Synthesis and Characteristics of CoAPSO-34s, and Their Catalytic Performance on Methanol Conversion

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(Received January 8, 1998; Accepted March 3, 1999)

Abstract: The influence of cobalt incorporation into the framework of SAPO-34 on the catalytic performance on methanol conversion was investigated. CoAPSO-34 catalysts with a high crystallinity and a sharp particle size distribution with various Si/Co(Si/Co=∞, 40, 20, and 5) were acquired employing the rapid crystallization method. From the results of MAS-NMR of $^{27}$Al and $^{31}$P, incorporation of Co into the framework of SAPO-34 was confirmed. These CoAPSO-34 catalysts exhibited a minor methanation on methanol conversion compared with that with Ni-incorporated SAPO-34 catalysts(NiAPSO-34) reported in previous papers and the methanol conversion increased. On the other hand, the ethylene selectivity after 1 h of time on stream on CoAPSO-34 decreased compared with non-metal incorporated catalyst. In particular, high methanol conversion(over 98%) was maintained for 6 h for CoAPSO-34 with Si/Co = 5.

Keywords: CoAPSO-34, rapid crystallization method, methanol conversion

1. Introduction

After the innovation in the synthesis of alumino-phosphate molecular sieves by UCC [1], a trial of methanol conversion had been done using SAPO-34 as the catalyst for methanol conversion [2-5]. A rather high selectivity to ethylene and propylene were observed without causing serious coke formation, although the catalyst has an isomorph of chabazite. Remarkable results were then found by using NiAPSO-34 [6], on which ethylene was obtained from methanol with a selectivity of 88%, expressed by carbon weight percentage, at a medium temperature of 450 °C, at 100% methanol conversion without coke formation.

However, it was suggested in our previous papers [7,8] that the extra-framework nickel component relates closely to the methanation activity which resulted in decrease in ethylene selectivity in methanol conversion. In order to restrain the adverse effect of extra-framework nickel ingredient, the effects of sulfidation by SO$_2$ or H$_2$S addition in methanol conversion were investigated. Subsequently, it was established that such sulfidation treatment can control the methane yield in methanol conversion; with addition of H$_2$S, CH$_4$ yield decreased to half of that corresponded to the result in reaction without addition of H$_2$S. However, these sulfur compounds are a concerning problem for air pollution. Therefore, in this present study, it was tried to synthesis CoAPSO-34 crystal, substituting cobalt for nickel and applied to the methanol conversion reaction, expecting to decrease the methanation in methanol conversion.

The synthesis and characterization of aluminophosphate molecular sieves and isomorphously substituted analogues have attracted a great interest. Several works are available discussing the synthesis conditions in relation to the structure types obtained [9,10]. Furthermore, the characterization of cobalt species in cobalt-containing molecular sieves has been the subject of many investigations [11-15]. Most of these

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reports deal with the substitution of Al by bivalent metal ions, creating Brønsted acid sites, namely acidic P-OH groups, as well as Lewis acid sites. In the case of Co-substituted aluminophosphates, both redox and acidic properties can develop [16-20]. Reduction of Co$^{3+}$ to 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 remained unclear, and the reports on the hydrocarbon synthesis using CoAPO-34 are very scarce.

In this work, characterization and the catalytic performance of SAPO-34s relatively high concentration of Co synthesized by reliable procedure were investigated. In particular, its performance for the methanol conversion was investigated in detail.

2. Experimental

2.1. Catalyst Preparation

In Figure 1, the typical preparation procedure of the CoAPO-34 catalyst is shown. Reagents used for preparation of the gel mixture were as follows: 35 wt.-% aqueous solution of tetraethyl ammonium hydroxide (TEAOH, Aldrich) was used as the organic template. Aluminum isopropoxide (AlP, Wakopure Chem. Industries), cataloid-30 (30 wt.-% SiO$_2$, Kasei Tesque), phosphoric acid (85 wt.-% H$_3$PO$_4$, Nacalai Tesque), and cobalt nitrate ((Co(NO$_3$)$_2$ 6H$_2$O, Nacalai Tesque) were used as the starting materials of Al, Si, P, and Co ingredients of CoAPO-34, respectively. The order of mixing of these starting materials is important to obtain a homogeneous gel mixture, which was confirmed in our previous paper [21]. The gel mixtures for all catalysts were crystallized by applying the rapid crystallization method [21].

2.2. Characterization

The crystallinity and phase purity of the samples synthesized here were identified by powder X-ray diffraction (XRD) using Shimazu XD-DI with Nickel filtered Cu $K\alpha$ radiation (30 kV, 30 mA) in the 2$\theta$ range from 5 to 50 degree. Chemical compositions were analyzed by ICP (inductively coupled plasma), Shimadzu ICP-100III. Crystal size and shape of catalysts were observed by using Hitachi S-2500CX scanning electron microscope (SEM). BET surface areas of crystals were measured by nitrogen gas adsorption at the liquid nitrogen temperature in mixed gas of nitrogen and helium flow as the carrier gas with Shimadzu Flow sorbs 2-2300. Particle size distribution was measured by DLS (Dynamic of light scattering) system of Photol Otsuka Electronics; the samples were dispersed by ultrasonic treatment

![Figure 1. Preparation procedure of CoAPO-34 catalyst.](image)

for 10 min with 120 watt in water. The analysis was determined by weight based distribution.

In order to determine the coordination of Al and P in the framework, the local structure in crystalline was analyzed by magic angle spinning (MAS) NMR with a JEOL GSX-270 solid state, high resolution spectrometer; the scan times were over 400 while the Al(NO$_3$)$_3$ and H$_3$PO$_4$ were used as the standard references. High-power decoupling experiments were carried out at 40$^\circ$ with 40.4 MHz for $^{27}$Al and at 40$^\circ$ with 193 MHz for $^{31}$P.

The acidity of catalyst was estimated by TPD profiles of pre-adsorbed NH$_3$ determined by Quadruple Mass Spectrometer [M-QA100F] of BEL JAPAN INC. To restrain the influence of water during NH$_3$ adsorption, the adsorption was conducted at temperatures higher than 100 $^\circ$C.

The amount of coke deposited on the catalyst after the reaction was measured by temperature-programmed oxidation (TPO) on a Shimadzu DT-40 thermogravimeter with a heating rate of 10 $^\circ$C/min in a 40 mL/min air flow. The profiles were calculated from the weight-loss from 300 $^\circ$C to 800 $^\circ$C.

2.3. Catalytic Reaction

Each methanol conversion reaction was carried out by using an ordinary continuous flow reactor. A 0.325 g portion (0.35 mL) of the catalyst was packed into a quartz tubular reactor having 0.5 cm inner diameter, and a reaction gas composed of 15 mol % methanol and 85 mol % N$_2$ was allowed to flow with a gaseous space velocity (GHSV) of 1000 h$^{-1}$ at

Table 1. Physical Properties of CoAPS0-34 Catalysts Synthesized with Various Si/Co Molar Ratios

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallinity (%)</th>
<th>Composition in crystal (molar ratio)</th>
<th>Surface area (m²/g)</th>
<th>Particle size (μm)</th>
<th>Mean of particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Co = ∞</td>
<td>98</td>
<td>0.435 0.130 0.435 0 0 ∞</td>
<td>500</td>
<td>0.8–2.0</td>
<td>420</td>
</tr>
<tr>
<td>Si/Co = 40</td>
<td>95</td>
<td>0.435 0.130 0.433 0.003 43.33</td>
<td>508</td>
<td>1.0–1.5</td>
<td>500</td>
</tr>
<tr>
<td>Si/Co = 20</td>
<td>95</td>
<td>0.432 0.130 0.432 0.006 21.67</td>
<td>497</td>
<td>1.0–1.5</td>
<td>1100</td>
</tr>
<tr>
<td>Si/Co = 5</td>
<td>100</td>
<td>0.424 0.127 0.424 0.025 5.08</td>
<td>502</td>
<td>1.5–2.0</td>
<td>1400</td>
</tr>
</tbody>
</table>

Determination method | XRD | ICP | BET | SEM | DLS |

450 °C for 1...

The products were analyzed by three FID-type gas chromatographs, Shimadzu GC7A, 12A, and 14A, equipped with integrators. Analyses for methanol and dimethyl ether, C₃–C₄ hydrocarbons, gasoline range hydrocarbons, and CO, were carried out by using columns porapak T, VZ-10, and silicon OV-101, respectively.

The deposited coke was determined by combustion using a micro-thermogravimetric analyzer Shimadzu DTG-50.

3. Results and Discussion

3.1. Characterization of CoAPS0-34 Catalysts

The physical properties of synthesized CoAPS0-34 catalysts are summarized in Table 1. XRD patterns of all the catalysts match well with that of the SAPO-34 reference, and the crystallinity of these catalysts was almost identical. In general, when the amount of metal substituted into framework increased, the crystallinity determined from the intensity decreased. However, in this study, despite of an increase in Co amounts in framework the crystallinity was remained almost identical to that of pure SAPO-34. In addition, in the crystal the more sharp and high peaks were obtained with Si/Co=5. The BET-surface areas for all catalyst were almost the same about 500 m²/g. This is ascribed to the fact that the rate of crystal growth was enhanced followed by increases in Co amount at gel preparation. From the result of ICP data, it can be confirmed that the molar ratios of Si/Co added in the starting gel mixture are almost identical with those of synthesized crystals. This result is a proof that this procedure adapted for CoAPS0-34 synthesis is very stable and reliable. The morphologies of all the crystals observed by SEM showed regular cubic crystals with uniform size distribution of 1.0–2.0 μm, and the particle size of catalysts contained higher loading of Co was larger than catalysts with a smaller amount of Co. These results matches well DLS data which showed particle size distribution with increasing Co amount in crystals.

3.2. Acidic Property

In Figure 3, NH₃-TPD profiles for four typical kinds of catalysts are shown. In general, aluminophosphates (AlPO₄-n) are prepared in the presence of cationic or neutral amine additives and crystallize with a composition ratio of Al/P of one, resulting in no net charge on the framework. However, as silica (SAPO) and/or other metal ions are introduced into the structure, both ion exchange capacity and catalytic acid activity develop. The incorporation of silica into framework displayed Brønsted acid sites in SAPO. Furthermore, incorporation of metal into the SAPO framework can cause, the strength and number of Brønsted acid sites to change. Those profiles obtained in this study consist of two peaks: one appears at a low temperature range of around 150–200 °C and the another appears at a higher temperature range around 420–470 °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 by the strong acidity at high temperatures. At the low temperature, the amounts of acid sites decreased with an increase in Co amount. Therefore, it was reconfirmed that the Si sites were partly substituted by Co atom from the result at high temperature. However, the total acidity decreased but the amount of strong acid sites rather increased with Co introduced. The total amount of acid sites on the
Figure 2. $^{27}$Al and $^{31}$P MAS-NMR spectra for CoAPO-34 crystals with various Si/Co ratios.

Surface of crystals were calculated on the basis of BET-surface area and the NH$_3$-TPD; the values were 7.55, 6.23, 5.90, and 5.95 $\mu$mol/m$^2$ corresponded to Si/Co = $\infty$, 40, 20, and 5, respectively.

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 Figure 4. When the Al/(Al+Co) ratio increased, the NMR peaks for Al shifted to upward, and a straight line could be drawn. From this result, it was confirmed that the Co atom was incorporated into framework of SAPO-34 crystal, in place of Al atom. Furthermore, when the P/(P+Co) ratio increased,
the NMR peaks for P shifted to upward, and a straight line could be drawn. From this result, it can be confirmed that the incorporated Co atom is located at the side of P atom. Therefore, it can be supposed that the incorporated Co atom partly substituted to both sites of Si and P from results of Figures 3 and 4.

3.3. Catalytic Performance

In Figure 5, product distributions for CoAPSO-34 catalysts on methanol conversion are shown. The methanol conversion has almost the same for all the catalysts. The ethylene selectivity decreased with a decrease in Si/Co molar ratio. This is ascribed to increases in particle size and of acidity in CoAPSO-34. However, the methane yield remarkably decreased on CoAPSO-34 compared with on NiAPSO-34 with about 10% methane selectivity in previous paper [8]. Therefore, it was confirmed that introduction of Co in place of Ni was useful the decrease of methanation.

Changes in catalytic performance on CoAPSO-34s as a function of time on stream are shown in Figure 6. As shown, with increasing of time on stream the conversion of methanol and ethylene decreased on all catalysts. However, the decreasing tendencies were smaller on catalyst containing higher Co amounts than that on SAPO-34. In particular, the high methanol conversion on CoAPSO-34 with Si/Co=5 was maintained for 6 hs.

The coke deposited on the catalysts was analyzed by temperature-programmed oxidation (TPO) and the profiles are shown in Figure 7. For the CoAPSO-34 with Si/Co=5, the amount of deposited coke slightly decreased compared with pure SAPO-34 however the combusted temperature was higher on CoAPSO-34. This is ascribed to the increase in the number of strong acid sites on CoAPSO-34 compared with

Figure 5. Product distribution for methanol conversion on CoAPSO-34 catalysts with various Si/Co ratios. Reaction condition: 15 mol % MeOH-balance N₂; GHSV, 1000/h; Temperature, 450 °C; Time on stream, 1 h.

Figure 6. Change in catalytic performance on CoAPSO-34s as a function of time on stream. Reaction condition: 15 mol % MeOH-balance N₂, Temperature 450 °C, GHSV 1000/h.

SAPO-34.

4. Conclusions

This study had been focused on the influence of cobalt incorporation into framework of SAPO-34 on the catalytic performance of methanol conversion. The results can be summarized as follows:

1) by rapid crystallization method, the crystals having a high crystallinity and a sharp particle size distribution were obtained.

2) with an increase in Co amount into framework,
the number of strong acid sites increased.

3) the methanol conversion obtained were almost same for all catalysts, however the ethylene selectivity decreased with a decrease in Si/Co molar ratio.

4) with an increase in time on stream the conversion of methanol and ethylene yield decreased on all the catalysts. However, the decreasing tendencies were smaller on catalyst containing higher Co concentration than that on SAPO-34.

5) for the CoAPSO-34 with Si/Co=5, the amount of deposited coke was decreased compared with pure SAPO-34 however, the coke combustion temperature was higher on CoAPSO-34 with Si/Co=5.

References
