[Regular Paper]

NO Storage-reduction Reaction over Pt-Li₂O/TiO₂-Al₂O₃ Catalysts under SO₂-containing Conditions

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The NO storage-reduction properties of 1 wt% Pt-10 wt% Li₂O/TiO₂-Al₂O₃ catalysts prepared by the impregnation and sol-gel methods were investigated in the presence and absence of SO₂. The surface area and NO storage amount of catalysts were smaller for the Pt-Li₂O/TiO₂-Al₂O₃ catalyst than for the Pt-Li₂O/Al₂O₃ catalyst. However, the Pt-Li₂O/TiO₂-Al₂O₃ sample with mixed oxide support achieved high NO removal efficiency for a long period, although the reduction of NO sorption amount by sulfur poisoning was comparable for all catalysts. These results revealed that the mixed oxide support in the catalyst is a key component for continuous NO removal. The preparation method affected the NO storage amount and the crystalline phases of catalysts. The strong diffraction peak of Li₂TiO₃ phase was observed in the XRD pattern of sample prepared by the impregnation method. The formation of Li₂TiO₃ weakened the basicity of the catalyst, resulting in decreased NO storage capacity under a SO₂-free atmosphere and the enhancement of tolerance to sulfur poisoning.

Keywords

Nitrogen oxide storage-reduction, Sulfur poisoning, Platinum lithia catalyst, Diesel engine

1. Introduction

Diesel engines operating in the lean combustion region are one of the most important technologies to improve fuel economy and suppress CO_2 emissions. Harmful exhaust species from these engines are mainly nitrogen oxide (NO_x), carbon monoxide (CO), unburned hydrocarbons (HC), and particulate matter (PM). The exhaust emission regulations for these pollutants have been tightened every year. The conventional threeway catalyst effectively reduces the emission of NO_x, CO, and HC under combustion conditions with air to fuel (A/F) ratios of around 14.7¹). However, the exhaust gas from diesel engines contains several percent of oxygen and the A/F ratio is generally higher than 14.7. Therefore, the NO_x emitted from these engines can not be purified by the three-way catalyst²).

NO_x reduction techniques have been developed by many researchers to reduce NO_x emissions under lean combustion conditions^{3)~22)}. In the middle of the 1990s, the NO_x reduction approach with NO_x storagereduction (NSR) catalysts was first proposed as a promising technology^{3),4)}. This catalyst system consists of precious metals (such as Pt) and basic metal oxides (such as BaO) supported on metal oxides (such as Al₂O₃). In this technology, NO_x reduction is per-

formed by alternating fuel lean and rich conditions. The NO_x oxidized over the precious metal is stored as nitrate ion in the storage materials under oxidizing atmospheres. Subsequently, the trapped NO_x is reduced to N₂ over the precious metal and the catalyst is regenerated during the short period under rich conditions. Relatively high NO_x conversion is achieved with the NSR technique, but high performance of the catalysts must be maintained during cyclic operations for a long time. The storage materials of basic metal oxides in NSR catalysts can absorb NO_x as well as SO_x , which is formed from the oxidation of sulfur species in fuels. Sulfates are more chemically stable than nitrates, resulting in deterioration in NO_x storage capacity $^{14)\sim16)}$. Although the degraded catalysts can be desulfurized by heat-treatment, reactivation at high temperatures also causes sintering resulting in deteriorated catalytic activity¹⁷⁾. Therefore, high tolerance to sulfur poisoning and sintering are essential for NSR catalysts in practical diesel engine applications^{18/ \sim 21).}

Previously, we investigated the effect of basic oxide added to Pt/TiO₂ on the NO sorption capacity and the tolerance to SO₂ poisoning in the presence and absence of SO₂¹⁹⁾. Less amount of NO was absorbed over Pt-Li₂O/TiO₂ catalyst than over other modified catalysts under SO₂-free conditions. However, the NO storage capacity over Pt-Li₂O/TiO₂ remained unchanged in the presence of SO₂, in contrast to remarkable deterioration of activity for other catalysts. Furthermore, the TiO₂

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Fig. 1 Schematic Drawing of the Procedure for Sequential NO Sorption-desorption Tests

support is known to be resistant to sulfur poisoning because of the low stability of sulfate on this material^{22),23)}. In contrast, the NSR catalysts based on Al₂O₃ supports attain relatively high NO_x storage capacity due to the high surface area and thermal stability of the support. The sulfur poisoning, however, is severe for the catalysts based on Al₂O₃ supports.

The present study focused on NSR catalysts consisting of Pt and Li₂O supported on mixed TiO₂ and Al₂O₃, Pt-Li₂O/TiO₂-Al₂O₃. The effect of mixed oxide as a support material on the NO_x storage capacity and the tolerance to sulfur poisoning of catalysts was investigated. Moreover, the catalytic property of samples prepared by different methods was also examined in the absence and presence of SO₂.

2. Experimental

2.1. Catalyst Preparation

The amounts of Pt and Li₂O in the catalysts were fixed at 1 and 10 wt%, respectively. The catalysts of Pt-Li₂O/Al₂O₃, Pt-Li₂O/TiO₂-Al₂O₃ (weight ratio of TiO_2 : $Al_2O_3 = 1 : 1$), and $Pt-Li_2O/TiO_2$ were prepared by the impregnation method, and named PLA(imp), PLTA(imp), and PLT(imp), respectively. Commercial Al₂O₃ (JRC-ALO-8, The Catalysis Society of Japan) and/or TiO₂ (SSP-25, Sakai Chemical Industry Co., Ltd.) were used as support materials for the catalysts. For the PLTA(imp) sample, Al₂O₃ and TiO₂ were mixed with mortar and pestle. The support material was impregnated with solution of Pt(NO₂)₂(NH₃)₂ (Tanaka Kikinzoku Kogyo) and LiNO3 (Wako Pure Chemical Industries, Ltd.). The mixture was kept on a steam bath at 80 °C until the solvent was evaporated. The obtained powder was calcined at 450 °C for 6 h in 20 % H_2/N_2 . Pt-Li₂O/TiO₂-Al₂O₃ (weight ratio of TiO₂ : $Al_2O_3 = 1:1$) catalyst was also fabricated by the sol-gel method, and named PLTA(sol-gel). Aluminum and titanium iso-propoxides (Nakalai Tesque Inc.) were used as starting materials. The alkoxides were mixed

in 2-propanol and stirred thoroughly. The mixed solution of $Pt(NO_2)_2(NH_3)_2$ and $LiNO_3$ was added dropwise to the solution. The resultant gel was heated at 110 °C for 8 h to dryness and calcined at 600 °C for 6 h in 20 % H_2/N_2 .

2. 2. NO Sorption-desorption Test

The catalyst powders were formed into tablets and then pulverized to 7-11 mesh. NO sorption-desorption performance was evaluated with a fixed-bed reactor at 350 °C under atmospheric pressure. The 0.25 g sample was fixed in the quartz tube with 8 mm inner diameter. A gaseous mixture of 800 ppm NO, 10 % O₂, and the balance He was fed for 1 h at a flow rate of 60 mL · min⁻¹ (*W*/*F* = 0.25 g · s · cm⁻³) to examine the NO sorption capacity of catalysts under SO₂-free condition. Gaseous SO₂ was added to the supplied gas at 500 ppm in the case of SO₂-containing condition. Such relatively highly concentrated SO₂ was supplied for acceleration of deactivation.

Cyclic NO sorption-desorption tests were conducted under SO₂-containing conditions. Figure 1 shows the standard procedure for sequential sorption-desorption. A mixture of 800 ppm NO, 500 ppm SO₂, 10 % O₂, and the balance He was supplied for 1 h at 60 mL·min⁻¹ in the sorption process. A 5 % C₃H₈/He mixture was fed for 30 min in the desorption process. Three cycles of sorption-desorption reaction were repeated in a sequence. Heat-treatment was subsequently carried out at 600 $^\circ\!\!\!C$ for 1 h in 5 % H_2/He to remove sulfur species. After that, three cycles were performed again in the next sequence. The NO sorption reaction is expressed as follows; e.g. the second sorption reaction in the first sequence is 1-2nd. Furthermore, the sorptiondesorption characteristics of catalysts were evaluated at 350 °C under low SO₂-containing condition. A mixture of 800 ppm NO, 30 ppm SO₂, 10 % O₂, and the balance He was fed for 1 h in the sorption process and the condition for desorption process was the same as that mentioned above. The sorption-desorption reaction was repeated several times without heat-treatment for removal of sulfur species.

2.3. Characterization

Crystal structure of the catalysts was analyzed by X-ray diffraction (XRD, Rigaku, Ultima IV X-ray diffractometer). The typical working condition was 40 kV and 40 mA with a scanning rate of 2° min⁻¹. The specific surface area was measured by the BET method with N2 adsorption (BEL Japan, Bellsorp-mini II). Prior to the measurement, the sample was heated at 300 °C for 30 min in a vacuum. Temperature programmed desorption (TPD) was measured to study the desorption behavior of sulfur species and the basicity of samples. A weighed amount (0.25 g) of the sample was placed in a fixed-bed reactor. For evaluation of the desorption behavior of sulfur species, the sample was exposed to a gaseous mixture of 500 ppm SO₂, 10 % O₂, and the balance He at 350 $^{\circ}$ C for 3 h, cooled to room temperature, and then heated at 10 $^{\circ}$ C \cdot min⁻¹ up to 900 $^{\circ}$ C in 5 % H₂/He. The basicity of sample was examined as follows: The sample was exposed to 5 % CO₂/He at 100 \degree C for 30 min after heating at 500 \degree C for 30 min in He. Then, the temperature was raised to 800 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C \cdot min⁻¹ in He. The effluent from the reactor in both measurements was analyzed with a quadruple mass spectrometer (ANELVA, M-200QA-M).

3. Results and Discussion

3.1. Effect of Mixed Oxide on the Characteristics of Catalysts

The three types of catalysts with different support materials were prepared by the impregnation method. The XRD patterns of the catalysts calcined at 450 $^\circ C$ in $20 \% H_2/N_2$ are shown in **Fig. 2**. No diffraction lines attributable to platinum species were detected in all the patterns, indicating that the metallic platinum should be highly dispersed on the support materials. The patterns of lithium components were identical to those of Li₂TiO₃ and LiAlO₂, whereas the diffraction peaks of Li2O were not observed. The specific surface area of the catalysts is summarized in **Table 1**. The PLT(imp) catalyst attained the lowest surface area, which corresponded to its high crystallinity observed in Fig. 2. The catalysts with higher Al₂O₃ content possessed higher surface area. Table 1 shows the amount of NO sorption for the three catalysts under the gaseous mixture of 800 ppm NO, 10 % O₂, and the balance He at 350 $^{\circ}$ C. The amount of NO storage was also strongly associated with the support materials. The increase in Al₂O₃ content enhanced the surface area and the NO storage capacity of catalysts. Considering that the platinum and lithium species were highly-dispersed on the support with high surface area, the extent of dispersion was important in NO sorption reaction.

Prior to the evaluation of NO storage capacity of cat-



 (\bigcirc) TiO₂ (anatase), (\diamondsuit) Al₂O₃, (\bigtriangledown) Li₂TiO₃, and (\diamondsuit) LiAlO₂.

Fig. 2 XRD Patterns of PLA, PLTA, and PLT Samples Prepared by the Impregnation Method

 Table 1
 Specific Surface Area and Amount of NO Sorption of PLA, PLTA, and PLT Samples Prepared by the Impregnation Method

Catalyst	Specific surface area [m ² ·g ⁻¹]	Amount of NO sorption $[10^{-4} \text{ mol} \cdot \text{g}^{-1}]$
PLA(imp)	120	3.86
PLTA(imp)	95	2.92
PLT(imp)	58	2.00

alysts under SO₂-containing condition, the desorption behavior of sulfate species absorbed on the catalysts was examined as shown in Fig. 3. TPD measurement was conducted under H₂ after exposure to an oxidizing atmosphere containing SO₂. The formed sulfates were desorbed only as H₂S from the catalysts. A much smaller amount of sulfates was formed over the PLT(imp) catalyst than over the other catalysts due to the stronger acidity of TiO_2 compared to Al_2O_3 . A specific peak was observed at ca. 600 °C for the PLTA(imp) sample. For the PLA(imp) sample, the sulfur species were gradually desorbed, and then a large peak of H₂S formation with a top at *ca*. 740 \degree C was detected. These results clarified that SO₂ was readily absorbed over the catalysts containing Al₂O₃, resulting in the formation of stable sulfates.

The NO sorption-desorption performance of the catalysts in two sequential operations was examined under 500-ppm SO₂-containing atmosphere. Heat-treatment under the reducing atmosphere in the sequential NO sorption-desorption test was conducted at 600 $^{\circ}$ C to remove sulfur species. **Figure 4** shows the NO sorption amounts during the first and third sorption reactions.



Fig. 3 Partial Pressures of H₂S Desorbed over PLA(imp), PLTA(imp), and PLT(imp) Samples under 5 % H₂/He after Exposure to a Gaseous Mixture of 500 ppm SO₂, 10 % O₂, and the Balance He at 350 °C for 3 h



Fig. 4 Amounts of NO Sorption by PLA(imp), PLTA(imp), and PLT(imp) Samples during NO Sorption Reaction in Two Sequences of Three Cycles under 500-ppm SO₂-containing Atmosphere

The sorption amount in the 1-1st operation under SO₂containing condition was lower than that under SO₂free condition for all the catalysts (**Table 1**). SO₂ sorption and the formation of stable sulfates were dominant, resulting in the inhibition of the NO sorption over the catalysts in the presence of SO₂. Note that the amounts of NO sorption in the presence of SO₂ were almost the same for the PLA(imp) and PLTA(imp) samples, although the former catalyst sorbed NO in much larger amount than the latter in the absence of SO₂.



Fig. 5 First NO Detection Times in NO Sorption Reaction over PLA(imp), PLTA(imp), and PLT(imp) Samples during Two Sequences of Three Cycles under 500-ppm SO₂-containing Atmosphere

This result suggests that the addition of TiO₂ to Al₂O₃ support provided positive effect on the NO sorption capacity of the catalysts. The amount of sorbed NO reduced as the number of sorption-desorption cycles increased within each sequence. Thus, the sulfur species were not completely desorbed by switching to the reducing atmosphere for the desorption process, but were continuously accumulated in the catalyst throughout one sequence. The rate of decrease in NO sorption amount from the first to third reactions in each sequence was comparable for all the catalysts. For the PLA(imp) sample, NO sorption capacity was not recovered after heat-treatment at 600 $^\circ$ C between sequences. Considering the desorption behavior of sulfur species over this catalyst in Fig. 3, the accumulated sulfates were scarcely removed at 600 $^{\circ}$ C and thus the NO sorption amount was significantly decreased in the 2-1st operation. In contrast, the other samples achieved partial recovery of NO sorption amount. The duration of NO removal, as well as the NO sorption amount, is important properties for NSR catalysts. The first NO detection time is defined as the time when NO removal fell below 95 % from the start of NO sorption, and is summarized in Fig. 5. The first NO detection time was shortened with the repeated sorption-desorption cycles in each sequence. Heat-treatment between two sequences recovered NO removal for all catalysts, indicating that sulfur poisoning also significantly deteriorated the duration time and NO removal capability. The PLTA(imp) sample was remarkably superior in continuous NO removal to the other catalysts, whereas the first detection time for the PLA(imp) sample was sharply re-



Table 2 Specific Surface Area and Amount of NO Sorption of PLTA Samples in the Presence or Absence of 500 ppm SO₂



(\bigcirc) TiO₂ (anatase), ($\textcircled{\bullet}$) TiO₂ (rutile), ($\textcircled{\bullet}$) Al₂O₃, (\bigtriangledown) Li₂TiO₃, and (\diamondsuit) LiAlO₂.

Fig. 6 XRD Pattern of PLTA Samples Prepared by (a) the Impregnation and (b) the Sol-gel Methods

duced at the 1-2nd operation. Thus, the effect of mixed oxide with TiO_2 and Al_2O_3 as a support material was positively demonstrated in NO storage-reduction operations under SO₂-containing conditions.

3.2. Comparison of the Catalysts Prepared by Different Methods

The influence of preparation method on the property of catalysts was investigated for the 1 wt% Pt-10 wt% $Li_2O/TiO_2-Al_2O_3$ catalyst with a weight ratio of TiO_2 : $Al_2O_3 = 1$: 1, which could continuously sorb NO over the long term under a SO₂-containing atmosphere. The PLTA samples were prepared by the impregnation and sol-gel methods. The amount of NO sorption in the absence and presence of 500 ppm SO₂, and the specific surface area of catalysts are summarized in
 Table 2.
 The NO sorption capacity and the tolerance
 to sulfur poisoning were dependent on the preparation methods, regardless of the small difference in the surface area of the samples. Compared with the PLTA(imp) catalyst, the PLTA(sol-gel) attained the larger amount of NO sorption in the absence of SO₂. However, the coexistence of SO₂ in the reactant gas remarkably degraded the PLTA(sol-gel) catalyst. The crystalline phases of the PLTA catalysts as prepared are shown in the XRD pattern of Fig. 6. The TiO_2 was composed only of anatase phase in PLTA(imp), and anatase and rutile phases in PLTA(sol-gel). Furthermore, the relatively strong diffraction peaks of Li₂TiO₃ phase in the PLTA(imp) sample indicated that the formation of lithium and titanium composite oxide was promoted.



Fig. 7 Partial Pressures of CO₂ Desorbed over PLTA(imp) and PLTA(sol-gel) Samples in He after the Exposure to 5 % CO₂/ He at 100 $^\circ$ C for 30 min

This interpretation is supported by the CO₂ TPD profiles for these two samples shown in **Fig. 7**; the smaller amount of desorbed CO₂ at 600-900 $^{\circ}$ C for PLTA(imp) implied this sample contained a larger amount of Li₂TiO₃ with low basicity. Accordingly, because the reaction of Li₂O and TiO₂ in catalysts weakened the basicity of the samples, the PLTA(imp) catalyst exhibited lower NO storage capacity under the SO₂-free atmosphere and higher tolerance to sulfur poisoning.

3.3. Durability of the Catalyst under SO₂containing Condition

The durability of NO sorption capacity for the sulfurtolerant PLTA(imp) catalyst was examined in seven sequences of cyclic NO sorption-desorption reactions under a 500-ppm SO₂-containing atmosphere. Figure 8 shows the amount of NO sorption during the first and third sorption reactions in the odd-numbered sequences. The NO sorption amount continuously fell with cycles and sequences in the initial five sequences. The platinum and lithium species were agglomerated by heat-treatment at 600 °C because of the calcination temperature of 450 $^{\circ}$ C in the preparation procedure. Heattreatment at 600 $^{\circ}$ C under a reducing atmosphere could recover the NO storage capacity completely in the fifth to seventh sequences due to the removal of sulfur species in the sample, although SO₂ poisoning deteriorated the catalytic activity with subsequent cycles in each



Fig. 8 Amounts of NO Sorption by PLTA(imp) Sample during NO Sorption Reaction in Seven Sequences of Three Cycles under 500-ppm SO₂-containing Atmosphere



 (\bigcirc) TiO₂ (anatase), (\diamondsuit) Al₂O₃, (\bigtriangledown) Li₂TiO₃, and (\diamondsuit) LiAlO₂.

Fig. 9 XRD Pattern of PLTA(imp) Sample (a) before and (b) after Seven Sequences of Three Cyclic Tests

sequence. The XRD patterns of the samples before and after this sequential operation are shown in **Fig. 9**. The peak intensities of Li_2TiO_3 and TiO_2 anatase phases relatively increased and decreased, respectively, compared with the intensities before this operation. This result suggests that the reaction of TiO_2 and Li_2O to form Li_2TiO_3 proceeded during the sequential operation. Consequently, the consumption of strongly-basic Li_2O also should be attributed to the gradual decrease in NO sorption capacity of the catalyst within the initial five sequences.

Nowadays, the desulfurization of fuel has reached high levels due to the severity of exhaust emission regulations, resulting in low SO₂ concentrations in exhaust gas. Therefore, the NO sorption-desorption characteristics of PLTA(imp) were investigated at 350 $^{\circ}$ C by supplying a gaseous mixture of 800 ppm NO, 30 ppm SO₂, 10 % O₂, and the balance He in sorption reaction. The catalyst achieved 80 % of initial NO sorption amount even after 25 cycles in the presence of 30 ppm SO₂, although the amounts of NO sorption decreased by 16-22 % within three cycles in each sequence under 500 ppm SO₂-containing condition as shown in **Fig. 8**. This result indicated the SO₂ concentration in exhaust gas significantly affected the NO sorption capacity of the catalyst, and the PLTA catalyst is expected to exhibit high durability under practical conditions.

4. Conclusions

The NO sorption-desorption reaction over 1 wt% Pt-10 wt% Li2O/TiO2-Al2O3 was investigated to develop sulfur-tolerant NSR catalysts. The addition of TiO₂ to the support material reduced the surface area of the catalyst and suppressed the NO sorption reaction. However, the positive effect of mixed oxide support with TiO₂ and Al₂O₃ on the NO sorption characteristics remarkably appeared during the period of high NO removal efficiency under the SO₂-containing atmosphere; the sample with TiO_2 : Al₂O₃ ratio of 1 : 1 exhibited continuous NO removal for a long period. Furthermore, the formed sulfates could be removed at lower temperature in a reducing atmosphere by using the mixed oxide support, as compared with the Al_2O_3 support. Thus, sintering of the catalyst was expected to be suppressed during the reduction treatment for removal of the sulfur species. When the catalyst was prepared by the impregnation method, the diffraction pattern of the Li₂TiO₃ phase strongly appeared. This sample possessed lower NO storage amount in the absence of SO₂ and higher tolerance to SO₂ compared with the sample prepared from the sol-gel method. As a result, the consumption amount of strongly-basic Li2O by the formation of Li₂TiO₃ should be significantly associated with NO sorption characteristics. Although sulfur poisoning damaged the NO sorption capacity throughout this study, stable performance of the catalyst was achieved during several sequences. Furthermore, the developed catalysts maintained relatively high NO sorption capacity under low SO₂-containing condition. Consequently, this study could demonstrate the potential of Pt-Li₂O/TiO₂-Al₂O₃ system as NSR catalysts for the purification of exhaust gas from diesel engines.

References

- 1) Taylor, K. C., Catal. Rev. Sci. Eng., 35, 457 (1993).
- 2) Frost, J. C., Smedler, G., Catal. Today, 26, 207 (1995).
- Fritz, A., Pitchon, V., Appl. Catal. B: Environment, 13, 1 (1997).
- 4) Shelef, M., Chem. Rev., 95, 209 (1995).
- 5) Bisca, G., Lietti, L., Ramis, G., Berti, F., Appl. Catal. B:

Environment, 18, 1 (1998).

- Burch, R., Breen, J. P., Meunier, F. C., *Appl. Catal. B: Environment*, **39**, 283 (2002).
- Takahashi, N., Shinjoh, H., Iijima, T., Suzuki, T., Yamazaki, K., Yokota, K., Suzuki, H., Miyoshi, N., Matsumoto, S., Tanizawa, T., Tanaka, T., Tateishi, S., Kasahara, K., *Catal. Today*, **27**, 63 (1996).
- 8) Matsumoto, S., *Catal. Today*, **29**, 43 (1996).
- 9) Hodjati, S., Bernhardt, P., Petit, C., Pitchon, V., Kiennemann, A., *Appl. Catal. B: Environment*, **19**, 209 (1998).
- Milt, V. G., Querini, C. A., Miró, E. E., Ulla, M. A., J. Catal., 220, 424 (2003).
- Muncrief, R. L., Kabin, K. S., Harold, M. P., AIChE J., 50, (10), 2526 (2004).
- 12) Kabin, K. S., Muncrief, R. L., Harold, M. P., *Catal. Today*, **96**, 79 (2004).
- Epling, W. S., Parks, J. E., Campbell, G. C., Yezerets, A., Currier, N. W., Campbell, L. E., *Catal. Today*, 96, 21 (2004).

- 14) Engström, P., Amberntsson, A., Skoglundh, M., Fridell, E., Smedler, G., Appl. Catal. B: Environment, 22, L241 (1999).
- Matsumoto, S., Ikeda, Y., Suzuki, H., Ogai, M., Miyoshi, N., Appl. Catal. B: Environment, 25, 115 (2000).
- 16) Sedlmair, Ch., Seshan, K., Jentys, A., Lercher, J. A., Catal. Today, 75, 413 (2002).
- 17) Matsumoto, S., Catal. Today, 90, 183 (2004).
- 18) Huang, H. Y., Long, R. Q., Yang, R. T., Appl. Catal. B: Environment, 33, 127 (2001).
- 19) Yamamoto, K., Kikuchi, R., Takeguchi, T., Eguchi, K., J. Catal., 238, 449 (2006).
- 20) Happel, M., Desikusumastuti, A., Sobota, M., Laurin, M., Libuda, J., J. Phys. Chem. C, 114, 4568 (2010).
- 21) He, J. J., Meng, M., Zou, Z. Q., He, X. X., *Catal. Lett.*, **136**, 234 (2010).
- 22) Chen, Y., Chen, Y., Li, W., Sheng, S., Appl. Catal., 63, 107 (1990).
- 23) Matsuda, S., Kato, A., Appl. Catal., 8, 149 (1983).

要 旨

SO₂共存下における Pt-Li₂O/TiO₂-Al₂O₃触媒の NO 吸蔵還元特性

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1 wt% Pt-10 wt% Li₂O/TiO₂-Al₂O₃触媒を含浸法とゾル-ゲル法 で調製し, TiO₂-Al₂O₃混合担体が NO 吸蔵還元特性に与える影 響を検討した。Pt-Li₂O/TiO₂-Al₂O₃触媒は Pt-Li₂O/Al₂O₃触媒よ りも低い表面積および NO 吸収量を示した。SO₂共存下におけ る NO 吸蔵還元反応では、すべての触媒について NO 吸収量が 低下したが、Pt-Li₂O/TiO₂-Al₂O₃触媒を用いた場合、比較的高 い NO 吸収能が長時間にわたり維持された。この結果より、 TiO₂-Al₂O₃担体は SO₂共存下における継続的な NO 吸収に効果 的であることが明らかとなった。Pt-Li₂O/TiO₂-Al₂O₃触媒につ いて,調製法は NO 吸収量と結晶相に影響を及ぼした。含浸法 で調製した触媒では Li₂TiO₃相の強い回折ピークが認められた。 Li₂TiO₃の生成は触媒の塩基性度を弱め,NO 吸収能の低下と硫 黄成分への被毒耐性の向上をもたらしたと考えられる。

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