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Properties and catalytic activity of NO_X reduction of alumina-titania catalysts prepared by sol-gel method

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The alumina-titania catalysts were prepared from various alumina and titania sources by sol-gel method, which were metal alkoxide and metal alkoxide modified with organic groups. Specific surface area, pore size distribution, solid acidity and catalytic activity of NO reduction for the alumina-titania catalysts depended on the alumina and titania sources. The alumina-titania catalyst prepared from metal alkoxide for alumina source and metal alkoxide modified with organic groups for titania source exhibited higher activity of NO reduction than the other alumina-titania catalysts. Catalytic activity of NO reduction for the alumina-titania catalysts depended on specific surface area and solid acidity. It was suggested that solid acidity of the alumina-titania catalysts depended on the coordination structure of Al atoms and the homogeneity of alumina and titania components.

1. Introduction

Removal of nitrogen oxides emission has become one of the most pressing issues to be solved for environmental protection. Catalytic reduction of nitrogen oxides by hydrocarbons is a promising method for the removal of dilute nitrogen oxides from engine exhausts which contain a significant amount of oxygen [1–9]. The catalysts found so far can be classified into zeolites, noble metals, and metal oxides such as alumina, zirconia, titania and alumina-silica [7]. Zeolite catalysts such as Cu-ZSM-5 show high activity, but low hydrothermal stability. Noble metals such as supported platinum are active at low temperature. Metal oxides catalysts such as alumina-based materials show relatively high activity and durability.

We have reported the effects of starting materials on the catalytic activity and properties of the alumina-zirconia catalysts prepared by sol-gel method [10, 11]. Selective reduction of nitrogen oxide with propylene in oxygen-rich atmosphere on the alumina-zirconia catalyst (denoted as AZ) prepared from ethyl acetoacetate aluminum di-isopropoxide and zirconium tetra-*n*-butoxide was superior to that on the alumina-zirconia catalyst prepared from aluminum tri-*sec*-butoxide and zirconium tetra-*n*-butoxide [10]. Kawabata *et al.* accounted for it as the alumina component and the zirconia component in AZ were mixed homogeneously at the atomic level [11]. On the other hand, it was reported that an alumina-titania catalyst showed higher activity of NO reduction than an alumina-zirconia catalyst in alumina-based materials [7]. Thus we also prepared alumina-titania catalysts by a sol-gel method. In this paper, we report the effects of starting materials on their catalytic activity and properties.

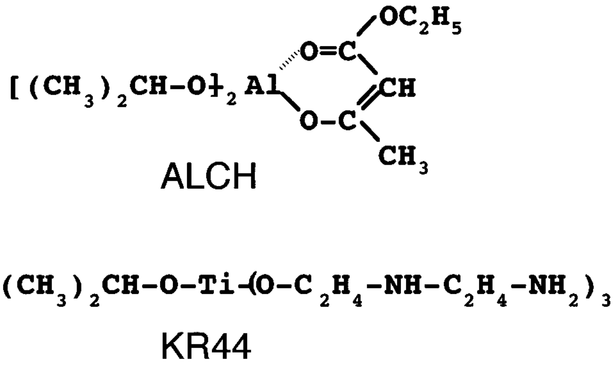
2. Experimental

We used aluminum tri-*sec*-butoxide (denoted as ASBD), ethyl acetoacetate aluminum di-isopropoxide (denoted as ALCH), titanium tetra-isopropoxide (denoted as TIP) and isopropyl tri(*N*-amidoethyl-aminoethyl)titanate (denoted as KR44) for the starting materials of the alumina-titania catalysts. Fig. 1 illustrates the monomeric structure of ALCH and KR44. ALCH and KR44 are metal alkoxides modified with organic groups (denoted as modified metal alkoxide). Mixtures of the starting materials for alumina and titania (0.3 mol in total with a molar ratio of

TABLE I The sample names and starting materials for the alumina-titania catalysts

Sample name		Starting material	
		Alumina	Titania
A	A-series	ASBD	No use
AT		ASBD	TIP
AT*		ASBD	KR44
A*	A*-series	ALCH	No use
A*T		ALCH	TIP
A*T*		ALCH	KR44

ASBD: aluminium tri-*sec*-butoxide.
ALCH: ethyl acetoacetate aluminium diisopropoxide.
TIP: titanium tetra-isopropoxide.
KR44: isopropyl tri(*N*-amidoethyl-aminoethyl)titanate.



$(CH_3)_2CH\text{-}O\text{-}Ti\text{-}(O\text{-}C_2H_4\text{-}NH\text{-}C_2H_4\text{-}NH_2)_3$

Figure 1 Structures of ALCH and KR44.

$Al : Ti = 8 : 1$) were dissolved in 3 mol isopropyl alcohol. The solutions were gelled at 30 °C by the addition of a 9 : 3 molar ratio mixture of distilled water and isopropyl alcohol at a rate of 0.5 ml · s^{-1}. The gels were kept at 50 °C for 12 h in air, dried at 50 °C for 6 h in vacuum, and ground. The alumina-titania catalysts were obtained by heating the dry gels at a rate of 300 °C · h^{-1} up to 700 °C in air and holding at that temperature for 2 h. The alumina catalysts were prepared by the use of ASBD or ALCH for comparison. Table I shows the sample names and the starting materials for the alumina-titania catalysts.

The thermal behavior of the dry gels heated at 110 °C was traced by TG-DTA (Thermal Gravimetry-Differential Thermal Analysis) techniques up to 1000 °C in air with a heating rate of 10 °C · min^{-1}. Nitrogen adsorption isotherms were recorded at 77 K. The samples were outgassed at 200 °C for 4 h to a vacuum of $<10^{-2}$ Pa. Specific surface area (denoted as SSA) was measured with application of the Brunauer-Emmett-Teller (BET) equation; the linear range of the BET equation was usually located between 0.05 and 0.35 P/P_0, taking the area of the nitrogen molecule as 0.162 nm^2. Pore size distribution was derived by the DH (Dollimore-Heal) analysis on the desorption isotherm [12, 13]. The crystalline phases in the heated powders of the alumina-titania catalysts were identified using the X-ray diffraction (XRD) technique with CuK_α radiation. Solid acidity of the alumina-titania catalysts was evaluated from NH_3-TPD (Temperature Programmed Desorption) spectra measured on a conventional apparatus [14]. The samples were dried in vacuo at 500 °C for 1 h, exposed to NH_3 at100 °C for 10 min, and then purged by evacuation at 100 °C for 1 h. TPD was done from 100 to 600 °C with a heating rate of 10 °C · min^{-1} and with helium as the carrier gas. The desorbed species were detected by a mass spectrometer. The amount of acid sites was derived from the amount of desorbed NH_3 using a zeolite (JRC-Z5-25H) as the standard material, offered by Catalysis Society of Japan [15]. ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra were recorded on a spectrometer (CMX-300, CHEMAGNETICS) operating at 78.237 MHz. The samples were spun at up to 11.0 kHz. The signals of 2048 scans were accumulated before Fourier transformation. A 1.0 μs pulse was used with a repetition time of 0.5 s between pulses. The chemical shift values were assigned relative to the reference, $Al(H_2O)_6^{3+}$. The surface morphology of the alumina-titania catalysts was observed under a field emission type scanning electron microscope (FE-SEM). The catalytic reaction was carried out with a fixed-bed flow reactor by passing a gas mixture of 10% O_2-90% N_2 containing 900 ppm NO and 900 ppm propylene at a rate of 1000 cm^3 · min^{-1} over 1 g catalyst. The NO content in the effluent gas was analyzed by chemiluminescence detection method. The catalytic activity for NO reduction was expressed in terms of the fraction of NO conversion.

3. Results

3.1. Thermal gravimetric analysis

Fig. 2 shows TG curves for the dry gels. Weight loss was observed between 100 and 600 °C. It was accompanied by sharp and broad exothermic peaks for AT*, A*T and A*T*, which were due to the combustion of some organic components in the dry gels, whereas no remarkable exothermic peaks were observed for AT. The weight loss for AT, A*T, AT* and A*T* at 1000 °C was 20, 33, 51 and 58% respectively. That is, ALCH is likely to lead to a larger weight loss than ASBD when the same titania source is used for the catalysts.

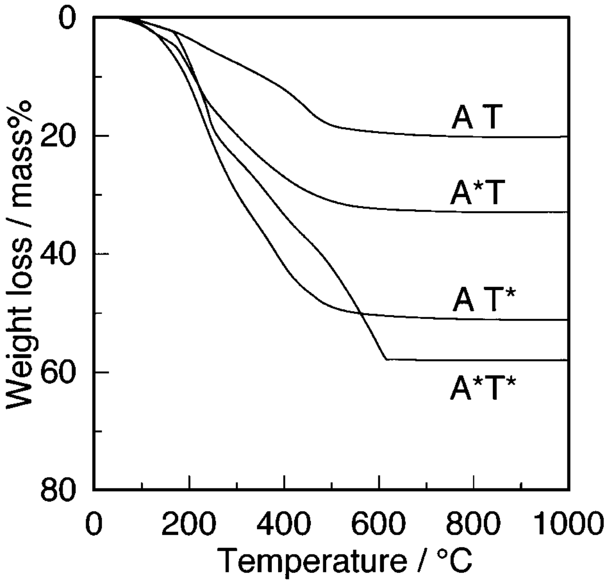


Figure 2 TG curves of the alumina-titania dry gels. Heating: 10 °C · min^{-1} in air. See Table I for sample notation.

Similarly, the weight loss of the alumina-titania dry gels prepared from KR44 was larger than that prepared from TIP when the same alumina source was employed. It follows that the dry gel prepared from the modified metal alkoxides has more amount of organic components than that prepared from the metal alkoxide. That is, some organic components remained in the dry gels prepared from the modified metal alkoxides after hydrolysis and condensation.

3.2. Specific surface area and pore size distribution

Fig. 3 shows the adsorption isotherms of nitrogen gas on the alumina-titania catalysts. The alumina-titania catalysts gave a Type IV isotherm that implies the mesoporous character in BDDT (Brunauer, Deming, Deming, Teller) classification [16]. The adsorption isotherms at $P/P_0 = 0$–0.4 indicated the difference in SSA for the alumina-titania catalysts. A plateau in high pressure ranges and a hysteresis loop on desorption in each curve referred to the difference in the pore size distributions. Fig. 4 shows the pore size distribution as well as the SSA in the range of 170–355 $m^2 \cdot g^{-1}$. For the alumina catalysts (A and A*), A* had a larger SSA than A. Similarly SSA of the alumina-titania catalysts prepared from ALCH (A*-series) was larger than that prepared from ASBD (A-series) when the same titania source was used. One may notice A*T* $<$ A*T and AT $<$ AT* in SSA. Moreover, AT gave smaller SSA than the other alumina-titania catalysts. The results indicated that the modified metal alkoxide results in larger SSA than the metal alkoxide for the alumina source. From the pore size distribution curves, the mesopore size depended on the alumina source: the alumina-titania catalysts prepared from ALCH (A*-series) gave the mesopores in the range of 1–3 nm for pore radius, while those prepared from ASBD (A-series) gave the mesopores in the range of 2–5 nm for pore radius. That is, the modified Al alkoxide (ALCH) gave smaller mesopores than the Al alkoxide (ASBD). It is generally acceptable that smaller pores result in higher SSA. It was thus suggested that smaller pores of A*-series than those of A-series result in higher SSA of A*-series than those of A-series.

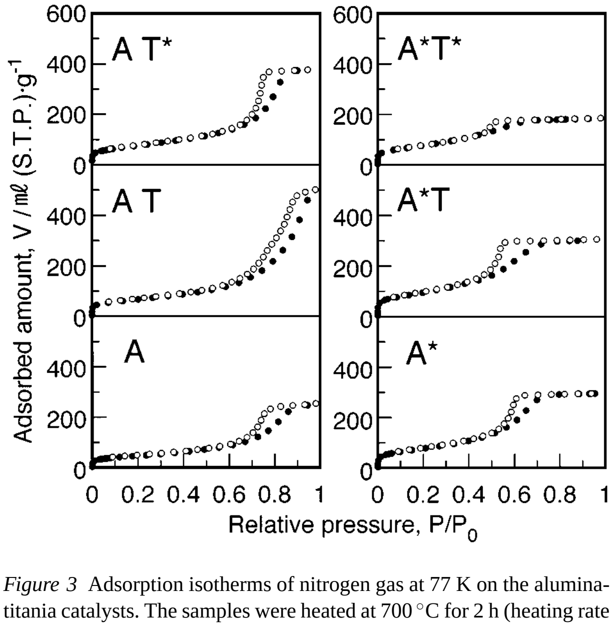


Figure 3 Adsorption isotherms of nitrogen gas at 77 K on the alumina-titania catalysts. The samples were heated at 700 °C for 2 h (heating rate 5 °C · min^{-1}). ●: adsorption, ○: desorption.

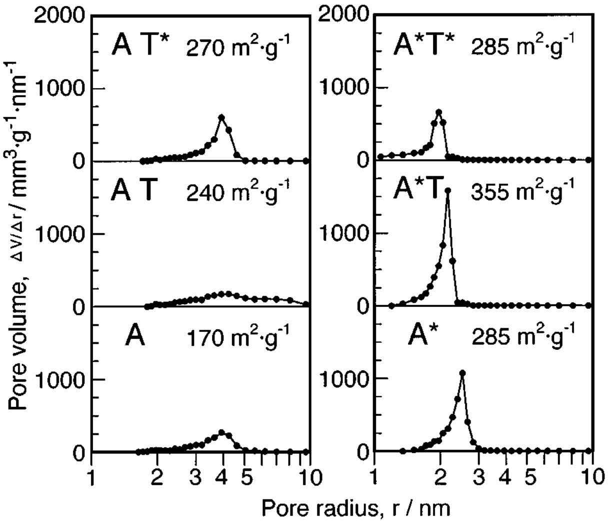


Figure 4 Pore size distribution and specific surface area of the alumina-titania catalysts heated at 700 °C for 2 h.

3.3. Crystalline phase and ^{27}Al MAS-NMR spectra

Table II summarizes the crystalline phases in the alumina-titania catalyst powders after the heat treatment up to 1100 °C. The alumina-titania powders were amorphous in the range of 700–800 °C. AT gave the peaks of rutile TiO_2, whereas the other alumina-titania powders were amorphous after the heat treatment at 900 °C. The all alumina-titania powders gave the peaks of rutile TiO_2 and corundum Al_2O_3 in the range of 1000–1100 °C.

The alumina-titania catalysts heated at 700 °C were investigated by measurement of ^{27}Al MAS-NMR spectra. Fig. 5 shows two signals centered at 0 and 65 ppm, which are assigned to 6- and 4-coordinated aluminum, respectively [17–22]. Another peak was detected for A*T around 30 ppm that may be due to the 5-coordinated aluminum [17–21]. The fraction of 4- and 6-coordinated Al atoms depended on the starting materials for alumina: the fraction of 4-coordinated Al atoms for the alumina-titania catalysts prepared from ASBD (A-series) was slightly larger than those prepared from ALCH (A*-series). The addition of titania component

TABLE II Crystalline phases in the alumina-titania powders

Temperature (°C)	AT	AT*	A*T	A*T*
700	Amorphous	Amorphous	Amorphous	Amorphous
800	Amorphous	Amorphous	Amorphous	Amorphous
900	T_R	Amorphous	Amorphous	Amorphous
1000	T_R, A_α	T_R, A_α	T_R, A_α	T_R, A_α
1100	T_R, A_α	T_R, A_α	T_R, A_α	T_R, A_α

T_R: TiO_2 (Rutile), A_α: α-Al_2O_3 (Corundum).
Heating rate: 5 °C · min^{-1}, holding time: 2 h.

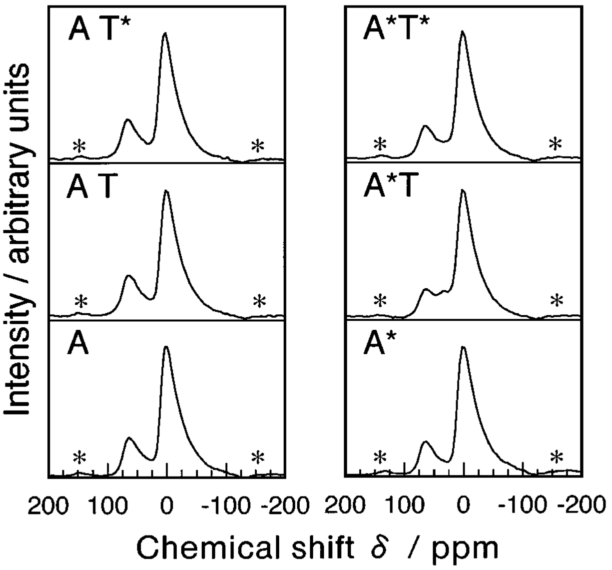


Figure 5 ^{27}Al MAS-NMR spectra of the alumina-titania catalysts heated at 700 °C for 2 h. The asterisk (*) shows spinning side bands.

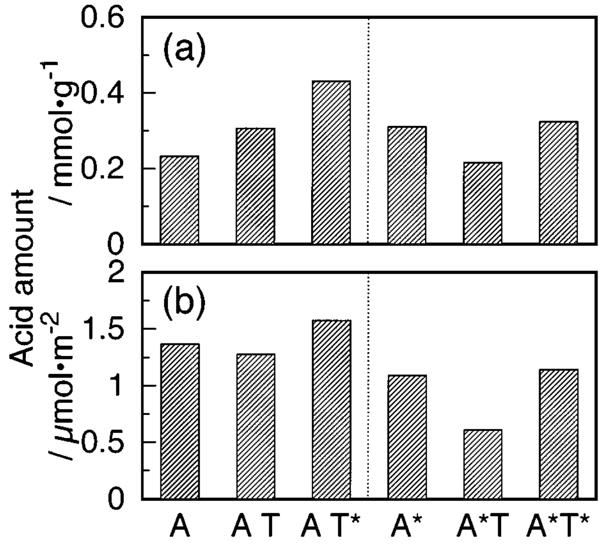


Figure 6 Acid amount of the alumina-titania catalysts heated at 700 °C for 2 h.

and the kind of starting materials for titania did not affect the coordination state of the Al atoms where the starting material for alumina was ASBD (A-series). However, the coordination state of the Al atoms for A*T was different from that for A*T* despite that both were derived from the same alumina source: ALCH (A*-series).

3.4. Solid acidity

Fig. 6 shows the acid amount of the alumina-titania catalysts where it is normalized to unit weight (l g) (Fig. 6a) and to unit area (1 m^2) (Fig. 6b). Each of the acidity parameter is in the ranges of 0.22–0.43 mmol · g^{-1} and 0.6–1.6 μmol · m^{-2}. AT* had higher acidity than the other alumina-titania catalysts. The alumina-titania catalysts prepared from ASBD (A-series) had higher acidity than those prepared from ALCH (A*-series) due to comparison between A and A*, AT and A*T, AT* and A*T*, respectively. In contrast, comparison between AT and AT*, A*T and A*T* shows that the alumina-titania catalysts prepared from KR44 had higher acidity than those prepared from TIP. It is thus indicated that the use of metal alkoxide gave higher acidity than that of modified metal alkoxide for the starting material of alumina, and the use of modified metal alkoxide gave higher acidity than that of metal alkoxide for the starting material of titania.

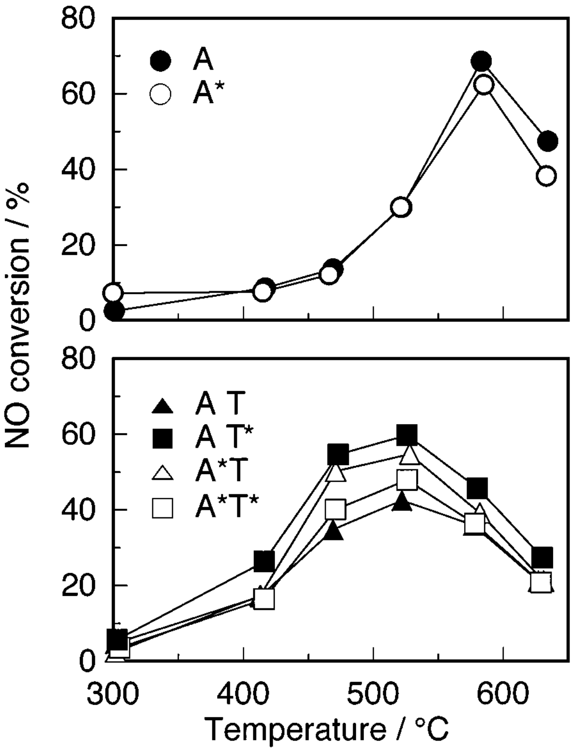


Figure 7 Reduction of NO by propylene over the alumina and the alumina-titania catalysts heated at 700 °C as a function of reaction temperature. Reaction conditions: catalyst weight = 1 g, flow rate = 1000 ml · min^{-1}; feed concentrations, NO = 900 ppm, C_3H_6 = 900 ppm, O_2 = 10%, N_2 = balance.

3.5. Catalytic activity of NO reduction

Fig. 7 shows catalytic activity of NO reduction by propylene on the alumina-titania catalysts. The alumina catalysts (A and A*) showed approximately the same activity in the range of 300–630 °C. The NO conversion for A and A* was only <30% below 500 °C, although A and A* had relatively high activity (>40%) above 550 °C. The alumina-titania catalysts showed higher activity than those alumina catalysts in the practical temperature region. The fraction of NO conversion was more than 40% at 520 °C for the alumina-titania catalysts. The NO conversion for AT, A*T*, A*T and AT* was 43, 48, 55 and 60%, respectively. Catalytic activity of NO reduction for the alumina-titania catalysts thus depended on the alumina and titania sources. AT* had the highest activity among the alumina-titania catalysts.

4. Discussion

4.1. The effects of specific surface area and acidity on catalytic activity of NO reduction

Generally, the increase of SSA may improve the catalytic activity. However, Figs 4 and 7 indicate that the improvement of the catalytic activity is not always

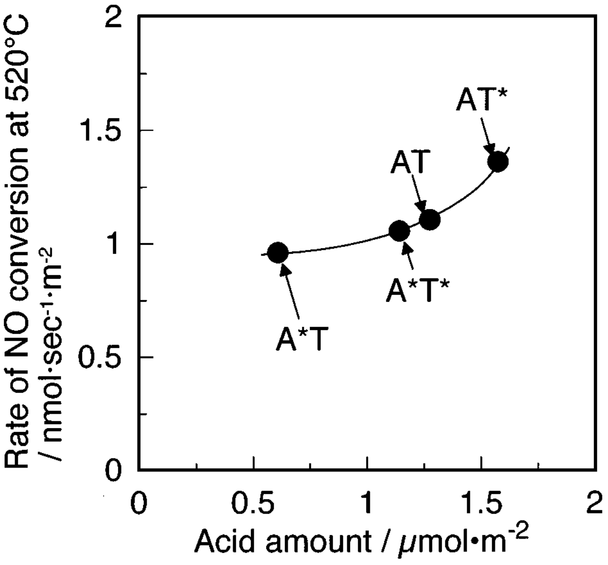


Figure 8 The rate of NO conversion at 520 °C as a function of acid amount of the alumina-titania catalysts.

related to the increase of SSA. Therefore, the difference of catalytic activity for NO reduction can be explained by the effect of not only SSA but a few more factors, like acidity of the catalysts as indicated by Hamada *et al.* [6, 7].

Fig. 8 shows the relation between the rate of NO conversion at 520 °C and the acid amount per 1 m^2 of the alumina-titania catalysts. The rate of NO conversion increased with the increase of the acid amount. We have thus confirmed that the acid amount has a profound effect on the catalytic activity of NO reduction by propylene on the alumina-titania catalysts.

4.2. The effects of the starting materials for alumina and titania on specific surface area and acidity

Fig. 4 suggests that the increase of the SSA by use of modified Al alkoxide (ALCH) depended on the pore size distribution. Fig. 9 shows the scanning electron micrographs of the alumina-titania catalysts. The primary particles in the range of about 10–50 nm in diameter were closely packed for AT*, A*T and A*T*, while the primary particles in the range of about 10–100 nm in diameter were loosely packed for AT. It is considered that mesopore is formed by the space between the primary particles in the range of 1–100 nm in diameter of the catalysts prepared by a sol-gel method [25]. Therefore, it seems that the decrease of mesopore size due to the use of the modified Al alkoxide was caused by the decrease of the primary particle size.

The effects of the starting materials for alumina on acidity are to be discussed. Fig. 6b shows that smaller acid amounts per 1 m^2 resulted from the use of modified Al alkoxide (ALCH), while Fig. 5 shows that the fraction of 4-coordinated Al atoms for the alumina-titania catalysts prepared from ASBD (A-series) was slightly larger than that prepared from ALCH (A*-series). It is

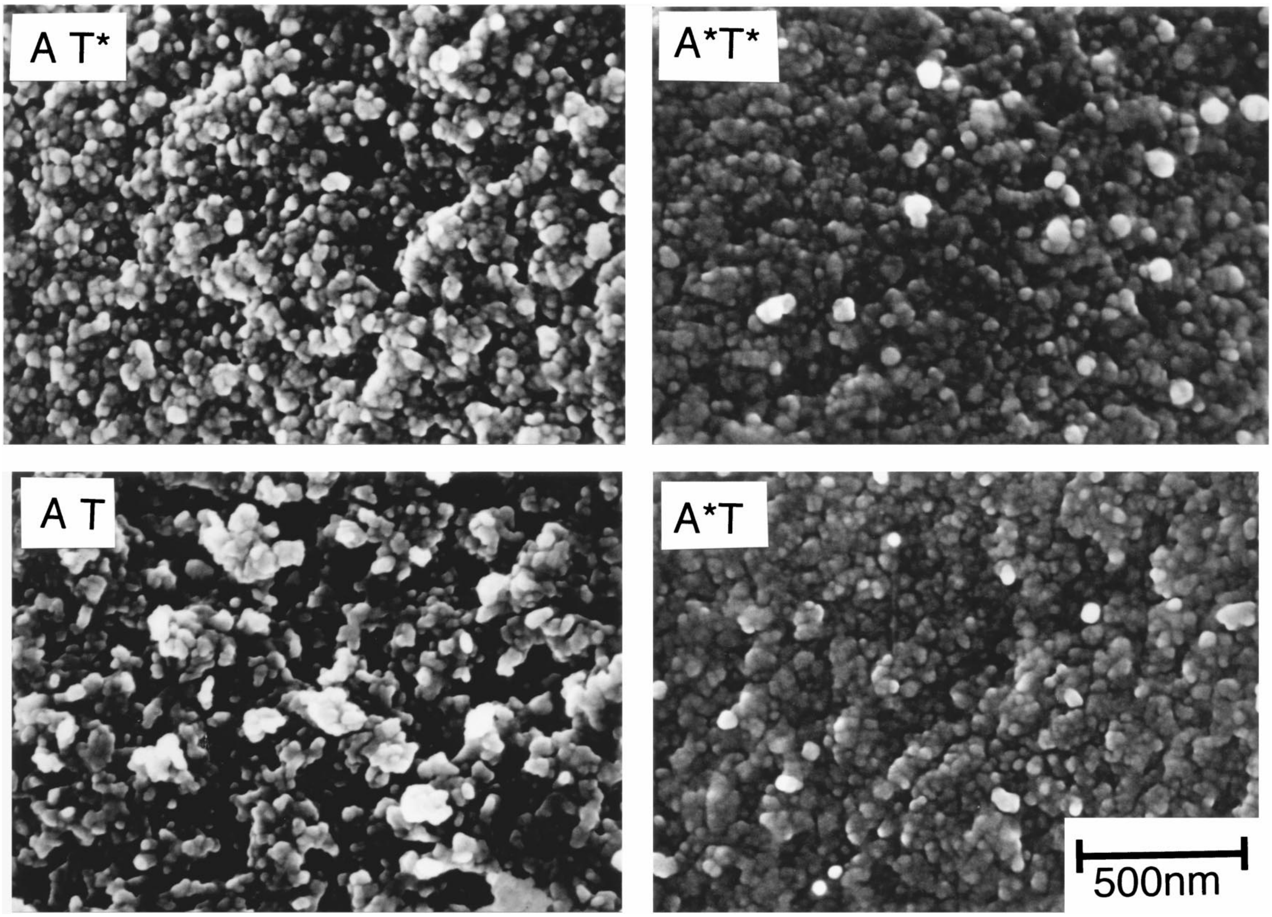


Figure 9 Scanning electron micrographs of the alumina-titania catalysts heated at 700 °C for 2 h.

reported that the acidity of alumina catalysts is related to the coordination state of Al atoms [26]. Therefore, it is considered that the decrease of acid amount by use of ALCH was caused by the change of the coordination state of Al atoms despite that the difference of the acidity among alumina catalysts may be explained by the effects of not only the coordination state of Al atoms but also a few more factors, like the lattice oxygen defects and the atomic configuration of the site, i.e., Al-O distance and O-Al-O angles as proposed by Kawakami *et al*. [26].

Then, the effects of the starting materials for titania on acidity are to be discussed. The acid amount was increased by the use of the modified metal alkoxide for the starting material for titania as compared with the use of the metal alkoxide. As shown in Table II, AT gave the peaks of rutile TiO_2 after the heat treatment at 900 °C, whereas the other alumina-titania catalysts were amorphous. In the case of AT and AT* derived from ASBD for the starting material for alumina, the difference of acid amount between AT and AT* cannot be attributed to the effects of Al coordination structure because both had the same Al coordination distribution. Since titania is precipitated from AT* at a higher temperature than from AT, it is suggested according to Toba [27] that the titania component in AT* was more homogeneously dispersed than in AT. Toba also reported [27] that the amount of "Al-O-Ti" bonds in the alumina-titania systems increases with increase of the homogeneity of each component and that the acid amount increases as a result of the increase of the amount of "Al-O-Ti" bonds. Therefore, one may attribute the greater acid amount for AT* derived from KR44 to the better homogeneity of the titania component than for AT derived from TIP. In the course of gelation, AT passes through the state of a mixture of fine grain aluminium and titanium hydroxides as a result of the different rate of hydrolysis between the metal alkoxides and thus condensation among metal-OH units of a kind. In contrast, AT* gel had better homogeneity. It is accounted for by the effect of the modifying organic component in KR44 that keeps from condensation among the species of a kind. The high homogeneity of alumina and titania in AT* after heating is thus derived from the high homogeneity of the dry gel in AT*.

On the other hand, the fact that the acid amount for A*T* is larger than that for A*T, both from ALCH as the alumina source, cannot be explained by the more homogeneous distribution of the titania component because of the same precipitation temperature of titania as shown in Table II. In this case, as shown in Fig. 5, the coordination state of Al atoms for A*T was different from that for A*T*. It is thus considered that the acid amount of A*T* is higher than that of A*T because of the change of the coordination state of Al atoms between A*T and A*T*.

5. Conclusions

The alumina-titania catalysts were prepared from various alumina and titania sources by sol-gel method, which were metal alkoxide and metal alkoxide modified with organic groups. Specific surface area, pore size distribution, solid acidity and catalytic activity of NO reduction for the alumina-titania catalysts depended on the alumina and titania sources. The alumina-titania catalyst prepared from metal alkoxide for alumina source and metal alkoxide modified with organic groups for titania source exhibited higher activity of NO reduction than the other alumina-titania catalysts. Catalytic activity of NO reduction for the alumina-titania catalysts depended on specific surface area and solid acidity. It was suggested that solid acidity of the alumina-titania catalysts depended on the coordination structure of Al atoms and the homogeneity of alumina and titania components.

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