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Outstanding low temperature HC-SCR of NOx over platinum-group catalysts supported on mesoporous materials expecting diesel-auto emission regulation

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Abstract

Outstanding low temperature HC-SCR of NOx over platinum-group catalysts supported on mesoporous materials, which does not rely on the conventional NOx-absorption–reduction-catalysts, is presented for the purpose of de-NOx of diesel-auto emissions. The established catalysts basically consist of mesoporous silica or metal-substituted mesoporous silicates for supports and platinum for active species, which is operated under lean- and rich-conditions. The new catalysts are very active at 150–200 °C and free from difficult problems of SOx-deactivation and hydrothermal ageing of the NOx-absorption–reduction catalyst.

Keywords: De-NOx catalysts; HC-SCR; Mesoporous; NOx-absorption–reduction; Lean-burn emissions

1. Introduction

In 1997 at the Kyoto conference, a protocol regarding the regulation of greenhouse warming CO_2 emission, i.e., the Kyoto Protocol, was adopted. According to the presentation by the Japanese Ministry of Economy, Trade and Industry (METI), the energy-conservation over 12% will be imposed on the Transport Department no later than year 2010. A diesel-auto is so extremely more fuel-efficient than a gasoline-auto that the dieselization of only 10% of the gasoline-auto can achieve a numerical target of the energy-conservation. However, the diesel-auto has been unfamiliar in Japan. To popularize the diesel-auto, cleaning techniques for diesel-emissions should be developed. But, the conventional three-way catalysts (Pt–Rh–Pd) used for gasoline-auto emissions are momentarily deactivated because of easy oxidative poisoning of the Rh and Pd metals even in an atmosphere of 2–3% O_2 at moderate temperatures. The oxygen content in the diesel-auto emissions is usually 10–14% (lean-burn emissions) whereas the gasoline-auto emissions are controlled with O_2 content below 1% (rich-burn emissions). Exhaust temperatures of the diesel-auto in Japan is in the range 150–400 °C (the JC08 mode), but de-NOx of the emissions below 200 °C has been very difficult due to low activity of the catalysts. Expecting the diesel-auto NOx-emission regulation, many researchers working in the automobile-catalyst field have attended to a NOx-absorption(storage)–reduction type of catalysts. The concept of the method is: NO_2-absorption in a lean (oxidative) atmosphere below 200 °C with NOx-absorbing agents and successive reduction of desorbed NO_2 in a rich (reductive) atmosphere over 200 °C with noble metal catalysts using hydrocarbons. The catalysts composed of Pt, Rh, alkali metals, alkali earth metals, alumina, zirconia, titania, ceria and lanthanides, etc. have been patented [1–7], where alkali metals and alkali earth metals are used as NOx-absorbing agents. This type of catalysts have several essential problems such as deactivation of NOx-absorbing agents in a stream of several ppm SOx (SOx poisoning or stoichiometric sulfation), water-elution of NOx-absorbing agents, time lags between catalytic NOx-reduction and NOx-desorption rates and long waiting until reaching steady-state conditions at certain temperatures. Also in present, the NOx-absorption–reduction method can scarcely achieve de-NOx below 200 °C. Considering the ageing of the catalysts, a large excess of noble metal loading and/or regular regenerating of the

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catalysts in the range 750–850 °C (decomposition temperatures of the sulfates of NOx-absorbing agents) have been carried out.

On the other hand, the hydrocarbon-selective catalytic reduction (HC-SCR) method [8–15] had been studied before the presentation of the NOx-absorption–reduction method. A basic composition of the HC-SCR catalysts was a combination of noble metals and alumina (or silica) or transition metals and ZSM-5. The catalysts are free from deactivation with SOx [14,15]. The main problem of this method is that the catalysts are scarcely active below 200 °C. That is, the difficult NOx-removal below 200 °C has been remaining open as a common problem of both methods. Considering the many problems of SOx-deactivation, hydrothermal ageing, reproduction of the catalysts and complex O_2-regulation for the NOx-absorption–reduction system, the HC-SCR method has clearly an aptitude and is reasonable rather than the former requiring the NOx-removal via NOx-absorbing agents. In addition, the concept of the NOx-absorption–reduction method is self-contradictory, because it can be hardly said that the NOx-absorbing agents absorb NO_2 below 200 °C despite of the catalysts inactive below 200 °C.

From these backgrounds, this work presents an advanced HC-SCR type of mesoporous catalysts, which mean the HC-SCR catalysts supported on mesoporous materials, to effectively achieve de-NOx of the lean-burn emissions below 200 °C. Also, the HC-SCR of NOx over the mesoporous catalysts will be discussed from the viewpoint of surface-active acid-base properties of the supports.

2. Experimental

2.1. Sample preparation

Mesoporous silica (MPS) was prepared as follows. To a mixture of distilled water (300 g), ethanol (240 g) and dodecylamine (30 g), TEOS (125 g) were added. The mixture was stirred for 22 h at room temperature. The resulting precipitate was separated by filtration under suction, washed with distilled water, evaporated to dryness at 110 °C, followed by calcination in air at 550 °C for 5 h to remove the template. Al-, B-, W-, Ti-, Nb- and Gd-substituted mesoporous silicates (M-MPS) were prepared in a similar manner as above except for addition of a mixture of tetraorthosilicate (TEOS) and each substituent precursor as a source of the silicate: for B-substituted silicate, a mixture of TEOS (112 g) and $B(OCH_3)_3$ (5.6 g); for W-substituted one, a mixture of TEOS (99.6 g) and $(NH_4)_2WO_4\cdot 5H_2O$ (40 g); for Nb-substituted one, TEOS (112 g), $Nb(OC_2H_5)_5$ (19.0 g) and ethanol (5 g); for Ti-substituted one, a mixture of TEOS (124.8 g), $Ti(OC_2H_5)_4$ (9.1 g) and ethanol (5 g); for Al-substituted one, a mixture of TEOS (125 g) and $Al(O\text{–}i\text{–}C_3H_7)_3$ (24 g); for Gd-substituted one, TEOS (125 g), $Gd(OC_2H_5)_3$ (2.9 g) and ethanol (5 g). MCM-41 mesoporous silica and mesoporous alumina (MPA), were prepared in the presence of cetyltrimethylammonium hydroxide and dodecanoic acid, respectively [16,17]. The other supports, silica, silica–alumina, zirconia, γ-alumina and ZSM-5, were commercially available. Supported catalysts were prepared by impregnating each support with an aqueous solution of catalyst sources, evaporated to dryness at 110 °C, followed by reduction with hydrogen at 300 °C for 1 h. As catalyst sources, H_2PtCl_4 and $Fe(OH)(CH_3CO_2)_2$ were used. For comparison, a 2%Pt–0.12%Rh–2.8%Ba catalyst supported on γ-alumina as a model of the NOx-absorption–reduction catalysts was prepared with an aqueous solution of H_2PtCl_4, $RhCl_3\cdot 3H_2O$ and $Ba(CH_3CO_2)_2$ in the same way as above. The impregnation amount of all the catalysts was precisely adjusted to obtain a 2 mass% of the platinum metal loading.

2.2. Characterization of the samples

Specific surface areas and pore size distribution of the supports were measured using nitrogen adsorption at 77 K and determined by BET and BJH methods. Crystallite sizes of the catalysts were estimated by powder XRD measurements and confirmed by HRTEM observations. Homogeneities of the supports and catalysts were confirmed by FESEM, scanning-TEM (STEM) and HRTEM observations. The metal content was determined by ICP mass analysis. Functional groups of the samples were identified by FTIR spectroscopy.

2.3. Measurements of HC-SCR of NOx

The catalytic NOx reduction with hydrocarbons was carried out using a three-necked quartz tubular downflow reactor (20 mm in i.d. and 400 mm in length) inserted with a thermocouple. A supported catalyst of 0.6 g that was in advance homogeneously mixed with commercially available sea-sands (20–30 mesh) of 13 g (10 ml) was charged into the reactor, and on this fixed bed the same amount of sea-sands was charged to make the reaction undergo at a homogeneous reaction gas flow. The reactor was placed in a temperature-programmed cylindrical electric furnace. Through a mass-flow controller, the reaction mixture comprising a lean-conditioning gas of 0.1%NO, 0.3%C_3H_6 and 14%O_2 balanced with He or a rich-conditioning gas of 0.1%NO, 1%C_3H_6 and 1%O_2 balanced with He was introduced into the reactor at a flow rate of 100 ml min^{-1}. After reaching steady-state conditions, the effluent gas was analyzed by a chemiluminescence NOx detector to measure NO-conversion.

2.4. Ageing tests of the supports and catalysts

Heat-resistance of the catalysts was estimated from the catalyst activities before and after heating in air at 750 °C for 24 h. In order to investigate the effect of sintering of the catalysts on the activities, the heat-treated samples were reproduced by reduction with hydrogen at 500 °C for 1 h. Hydrothermal resistance at atmospheric pressure (abbr. hydrothermal ageing) of the supports was assessed using each sample of 0.6 g that was treated under the conditions of 0.5%O_2 and 10%H_2O balanced with N_2 at a flow rate of 100 ml min^{-1} at 750 °C for 5 h. SOx ageing of the catalysts was assessed using each sample of 0.6 g that was previously SOx-treated. The SOx-treatment was as follows: the fresh catalyst of 1 g was boiled in fuming sulfuric acid of 30 g for 10 min under reflux using a reflux condenser, diluted with distilled water, the remaining powders was then filtered under suction, washed with distilled water and evaporated to dryness at 110 °C.

3. Results and discussion

3.1. Characterization of the supports

Table 1 shows the characterizations of the fresh supports and the hydrothermally aged ones. Mesoporous silica and metal-substituted mesoporous silicates hold high specific surface areas ranging 500–1400 $m^2 g^{-1}$ and nanopores of several nm in diameter even after the hydrothermal treatment. In particular, Gd-substituted mesoporous silicate is very tough to the hydrothermal treatment. This tendency was also found for other lanthanoids such as Ce and Sm, probably due to the lanthanoid construction. On the other hand, it was reconfirmed that light metals such as B and Al in the silicates are hydrothermally eluted, as already reported [18]. This is also the case for ZSM-5. The heavy metal-substituted silicates such as W-MPS, Nb-MPS and Ti-MPS were comparatively durable under the hydrothermal condition. As-obtained mesoporous alumina has a specific surface area of 300–400 $m^2 g^{-1}$ and pores of around 3 nm in diameter, but after the hydrothermal treatment remarkably decreases the specific surface area up to the same low level as that of γ-alumina. Commercially available silica, silica–alumina, zirconia and γ-alumina have too large pores or too small specific surface areas to use for a support of de-NOx catalysts.

3.2. Low-temperature activity of the catalysts

Table 2 shows the NO-conversions over the fresh catalysts, which were measured under lean and rich conditions. Platinum catalysts supported on the mesoporous silica and metal-substituted silicates established high NO-conversions below 200 °C. The produced gases were composed of N_2, N_2O, CO_2 and H_2O, excepting unchanged NO. The selectivity was N_2:N_2O = 0.45:0.55 at 200 °C. In particular, Pt/B-MPS and Pt/W-MPS gave almost perfect NO-conversions at 160 °C lower than the temperature (ca. 165 °C) at the maximum NO conversion over Pt/MPS. This phenomenon means that the NO-conversion is affected by metal substitution of the silicates (the effect of supports in the general meaning), which relates to the support acidity. The effect of the metal substituents upon the lower temperature shift tended to increase in order of $B > W \gg Si > Nb > Ti > Al > Gd$, where substitution by B and W usually increase the Bronsted acidity of the supports and Ti and Al increase the Lewis acidity. Silica–alumina and zeolites were reported to show the existence of the Lewis acidity [19]. Ward reported that NH_4^+-zeolites increase the Lewis acidity with increasing temperature [20]. Also, it was found that alumina and zirconia after acid-treatment show a lower temperature shift of 30 and 20 °C, respectively, and that the supports after the acid-treatment indicate two or three new IR absorption peaks in the range 1040–1220 cm^{-1} which are assigned to the Bronsted OH groups or $M–O^-$ ion (M = metal). Therefore, the Bronsted acidity or $M–O^-$ ion on the support surfaces is closely related to the lower temperature activity of the catalyst.

Two reasons for explaining the low temperature activity: concentration of the reaction substrates on the supports; improvement in the catalysis of platinum by certain interactions between platinum and the substituted metals of the supports; are conceivable. The supports have no redox-property to NOx but are able to adsorb the reaction substrates; the co-precipitation of B or W or Si and Pt does not increase the catalyst activity; accordingly, the concentration of the substrates on the supports is probable. The basic supports such as mesoporous alumina, γ-alumina and zirconia remarkably decrease the catalytic activity compared to the mesoporous silica and silicates. Differently from activated carbons, which preferentially adsorb a solute dissolved in the solvent, γ-alumina as being more adsorptive than silica traps the solute in the pores when an aqueous solution impregnated in the pores is evaporated. The STEM and HRTEM observations confirmed that γ-alumina holds monodispersed Pt-nanoparticles at places

Table 1
Characterizations of the fresh supports and the hydrothermally treated (aged) ones

Supports	Si/metal (molar ratio)		Specific surface area ($m^2 g^{-1}$)		Pore diameter (nm)	
	Fresh	Aged	Fresh	Aged	Fresh	Aged
MPS	–	–	1252	1291	2.5	2.2
MCM-41	–	–	1450	686	2.4	0.8–1.0
MPA	–	–	379	144	3.2	3.8
B-MPS	10/1	10/0.2	1206	724	2.4	1.8
W-MPS	60/1	60/1	906	690	2.8	2.2–3.2
Nb-MPS	30/1	–	791	685	3.2	3.2
Ti-MPS	15/1	–	710	648	3.2	3.0
Al-MPS	5/1	–	756	776	3.2	2.2
Gd-MPS	60/1	60/1	1144	1397	2.2	2.2
Silica	–	–	428	401	Nonporous	20,40
Silica–alumina	5/1	–	412	397	3.8	4
Zirconia	–	–	128	34	7	16
γ-Alumina	–	–	250	178	6.2	8.7
ZSM-5	47/1	–	391	428	0.5	1.6

Table 2
NO-conversions over the fresh catalysts measured under the lean- and rich-conditions

Supported catalysts	NO conversion (%)						
	Lean-condition					Rich-condition	
	160 °C	170 °C	200 °C	250 °C	300 °C	400 °C	500 °C
2%Pt/MPS	73	99	99	97	92	100	100
2%Pt/MCM-41	13	19	94	72	48	–	–
2%Pt/MPA	20	23	54	89	84	–	–
2%Pt/B-MPS	100	100	97	87	82	–	–
2%Pt/W-MPS	97	99	93	89	80	–	–
2%Pt/Nb-MPS	57	99	94	89	82	–	–
2%Pt/Ti-MPS	34	74	94	85	81	–	–
2%Pt/Al-MPS	34	58	96	77	51	–	–
2%Pt/Gd-MPS	16	17	94 (205 °C)	81	70	–	–
2%Pt/silica	94	94	89	82	75	–	–
2%Pt/silica–alumina	39	65	97	82	66	–	–
2%Pt/zirconia	23	37	92	89	89	–	–
2%Pt/γ-alumina	18	24	44	72	70	–	–
2%Pt/ZSM-5	45	64	99 (180 °C)	95	90	–	–

deeper than 100 nm in depth in the pore inside, on the contrary the mesoporous silica traps them in the shallow pits of the pores. Although the low temperature activity of the catalysts results from homogeneous dispersion of active nanoparticles on high specific surface areas of mesoporous supports, the depth in which the catalysts are located must greatly influence the NO-conversion, because the solid–gas NOx-reduction is occurring in the catalyst surface-nano-space. The activities of Pt/MCM-41 and Pt/ZSM-5 are lower than that of Pt/MPS. The prepared mesoporous silica is nanoparticles below 100 nm in size and has disordered and shallow pores, on the contrary MCM-41 and ZSM-5 are large aggregates above 300 nm in size and have well-ordered very long pores. The low activity of Pt/MCM-41 and Pt/ZSM-5 may be due to organized very long pores or channels in the supports. The NO-conversion begins to decrease from around 300 °C because of waste combustion of the reductant, thus, an use of excess amounts of the reductant is found to be effective to establish high NO-conversions at temperatures in the range 300–600 °C.

3.3. Ageing of the catalysts

Table 3 shows the NO-conversions over the fresh 2%Pt/MPS and the heat-treated one. The fresh 2%Pt/MPS having the highest activity in this work remarkably decreased the low temperature activity after the heat-treatment in air at 750 °C for 24 h (the activity remaining after the heat-treatment corresponds to the activity after 80,000 km-traveling on the diesel-auto). The temperature at the maximum NO-conversion was shifted from 170 to 240 °C. This deactivation is due to the superposition affects of sintering and oxidation of the catalyst. The heat-treatment made the crystallite size of the catalyst greatly increase from 2.3 nm (fresh) to 32–34 nm (aged).

In order to separate the effect of sintering from that of oxidation of the catalyst on the heat ageing, the hydrogen-reduction of the catalyst after the heat-treatment was made. In Table 3, is also shown the NO-conversion over the regenerated catalysts. The low temperature activity of the aged 2%Pt/MPS was slightly recovered and the temperature at the maximum NO-conversion was lowered by 10 °C. The aged catalyst was observed to contain Pt–O species in addition to Pt–Pt species by EXAFS measurements, although platinum is generally never oxidized under the present experimental condition. Probably, the above slight recovery in the low temperature activity is due to the reduction of the Pt–O species into Pt(0). From these results, it was found that the affect of sintering is greater than that of oxidation.

An addition of very small amounts of Fe to Pt (0.01–0.1 mass% Fe to Pt) was found to appreciably reduce the affect of sintering. Fig. 1 shows the NO conversions over the fresh 2%Pt–0.03%Fe/MPS, the aged one and the regenerated one after the heat-treatment. In the fresh or aged state, the catalyst shows almost the same de-NOx activity as that of the fresh or aged 2%Pt/MPS, and in the regenerated state, lowers the temperature at the maximum NO-conversion by 20 °C in comparison to the regenerated 2%Pt/MPS. The powder XRD

Table 3
NO-conversions over the fresh catalysts and the heat-treated (aged) catalysts

Catalyst	NO conversion (%) under the lean-condition								
2%Pt/MPS	Fresh			Aged			Reproduced		
	170 °C	200 °C	240 °C	170 °C	200 °C	240 °C	170 °C	200 °C	230 °C
	99	99	99	7	20	98	10	28	98

Table 4
NO-conversions over the mesoporous catalyst and the typical NOx-absorption–reduction catalyst before and after the SOx-treatment

Supported catalysts	NO conversion (%) under the lean-condition					
	Fresh			SOx-treated		
	170 °C	200 °C	230 °C	170 °C	200 °C	230 °C
2%Pt–0.03%Fe/MPS	99	99	99	98	97	96
2%Pt–0.12%Rh–2.8%Ba/γ-alumina	24	42	80	Not measures	Not measures	Not measures

measurements and HRTEM observations showed that the crystallite size of platinum in the aged 2%Pt–0.03%Fe/MPS is scarcely different from that for the aged 2%Pt/MPS. However, these measurements failed to detect trace amounts of Fe. Although the apparent sintering of platinum was observed, the addition of Fe probably prevents platinum particles from its self-diffusion. State-of-the-art local analysis such as EXAFS is under studying to demonstrate the hypothesis that thin films of Fe atoms may be lying at the boundaries of Pt-nanoparticles as if inhibiting the coagulation.

Table 4 shows the NO-conversions over the mesoporous catalysts before and after the SOx-treatment, which were compared with those for the typical NOx-absorption–reduction catalyst. The SOx-treated mesoporous catalyst shows slightly lower NO conversion than that of the fresh catalyst, that is, the catalyst is almost free from SOx-deactivation. On the contrary, the typical NOx-absorption–reduction catalyst was so much decomposed into water-soluble $Al_2(SO_4)_3$ and separated into Pt and Rh particles that the assessment of the aged catalyst was not measured. Burch et al. already reported that the Pt catalyst supported on γ-alumina is not deactivated with SOx but the alumina-support is completely sulfated by an ex situ treatment of the catalyst with SO_2 under oxidizing conditions [14,15]. A mechanism of the SOx-deactivation of the NOx-absorption–reduction type of catalysts is probably (1) oxidation of SO_2 into SO_3 over the platinum catalyst, (2) sulfation of the Al_2O_3-support and Ba into $Al_2(SO_4)_3$ (water-soluble) and $BaSO_4$, respectively, with SO_3, (3) separation, coagulation and peeling of the supported platinum particles from the support. This is also for the case of other basic supports such as zirconia, ceria, titania and magnesia. The silica-support of the mesoporous catalyst is inert to SO_3, so, the mesoporous catalyst is stable. That is, the essential problem of the NOx-absorption–reduction catalysts is that the basic supports of the catalyst are destroyed with SOx under hydrothermal conditions rather that the NOx-absorbing agents aged with SOx cannot absorb NO_2-spillover on the support.

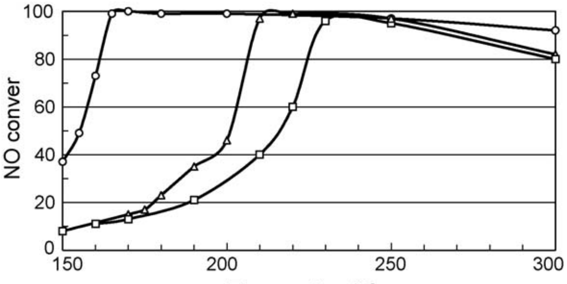

Fig. 1. NO conversion over 2%Pt–0.03%Fe/MPS under the lean-condition: (○) the fresh catalyst; (△) the regenerated; (□) the heat-treated.

4. Conclusions

This work reports new catalysts, “advanced HC-SCR mesoporous catalysts” meaning the catalysts supported on mesoporous materials without NOx-absorption agents and different from the conventional NOx-absorption(storage)–reduction-catalysts, for the purpose of cleaning diesel-auto lean-burn NOx emissions. Porous materials as supports were assessed with respect to pore-characteristics and hydrothermal durability, and compared with those for the conventional support materials. For the catalyst species, platinum were selected from oxidation resistance and SOx resistance viewpoints and assessed with regard to the de-NOx properties after the heat-treatment and SOx-deactivation treatment. The de-NOx properties of the HC-SCR mesoporous catalysts were compared with those for a typical NOx-storage–reduction-catalyst. The new catalysts, which basically consist of mesoporous silica or metal-substituted silicates for supports and platinum for catalytically active species, were found to be very useful for cleaning lean-burn NOx emissions and alternative to the conventional NOx-absorption–reduction-catalysts. The catalysts show the highest activity under lean-conditions in the temperature range 160–200 °C, which has not ever been known, and achieve perfect de-NOx in the range 300–600 °C with excess amounts of hydrocarbons as a reductant (rich-conditions). The catalyst system is greatly with hydrothermal-resistance and principally free from SOx-deactivation. Ageing of the catalyst after the harsh heat-treatment was inhibited with addition of very small amounts of Fe to the Pt-catalysts.

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