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Effect of modification by alkali on the γ -Ga₂O₃–Al₂O₃ mixed oxides prepared by the solvothermal method

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Abstract

The solvothermal reaction of the mixtures of aluminium triisopropoxide (AIP) and gallium triacetylacetonate at 300 °C directly yielded γ -Ga₂O₃–Al₂O₃ mixed oxides (solid solutions, but Ga³⁺ ions preferentially occupied the tetrahedral sites of the defect spinel structure). The reaction of AIP alone in 2-(methylamino)ethanol yielded γ -Al₂O₃, and the reaction of the mixture of AIP and Ga(acac)₃ yielded γ -Ga₂O₃–Al₂O₃ mixed oxides having an Al ratio identical to the charged ratio. Although the reaction of AIP alone in toluene at 315 °C yielded χ -Al₂O₃, the reaction at 300 °C gave an amorphous product, while the reaction of Ga(acac)₃ alone afforded γ -Ga₂O₃ at 300 °C. The reaction of the mixtures of the two starting materials yielded the γ -type mixed oxide even with extremely high charged ratio of Al. It was concluded that, in toluene, the initial formation of γ -Ga₂O₃ nuclei controlled the crystal structure of the mixed oxide. The mixed oxide catalysts with lower acid density showed lower methane consumption by combustion in selective catalytic reduction of NO with methane. By alkali modification of the catalyst, the acid density of the mixed oxide decreased, and the CH₄ combustion rate was diminished. Although NO conversion activity was also decreased by the modification, the efficiency of methane used for NO reduction was improved.

1. Introduction

Nitrogen oxides in the exhaust gases from the stationary combustion sources are removed by selective catalytic reduction (SCR) on the V₂O₅/TiO₂-based catalysts with ammonia as the reducing agent [1]. However, because of toxicity and the expensiveness of ammonia, safer and less expensive reducing agents such as hydrocarbons have been sought. Methane is one of the candidates [2–5], because it is the main component of natural gas, an abundant resource, and

a fuel for the power stations. Moreover, excess methane can be removed easily by catalytic combustion even if methane is leaked from the SCR device.

We have been exploring the synthesis of inorganic materials in organic media at temperatures higher than their boiling points. When glycols are used as the reaction medium, the reaction is called ‘glycothermal’ because of the use of glycol in place of water for hydrothermal reaction, and the synthesis of ultrafine particles of various metal oxides has been developed [6–10].

Shimizu *et al* reported that γ -alumina-supported gallium oxide ($\text{Ga}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$) catalyst prepared by the impregnation of a commercial alumina (JRC ALO4) with a gallium nitrate solution showed high activity for the SCR of NO with methane [4, 5]. We have reported that $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide, obtained directly by the glycothermal reaction of the mixtures of aluminium triisopropoxide and gallium triacetylacetonate, exhibited higher activity for this reaction than the catalyst prepared by the conventional method [8]. It was also found that Ga^{3+} ions preferentially occupied the tetrahedral sites in the defect spinel structure of the mixed oxide, while Al^{3+} ions preferentially occupied the octahedral sites. Since the glycothermal reaction of AIP alone afforded the glycol derivative of boehmite (GDB), higher charged ratios of Al resulted in the contamination of the products with GDB, and the actual Al ratio in the mixed oxide was lower than the charged ratio.

A clear relationship between the acid density of the mixed oxide and the ratio of the amount of CH_4 consumed by combustion to the total CH_4 conversion for CH_4 -SCR was found [11]. With the increase in acid density per surface area of the mixed oxide, the CH_4 combustion rate increased. In the present study, synthesis of the $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide using various reaction media and alkali modification of the catalyst was examined in order to reduce the acid density of the catalyst surface.

2. Experimental details

$\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxides were prepared by the solvothermal method. Gallium acetylacetonate ($\text{Ga}(\text{acac})_3$; Mitsuwa Chemical) and an appropriate amount of aluminium triisopropoxide (AIP; Nacalai Tesque) were suspended in 80 ml of an organic solvent (2-(methylamino)ethanol, toluene, diethylenetriamine, triethanolamine, or diethanolamine) in a test tube, serving as an autoclave liner, and the test tube was placed in a 200 ml autoclave. An additional 30 ml of the solvent was placed in the gap between the autoclave wall and the test tube. The autoclave was completely purged with nitrogen, heated to 300 °C at a rate of 2.5 °C min^{-1} , kept at that temperature for 2 h, and cooled down to room temperature. The product was washed with acetone by vigorous mixing and centrifuging, and then air-dried.

Alkali modification was performed by the impregnation method, using an aqueous solution of NaNO_3 or CsNO_3 . The $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide prepared in diethylenetriamine with a charged molar ratio of $\text{Ga}/\text{Al} = 30/70$ (30/70 $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$), which showed the highest NO conversion for CH_4 -SCR of NO, was used.

Catalyst tests for the SCR of NO with methane were carried out in a fixed-bed flow reactor. The mixed oxide in powder form was calcined at 700 °C, tabletted, and pulverized into 10–22 mesh, and 0.50 g of the catalyst was set in the reactor. The catalyst bed was heated to 600 °C in a helium gas flow and held at that temperature for 30 min. Then, the reaction gas, which was composed of 1000 ppm NO, 1000 ppm CH_4 , 6.7% O_2 , and helium balance, was introduced to the catalyst bed at $W/F = 0.3 \text{ g s ml}^{-1}$ ($SV = \sim 11\,000 \text{ h}^{-1}$), and the effluent gases from the reactor were periodically analysed with an on-line gas chromatograph (columns: molecular sieve 5 A at 80 °C; porapak Q at 40 °C) while gradually decreasing the reaction temperature.

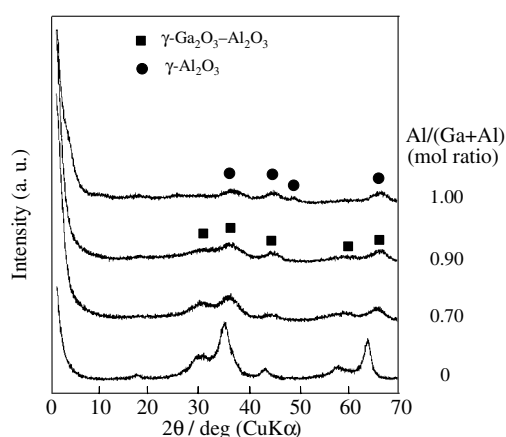


Figure 1. XRD patterns of the products obtained from the reaction of AIP and Ga(acac)₃ in 2-(methylamino)ethanol at 300 °C for 2 h.

Powder x-ray diffraction (XRD) patterns were measured on a Shimadzu XD-D1 diffractometer using Cu K α radiation and a carbon monochromator. The crystallite size was calculated from the half-height width of the (440) diffraction peak of the γ -Ga₂O₃-Al₂O₃ solid solutions using the Scherrer equation. Simultaneous thermogravimetric (TG) and differential thermal (DTA) analyses were performed on a Shimadzu DTG-50 analyser at a heating rate of 10 °C min⁻¹ in a 40 ml min⁻¹ flow of dried air. The morphologies of the samples were observed with a transmission electron microscope (Hitachi, H-9000UHR III). The Brunauer-Emmett-Teller (BET) surface area was calculated using the single-point method on the basis of the nitrogen uptake measured at 77 K. Nitrogen adsorption isotherms were determined using a volumetric gas-sorption system (Yuasa-Ionics, Quantachrome, Autosorb-1). The samples were evacuated at 300 °C for 30 min prior to the measurement. The pore size distribution was calculated using the Barret-Joyner-Halenda (BJH) method with the desorption branch of the isotherm. The chemical composition of the γ -Ga₂O₃-Al₂O₃ solid solution was determined by inductively coupled plasma (ICP) emission spectroscopy (Shimadzu, ICPS1000-III). Temperature-programmed desorption profiles of NH₃ were obtained using a Bel Japan TPD-1-AT apparatus with a Q-Mass detector. The sample was pre-treated in a 50 ml min⁻¹ He flow at 600 °C for 1 h and saturated with 0.1 MPa ammonia at 100 °C for 6 h. After purging ammonia with He for 30 min, the sample was heated to 600 °C at a heating rate of 10 °C min⁻¹ in a He flow, and desorbed NH₃ was analysed.

3. Results and discussion

3.1. Solvothermal synthesis of the γ -Ga₂O₃-Al₂O₃ mixed oxides

The XRD patterns of the products obtained from the reaction of the mixtures of Ga(acac)₃ and AIP in 2-(methylamino)ethanol at 300 °C for 2 h are shown in figure 1. The reaction of AIP alone in 2-(methylamino)ethanol yielded γ -Al₂O₃ with a crystal structure identical to that of γ -Ga₂O₃ obtained from the reaction of Ga(acac)₃ alone. Therefore, γ -Ga₂O₃-Al₂O₃ mixed oxide without contamination of the byproducts was directly obtained even with an extremely high charged Al ratio.

Figure 2 shows the relationship between the charged molar percentage of Ga₂O₃ and the 440 spacing of the mixed oxide synthesized in 2-(methylamino)ethanol. For comparison, data

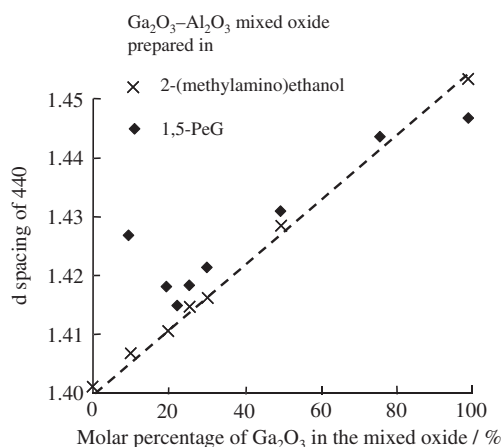


Figure 2. The 440 spacing of the Ga₂O₃-Al₂O₃ binary oxides versus the molar percentage of Ga₂O₃.

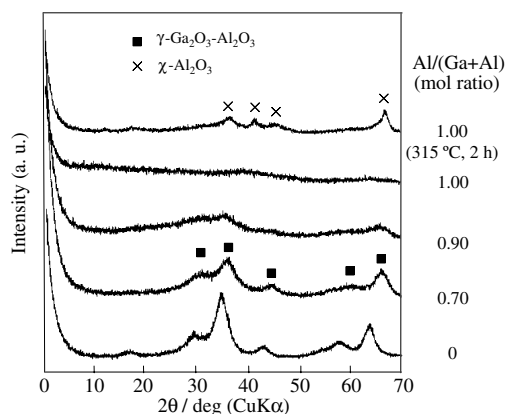


Figure 3. XRD patterns of the products obtained from the reaction of AIP and Ga(acac)₃ in toluene at 300 °C for 2 h.

for the sample obtained in 1,5-pentanediol (1,5-PeG) are also plotted. The broken line in figure 2 represents the ideal 440 spacing of the Ga₂O₃-Al₂O₃ mixed oxides linking between the 440 spacings of γ-Ga₂O₃ and γ-Al₂O₃ (data from JCPDS cards No.20-426 and 10-425, respectively). The 440 spacing of the Ga₂O₃-Al₂O₃ mixed oxides obtained using the glycothermal method was lower than that expected from the charged ratio, indicating that the actual Al ratio of the synthesized mixed oxide was lower than that expected from the Al charged ratio [8]. On the other hand, the 440 spacing of the Ga₂O₃-Al₂O₃ mixed oxides prepared in 2-(methylamino)ethanol was identical with that expected from the charged ratio. Furthermore, with increasing Al ratio, the 440 spacing of the mixed oxides continued to decrease, indicating that the solvothermal reaction in 2-(methylamino)ethanol directly yielded the γ-Ga₂O₃-Al₂O₃ mixed oxide with a molar ratio of Ga/Al identical to the charged ratio.

As shown in figure 3, reaction of AIP alone in toluene at 315 °C for 2 h yielded χ-Al₂O₃ [9, 10] and reaction at 300 °C for 2 h gave an amorphous product, while the reaction of Ga(acac)₃ alone afforded γ-Ga₂O₃. However, the reaction of the mixtures of Ga(acac)₃ and

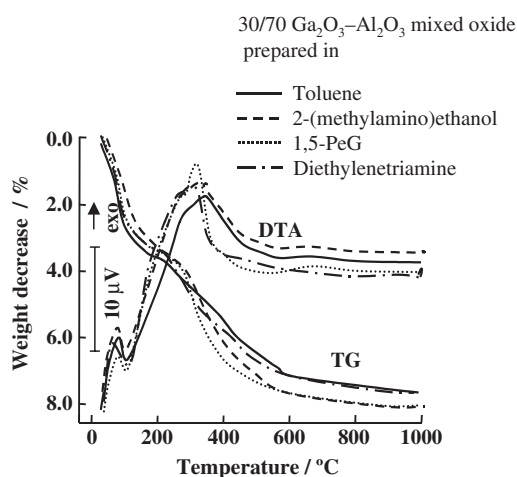


Figure 4. TG-DTA profiles of 30/70 γ -Ga₂O₃-Al₂O₃ synthesized in various reaction media.

AIP in toluene at both 315 and 300 °C for 2 h yielded Ga₂O₃-Al₂O₃ mixed oxide having the γ -type crystal structure. These results suggest that initially formed γ -Ga₂O₃ nuclei controlled the crystal structure of the mixed oxide when toluene was used as a reaction medium.

Although some organic solvents (i.e. diethanolamine, triethanolamine, or diethylenetriamine) gave amorphous products by the reaction of AIP alone, γ -Ga₂O₃-Al₂O₃ mixed oxide was obtained in these solvents (data not shown). These results indicate that, in solvothermal synthesis, the crystal structure of the mixed oxide was controlled by the γ -Ga₂O₃ nuclei. In other words, the reaction media, which afforded γ -Ga₂O₃ in the reaction of Ga(acac)₃ alone, gave γ -Ga₂O₃-Al₂O₃ mixed oxide by the reaction of the mixtures of Ga(acac)₃ and AIP.

3.2. Thermal stability of the mixed oxides

The TG-DTA profiles of Ga₂O₃-Al₂O₃ mixed oxides obtained in various solvents (Ga/Al = 30/70) are shown in figure 4. The weight loss at ~100 °C, accompanied by an endothermic response in DTA, is due to the desorption of physisorbed water and/or organic molecules. The exothermic weight-loss process at 200–400 °C is due to the combustion of the organic moieties remaining on the surface of the product. The profiles of the mixed oxides obtained in various reaction media were essentially identical, and no indication for phase transformation was obtained, indicating that thermal stability of the mixed oxides (Ga/Al = 30/70) was not affected by the reaction media for the solvothermal synthesis. Note that, for a sample with low Al content, a broad exothermic response was observed at 600–900 °C due to the phase transformation from γ -Ga₂O₃ to β -Ga₂O₃ [8].

3.3. The properties of the mixed oxides

Some properties of these mixed oxides are summarized in table 1. The molar content of Ga₂O₃ in the mixed oxide, determined by ICP emission spectroscopy, was essentially identical with charged ratio (Ga/(Ga+Al)), indicating that all the starting materials charged for the solvothermal reaction were precipitated under the reaction conditions. The Ga content determined by XPS was lower than that determined by ICP emission spectroscopy. The Ga concentration in the core of crystals was higher than that in the surface region. This result

Table 1. Some properties of γ -Ga₂O₃-Al₂O₃ mixed oxides prepared by the solvothermal method.

Reaction medium	Molar ratio of Ga/%				Surface area calculated at 700 °C (m ² g ⁻¹)	Crystallite size calculated from XRD (nm)	Particle size calculated surface area (nm)	Mode pore diameter (nm)	Acid amount (μ mol g ⁻¹)	Acid density (μ mol m ⁻²)	Reference
	Charged	Determined by		XRD							
		ICP	XPS								
1,5-pentanediol	100	—	—	γ -type structure	71	—	—	12	—	—	[8]
	75	77	74	γ -type structure	113	—	—	10	111	0.98	[8]
	50	51	—	γ -type structure	144	—	—	8	148	1.03	[8]
	30	26	19	γ -type structure	200	4.8	4.6	7	196	0.98	[8]
	10	10	6	γ -type structure +GDB	157	—	—	7	165	1.05	[8]
	0	—	—	GDB	140	—	—	—	—	—	[6–8]
2-(methylamino)- ethanol	100	—	—	γ -type structure	—	—	—	—	—	—	This work
	30	30	22	γ -type structure	240	3.9	3.6	6	394	1.64	
	10	9	8	γ -type structure	220	—	—	—	370	1.68	
	0	—	—	γ -type structure	201	—	—	—	—	—	
Toulene	100	—	—	γ -type structure	—	—	—	—	—	—	This work
	30	28	21	γ -type structure	184	4.3	4.7	7	236	1.28	
	10	—	—	Amorphous product	173	—	—	—	225	1.30	
	0	—	—	γ -type structure	161	—	—	—	—	—	
Diethanolamine	30	28	22	γ -type structure	251	4.4	4.6	7	331	1.32	This work
Triethanolamine	30	29	22	γ -type structure	216	4.3	5.5	7	292	1.35	This work
Diethylenetriamine	30	29	21	γ -type structure	151	9.5	6.4	12	112	0.74	This work

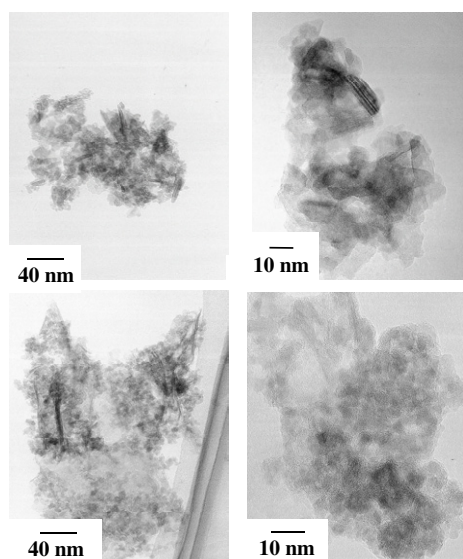


Figure 5. Transmission electron micrograph of the γ -Ga₂O₃-Al₂O₃ sample synthesized in diethylenetriamine (Ga/Al = 30/70; upper), followed by calcination at 700 °C, together with the sample synthesized in 1,5-PeG (Ga/Al = 22/78; lower) [8] for comparison. The average particle size prepared in diethylenetriamine was 9.8 nm, while the crystallite size determined by XRD and the particle size calculated from the surface area are 9.5 and 6.4 nm, respectively.

supports the argument that the initial formation of γ -Ga₂O₃ nuclei controlled the crystal structure of the mixed oxide.

The γ -Ga₂O₃-Al₂O₃ mixed oxides prepared in 2-(methylamino)ethanol had large surface areas and small crystallite sizes. On the other hand, diethylenetriamine gave mixed oxide with a small surface area and large crystallite size. The crystallite size for the γ -Ga₂O₃-Al₂O₃ mixed oxides depends on the reaction medium used for solvothermal synthesis. The particle size calculated from the surface area was approximately identical to the crystallite size calculated from the XRD data by the Scherrer equation, suggesting that the primary particle is a single crystal of the mixed oxide.

3.4. Morphology and pore texture of the mixed oxides

Figure 5 shows the transmission electron microscopy (TEM) images of the 700 °C calcined products obtained in 1,5-PeG (Ga/Al = 22/78) [8] and diethylenetriamine (Ga/Al = 30/70). The primary particles obtained in 1,5-PeG are nearly spherical, while those obtained in diethylenetriamine are rod-shaped. The average sizes of the primary particle were 5.1 and 9.8 nm, respectively, which were essentially identical to the corresponding crystallite sizes of these mixed oxides, as shown in table 1. These results strongly suggest that each primary particle is a single crystal of the mixed oxide. As shown in figure 5, the lattice images were observed clearly. The lattice plane spacing was 2.4 Å, which is in good agreement with the 113 spacing of the mixed oxides (2.4 Å). The lattice fringe of the mixed oxide prepared in diethylenetriamine was observed more clearly than that prepared in 1,5-PeG, indicating that the crystallinity of the former product was higher than that of the latter.

The nitrogen adsorption isotherm and the pore-size distribution of the 30/70 Ga₂O₃-Al₂O₃ sample obtained in diethylenetriamine are shown in figure 6. A hysteresis loop was seen at high

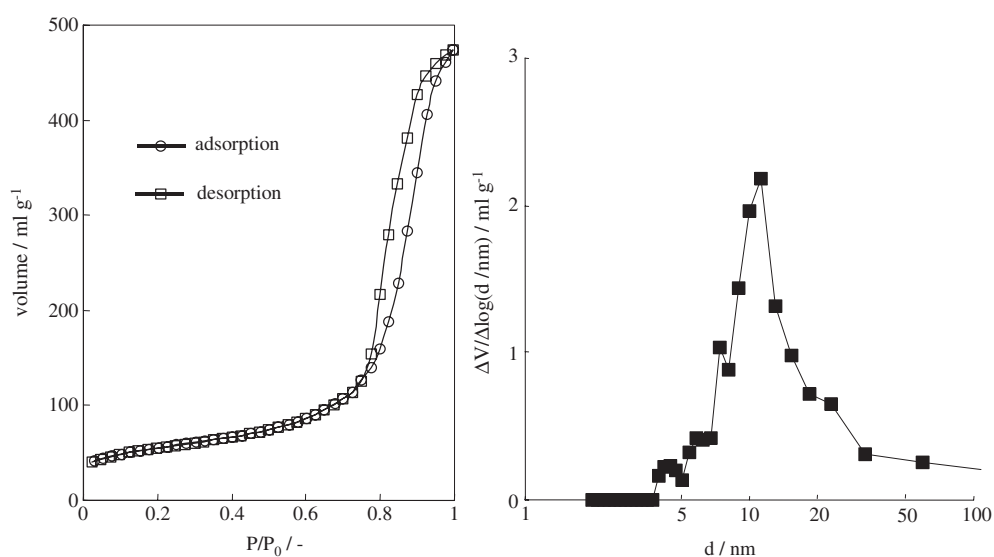


Figure 6. N_2 adsorption isotherm of the 30/70 γ - Ga_2O_3 - Al_2O_3 catalyst prepared in diethylenetriamine, followed by calcination at $700^\circ C$, together with the pore size distribution calculated on the basis of the desorption branch of the N_2 adsorption isotherm.

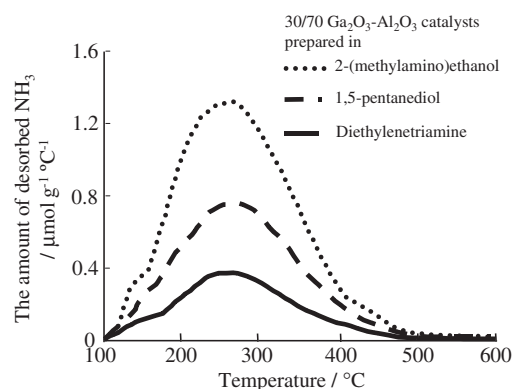


Figure 7. NH_3 -TPD profiles of the mixed oxide catalyst ($Ga/Al = 30/70$) prepared in various reaction media.

relative pressure in the isotherm, suggesting that the product has the mesopore structure. The product exhibited a relatively broad pore-size distribution peak, and the mode pore diameter of the mixed oxide was ~ 12 nm. This size is slightly larger than the crystallite size of the mixed oxide (9.5 nm). As shown in table 1, a similar tendency was also observed for the mixed oxides prepared in the other solvents, and the mode pore diameter of the mixed oxides increased with an increase in the crystallite size of the mixed oxides. Therefore, the mesopores are attributed to the space between loosely coagulated primary particles.

3.5. Acid density of the mixed oxide

As shown in figure 7, the acid strength was essentially identical for all of the catalysts examined. However, the amount of acid, as assessed by the total amount of ammonia desorbed from

Table 2. Results for CH₄-SCR of NO on 30/70 Ga₂O₃-Al₂O₃ mixed oxide prepared in diethylenetriamine. (Reaction conditions: NO, 1000 ppm; CH₄, 1000 ppm; O₂, 6.7%; He balance; W/F = 0.30 g s ml⁻¹)

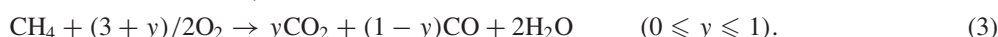
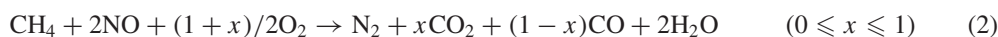
Temperature (°C)	Formation (ppm)				<i>x</i> in equation (1)	<i>y</i> in equation (2)
	N ₂	N ₂ O	CO ₂	CO		
350	91	1	39	50	0.4	—
400	253	3	125	128	0.5	—
450	437	3	428	80	0.82–0.98	0–1.0
500	480	5	708	8	0.98–1	0.97–1.0
550	469	2	1000	0	1.0	1.0
600	401	1	1000	0	1.0	1.0

the catalyst, depended strongly on the medium used for the preparation of the catalyst. It is rather surprising to note that the amount of acid was only slightly affected by the catalyst composition of the mixed oxide (table 1). In the previous paper, we reported that the Fourier transform infrared (FT-IR) spectra of the pyridine that was adsorbed on the catalysts suggested the presence of only Lewis acid sites [6]. The present result implies that the acid sites were created randomly on both the Al and Ga sites.

The amount of acid of the catalyst increased with an increase in the surface area of the catalyst (table 1). Therefore, the acid density on a unit surface area was calculated, and the data are summarized in table 1. For all catalysts listed in the table, the acid density still has a tendency to increase with an increase in the surface area. Since the surface area of the catalyst was inversely correlated with the crystallite size, the result may be interpreted by the fact that the acid density increased with a decrease in the crystallite size. As shown in figure 5, the primary particles of the catalyst with a large surface area (i.e. small crystallite size) were spherical, so the particles should expose high Müller index surfaces. Such surfaces are composed of steps and kinks in the oxygen sublattice. Therefore, the acid sites of the present catalyst system seem to be created at the surface defect sites.

3.6. Stoichiometry

Detailed product distributions for the CH₄-SCR of NO on 30/70 Ga₂O₃-Al₂O₃ prepared in diethylenetriamine are summarized in table 2. The stoichiometry below (equation (1)) was suggested for the SCR of NO with methane in the presence of O₂, based on the fact that the NO conversion rate was four times larger than the CO₂ formation rate at 400 °C [11]. However, taking into account the CO formation, the NO conversion rate was calculated to be two times larger than the CH₄ conversion rate, and therefore it seems to be reasonable that the reaction on the present catalyst system proceeded according to the stoichiometry shown in equations (2) and (3):



Equation (2) represents the SCR of NO with methane, where *x* is the selectivity of methane converted to CO₂ by the reaction with NO. On the other hand, equation (3) shows the consumption of methane by combustion, where *y* is the selectivity to CO₂ formed by methane combustion. With an increase in reaction temperature, the values of *x* and *y* increased. These

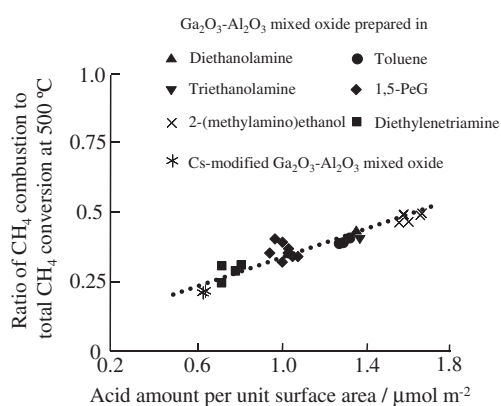


Figure 8. Ratio of CH₄ combustion to total CH₄ conversion versus acid density.

stoichiometries were slightly different from those reported by other researchers on various catalyst systems (Co-ZSM-5 [2], Ga₂O₃/Al₂O₃ [4], Pd/H-ZSM-5 [12], and Ba/MgO [13]). In their reports, the formation of CO was not mentioned, and therefore the equations (2) and (3) with $x = y = 1$ were suggested.

3.7. Effect of acid density on the CH₄ consumption

The relative CH₄ consumption ratio (i.e. the ratio of the amount of CH₄ consumed by combustion to the total CH₄ conversion) was calculated by using equations (2) and (3) and plotted against the acid density. As shown in figure 8, the amount of CH₄ consumption increased with an increase in acid density. These results indicate that Ga₂O₃-Al₂O₃ mixed oxide with a lower acid density showed lower CH₄ combustion activity, and therefore increased the efficiency of methane for the SCR of NO.

3.8. Modification of the catalyst with alkali component

The acid density can be reduced by alkali modification [14–18]. Therefore, we examined the modification of the catalyst (parent catalyst: 30/70 Ga₂O₃-Al₂O₃, prepared in diethylenetriamine) with alkali elements to reduce its acid density and thus increase the methane efficiency.

Some properties of the Na-modified catalysts are summarized in table 3. BET surface areas and crystallite sizes of the catalysts were essentially identical to those of the parent catalyst. The crystal structure was not affected by the alkali modification. With an increase in the amount of alkali, the acid density of the catalyst decreased. However, the catalytic activities were slightly decreased by Na modification. Since the surface properties of alkali-modified catalysts are strongly influenced by the alkali metal modifier [15–20], Cs modification was examined.

Cs modification did not alter the XRD pattern, and no peak shifts were observed, indicating that Cs ions were not incorporated in the spinel structure. Figure 9 shows the results for the SCR of NO with methane on the Cs-modified catalysts. The catalysts showed lower NO conversion to N₂ and CH₄ conversion to CO₂ than the parent catalyst, and both NO conversion and CH₄ conversion decreased with an increase in the amount of Cs modification. However, the extent of the decrease in CH₄ conversion by modification with Cs was much larger than that in NO conversion; efficiency of methane used for the SCR of NO increased and higher CH₄ efficiency was attained using 0.05 wt% Cs/Ga₂O₃-Al₂O₃ catalyst, in which the amount of Cs

Table 3. Some properties of alkali-modified Ga₂O₃-Al₂O₃ mixed oxides.

Catalyst	Alkali loading (wt%)	M ⁺ /acid site	XRD	Surface area calcined at 700 °C (m ² g ⁻¹)	Crystallite size calculated from XRD (nm)	Acid amount (μ mol g ⁻¹)	Acid density (μ mol m ⁻²)	NO conversion at 500 °C ^a (%)	CH ₄ conversion at 500 °C ^a (%)	CH ₄ combustion/total CH ₄ conversion at 500 °C
Ga ₂ O ₃ -Al ₂ O ₃	—	—	γ -type structure	151	9.5	112	0.74	100	75	0.33
Na/Ga ₂ O ₃ -Al ₂ O ₃	0.005	0.5	γ -type structure	150	9.5	110	0.73	95	68	0.30
	0.01	1.0	γ -type structure	150	9.4	106	0.71	90	64	0.30
	0.02	1.5	γ -type structure	148	9.0	100	0.68	80	65	0.38
Cs/Ga ₂ O ₃ -Al ₂ O ₃	0.03	0.5	γ -type structure	150	9.0	95	0.63	84	52	0.21
	0.05	1.0	γ -type structure	145	8.6	90	0.62	82	51	0.20
	0.10	1.5	γ -type structure	142	8.0	80	0.56	45	45	0.50

^a Reaction conditions: NO, 1000 ppm; CH₄, 1000 ppm; O₂, 6.7%; He balance; W/F = 0.30 g s ml⁻¹.

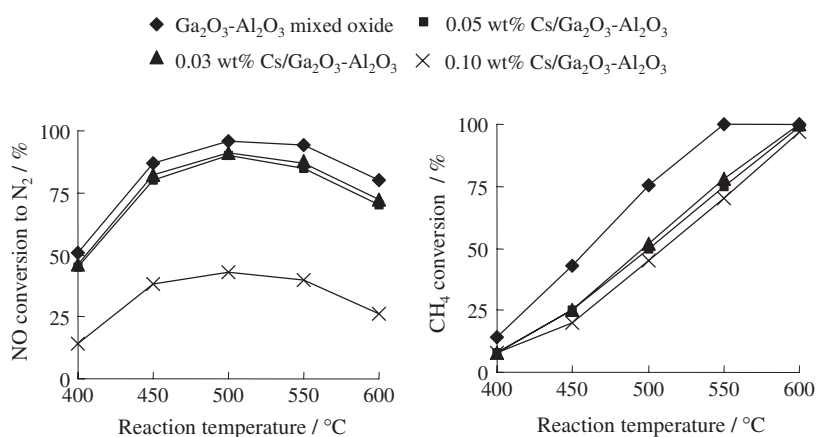


Figure 9. Results for SCR of NO with methane on the Cs-modified Ga₂O₃-Al₂O₃ mixed oxides. Reaction conditions: NO, 1000 ppm; CH₄, 1000 ppm; O₂, 6.7%; He balance; W/F = 0.30 g s ml⁻¹.

was equivalent to the acid density of the parent catalyst. A further increase in the amount of Cs caused an abrupt decrease in NO conversion.

In figure 8, the data for the Cs-modified catalyst are also plotted. Note that a further decrease in the relative CH₄ consumption rate was observed. This result confirmed our previous postulation that the combustion activity of the present catalyst system increased with an increase in the acid density [11]. Choudhary *et al* examined alkali-metal-promoted MgO catalyst for oxidative coupling of methane to C₂ hydrocarbons [15] and found a close relationship between the surface density of strong basic sites and C₂ hydrocarbon formation rate per surface area, strong acid sites preferring the formation of CO₂ over C₂ hydrocarbons. Their findings somewhat resemble the present results for the relationship between the acid density and the total-oxidation activity. Lisi *et al* reported a deactivating effect of alkali metal modification on the NO conversion of the commercial catalysts for NH₃-SCR [18]. A decrease in NO conversion on alkali modification was also observed in the present study. However, alkali modification caused a larger decrease in CH₄ conversion than the decrease in NO conversion, and the efficiency of methane used for this reaction increased on modification with an adequate amount of alkali.

4. Conclusion

The γ -Ga₂O₃-Al₂O₃ mixed oxides with various crystallite sizes were obtained using the solvothermal method. In this reaction, the initial formation of γ -Ga₂O₃ nuclei controlled the crystal structure of the mixed oxide. The mixed oxides were composed of nanoparticles with a mesopore system between the primary particles. The particle size of the mixed oxide depended on the organic medium used as the solvent, while the thermal stability of the mixed oxide (Ga/Al = 30/70) was independent of the reaction media. The primary particle is a single crystal of the mixed oxide. Acid sites of the mixed oxides seem to be created at the surface defect sites. A de-NO_x reaction with methane on the present catalyst system proceeded competitively according to the stoichiometry shown by equations (2) and (3).

The mixed oxide with a lower acid density showed a higher efficiency of methane used for the SCR of NO. The acid density was reduced by alkali modification. The alkali-modified mixed oxide catalyst showed higher methane efficiency than the parent catalyst, although activity for the SCR of NO was also decreased.

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