State of the Art of de-NOx Technology Using Zeolite Catalysts in Automobile Engines

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Abstract: This review focuses on recent aspects of the use of precious metals or metal ion-exchanged zeolites as de-NOx catalysts. We focus especially on the NO conversion efficiency of precious metal ion-exchanged zeolites and the reactions of NOx with hydrocarbon reactants over metal ion-exchanged zeolite catalysts as a function of reaction temperature. We discuss the possibility of realizing automotive catalysts from such metal ion-exchanged catalysts. Precious metals or metal ion-exchanged zeolite catalysts performed very well in the reduction of NOx when water vapor was present. The effectivity of reduction reactants for the NO conversion on zeolite catalysts decrease in the order aromatics > olefins > paraffins. The present NO conversion values suggest the possibility for development of de-NOx catalysts for future lean-burning engines using ZSM-5 catalysts.

Keywords: catalyst, diesel engine, emission, after-treatment, NOx, zeolite, ZSM-5

Introduction

Diesel engines are useful for heavy-duty power applications (trucks, middle-and heavy-duty cogenerators, marine, vessels) because of their fuel efficiency, reliability, durability, and comparatively low fuel price. However, further development of diesel engines must focus on their adverse effects on the environment and human health, which are caused by nitrogen oxidation materials (NOx) and particulate matter (PM).

Advanced technologies, such as homogenous charge compression ignition (HCCI) engines, can result in very low emissions of both NOx and PM, as well as high thermal efficiency at part-load. However, there are some difficulties in applying HCCI combustion to diesel engines. Therefore, the NOx and PM that are exhausted from current diesel engines are important byproducts that must be purified by an after-treatment technology. The Cu-ZSM-5 catalyst developed by Iwamoto [1] that is used as an exhaust after-treatment technology has demonstrated that noble metals or metal ion-exchanged catalyst technologies are beneficial for NOx reduction in industry-leading vehicles [2-22].

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This review focuses on recent aspects of the use of precious metals or metal ion-exchanged zeolites as de-NOx catalysts, but it is not intended to be a comprehensive review. We focus especially on the NO conversion efficiency of precious metal ion-exchanged zeolites, the reactant of NOx with hydrocarbon reactants over metal ion-exchanged zeolite catalysts as a function of reaction temperature. In addition, we discuss the possibility of realizing automotive catalysts form such metal ion-exchanged catalysts.

Effect of Zeolites, Catalysts and Additives

The catalytic activities of (a) Na-ZSM-5, (b) H-ZSM-5, (c) Ag-H-ZSM-5, (d) Ag-Na-ZSM-5 catalysts have been measured as a function of catalyst temperature [2]. These experiments were conducted using 2000 ppm NO, 2000 ppm CH4, and 10% O2, with SV = 12000 1/h. In Figure 1, the conversion of NO to N2 was much higher over the H-ZSM-5 catalyst than it was over the Na-ZSM-5 catalyst. A higher NO conversion was obtained over Ag-Na-ZSM-5 catalyst than over Ag-H-ZSM-5 catalyst. The highest NO conversion was observed at 450°C over the Ag-Na-ZSM-5 catalyst. Complete CH4 conversion occurred at 450°C over the Ag-Na-ZSM-5 catalyst.
Figure 1. NO and CH₄ conversion over ZSM-5 catalysts [2].

Figure 2. Effect of C₃H₈/NO ratio on NO reduction over Cu-Mordenite; SV = 2800 l/h, O₂ = 2%; (open squares) C₃H₈/NO = 0.5, NO = 1000 ppm; (triangles) C₃H₈/NO = 1, NO = 1000 ppm; (open circles) C₃H₈/NO = 2, NO = 750 ppm [3].

Figure 2 shows the NO conversion over Cu-MOR (mordenite) in 2% O₂ at low and high SV (16,270 ~ 102,000/l/h) [3]. The maximum NO conversion was 90% at 350°C at C₃H₈/NO = 2. This result is a higher NO conversion than that reported by Konno and coworkers [20] for their diesel engine (25% NO conversion). At the same SV, the NO conversion ratio at C₃H₈/NO = 2 is higher than that at C₃H₈/NO = 1.

Figure 3 shows the catalytic activities of Ga- and In-ZSM-5 catalysts [4]. The contents of every additives with respect to In-ZSM-5 were controlled at 1 wt%. The reaction was performed in a fixed-bed flow reactor by passing 1000 ppm NO, 1000 ~ 2000 ppm CH₄, 10% O₂, and 0 ~ 10% H₂O. Without H₂O, the NO conversions of Ga-ZSM-5 and In-ZSM-5 catalysts were 80% at 400°C and 65% at 500°C, respectively.

The NO conversions over Ce-H-FER-22, Ce-H-Beta, and Ce-ZSM-5 with various cerium contents are presented in Figure 4 [5]. The Ce-H-FER catalyst appears to be more active than the other catalysts and shows maximum conversions in the temperature range 300 ~ 400°C. The NO conversions at 350°C follow the order Ce(75)-H-FER (87%) > Ce(51)-H-FER (80%) > Ce(27)-H-FER (65%). The conversion of propene appears to be positively correlated to the cerium content.

In Ni-exchanged MOR, the Ni weight contents were 1.8 ~ 2.0 wt%. The NO and hydrocarbon conversions over Ni-Na-MOR2.1 during reduction of NO with propene and propane are compared in Figure 5 [6]. A lower temperature was observed for the maximum NO conversion with propene, relative to propane: 400 and 450°C, respectively. The conversions of the reducing agent showed significant differences.

Figure 6 shows the conversion of NO to N₂ as a function of temperature for the Co-ZSM-5, Zn-ZSM-5, and Co-Zn-ZSM-5 catalysts [7]; the gas composition was NO = 2500 ppm, CH₄ = 2000 ppm, and O₂ = 2.0%, with SV = 3600 l/h. The Zn-Co-ZSM-5 (1:1:50) catalyst exhibits a higher activity for NO conversion than do the other catalysts. The result indicates that Zn can effectively promote the selectivity and activity of Co-ZSM-5. The incorporation of Pt into Co-ZSM-5 increases both the selectivity to N₂ and the resistance to water vapor inhibition [8]. The NO conversion over Co-ZSM-5 was 17% when using CH₄ as the reactant at 500°C, while over Pt-Co-ZSM-5 it was 22.7%. The NO conversion was
evaluated over various metal ion-exchanged (Co, Mn, Ni, Cu) ZSM-5 catalysts using CH₄ as the reactant [9]. Table 2 shows the NO conversions over various cation-ZSM-5 catalysts at the maximum conversion temperature of 450°C. Although the metal loadings are different, the maximum NO conversion decreases in the following order: Co-ZSM-5 = Co-H-ZSM-5 > Mn-ZSM-5 > Ni-ZSM-5 > Cu-ZSM-5 > H-ZSM-5.

Table 1. NO and CH₄ Conversions over Metal-ZSM-5 Catalysts [9]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal loading (wt%)</th>
<th>Conversion (%) at 450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NO</td>
</tr>
<tr>
<td>Co-ZSM-5</td>
<td>4.0</td>
<td>34</td>
</tr>
<tr>
<td>Mn-ZSM-5</td>
<td>3.1</td>
<td>30</td>
</tr>
<tr>
<td>Ni-ZSM-5</td>
<td>4.3</td>
<td>26</td>
</tr>
<tr>
<td>Cu-ZSM-5</td>
<td>3.7</td>
<td>8</td>
</tr>
<tr>
<td>Co-H-ZSM-5</td>
<td>2.3</td>
<td>34</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>-</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 4 compares the NO reduction activities of H-ZSM-5, Cu-ZSM-5, and Ga-ZSM-5 using C₃H₆ as the reactant [10]. The maximum conversion of NO was expected to be 50%. The Ga-ZSM-5 catalyst showed high activity over a wide range of reaction temperatures (400–600°C); the NO conversion reached 50% at temperatures above 400°C.

NO reduction with ethanol was performed in a continuous micro-reactor. Figure 5 shows the NO conversions over H-ZSM-5, Pd-ZSM-5, Mo-ZSM-5, and Pd-Mo-ZSM-5 catalysts as a function of reaction temperature [11]. The Pd and Mo loadings were 0.67 and 2.5 wt%, respectively. The NO conversion for Pd-Mo-ZSM-5 was superior to the sum of the conversions of Pd-ZSM-5 and Mo-ZSM-5, proving that synergy exists between Pd and Mo.

The other Pd-ZSM-5 catalyst was prepared using the following steps: impregnation, drying, glow discharge plasma treatment, and thermal calcinations. The incipient
Figure 6. NO conversions over Co-ZSM-5 (1:50), Zn-ZSM-5 (1:50), and Co-Zn-ZSM-5 (1:1:50) [7].

Figure 7. NO conversions over Ga-ZSM-5 (open circle), H-ZSM-5 (open triangle), and Cu-ZSM-5 (open square); reaction conditions: NO = 1000 ppm, C\(_6\)H\(_4\) = 250 ppm, O\(_2\) = 10% [10].

Figure 8. NO conversions using ethanol over H-ZSM-5, Pd-ZSM-5, Mo-ZSM-5, and Pd-Mo-ZSM-5 [11].

while with plasma treatment of the Pd-ZSM-5 catalyst, the CH\(_4\) conversion reached 90% at 400°C [12].

Fe-ZSM-5 was synthesized in a nitrogen atmosphere [13]. Figure 9 shows the catalytic test results of NO with \(i-C_4H_{10}\). The reaction gas components were NO = 2000 ppm, O\(_2\) = 3%, and \(i-C_4H_{10}\) = 2000 ppm, with SV = 42000 h\(^{-1}\). The Fe/Al ratios of samples 1 and 2 were 0.29 and 0.11, respectively; For samples 4 and 5 they were 0.52 and 0.50, respectively. Sample 1 shows a maximum NO conversion of 55% at 350°C.

Figure 10 shows the effect that additives (1 wt%) to In-H-ZSM-5 catalysts have on the NO conversions with CH\(_4\) at 500°C [4]. Among these metals, Pt, Rh, and Ir showed enhanced effects on the catalytic activity of In-ZSM-5, because these metal sites can work as active sites for NO oxidation even in the presence of water vapor. Co and Mn showed negative effects for their NO conversions.

Keiski and coworkers [14] reported the NO conversions of various metal-ZSM-5 catalysts. They found that the maximum NO conversion over Pt-ZSM-5 was 40% at 210°C, but the conversion window was very narrow. Cu-ZSM-5 had the highest NO conversion (max: 80%) at 350°C.

**Effect of Reactant Gases**

Figure 11 displays NO conversions over Cu-ZSM-5 catalyst using C\(_6\)H\(_6\) and C\(_3\)H\(_8\) at an A/F ratio of 18.0 [15]. The Cu/Al atom ratio was 0.295–2.15; the best NO conversion was observed at the 150–200% exchange level. Catalysts were evaluated using a simulated lean-burn engine exhaust emission. The model A/F 18 gas
mixture contained 300 ppm CO, 1000 ppm H₂, 1600 ppm C₃H₆, 1200 ppm NO, 3.2% O₂, 10% CO₂, and 10% H₂O. NO conversion was much higher when propene was the hydrocarbon compound used.

Mosqueda-Jimenez and coworkers [16] studied the effect of the reactant (C₃H₆ or C₃H₈) over Ni-ZSM-5. Figure 12 shows the reduction of NO to N₂ using propane the over Ni-ZSM-5 catalyst (0.3 mmol/g content). The maximum NO conversions followed the order Ni-

Figure 9. NO and i-C₃H₁₀ conversions over Fe-ZSM-5: samples 1 (circle), 2 (square), 3 (triangle), 4 (reverse triangle), 5 (diamond) [13].

Figure 10. Effects that additives (1 wt%) to In-H-ZSM-5 have on NO conversion using CH₄ at 500°C; NO = 1000 ppm, CH₄ = 1000 ppm, O₂ = 10% [4].

Figure 11. NO conversions using C₃H₆ and C₃H₈ over the Cu-ZSM-5 catalyst; A/F = 18 [15]. ZSM-5 (80% NO conversion at 430°C) > Ni-MOR (70% NO conversion at 470°C) > Ni-MCM-22 (50% NO conversion at 530°C). The reduction of NO is limited by the reducing agent. For propene, at a low Ni concentration, the maximum NO conversion increased from almost 0 to 50%, but increased only to 80% for a catalyst containing 3.7 wt% Ni. In contrast, for the NO reduction with propane, the catalyst having a low Ni loading was less active (18% NO conversion), but the activity increased up to 80% NO conversion for the catalyst having the highest Ni loading (Figure 13). The NO conversion
Figure 12. NO conversion to N₂ (solid line) and C₃H₆ conversion (dashed line) over (diamond) Ni-MOR, (square) Ni-ZSM-5, and (triangle) Ni-MCM-22 [16].

Figure 13. NO conversion with respect to the concentration of Ni for NO reduction using C₃H₆ (square) and C₃H₈ (diamond) over Ni-MOR [6].

decreased in the order aromatics > olefins > paraffins (Figure 14).

Suitability as Automotive Catalysts

The exhaust emissions range of diesel engines are as follows: NOx = 350~1000 ppm, HC = 50~330 ppmC, CO = 300~1200 ppm, O₂ = 10~15%, H₂O = 1.4~7%, CO₂ = 7%, SOx = 10~100 ppm, PM = ca. 65 mg/m³; the maximum exhaust temperature is ca. 650°C. The SV (space velocity) range is 5000~100000 l/h. The excess air ratio of the lean limit is ca. 2.0 (A/F = 28) [18]. The use of ZSM-5 catalysts for diesel de-NOx should be especially affected by the water vapor, O₂, and SOx concentrations, the SV, and the exhaust gas temperature.

Figure 15 shows the NO conversions over 8Ce₁₃In-H-ZSM-5 catalysts [19]. The nomenclature of 8Ce₁₃In-H-ZSM-5 means that the metal weight contents were 8 wt% Ce and 13 wt% In. This metal composition gave the best NO conversion in that study. Increased N₂ formation was also obtained with a wet feed. Similar effects were observed upon variation of the propane concentration. Konno and coworkers [20] reported the effect of water vapor on Cu-ZSM-5; when the diesel exhaust was introduced directly to the Cu-ZSM-5 catalyst (H₂O = 7%), the NO conversion decreased by ca. 7%. Kikuchi and coworkers [4] studied the effect of H₂O on Ga- and In-ZSM-5 catalysts, and found that NO oxidation was strongly inhibited by H₂O (see Figure 3). The adverse effect of H₂O appears to be a major issue for the application of metal-ZSM-5 catalysts to diesel engines.

In the absence of O₂, almost no NOx conversion was achieved (Figure 16) [17]. This finding reveals that the
Figure 16. NOx conversion as a function of temperature at various O₂ concentrations [17].

![NOx Conversion Graph](image1)

Space velocity (1/h)  
NO conversion (%)  
0 30000 60000 90000 120000

Figure 18. Effect of SV on NO reduction over Cu-ZSM-5 at 300°C; NO = 1050 ppm, C₃H₈ = 1320 ppm, O₂ = 2% [3].

The oxidation of HC has an important influence on NOx reduction. By increasing the O₂ concentration from 0 to 12%, the NOx conversion increases.

Figure 17 shows the conversions of NO and C₃H₈ over various Co-ZSM-5 catalysts [21]. The maximum NO conversion decreased in the following order: Co-ZO2 (Co = 1.15%) > Co-ZO4 (Co = 0.16%) > ZO5 (Co = 4.21%, no ion-exchange). The maximum NO conversions in the presence of 15% O₂ were higher than that in the presence of 5% O₂.

Additives to the Co-ZSM-5 catalyst were studied to improve the NO conversion [7,8]. The mixed Co-Zn-ZSM-5 catalyst was prepared by impregnating H-ZSM-5 with an aqueous solution of cobalt nitrate [Co(NO₃)₂] and zinc nitrate [Zn(NO₃)₂] mixed according to the desired Co and Zn loadings.

The effect that the space velocity (Figure 17) has on NO conversion was determined for Cu-ZSM-5 over the range 4000~102000 1/h at a temperature of 300°C [3]. The NO conversion decreased upon increasing the SV. Cu-ZSM-5 maintains a high conversion (87%) at a reasonably high SV (102000 1/h). If the catalyst volume of the diesel engine is the same as the engine displacement, the SV of the catalyst will be ca. 120000 1/h. Konno and coworkers [20] reported the same effect of SV in a diesel engine experiment. Engler [17] also reported that NOx conversion of the fresh catalyst of vehicle A was 22%, while that of a 100-h engine-aged catalyst was 18%.

Figure 19 shows the conversion for vehicle A measured in the ECE (European) test cycle using the Pt-ZSM-5 catalyst [17]. The NOx conversion of Vehicle A was measured to be over 30%. This NOx conversion of the Pt-ZSM-5 catalyst is not high enough for application as...
automobile after-treatment equipment. However, this result demonstrates the possibility of developing de-NOx catalysts for future lean-burn engines using ZSM-5 catalysts.

**Summary**

Previous studies on the performance of de-NOx catalysts prepared from various precious metals or metal ion-exchanged zeolites have been reviewed. From this review, the following summary is given:

1. Because zeolite catalysts are prepared using different manufacturing methods and have been studied using various performance evaluation methods, it is hard to decide the uniform order relating to the performance of NOx reduction. However, precious metal (Pt, Pd, Rh, Ru, Ir) or metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Zr, Mo, Ba, La, Ce) ion-exchanged zeolite catalysts performed very well in the reduction of NOx when water vapor was present.

2. The results could be summarized with respect to the reaction characteristic of the reduction reactants (CH₄, C₂H₆, C₃H₈, C₅H₁₀) and the temperature window. The reduction reactants of the NO conversion on zeolite catalysts decrease in the order aromatics > olefins > paraffins.

3. NO oxidation is strongly inhibited by H₂O molecules in the space velocity. The NO conversion increases as the presence of O₂ in the exhaust emission increases.

4. The NOx conversions of the ZSM-5 catalysts were not high enough for applications as automobile after-treatment equipment. However, these values demonstrate the possibility for the development of de-NOx catalysts for the future lean-burn engines using ZSM-5 catalysts.

The results of the review also suggest that the following areas need additional study:

1. The kinds of reduction agents and zeolites for the NOx reduction of lean-burn engine should be optimized with respect to the exhaust gas components; the loading and concentration of the (precious) metals also should be optimized for NOx reduction.

2. The intermediate components of the catalytic reactions over de-NOx catalysts should be defined.

3. There is a need to understand the synergy effects between (precious) metals if composite metal ion-exchange catalysts are to improve their de-NOx performance.

4. There is a need to clarify the de-NOx reaction mechanisms for the precious metals or metal-exchanged zeolite catalysts.

5. It must be possible to design the precious metal or metal ion-exchanged zeolite catalysts more simply by using a numerical calculation that considers the de-NOx reaction mechanism of the zeolite catalysts.

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