[Review Paper]

Solvothermal Synthesis of Inorganic Materials and Their Performance as Catalysts

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The synthesis of inorganic materials was investigated in organic solvents at temperatures (200–300°C) higher than their boiling points (solvothermal method), and various inorganic materials were directly obtained. The solvothermal products had high surface areas, superior thermal stabilities, and characteristic morphologies as well as unique surface properties with high potential for catalytic applications. Here, two recent studies on catalytic applications of nanocrystalline mixed oxides synthesized by the solvothermal method are reviewed. First, the solvothermal synthesis of gamma-type $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ solid solutions and their activities for selective catalytic reduction of NO using methane as a reducing agent are described. $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ catalyst prepared in diethylenetriamine exhibited quite high activity for this reaction. The physicochemical properties of the catalysts as well as the active sites for this reaction are discussed. Second, the synthesis of nanocrystalline silica-modified titanias with large surface areas and high thermal stabilities by the glycolthermal treatment of the mixture of titanium tetraisopropoxide and tetraethyl orthosilicate in 1,4-butanediol is described. The products were characterized by several techniques and the origin of the thermal stability of the products is discussed. The recovery of silica-modified titania particles as xerogels by flash evaporation of the reaction medium after the glycolthermal reaction is described. Photocatalytic activities of the products under UV light irradiation and the visible light responsive photocatalytic activity of N-doped silica-modified titanias are also discussed.

Keywords

Solvothermal synthesis, Alumina-galia solid solution, Nitric oxide selective reduction, Silica-modified titania, Thermal stability, Photocatalyst

1. Introduction

Inorganic nanomaterials have become important in various scientific fields because of their potential applications such as catalysis, electronics, optics, and ceramics. Consequently, the development of techniques for the preparation of inorganic materials/nanoparticles with desired shapes, sizes, and forms is of great importance. Conventional procedures for the fabrication of various ceramic materials are based on solid state reactions of suitable precursors at high temperatures, which usually provide products consisting of aggregated particles, with quite low surface areas and pore volumes. Liquid phase syntheses are preferred for the preparation of inorganic materials with well-defined morphologies and smaller particle sizes. Hydrothermal synthesis is the most common technique, in which high temperature water acts as the transfer medium of heat, as the solvent which dissolves or precipitates the solid materials, and as a reagent (mineralizer). Various other substances

are also used as reaction media. Generally, these processes are known as ‘solvothermal methods.’ The prefix, ‘solvo-’ indicates any type of solvent including water, aqueous alkali or acid solutions, inorganic liquids including NH_3 , HF and CO_2 , and various organic solvents. In this sense, the hydrothermal technique is one type of solvothermal process, and can be regarded as a special case with water solvent.

In the last two decades, however, thermal reaction in organic solvents has been attracting increasing interest in the fields of inorganic synthesis and material science^{1)–4)}. This synthetic technique can be carried out under relatively mild conditions, and is often compared with the hydrothermal reaction. In the present paper, ‘solvothermal’ will be used to describe reaction in organic solvents.

The synthesis of inorganic materials has been explored in organic media at high temperatures (200–300°C) under the autogenous pressure of the organic media since 1984⁵⁾. Some oxides such as α -alumina can be crystallized in glycols at temperatures lower than that required by the hydrothermal reaction⁶⁾. This method is termed ‘glycolthermal’ because glycols are used in

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place of water for the hydrothermal reaction^(6),7). Various single oxides and mixed oxides were directly obtained by the glycothermal method in 1,4-butanediol (1,4-BG) at 200–300°C^(8)~21). Crystalline products were synthesized by the solvothermal reaction of appropriate starting materials in suitable organic media other than glycols^(22)~31). Reaction mechanisms and the effects of starting materials and solvents were discussed previously^(4),17),32),33). Products from solvothermal synthesis have large surface areas, unique morphologies and specific surface properties; therefore they show superior catalytic performances, for example, in partial oxidation or autothermal reforming of methane^(34),35), steam reforming of methanol⁽³⁶⁾, synthesis of carbon nanotubes by methane decomposition^(37)~40), and photocatalytic reactions^(27)~29),41).

Here, two recent studies on catalytic applications of solvothermally obtained products are described: the solvothermal synthesis of γ -type $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ solid solutions for selective catalytic reduction (SCR) of NO using methane^(21),42)~46), and the glycothermal synthesis of silica-modified titanias for photocatalytic applications^(47)~56).

2. Solvothermal Synthesis of $\gamma\text{-Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ Solid Solutions and Their Catalytic Performance for SCR of NO with Methane

Nitrogen oxides in the exhaust gases of stationary combustion sources are now removed by SCR over $\text{V}_2\text{O}_5/\text{TiO}_2$ -based catalysts with ammonia as the reducing agent⁽⁵⁷⁾. However, ammonia is toxic and expensive, and therefore, safer and less expensive reducing agents such as hydrocarbons are desirable. Methane is one of the candidates^(58)~64), because it is the main component of natural gas, an abundant resource, as well as a fuel for power stations. Ga-containing zeolite catalysts are active for NO_x removal using hydrocarbons as reducing agents^(62),63). Previously, it was reported that γ -alumina-supported gallium oxide catalyst ($\text{Ga}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$) prepared by the impregnation of $\gamma\text{-Al}_2\text{O}_3$ (JRC-ALO-4) with gallium nitrate showed high activity for the SCR of NO_x with methane^(58),59). $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ catalysts prepared by a sol-gel method also exhibited high activities for SCR of NO with propene⁽⁶⁴⁾.

We found that the glycothermal reaction of mixtures of gallium acetylacetonate ($\text{Ga}(\text{acac})_3$) and aluminum isopropoxide (AIP) yielded $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ binary oxides with a gamma-type defect spinel structure⁽⁴²⁾. Here, solvothermal synthesis of $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ mixed oxides in various organic media and their catalytic activities for selective catalytic reduction of NO with methane are described.

2.1. Procedure for Catalyst Preparation

Appropriate amounts of $\text{Ga}(\text{acac})_3$ and AIP were suspended in 80 ml of an organic solvent, for example

Fig. 1 Powder X-ray Diffraction Patterns of the Products Obtained by Reaction of Aluminum Triisopropoxide (AIP) and Gallium Acetylacetonate ($\text{Ga}(\text{acac})_3$) in 1,5-Pentandiol (1,5-PeG) at 300°C for 2 h

1,5-pentandiol (1,5-PeG), in a test tube, 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 the desired temperature (usually 300°C) at a rate of 2.5°C/min, and held at that temperature for 2 h. After the assembly was cooled, the solid product was washed with acetone by vigorous mixing and centrifuging, and then air-dried.

2.2. Synthesis of $\text{Al}_2\text{O}_3\text{--Ga}_2\text{O}_3$ in 1,5-PeG

The glycothermal reaction of $\text{Ga}(\text{acac})_3$ alone afforded $\gamma\text{-Ga}_2\text{O}_3$ ⁽¹⁷⁾, whereas the reaction of AIP alone yielded the glycol derivative of boehmite (GDB; $\text{AlO}(\text{OH})_x(\text{O}(\text{CH}_2)_n\text{OH})_{1-x}$)⁽⁶⁵⁾. The X-ray diffraction (XRD) patterns of the products obtained by the reaction of the mixtures of these two materials in 1,5-PeG at 300°C for 2 h are shown in **Fig. 1**. With low Al content, $\text{Al}/(\text{Ga}+\text{Al})$, in the starting mixture, the XRD patterns of the products were essentially identical to that of $\gamma\text{-Ga}_2\text{O}_3$. With higher Al content, the diffraction peaks gradually shifted to the higher angle side, indicating that $\gamma\text{-Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ solid solution was directly obtained by the glycothermal reaction. With $\text{Al}/(\text{Ga}+\text{Al})$ charged ratio higher than 0.80, GDB and boehmite (AlOOH) were formed as by-products. The diffraction peaks of the $\gamma\text{-Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ solid solution shifted to the lower angle side, suggesting that at $\text{Al}/(\text{Ga}+\text{Al}) > 0.80$, the Al content in the $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ solid solution decreased despite the $\text{Al}/(\text{Ga}+\text{Al})$ charged ratio. **Figure 2** shows the relationship between the charged ratio of Al and the 440 spacing of the solid solution synthesized in

Fig. 2 440 Spacing of the $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ Binary Oxides vs. the Al Charged Ratio

1,5-PeG. The maximum 440 spacing occurred at $\text{Al}/(\text{Ga}+\text{Al})=0.778$, indicating that formation of GDB became predominant as Al content in the starting mixture exceeded this value. The broken line in **Fig. 2** represents the theoretical 440 spacing of the $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solution, linking the 440 spacings of $\gamma\text{-Ga}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ (data from JCPDS cards nos. 20-426 and 10-425, respectively). The plot of d spacing of the $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solution obtained by the glycothermal method was lower than the theoretical d spacing line, indicating that the solid solution had an Al content lower than the charged ratio, so that the sample was contaminated with a small amount of GDB, although this phase was not detected in the samples with low Al contents.

2.3. Synthesis of $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ Using Glycols Other than 1,5-PeG

To synthesize solid solutions with higher Al contents from the starting composition of $\text{Al}/(\text{Ga}+\text{Al})=0.778$, various glycols were examined as the solvent. Using ethylene glycol (EG), amorphous product was obtained, whereas 1,3-propanediol (1,3-PG) yielded solid solution with a relatively small crystallite size (3.4 nm). Using 1,6-hexanediol (1,6-HxG), solid solution without contamination of GDB was obtained, and glycols with higher carbon numbers, 1,8-octanediol (1,8-OG) and 1,9-nonanediol (1,9-NG), also yielded GDB-free solid solutions. The crystallite size of the solid solution obeyed the following order: $2 < 3 < 4 < 6 < 5 > 6 > 8 > 9$ (carbon number of glycol).

Reaction of AIP yielding GDB proceeded easily according to the following order of carbon number of glycol: $2 < 3 < 6 < 4^{(65),(66)}$. This result can be explained in terms of the heterolytic cleavage of the C-O bond of aluminum glycoxide formed by alkyl exchange reaction of AIP with the solvent glycol. As the electron-withdrawing property of the intramolecular hydroxyl

group disturbs the cleavage of the C-O bond, ethylene glycol gives a poorly crystallized product. The high reactivity observed in 1,4-BG can be explained by participation⁽⁶⁷⁾ of the intramolecular hydroxyl group as depicted below⁽⁶⁶⁾:

Mixed-oxide formation is also controlled by the heterolytic cleavage of the C-O bond of glycoxides. In the case of 1,5-PeG, a six-membered ring is formed at the transition state, which is also favored as for the five-membered ring as shown in the scheme above. Formation of seven- or more-membered rings is difficult because of the proximity effect of transannular hydrogen atoms⁽⁶⁸⁾. In the cases of higher carbon number, the heterolytic cleavage of the C-O bond seems to be disturbed by the low dielectric constant of the glycol, yielding poorly crystallized products.

In the $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ system, competition between formation of GDB and the mixed oxide may give slightly different results than expected for the reaction of AIP alone. The increase in the carbon number of the glycol increases the temperature required for the formation of GDB, because the thermodynamical stability of the boehmite layers decreases with increasing carbon number of the glycol⁽⁶⁾. Therefore, in the case of 1,6-HxG or higher carbon-number glycols, the solid solution was obtained without contamination of GDB even with a higher Al-charged ratio, 0.778.

2.4. Solvothermal Synthesis of $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ Using Various Solvents

The reaction of AIP alone in 2-(methylamino)ethanol yielded $\gamma\text{-Al}_2\text{O}_3$ with the crystalline structure identical to that of $\gamma\text{-Ga}_2\text{O}_3$ obtained by the reaction of $\text{Ga}(\text{acac})_3$ alone. Therefore, $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide without contamination of by-products was directly obtained even with an extremely high $\text{Al}/(\text{Ga}+\text{Al})$ feed ratio. **Figure 2** shows the relationship between the feed ratio of $\text{Al}/(\text{Ga}+\text{Al})$ and the 440 spacing of the mixed oxide synthesized in 2-(methylamino)ethanol. Whereas the plots for the glycothermal products had an apparent inflection at $\text{Al}/(\text{Ga}+\text{Al})=0.778$ because of the formation of GDB, the plots for the products obtained in 2-(methylamino)ethanol were a straight line over the entire range of the $\text{Al}/(\text{Ga}+\text{Al})$ ratio, indicating that the solvothermal reaction in 2-(methylamino)ethanol directly yields the $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxides with the $\text{Al}/(\text{Ga}+\text{Al})$ ratios used in the feed.

The reactions of mixtures of $\text{Ga}(\text{acac})_3$ and AIP in toluene, diethanolamine, triethanolamine, and diethylene-triamine at 300°C for 2 h also yielded $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxides with the γ -type crystalline structure.

Table 1 Some Properties of $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ Mixed Oxides Prepared by the Solvothermal Method

Reaction medium	Al/(Ga + Al)	XRD	Surface area after calcination at 700°C [m ² /g]	Crystallite size calculated from XRD [nm]	Particle size calculated from surface area [nm]	Acid amount [μmol · g ⁻¹]	Acid density [μmol · m ⁻²]
1,5-Pentanediol	0	γ-type structure	71	—	—	—	—
	0.25	γ-type structure	113	—	—	111	0.98
	0.50	γ-type structure	144	—	—	148	1.03
	0.70	γ-type structure	200	4.8	4.6	196	0.98
	0.778	γ-type structure + GDB	188	5.2	5.1	165	1.05
	0.90	γ-type structure + GDB	157	—	—	—	—
	1.00	GDB	140	—	—	—	—
2-(Methylamino)ethanol	0	γ-type structure	—	—	—	—	—
	0.70	γ-type structure	240	3.9	3.6	394	1.64
	0.90	γ-type structure	220	—	—	370	1.68
	1.00	γ-type structure	201	—	—	—	—
Toluene	0	γ-type structure	—	—	—	—	—
	0.70	γ-type structure	184	4.3	4.7	236	1.28
	0.90	γ-type structure	173	—	—	225	1.30
	1.00	amorphous product	161	—	—	—	—
Diethanolamine	0.70	γ-type structure	251	4.4	4.6	331	1.32
Triethanolamine	0.70	γ-type structure	216	4.3	5.5	292	1.35
Diethylenetriamine	0.70	γ-type structure	151	9.5	6.4	112	0.74

2.5. Some Properties of $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ Solid Solutions

The physical properties of the products obtained in various solvents are summarized in **Table 1**. $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxides prepared in 2-(methylamino)ethanol had large surface areas and small crystallite sizes, whereas those prepared in diethylenetriamine had small surface areas and large crystallite sizes. The crystallite size calculated from the XRD was approximately identical with the particle size calculated from the surface area, assuming that the primary particle is spherical. This result suggests that the primary particle is a single crystal of the mixed oxide and that the primary particles are well dispersed. The crystallite size of the $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxides depends on the reaction medium used for the solvothermal synthesis, although no correlation between the properties of the reaction medium and the crystallite size of the product has been found so far.

Figure 3 shows the XRD patterns of the products obtained in 1,5-PeG after calcination at 700°C. $\gamma\text{-Ga}_2\text{O}_3$ was partially transformed to $\beta\text{-Ga}_2\text{O}_3$. However, the XRD patterns of the $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions calcined at 700°C were essentially identical to those of the as-synthesized products except for the disappearance of the peaks due to GDB and boehmite. The crystallite size of the solid solution was little increased by calcination at 700°C. After calcination at 900°C, $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions with lower Al contents were completely transformed into $\beta\text{-Ga}_2\text{O}_3\text{-}\theta\text{-Al}_2\text{O}_3$, whereas those with higher Al contents retained the γ -type structure. These results indicate that the thermal stability of the gamma structure increased

Fig. 3 Powder X-ray Diffraction Patterns of the Products Obtained by Reaction of Aluminum Triisopropoxide (AIP) and Gallium Acetylacetonate ($\text{Ga}(\text{acac})_3$) in 1,5-Pentanediol (1,5-PeG) at 300°C for 2 h, Followed by Calcination at 700°C

with higher Al content.

^{71}Ga and ^{27}Al magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of the catalysts suggested that Ga^{3+} ions preferentially occupied the tetrahedral sites of the spinel structure, and the Al^{3+} ions occupied the octahedral sites^{(21), (42)}. The increase in the Al/(Ga + Al) ratio caused the increase in the ratio of tetrahedral Ga^{3+} ions to total Ga^{3+} ions.

The acid strength measured by temperature-programmed desorption (TPD) of NH_3 method was

Data for $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts previously reported^{(58), (59)} are also plotted. Reaction conditions: 550°C; NO, 1000 ppm; CH_4 , 1000 ppm; O_2 , 6.7%; He balance.

Fig. 4 NO Conversion over Catalysts Prepared in Various Media

essentially identical for all catalysts examined. However, the amount of acid, assessed by the total amount of ammonia desorbed from the catalyst, strongly depended on the medium used for the preparation of the catalyst (Table 1), and increased with higher surface area of the catalysts. The *acid density* also tended to increase with higher surface area. Since the surface area of the catalyst was inversely correlated with the crystallite size, the acid density increased with smaller crystallite size. Transmission electron microscope (TEM) showed that the primary particles of the catalyst with high surface area (*i.e.* small crystallite size) were spherical; therefore, the particles should expose high Müller index surfaces. Such surfaces consist of steps and kinks in the oxygen sublattice. Therefore, the acid sites of the present catalyst system apparently occur at the surface defect sites. Fourier transform infrared (FT-IR) spectra of pyridine adsorbed on the catalysts suggested the presence of only Lewis acid sites⁽⁴²⁾.

2. 6. Catalytic Activity of $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ Synthesized in 1,5-PeG for SCR of NO with CH_4

Figure 4 shows the results for SCR of NO with methane at 550°C over the $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions synthesized in various media. For the catalyst synthesized in 1,5-PeG, the NO conversion to N_2 increased with higher Al content, and the solid solution with $\text{Al}/(\text{Ga} + \text{Al}) = 0.778$ exhibited the highest activity. The increase in activity was much larger than that expected

from the increase in the surface area (Ga_2O_3 , 71 m^2/g ; $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solution ($\text{Al}/(\text{Ga} + \text{Al}) = 0.778$), 188 m^2/g), and therefore, the high activity is probably connected with the crystalline structure of the solid solution. At higher $\text{Al}/(\text{Ga} + \text{Al})$ ratio (>0.778), the activity abruptly decreased, partially due to the formation of GDB causing lower actual $\text{Al}/(\text{Ga} + \text{Al})$ ratio in the solid solution. For comparison, the activity of a γ -alumina-supported gallium oxide catalyst ($\text{Ga}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$) prepared by impregnation of commercial alumina (JRC-ALO-4) with gallium nitrate solution is also plotted in Fig. 4 together with that previously reported^{(58), (59)}. The $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solution catalyst had higher activity than the impregnation catalysts.

Since Ga^{3+} ions preferentially occupy the tetrahedral sites of the defect spinel structure, these results indicate that the tetrahedral Ga^{3+} ions are the active sites for this reaction. However, $\gamma\text{-Ga}_2\text{O}_3$ and solid solutions with high Ga contents did not show high activities despite containing tetrahedral Ga^{3+} . Therefore, we concluded that tetrahedral Ga^{3+} ions with Al^{3+} ions in the next-nearest-neighbor (NNN) sites are the active sites for the reaction. A similar conclusion was reached for $\text{Ga}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ ⁽⁵⁹⁾.

The reaction proceeded according to the stoichiometry shown in Eq. (1) at low temperature, but the combustion of methane increased with higher temperature as shown in Eq. (2)⁽⁴³⁾.

The reaction orders of NO and CH_4 with respect to the formation of N_2 at 350°C were 0.20 and 0.68, respectively, suggesting that activation of CH_4 is the key step for this reaction.

To evaluate the activation of CH_4 , $\text{CH}_4\text{-D}_2$ isotope exchange over $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions with various $\text{Al}/(\text{Ga} + \text{Al})$ ratios was examined at 450°C⁽⁴³⁾. The isotopic compositions of CH_3D_y were calculated by using the least square method. The activity of the solid solutions for the isotope exchange reaction was proportionally correlated with the rate for the $\text{CH}_4\text{-SCR}$ of NO as shown in Fig. 5. These results strongly suggest that two reactions take place on the same active sites, tetrahedral Ga^{3+} ions with Al^{3+} ions in the NNN sites, and that activation of CH_4 is the key step for the $\text{CH}_4\text{-SCR}$ of NO over $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions.

Figure 6 shows NO conversion at 500°C over solid-solution catalysts ($\text{Al}/(\text{Ga} + \text{Al}) = 0.778$) prepared in various glycols plotted against the carbon number of the glycol. The solid solution prepared in 1,6-HxG showed better performance than those prepared in 1,4-BG or 1,5-PeG. This result is attributed to the formation of $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solution with $\text{Al}/(\text{Ga} + \text{Al}) = 0.778$ without contamination of by-products. The reduced performances of the catalysts prepared in high glycols are due to the low crystallinity of the products.

Reaction conditions: CH₄-D₂ isotope exchange reaction; CH₄, 18,500 ppm; D₂, 74,000 ppm; He balance; W/F = 0.15 g·s·mL⁻¹. CH₄-SCR: NO, 1000 ppm; CH₄, 1000 ppm; O₂, 6.7%; He balance; W/F = 0.3 g·s·mL⁻¹.

Fig. 5 Activities for CH₄-D₂ Isotope Exchange Reaction and for CH₄-SCR of NO of Ga₂O₃-Al₂O₃ Solid Solutions with Various Al/(Ga+Al) Ratios

Reaction conditions: 500°C; NO, 1000 ppm; CH₄, 1000 ppm; O₂, 6.7%; He balance; SV = 11,000 h⁻¹.

Fig. 6 NO Conversion over Catalysts Prepared from the Starting Composition of Al/(Ga+Al) = 0.778 in Glycols with Various Carbon Numbers

As shown in **Fig. 4**, the NO conversion to N₂ increased with higher Al/(Ga+Al) ratio in the feed up to *ca.* 0.75, regardless of the reaction medium used for the synthesis of the catalysts. However, the catalytic activity strongly depended on the organic solvent used in the solvothermal synthesis, and the highest activity was attained by the catalyst prepared in diethylenetriamine. This result indicates that the catalyst activity increases with greater crystallite size despite the lower surface area of the catalyst⁴⁶.

NO conversion to N₂ was four times as large as the CH₄ conversion to CO₂ at a relatively low temperature. Therefore, we proposed that the reaction over the pres-

ent catalyst system proceeded according to the stoichiometry shown in Eq. (1)⁴³. The ratio of the NO conversion to the CH₄ conversion decreased at higher reaction temperature, because methane is progressively consumed by combustion, as shown in Eq. (2). SCR of NO with methane in the presence of O₂ is widely accepted to proceed according to Eq. (3), which competes with the combustion shown by Eq. (2).

However, the stoichiometry of reaction (3) cannot be applied to the present catalyst system, since no O₂ was consumed at low temperatures, and the ratio of CH₄ conversion to NO conversion was four. We estimated the ratio of the amount of CH₄ consumed by Eq. (1) to that consumed by the competitive combustion reaction as expressed by Eq. (2), and found that this ratio was essentially constant irrespective of the feed Al/(Ga+Al) ratio, but increased with higher density of acid sites. These results indicate that the combustion activity of the catalysts increases with higher density of acid sites. The promoting effect of acidity of the catalyst on the combustion activity has been reported in various catalyst systems^{69)~71)}. In the present catalyst system, the acidity of the catalyst rather promoted combustion of methane, and therefore, had a negative effect on CH₄-SCR. Since the mixed oxide prepared in diethylenetriamine has a low acid-site population, the Ga₂O₃-Al₂O₃ catalyst prepared in this solvent utilizes methane more effectively for SCR of NO and so provides higher activity.

3. Glycothermal Synthesis of Silica-modified Titanias and Their Photocatalytic Performance

Preparation of titania is important because of its various catalytic applications, for example, as a support for SCR of NO_x with ammonia⁵⁷⁾ and the selective oxidation of hydrocarbons⁷²⁾. In recent years, titania has also become used as a semiconductor photocatalytic material^{73),74)}. Amorphous titania with extremely high surface area has been prepared by sol-gel methods^{75)~77)}, but crystallizes into anatase at around 500°C, accompanied by a marked decrease in surface area^{77)~79)}. Previously, nanocrystalline anatases with large surface areas were obtained by solvothermal reactions^{22),27),80)}. However, calcination at high temperatures transforms the metastable anatase phase to the thermodynamically stable rutile phase, accompanied by drastic decreases in surface area and porosity^{77),81)}. To improve the thermal stability of titania, addition of small amounts of other components have been examined^{79),82)~86)}.

Recently, we examined the thermal reaction of mixtures of titanium tetraisopropoxide (TIP) and tetraethyl orthosilicate (TEOS) in 1,4-butanediol, and obtained nanocrystalline silica-modified titanias with quite high surface areas and excellent thermal stabilities⁴⁷⁾. Here,

Fig. 7 XRD Patterns of the Products Formed by the Reaction of Titanium Tetraisopropoxide and Tetraethyl Orthosilicate with the Charged Ratio of: (a) Si/Ti = 0; (b) Si/Ti = 0.1; in 1,4-butanediol at 300°C and after calcination at various temperatures

the characterization of these products as well as their photocatalytic activity is described.

3. 1. Preparation of Materials

Silica-modified titanias were prepared by the glycothermal method from TIP and an appropriate amount of TEOS. These products are designated as GT(*x*), where *x* is the Si/Ti charged ratio. The products were also collected by flash evaporation of the solvent. After the glycothermal reaction, one valve of the autoclave connected to a stainless steel Liebig condenser was slightly opened to remove the organic vapor from the autoclave while keeping the autoclave temperature at 300°C. After the pressure inside decreased to the atmospheric level, nitrogen gas was introduced into the autoclave (up to 30 kg/cm²) and then released to remove all volatile matter. After cooling, the bulk solid products (xerogels) were directly obtained. The products are designated as XG(*x*), where *x* is the Si/Ti charged ratio. Calcination of the products was carried out at the desired temperature for 30 min. The calcined samples are designated by adding “-(calcination temperature)” after the sample names; *e.g.*, GT(0.1)-600 means the GT(0.1) sample calcined at 600°C.

N-doped samples were obtained as follows: XG(*x*) samples calcined at 500°C were placed in a quartz tube heated to the desired temperature in an argon flow and then treated in an NH₃ flow (100 ml/min) for 1 h. After the NH₃ treatment, the sample was annealed in air in a box furnace at the desired temperature (400-600°C) for 30 min. The nitrified and annealed samples are designated as XG(*x*)-N(temp-1)-A(temp-2), where “temp-1” and “temp-2” are the nitrification and annealing temperatures, respectively.

3. 2. Characterization of Silica-modified Titanias Synthesized by the Glycothermal Method

The reaction of TIP alone in 1,4-BG at 300°C yielded anatase particles with crystallite size of 17 nm and BET surface area of 91.5 m²/g. The products obtained by the addition of TEOS also had the anatase structure, and no other phases were detected by XRD. Higher amounts of TEOS added resulted in decreased crystallite size of the products and significantly increased BET surface area. **Figure 7** shows the XRD patterns of the silica-modified titanias calcined at high temperatures, and **Table 2** shows the BET surface area, crystallite size, and crystalline phase of the calcined samples. For GT(0), the BET surface area was relatively large after calcination at 600°C, but decreased significantly after calcination at 800 and 1000°C, accompanied by the transformation to the rutile phase. On the other hand, the silica-modified titanias preserved quite large surface areas. The phase transformation into rutile was significantly retarded by the addition of TEOS. For example, the samples with *x* > 0.02 preserved the anatase structure even after calcination at 1000°C.

Unit cell parameters, *a* and *c*, of GT(*x*) samples calcined at 600°C decreased monotonously with increasing Si/Ti ratio up to 0.1, which suggests that Si atoms are incorporated in the anatase structure⁵⁰.

The surface properties of the products were assessed by 2-propanol-TPD⁴⁸. 2-Propanol adsorbed on TiO₂ at room temperature decomposed to C₃H₆ and H₂O at ~200°C, whereas only a small amount of 2-propanol was adsorbed on SiO₂^{83,87}. Therefore, the amount of desorbed C₃H₆ in 2-propanol-TPD is a measure of the TiO₂ (or TiO₂-like) surface area. As shown in **Fig. 8(a)**, small amounts of added Si significantly increased the C₃H₆ desorption, which reached a maximum at Si/Ti =

Table 2 Physical Properties of Silica-modified Titanias Calcined at High Temperatures

Sample	Phase ^{a)}			BET surface area [$\text{m}^2 \cdot \text{g}^{-1}$]				D_{101} ^{b)} [nm]				Pore volume [$\text{ml} \cdot \text{g}^{-1}$]	
	800°C	1000°C	1100°C	300°C	600°C	800°C	1000°C	as-syn	600°C	800°C	1000°C	$d < 50 \text{ nm}^{\text{c)}$	total ^{d)}
GT(0)	A+R	R+A	R	92	62	12	2	17	22	95	320	0.19	1.15
GT(0.01)	A+R	A+R		138	102	45	14	10	13	37	120		
GT(0.02)	A	A		154	128		17	10	11	28	85		
GT(0.04)	A	A		150	145	96	30	10	10	16	48		
GT(0.06)	A	A		174	165	112	36	9	9	12	37		
GT(0.1)	A	A	A+R	161	157	125	50	10		11	26	0.58	1.49
GT(0.2)	A	A		194	189	168	72	9		9	17		
XG(0)	A	A+R	R+A	79	80	51	17	18	19	35	83	0.29	7.87
XG(0.02)	A	A		106	112	88	52	15	16	21	39		
XG(0.04)	A	A		101	107	93	73	14	14	17	23	0.48	5.59
XG(0.06)	A	A+R		154	168	133	74	11	12	13	24		
XG(0.1)	A	A	A	149	151	121	65	11	11	11	23	0.66	4.74
XG(0.2)	A	A		149	190	179	78	10	10	10	22		

a) A, anatase; R, rutile.

b) Crystallite size of anatase calculated from the 101 diffraction peak.

c) Calculated from the N_2 adsorption method.

d) Calculated from mercury porosimetry.

Fig. 8 Amount of C_3H_6 Desorbed from GT(x) Samples Calcined at 600°C: (a), amount of C_3H_6 desorbed from a unit weight of the sample and (b), amount of C_3H_6 desorbed from a unit surface of the sample

0.06 and then decreased gradually. **Figure 8(b)** shows the amounts of C_3H_6 desorbed from a unit surface area of the products. This value was essentially identical for all samples with Si/Ti range of 0–0.1, suggesting that small amounts of added silicon did not alter the surface property of the titania particles. However, this value abruptly decreased for samples with higher Si contents, indicating that part of the surface of the particles was covered with SiO_2 -like matter.

We also investigated the surface acidity of the samples by the NH_3 -TPD method and found that small amounts of added silica, $\text{Si/Ti} < 0.1$, did not alter the acid strength^{47),48)}. This result also suggests that amorphous TiO_2 - SiO_2 is not present in GT(x) with lower Si content, and hence Si is incorporated in the titania matrix.

Figure 9 shows O 1s X-ray photoelectron spectroscopy (XPS) spectra of GT(0.1) and two reference sam-

ples calcined at higher temperatures⁵¹⁾. For GT(0.1), the main peak was observed at 530 eV binding energy (BE) together with a shoulder peak at 532 eV BE. The former peak was due to the oxygen in titania with the anatase structure, and the latter to the oxygen atoms associated with the Si–O–Ti bond⁸⁸⁾. The proportion of the shoulder peak in GT(0.1)-600 was smaller than that of a reference sample (ES(0.1)) prepared by impregnation of TEOS (Si/Ti ratio = 0.1) on glycothermally-prepared TiO_2 , indicating that the silicon is distributed to deeper regions in the particles of GT(0.1). The spectra of the other reference sample (SS(0.1)) prepared by impregnation of silica sol on TiO_2 clearly showed a large peak at 533 eV, attributed to the oxygen atoms in SiO_2 . The absence of the 533 eV peak in GT(0.1) indicates that the silicon atoms are preferentially attached

Fig. 9 O 1s XPS Spectra of the Silica-modified Titanias Prepared by: (a), glycothermal method; (b), impregnation using TEOS (ES(0.1)); and (c), impregnation using silica sol (SS(0.1)); after calcination at various temperatures

to the Ti atoms through oxygen without forming silica particles.

Figure 10 shows the normalized Si K-edge X-ray absorption near edge structure (XANES) spectra of GT(*x*) samples and amorphous silica (A-SiO₂)⁵¹⁾. The spectrum of A-SiO₂ contained a strong absorption peak at 1846.8 eV, which is typical for tetrahedrally coordinated Si, [⁴Si]. The XANES spectra of the GT samples were quite similar to that of silica sol, suggesting that the silicon atoms in the GT samples are similar to [⁴Si]. However, some small but significant differences were observed. The peak top positions of the GT samples were shifted toward the higher energy side and a shoulder peak at the higher energy side of the main peak was recognized. Since [⁴Si] presents a strong absorption peak at 1846.8 eV whereas octahedrally coordinated Si, [⁶Si], shows a main absorption peak at 1849 eV^{89)~93)}, the observed spectra of the silica-modified titanias were considered to be combined spectra of [⁶Si] and [⁴Si]. To estimate the ratios of the [⁶Si] and [⁴Si] in the sample, curve-fitting analysis was carried out. Since we observed a small absorption peak at 1844 eV, originating from an impurity in the adhesive carbon tape used to mount the samples on the holder, the spectra were fitted to one common background and three Gaussian components, two for the edge peaks of [⁴Si] and [⁶Si], and one for the impurity. The deconvoluted spectra are shown in **Fig. 10**. The proportion of [⁶Si] was highest for GT(0.02), and decreased as the Si/Ti charged ratio increased, because of the low stability of [⁶Si] as compared to [⁴Si].

The population of [⁶Si] was much higher in GT(0.1) compared with the reference samples prepared by the impregnation method. Therefore, the glycothermal

method is suitable for incorporating silicon atoms in the unique octahedral sites in the titania matrix. Substitution of Ti with Si would be difficult after formation of the anatase structure because this implies the diffusion of Si from the surface and the back diffusion of Ti toward the surface with breaking of the Ti–O bond in the anatase structure. This seems to be the reason for the low proportion of [⁶Si] in the reference samples, prepared by “post-synthesis modification.” To obtain octahedrally coordinated Si atoms, as demonstrated in the glycothermal products, the crystallization must proceed in the presence of both Ti and Si sources.

Figure 11 shows the structure of anatase⁹⁴⁾. Two unit cells are depicted with a common edge along the *c* axis. The TiO₆ octahedron in the anatase structure has two Ti–O bonds longer than the other four Ti–O bonds. The titanium ions occupy one-half of the octahedral holes between the layers of oxide ions in a zigzag row, and the other half of the octahedral holes is vacant, designated as (h). Because the anatase structure has a distorted oxygen packing, the (h)O₆ is also a distorted octahedron, in which two of the (h)–O distances (2.8 Å, 1 Å = 10^{–10} m) are much longer than the other four (h)–O (1.9 Å). Therefore, the (h)O₆ octahedral hole is essentially a distorted tetrahedral hole.

The XPS and XRD data as well as TPD results indicate that the silicon atoms are included in the titania matrix, whereas the XANES results reveal that most of the silicon atoms are present in the tetrahedral sites. These results indicate that the silicon atoms are located in the tetrahedral holes shown as the closed circles in **Fig. 11**.

Insertion of Si atoms into the vacant holes causes unbalanced positive charges, which can be compensated

Fig. 10 Deconvolution of the Si K-edge XANES Spectra of the As-synthesized Silica-modified Titanias and Simulated Spectra

by several mechanisms, such as incorporation of interstitial oxide ions, change of the valence of titanium, or increase of the negative surface electric charge. We measured the concentration of the surface OH groups of the silica-modified samples, and found that the OH group concentration decreased with TEOS addition as shown in Fig. 12⁴⁸⁾. This result indicates substitution of the surface OH groups with surface oxide ions to form negative surface charge, compensating for the positive charge caused by the insertion of the Si into the vacant holes of the anatase structure. The OH group concentration on the surface is directly correlated to the free energy of the surface, and therefore, the insertion of Si atoms is critical for the stabilization of the silica-modified titanias.

Silica coating models have been proposed for the stabilization mechanism for silica-modified titanias^{95),96)}. However, if the surface is covered with a second component, the surface property, which can be estimated by

Fig. 11 Structure of Anatase

the TPD technique and catalytic test, should be changed. The present data suggest that the surface property did not change with a small amount of added Si. Therefore, the coating model cannot explain the present system.

The anatase structure contains oxide ions in the face-centered cubic arrangement, whereas the rutile structure has a hexagonal packing of oxide ions. Therefore, cleavage of some of the Ti-O bonds is involved in the transformation from anatase to rutile. The presence of silicon atoms in the anatase matrix results in the formation of Si-O-Ti bonds, and consequent retardation of the structural change. In addition to this effect, we believe that the decrease in the surface energy caused by substitution of the surface OH groups with oxide ions contributes to the thermal stability of the present products.

3.3. Photocatalytic Activity of Silica-modified Titanias

As the silica-modified titanias have quite high surface areas, they are expected to show high photocatalytic activities. The photocatalytic activities of the silica-modified titanias prepared by the glycothermal method were examined. However, compared with standard TiO₂, JRC-TIO-4, the glycothermally synthesized samples exhibited rather low activities for the photocatalytic decomposition of acetic acid in an aqueous solution⁴⁹⁾. Relatively rapid sedimentation was observed for GT(*x*) samples, suggesting low dispersibility of GT(*x*) in the suspension. The as-synthesized glycothermal products were well dispersed in methanol during the washing stage. However, the wet gel product became a stiff solid after air drying. Since the glycothermal products contain organic moieties, *e.g.* glycoxides, on the surface, the OH groups of the surface organic moiety

Fig. 12 Surface Hydroxyl Group Content of GT(x)-600s

Fig. 13 Pore Size Distributions of GT(0.1)-600 and XG(x)-600s Calculated on the Basis of the Desorption Branch of the N_2 Adsorption Isotherm

interact with the dispersant liquid, resulting in increased surface tension of the liquid between the particles in the drying stage, and coagulation of the fine particles. The pore-size distribution calculated from the N_2 adsorption isotherm, as depicted in Fig. 13, shows that GT(0) has a sharp peak at the pore diameter of 9 nm. This value is half of the crystallite size of this material (17 nm), and the pores in this range can be attributed to the voids between tightly coagulated nanoparticles.

In order to avoid such coagulation, the organic vapor was removed by a flash evaporation method after the glyothermal reaction to obtain bulk solid powder products, XG(x). The pore size distribution of XG(x) had no clear distribution peaks in the mesopore range as shown in Fig. 13. The pore-size distribution of XG(x) measured by mercury porosimetry exhibited significant pore volumes in the macropore range. The pore volumes of XG(x) were much larger than those of GT(x) samples as shown in Table 2, indicating that coagulation during drying of the wet gels due to the surface tension of the liquid was effectively prevented. Highly dispersed suspensions were easily obtained from the XG(x) samples and showed improved photocatalytic

activities⁴⁹.

3. 4. Nitrification of Silica-modified Titanias and Their Photocatalytic Activities under Visible Light Irradiation

The photocatalytic reaction with anatase-type TiO_2 photocatalysts proceeds only under irradiation of ultra-violet (UV) light (wavelength (λ) < 388 nm) since the band gap of anatase TiO_2 is 3.2 eV^{73,74}. In order to utilize solar energy more efficiently, a number of attempts have recently been made to expand the photo-sensitivity of TiO_2 -based photocatalysts into the visible-light region. Since nitrogen-doping into TiO_2 may exhibit visible light-induced photocatalytic activity^{97,98}, nitrification of the silica-modified titania xerogels was examined^{52,54}.

White mother TiO_2 powders, XG(0), turned gray after NH_3 treatment at 600°C and annealing treatment at 400°C. The spectrum of the NH_3 -treated and annealed XG(0) sample had a shoulder absorption band at 400-500 nm and a broad band at higher wavelength (> 500 nm). The former band can be attributed to the nitrogen doped into the anatase structure and the latter band to the formation of Ti^{3+} ⁹⁹. In the case of XG(0.1), the NH_3 -treated and annealed sample was bright yellow, and the UV-vis absorption spectrum, contained a much stronger shoulder band at 400-500 nm, whereas the absorbance at the higher wavelength region was apparently lower. These results indicate that the formation of Ti^{3+} was effectively suppressed, and nitrogen was stably doped in the silica-modified titania.

As shown in Fig. 14 (inset), the N 1s XPS spectrum of XG(0) without NH_3 treatment exhibited a peak at 400 eV BE, due to nitrogen adsorbed on the surface¹⁰⁰. On the other hand, after the NH_3 treatment, another peak appeared at 396 eV BE, assigned to nitrogen doped in TiO_2 . The intensity of the peak at 396 eV in nitrified XG(0.1) was larger than that in nitrified XG(0). The N/Ti ratios calculated from the intensities of the Ti and $N_{396\text{ eV}}$ peaks are plotted as a function of the NH_3

(Δ) and ($\blacktriangle$), for XG(0.1); ($\circ$) and ($\bullet$), for XG(0): open symbols, after NH_3 treatment; solid symbols, after NH_3 treatment followed by annealing at 400°C in air for 30 min. The inset shows N 1s XPS spectra of: (a), XG(0.1); (b), XG(0); treated in an NH_3 flow at 600°C for 1 h and annealed in air at 400°C for 30 min, and (c), XG(0).

Fig. 14 N/Ti Ratios of the Nitrified Samples Determined by XPS

treatment temperature in **Fig. 14**. The N/Ti ratio increased with higher treatment temperature, and NH_3 -treated XG(0.1) showed higher N/Ti ratios at temperatures up to 650°C than NH_3 -treated XG(0). The abrupt increase in the N/Ti ratio of NH_3 -treated XG(0) at 700°C was due to the formation of TiN, as observed by XRD⁵⁴. After annealing at 400°C , the N/Ti ratio decreased in both samples, but the N/Ti ratios of nitrified XG(0.1) were several times higher than those of nitrified XG(0), suggesting that a larger amount of nitrogen was doped in XG(0.1) than in XG(0). In the silica-modified titanias, silicon atoms were inserted in the distorted octahedral vacant sites in the anatase structure, which caused unbalanced positive charges in the particles⁵¹. On the other hand, the substitution of O^{2-} with N^{3-} caused excess negative charge. In the case of nitrified silica-modified titanias, the positive charge formed by the Si insertion was compensated by the negative charge introduced by the substitution of O^{2-} with N^{3-} . This mechanism explains the more stable doping of nitrogen in the silica-modified titanias than in titanias.

In the photocatalytic decomposition of acetaldehyde, XG(0.1)-N(600)-A(400) exhibited two times higher activity than XG(0) and JRC-TIO-4 nitrified and annealed in the same way^{52,54}. This enhanced photocatalytic activity is due to the increase in absorption at 400–500 nm, which in turn results from the increase in the amount of doped nitrogen without the formation of Ti^{3+} . By optimizing the amount of Si addition and the annealing temperature, a catalyst, XG(0.2)-N(600)-A(500), was obtained with three times higher photocatalytic activity compared with XG(0.1)-N(600)-A(400)¹⁰¹.

4. Conclusions

We have been investigating the solvothermal synthesis of inorganic materials using various organic solvents and the catalytic applications of the products. Here, two recent studies are reviewed; the solvothermal synthesis of γ -type Ga_2O_3 - Al_2O_3 solid solutions for selective catalytic reduction of NO using methane, and the glycothermal synthesis of silica-modified titanias for photocatalytic applications.

γ - Ga_2O_3 - Al_2O_3 solid solutions were directly obtained by solvothermal reaction of $\text{Ga}(\text{acac})_3$ and AIP in various organic media. The solid solutions exhibited high catalytic performance for SCR of NO with methane. The rate-determining step for the reaction was the activation of CH_4 , and tetrahedral Ga^{3+} ions with Al^{3+} ions in the NNN sites were the active sites. The solid solutions with a higher acid density showed higher methane combustion rates and lower NO conversions. Ga_2O_3 - Al_2O_3 catalyst prepared in diethylenetriamine showed significantly enhanced activity since they had lower density of acid sites than those obtained in other solvents and methane was more effectively used for SCR of NO.

Silica-modified titanias with various silica contents were directly synthesized by the thermal reaction of TIP and TEOS in 1,4-butanediol. The products possessed significantly higher surface areas and smaller crystallite sizes, and exhibited remarkable thermal stabilities. XPS, XRD, and TPD showed the products were solid solutions of SiO_2 - TiO_2 . Si K-edge XANES spectra revealed that most of the Si atoms were located in the tetrahedral sites of the anatase structure. Such insertion of Si atoms caused decreased surface energy of the particles and retarded the anatase-to-rutile phase transformation, thus contributing to the thermal stability of the silica-modified titanias. Xerogels of these materials were obtained by removal of the organic vapor in the autoclave by flash evaporation after glycothermal reaction. The xerogel catalysts exhibited high photocatalytic activity because coagulation of the ultrafine particles due to the surface tension of the liquid between the particles in the drying stage was prevented. NH_3 treatment at high temperatures afforded N-doped silica-modified titanias with high N contents, which showed strong absorption in the visible region (400–500 nm) and exhibited high photocatalytic activities under visible light irradiation.

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要 旨

ソルボサーマル法を用いる無機材料の合成とその応用

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我々は無機材料原料の有機溶媒中での加熱処理（ソルボサーマル（ST）法）に関する研究を行っており、本方法で多様な無機材料が直接得られることを種々報告している。本稿では、最近の二つの研究、 $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ 固溶体の ST 合成とそのメタン脱硝性能、シリカ修飾チタニアの ST 合成とその光触媒能に関し概説する。ガリウムアセチルアセトナートとアルミニウムトリイソプロポキシドの ST 反応では、スピネル型 $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ 固溶体を得られ、これがメタンを還元剤とする選択的 NO 還元反応に高活性を示した。本反応では CH_4 の活性化が律速過程であり、また第二近接が Al^{3+} である 4 配位 Ga^{3+} が活性点であ

ると考えられる。ジエチレントリアミン中での ST 反応で得た触媒は特に高活性を示したが、これは触媒の表面酸点密度が低く、メタン燃焼が抑制されたためと考えられる。一方、チタニテトライソプロポキシドとオルソケイ酸エチルの ST 反応では、熱安定性に優れたアナタース型シリカ修飾チタニアが得られた。ST 反応後、高温を維持して系内の気相成分を留去すると生成物をキセロゲルとして回収でき、これが高い光触媒活性を示した。さらに、これに窒素ドーピングした試料は可視光照射下でも高い活性を示した。

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