

## Synthesis of Fe-Mn Bimetallosilicate and Its Catalytic Performance on NO Decomposition

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### Abstract

This study has been focused on NO conversion for metal-incorporated silicates (Fe-silicate, Mn-silicate, and Fe-Mn-bimetallosilicate) with a similar MFI type. Used metallosilicates were prepared by the rapid crystallization method. Their catalytic performance for the conversion of NO under excess O<sub>2</sub> (10%) condition with the addition of hydrocarbon of low concentration (1,100 ppm n-C<sub>8</sub>H<sub>18</sub>) were investigated. As a result, the NO conversion on the Fe-Mn-bimetallosilicate was enhanced compared with on the Fe- or Mn-silicates. Furthermore, the performances for NO conversion on Fe-Mn-bimetallosilicate more increased with an increase in n-C<sub>8</sub>H<sub>18</sub> concentration, a decrease in NO concentration, and an increase in O<sub>2</sub> concentration.

**Key words** : Rapid crystallization method, Metallosilicate, Fe-Mn bimetallosilicate, NO conversion

### 1. INTRODUCTION

Over the past 35 years developed industrialized nations have experienced especially severe pollution problems. The control technology of nitrogen oxide (NO<sub>x</sub>) is of great importance because NO<sub>x</sub> is an air-polluting component. Ambient air quality standards were set and stringent emission regulations were enforced since the early 1970s in the USA (Rhoads, 1982) and Japan (Nakajima, 1982). At that time local or nation-wide improvement of standards was regarded as the best countermeasure to treat pollution problems. In the 1980s, however, analysis technology and monitoring systems improved greatly (Matsuzaki, 1990), leading to increased public awareness of a variety of local global environmental problems (Brown, 1992). Increasing concerns about air quality and the environ-

ment 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 O<sub>2</sub> and a low concentration of hydrocarbon has been intensively studied to decrease the NO<sub>x</sub> in the exhaust gas from diesel engines and lean-burn facilities up to a harmless level. A variety of catalysts, such as alumina (Sasaki *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 Arnot, 1992; Misono and Kondo, 1991; Iwamoto *et al.*, 1990; Sato *et al.*, 1990) have been used to remove NO<sub>x</sub> from exhaust gas. Above all, microporous materials, including a wide range of crystalline and amorphous solid

such as zeolites and related materials, carbon molecular sieves, pillared clay, and microporous materials may have a potential to create a new field in scientific and practical way. Their ion-exchange, molecular sieving, and catalytic properties make them more attractive (Flanigan, 1991). Especially, metal-containing microporous crystals are gaining a great interest as a number of promising catalytic performances have been revealed (Corma, 1991). Those materials are expected to have two functions: molecular sieves and metal oxides. When some elements are incorporated in the crystal lattice, they are atomically dispersed and firmly supported on the mother 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 thanks to metal-supported interaction (Inui, 1993). In particular, Cu-ion-exchanged zeolites were found to catalyze the NO decomposition (Iwamoto *et al.*, 1990). However, these catalysts have a limitations owing to the properties of their mother zeolites such as thermal stability, acidic property and ion exchange capacity (Inui *et al.*, 1991; Kikuchi *et al.*, 1991).

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). In fact, many promising results were already reported using MFI-type metallosilicates (Inui *et al.*, 1992; Inui, *et al.*, 1987) and others (Inui, 1993; Inui *et al.*, 1990). The validity of metallosilicates for the deNOx reaction was also shown using MFI-type Co-containing silicates (Inui *et al.*, 1994). An H-Co-silicate exhibited the highest performance, and the stability of NO conversion performance against H<sub>2</sub>O and SO<sub>2</sub> was confirmed. Those properties were attributed to the high and stable distribution of the incorporated elements. However, it is still well established between the catalytic activity of NOx and the charac-

teristics contributes to the NO conversion reaction. In this point, we supposed that if the incorporated metal is easily reduced, the NO conversion to N<sub>2</sub> on the coporated metal should be increased.

Therefore, In this study, to help the Fe<sup>3+</sup> reduction, the synthesis of Fe-Mn bimetallosilicate introduced the Mn<sup>2+</sup> was tried by the rapid crystallization procedure, and its catalytic performance on NO conversion was investigated. In particular, the NO conversion for Fe-Mn-bimetallosilicate at various reaction conditions was discussed.

## 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 used reagents were listed in Table 1. As the source of metals, nitrate compounds of Fe and Mn were used. The charged metal contents, expressed as atomic ratio of Si/metal were 100. 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 Irikai-kikai). The precipitated gel mixture was milled for 1 h in a motor-driven mortar (Yamato-Nitto, UT-21). Solution 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/cm<sup>2</sup> 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 it cooled down, the solid products were washed with distilled water and centrifugally separated. 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. They were

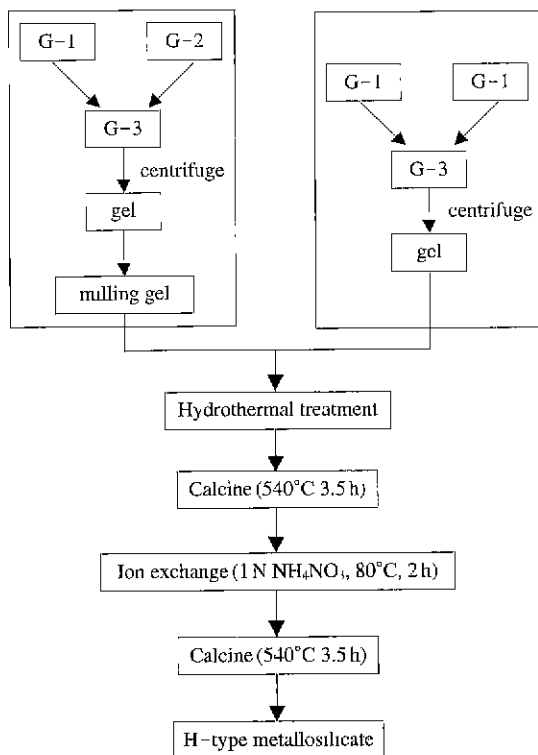


Fig. 1. The preparation of Metallosilicate with MFI type.

Table 1. Reagents used for the preparation of metallosilicate.

Solution	Reagent	Weight
G-1 (S-1)	distilled water	60 ml (60 ml)
	H <sub>2</sub> SO <sub>4</sub>	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 <sub>2</sub> SO <sub>4</sub>	1.55 ml (-)

ion-exchanged as follows: A 1.0 g portion of calcined sample was put in 40 ml of 1 N NH<sub>4</sub>NO<sub>3</sub> 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), Shimazu XD-DI with Nickel filtered Cu K $\alpha$  radiation (30 kV, 30 mA) at an angle of 2 $\theta$  range from 5 to 50 degree.

Composition of elements were analyzed by ICP (inductively coupled plasma), Shimadzu ICPS-1000 III.

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 BaSO<sub>4</sub> was used as the reflectance standard.

Acidity of catalyst was estimated by TPD profiles of pre-adsorbed NH<sub>3</sub>, determined by Quadruple Mass Spectrometer [(M-QA100F) of BEL JAPAN INC]. To restrain influence of water during NH<sub>3</sub> adsorption, which 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 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 to provide for the reaction. A 0.5 g (0.7 ml) portion of the catalyst was packed in a quartz tabulated 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 200 to 500°C with an SV 30000 h<sup>-1</sup>. The reaction and products gases were analyzed by using a gas chromatography (Shimadzu GC-4CPT, MS-5A column).

## 3. RESULTS AND DISCUSSION

### 3. 1 Characteristics of metallosilicate catalysts

XRD patterns for all the metallosilicates are shown in Figure 2 and the composition analyzed by ICP test

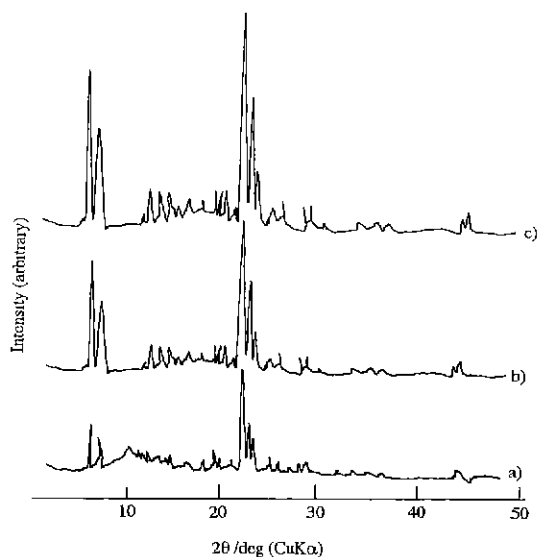


Fig. 2. XRD patterns of metallosilicates. a) Fe-silicate, b) Mn-silicate, and c) Fe-Mn-bimetallosilicate.

Table 2. The compositions in gel mixture and crystals and BET surface areas.

Catalyst	Composition in gel mixture (Si/metal)	Composition in crystal (Si/metal)	BET surface area (m <sup>2</sup> /g)
Fe-silicate	100	65	350
Mn-silicate	100	175	360
Fe-Mn-bi metallosilicate	100~100	45~200	385

depicts in Table 2. XRD patterns of all the samples coincide with that of the reference of MFI type, although differences in the peak heights were evident. In general, when the amount of metal substituted into framework increased, the crystallinity decreased. Therefore, from this result of XRD pattern, it is expected that the Fe component was much more than the Mn component in the crystals. This result was well accord with ICP data in Table 2. On the other hand, as a surprising result, the peak intensity more increased in Fe-Mn-bimetallosilicate, in addition, the BET surface area also increased in Fe-Mn-bimetallosilicate compared with that in Fe or Mn-silicates. This result shows that the incorporation of Mn into framework was more difficult compared with the Fe, and the Fe component

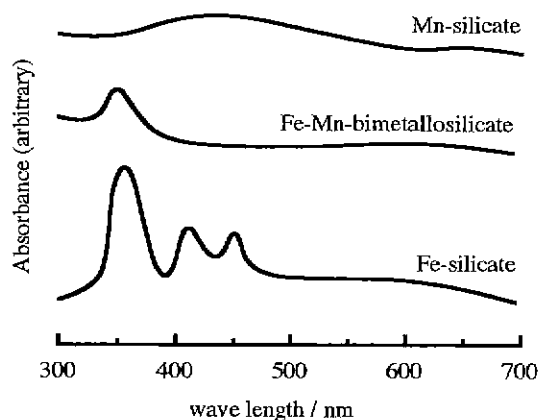


Fig. 3. UV-visible spectra of metallosilicates.

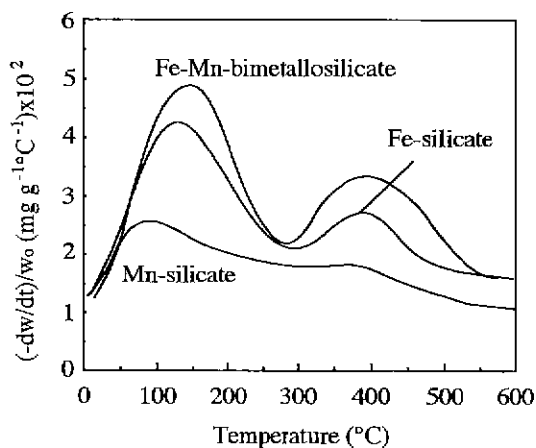


Fig. 4. NH<sub>3</sub>-TPD profiles of metallosilicates.

in framework was more stable.

In Figure 3, UV-visible spectra are profiled. The coordination states of Fe observed by UV-Visible measurement for Fe-silicates were appeared at 370, 410, and 435 nm that indicated Fe<sup>3+</sup>, however, the specific peak for Mn-silicate was not shown. On the other hand, the peaks at 410 and 435 nm disappeared in Fe-Mn-bimetallosilicates, and a peak at 370 nm just was observed.

### 3.2 Acidic property

In Figure 4, NH<sub>3</sub>-TPD profiles for three typical

kinds of catalysts are shown. In case of MFI type catalyst, because the incorporation of metal into framework, the Bronsted acid sites were changed. These profiles consist of two peaks: one appears at a low temperature range around 130~180°C and another appears at a high temperature range around 370~420°C. The low and high temperature peaks correspond to the weak and strong acid sites, respectively. In general, it was well known that the catalytic performance was effected to the strong acidity at high temperature (Kang *et al.*, 1999). The order for acidities in these catalysts follows next : Fe-Mn-bimetallosilicates > Fe-sil-icate > Mn-silicate.

### 3. 3 Performance of NO decomposition on metallosilicates

In a) of Figure 5, the hydrocarbon conversion is expressed as a function of the reaction temperature in a presence of  $n\text{-C}_8\text{H}_{18}$  on metallosilicates. As shown, with an increase in reaction temperature the performances for the hydrocarbon conversion on all the catalysts increased. In addition, the combustion temperature of hydrocarbon on Fe-Mn-bimetallosilicate was low-

er than that on Fe or Mn-silicate. Furthermore, the yield into CO on Fe-Mn-bimetallosilicate was very small compared with that into  $\text{CO}_2$ . On the other hand, the NO conversion to  $\text{N}_2$  is shown in b) of Figure 5. The Fe-Mn-bimetallosilicate exhibited the highest conversion. However the performance for NO conversion on Fe-silicate and Mn-silicate almost was the same as 27%. From this result, it was supposed that the incorporated Fe-Mn bimetal element had effected to reduction of NO and oxidation of hydrocarbon compared with the only incorporated-Fe or -Mn

In Table 3, the NO conversion to  $\text{N}_2$  with a presence of various hydrocarbons on Fe-Mn-bimetallosilicate are compared. As shown, the performances for NO conversion in a presence of  $n\text{-C}_8\text{H}_{18}$  were enhanced compared with that under the other hydrocarbons. Furthermore, in olefin, the NO conversion increased also compared with that in paraffin. This is ascribed to the combustibility of hydrocarbons.

Effect of the  $n\text{-C}_8\text{H}_{18}$  concentrations on NO conversion to  $\text{N}_2$  and  $n\text{-C}_8\text{H}_{18}$  conversion for Fe-Mn-bimetallosilicate are shown in Figure 6. As shown, the conversions were variously exhibited following as

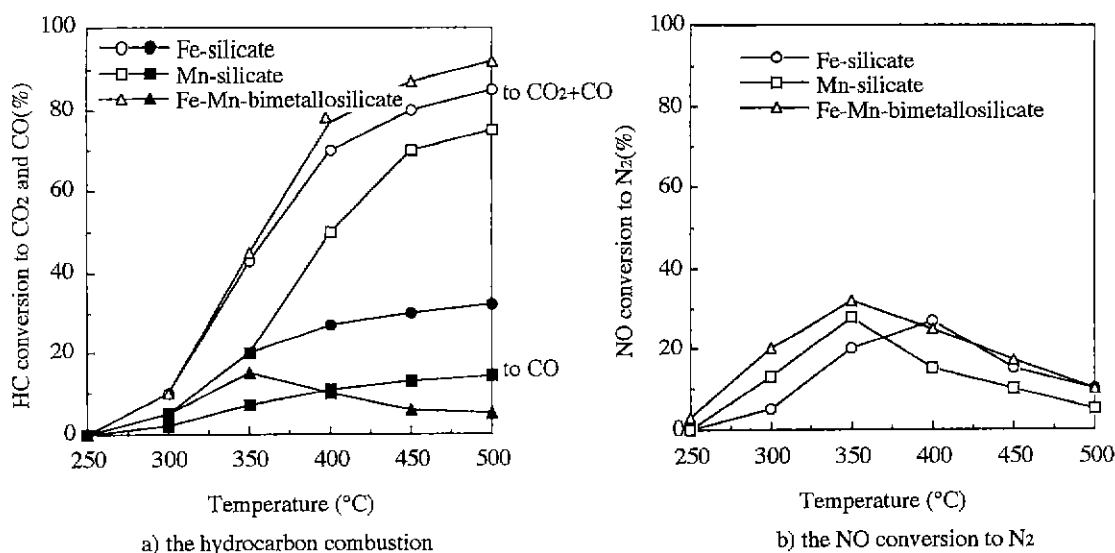
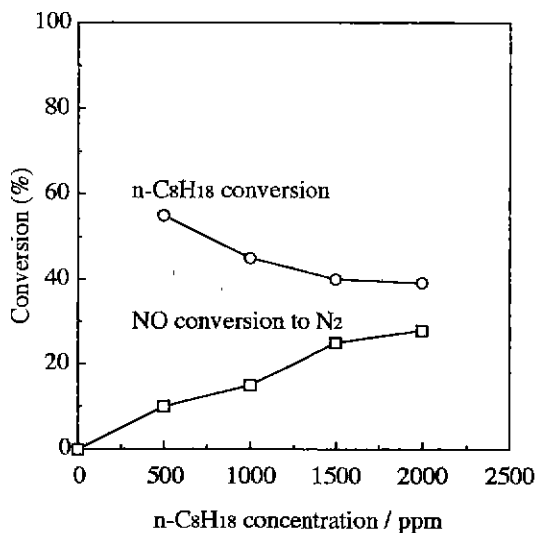


Fig. 5. The performances of the NO and hydrocarbon conversion for metallosilicates under the presence of  $n\text{-C}_8\text{H}_{18}$ . Reaction condition: 1000 ppm NO, 1100 ppm  $n\text{-C}_8\text{H}_{18}$ , 10%  $\text{O}_2$ , balance  $\text{N}_2$ , SV = 30000/h.

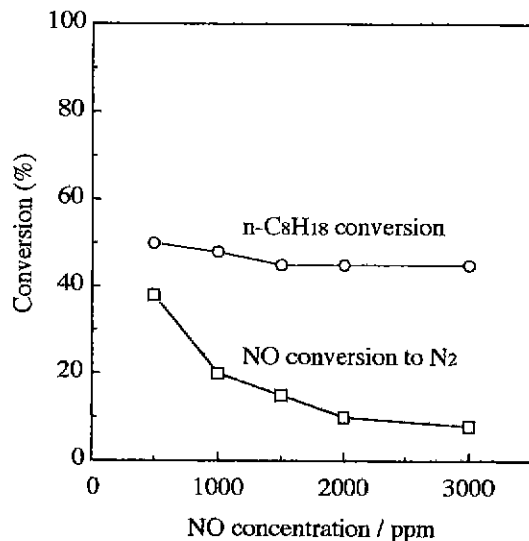
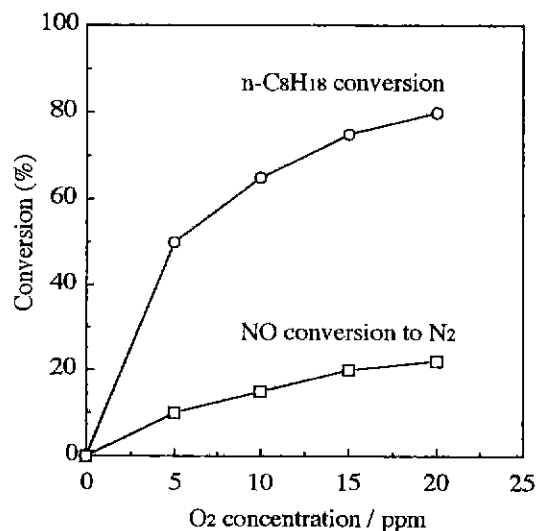
**Table 3. The NO conversions in changes of hydrocarbon species.**

Hydrocarbon species	Concentration (ppm)	Temperature (°C)	The NO conversion to N <sub>2</sub> (%)
CH <sub>4</sub>	2000	475	1.7
C <sub>2</sub> H <sub>6</sub>	2000	475	7.0
C <sub>2</sub> H <sub>4</sub>	2000	475	12
C <sub>3</sub> H <sub>6</sub>	2000	475	15
n-C <sub>8</sub> H <sub>18</sub>	2000	475	16

**Fig. 6. Effect of the n-C<sub>8</sub>H<sub>18</sub> concentration for NO conversion reaction on Fe-Mn-bimetallosilicate. Reaction condition: 1000 ppm NO, 10% O<sub>2</sub>, balance N<sub>2</sub>, SV=30000/h, temp 400°C.**

change of concentration of n-C<sub>8</sub>H<sub>18</sub>. With an increase in n-C<sub>8</sub>H<sub>18</sub> concentration the NO conversion increased and the n-C<sub>8</sub>H<sub>18</sub> conversion decreased, however, these tendencies were kept at over hydrocarbon concentration 1500 ppm. This is a proof that the NO was more well reduced by hydrocarbon combustion.

In addition, effect of the NO concentrations on NO conversion to N<sub>2</sub> and n-C<sub>8</sub>H<sub>18</sub> conversion for Fe-Mn-bimetallosilicate are shown in Figure 7. As shown, with an increase in NO concentration the NO conversion decreased and the n-C<sub>8</sub>H<sub>18</sub> conversion was not changed. This result accorded to general result that with a decrease in feed gas the catalytic performance

**Fig. 7. Effect of the NO concentration for NO conversion reaction on Fe-Mn-bimetallosilicate. Reaction condition: 1000 ppm NO, 10% O<sub>2</sub>, 1100 ppm n-C<sub>8</sub>H<sub>18</sub>, balance N<sub>2</sub>, SV=30000/h, temp 400°C.****Fig. 8. Effect of the O<sub>2</sub> concentration for NO conversion reaction on Fe-Mn-bimetallosilicate. Reaction condition: 1000 ppm NO, 1100 ppm n-C<sub>8</sub>H<sub>18</sub>, balance N<sub>2</sub>, SV=30000/h, temp 400°C.**

increased in catalytic reaction used Brönsted acid sites.

On the other hand, in Figure 8, the effect of O<sub>2</sub> con-

centration on NO conversion to  $N_2$  and  $n-C_8H_{18}$  conversion for Fe-Mn-bimetallosilicate are shown. As shown, with an increase in  $O_2$  concentration the both of NO and hydrocarbon conversions increased. This results from that the hydrocarbon was well combusted by  $O_2$  addition. From Figures 6, 7, and 8. it was confirmed that higher  $n-C_8H_{18}$  concentration, lower NO concentration, and higher  $O_2$  concentration were very useful on the good performance of NO conversion on Fe-Mn-bimetallosilicate.

#### 4. CONCLUSION

This study has been a focus on NO conversion on metal-incorporated silicates (Fe-silicate, Mn-silicate, and Fe-Mn-bimetallosilicate) with MFI type under the reaction condition of oxygen presence with various hydrocarbons. These results were exhibited as follows;

1) metallosilicates introduced Fe or Mn were synthesized by the rapid crystallization method.

2) the NO conversion on Fe-Mn-bimetallosilicate was enhanced compared with those on the Fe- or Mn-silicates.

3) the performances for NO conversion on the Fe-Mn-bimetallosilicate increased with an increase in  $n-C_8H_{18}$  concentration, a decrease in NO concentration, and an increase in  $O_2$  concentration.

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## Fe-Mn bimetallosilicate의 합성과 NO 분해에 통한 촉매적 활성

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### 초 록

본 연구는 MFI 형태를 갖는 metal (Fe-, Mn-, 그리고 Fe-Mn)함유 실리케이트에 통한 NO전환성능에 초점을 맞추었다. 사용된 메탈로실리케이트는 신속결정화법에 의해 합성되었다. 10%의 산소와 1100 ppm의 옥탄 존재하에서 Fe-실리케이트와 Mn-실리케이트와 비교하여 Fe-Mn bimetallosilicate에서 NO전환율이 향상되었다. 더우기 첨가된 옥탄농도가 증가할수록, NO농도가 증가할수록, 그리고 산소의 농도가 증가할수록 NO전환성능이 더욱 증가하였다.