

Synthesis of Ga-silicate and Its Catalytic Performance for NO Removal under the Presence of Water

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Abstract

Catalytic performance for NO_x removal by Ga-incorporated silicates (Ga-silicate; Gallosilicate) with MFI type synthesized by the rapid crystallization method was reported in this study. NO_x removal was investigated under the condition of O₂ excess (10%), with various hydrocarbons of low concentrations. Effect of H₂O (2%) addition was also considered. The result showed that the conversion from NO_x to N₂ was enhanced on the Ga-silicate compared with the Al-silicate. Furthermore, the performance for NO_x conversion on the Ga-silicate increased with addition of water.

Key words : Rapid crystallization method. Ga-silicate. NO removal

1. INTRODUCTION

In the 1980s, analysis technology and monitoring systems improved greatly (Matsuzaki, 1990), leading to increased public awareness of a variety of local and global environmental problems (Brown, 1992). Increasing concerns about air quality and the environment have led to tougher standards in many countries throughout world in the control of exhaust emission in mobile and stationary engines, and even more stringent regulation are expected to be introduced in the near future (Kim, 1992).

Up to now, catalytic conversion of NO in the presence of excess O₂ and low concentration of hydrocarbons has been intensively studied to decrease the NO_x in the exhaust gas from diesel engines and lean-burn facilities. A variety of catalysts, such as alumina (Sasa-

ki *et al.*, 1992; Hamada *et al.*, 1990), other metal-oxides (Hamada *et al.*, 1991; Hamada *et al.*, 1991) and microporous crystalline catalysts (Yogo *et al.*, 1993; Li and Armor, 1992; Misono and Kondo, 1991; Iwamoto *et al.*, 1990; Sato *et al.*, 1990) have been used to remove NO_x from exhaust gas. Above all, metal-containing microporous crystals are gaining a great interest as a number of promising catalytic performances have been reported (Corma, 1991). Those materials are expected to have two contributions from components molecular sieves and metal oxides. When some elements are incorporated in the crystal lattice, they are atomically dispersed and firmly supported on the host structure. Even though those metals are not incorporated in the crystal lattice, very small particles incorporated in the crystal structure would exhibit interesting properties. The unique catalytic properties of metal-containing zeolite materials and zeolite like materials

have been reported (Inui, 1993).

In particular, Cu-ion-exchanged zeolites were found to catalyze the NO decomposition (Iwamoto *et al.*, 1990). However, it has been recognized that ion-exchanged ZSM-5, especially Cu-ion exchanged H-ZSM-5, gradually deteriorates in the presence of water vapor under high temperature conditions owing to both sintering of copper atoms and dislocation of the aluminum ingredient from the framework position. These kinds of disadvantages would be extended to other transition metal ion-exchanged zeolites.

In order to overcome this disadvantage, metallosilicates, which were synthesized by the rapid crystallization method adding the other elements in the reaction gel in the hydrothermal stage, have significant potential for precise modification of the catalytic properties (Inui, 1989). Especially, the validity of metallosilicates for the deNO_x reaction was shown using MFI-type Co-containing silicates (Inui *et al.*, 1994). An H-Co-silicate exhibited the highest performance, and actually, the stability of NO conversion performance against H₂O and SO₂ was confirmed. Those properties were attributed to the high and stable distribution of the incorporated elements.

In this study, the synthesis of metallosilicate containing Ga by the rapid crystallization procedure and its catalytic performance on NO conversion under condition with O₂ excess (10%), various hydrocarbons of low concentration, and addition of H₂O (2%) was investigated. In addition, we had tried to find the relationship between the performance of the NO conversion and the combustion of hydrocarbons.

2. MATERIALS AND METHODS

2.1 Preparation of materials using as a catalyst

In Figure 1, the typical rapid crystallization procedure of the metallosilicate catalyst is shown and reagents used are listed in Table 1. As the source of metals, nitrates for Al and Ga were used. The charged metal contents were expressed as atomic ratio and the

Si/metal ratios were 20. First, a gel mixture was prepared by adding solution G-1 and G-2 into G-3 while maintaining a pH at 9-11 at room temperature and vigorously stirring with an ultra-disperser (Nichion Irika-kikai). The precipitated gel mixture was milled for 1 h in a motor-driven mortar (Yamato-Nitto, UT-21). Solutions S-1, S-2, and S-3 were mixed together similarly and the supernatant solution was obtained from it by centrifuge. The milled gel from G-1, G-2, and G-3 and the supernatant from S-1, S-2, and S-3 were mixed together in the mortar. Then the mixture was transferred into a glass vessel in a 1 liter stainless-steel autoclave. The atmosphere in autoclave was replaced by nitrogen gas with 3 kg/cm² gauge. This was heated from room temperature to 160 °C with a constant heating rate of 1.5 °C/min, and then up to 210 °C with a constant heating rate of 12 °C/h. After being cooled down, the solid products were washed with distilled water and centrifuged separated.

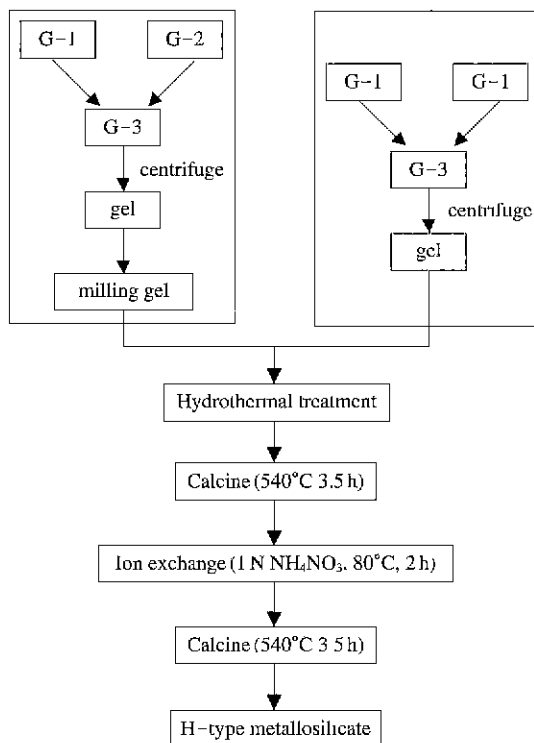


Fig. 1. The preparation of Metallosilicate with MFI type.

Table 1. Reagents used for the preparation of metallosilicate.

Solution	Reagent	Weight
G-1(S-1)	distilled water	60 ml (60 ml)
	H ₂ SO ₄	3.4 ml (3.4 ml)
	metal salts	x g (x g)
G-2(S-2)	distilled water	45 ml (45 ml)
	water glass	69 g (69 g)
G-3(S-3)	distilled water	45 ml (45 ml)
	NaCl	52.55 g (26.3 g)
	TPAB	5.75 g (5.75 g)
	NaOH	2.4 g (-)
	H ₂ SO ₄	1.55 ml (-)

Washing was repeated until the mother solution became neutral. They were dried at 120°C overnight and heated in air at 550°C for 3.5 hrs to burn off the organic template. Subsequently they were ionexchanged as follows: A 1.0 g portion of calcined sample was put in 40 ml of 1 N NH₄NO₃ solution, heated at 80°C for 2 h with stirring, and then washed with distilled water. This procedure was repeated again, and then followed by drying at 120°C overnight. Finally, they were calcined at 550°C in air for 3.5 hrs to be converted into H-type silicates.

2.2 Characterization of catalyst

Synthesized samples were identified by powder X-ray diffraction analysis (XRD). Shimadzu XD-DJ with Nickel filtered Cu K α radiation (30 kV, 30 mA) at an angle of 2 θ range from 5 to 50 degree. Elemental analysis was performed on an ICP (inductively coupled plasma), Shimadzu ICPS-1000III. BET surface areas of crystals were measured by nitrogen gas adsorption at the liquid nitrogen temperature in mixing gas of nitrogen and helium flow as the carrier gas with Shimadzu Flow sorbs 2~2300. UV-visible spectra were recorded on a Shimadzu MPS-2000 spectrometer, and BaSO₄ was used as the reflectance standard. Acidity of catalyst was estimated by TPD profiles of pre-adsorbed NH₃, determined by Quadruple Mass Spectrometer [(M-QA100F) of BEL JAPAN INC]. To restrain influence of water during NH₃ adsorption, the adsorption was done at above 100°C.

2.3 Reaction and analysis

The catalytic test of materials prepared was carried out by using a conventional flow apparatus which was shown in our previous paper (Kang *et al.*, 1998). The catalyst in powder form was tabulated with a tablet machine. It was crushed and sieved to 15~24 mesh for the reaction. A 0.5 g (0.7 ml) portion of the catalyst was packed in a quartz reactor of 8 mm inner diameter. The catalyst-bed length was 14 mm. After drying in a helium flow at 400°C for 30 min, a reaction gas was introduced in a temperature range from 300 to 600°C with an SV 30,000 h⁻¹. The reaction and product gases were analyzed by using a gas chromatography (Shimadzu GC-4CPT, MS-5A column) equipped with an integrator.

3. RESULTS AND DISCUSSION

3.1 Characteristics of metallosilicate catalysts

XRD patterns for all the metallosilicates are shown in Figure 2 and their oxide compositions analyzed by ICP test is shown in Table 2. The XRD patterns of all the samples coincide with that of the reference MFI type. The peak intensity on two samples was almost the same, and the metal amount acquired from ICP test

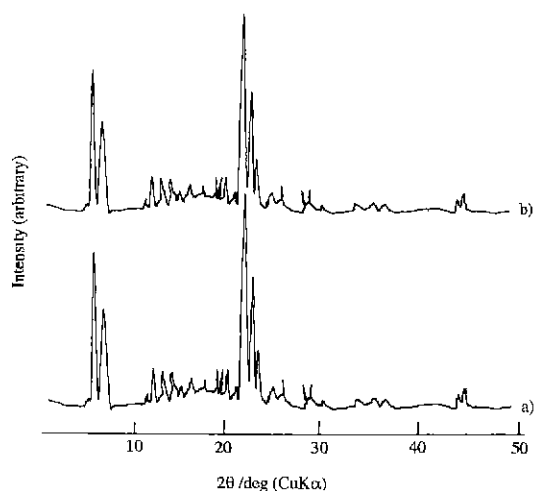


Fig. 2. XRD patterns of metallosilicates. a) Al-silicate and b) Ga-silicate.

Table 2. Composition and BET surface area in metallosilicates.

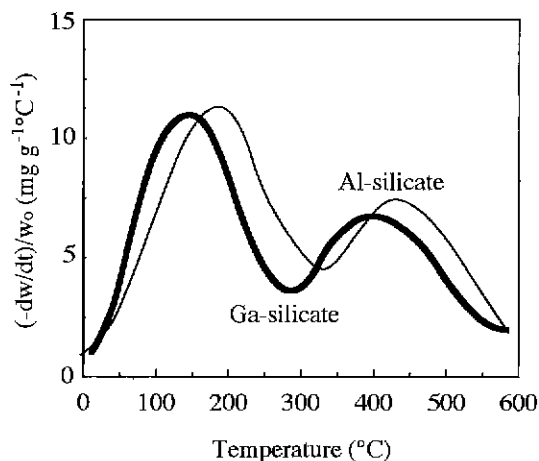
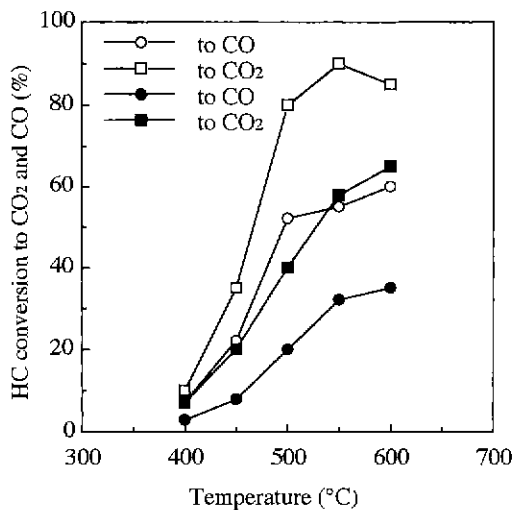
Catalyst	Composition before reaction		BET surface area (m ² /g)
	In gel (Si/Metal)	In crystal (Si/Metal)	
Al-silicate	20	16	308
Ga-silicate	20	17	281

was also same as shown Table 2. On the other hand, despite the identical structure, the BET surface area was smaller on Ga-silicate than Al-silicate.

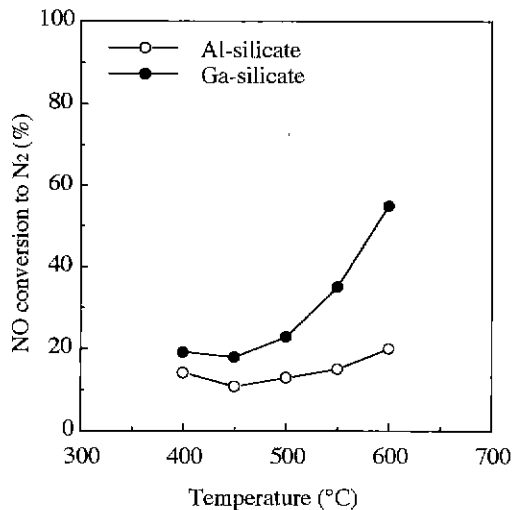
3. 2 Acidic property

In Figure 3. NH₃-TPD profiles for the two catalysts are shown. In the case of MFI type catalyst, the Brønsted acid sites were changed because of the incorporation of metal into framework. These profiles consist of two peaks: one appearing at a low temperature range around 130~180°C and another at a high temperature range around 370~420°C. There low and high temperature peaks correspond to the weak and strong acid sites, respectively. In general, it is well known that the catalytic performance of zeolites and

related materials is effected by the strong acidity at high temperature. As shown in Figure 3, the acidity decreased in Ga-silicate compared with Al-silicate. From this result, it was confirmed that the difference of acidity has influence on the performance of NO conversion as will be shown Figure 4.

**Fig. 3. NH₃-TPD profiles of metallosilicates.**

a) the hydrocarbon combustion



b) the NO conversion

Fig. 4. The performances for the NO and hydrocarbon conversion of Al-silicate and Ga-silicate. Reaction condition: 1000 ppm NO, 1100 ppm n-C₄H₁₀, 10% O₂, balance N₂, SV = 30000/h. Opened symbol; Al-silicate, Closed symbol; Ga-silicate.

3.3 Performance for NO conversion

In Figure 4, the results of the NO removal and hydrocarbon conversion are expressed as a function of the reaction temperature under a presence of $n\text{-C}_8\text{H}_{18}$ on Al- and Ga-silicates. As shown, with an increase in reaction temperature, the performances for the hydrocarbon conversion to CO and CO_2 on both catalysts increased. However, the tendency on Ga-silicate decreased compared with on Al-silicate. Furthermore, the combustion temperature of hydrocarbon on Al-silicate was lower than that on Ga-silicate. Its difference was over 20% at high temperature. The conversion into CO was far smaller than that into CO_2 . On the other hand, the performance for NO conversion was enhanced on Ga-silicate compared with Al-silicate and, in particular, the conversion on Ga-silicate also increased significantly when the temperature increased.

3.4 Effect of the presence of water on NO conversion

In Figure 5, the performance for the NO removal and hydrocarbon conversion under the presence of water on Al-Ga-silicates are shown. It is clear that

with an increase in reaction temperature, the performances for the hydrocarbon conversion to CO and CO_2 on both catalysts increased. The combustion temperature of hydrocarbon on Al-silicate was lower than that on Ga-silicate as shown in Figure 4. However, it was noteworthy that the hydrocarbon conversion increased in Ga-silicate in condition with H_2O addition compared with the result without H_2O addition shown in Figure 4. The performance for NO conversion on Ga-silicate was higher as compared with Al-silicate.

The performances for the NO conversion with and without water addition on Al- and Ga-silicate are compared in Figure 6. As shown, surprisingly, the performances of NO conversion on both catalysts increased when the water was added to feed gas in reaction. Furthermore, compared with Al-silicate, the performance on Ga-silicate increased more and the difference was over 40% at 600°C .

3.5 Effect of H_2O concentration on the NO conversion

The influence of H_2O concentration in reaction gas

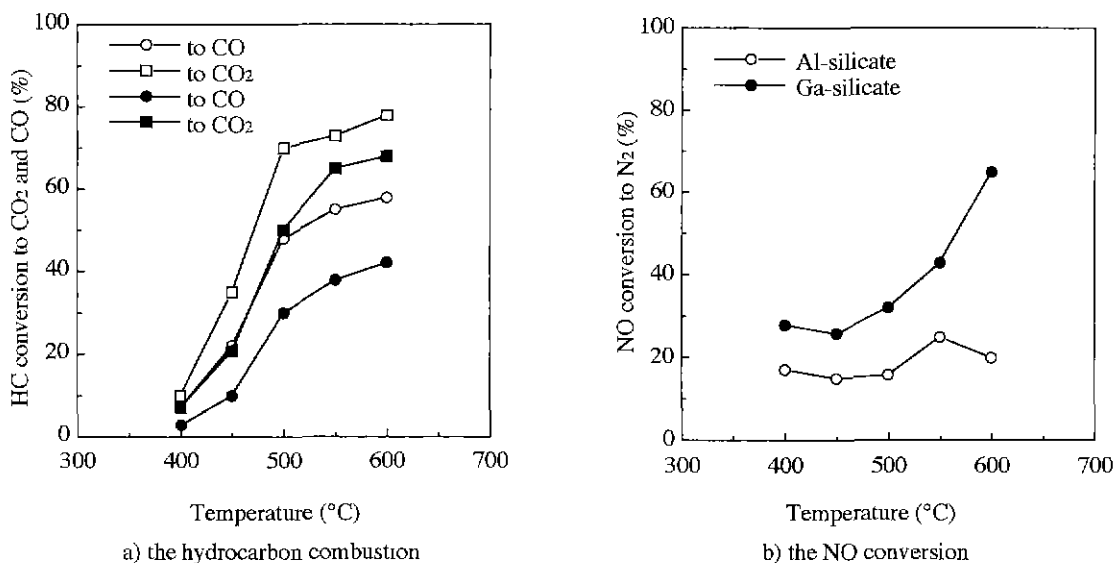


Fig. 5. The performances for the NO and hydrocarbon conversion in the presence of water on Al-silicate and Ga-silicate. Reaction condition: 1000 ppm NO, 1100 ppm $n\text{-C}_8\text{H}_{18}$, 10% O_2 , 2% H_2O , balance N_2 , SV = 30000/h. Opened symbol; Al-silicate, Closed symbol; Ga-silicate.

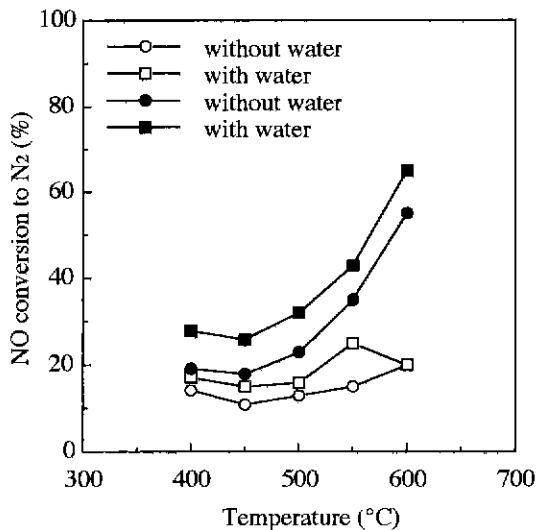


Fig. 6. Comparison of performances for the NO conversion with and without water on Al-silicate and Ga-silicate. Reaction condition: 1000 ppm NO, 1100 ppm $n\text{-C}_8\text{H}_{18}$, 10% O_2 , 0 or 2% H_2O , balance N_2 , SV = 30000/h. Opened symbol; Al-silicate, Closed symbol; Ga-silicate.

on the catalytic activity of Ga-silicate at 500°C and 600°C are presented in Figure 7. With an increase in H_2O concentration the NO conversion at 600°C decreased, however the conversion was kept on about 40% under reaction condition with above H_2O 5%. On the other hand, the NO conversion at 500°C was almost the same despite with an increase in H_2O concentration.

3. 6 Combustion of hydrocarbon on metallosilicate

The amounts of produced H_2 and CO on Al- and Ga-silicate with or without H_2O are compared in Table 3. The addition of H_2O has clearly influenced the formation of these products, and this indicates that the steam reforming reaction progress in these systems even in an oxygen rich condition. Without H_2O the amounts of CO on Al-silicate decreased compared with that with H_2O , while such trend is more pronounced with Ga-silicate. Apparently, most of the $n\text{-}$

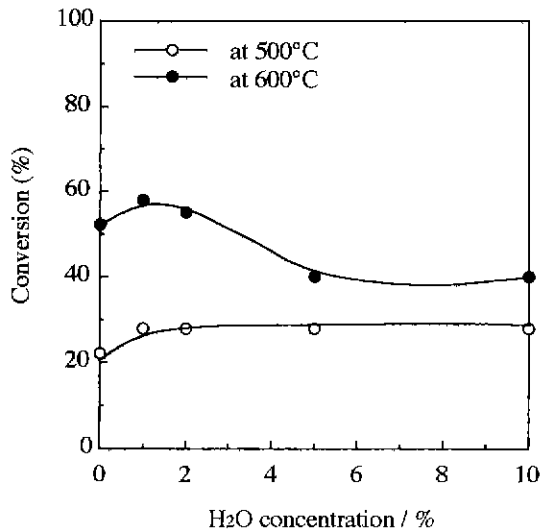


Fig. 7. Effect of the H_2O concentration for NO conversion reaction of Ga-silicate. Reaction condition: 10% O_2 , 1100 ppm $n\text{-C}_8\text{H}_{18}$, balance N_2 , SV=30000/h.

Table 3. Comparison of amounts of H_2 and CO in $n\text{-C}_8\text{H}_{18}$ combustion on metallosilicates.

Catalyst	Temperature (°C)	Without H_2O		With H_2O	
		H_2 (ppm)	CO (ppm)	H_2 (ppm)	CO (ppm)
Al-silicate	400	21	650	28	760
	500	51	4,750	93	4,190
	600	340	5,530	470	5,080
Ga-silicate	400	91	300	43	350
	500	630	1,890	780	2,740
	600	770	3,110	1,070	3,750

octane molecules added were oxidized into CO or CO_2 and the addition of H_2O has little influence on Ga-silicate. However, it is difficult to prove whether the steam reforming reaction takes place on metallosilicate or not.

In Table 4, the formation of H_2 and CO on Al- and Ga-silicate under presence of NO are summarized. The CO formation was much high compared with the results of simple combustion experiments mentioned in Table 3. This is a proof that CO formed on-site is rapidly oxidized on metallosilicate as having high oxidation activity especially in the presence of excess

Table 4. Comparison of amounts of H₂ and CO formed in NO removal on metallosilicates.

Catalyst	Temperature (°C)	Without H ₂ O		With H ₂ O	
		H ₂ (ppm)	CO (ppm)	H ₂ (ppm)	CO (ppm)
Al-silicate	400	10	540	16	770
	500	37	2,350	60	2,770
	600	160	5,270	25	4,680
Ga-silicate	400	33	700	41	850
	500	450	4,070	600	4,140
	600	180	5,330	270	5,300

* Reaction condition: NO 1000 ppm, n-C₈H₁₈ 1100 ppm, O₂ 10%, H₂O 0 or 2%, balance N₂, SV 30000/h

Table 5. Comparison of amounts of H₂ and CO under various hydrocarbon combustion on Ga-silicate at 400°C.

Hydrocarbon	Without H ₂ O addition		With H ₂ O addition	
	H ₂ (ppm)	CO (ppm)	H ₂ (ppm)	CO (ppm)
CH ₄	0	0	0	0
C ₃ H ₆	990	95	110	35
n-C ₈ H ₁₈	2,050	97	1,160	81

* Reaction condition: CH₄ 6000 ppm, C₃H₆ 2000 ppm, n-C₈H₁₈ 750 ppm, H₂O 0 or 2%, balance N₂, SV 25000/h

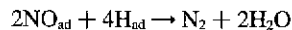
oxygen. In particular, the oxidation tendency was more pronounced on Ga-silicate in NO conversion reaction compared with non-reaction. In addition, the CO formed was similar with or without H₂O. On the other hand, the CO formed on Al-silicate decreased in reaction NO conversion compared with non-reaction as shown Table 3.

To study the role of acidic property, hydrocarbon conversion in the absence of oxygen was examined on Ga-silicate. The conversion of various hydrocarbon on Ga-silicate was examined in detail to Table 5. As shown, the formed CO increased gradually with an increase in carbon chain. In the previous paper (Kang *et al.*, 1998), it was found that higher hydrocarbon was more effective to the NO conversion reaction.

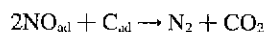
3. 7 Mechanism expected on metallosilicate

If the NO reacts selectively with the adsorbed hydrocarbon species and gives N₂ and complete combustion products CO₂ and H₂O, the elementary reaction

steps must involve the following simple reduction reactions.



or



However, as described above, the number and kinds of combustion products on the effective catalysts for NO removal are considerable. Therefore, the possibility of the rapid occurrence of such simple reductants: hydrogen, carbon monoxide, and carbon, before the reaction with NO, would be very small except in the cases that simple hydrocarbons such as methane and C₂-C₃ olefins hydrocarbons are added in the feed gas. This means that direct reactions between very small amounts of adsorbed NO or gaseous NO hardly occur under excess oxygen conditions.

4. CONCLUSION

This study focused on the catalytic performance for NO_x removal under condition with O₂ excess (10%), hydrocarbons of low concentration (1,100 ppm n-C₈H₁₈), and addition of H₂O (2%). The results can be summarized as follows;

- 1) Al- or Ga-incorporated metallosilicates (Al-silicate or Ga-silicate) were synthesized successfully by the rapid crystallization method.
- 2) the NO removal on Ga-silicate was higher compared with that on the Al-silicates.
- 3) the performance for NO conversion with addition of H₂O was enhanced.

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Ga-silicate의 합성과 물 존재하에서의 NO 제거에 놓인 촉매적 활성

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초 록

신속결정화법에 의해 합성된 Ga 함유 silicate (Gallosilicate)에 놓인 NOx 제거에 관한 촉매적 성능이 연구되었다. 10% 산소와 다양한 탄화수소 존재하의 NOx 제거성과 아울러 물의 영향도 조사되었다. 그 결과로써, NOx에서 N₂로의 전환성능은 Al 함유 실리케이트, 비교하여 Ga 함유 실리케이트에서 증가되었으며, 더우기 물의 첨가될 경우 더욱 증가하였다.