Outstanding HC-SCR of Lean NOx Over Pt/Mesoporous-Silica Catalysts

Tamikuni Komatsu*, Keizou Tomokuni, Mitsuo Konishi and Takashi Shirai

The Noguchi Institute, Asahi-Kasei Corporation, 1-8-1 Kaga, Itabashi-Ku, Tokyo 173-0003, Japan

Abstract: Perfect de-NOx over a wide temperature range above 170 °C was achieved using a new Pt-catalyst supported on mesoporous silica (Pt/MPS) and a stoichiometric amounts of long-chain hydrocarbons as reducing agents for NOx-purification. Kinetic investigation of the HC-SCR of lean NOx over Pt/MPS, Pt/alumina and Pt/zirconia showed that such a remarkable activity of Pt/MPS is due to a large frequency factor but not to activation energy. Acid-treatment of the supports increased the activities of the catalysts and generated new IR-peaks in the range 1000-1200 cm⁻¹, which suggests the support-effects on the catalyst-activities to be related to the special surface functional groups of the supports. The present HC-SCR must be very useful to remove diesel-NOx by means of pulse-injection of diesel fuel into the exhaust.

Keywords: HC-SCR, lean NOx, de-NOx, diesel exhaust, mesoporous, mesoporous silica, diesel fuel.

INTRODUCTION

The regulation of greenhouse warming due to CO₂ discharged by automobiles has become quite severe all over the world. To decrease CO₂ emission, changes such as gasoline-autos into diesel-autos with higher fuel efficiency have been expected. However, how to purify diesel-NOx is still unresolved. The O₂-content of the gasoline-exhaust is controlled below 0.5% (rich burn) but the O₂-content of the diesel-exhaust is usually 24% O₂ (lean burn). This makes purification of the diesel-NOx very difficult, because of the low activities of the conventional catalysts below 200 °C. Diesel-fuel consists of C₆-C₁₆ HCs including aromatic compounds. However, the fuel was not directly used as the reducing agents because of low reducing performance, while a usage of diesel-fuel for reduction of NOx is essentially necessary for such de-NOx catalysts as remove NOx by means of pulse-injection of diesel-fuel into the exhaust.

The recent de-NOx methods such as the urea-SCR and NOx-storage-reduction (LNT: lean-NOx-trap) were reviewed [1]: (1) the urea-SCR has unresolved problems that the method requires storing a solution of urea and that a usage of diesel-fuel for reduction of NOx is essentially necessary for such de-NOx catalysts as remove NOx by means of pulse-injection of diesel-fuel into the exhaust.

However, the fuel was not directly used as the reducing agents because of low reducing performance, while a usage of diesel-fuel for reduction of NOx is essentially necessary for such de-NOx catalysts as remove NOx by means of pulse-injection of diesel-fuel into the exhaust.

Perfect de-NOx over a wide temperature range above 170 °C was achieved using a new Pt-catalyst supported on mesoporous silica (Pt/MPS) and a stoichiometric amounts of long-chain hydrocarbons as reducing agents for NOx-purification. Kinetic investigation of the HC-SCR of lean NOx over Pt/MPS, Pt/alumina and Pt/zirconia showed that such a remarkable activity of Pt/MPS is due to a large frequency factor but not to activation energy. Acid-treatment of the supports increased the activities of the catalysts and generated new IR-peaks in the range 1000-1200 cm⁻¹, which suggests the support-effects on the catalyst-activities to be related to the special surface functional groups of the supports. The present HC-SCR must be very useful to remove diesel-NOx by means of pulse-injection of diesel fuel into the exhaust.

Keywords: HC-SCR, lean NOx, de-NOx, diesel exhaust, mesoporous, mesoporous silica, diesel fuel.

INTRODUCTION

The regulation of greenhouse warming due to CO₂ discharged by automobiles has become quite severe all over the world. To decrease CO₂ emission, changes such as gasoline-autos into diesel-autos with higher fuel efficiency have been expected. However, how to purify diesel-NOx is still unresolved. The O₂-content of the gasoline-exhaust is controlled below 0.5% (rich burn) but the O₂-content of the diesel-exhaust is usually 24% O₂ (lean burn). This makes purification of the diesel-NOx very difficult, because of the low activities of the conventional catalysts below 200 °C. Diesel-fuel consists of C₆-C₁₆ HCs including aromatic compounds. However, the fuel was not directly used as the reducing agents because of low reducing performance, while a usage of diesel-fuel for reduction of NOx is essentially necessary for such de-NOx catalysts as remove NOx by means of pulse-injection of diesel-fuel into the exhaust.

The recent de-NOx methods such as the urea-SCR and NOx-storage-reduction (LNT: lean-NOx-trap) were reviewed [1]: (1) the urea-SCR has unresolved problems that the method requires storing a solution of urea and that a usage of diesel-fuel for reduction of NOx is essentially necessary for such de-NOx catalysts as remove NOx by means of pulse-injection of diesel-fuel into the exhaust.

Previously, we presented outstanding low-temperature active Pt/MPS to purify diesel-NOx exhaust [13]. The present study will report the kinetics of HC-SCR of NOx over Pt/MPS and an application to perfect purification of diesel-NOx in a wide temperature range over 170 °C with diesel-fuel.

MATERIALS AND METHODOLOGY

Sample Preparation

Mesoporous silica (MPS) was prepared by a sol-gel method using tetraethyl orthosilicate (TEOS) as a silica-source and dodecylamine as a template. Pt/MPS was prepared by impregnating MPS with an aqueous solution of H₂PtCl₆ as the Pt-source. The experimental details were described in the previous report [13]. For comparison, Pt/silica, Pt/silica-alumina, Pt/alumina, Pt/zirconia and a NOx-absorption-reduction catalyst (LNT) were prepared in a similar manner as above using commercially available support-materials. The precious metal loading was 5 mass % Pt and 0.3 mass % Rh for Pt/MPS, and 2 mass % Pt and 0.12 mass % Rh for Pt/silica, Pt/silica-alumina, Pt/alumina and Pt/zirconia. The LNT was 2%Pt-0.12%Rh/alumina (80%)-ceria (10%)-zirconia (10%) including BaCO₃ (3%), La₂O₃ (1%) and KOH (1%). In addition, Pt-catalysts using acid-treated supports of MPS, γ-alumina and zirconia were also prepared. The acid-treatment of the supports was carried out as follows: boiling in a 0.1 mass % solution of equimolar HNO₃ and H₂SO₄ for 3 h, followed by washing with distilled water. A honeycomb catalyst was prepared using the Pt/MPS powders as follows: a slurry of the Pt/MPS powders mixed with alumina-sol was prepared, coated on a full-size cordierite-honeycomb (φ143.8 mm×118 mm, 4.5 mil/400 cpsi), followed by calcination at 600 °C for 1h in air. A coating mass of Pt/MPS was 80 g per 1 liter of the
honeycomb. Assessment of the heat-resistance of Pt/MPS was carried out using the sample after the heat-treatment under each condition of 600 °C-50 h, 700 °C-50 h and 800 °C-50 h in air containing 10% steam.

**Characterization of the Samples**

The specific surface areas and pore sizes of the supports were measured using nitrogen adsorption at 77 K. The pore-structure of the supports was characterized by small-angle X-ray diffraction (SAX) and selected-area electron diffraction (SAED). Exposed active sites of Pt/MPS for estimation of turn over frequency (ToF) were measured by CO-chemisorption. Crystallite sizes of the catalysts were directly measured by high-resolution TEM (HRTEM) observation. The average size of the crystallites was estimated from the half-width of the (111) reflection by powder XRD measurements. Homogenieties of the supported catalysts were confirmed by HRTEM observations.

**Measurements of HC-SCR of NOx**

The experiment of HC-SCR of NOx was carried out using a three-necked quartz tubular downflow reactor (20 mm i.d and 400 mm length). A mini honeycomb-catalyst (2 ml in volume) or powder catalyst was charged into the reactor. NO, NO2 and N2O contained in the effluent gas. The specific surface areas and poresizes of MPS were 1250 m2 g-1 and 2.5 nm, respectively. An estimated thickness of mesopore-walls for MPS was ca. 2 nm which is about twice larger than that for MCM-41. Relative IR-intensity around at 3400 cm-1 showed that MPS is covered with hydrolytic OH-groups in comparison to MCM-41. The exposed active site of Pt/MPS which was estimated from the experimental CO-chemisorption was ca. 5%. The HRTEM image of Pt/MPS indicated that many Pt-particles of 1-3 nm in diameter are homogeneously dispersing on the support surface. The average diameter of the Pt-particles was 2 nm which is very close to the pore diameter of MPS. This indicates the Pt-particles of the catalyst to be supported in the inside of mesopores. On the other hand, those for Pt/alumina, Pt/silica-alumina, Pt/silica, LNT and Pt/zirconia were 2, 4, 5, 6 and 21 nm, respectively. Since the average diameter of Pt/silica-alumina is smaller than the pore diameter, the Pt-particles of the catalyst may be in the inside of mesopores. However for Pt/silica and Pt/zirconia, the Pt-particles are supported in the outside of mesopores. Also, the Pt-particles of Pt/alumina and LNT may be supported in the outside of mesopores, because adsorption ability of γ-alumina is much stronger than those of the other supports.

**RESULTS AND DISCUSSION**

**Characterization of the Pt-Catalysts**

Table 1 shows the characterization of the used Pt-catalysts and supports. The SAX profile of MPS showed a strong singlet-peak at 2θ=2.72 °(d=3.25 nm). The SAED image showed a hallow pattern. The results mean that MPS is completely disordered in the pore-arrangement differently from well-ordered MCM-41. The specific surface area and pore diameter of MPS were 1250 m2 g-1 and 2.5 nm, respectively. An estimated thickness of mesopore-walls for MPS was ca. 2 nm which is about twice larger than that for MCM-41. Relative IR-intensity around at 3400 cm-1 showed that MPS is covered with hydrolytic OH-groups in comparison to MCM-41. The exposed active site of Pt/MPS which was estimated from the experimental CO-chemisorption was ca. 5%. The HRTEM image of Pt/MPS indicated that many Pt-particles of 1-3 nm in diameter are homogeneously dispersing on the support surface. The average diameter of the Pt-particles was 2 nm which is very close to the pore diameter of MPS. This indicates the Pt-particles of the catalyst to be supported in the inside of mesopores. On the other hand, those for Pt/alumina, Pt/silica-alumina, Pt/silica, LNT and Pt/zirconia were 2, 4, 5, 6 and 21 nm, respectively. Since the average diameter of Pt/silica-alumina is smaller than the pore diameter, the Pt-particles of the catalyst may be in the inside of mesopores. However for Pt/silica and Pt/zirconia, the Pt-particles are supported in the outside of mesopores. Also, the Pt-particles of Pt/alumina and LNT may be supported in the outside of mesopores, because adsorption ability of γ-alumina is much stronger than those of the other supports.

**Table 1. Characterization of the Used Pt-Catalysts (Powders) and Supports**

<table>
<thead>
<tr>
<th>Pt-Catalysts</th>
<th>Pt-Particles Average Diameter/nm</th>
<th>Support</th>
<th>Specific Surface Area/m2 g-1</th>
<th>Pore Diameter/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/MPS</td>
<td>2</td>
<td>1250</td>
<td>2.5</td>
<td>non-porous</td>
</tr>
<tr>
<td>Pt/Silica</td>
<td>5</td>
<td>428</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/Silica-Alumina</td>
<td>4</td>
<td>412</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Pt/Alumina</td>
<td>2</td>
<td>250</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Pt/Zirconia</td>
<td>21</td>
<td>128</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>LNT Type Catalyst</td>
<td>6</td>
<td>210</td>
<td>6-20</td>
<td></td>
</tr>
</tbody>
</table>

**Heat-Resistance of MPS and Pt/MPS**

The specific surface areas and poresizes of MPS before and after the heat-treatment at 700 °C-50 h in air containing 10% steam were confirmed by HRTEM observations.

---

1 Sea-sand (quartz-sand) is generally used as a dispersant because of inactivity in catalysis.
2 The diminished-pressure chemiluminescence NOx detector, Japan Thermo Corp. Model 42—HL & 46 C—H, which performs simultaneous detection of NO, NO2 and N2O contained in the effluent gas.
3 From the experimental NOx-conversion and NO : NO2 ratio, contribution of NO or NO2 to the NOx-conversion can be estimated, since NOx-conversion is defined as the conversion of NOx (total of NO and NO2) into nonhazardous N-containing compounds such as N2 and N2O.
10% steam were almost unchanged. The hydrothermal durability of MPS was much higher than that of MCM-41. According to our experiment, MCM-41 lost half of the specific surface area and mesopores after ageing at 600 °C-24 h in air containing 10% steam. Probably the high heat-resistance of MPS is due to the thick mesopore-walls and minor amounts of hydrolytic OH-groups, because under hydrothermal conditions H2O molecules attacks -Si-O-skeletons to destroy mesoporous structures. Fig. (1) shows the relationship between NOx-conversion and ageing conditions for Pt/MPS. Until 600 °C-50 h, a maximum NOx conversion (70%) and corresponding temperature (the lower limit in temperature: 170 °C) were similar to those of fresh Pt/MPS. After 700 °C-50 h, the NOx conversion was not changed but the lower limit in temperature rose to 210 °C (40 °C rise). After 800 °C-50 h, the NOx conversion dropped to 45% (25% drop) and the lower limit in temperature rose to 230 °C (60 °C rise). In order to elucidate whether such a higher temperature shift is due to permanent deterioration or not, the heat-treated Pt/MPS was reduced with hydrogen at 300 °C-1 h, followed by the same HC-SCR of NOx. The result showed remarkable restoration close to the temperature for fresh Pt/MPS. On the other hand, the powder XRD measurements of the heat-treated Pt/MPS showed that an averaged size of Pt-particles was scarcely changed until 600 °C-50 h, increased to 4-5 nm (3 times larger than that of fresh Pt/MPS) after 700 °C-50 h, remarkably increased to 10 nm after 800 °C-50 h. The result teaches that the higher temperature shift for the heat-treated Pt/MPS is due to both oxidation and enlargement of the supported Pt-particles. The former factor may be gradually restored by reduction with HC's contained in rich burn exhausts and the latter greatly influences the activity of the catalyst over 800 °C. A similar relationship between the Pt-size and ageing conditions was observed for conventional Pt/alumina. The high heat resistance of Pt/MPS is found due to mechanically strong encapsulation in the mesopores which is different from chemically strong adsorptive ability of γ-alumina supports, because MPS is much inferior to γ-alumina with respect to adsorptive ability. The activity of Pt/MPS remaining after ageing at 700 °C-50 h corresponds to an estimation of a million km-traveling on the heavy duty diesel cars, on the basis of the Arrhenius plots (the logarithm of ageing hour vs 1/T relationships in the range 400 - 700 °C).

Kinetics of HC-SCR of Lean-NOx over the Pt-Catalysts with Propylene

Fig. (2) shows the NOx-conversion over Pt/MPS, Pt/alumina and Pt/zirconia using model-gas (1). Pt/MPS provides a peak NOx-conversion of 70% at 170 °C, while Pt/alumina and Pt/zirconia respectively show 40% at 240 °C and 33% at 260 °C. The ToF of Pt/MPS in terms of NOx conversion, which was calculated on the basis of the experimental exposed active sites, was 0.7 at 70% NOx-conversion. The gas after the treatment was composed of N2, N2O, CO2 and H2O, except for unchanged NO. The selectivity for N2 was 10-30% below 200 °C and over 95% above 250 °C, which was almost the same as the selectivity of the gasoline-auto emission purification over the conventional three-way-catalysts. The curve of NOx-conversion before the peak for each catalyst is almost the same as that of NO-conversion, that is, the NOx-conversion is almost the same as the conversion of NO2. After the peak, the NO-conversion continues to increase up to 250 °C followed by a slight decrease above 250 °C. The NOx-conversion tends to decrease after the peak, which means that an increase in NO2 does not contribute to the NOx-conversion. This is due to wasteful consumption of propylene above 180 °C, because propylene is very combustible with oxygen. According to our experiment, the conversion of propylene over Pt/MPS with 10% O2 begins at 100 °C and increases rapidly at 110 °C, reaching 100% at 150 °C. Apparent activation energies and frequency factors estimated from the conversion curve were 104 kJ mol-1 and 2.4×107 s⁻¹, respectively. The smaller NOx-conversions of Pt/alumina and Pt/zirconia are not only due to the low activities of the catalysts but also to unselective conversion of propylene above 200 °C.

Fig. (3) shows the Arrhenius plots (the logarithm of conversion rate vs 1/T relationships) of the observed NOx-conversions shown in Fig. (2). These results show that the E-values for NOx-conversions of Pt/MPS, Pt/alumina and Pt/zirconia are scarcely different. The obtained values are slightly different from those reported previously [14-17] (E_NO=91.2

Fig. (2). NOx-conversion over the Pt-catalysts (powders) with model-gas (1): (●), (▲) and (■) depict the NOx-conversion over Pt/MPS, Pt/alumina and Pt/zirconia, respectively; (○), (△) and (□) depict the NO-conversion over the Pt/MPS, Pt/alumina and Pt/zirconia, respectively.

Fig. (3) shows the Arrhenius plots (the logarithm of conversion rate vs 1/T relationships) of the observed NOx-conversions shown in Fig. (2). The obtained apparent activation energies E and frequency factors A are summarized in Table 2. These results show that the E-values for NOx-conversions of Pt/MPS, Pt/alumina and Pt/zirconia are scarcely different. The obtained values are slightly different from those reported previously [14-17] (E_NO=91.2
kJ mol\(^{-1}\) and \(E_{C_3H_6}=108.5\) kJ mol\(^{-1}\) reported by Ioan et al [14]), because of the different reaction conditions. The A-value of Pt/MPS is larger by at least two orders of magnitude than those of Pt/alumina and Pt/zirconia. Therefore, the difference in activity among the catalysts must be affected by frequency factors rather than activation energies. On the other hand, the Pt-particle size of Pt/MPS is similar to that of Pt/alumina as shown in Table 1. The results suggest that the remarkable low-temperature activity of Pt/MPS is due to the MPS-support.

The Effects of Supports on NO\(_x\)-Conversion

To elucidate a mechanism of the HC-SCR of NOx over Pt/MPS, the NO\(_x\)-purification process was formally divided into two stages: (1) [1\(^{st}\)-stage] oxidation of NO into NO\(_2\), and (2) [2\(^{nd}\)-stage] successive reduction of NO\(_x\) with propylene. From Fig. (5a), it is found that Pt/MPS slowly oxidizes NO to NO\(_2\) with O\(_2\), because the conversion of NO to NO\(_2\) is much lower than that predicted from the equilibrium. The apparent activation energies and frequency factors estimated from Fig. (5a) were 108 kJ mol\(^{-1}\) and 5\(\times\)10\(^4\) s\(^{-1}\), respectively. Fig. (5b) shows that all of the NO\(_2\) produced in the first stage is reduced into N\(_2\)O and N\(_2\) below 170 °C, because the NO\(_2\) ratio is zero % from the beginning of reaction (150 °C) to a maximum NO\(_x\) conversion (170 °C). Fig. (5c) shows the result of HC-SCR of NO\(_2\) over Pt/MPS with propylene. The estimated apparent activation energy was 64 kJ mol\(^{-1}\). That is, [2\(^{nd}\)-stage] reduction of NO\(_2\) with propylene is very faster than [1\(^{st}\)-stage] oxidation of NO into NO\(_2\). Therefore, oxidation of NO into NO\(_2\) is the rate-determining step. The results also notify that NO\(_2\)-molecules can be purified into N\(_2\)O and N\(_2\) over Pt-catalysts with HCs but NO-molecules are difficult. The appearance of the Brønsted-acid sites on the acid-treated supports may influence the rate-determining step. If NO\(_2\) is more effective for NO\(_x\)-conversion than NO, the HC-SCR of NO\(_2\) may be more advantageous than that of NO, as reported in ref. [5]. As shown in Fig. (5c), in spite of the HC-SCR of NO\(_2\) (\(E_{NOx} = 64\) kJ mol\(^{-1}\)) much faster than that of NO, the maximum NO\(_x\)-conversion (75%) and its temperature (170 °C) were not much different from those for the HC-SCR of NO. Reduction of NO\(_2\) into NO quickly occurred around 150-160 °C (the conversion of NO\(_2\) into NO was 77% at 150 °C). That is, the HC-SCR of NO\(_2\) over Pt/MPS is also unselective. The following is a reaction diagram of the HC-SCR of lean-NO\(_x\) over Pt/MPS which was confirmed from the results.

![Figure 4](image_url)  
Fig. (4). NO\(_x\)-conversion over the Pt-catalysts (powders) supported on acid-treated supports with model-gas: (●) Pt/MPS; (▲) Pt/alumina; (■) Pt/zirconia.
Oxidation of \([\text{NO–O}_2]\) \(\rightarrow\) \(\text{NO}_2\) [equilibrium] \(\Delta H = 108 \text{ kJ mol}^{-1}, A = 5 \times 10^4 \text{ s}^{-1}\) \(\text{(1)}\)

Reduction of \([\text{NO}_2–\text{C}_3\text{H}_6–\text{O}_2]\) \(\rightarrow\) \(\text{N}_2\text{O}, \text{N}_2, \text{H}_2\text{O}, \text{CO}_2\) [fast below 170 °C] \(\text{(2)}\)

Reduction of \([\text{NO}_2–\text{C}_3\text{H}_6–\text{O}_2]\) \(\rightarrow\) \(\text{NO}\) [fast below 170 °C] \(\text{(3)}\)

Partial reduction of \([\text{NO–C}_3\text{H}_6–\text{O}_2]\) \(\rightarrow\) \(\text{N}_2\text{O}, \text{N}_2\) [difficult] \(\text{(4)}\)

Oxidation of \([\text{C}_3\text{H}_6–\text{O}_2]\) \(\rightarrow\) \(\text{H}_2\text{O}, \text{CO}_2\) [fast above 200 °C] \(\Delta H = 104 \text{ kJ mol}^{-1}, A = 2.4 \times 10^7 \text{ s}^{-1}\) \(\text{(5)}\)

Total HC-SCR of \([\text{NO–C}_3\text{H}_6–\text{O}_2]\) \(\rightarrow\) \(\text{N}_2\text{O}, \text{N}_2, \text{H}_2\text{O}, \text{CO}_2\) [fast below 200 °C] \(\text{(6)}\)

\[ E_{\text{NOx}} = 102 \text{ kJ mol}^{-1}, A_{\text{NOx}} = 8.6 \times 10^6 \text{ s}^{-1} (\lesssim 170 ^\circ \text{C}), E_{\text{C}_3\text{H}_6} = 124 \text{ kJ mol}^{-1}, A_{\text{C}_3\text{H}_6} = 1.4 \times 10^9 \text{ s}^{-1} (\lesssim 170 ^\circ \text{C})\]

Total HC-SCR of \([\text{NO}_2–\text{C}_3\text{H}_6–\text{O}_2]\) \(\rightarrow\) \(\text{NO}, \text{N}_2\text{O}, \text{N}_2, \text{H}_2\text{O}, \text{CO}_2\) [fast below 200 °C] \(\text{(7)}\)

\[ E_{\text{NOx}} = 64 \text{ kJ mol}^{-1} (\lesssim 170 ^\circ \text{C})\]

Fig. (5a). [1st stage] oxidation of NO into \(\text{NO}_2\) over Pt/MPS (honeycomb) with \(\text{O}_2\): (●) and (▲) depict the NO ratio and \(\text{NO}_2\) ratio, respectively; (---) the equilibrium between \(\text{NO}_2\) and NO (ref. [5]). The result of the second stage is also shown: (○) NOx-conversion by injection of \(\text{C}_3\text{H}_6\) into the first stage outlet-gas.

Fig. (5b). [2nd stage] reduction of the 1st stage outlet-gas over Pt/MPS (honeycomb) with propylene: (●) and (▲) depict the NO ratio and \(\text{NO}_2\) ratio, respectively; (○) NOx-conversion.

HC-SCR of Lean-NOx over Pt/MPS with Long-Chain HCs

Fig. (6) shows the purification of NOx over Pt/MPS using model-gas (2). The results show that Pt/MPS is able to perfectly purify lean NOx with stoichiometric HCs (where, stoichiometric HCs mean the quantitative HCs required for the perfect consumption of HC with 10% \(\text{O}_2\)) above 170 °C. The apparent order of the reducing activities among the hydrocarbons (in regard to the temperature acting as a reducing agent of NOx) was propylene (100% in NOx-conversion at 170 °C) and n-octane (100% at 170 °C) > n-cetane (100% at 180 °C) > light oil (100% at 200 °C) and toluene (100% at 200 °C). The NOx-conversion curves and the hydrocarbon-consumption curves were synchronized with each other. The steep slope \([\Delta (\text{NOx-conversion}) / \Delta T] \) of each NOx-conversion curve is almost the same 10% K^1 for each HC. The results show that the HC-SCR of lean NOx with stoichiometric HCs proceeds rapidly with the catalytic consumption of HCs. Many HCs are combustible over Pt/MPS with excess amounts of oxygen at comparatively mild temperatures. The difference in reducing activity among HCs is not clearly associated with the chain-length of HCs. Most aliphatic and aromatic HCs can be used as the reducing agents for lean NOx over Pt/MPS.

Fig. (5c). HC-SCR of \(\text{NO}_2\) over Pt/MPS (honeycomb) with model-gas (2): (●) and (▲) depict the NO ratio and \(\text{NO}_2\) ratio, respectively; (○) NOx-conversion.

Fig. (6). HC-SCR of lean NOx over Pt/MPS (honeycomb) with model-gas (3) containing long chain HCs.
CONCLUSION

The HC-SCR of lean NOx at low temperatures below 200 °C was remarkably improved using the Pt-catalyst supported on mesoporous silica (Pt/MPS). Such remarkable low-temperature activity of Pt/MPS is primarily due to the acidity of MPS rather than the sizes of Pt-particles and mesopores. The kinetic investigation of HC-SCR of NOx over Pt/MPS elucidated that the NOx-conversion below 200 °C is determined by the oxidation of NO to NO2 which is the rate-determining step. It was also found that the acid-treatment of the supports increases the activities. The active protons on the supports which may be acting as the Brønsted-acid sites probably influence the rate-determining step. It was also found that the HC-SCR of lean NOx is perfectly achieved with stoichiometric C6-C16 HCs over a wide temperature range from 170 °C to 400 °C. The present HC-SCR must be very useful for de-NOx of diesel-exhaust by means of pulse-injection of diesel-fuel into the exhaust.

REFERENCES


© Komatsu et al.; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.