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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 CO_2 discharged by automobiles has become quite severe all over the world. To decrease CO_2 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 O_2-content of the gasoline-exhaust is controlled below 0.5% (rich burn) but the O_2-content of the diesel-exhaust is usually 24% O_2 (lean burn). This makes purification of the diesel-NOx very difficult, because of immediate deactivation of the conventional three-way catalysts by oxygen at 1%. Also, comparatively low temperatures of the diesel-exhaust which are usually 100-400 °C make purification very difficult because of the low activities of the conventional catalysts below 200 °C. Diesel-fuel consists of C_6-C_{16} 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 large portion of NOx may be discharged in the form of nitrates and nitrites at low temperatures; (2) the LNT has essential problems such as deactivation of NOx-storage agents by a small SOx-content and very low activities below 200 °C. The other method, the HC-SCR [2-6] has a problem that the purification is limited to narrow temperature ranges around 200 °C, although the catalysts are free from deactivation by SOx [7]. To improve the HC-SCR method, the presentation of Pt-catalysts supported on MCM-41 type mesoporous silica [8], the intermediate addition of reducing agents [9], a secondary fuel-injection method [10], a double-washed honeycomb coating with two kinds of Pt-catalysts [11], and a fast SCR process [12] were studied. However, the HC-SCR method has not been considered for mainstream lean burn NOx-purification, because of the low activities of the catalysts below 200 °C and a narrow temperature window.

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 H_2PtCl_4 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 $BaCO_3$ (3%), La_2O_3 (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 HNO_3 and H_2SO_4 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

*Address correspondence to this author at 2-24-4 Sakura, Tsukuba-shi, Ibaraki 305-0003, Japan; Tel: +81 29-857-7325; Fax: +81 29-857-7325; E-mail: BRA01367@nifty.com

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. Homogeneities 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, a small amount of glass wool was placed on the catalyst, and 10 ml of sea-sand[1] as a dispersant of reaction gases was placed on the glass wool to initiate the reaction over the catalyst in a homogeneous reaction gas flow. The mini honeycomb catalyst was cut from the full-size honeycomb catalyst. The powder catalyst (160 mg of 5% Pt-catalysts or 400 mg of 2% Pt-catalysts) was mixed in advance with commercially available sea-sand (20-30 mesh) at 2.6 g (2 ml) and charged into the reactor. The reactor containing the catalyst was placed in an electric furnace. As an exhaust gas for NOx-purification experiments, three model-gases, (1) a reaction mixture comprising 250 ppm NO, 400 ppm C_3H_6 and 10% O_2 balanced with He, (2) a reaction mixture comprising 250 ppm NO_2, 400 ppm C_3H_6 and 10% O_2 balanced with He, (3) a reaction mixture comprising 250 ppm NO, 2000-7000 ppm liquid of long chain HCs and 10% O_2 balanced with He, were used. Each model-gas was introduced into a gas-inlet of the reactor at a flow rate of 1000 ml min^{-1} (SV=30,000 h^{-1} or GHSV=7.5 m^3 h^{-1} per g of Pt) through a mass-flow controller. The liquid HCs were supplied upstream along the inner wall of the reactor by a syringe-type micro-feeder. The temperature of the reactor was increased at a rate of about 10 °C min^{-1} and was held at the prescribed temperature for 10 min. The NOx measurement of the effluent gas was carried out during a period held at the prescribed temperature using a chemiluminescence NOx-detector[2]. To confirm the mechanism of the HC-SCR, two reactors containing the honeycomb catalyst were connected in series. The first stage (oxidation of NO into NO_2 with O_2) was carried out by introducing a reaction mixture of 250 ppm NO and 10% O_2 balanced with He into the gas-inlet of the first-stage reactor at a flow rate of 1000 ml min^{-1} (SV=30,000 h^{-1}) and the second stage (reduction of NOx with propylene) was carried out by introducing 400 ppm C_3H_6 into the gas-inlet of the second-stage reactor at a flow rate of 1000 ml min^{-1}. The result was analyzed using the experimental NOx-conversion and NO:NO_2 ratio[3].

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 m^2 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 minor amount of 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

Pt-Catalysts	Pt-Particles Average Diameter/nm	Support	
		Specific Surface Area/m^2 g^{-1}	Pore Diameter/nm
Pt/MPS	2	1250	2.5
Pt/Silica	5	428	non-porous
Pt/Silica-Alumina	4	412	3.8
Pt/Alumina	2	250	6.2
Pt/Zirconia	21	128	7
LNT Type Catalyst	6	210	6-20

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

[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 i—HL & 46 C—H, which performs simultaneous detection of NO, NO_2 and N_2O contained in the effluent gas.

[3] From the experimental NOx-conversion and NO : NO_2 ratio, contribution of NO or NO_2 to the NOx-conversion can be estimated, since NOx-conversion is defined as the conversion of NOx (total of NO and NO_2) into nonhazardous N-containing compounds such as N_2 and N_2O.

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 H_2O 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 HCs 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).

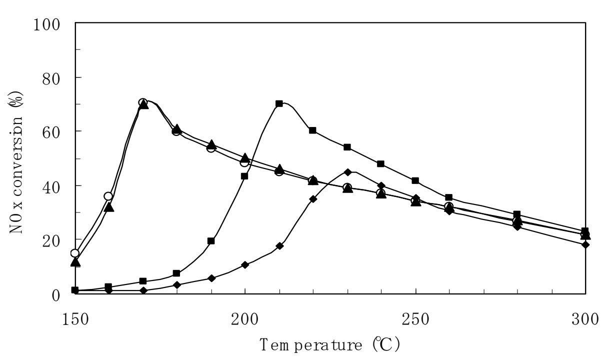

Fig. (1). The heat-resistance of Pt/MPS (powders): (○) fresh; (▲) after 600 °C-50 h in air containing 10% steam; (■) after 700 °C-50 h in air containing 10% steam; (◆) after 800 °C-50 h in air containing 10% steam.

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 N_2, N_2O, CO_2 and H_2O, except for unchanged NOx. The selectivity for N_2 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 NO_2. 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 NO_2 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% O_2 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 2.4×10^7 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.

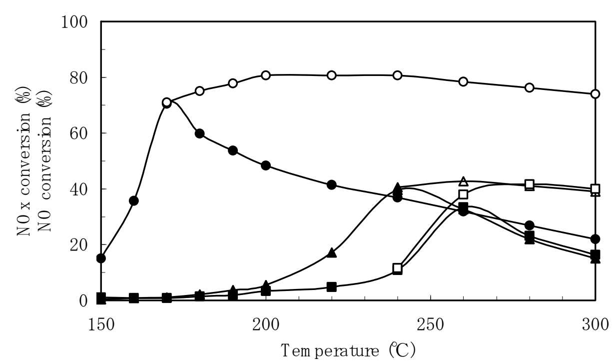

Fig. (2). NOx-conversion over the Pt-catalysts (powders) with model-gas (1): (●), (▲) and (■) depict the NOx-conversion over Pt/MPS, Pt/alumina and Pt/zirconia, respectively; (○), (△) and (□) depict the NO-conversion over the Pt/MPS, Pt/alumina and Pt/zirconia, respectively.

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_{C3H6}=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.

Table 2. Apparent Activation Energies and Frequency Factors of Pt-Catalysts (Powders) Estimated from Fig. (2)

Pt-Catalysts	NOx-Conversion		C_3H_6-Conversion	
	E/kJ mol^{-1}	A/s^{-1}	E/kJ mol^{-1}	A/s^{-1}
Pt/MPS	102	8.6×10^6	124	1.4×10^9
Pt/Alumina	102	2.6×10^4	—	—
Pt/Zirconia	101	5.9×10^3	—	—

Estimations of E and A of the C_3H_6 conversion for Pt/alumina and Pt/zirconia were useless because of wasteful combustion of propylene above 200 °C.

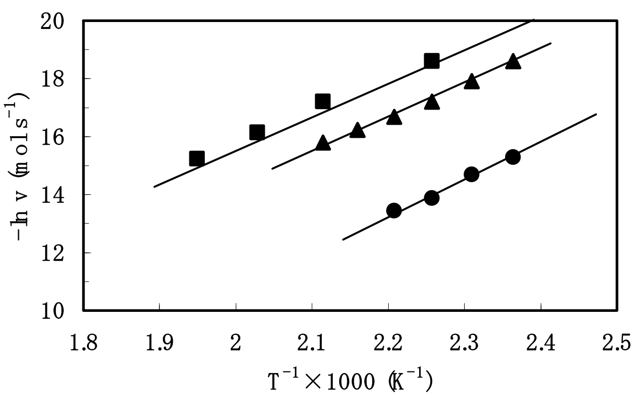

Fig. (3). Arrhenius plots (the logarithm of conversion rate *vs* 1/T relationships) of the observed NOx-conversions over Pt/MPS, Pt/alumina and Pt/zirconia shown in Fig. (**2**): (●) Pt/MPS; (▲) Pt/alumina; (■) Pt/zirconia.

The Effects of Supports on NOx-Conversion

To clarify the above effects of supports to the NOx-conversion, acid-treatment of the supports was carried out. Fig. (**4**) shows the NOx-conversions over the Pt-catalysts using acid-treated γ-alumina and zirconia. As seen from the comparison with Fig. (**2**), the acid-treatment of the supports gives a remarkable increase in NOx-conversion and low-temperature shifts of the peak-temperatures. The acid-treatment of MPS also increases the NOx-conversion by several %. The IR spectra of γ-alumina and zirconia after the acid-treatment were investigated. Resultantly, new peaks appeared at 1152 and 1065 cm^{-1} for γ-alumina and 1211, 1141 and 1047 cm^{-1} for zirconia. Since the absorption bands in this finger-print region are generally assigned to the stretching bands of SiO_2-skelton, the observed peaks are probably due to protons bonded to the metal oxide skeletons because stretching bands of Si-O in Si-OH groups are generally known to be observed in the range 800-1000 cm^{-1}. It is also well-known that a portion of active OH-groups on solid-acids is acting as the Brφnsted-acid sites. Then, the high activity of Pt/MPS and increased activities of Pt/alumina and Pt/zirconia using the acid-treated supports are probably due to active protons incorporated with the supports.

Mechanism of the HC-SCR of Lean-NOx

To elucidate a mechanism of the HC-SCR of NOx over Pt/MPS, the NOx-purification process was formally divided into two stages: (1) [1st-stage] oxidation of NO into NO_2 with O_2, (2) [2nd-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 5×10^4 s^{-1}, respectively. Fig. (**5b**) shows that all of the NO_2 produced in the first stage is reduced into N_2O and N_2 below 170 °C, because the NO_2 ratio is zero % from the beginning of reaction (150 °C) to a maximum NOx 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, [2nd-stage] reduction of NO_2 with propylene is very faster than [1st-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_2O and N_2 over Pt-catalysts with HCs but NO-molecules are difficult. The appearance of the Brφnsted-acid sites on the acid-treated supports may influence the rate-determining step. If NO_2 is more effective for NOx-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 NOx-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-NOx over Pt/MPS which was confirmed from the results.

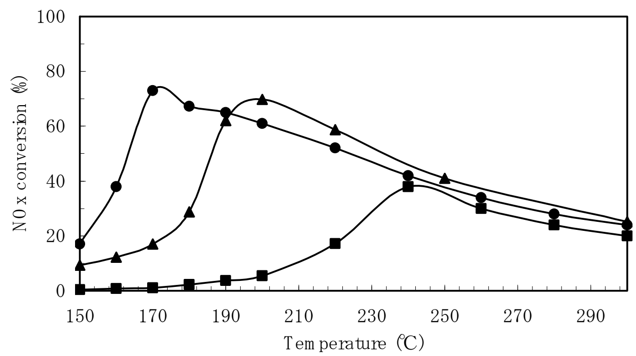

Fig. (4). NOx-conversion over the Pt-catalysts (powders) supported on acid-treated supports with model-gas (1): (●), (▲) and (■) depict the NOx-conversion over Pt/[acid-treated MPS], Pt/[acid-treated alumina] and Pt/[acid-treated zirconia], respectively.

Oxidation of [NO—O_2] $\longleftrightarrow$ NO_2 [equilibrium] E=108 kJ mol^{-1}, A=5×10^4 s^{-1} (1)

Reduction of [NO_2—C_3H_6—O_2] $\longrightarrow$ N_2O, N_2, H_2O, CO_2 [fast below 170 °C] (2)

Reduction of [NO_2—C_3H_6—O_2] $\longrightarrow$ NO [fast below 170 °C] (3)

Partial reduction of [NO—C_3H_6—O_2] $\xrightarrow{\times}$ N_2O, N_2 [difficult] (4)

Oxidation of [C_3H_6—O_2] $\longrightarrow$ H_2O, CO_2 [fast above 200 °C] E=104 kJ mol^{-1}, A=2.4×10^7 s^{-1} (5)

Total HC-SCR of [NO—C_3H_6—O_2] $\longrightarrow$ N_2O, N_2, H_2O, CO_2 [fast below 200 °C] (6)

E_{NOx}=102 kJ mol^{-1}, A_{NOx}=8.6×10^6 s^{-1} (≤170 °C), E_{C3H6}=124 kJ mol^{-1}, A_{C3H6}=1.4×10^9 s^{-1} (≤170 °C)

Total HC-SCR of [NO_2—C_3H_6—O_2] $\longrightarrow$ NO, N_2O, N_2, H_2O, CO_2 [fast below 200 °C] (7)

E_{NOx}=64 kJ mol^{-1} (≤170°C)

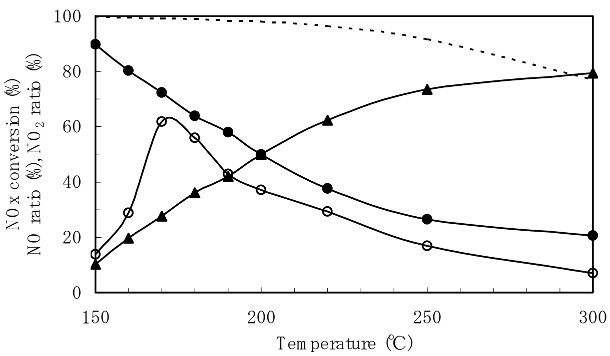

Fig. (5a). [1st stage] oxidation of NO into NO_2 over Pt/MPS (honeycomb) with O_2: (●) and (▲) depict the NO ratio and NO_2 ratio, respectively; (---) the equilibrium between NO_2 and NO (ref. [5]). The result of the second stage is also shown: (○) NOx-conversion by injection of C_3H_6 into the first stage outlet-gas.

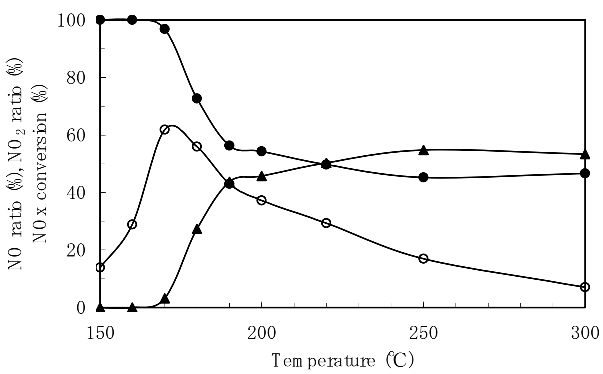

Fig. (5b). [2nd stage] reduction of the 1st stage outlet-gas over Pt/MPS (honeycomb) with propylene: (●) and (▲) depict the NO ratio and NO_2 ratio, respectively; (○) NOx-conversion.

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% 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 [Δ (NOx-conversion) /ΔT] 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.

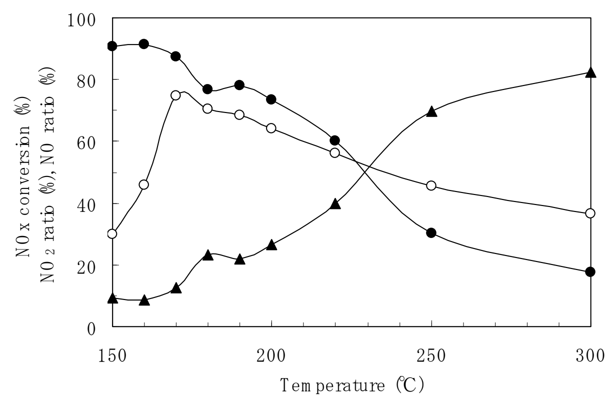

Fig. (5c). HC-SCR of NO_2 over Pt/MPS (honeycomb) with model-gas (2): (●) and (▲) depict the NO-ratio and NO_2- ratio, respectively; (○) NOx-conversion.

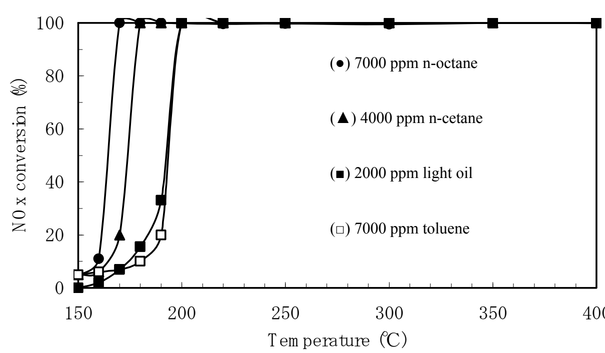

Fig. (6). HC-SCR of lean NOx over Pt/MPS (honeycomb) with model-gas (3) containing long chain HCs.

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 NO_2 which is the rate-determining step. The acid-treatment of the supports generates new functional groups assignable to active protons incorporated with the supports and makes the Pt-catalysts increase the activities. The active protons on the supports which may be acting as the Brφnsted-acid sites probably influence the rate-determining step. It was also found that the HC-SCR of lean NOx is perfectly achieved with stoichiometric C_6-C_{16} 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

[1] Narula, C. K.; Daw, C. S.; Hoard, J. W.; Hammer, T. Materials issues related to cataltsts for treatment of diesel exhaust. *Int. J. Appl. Ceram. Technol.*, **2005**, *2*, 452-466.

[2] Iwamoto, M.; Yahiro, H. Novel catalytic decomposition and reduction of NO. *Catal. Today*, **1994**, *22*, 5-18.

[3] Bell, V. A.; Feeley, J. S.; Deeba, M.; Farrauto, R. J. In situ high temperature FTIR studies of NOx reduction with propylene over Cu/ZSM-5 catalyst. *Catal. Lett.*, **1994**, *29*, 15-26.

[4] Burch, R.; Millington, P. J. Selective reduction of nitrogen oxides by hydrocarbons under lean-burn conditions using supported platinum group metal catalysts. *Catal. Today*, **1995**, *26*, 185-206.

[5] Iwamoto, M.; Fernandez, A. M.; Zengyo, T. Oxidation of NO to NO_2 on Pt-MFI zeolite and subsequent reduction of NOx by C_2H_4 on In-MFI zeolite: a novel de-NOx strategy in excess oxygene. *Chem. Commun.*, **1997**, 37-38.

[6] Shichi, A.; Satsuma, A.; Iwase, M.; Shimizu, K.; Komai, S., Hattori, T. Catalyst effectiveness factor of cobalt-exchanged mordenites for the selective catalytic reduction of NO with hydrocarbons. *Appl. Catal. B-Environ.*, **1998**, *17*, 107-113.

[7] Burch, R.; Watling, T. C. The effect of sulphur on the reduction of NO by C_3H_6 and C3H8 over Pt/Al_2O_3 under lean-burn conditions. *Appl. Catal. B-Environ.*, **1998**, *17*, 131-139.

[8] Schieβer, W.; Vinek, H.; Jentys, A. Catalytic reduction of NO_2 over transition-metal containing MCM-41. *Catal. Lett.*, **1998**, *56*, 189-194.

[9] Iwamoto, M.; Zengyo, T.; Hernandez, A. M.; Araki, H. Intermediate addition of reductant between an oxidation and a reduction catalyst for highly selective reduction of NO in excess oxygen. *Appl. Catal. B-Environ.*, **1998**, *17*, 259-266.

[10] Nakatsuji, T.; Yasukawa, R.; Tabata, K.; Ueda, K.; Niwa, M. Catalytic reduction system of NOx in exhaust gases from diesel engines with secondary fuel injection. *Appl. Catal. B-Environ.*, **1998**, *17*, 333-345.

[11] Centi, G.; Perathoner, S. Novel catalyst design for multiphase reactions. *Catal. Today*, **2003**, *79-80*, 3-13.

[12] Irfan, M. F.; Goo, J. H.; Kim, S. D. Co_3O_4 based catalysts for NO oxidation and NOx reduction in fast SCR process. *Appl. Catal. B-Environ.*, **2008**, *78*, 267-274.

[13] Komatsu, T.; Tomokuni, K; Yamada, I. Outstanding low temperature HC-SCR of NOx over platinum-group catalysts supported on mesoporous materials expecting diesel-auto emission regulation. *Catal. Today*, **2006**, *116*, 244-249.

[14] Ioan, B.; Miyazaki, A.; Aika, K. On the kinetic and structure sensitivity of lean reduction of NO with C_3H_6 over nanodispersed Pt catalysts. *Appl. Catal. B-Environ.*, **2005**, *59*, 71-80.

[15] Bueno-Lopez, A.; Illan-Gomez, M. J.; Salinas-Martinez de Lecea, C. Effect of NOx and C_3H_6 partial pressures on the activity of Pt-beta-coated cordierite monoliths for deNOx C_3H_6-SCR. *Appl. Catal. A-General*, **2006**, *302*, 244-249.

[16] Botas, J. A.; Miguel, A.; Gutierrez-Ortiz, M. P.; Gonzalez-Marcos, J. A.; Gonzalez-Marcos, J. R.; Gonzalez-Velasco, Kinetic considerations of three-way catalysis in automobile exhaust converters. *Appl. Catal. B-Environ.*, **2001**, *32*, 243-256.

[17] Marnellos, G. E.; Efthimiadis, E. A.; Vasalos, I. A. Mechanistic and kinetic analysis of the NOx selective catalytic reduction by hydrocarbons in excess O_2 over In/Al_2O_3 in the presence of SO_2 and H_2O. *Appl. Catal. B-Environ.*, **2004**, *48*, 1-15.

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