Nitric Oxide Decomposition over
Metal Ion-Modified Cu-ZSM-5 Catalysts

By

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Abstract

In this thesis, nitric oxide decomposition into nitrogen and oxygen over copper ion-exchanged ZSM-5 (Cu-ZSM-5) and metal ion-modified Cu-ZSM-5 (M/Cu-ZSM-5) catalysts were studied in a laboratory-scale fixed-bed reactor equipped with gas chromatograph and NOx chemiluminescence analyzer. The fresh and used catalysts were characterized by using ICP, XRD, STEM/EDX, luminescence and XPS analyses.

Preparation of Cu-ZSM-5 from the aqueous cupric acetate solution at pH ≥ 6.5 leads to not only ion-exchanged Cu but also Cu deposition on the zeolite surface forming inactive copper CuO particles, which are identified by STEM/EDX and XRD, while at pH ≤ 5.0 it leads to low Cu exchange level and ZSM-5 protonation. The optimal pH of the solution is 5.7. There are two copper ion-exchanged sites in ZSM-5 zeolite: one associated with two framework Al atoms and preferentially occupied by cations-inactive, another close to one framework Al atom- active for NO decomposition.

Alkaline earth and transition metal ion-modified Cu-ZSM-5 catalysts promotes the catalytic activity of Cu-ZSM-5 materials at high temperature (450- 600°C), while rare earth metal ion-modified Cu-ZSM-5 materials enhance the Cu-ZSM-5 activity at low temperatures (≤ 400°C). Coexistence of Mg and Ce ions promotes the Cu-ZSM-5 activity over the whole temperature range of 350- 600°C. Cations also moderate reaction inhibition by oxygen. These phenomena are explained by that the inert cocations first occupy the inactive sites and copper ions take active sites subsequently.

Cerium addition to Cu-ZSM-5 promotes the activity of the latter for the NO decomposition in wet gas streams. Wet conditions drastically decrease the NO decomposition activity of Cu-ZSM-5 catalysts. Activity is partially recovered upon removal of water vapor. Copper migration leading to CuO formation inside the zeolite particles has been identified by STEM/EDX, XRD and XPS as the major pathway to deactivation. The cerium ion-modified Cu-ZSM-5 displays higher wet-gas activity for NO decomposition, and recovers a higher fraction of its initial dry-gas activity than the Cu-ZSM-5 after removal of water vapor. The presence of cerium suppresses CuO formation and dealumination, providing higher hydrothermal stability for the zeolite structure and higher copper dispersion. All of these factors contribute to better catalytic performance of the Ce/Cu-ZSM-5 catalyst.

Kinetics of NO decomposition over Cu-ZSM-5 and M/Cu-ZSM-5 were studied and a simple mechanism was proposed. O2-TPD and O2 uptake capacity for the above materials were performed to examine the interaction of Cu with O2.

Thesis Supervisors: Maria Flytzani-Stephanopoulos Visiting Professor of Chemical Engineering Adel F. Sarofim Lammot duPont Professor of Chemical Engineering

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DEDICATION

THIS THESIS IS DEDICATED TO

SHUXIANG, TRACEY
AND MY PARENTS
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This section- Acknowledgments, I finally realized, is the most difficult part of the thesis to write, since so many people have influenced this final product. Thus, I appreciate you all in advance in case any omissions.

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Chapter 1

INTRODUCTION

Environmental problems related to energy and goods production and waste treatment are given more attention by human beings as their standard of living continually improves. The standard of living is proportional to the energy consumed. The increasing population of the earth demands even more energy. Energy production principally from combustion of fossil fuels, such as wood, coal, oil or nature gas, in an environmentally benign manner is a challenge faced presently by the United States and the world. This is determined by the global needs and expansion in the use of fossil fuels, which in turn impose environmental and health problems resulting from emissions of combustor exhausts. The main pollutants from fuel combustion are NO\textsubscript{X} (NO and NO\textsubscript{2}), SO\textsubscript{2}, VOC (volatile organic compounds), PAH and particulates.

This thesis addresses the issues involved in NO\textsubscript{X} removal from exhaust gases. In this chapter, background information and literature related to the research of this thesis will be reviewed. Finally, the thesis objectives will be presented.

1.1 BACKGROUND

1.1.1 Pollutant Emission from Combustion Sources

The main environmental and health concern from NO\textsubscript{X}, SO\textsubscript{2} and particulate emissions is acid rain, which is most closely associated with damage to aquatic systems, forests, buildings and other structures, and toxic to living organisms [1, 2]. Table 1.1 summarizes these health and which is environmental concerns in more detail. In addition, NO\textsubscript{X} is a precursor of photochemical smog, a major problem in urban areas.

As mentioned above, all fossil combustors are possible sources of NO\textsubscript{X} emissions. Stationary sources, such as utility and industrial coal-fired boilers, oil and gas-fired boilers, and mobile sources, such as motor vehicles, motor cycles and diesel engines, contribute 35%, and 45% of total NO\textsubscript{X} emissions, respectively. Chemical process industries, e.g., a nitric acid plant emitting (dry basis) 3,000- 4,000 ppm NO [3], contribute the rest. NO\textsubscript{X} emissions in the US
increased from 19 million short tons in 1975 to 20 million short tons in 1984 [4]. Coal combustors in coal-fired power plants emitted 4 to 6 million short tons in total NO\textsubscript{X} emissions in 1975 and 1986, respectively.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Health Concern</th>
<th>Environmental Concern</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{X}</td>
<td>Respiratory Illness and Lung Damage</td>
<td>Acid Deposition; Damage to Lakes, Streams, and Forests; Lowering Visibility and Increasing Ozone</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>Respiratory Trace Problems; Permanent Harm to Lung Tissue</td>
<td>Acid Deposition and Lowering Visibility</td>
</tr>
<tr>
<td>Airborne particulate matter</td>
<td>Eye and Throat Irritation; Bronchitis and Lung Damage</td>
<td>Lowering Visibility</td>
</tr>
</tbody>
</table>

The U. S. Clean Air Act Amendments of 1970 and 1977 were the driving forces for the development of new technology to control NO\textsubscript{X} emission from various sources to meet federal environmental requirements. The Clean Air Act Amendments of 1990 have more stringent regulations on stacks and tailpipes, calling for a 30% reduction of NO\textsubscript{X} emissions and 50% reduction of SO\textsubscript{2} emissions.

Standards for NO\textsubscript{X} emissions vary with the fuel and type of utility (ca. 300 ppm for coal, 150 ppm for oil, and 10 ppm for gas [5]). For coal-fired boilers, NO\textsubscript{X} emission control is achieved by adjusting combustion conditions and cleaning flue gas in post-combustion. For motor vehicles, the 1970 Clean Act Amendments directed major reductions in tailpipe emissions with goals of 90% HC and CO and 70% of NO\textsubscript{X}. The oil industry was asked to change fuels, which produced some reductions in some pollutants by perhaps 10-15%. However, the vehicle manufacturers were required to reduce 70% HC
and CO and 90% of NOx [6]. Consequently, for gasoline products, the refiner started to take out the lead (starting, July 1974) and add deposited control additives (1985) and control vapor pressure (1989) [7]. The NOx emissions of car tailpipes with model year 1981 were limited to 1.0 g/mile by the Clean Air Act Amendments of 1977. Motor vehicle pollution limits, including existing limits and requirements of the Clean Air Act Amendments of 1990, and U.S. heavy duty diesel emission regulations are summarized in Table 1.2. For gas turbine emissions [8] the U.S. EPA proposed emission standards for stationary gas engines and gas turbines in the mid-1970's. There were no national New Source Performance Standards (NSPS) for emissions from stationary engines. There are, however, requirements for Prevention of Significant Deterioration (PSD) and for emission control in areas that do not meet National Ambient Air Quality Standards (NAAQS), and in some areas the control requirements are very stringent, for example in California. Rules of NOx emission in California are listed in Table 1.3 [9]. The overall average NOx emission from in-use natural gas-engines is 11 to 12 g/bhp-h, with a range from a low of about 6 to a high of over 20 g/bhp-h. Current production standard engines generally produce NOx emissions near or below the overall average value: 12 g/bhp-h. The NOx emission from low emission engines (e.g., clean-burn) is not higher than 2.5 g/bhp-h. Obviously, flue gas clean-up is urgently needed to get NOx down for in-use gas engines with high NOx emissions.

<table>
<thead>
<tr>
<th>Table 1.2</th>
<th>U.S. Vehicle Pollution Limits (g/mile)</th>
</tr>
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<tr>
<td><strong>Existing Limits:</strong></td>
<td><strong>CO</strong></td>
</tr>
<tr>
<td>Passenger Car</td>
<td>3.4</td>
</tr>
<tr>
<td>(GVW&lt; 6,000 LB)</td>
<td></td>
</tr>
<tr>
<td>Light Truck</td>
<td>10.0</td>
</tr>
<tr>
<td>(6,000 LB ≤ GVW ≤ 8,500 LB)</td>
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### Table 1.2  U.S. Vehicle Pollution Limits (g/mile)-Conn.

<table>
<thead>
<tr>
<th>Clean Air Act Amendments of 1990:</th>
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<th>HC</th>
<th>NOx</th>
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<tr>
<td>Tier I</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Passenger Car 1994</td>
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<td>0.4</td>
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<tr>
<td>Light Truck 1995</td>
<td>5.0</td>
<td>0.39</td>
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<tr>
<td>Tier II</td>
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<tr>
<td>Passenger Car 2004</td>
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<td>0.2</td>
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<table>
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<tr>
<th>U. S. EPA Heavy Duty Diesel Emission Regulations (g/hp-h):</th>
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<th>PM</th>
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<tr>
<td>1988 (all)</td>
<td>10.7</td>
<td>0.6</td>
</tr>
<tr>
<td>1991</td>
<td>5.0</td>
<td>0.25</td>
</tr>
<tr>
<td>1994 (trucks)</td>
<td>5.0</td>
<td>0.1</td>
</tr>
<tr>
<td>1994 (urban buses)</td>
<td>2.5</td>
<td>0.05</td>
</tr>
<tr>
<td>1998 (trucks)</td>
<td>4.0</td>
<td>0.1</td>
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</table>

<table>
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<tr>
<th>CARB Car Standards, Gasoline Fueled (g/mile):</th>
<th>NMOG¹</th>
<th>CO</th>
<th>NOx</th>
<th>PM²</th>
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<tbody>
<tr>
<td>1993</td>
<td>0.25</td>
<td>3.4</td>
<td>0.4</td>
<td>0.008</td>
</tr>
<tr>
<td>TLEV</td>
<td>0.125</td>
<td>3.4</td>
<td>0.4</td>
<td>0.08</td>
</tr>
<tr>
<td>LEV</td>
<td>0.075</td>
<td>3.4</td>
<td>0.4</td>
<td>0.08</td>
</tr>
<tr>
<td>ULEV</td>
<td>0/04</td>
<td>1.7</td>
<td>0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>ZEV</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

¹ Non-methane organic gases included H, oxygenated HC
² For diesel vehicles only

### Notes:
- TLEV- Transitional low emission vehicles
- LEV- Low emission vehicles
- ULEV- Ultra-low emission vehicles
- ZEV- Zero emission vehicles
Table 1.3  California NO\textsubscript{x} Emission Regulations for Gas Turbines

<table>
<thead>
<tr>
<th>Exhaust Oxygen Content</th>
<th>Required Reduction</th>
<th>Limit in ppm at 15% O\textsubscript{2}</th>
<th>Approximated g/bhp-h</th>
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<tr>
<td>&lt;4%</td>
<td>90%</td>
<td>90</td>
<td>1.2</td>
</tr>
<tr>
<td>&gt;4%</td>
<td>80%</td>
<td>150</td>
<td>2.0</td>
</tr>
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</table>

1.1.2 NO\textsubscript{x} Removal

Many efforts have been made to remove NO from combustion emission exhaust in addition to efforts at reducing production of NO\textsubscript{x} by controlling combustion conditions. For electric utility or industrial boilers generated flue gas that contains excess oxygen, a demonstrated technology for NO removal, known as Selective Catalytic Reduction (SCR), that uses V\textsubscript{2}O\textsubscript{5}-TiO\textsubscript{2} supported on ceramic or metallic monoliths as catalyst, is presently commercially available only in Japan and Europe [10]. This method reduces NO to N\textsubscript{2} over the catalyst using gaseous ammonia as the reductant. It is also applicable to gas-fired engines containing significant concentrations of oxygen in the exhaust, but it has not been practiced commercially. With regard to moving-source NO\textsubscript{x} emission, the three-way catalyst in the automobile exhaust line controls NO\textsubscript{x}, hydrocarbons (HCs) and CO emissions well [11]. The noble metal catalyst reduces NO\textsubscript{x} by operating the engine at near stoichiometric conditions. The situation is different for diesel engines, operating under lean combustion, i.e. with excess oxygen. It is well known that diesel engines contribute to NO\textsubscript{x} emissions. The new Clean Air Act Amendments of 1990 have provisions or regulating NO\textsubscript{x} emissions for diesel engines. Among other technologies under development for flue gas clean up are the thermal DeNO\textsubscript{x}, urea injection, NO\textsubscript{x}SO [12], the copper oxide method and lean combustion [13]. In hardware design a lot of efforts on combustion modification for future installations have produced new designs of coal combustors that can greatly reduce NO\textsubscript{x} emissions, e.g., staged combustion [14].
Even though considerable reduction of NO$_x$ emissions from various sources has been achieved in the last two decades, further NO$_x$ control is still necessary to meet more and more stringent regulations on pollutant emissions, directed nationally by the Clean Air Act Amendments of 1990, the New Source Performance Standards and by regional requirements (often more stringent).

SCR and three-way catalysts have some problems. As mentioned above, SCR is available presently for NO$_x$ removal from industrial boiler flue gas, and is unique in that it reduces NO$_x$ by NH$_3$ in the presence of several percents of oxygen. The main drawbacks of this process are that it is: (1) expensive, since it consumes a large amount of ammonia; (2) a source of secondary pollution by NH$_3$ slip due to incomplete reaction; also N$_2$O (presently unregulated), a potent greenhouse gas, is an undesired by-product; (3) difficult to control; and (4) a catalyst poison. SCR with ammonia cannot be used in automobiles. The current automotive catalyst, Rh-Pt-Pd/Al$_2$O$_3$, has been very successful in reducing all three pollutants by more than 80%. However, this catalyst works well only in the environment of a properly stoichiometrically balanced exhaust gas composition, which is maintained by controlling the ratio of air to fuel using an on-board microprocessor. To some engineers, the three-way catalyst represents a major obstacle to improving the efficiency of motor vehicles. An improvement of as much as 10 percent (1.1 million barrels of crude oil every day based on 1989 statistical data [6]) is attainable from very lean-burning engines, but cannot be commercialized because the NOx removal efficiency of the present 3-way catalyst drastically drops when the exhaust gas contains excess oxygen.

Studies of selective nitric oxide reduction with hydrocarbons are currently underway. Held and coworkers [15] and Iwamoto and coworkers [16, 17] first reported that the catalytic activity of Cu-ZSM-5 could be greatly enhanced in an excess of oxygen by the presence of small amounts of non-methane hydrocarbons, such as C$_2$H$_4$, C$_3$H$_6$ or C$_3$H$_8$. Since then, many catalysts have been reported to be active for this reduction, for example, H$^+$- [18], Co- [19], cerium ion- [20] exchanged zeolites, Fe-silicate [21], alumina [22] and silica-alumina [23], Cu-ZrO$_2$ [24], etc. Among these, the copper ion-exchanged ZSM-5 zeolite is the most active catalyst [25]. The main drawback of this catalyst is its hydrothermal instability. Intensive efforts here and abroad are underway to develop these lean-NO$_x$ catalysts.
1.2 LITERATURE REVIEW: NITRIC OXIDE DECOMPOSITION CATALYSTS

Direct decomposition of nitric oxide to nitrogen and oxygen would be the most attractive process for NO control, since no reductant is needed. Except at very high temperatures, NO decomposition to \( \text{N}_2 \) and \( \text{O}_2 \) is thermodynamically favorable, as seen in Table 1.4 [26]. This table shows thermodynamic equilibrium constants for the reactions of 2 NO \( \rightleftharpoons \text{N}_2 + \text{O}_2 \), 2 NO + O\(_2\) \( \rightleftharpoons \) 2 NO\(_2\) and 2 NO + N\(_2\) \( \rightleftharpoons \) 2 N\(_2\)O. There are many papers dealing with the catalytic decomposition of NO. The catalysts for NO decomposition reported so far can be classified into three groups: metal and metal oxides, copper ion-exchanged zeolites and metal ion modified Cu ion-exchanged ZSM-5 (or M-Cu-ZSM-5, for simplicity) zeolites. In this section, a brief review of studies of these catalysts is presented.

<table>
<thead>
<tr>
<th>Table 1.4 Thermodynamic Equilibrium Constants of NO Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K) 298 400 500 600 800 1000</td>
</tr>
<tr>
<td>Reaction: 2NO ( \rightleftharpoons ) N(_2) + O(_2)</td>
</tr>
<tr>
<td>1.71x10(^{30})</td>
</tr>
<tr>
<td>Reaction: 2NO + O(_2) ( \rightleftharpoons ) 2NO(_2)</td>
</tr>
<tr>
<td>1.96x10(^{12})</td>
</tr>
<tr>
<td>Reaction: 2NO + N(_2) ( \rightleftharpoons ) 2N(_2)O</td>
</tr>
<tr>
<td>5.80x10(^{-7})</td>
</tr>
</tbody>
</table>

1.2.1 Metal and Metal Oxide Catalysts

Many efforts have been made to decompose NO directly into N\(_2\) and O\(_2\). Unfortunately, as Hightower and Van Leirsburg [27] reported, as of 1974, no solid catalyst had been found to effectively work for this direct decomposition. A number of catalysts, e.g., Pt, Rh, Ru, MgO, NiO, ZnO, CaO, SrO, Al\(_2\)O\(_3\), GaO, Fe\(_2\)O\(_3\), Cr\(_2\)O\(_3\), CeO\(_2\), ZrO\(_2\), Co\(_3\)O\(_4\), TiO\(_2\), IrO\(_2\), Sc\(_2\)O\(_3\), Y\(_2\)O\(_3\), Er\(_2\)O\(_3\), Tm\(_2\)O\(_3\), Lu\(_2\)O\(_3\), etc. had been tried and were found to decompose NO, but none of these catalysts had sufficiently high activity to be of practical interest [28, 29]. Of these catalysts, Co\(_3\)O\(_4\) was the most active [30]. The NO reacts with reduced sites in catalysts but the reduced catalyst sites would be rapidly oxidized by the
oxygen released from the decomposed NO with a concomitant loss in catalyst activity was lost. High temperature and/or gaseous reductants were required to remove the surface oxygen and regenerate the catalytic activity. Amirnazmi et. al. [31] investigated NO decomposition over Pt and oxides of Fe, Co, Ni, Cu and Zr at temperatures up to 700°C. They reported that the kinetics were of the Langmuir-Hinshelwood form. Recently, the interaction of NO with perovskite oxides, including the super-conducting oxide YBaCu3O7-y, has been reported [32-34]. Experimental results indicated that perovskite-type oxides, such as La1-xSrxCo1-yM1-yO3, where M is one of the metals Cr, Mn, Fe, Co, Ni, Cu, are promising NO decomposition catalysts having a steady state activity at high temperatures (≥ 750°C) and thermal stability [34]. NO decomposition over YBaCu3O7-y took place at high temperature, e.g., 20% of NO conversion to nitrogen at 1073K, and the catalytic activity increased with increasing surface area of the catalyst.

Inhibition of NO decomposition by oxygen over Pt and oxides of Fe, Co, Cu, and Zr was investigated by Amirnazmi et al [13]. It was found that reaction order with respect to O2 was minus one.

1.2.2 Copper Ion-Exchanged Zeolites
Cobalt(II) ion-exchanged Y-type zeolite was a first reported metal ion-exchanged zeolite for nitric oxide decomposition. The catalyst exhibited an activity but was poisoned by trace amount of water [35]. In the early 1980s, Iwamoto and coworkers discovered that copper ion-exchanged zeolite catalysts had a stable steady-state catalytic activity for NO decomposition even in presence of oxygen[36-39]. It has been reported [36] that Cu-exchanged Y zeolite (Si/Al = 2.4) displayed 42% conversion of NO to N2 in a mixture of 4% NO-He at 500°C and a contact time, defined as the ratio of the catalyst weight in use to the total flow rate, of 7.8 g s/cm³; The catalytic activity of the CuNa-Y was low until the Cu exchange level was 42%, where 100% Cu exchange was defined as Cu/Al = 0.5 in the catalyst; Pretreatment with a 1% H2O-He at 500°C for 1 hour did not affect the catalytic activity. Cu ion exchanged-Mordenite (Si/Al = 5) catalyst had higher catalytic activity than Cu-Y (Si/Al = 2.6) and Cu-X (Si/Al = 1.05) for NO decomposition in a gas mixture of 4% NO-He at 550°C and 4.0 g s/cm³ [38]. Addition of Co3+ or Ni2+ ions to Cu-Y catalysts enhanced Cu catalytic activity for NO decomposition while Ca2+, Mn2+, Fe2+ and Zn2+ decreased the catalytic activity [39].
The best performance was obtained from a Cu-ZSM-5 catalyst, which showed 80% conversion of nitric oxide to nitrogen and oxygen in a mixture of 4% NO- 96% He with a contact time of 4.0 g s/cm³ at a temperature of around 500°C [38]. This catalyst is different from the above conventional metal, metal oxide, perovskite oxide catalysts in the catalytic activity for NO decomposition and catalyst structure. Subsequently many studies [such 40- 46] of this catalyst system have followed, the results of which will be reviewed in the rest of this Chapter.

The performance of Cu-ZSM-5 catalysts for NO decomposition [37, 38, 40, 44 and 45] is summarized as follows:

- Cu-ZSM-5, with Cu exchange level lower than 40%, has low activity [37, 38]. Above this level, the catalytic activity increases non-linearly with the amount of exchanged copper. This increase in activity continues up to ~140% Cu exchange level.

- The Cu-ZSM-5 catalysts display a maximum reaction temperature for NO conversion to N₂, which is about 500°C, in a dry-gas mixture. Higher than this temperature, the catalytic activity decreases, and more quickly for lower Cu ion-exchanged ZSM-5 materials. This maximum can be found either in ascending or descending temperature sequence. Therefore, Cu sintering or other catalyst deactivation processes at high temperatures can be ruled out. At the present time, no consensus exists in the literature for this phenomena.

- The kinetics of NO decomposition over Cu-ZSM-5 catalyst have a reaction order of 1.6 ± 0.4 [40] or first order [44] in partial NO pressure, and is inhibited by oxygen, with a minus half order [43]. Oxygen inhibition decreases with increasing temperature [44, 45].

- The specific rate per unit Cu, i.e. the turnover frequency, increases with increasing Si/Al ratio [38], opposite to the observations of Li, et al [44]. Recently, Moretti [47] reviewed published rate data, and concluded that the specific rate per unit Cu increases with the number of aluminum per unit cell; and speculated that two Cu sites are needed to decompose nitric oxide.

SO₂ and H₂O vapor in the flue gas affect the catalytic activity of Cu-ZSM-5 greatly [39]. It is reported that SO₂ completely poisons the activity at 400-650°C [48]. But the poisoned catalysts are regenerable after treatment at a higher temperature to desorb SO₂. Adding 2% H₂O vapor into the NO reaction stream reduced the NO conversion from 92% to 72 % at 500°C, but full recovery of the conversion was possible [46]. However, the detailed
experiment was not given in the literature. More recently, Kharas and coworkers [50] found that Cu-ZSM-5 was quickly and severely deactivated in a simulated lean-burn gas mixture, including 10% H2O, at GHSV = 127,000 h⁻¹ at 600 and 800°C. The authors claimed that sintering of the catalytically active components, rather than degradation of the metastable zeolitic support, probably dominates deactivation.

The shortcomings of Cu-ZSM-5 catalysts are, therefore, low activity at high temperatures (≥ 500°C), oxygen and more so water vapor inhibition.

1.2.3 Cocation Modified Cu Ion-Exchanged Zeolites
In recent work, Kagawa et al. [50] reported that the incorporation of cocations, such as alkaline earth and transition metals, into Cu-ZSM-5 catalysts promoted the catalytic activity of Cu-ZSM-5 for the direct NO decomposition in 0.5% NO- He at a contact time of 4.0 g s/cm³ at temperatures above 450. Alkaline earth and transition metals were equally effective cocations in Cu-ZSM-5 at 550°C. Negative results were obtained with alkali metal ions. No explanation of the cocation promotion effect was given. However, it is clear that the cocation effect is not due to the presence of cocations in the catalysts since, in absence of copper, the cocation ion-exchanged ZSM-5 materials did not have any catalytic activity for NO decomposition. In the same paper, the effect of O₂ and H₂O vapor on the M/Cu-ZSM-5 catalytic activity was not examined.

1.2.4 Characterization of Cu-ZSM-5 Catalysts
The interaction of NO and O₂ with Cu-ZSM-5 catalysts has been extensively characterized by Temperature-Programmed-Desorption (TPD), Temperature-Programmed-Reduction (TPR), Fourier Transform Infrared spectroscopy (FT-IR), X-ray Photoelectron Spectroscopy (XPS), Electron Spin Resonance (ESR), Extended X-ray Adsorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) techniques in efforts to understand the mechanism of NO decomposition over Cu-ZSM-5 catalysts.

Iwamoto [41] first reported that two NO peaks at about 100- 200°C and 380°C, respectively, were observed in his earlier nitric oxide TPD on Cu-ZSM-5, accompanied by O₂ desorption peak at 380°C. More recently, the adsorption and desorption properties were examined by the same research group [51] in more detail by using quadrupole mass spectrometry (QPMS) and IR to detect
the desorption products of NO on Cu-ZSM-5. They observed three desorption peaks of NO at 127, 190 and 390°C, one N2O desorption peak at 127°C K, and one O2 desorption peak at 390°C. They assigned most of the NO reversibly adsorbed on Cu-ZSM-5 to the NO\(^+\) on Cu\(^{2+}\), and the NO irreversibly adsorbed to the residual of NO\(^+\), nitrate (NO\(^3^-\)), nitrite (NO\(^2^-\)) and NO\(^2+\). In the latter species, NO\(^+\) can desorb at 77- 277°C, and NO\(^2+\), NO\(_2\), and NO\(^3-\) decompose to yield NO and O\(_2\) around 387 K.

Li and Armor [52] observed several NO and N\(_2\)O peaks from NO-TPD on Cu-ZSM-5 samples pretreated in pure He at 500°C. Four NO desorption peaks at 90, 140, 250 and 360°C were found. Also desorption of O\(_2\) at 360°C and two N\(_2\)O peaks at 90 and 140°C were observed. However, on CO-reduced Cu-ZSM-5 materials, the O\(_2\) peak was dramatically decreased. Compared to NO-TPD on the He-pretreated Cu-ZSM-5, an additional N\(_2\)O peak and an additional NO peak at about 240°C were observed. A TPD of NO on O\(_2\)-pretreated Cu-ZSM-5 showed that the N\(_2\) and N\(_2\)O peaks totally disappeared, while four NO peaks and one O\(_2\) peak still remained. Hierl, et al [53] obtained a similar NO TPD on Cu/Al\(_2\)O\(_3\) to that reported by the Iwamoto group on Cu-ZSM-5.

Teraoka, et al [54] have reported that the TPD profile of O\(_2\) on Cu-ZSM-5 became more pronounced, and the number of O\(_2\) desorption peaks increased from one above 400°C at 30% Cu exchange level to three peaks at 120, 380 and 630°C at 130% Cu exchange level. The desorption peak of O\(_2\) at 120°C did not exist at low Cu exchange level. The O\(_2\) desorption peak at 630°C was attributed to lattice oxygen. Valyon and Hall [55] reported the O\(_2\)-TPD temperatures at 125, 218, 410 and 537°C. Higher temperature shift was observed compared to that reported by Teraoka, et al [54]. They proposed that the low-temperature O\(_2\) desorption resulted from O\(_2\) chemisorption, while those with substantial binding energies desorbed at high temperatures were dissociated automatically bound extralattice oxygen.

FT-IR investigation of NO interaction with Cu-ZSM-5 at low temperatures by Iwamoto [39, 40] showed seven adsorption peaks at 1734, 1813, 1827, 1906, 1964, 2125 and 2238 cm\(^{-1}\) after NO had adsorbed on Cu-ZSM-5 at room temperature and a gas pressure of 40 Torr. These peaks were attributed to species such as Cu\(^{2+}\)NO\(^-\), Cu\(^+\)(NO)\(_2\), Cu\(^+\)(NO)\(^-\), etc., among which Cu\(^+\)(NO)\(^-\) species contribute mostly to N\(_2\) formation. Spoto and coworkers [41] used FT-IR to examine the evolution of adsorbed gaseous
species on Cu+-ZSM-5 prepared by reaction between the acidic protons of H-ZSM-5 and CuCl in the gas phase in high vacuum, after NO was introduced into the IR cell. They proposed the reaction scheme as follows (in presence of excess NO): Cu+ (NO) + NO ---> NO-Cu+-NO ---> O--Cu2+-(N2O)+ NO ---> N2O + O--Cu2+-NO, and O--Cu2+-NO + NO ---> NO2--Cu2+-NO, whereby the oxidation of Cu+ to Cu2+ is associated with the decomposition of dinitrosylic complex to give N2O and O-. Finally, NO2--Cu2+-NO is formed. It was proposed that the NO2--Cu2+-NO could further evolve to give N2 and O2. Using FT-IR and EPR, however, Giamello, et al [42] proposed another reaction scheme, which is described as follows: Cu+ + NO ---> (Cu+NO) at low NO pressure (<1 Torr); (Cu+NO) + NO ---> NO-Cu+-NO at high NO pressure (5~ 30 Torr); NO-Cu+-NO ---> N2Oads + Cu2+-O--; N2Oads ---> N2O (gas) and Cu2+-O- + NO ---> Cu2+(NO2--); Cu2+(NO2--) + NO ---> Cu+Δ+- NOΔ'+ + NO2--ads, where Δ + Δ' = 1.

XPS was used by Jirka, et al [56] to examine the oxidation state of Cu ions in Cu-ZSM-5. A gradual disappearance of the Cu2+ shake-up satellites and binding energy shift were observed as the exposure time of the Cu-ZSM-5 to the X-ray beam increased. This phenomenon suggests the reduction of Cu2+ by the X-ray beam, which makes it difficult to obtain information about the Cu2+/Cu+ distribution in Cu-ZSM-5 by using XPS. A mechanism of Cu2+ reduction was proposed that water decomposition (H2O ionization: 2Cu + 2H2O ---> 2Cu2+ + H+ + 2OH--; O2 and H2O desorption: 2OH---> H2O + 1/2 O2 + 2e--; Cu2+ reduction: 2Cu2+ + 2e---> 2Cu+) by zeolites into oxygen leads to Cu2+ reduction. However, Haack, et al. [57] recently found that this result could not be confirmed by Cu-ZSM-5 characterization by XPS. The two XPS peaks observed were both assigned by Haack, et al. to cupric ions. They found that heat treatment under oxidizing conditions could induce a redistribution of Cu2+ ions in different spatial coordination. As both Jirka, et al. and Haack, et al. stated, the technical problem encountered for characterizing Cu-ZSM-5 samples with XPS is that X-ray irradiation on the Cu-ZSM-5 during data acquisition induced reduction of Cu2+ to Cu+. More recently, Shpiro, et al [43] reported that maintaining the Cu-ZSM-5 sample at 170- 200 K and using a lower beam energy (200W: 10 keV x 20 mA) would avoid X-ray induced Cu2+ reduction to Cu+. Hence, the amount of reduced Cu2+ was estimated after Cu-ZSM-5 was treated under different conditions. It was found that copper in ion-exchanged Cu-ZSM-5 sample becomes well dispersed throughout the
bulk upon exposure to reducing conditions or reactive atmospheres, although it initially enriches the external surface of the zeolite. In impregnated Cu-ZSM-5, large aggregated copper species were found on the external surface of the zeolite. Valyon and Hall also observed both Cu$^{2+}$ and Cu$^+$ in Cu-ZSM-5 by using XPS [58].

Kucherov and coworkers [59-61] have conducted a comprehensive EPR study of Cu-ZSM-5. The Cu-ZSM-5 was prepared by incorporating Cu ions into NH$_4$-ZSM-5 (Si/Al = 21) zeolite in aqueous solutions of Cu(NO$_3$)$_2$ or Cu$_3$(PO$_4$)$_2$ followed by calcination. They found that Cu$^{2+}$ in Cu-ZSM-5 exists as isolated cations. Two types of the isolated Cu cations were identified after calcination of Cu-ZSM-5 at 550°C, one in a square planar four-coordinated configuration, the other in a square pyramidal five-coordinated. The results of the investigation also indicated that the preferable formation of five-coordinated Cu$^{2+}$ cations takes place at low copper exchange level. The four-coordinated square planar Cu$^{2+}$ was more reducible by CO reduction, indicating that this type of Cu$^{2+}$ was more accessible than the five-coordinated Cu$^{2+}$. These more accessible Cu$^{2+}$ cations may be responsible for the activity of Cu-ZSM-5 for methane oxidation. This hypothesis was supported by a very good linear correlation between the conversion of CH$_4$ oxidation and the number of the four-coordinated Cu$^{2+}$ [60]. The same group also used the EPR technique to follow and prove the Cu$^{2+}$ migration from the external surface of zeolites into the ZSM-5 channels by solid-state Cu$^{2+}$ ion-exchange [62].

Janssens, et al [63], Schoonheydt [64, 65] and Karge, et al [66] have used EPR to characterize solid-state Cu$^{2+}$ ion exchange. Schoonheydt [61] found that there are two distinct sites for isolated Cu$^{2+}$ in large prismatic and cubic crystals with smaller g value, but three sites in microcrystalline materials with higher g value. In a recent article [65], Schoonheydt discussed the sittings and energetics of Cu$^{2+}$ in zeolites by using results from EPR and Diffuse-Reflectance IR Spectroscopy. Coordination models of Cu$^{2+}$ to oxygen at the wall of the channels of dehydrated ZSM-5 were presented in that review. Karge's EPR results [66] are in agreement with Kucherov's observations [59-61]. By solid state ion exchange of H-ZSM-5 with CuCl$_x$·2H$_2$O, Karge, et al observed the presence of four-coordinated and five-coordinated Cu$^{2+}$ in the channels of ZSM-5.
Anderson and Kevan [67] and Sass and Kevan [68, 69] have conducted Electron Spin Echo Modulation (ESEM) EPR to investigate the interaction of adsorbates with Cu$^{2+}$ in ZSM-5. Upon dehydration (removal of ligand water molecules coordinated to Cu$^{2+}$ ions), Cu$^{2+}$ cations moved away from the intersection of straight channels with the zig-zag channels and approached the wall of the zeolite framework. These cations, however, migrated back to channel intersections upon exposure to water where the large hydrated cations could better fit. Similarly, polar molecules, such as ammonia, pyridine and alcohol, also caused rapid migration of Cu$^{2+}$ cations to the main channel positions. However, Slinkin, et al. [62] disagreed with Kevan's explanation of the Cu$^{2+}$ redistribution due to exposure of Cu$^{2+}$ to polar molecules. He investigated the interaction of NH$_3$, pyridine, methanol, dimethyl ether, propylene and p-xylene molecules with Cu$^{2+}$ in ZSM-5 by EPR and performed quantum-chemical calculation on spin densities and the g tensors of Cu$^{2+}$ in ZSM-5, finally concluding that all changes of Cu$^{2+}$ EPR signals observed by introducing the polar molecules were mainly caused by changes of the coordination environments around Cu$^{2+}$ cations, such as changes of coordination numbers and slight geometric displacements of Cu$^{2+}$ ions in their chelate sites.

Anderson and Kevan [67] reported a cocation effect on Cu$^{2+}$ siting by EPR of Cu-ZSM-5. They found that the valence of cocations in Cu/M-ZSM-5 determined the locations of Cu$^{2+}$ ions. The cupric cations in Cu/Ca-ZSM-5 were closer to aluminum than in Cu/K-ZSM-5 because an aluminum modulation on Cu$^{2+}$ EPR was observed only with Cu/Ca-ZSM-5. It should be pointed out that both samples were fully hydrated. Later on, they [70] also reported that in the hydrated zeolite the Cu$^{2+}$ is octahedrally coordinated to six water molecules with the complex located at the intersection between two zeolite channels. Evacuation at room temperature removed three water molecules from Cu$^{2+}$ which anchored to the zeolite lattice by coordination of zeolite oxygen. Activation to 400°C produces one Cu$^{2+}$ species which is either recessed from or inaccessible to the main channels.

Sass and Kevan [69] reported another result that Cu$^{2+}$ cations in ZSM-5 with Si/Al = 26 were not preferentially adjacent to the negatively charged AlO$_2^-$ lattice units until the Cu$^{2+}$ concentration was high (4 Cu$^{2+}$/40 unit cell) enough or unless a divalent cocation (Ca$^{2+}$ or Mg$^{2+}$) was present. At higher Si/Al ratios (40 and 70), the preferred location of Cu$^{2+}$ was always
close to AlO$_2^-$ . These EPR experiments were carried out with very low Cu$^{2+}$ loading of the ZSM-5 to obtain better resolved EPR spectra; hence, extrapolation of these results to the Cu-ZSM-5 with high Cu$^{2+}$ exchange level (> 100%) is not straightforward.

Giamello, et al [42] conducted a series of Cu$^{2+}$ EPR measurements on Cu-ZSM-5 after various pretreatments. Two types of Cu$^{2+}$ were observed in Cu-ZSM-5 dehydrated at 400°C under vacuum, and an additional signal appeared at 500°C, based on g factors. However, a specific assignment of three types of Cu$^{2+}$ were not given in the article. Due to high Cu$^{2+}$ content, the resulting dipolar interaction among neighboring Cu$^{2+}$ caused very intense, broad and poorly resolved EPR signals. Even after exposure to H$_2$ for 30 minutes, Cu$^{2+}$ signal was still observed. Other research groups [71- 73] obtained similar results to those reported by Kucherov, et al [59- 61]. Iwamoto and coworkers [47] reported that upon treatment of Cu-ZSM-5 (Si/Al = 11.7, copper exchange: 116%) in oxygen at 500°C for 30 minutes, about 50% of copper ions exists as Cu$^{2+}$. This was concluded by comparison of the doubly integrated EPR spectrum with that of the standard sample (CuSO$_4$·5H$_2$O).

Larsen, et al [74] reported the EPR measurements for Cu-ZSM-5 material and proposed a mechanism for autoreduction of copper. They found that the copper concentration in the EPR spectra of pretreated Cu-ZSM-5 samples only accounted for about 40~60% of total copper present in the samples, suggesting that cupric ions were reduced to cuprous ions. The reduction process was reversible in the presence of water. They proposed a reduction process: 2[Cu$^{2+}$OH$^-$]$^+ \rightarrow$ Cu$^{1+} +$ Cu$^{2+}$O$^- +$ H$_2$O. No evidence of [CuOCu] in Cu-ZSM-5 was found. They concluded that a redox process between Cu$^{2+}$ sites and Cu$^{2+}$O$^-$ and Cu$^{1+}$ is not responsible for high-temperature nitric oxide decomposition and that Cu$^{2+}$O$^-$ (Cu$^{2+}$O$^- +$ NO $\rightarrow$ Cu$^{2+}$NO$_2^-$) and Cu$^{1+}$ (Cu$^{1+} +$ O$_2$ $\rightarrow$ Cu$^{2+}$O$_2^-$ + NO $\rightarrow$ Cu$^{2+}$NO$_3^-$) sites are responsible for the catalytic activity of Cu-ZSM-5.

However, Iwamoto, et al [47], Sarkany, et al [75, 76] reported an oxygen bridged copper dimer, [Cu-O-Cu]$^{2+}$, which was not observed by Larsen, et al [74].

Recently, Kucherov, et al [77, 78] studied the oxidation and coordination states of copper in Cu-ZSM-5 using in-situ EPR measurement. They mainly concluded that below 500°C the cupric ions are not spontaneously reduced to cuprous ions in vacuo or in flowing, purified He; at 500°C the EPR signal of
Cu$^{2+}$ was not changed by the presence of NO, O$_2$ or their mixture in the gas phase. Larsen, et al [74] argued that the intensity of Cu$^{2+}$ signal following pretreatment and calcination in oxygen did not represent a measure of the total amount of Cu in the zeolite, since EPR-silent Cu$^{2+}$O$_2^-$ was produced during oxidation. However, the normalized double integral of the EPR spectra of the Cu-ZSM-5 pretreated in oxygen flow at 500$^\circ$C and saturated with water vapor at 20$^\circ$C was in good agreement with that of standard CuSO$_4$ solution [77].

All Cu$^{2+}$ EPR results consistently showed that two types of Cu$^{2+}$ sites were present in Cu-ZSM-5 after pretreatment at 500$^\circ$C, and most likely only one of them, the four-coordinated square planar Cu$^{2+}$, contributed to the catalytic activity of Cu-ZSM-5 for NO decomposition. The disadvantages of the EPR technique are that it cannot detect all Cu species in Cu-ZSM-5, and it cannot be used at high temperatures since the high temperature leads to an unwanted electron Boltzman distribution and fast electron relaxation. In combination with other techniques, EPR can be used to distinguish isolated, catalytically active Cu$^{2+}$ sites from other species.

X-ray diffraction (XRD) has been used to examine the loss of crystallinity and the formation of CuO particles in Cu-ZSM-5 [79, 80]. Kharas, et al [80] found evidence of an amorphous halo after exposure to lean-combustion exhaust gas containing 10% water vapor at 600 and 800$^\circ$C. With a very high Cu loading (nominally corresponding to 387% copper exchange level) in ZSM-5, they found CuO particle formation in ZSM-5 after reaction (lean NO reduction) for 1 hour at 600 and 800$^\circ$C. Water vapor-induced dealumination was identified by Grinsted, et al [79] using $^{27}$Al Magic Angle Spinning (MAS) NMR, while XRD analysis did not show framework structure damages on the same sample which was aged by heating in air-containing 10% water vapor at 410$^\circ$C for 113 hours.

Three crystal structures of M-ZSM-5 have been determined by using the powder X-ray diffraction technique, which provided some information about cation locations in ZSM-5 zeolites [81- 83]. However, only one of them involved a transition metal cation, Ni$^{2+}$, and no information is available for Cu$^{2+}$. Two Ni$^{2+}$ cation sites were identified by XRD structure refinements [83]: one in a small cage (site I) and the other in the zig-zag channel parallel to (100) direction (site II). Ni$^{2+}$ at site II, a very accessible site, was found to be three-oxygen coordinated, while as mentioned earlier, a four-coordinated
Cu$^{2+}$ was reported by Kucherov, et al [59]. This difference may be due to the different affinity of Cu$^{2+}$ and Ni$^{2+}$ to oxygen. All the above crystal structures [81-83] regarding cation locations were very poorly refined and not very reliable because the XRD data were collected using a conventional X-ray source, which cannot provide high resolution data for powder structure refinement.

Solid state MAS-NMR has been used widely for zeolite characterization, even for the high siliceous ZSM-5 [84, 85]. This technique provides direct information about dealumination and changes of chemical coordination environments of Al and Si in the zeolites. Mastikhin, et al [86, 87] studied NO decomposition and reduction on H-ZSM-5 with $^{15}$N-NMR. By using isotopic-exchange experiments, they identified N$_2$ and N$_2$O as products of NO disproportionation over H-ZSM-5. The N$_2$ product cannot be detected by FT-IR. Grinsted, et al [79] presented a very well resolved $^{27}$Al-MAS NMR evidence for dealumination in ZSM-5 caused by water vapor in the reaction stream. A sharp decrease of the $^{27}$Al-MAS NMR peak at 54 ppm was observed on both H-ZSM-5 and Na/Cu-ZSM-5 after steaming at 700°C, but the extent of dealumination on Na/Cu-ZSM-5 was 75% compared to 97% on H-ZSM-5. This result indicates that the introduction of Cu$^{2+}$ into ZSM-5 stabilizes the framework structure. However, the extracted aluminum from the zeolite framework was hard to identify by an increase in the peak associated with octahedral Al because this small amount of Al may exist in small aggregates of low symmetry (amorphous) [88].

EXAFS and XANES are powerful tools for characterizing the local coordination of catalytic centers and the oxidation states, even for obtaining information on the secondary coordination of catalytically active centers. This information cannot be obtained with the conventional X-ray diffraction method. An increase in the coordination number of copper ions with oxygen was observed with EXAFS and XANES from 3.5 to 3.8 after calcination of Cu-ZSM-5 in the presence of oxygen [54]. More recently, Liu and Robata [89] used XANES to correlate the catalytic activity of Cu-ZSM-5 for NO decomposition with the amount of cuprous ion, Cu$^+$, present. They found that Cu$^{1+}$ signal intensity increased with increasing temperature up to 500°C in a pattern similar to NO decomposition. The Cu$^{1+}$ signal intensity still increased with temperature after 500°C, however, the Cu-ZSM-5 activity decreased.
Dedecek, et al [90] studied sitting and redox behavior of Cu ions in Cu/H-ZSM-5 zeolites using photoluminescence. The Cu/H-ZSM-5 catalysts were prepared by ion exchange using an aqueous CuCl₂ solution with a molar concentration ranging from 0.001 to 0.01 at a temperature of 27 or 57 and over a time period of 1-12 hours. The Cu exchange levels in ZSM-5 with a low ratio of Si/Al (17.3) were changed from 1.9 to 45%, while in ZSM-5 with a high ratio of Si/Al (22.6) from 5.4 to 46%. They identified the Cu²⁺ ions at two exchangeable sites in the Cu/H-ZSM-5 after Cu²⁺ reduction to Cu¹⁺. The one site was reflected in the blue (480 nm) band, close to the two framework aluminum atoms, and another in the yellow-green (540 nm) band, adjacent to one framework aluminum atom. The sites close to the two aluminum atoms are preferentially occupied. The Cu²⁺ dominates in the Al-rich zeolites (low Si/Al ratio) and low Cu content. On the other hand, in the silica-rich zeolites (high Si/Al ratio) with a high Cu exchange level, the Cu ion entities with an extra ligand prevail. In zeolites with high Si/Al ratio the reduction of Cu ions is much easier than in those with low Si/Al ratio.

In summary, various techniques have been used to characterize Cu-ZSM-5, and some information on Cu sitting and oxidation states of Cu in ZSM-5 has been obtained. However, most of the data were collected at room temperature or lower, which may not reflect the actual sitting and oxidation distribution of copper during the reaction. At the present time, no data on Cu²⁺ and Cu⁺ distribution in Cu-ZSM-5 is available under reaction temperature (350-600°C). This work needs to be performed to gain more insight into the NO decomposition mechanism over Cu-ZSM-5.

1.2.5 Mechanic Studies of NO Decomposition

Two mechanisms of NO decomposition over Cu-ZSM-5 catalysts have been proposed. Mechanism I is the Redox mechanism [40, 44] in which the reaction network is simplified as follows:

\[
\begin{align*}
2 \text{Cu}^{2+} & \xrightarrow{\text{elevated T}} \text{Cu}^{2+} - \text{O}_2 \\
& \quad \downarrow \\
2 \text{Cu}^{2+} + 2 \text{NO} & \rightarrow 2 \text{Cu}^{2+} - \text{O}_2, \text{N}_2
\end{align*}
\]
Mechanism II [91] proposes that Cu\(^{2+}\) ions are the active sites, instead of Cu\(^{+}\) as suggested in mechanism I. These sites are positioned to chemisorb NO molecules in the gem-dinitrosyl form. The pair of adsorbed NO molecules desorbs as N\(_2\) and O\(_2\). The reaction path is given as:

\[
\text{Cu}^{2+}: \text{NO} + \text{NO}_2 \rightleftharpoons \text{Cu}^{2+} \, \text{(gem-dinitrosyl)} \quad (2).
\]

The main unsolved question about mechanism I is that the pairing of nitrogen by the interaction of the two NO species, each adsorbed on a different copper site, does not seem probable since the copper ions are spaced too far apart in high-silica zeolites. More recently, the desorption of O\(_2\) during NO decomposition on Cu-ZSM-5 reported by Valyon, et al. [92] showed high mobility of the lattice oxygen ions in self-diffusion. The authors stated that this result could be used to explain the problem of how two extralattice oxygen atoms located at positions remote from each other may combine to form the O\(_2\) molecules which are spontaneously desorbed in these redox reactions. For mechanism II, if equation (2) is the reaction limiting step, the catalytic activity is more likely to be second order in NO partial pressure. More experimental data are needed to support this mechanism. There are conflicting reports on the reaction order in NO, between 1 - 1.6 [40, 44].

### 1.3 Thesis Objectives

Copper ion-exchanged ZSM-5 zeolite is presently the most active catalyst for direct decomposition of nitric oxide (2 NO \(\rightarrow\) N\(_2\) + O\(_2\)) in the effluent gas streams from combustion flue gases. The drawbacks of Cu-ZSM-5 catalysts for the reaction are low catalytic activity at both low (< 400°C) and high (> 550°C) temperatures, O\(_2\) inhibition of the catalytic activity, and hydrothermal stability of the Cu-ZSM-5 structure. Preliminary work has indicated that addition of other metal ions into Cu-ZSM-5 may be beneficial. The overall objective of this thesis was to improve the performance of Cu-ZSM-5 catalysts for NO decomposition in O\(_2\)-containing gas streams as well as wet gases, and to shed more light on the mechanism of NO decomposition over Cu-ZSM-5 catalysts.

The specific objectives of the thesis are:

1. To examine effects of catalyst preparation on the copper distribution in ZSM-5 zeolite and catalytic activity;
(2) To conduct a parametric study of the effects of cocations on the catalytic activity of Cu-ZSM-5 under various conditions;

(3) To examine the water vapor effects on the Cu-ZSM-5 active sites, and structural changes of Cu-ZSM-5 and metal-ion modified Cu-ZSM-5;

(4) To measure the NO decomposition kinetics in the presence and absence of oxygen in Cu-ZSM-5 and metal-ion modified Cu-ZSM-5.
Chapter 2

EXPERIMENTAL METHODOLOGIES

Metal ion modified ZSM-5, including Cu-ZSM-5 and M/Cu-ZSM-5, catalysts are highly complex materials, as mentioned in Chapter 1, and fundamental problems exist on how to prepare the materials to show better catalytic activity for NO decomposition and how to correlate the catalytic behavior with physical and chemical properties. In this Chapter, the procedure of catalyst preparation developed in this research will be first presented and discussed. Bulk elemental composition of the resulting materials was analyzed by Inductively Coupled Plasma Spectrometry (ICP) and Atomic Absorption (AA) Spectrometry. Catalytic activities and deactivation of Cu-ZSM-5 and M/Cu-ZSM-5 catalysts were evaluated in a laboratory-scale fixed bed reactor constructed in this study. Analytical methods used for characterizing the zeolite crystal structure, phase composition, surface properties, and elemental distribution in the catalysts were X-Ray Diffraction (XRD), Scanning Transmission Electron Microscopy coupled with Energy Dispersion X-Ray microprobe analysis (STEM/EDX), X-ray Photoelectron Spectroscopy (XPS) and Photoluminescence.

2.1 ZSM-5 ZEOLITE AND ION EXCHANGE

ZSM-5, patented by Argauer and Landolt [93] and widely used in the conversion of methanol to gasoline, dewaxing of distillates, and the interconversion of aromatic compounds [94], is a 10-oxygen member ring zeolite with two distinct sets of the intersecting channels. One is zig-zag and has essentially circular openings (0.54 x 0.56 nm) parallel to the a-axis or [100]; the other straight with slightly elliptical openings (0.51 x 0.55 nm) parallel to the b-axis or [010]. Flanigen, et al [95] calculated the free cross section by assuming that oxygen ions have radius of 1.3 Å. Figures 2.1a and 2.1b show ZSM-5 structure on planes (100) and (010) [96]. The intersecting channels form a three-dimensional framework with a coordination number of 4; each intersection connects to four other neighboring intersection channels. The size of the intersections is about 9 Å in diameter [97]. The distances between intersections are about 10 Å for straight channels and 12.0 Å for sinusoidal
Figure 2.1a Diagram of the (010)-face of the ZSM-5 unit cell. The x-axis is horizontal and the z-axis is vertical. Atom on a corner is either Si or Al. The line represents -O-. The 10-membered ring apertures shown are the straight channels which is parallel to [010] (from reference [96]).

Figure 2.1b Diagram of the (100)-face of the ZSM-5 unit cell. The y-axis is horizontal and the z-axis is vertical. Atom on a corner is either Si or Al. The line represents -O-. The nearly circular 10-membered ring apertures shown are the sinusoidal channels which is parallel to [100] (from reference [96]).
channels, respectively [98].

ZSM-5 crystallizes in the idealized orthorhombic system with space group Pnma and lattice constants of \( a = 20.1 \), \( b = 19.9 \), \( c = 13.4 \) Å; monoclinic symmetry has also been observed [96, 99]. A unit cell of ZSM-5 contains 96 Tetrahedral (T) Si or Al and 192 oxygen atoms, and the ratio of Si to Al usually is larger than 10. Aluminum is trivalent, whereas silicon is tetravalent. Thus, cations are needed to neutralize the negative charges associated with the framework aluminum ions because of the presence of \((\text{AlO}_2)^-\) in the ZSM-5 crystal. Therefore, the unit cell formula is usually written as

\[
M^{n+}x/n[(\text{AlO}_2)^-x(\text{SiO}_2)^{98-x}](\text{H}_2\text{O})_y
\]

where \( M \) is the cation of valence \( n \). In commercial ZSM-5 zeolite, \( M \) is either \( \text{H}^+ \) or \( \text{Na}^+ \), and can be replaced by other cations, such as alkali, alkaline earth or transition metal ions. In some cases, the exchange reaction may occur to completion or fail to do so, depending on the nature of ion and reaction temperature.

The replacement of ion \( B^{b+} \) in ZSM-5 by ion \( A^{a+} \) in aqueous solution can be simply expressed by the following charge-balanced equation:

\[
b A_s^{a+} + a B_2^{b+} \rightleftharpoons b A_2^{a+} + a B_s^{b+}
\]

An equilibrium is established for the reaction (2.2). The overall thermodynamic equilibrium constant \( K \) is defined as:

\[
K = \frac{f_A^b Z_A^{b} Z_B^{a} M_A^b}{f_B^a Z_A^{a} Z_B^{b} M_B^a} = N_K A^{f_A^b} A^{f_B^a}
\]

where \( a \) and \( b \) are the ionic charges of ions \( A^{a+} \) and \( B^{b+} \); \( f_a \) and \( f_b \) are the rational single ion activity coefficients in the zeolite phase; \( \mu_A \) and \( \mu_B \) are the molar single ion activity coefficients in the zeolite phase; \( Z_a \) and \( Z_b \) are the equivalent fraction in the zeolite phase. \( M_a \) and \( M_B \) are the molarities of ions \( A \) and \( B \) in the solution phase, \( K \) is the thermodynamic equilibrium constant for the ion exchange reaction, \( s \) and \( z \) are subscripts which identify the
solution and zeolite phases, and $N_{K_b}A$ is the rational selectivity coefficient [100].

In equilibrium studies, the function of primary interest is the selectivity of the ion exchanged. This is defined quantitatively in terms of the separation factor ($\alpha_B^A$) such as

$$\alpha_B^A = \frac{Z_A S_B}{Z_B S_A}$$ (2.4)

where $\alpha_B^A$ is the separation factor of ion A over ion B and $Z_A$, $Z_B$, $S_A$, and $S_B$ are ionic fractions of A and B in the zeolite and solution phase, respectively.

Chu and Dwyer [101] studied a number of monovalent, divalent and trivalent metal ions-Na$^+$ isotherms, and obtained the $\alpha_{Na}^X$ with an equimolar equilibrating solution ($S_X = S_{Na} = 0.5$) at 25°C. All Na$^+$ ions are replaced by divalent ions and their selectivity sequence is

$$\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Ba}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}$$

With the monovalent ion series, the selectivity is directly proportional to the bare ionic radius, i.e., the larger the bare ionic radius the higher the selectivity. The selectivity is in following order:

$$\text{Cs}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Ag}^+ > \text{Na}^+ > \text{Li}^+$$

For trivalent ions, the selectivity sequence is

$$\text{La}^{3+} > \text{Al}^{3+}.$$  

From the above results, we can foresee that it is difficult to reach high ion exchange level for the low-selectivity metal ion if Na-ZSM-5 is simultaneously ion-exchanged with two metals of very different selectivity.

2.2 DEVELOPMENT OF PREPARATION TECHNIQUES AND ELEMENTAL ANALYSIS OF CATALYSTS
2.2.1 Development of Catalyst Preparation Techniques
In this work, Cu-ZSM-5 and metal ion modified Cu-ZSM-5 were prepared by incorporating metal cations into ZSM-5 zeolite supports through ion exchange in a dilute aqueous solution. The starting material was Na\(^+\) form of ZSM-5 zeolite (Na-ZSM-5) with Si/Al ratio of 21.5 synthesized by the Davison Chemical Division of W. R. Grace & Co. This zeolite was in the form of fine powder (<5\(\mu\)m). The as-received analyses of the Na-ZSM-5 are listed in Table 2.1.

<table>
<thead>
<tr>
<th>SiO(_2)/Al(_2)O(_3)</th>
<th>Al(_2)O(_3) (wt.%)</th>
<th>SiO(_2)</th>
<th>Surface Area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>3.716</td>
<td>94.0</td>
<td>400</td>
</tr>
</tbody>
</table>

Data provided by Davison, W. R. Grace & Co.

The Na-ZSM-5 materials can be represented by the following simplified structure:

\[
\begin{array}{c}
\text{Na}^+ \\
\text{Si} \\
\text{Al} \\
\text{Si} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Na}^+ \\
\text{Si} \\
\text{Al} \\
\text{Si} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]

(2.5)

If Na\(^+\) is replaced by Cu\(^{2+}\), the structure becomes

\[
\begin{array}{c}
\text{Cu}^{2+} \\
\text{Si} \\
\text{Al} \\
\text{Si} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]

(2.6)
Here one Cu\(^{2+}\) ion will neutralize the negative charges associated with two (AlO\(_2\))\(^{-}\) groups. Therefore, 100% metal ion (of n valence) exchange level in the catalysts is defined as one metal ion replacing n Na\(^{+}\) [or neutralizing n (AlO\(_2\))\(^{-}\)] and the atomic ratio of (metal ion)/Al = 1/n, e.g., Cu\(^{2+}\)/Al = 0.5. The ion exchange level can be calculated by n x (metal ion/Al) x 100%, where the metal ion/Al ratio was measured by ICP.

Repetition exchange of Cu ion with Na-ZSM-5 could lead to Cu "over-exchanged" Cu-ZSM-5, even before ion exchange, Na\(^{+}\) cations neutralize the negative charge associated with the T-aluminum in the ZSM-5 framework. For stoichiometric exchange of copper for sodium, the Cu/Al ratio should be 0.5 assuming that one Cu\(^{2+}\) charge compensates two aluminum sites (or exchange for two sodium ions). The over exchanged copper is attributed to formation and exchange of [Cu\(^{2+}\)OH\(^{-}\)]\(^{+}\) [102]. Using this hypothesis, Larsen, et al [74] reported that the sum of Cu/Al and Na/Al was unity for Cu copper exchange levels below ~70% but that was not the case for 92-100% exchange, implying either that some copper is exchanged into Na-ZSM-5 as bare ion or that H-Brösted acid sites were also formed in the sample with high copper loading. However, it is still not clear how much Cu\(^{2+}\) is in the form of [Cu\(^{2+}\)OH\(^{-}\)]\(^{+}\) in the samples.

In this study, the procedures of catalyst preparation were developed to obtain materials with improved catalytic activity and hydrothermal stability for NO decomposition. For catalysts containing copper only, the Na-ZSM-5 zeolites were ion-exchanged with Cu\(^{2+}\) in an aqueous cupric acetate solution with concentration of 0.007 M. This is according to well-established procedures in the literature [37, 38]. The number of Cu\(^{2+}\) ions in the solution were twice as many as what is needed stoichiometrically to replace all Na\(^{+}\) ions in the zeolite phase. The slurry was vigorously stirred by a magnetic stirrer at room temperature for 19 hours. After the Cu ion exchange, the sample was filtered, and washed with deionized water at room temperature for 30 minutes to 2 hours. The initial pH of the aqueous cupric acetate solution was 5.74 and the final pH was 5.65. High Cu\(^{2+}\) exchange level was achieved by repetition of the above procedures. The Cu-ZSM-5 was finally dried in air at 100°C for 10 hours and kept in a dessicator.

Na-ZSM-5 ion exchange with Cu cations is a slow process at room temperature, especially when a Cu exchange level in ZSM-5 of over 100% was
reached in a prior step. Raising temperature of the aqueous slurry of cupric acetate and ZSM-5 accelerates the exchange reaction. However, it was found that Cu would precipitate in the pores of ZSM-5 crystal if the temperature was higher than 40°C. Such Cu-ZSM-5 materials were found less active for NO conversion to N₂ and O₂, compared with catalysts prepared with the same Cu/Al ratio at 20°C. Therefore, all Cu ion-exchanges with Na-ZSM-5 zeolite were performed at room temperature.

The preparation procedures of metal ion modified Cu-ZSM-5 were different from that of Cu-ZSM-5. The ZSM-5 zeolite was first ion-exchanged with theocation in dilute aqueous nitrate solution (0.007 M). The exchanges were made either at room temperature for 10 hours or at 85°C for 2 hours. After filtration, the metal ion-exchanged ZSM-5 materials were dried at 100°C for 10 hours, some of them were further calcined in air at 500°C for 2 hours. To obtain high cocation exchange level, the same procedure would be repeated. The M-ZSM-5 materials were further ion-exchanged with Cu²⁺ in an aqueous solution (0.007 M) of cupric acetate at room temperature for 19 hours. This was repeated several times, depending on the desired Cu exchange levels. Finally, the catalysts were washed with deionized water at room temperature and dried at 100°C for 10 hours.

The mode of exchange described above was the evolution of several different preparation methods. A summary of the observations made during this procedure when using M (of valence n ≥ 2) as the cocation is as follows: (a) exchanging copper ions first or co-exchanging copper and Mⁿ⁺ ions with the Na-ZSM-5 zeolites did not succeed in high-exchange levels of Mⁿ⁺ in the zeolites; (b) even when Mⁿ⁺ was ion-exchanged first followed by copper ion exchange, we would observe loss of most Mⁿ⁺ from the ZSM-5 back to solution. Both (a) and (b) can be explained by fact that the separation factor of ion Cu²⁺ over ion Na⁺ is higher than those of the ion Mⁿ⁺ over ion Na⁺ [101], i.e., the result of a more favorable exchange equilibrium for Cu²⁺/Na⁺; (c) when the Mⁿ⁺ ion solution was heated to 85°C, and was stirred with the Na-ZSM-5 for 2 hours, higher levels of exchange were achieved and better stability in subsequent room temperature copper ion exchange. However, a number of Mⁿ⁺ ions were still replaced by Cu²⁺; (d) air calcination of Mⁿ⁺-ZSM-5 zeolites at 500°C for 2 hours was very effective to keeping the Mⁿ⁺ exchange high even after subsequent copper ion exchanges. During ion exchange, hydrated or hydrolyzed metal may be exchanged into ZSM-5.
During air calcination metal dehydration or decomposition of the hydrolyzed form produce bare ions which are more strongly associated with the framework aluminum. Therefore, the metal stability in the ZSM-5 is improved. This procedure, summarized in Table 2.2, was followed in preparing all metal ion modified Cu-ZSM-5 catalysts in this study. Kagawa, et al [50] have also reported that a positive effect of cocation on Cu-ZSM-5 activity in a dry, O2-free reaction stream was shown only when Na-ZSM-5 was ion exchanged with cocation followed by Cu ion exchange.

Table 2.2 Procedures of Catalyst Preparation

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Na-ZSM-5 (Si/Al= 21.5)}$</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Exchange } M^{n+}$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Aqueous Solution } 0.007 \text{ M, } M(\text{NO}_3)_n$</td>
</tr>
<tr>
<td>4</td>
<td>Dry at $100^\circ\text{C, 10 h.}$, Calcine at $500^\circ\text{C, 2 h.}$</td>
</tr>
<tr>
<td>5</td>
<td>$\text{Exchange } \text{Cu}^{2+}$</td>
</tr>
<tr>
<td>6</td>
<td>$\text{Aqueous Solution } 0.007 \text{ M, } \text{Cu(Ac)}_2$</td>
</tr>
<tr>
<td>7</td>
<td>$20^\circ\text{C, 20 h.}$, 1- 3 times</td>
</tr>
<tr>
<td>8</td>
<td>$\text{Heat Treatment}$</td>
</tr>
<tr>
<td>9</td>
<td>Wash, Dry at $100^\circ\text{C, 10 hours}$</td>
</tr>
</tbody>
</table>

\text{Catalyst Ready for Use}
These procedures were also used for preparation of rare earth ion-modified Cu-ZSM-5. However, it should be noted that for the rare earth ion exchanges, the importance of the exchange sequence and/or the intermittent calcination was not checked.

2.2.2 Elemental Analysis of Catalysts
Catalyst elemental analyses were performed by Inductively Coupled Plasma Spectrometry (ICP: Perkin-Elmer Plasma 40). Multi-elements can be measured simultaneously, after Cu-ZSM-5 or M/Cu-ZSM-5 materials were dissolved in HF (48%). Atomic Absorption Spectroscopy (AA) was used to verify some results measured by ICP.

For Cu-ZSM-5 and M/Cu-ZSM-5 (M ≠ Ce) materials, about 0.03 g of the sample was added in 4 ml of 48% HF to dissolve the zeolite. The solution was then shaken by hand for 10 minutes, then diluted by adding 96 ml of deionized water.

Preparation of Ce/Cu-ZSM-5 sample for ICP analysis is different from that described above, since Ce cation is fluoride insoluble. The special dissolution reagents purchased from UniSol consist of three types of solutions: UA-4, UNS-2A and UNS-2B. The UA-4, containing HF, dissolves the catalysts, the UNS-2A and UNS-2B neutralize and stabilize the solution to (a) deactivate the HF by increasing the pH to a value of 7.5 to 8.0, and (b) maintain solubility of the samples. Standard solutions were prepared by keeping the same amount of each reagent as that in the sample solutions. As a result, standard solutions would have similar viscosity to sample solution.

ICP standard solutions for the elements, such as Si, Al, Na, Li, K, Mg, Ca, Sr, Ba, Y, Ce, Mn, Co, Ni, Pd, Cu, Ag, and Zn, were purchased from Scientific Products. The ICP instrument was first calibrated with the standard solutions of different metal concentrations before measurements were carried out. Characteristic emission wavelengths, at which radiation intensity was measured, for some of those elements are as follows:

<table>
<thead>
<tr>
<th>element</th>
<th>Si</th>
<th>Al</th>
<th>Na</th>
<th>Li</th>
<th>K</th>
<th>Mg</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength (Å)</td>
<td>251.6</td>
<td>396.2</td>
<td>589.6</td>
<td>670.8</td>
<td>766.5</td>
<td>279.6</td>
<td>407.8</td>
<td>455.4</td>
</tr>
<tr>
<td>element</td>
<td>Y</td>
<td>Ce</td>
<td>Mn</td>
<td>Co</td>
<td>Ni</td>
<td>Pd</td>
<td>Cu</td>
<td>Ag</td>
</tr>
<tr>
<td>wavelength (Å)</td>
<td>371.0</td>
<td>394.3</td>
<td>257.6</td>
<td>238.9</td>
<td>221.6</td>
<td>340.5</td>
<td>324.8</td>
<td>328.1</td>
</tr>
</tbody>
</table>
Figure 2.2 is representative of ICP calibration curves, in which a linear relationship between copper, magnesium and sodium emission intensities and the elemental concentrations in the standard solutions is displayed.

After the ICP instrument had been calibrated, sample solution was injected into the ICP plasma torch to be analyzed. The concentration of each metal in the solution was calculated and printed out by computer.

Atomic Absorption Spectroscopy was used to check the results obtained by ICP. It was found that the results obtained by two techniques were in good agreements (± 6.5%). Table 2.3 shows two of these sample comparisons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu Concentration in Solution (ppm)</th>
<th>Measured by ICP</th>
<th>Measured by AA</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>10.1</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>#2</td>
<td>11.6</td>
<td>12.3</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.2a  Calibration of ICP for elements Na and Cu
2.3 EXPERIMENTAL SETUP

A laboratory-scale fixed-bed reactor system, as shown schematically in Figure 2.3, built in this work was used to evaluate the nitric oxide decomposition activity of the catalysts. The reactor consists of a 60 cm long quartz tube with inside diameter equal to 1.1 cm (for NO conversion measurements) or 0.4 cm (for kinetic studies). A porous quartz fritted disk was placed in the middle of the reactor tube to support the catalyst bed. The reactor was placed in a temperature-programmed, three-zone heated furnace that was electrically heated and controlled by a temperature controller (Tetrahedron: Model Wizard). Three mass flow controllers were used to measure flow rates of NO-He, O₂-He and He. The O₂-He line was electrically heated upstream of the reactor to avoid the reaction between NO and O₂ which is thermodynamically favorable at low temperature. A Matheson certified standard gas mixture of 4% NO-He was used to blend with other gases to get a desired mixture. A pure He or O₂-He flowing through deionized water in an electrically heated bath entrained water vapor to the reactor. An electrically heated stainless steel tubing connected the water bath and the reactor. Water vapor pressure in the saturator was adjusted by varying the bath temperature.
Figure 2.3 Laboratory-scale fixed bed reactor system.
Mass flow controllers were calibrated for each gas, accordingly, at a gas pressure of 40 psig.

A gas chromatograph (Hewlett Packard: Model 5890) with a thermal conductivity detector and a 5Å molecular sieve column of 1/8 inch O.D. by 6 feet long was used to measure the concentrations of N₂, O₂, and NO in the effluent gas stream. The GC was calibrated for NO, N₂ and O₂ at a total flow of 60 cm³/minute and an oven temperature of 35°C. A NO-NOₓ analyzer (Thermo Electron: Model 14A), which can measure NO and NOₓ concentrations ranging from 0.001 ppm to 2,500 ppm, was occasionally used to monitor NO and NO₂ concentration. A dry-ice cold trap was attached to the exit of the reactor to condense the water vapor before the exhaust stream reached the gas chromatograph. The NO conversion to N₂ was calculated as 
\[(2 \times \text{N}_2 \text{ concentration in the effluent flow})/(\text{NO concentration in the feed gas}) \times 100\%\]

An amount of 0.5 gram of the catalyst was placed in the reactor for NO conversion measurements, or 0.03 g for kinetics studies. Because the catalyst was in fine powder form (≤ 5µm), the pressure drop in the reactor was in the range of 1.2–1.6 atm depending on the flow rate used. The contact time, W/F, defined as the ratio of the catalyst weight in the reactor to the total flow rate of the feed stream, was equal to 1.0 g s/cm³ (NTP) for the NO conversion measurements, or 0.03 g s/cm³ (NTP) for the kinetics studies.

In a typical run, the fresh catalyst was pretreated in pure He stream at 500°C for 2 hours, after it had been dried in pure He at 150°C for 30 minutes. Then, the sample was exposed to the reactant gas stream. All measurements were made after reaction had reached a steady-state.

2.4 CATALYST CHARACTERIZATION

Characterization of fresh and used catalysts by XRD, STEM/EDX, XPS and Photoluminescence was performed to correlate the catalytic behavior with physical and chemical properties. Sample preparation and measurement procedure for each individual technique are summarized in the following sections.
2.4.1 X-Ray Powder Diffraction
A Rigaku RU-300 X-ray powder diffractometer equipped with a rotating copper anode generator was used to examine the crystal structures in fresh and used catalysts. X-Ray diffraction from various crystallographic planes follows Bragg’s law [103]:

\[ n\lambda = 2d\sin\theta \]  \hspace{1cm} (2.7)

where \( \lambda \) is the X-ray wavelength, \( d \) is the d-spacing of plane, \( \theta \) is the diffraction angle, and \( n \), the order of diffraction, is an integer. In this study, a copper anode generator was used at 1.54 Å wavelength. In crystalline specimens, scattering of the incident X-ray beam occurs in specific directions defined by equation (2.7).

A small amount of sample was well mixed with colloid by hand. A layer of the mixture was placed on a 0.5” x 1.0” glass, and dried in an oven at 100°C for about 1 hour. An aluminum frame was used to support sample. The diffraction patterns were taken in the 2\( \theta \) range of 5-80° at a scanning speed of 1° per minute.

A DEC VAX Station II computer was used for instrument control and data acquisition as well as for data processing. Diffraction peak identification, compound (search/match) identification, lattice parameter determination and unit cell indexing, etc. were performed using data analysis software.

2.4.2 Scanning Transmission Electron Microscopy and Electron Microprobe Analysis
A scanning transmission electron microscope (STEM) is a transmission electron microscope that can be used to examine thin sample sections in a scanning mode. The principles of STEM operation are based on several important interactions, which contribute electron image, of the electron beam with the specimen. They are electron absorption, diffraction, elastic scattering, and inelastic scattering. Incident electrons from the beam, are transmitted through the specimen to form three types of electrons: unscattered, inelastically scattered (low angle), and elasticity scattered (high angle). The directly transmitted electrons form bright-field image, while the widely scattered electrons from the specimen form a dark-field image. Since the primary electron beam is focused on a point source and scans the
specimen, sections of greater thickness can be examined under scanning mode, and better analytical resolution can be obtained by X-ray analysis.

A top-of-the-line Vacuum Generators HB603 Scanning Transmission Electron Microscope operated at 300kV was used to characterize the fresh and used catalyst samples. The electron source is of the field-emission type, enabling very small high intensity electron probes to be formed. Ultimately the imaging resolution can approach 0.14 nm. The windowless X-ray detector has very high geometrical efficiency, leading to exceptional X-ray microanalytical capability. The fresh samples were calcined in a muffle furnace in air at 500°C for 2 hours. The catalyst samples were supported by a 200 mesh, carbon film-covered, plain nickel in the STEM chamber. The plain nickel-supported samples were coated by carbon in vacuum to further ensure no particle charging during STEM analyses. The elemental composition of interested areas on the samples was analyzed by Energy Dispersive X-ray Micro Probe technique, and elemental distributions were simultaneously obtained by the X-ray mapping technique.

2.4.3 Surface Composition Analyses by X-ray Photoelectron Spectroscopy (XPS)
The theoretical foundation of XPS was Einstein’s well-known photoeffect equation:

\[ h\nu = E_b + E_k \]  \hspace{1cm} (2.8)

where \( h\nu \) is the energy of incident electron, \( E_b \) the binding energy of the electron in the sample material and \( E_k \) the kinetic energy of the ejected electron from the specimen. The method of the XPS can be summarized as the measurement of the kinetic energy of the inner electron ejected by an incident photon with a known energy \( h\nu \). In reality, equation (2.8) is modified as

\[ E_b = h\nu - E_k - \phi \]  \hspace{1cm} (2.9)

where \( \phi \) is the work function of spectrometer materials. From the values of the energies on the right hand side of equation (2.9), it is easy to calculate \( E_b \), the binding energy, which is a sensitive characteristic of elements and chemical state in a compound.
In this study, X-ray-excited photoelectron spectroscopy (Perkin Elmer, model 548 ESCA) with 2 mm spatial resolution was used to determine the elemental concentrations of copper, silicon, aluminum, oxygen and cerium on the surface of materials. A MgKα anode X-ray source (300 W, 15 kV by 20 mA) provides high signal intensity, and 178 eV of a fixed pass energy was used. Base pressure was lower than 7.5 x 10^-8 torr in vacuum chamber.

A layer of catalyst samples in powder form was pressed on a double-sided transfer tape adhered on a 1" x 0.5" aluminum sheet. The sample, then, was introduced into XPS vacuum chamber, after it had been placed on a sample holder. XPS analyses were performed after a desired low pressure was reached in the vacuum chamber.

2.4.4 Ce-Containing Catalyst Characterization by Luminescence

Cerium(III) luminescence spectra were recorded on a SPEX spectrofluorometer (Model No. 1501 and 1502) equipped with DM 3000 Software, SPEX Industries, Co. Spectra of fresh and used Ce-ZSM-5 and Ce/Cu-ZSM-5 catalysts were recorded by loading about 0.3 grams of the material into a quartz cell.

Luminescence measurements were performed by two steps. The first was to find the excitation wavelength at which the maximum intensity of Ce³⁺ photoluminescence would be achieved. Radiation energy of Ce³⁺ was measured at a wavelength of 359 nm, which was characteristic Ce³⁺ luminescence in Ce³⁺ ion-exchanged Y zeolites [104] when the wavelength of the excitation light was changing from 240 to 329 nm. The maximum intensity of Ce³⁺ luminescence was detected when the wavelength of excitation light was 295 nm. The second step was to take the Ce³⁺ luminescence spectra in the wavelength range of 320~510 nm when a sample was exposed to the light of 295 nm.

2.5 SUMMARY

The procedures of catalyst synthesis, evaluation and characterization are summarized in this Chapter. Active Cu-ZSM-5 catalysts were prepared by ion exchange between Cu²⁺ cations and Na⁺-ZSM-5 materials in dilute aqueous cupric acetate solution at room temperature. M/Cu-ZSM-5 catalysts were synthesized by incorporating M¹⁺ into Na-ZSM-5 first at 85°C for 2 hours,
then drying at 100°C for 10 hours. After the M-ZSM-5 had been calcined in air at 500°C for 2 hours, it was ion-exchanged with Cu$^{2+}$ at room temperature. The experimental procedures of running the reactor system and analyzing gas products, catalyst elemental analysis, and characterization techniques used in this study were briefly summarized in this Chapter.
Chapter 3

NITRIC OXIDE DECOMPOSITION
OVER CU-ZSM-5 CATALYSTS

As reviewed in Chapter 1, the copper ion-exchanged ZSM-5 zeolite is the most active catalyst for nitric oxide decomposition. Conversion of NO to N₂ and O₂ over Cu-ZSM-5 materials is not a linear function of copper ion-exchanged level, and very low catalytic activity exists for up to 30% Cu exchange level [38- 40]. Excessively-exchanged Cu-ZSM-5 catalysts are more active since either copper ions adequately populate sites accessible to NO or catalytic activity only emerges if enough adjacent copper active sites exist [44, 51, 105]. However, Campa, et al [106] reported the excessively exchanged portion of the Cu ions to be completely inactive. The mechanism of NO decomposition was proposed to involve a redox process of Cu²⁺ ←→ Cu¹⁺ [40, 44, 58]. Using in-situ XANES measurements, Liu. et al [89, 107] reported that the Cu¹⁺ concentration increased in a dry NO mixture with increasing reaction temperature. Therefore, the authors claimed that the NO decomposition is a redox process. However, Shelef [91] proposed that single Cu²⁺ ions are the active sites for dinitrosyl intermediates, instead of two Cu¹⁺ sites suggested by the redox mechanism.

In this chapter, Cu-ZSM-5 catalysts with different copper ion-exchanged levels ranging from 10- 141% are prepared in aqueous copper acetate solutions. NO conversion to N₂ over the Cu-ZSM-5 catalysts, effect of catalyst pretreatment on the Cu-ZSM-5 catalytic activity are examined. The Cu-ZSM-5 catalytic activities are correlated with the amount of square planar four-coordinated Cu²⁺ cations in Cu-ZSM-5 catalysts. Issues of Cu cation oxidation state, and interaction with NO and O₂ during the NO decomposition is not considered in the chapter.

3.1 EXPERIMENTAL

3.1.1 Catalyst Preparation and Characterization
Cu-ZSM-5 catalysts were prepared by exchanging Cu$^{2+}$ cations into Na$^+$ form of ZSM-5 zeolite in dilute aqueous copper acetate, Cu(C$_2$H$_3$O$_2$)$_2$, solutions. The parent Na-ZSM-5 (Si/Al = 21.5) was in fine powder form (< 5µm) obtained from the Davison Chemical Division of W. R. Grace & Co. The Cu-ZSM-5 materials were prepared by following the procedures described in Chapter 2. Low Cu exchange levels were achieved by adjusting the ratio of Cu$^{2+}$ to Na$^+$ in the slurry of Na-ZSM-5 and cupric acetate. Repetition exchanges were made to get the excessively copper-exchanged Cu-ZSM-5.

It is noteworthy that some copper easily precipitates on the ZSM-5 instead of ion-exchanged when the Cu exchange process was carried out at temperatures higher than 40°C since Cu(OH)$_x$ decomposed to form CuO, which is inactive for the NO decomposition. Copper loading on the ZSM-5 zeolite was found to vary greatly with the pH of the cupric acetate solution. For low pH, Na cations in ZSM-5 will be replaced by not only Cu ions but also protons. The exchange between the Na$^+$ and H$^+$ leads to low copper ion exchange level. However, if Cu ion exchange is made at high pH, copper deposits on the external surfaces and voids of the ZSM-5 crystals. It was found that the optimal pH was about 5.7, which was used later. The Cu-ZSM-5 preparation effects on the copper states will be examined in next chapter.

Elemental analyses were performed by ICP after the catalyst samples were dissolved in HF solution. Analytical results of the prepared Cu-ZSM-5 are listed in Table 3.1. A Na/Al ratio of unity indicates that sodium cations stoichiometrically neutralize the negative charges associated with the framework aluminum atoms in the as-received Na-ZSM-5. For stoichiometric exchange of copper for sodium, one Cu$^{2+}$ charge compensates two aluminum sites. Table 3.1 shows that the (2 Cu + Na)/Al approximately equals 1.0 for the catalysts with copper exchange level up to about 73%. These results imply that the bare Cu$^{2+}$ dominates in the low Cu exchanged ZSM-5 materials, which is in agreement with the literature [90]. However, the Cu$^{2+}$ ion-exchanged level can exceed 100% (2 Cu/Al x 100%), e.g., in Cu(141)-ZSM-5, this suggests that some Cu$^{2+}$ hydrolyzes and exchanges into ZSM-5 as [Cu$^{2+}$(OH)]$^+$ [102]. Larsen, et al [74] proposed all copper was exchanged into Na-ZSM-5 as [Cu$^{2+}$(OH)$^-$]$^{1+}$ with the rest of the charge compensation provided by protons.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Cu/Al</th>
<th>Na/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received Na-ZSM-5</td>
<td>21.5 (supplier's)</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>Cu(10)(^2)-ZSM-5</td>
<td>20.5</td>
<td>0.15</td>
<td>0.89</td>
</tr>
<tr>
<td>Cu(30)-ZSM-5</td>
<td>19.1</td>
<td>0.25</td>
<td>0.62</td>
</tr>
<tr>
<td>Cu(50)-ZSM-5</td>
<td>19.4</td>
<td>0.37</td>
<td>0.44</td>
</tr>
<tr>
<td>Cu(72)-ZSM-5</td>
<td>21.3</td>
<td>0.48</td>
<td>0.20</td>
</tr>
<tr>
<td>Cu(97)-ZSM-5</td>
<td>21.9</td>
<td>0.51</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu(102)-ZSM-5</td>
<td>19.0</td>
<td>0.71</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu(142)-ZSM-5(^3)</td>
<td>20.3</td>
<td>0.82</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu(164)-ZSM-5</td>
<td>20.2</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

1. Catalysts were prepared at pH = 5.7 in cupric acetate solution (0.007 M) at room temperature for 19 hours once.
2. The values in parentheses are ion exchange levels, based on Al and Cu contents as measured by ICP.
3. Cu-ion exchanged with Na-ZSM-5 at room temperature for 19 hours thrice.

In this chapter, the catalysts are identified in the following way: Cu(percent exchange level)-ZSM-5 for materials prepared at pH = 5.7.

3.1.2 Catalytic Activity Measurements
Conversion and kinetic studies were performed in the laboratory-scale packed-bed reactor system. An amount of 0.5 grams of catalyst was placed in the 1.1 cm O.D.-reactor for conversion measurements, and 0.03 g in the 0.4 cm O.D.-reactor for kinetic studies. The catalyst packing density in the reactors was about 0.5 g/cm\(^3\). Contact times were 1.0 g s/cm\(^3\) (NTP) for the conversion measurements and 0.03 g s/cm\(^3\) for the kinetic studies, respectively. The NO concentrations varied from 0.2 to 4 mol.% in He, and the temperature was in the range of 300-700\(^\circ\)C. All measurements were made after reaction had reached steady state.
3.2 RESULTS AND DISCUSSION

3.2.1 Nitric Oxide Decomposition over Cu-ZSM-5 Catalysts

The catalytic activity of the Cu-ZSM-5 was evaluated in the reactor system in a mixture of 2% NO - He at a contact time of 1.0 g s/cm\(^3\) in the temperature range of 350- 600\(^\circ\)C. The catalyst in the reactor was pretreated in pure He at 100\(^\circ\)C for 30 minutes to remove physically adsorbed water molecules from the catalyst followed by raising the catalyst temperature to 500\(^\circ\)C at a heating rate of 10\(^\circ\)C/minute. The catalyst was in He at 500\(^\circ\)C for two hours before introducing the reactant mixture into the reactor.

![Graph of NO Conversion to N2 vs Reaction Temperature](image)

Figure 3.1 Catalytic performance of Cu-ZSM-5 catalysts in a gas mixture of 2% NO- He at W/F= 1.0 g s/cm\(^3\) (NTP).

The profiles of NO conversion to N\(_2\) over the catalysts with different Cu exchange levels ranging from 10 to 141\% are shown in Figure 3.1. The catalyst performance for NO decomposition generally was in very good agreement
with that reported in the literature [35-42]: (1) Cu-ZSM-5 catalysts, with less than 30% Cu exchange level, are not active for NO decomposition; (2) The catalytic activities increased with reaction temperature, reached a maximum at 500°C, and then decreased; (3) this falloff was reversible with a drop in reaction temperature.

Figure 3.2 is a plot of the NO conversion to N\textsubscript{2} vs. the copper ion exchange level at 400, 500 and 600°C. This shows that the NO conversion over Cu-ZSM-5 catalysts increases non-linearly with Cu ion exchange level. The slope of this curve can be used to find which portion of copper is more active for NO decomposition. The value of the slope depends on reaction temperatures. At 400°C, the highest slope is for Cu-exchange level in the range of 50 to 97%, while at 500 and 600°C it is observed for copper exchange in the range of 30 to 72%. It is interesting that Cu(141)-ZSM-5 displayed a plateau in NO conversion to N\textsubscript{2} in the temperature range of 450 to 600°C.

![Figure 3.2](image) The change of catalytic activity of Cu-ZSM-5 with copper exchange levels at 400, 500 and 600°C in a gas mixture of 2% NO - He at W/F = 1.0 g s/cm\textsuperscript{3} (NTP).
Based on the experimental data shown in Figure 3.2, the slope of NO conversion to \( \text{N}_2 \) vs. copper exchange level can be estimated using \( \Delta = \) (change in percent NO conversion to \( \text{N}_2 \)/change of Cu exchange level). The results are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Cu exchange level (%)</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>72</th>
<th>97</th>
<th>141</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta ) at 400(^\circ)C</td>
<td>0.26</td>
<td>0.48</td>
<td>0.86</td>
<td>0.88</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>( \Delta ) at 500(^\circ)C</td>
<td>0.50</td>
<td>1.33</td>
<td>1.16</td>
<td>0.36</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>( \Delta ) at 600(^\circ)C</td>
<td>0.37</td>
<td>1.17</td>
<td>0.68</td>
<td>0.36</td>
<td>0.74</td>
<td></td>
</tr>
</tbody>
</table>

To get higher copper ion exchange level, Na-ZSM-5 was ion-exchanged with Cu\(^{2+}\) more than thrice, based on the procedure described in Chapter 2. It was found that when a Cu-ZSM-5 catalyst was further exchanged with Cu\(^{2+}\) after the Cu exchange level had reached about 150\%, the catalyst color would change from light blue to brown, e.g. Cu(164)-ZSM-5 as shown in Table 3.1. Measurements of NO decomposition to \( \text{N}_2 \) showed that the Cu(164)-ZSM-5 activity was lower than the Cu(141)-ZSM-5. For the Cu(164)-ZSM-5, the catalytic activity no longer increased with increasing copper content. This phenomenon can be explained by Cu(OH)\(_x\) precipitation on the surface of ZSM-5, since high concentrations of Cu\(^{2+}\), [Cu\(^{2+}\)(OH)\(^-\)]\(^+\) and (OH)\(^-\) exist in the vicinity of zeolite particles during the late copper exchange step. Adding NH\(_4\)OH into solution can easily exceed 150\% copper loading. However, the NO conversion over such catalysts was the same as that over the light-blue colored ones with about 100\% Cu exchange level, as will be discussed in Chapter 4. This is attributed to inactive CuO particle formation by Cu(OH)\(_x\) decomposition. Thus, under our conditions, the highest amount of ion-exchanged Cu is approximately 150\%.

Assuming that copper ions exist only in two forms, one in bare Cu\(^{2+}\), and another in [Cu\(^{2+}\)(OH)]\(^+\), and electrical charges are balanced in a ZSM-5 material with 150\% copper exchange level, we can estimate the fraction of Cu\(^{2+}\) in each form by the following equations:
Copper conservation: \[ X + Y = 0.75 \]  \hspace{1cm} (4.1)  
Charge balance: \[ 2X + Y = 1.0 \]  \hspace{1cm} (4.2)

where \( X \) and \( Y \) are ratios of the number of the bare \( \text{Cu}^{2+} \), and \( [\text{Cu}^{2+}(\text{OH})]^+ \) to Al. Solving the above two equations, we have \( X \) and \( Y \) equal to 0.25 and 0.5, respectively, that is one third of copper is in the form of bare \( \text{Cu}^{2+} \) ions, and the rest \([\text{Cu}^{2+}(\text{OH})]^+\). Certainly, this is an oversimplified way to estimate Cu ion distributions. Another possibility, as Li, et al [44] suggested, leading to high copper ion exchange level is due to the presence of silanols, in which proton could be replaced by copper ion.

EPR results by Sass, et al [68, 69] and luminescence data by Dedecek, et al [90] have shown that copper ion preferentially occupies the sites close to the two framework aluminum atoms in Cu-ZSM-5 at low copper content; on the other hand, with a high Cu exchange level (or low aluminum content), the \( \text{Cu}^{2+} \) is located nearer to one framework aluminum. It is plausible to suggest that the catalytic activity of Cu-ZSM-5 for NO decomposition is related to the \( \text{Cu}^{2+} \) position in ZSM-5. The closer to framework aluminum \( \text{Cu}^{2+} \) is, the higher the catalytic activity. This is supported by the increase of the specific NO decomposition rate per copper with Si/Al ratio [38]. The low catalytic activity, thus, of Cu-ZSM-5 with low copper exchange level is due to copper ions away from framework aluminum atoms.

The excessively exchanged copper ions in Cu(141)-ZSM-5 are found to be active. STEM/EDX mapping of copper and aluminum in the Cu(141)-ZSM-5 showed that the copper cations uniformly distributed and strongly associated with aluminum (see Chapter 6). That is why the excessively exchanged Cu cations are active in our catalyst. However, deposited copper cations, if they are the excessively exchanged, are not active for the reaction.

Effects of inlet NO concentration and contact time on the catalytic activity of Cu(97)-ZSM-5 were examined in a mixture of 0.2 to 4.0% NO - He balance at 525°C and \( W/F = 0.75 - 4 \) g s/cm³ (NTP) by using the chemiluminescence NOx analyzer to measure NO in the effluent gas stream. Figure 3.3 shows NO conversions over the catalyst Cu(97)-ZSM-5 with
Figure 3.3 Effect of the inlet NO concentration on the catalytic activity over Cu(97)-ZSM-5 at 525°C and W/F = 4.0 g s/cm³ (NTP) as measured by NOx analyzer.

Figure 3.4 Effect of the contact time on catalytic activity over Cu(97)-ZSM-5 in 0.2% (or 4%) NO - He at 525°C.
different NO inlet concentration at a contact time of 4 g s/cm$^3$ (STP). The NO conversion increased with increasing inlet NO concentration. The effect of the contact time on catalytic activity is shown in Figure 3.4 in a mixture of 0.2% NO - He at 525°C. The catalytic activity decreases with increasing contact time. Higher NO conversion was achieved for higher inlet NO concentration over the tested range of the contact time.

3.2.2 Effect of Pretreatment on Catalytic Activity
Fresh Cu(97)-ZSM-5 catalyst was pretreated in four different gas compositions, i.e., pure He, 10% O$_2$ - He, 2% NO - He and 4% H$_2$O - He, at 500°C for 4 hours (2 hours in pure He). After each pretreatment, the catalyst performance was measured in a gas mixture containing 2% NO - He at 500°C and a contact time of 1.0 g s/cm$^3$ (NTP). Test results showed that the steady state catalytic activity is not sensitive to pretreatment, except when water vapor was used, as shown in Figure 3.5.

![Figure 3.5 NO decomposition over Cu(97)-ZSM-5 in 2% NO - He at 500°C and W/F = 1.0 g s/cm$^3$ (NTP) after pretreatments of the fresh catalyst Cu(97)-ZSM-5 in different gas composition at 500°C](image)
After the oxygen-containing gas pretreatment, 63% NO conversion to N₂ was found one hour and half after the introduction of NO into the reactor, while 75% conversion was obtained after treatments in pure He or 2% NO-He gases. The results suggest that adsorbed oxygen caused partial deactivation during the O₂-containing gas treatment. This was reversible upon removal of oxygen. The treatment in water vapor-containing He stream decreased the catalytic activity. In this case, permanent loss of some active sites took place. Effects of water vapor on the catalytic activity for NO decomposition will be described in detail in Chapter 6. Deactivation by water has adverse practical implications; all combustion exhaust gases contain a significant amount of water vapor (2-15%).

3.2.3 Correlation of Cu-ZSM-5 Activity with Cu²⁺ Ions
At the present time, no consensus can be found in the literature on the mechanism of NO decomposition over Cu-ZSM-5 catalysts. Using FT-IR measurements at room temperature, Iwamoto, et al. [40, 47, 105], Hall, et al. [44, 108] reported the intermediate species formed on the catalyst surface, and proposed a mechanism for NO decomposition into N₂ involving a redox mechanism for NO decomposition involving Cu²⁺ and Cu⁺ cations. Liu and Robota [89] reported that the Cu⁺ population in Cu-ZSM-5 materials increases, and reaches a maximum at 500°C with temperature. However, Kucherov, et al. recently reported that no spontaneous thermal reduction (autoreduction) of the cupric ions was observed by in-situ EPR measurements in flowing He, and O₂ up to 500°C [77]. In earlier reports [59, 60], Kucherov and coworkers investigated Cu²⁺ coordination by ESR, and found that Cu-ZSM-5 contained two types of isolated Cu²⁺ cations: one in a four-coordinated square planar configuration, the other in a five-coordinated square pyramidal. The results of the investigation also indicated that the preferred formation of five-coordinated Cu²⁺ cations takes place at low copper exchange level. According to these results, Shelef [91] proposed another mechanism for the reaction of NO decomposition over Cu-ZSM-5 catalysts. This involves the more coordinately unsaturated Cu²⁺ sites on which NO molecules are chemisorbed in the gem-dinitrosyl form, from which N₂ and O₂ are produced. This can explain the negligible activity of Cu-
ZSM-5 catalysts with low Cu exchange level (<30%). From the EPR study of a fresh Cu-ZSM-5 catalyst with 116% exchanged Cu Iwamoto and coworkers [48] reported that approximately 50% of copper cations exist as Cu$^{2+}$, while the rest of copper are Cu$^+$, which is different from the above results [77]. To the author's knowledge, no further data has been reported on distribution of Cu$^{2+}$ and Cu$^+$ in the Cu-ZSM-5 materials with different Cu cation exchange levels.

Figure 3.6 is a plot of the dependence of NO conversion to N$_2$ on the Cu ion exchange levels over the Cu-ZSM-5 catalysts at 500°C found in this thesis work. The results are in good agreement with those reported by Iwamoto [40]. The two sets of data are shown together in Figure 3.6 for comparisons.

![Graph showing NO conversion to N$_2$ vs. Total Cu Exchange Level](image)

Figure 3.6  Dependence of NO conversion to N$_2$ on total Cu exchange level [this study: NO = 2%, 500°C and W/F = 1.0 g s/cm$^3$ (NTP); Iwamoto's data [40]: NO = 1%, 500°C and W/F = 4.0 g s/cm$^3$].

Examining the data in Figure 3.6 and the distribution of four-coordinated square planar Cu$^{2+}$ in Cu-ZSM-5 for various Cu exchange levels reported by Kucherov, et al [60], we found them similar. We assume that the correlation between the concentrations of four- and five-coordinated Cu$^{2+}$ ions and the total Cu loading [60] is applicable to our Cu-ZSM-5 catalysts, since the Si/Al
ratio, 21.5, of the parent ZSM-5 in this study is similar to that (= 21) of the parent ZSM-5 used by Kucherov. It was found that the NO conversion to N₂ linearly increased with the amount of four-coordinated Cu²⁺, as shown in Figure 3.7. This implies that the active sites for NO conversion to N₂ are the four-coordinated square planar Cu²⁺ in the Cu-ZSM-5 catalysts. By assuming that the distribution of four- and five-coordinated Cu²⁺ at a certain Cu exchange level is the same for all Cu-ZSM-5 with different Si/Al ratios, Iwamoto’s data [40] were treated in the same manner as above. Once again, a linear relation was found between NO conversion and the four-coordinated Cu²⁺ (see Figure 3.7). Furthermore, the same correlation was found for the data reported by Kagawa [50], as shown in Figure 3.8. The catalytic activities of Cu-ZSM-5 catalysts for NO decomposition may, thus, be attributed to square planar four-coordinated Cu²⁺. This has been reported for methane oxidation [60]. Of the two isolated Cu²⁺ sites, the coordination of the four-coordinated Cu²⁺ is more unsaturated. Accordingly, NO chemisorption occurs preferentially on square planar Cu²⁺. The redox process may take place on the four-coordinated Cu²⁺ site which is in dynamic equilibrium with Cu⁺ during the NO decomposition.

Figure 3.7  Dependence of NO Conversion to N₂ on square planar Cu²⁺ exchange level (the same as conditions as those in Figure 3.1).
Figure 3.8  Dependence of NO conversion to N₂ on square planar Cu²⁺ exchange level (NO = 0.48% and W/F = 4.0 g s/cm³ [50]).

It is noted that all Cu cations in the above calculation were assumed as Cu²⁺, since there are no Cu⁺ and Cu²⁺ distribution data available for catalysts with various Cu cation exchange levels. The previous cited literature [44, 77] reported that a major part (perhaps all) of Cu cations were in Cu²⁺ rather than Cu⁺ state. If both Cu²⁺ and Cu⁺ are involved in the reaction, as reported in the literature [3, 10, 12], an equilibrium between the two Cu cation states must be established at each temperature.

From the results reported by Kuchercov, et al [59-61], Sass, et al [69], and Dedecek, et al [90], we surmise that the five-coordinated copper ions are at sites associated with two framework aluminum atoms, while the four-coordinated copper at sites adjacent to one framework aluminum atom.

3.2.4 Estimation of Apparent Activation Energy
The microreactor described in Chapter 2 was used for kinetic studies and measurements of turnover frequencies over the Cu-ZSM-5 catalysts. At contact time of 0.03g s/cm³ (NTP) the reaction was in the kinetic control
region. Actually, this is true for contact time up to 0.08 g s/cm³. This will be discussed in detail in Chapter 7.

Figure 3.9 shows Arrhenius-type plots for the turnover frequencies over Cu-ZSM-5 catalysts for NO decomposition. The turnover frequency (TOF), defined here as the number of NO molecules to N₂ per second per square planar four-coordinated Cu²⁺, is independent on the total Cu exchange levels under same experimental conditions. This weakens the possibility that catalytic activity only emerges if enough adjacent copper active sites exit. The increase in NO conversion to N₂ with the copper exchange level, as shown in Figure 2, may simply be due to increasing concentration of the square planar four-coordinated copper. If this is true, it is important to find ways to stabilize four-coordinated Cu²⁺ sites in the zeolite to improve the catalytic activity of Cu-ZSM-5 materials for NO decomposition in practice.

![Arrhenius plots for NO decomposition over Cu-ZSM-5 catalysts at 4% NO and 1 atm of total pressure.](image)

Figure 3.9 Arrhenius plots for NO decomposition over Cu-ZSM-5 catalysts at 4% NO and 1 atm of total pressure.

If the TOF for all catalysts in Figure 3.8 were averaged at the same temperature, the average apparent activation energy would be 11.8 Kcal/mole in the low temperature region, changing over to a negative value of -7.3
Kcal/mole for the high temperature region. These values are close to those in our early report [109].

At the present time, no consensus exists in the literature on why the NO decomposition has a negative apparent activation energy at high temperatures (> 500°C) over Cu-ZSM-5 catalysts. There are three possibilities which can attribute to this phenomenon: (1) the change of reaction mechanism; (2) the distortion of active copper coordination and (3) larger heat of chemisorption than true activation energy for the reaction process. The above hypotheses are subject to change as more experimental data become available.

3.3 CONCLUSION

Conversion of NO to N₂ over Cu-ZSM-5 catalysts increases nonlinearly with Cu ion-exchange level in Cu-ZSM-5 catalysts. Oxygen adsorption on active sites inhibits the reaction, while water vapor permanently deactivates active sites. The catalytic activity of Cu-ZSM-5 for NO decomposition may be related to the Cu²⁺ position in ZSM-5. The closer to framework aluminum Cu²⁺ is, the higher its catalytic activity. Experimental evidence has suggested that the catalytic activity of Cu-ZSM-5 materials for nitric oxide decomposition is related to the amount of square planar four-coordinated Cu²⁺ cations. Perhaps, the redox involving Cu²⁺ and Cu⁺ takes place between square planar four-coordinated Cu²⁺ cations and Cu⁺. By correlating with Kucherov, et al [60] active copper site population, it is shown that the conversion of NO to N₂ and O₂ increases linearly with increasing square planar four-coordinated Cu²⁺, and that the turnover frequency of the NO decomposition over the catalysts is independent of the total copper exchange level in the Cu-ZSM-5 catalysts.
Chapter 4

PREPARATION EFFECTS ON THE ACTIVITY OF CU-ZSM-5 CATALYSTS FOR NO DECOMPOSITION

As pointed out in Chapter 1, the direct catalytic decomposition of nitric oxide is the simplest method for removing NO\textsubscript{X} from flue gas streams since it involves no reductant addition, such as ammonia or hydrocarbons. Reports of Cu-ZSM-5 catalyst activity agree that excessively copper ion-exchanged ZSM-5 catalysts give higher N\textsubscript{2} yields [37, 40, 44], however, one report disagrees it [106]. Here, "excessively" indicates above the theoretical ion exchange level, corresponding to one divalent Cu\textsuperscript{2+} ion for every two [AlO\textsubscript{2}]\textsuperscript{-} sites in the zeolites.

The "excessively-exchanged" copper has been attributed to [CuOH]\textsuperscript{+}, i.e., to both cupric cations, Cu\textsuperscript{2+}, and anions, OH\textsuperscript{-}, carried into the zeolite from an aqueous solution [110-112, 102]. Iwamoto, et. al. [112] reported that it is impossible to prepare excessively copper ion-exchanged ZSM-5 zeolites from aqueous solutions of cupric nitrate or sulfate. However, increasing the pH of the solution by addition of basic compounds readily achieved "excessively-exchanged" copper in the ZSM-5 [113]. The Cu loading increased with pH from 4 to 9 and reached a nearly constant value above pH = 9. The conversion of nitric oxide to nitrogen over catalysts with Cu\textsuperscript{2+} exchange from 130- 150% was approximately the same. Campa et al. [106] also reported that the catalytic activity remains almost constant above 100% Cu\textsuperscript{2+} exchange and was suggested to be due to formation of Cu\textsubscript{x}O\textsubscript{y} microclusters on the surface. Recently, Valyon and Hall [102] reported that the NO decomposition activity of ZSM-5 catalysts correlated with the pH values, 4 and 6, of the aqueous cupric acetate solution used for ion exchange.

Presently, it is still not known what the state of "over-exchanged" copper is in the ZSM-5 materials. The probability exists that at higher pH values deposition of Cu(OH)\textsubscript{2} in the zeolite pores takes place, resulting in "deposited" rather than "exchanged" copper. Recently, Sarkany, et. al. [75] used TPR/TPD and FTIR to characterize the "over-exchanged" copper in ZSM-5. An aqueous solution of Cu(ac)\textsubscript{2} at pH = 7 was used for the exchange. Two copper-oxygen species were identified in addition to Cu\textsuperscript{2+} ions and attributed to CuO and [Cu-O-Cu]\textsuperscript{2+} [100]. These results were not correlated...
with the pH of the salt solution. Thus, it remains unclear whether the oxidic copper is the result of Cu(OH)$_2$ precipitation or [CuOH]$^+$ exchange.

In this Chapter, effects of catalyst preparation on Cu states and catalytic activity of Cu-ZSM-5 catalysts were examined for nitric oxide decomposition. The Cu-ZSM-5 catalysts were prepared from aqueous Cu(ac)$_2$ solutions adjusting the pH in the range of 4.5-7.5, and analyzed the activity of the resulting materials for nitric oxide decomposition. The "over-exchanged" copper was characterized by a wet chemical technique (aqueous ammonia wash), followed by ICP spectrometry and by STEM equipped with EDX microprobe analysis.

### 4.1 EXPERIMENTAL

#### 4.1.1 Catalyst Preparation and Composition Analysis

Catalysts were prepared by exchanging Cu$^{2+}$ cations into ZSM-5 from dilute aqueous Cu(ac)$_2$ solutions. The parent zeolite was a Na$^+$-ZSM-5 (Si/Al= 21.5) zeolite in fine powder form obtained from the Davison. The following preparation procedure was used in this study. First, cupric acetate was dissolved in deionized water to form an aqueous solution with a concentration of 0.007 M and initial pH of 5.74. Second, the pH of the solution was adjusted by adding either acetic anhydride or aqueous ammonia into the solution to a desired pH value. The ZSM-5 particles were added into the solution in amounts corresponding to replacing all the Na$^+$ ions in the ZSM-5 by half the number of Cu$^{2+}$ in the cupric acetate solution. The mixture was then vigorously stirred by a magnetic stirrer at room temperature for 19 hours. Finally, the sample was washed with deionized water at room temperature for 30 minutes. After filtration, the samples were dried in air at 100°C overnight. Seven Cu-ZSM-5 catalysts were prepared according to this procedure at pH of 4.5, 4.9, 5.74, 6.0, 6.5, 7.0 and 7.5.

Another Cu-ZSM-5 catalyst was prepared in a different fashion for comparison. The ZSM-5 zeolite was first ion-exchanged with Cu$^{2+}$ using the same procedure as above, except that aqueous ammonia was gradually added to the slurry of ZSM-5 and cupric acetate solution to a final pH value of 7.0, after the ZSM-5 zeolite had reached equilibrium in exchange with Cu$^{2+}$ at the pH value of 5.7 at room temperature for 19 hours. This catalyst was tested for
NO decomposition to examine the effect of increasing the pH of the solution after Cu$^{2+}$-exchange had taken place at lower pH.

Elemental analyses were performed by ICP after the catalyst samples were dissolved in HF (48%) solution, and the solution was diluted to 2% HF by deionized water. Metal ratios, such as Si, Cu and Na, to Al were calculated based on the elemental contents measured by ICP. In the text, the catalysts are identified in the following way: Cu(exchange level)-ZSM-5-(pH), for example, Cu(97)-ZSM-5-(6.0), where 100% nominal Cu$^{2+}$ exchange level denotes one Cu$^{2+}$ ion neutralizing two Al$^{3+}$, i.e. the atomic ratio Cu/Al = 0.5.

Activity of the Cu-ZSM-5 catalysts prepared in this chapter will be compared with that of the Cu-ZSM-5 synthesized from solutions of pH = 5.7 (see Table 3.1 in Chapter 3).

The preparation and properties of the Cu-ZSM-5 catalysts in this study are listed in Table 4.1. It is worth noting that the Cu$^{2+}$ ion-exchange with Na$^+$ is non-stoichiometric in the samples.

4.1.2 Partial Removal of Copper from Cu-ZSM-5
The prepared materials were evaluated with respect to copper loss in short-time wash experiments with aqueous ammonia solutions. For these experiments, 0.1 g of Cu-ZSM-5 catalyst was washed with aqueous ammonia (5 ml of 29.5% aqueous ammonia + 50 ml of deionized water) at room temperature for six minutes. The washed Cu-ZSM-5 samples were analyzed by ICP to determine potential copper loss from the Cu-ZSM-5 samples.

The catalysts prepared in this study were characterized by X-Ray Diffraction to examine the crystal structures, as well as CuO formation on the samples. The diffraction patterns were taken in the 2θ range of 5 - 80° at a scanning speed of 1° per minute. Characterization of the Cu-ZSM-5 samples by STEM/EDX was also performed to examine Cu distribution in the Cu-ZSM-5 samples. Elemental mapping was performed with the X-ray microanalytical probe on the basis of 128 x 128 data matrix.

4.1.3 NO Conversion to N$_2$ Measurement and Kinetic Study
The activity of the Cu-ZSM-5 catalysts for NO decomposition was evaluated in laboratory-scale packed-bed, quartz-tube reactors, as described in Chapter 2. An amount of 0.5g or 0.03g of catalyst was used in conversion and kinetic
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al$^2$</th>
<th>Cu/Al$^2$</th>
<th>Na/Al$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-received Na-ZSM-5</td>
<td>21.5 (supplier's)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>First set of samples$^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(40)-ZSM-5(4.5)</td>
<td>19.1</td>
<td>0.20</td>
<td>0.09</td>
</tr>
<tr>
<td>Cu(74)-ZSM-5(4.9)</td>
<td>19.2</td>
<td>0.37</td>
<td>0.20</td>
</tr>
<tr>
<td>Cu(102)-ZSM-5(5.7)</td>
<td>19.0</td>
<td>0.51</td>
<td>0.20</td>
</tr>
<tr>
<td>Cu(97)-ZSM-5(6.0)</td>
<td>19.0</td>
<td>0.48</td>
<td>0.18</td>
</tr>
<tr>
<td>Cu(154)-ZSM-5(6.5)</td>
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<td>0.77</td>
<td>0.11</td>
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<tr>
<td>Cu(165)-ZSM-5(7.0)</td>
<td>19.0</td>
<td>0.83</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu(154)-ZSM-5(7.5)</td>
<td>18.4</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>Cu(136)-ZSM-5(5.7/7.0)$^4$</td>
<td>18.1</td>
<td>0.68</td>
<td></td>
</tr>
</tbody>
</table>

1 pH measured before contacting Na-ZSM-5 with the aqueous cupric acetate solution.

2 Si, Al, Cu and Na contents as measured by ICP.

3 Cu ion-exchanged with Na-ZSM-5 at room temperature for 19 hours once.

4 Cu first ion-exchanged with Na-ZSM-5 at room temperature and pH= 5.8 for 19 hours, then gradually adding aqueous ammonia into the slurry of Na-ZSM-5 and cupric acetate solution to pH=7.0.

Tests, respectively. The catalyst packing density in the reactor was 0.5g/cm$^3$. The contact time, defined as the ratio of catalyst weight to the total flowrate of the feed gas, was 1g s/cm$^3$ or 0.03g s/cm$^3$ (NTP). The NO concentration was 2 or 4 vol.% in the feed gas stream. All measurements were made after steady state had been reached.

### 4.2 RESULTS

#### 4.2.1 Effect of pH on Cu Exchange Level

Figure 4.1 shows the pH dependence of Cu$^{2+}$ ion-exchange levels in Cu-ZSM-5 samples. The Cu$^{2+}$ exchange level increased with increasing pH, leveled off at about pH = 6.0, then increased further showing a maximum at pH = 7.0. Aluminum was not found by ICP in residual solutions, and no structural
change of the zeolite was observed from X-ray diffraction patterns of the Cu-ZSM-5 samples after the ion exchange, which is in agreement with what was reported by Iwamoto, et al [103]. Figure 4.2 shows XRD patterns of the as-received Na-ZSM-5, the Cu(74)-ZSM-5(4.9) and Cu(154)-ZSM-5(6.5). In a separate test, the Cu ion uptake capacity (at pH = 5.7) of the parent zeolite (Na-ZSM-5) after exposure to an acetic anhydride solution at pH = 4.0 at room temperature for 19 hours remained unchanged.

![Graph showing Cu Loading (%) vs pH of solution]

Figure 4.1. Dependence of Cu loading on pH of starting cupric acetate solution.

The mode of adding aqueous ammonia to the ion-exchange solution affects the Cu exchange level. The Cu exchange level reached 136.8%, when the pH of the slurry of aqueous cupric acetate and ZSM-5 zeolite was adjusted to 7.0 after Cu ion-exchange at pH = 5.7 had carried out for 19 hours. This sample is designated as Cu(136)-ZSM-5(5.7/7.0), where 5.7 and 7.0 refer to the two pH values used. However, the Cu$^{2+}$ exchange level of the sample Cu(165)-ZSM-5(7.0) was higher than that of Cu(136)-ZSM-5(5.7/7.0). The former was exchanged once at pH = 7.0 for 19 hours.
Figure 4.2  XRD patterns of (a) the parent Na-ZSM-5; (b) Cu(74)-ZSM-5(4.9); and (c) Cu(154)-ZSM-5(6.5).
4.2.2 Effect of pH on NO Conversion To N₂

The catalytic activities of the catalysts prepared in this work were evaluated for NO decomposition in a mixture of 2% NO-He at a contact time of 1.0 g s/cm³ (NTP) and temperature in the range of 350-600°C. NO was introduced into the inlet stream after the catalyst was pretreated in the reactor in pure He stream at 500°C for 2 hours at a total pressure of 1.3 atm.

Figure 4.3. Effects of catalyst preparation on catalytic activity for NO conversion to N₂ in 2%NO+He and 1g s/cm³ (NTP): (a) Cu(40)-ZSM-5(4.5); (b) Cu(74)-ZSM-5(4.9); (c) Cu(102)-ZSM-5(5.7); (d) Cu(97)-ZSM-5(6.0); (e) Cu(165)-ZSM-5(7.0); (f) Cu(154)-ZSM-5(7.5).

Figure 4.3 shows the results for the Cu-ZSM-5 samples. The activity of these catalysts for NO decomposition to N₂ increased with the Cu exchange level when the pH used in preparation was less than 5.74. However, over the rest of the catalysts, including Cu(136.8)-ZSM-5(5.7/7.0), prepared at higher pH with high nominal Cu²⁺ exchange levels, the NO conversion to N₂ curves overlap with that of Cu(102)-ZSM-5(5.7) over the whole temperature range. Here, the catalytic activity no longer increases with the Cu²⁺ exchange level. This suggests that part of the copper contained in these samples is not active for NO decomposition. It is noted that the NO conversion to N₂ over the
Cu(96)-ZSM-5(6.0) catalyst was almost 20% lower than that over the Cu(102)-ZSM-5(5.74). This is not the case for two catalysts with similar Cu$^{2+}$ exchange levels (here, 97% and 102%) in the Cu-ZSM-5 samples, both prepared at pH = 5.74 (Table 3.1 and Figure 3.6).

Contrary to the samples prepared in this Chapter, the catalytic activities of the Cu-ZSM-5(5.7) samples synthesized in Chapter 3 increased monotonically with the Cu exchange level. The NO conversion to N$_2$ at 500°C over these samples is depicted in Figure 3.6 as a function of Cu exchange level.

4.2.3 Measurements of Turnover Frequency
The microcatalytic reactor was used with samples weighing 0.03 g for kinetic studies and measurements of turnover frequencies of NO decomposition over the first set of the Cu-ZSM-5 samples. A short contact time, 0.03g s/cm$^3$ (STP), was chosen at which the reaction was controlled by kinetics. Figure 4.4a shows Arrhenius plots for the turnover frequencies over six typical Cu-ZSM-5 catalysts (see Table 4.1), while Figure 4.4b displays the TOF as a function of the pH at the temperature of 500°C. The turnover frequency (TOF) defined, here, as the number of NO molecules converted to N$_2$ per Cu (based on total Cu) per second, generally increases with temperature, reaches a maximum at 500°C [450°C for Cu(40)-ZSM-5(4.5)], then decreases at higher temperatures. The TOF in Figure 4.4b increases with the pH up to a value of 5.7 for the catalyst Cu(102)-ZSM-5(5.7), then decreases for the samples prepared at higher pH. This is in good agreement with the NO conversion measurements.

4.2.4 Identification of "Surface Copper"
As shown in Figures 4.3 and 4.4, a certain amount of copper ions in the samples prepared at high pH were not active for NO decomposition, since the NO conversion did not increase with the copper exchange level. The Cu$^{2+}$ distribution in the catalysts can be evaluated in terms of "surface Cu" and "ion-exchanged Cu" cations. Unlike the samples prepared in different pH, Cu$^{2+}$ cations in the Cu-ZSM-5(5.7) catalysts were approximately stoichiometrically ion-exchanged with Na$^+$ ions, as shown in Table 3.1 in Chapter 3, when Cu ion exchange level was lower than about 90%. The correlation of catalytic activity with the amount of ion-exchanged Cu, as shown in the Figure 3.6, can be used as a standard to determine how much
Figure 4.4a The effect of catalyst preparation on the catalytic activity (TOF) for NO decomposition in 4%NO-He and 0.03g s/cm³ (NTP): (1) Arrhenius plots: (a) Cu(40)-ZSM-5(4.5); (b) Cu(74)-ZSM-5 (4.9); (c) Cu(102)-ZSM-5(5.7); (d) Cu(97)-ZSM-5(6.0); (e) Cu(165)-ZSM-5(7.0); (f)Cu(154)-ZSM-5(7.5).

Figure 4.4b Correlation of TOF with the pH at 500C.
copper was "ion-exchanged" in each of the Cu-ZSM-5 samples prepared in this Chapter. The difference between the total Cu and "ion-exchanged Cu" is, here, designated as "surface Cu," which is not active for NO decomposition. The Cu distribution in the samples is shown in Figure 4.5.

![Figure 4.5. Cu distribution in the catalysts prepared at different pH.](image)

In order to further examine the contribution of the "surface Cu" and "ion-exchanged Cu" to the catalytic activity, the Cu-ZSM-5 catalysts was washed by aqueous ammonia solutions (2.7% assay). The amounts of Cu washed out from two samples, namely Cu(97)-ZSM-5-(6.0) and Cu(165)-ZSM-5-(7.0), did not change one minute after the catalyst samples were contacted with the solutions, as shown in Figures 4.6 and 4.7. It was decided to contact all samples with the aqueous ammonia solution for six minutes, which is long enough for all cations in the slurry to reach a surface equilibrium. The amount of Cu removed by the aqueous ammonia solutions from each catalyst is determined by the difference of the initial total Cu and the remaining Cu in the samples (as specified by ICP). The results are shown in Figure 4.8. It can be seen that a little amount of Cu was removed from the catalysts prepared at low pH. However, considerable amount of copper was extracted from the catalysts prepared at high pH. The "surface Cu" and the Cu$^{2+}$ washed out by aqueous ammonia were approximately equal as shown in Figure 4.8. The Cu
Figure 4.6. Change of removal of copper from Cu(97)-ZSM-5(6.0) by aqueous ammonia with time.

Figure 4.7. Change of removal of copper from Cu(165)-ZSM-5(7.0) by aqueous ammonia with time.
removed by aqueous ammonia from the samples prepared at pH values of 4.5, 4.9 and 5.7 is part of the ion-exchanged copper. This is concluded from the following tests. First, the same amount of Cu was removed by aqueous ammonia after calcination of these samples in air at 500°C for 2 hours. Second, the same tests for the materials prepared at high pH values showed that only a small amount of Cu (~ 3%) could be removed. It was found by XRD that CuO was formed by the “surface Cu” after calcination in air. A separate test revealed that CuO cannot be removed by the ammonia wash method. Therefore, the removed Cu is the ion-exchanged Cu cations.

![Graph showing the amount of Cu (%) at different pH values](image)

**Figure 4.8.** Comparison of "surface Cu" and Cu washed by aqueous ammonia.

Kinetic studies showed that the TOF values of the ammonia-washed catalysts were the same as those of the original samples (prior to washing). This confirms that the extracted Cu was not active for the reaction. The TOF for the catalysts Cu(96)-ZSM-5(6.0) and Cu(165)-ZSM-5(7.0) before and after the ammonia wash is shown in Figure 4.9. Here the TOF is defined as the number of NO molecules converted to N₂ per Cu (based on ion-exchanged Cu) per second.
Figure 4.9. Activity comparisons of fresh with aqueous ammonia washed-samples for NO decomposition in 4%NO-He and 0.03g s/cm³ (NTP): Cu(97)-ZSM-5(6.0) (a) fresh; (b) washed; Cu(165)-ZSM-5(7.0) (c) fresh; (d) washed.

When the catalyst Cu(141)-ZSM-5(5.7) was washed with the aqueous ammonia solution under the same conditions as above, it was found that only 6% of total Cu was removed. However, the catalyst Cu(153)-ZSM-5(7.5) lost 28% of its total Cu. Thus, the "surface Cu" is easily removed by aqueous ammonia.

4.2.4 Characterization of Catalysts by STEM/EDX and XRD

Figure 4.10a shows a STEM micrograph of the 500°C, 2h-air calcined Cu(165)-ZSM-5(7.0) sample. This is representative of the catalysts prepared at high pH (> 6.0). The phase contrast imaging demonstrated formation of copper particles (up to 6 nm) clearly distinguishable from the zeolite support. The X-ray spectra of a copper aggregate and the Cu-ZSM-5 background are shown in Figure 4.10b, in which a very strong copper signal was obtained on the bright spots of the dark field STEM micrograph (Figure 4.10a). Copper X-ray mapping shows homogeneously dispersed copper in the sample, and confirms formation of copper particles on the edges and voids of the zeolite.
Figure 4.10a Characterization of the calcined Cu(165)-ZSM-5(7.0) by STEM: dark field micrograph showing copper aggregates (bright spots).
Figure 4.10b X-ray spectrum of copper aggregates (dots) and catalyst background (bars).
crystal. This can be seen in the X-ray mapping of Cu and Si, as shown in Figure 4.11 (scale of one elemental mapping: 100 nm by 120 nm), for the same area as that in Figure 4.10a.

XRD patterns similar to that of the parent ZSM-5 zeolite were obtained for all the materials prepared in this work. No other crystalline phase, such as CuO, was found by XRD in the fresh samples. However, CuO could be clearly seen by XRD in samples prepared at high pH after air calcination. An example is shown in Figure 4.12 for the Cu(154)-ZSM-5(7.5) after 2h-air calcination at 500°C. For comparison, Figure 4.12 shows the XRD pattern of this sample as well as that of the parent ZSM-5 in the range of 2θ = 34-40° in which CuO has the strongest diffraction peaks.

4.3 DISCUSSION

The experimental results in Figures 4.1 and 4.3 show that the Cu\(^{2+}\) loading and activity are strongly dependent on the initial pH of the starting aqueous cupric acetate solution. It is well known that there are three types of terminal silanol OH-groups in zeolites. The first type is always present at the outer surface of the zeolithic crystals to terminate the structure [114], while the second and third silanol groups exist in the framework of zeolites. At low pH, OH-groups adsorb protons and become positively charged. At high pH, they deprotonate, and the edges become negatively charged and have a cation exchange capacity [115]. Adding acetic anhydride into the cupric acetate solution lowers the pH, i.e., more protons are present in the solution. When a certain amount of Cu\(^{2+}\) cations exist in the solution, Na\(^+\) cations in the ZSM-5 zeolites will be exchanged by both Cu\(^{2+}\) and H\(^+\), and an equilibrium will be reached. Hence, the presence of H\(^+\) cations in the solution inhibits the ion exchange between Cu\(^{2+}\) and Na\(^+\) cations. The higher the H\(^+\) concentration in the solution, the lower the Cu\(^{2+}\) ion exchange level. This is the reason why the Cu\(^{2+}\) ion exchange with Na\(^+\) is not stoichiometric for the first set of samples shown in Table 4.1. Since OH-groups adsorb protons and become positively charged, Cu\(^{2+}\) cations exchanged in the zeolite would only replace Na\(^+\) cations associated with Al in the zeolite framework. This can also be concluded by the low amount of "surface Cu" present in the samples prepared at low pH values. However, by adding aqueous ammonia to the cupric acetate solutions, some Cu complexes can be formed with positive
Figure 4.11  X-ray mapping of Si and Cu in the calcined Cu(165)-ZSM-5 (7.0) sample.
Figure 4.12 XRD patterns of (a) 500°C, air-calcined Cu(154)-ZSM-5(7.5) showing CuO formation, and (b) parent Na-ZSM-5.
charges. The typical complexes are \([\text{Cu(NH}_3)_4]^{2+}\) [116], mononuclear \([\text{CuOH}]^+\), and polynuclear \([\text{Cu}_2\text{(OH)}_2]^{2+}\), \([\text{Cu}_2\text{OH}]^{3+}\), etc. [117]. It is possible for the positively charged \(\text{Cu}^{2+}\) complexes and negatively charged edges of the zeolites to attract each other. Thus, some part of copper is deposited in the zeolite pores while the other exchanges with the \(\text{Na}^+\) cations associated with \((\text{AlO}_2^-)\) in the framework. As a result, higher nominal \(\text{Cu}^{2+}\) exchange levels are measured by ICP in the samples. The STEM X-ray maps of copper and silicon support this explanation.

From Figure 4.8, it is further seen that a part of \(\text{Cu}^{2+}\) cations is easy to remove by the aqueous ammonia solution. The amount of the removed Cu is approximately equal to the increment of the Cu loading at the higher pH, on the basis of \(\text{Cu}(102)-\text{ZSM-5}(5.74)\). Therefore, it is concluded that the removed Cu is the deposited Cu.

The copper aggregates seen by STEM/X-ray microprobe analysis in the Cu-ZSM-5 samples are formed by the deposited Cu on the ZSM-5 crystals, which are labile and upon calcination can form copper oxide particles on the crystal edges and voids. The deposited copper on the zeolite is similar to impregnated Cu-ZSM-5, which is not active for NO decomposition. Characterization of impregnated Cu-ZSM-5 by XPS showed a higher Cu/Si ratio in the zeolite surface region than the bulk value, and was attributed to large copper aggregates [43].

The catalytic activity of Cu-ZSM-5 catalysts depends on the copper exchanged in the zeolite channels. The deposited copper is inactive. As can be seen in Figure 4.3, the NO conversion to \(\text{N}_2\) increases with \(\text{Cu}^{2+}\) exchange levels for the Cu-ZSM-5 catalysts prepared at starting solution pH equal to or lower than 5.74, but not for those samples prepared at higher pH values. The results from the kinetic study of NO decomposition over these catalysts, shown in Figure 4.4, are in good agreement with the NO conversion measurements of Figure 4.3.

From the XRD analyses, it can be concluded that the deposited Cu coalesced and formed CuO after calcination of the Cu-ZSM-5 samples prepared at high pH in air at 500°C for 2 hours.
4.4 CONCLUSION

"Over-exchanged" Cu-ZSM-5 is desirable as it is a more active catalyst for the NO decomposition reaction than under-exchanged Cu-ZSM-5. While a single-step ion-exchange from a dilute copper salt solution at pH>6.5 can achieve a high copper loading in ZSM-5, not all the copper exists in the ion-exchanged state in the zeolite channels; a fraction of the copper is on the surface, easily forming oxide particles after calcination. This surface deposited copper is inactive for NO decomposition. The reported multi-step ion-exchange process from dilute cupric salt solutions at pH = 5.5-6.0, even if more tedious, is presently the only one that can safeguard the active "over-exchanged" Cu-ZSM-5 state.
Chapter 5

NITRIC OXIDE DECOMPOSITION
OVER METAL ION-MODIFIED CU-ZSM-5 CATALYSTS

As mentioned in previous chapters, while Cu-ZSM-5 is presently the most active catalyst for NO direct decomposition, its obvious shortcomings are low catalytic activity at both low (≤ 400°C) and high temperatures (≥ 500°C), inhibition by oxygen, as well as loss of activity due to steam aging. As shown in Chapters 3 and 4, the conversion of NO to N₂ over Cu-ZSM-5 materials is not a linear function of the copper ion-exchange level. Rather, very low activity exists for up to 30% exchange level, above which conversion increases rapidly with the exchange level. At least two Cu²⁺ sites are suggested, one inactive and another active for nitric oxide decomposition. Over exchanged (>100%) Cu-ZSM-5 improves catalytic activity, either because copper ions adequately populate sites accessible to NO (i.e., in the 10-membered rings of the ZSM-5) or because catalytic activity only emerges if enough adjacent copper active sites exist [67]. In Chapter 3, we proposed that the siting of copper cations in Cu-ZSM-5 affects catalytic activity for NO decomposition, based on the EPR results by Sass, et al [69], luminescence data by Dedecek, et al [90] and NO conversion to N₂ over Cu-ZSM-5 catalysts. We concluded that copper ions associated with one framework aluminum are active for NO decomposition. This hypothesis is supported by the increase in the specific NO decomposition rate per copper with Si/Al ratio [38]. Following this further, it is important to find ways to stabilize Cu cations on active sites to improve the catalytic activity of Cu-ZSM-5 materials for NO decomposition in practice.

In recent work, Kagawa, et al [50] reported that the incorporation of cocations into Cu-ZSM-5 promoted the catalytic activity of Cu ion for the direct NO decomposition in O₂-free gas streams at temperatures above 450°C. Transition or alkaline earth metals were equally effective cocations in Cu-ZSM-5 at 550°C. The mode of ion exchange was important, i.e., the cocation had to be exchanged first followed by copper ion exchange, for the effect to show. The effect of oxygen on the conversion of NO to N₂ was not examined
in that work. Oxygen has been reported to inhibit the reaction over unpromoted Cu-ZSM-5 catalysts, but the inhibition decreases with temperature [44, 45].

Cocations are presently under study for hydrocarbon-selective-catalytic reduction of nitric oxide. Following the study of NO decomposition over metal ion-modified Cu-ZSM-5, the group of Kagawa, et al [118] used similar catalysts to reduce NO by ethene (C2H4).

In this chapter, theocation effect on the NO decomposition reaction is examined in O2-containing gases over M/Cu-ZSM-5 catalysts, where M is an alkaline earth, transition or rare earth metal ion. The importance of the preparation method is discussed in terms of active (Cu ion) site stabilization.

5.1 EXPERIMENTAL

5.1.1 Catalyst Preparation and Characterization
Catalysts were prepared by incorporating metal cations into ZSM-5 zeolite supports according to ion exchange procedures described in Chapter 2. The elemental analyses were performed by ICP, after catalyst samples were dissolved in HF(48%). It is noted that a small amount of Si and Al was extracted from the zeolite during the ion exchanges. Sample solutions for cerium-containing catalysts were prepared by the techniques described in Chapter 2. It is worth to point out that both sample and standard solutions had the same volume fraction of each dissolution reagent. This enabled the sample and standard solutions to have the same viscosity. Hence, the sample and standard solutions were identically atomized in the plasma jet of ICP. More accurate results would are obtained this way.

In the text, the catalysts are identified in the following way: M (percent exchange level)/Cu(percent exchange level)-ZSM-5, where M represents a cocation, and the metal ion exchange level was defined in section 2.2.1.

Four Cu-ZSM-5 catalysts were synthesized in this Chapter. Their syntheses and properties are summarized in Table 5.1.

The metal ion-modified Cu-ZSM-5 preparation technique, as presented in Chapter 2, was developed with the evolution of different Mg ion-modified Cu-ZSM-5. As reviewed in Chapter 2, the separation factor of ion Cu2+ over
### Table 5.1  Summary of Cu-ZSM-5 Synthesis and Properties\(^1\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Cu/Na</th>
<th>Na/Al</th>
<th>Cu exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(50)-</td>
<td>19.4</td>
<td>0.25</td>
<td>0.44</td>
<td>once, RT</td>
</tr>
<tr>
<td>Cu(72)-</td>
<td>21.3</td>
<td>0.37</td>
<td>0.20</td>
<td>once, RT</td>
</tr>
<tr>
<td>Cu(97)-</td>
<td>21.9</td>
<td>0.48</td>
<td>0.13</td>
<td>once, RT</td>
</tr>
<tr>
<td>Cu(141)-</td>
<td>20.3</td>
<td>0.71</td>
<td>0.0</td>
<td>thrice, RT</td>
</tr>
</tbody>
</table>

1. Catalysts were prepared at pH = 5.7 in cupric acetate solution (0.007M) at room temperature. One exchange was made for 19 hours.

### Table 5.2  More Favorable Cu Exchange than Mg in ZSM-5\(^1\)

<table>
<thead>
<tr>
<th>Ion exchange</th>
<th>Mg, Cu compound concentration (M)</th>
<th>Mg exchange level (%)</th>
<th>Cu exchange level (%)</th>
<th>Na replaced level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.011</td>
<td>50.6</td>
<td></td>
<td>62.8</td>
</tr>
</tbody>
</table>

Test 1: The Mg ion-exchanged ZSM-5 was subsequently ion-exchanged with

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Mg exchange level (%)</th>
<th>Cu exchange level (%)</th>
<th>Na replaced level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.007</td>
<td>-38.2</td>
<td>81.2</td>
<td>34</td>
</tr>
<tr>
<td>washing catalyst</td>
<td>-4.6</td>
<td>-9.3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Final exchange</td>
<td>7.8</td>
<td>71.9</td>
<td>96.8</td>
<td></td>
</tr>
</tbody>
</table>

Test 2: The Mg ion-exchanged ZSM-5 was dried in air at 100°C for 15 hours, calcined at 500°C for 2 hours, then was further ion-exchanged with

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Mg exchange level (%)</th>
<th>Cu exchange level (%)</th>
<th>Na replaced level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.007</td>
<td>-4.8</td>
<td>70.6</td>
<td>33.9</td>
</tr>
<tr>
<td>Cu</td>
<td>0.007</td>
<td>-1.4</td>
<td>18.5</td>
<td>5.3</td>
</tr>
<tr>
<td>washing catalyst</td>
<td>0</td>
<td>-9.1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Final exchange</td>
<td>44.2</td>
<td>80.0</td>
<td>~100</td>
<td></td>
</tr>
</tbody>
</table>

1. Na-ZSM-5 was ion-exchanged with Mg\(^{2+}\) in Mg(NO\(_3\))\(_2\) solution at 90°C for 2.5 hours; the resulting Mg-ZSM-5 was ion-exchanged with Cu\(^{2+}\) in Cu(ac)\(_2\) solution at room temperature for 19 hours.
ion Na$^+$ is higher than that of ion Mn$^{n+}$ (n≥ 2) over ion Na$^+$, i.e. a more favorable exchange equilibrium for Cu$^{2+}$/Na$^+$. The results in Table 5.2 shows this fact. The Na-ZSM-5 was first ion-exchanged with Mg(NO$_3$)$_2$ at 90°C for 2.5 hours. A 50.6% Mg exchange level was achieved. In test 1, the Mg ion-exchanged ZSM-5 was directly ion-exchanged with Cu$^{2+}$. It was found that most of the Mg ions in the ZSM-5 were removed by the Cu cations. Therefore, the stabilization of cocation in ZSM-5 is needed. In test 2, the Mg ion-exchanged ZSM-5 was dried in air at 100°C for 14 hours, then calcined in air at 500°C for 2 hours. It was observed that only small fraction of the Mg ions were replaced by Cu cations in later Cu ion exchange processes. The procedure of air-calcination for Mn$^{n+}$-ZSM-5 was followed, and it was found that this is effective to keeping the Mn$^{n+}$ exchange level high even after subsequent copper ion exchanges.

The Mg(40)/Cu(91)-ZSM-5, as listed in Table 5.3, was prepared in a different method. The ZSM-5 zeolite was first ion-exchanged with Mg$^{2+}$ in a 0.005M aqueous solution of Mg(NO$_3$)$_2$ at 90°C for 2 hours. A 45.2% of Mg exchange level was achieved. The produced Mg-ZSM-5 material was ion-exchanged with Mg$^{2+}$ and Cu$^{2+}$ in a solution of Cu(ac)$_2$ (0.007M) and Mg(NO$_3$)$_2$ (0.035M) at room temperature for 19 hours twice. The ratios of Cu/Al and Mg/Al were 0.75 and 5 in the slurry, respectively. The excess Mg ions in the slurry was necessary to keep Mg in ZSM-5. Finally, the Mg exchange level was 40% and the Cu was 91%.

Great efforts have been made to make a Mg/Cu-ZSM-5 with about 50% Mg exchange level and a high Cu exchange level (≥ 110%). This was attempted by varying the ion-exchange conditions, such as the pH of solution, exchange time and solution temperature, etc. It was found that the catalyst color changed from light blue to brown when the maximum sum of Mg and Cu exchange levels exceeded about 150%. The color change is an indication of copper precipitation on zeolite particles, as discussed in Chapter 3. Table 5.3 shows two, Mg(50)/Cu(182)-ZSM-5 and Mg(62)/Cu(154)-ZSM-5, of these samples. The rest of Mg/Cu-ZSM-5 in Table 5.3 were prepared by following procedures in Table 2.2.
Table 5.3  Summary of Mg/Cu-ZSM-5 Syntheses and Properties

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Si/Al</th>
<th>Cu/Al</th>
<th>Mg/Al</th>
<th>Na/Al</th>
<th>color after Cu change</th>
<th>Cu exch.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(40)/Cu(91)</td>
<td>18.0</td>
<td>0.456</td>
<td>0.202</td>
<td>~0</td>
<td>light blue</td>
<td>twice, RT</td>
</tr>
<tr>
<td>Mg(34)/Cu(86)</td>
<td>17.1</td>
<td>0.43</td>
<td>0.170</td>
<td>~0</td>
<td>light blue</td>
<td>twice, RT</td>
</tr>
<tr>
<td>Mg(50)/Cu(182)</td>
<td>19.9</td>
<td>0.91</td>
<td>0.25</td>
<td>~0</td>
<td>brown</td>
<td>thrice, RT</td>
</tr>
<tr>
<td>Mg(52)/Cu(66)</td>
<td>19.5</td>
<td>0.33</td>
<td>0.26</td>
<td>~0</td>
<td>light blue</td>
<td>twice, RT</td>
</tr>
<tr>
<td>Mg(60)/Cu(97)</td>
<td>19.0</td>
<td>0.48</td>
<td>0.20</td>
<td>~0</td>
<td>light blue</td>
<td>twice, RT</td>
</tr>
<tr>
<td>Mg(62)/Cu(154)</td>
<td>19.7</td>
<td>0.77</td>
<td>0.31</td>
<td>~0</td>
<td>brown</td>
<td>thrice, RT</td>
</tr>
<tr>
<td>Mg(45)/Cu(104)</td>
<td>21.2</td>
<td>0.52</td>
<td>0.52</td>
<td>~0</td>
<td>light blue</td>
<td>twice, RT</td>
</tr>
<tr>
<td>Mg(65)/Cu(104)</td>
<td>17.9</td>
<td>0.52</td>
<td>0.327</td>
<td>~0</td>
<td>light brown</td>
<td>twice, RT</td>
</tr>
</tbody>
</table>

1. Cations exchanged once with Na/ZSM-5 at 85°C for 2 hours.
2. Cation exchanged once with Na/ZSM-5 overnight at RT.
3. The cation-exchanged ZSM-5 catalysts were dried in air at 100°C overnight, and calcined at 500°C for 2 hours.

Table 5.4 lists alkaline earth and transition metal ion-modified Cu-ZSM-5 catalysts. The same preparation procedures were followed for the sample preparation. It is worth pointing out that ion exchange between Ag⁺ and Na-ZSM-5 was made in the dark to prevent Ag⁺ reduction to form metallic Ag⁰.

Rare earth ion-modified Cu-ZSM-5 catalysts, four Ce-ZSM-5, three Ce/Cu-ZSM-5 and one La/Cu-ZSM-5, were prepared according to the procedures presented in Chapter 2. The syntheses and properties of the catalysts were summarized in Table 5.5.

Table 5.6 shows the syntheses and properties of Mg/Ag-ZSM-5, Mg/Ce-ZSM-5, Ce/Mg/Cu-ZSM-5 and Mg/Ce/Cu-ZSM-5. The former two catalysts were prepared by incorporating Mg ions into Na-ZSM-5. The resulting Mg-ZSM-5 was calcined in air at 500°C for 2 hours, then was ion-exchanged with Ag or Ce. Each ion exchange was made at 85°C for 2 hours. The latter two catalysts were ion-exchanged with Mg (or Ce), Ce (or Mg) and Cu in series. The cocation exchange was done at 85°C for two hours followed by 500°C air-
### Table 5.4  Summary of M/Cu-ZSM-5 Syntheses and Properties

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>M/Al</th>
<th>Cu/Al</th>
<th>Na/Al</th>
<th>M, Cu exchange times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(5)/Cu(98)-</td>
<td>20.5</td>
<td>0.05</td>
<td>0.49</td>
<td>0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Sr(39)/Cu(104)-</td>
<td>20.8</td>
<td>0.194</td>
<td>0.52</td>
<td>0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Ba(5)/Cu(126)-</td>
<td>22.1</td>
<td>0.025</td>
<td>0.63</td>
<td>0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Y(13)/Cu(135)-</td>
<td>22.4</td>
<td>0.045</td>
<td>0.675</td>
<td>0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Mn/Cu(73)-</td>
<td>19.2</td>
<td>NA</td>
<td>0.37</td>
<td>0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Ni/Cu(95)-</td>
<td>20.8</td>
<td>NA</td>
<td>0.478</td>
<td>0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Pd(88)/Cu(90)-</td>
<td>20.7</td>
<td>0.44</td>
<td>0.45</td>
<td>0</td>
<td>1, 2</td>
</tr>
</tbody>
</table>

1. Na-ZSM-5 was ion-exchanged with copper ion in a 0.007 M nitrate salt solution once at about 85°C for 2 hours, dried in air at 100°C overnight, and calcined in air at 500°C for 2 hours; the cation exchanged ZSM-5 was further ion-exchanged with Cu in a 0.007 M Cu(ac)₂ solution at room temperature for 19 hours.

### Table 5.5  Summary of Ce- and Ce/Cu-ZSM-5 Syntheses and Properties

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Ce/Al or La/Al</th>
<th>Cu/Al</th>
<th>Na/Al</th>
<th>Ce, Cu exchange times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(5)-</td>
<td>20.8</td>
<td>0.017</td>
<td>0.79</td>
<td>1, 0</td>
<td></td>
</tr>
<tr>
<td>Ce(11)-</td>
<td>20.4</td>
<td>0.034</td>
<td>0.72</td>
<td>1, 0</td>
<td></td>
</tr>
<tr>
<td>Ce(26)-</td>
<td>20.7</td>
<td>0.088</td>
<td>0.58</td>
<td>2, 0</td>
<td></td>
</tr>
<tr>
<td>Ce(60)-</td>
<td>20.8</td>
<td>0.20</td>
<td>0.52</td>
<td>3, 0</td>
<td></td>
</tr>
<tr>
<td>Ce(5)/Cu(106)-</td>
<td>20.7</td>
<td>0.017</td>
<td>0.53</td>
<td>~0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Ce(11)/Cu(119)-</td>
<td>21.2</td>
<td>0.036</td>
<td>0.596</td>
<td>~0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Ce(60)/Cu(138)-</td>
<td>19.8</td>
<td>0.20</td>
<td>0.69</td>
<td>0</td>
<td>3, 3</td>
</tr>
<tr>
<td>La(18)/Cu(123)-</td>
<td>19.4</td>
<td>0.06</td>
<td>0.627</td>
<td>0</td>
<td>1, 2</td>
</tr>
</tbody>
</table>

1. Conditions were the same as those in the note 1 of Table 5.4.
calcination for 2 hours, while the Cu ion exchange took place at room temperature for 19 hours.

Table 5.6  Summary of Mg/M- and Ce/Mg/Cu-ZSM-5 Syntheses and Properties

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Mg/Al</th>
<th>Ag/Al</th>
<th>Ce/Al</th>
<th>Cu/Al</th>
<th>Mg, Ag, Ce &amp; Cu exchange times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(40)/Ag(5)-</td>
<td>21.8</td>
<td>0.20</td>
<td>0.05</td>
<td></td>
<td></td>
<td>1, 1</td>
</tr>
<tr>
<td>Mg(42)/Ce(12)-</td>
<td>22.0</td>
<td>0.21</td>
<td></td>
<td>0.04</td>
<td></td>
<td>1, 1</td>
</tr>
<tr>
<td>Mg/Ce/Cu-</td>
<td>22.4</td>
<td>0.29</td>
<td></td>
<td>0.078</td>
<td>0.277</td>
<td>1, 1, 1</td>
</tr>
<tr>
<td>Ce/Mg/Cu-</td>
<td>21.2</td>
<td>0.13</td>
<td></td>
<td>0.144</td>
<td>0.48</td>
<td>1, 1, 2</td>
</tr>
</tbody>
</table>

1. Na-ZSM-5 was ion-exchanged with cocation in a 0.007M nitrate salt solution once at about 85°C for 2 hours, dried in air at 100°C overnight, and calcined in air at 500°C for 2 hours; the cocation exchanged ZSM-5 was further ion-exchanged with Cu in a 0.007 M Cu(ac)2 solution at room temperature for 19 hours.

Catalyst materials were characterized using XRD, luminescence, XPS and STEM/EDX. Structures of fresh and used catalysts were examined by the X-ray powder diffractometer. The diffraction patterns were taken in the 2θ range of 5-100° at a scanning speed of 1° per minute. Cerium(III) luminescence spectra were recorded on a SPEX spectrofluorometer. Spectra of air-calcined Ce-ZSM-5, and fresh and catalytically used Ce/Cu-ZSM-5 materials were collected by loading about 0.3 gram of the material into a quartz cell. Surface atomic ratios of Cu/Si and Ce/Si were measured by XPS and Ce distribution in the Ce/Cu-ZSM-5 was mapped by STEM/EDX.

5.1.2 Conversion Measurements and Kinetic Studies

The onversion of NO to N2 over the catalysts at different contact times was followed in a laboratory-scale packed-bed reactor, as described in Chapter 2. An amount of 0.5 g of catalyst was placed in reactor, and the catalyst packing density in the reactor was about 0.5 g/cm³. The contact time, W/F, was 0.05-
1.0 g s/cm³ (NTP). The total gas pressure in the reactor was 1.5 atm. NO concentrations varied from 0.2 to 2% in the feed stream, O₂ from 0 to 5%, balance He. The O₂-He stream was heated to 150°C before it was mixed with NO-He at the inlet of the reactor to avoid NO₂ formation [46]. All measurements were made after steady state had been reached.

5.2 RESULTS

5.2.1 Nitric Oxide Decomposition in Oxygen-Free Gas
The Cu-ZSM-5 and Mg/Cu-ZSM-5 catalysts shown in Tables 5.1 and 5.3 were evaluated in a gas containing 2% NO-He, at contact time of 1 g s/cm³ (NTP) over the temperature range of 350-600°C. Control experiments with Mg-ZSM-5 materials verified that the activity of Mg/Cu-ZSM-5 was exclusively due to Cu ions. Figures 5.1 shows the NO to N₂ conversion profiles obtained for the Cu(72)-ZSM-5, Cu(97)-ZSM-5, Mg(52)/Cu(66)-ZSM-5 and Mg(34)/Cu(86)-ZSM-5 catalysts tested under these conditions.

For the same copper ion-exchange level (~70%), the Mg(52)/Cu(66)-ZSM-5 catalyst shows a positive effect, i.e., higher NO to N₂ conversion than the Cu(72)-ZSM-5 material, in the high temperature region (450-600°C), as can be seen in Figure 5.1. These results are in agreement with what was report by Kagawa, et al [50]. Nitric oxide decomposition to nitrogen over catalysts Cu(97)-ZSM-5 and Mg(34)/Cu(86)-ZSM-5 shows that the cations enhance the catalytic activity of Cu-ZSM-5. However, the relative increment of NO conversion to N₂ is smaller than that over the low Cu ion-exchanged Mg/Cu-ZSM-5. This suggests that the cocation effect can be shown only when Cu exchange level is low (<100%). This is further supported by the similar activity of catalysts, Cu(103)-ZSM-5 and Mg(40)/Cu(104)-ZSM-5, in a mixture of 2% NO-He, at contact time of 1.0 g s/cm³ (NTP) and a temperature of 500°C.
Figure 5.1  Comparison of NO conversion to N₂ over Mg(34)/Cu(86)-ZSM-5 and Cu(97)-ZSM-5; Mg(52)/Cu(66)-ZSM-5 and Cu(72)-ZSM-5 in 2% NO- He and W/F= 1.0 g s/cm³ (NTP).

Within the group of the Mg/Cu-ZSM-5 catalysts, preparation conditions were important. As mentioned in the previous section, heating of the solution during Mg²⁺-exchange was necessary to preserve the Mg ions in the zeolite upon subsequent exchange with copper ion solutions. The effect of intermittent air calcination of Mg-ZSM-5 material at 500°C for two hours on the catalytic activity has been evaluated. The precalcined catalyst, Mg(34)/Cu(86)-ZSM-5, gave higher NO to N₂ conversion over the whole temperature range (350- 600°C) than the catalyst Mg(40)/Cu(91)-ZSM-5 without intermittent air calcination, as shown in Figure 5.2.
Figure 5.2  Effect of intermittent Mg-ZSM-5 calcination on Mg/Cu-ZSM-5 catalyst activity for NO conversion to N2 in 2% NO- He and W/F= 1.0 g s/cm3 (NTP): calcined Mg(34)/Cu(86)-ZSM-5 and non-calcined Mg(40)/Cu(91)-Z.

When the sum of Mg and Cu exchange levels was higher than about 150%, precipitation of copper took place. Figure 5.3 shows NO conversion to N2 over catalysts Mg(34)/Cu(86)-, Mg(45)/Cu(104)-, Mg(60)/Cu(97)-, Mg(65)/Cu(104)- and Mg(62)/Cu(154)-ZSM-5, as well as Cu(141)-ZSM-5. The catalytic performance of the first four catalysts is similar. It is noted that the fresh catalysts Mg(65)/Cu(104)-ZSM-5 and Mg(62)/Cu(154)-ZSM-5 had brown color which was caused by copper deposition. The NO conversion to N2 over the Mg(62)/Cu(154)-ZSM-5 catalyst is higher than over the rest of Mg/Cu-ZSM-5 catalysts, but lower than over Cu(141)-ZSM-5 material. It is found that catalytic activity of Mg(62)/Cu(154)-ZSM-5 was constant in terms of NO conversion to N2 in temperature range of 450- 500°C.

We found that the cocation effect on the Cu-ZSM-5 activity is not sensitive to the type of divalent cocation chosen for the conditions used in this thesis work. Figure 5.4 shows the NO conversion to N2
Figure 5.3  NO decomposition over Mg/Cu-ZSM-5 and Cu(141)-ZSM-5 catalysts in 2% NO- He and W/F= 1.0 g s/cm³ (NTP).

Figure 5.4  Same catalytic activities are shown for selected M/Cu-ZSM-5 in 2% NO- He and W/F= 1.0 g s/cm³ (NTP).
over several precalcined M/Cu-ZSM-5, where M is a divalent metal ion. When Cu ion exchange level is high, however, Ba(5)/Cu(126)-ZSM-5 displayed lower catalytic activity than Cu(141)-ZSM-5 at temperatures higher than 550°C (see Figure 5.5). The similar performance of Y(13)/Cu(135)-ZSM-5 is also shown in Figure 5.5 for comparison, even though Y is trivalent ion. In regard to monovalent metal ion, nitric oxide decomposition over the Ag(5)/Cu(98)-ZSM-5 catalyst was higher than that over the Cu(97)-ZSM-5 at high temperatures, and slightly lower at low temperatures (Figure 5.6). However, alkali metal ion-modified Cu-ZSM-5 was reported to have lower catalytic activity than Cu-ZSM-5 [50].

Three Ce-ZSM-5 materials, and three rare earth ion-modified Cu-ZSM-5 catalysts, namely La(18)/Cu(123)-ZSM-5, Ce(11)/Cu(119)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5, shown in Table 5.5, were evaluated and compared to Cu(141)-ZSM-5 in a gas mixture of 2% NO-He at contact time of 1.0 g s/cm³ (NTP) over the temperature range of 300-600°C. Figure 5.7 shows the NO conversion to N₂ profiles obtained for these catalysts under the above conditions.

The coexistence of rare earth ions with copper in the ZSM-5 produced a markedly different effect promoting the activity of copper ions for the NO decomposition at low temperatures (300-400°C). The Ce(11)-, Ce(26)- and Ce(60)-ZSM-5 material have very low (but measurable) activity, less than 7% conversion of NO to N₂, over the temperature region of 300-500°C, as shown in Figure 5.7. However, the Ce(11)/Cu(119)-ZSM-5 and La(18)/Cu(123)-ZSM-5 catalysts showed higher conversion of NO to N₂ than the over exchanged Cu(141)-ZSM-5 catalyst at temperatures in the range of 300-400°C. When a 50% - 50% mixture (by weight) of Ce(11)/Cu(119)-ZSM-5 and Cu(141)-ZSM-5 was tested, its catalytic activity was between Cu(141)-ZSM-5 and Ce(11)/Cu(119)-ZSM-5, as shown in Figure 5.8.

From the above results, we conclude that alkaline earth and transition metal ions improve Cu-ZSM-5 activity at high temperatures (≥ 450°C), while rare earth ions enhance Cu-ZSM-5 activity at low temperatures (≤ 400°C). The coexistence of Mg and Ce in Cu-ZSM-5 greatly improves the Cu-ZSM-5 activity over whole temperature range of 300-600°C. Figure 5.1 shows that Mg(34)/Cu(86)-ZSM-4 had slightly higher activity than Cu(97)-ZSM-5.
Figure 5.5  Comparisons of NO conversion to N₂ over Ba(5)/Cu(126)-ZSM-5 and Y(13)/Cu(135)-ZSM-5 with that over Cu(141)-ZSM-5 in 2% NO-He and W/F = 1.0 g s/cm³ (NTP).

Figure 5.6  NO conversion to N₂ over Ag(5)/Cu(98)-ZSM-5 and Cu(97)-ZSM-5 catalysts in 2% NO-He and W/F = 1.0 g s/cm³ (NTP).
Figure 5.7  Comparison of NO conversion to N₂ over Ce-ZSM-5, Ce/Cu-ZSM-5, La/Cu-ZSM-5 and Cu-ZSM-5 catalysts in 2% NO-He and W/F= 1.0 g s/cm³ (NTP).

Figure 5.8  Comparison of NO conversion to N₂ over a mixture of 50 wt.% Ce(11)/Cu(119)- and 50 wt.% Cu(141)-ZSM-5, Ce(11)/Cu(119)- and Cu(141)-ZSM-5 in 2% NO-He and W/F= 1.0 g s/cm³ (NTP).
However, the existence of Ce in the catalyst Ce(42)/Mg(26)/Cu(96)-ZSM-5 further promoted Mg/Cu-ZSM-5 catalytic activity, as depicted in Figure 5.9. For Mg/Ce/Cu-ZSM-5 material with low Cu exchange level, this effect of cocations on the catalytic activity is even more pronounced. The Mg(60)/Ce(23)/Cu(55)-ZSM-5 shows much higher catalytic activity for NO decomposition than Cu(50)-ZSM-5 in temperature range of 350-600°C.

![Graph showing NO conversion to N2 (%) vs. Reaction Temperature (°C)](image)

Figure 5.9 Effect of coexistence of Mg and Ce cations on Cu-ZSM-5 activity in 2% NO-He and W/F=1.0 g s/cm³ (NTP).

Finally, no catalytic activity was found for NO decomposition over Mg/Ag-ZSM-5 and Mg/Ce-ZSM-5 materials. This further confirms that Cu is the active center in metal ion-modified Cu-ZSM-5 catalysts.

5.2.2 NO Decomposition in O2-Containing Gases
Oxygen has been reported to inhibit the NO decomposition reaction, but the inhibition decreases with temperature [44]. The oxygen effect was studied on Cu-ZSM-5 catalysts using high NO concentrations (1-4%) in the feed gas. Iwamoto, et al [48] have reported that in oxygen-containing gas the NO
conversion to N2 does not decrease as much for over-exchanged Cu-ZSM-5 catalysts. However, a large decrease was shown for low Cu ion-exchanged Cu-ZSM-5.

In the present work we examined the effect of oxygen both with excessively exchanged Cu-ZSM-5 as well as with the cocation-modified M/Cu-ZSM-5 catalysts. Figure 5.10 shows typical conversion-temperature plots for the Cu (141)-ZSM-5 catalyst with 0 and 5% O2 containing gases with NO content fixed at either 2% or 0.2%, W/F = 1g s/cm³ (NTP). The data display strong O2-inhibition and the lower-sensitivity to O2 at high temperature mentioned above. However, it is very interesting that a similar plot for low NO-content (0.2%) in the gas, shows much less inhibition by oxygen at low temperatures and less oxygen-effect in the high-temperature region.

Figure 5.10 Effect of O2 and NO concentrations on the Cu(141)-ZSM-5 activity for NO decomposition at W/F = 1.0 g s/cm³ (NTP) in different reaction gas streams.
Similar experiments were run with the Mg/Cu-ZSM-5 catalysts. Typical results are shown in Figure 5.11 for the Mg (34)/Cu (86)-Z material. Similar trends to those in Figure 5.10 for the Cu(141)-ZSM-5 catalyst are seen for a feed gas with 2% NO, 0% or 5% O₂, and 1.0 g s/cm³ contact time. When the inlet concentration of NO was 0.2%, however, the NO to N₂ conversion in the presence of 5% O₂ was higher than that in the absence of O₂ at temperatures above 450°C.

![Graph showing NO conversion to N₂ (%) over reaction temperature (°C)](image)

Figure 5.11 Effect of O₂ and NO concentrations on the Mg(34)/Cu(86)-ZSM-5 activity for NO decomposition at W/F= 1.0 g s/cm³ (NTP) in different reaction gas streams.

The other Mg/Cu-ZSM-5 catalysts gave conversions similar to those in Figure 5.11 for the catalyst Mg(34)/Cu(86)-ZSM-5. Furthermore, NO conversion to N₂ in 0.2% NO- 5% O₂ - He was higher than that in 0.2% NO - He when the temperature was higher than 550°C. The conversion of NO to N₂ is less inhibited by oxygen in the high temperature region (500-600°C).

Another feature of the conversion-temperature profiles becomes evident by comparing the data of Figures 5.10 and 5.11 for the 5% O₂-containing feed
gas with low (0.2%) or high (2%) NO content. For both the Cu (141)-ZSM-5 and Mg (34)/Cu (86)-ZSM-5 catalysts, the conversion of NO to nitrogen increases as the NO-content decreases at temperatures below 450°C. Assuming that O₂ and NO compete for adsorption sites, oxygen would inhibit the reaction, especially at low temperatures. Under these conditions, NO₂ formation may be favored reducing the selectivity to N₂. It is not clear, however, why oxygen appears to inhibit the decomposition reaction more for the high NO concentration gas. Therefore, more experimental work is warranted.

Figure 5.1 shows that in the absence of oxygen, NO conversions over the Mg(34)/Cu(86)-ZSM-5 catalyst were slightly higher than these over Cu(97)-ZSM-5. However, a more pronounced positive effect was found in the presence of oxygen (2% NO-5% O₂-He), as shown in Figure 5.12. The performance of Ag(5)/Cu(98)-ZSM-5 was similar to that of the Mg(34)/Cu(86)-ZSM-5 under the same conditions.

![Graph showing NO conversion to N₂](image)

**Figure 5.12** Cocation moderates the reaction inhibition by O₂ in 2% NO-5% O₂-He at W/F = 1.0 g s/cm³ (NTP).
The Ce ion effect on the Cu-ZSM-5 catalytic activity was further evaluated in gas mixtures of 2% NO- 5% O2- He at contact time of 1.0 g s/cc when both Ce and Cu ion exchange levels were high. The NO conversion to N2 over catalysts Ce(60)/Cu(138)-ZSM-5 is shown in Figure 5.12 under the above experimental conditions. For comparison, the NO conversion to N2 over the Cu(141)-ZSM-5 is also shown in Figure 5.12. The catalytic activity of the Ce(60)/Cu(138)-ZSM-5 is higher than that of the Cu(141)-ZSM-5 at low temperature in the oxygen-free gas (Figure 5.7) and at high temperature in the oxygen-containing gas (Figure 5.12). This further shows thatocations moderate reaction inhibition by oxygen in the reactant stream.

5.2.3 Catalyst Characterization by XRD, Luminescence, XPS and STEM/EDX

Structures of the fresh and used catalysts were examined by XRD. No structure change was found for the samples, compared with as-received Na-ZSM-5. Typical X-ray diffraction patterns of fresh and used Cu(97)-ZSM-5 and Mg(34)/Cu(86)-ZSM-5 as well as the parent Na-ZSM-5 are shown in Figure 5.13. It was found that the XRD patterns of ion-modified ZSM-5 are the same as the as-received ZSM-5. No diffraction peak of copper, and cerium oxide crystals were found on XRD patterns.

Hydrated and dehydrated (calcined in air at 500°C) Ce3+ ion-exchanged ZSM-5, fresh and catalytically used Ce/Cu-ZSM-5 materials were examined by the luminescence to identify whether Ce3+ had been ion-exchanged into ZSM-5 or not. When the Ce3+ ions were deposited on the ZSM-5, i.e., not ion-exchanged, the Ce3+ would be oxidized to Ce4+, which is nonluminescent species, by treatment at 500°C in air for two hours.

Luminescence measurements were performed by two steps. The first was to find the excitation wavelength at which the maximum intensity of Ce3+ photoluminescence would be achieved. Radiation energy of Ce3+ was measured at a wavelength of 359 nm, which has characteristic Ce3+ luminescence in Ce3+ ion-exchanged Y zeolites [104] when the wavelength of the excitation light was changing from 240 to 329 nm. It was found that the maximum intensity of Ce3+ luminescence was detected when the wavelength of excitation light was 295 nm. This result is shown in Figure
Figure 5.13  XRD patterns of (a) fresh and (b) used Cu(97)-ZSM-5, (c) fresh and (d) used Mg(34)/Cu(86)-ZSM-5 as well as (e) as-received Na-ZSM-5 zeolite.
5.14. The second was to take the Ce$^{3+}$ luminescence spectra in the wavelength range of 320–510 nm when a sample was exposed to the light of 295 nm.

![Graph showing luminescence intensity vs. excitation wavelength](image)

**Figure 5.14** Maximum intensity of Ce$^{3+}$ photoluminescence evident at 359 nm for the hydrated Ce(5)-ZSM-5 when the wavelength of excitation light being 295 nm.

Luminescence spectra of hydrated and calcined (in air at 500°C for 2 hours) Ce(5)-ZSM-5 are shown in Figures 5.15 and 5.16 with a doublet at 346.4 and 358.3 nm. Assignments of Ce$^{3+}$ transitions for the doublet are $^2\!D \rightarrow ^2\!F_{5/2}$ for 346.4 nm and $^2\!D \rightarrow ^2\!F_{7/2}$ for 358.3 nm by analogy to that of Ce$^{3+}$ in zeolites X and Y [119]. Calcination of the sample causes loss of bulk and bound water molecules. It was found that there is no change in peak position and peak number by comparing the spectrum of the hydrated sample with that of the calcined material. However, the luminescence intensity of the calcined Ce(5)-ZSM-5 was about 50% of that for the hydrated sample. The luminescence intensity at 358.3 nm is higher than that at 346.4 nm for the hydrated sample, while the intensity at 346.4 nm is stronger than that at 358.3 nm for the calcined sample.
Figure 5.15  A doublet peak of Ce$^{3+}$ photoluminescence shown for the hydrated Ce(5)-ZSM-5, $\lambda_{exc}=295$ nm.

Figure 5.16  Ce$^{3+}$ photoluminescence intensity decreased after calcination of the Ce(5)-ZSM-5 in air at 500°C for 2 hours, $\lambda_{exc}=295$ nm.
The spectrum of fresh Ce(5)/Cu(135)-ZSM-5 shown in Figure 5.17 is similar to those of the hydrated and calcined Ce(5)-ZSM-5 materials. The spectrum intensity is smaller after the calcined Ce(5)-ZSM-5 was ion-exchanged with Cu\(^{2+}\) in aqueous solutions at room temperature thrice. The intensity at 358.3 nm is again higher than that at 346.4 nm.

![Graph showing the intensity of photoluminescence versus wavelength.]

Figure 5.17 Ce\(^{3+}\) photoluminescence of the fresh Ce(5)/Cu(135)-ZSM-5, \(\lambda_{exc}=295\) nm.

Same measurements were performed for the calcined Ce(60)-ZSM-5, the fresh Ce(60)/Cu(138)-ZSM-5, and catalytically used Ce(60)/Cu(138)-ZSM-5 in 2% NO - He over temperature range of 350~600\(^{\circ}\)C for 24 hours, followed by in 2% NO-5% O\(_2\)-He for 24 hours. These results are shown in Figures 5.18-5.20. The spectra are similar to each other, except the luminescence intensity is different. Comparing Figure 5.19 with Figure 5.20, the Ce\(^{3+}\) luminescence was decreased after Ce(60)/Cu(138)-ZSM-5 was used to decompose nitric oxide.

The surface ratios of Ce/Si of 500\(^{\circ}\)C air-calcined Ce(11)/Cu(119)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 samples were measured by XPS. The bulk Ce/Si ratio measured by ICP is 0.002 for the catalyst Ce(11)/Cu(119)-ZSM-5, while the bulk Ce/Si is 0.01 for the Ce(60)/Cu(138)-ZSM-5. The surface Ce/Si in the Ce(11)/Cu(119)-ZSM-5 was the same as the bulk value. However, the cerium
Figure 5.18 Ce\(^{3+}\) photoluminescence of calcined Ce(60)-ZSM-5, \(\lambda_{\text{exc}}=295\) nm.

Figure 5.19 Ce\(^{3+}\) photoluminescence of the fresh Ce(60)/Cu(138)-ZSM-5, \(\lambda_{\text{exc}}=295\) nm.
Figure 5.20  Ce$^{3+}$ photoluminescence of the used Ce(60)/Cu(135)-ZSM-5 in dry gas, $\lambda_{exc}=295$ nm.

concentration (Ce/Si = 0.27) in the Ce(60)/Cu(138)-ZSM-5 was much higher than the bulk value.

STEM/EDX mapping of cerium, aluminum and copper were performed for the calcined fresh Ce(26)-ZSM-5 (Figure 6.19) and Ce(60)/Cu(138)-ZSM-5 (Figure 6.20). For the Ce(26)-ZSM-5 material, it was found that Ce ions were uniformly distributed, and that cerium ions enriched the surface region. For the Ce(60)/Cu(138)-ZSM-5, it was observed that cerium, aluminum and copper were uniformly distributed, and the copper was associated not only with aluminum but also with cerium.

5.3 DISCUSSION

The cocation effect, the importance of ion exchange sequence and catalyst heat treatment on the NO decomposition activity may all be explained in terms of stabilizing copper at active sites. In their EPR studies, Sass and Kevan [69] reported that Cu$^{2+}$ cations in ZSM-5 were not preferentially adjacent to the negative charged AlO$_2^-$ until the Cu$^{2+}$ concentration was high enough or
unless a divalent cation (Ca$^{2+}$ or Mg$^{2+}$) was present. The luminescence
data by Dedecek, et al [90] also showed that copper ion preferentially occupied
the sites close to the two framework aluminum atoms in Cu-ZSM-5 with a
low copper content; on the other hand, with high Cu exchange level, the
Cu$^{2+}$ was located nearer to one aluminum. Kucherov, et al [59, 60] have
identified two types of isolated Cu$^{2+}$ ions: one in a square pyramidal five-
coordinated configuration, the other in a square planar four-coordinated. At
low Cu exchange level, the five-coordinated Cu$^{2+}$ ions were preferably
formed [59]. In Chapter 3, we also presented a correlation of the NO
conversion to N$_2$ over various Cu-ZSM-5 catalysts as a function of the
amount of square planar Cu$^{2+}$ ions, calculated from the data given in
Kucherov, et al [59]. We assumed that this data could be extended to our
ZSM-5 which has Si/Al ratio equal to 21.5. A linear correlation was found.

Based on the above observations, we have concluded that Cu cation sites
near to one framework aluminum, which are four-coordinated, are active for
NO decomposition. It is plausible that the inert Mg ions occupy the sites
associated with two framework aluminum atoms, which forces Cu cations
subsequently exchanged into ZSM-5 to take active sites. Therefore, the
relatively high population of four-coordinated Cu$^{2+}$ ions results in high NO
conversion to N$_2$, as shown in Figure 5.1. The cations are inert for the NO
decomposition, and a limit of maximum cation exchange sites exists in ZSM-
5, therefore, the positive cocation effect should be more pronounced for low
Cu exchange levels. The results shown in Figures 5.1 and 5.5 support this
argument.

The intermittent calcination effect may be explained by strong bonding of
Mg$^{2+}$-bare ions to zeolite framework oxygen, upon dehydration during
calcination from their respective larger hydrated complex ions. This would
effectively keep the Mg$^{2+}$ in the inactive sites. Hence, a higher NO
conversion to N$_2$ is expected for the pre-calcined Mg(34)/Cu(86)-ZSM-5 over
the non-calcined Mg(52)/Cu(91)-ZSM-5 catalyst as shown in Figure 5.2.

The observed cocation effect in Kagawa, et al [50] and the present work,
therefore, is one of stabilization of the copper cations in active sites. To
pursue this argument further, the performance shown in Figure 5.1 should
not be sensitive to the type of cocation chosen. Figure 5.4 shows the NO
conversion to N₂ over several precalcined M²⁺/Cu-ZSM-5 catalysts with similar Cu²⁺ exchange level, where M is a divalent transition metal or alkaline earth ion. Similar catalytic activity is indicated by the overlapping conversion profiles of Figure 5.4.

In Chapter 3, we found that copper precipitation took place when Cu ion exchange level was higher than about 150%. The failure to prepare an active Mg/Cu-ZSM-5 with the sum of Cu and Mg exchange level exceeding 150% further suggests that Mg cations occupy the same sites as Cu ions in ZSM-5 zeolite. The performance of metal ion-modified Cu-ZSM-5 supports this.

The preparation of Ce-ZSM-5 by ion exchange at 85°C, 2h achieves partial exchange with Na ions, as shown in Table 5.5. In addition, during the exchange, partial protonation of the sites must have occurred as indicated by the lack of charge balance in Table 5.5. The data of Table 5.5 also show that a limit to cerium ion exchange exists after two sequential exchanges. Thus, the higher uptake of Ce in the third exchange must be due to surface deposition rather than ion exchange. STEM/EDX and XPS data confirm this (Figures 6.19 and 6.20 and higher surface Ce/Si than the bulk value). However, the oxidic cerium is not highly crystallized, as no CeO₂ peaks could be detected by XRD. Based also on the luminescence evidence of Ce³⁺ in both low- and high-cerium containing ZSM-5 samples (Ce³⁺ luminescence signal intensity does not increase linearly with Ce loading); XPS evidence (the surface Ce/Si is equal to the bulk value for Ce(11)/Cu(119)-ZSM-5; but much higher than the bulk value for the Ce(60),Cu(138)-ZSM-5); and STEM/EDX evidence (uniform bulk signal of cerium), we conclude that our working catalysts comprise a small fraction of cerium as Ce³⁺ ions associated with the framework aluminum as well as Ce⁴⁺ in oxidic form on the zeolite surface; the latter is predominant in the Ce(60)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5, while the former dominates in the Ce(11)-ZSM-5 and Ce(11)/Cu(119)-ZSM-5 materials. It appears that the Ce³⁺ form is the activity promoter, as indicated by activity comparisons of Ce(60)/Cu(138)-ZSM-5 and Ce impregnated Ce(60)/Cu(136)-ZSM-5 (for the latter catalyst preparation, see Chapter 6). The latter catalyst contains only Ce⁴⁺ oxide on the surface and shows similar catalytic performance as Cu-ZSM-5, i.e. no enhancement. This is because there is no possibility for ion exchange between the Cu(136)-ZSM-5 and cerium ions
under the conditions used for impregnation (Table 6.1). In Figure 5.7, the
concerted effect of Ce$^{3+}$ and active copper sites is clearly shown by higher NO
conversion to N$_2$ over the Ce(11)/Cu(119)-ZSM-5 than the Cu(141)-ZSM-5
catalyst in the low temperature range (300-450°C). The reduced effectiveness
of Ce(60)/Cu(138)-ZSM-5 in this region may be due to lower Ce$^{3+}$
concentration. In catalysts prepared by sequential exchange, the Ce$^{3+}$ ion was
exchanged first; then air calcination was used prior to exchanging the copper
ions. The role of heat treatment on the cerium stability in ZSM-5 may be
similar to that of Ce-Y zeolite, which has been reported to cause stronger
binding of Ce cations to the zeolite framework in Na-Y [120]. It is interesting
that even after several such air calcinations, a small fraction of Ce$^{3+}$ exists in
the zeolite, as shown in Figure 5.20. As STEM/EDX measured, Cu ions are
associated not only with aluminum but also with cerium. The interaction of
Ce and Cu may contribute to the effect of Ce on Cu-ZSM-5 activity for NO
decomposition.

The presence of both Ce and Mg promotes Cu-ZSM-5 catalytic activity in
both low and high temperatures, especially for low copper exchange level, as
shown in Figure 5.9. Figure 5.1 shows that Mg ions promoted the Cu-ZSM-5
activity at temperature higher than 450°C, while Ce cations enhanced the
activity at temperatures below 400°C. Interestingly, the Cu-ZSM-5 activity was
greatly improved by the coexistence of Ce and Mg in temperature of 400-
450°C. This indicates that Ce and Mg ions may not interact with Cu ions
independently.

The effect of cocation on inhibition of NO decomposition by oxygen over
metal ion-modified Cu-ZSM-5 will be presented in Chapter 7.

5.4 CONCLUSION

Alkaline earth and transition metal ion-exchanged ZSM-5 zeolites further
exchanged with copper ions show promotion effects over the catalytic activity
of Cu-ZSM-5 materials for NO decomposition in the present and absence of
oxygen at high temperature (≥450°C). The performance of rare earth ion-
modified Cu-ZSM-5 is different, the cocation effect being one of promotion of
the Cu-ZSM-5 activity at low temperatures (≤400°C). Furthermore,
coexistence of Mg and Ce cations enhances the Cu-ZSM-5 activity for the reaction over the whole temperature range of 350- 600°C.

An explanation of the promotion effect may be that the inert cocations are exchanged into the inactive sites in ZSM-5 zeolite. The copper ions are subsequently forced to occupy the active sites. For metal ion-modified Cu-ZSM-5 and Cu-ZSM-5 with same copper exchange level, therefore, the former has a higher fraction of copper at the active sites than the latter. Hence, the relatively high population of active Cu ions in the metal ion-modified Cu-ZSM-5 results in high conversion of NO to N₂ and O₂.

Stabilization of inert cocation at inactive sites is crucial for the positive cocation effect, since the separation factor of ion Cu²⁺ over ion Na⁺ is higher than those of ion Mn⁺ (n≥ 2) over ion Na⁺. The 500°C-air calcination of M-ZSM-5 is effective in keeping the Mn⁺ exchange level high even after subsequent copper ion exchanges. The cocation stability is due to its strong coordination to the zeolite framework.
Chapter 6

HYDROTHERMAL STABILIZATION OF CU-ZSM-5
BY CERIUM FOR NITRIC OXIDE DECOMPOSITION

Cations in Cu-ZSM-5 display positive effects on the catalytic activity, as discussed in the previous Chapter. The incorporation of rare earth metal cocation to Cu-ZSM-5 improves the low temperature catalytic activity in oxygen-free gases, while addition of alkaline earth and transition metal cocation improves the high temperature catalytic activity. The latter is in good agreement with recently reported work [50]. Furthermore, it was found that cocations in Cu-ZSM-5 moderate the oxygen inhibition of catalytic activity for nitric oxide decomposition.

All NO\(_x\)-containing combustion gases also contain a significant amount of water vapor (2-15%), hence the hydrothermal stability of the catalyst is of great importance for practical application. In Chapter 3, it was shown that Cu-ZSM-5 deactivated when it was exposed to water vapor in reaction stream. Iwamoto, et al. [48], and Li and Hall [46] reported that the catalytic activity of Cu-ZSM-5 for NO conversion to N\(_2\) was decreased in the presence of 2% water vapor, but could be recovered after removal of water vapor. Details about these tests were not given in the articles. However, Kharas and coworkers [49] found that Cu-ZSM-5 was quickly and severely deactivated in a simulated lean-burn gas mixture, including 10% H\(_2\)O, at GHSV= 127,000 h\(^{-1}\) at 600 and 800\(^{\circ}\)C. The authors claimed that sintering of the catalytically active components, rather than degradation of the metastable zeolitic support, probably dominates deactivation.

Understanding the Cu-ZSM-5 deactivation, developing catalysts which have more tolerance to water poison, and characterizing these new catalysts are the subject of this Chapter. The parent Na-ZSM-5 zeolite was steamed in water vapor-containing gas at different temperatures to examine the structural change of the zeolite. Work is focused on detailed comparisons of Ce/Cu-ZSM-5 with Cu-ZSM-5 catalysts under various wet NO decomposition reaction conditions. Fresh, steamed and catalytically reacted catalyst samples were examined by scanning transmission electron microscopy (STEM).
equipped with X-ray microprobe analysis, powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) to identify differences in the state and distribution of copper, cerium and aluminum in the catalyst samples. Chemical and physical structure changes are correlated with catalyst behavior.

6.1 EXPERIMENTAL

6.1.1 Catalyst Preparation and Composition Analysis
Table 6.1 shows the preparation and composition of the catalysts used in this study. Four types of catalysts, Cu$^{2+}$ ion-exchanged, Ce$^{3+}$ ion-exchanged, Mg$^{2+}$, Ba$^{2+}$, Y$^{3+}$, Ce$^{3+}$ modified Cu$^{2+}$ ion-exchanged ZSM-5, and Ce$^{3+}$ impregnated Cu$^{2+}$ ion-exchanged ZSM-5, were prepared. Meta$^1$ ion-exchanged ZSM-5 zeolite catalysts were prepared incorporating metal cations into the parent Na-ZSM-5 zeolite (Si/Al = 21.5, SMR 6-2670-1191, Davison) according to the ion exchange procedures developed in this thesis research work, while the Ce-impregnated Ce/Cu-ZSM-5 was synthesized by impregnating the copper ion-exchanged ZSM-5 with cerium nitrate.

The Cu ion-exchanged ZSM-5 catalysts were prepared by copper exchange with sodium in the Na-ZSM-5 following the procedure presented in Chapter 2. pH of cupric acetate solution used here was monitored by a digital pH meter (Beckman Product, Model 3500). pH indicator strips were also used to double check the measured values. The initial pH of the solution was 5.74, and the final pH was 5.65. The ZSM-5 particles were added into the solution in amounts corresponding to replacing all the Na$^+$ ions in the ZSM-5 by half the number of Cu$^{2+}$ in the cupric acetate solution. The Cu-exchange process was carried out once for low Cu ion exchange level and thrice for high copper exchange.

The metal ion-modified Cu-ZSM-5 catalysts were synthesized following the procedures developed in this thesis work, as described in Chapter 2.

The Ce-impregnated Ce/Cu-ZSM-5 catalysts was prepared as follows: after cerium nitrate was dissolved in deionized water, a certain amount of Cu(136)-ZSM-5 was added to the cerium nitrate solution corresponding to an atomic ratio of Ce/Al = 0.2. This atomic ratio gave the same total amount of cerium as in the ion-exchanged Ce(60)/Cu(138)-ZSM-5 catalyst (see Table 6.1).
The slurry was left at 25°C for 5 days, then dried in air at 100°C for 10 hours. The materials were finally calcined in air at 500°C for 2 hours.

Table 6.1 Summary of Catalyst Preparation and Properties

<table>
<thead>
<tr>
<th>Catalyst (M/Cu-ZSM-5) as-received</th>
<th>Si/Al</th>
<th>Cu/Al&lt;sup&gt;2&lt;/sup&gt;</th>
<th>M/Al&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Na/Al&lt;sup&gt;2&lt;/sup&gt;</th>
<th>M, Cu exchange times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(72)-</td>
<td>21.5</td>
<td>0.36</td>
<td>0.25</td>
<td></td>
<td>0, 1</td>
</tr>
<tr>
<td>Cu(97)-</td>
<td>21.9</td>
<td>0.48</td>
<td>0.13</td>
<td></td>
<td>0, 1</td>
</tr>
<tr>
<td>Cu(141)-</td>
<td>20.3</td>
<td>0.705</td>
<td>~0</td>
<td></td>
<td>0, 3</td>
</tr>
<tr>
<td>Mg(52)/Cu(66)-</td>
<td>19.5</td>
<td>0.33</td>
<td>0.26</td>
<td>~0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Mg(34)/Cu(86)-</td>
<td>17.1</td>
<td>0.43</td>
<td>0.17</td>
<td>~0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Ba(5)/Cu(1126)-</td>
<td>22.1</td>
<td>0.63</td>
<td>0.025</td>
<td>~0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Y(13)/Cu(135)-</td>
<td>22.3</td>
<td>0.675</td>
<td>0.044</td>
<td>~0</td>
<td>1, 3</td>
</tr>
<tr>
<td>Ce(11)/Cu(119)-</td>
<td>19.5</td>
<td>0.60</td>
<td>0.033</td>
<td>~0</td>
<td>1, 2</td>
</tr>
<tr>
<td>Ce(40)/Cu(135)-</td>
<td>20.7</td>
<td>0.675</td>
<td>0.133</td>
<td>~0</td>
<td>3, 3</td>
</tr>
<tr>
<td>Ce(60)/Cu(138)-</td>
<td>19.8</td>
<td>0.69</td>
<td>0.20</td>
<td>~0</td>
<td>3, 3</td>
</tr>
<tr>
<td>Ce(60)/Cu(136)-&lt;sup&gt;4&lt;/sup&gt;</td>
<td>20.2</td>
<td>0.695</td>
<td>0.20</td>
<td>~0</td>
<td>impre., 3</td>
</tr>
</tbody>
</table>

1 Cation, M, exchanged with Na-ZSM-5 at 85°C for 2 hours, while Cu exchanged at 22°C.
2 The ratios are calculated based on Al and cation contents as measured by ICP.
3 as-received Na-ZSM-5: SMR-2670-1191 (Davison).
4 Ce was impregnated on Cu(136)-ZSM-5 at room temperature.

Elemental analyses were performed by inductively coupled plasma emission spectrometry, as described in Chapter 2. In this Chapter, the catalysts are identified in the same way as that in Chapter 5: M(percent cocation exchange level)/Cu<sup>2+</sup>(percent exchange level)-ZSM-5, where 100% metal ion (of n valence) exchange level in the catalysts is defined as one metal ion replacing n Na<sup>+</sup> [or neutralizing n (AlO<sub>2</sub>)<sup>-</sup>] and the atomic ratio of (metal
ion)/Al = 1/n, e.g., Cu$^{2+}$/Al = 0.5. The metal ratios were measured by ICP. Table 6.1 shows the ratios of Na, Cu, Ce, Mg, Ba, Y to Al after the exchange steps of the catalysts examined in this study.

6.1.2 Hydrothermal Effect on Na-ZSM-5 Structure
Hydrothermal effects on the structure and Cu$^{2+}$ ion exchange capacity of the parent Na-ZSM-5 zeolites, and on the catalytic activity of the Cu-ZSM-5 and metal ion modified Cu-ZSM-5 catalysts for NO decomposition were evaluated. The parent Na-ZSM-5 zeolite was pretreated for 20 hours in a gas mixture containing 20% H$_2$O- 4% O$_2$- He at temperatures of 500, 600 and 750$^\circ$C to examine zeolitic structural changes of the steamed Na-ZSM-5. Micropore volumes of the as-received and the steamed Na-ZSM-5 zeolites were measured by nitrogen uptake in a Micropore Analyzer (Micromeritics, ASAP 2000), as well as by n-hexane adsorption in a TGA at 25$^\circ$C. The amount of n-hexane adsorbed was obtained after the sample weight no longer increased with time in a n-hexane and nitrogen stream. Assuming liquid n-hexane (density: 0.62 g/cc) in the pores, the volume of n-hexane is equal to the sample micropore volume. No correction for surface adsorbed n-hexane was made here [99, 121]. The Cu$^{2+}$ uptake capacity of the steamed samples was measured by ICP after copper ion exchange using the procedure described earlier. Nitric oxide conversions to nitrogen were measured for the Cu-ZSM-5 synthesized from the steamed Na-ZSM-5.

6.1.3 Measurements of Nitric Oxide Decomposition
The NO decomposition activity of the catalysts was evaluated in a laboratory-scale reactor system described in Chapter 2. An amount of 0.5 gram of catalyst was placed in the reactor for NO conversion measurements. The contact time, W/F, defined as the ratio of catalyst weight in the reactor to the total flowrate of the feed gas stream, was 1.0 g s/cm$^3$ (corresponding GHSV = 1,800 h$^{-1}$, NTP). Pure He (Airco, 99.999%) flowing through deionized water in a water saturator with constant temperature was used to entrain water vapor to the reactor via an electrically heated line. The water vapor entrained by He was calibrated at different temperatures. A gas mixture of 2% NO, 0-5% O$_2$, 0-20% H$_2$O and balance He was used in the tests. A dry-ice cold trap was
installed at the exit of the reactor to condense the water vapor prior to analyzing the exhaust gas in a gas chromatograph. The fresh catalysts were pretreated in pure He in the reactor at 500°C for two hours before they were exposed to the reactant stream. The catalyst activity was evaluated in both dry and wet gas mixtures. All measurements were made after reaction had reached steady-state.

6.1.4 Characterization of Catalyst Samples
A VG SB601 STEM was used to characterize the fresh and steamed catalyst samples. The catalyst samples were supported by a 200 mesh, carbon filmed-covered, plain nickel grid (Ernest F. Fullam Inc. Part No. 14581) in the STEM chamber. The sample preparation was the same as that described in Chapter 2. The surface composition of the catalyst samples was analyzed by energy dispersive X-ray (EDX) micro-probe technique (spot size: 0.5 nm by 1.0 nm), and copper, cerium, silicon, and aluminum distribution in catalysts were simultaneously collected by an X-ray mapping technique with a magnification of \(1 \times 10^6\).

A Rigaku 300 X-Ray powder diffractometer was used to examine the crystal structures of the fresh and steamed catalysts, as well as check for CuO particle formation. The samples were evacuated at 55°C for 24 hours, then placed in a dessicator. The diffraction patterns were taken in the 2θ range of 5-80° at a scanning speed of 1° per second.

The Perkin Elmer, Model 548 (ESCA) instrument with 2 mm spatial resolution was used to determine the elemental concentrations of copper, cerium, oxygen and silicon on the surfaces of the catalyst samples. The procedure of XPS analysis was presented in Chapter 2. Total time of acquisition of the Cu, Ce, O, and Si core level spectrum was 20 minutes after the sample had been exposed to X-ray for 10 minutes. Atomic ratios of copper, cerium, and oxygen to silicon in the surface region of catalyst crystal were determined based on these core level photoelectron spectra.
6.1.5 Change of Ion Exchange Sites in Steamed Catalysts

Understanding catalyst deactivation due to steaming is important for application of these catalysts. However, it is difficult quantitatively to distinguish copper-induced and dealumination-induced catalyst deactivation by using XRD and STEM/EDX analyses. The loss of ion exchange capacity and decrease of catalytic activity of steamed catalysts were used to examine the extent of dealumination. In this test, the Ce(40)/Cu(135)-ZSM-5 was used in place of the Ce(60)/Cu(138)-ZSM-5. These experiments were conducted as follows: The steamed catalysts were removed from the reactor, and treated with 0.05 M HNO₃ solution at room temperature for 4 hours to dissolve all ion-exchanged copper. This procedure does not affect the framework aluminum. The Cu-extracted materials were then washed with deionized water, exchanged with Na⁺ using 0.01M NaNO₃ solution for 10 hours; dried in air at 100°C for 10 hours and heated at 500°C for 2 hours. A small amount of the catalyst sample was analyzed by ICP to determine the residual amount of copper. The remaining was ion-exchanged with copper acetate solution thrice, following the procedures described earlier. The catalysts were filtered and dried overnight in air at 100°C, and the amount of re-exchanged copper ion was measured using ICP. Subsequently, the NO conversion to N₂ over the Cu re-exchanged catalysts was measured in the fixed-bed reactor. The analyses of the catalysts and the conditions of steaming are given in Table 6.2.

The parent Na-ZSM-5 was ion-exchanged with copper after it had been treated in HNO₃ solution based on the above procedures and conditions. It was found that its copper exchange level was 134% and activity in terms of NO conversion to N₂ was 90% in 2% NO - He at 500°C and W/F = 1.0 g s/cm³. The copper exchange level of the HNO₃-washed Na-ZSM-5 was slightly less than the parent Na-ZSM-5, while the catalytic activity of the derivative Cu-ZSM-5 was almost the same as the Cu(141)-ZSM-5 prepared directly from the parent Na-ZSM-5. It can be concluded that 0.05 M HNO₃ does not change the ion exchange sites, i.e. the framework aluminum, of the Na-ZSM-5. This result is shown in Table 6.2.

As we know, the copper cations in the Cu(141)-ZSM-5 used at 500°C in a gas mixture of 2% NO- He for 20 hours do not deactivate. They can completely be extracted by HNO₃ solution using the above method (see Table
<table>
<thead>
<tr>
<th>Catalyst (cation-ZSM-5)</th>
<th>Si/Al</th>
<th>Cu/Al (remained Cu)</th>
<th>Cu/Al (removed Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(141)-1</td>
<td>20.3</td>
<td>0.17</td>
<td>0.54</td>
</tr>
<tr>
<td>Cu(141)-2</td>
<td>22.8</td>
<td>0.30</td>
<td>0.41</td>
</tr>
<tr>
<td>Cu(141)-3</td>
<td>20.2</td>
<td>0.13</td>
<td>0.58</td>
</tr>
<tr>
<td>Cu(141)-4</td>
<td>21.1</td>
<td>0.07</td>
<td>0.64</td>
</tr>
<tr>
<td>Ce(40)/Cu(135)-1</td>
<td>21.5</td>
<td>0.19</td>
<td>0.49</td>
</tr>
<tr>
<td>Ce(40)/Cu(135)-2</td>
<td>22.8</td>
<td>0.32</td>
<td>0.36</td>
</tr>
<tr>
<td>Na-ZSM-51</td>
<td>20.5</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Ce(60)-2, 5</td>
<td>22.0</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The following are ICP measurements after the above samples were ion-exchanged with Cu\(^{2+}\) at room temperature for 20 hours thrice.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Cu/Al</th>
<th>Cu/Al (re-exchanged)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(141)-1</td>
<td>20.4</td>
<td>0.65</td>
<td>0.47</td>
</tr>
<tr>
<td>Cu(141)-2</td>
<td>22.9</td>
<td>0.57</td>
<td>0.27</td>
</tr>
<tr>
<td>Cu(141)-3</td>
<td>20.3</td>
<td>0.68</td>
<td>0.56</td>
</tr>
<tr>
<td>Cu(141)-4</td>
<td>21.3</td>
<td>0.78</td>
<td>0.71</td>
</tr>
<tr>
<td>Ce(40)/Cu(135)-1</td>
<td>21.0</td>
<td>0.77</td>
<td>0.60</td>
</tr>
<tr>
<td>Ce(40)/Cu(135)-2</td>
<td>22.9</td>
<td>0.67</td>
<td>0.35</td>
</tr>
<tr>
<td>Ce(60)-2, 5</td>
<td>22.1</td>
<td>-</td>
<td>0.41</td>
</tr>
<tr>
<td>Na-5, 6</td>
<td>22.1</td>
<td>-</td>
<td>0.10</td>
</tr>
</tbody>
</table>

1 steamed in 20% H\(_2\)O- 2% NO- He for 10 hours, then in 2% NO- He for 20 hours at 500°C.
2 steamed in 20% H\(_2\)O- 2% NO- He for 10 hours, then in 2% NO- He for 20 hours at 600°C.
3 steamed in 20% H\(_2\)O- 4% NO- He for 10 hours and reacted in 2% NO- He for 20 hours at 500°C.
4 reacted in 2% NO- He for 20 hours at 500°C.
5 steamed in 20% H\(_2\)O- 2% NO- He for 10 hours, then in 2% NO- He for 20 hours at 600°C.
6 at 600°C steamed in 20% H\(_2\)O- 4% NO- He for 10 hours, then in 2% NO- He for 20 hours.
6.2). The same amount of copper could be re-exchanged into this copper-extracted material. The re-exchanged copper ions were equally active as these directly incorporated in the parent Na-ZSM-5. It is suggested that the active copper can be completely removed by the 0.05 M HNO₃ solution.

6.2 RESULTS

6.2.1 Hydrothermal Stability of Na-ZSM-5
It was reported that addition of water vapor into reactant stream decreased the Cu-ZSM-5 activity. However, the activity could be totally recovered after removal of water vapor from the reaction stream [46, 48]. The following accelerated tests were intended to verify this results. The catalytic activities of Cu(97)-ZSM-5 and Mg(34)/Cu(86)-ZSM-5 catalysts were evaluated over the temperature range of 400- 600°C in 2% NO - 5% O₂ - He before and after the catalysts were exposed to a gas mixture of 20% H₂O - 4% O₂ - He at 650°C for 20 hours. It was found that the activity was permanently lost after steaming, as shown in Figures 6.1 and 6.2.

The loss of catalytic activity after steaming may be attributed to either dealumination of the ZSM-5 material or deactivation of copper, or both. To correlate dealumination to steaming conditions, the parent Na-ZSM-5 zeolite was pretreated at 500, 600, and 750°C in a gas mixture containing 20% H₂O- 4% O₂-He for 20 hours. It was found that the micropore volume decreased from 0.11 cm³/g for the as-received Na-ZSM-5 to practically zero after the treatment at 600°C, while the subsequent Cu²⁺ ion exchange capacity was reduced from 141% to 20% (or 15% for the sample steamed at 750°C). The procedures of Cu ion exchange were the same as that described in Chapter 2. The Cu(20)-ZSM-5 and Cu(15)-ZSM-5 catalysts had 8 and 5% conversion of NO into N₂ at 500°C and W/F= 1.0 g s/cm³ in 2% NO- He, respectively. The Cu(132)-ZSM-5 prepared from the 500°C-steamed Na-ZSM-5 had similar activity to the Cu(141)-ZSM-5. The results are summarized in Table 6.3. Lago, et al [122] used Cs ion exchange capacity in steamed H-ZSM-5 catalysts to evaluate the content of dealumination, and found the result in good agreement with that obtained using ²⁷Al-NMR.
Figure 6.1  NO conversion to N\textsubscript{2} over the Cu(97)-ZSM-5 in 2\% NO- 5\% O\textsubscript{2}-He at 1.0 g s/cm\textsuperscript{3} (NTP) before and after steaming in 20\% H\textsubscript{2}O- 5\% O\textsubscript{2}-He at 650\textdegree C for 20 hours.

Figure 6.2  NO conversion to N\textsubscript{2} over the Mg(34)/Cu(86)-ZSM-5 in 2\% NO- 5\% O\textsubscript{2}-He at 1.0 g s/cm\textsuperscript{3} (NTP) before and after steaming in 20\% H\textsubscript{2}O- 5\% O\textsubscript{2}-He at 650\textdegree C for 20 hours.
### Table 6.3 Hydrothermal Effects on Na-ZSM-5\(^1\)

<table>
<thead>
<tr>
<th>Catalyst Steaming</th>
<th>as-received Na-ZSM-5(^2)</th>
<th>Steamed Na-ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>-</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>750</td>
</tr>
<tr>
<td>Micropore Volume</td>
<td>0.11(^3)</td>
<td>0.11(^3)</td>
</tr>
<tr>
<td>(cm(^3)/g)</td>
<td>(0.147)(^4)</td>
<td>(0.109)(^4)</td>
</tr>
<tr>
<td></td>
<td>(0.0)(^4)</td>
<td>NM</td>
</tr>
<tr>
<td>Cu Exchange Capacity (%)</td>
<td>141(^5)</td>
<td>132(^5)</td>
</tr>
<tr>
<td></td>
<td>206</td>
<td>156</td>
</tr>
<tr>
<td>NO conversion to N(_2) (%)</td>
<td>92</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>5</td>
</tr>
</tbody>
</table>

1. in 20% H\(_2\)O- 4% O\(_2\)- 76% He; 20 hours.
2. Davison: Si/Al = 21.5.
4. Measured by n-hexane adsorption.
5. Cu was ion-exchanged with Cu in 0.007 M Cu(ac)\(_2\) aqueous solution for 19 hours at room temperature thrice.
6. Cu was ion-exchanged with Cu in 0.007 M Cu(ac)\(_2\) aqueous solution for 19 hours at room temperature thrice.
7. at 500°C and W/F= 1.0 g s/cm\(^3\) in 2% NO- He.

NM not measured.

The effects of steaming on the zeolite structure were further examined using XRD analysis. Figure 6.3 shows the diffractograms of the as-received, the 500°C- and 600°C-steamed Na-ZSM-5 materials. Except for very fine particle appearance indicated by small angle scattering of X-ray and very small diffraction peak shifts (will be presented in section 6.2.6 in details), no significant structure change is observed for the 500°C-steamed sample by comparing its XRD pattern with that of the as-received Na-ZSM-5. However, after steaming at 600°C, vitreous glass formation [123] is evident by the appearance of an amorphous background (halo) on the diffraction pattern at 2\(\theta\) = 10- 40°. The ensuing very low copper cation exchange capacity, and micropore volume loss (Table 6.2) together with Figure 6.3 provide evidence
Figure 6.3  XRD patterns of the Na-ZSM-5 samples reveal evolution of vitreous glass formation with steaming temperature (in 20% H₂O- 4% O₂- He for 20 hours).
of a major structural change for the 600°C-treated Na-ZSM-5. This severe steaming can also lead to dealumination, which is best indicated by the reduced ion-exchange uptake capacity, since framework (AlO₂)⁻ is major cation exchange site in the Na-ZSM-5. On the other hand, little micropore volume loss and Cu²⁺ uptake capacity loss were found for the 500°C-steamed Na-ZSM-5. This suggests that the 500°C-steamed Na-ZSM-5 has less significant structural change, compared with the 600°C-steamed Na-ZSM-5. Therefore, it is at this temperature of 500°C that the effect of water vapor on the catalytic activity for all Cu-ZSM-5 and metal modified Cu-ZSM-5 materials was examined to correlate it with the stability of copper under no structural modifications of the zeolite.

6.2.2 Cocation Effects on Cu-ZSM-5 Activity in Wet NO-Decomposition

A series of tests was performed in 2% NO-He at contact time 1 g s/cm³ (NTP) and 500°C under both dry (0% H₂O) and wet (2-20% H₂O) conditions over Cu-ZSM-5 and metal modified Cu-ZSM-5 catalysts. Figure 6.4 shows the steady-state NO conversion to N₂ over the catalysts Cu(72)-, Cu(141)-, Mg(52)/Cu(66), Ba(5)/Cu(126)-, Y(13)/Cu(135)-, and Ce(60)/Cu(138)-ZSM-5 in dry gas (2% NO-He) and the wet gas mixture (20% H₂O- 2% NO-He). After the catalysts were treated in pure He for two hours and in 2% NO-He for four hours at 500°C and W/F= 1.0 g s/cm³ (NTP), water vapor was introduced in the reactant gas mixture. The presence of water vapor drastically decreased the NO conversion to N₂. The wet-gas activities reached a steady state corresponding to 8% conversion of NO to N₂ for all catalysts, except for 20% conversion over Ce(60)/Cu(138)-ZSM-5, in two hours.

The activity recovery in dry NO-gas after removal of water vapor is shown in Figure 6.4. The Mg(52)/Cu(66)-ZSM-5 gradually restored some of its activity to ca 45% of its original value. However, no recovery was found for the Cu(72)-ZSM-5 catalyst. For the excessively-exchanged Cu(141)-ZSM-5, about 30% of its original dry gas conversion was recovered after removal of water vapor. The cocation (Mg²⁺, Ba²⁺, Y³⁺ and Ce³⁺) modified Cu-ZSM-5 catalysts recovered a larger fraction of their original catalytic activity than Cu(141)-ZSM-5. Among these cations, Ce³⁺ modified Cu-ZSM-5 was superior to Cu-ZSM-5 and the other catalysts, as shown in Figure 6.4, in the wet gas-
activity and dry gas-activity recovery (more than 66%). The Ce(60)/Cu(138)-ZSM-5 catalyst was, thus, chosen for additional testing.

![Graph showing NO conversion to N2 over different catalysts](image)

**Figure 6.4** Effect of H2O vapor on the NO conversion to N2 at 500°C over the (a) Cu(72)-; (b) Mg(52)/Cu(66)-; (c) Cu(141)-; (d) Ba(5)/Cu(126)-; (e) Y(13)/Cu(135)-; (f) Ce(60)/Cu(138)-ZSM-5 catalysts in 20% H2O- 2% NO- He, W/F = 1.0 g s/cm³ (NTP).

Activities of the catalysts Ce(60)/Cu(138)-ZSM-5 and Cu(141)-ZSM-5 were measured in a gas mixture of 2% NO - He with varying water vapor contents from 2 to 20% at 500°C and 1 g s/cm³ (NTP). Cyclic activity tests in dry and wet conditions were conducted. The results of gas cycling for the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 are shown in Figures 6.5 and 6.6, respectively, where the relative catalytic activity, defined as the ratio of steady state catalytic activities are shown by the horizontal lines. The catalysts were pretreated in He at 500°C for two hours prior to introduction of the reactant gas stream (2% NO- He). Following this dry-gas test for two hours, the catalysts were exposed to 2% water vapor for 10 hours followed by dry reaction for 20 hours. Next,
Figure 6.5  Cyclic performance of the Cu(141)-ZSM-5 in dry/wet NO decomposition in 2% NO-He, at W/F = 1.0 g s/cm³ (NTP) and 500°C.

Figure 6.6  Cyclic performance of the Ce(60)/Cu(138)-ZSM-5 in dry/wet NO decomposition in 2% NO-He, at W/F = 1.0 g s/cm³ (NTP) and 500°C.
NO conversion to N₂ was measured in cycles of wet and dry reaction gases (with different water vapor contents). The transition time between dry/wet to wet/dry-gas conversion was about two hours. The Cu(141)-ZSM-5 catalyst was inferior to the Ce(60)/Cu(138)-ZSM-5 under all conditions. The latter displays twice as high activity as the former in all wet gas mixtures. These results indicate that Ce³⁺ cations can promote the catalyst activity in wet NO decomposition, and restore the activity to a larger extent after removal of water vapor from the gas stream. Therefore, the cocations, especially Ce³⁺, can preserve the copper activity better in wet NO decomposition, and restore to a larger extent the activity of the Cu active sites after the removal of water vapor from the gas stream. It is worth pointing out here that the dry-gas catalytic activities over the above steamed samples were not affected by heat-treatment in pure He at high temperatures (600- 750°C).

![Effect of H₂O vapor (20% H₂O) on the relative catalytic activity (NO conversion over the catalyst/NO conversion over fresh material) over the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 in 2% NO- He at W/F = 1.0 g s/cm³ (NTP) and 400°C.](image)

**Figure 6.7** Effect of H₂O vapor (20% H₂O) on the relative catalytic activity (NO conversion over the catalyst/NO conversion over fresh material) over the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 in 2% NO- He at W/F = 1.0 g s/cm³ (NTP) and 400°C.
Figure 6.7 shows relative NO conversion to N₂ over the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 in dry (2% NO - He) and wet gas (20% H₂O - 2% NO - He) mixtures at 400°C. After water vapor was removed from the reaction stream, the dry gas activity of each catalyst was recovered much more for the 500°C steamed samples. Again, the Ce(60)/Cu(138)-ZSM-5 restored a larger-fraction of its original activity than the Cu(141)-ZSM-5. Figure 6 also shows differences in the rate of activity recovery between two catalysts. Raising the reaction temperature to 500°C, the relative catalytic activity slightly increased for the Ce(60)/Cu(138)-ZSM-5, compared with the Cu(141)-ZSM-5.

![Graph showing NO conversion over Cu(141)-ZSM-5](image)

Figure 6.8. NO conversion to N₂ over Cu(141)-ZSM-5 in 5% and 10% H₂O-2% NO- He at 400°C; and in 2% NO- He at 400 and 500°C, respectively, at W/F= 1.0 g s/cm³ (NPT).

Figure 6.8 shows relative NO conversion to N₂ over the Cu(141)-ZSM-5 in dry (2% NO- He) and wet gas (5% and 10% H₂O- 2% NO- He) mixtures at 1.0 g s/cm³ (NTP) at 400°C. Upon introduction of 5% H₂O to the reaction stream, the relative catalytic activity rapidly decreased to 42% and remained constant in the wet gas for 77 hours. Its 500°C-dry gas activity was completely recovered after removal of water vapor from the reaction stream. After
further steaming at 400°C in 10% H2O-containing gas for 54 hours, followed by removing the water vapor, the catalytic activity was restored to 85% of its dry-gas activity at 500°C. However, the 400°C-dry gas activity recovery is lower than the 500°C-dry gas activities in both cases.

The wet (20% H2O- 2% NO- He) NO decomposition activity was lower at 600°C than at 500°C for both the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 catalysts. After water vapor was removed from the reaction stream, the reaction temperature was lowered to 500°C. It was found that NO conversion to N2 was only 5% over the Cu(141)-ZSM-5. As shown in Figure 6.9, heat treatment in 2% NO- He at 500- 750°C did not restore the 500°C-catalyst activity at all. Figure 6.10 shows the performance of the Ce(60)/Cu(138)-ZSM-5 under the same experimental conditions. Both wet and wet-gas activities of Cu(60)/Cu(138)-ZSM-5 were higher than these of the Cu(141)-ZSM-5. Again, the heat treatment of this 600°C-steamed catalyst did not change the dry-gas activity (see Figure 6.10).

![Figure 6.9](image)

Figure 6.9 Heat treatment effect on the 500°C dry-gas activity of the Cu(141)-ZSM-5 in 2% NO- He at W/F = 1.0 g s/cm³ (NTP) after 10 hours in 20% H2O- 2% NO- He at 600°C.
Figure 6.10  Heat treatment effect on the 500°C dry-gas activity of the Ce(60)/Cu(138)-ZSM-5 in 2% NO- He at W/F = 1.0 g s/cm³ (NTP) after 10 hours in 20% H₂O- 2% NO- He at 600°C.

Effects of cerium content and preparation on the Cu-ZSM-5 were also studied under the same experimental condition as that in Figure 6.4. It is interesting that Ce-impregnated Cu(139)-ZSM-5 showed a similar performance to Cu(141)-ZSM-5 in wet NO decomposition as well as in dry-gas recovery. NO conversion to N₂ over the Ce(11)/Cu(119)-ZSM-5 in wet gas was about 8%, and gradually increased to about 40% of the original value. These results are shown in Figure 6.11.

XRD, STEM/EDX, and XPS were performed to examine physical and chemical changes of the fresh and catalytically used Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 samples. Luminescence was used to check for trivalent cerium ion in the cerium-containing materials. Fresh, 100°C-dried samples are referred to as-synthesized. Air-calcined samples were prepared by calcining the as-synthesized samples in air at 500°C for two hours. For the catalysts used in dry- and wet-gas streams, there are three kinds treatments: (1) ir. He for 2 hours, then in 2% NO - He at 500°C for hours; (2) in 20% H₂O - 2% NO - He at 500°C for 10 hours following the first treatment; (3) in 2% NO - He at 500°C for 20 hours following treatment-2 (refer to Figure 6.4).
Figure 6.11 Effect of Ce/Cu-ZSM-5 preparation on catalytic activity in wet-gas NO decomposition [20% H₂O- 2% NO- He, 1.0 g s/cm³ (NTP) and 500°C].

6.2.3 Micropore Volume Measurements

Table 6.3 summarizes the micropore volumes of the fresh and catalytically used samples, which were measured by n-hexane adsorption. The effect of water vapor on the catalyst structure was examined by comparing relative pore volume changes after various treatments. After treatment-3, the micropore volume decrease of Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 was 19% and 15%, respectively. Micropore volume loss is attributed to amorphous formation, which blocks zeolite channels. Lower decrease in the micropore volume suggests that Ce cations stabilize the crystal structure and increase its tolerance to water vapor in the Ce(60)/Cu(138)-ZSM-5 catalyst. In wet NO-decomposition (20% H₂O - 2% NO - He) at 600°C, the Ce(60)/Cu(138)-ZSM-5 catalyst lost its activity drastically, and simultaneously lost 32% of its micropore volume. The decrease in micropore volume of the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 catalysts was less than 600°C-steamed Na-ZSM-5 sample, as shown in Tables 6.3 and 6.4.
### Table 6.4 Micropore Volume of Catalysts\(^a\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fresh</th>
<th>Used(^b)</th>
<th>Volume Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(141)-ZSM-5</td>
<td>0.178 cm(^3)/g</td>
<td>0.145 cm(^3)/g at 500(^\circ)C</td>
<td>18.6%</td>
</tr>
<tr>
<td>Ce(60)/Cu(138)-ZSM-5</td>
<td>0.159 cm(^3)/g</td>
<td>0.136 cm(^3)/g at 500(^\circ)C</td>
<td>14.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.109 cm(^3)/g at 600(^\circ)C</td>
<td>31.7%</td>
</tr>
<tr>
<td>Na-ZSM-5</td>
<td>0.147 cm(^3)/g</td>
<td>0.109 cm(^3)/g at 500(^\circ)C</td>
<td>26.0%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0 cm(^3)/g at 600(^\circ)C</td>
<td>100%</td>
</tr>
</tbody>
</table>

\(^a\) Measured by n-hexane adsorption.

\(^b\) in 20% H\(_2\)O- 2% NO- He for 10 hours, then in 2% NO- He for 20 hours.

#### 6.2.4 Catalyst Characterization by STEM/EDX

Electron micrographs representative for the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 catalysts in the freshly calcined state are shown in Figures 6.12 and 6.13. No aggregate in the freshly calcined Cu(141)-ZSM-5 are found, as shown in Figure 6.12. It is observed that one particle is on the external surface of lower right of the crystal particle of the Ce(60)/Cu(138)-ZSM-5 (see Figure 6.13). The 500\(^\circ\)C-steamed Cu(141)-ZSM-5 catalyst (after treatment-3), however, shows many particles with mean aggregate sizes of 4-6 nm (bright spots on dark field image as seen in the Figure 6.14) in the particle edge, and about 15 nm within particle body (see Figure 6.15). The phase contrast imaging demonstrated formation of particles clearly distinguishable from the support. On the other hand, a few very fine particles are shown for the steamed Ce(60)/Cu(138)-ZSM-5, as shown in Figure 6.16. Focusing electron beam on an aggregate in the steamed Cu(141)-ZSM-5, a similar energy dispersive spectrum to Figure 4.10 was obtained. Therefore, aggregates were identified as copper compound. However, it couldn't identify what kinds of copper compound were in the aggregates.

STEM/EDX mappings (scale of a mapping: 10 nm by 120 nm) of aluminum and copper, for the Cu(141)-ZSM-5 in the freshly 500\(^\circ\)C-calcined state, and after 10 hour wet- followed by 20 hour dry-NO decomposition
Figure 6.12  Scanning transmission electron micrograph of the fresh Cu(141)-ZSM-5.
Figure 6.13  Scanning transmission electron micrograph of the fresh Ce(60)/Cu(138)-ZSM-5.
Figure 6.14  Aggregates (bright spots) evident on the scanning transmission electron micrograph of the 500°C-steamed Cu(141)-ZSM-5.
Figure 6.15  Large particles (bright spots) evident within the body of the 500°C-steamed Cu(141)-ZSM-5 on STEM picture.
Figure 6.16  No significant aggregates found on the scanning transmission electron micrograph of the 500°C-steamed Ce(60)/Cu(138)-ZSM-5.
(treatment-3), are shown in Figures 6.17 and 6.18. Uniform Al and Cu distribution, and strong Cu cation association with Al on the freshly calcined Cu(141)-ZSM-5 sample are found, as shown in Figure 6.17 (the Al mapping is on the upper left corner, the Cu mapping is on the upper right corner, and an overlapping of the Al and Cu mappings is on the lower left corner). The 500°C-steamed Cu(141)-ZSM-5 catalyst, however, shows many Cu aggregates, Figure 6.18. This mapping area was the same as that shown in Figure 6.14. It is very interesting to see formation of aluminum aggregates which indicates partial dealumination of the zeolite. It is well known that dealumination leads to the loss of tetrahedral aluminum from the zeolite framework, and subsequently Cu$^{2+}$ cations are forced to change coordination in the zeolite if the dealumination takes place first. Copper migration and zeolite dealumination leading to copper aggregates cause the loss of catalytic activity. It is worth pointing out that the Al and Cu distributions in the fresh 500°C-calcined Cu(141)-ZSM-5 sample are similar to those in the Cu(141)-ZSM-5 reacted in dry 2% NO - He at 500°C.

Cerium and aluminum distributions were obtained for the Ce(26)-ZSM-5 after it had been calcined in air at 500°C for 2 hours. This result is shown in Figure 6.19. Ce ions uniformly distributed in ZSM-5 zeolite. However, it is observed that the cerium ions enriched in the surface region. It is plausible that the Ce on the external surface of ZSM-5 is in oxide form, and the uniformly distributed Ce ions are associated with zeolite framework aluminum. From Table 6.1, the Na/Al ratio is reduced confirming the ion exchange between Ce$^{3+}$ and Na$^+$. This result is in good agreement with the Ce$^{3+}$ luminescence measurements.

Three samples of the Ce(60)/Cu(138)-ZSM-5 were examined by using STEM/EDX mapping: sample 1 is fresh, 500°C air-calcined materials, sample 2 reacted in the gas stream under the conditions of treatment-2, and sample 3 used in that under treatment-3 (refer to Figure 6.4). Copper, cerium and aluminum mappings of the fresh Ce(60)/Cu(138)-ZSM-5 on lower right area in Figure 6.13 are shown in Figure 6.20. It is observed that Cu, Al and Ce are uniformly distributed in the sample-1 except one Ce/Cu aggregate on the right-side of the crystal (also see Figure 6.13). It is interesting that copper is associated not only with aluminum but also with cerium. Figure 6.21 shows
Figure 6.17  Cu uniformly distributed and strongly associated with Al on STEM/EDX mapping of Al and Cu cations in the calcined Cu(141)-ZSM-5.
Figure 6.18  Cu aggregates evident on STEM/EDX mapping of Al and Cu cations in the Cu(141)-ZSM-5 under treatment-3 (same area as that shown in Figure 6.12).
Figure 6.19  Ce and Al distribution in the Ce(26)-ZSM-5 measured by STEM/EDX.
Figure 6.20  STEM/EDX mapping of Cu, Al and Ce in the calcined fresh Ce(60)/Cu(138)-ZSM-5.
Figure 6.21 STEM/EDX mapping of Cu, Al and Ce in the Ce(60)/Cu(138)-ZSM-5 after the treatment-2.
Cu, Al and Ce mappings for the sample-2. The copper in this sample is enriched on the edges of the catalyst crystal. Unlike the catalytically used Cu(141)-ZSM-5 shown in Figure 6.18, no apparent Al aggregates are found. After removal of water vapor from the reactant stream (under treatment-3), the Cu cations redistribute in the Ce(60)/Cu(138)-ZSM-5 sample, which leads to the high catalytic activity recovery as shown in Figure 6.22. From comparison of the copper distribution in sample-3 with that in the fresh Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5, it was found that the redistributed Cu cannot reach the same uniform dispersion as in the fresh samples. Therefore, 100% recovery of catalytic activity cannot be achieved.

6.2.5 X-Ray Diffraction Patterns

Preliminary study of catalyst structural change was first performed using XRD for the catalyst Cu(97)-ZSM-5 after reaction in 20% H2O - 2% NO - He at 650°C for 19 hours, whose catalytic activity in terms of NO conversion to N2 is shown in Figure 6.1. A halo background at 2θ = 10-35° is shown on XRD pattern, which is similar to that in Figure 6.3 for the 600°C-steamed Na-ZSM-5. Crystallinity loss of catalyst materials may cause the catalyst deactivation. Detailed XRD studies for the catalysts Cu-ZSM-5 and metal ion-modified Cu-ZSM-5 are presented as follows.

The crystal structures of the fresh and steamed Cu(72)-ZSM-5 and Mg(52)/Cu(66)-ZSM-5 catalysts were examined by XRD. The steamed samples were treated in 2% NO - He for 4 hours, then in 20% H2O - 2% NO - He for 20 hours followed by in 2% NO - He for 10 hours at 500°C and W/F = 1.0 g s/cm³ (refer to Figure 6.4). Figures 6.23 and 6.24 show XRD patterns of two catalyst samples, the fresh and steamed, respectively. For the steamed samples, the diffractograms show some loss of the crystallinity by the appearance of an amorphous background (halo) compared with the fresh catalysts. The loss of the crystallinity for the steamed Cu(72)-ZSM-5 was more than that for the steamed Mg(52)/Cu(66)-ZSM-5. Both steamed samples were to form very fine particles indicated by small angle scattering of X-Ray. However, the slope of the small angle scattering for steamed Mg(52)/Cu(66)-ZSM-5 is smaller than that for the steamed Cu(72)-ZSM-5.
Figure 6.23  X-ray diffraction patterns of the (a) fresh; (b) 500°C-steamed Cu(72)-ZSM-5.
Figure 6.24 X-ray diffraction patterns of the (a) fresh; (b) 500°C-steamed Mg(52)/Cu(66)-ZSM-5.
XRD analyses of the fresh and used Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 after treatment-3 showed similar pattern to the parent Na-ZSM-5, except for diffraction peak shifts of the steamed samples. Figure 6.25, normalized X-ray diffraction patterns, shows that the fresh Cu(141)-ZSM-5, Ce(60)/Cu(138)-ZSM-5 and the parent Na-ZSM-5 have the same XRD pattern. This indicates that the ion-exchange processes do not change the zeolitic structure, even after three Ce\(^{3+}\)-ion exchanges with the Na-ZSM-5 at 85\(^\circ\)C for 2 hours each. However, the 500\(^\circ\)C-steamed samples show diffraction peak shift to lower 2\(\theta\), as shown in Figure 6.26. Hence, the steaming treatment of samples leads to increased the d-spacing of zeolite crystal, based on Bragg's Law. The shift (2\(\theta\)) for the 500\(^\circ\)C-steamed Cu(141)-ZSM-5 sample was more than that for the 500\(^\circ\)C-steamed Ce(60)/Cu(138)-ZSM-5 and the 500\(^\circ\)C-steamed Na-ZSM-5 (Figure 6.26 and Table 6.5). Differentiating Bragg's equation, we have

\[
\delta d = -\frac{\lambda \cos\theta}{2 \sin^2 \theta} \delta \theta
\]  

(6.1).

The increment of d-spacing can be calculated for the planes which give the strongest diffraction peaks. The position shifts of the five strongest diffraction peaks and d-spacing of corresponding planes for the parent and 500\(^\circ\)C-steamed Na-ZSM-5, fresh and 500\(^\circ\)C-steamed Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 samples are listed in Table 6.5.

Compared with the above 500\(^\circ\)C-steamed samples, the 400\(^\circ\)C-steamed Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 (refer to Figure 6.7) had smaller diffraction peak shift. It is noteworthy that the 500\(^\circ\)C- and 600\(^\circ\)C-steamed Na-ZSM-5 materials had similar diffraction shifts as did the 500\(^\circ\)C- and 600\(^\circ\)C-steamed Ce(60)/Cu9138)-ZSM-5 materials. However, the shifts of Na-ZSM-5 were smaller than these of Ce(60)/Cu(138)-ZSM-5, as shown in Table 6.5.

Based on XRD spectrum, the dimensions of a unit cell were estimated on the Rigaku 300 instrument by using the Least Square Unit Cell Refinement- a least square fitting of unit cells with peak position. It was assumed that the ZSM unit cell is orthorhombic. The fitting results for the fresh and 500\(^\circ\)C steamed Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 are shown

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### Table 6.5 Summary of Diffraction Peak Shifts

<table>
<thead>
<tr>
<th></th>
<th>Parent Na-ZSM-5 (as-received):</th>
<th>500°C-steamed Na-ZSM-5:</th>
<th>Fresh Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5:</th>
<th>500°C-Steamed Cu(141)-ZSM-5:</th>
<th>500°C-Steamed Ce(60)/Cu(138)-ZSM-5:</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (°)</td>
<td>8.05</td>
<td>7.95</td>
<td>8.05</td>
<td>7.85</td>
<td>7.90</td>
</tr>
<tr>
<td>d-spacing (Å)</td>
<td>10.9742</td>
<td>11.120</td>
<td>10.9742</td>
<td>11.2534</td>
<td>11.112</td>
</tr>
<tr>
<td>δd(steamed – parent)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>1.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d_fresh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δd(fresh – parent)</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δd(steamed – fresh)</td>
<td>2.55</td>
<td>2.28</td>
<td>0.64</td>
<td>0.83</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>x100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.55</td>
<td>2.28</td>
<td>0.64</td>
<td>0.83</td>
<td>1.25</td>
</tr>
<tr>
<td>δd(steamed – fresh)</td>
<td>1.25</td>
<td>1.13</td>
<td>0.64</td>
<td>0.62</td>
<td>0.40</td>
</tr>
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<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.55</td>
<td>2.28</td>
<td>0.64</td>
<td>0.83</td>
<td>1.25</td>
</tr>
</tbody>
</table>

1. at 500°C in He for 2 hours, then in 2% NO - He for 4 hours; then, in 20% H2O -2% No -He for 10 hours followed by in 2% NO -He for 20 hours.
Figure 6.25  (a) As-received Na-ZSM-5; (b) fresh 500°C-calcined Cu(141)-ZSM-5; (b) fresh 500°C-calcined Ce(60)/Cu(138)-ZSM-5.
Figure 6.26  (a) As-received Na-ZSM-5; (b) 500°C-steamed Na-ZSM-5 in 20% H₂O- 4% O₂- He; (c) 500°C-steamed Ce(60)/Cu(138)-ZSM-5; (d) 500°C-steamed Cu(141)-ZSM-5 in 20% H₂O- 2% NO- He for 10 hours, then in 2% NO- He for 20 hours. Insets: 2θ = 7- 10° (upleft); 2θ = 22- 25° (upright).
in Table 6.6. From the calculation, the dimensions along the $\tilde{a}$ and $\tilde{c}$ directions slightly increased, while a decrease along $\tilde{b}$ took place. The unit cell dimensions do not significant change after the catalysts are steamed.

<table>
<thead>
<tr>
<th>Ion(s)-ZSM-5</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Cu(141)-</td>
<td>20.0709± 0.0145</td>
<td>19.9028± 0.0000</td>
<td>13.4824± 0.0105</td>
</tr>
<tr>
<td>Steamed Cu(141)-</td>
<td>20.0845± 0.0100</td>
<td>19.8933± 0.0000</td>
<td>13.4851± 0.0452</td>
</tr>
<tr>
<td>Fresh Ce(60)/Cu(138)-</td>
<td>20.0732± 0.0040</td>
<td>19.9503± 0.0000</td>
<td>13.4485± 0.0130</td>
</tr>
<tr>
<td>Steamed Ce(60)/Cu(138)-</td>
<td>20.0840± 0.0083</td>
<td>19.9301± 0.0000</td>
<td>13.4902± 0.0236</td>
</tr>
</tbody>
</table>

From STEM/EDX mapping, one cannot tell what kind of copper compound copper aggregates contain. Identification of the copper compound was accomplished by X-ray diffraction. Figure 6.27 shows the XRD patterns of the fresh 500°C-air calcined Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 as well as the parent Na-ZSM-5 in the range of $2\theta$ = 34- 40° in which CuO crystal has the strongest diffraction peaks. No CuO phase is present in the samples. However, Figure 6.28 shows CuO formation for the Cu(141)-ZSM-5 under treatment-3. On the other hand, CuO formation was not observed from the XRD-pattern of the Ce(60)/Cu(138)-ZSM-5, which retained 67% of the original dry-gas activity, under the same treatment. Some clusters were observed in Figure 6.17. If some of them are CuO particles, maybe the particle size is too small to be observed using XRD analysis. No other crystalline phases involving copper or cerium were identified by XRD in these samples.

The XRD comparison was made for the Cu(141)-ZSM-5 samples after treatment-2 and -3, as shown in Figure 6.29. It is found that CuO diffraction peaks are identical in the two cases, which indicates that average size of CuO particles is the same. Hence, we could conclude that CuO particles were formed during steaming, and the mean CuO particle size did not change in dry NO decomposition.
Figure 6.27  XRD patterns of the (a) fresh, calcined Cu(141)-ZSM-5; (b) fresh, calcined Ce(60)/Cu(138)-ZSM-5; and (c) as-received Na-ZSM-5: no CuO was detected.
Figure 6.28 CuO evident in the 500°C-steamed Cu(141)-ZSM-5, not in 500°C-steamed Ce(60)/Cu(138)-ZSM-5.
Figure 6.29  XRD patterns of the Cu(141)-ZSM-5 after treatment-2 and -3.
Using Scherrer’s formula, the volume-weighted mean crystal diameter of CuO particles can be estimated if internal strain, instrumental broadening, etc. are neglect. Let’s take a diffraction peak of CuO at $2\theta=35.45^\circ$ as a sample to compute the particle size. The peak width at half height, $B$, is 0.0073 grade (Figure 6.28). The wavelength, $\lambda$, of X-ray is 1.54Å. Substituting those data into the Scherrer formula:

$$B = \frac{0.9\lambda}{D\cos\theta} \tag{6.2}$$

we have

$$D = \frac{0.9\lambda}{B\cos\theta}$$

$$= (0.9 \times 1.54\text{Å})/[0.0073 \times \cos (35.45/2)]$$

$$= 20 \text{ nm}$$

The size estimate of CuO particle from XRD gives a volume-weighted mean diameter. The STEM picture, Figure 6.15, of the 500°C-steamed Cu(141)-ZSM-5 showed similar Cu aggregate size to that calculated from XRD pattern.

For the 400°C-steamed Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 samples, under the conditions of Figures 6.7 and 6.8, CuO diffraction peaks were not observed on their XRD patterns.

CuO particles on the Cu-ZSM-5 crystal were also observed by Kharas, et al [49], after Cu(207)-ZSM-5, prepared from an ion-exchange solution of pH = 7.5, was tested in a simulated lean-burn gas mixture in the temperature range of 600-800°C. However, the CuO particles observed by these authors may not be exclusively attributed to CuO sintering induced by Cu-ZSM-5 degradation. In experiments of Chapter 4, we have shown that CuO particle with a mean size of 5 nm were found on the surface of the fresh Cu(165)-ZSM-5 calcined in air at 500°C for 2 hours after ion-exchange process in a cupric acetate solution of pH = 7.0, and dried in a muffle furnace in air at 100°C overnight. This CuO particle formation is due to Cu(OH)$_x$ precipitation on the zeolite in high pH (> 6.0) solutions.
6.2.6 Cation Re-Exchange Capacity of Steamed Catalysts

Part of the catalyst activity of the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 catalysts was permanently lost after steaming at 500 and 600°C. The permanent loss of catalytic activity is attributed to isolated copper loss and copper oxide sintering, and dealumination as indicated by the STEM/EDX and XRD analyses. Effect of steaming on cation exchange sites of ZSM-5 was examined by uptake capacity of re-exchanged copper ions and catalytic activity of Cu re-exchanged Cu-ZSM-5.

The copper uptake capacity of the 500°C- and 600°C-steamed materials was measured after removal of copper with dilute nitric acid according to the procedure mentioned above. Table 6.2 shows the ICP analyses. The steamed Na-ZSM-5 materials were directly exchanged with copper acetate solution, the copper exchange levels are shown in Table 6.3. For the Cu(141)-ZSM-5 samples after wet NO decomposition at 500 and 600°C, the re-exchanged copper ion capacities were Cu/Al = 0.47 and 0.27, respectively. The latter is higher than the Cu/Al value of 0.1 for the 600°C-steamed Na-ZSM-5 (as shown in Table 6.3). The Ce(40)/Cu(135)-ZSM-5 samples after wet NO decomposition at 500 and 600°C showed higher copper re-exchange capacities with Cu/Al values of 0.60 and 0.35, respectively.

In a separate control experiment, Ce(60)-ZSM-5 was treated under a similar wet NO decomposition condition at 600°C. The steamed sample had medium-high copper ion exchange capacity with Cu/Al = 0.41 (Table 6.2). This shows that the steamed cerium ion-exchanged ZSM-5 had also more copper ion exchange sites than the 600°C-steamed Na-ZSM-5.

Catalytic activities of the copper re-exchanged ZSM-5 materials prepared from the steamed catalysts as well as the Cu-ZSM-5 synthesized from the 600°C-steamed Ce(60)-ZSM-5 were evaluated in 2% NO - He at 500°C and W/F = 1.0 g s/cm³. However, it was found that not all re-exchanged copper ions were active for NO decomposition. Table 6.7 shows comparisons of NO conversion over the Cu re-exchanged materials with those over their parent steamed catalysts, and fresh Cu-ZSM-5 prepared directly from the as-received Na-ZSM-5.
Table 6.7. Activity Comparisons of Copper Re-exchanged ZSM-5 with Steamed and fresh Cu-ZSM-5

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>NO Conversion to N₂ (%)(^1)</th>
<th>Corresponding Active Cu (%)(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu re-exchanged Cu(94)-ZSM-5 from 500°C-steamed Cu(141)-ZSM-5</td>
<td>28.0</td>
<td>42</td>
</tr>
<tr>
<td>Cu re-exchanged Cu(120)-ZSM-5 from 500-steamed Ce(40)/Cu(135)-ZSM-5</td>
<td>30.1</td>
<td>43</td>
</tr>
<tr>
<td>Cu exchanged Cu(108)-ZSM-5 from 600°C-steamed Ce(60)-ZSM-5</td>
<td>13.7</td>
<td>31</td>
</tr>
<tr>
<td>Cu(141)-ZSM-5 after 500°C-steaming</td>
<td>29.0</td>
<td>42.5</td>
</tr>
<tr>
<td>Cu(40)-ZSM-5 after 500°C-steaming</td>
<td>53.0</td>
<td>61</td>
</tr>
<tr>
<td>Fresh Cu(94)-ZSM-5</td>
<td>72</td>
<td>94</td>
</tr>
<tr>
<td>Fresh Cu(108)-ZSM-5</td>
<td>77.5</td>
<td>108</td>
</tr>
<tr>
<td>Fresh Cu(120)-ZSM-5</td>
<td>82.5</td>
<td>120</td>
</tr>
</tbody>
</table>

\(^1\) in 2% NO-He at 500°C and W/F = 1.0 g s/cm³

\(^2\) Active copper was estimated based on the catalytic activity data of the Table 3.5.

The residual catalytic activity of the Cu(141)-ZSM-5 after 500°C-steaming was the same as that of the Cu(94)-ZSM-5 resulted from the re-exchanged 500°C-steamed Cu(141)-ZSM-5 (Table 6.7). However, the Cu re-exchanged catalyst prepared from the 500°C-steamed Ce(40)/Cu(135)-ZSM-5 showed
lower conversion of NO to N₂ (29%) than the original steamed material (58%). Also shown in Table 6.7 are conversions of NO to N₂ over fresh Cu-ZSM-5 materials containing the same nominal Cu/Al ratios. These materials have much higher catalytic activity than the Cu re-exchanged ZSM-5 materials.

6.2.7 Catalyst Characterization by XPS

It has been shown that the incorporation of cerium ions into Cu-ZSM-5 stabilized active Cu for NO decomposition in water vapor-containing gases by suppressing CuO particle formation. However, it is not clear where CuO was formed and how the state of copper and cerium changed before, during, and after the steaming process. Understanding these changes is needed to elucidate how Cu-ZSM-5 catalyst deactivates, and what role cerium ions play in stabilizing active copper in ZSM-5. XPS characterization of catalyst samples will give us information about changes of surface elemental concentration after the various treatments.

A photoelectron spectrum from raw data is shown in Figure 6.30 for the as-synthesized Ce(60)/Cu(138)-ZSM-5 sample, while in Figure 6.31 for the as-synthesized Cu(141)-ZSM-5. It was found that peak positions of Cu₂p₃, Ce₃p, O₁s and Si₂p remained the same after the different treatments. Binding energy was referred to C₁s = 284.6 eV, which was found that the C₁s line shifted 3.0 eV higher than 284.3 eV. This shift is attributed to sample charging because the catalyst materials are not conductive.

The surface ratios of copper, cerium, oxygen to silicon of the fresh and used Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 samples were measured by XPS. These results are shown in Figures 6.32-6.34 for both catalysts after different treatments. The bulk Cu/Si ratio measured by ICP is 0.035 for catalysts Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5, while the bulk Ce/Si is 0.01 for the Ce(60)/Cu(138)-ZSM-5. The O/Si of the as-received Na-ZSM-5 equals 2.72. The O/Si ratios, as shown in Figure 6.32, of the as-synthesized, treated-1, -2, and -3 samples of each catalyst are approximately constant, and are higher than the 2.72 of the parent Na-ZSM-5, implying coverage of the zeolitic crystal by cations.

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Figure 6.30  XPS survey of the fresh Ce(60)/Cu(138)-ZSM-5 (300W, 15KV; pass energy: 178eV).
Figure 6.31  XPS survey of the fresh Cu(141)-ZSM-5 (300 W, 15 KV; pass energy: 178 eV).
Figure 6.32  Atomic O/Si ratios of the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 measured by XPS (300 W, 15 KV; pass energy: 178 eV).
Figure 6.33  Atomic Cu/Si ratios of the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 measured by XPS (300 W, 15 KV; pass energy: 178 eV).
Figure 6.33  Atomic Ce/Si ratios of the Ce(60)/Cu(138)-ZSM-5 measured by XPS (300 W, 15 KV; pass energy: 178 eV).
Figure 6.33 shows the change of Cu/Si ratio with treatment for the Ce(60)/Cu(138)-ZSM-5. The Cu/Si (= 0.395) of the as-synthesized sample is much higher than the bulk value (Cu/Si= 0.035). After treatment-1, copper migrated into the ZSM-5 zeolite leading to lower Cu/Si value, from 0.395 to 0.071. When water vapor was present in the reactant stream, i.e., under treatment-2, copper migrated out and enriched the surface region of the catalyst particles. The same amount of surface copper moved back to the bulk of the catalyst again under treatment-3, which indicated copper redistribution. These results are in good agreement with STEM/EDX analyses.

Cerium ions were not as mobile as copper ions. This is indicated by Ce concentrations on the surface regions of the Ce(60)/Cu(138)-ZSM-5 materials only slightly different under treatments-2 and -3, from that of the as-synthesized sample. The surface cerium concentration was much higher than the bulk value in each case, indicating cerium oxide formation. These results are shown in Figure 6.34. However, the Ce/Si ratio of the Ce(11)/Cu(119)-ZSM-5 material was equal to the bulk value.

Surface Cu/Si ratios in the Ce(141)-ZSM-5 were lower than in the Ce(60)/Cu(138)-ZSM-5 under the same treatments, as shown in Figure 6.33. The as-synthesized sample had higher surface copper concentration (Cu/Si = 0.088) than the bulk (0.035). After treatment-1, copper also migrated into ZSM-5 zeolite leading to surface Cu/Si equal to the bulk value (0.034). The Cu/Si increased to 0.06 after treatment-2, and then decreased again after water vapor was removed from the reaction gas stream (treatment-3).

Auger parameters of copper and cerium were also measured. Unfortunately, the Auger peaks are too broad to exactly identify their positions. Therefore, copper and cerium oxidation states were not completely assigned in this study.

6.3 DISCUSSION
6.3.1 Change in Active Copper Sites
The cyclic dry/wet NO decomposition tests over the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5, Figures 6.4- 6.8, clearly show that both reversible and irreversible loss of active copper sites take place under the conditions employed. Moreover, a beneficial effect of the presence of cerium is displayed
by higher wet-gas activity as well as higher dry-gas activity recovery. In all cycles, a rather rapid (≈ 2 hours) approach to steady-state conversion of NO to N₂, indicates an equilibrium process at play. This can be thought of as a hydration-dehydration process and is, thus, a function of water content and temperature. Irreversible loss of activity may occur either through zeolitic structural changes due to steaming or copper migration/aggregation or both.

We may, therefore, distinguish three types of copper sites: active in wet gas stream, reversibly active sites (inactive in wet gas, however, recovering activity after removal of the water vapor), and inactive (permanent copper deactivation due to water vapor). We propose that the reversibly active sites are mainly hydrated and hydrolyzed copper complexes, and inactive sites are attributed to CuO formation. By using the correlation of the NO conversion to N₂ with various Cu ion-exchange levels, as shown in Figure 3.6, the ion-exchanged Cu corresponding to the NO conversion measured in Figures 6.5 and 6.6 was calculated. Figures 6.35 and 6.36 show the distribution of the three types of copper in the 500°C-steamed Cu(141)- and Ce(60)/Cu(138)-ZSM-5 under various conditions.

![Cu Distribution vs Water Content](image)

Figure 6.35  Estimated copper site distribution of the Cu(141)-ZSM-5 during the dry/wet NO decomposition.
An amount of the active copper sites decreases very fast in low partial water vapor pressure region, then deactivated slowly with increasing water vapor content in the reaction streams. This may be attributed to a fast copper migration at 500°C. For copper deactivation, an equilibrium between active and inactive copper ion is suggested by the experimental results as shown in Figure 6.5 and 6.6.

![Graph showing copper distribution vs water content](image)

Figure 6.36 Estimated copper site distribution of the Ce(60)/Cu(138)-ZSM-5 during the dry/wet NO decomposition.

### 6.3.2 Mechanism of Cu-ZSM-5 Deactivation

As we pointed out earlier, the introduction of O₂ into reaction stream lowers catalytic activity. However, the catalytic activity can be fully recovered after removal of O₂ from the stream. The reversible activity indicates no reaction between Cu cations and O₂ to form CuO. The formation of CuO in steamed Cu-ZSM-5 must be attributed to reaction of water molecules with active copper sites.

Hydrated and hydrolyzed copper complexes are formed when Cu-ZSM-5 is exposed to water vapor at reaction temperatures. These copper complexes are more mobile than Cu²⁺ cations alone, since the complexes have lower
surface charge density. Therefore, hydrolyzed copper complexes migrate in zeolite channels, which leads to the formation of Brønsted acids on the sites left behind. Upon dehydration, aggregation leads to CuO particle formation and catalyst deactivation. The following simplified scheme is proposed for Cu-ZSM-5 deactivation:

\[
\text{Cu}^{2+} = Z + x \text{H}_2\text{O} \leftrightarrow \text{Cu}^{2+}(\text{H}_2\text{O})_x = Z
\]  

(6.3)

The electrostatic field of divalent Cu cations is assumed to generate protons through dissociation of water molecules in the following way [124, 125]:

\[
\text{Cu}^{2+}(\text{H}_2\text{O})_x = Z \leftrightarrow [\text{Cu}^{2+}(\text{OH})^-(\text{H}_2\text{O})_{x-1}]^+ - Z - \text{H}^+
\]  

(6.4)

and,

\[
[Cu^{2+}(OH)^-(H_2O)_{x-1}]^+ - Z - H^+ \leftrightarrow Cu(OH)_2 + H^+ - Z - H^+ + (x-2)H_2O
\]  

(6.5)

Finally, CuO is formed by decomposition:

\[
\text{Cu(OH)}_2 \leftrightarrow \text{CuO} + \text{H}_2\text{O}
\]  

(6.6)

Z is the ZSM-5 substrate, Cu\(^{2+}(\text{H}_2\text{O})_x\) and \([\text{Cu}^{2+}(\text{OH})^-(\text{H}_2\text{O})_{x-1}]^+\) are potential hydrated and hydrolyzed copper complexes, and H\(^+\) is a Brønsted acid. In wet-NO decomposition process, the steady state catalytic activities at different water vapor contents suggest that an equilibrium is established between Cu\(^{2+}\) and water vapor, otherwise 2% water vapor in the reaction stream is enough to deactivate all the active copper sites. This is because the total number of \(\text{H}_2\text{O}\) molecules fed through the catalyst bed during 10 hour steaming at 2% \(\text{H}_2\text{O}\) was about 100 times the Cu atoms in Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5.

The proposed mechanism of Cu-ZSM-5 deactivation is supported by the appearance of CuO diffraction peaks on the XRD pattern of the Cu(141)-ZSM-5 after the catalyst was steamed in 20% \(\text{H}_2\text{O}\)-\(\text{He}\) at 500°C for 10 hours, i.e., in the absence of reaction and oxygen. Figure 37 shows this result. The detailed catalyst treatment is described as follows. The Cu(141)-ZSM-5 catalyst was
Figure 6.37  CuO evident in the 500°C-steamed Cu(141)-ZSM-5 in 20% H₂O-He for 10 hours.
pretreated with pure He (99.999% purity) at 500°C for 2 hours. At the same
time, the deionized water was flushed to remove dissolved O₂ molecules.
Then, the water vapor was entrained into the reactor by pure He. After
steaming, the Cu(141)-ZSM-5 was dried in He at 100°C, and the diffraction
pattern was taken.

Upon water vapor removal from the reactant stream, only a part of the
dry gas-catalytic activity is restored. This partial activity recovery must be
mainly attributed to dehydration of the hydrolyzed or hydrated copper
complexes. However, CuO formed during the process of wet NO-
decomposition does not likely form any active copper under our
experimental conditions. Irreversible CuO particle formation causes
permanent catalyst deactivation.

Data shown in Figure 6.8 indicates that no dealumination or CuO
formation took place during wet NO decomposition in a 5% H₂O-containing
reaction stream at 400°C for 77 hours, because the 500°C-dry gas activity was
fully restored. Hydration of the Cu(141)-ZSM-5 is attributed to low catalytic
activity in wet NO decomposition. CuO would be produced if Cu(OH)₂ was
formed in the material since the decomposition temperature of Cu(OH)₂ is
about 90°C. Thus, reaction (6.6) proceeds quickly at high temperatures (≥
400°C). We conclude that reactions (6.4) and (6.5) are the controlling steps for
catalyst deactivation. Higher water vapor pressure in the reaction stream will
favor the forward reaction to deactivation at 400°C.

Active copper loss and activity recovery pathways can be summarized in
the following scheme:
The mechanism of Y-zeolite dealumination induced by steaming has been discussed by Kerr [126, 127] and McNicol and Pott [128]. The scheme of the zeolite dealumination in this study is considered similar to that of the Y-zeolite dealumination after H-ZSM-5 is formed in wet NO decomposition. The H-ZSM-5 form is the most hydrothermally unstable, while M-ZSM-5, where M is alkali or alkaline metals, are more stable forms [129, 130]. Aluminum ions dislocate from the crystal framework, losing their tetrahedral coordination. Thus, dealumination takes place. This cation site loss can cause permanent loss of tetrahedral framework aluminum sites, since (AlO2)− cannot be restored again in the zeolite framework. STEM/EDX mapping (Figure 6.18) suggests that dealumination took place in the Cu(141)-ZSM-5 sample.

6.3.3 Transport of CuO in ZSM-5
As we discussed above, copper oxide formation is due to interaction of copper cations with water molecule, and CuO particles were formed in steamed Cu-ZSM-5. In this section, a mechanism of formation of CuO particles is proposed to explain how CuO particles form, and location of CuO particles is discussed.

Initially, the CuO can be present in the form of separate molecules or in the form of a two-dimensional cluster after reaction (6.6) takes place. Generally, the two-dimensional cluster is more stable than individual molecules, so individual molecules can "surface"-diffuse to form two-dimensional rafts [3]. Very small CuO particles are formed by crystallite migration. Small crystallites have a large fraction of surface atoms, which become mobile at relatively low temperature. When the particle size is more than about 4 nm, CuO particles grow mainly through interparticle transfer. The driving force is the larger free energy of smaller crystallites. The free energy can be represented by the following equation:

$$RT\ln\frac{a}{a_0} = \frac{2\gamma V_m}{r}$$

(6.7)

where a and a₀ are particle activity and reference state activity, respectively; R
is ideal gas constant, $T$ the temperature (K), $\gamma$ the surface tension, $V_m$ the molar volume of CuO, and $r$ the particle radius.

From CuO melting temperature ($1326^\circ$C), the Tammann temperature, at which lattices begin to be appreciably mobile, and the Hüttig temperature, at which surface atoms become significantly mobile, can be simply calculated as following: Tammann Temperature $= T_m(K)/2 = 523^\circ$C, and Hüttig temperature $= T_m(K)/3 = 260^\circ$C. The reaction temperature of 500$^\circ$C for steaming Cu(141)-ZSM-5 is very close to Tammann temperature. Therefore, CuO particles can grow to large sizes. The above proposed mechanism could explain the observation of CuO particle formation in steamed Cu-ZSM-5.

It is interesting in finding out where the CuO was formed in the steamed catalysts. First, let us assume that CuO particles form on the external surfaces of catalyst particles. It is easy to estimate the change of Cu concentration in the surface regions before and after CuO formation. From Table 6.5, the active copper kept only 42% exchange level. The inactive copper ions are assumed to form CuO. If we have a Cu(141)-ZSM-5 particle with a diameter of 5 micron (the volume of the particle: $6.544 \times 10^{10}$ nm$^3$), the particle contains a number of Cu:

$$\text{(particle volume/unit cell volume)} \times \text{Cu/unit cell}$$
$$= \left[\frac{1}{6\pi} \times (5 \times 10^3)^3 \text{nm}^3\right] / [5.32 \text{nm}^3/\text{cell}] \times 2.9869 \text{Cu/cell}$$
$$= 3.675 \times 10^{10}$$

and,

the number of inactive Cu atoms $= 3.675 \times 10^{10} \times (1 - 42.5\%/141\%) = 2.567 \times 10^{10}$ after steaming.

If the CuO is formed on the catalyst surface region within a depth of 20 nm, the volume of the shell on the catalyst particle is $1.558 \times 10^9$ nm$^3$. The amount of copper atoms migrated to the shell from the core of the particle is about $2.55329 \times 10^{10}$. Therefore, the increment of the Cu concentration in the shell is

$$2.55329 \times 10^{10} \text{Cu}/(\text{the number of the unit cells contained in the shell})$$
$$= 2.55329 \times 10^{10} / [1.558 \times 10^9 \text{nm}^3/(5.32 \text{nm}^3/\text{unit cell})]$$
$$= 87 \text{Cu/unit cell}.$$
Now, the concentration of the Cu in the shell is about 30 times \([(87 + 2.9869)/2.9869)]\) as high as that before catalyst steaming! The XPS analysis, however, as shown in Figure 6.33, does not show accumulation of Cu on the surface. Rather, a reversible migration to the surface (upon steaming) and back into the bulk of the catalysts (after removal of water vapor). Figure 6.29 shows that the CuO particle size was the same in the steamed Cu(141)-ZSM-5 after treatments- 2 and 3. The experimental data do not support the above assumption that CuO particles are on the external surface of zeolite particles. Thus, the irreversible CuO particle formation must be in the bulk of zeolite particles!

However, CuO particle sizes observed by STEM and XRD are much bigger than 1 nm which is about the diameter of the ZSM-5 channel cross-sections. The size of these CuO particles is too large to be accommodated by mere crystal expansion. We can only conclude that the zeolite structure is destroyed around these CuO particles.

The following simple calculation is to estimate pressure inside CuO particle with a diameter of 1 nm:

CuO: density, \(\rho, \approx 6.4 \text{ g/cm}^3\), melting point, \(T_m, = 1326^\circ\text{C}\)

molar volume, \(V_m, = 12.429 \text{ cm}^3/\text{mole}\)

Surface tension, \(\gamma\), is calculated by the following equation [122]

\[
\gamma = 3.26T_mV_m^{-2/3} = 971.4 \text{ erg/cm}^2
\]

The pressure: \(\Delta P = 2\gamma/r = 1.9 \times 10^4 \text{ atm}\), if the CuO diameter particle is assumed as 1 nm. The pressure is so high that it is feasible for CuO particles to break the zeolite structure.

However, catalyst characterization by XRD showed that major crystal structure was preserved after catalyst steaming. How much can CuO formation attribute to zeolite structure change? As an estimate, the volume ratio of a CuO particle to zeolite crystal, in which if all Cu ions are used to form this CuO particle, is calculated as follows:

Assuming a CuO diameter \(d = 2^n \text{ nm} = 20 \times 10^{-7} \text{ cm}\), then

the volume of the CuO particle: \(V = 1/6\pi d^3 = 4.18879 \times 10^{-18} \text{ cm}^3\)
Weigh of the CuO particle: \( w = \rho \times v = 2.680825 \times 10^{-17} \text{ g} \)

Number of Cu atoms in the CuO particle: \( N = (w \times 6.02 \times 10^{23}) / 79.546 \text{ g/mole CuO} = 2.028835 \times 10^5 \)

Number of Cu atoms in one unit cell: \( \text{Cu/Al} \times \text{Al/unit cell} = 0.7 \times 4.267 = 2.9869 \text{ Cu atoms/unit cell} \)

Number of unit cells containing \( N \) Cu atoms: \( N_1 = 2.028835 \times 10^5 \text{ Cu/(2.9869 Cu per unit cell)} = 6.7924 \times 10^5 \text{ unit cells} \)

Volume of one unit cell: 5.32 nm\(^3\)

Volume of \( N_1 \) unit cells: \( v_1 = 4.29282 \times 10^5 \text{ nm}^3 \)

The volume ratio of the CuO particle to \( N_1 \) unit cells: \( f = 1.159 \times 10^{-3} = 0.1\% \). Therefore, CuO formation causes about 0.1% deformation for zeolite structure, i.e. the damage remains sparse. Hence, the XRD pattern does not change significantly.

6.3.4 Cu-ZSM-5 Stabilization by Cerium Cations

Structural changes of zeolites due to high temperature steaming are well established in the literature [132]. While the highly siliceous ZSM-5 structure is more hydrothermally stable than the Y-zeolite, severe steaming at 600°C can lead to extensive structural changes. Using \(^{27}\text{Al-NMR},\) Grinsted, et al [79] have reported aluminum stabilization in H-ZSM-5 by Cu cations after the sample had been steamed at 700°C. The results of the section 6.2.8 and Figure 6.38 show that the Ce/Cu-ZSM-5 is more stable structurally than the Na-ZSM-5 material after exposure to 20% H\(_2\)O-containing gas at 600°C for 10 hours. The appearance of an amorphous background (halo) at \( 2\theta = 10-40^\circ \) is clearly seen for the Na-ZSM-5 material but not for the Ce(60)/Cu(138)-ZSM-5 in Figure 6.38. The NO conversion to N\(_2\) over Ce(60),Cu(108)-ZSM-5, where the copper was exchanged after 600°C-steaming of the Ce(60)-ZSM-5 material, was 13.7% (see Table 6.7), while the Cu(20)-ZSM-5 prepared from the 600°C-steamed Na-ZSM-5 showed only 5% conversion of NO to N\(_2\) (see Table 6.3).

We have found that steaming of Na-ZSM-5 at 500°C does not change the XRD pattern, except for small diffraction peak shifts and also retains the pore volume and the Cu\(^{2+}\) uptake capacity of the material. Hence, the data reported here for 400 and 500°C can be used to correlate loss of activity with
changes in the state of copper in the absence of structural modification of the zeolite.

Figures 6.5 and 6.6 and the corresponding characterization data in Figures 6.12-6.22, 6.25-6.29 and 6.38, may be used to show that CuO particle formation (sintering) causes the observed irreversible loss of activity after wet-gas NO decomposition. Cerium suppresses this sintering as indicated by the absence of CuO phase from the steamed Ce(60)/Cu(138)-ZSM-5, as shown in Figures 6.28 and 6.6.22. In this material, cerium exists primarily as an oxidic phase on the surface, as seen in Figures 6.19, 6.20, and Table 6.7, along with a certain amount of Ce$^{3+}$ ions in the zeolite channels, as shown in Figures 6.19, 6.20, 5.19 and 5.20 and Table 6.1. From Figures 6.20 and 6.33, it can be concluded that Cu cations are not only associated with framework aluminum but also with cerium ions. This indicates that there is an interaction between Cu and Ce in the Ce(60)/Cu(138)-ZSM-5 catalysts.

Certainly, cerium does not seem to suppress the mobility of Cu ions, e.g. Figures 6.21, 6.22, and 6.33. However, it enhances the dispersion of copper, and thus, its reversibility. We have concluded that CuO formed in the bulk of steamed catalysts and the zeolitic structure was destroyed around the CuO particles. This could cause the distortion of crystal structure. The crystal expansion is indicated by the increase of d-spacing for the 500°C-steamed materials, which changes in the following order: Cu(141)-ZSM-5 > Ce(60)/Cu(138)-ZSM-5 > Na-ZSM-5. This order is in the same sequence as the CuO particle sizes found in the above materials. However, the damage remains sparse for the low total loading of copper (~ 3 wt.%) used here. Consequently, the XRD pattern does not change significantly. Copper migration into ZSM-5 has been recently reported by Shpiro, et al [42] after heat treatment at 500°C in oxygen, and in nitric oxide. However, it was observed by Haack, et al [53] that copper migrated out to the crystal surface region after heat treatment in oxygen and argon followed severe reduction in hydrogen. In Cu-Y zeolite, copper has much less mobility [133] than that in Ce(60)/Cu(138)-ZSM-5.

Figure 6.38 shows amorphous material formation for the 600°C-steamed Na-ZSM-5, but not for the 600°C-steamed Ce(60)/Cu(138)-ZSM-5. However, the diffraction peak shift on XRD of the former material was less than for the
latter. These results together with these at 500°C discussed above provide strong evidence that the more pronounced diffraction peak shifts in the steamed Cu-containing materials were caused by CuO particle formation in the zeolites.

As we discussed in the previous section, the irreversible CuO particle formation/sintering causes permanent catalyst deactivation. In recent work, Kharas, et al [49] showed that such sintering is fast and extensive even in short-time runs at 600 and 800°C in 10% H₂O-containing lean exhaust gases. The corresponding structural changes of the zeolitic matrix were reported to be minor, even though XRD analysis indicated amorphous material formation gradually with temperature over the range of 2θ = 10-40°. In the long-time hydrothermal tests reported here, structural changes (e.g. diffraction peak shifts) do occur, even at lower temperature. However, we attribute these to de-stabilization of the zeolite structure upon migration of copper ion complexes away from the framework aluminum. Thus, according to the scheme of reactions (6.4) and (6.5), a partially protonated ZSM-5 is formed, which is less stable than the metal exchanged form, i.e., more prone to dealumination by steaming. As Figures 6.5-6.8 and Tables 6.2 and 6.7 indicate that this phenomenon is more pronounced at the higher temperatures of 500 and 600°C. At 400°C and low water vapor contents, crystalline CuO is not formed even after several days in operation, and this preserves the structural integrity of the zeolite as well.

It is noteworthy that the presence of Ce³⁺ is beneficial even at the mild conditions of Figure 6.7. The possible explanations for the positive effect of cerium ions on the hydrothermal stability of Cu-ZSM-5 are: (i) cerium imparts stabilization of copper ions in the active coordination with the Al-O of the framework. This would suppress copper ion complex migration away from the framework aluminum; (ii) even when migration occurs, the cerium-copper interaction is strong and prevents aggregates from forming crystallites of CuO that may sinter and be lost irreversibly. Rather, highly dispersed small copper clusters prevail (see Figure 6.7) and these may slowly recover activity by exchanging with protons on AlO₂⁻ sites. It has been reported that sintering of platinum particles was inhibited by a chemical interaction of Pt and Y₂O₃, which was formation of an yttrium-rich phase on
Figure 6.38  XRD patterns of (a) steamed Na-ZSM-5 (20 hours) in 20% H2O-4% O2- He; and (b) Ce(60)/Cu(138)-ZSM-5 (10 hours) in 20% H2O-2% NO- He at 600°C.
the surface of the particles [134]. Hydration of the cerium ions may also occur, but this can not be used to explain the consistently twice as high activity of the Ce(60)/Cu(138)-ZSM-5 material versus the Cu(141)-ZSM-5 at all wet gas compositions (2- 20% H₂O, see Figures 6.5 and 6.6).

Finally, the results with re-exchanged materials after steaming and extraction of the ionic copper are interesting as they both complement the XRD and STEM/EDX analyses as well as provide some new information. As Table 6.2 shows, the high copper re-exchange capacity of the steamed materials does not correlate with the resulting activity for NO decomposition (Table 6.7). This indicates that the steamed materials contain either extra-framework tetrahedral aluminum or other negatively charged sites, e.g., hydroxylated fragments [135] that have copper uptake capacity but no activity. In the re-exchanged materials copper deposition on the surface can be ruled out since the color of the re-exchanged materials remained light blue and no CuO phase was detected by XRD. Also, the process of copper extraction used here prior to re-exchange does not extract framework aluminum. This is shown in Table 6.2. The fresh parent Na-ZSM-5 zeolite, after the same treatment (washed with 0.05M HNO₃ solution at room temperature for 4 hours), could exchange copper ions as much as the untreated material, and the copper was equally active in both cases. It has been reported that even with 1M HNO₃ solution, i.e., much higher concentration than 0.05M solution used here, only non-framework aluminum was partially extracted from steamed ZSM-5 [136]. The Cu re-exchanged catalyst prepared from the 500°C-steamed Ce(40)/Cu(135)-ZSM-5 according to the above technique was less active for NO decomposition than the original steamed material (Table 6.7). This suggests the existence of a stabilized Cu-...Ce-...Al-O site, which is active for NO decomposition, but is destroyed in dilute HNO₃ solution. These metastable active sites exist only in the presence of Ce ions in Cu-ZSM-5, and serve to prove that cerium enhances the stability of active copper sites in wet NO decomposition.

The Cu-ZSM-5 deactivation and the interaction of Cu with Ce are shown schematically in Figures 6.39 and 6.40.

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6.4 CONCLUSION

We have shown that cerium addition to Cu-ZSM-5 promotes the activity of the latter for the NO decomposition in wet gas streams at temperatures in the range of 400-600°C. From extensive analysis of unmodified Cu-ZSM-5, it appears that the mechanism of copper deactivation in wet NO decomposition is twofold: (i) equilibrium hydration (reversible); (ii) migration/aggregation and CuO crystallite formation/sintering (irreversible). The second path is thermally activated, hence, high temperature of reaction will exacerbate it. We think that dealumination happens as a result of partial protonation of sites vacated by the mobile copper ion complexes; thus, dealumination appears to be a secondary issue in the deactivation process. The partial recovery of dry-gas activity upon removal of water indicates that not all copper sites are equally unstable in wet gas streams; there is a fraction of active copper sites of apparently a strong coordination with the framework (non-mobile). Cerium serves to increase the stability of additional copper sites. Certainly, the material used here is not optimized. If the presence of Ce$^{3+}$ ions is important, the catalyst Ce(60)/Cu(138)-ZSM-5 only contains but a small fraction of these.
Figure 6.39  Schematic of CuO formation in steamed Cu-ZSM-5.
Figure 6.40 Interaction of Ce with Cu leading to suppressing CuO formation.
Chapter 7

KINETICS OF NITRIC OXIDE DECOMPOSITION OVER CU- AND METAL ION-MODIFIED CU-ZSM-5

Kinetics of NO decomposition over Pt and the oxides of Fe, Co, Ni, Cu, and Zr at temperatures up to 1,000°C was investigated by Amirnazmi, et al [31]. It was reported that the kinetics were of Langmuir-Hinshelwood form with oxygen inhibition of the first order. More recently, Li and Hall [44] reported that the NO decomposition rate over Cu-ZSM-5 was first order in NO and was inhibited by oxygen (-0.5 order). From this thesis work, we found that alkaline earth and transition metal ion-modified Cu-ZSM-5 displayed higher catalytic activity at high temperatures (>450°C), which is in good agreement with the literature [50], and rare earth metal ion-modified Cu-ZSM-5 promoted the activity at low temperatures (<400°C). Interestingly, the presence of cations in the Cu-ZSM-5 moderates the oxygen inhibition of NO decomposition. These findings lead to some interesting questions. How do metal cations affect the NO decomposition rate over Cu-ZSM-5? Is the decomposition reaction rate expression over metal ion-modified Cu-ZSM-5 the same as that over Cu-ZSM-5?

In this chapter, kinetic tests are conducted to obtain the rate expressions. A simple mechanism is proposed for nitric oxide decomposition over Cu(72)-, Cu(141)-, Mg(52)/Cu(66)- and Ce(60)/Cu(138)-ZSM-5 catalysts. The reaction orders with respect to NO and O₂ concentrations are determined at different reaction temperatures. The kinetic data are used to explain the catalyst performance for the NO conversion to N₂ as presented in previous Chapters. A first attempt at elucidating the interaction between Cu and Ce ions in ZSM-5 was made by measuring the oxygen uptake capacity in a thermogravimetric analyzer (TGA) and by Temperature-Programmed-Desorption (TPD) coupled with mass spectrometry (MS) for the catalysts Cu-ZSM-5, Ce-ZSM-5 and metal ion-modified Cu-ZSM-5.
7.1 EXPERIMENTAL

The catalysts used in the kinetic studies were the low copper-containing Cu(72)-ZSM-5 and Mg(52)/Cu(66)-ZSM-5, and the excessively copper exchanged Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5. Preparation and properties of the two Cu-ZSM-5 catalysts were discussed in Chapter 3, while the two metal ion modified Cu-ZSM-5 materials in Chapter 5.

The kinetic studies were made using mixtures of NO- He or NO- O2- He in the microreactor, as described in Chapter 2. Experimental procedures were described in Chapter 4. Samples weighing about 30 mg were placed in the reactor. The NO concentration in the feed gas was varied from 0.075 to 4%, and the O2 from 1 to 5%. The gas pressure in the reactor was about 1.5 atm. The catalysts were treated using pure He at 500°C for 2 hours in the reactor before being exposed to reaction streams. The turnover frequency of NO decomposition was expressed as the number of NO molecules converted into N2 per Cu per second.

Figure 7.1 shows the NO conversion to N2 (%) as a function of contact time, W/F, over the catalysts Mg(52)/Cu(66)-ZSM-5 and Cu(141)-ZSM-5. NO conversions to N2 increase linearly with increasing W/F up to 37% and 51%, respectively, for the above two catalysts. Straight lines indicate that the reaction took place in the kinetic regime. Similar experiments were performed for the catalysts Cu(72)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5. A value of the W/F = 0.03 g s/cm³ was chosen for all kinetic tests to ensure that reaction rate was measured in the kinetic regime for the above catalysts.

The oxygen uptake capacities of Ce(60)-ZSM-5, Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 materials were measured in TGA (ATI: Cahn TG 121) in flow mode at 500°C. The experimental procedure was as follows: the sample weighing about 50 mg was placed in the quartz pan; the sample was first heated in dry air at a heating rate of 15°C/min up to 500°C, and was left at 500°C for 1 hour in dry air flow. Then a mixture of 10% CO- He was switched on to replace the dry air stream; the oxidized sample was reduced at 500°C for 1 hour. Finally, the sample was purged at 500°C in He flow to remove adsorbed CO from the sample. The oxygen uptake capacity could be measured by weight difference between oxidized and reduced samples.
Figure 7.1  NO conversion to N₂ vs. W/F over Mg(52)/Cu(66)-ZSM-5 and Cu(141)-ZSM-5 in 4% NO- He at 500°C and 1.5 atm.

Oxygen Temperature-Programmed-Desorption (TPD) studies were made in the micro-reactor equipped with a mass spectrometer (MKS Instruments: Quadruple Residual Gas Analyzer). The samples were evacuated at 40°C overnight. The pretreated samples weighing 105 mg were placed in the microreactor. The reactor system was first flushed by pure He with a flow rate of 30 cm³/min at 150°C for 1 hour to remove adsorbed water from the samples. The reactor temperature was then lowered to room temperature in He flow. Pure flowing oxygen at a flowrate of 30 cm³/min was introduced into the system at this point. The samples were heated from room temperature to 500°C at a heating rate of 10°C/min, stayed at 500°C for 2 hours, then cooled to room temperature all in oxygen flow. Then, the samples were purged with He flowing at 30 cm³/min at room temperature for 10 hours to remove oxygen adsorbed on the reactor system. TPD started by raising temperature at a heating rate of 10°C/min to 550°C, where it was maintained for an additional 35 minutes. The amount of oxygen desorbed was continuously monitored by the mass spectrometer.
7.2 KINETICS MEASUREMENTS IN THE MICROREACTOR

The turnover frequencies for NO decomposition over the Cu(72)/Cu-ZSM-5 and Mg(52)/Cu(66)-ZSM-5 are shown in Figure 7.2 in the form of Arrhenius-plots. The turnover frequency over the Cu(72)-ZSM-5 is higher than that over the Mg(52)/Cu(66)-ZSM-5 catalyst in the low temperature range (<450°C), and lower at high temperatures. These results are in good agreement with the conversion-temperature plot of Figure 5.1. In this study, the TOF measurements were extended to higher temperatures to measure the corresponding apparent activation energy. As can be seen in Figure 7.2, the apparent energy for NO decomposition over the Mg(52)/Cu(66)-ZSM-5 is 18.4 Kcal/mole in the low temperature region (< 450°C), changing over to a negative value of -7.9 Kcal/mole in the high temperature region (> 550°C). Over the Cu(72)-ZSM-5 material, different values of the apparent activation energies, 10.1 Kcal/mole for the low temperature region and -15.4 Kcal/mole for the high temperature region, were obtained. The apparent activation energies are for the linear parts of the Arrhenius plots for the low and high temperature regions. As we have pointed out in Chapter 4, a changing reaction mechanism or distortion of active copper coordination (the original coordination can be restored by lowering the reaction temperature), or the higher heat of reactant chemisorption than the true activation energy may be used to explain the observed reaction rate maximum.

Figure 7.3 shows Arrhenius-type plots for the turnover frequencies over the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5. The TOF for the Ce(60)/Cu(138)-ZSM-5 is higher than that for the Cu(141)-ZSM-5 over the whole temperature range. The apparent activation energies of NO decomposition over the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 are 12.8 Kcal/mol and 14.3 Kcal/mol in low temperature regime (< 450°C), and -3.4 Kcal/mol and -2.8 Kcal/mol in high temperature (> 550°C), respectively.
Figure 7.2  Arrhenius-type plots for Cu(72)-ZSM-5 and Mg(52)/Cu(66)-ZSM-5 in 4% NO- He at W/F = 0.03 g s/cm³ and 1.5 atm.

Figure 7.3  Arrhenius-type plots for Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 in 4% NO- He at W/F = 0.03 g s/cm³ and 1.5 atm.
Initially, a simple power law was used to fit the data, which is written as

\[ r = k P_{\text{no}}^m P_{\text{O}_2}^n \]  \hspace{1cm} (7.1)

where \( P_{\text{no}} \) is the NO partial pressure (Pa), \( P_{\text{O}_2} \) is the \( \text{O}_2 \) partial pressure (Pa), \( m \) is the reaction order with respect to NO and \( n \) is the reaction order with respect to \( \text{O}_2 \). To determine \( m \), the \( \ln (r) \) vs. \( \ln (P_{\text{no}}) \) was plotted at each reaction temperature. The slope of the straight line of the \( \ln (r) \) vs. \( \ln (P_{\text{no}}) \) is the reaction order, \( m \), in NO. The concentration of NO was varied in the feed gas stream, while keeping the total flow rate constant. Similarly, the reaction order, \( n \), for \( \text{O}_2 \) was obtained from the slope of the straight line of the \( \ln (r) \) vs. \( \ln (P_{\text{O}_2}) \) at each reaction temperature while \( P_{\text{no}} \) and total the flow rate kept constant.

The dependence of the NO decomposition rate on the partial pressures of nitric oxide and oxygen was investigated over the Cu(72)-ZSM-5 and Mg(52)/Cu(66)-ZSM-5 catalysts at different reaction temperatures. The NO concentration was varied from 0.5% to 4%, and \( \text{O}_2 \) from 1 to 5%. The reaction rate was first order in partial pressure of nitric oxide over the Cu(72)-ZSM-5 in the temperature range of 400 to 600°C, as shown in Figure 7.4. However, Figure 7.5 shows the reaction order of NO decomposition over the Mg(52)/Cu(66)-ZSM-5 being temperature dependent, first order at 400°C and 1.4 at 600°C. The reaction rates, as shown in Figures 7.6 and 7.7, are inhibited by oxygen for both catalysts.

The reaction order with respect to NO for the Cu(141)-ZSM-5 increases from 0.5 to 1.0 for reaction temperature in the range from 350 to 600°C, where the NO concentration varied from 0.075% to 4%. Li, et al [44] studied the kinetics of NO decomposition over a Cu(166)-ZSM-5 (Si/Al = 26) at temperatures ranging from 350 to 550°C. They found that the reaction rate was first order in NO. However, our findings are different at low temperatures, with the reaction order equal to 0.5 and 0.7 in \( P_{\text{no}} \) at 350 and 400°C, respectively. Amirnazmi et al [31] investigated the reaction rate of NO decomposition over Pt and some metal oxides at temperatures above 600°C, and found it first order in NO. Over the Ce(60)/Cu(138)-ZSM-5 we found the
Figure 7.4  The dependence of the NO decomposition rate on the pressure of NO over Cu(72)-ZSM-5 at W/F= 0.03 g s/cm³ (NTP) and 1.5 atm.

Figure 7.5  The dependence of the NO decomposition rate on the pressure of NO over Mg(52)/Cu(66)-ZSM-5 at W/F= 0.03 g s/cm³ (NTP) and 1.5 atm.
Figure 7.6 The dependence of the NO decomposition rate on the pressure of O₂ for Cu(72)-ZSM-5 at W/F= 0.03 g s/cm³ (NTP) and 1.5 atm. The concentration of NO (2%) was constant.

Figure 7.7 The dependence of the NO decomposition rate on the pressure of O₂ for Mg(52)/Cu(66)-ZSM-5 at W/F= 0.03 g s/cm³ (NTP) and 1.5 atm. The concentration of NO (2%) was constant.
rate to be first order in NO. The reaction orders with respect to NO partial pressure are summarized in Table 7.1.

The reaction order in O₂ varies from -1.0 to -0.5 in the temperature range from 350 to 600°C for the Cu(141)-ZSM-5 material. The first order in denominator term means stronger O₂ adsorption on the active Cu sites at low temperatures. This is why NO conversions to N₂ over the Cu(141)-ZSM-5 were very low in the low temperature region after introduction of 5% O₂ into the reaction stream (see Figure 5.11). The reaction order in O₂ is -1/4 for the Ce(60)/Cu(138)-ZSM-5 based on the plot of ln (r) vs. ln (P O₂). The detailed data are shown in Table 7.1.

Table 7.1 Reaction Orders in NO and O₂¹

<table>
<thead>
<tr>
<th>Catalyst-</th>
<th>in NO²</th>
<th></th>
<th></th>
<th></th>
<th>in O₂³</th>
<th></th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>ZSM-5</td>
<td>350°C</td>
<td>400°C</td>
<td>500°C</td>
<td>600°C</td>
<td>350°C</td>
<td>400°C</td>
<td>500°C</td>
<td>600°C</td>
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<tr>
<td>Cu(72)-</td>
<td>1.0</td>
<td>0.98</td>
<td>0.98</td>
<td></td>
<td>-0.50</td>
<td>-0.51</td>
<td>-0.45</td>
<td></td>
</tr>
<tr>
<td>Mg(52)/Cu(66)-</td>
<td>1.0</td>
<td>1.14</td>
<td>1.37</td>
<td></td>
<td>-0.40</td>
<td>-0.41</td>
<td>-0.41</td>
<td></td>
</tr>
<tr>
<td>Cu(141)-</td>
<td>0.51</td>
<td>0.84</td>
<td>1.0</td>
<td>1.1</td>
<td>-1.0</td>
<td>-0.86</td>
<td>-0.43</td>
<td>-0.45</td>
</tr>
<tr>
<td>Ce(60)/Cu(138)-</td>
<td>0.96</td>
<td>1.0</td>
<td>1.1</td>
<td></td>
<td>-0.27</td>
<td>-0.26</td>
<td>-0.27</td>
<td></td>
</tr>
</tbody>
</table>

¹ The contact time, W/F, was 0.03g s/cm³ (NTP).
² The NO content varied from 0.5 to 4% for the Cu(72)-ZSM-5, and 0.057 to 4% in the absence of O₂.
³ The O₂ content varied from 0.5 to 5% while the NO content was kept constant at 2%.

Experimental tests were made to examine the reaction order in NO at 500°C in 2% O₂-containing reaction streams over the above catalysts. It was found that the reaction order in NO was similar to the values shown in Table 7.1 obtained in O₂-free decomposition.
7.3 MODELING THE NO DECOMPOSITION

The experimental data were fitted by using different rate expressions. The following rate expression best fitted the data for the Cu(72)-ZSM-5, Mg(52)/Cu(66)-ZSM-5, Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 catalysts:

\[ r = \frac{k[NO]^m}{[1 + K[O_2]^n]^2} \]  \hspace{1cm} (7.2)

This was true both in the presence and absence of oxygen in the reaction gases. The \( m \) and \( n \) in equation (7.2) are dependent on the catalysts and reaction temperatures.

The rate expression for the Cu(141)-ZSM-5 can be written as follows:

\[ r = \frac{k[NO]}{[1 + K[O_2]]^2} \]  \hspace{1cm} (7.3)

at low temperatures (≤ 450°C), and

\[ r = \frac{k[NO]}{[1 + K[O_2]^{1/2}]^2} \]  \hspace{1cm} (7.4)

at high temperatures (≥ 500°C). The values of the parameters, \( k \) and \( K \), are summarized for Cu(141)-ZSM-5 at various reaction temperatures in Table 7.2.

Comparisons of experimental data with the fitted values using Equations (7.3) and (7.4) and the values of the parameters listed in Table 7.2 are shown in Figures 7.8 and 7.9. A good agreement between them is found.

The kinetic rate of NO decomposition over the Ce(60)/Cu(138)-ZSM-5 catalyst was fitted by the following expression:

\[ r = \frac{k[NO]}{[1 + K[O_2]^{1/4}]^2} \]  \hspace{1cm} (7.5)
Table 7.2  Kinetic Parameters of Cu(141)-ZSM-5

<table>
<thead>
<tr>
<th>Reaction Temperature (°C)</th>
<th>$k^1$</th>
<th>$K^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>3.3</td>
<td>1923.9</td>
</tr>
<tr>
<td>400</td>
<td>11.9</td>
<td>1385.5</td>
</tr>
<tr>
<td>500</td>
<td>35.3</td>
<td>36.6</td>
</tr>
<tr>
<td>600</td>
<td>31.1</td>
<td>34.5</td>
</tr>
</tbody>
</table>

1. The units of $k$ are (# of NO converted to N$_2$/Cu s)/(mole/liter).
2. The units of $K$ are (mole/liter)$^{-1}$ for temperatures of 350 and 400°C, and (mole/liter)$^{-1/2}$ for 500 and 600°C.

Figure 7.8  Turnover frequencies of NO decomposition vs. concentration of NO over Cu(141)-ZSM-5 in O$_2$-free stream at $W/F = 0.03$ g s/cm$^3$ (NTP) and 1.5 atm. The symbols are experimental data, while the solid lines are the predicted values by using rate expressions (7.3) and (7.4).
Figure 7.9  Turnover frequencies of NO decomposition vs. concentration of O\textsubscript{2} for Cu(141)-ZSM-5 at W/F = 0.03 g s/cm\textsuperscript{3} (NTP) and 1.5 atm. The concentration of NO (2\%) was constant. The symbols are experimental data, while the solid lines are the predicted values by using rate expressions (7.3) and (7.4).

The reaction order with respect to oxygen on the Ce-modified Cu-ZSM-5 catalyst, equation (7.5), is different from these on the Cu-ZSM-5 material in equations (7.3) and (7.4). The negative quarter order in the [O\textsubscript{2}] term in Equation (7.5) suggests that the presence of Ce ions in the Cu-ZSM-5 moderates the reaction inhibition by oxygen. The parameters, k and K, in the rate expression (7.5) are listed in Table 7.3. The calculated turnover frequencies for NO decomposition in the absence and presence of oxygen are shown in Figures 7.10 and 7.11 at different [NO] and [O\textsubscript{2}] concentrations. A good fit is shown by comparison with the experimental data.

The kinetic parameters in Equation (7.2) for NO decomposition over the catalysts Cu(72)-ZSM-5 and Mg(52)/Cu(66)-ZSM-5 are listed in Table 7.4. Interestingly, only for the Mg(52)/Cu(66)-ZSM-5, the reaction order in [NO] concentration changes with increasing temperature. It is not clear why reaction order in O\textsubscript{2} is -1/2 over the Cu(72)-ZSM-5 catalyst at 400\degree C, while it is -1 over Cu(141)-ZSM-5.
Figure 7.10 Turnover frequencies of NO decomposition vs. concentration of NO over Ce(60)/Cu(138)-ZSM-5 (0% O2) at W/F= 0.03 g s/cm³ (NTP) and 1.5 atm. The symbols are experimental data, while the solid lines are predicted values by using rate expression (7.5).

Figure 7.11 Turnover frequencies of NO decomposition vs. concentration of O2 for Ce(60)/Cu(138)-ZSM-5 at W/F= 0.03 g s/cm³ (NTP) and 1.5 atm. The concentration of NO (2%) was constant. The symbols are experimental data, while the solid lines are the predicted values by using rate expression (7.5).
Table 7.3  Kinetic Parameters over Ce(60)/Cu(138)-ZSM-5

<table>
<thead>
<tr>
<th>Reaction Temperature (°C)</th>
<th>$k^1$</th>
<th>$K^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>12.5</td>
<td>6.9</td>
</tr>
<tr>
<td>500</td>
<td>43.3</td>
<td>5.3</td>
</tr>
<tr>
<td>600</td>
<td>34.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

1. The units of $k$ are (# of NO conversion to N$_2$/Cu s)/(mole/liter).
2. The units of $K$ are (mole/liter)$^{-1/4}$.

Table 7.4  Kinetic Parameters of Cu(72)- and Mg(52)/Cu(66)-ZSM-5$^1$

<table>
<thead>
<tr>
<th></th>
<th>$m$</th>
<th>$n$</th>
<th>$k$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(72)-ZSM-5</td>
<td>1.0</td>
<td>1/2</td>
<td>15.6</td>
<td>45.8</td>
</tr>
<tr>
<td>400°C</td>
<td>1.0</td>
<td>1/2</td>
<td>32.5</td>
<td>13.8</td>
</tr>
<tr>
<td>600°C</td>
<td>1.0</td>
<td>1/2</td>
<td>19.6</td>
<td>9.4</td>
</tr>
<tr>
<td>Mg(52)/Cu(66)-ZSM-5</td>
<td>1.0</td>
<td>1/2</td>
<td>9.4</td>
<td>10.2</td>
</tr>
<tr>
<td>400°C</td>
<td>1.1</td>
<td>1/2</td>
<td>67.3</td>
<td>9.7</td>
</tr>
<tr>
<td>600°C</td>
<td>1.5</td>
<td>1/2</td>
<td>975.7</td>
<td>9.0</td>
</tr>
</tbody>
</table>

1. The units of $k$ are (# of NO converted to N$_2$/Cu s)/(mole/liter)$^{-m}$.
2. The units of $K$ are (mole/liter)$^{-1/2}$.

The experimental data and predicted values using the above parameters are shown in Figures 7.12 and 7.13 for the Cu(72)-ZSM-5, and Figures 7.14 and 7.15 for the Mg(52)/Cu(66)-ZSM-5. From the above results, the reaction order in O$_2$ over the Mg(52)/Cu(66)-ZSM-5 is the same as that over the Cu(72)-ZSM-5. However, The Mg ions in the Mg(34)/Cu(86)-ZSM-5, however, moderate the reaction inhibition by oxygen, as shown in Figure 5.12. This may be attributed to a ratio of Mg to Cu in the materials.
Figure 7.12  TOF of NO decomposition vs. concentration of NO over Cu(72)-ZSM-5 in O$_2$-free stream at W/F = 0.03 g s/cm$^3$ (NTP) and 1.5 atm. The symbols are experimental data, while the solid lines are the predicted values using rate expression (7.2) and kinetic parameters in Table 7.4.

Figure 7.13  Turnover frequencies of NO decomposition vs. concentration of O$_2$ for Cu(72)-ZSM-5 at W/F = 0.03 g s/cm$^3$ (NTP) and 1.5 atm. The concentration of NO (2%) was constant. The symbols are experimental data, while the solid lines are the predicted values using rate expression (7.2) and kinetics parameters in Table 7.4.
Figure 7.14  Turnover frequencies of NO decomposition vs. concentration of NO over Mg(52)/Cu(66)-ZSM-5 in O2-free stream at W/F= 0.03 g s/cm³ (NTP) and 1.5 atm. The symbols are experimental data, while the solid lines are the predicted values using rate expression (7.2) and kinetic parameters in Table 7.4.

Figure 7.15  Turnover frequencies NO decomposition vs. concentration of O2 for Mg(52)/Cu(66)-ZSM-5 at W/F= 0.03 g s/cm³ (NTP) and 1.5 atm. The concentration of NO (2%) was constant. The symbols are experimental data, while the solid lines are the predicted values by using rate expression (7.2) and kinetics parameters in Table 7.4.
7.4 INTERACTION OF CU IONS AND OXYGEN

As discussed in Chapter 5, higher conversions of NO to N₂ were measured over metal ion modified Cu-ZSM-5 catalysts than that over Cu-ZSM-5 materials in O₂-containing gas mixtures. In this section, the interaction of Cu with oxygen in the presence and absence of cations was investigated using the TGA, and the microreactor equipped with on-line mass spectrometry.

The presence of cerium ions in Cu-ZSM-5 moderates the reaction inhibition by oxygen in the reaction streams, as shown in Figure 5.12 and the kinetic rates in Figures 7.11. In the reaction rate expressions, the reaction order in oxygen is -1/4 (Equation 7.5) over Ce(60)/Cu(138)-ZSM-5, while it is -1 or -0.5 order over the Cu(141)-ZSM-5 (Equations 7.3 and 7.4). The presence of Ce ions, thus, appears to change the interaction between active Cu cations and oxygen.

To shed more light on this interaction, the oxygen uptake capacity of the Cu(141)-ZSM-5, Ce(60)/Cu(138)-ZSM-5 and Ce(60)-ZSM-5 materials was measured using the TGA. It was found that the oxygen uptake capacity was 0.161% (by weight, using the reduced sample weight as a basis) for Cu(141)-ZSM-5, 0.218% for the Ce(60)/Cu(138)-ZSM-5, and 0.01% for the Ce(60)-ZSM-5 material. Since the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 both contain a similar number of copper atoms, their oxygen uptake capacities can directly be compared. The oxygen uptake capacity of the Ce(60)/Cu(138)-ZSM-5 is 35% higher than that of Cu(141)-ZSM-5. The negligible oxygen uptake capacity (0.01 wt.%) of the Ce(60)-ZSM-5 material indicates that no Ce³⁺ \rightarrow Ce⁴⁺ took place. Therefore, the increase of oxygen uptake capacity of the Ce(60)/Cu(138)-ZSM-5 catalyst is attributed to the effect of Ce on Cu ions.

The O₂-TPD of the samples weighing 105 mg was made in the micro-reactor system coupled with the mass spectrometer. The O₂ desorption profiles for the as-received Na-ZSM-5, Cu(141)-ZSM-5, Ce(60)/Cu(138)-ZSM-5 and Ce(60)-ZSM-5 materials are shown in Figure 7.16. The parent Na-ZSM-5 has three O₂ desorption peaks at temperatures of 55, 295 and 540°C. The first two peaks are much smaller than the latter. However, Na-ZSM-5 adsorbed O₂, which was not observed at temperatures up to 550°C by Vallyon and Hall [55]. For the catalyst Cu(141)-ZSM-5, four O₂ adsorption peaks are observed at 45, 150, 420
Figure 7.16  Temperature-programmed-desorption of O₂ from the Na-ZSM-5, Ce(60)-ZSM-5, Mg(52)/Cu(66)-ZSM-5, Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5.
and 540°C, while for Ce(60)/Cu(138)-ZSM-5 at 45, 200, 313, 403, 540°C. The latter two peaks for the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 are the strongest ones, which contribute to NO decomposition. A lower oxygen desorption temperature for the major peak may be used to explain lower reaction inhibition by oxygen during reaction. Also, this could explain the difference of the reaction orders in oxygen, as shown in Equations (7.4-7.6).

It is worth pointing out that no oxygen desorption peak was observed in the O₂-TPD of Ce(60)-ZSM-5. This is in good agreement with what was measured by TGA (practically no oxygen uptake capacity was observed).

The O₂-TPD for the Mg(52)/Cu(66)-ZSM-5 catalyst is also shown in Figure 7.16. The profile is similar to that of Cu(141)-ZSM-5. The amount of desorbed oxygen from Mg(52)/Cu(66)-ZSM-5 is less than that from Cu(141)-ZSM-5 since its Cu exchange level is low.

The amount of desorbed oxygen can be estimated by integrating the area of under the oxygen TPD peaks. The ratios of the oxygen desorbed from Na-ZSM-5, Mg(52)/Cu(66)-ZSM-5, Cu(141)-ZSM-5, and Ce(60)/Cu(138)-ZSM-5 are 1: 3.36: 9.18: 11.57. The integrated area for Ce(60)/Cu(138)-ZSM-5 was about 26% higher than that for Cu(141)-ZSM-5, which is in agreement with the oxygen uptake capacities measured by TGA. The absolute amount of the adsorbed oxygen in Mg(52)/Cu(66)-ZSM-5 catalyst is less than in Cu(141)-ZSM-5, since the copper exchange level in the former catalyst is lower than the latter. Therefore, ratio of desorbed oxygen normalized to the copper contents is 1: 1.28.

7.5 DISCUSSION

The apparent activation energy over the Cu(141)-ZSM-5 is slightly higher than that over the Cu(72)-ZSM-5 in the low temperature region, while the absolute negative apparent activation energy was lower in the high temperature region. The low absolute activation energy at high temperatures can explain the plateau in NO conversion to N₂ in the temperature range of 500 to 650°C over the Cu(141)-ZSM-5, as shown in Figure 3.1. The reason for this may be that the active copper cations are located closer to one framework aluminum in excessively Cu ion-exchanged Cu-ZSM-5 and are more stable at
high temperatures than in the low Cu ion-exchanged catalyst. The stable active copper cations maintain the catalyst activity for NO decomposition, which results in the higher TOF over the Cu(141)-ZSM-5.

As reported in literature [67, 69], addition of Mg$^{2+}$ ions into Cu-ZSM-5 forces Cu ions to move closer to the framework aluminum atoms. We have proposed in Chapter 5 that this increases the Cu-ZSM-5 catalytic activity. The high catalytic activity, i.e. lower negative apparent activation energy, of Mg(52)/Cu(66)-ZSM-5 may be due to more Cu cations close to one T-Al in this material than in the Cu(72)-ZSM-5 catalyst.

The specific rate of NO decomposition over the Ce(60)/Cu(138)-ZSM-5 is higher than the Cu(141)-ZSM-5 over the whole temperature range of 350-650°C (Figure 7.3). The activity differences between the two samples were higher at high temperatures. However, the measurements of NO conversion to N$_2$ (Figure 5.7) only show that Ce ions improve the Cu-ZSM-5 activity in low temperature region, not in high temperature region. This may be due to diffusion limitation at high temperatures for the conversion measurements. By using STEM/EDX and XPS analyses, we have shown that Cu cations are associated not only with T-Al but also with Ce ions in Ce/Cu-ZSM-5. The effect of Ce ions on the Cu-ZSM-5 activity may be attributed both to interaction of Cu and Al, as well as Cu and Ce.

As shown in Figure 5.10, the NO conversion to N$_2$ over the Cu(141)-ZSM-5 catalyst is very low at temperatures below 400°C when oxygen is present in the reaction stream. This suggests that oxygen strongly adsorbs on the active Cu sites at low temperature, which is in good agreement with the O$_2$-TPD measurement. At high temperature, oxygen desorbs and reduced Cu sites are produced. The desorption of oxygen from the Cu sites provides NO with more adsorption sites and consequently the activity increases. Tables 7.2-7.4 show that K decreases with reaction temperature. Interestingly, K for the Mg ion-modified Cu-ZSM-5 is smaller than that for Cu(72)-ZSM-5. This indicates that oxygen adsorbs less strongly on active sites in metal ion-modified Cu-ZSM-5 materials. The higher reaction order than unity in NO over the Mg(52)/Cu(66)-ZSM-5 is attributed to more active copper available in this material, compared to Cu(72)-ZSM-5 with similar copper exchange level.
From our kinetic data, Equations (7.3) and (7.4), a simplified mechanism of NO decomposition over the Cu(141)-ZSM-5 is as follows:

\[
\text{NO} + [S] \rightleftharpoons \text{NO-[S]} \quad (7.6)
\]

\[
\text{NO-[S]} + [S] \rightarrow (1/2 \text{N}_2)-[S] + (1/2 \text{O}_2)-[S]
\rightarrow 1/2 \text{N}_2 + (1/2 \text{O}_2)-[S] + [S] \quad (7.7)
\]

\[
\text{O}_2-[S] \rightleftharpoons \text{O}_2 + [S] \quad (7.8)
\]

where NO and O\(_2\) are in the gas phase; [S] represents an active site; NO-[S] and O\(_2\)-[S] are adsorbed NO and O\(_2\), respectively. At low temperatures, the oxygen molecules directly adsorb on the Cu active sites without dissociation. Assuming that reaction (7.7) is the rate-controlling step and that reactions (7.6) and (7.8) are in equilibrium, it follows that

\[
\text{NO-[S]} = K_{\text{NO}}[\text{NO}][S] \quad (7.9)
\]

and

\[
[\text{O}_2][S] = K_{\text{O}_2} \{\text{O}_2 - [S]\} \quad (7.10)
\]

The conservation of active sites gives

\[
[S] + \text{NO-[S]} + \text{O}_2-[S] = C \quad (7.11)
\]

Where c is constant. It was found that Cu-ZSM-5 is in nearly completely oxidized state [43]; it may be assumed that NO-[S] is very small compared with O\(_2\)-[S] and can be neglected. Thus, combining Equations (7.10) and (7.11) leads to

\[
[S] = \frac{C}{1 + K[O_2]} \quad (7.12)
\]

where, \(K = 1/K_{O_2}\).

Based on Equation (7.7), the reaction rate can be written as
\[ r = k[\text{NO} - [S]][S] \]  
(7.13)

Substituting equations (7.9) and (7.12) into equation (7.13), we obtain

\[ r = \frac{kC[\text{NO}]}{[1 + K[\text{O}_2]]^2} = \frac{k'[\text{NO}]}{[1 + K[\text{O}_2]]^2} \]  
(7.14)

where \( k' = kC \).

At high temperatures, adsorbed oxygen could dissociate into oxygen atoms. Thus, Equations (7.7) and (7.8) are modified as follows:

\[
\text{NO-[S] + [S] \rightarrow (1/2 \text{ N}_2)-[S] + \text{O-[S]}}
\]

\[
\quad \rightarrow 1/2 \text{ N}_2 + \text{O-[S]} + [\text{S}] \]  
(7.15)

\[ 2 \text{[O-[S]]} \leftrightarrow \text{O}_2 + 2 \text{[S]} \]  
(7.16a)

or

\[ \text{O-[S]} = [\text{O}_2]^{1/2} \text{[S]} / K_{\text{O}_2}^{1/2} \]  
(7.16b)

Combining Equation (7.9), (7.11) and (7.16b) and using the same analysis as above, we have

\[ [S] = \frac{C}{1 + K[\text{O}_2]^{1/2}} \]  
(7.17)

Thus, the reaction rate at high temperatures is expressed by

\[ r = \frac{C[\text{NO}]}{[1 + K[\text{O}_2]^{1/2}]^2} \]  
(7.18)

In this analysis, the nature of the active centers is not defined. From kinetics alone, one can never establish a mechanism for a reaction. The mechanism of NO decomposition over Cu-ZSM-5 presented above is probably not unique, and subject to modification by in-situ spectroscopy.
The effect of Ce ions on the NO decomposition into N\textsubscript{2} and O\textsubscript{2} can be explained by a "spillover" effect, which has been reported for hydrogenation processes [137, 138]. It is proposed that oxygen first adsorbs on the active Cu, then leaves Cu to diffuse to Ce ions, since the reduction potential, $E^0 = 1.72$ eV, of Ce\textsuperscript{4+} + e\textsuperscript{-} = Ce\textsuperscript{3+} is higher than that, $E^0 = 0.153$ eV, of Cu\textsuperscript{2+} + e\textsuperscript{-} = Cu\textsuperscript{+} [125]. This, in turn, creates more vacant sites for NO decomposition. The results of O\textsubscript{2}-TPD measurements showed that the temperature of the major O\textsubscript{2} desorption peak (403°C) from the Ce(60)/Cu(138)-ZSM-5 is 17°C lower than that from the Cu(141)-ZSM-5. As discussed earlier, this can explain the observed kinetics showing lower oxygen inhibition for the former catalyst.

7.5 CONCLUSION

The NO decomposition rate over Cu-ZSM-5 is first order with respect to NO concentration, and negative first order at low temperature (≤ 400°C) and negative half order at high temperatures with respect to O\textsubscript{2} concentration. The change in reaction order with respect to O\textsubscript{2} can be explained by molecular oxygen adsorption at low temperatures and dissociated oxygen adsorption at high temperatures.

The reaction order in NO concentration over Mg modified Cu-ZSM-5 is temperature dependent, and increases as temperature increases. The reaction order in O\textsubscript{2} concentration is the same as that over Cu-ZSM-5, except for a negative 1/2 order at 400°C. The presence of Mg cations may bring copper ions closer to one T-Al which enhances activity for NO decomposition.

The presence of cerium ions in Cu-ZSM-5 moderates the reaction inhibition by oxygen. It was found that Ce promotes the oxygen uptake capacity of Cu-ZSM-5, and shifts desorption of oxygen to lower temperature. It is proposed that the effect of Ce ions on NO decomposition over Cu-ZSM-5 is due to oxygen "spillover", which facilitates oxygen desorption and free active sites for NO adsorption.

Nitric oxide decomposition proceeds involving two sites may be invoked to fit the kinetics. However, the mechanism of NO decomposition over Cu-ZSM-5 presented here is subject to refinement as further information becomes available regarding the nature of active sites.
Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

In attempting to meet the objectives of this thesis as set out in Chapter 1, work has been performed and a new body of data was obtained and analyzed to improve our knowledge of the nitric oxide decomposition over copper ion-exchanged and metal ion-modified copper ion-exchanged ZSM-5 catalysts. The following conclusion are drawn from this thesis work:

(1) Based on the results of Cu$^{2+}$-sitting and Cu$^{2+}$ coordination in ZSM-5 reported in literature [59, 60, 69, 90] and performance of Cu-ZSM-5 for NO conversion to N$_2$ and O$_2$, we proposed that Cu ions at sites associated with two framework aluminum atoms and preferentially occupied by cations are inactive, while Cu ions at sites close to one framework aluminum are active for NO decomposition. It was found that the conversion of NO to N$_2$ and O$_2$ increases linearly with increasing square planar four-coordinated Cu$^{2+}$, and that the turnover frequency of the NO decomposition over the Cu-ZSM-4 catalysts is independent on the total copper exchange level.

(2) Preparation of Cu-ZSM-5 at high pH ($\geq$ 6.5) of cupric acetate solution leads to not only ion-exchanged copper but also copper deposition on the zeolite surface and voids forming inactive copper CuO, which is identified by using STEM/EDX and XRD, while at pH $\leq$ 5.0 to low copper exchange level and ZSM-5 protonation. The multi-step ion-exchange process from dilute cupric acetate at pH = 5.7 is presently the only one that can safeguard the active "excessively exchanged" Cu-ZSM-5.

(3) Alkaline earth and transition metal ion-exchanged ZSM-5 zeolites further exchanged with copper ions show promotion effects over catalytic activity of Cu-ZSM-5 materials for NO decomposition in the present and absence of oxygen at high temperature ($\geq$ 450°C). The performance of rare earth ion-modified Cu-ZSM-5 is different, the cocation effect being promotion of the Cu-ZSM-5 activity at low temperatures ($\leq$ 400°C).
Furthermore, coexistence of Mg and Ce cations enhances Cu-ZSM-5 activity for the reaction over whole temperature range of 350-600°C.

By exchanging the inert cations first, we attempt to let the cations occupy the inactive sites in ZSM-5 zeolite. The copper ions are subsequently exchanged so that they occupy the active sites. For metal ion-modified Cu-ZSM-5 and Cu-ZSM-5 with same copper exchange level, therefore, the former has a higher fraction of copper at the active sites than the latter. Therefore, the relative high population of active Cu ions in the metal ion-modified Cu-ZSM-5 results in high conversion of NO to N₂ and O₂.

Stabilization of inert cation, $M^{n+}$, at inactive sites is crucial for the positive cation effect to be displayed, because $M^{n+}$ can easily be replaced by ion Cu$^{2+}$ in the subsequent exchange. It was found that 500°C air calcination of M-ZSM-5 is effective in keeping the $M^{n+}$ exchange level high even after subsequent copper ion exchanges. The stabilization is due to strong bonding of cations to the zeolite framework.

(4) Wet conditions drastically decrease the NO decomposition activity of Cu-ZSM-5 catalysts. The activity is partially recovered upon removal of water vapor. The mechanism of copper deactivation in wet NO decomposition is twofold: equilibrium hydration (reversible); migration/aggregation and CuO particle formation/sintering (irreversible). The second path is thermally activated, hence, high temperature of reaction will exacerbate it. We have proposed that dealumination occurs as a result of partial protonation of sites vacated by the mobile copper complexes; thus, dealumination appears to be a secondary issue in the deactivation process.

The partial recovery of dry-gas activity upon removal of water vapor indicates that not all copper sites are equally unstable in wet gas stream; there is a fraction of active copper sites apparently in strong coordination with the framework (non-mobile). Cerium ion addition to Cu-ZSM-5 promotes the catalytic activity of the latter for the NO decomposition in wet gas streams at temperatures in the range of 400-600°C. Cerium cations stabilize copper ions in wet-gases by decreasing copper aggregation and suppressing CuO formation/sintering. An interaction between cerium and copper has been identified, which attributes to active copper stabilization.
(5) The NO decomposition rate over Cu-ZSM-5 is first order in NO, and negative first order at low temperatures (≤ 400°C) and negative half order at high temperatures in O₂. The change in reaction order with respect to O₂ may be due to molecular oxygen adsorption at low temperatures and dissociated oxygen adsorption at high temperatures.

The reaction order in NO over Mg modified Cu-ZSM-5 is temperature dependent, and increases as temperature increases. The reaction order with respect to O₂ concentration is the same as that over Cu-ZSM-5, except for a negative 1/2 order at 400°C. The presence of Mg cations may force copper ions to occupy the sites close to one T-Al, which enhances the activity for NO decomposition.

The presence of cerium ions in Cu-ZSM-5 moderates the reaction inhibition by oxygen. It was found that Ce promotes oxygen uptake capacity of Cu-ZSM-5, and shifts desorption of oxygen to lower temperature. It is proposed that the effect of Ce ions on NO decomposition over Cu-ZSM-5 is due to oxygen "spillover," which facilitates oxygen desorption and frees vacant sites to NO adsorption.

8.2 RECOMMENDATIONS

This thesis work has produced some key new findings in regard to the effects of cocations on the activity and stability of Cu-ZSM-5 catalyst for lean NO decomposition. The following recommendations are made for future work aimed at elucidating further the mechanistic aspects of cation interaction in the zeolite.

(1) The effect of metal cocations on Cu ion-siting and Cu²⁺ coordination needs to be studied using luminescence and EPR. Both divalent and trivalent metal ion-modified Cu-ZSM-5 catalysts with various ion exchange levels should be investigated, since Cu ions interact with these cations differently.

(2) The importance of Ce oxidation state on the catalytic activity of Cu-ZSM-5 needs to be further explored. Additionally, low-exchanged Ce/Cu-ZSM-5 should be studied systematically to identify whether an electronic interaction dominates.
(3) The changes in T-Al in fresh and steamed Ce-ZSM-5, Cu-ZSM-5 and Ce/Cu-ZSM-5 materials should be examined by using Al$^{27}$-NMR to identify whether Ce ions stabilize T-Al or not. In this thesis, the analyses of the fresh and steamed Ce-ZSM-5, Cu-ZSM-5 and Ce/Cu-ZSM-5 by XRD, STEM/EDX and XPS have shown that Ce ions impact the ZSM-5 crystallinity, CuO formation, cation distribution and migration, but little work was done on the effect of Ce ions on T-Al.

(4) The interaction of oxygen with Cu ions in metal ion-modified Cu-ZSM-5 using TGA and O$_2$-TPD can reveal differences between different Cu ion coordination. Based on the work presented in Chapter 7, it is concluded that oxygen uptake capacity per Cu ion is affected not only by Cu ion-exchange level, but also by the Cu position in ZSM-5. Additional work with various catalyst compositions along this line is recommended.

(5) The adsorption/desorption of water on/from Cu-ZSM-5 and Ce/Cu-ZSM-5 should be investigated in detail at various temperatures and water contents to improve our understanding of Cu-ZSM-5 deactivation by hydrothermal aging.
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17. Iwamoto, M., Catalysis, 33 (1990) 430.


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