Effects of addition of Na and S to alumina catalyst for the selective reduction of nitrogen monoxide with ethene in excess oxygen

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The addition of Na and S into alumina catalysts brought about a decrease in the catalytic activity for the reduction of NO with ethane in excess oxygen. Aluminas containing Na or S in different amounts were subjected to activity tests for the related reactions to elucidate the causes of the suppressive effects of the addition of Na and S on the reduction of NO. The reactions taken as test reactions were the oxidation of NO with oxygen, the reaction of NO_2 with ethene in the absence of oxygen, and the reaction of ethene with oxygen. The addition of Na suppressed the oxidation of NO, and the reaction of NO_2 with ethene to form N_2, but promoted the reaction of ethene with oxygen to a great extent. The addition of Na also caused the formation of NO in the reaction of NO_2 with ethene. The changes which the addition of Na brought about are all unfavorable directions for the reduction of NO. The most important effect of the addition of Na on the decrease in the reduction of NO is suggested to be due to the enhancement of the reaction of ethene with oxygen. The addition of S suppressed the oxidation of NO to a great extent, but did not affect much the reaction of ethene with oxygen. Like the case of the Na addition, the addition of S caused the formation of NO in the reaction of NO_2 with ethene.

KEY WORDS: selective catalytic reduction; nitrogen oxide; nitrogen dioxide; hydrocarbons; Al_2O_3; oxidation of nitrogen oxide to nitrogen dioxide; effects of addition of Na and S to alumina.

1. Introduction

The selective catalytic reduction of NO_x by hydrocarbons (HC) in the presence of excess oxygen (denoted as $NO_x + HC + O_2$) has been attracting much attention for the abatement of nitrogen oxides [1–16]. For this reaction, alumina is proposed to be a potential catalyst [8–16]. However, there are a number of aluminas commercially available. We reported that the catalytic activity of alumina varied with the type of alumina [14]. It is important to find out the reasons why different types of alumina showed different catalytic activities for the reduction of NO. Most of the commercially-available aluminas contain Na and S as impurities in different levels [17]. Nevertheless, the effects of the presence of Na and S in aluminas on the catalytic activity for the reduction of NO have never been studied extensively. The present study aims at elucidating the effects of the addition of Na and S into alumina catalyst.

It is widely accepted that the reduction of NO with hydrocarbons in excess oxygen proceeds by the successive reactions (1) and (2)

$$NO + \tfrac{1}{2}O_2 \longrightarrow NO_2 \qquad (1)$$

$$NO_2 + \text{hydrocarbon} \longrightarrow N_2 + CO_x + H_2O \qquad (2)$$

In addition to reactions (1) and (2), reaction (3) occurs as an undesirable side reaction:

$$\text{hydrocarbon} + O_2 \longrightarrow CO_x + H_2O \qquad (3)$$

In order to clarify the effects of the addition of Na and S to alumina, we prepared aluminas containing different amounts of Na and S, and measured the catalytic activities of these aluminas not only for the reduction of NO with ethane in excess oxygen, but also for the related reactions (1), (2) and (3).

2. Experimental

2.1 Preparation of catalyst

Alumina was prepared from aluminum tri-isopropoxide by hydrolysis with deionized water. Aluminum tri-isopropoxide was purchased from Koujundo Chemical Lab. Co. Ltd. and purified by repeated distillation three times, and poured dropwise into a deionized water kept at 0 °C with vigorous stirring. Aluminum hydroxide was precipitated. The precipitate was filtered and washed thoroughly with deionized water. The resulting material was dried at 120 °C for 24 h, and then calcined at 600 °C for 24 h in air to form alumina which is denoted by ALOA. In ALOA, neither Na nor S was contained, which was confirmed by XRF.

The alumina catalysts containing Na or S were prepared as follows. For alumina containing Na, ALOA was impregnated with an aqueous solution of $NaHCO_3$. The water was removed by evaporation at 50 °C under reduced pressure with a rotary evaporator.

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Then the resulting material was dried at 120 °C in air for 24 h, followed by calcination at 500 °C for 4 h in air. The contents of Na were adjusted to be 0.03, 0.2 and 1.0 wt% by the use of aqueous $NaHCO_3$ of appropriate concentration. For alumina catalysts containing S, ALOA was impregnated with an aqueous solution of $(NH_4)_2SO_4$ by similar procedures. The contents of S were adjusted to be 0.3, 1.0 and 2.0 wt%. The aluminas containing Na or S are denoted as ALOA (Na or S, content of Na or S in wt%), *e.g.* ALOA (Na, 0.03). All catalysts obtained in the form of powder were pressed into pellet followed by crushing and sieving to 30–42 mesh.

2.2 Characterization

The surface areas of the alumina samples calcined were measured by the BET method after calcination at 800 °C for 4 h in air. The contents of Na and S in the samples were determined by XRF. X-ray powder diffraction (XRD) patterns were taken with a Rigaku diffractometer RINT-1200 using monochromatic Cu K_α radiation.

2.3 Reaction procedures

A fixed-bed flow reactor was employed for carrying out the reactions at a W/F of 0.18 g s cm^{-3} (catalyst, 0.40 g; total flow rate, 130 cm^3 min^{-1}) at temperatures ranging from 300 to 800 °C. Prior to use for the reaction, the catalyst was calcined at 800 °C for 4 h in air. The catalyst was placed in a quartz tubing reactor (6 mm i.d.) with quartz wool plugs and heated in an He stream (30 cm^3 min^{-1}) at 300 °C for 0.5 h.

The following reactions were performed: the reduction of NO with ethene in excess oxygen, the oxidation of NO with oxygen, the reaction of NO_2 with ethene in the absence of oxygen, and the oxidation of ethene with oxygen. The compositions of NO, NO_2, O_2 and ethene, when contained, were 1000 ppm, 1000 ppm, 2.0% and 500 ppm, respectively, with all He balance. The outflow gases during reactions, except $NO + O_2$, were analyzed by gas chromatography, two columns packed with 5 Å molecular sieves (3 m; separation for N_2, O_2, CO and NO), and with Porapak Q (3 m; separation for CO_2, C_2H_4 and N_2O) being used. The outflow gas during $NO + O_2$ was analyzed by FTIR.

3. Results and discussion

3.1. Characterization

Table 1 shows the surface area and crystal phase of the doped samples. The surface areas of aluminas containing Na were independent of Na content, while those of aluminas containing S increased slightly with an increase in S content. The XRD patterns of all the samples were almost the same, indicating they are of γ-type.

Table 1
The specific surface areas and crystal phase of various alumina catalysts

Catalyst	Surface area (m^2 g^{-1})	Crystal phase
ALOA	145	γ
Na (0.03 wt%)/ALOA	145	γ
Na (0.2 wt%)/ALOA	144	γ
Na (1 wt%)/ALOA	142	γ
S (0.3 wt%)/ALOA	147	γ
S (1 wt%)/ALOA	152	γ
S (2 wt%)/ALOA	157	γ

3.2. Catalytic properties for the reduction of NO with ethene in excess oxygen

Figure 1 shows the results of the reduction of NO with ethene in excess oxygen over aluminas containing different amounts of Na. The conversions of NO to N_2, and those of ethene to CO and CO_2, are plotted against the reaction temperature in figures 1(a) and (b), respectively. The plots show that the conversions have maxima at the reaction temperature of 550 °C for all catalysts. The maximum conversions decreased with an increase in the amount of Na added to the alumina. It is noted that the maximum conversion decreased by 20% by addition of Na in a small amount of 0.03 wt%, which is the same level of Na contained in a commercial alumina as an impurity.

The conversions of C_2H_4 to CO_x (CO and CO_2) were not affected by Na addition to the alumina. The conversion was slightly lower for Na-free alumina than for Na-added aluminas when the reaction was carried out at 500 °C. The conversion of C_2H_4 to CO_x is the sum of the CO_x formation accompanying the conversion of NO to N_2 (reaction (2)) and the CO_x formation by the reaction of C_2H_4 with oxygen (reaction (3)). Although the conversion of NO to N_2 decreased by addition of Na to the alumina, the conversion of C_2H_4 to CO_x remained almost constant. This indicates that the formation of CO_x due to the reaction of C_2H_4 with oxygen increases by the addition of Na to the alumina.

Figure 2 shows the results of the reduction of NO with ethene in excess oxygen over aluminas containing different amounts of S. The conversions of NO to N_2, and those of ethene to CO and CO_2, are plotted against the reaction temperature in figures 2(a) and (b), respectively. The conversions of NO to N_2 have maxima against the reaction temperature, but the temperatures to give maximum conversions shifted to a higher temperature with the S content. The maximum conversions decreased with the S content.

Unlike the case of Na addition, the conversion of C_2H_4 to CO_x decreased greatly with the S content, which is in contrast to a slight decrease of the conversion when Na was added. One of the factors to decrease the

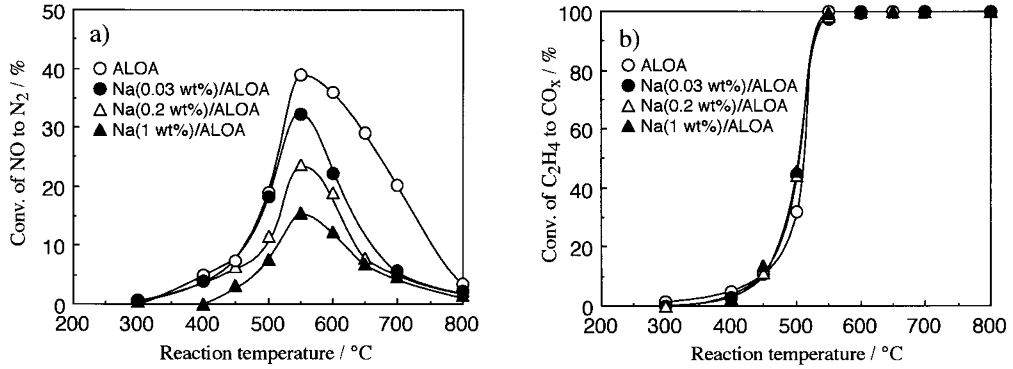

Figure 1. Temperature dependence of the catalytic activity for the reduction of NO with ethene in excess oxygen over the aluminas containing different amounts of Na.

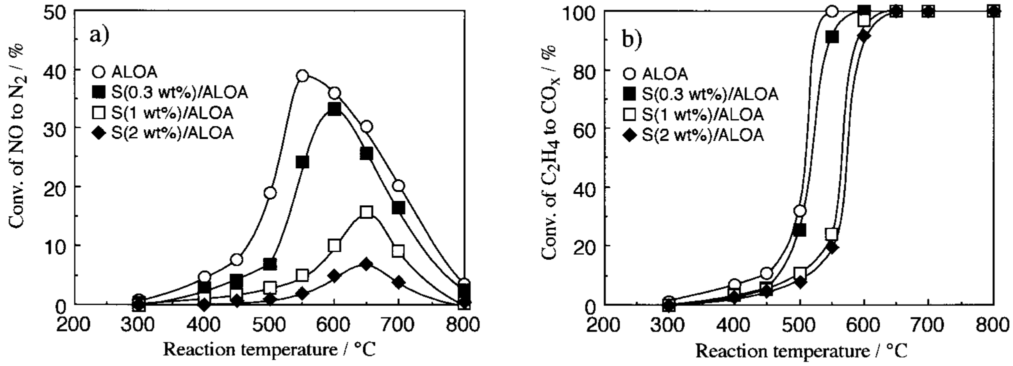

Figure 2. Temperature dependence of the catalytic activity for the reduction of NO with ethene in excess oxygen over the aluminas containing different amounts of S.

conversion of C_2H_4 to CO_x is the decrease in the conversion of NO to N_2 by reaction (2). It is not certain at present whether the change in the activity for reaction (3) contributed to the decrease in the conversion of C_2H_4 to CO_x upon increase in the S content.

3.3. Catalytic properties for the reactions related to the reduction of NO with ethylene

3.3.1. Oxidation of NO with oxygen

The conversions of NO to NO_2 are plotted against the reaction temperature for the aluminas containing Na and the aluminas containing S in figures 3(a) and (b), respectively. The conversions in the blank experiments are also included. The blank experiments were carried out with the reaction in which quartz wool was used instead of catalyst. For both aluminas containing Na and S, the conversions decreased with the contents of Na and S with one exception: the exception was observed for the alumina containing 2 wt% S, whose conversion was slightly higher than that for the alumina containing 1 wt% S at the reaction temperature of 700 °C. In particular, the addition of S to the alumina caused severe deactivation for the conversion of NO with oxygen to NO_2.

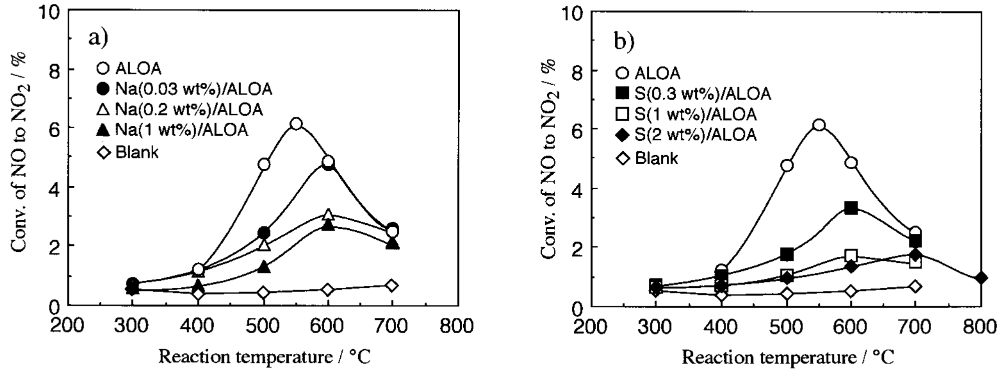

Figure 3. Temperature dependence of the catalytic activity for the oxidation of NO with oxygen to NO_2 over the aluminas containing (a) Na and (b) S.

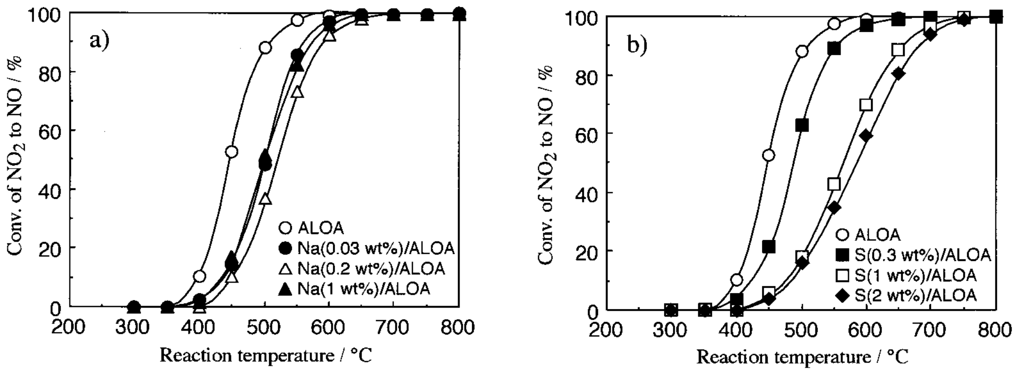

Figure 4. Temperature dependence of the catalytic activity for the decomposition of NO_2 to NO and O_2 over the aluminas containing (a) Na and (b) S.

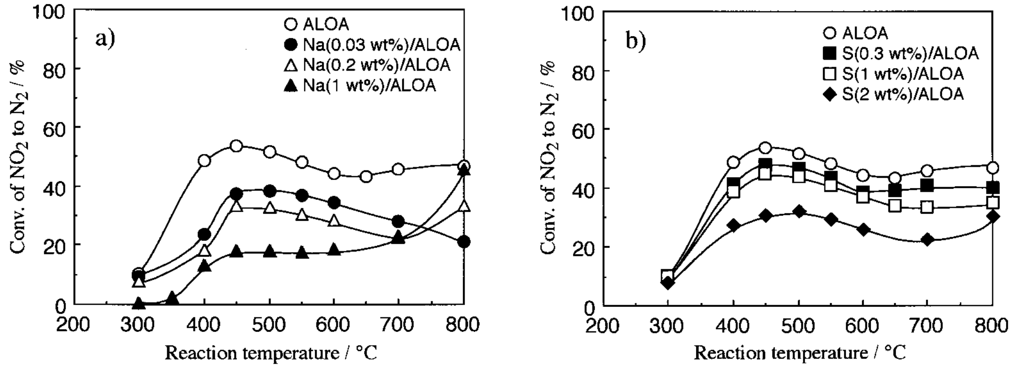

Figure 5. Temperature dependence of the catalytic activity for $NO_2 + C_2H_4$ reaction over the aluminas containing (a) Na and (b) S.

3.3.2. Decomposition of NO_2 to NO and O_2

Since it was shown that the oxidation of NO with oxygen to NO_2 is suppressed by the addition of Na and S to alumina, the reverse reaction of the NO_2 to NO and O_2 is expected to be suppressed by the addition of Na and S. To confirm the effects of the addition of Na and S to alumina, the decomposition of NO_2 was performed, and the results are shown in figure 4, in which the conversions of NO_2 to NO are plotted against the reaction temperature for the aluminas containing Na (figure 4(a)) and for aluminas containing S (figure 4(b)). As expected, both additions of Na and S suppressed the conversion.

3.3.3. Reaction of NO_2 with ethene

The conversions of NO_2 to N_2 are plotted against the reaction temperature for the aluminas containing Na and the alumina containing S in figures 5(a) and (b), respectively. The conversions were suppressed by additions of both Na and S to the alumina. The suppression effect was much stronger with Na than with S.

It should be noted that NO was also formed to a considerable extent in the reaction of NO_2 with ethene for the aluminas containing Na and S. The conversions of NO_2 to NO are plotted against the reaction temperature for the aluminas containing Na and the alumina containing S in figures 6(a) and (b), respectively. In

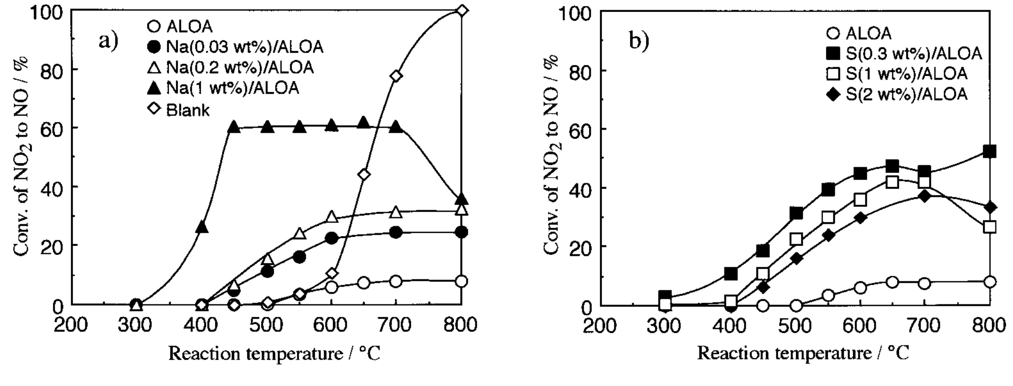

Figure 6. Temperature dependence of the decomposition of NO_2 to NO for $NO_2 + C_2H_4$ reaction over the aluminas containing (a) Na and (b) S.

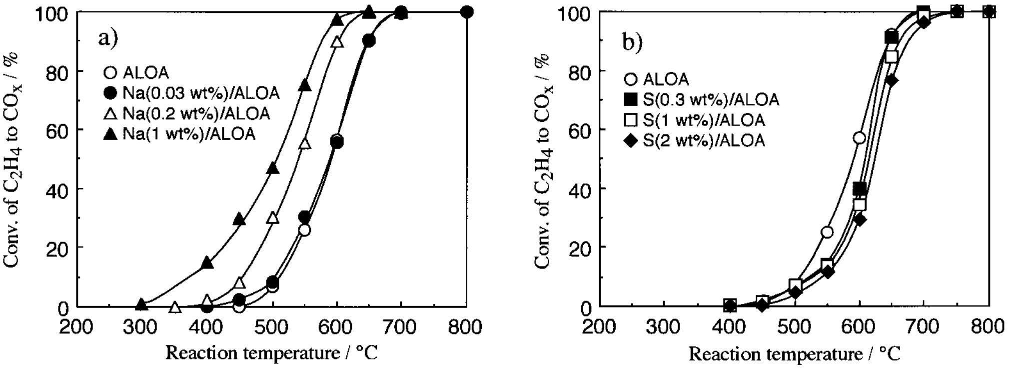

Figure 7. Temperature dependence of the catalytic activity for the oxidation of ethene with oxygen to CO_x over the aluminas containing (a) Na and (b) S.

particular, the alumina containing Na formed a large amount of NO. For the alumina containing Na by 1 wt%, the formation of NO exceeded that of N_2. The formation of NO may result from both the decomposition of NO_2 to NO and O_2 and the reaction of NO_2 with C_2H_4. Considering that the decomposition of NO_2 was suppressed by the addition of Na and S as shown in figure 4, the enhancement of the NO formation in the presence of C_2H_4 for the aluminas containing Na and S should be caused by the enhancement of the reaction of NO with C_2H_4. Ethene is consumed not for the formation of N_2, but for the conversion of NO_2 to NO.

3.3.4. Oxidation of ethene with oxygen

The oxidation of ethene with O_2 to form CO_2 is an undesirable side reaction which consumes ethene without use for the reduction of NO to N_2. The conversions of C_2H_4 to CO_2 are plotted against the reaction temperature for the aluminas containing Na and the alumina containing S in figures 7(a) and (b), respectively. Addition of Na to the alumina resulted in the enhancement of the conversion to CO_x. On the contrary, the addition of S did not affect much; it slightly suppressed the conversion of C_2H_4 to CO_x. It is noted that the addition of Na to the alumina enhanced the oxidation of ethane, but suppressed the oxidation of NO as shown in figure 3, though both reactions are oxidation.

4. Discussion

The addition of Na and S to alumina catalysts brought about a decrease in the activity for the reduction of NO with ethene in excess oxygen. The decrease in the activity is considerable even when the contents of Na and S are at the level of impurity. We have reported that the catalytic activities of aluminas commercially available are greatly different, and the alumina containing lesser amounts of impurity show the highest activity. It is now clear that the presence of Na and S in alumina is responsible for the activity decrease.

The reduction of NO with ethene in excess oxygen is supposed to proceed by the successive reactions of the oxidation of NO to NO_2 and the reaction of NO_2 with ethene to form N_2. Undesirable side reaction of the oxidation of ethene to form CO_2 occurs simultaneously. The effects of the additions of Na and S to the alumina on each of these reactions are as follows.

The addition of Na to the alumina decreases the activities for the oxidation of NO with O_2 to form NO_2, and the reduction of NO_2 with ethene to N_2, but increases the oxidation of ethene to CO_x. In addition, the formation of NO by the reaction of NO_2 with ethene is enhanced. Among these changes in catalytic activities brought by the addition of Na, the enhancement of the oxidation of ethene is most prominent and is considered to affect most strongly the decrease in the activity for the reduction of NO with ethene in excess oxygen.

The addition of S to the alumina decreased the activities for the oxidation of NO with O_2 to form NO_2, and the reduction of NO_2 with ethene to N_2. The formation of NO by the reaction of NO_2 with ethene is enhanced. These effects brought about by the addition of S are the same as those observed for the Na-added aluminas. However, the addition of S does not enhance the oxidation of ethene with oxygen to CO_x. Among these changes in catalytic activities brought about by the addition of S, the suppression of the oxidation of NO to form NO_2 is most prominent and is considered to affect most strongly the decrease in the activity for the reduction of NO with ethene in excess oxygen.

References

[1] M. Iwamoto and H. Yahiro, Catal. Today 22 (1994) 5.
[2] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yuu and N. Mizuno, Appl. Catal. 69 (1991) L15.
[3] S. Sato, Y. Yuu, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal. 70 (1991) L1.
[4] W. Held, A. Koenig, T. Richter and L. Puppe, SAE Paper 900496 (1990).
[5] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 64 (1990) L1.
[6] C. Yokoyama and M. Misono, Catal. Today 22 (1994) 59.

[7] E. Kikuchi and K. Yogo, Catal. Today 22 (1994) 73.

[8] H. Hamada, Catal. Today 22 (1994) 21.

[9] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, Catal. Lett. 6 (1990) 239.

[10] Y. Torikai, H.Yahiro, N. Mizuno and M. Iwamoto, Catal. Lett. 9 (1991) 91.

[11] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 75 (1991) L1.

[12] N. Okazaki, Y. Katoh, Y. Shiina, A. Tada and M. Iwamoto, Chem. Lett. (1997) 889.

[13] N. Okazaki, S. Tsuda, Y. Shiina and A. Tada, Chem. Lett. (1998) 51.

[14] N. Okazaki, Y. Shiina, H.Itoh, A. Tada and M. Iwamoto, Catal. Lett. 49 (1997) 169.

[15] H. Hamada, Y. Kintaichi, M. Tabata, M. Sasaki and T. Ito, Sekiyu Gakkaishi 36 (1993) 149.

[16] H. Hamada, Y. Kintaichi, M. Tabata, M. Sasaki and T. Ito, Chem. Lett. (1991) 2179.

[17] T. Uchijima, *Catal. Sci. Tech.*, Vol. 1, eds. S. Yoshida, N. Takezawa and T. Ono (Kodansha, Tokyo, 1991), p. 393.