Special Issue

Selective Reduction of NO over Pt-Mo Catalysts under Lean Static Conditions

Toshiyuki Tanaka, Koji Yokota, Noritake Isomura, Haruo Doi, Masahiro Sugiura

酸素過剰雰囲気下におけるPtMo触媒上のNO選択還元反応

田中寿幸，横田幸治，磯村典武，土井晴夫，杉浦正洽

Abstract

The selective reduction of NO_x on various PtMoX-catalysts (X: Li, Na, K, Mg and Ca) loaded on metal oxides such as SiO_2, Al_2O_3, TiO_2, ZSM-5 and silicalite was studied in simulated exhaust gases from an automotive lean-burn engine and a stoichiometric engine and compared with that on PtMo/SiO_2, PtNa/SiO_2, and Pt/SiO_2 catalysts. The temperature window for the selective reduction of NO_x on the PtMoLi-, PtMoNa- and PtMoK-catalysts loaded on SiO_2 was found to be wider and to shift to a higher temperature than that on the other catalysts under lean static conditions. The redox ratio window, in which three-way activity occurred on a PtMoNa catalyst loaded on SiO_2, was also found to be wider than that on PtMo/SiO_2, catalysts and Pt/SiO_2 around the stoichiometric point. On the other hand, XPS, IR and CO adsorption data indicated that the oxidation of Pt on PtMoNa/SiO_2 catalysts was depressed by the added Mo and Na even under excess oxygen conditions, so that the reaction characteristics of the PtMoNa/SiO_2 catalysts were improved.

要　旨

SiO_2，Al_2O_3，TiO_2，ZSM-5，およびsilicaliteを担体とするPtMoX触媒 (X: Li，Na，K，MgおよびCa) のリーンバーンおよびストイキエンジンの排気モデルガスにおけるNO_x選択還元反応を調べ，PtMo/SiO_2，PtNa/SiO_2，およびPt/SiO_2触媒と比較した。SiO_2を担体とするPtMoLi，PtMoNa，およびPtMoK触媒は，リーン雰囲気下において比較触媒よりも高温側の広い温度域において高いNO_x選択還元活性を示した。また，PtMoNa/SiO_2はストイキ雰囲気近傍で広いA/F域においてNO_x還元活性を示した。PtMoNa/SiO_2に関するXPS，IRおよびCO吸着による解析より，上述のように反応特性が変化する要因は，MoおよびNaの添加によって酸素過剰下においてもPtの酸化が抑制されることであると結論した。

keywords　Exhaust catalysts, Molybdenum, NO selective reduction, Platinum, Silica, Sodium

1. Introduction

Lean-burn gasoline and diesel engines achieve high fuel economy using a higher air/fuel ratio (A/F). However, it is difficult to remove NO_x in exhaust gases from these engines under excess oxygen conditions. Selective catalytic reduction of NO_x under such excess oxygen conditions has been an object of study for several years. Extensive research has been carried out to develop a catalyst suitable for practical use. It has been reported that copper ion-exchanged zeolites such as Cu-ZSM-5[1〜5] are efficient for the reduction of NO_x. Some noble metal catalysts[6〜13] are found to be superior in durability to the copper zeolite system under both oxidizing and reducing conditions.

It is well-known that supported noble metal catalysts are active for the reaction of NO with H_2, CO or NH_3[14, 15]. Three-way catalysts (TWCs) which consist of noble metals and several oxides have been used for the catalytic control of automotive emissions. Such catalysts function efficiently in engine exhaust oscillating just rich of the stoichiometric air-to-fuels (A/F) ratio in a narrow A/F window, so that conversion of NO_x, CO and hydrocarbons (HC) occurs, but do not work in a lean static exhaust[16]. Recently, a new concept TWC, which removes NO_x, CO and HC under rich-lean dynamic conditions, has been developed and practically used[17, 18]. However the new concept TWC is not expected to remove NO_x under lean static conditions.

Bimetallic Pt-Mo and Pd-Mo catalysts have been demonstrated to modify the catalysis of each component and to create new catalytic properties : such as hydrogenolysis[19〜21], hydrogenation[22], NO_x reduction[23〜25], and unusual characterization[26〜28].

The purpose of this study was to examine NO_x reduction and three-way activity of the PtMo-catalysts with various additives and supports[29]. Another purpose was to present XPS, IR and CO adsorption results to clarify the state of Pt on these catalysts in the simulated model gases[34].

2. Experimental

2. 1 Catalyst preparation

Sixteen catalysts composed of Pt, MoO_3, basic additives and various metal oxides were prepared by an impregnation method as summarized in **Table 1**. The PMNS2 catalyst was prepared by the same method using SiO_2 powder (AEROSIL TT600, Nippon Aerosil Corp., 200m^2/g), $CH_3COONa\cdot 3H_2O$ (Wako Pure Chemical Industries), $(NH_4)_6Mo_7O_{27}\cdot 4H_2O$ (Wako Pure

Table 1 Catalyst formulations.

Catalyst	Pt loading (wt%)	MoO_3 loading (wt%)	additive	loading (wt%)	Support
PMNS1	1.67	12.3	Na_2O	0.05	SiO_2
PMNS2	1.67	12.3	Na_2O	0.1	SiO_2
PMNS3	1.67	12.3	Na_2O	1.0	SiO_2
PMLS	1.67	12.3	Li_2O	0.1	SiO_2
PMKS	1.67	12.3	K_2O	0.1	SiO_2
PMMS	1.67	12.3	MgO	0.1	SiO_2
PMCS	1.67	12.3	CaO	0.1	SiO_2
PMNA	1.67	12.3	Na_2O	0.1	Al_2O_3
PMNT	1.67	12.3	Na_2O	0.1	TiO_2
PMNZ	1.67	12.3	Na_2O	0.1	ZSM-5
PMNs	1.67	12.3	Na_2O	0.1	silicalite
PMS	1.67	12.3	-	0	SiO_2
PNS	1.67	0	Na_2O	0.1	SiO_2
PS	1.67	0	-	0	SiO_2
MS	0	12.3	-	0	SiO_2
NS	0	0	Na_2O	0.1	SiO_2

Chemical Industries) and $Pt(NH_3)_2(NO_2)_2$ (Tanaka Precious Metal Co.), and calcined at 500℃ for 3h in flowing 10% H_2 / N_2. The Pt, MoO_3 and Na_2O loading amounts were 1.67wt%, 12.3wt% and 0.1wt%, respectively. Other catalysts were prepared in the same way as described above starting from the corresponding additives and supports as shown in Table 1. The prepared catalysts were pressed into disks and pulverized to a 300～700μm size.

2．2 Activity measurement

The laboratory reactor system used in this experiment is similar to the previously described system 30). Catalytic activity data were obtained using a conventional fixed-bed flow reactor at atmospheric pressure. A quartz tube with an inner diameter of 18mm was chosen as the reactor tube. 0.5 g catalyst (～1 cm^3) was placed on a quartz filter at the middle part of the reactor. The upper part of the catalyst bed was packed with 7 cm^3 of inactive SiC spheres (3 mm o.d.) for preheating the feed gas. Furnace temperature was controlled with a maximum variation of 2℃ by an automatic temperature controller. The gas leaving the reactor was led to a condenser to remove the water vapor. The remaining components were continuously analyzed by nondispersive infrared (CO and CO_2), flame ionization (hydrocarbon, HC) , magnetic susceptibility (O_2), and chemiluminescence (NO_x) equipped with a gas analyzer (Horiba MEXA-8120).

We chose propene to simulate a hydrocarbon in the feedstream in order to measure the activity of the prepared catalysts under hard conditions.

The redox ratio, S, used to identify the redox characteristic of the model gas mixtures is defined as

$$S = \frac{NO + 2 \times O_2}{H_2 + CO + 9 \times C_3H_6} \quad \cdots\cdots\cdots\cdots\cdots(1)$$

When $S < 1.0$, $S = 1.0$, and $S > 1.0$, the composition of the feedstream is net reducing, stoichiometric, and net oxidizing, respectively.

The feed compositions and reaction conditions used in this study were as follows:(1) The simulated oxidizing feedstream consisted of 4.3 % O_2, 0.12 % NO, 800 ppm C_3H_6, 0.12 % CO, 400 ppm H_2, 12.3 % CO_2, 3 % H_2O and the balance of N_2. This mixture corresponded to $S = 9.91$ and simulated an A/F ratio of 18 (lean mixture). For each light-off test, catalysts were exposed to the simulated exhaust at 3.3 l/min while the temperature was decreased from 600℃ to 100℃ at 5℃/min and at 9.91 × 10^{-3} g·sec/cc W/F.

(2) The simulated exhaust gases for the S-scan were composed of 0.40～1.21 % O_2, 0.12 % NO, 490～620 ppm C_3H_6, 0.45~1.50 % CO, 0.15～0.50 % H_2, 10.0 % CO_2, 3.0 % H_2O and the balance of N_2. Catalytic activities of the catalysts were expressed as percent conversion of NO_x. Conversion data were measured at 450℃ and 9.91 × 10^{-3} g·sec/cc W/F. The activity measurements as a function of S are designated as the S-scan. In this experiments, S is changed gradually from reducing to oxidizing conditions by adjusting the O_2, C_3H_6, CO and H_2 contents at the inlet of the reactor.

2．3 Infrared Spectroscopy

IR spectra were recorded on a JASCO FTIR-8900 spectrometer equipped with an MCT detector and a diffuse reflectance IR cell. The catalyst sample placed in an in situ IR cell with a KBr window was pretreated at 400℃ for 1 h in flowing 7 % O_2/N_2 (O_2 pretreatment), and then cooled to 200℃. CO was adsorbed at 200℃ in flowing 0.28% CO/N_2 and the IR spectra were measured. The IR spectra of CO adsorbed on the sample were obtained by subtracting the spectra before CO adsorption from those after that. In another IR measurement, other catalyst samples were pretreated in flowing N_2 (N_2 pretreatment) and 7 % H_2/N_2 (H_2 pretreatment) by the same procedure as mentioned above except for pretreating in flowing 7 % O_2/N_2.

2．4　X-ray Photoelectron Spectroscopy (XPS)

In-situ XPS measurements were performed on a V.G. SCIENTIFIC ESCALAB MK III with Mg-Kα X-rays. The catalyst sample was placed on a grid and preheated under 1×10^{-7} torr O_2 pressure at 400℃ for 1 h. The preheated sample was cooled to room temperature under the same atmosphere and then transferred onto the XPS measurement stage. The binding energy was calibrated using the Si 2p (103.4eV).

2．5　X-ray diffraction (XRD)

XRD measurement was recorded on a RIGAKU RU-3L equipped with a Co source (Co-Kα radiation). Samples of catalyst powder were pressed into wafers and affixed to standard-sized microscope slides. Calculations of average crystallite size were made using the Pt(111) linewidth in Scherrer's equation with the Gaussian lineshape approximation.

2．6　Chemisorption of CO

Chemisorption measurement of CO was carried out by a pulse technique with chromatographic analysis. Catalyst samples placed in a flow reactor were pretreated at 400℃ for 15 min in flowing H_2 and cooled to 25℃. After that, several pulses of CO were introduced to the reactor until equilibrium was reached. The surface dispersion of Pt was calculated assuming that one molecule of CO adsorbs on an atom of Pt.

3．Results and discussion

3．1　Catalytic activity under excess oxygen conditions

Fig. 1 shows the conversions of NO_x on PS, PNS, PMS, PMNS1, PMNS2, and PMNS3 catalysts in a simulated oxidizing feedstream as a function of temperature. The PS and PNS catalysts showed maximum conversions of NO_x at temperatures from 250 to 260℃. The conversions of NO_x by these catalysts rapidly decreased with increasing temperature above 260℃. The temperature of the maximum NO_x conversion (300℃) on the PMS catalyst was about 50℃ higher than that on the PS catalyst. The conversion of NO_x gradually decreased with increasing temperature above 300℃. On the other hand, the maximum NO_x conversion temperatures (400～450℃) on the PMNS1, PMNS2 and PMNS3 catalysts were about 150 to 250℃ higher than that on the PS catalyst.

Fig. 2 shows the conversions of NO_x on the PMLS, PMKS, PMMS and PMCS catalysts as a function of temperature. The

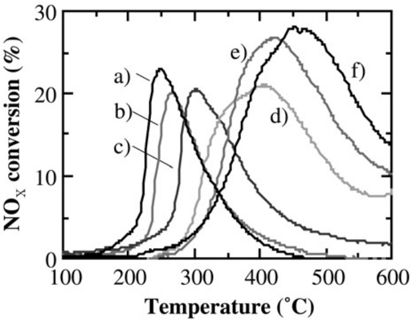

Fig. 1　NO_x conversion efficiency as a function of temperature in simulated oxidizing feedstream. The following catalysts are indicated: a) PS, b) PNS, c) PMS, d) PMNS1, e) PMNS2 and f) PMNS3.

PMLS and PMKS catalysts showed maximum conversion of NO_x at temperatures from 400 to 500℃. The temperature dependence of NO_x conversion on these catalysts had features similar to those of the PMNS2 catalyst in Fig. 1. On the other hand, the PMMS and PMCS catalysts showed maximum conversion of NO_x below 350℃, and the features were similar to those the PMS catalyst in Fig. 1.

Fig. 3 shows the conversions of NO_x on PMNA, PMNT, PMNZ and PMNs catalysts as a function of temperature. The PMNA and PMNT catalysts showed maximum conversions of NO_x below 300℃ and had features similar to those of the PMS catalyst. The conversions of NOx on PMNZ and PMNs catalysts were higher than those of the PMNA and PMNT catalysts at temperatures from 400 to 500℃. However, the NO_x conversion curves of these catalysts were not similar to that of the PMNS2 catalyst.

MS and NS catalysts do not have activity for NO_x reduction in a simulated oxidizing feedstream in a temperature range under 600℃.

As shown in Figs. 1-3, the NO_x conversion curves are classified into three groups : The first group is composed of the NO_x conversion curves on the catalysts without Mo such as the PS and PNS catalysts, the second group is of that on the catalyst with Mo and without alkaline metal or an SiO_2 support such as the PMS, PMMS, PMCS, PMNA, PMNT, PMNZ and PMNs catalysts, and the third group is of those on the catalysts with Mo, alkaline metals and an SiO_2 support such as the PMNS1, PMNS2, PMNS3, PMLS and PMKS catalysts.

In the first group, the PS and PNS catalysts show maximum conversion of NO_x at temperatures from 250 to 260℃. This temperature dependence of NO_x selective reduction had already been described5～7). This result indicates that the addition of Na to the PS catalyst does not play a significant role in the reactivity of Pt on the PNS catalyst.

In the second group, the maximum NO_x conversion temperature (300℃) is about 50℃ higher than those on PS catalyst. The conversion of NO_x gradually decreases with increasing temperature above 300℃. These results indicate that the addition of Mo plays a significant role in the reactivity of Pt catalysts.

In the third group, the maximum NO_x conversion temperatures (400～450℃) are

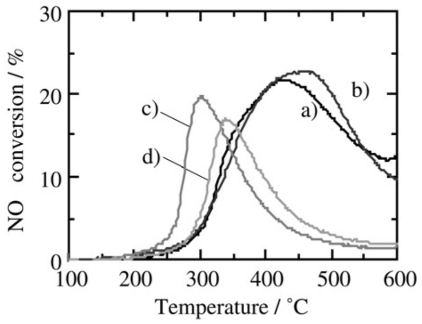

Fig. 2 NO_x conversion efficiency as a function of temperature in simulated oxidizing feedstream. a) PMLS, b) PMKS, c) PMMS and d) PMCS.

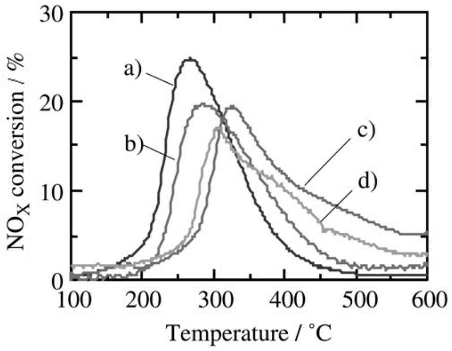

Fig. 3 NO_x conversion efficiency as a function of temperature in simulated oxidizing feedstream. a) PMNA, b) PMNT, c) PMNZ and d) PMNs.

about 150 to 250℃ higher than those on PS catalyst as shown in Figs. 1 and 2. The maximum NO_x conversion and its temperature on PMNS1, PMNS2 and PMNS3 catalysts increase with increasing amount of Na added to these catalysts as shown in Fig. 1. These results indicate that the addition of Mo and alkaline metals plays a significant role in the reactivity of Pt on an SiO_2 support.

A number of papers had already described that the temperature of the maximum NO_x conversion for selective reduction of NO_x on Pt catalysts changed with the Pt loading 7), the Pt precursor 8), and the aging conditions. In these cases, the maximum NO_x conversion decreased with increasing temperature, which has been explained by the changing of the number of active sites on Pt. On the other hand, for selective reduction of NO_x on the catalysts in the third group, the maximum NO_x conversion increases as the temperature increases. This result can be explained by the improvement in the reaction characteristics of Pt inherent in the addition of Mo and alkaline metals, as mentioned below.

3．2　Catalytic activity near the stoichiometric point

Fig. 4 shows the conversions of NO_x at 450℃ on the PS, PNS, PMS, PMNS1, PMNS2 and PMNS3 catalysts, respectively, when *S* changes from reducing to oxidizing conditions around the stoichiometric point. The reaction temperature was chosen as 450℃ at which the effect of the addition of Mo and Na appeared. All the catalysts have high conversion activity of NO_x when *S* is nearly equal to 1. The NO_x conversion curves are also classified into the three groups described above.

In the first group, the PS and PNS catalysts show poor NO_x conversion activity except for around the stoichiometric point ($S = 1$). This characteristic feature is the same as that of the supported Pt catalysts reported previously 23). It is assumed that NO reductions inhibited by O_2 and CO 31) adsorbed on Pt under lean and rich conditions, respectively.

In the second group, the PMS catalyst has higher NO_x conversion activity than the catalysts of the first group. As shown in Fig. 4, the addition of Mo has the effect of enhancing the NO_x reduction activity under lean and rich conditions compared with the PS and PNS catalysts. Gandhi and Shelef et al. 23～25) had already described similar results in which Mo in $PtMo/Al_2O_3$ and $PdMo/Al_2O_3$ catalysts improved NO_x reduction under slight lean conditions compared with Pt/Al_2O_3 and Pd/Al_2O_3 catalysts.

In the third group, the PMNS1, PMNS2 and PMNS3 catalysts show much higher conversion in $S > 1$, compared with the catalysts without Mo or Na in the first and second groups. As shown in Fig. 4, the conversion of NO_x on the PMNS1, PMNS2

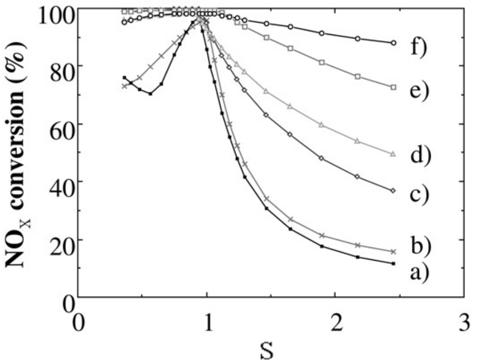

Fig. 4　NO_x conversion efficiency as a function of redox ratio in simulated exhaust for *S*-scan at 450 ˚C. The following catalysts are indicated: a) PS, b) PNS, c) PMS, d) PMNS1, e) PMNS2 and f) PMNS3.

and PMNS3 catalysts under rich, lean and stoichiometric conditions increase with the increasing addition of Na. When 1 wt% Na_2O (PMNS3 catalyst) is added, the conversion of NO_x was over 90 % at $0.36 < S < 2.45$. This result indicates that Na and Mo on a Pt catalyst improves the conversion of NO_x more significantly than Mo on a Pt catalyst. It is suggested that the addition of Mo and Na to a Pt catalysts has the effect of expanding the active S window in which three-way activity occurs, in particular, the window of the conversion of NO_x.

The MS and NS catalysts do not have activity for NO_x reduction when S changes gradually from reducing to oxidizing conditions around the stoichiometric point at 450 ℃.

3．3　Selectivity of NO

NO selectivity, for the selective reduction of NO_x in the presence of excess oxygen, is given by the following expression.

$$NO\ selectivity = \frac{NO\_\ consumption}{NO\_\ consumption + O_2\_\ consumption} \times 100(\%) \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

Fig. 5 shows the NO selectivity in the model gas reaction at 450℃ when S changes from 0.36 to 9.91. In Fig. 5, no symboled line indicates the partial pressure ratio of NO in the inlet NO and O_2 gases. At $S < 1$, the NO selectivity of both PS and PMNS3 is nearly the same as the partial pressure ratio of NO in the inlet NO and O_2 gases. This result indicates that NO functions as an oxidant as dose oxygen at $S < 1$. At $S > 1$, the NO selectivity of PS is less than the partial pressure ratio of NO, while, the NO selectivity of the PMNS3 catalyst is higher than the partial pressure ratio of NO at $S > 1$. Thus, the $PtMoNa/SiO_2$ catalyst has the feature that the reaction in which oxygen participates is inhibited by excess oxygen, so that the reaction in which NO participates as an oxidant proceeds preferentially. The effect of the inhibition of the reaction induced by O_2 is assumed to lead to widening of the S window of NO_x reduction activity around the stoichiometric point and the enhancement of NO_x reduction activity under lean conditions.

3．4　Characterization of catalysts

We examined the oxidation state of Pt on PS, PMS, PMNS2 and PMNS3 catalysts by an IR study using CO as a probe molecule. **Table 2** shows the wavenumbers of the stretching vibration of CO adsorbed on Pt, $\nu(CO_{ads})$, when the catalysts were pretreated

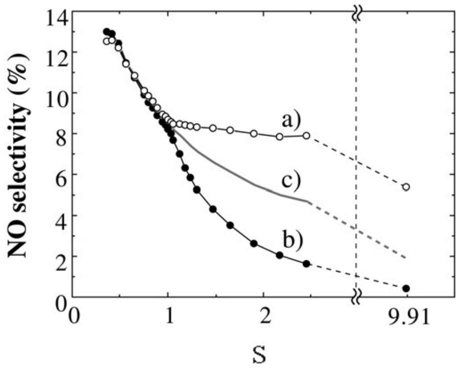

Fig. 5　NO selectivity for NO reduction as a function of redox ratio in simulated exhaust for S-scan at 600 ˚C. The following catalysts are indicated: a) PMN3 and b) PS. C) indicates partial pressure ratio of NO in inlet NO and O_2 gases.

Table 2　The wavenumbers of $\nu(CO_{ads})$.

Catalyst	wavenumbers (cm^{-1}) pretreatment (balance, N_2)		
	O_2	N_2	H_2
PS	2087	2079	2074
PMS	2081	2078	-
PMNS2	2080	2075	-
PMNS3	2079	2075	-

in flowing 7 % O_2/N_2, 100 % N_2 and 7 % H_2/N_2, respectively, before IR measurement. In the measurement of Mo-containing catalysts, the intensity of diffuse reflectance IR was too weak to determine the position of wavenumbers of $\nu(CO_{ads})$. As for the PS catalyst, the positive shift of wavenumbers of $\nu(CO_{ads})$ is large in the order of flow of 7 % O_2 / N_2, 100 % N_2 and 7 % H_2/N_2. These results indicate that Pt exists in a high oxidation state under oxidizing conditions and exists in a low oxidation state under reducing conditions. On the other hand, the PMS, PMNS2 and PMNS3 catalysts have a negative shift compared with the PS catalyst. The difference in wavenumbers in $\nu(CO_{ads})$ on PtMoNa/SiO_2 after N_2 pretreatment and after O_2 pretreatment was less than that on the PS catalyst, and the wavenumbers of $\nu(CO_{ads})$ obtained on the PMS, PMNS2 and PMNS3 catalysts after O_2 pretreatment are similar to that on the PS catalyst after N_2 pretreatment. These results suggest that the electron density of the Pt atoms of PtMoNa/SiO_2 are maintained at a high level even under oxidizing conditions and that oxidation of Pt is inhibited.

Fig. 6 shows the relation between the wavenumbers of $\nu(CO_{ads})$ after O_2 pretreatment and the conversion of NO_x on the PtMoNa/SiO_2 catalyst at 450℃. When *S* is 2.45 and 9.91, the conversion of NO_x at 450℃ becomes higher as the wavenumbers of $\nu(CO_{ads})$ become lower. It is derived from this result that inhibition of the oxidation of Pt on the PtMoNa/SiO_2 catalysts caused increasing NO_x reduction activity.

The study of the oxidation state of Pt by XPS leads to the same conclusion mentioned above. **Fig. 7** shows the XPS spectra in the region of the Pt $4f_{7/2}$ emission band of the Mo-containing catalyst, such as PMS, PMNS2 and PMNS3 catalysts after O_2 pretreatment. The addition of Na causes a negative shift in the Pt $4f_{7/2}$ binding energy of the PtMoNa/SiO_2 catalysts. XPS spectra measured under oxidizing conditions also clarify that Pt on PMNS2 and PMNS3 catalysts is difficult to oxidize even under substantially O_2-rich conditions and the oxidation state of Pt becomes lower with increasing Na content.

Table 3 shows the amount of CO adsorbed

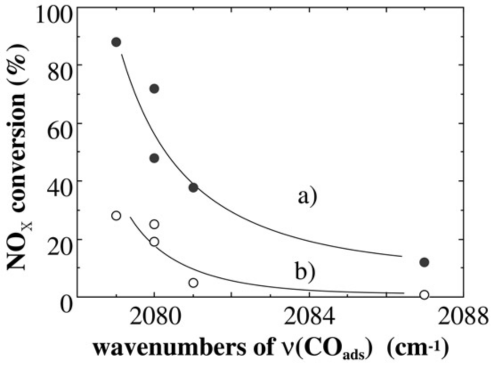

Fig. 6 The relation between the wavenumbers of $\nu(CO_{ads})$ after O_2 pretreatment and NO_x conversion on the PtMoNa/SiO_2 catalyst at 450˚C. The following redox ratio, *S*, are indicated: a) 2.45 (simulated A/F = 15.2) and b) 9.91 (simulated A/F = 18).

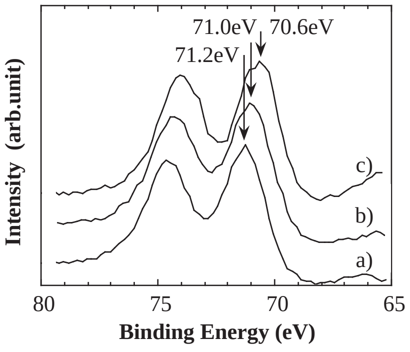

Fig. 7 XPS spectra of Pt 4f after O_2 pretreatment (1 × 10^{-7} torr O_2, 1h). The following catalysts are indicated: a) PMS, b) PMNS2 and c) PMNS3.

on the catalysts under reducing conditions. As for the PS and PNS catalysts, the amount of CO adsorbed on the catalyst is relatively large. This result indicates that a large amount of Pt exists on the surface of the catalyst. On the other hand, the catalysts including only Mo lose their ability to chemisorb CO, and the CO-to-Pt ratio (CO/Pt) becomes lower with increasing Na content, while XRD patterns show no crystalline Pt on the PtMoNa/SiO_2 catalysts in the third group. These results are in agreement with the model that Tri et al.[26] have already reported. As they have pointed out, it seems reasonable to suppose that physical masking around Pt atoms is caused by the Mo atoms deposited on the surface of the Pt atoms under reducing conditions. In addition, EXAFS and XPS analyses of PtMo/SiO_2 catalysts reported by Liu et al.[28] also support this model. In our case, as Na is added to PtMo/SiO_2 catalyst, Na probably assists Mo in masking more widely around the Pt atoms. Such an assumption is supported by the decrease in the amount of adsorbed CO.

3．5 The possible reason for the change in catalytic performance in PtMoNa/SiO_2

Only the Mo-supported catalyst and only the Na-supported catalyst showed no activity for NO_x reduction. Therefore, the active center of PtMoNa/SiO_2 is Pt, which determines the catalytic performance of NO_x reduction. The effect of the addition of Mo and Na is estimated to change the reaction characteristics of the Pt.

From the IR spectra of adsorbed CO and XPS spectra, it is demonstrated that the oxidation state of Pt on PtMoNa/SiO_2 catalysts is lower than that on the PS catalyst, that Na content strongly affects the oxidation state of Pt on PtMoNa/SiO_2 catalysts and that the oxidation state of Pt has a correlation with NO_x reduction activity. Further, the estimation of NO selectivity reveals that the PtMoNa/SiO_2 catalyst has the feature that the reaction in which oxygen participates was inhibited in the presence of excess oxygen.

These results described above can possibly be explained by the assumption that the oxidation of Pt corresponds to the activation of O_2 which leads to the oxidation of NO and reductants such as C_3H_6, CO and H_2. It is assumed that the adsorption or dissociation of O_2 causes oxidation of Pt and that O_2 becomes activated for the oxidation reaction through the adsorption and dissociation. In general, the dissociation rate of adsorbed O_2 is faster than that of adsorbed NO on a Pt surface[32], so that NO is a weaker oxidant than O_2 on the Pt surface and NO functions rather as a reductant and reacts with O_2 to produce NO_2 in the presence of excess oxygen. However, the addition of Mo and Na changes the characteristics of Pt under the conditions where oxygen sufficiently functions as an oxidant, so that the activation of O_2 is inhibited and NO is easily reduced. The reason for this is assumed to be the lower affinity between Pt and oxygen caused by the addition of Mo and Na.

Table 3 Amounts of CO adsorbed on catalysts.

Catalyst	adsorbed CO μmol/g-cat	CO/Pt ratio mol/mol
PS	32.8	38.4
PNS	29.0	33.9
PMS	1.9	2.2
PMNS1	1.5	1.7
PMNS2	0.6	0.7
PMNS3	0.3	0.4

From such structural information on $PtMoNa/SiO_2$ catalysts, it is concluded that a physical masking by Mo and Na exists around Pt, as mentioned before. Cáseres et al. have reported that MoO_3 exists in a poorly dispersed form and has a high reducibility on an SiO_2 support compared with other supports(33).

Perhaps, on the SiO_2 support, MoO_3, which has high reducibility, interacts physically or chemically with Pt and the interaction assisted by the addition of Na affects the electron density of the Pt atoms. As described above, Pt atoms on the $PtMoNa/SiO_2$ catalysts retains a high electron density even under excess oxygen conditions and accordingly resists oxidation. Under such environmental conditions, Pt atoms are assumed to be the active component of the characteristic NO_x selective reduction as described above and previously(35). It is assumed that the reason mentioned above explains not only the reactivity of the $PtMoNa/SiO_2$ but also that of $PtMo/SiO_2$ with alkaline metal additives such as Li and K instead of Na.

4. Conclusions

This paper has described the effects of the addition of Mo, alkaline metals and alkaline earth metals to Pt catalysts on various supports, compared with $PtMo/SiO_2$, $PtNa/SiO_2$ and Pt/SiO_2 catalysts. From the above results, we found that the $PtMo/SiO_2$ catalysts with alkaline metal additives have different characteristics from those of conventional Pt catalyst such as a Pt/SiO_2 catalyst. Some characteristics of $PtMoNa/SiO_2$ are described below.

1) Under lean static conditions, the temperature window of NOx reduction of the $PtMoNa/SiO_2$ is wider than that of the Pt/SiO_2 catalyst.

2) Under nearly stoichiometric condition, the $PtMoNa/SiO_2$ catalysts had wide redox ratio windows of NOx reduction compared with the Pt/SiO_2 catalyst.

3) The $PtMoNa/SiO_2$ catalysts have the reaction feature that NO is used selectively as an oxidant under oxidizing conditions.

4) The interaction of Mo and Na with Pt is assumed to lower the affinity between Pt and oxygen and results in the reaction characteristics of the $PtMoNa/SiO_2$ catalysts.

References

1) Iwamoto, M., et al. : Shokubai (Catalyst), **32**(1990), 430
2) Fujitani, Y., et al. : Jpn. Patent Publ (Kouhou), **63**-100919
3) Held, W., et al. : SAE Tech. Pap. Ser., No.900496, (1990)
4) Sato, S., et al. : Appl. Catal., **70**(1991), L1
5) Matsumoto, S., et al. : Catal. Today, **22**(1994), 127
6) Zhang, G., et al. : Appl. Catal., B: Environmental, **1**(1992), L15
7) Obuchi, A., et al. : Appl. Catal., B: Environmental, **2**(1993), 71
8) Burch, R., et al. : Appl. Catal. B: Environmental, **4**(1994), 65
9) Burch, R and Watling, T. C. : Catal. Lett. **37**(1996), 51
10) Tanaka, T., et al. : Appl. Catal. B:Environmental, **4**(1994), L1
11) Bamwenda, G. R., et al. : Appl. Catal. B: Environmental, **6**(1994), 311
12) Reyes, et al. : Catal. Lett., **37**(1996), 193
13) Engler, B. H., et al. : SAE Tech. Pap. Ser., No.930735 (1993)
14) Echigoya, E. : J. Jpn. Petrol. Inst., **23**(1980) 223
15) Jones, J. H., et al. : Environm. Sci. Tech., **5**(1971), 790
16) Yokota, K., et al. : SAE Tech. Pap. Ser., No.850129 (1985)
17) Takahashi, et al. : Catal. Today, 27(1996), 63
18) Miyoshi, N., et al. : SAE Tech. Pap. Ser., No.950809 (1995)
19) Yermakov, Y. I., et al. : Kinet. Katal., **16**(1975), 816
20) Yermakov, Y. I., et al. : Kinet. Katal., **42**(1976), 73
21) Tri, T. M., et al. : J. Catal., **85**(1984), 244
22) Yermakov, Y. I., et al. : Kinet. Katal. Lett., **2**(1975), 151
23) Gandhi, H. S., et al. in A. T. Bell and L. Hegedus (editors), : CS Symp. Ser. No.178, Catalysis Under Transient
24) Halasz, I., et al. : Appl. Catal. B: Environmental, **2**(1993), 131
25) Hoost, T. E., et al. : Catal. Lett., **38**(1996), 57
26) Tri, T. M., et al. : J. Catal., **79**(1983), 396

27) DeVries, J. E., et al. : J. Catal., 84(1983) 8
28) Liu, T., et al. : J. Catal., 135(1992) 367
29) Tanaka, T., et al. : Chem. Lett., 5(1997), 409
30) Muraki, H., et al. : Ind. Eng. Chem. Prod. Res. Dev., 19(1980), 293
31) Shelef, M. : Catal. Rev., 11(1975), 1
32) Litz, H-G. : Surf. Sci., 108(1981), L486
33) Cáceres, C. V., et al. : J. Catal., 122(1990) 113
34) Tanaka, T., et al. : Appl. Catal. B: Environmental, in press.
35) Yokota. K., et al. : Appl. Sur. Sci., **121/122**(1994), 273

Toshiyuki Tanaka was born in 1964. He received M.E. degree in molecular engineering from Kyoto University in 1990. He belongs to the catalyst Laboratory, where he works on automotive catalyst. He is a member of Catalysis Society of Japan.

Koji Yokota was born in 1953. He was graduated from Nagoya University in 1976. He is a manager of Catalysis Chemistry Laboratory, where he works on automotive catalyst. He is a member of the Chemical Society of Japan, the Japan Petroleum Institute, Catalysis Society of Japan, and Society of Automotive Engineers of Japan.

Masahiro Sugiura was born in 1942. He received Dr. Engineering in Faculty of Engineering From Nagoya University in 1994. He is a manager of Applied Catalysis Division, where he works on automotive catalyst. He is a member of Chemical Society of Japan, Catalysis Society of Japan,.Society of Automotive Engineers of Japan, the Clay Science Society of Japan, the Ceramic Society of Japan, the Japan Society of Adsorption, and the Japanese Society of Diatomology.

Haruo Doi joined Toyota Central R & D Labs. in 1969. He received Dr. Eng. in Applied chemistry from Hokkaido University in 1972. Science 1969 he engaged in the developments of catalysts for purification of NO_x in exhaust gas, and the modification of ceramics by ion implantation, etc. He was a manager of catalysis chemistry and catalyst Labs. between 1989 to 1994. He is a member of the Chemical Society of Japan, Catalysis Society of Japan, Japan Association of Zeolite, The Ceramic Society of Japan, Society of Automotive Engeers of Japan, and The Japan Society of Powder and Powder Metallurgy.

Noritake Isomura was born in 1968. He received M.E. degree in engineering science from Nagoya University. He belongs to Microbeam Analysis Laboratory, where he works on surface and interface analysis. He is a member of the Japan Society of Applied Physics.