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# Effect of cobalt incorporated into the framework of SAPO-34 (CoAPSO-34s) on NO removal

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## Abstract

This study has been focused on the effect of cobalt incorporated into SAPO-34 (CoAPSO-34s) for NO removal. The CoAPSO-34s with high crystallinity and sharp distribution in particle size were acquired by the rapid crystallization method. From results of the MAS-NMR of  $^{27}\text{Al}$  and  $^{31}\text{P}$ , incorporation of Co into the framework of SAPO-34 was identified. In addition, the NO conversion to  $\text{N}_2$  in presence of various hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_8\text{H}_{18}$ , and  $\text{C}_{16}\text{H}_{34}$ ) was investigated. The result showed that the NO conversion to  $\text{N}_2$  on the Co-incorporated catalysts was enhanced compared with the non-metal. In particular, the conversion was the highest for catalyst with  $\text{Si}/\text{Co} = 5$  in the presence of  $\text{C}_8\text{H}_{18}$ . © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* CoAPSO-34; Rapid crystallization method; NO removal

## 1. Introduction

Over the past 35 years, developed industrialized nations have experienced especially severe pollution problems. Ambient air quality standards were set and stringent emission regulations were enforced since the early 1970s in the US [1] and Japan [2]. At that time, local or nationwide improvement of standards was regarded as the best countermeasure to treat pollution problems. However, some analysis tech-

nologies and monitoring systems improved greatly [3], and then these lead to increase public awareness of a global environmental problem in the 1980s [4]. The environment crisis announced in the 1970s has returned more forcefully today. 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 regulations are expected to be introduced in the near future [5].

Recently, catalytic conversion of NO in the presence of excess  $\text{O}_2$  and a low concentration of hydrocarbon has been intensively studied to decrease the  $\text{NO}_x$  in the exhaust gas from diesel engines and lean-burn facilities up to a harmless level. A variety of catalysts, such as alumina [6,7], other metal-oxides

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[8,9], and microporous crystalline catalysts [10–14] have been used to remove  $\text{NO}_x$  from exhaust gas. Above all, microporous crystalline catalysts, such as zeolites and their related materials are promising due to the practical application [15,16]. Many different types of ion-exchanged zeolites have been investigated as catalysts for the  $\text{deNO}_x$  reaction. However, these catalysts have a limitation owing to the properties of their mother zeolites such as thermal stability, acidic property and ion exchange capacity [17,18]. 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 [19]. In fact, many promising results were already reported using MFI-type metallosilicates [20,21] and others [22,23]. The validity of metallosilicates for the  $\text{deNO}_x$  reaction was also shown using MFI-type Co-containing silicates [24]. An H-Co-silicate exhibited the highest performance, and the stability of NO conversion performance against  $\text{H}_2\text{O}$  and  $\text{SO}_2$  was actually 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  $\text{NO}_x$  and the characteristics contribute to the NO conversion reaction.

On the other hand, after the innovation in synthesis of aluminophosphate molecular sieves by UCC [25], the aluminophosphate-based molecular sieves family like SAPO, MeAPO, and MeAPSO was subsequently reported from 1986. Above all, coming to 1990, aluminophosphate family, SAPO-34, which had a similar pore structure of chabazite with 8-oxygen-membered rings attracted attention as the catalyst for light olefin synthesis, in particular, for high ethylene synthesis from methanol [26–28] ascribed to intermediate acidity and the smaller pore size (pore size of 0.38 Å). Use of the material is extending at various divisions recently and in particular, it has been tried as a catalyst in NO elimination. In case of Co-substituted aluminophosphates has a system which may combine both redox and acidic properties [29–32]. Reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  in CoAPOs leads to the increase of the concentration of acidic sites. However, the real nature and properties of these acidic sites in CoAPOs and other MeAPOs

have still not been cleared. In addition, the report about hydrocarbon synthesis using CoAPSO-34 is too seldom.

In this study, the synthesis of SAPO-34s containing much Co amount by a reliable procedure, and their catalytic performances on NO removal in the presence of various hydrocarbons were investigated. In particular, it has been focused on the effect of Co situation in the framework of SAPO-34 for NO removal and hydrocarbon combustion.

## 2. Experimental

### 2.1. Catalyst

In Fig. 1, the typical preparation procedure of the CoAPSO-34 catalyst is shown. Reagents used for preparation of the gel mixture were as follows: 35wt.% aqueous solution of tetraethyl ammonium hydroxide (TEAOH, Aldrich Chemical) was used as the organic template. Aluminum isopropoxide (AIP, Wako), cataloid-30 (30 wt.%  $\text{SiO}_2$ , Kasei Tesque), phosphoric acid (85 wt.%  $\text{H}_3\text{PO}_4$ , Nacali Tesque),

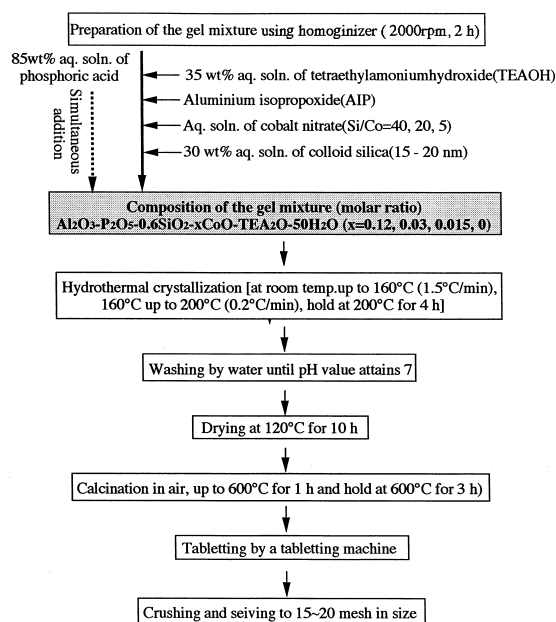


Fig. 1. Preparation procedure of CoAPSO-34 catalysts.

Table 1  
Physical properties of CoAPSO-34 catalysts synthesized with various Si/Co molar ratios

| Catalyst             | Si/Co molar ratio  |                | Crystallinity (%) | Surface area (m <sup>2</sup> /g) | Particle size (μm) | Mean of particle size (nm) |
|----------------------|--------------------|----------------|-------------------|----------------------------------|--------------------|----------------------------|
|                      | in the gel mixture | in the crystal |                   |                                  |                    |                            |
| Si/Co = ∞            | ∞                  | ∞              | 98                | 500                              | 0.8–2.0            | 420                        |
| Si/Co = 40           | 43.33              | 45.74          | 95                | 508                              | 1.0–1.5            | 500                        |
| Si/Co = 20           | 21.67              | 22.85          | 95                | 497                              | 1.0–1.5            | 1100                       |
| Si/Co = 5            | 5.08               | 5.77           | 100               | 502                              | 1.5–2.0            | 1400                       |
| Determination method | ICP                |                | XRD               | BET                              | SEM                | DLS                        |

and cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Nacalai Tesque) were used as the starting materials of Al, Si, P, and Co ingredients of CoAPSO-34, respectively.

The mixing order of these starting materials is important to obtain a homogeneous gel mixture, which was confirmed in our previous paper [33,34]. Catalysts shown in Table 1 are designated with various atomic ratios of Si/Co. The gel mixtures for all catalysts were crystallized by applying the rapid crystallization method [34].

## 2.2. Characterization of catalyst

Synthesized samples were identified by powder X-ray diffraction analysis (XRD), Shimadzu XD-DI with Nickel filtered Cu Kα radiation (30 kV, 30 mA) at an angle of 2θ range from 5° to 50°.

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

Crystal size and shape of catalysts were observed by using Hitachi S-2500 CX scanning electron microscope (SEM).

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.

Size distribution of particles was obtained by diffraction of light scattering (DLS) system of Photal Otsuka Electronics. The samples were dispersed by an ultrasonic wave treatment for 10 min with 120 W in water. The analysis was determined by weight-based distribution.

UV–Visible spectra were recorded on a Shimadzu MPS-2000 spectrometer, and BaSO<sub>4</sub> was used as the reflectance standard.

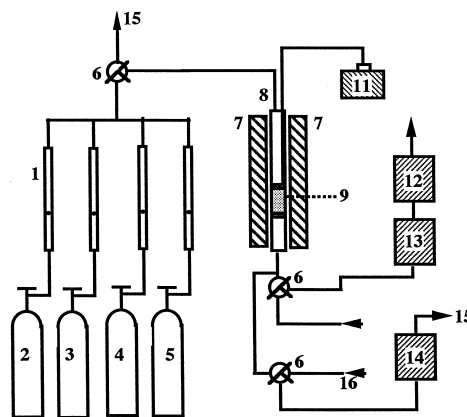
In order to determine the coordination of Al and P in the framework, a study for the local structure in

crystalline was analyzed by magic angle spinning (MAS) NMR with a JEOL GSX-270 solid state, high resolution spectrometer. The Al(NO<sub>3</sub>)<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> were used as the standard references. High-power decoupling experiments were carried out at 40° with 40.4 MHz for <sup>27</sup>Al and at 40° with 193 MHz for <sup>31</sup>P.

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. To restrain influence of water during NH<sub>3</sub> adsorption, the adsorption was done at 100°C.

## 2.3. Reaction and analysis

The catalytic performance of materials prepared was carried out by using a continually flow apparatus which is shown in Fig. 2. The catalyst with



1. Mass flow controller ; 2. Nitrogen ; 3. Oxygen ; 4. Hydrocarbon ; 5. Nitrogen Oxide ; 6. 3-way valve ; 7. Furnace ; 8. Quartz tube ; 9. Catalyst ; 10. Thermocouple ; 11. Temperature programmer ; 12. Oxygen analyzer ; 13. Nitrogen oxides analyzer ; 14. Carbon oxides analyzer ; 15. Purge ; 16. Air in

Fig. 2. Flow sheet of experimental apparatus.

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 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°C to 600°C with an SV 30 000 h<sup>-1</sup>.

The reaction and products 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 CoAPSO-34 crystalline catalysts

XRD patterns for all samples and the reference patterns of SAPO-34 [25] are shown in Fig. 3. XRD patterns of all samples coincided with that of the reference of SAPO-34, although the peak intensities were evident. In general, the crystallinity decreased

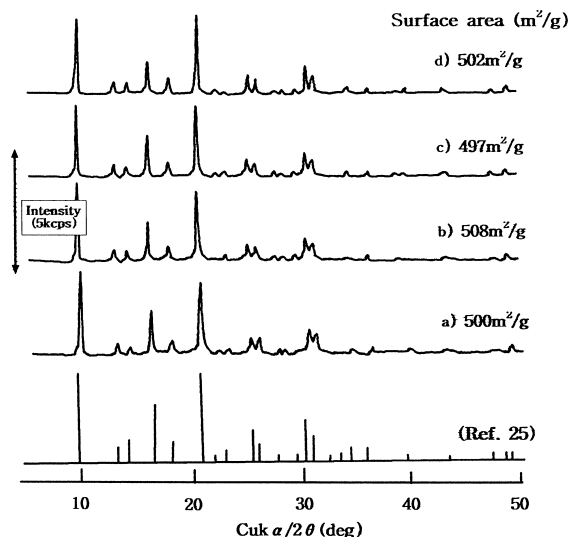


Fig. 3. XRD patterns of CoAPSO-34 crystals with various Si/Co ratios. (a) SAPO-34, (b–d): CoAPSO-34; (b) Si/Co = 40, (c) Si/Co = 20, and (d) Si/Co = 5.

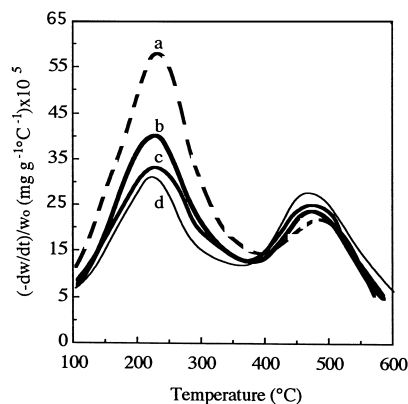


Fig. 4. NH<sub>3</sub>-TPD profiles of CoAPSO-34 catalysts with various Si/Co ratios. (a) Si/Co = ∞, (b) Si/Co = 40, (c) Si/Co = 20, and (d) Si/Co = 5.

with an increase of the metal amount substituted into the framework [34]. However, in this study, with an increase of Co amount in the framework, the crystallinity was almost accorded with that of a non-metal-incorporated sample (SAPO-34). In addition, the crystals with Co in the framework showed a sharper and higher peak. This is ascribed that the rate of crystal growth increased according to increase of Co amount at gel preparation.

The physical properties of synthesized catalysts are summarized in Table 1. The values of BET-surface area for all catalysts were almost the same. In ICP data, the ratios of Si/Co in gel mixture were almost accorded with that in synthesized crystals. This result is a proof that this procedure introduced in CoAPSO-34s synthesis is very stable and reliable. On the other hand, for all catalysts, not only cubic crystals with a uniform size distribution of 1.0–2.0 μm but no amorphous part also were observed by SEM. In addition, the particle size distribution of the catalyst which contained Co of much amount was larger than that of catalyst with Co of smaller amount.

#### 3.2. Acidic property

In Fig. 4, NH<sub>3</sub>-TPD profiles for four kinds of catalysts are shown. Zeolitic materials possess lots of acid sites and certain acidic strengths, attributed to their high Al contents and tetrahedral Al sites, re-

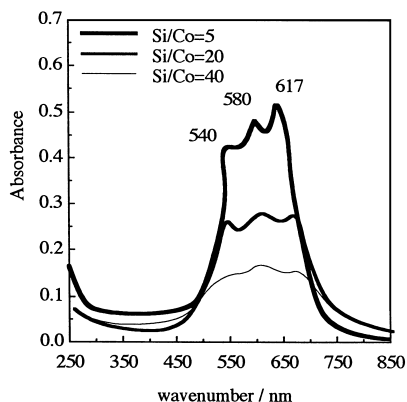


Fig. 5. UV-Visible spectra for CoAPSO-34s.

spectively. In general, aluminophosphates ( $\text{AlPO}_4-n$ ) are prepared in the presence of cation or neutral amine additives and crystallize with a composition ratio of Al/P of one, resulting in no net charge on the framework. However, with the addition of silica (SAPO) and/or other metal ions to the structure, both ion exchange capacity and catalytic acid activity were introduced. In particular, the incorporation of silica into the framework displayed Brönsted acid sites in SAPO. Therefore, the amount of acid sites was dependent on the Si amount. These profiles consist of two peaks: one appears at a low temperature range around 180–230°C and another appears at a high temperature range around 430–480°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 is effected by the strong acidity at high temperature. As a result in this study, at the low temperature, both the acidity and the amount of acid sites decreased with an increase of Co amount. However, at high temperature, the acidity decreased but the amount of acid sites rather increased. Therefore, it was reconfirmed that the Si sites were partly substituted by Co atom from the result at high temperature.

### 3.3. Cobalt situation in framework

UV-Visible spectra are profiled in Fig. 5. The absorbance of Co, which is observed by UV-Visible measurement, appeared at 540, 580, and 617 nm. These peaks are assigned to the tetrahedral situation. The peak intensity increased with an increase of Co amount. This result shows that some silicon sites are reliably substituted by cobalt component in the framework of SAPO-34.

On the other hand, a broad peak of Al around 38 ppm which is assigned to the tetrahedral generated from dehydration was observed in  $^{27}\text{Al}$  NMR spectra. With an increase of Co amount in the framework, the area of peak increased and it was shifted to the upfield. On the contrary, the peak for P around -40

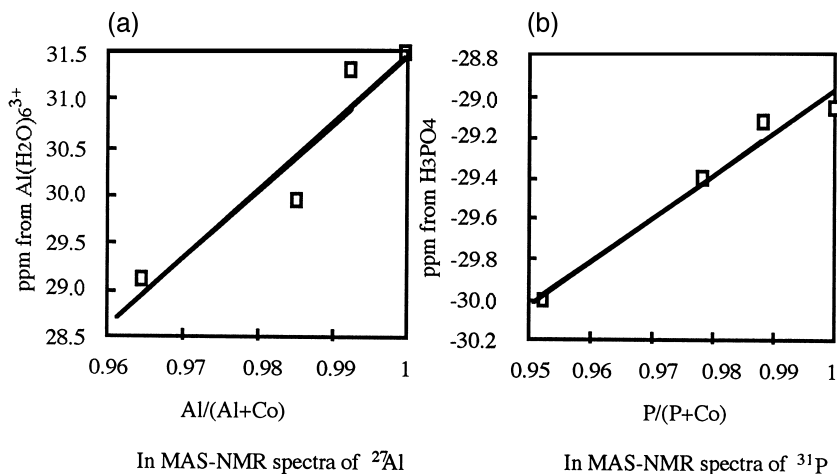


Fig. 6. Relationship between the Al/Al + Co and P/P + Co ratios and chemical shifts.

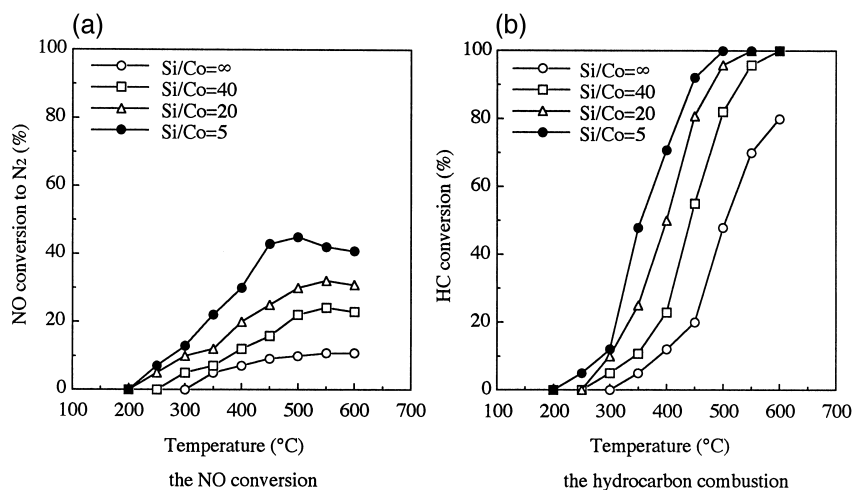


Fig. 7. Effect of temperature on NO removal and  $C_8H_{18}$  combustion for CoAPSO-34 catalysts. Reaction condition: 1000 ppm NO, 1100 ppm  $C_8H_{18}$ , 10%  $O_2$ , balance  $N_2$ , SV = 30 000  $h^{-1}$ .

ppm in  $^{31}P$  NMR spectra were rather shifted to downfield, and the widths of the peak were broader. From these results, the relations between Al/(Al + Co) ratios and chemical shift of Al peak, and P/(P + Co) ratios and chemical shift of P peak from standard samples are plotted in Fig. 6(a) and (b).

With a decrease in the Al/(Al + Co) ratio, the NMR peak for Al was shifted to upfield, and a straight line could be drawn as shown in (a). This result is ascribing that the Co component was incorporated into the framework of SAPO-34 crystal in place of Al component. Furthermore, when the P/(P + Co)

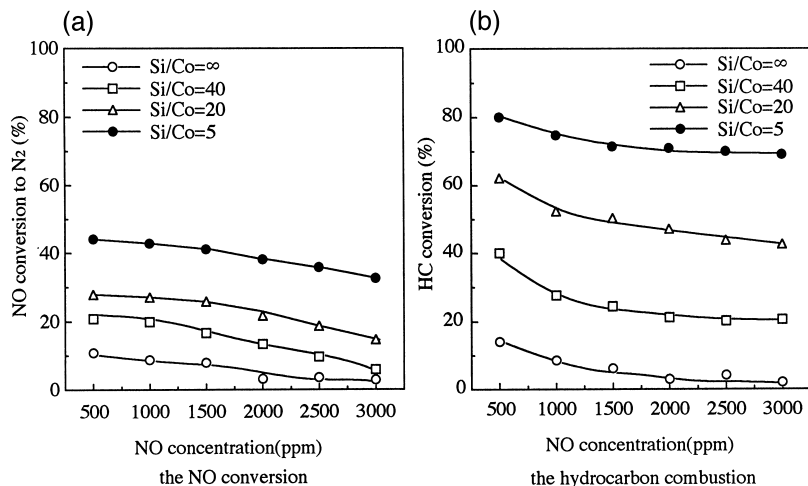


Fig. 8. Effect of the NO concentration on NO removal and  $C_8H_{18}$  combustion for CoAPSO-34 catalysts. Reaction condition: 1100 ppm  $C_8H_{18}$ , 10%  $O_2$ , balance  $N_2$ , SV = 30 000  $h^{-1}$ , temperature 400°C.

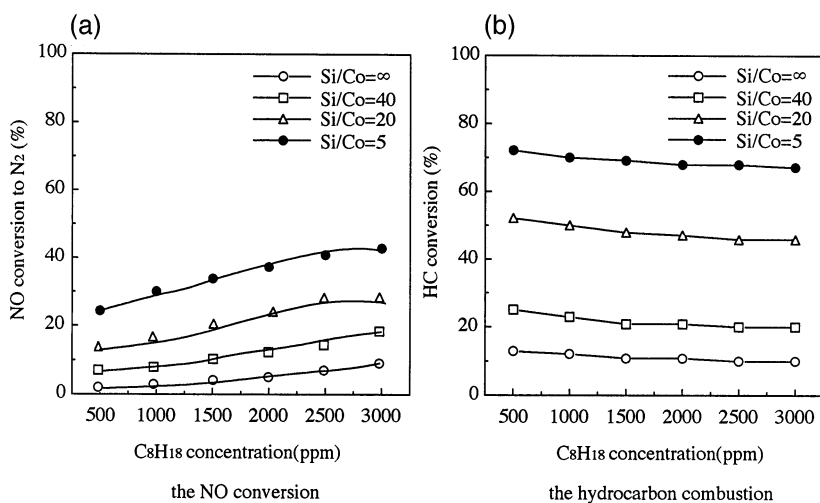


Fig. 9. Effect of the C<sub>8</sub>H<sub>18</sub> concentration on NO removal and C<sub>8</sub>H<sub>18</sub> combustion for CoAPSO-34 catalysts. Reaction condition: 1000 ppm NO, balance N<sub>2</sub>, SV = 30 000 h<sup>-1</sup>, temperature 400°C.

ratio increased the NMR peak for P was shifted to upfield, and a straight line could be drawn as shown in Fig. 6(b).

### 3.4. Performance for NO decomposition in a presence of various hydrocarbons on non-metal and Co-incorporated SAPO-34s

The effect of temperature on NO conversion and C<sub>8</sub>H<sub>18</sub> combustion for Co-incorporated SAPO-34s is

shown in Fig. 7(a) and (b). As shown, with an increase of reaction temperature from 300°C to 550°C, the performances for NO decomposition and hydrocarbon conversion on all the CoAPSO-34s were enhanced compared with SAPO-34. In particular, with an increase of Co amount in the framework, the conversion of NO to N<sub>2</sub> increased, furthermore, with the value highest for catalyst with Si/Co = 5. In addition, the combustion temperature of C<sub>8</sub>H<sub>8</sub> was lower for CoAPSO-34s than that for SAPO-34. This is a proof that the incorporated Co component has

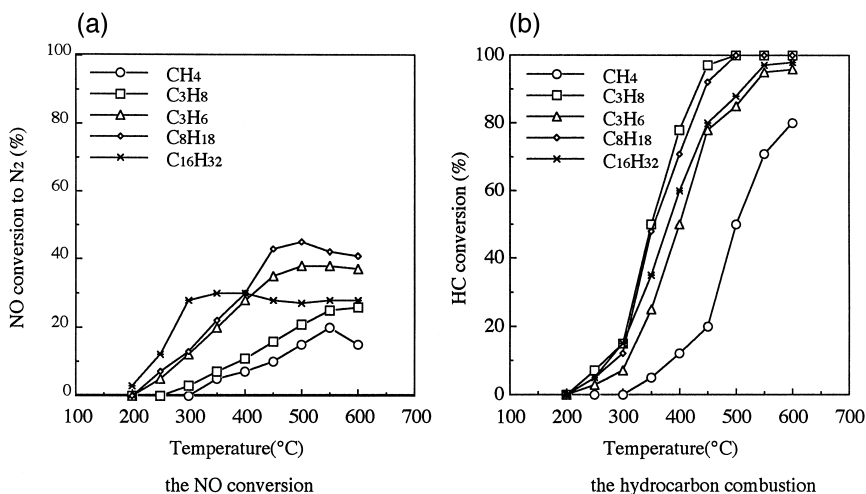


Fig. 10. Performances for NO removal and hydrocarbon conversion in the presence of various hydrocarbons (CH<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>8</sub>H<sub>18</sub>, and C<sub>16</sub>H<sub>32</sub>) on Co-incorporated SAPO-34 (Si/Co = 5). Reaction condition: 1000 ppm NO, balance N<sub>2</sub>, SV = 30 000 h<sup>-1</sup>.

closely influenced the reduction of NO and oxidation of hydrocarbon.

In Fig. 8(a) and (b), the effect of NO concentration on NO conversion and  $C_8H_{18}$  combustion is displayed. As shown, the NO conversion to  $N_2$  and  $C_8H_{18}$  combustion decreased for all catalysts with an increase of NO concentration. However, the decreasing rate for all catalysts was various. Particularly, in the catalyst with Si/Co = 5, the decreasing rate was the lowest.

On the other hand, the effect of  $C_8H_{18}$  concentration on NO conversion and  $C_8H_{18}$  combustion is shown in Fig. 9(a) and (b). With an increase of  $C_8H_{18}$  concentration, the NO conversion to  $N_2$  increased for almost catalysts. A value above 40% in a condition of 3000 ppm  $C_8H_{18}$  was attained in the catalyst with Si/Co = 5. On the contrary, the  $C_8H_{18}$  combustion increased with an increase of Co amount, and the value was not changed in spite of an increase in  $C_8H_{18}$  concentration. In particular, the initial value above 70% was kept within 3000 ppm on the reaction condition of  $C_8H_{18}$  of 3000 ppm for the catalyst with Si/Co = 5.

In addition, the catalytic performances for NO removal and hydrocarbon conversion in the presence of various hydrocarbons on Co-incorporated SAPO-34 (Si/Co = 5) are compared in Fig. 10(a) and (b). As shown, the performance for NO conversion in the presence of  $C_8H_{18}$  or  $C_3H_6$  was extinguishably enhanced at medium temperature around 400°C. On the contrary, in the presence of  $C_{16}H_{32}$ , the conversion increased at low temperature. On the other hand, the hydrocarbon conversion also increased in the presence of  $C_8H_{18}$  or  $C_3H_8$  compared with the presence of  $CH_4$ . From these results, it was confirmed that the  $C_8H_{18}$  was proper as a reductor on NO removal for CoAPSO-34 catalyst.

#### 4. Conclusions

By rapid crystallization method, the crystals having a high crystallinity and a sharp distribution in particle size were obtained. From results of the MAS-NMR of  $^{27}Al$  and  $^{31}P$ , and UV-Visible spectra, incorporation of Co into the framework of SAPO-34 was confirmed. On the other hand, the NO

decomposition on the Co-incorporated catalyst was enhanced compared with the non-metal. In particular, with an increase of Co amount incorporated to SAPO-34 framework, the NO conversion increased. In addition, the performance for NO conversion in the presence of  $C_8H_{18}$  for catalyst with Si/Co = 5 was the highest and the hydrocarbon combustion temperature was also the lowest.

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