

Low-Temperature Active Pt-catalysts Supported on Mesoporous Silica and Metal-Silicates for Cleaning Diesel-NOx Exhausts

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Abstract

New Pt-catalysts supported on mesoporous silica (MPS) and metal-silicates, which have high de-NOx capabilities over 70 % in NOx-conversion at temperatures around 170 °C under lean conditions, were developed. A new prototype honeycomb supporting Pt-catalyst allows high de-NOx of diesel-exhausts possible over the wide temperature range of 170-400 °C. The low-temperature activities of the catalysts are well correlated with the Brønsted acidity of the support materials. In view of the reaction mechanism of the de-NOx processes, the Brønsted acid-sites of the supports probably stimulate the oxidation of NO into NO₂, which is the rate-determining step of de-NOx processes, leading to the low-temperature activities.

Keywords: mesoporous silica, low-temperature activity, deNOx, diesel-NOx, kinetics, de-NOx mechanism, support effect

1. Introduction

The regulation of greenhouse warming due to CO₂ discharged by automobiles has become quite severe all over the world. The forthcoming Euro-6, which is the most strict exhaust emission standard legislation, will be implemented in Europe around 2014 on all the vehicles including light-, medium- and heavy-duty diesel vehicles. Because diesel-engines are extremely more fuel-efficient than gasoline engines, changes such as gasoline-autos into diesel-autos have been expected. However, the de-NOx of diesel-exhausts using the currently known HC-SCR catalysts (Iwamoto et al., 1997; Nakatsuji et al., 1998; Shich et al., 1998; Burch et al., 1998; Schieser et al., 1998; Centi et al., 2003; Narula et al., 2005; Irfan et al., 2008; Hickey et al., 2010) is very difficult due to lower exhaust-temperatures (100-200 °C) and low content of reductive HCs in the complete combustion of diesel-exhausts (24% O₂ concentration). For future catalysts to remove diesel-NOx, high de-NOx potential capabilities at temperatures of 100-200 °C using minimum diesel-fuels as reducing agents in an atmosphere of excess O₂ over 10% might be required.

We have previously reported the low-temperature active Pt/MPS (platinum-catalyst supported on mesoporous silica) (Komatsu et al., 2006, 2010). This paper describes a prototype Pt/MPS coated honeycomb for practical applications to remove the diesel-NOx. Also, several candidates of low-temperature active catalysts more active than Pt/MPS will be proposed through the elucidation of support effects on the low-temperature activities from the viewpoints of kinetics and reaction mechanisms of the de-NOx processes.

2. Experimental

2.1 Sample Preparation

Mesoporous silica (MPS) was prepared by a sol-gel method using tetraethyl orthosilicate (TEOS) as the silica-source and dodecylamine as the template. Mesoporous metal-silicates, such as W-, B-, Nb-, Ti-, Al- and Gd-silicate, in which each metal-element is incorporated in the silica-frameworks of the MPS were prepared in a similar manner as above except for the addition of a mixture of TEOS and each metal-element precursor as a source of the silicate. The silica/metal atom ratio was adjusted to 20/1. The experimental details were described in the previous report (Komatsu et al., 2006). The Pt-catalyst supported on MPS (Pt/MPS) and on the silicates (Pt/metal-silicate) were prepared by impregnating each support-material with an aqueous solution of H₂PtCl₄ and

RhCl₃·3H₂O, evaporated to dryness at 110 °C, followed by reduction with hydrogen at 300 °C for 1 h. The precious metal loading of the Pt-catalysts was adjusted at a 5 mass % Pt-0.3 mass % Rh.

A mixture of Pt/MPS and the solid oxide was prepared by mixing Pt/MPS (80 mg) and commercially available solid oxides (220 mg). MoO₃-Bi₂O₃ (1:1), WO₃-Co₃O₄ (1:1), WO₃-CeO₂ (1:1), BaO-CeO₂ (1:1) and ZrO₂-CeO₂ (1:1) mixture were used. For other additives, the zeolite materials were used. A mixture of Pt/MPS and zeolite was prepared by mixing Pt/MPS (80 mg) and the zeolite (220 mg). Commercially available mordenite, clinoptilolite, erionite, ferrierite, β-zeolite and A-zeolite were ion-exchanged with an aqueous solution of MgSO₄ before adding it to the Pt/MPS.

A prototype Pt/MPS coated honeycomb was prepared using Pt/MPS as follows: a slurry of Pt/MPS mixed with alumina-sol was prepared, coated on a full-size cordierite-honeycomb (φ143.8 mm×118 mm, 4.5 mil/400 cpsi), placed into an oven, followed by calcination at 600 °C for 1 h. The coating mass of Pt/MPS was 76 g per 1 liter of the honeycomb-support. This Pt/MPS coated full-size honeycomb (abbr. fresh honeycomb) was used for assessment of the de-NO_x capabilities. The honeycomb for the aging tests was prepared by aging the fresh honeycomb at 750 °C for 24 h in the atmosphere (abbr. aging honeycomb). The Pt/MPS coated mini-honeycombs (φ38 mm×50 mm, 56.7 ml in volume) as test pieces were prepared by cutting them out of the above full-size-honeycombs.

2.2 Characterization of the Samples

The specific surface areas and pore-size distribution of the supports were measured using nitrogen adsorption at 77 K and determined by the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method. The pore-structure of the supports was characterized by small-angle X-ray diffraction (SAX) and selected-area electron diffraction (SAED). The crystallite sizes of the catalyst were estimated from the half-width of the (111) reflection by powder XRD measurements and confirmed by high-resolution TEM (HRTEM) observations. The homogeneities of the supports and catalysts were confirmed by field-emission SEM (FESEM), scanning TEM (STEM) and HRTEM observations. The metal content was determined by an inductively coupled plasma mass (ICP-MS) analysis.

2.3 Aging Testes of the Support Materials and Powder Catalysts

Hydrothermal treatment of the support materials was carried out by treating each material charged in a column with flowing air containing 10 % steam at the flow rate of 100 ml min⁻¹ at 750 °C for 5 h. Heattreatment of Pt/MPS (powder) was carried out by heating the catalyst under each condition of 600 °C-50 h, 700 °C-50 h and 800 °C-50 h in the air containing 10 % steam.

2.4 Measurement of NO_x-conversions

The measurements of the NO_x-conversions for Pt/MPS and Pt/metal-silicate were carried out using a three-necked quartz tubular down-flow reactor (20 mm i.d. and 400 mm length). Before charging the catalyst into the reactor, each catalyst (80 mg) was mixed with 1.3 g (1 ml) of sea-sand (20-30 mesh). The catalyst was charged into the reactor, a small amount of glass wool was placed on the catalyst, followed by placing 10 ml of sea-sand on the glass wool. The mixture of Pt/MPS and the additives was charged into the reactor in a similar manner as described above. The sea-sand is used as a dispersant for achieving a homogeneous gas flow in the reactor. The reactor was then placed in an electric furnace. The temperature of the reactor was increased at the rate of ca. 10 K min⁻¹ and held at the prescribed temperature for 10 min. The lean-burn de-NO_x measurement was carried out using a lean-syngas comprised of 250 ppm NO, 400 ppm C₃H₆ and 10 % O₂ balanced with He. The rich-burn de-NO_x measurement was carried out using a rich-syngas comprised of 250 ppm NO, 4000 ppm C₃H₆ and 1 % O₂ balanced with He. A flow rate of the syngas was 30,000 ml h⁻¹ (SV=30,000 h⁻¹, GHSV=7.5 m³ h⁻¹ per g of Pt).

The measurement of de-NO_x capabilities of the Pt/MPS coated honeycomb was carried out using a large tubular down-flow reactor (40 mm i.d. and 400 mm length). The Pt/MPS coated mini-honeycomb (56.7 ml in volume) as the test piece was pre-treated at 600 °C for 1 h in an oven to stabilize the activities and charged them into the reactor. The reactor was placed in an electric furnace. The temperature of the reactor was increased at the rate of about 10 K min⁻¹ and was held at the prescribed temperature for 1 min. The lean-rich de-NO_x measurement was carried out by alternately flowing a lean-syngas comprised of 250 ppm NO, 400 ppm C₃H₆ and 10 % O₂ balanced with He and a rich-syngas comprised of 250 ppm NO, 4000 ppm C₃H₆ and 1 % O₂ balanced with He into the reactor at the flow rate of 1.7 m³ h⁻¹ every 1 min (SV=30,000 h⁻¹, GHSV=7.9 m³ h⁻¹ per g of Pt). The NO_x-measurement of the effluent gas was carried out during a period held at the prescribed temperature using a diminished-pressure chemiluminescence NO_x-detector which performs simultaneous detection of the NO, NO₂

and N_2O contained in the effluent gas through an online-system. The result was analyzed based on the experimental NO_x -conversions and $\text{NO}:\text{NO}_2$ ratios. The effluent gas after the C_3H_6 combustion was analyzed using a gas chromatograph-mass spectrometer (GC-MS).

3. Results and Discussion

3.1 Characterization and Hydrothermal Resistance of the Support Materials

The SAX profile of the MPS showed a strong singlet-peak at $2\theta=2.72^\circ$ ($d=3.25$ nm). The SAED images of all the prepared support materials showed hollow patterns. This result indicated that all the support materials are completely disordered in the pore-arrangement. The specific surface area and pore diameter of fresh MPS were $1250\text{ m}^2\text{ g}^{-1}$ and 2.5 nm, respectively. The estimated thickness of the mesopore-walls of the MPS was ca. 2 nm. After the hydrothermal treatment at 700°C - 50 h in the air containing 10% steam, the specific surface area and mesopore-size of MPS were $1290\text{ m}^2\text{ g}^{-1}$ and 2.2 nm, respectively, which were almost the same as those of the fresh. Based on our experiment, half of the specific surfaces and mesopores of MCM-41 and most of the Al-elements in ZSM-5 were lost upon exposure to the hydrothermal atmosphere. When compared to MCM-41 and ZSM-5, MPS has a very high hydrothermal resistance. The specific surface areas and pore diameters of the fresh silicates were W-silicate ($900\text{ m}^2\text{ g}^{-1}$, 2.8 nm), B-silicate ($1200\text{ m}^2\text{ g}^{-1}$, 2.4 nm), Nb-, Ti- and Al-silicate ($700\text{-}800\text{ m}^2\text{ g}^{-1}$, 3.2 nm) and Gd-silicate ($1140\text{ m}^2\text{ g}^{-1}$, 2.2 nm). After the hydrothermal treatment, the W-, B-, Nb- and Ti-silicates had decreased specific surface areas of $650\text{-}700\text{ m}^2\text{ g}^{-1}$ but had almost the same pore-diameters as those of the fresh ones. The specific surface areas and pore-diameters of the Al- and Gd-silicates before and after the treatment scarcely changed. The Si/metal atom ratios of the W-, Nb-, Ti- and Gd-silicate were almost unchanged before and after the treatment. However, the B and Al-contents of the silicates decreased to one fifth after the treatment.

3.2 Heat Resistance of Pt/MPS

The average diameters of the Pt-particles of the fresh Pt/MPS and Pt/metal-silicate were very close to the pore-diameters of the MPS and the corresponding metal-silicates, respectively. This indicated that the supported Pt-particles are located inside the mesopores of the supports. Certainly, the HRTEM images of the Pt/MPS and Pt/metal-silicate showed that the supported Pt-particles are close to the pore-diameter of each support and homogeneously distributed on each support particle (the particle size of MPS is 250 nm average size). The powder XRD measurements of the heat-treated Pt/MPS showed that the average size of the Pt-particles was almost unchanged until 600°C - 50 h, then increased to $4\text{-}5$ nm ($2\text{-}3$ times larger than that of fresh Pt/MPS) after 700°C - 50 h, remarkably increased to 10 nm after 800°C - 50 h. That is, the supported Pt-particles were gradually enlarged on the outside of the mesopores of MPS around 700°C . This is due to the thermal migrations of oxidized Pt-particles because oxidation of metallic Pt occurs around 700°C . Such an enlargement of the supported Pt-particles predictably decreased the de- NO_x activity of the catalyst, as previously reported (Komatsu et al., 2010). It was reconfirmed that up to 600°C - 50 h the NO_x -conversion vs. temperature profile of Pt/MPS is unchanged, after 700°C - 50 h the NO_x -conversion is not changed, but the corresponding temperature rises to 210°C (40°C rise), after 800°C - 50 h the NO_x -conversion drops to 45% (25% drop) and corresponding temperature rises to 230°C (60°C rise). The higher temperature shift of the NO_x -conversion temperature after the treatment at 700°C - 50 h was confirmed to be gradually restored by reduction with small HCs, such as CO and C_3H_6 . The activity of Pt/MPS remaining after aging at 700°C - 50 h corresponds to an estimation of a million-km-travel of the heavy duty diesel cars based on the Arrhenius plots (the logarithm of aging hour vs. $1/T$ relationships in the range of $400\text{-}700^\circ\text{C}$).

3.3 Assessment of Prototype Pt/MPS Coated Honeycombs

Figure 1 shows the de- NO_x profiles for fresh Pt/MPS and aging ones which were measured under lean and rich conditions. Under the lean condition, the de- NO_x reaction for fresh Pt/MPS begins around 140°C , rapidly increases to a maximum (ca. 70% in NO_x -conversion) at 170°C , followed by a gradual drop. Under the rich condition, the NO_x -conversion exponentially increases from 2% at 140°C to 99% at 210°C , followed by no change above 210°C . Since such exponential de- NO_x curves under the rich condition are due to a slight amount of O_2 in the rich syngas, the profiles may be made more precipitous with the increasing O_2 -concentration. The de- NO_x curves for the aged Pt/MPS are similar to the simulations in which the fresh curves were assumed to be shifted by ca. 40 K into the higher temperature region. From Figure 1, it is estimated that fresh Pt/MPS is able to remove ca. 14% of the lean-burn NO_x and ca. 6% of the rich-burn NO_x in the temperature range of $100\text{-}200^\circ\text{C}$ and that the de- NO_x capability of the aged Pt/MPS is only several %.

Figure 2 shows the de- NO_x profiles for the fresh Pt/MPS coated-honeycomb and aged one through the lean-rich cycle. The de- NO_x reaction for the fresh honeycomb starts around 150°C , rapidly increases to 90% in

NO_x-conversion at 200 °C, is constant at 93 % up to 250 °C, followed by a slow decrease to 70 % at 400 °C. For the aging one, the de-NO_x slowly increases from 170 °C up to 90 % at 250 °C, followed by a slow decrease similar to the fresh. If the unreacted NO₂ under the lean condition (the difference between NO-conv. and NO_x-conv. in Figure 3) is completely removed, the NO_x-conversions in the range of 200-400 °C are estimated to be 95 %. In order to bridge the gaps in the NO_x-conversion between the experiment and the above estimation, the addition of several zeolites was found to be very effective (Figure 4). From Figure 2, it is estimated that the fresh honeycomb is able to remove ca. 13 % of the NO_x in the temperature range of 100-200 °C and the aged one is ca. 8 %. However, the honeycomb indicates high activities in the range of 150-400 °C. Although the de-NO_x profiles for the powder catalyst and honeycomb were different from each other due to the differences in the gas-diffusion and thermal conductivity, the de-NO_x capabilities of both catalysts were approximately equal. Since Pt/MPS is able to utilize long-chain HCs contained in diesel-fuels as reducing agents (Komatsu et al., 2010), the honeycomb seems to be very useful to remove the NO_x of diesel-auto exhausts by combination of lean-rich techniques and post-injection of minimum diesel-fuels. For future catalysts to resolve the difficult problems regarding the de-NO_x of heavy duty diesel-exhausts, wider activities over the temperatures from 100 °C to 200 °C are required.

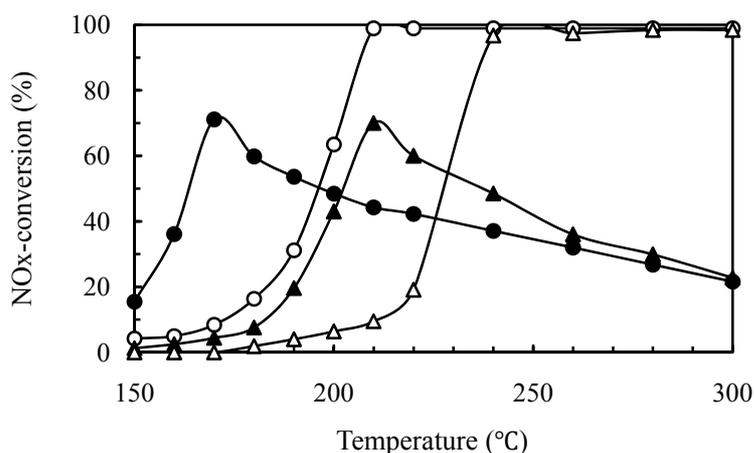


Figure 1. NO_x-conversions over fresh Pt/MPS (powder) and aged one under lean and rich conditions: (●) fresh Pt/MPS under the lean condition; (○) fresh Pt/MPS under the rich condition; (▲) aged Pt/MPS under the lean condition; (△) aged Pt/MPS under the rich condition

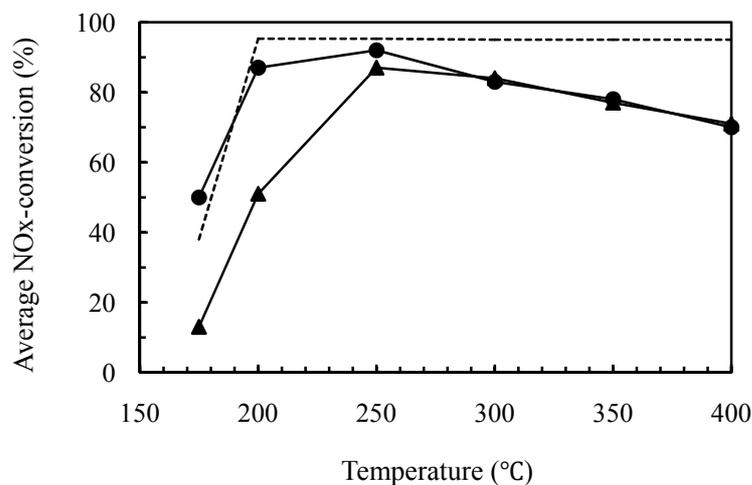


Figure 2. NO_x-conversions over the Pt/MPS coated honeycomb through lean (1 min)-rich (1 min) cycles: (●) fresh; (▲) after aging (750 °C-24 h); (---) estimation. The average NO_x-conversion is an average of NO_x-conversions at lean- and rich-gas flows

3.4 The Support Effect on NO_x-Conversion vs. Temperature Profiles for Pt/MPS and Pt/Metal-Silicate

Figure 3 shows the NO_x-conversions for Pt/MPS and Pt/metal-silicate with Pt/γ-alumina as the reference. The catalysts supported on MPS and the metal-silicates, except for Pt/γ-alumina indicate very high NO_x-conversions slightly over 70 % at temperatures around 170 °C. Although the NO_x-conversion gradually decreases above 170 °C, the NO_x-conversion increases even at temperatures above 170 °C. Since the difference {[NO-conv.] – [NO_x-conv.]} is equal to the unreacted NO₂, a volcano-form of the NO_x-conversion curves suggest that below 170 °C the HC-selective CR is occurring, and above 170 °C the HC-nonselective CR is occurring due to the competition of the oxidation of NO into NO₂ and consumption of the HCs. On the other hand, Pt/γ-alumina has NO_x-conversions as high as 40 % around 240 °C. The maximum NO_x-conversion for Pt/MPS can be raised to ca. 80 % with the decreasing O₂/C₃H₆ ratios of the initial syngas at the constant NO/C₃H₆ ratio (250/400), however, the maximum value under the standard condition is usually 70-72 %. A light-off temperature of the de-NO_x reactions can be dropped to 100 °C using H₂ as the reductant, however, the use of H₂ is difficult under practical applications due to the high expense.

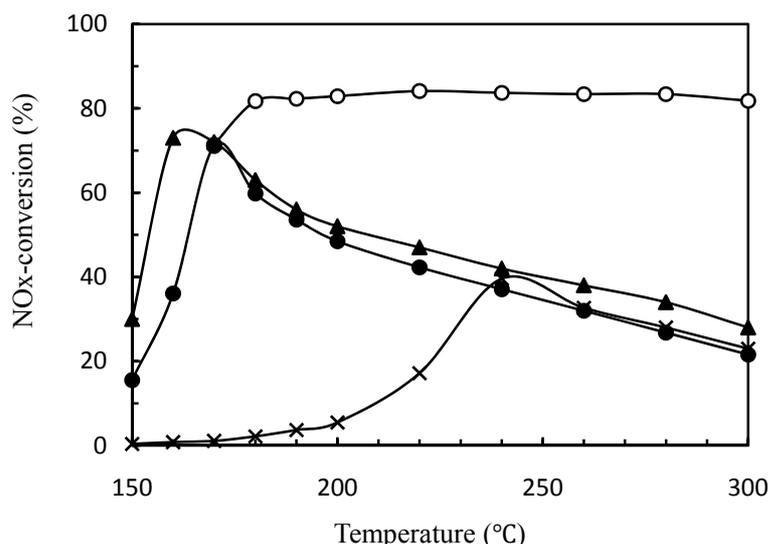


Figure 3. NO_x-conversions over the Pt-catalysts (powder): (●) Pt/MPS; (▲) Pt/W-silicate; (×) Pt/γ-alumina; (○) NO-conversion

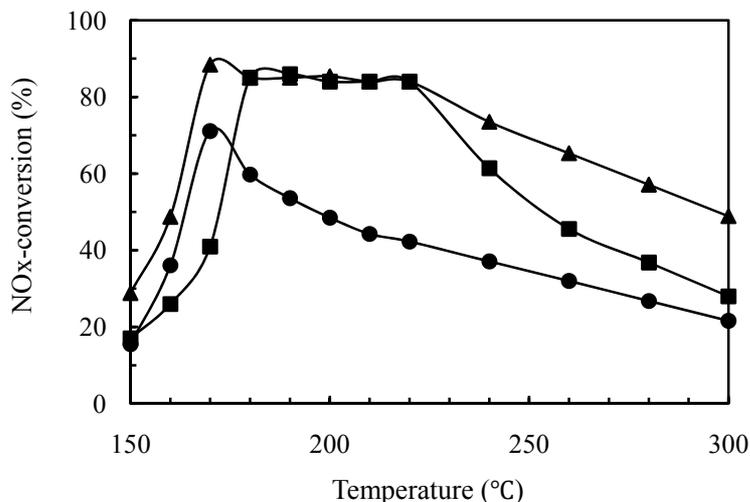


Figure 4. Effects of the additives on NO_x-conversions of Pt/MPS: (●) only Pt/MPS; (▲) addition of erionite; (■) addition of mordenite

Obviously, the MPS and metal-silicate supports produce the catalyst low-temperature activity, while γ -alumina produces the high-temperature activity. The average Pt-particle sizes of the Pt/MPS and Pt/ γ -alumina are the same at 2 nm. Both results suggest that the temperature regions in which the catalysts are the most active are related to the support materials (abbr. support effect). The Pt/W-silicate, Pt/B-silicate and Pt/MPS indicated high NO_x-conversions at temperatures lower than 170 °C in comparison with Pt/Nb-, Ti-, Al- and Gd-silicates. Among the catalysts, the de-NO_x activity of the Pt/W-silicate was significantly higher than those of the Pt/B-silicate and Pt/MPS. The Pt/W-silicate is able to extend the temperature window of de-NO_x by 10 °C on the lower temperature side in comparison with Pt/MPS as having NO_x-conversions higher than that of Pt/MPS (Figure 3). This is unlike the simple temperature shift of the NO_x-conversion curve for Pt/MPS.

Whether or not the additions of solid-oxides and several zeolite-materials to Pt/MPS affect the low-temperature activity was investigated. Figure 4 shows the effects of such additives on the NO_x-conversion profiles. None of the used solid oxides changed the NO_x-conversion profile for Pt/MPS. Even the addition of solid oxides, such as MoO₃ and WO₃, known as strong solid acids, indicated almost the same profile as that for Pt/MPS. Among the zeolites, the addition of mordenite and erionite increased the NO_x-conversions in the range of 170-300 °C, but were only slightly effective below 170 °C. Around the same time as the discovery of HC-SCR of NO_x over Cu-Zeolites, classical work for determining the active-sites of zeolites reported that the complex formation and transformation of nitrogen oxides (NO and N₂O) with cations and strong Lewis acid sites in zeolites (ZSM-5, MOR, LTA and FAU) yield strong NO^{δ+} and N₂O₃ species to oxidize CO and CH₄ into CO₂ (Kustov et al., 1995). The used zeolites ion-exchanged with Mg-ions in this study have no strong Lewis acid-sites in comparison with those exchanged with transition metal ions such as Fe³⁺, Cu²⁺, W⁶⁺, Mo⁶⁺ and Co³⁺. The Mg-zeolites in this study are not solid bases because Mg-ions are generally the very weak in their ion-exchange selectivity series: Cs⁺>Rb⁺>K⁺>NH₄⁺>Ba²⁺>Sr²⁺>Na⁺>Ca²⁺>Fe³⁺>Al³⁺>Mg²⁺>Li⁺ (Sherry, 2003). Accordingly, the effects of the zeolites used as additives are presumably due to the adsorption of HCs but not due to the adsorption of NO₂ similar to LNT (Lean-NO_x-Trap). The present zeolites are not solid bases, such as BaO usually used as LNT-agents, therefore, the materials have no problems such as deactivation with several ppm SO_x (SO_x poisoning or stoichiometric sulfation). Zeolites, such as HZSM-5 and MCM-41, produce low-temperature activities in the catalyst, as previously reported (Komatsu et al., 2006). These results strongly suggest that the support effect is due to the incorporated metals. The relative support effects dependent upon the incorporated metals tended to increase in the order of W>B>Si>Nb>Ti>Al>Gd. This order is similar to that of the Brønsted acidity of the solid oxides corresponding to the incorporated metals. MPS and the metal-silicates probably possess the Brønsted acid-sites, while γ -alumina contains Lewis acid-sites. The observation of the Brønsted acid-sites of transition-metal inserted MCM-41 was unsuccessful because of really ineffective pyridine adsorption FT-IR assessment (Zhang et al., 1998; Briot et al., 2000; Parvulescu et al., 2003). Although the measurement of acid-sites of MPS and the metal-silicates by the above standard method is very difficult, the support effect is undoubtedly due to the strong Brønsted acid-sites locally distributed on the support surfaces.

3.5 The Support Effect from a Kinetic View Point

A previous study (Komatsu et al., 2010) demonstrated that the rate-determining step of the de-NO_x processes over Pt/MPS with C₃H₆ as a reducing agent under lean-conditions is the oxidation of NO into NO₂ on the Pt-particle surfaces and that the low-temperature activity of Pt/MPS is due to the exceptionally high frequency factor A (8.6×10⁵ s⁻¹) rather than the apparent activation energy E (102 kJ mol⁻¹) for Pt/MPS in comparison with those for Pt/ γ -alumina (102 kJ mol⁻¹, 2.6×10⁴ s⁻¹) and Pt/zirconia (101 kJ mol⁻¹, 5.9×10³ s⁻¹). According to the Arrhenius theory, the frequency factor is related to the collision probabilities which are dependent upon the reaction temperatures. The reaction rate constants k₁ and k₂ for Pt/MPS and Pt/ γ -alumina are expressed by the Arrhenius eq. (1),

$$k=A \cdot e\left(-\frac{E}{RT}\right) \quad (1)$$

where a set of k₁, A₁, E₁ and T₁ is for Pt/MPS and a set of k₂, A₂, E₂ and T₂ is for Pt/ γ -alumina. R is the gas-constant (8.3144 J K⁻¹ mol⁻¹). A relative reaction rate of k₁/k₂ is equal to A₁/A₂ (=ca. 33) when E is equal between both catalysts. The relative k₁/k₂ is generally converted to the difference in the reaction temperature (T₂-T₁) from eq. 2.

$$k_1/k_2=A_1/A_2=e\left(\frac{E(T_2-T_1)}{RT_1T_2}\right) \quad (2)$$

A reaction temperature drop corresponding to the ratio of A₁/A₂(=ca. 33) is estimated to be ca. 70 K which is

close to the difference in the NO_x-conversion temperature between both catalysts. The thermal energies required for the de-NO_x reactions at lower light-off temperatures are supplied by the exothermic reactions, such as oxidations of NO and the HCs. Also, kinetic analysis of the Pt/metal-silicates in Figure 3 estimates the Pt/W-silicate (102 kJ mol^{-1} , $1.7 \times 10^6 \text{ s}^{-1}$) which are slightly higher or similar to those for Pt/MPS. It has been proposed that the intermediate NO⁺ and carbenium ions are generated from the respective NO₂ and HCs at the Brønsted acid-sites of HZSM-5, both intermediates react to form isocyanates, followed by oxidative decomposition into N₂ and N₂O (Ingelsten et al., 2006). Protons in the hydrothermal phase are strong electrophiles (oxidants) being quite able to stimulate oxidation of NO, NO₂, O₂ and the HCs. A hypothetical scheme that the Brønsted acid-strength of the support materials increases the Arrhenius frequency factor being directly correlated with the oxidation of NO into NO₂ to derive low-temperature activities is conceivable.

4. Conclusion

We developed new Pt-catalysts supported on mesoporous silica (MPS) and metal-silicates to remove lean-NO_x at temperatures around 170 °C. A prototype honeycomb supporting Pt/MPS allows the high de-NO_x of diesel-exhausts possible over the wide temperature range of 170-400 °C. Such remarkable low-temperature activities of the catalysts are dependent upon the supports (abbr. support effect) rather than the supported Pt-particle sizes and specific surface areas of the supports. The support effect is due to the Brønsted acid-sites of the support materials. The kinetic investigation of the de-NO_x over the Pt-catalysts predict that the Brønsted acid-sites of the support increase the frequency factors of the oxidation of NO into NO₂ which is the rate-determining step of the de-NO_x processes, in other words, that active protons on the Brønsted acid-sites of the support stimulate the oxidation of the HCs, NO and NO₂ adsorbed on the catalyst to produce the support effect. For future support materials, a strong Brønsted-acid type of material like mesoporous tungsten-silicate, which indicates higher support effects than MPS, appear promising.

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