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Synthesis and catalytic performance on methanol conversion of NiAPSO-34 crystals (II): catalytic performance under various reaction conditions

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Abstract

This work has been focused on the catalytic performance for methanol conversion of NiAPSO-34 catalysts which had been synthesized by various preparation methods. The deposited coke during the hydrocarbon transformation was analyzed by temperature-programmed oxidation (TPO) method. For a catalyst with small acid sites and sharp particle size distribution, the catalytic activity and selectivity to ethylene increased compared with other catalysts. It could be confirmed that the catalysts having different acidic densities on external surface and internal surface represented different catalytic activities. Furthermore, it was elucidated that amount of coke formation was strongly related to acidic density on the external crystal surface. On the other hand, catalytic performances under various reaction conditions were exhibited variously and the deposited coke amount was also various. In particular, a surprising result was that the catalytic performance was not changed on the revived catalyst by thermal treatment at 600°C for 3 h. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic activity; NiAPSO-34 catalyst; Methanol conversion; Acidic density; Coke formation

1. Introduction

The synthesis of light olefins from methanol on shape-selective catalysts is now considered to be one of the most promising routes for light olefin synthesis. Some zeolites with narrow pores have been found effective for this purpose [1–5]. In early stage of the investigation, some kinds of narrow pore zeolites such as chabazite [6–9] and ZSM-34 of mobil were found. How- ever, the most serious problem for these catalysts is the short catalyst life caused by coke deposition. To overcome the catalytic deactivation, Inui et al. [6,9] developed the rapid crystallization method, by which they prepared various metallosilicates having the pentasil structure which is expected as the catalyst for the olefin synthesis with high selectivity and long catalyst's life.

The long catalytic life of these metallosilicates is due to the three-dimensional pore structures preventing the conversion of alkylaromatics to polyalkylaromatics or fused-ring aromat-

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ics that are coke precursors. The replacement of Al ions in the pentasil type aluminosilicate (i.e., ZSM-5) with other metal ions would greatly modify the acid property. Furthermore, they had developed the rapid crystallization method together with some particular treatment, like an ultrasonic wave treatment and addition of seed crystal on NiAPSO-34 catalysts [9]. As this is operating, it could control the crystal size and acid property of NiAPSO-34 catalyst under gel preparation step before hydrothermal crystallization. Acquired, these catalysts could prevent the conversion of alkylaromatics to polyalkylaromatics or fused ring aromatics that are coke precursors.

In this work, the catalytic performances on methanol conversion for NiAPSO-34 catalysts synthesized by various preparation method, under various reaction conditions with various reaction temperatures, gas hourly space velocity (GHSV), and concentration of feed, were investigated. Moreover, this study had been focused on the coke formation related closely to the catalytic deactivation.

2. Experimental

2.1. Preparation of catalyst

The catalysts are prepared by applying the rapid crystallization method to the procedure for the synthesis of SAPO-34 as shown in Fig. 1. Reagents used for preparation of the gel mixture were as follows: 35 wt.% aqueous solution of tetraethyl ammonium hydroxide (TEAOH, Aldrich Chemical) was used as the organic template; aluminum isopropoxide (AIP, Wako), cataloid-30 (30 wt.% SiO_2, Kasei Tesque.), phosphoric acid (85 wt.% H_3PO_4, Nacali Tesque.), and nickel nitrate ($(Ni(NO_3)_2 \cdot 6H_2O$, Nacalai Tesque.) were used as the starting materials of Al, Si, P, and Ni ingredients of NiAPSO-34, respectively. The composition of gel formed was 0.2 M $(TEA)_2O$:0.2 M Al_2O_3:0.2 M P_2O_5:0.06 M SiO_2:0.0015 M NiO:10 M H_2O.

Preparation methods for gel mixture (for 1 h in homoginizer of 12000 rpm)

Composition of the gel mixture (molar ratio)
0.20AIP-0.20P₂O₅-0.060SiO₂-0.0015NiO-0.20(TEA)₂O-10H₂O

Addition of seed (SAPO-34, 0.8μm)

Milling for 1 h

Treatment of ultrasonic wave (47 KHz, 100 W, at room temp.)

Hydrothermal crystallization by appling the rapid crystallization method (at room temp. up to 200°C for 1 h, hold at 200°C for 10 h)

Washing with water until pH attaines 7

Drying (at 120°C for 10 h)

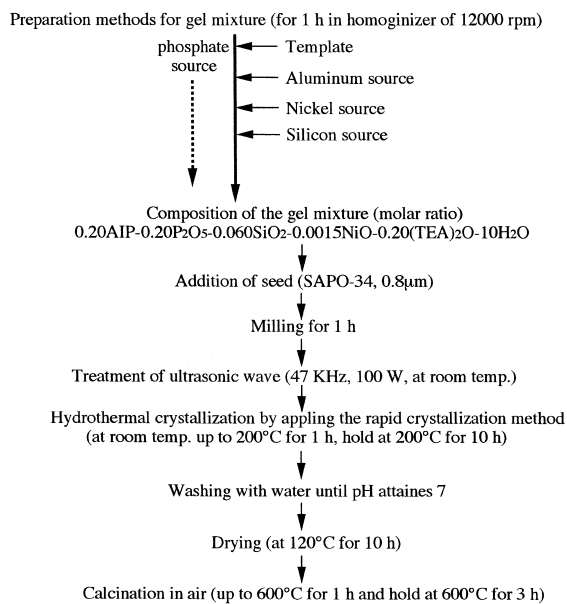Calcination in air (up to 600°C for 1 h and hold at 600°C for 3 h)

Fig. 1. Preparation for the gel mixtures on synthesis of NiAPSO-34 crystal.

The order of mixing of these starting materials is important to obtain a homogeneous gel mixture. In our previous study [9], we have found the best mixing order applied in this paper. Three kinds of different procedures are used for synthesis of samples such as using a homogenizer, addition of seed, and treatment of ultrasonic wave as shown in Fig. 1, and attained catalysts are listed in Table 1.

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 2θ ranges from 5° to 50°. The scan speed was 1°/min and time constant was 1 s. The diffraction angles of 22.0° and 9.7° were selected to discuss the crystallinity of synthesized samples.

Particle size distribution of catalyst was obtained by diffraction of light scattering (DLS) system of Photal Otsuka Electronics. The samples were dispersed by ultrasonic wave treat-

Table 1
Difference of treatment on gel mixture preparation

Preparation	Catalyst			
	CAT.1	CAT.2	CAT.3	CAT.4
Homogenizer operation	none	done	done	done
Addition of seed crystal	none	none	2.0 wt.%	5.0 wt.%
Ultrasonic wave treatment (one unit 5 min)	none	1	4	4

ment for 10 min with 120 W and the result was exhibited as distributed number (%).

The Brunauer–Emmet–Teller (BET) surface areas of catalysts were measured by nitrogen gas adsorption with continuous flow method using a gas chromatography at the liquid nitrogen temperature in mixing gas of nitrogen and helium flow as the carrier gas with Shimadzu Flow sorbs 2-2300.

The acidity of all the catalysts was estimated from temperature-programmed desorption (TPD) profiles of pre-adsorbed NH_3, determined by a Rigaku microthermogravimetic analyzer thermoflex TG 8110 equipped with thermal analysis station TAS 100. The acidic density on external surface of catalysts was assumed from TPD profiles of pre-adsorbed 4-methyl quinoline. The method was illustrated in previous paper [9].

2.3. Reaction method

The methanol to hydrocarbon conversion was carried out by using a continuous flow apparatus. The conditions detailed as follows: catalyst weight: 0.325 g; GHSV, gas compositions, reaction temperature, reaction time: arbitrary;

crushed catalyst size: 20–24 mesh; reaction column: inner size 0.5 cm; temperature of connected heating tape: above 50°C.

The reaction products were determined by three gas chromatography with flame ionization detector (FID)-type and one thermal conductivity detector (TCD)-type. The columns of VZ-10 for analysis of gaseous hydrocarbons, SILICON-OV-101 for analysis of gasoline range hydrocarbons, and Porapak T for analysis of methanol and dimethylether and activated carbon for CO and CO_2 were used.

2.4. Preparation of coke analysis

The deposited coke was investigated using differential thermogravimetry (DTG) techniques with DT-40 of Shimazu, detailed as follows: a weighed amount (ca. 20 mg) of a sample was placed in a sample pan and heated from 300° to 800°C at a heating rate of 10°C/min in a 40 ml/min air flow. The reference sample was 20 mg of *a*-alumina. The data was acquired from the decrease in weight.

3. Results and discussion

3.1. Physical properties of catalysts

The physical properties of catalysts are summarized in Table 2. The X-ray diffraction (XRD) patterns of catalysts were identified with U.S. Patent literature. All the catalysts had different crystallinities which were obtained from specific peak intensity (for angles of 22.5° and 9.7°). On the other hand, the CAT.3 had a

Table 2
Physical properties for synthesized NiAPSO-34 catalysts

Catalyst	Crystallite size hkl (Å)			Degree of crystallinity (%)	Surface area (m²/g)	Particle size (μm)	Atomic ratio (Al ≡ 1) Al/P/Si/Ni	Ni-coordination in catalyst	
	101	211	201					Oh	Td
CAT.1	640	601	540	87	552	1.0–1.5	1.00/2.00/0.26/0.0028	Oh	none
CAT.2	674	665	296	53	498	0.3–0.5	1.00/1.35/0.19/0.0020	Oh	Td
CAT.3	562	573	547	100	565	0.8–1.0	1.00/2.27/0.27/0.0029	Oh	Td
CAT.4	510	491	324	58	504	1.0–1.5	1.00/1.57/0.21/0.0030	Oh	Td
Measurement method		XRD		XRD	BET	SEM	ICP	UV–visible	

regular crystal growth, while the other catalysts had not regular. In the scanning electron microscopy (SEM) photograph, all the catalysts showed uniform cube type of chabazite structure; however, the particle sizes were various. The BET surface areas of calcined catalysts possessed wide areas above 500 m^2/g except for the CAT.2. On the other hand, the Al/Si ratio was three in CAT.3 and the ratio in CAT.1 was less than that of CAT.3; however, the contained Ni amount has similar value for all the catalysts. Furthermore, Ni^{2+} situation with six coordination numbers was observed for all the sample by UV-spectrum and a band corresponding to the tetrahedral structure was also observed except for the CAT.1.

The distributions of particle size were attained by DLS test. These results are shown in Fig. 2. CAT.1 had a distribution with broad type as compared with other catalysts. On the other hand, the distributions of particle size for catalysts synthesized with seed crystal addition were attained sharply as compared with the catalysts without seed crystal addition. However, with an increase in added seed crystal amount, the size distribution was changed to a broad type. From this result, it could be supposed that the added
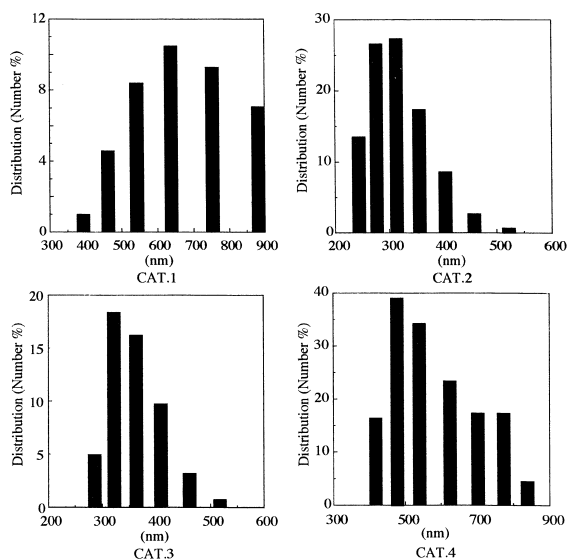
Table 3
Acidic property and catalytic performance for all catalysts. Reaction condition: MeOH 15 mol%–N_2 85 mol%, GHSV 1000 h^{-1}, 425°C, time on stream 1 h

Catalyst	CAT.1	CAT.2	CAT.3	CAT.4
Reaction score				
Methanol conversion (%)	94.5	100	94.5	100
Selectivity of C_2–C_4 olefin (C-wt.%)	88.9	76.3	89.7	89.0
Ethylene selectivity (C-wt.%)	64.0	72.5	78.3	70.9
Methane selectivity (C-wt.%)	2.61	20.7	6.85	4.47
Deposited coke amount (wt.%)	3.35	3.42	2.59	3.33
Acidic property				
Adsorption amount of NH_3 (mmol/g)	4.45	1.93	2.61	3.28
Adsorption amount of 4-MQ (mmol/g)	0.250	0.262	0.223	0.225

seed crystals had more influence on the crystallization than the creation of nucleus.

3.2. Methanol conversion reaction

The products after methanol conversion reaction at 425°C for 1 h on all catalysts are detailed in Table 3. On CAT.2 with the smallest particle size, the selectivity to ethylene and the methanol conversion was enhanced as compared with on CAT.1. Moreover, the methanol conversion and the selectivity to ethylene on CAT.3 with 2 wt.% seed had the best value as 100% and 78%, respectively. On the other hand, the ethylene selectivity on CAT.4 had a small value as compared with on that of CAT.3. It is ascribed to the intermediate transformation which resulted from longer staying time on CAT.4 with large size.

3.3. Correlationship between the acidic properties and catalytic performance

Table 3 also describes the acidic properties of all catalysts. Adsorption amount of NH_3 and

Fig. 2. Distribution of particle size for all the catalysts.

acidic density were much more in the CAT.1 than that in the other catalysts. On the other hand, the adsorbed NH_3 amount was the least in the CAT.2, extraordinarily. Acid sites on external surface obtained by 4-methyl quinoline-TPD are also exhibited in this table. The adsorption amount of 4-methyl quinoline was smaller on CAT.3 than those on the other catalysts. On the other hand, the adsorption amount of 4-methyl quinoline increased on CAT.2 and CAT.4.

Deposited coke amount was analyzed by temperature-programmed oxidation (TPO) method. In the temperature range of 623–973 K, almost all cokes were removed. Deposited coke amount after methanol conversion in catalysts is also summarized in Table 3. The coke amount almost resembled those of CAT.1, 2, and 4. On the other hand, the coke amount in CAT.3 was smaller than those in the other catalysts.

The correlationship between the selectivity to ethylene and the acid density on internal surface is shown in Fig. 3. As shown, when the acid density in internal surface increased, the selectivity decreased conversely. In particular, the selectivity to ethylene was attained with the best value of 78.3 C-wt.% for CAT.3 when adsorption amount of NH_3 was 2.61 mmol/g. With this result, it was reaffirmed that the selectivity was closely related to the acid density on inter-
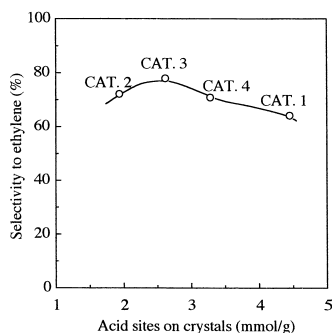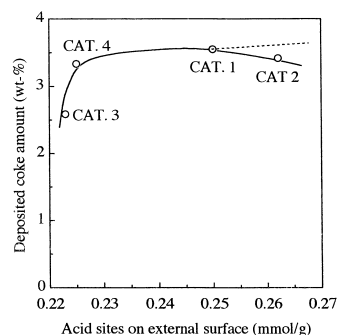

Fig. 4. Correlationship between the acid sites on external surface and the deposited coke amount. Reaction condition: GHSV 1000 h^{-1}, 425°C, time on stream 1 h. Gas composition; MeOH 15 mol%–N_2 85 mol%.

nal surface. However, in spite of having the small acid sites, the ethylene selectivity decreased in CAT.2. It is ascribed that the CAT.2 had the much more acidic density on external surface vs. internal surface as shown in Table 3. From this result, it could be supposed that the conversion reaction was progressed not only at acid sites on internal surface but also at that on external surface for CAT.2.

In Fig. 4, the correlated relation between the acid density on the external surface and deposited coke amount is indicated. The acid density on external surface has a strong influence on deposited coke amount. The coke amount decreased also when the acid density on exter-
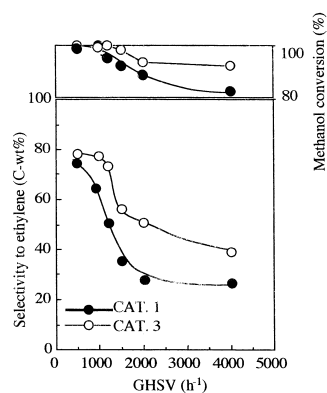

Fig. 3. Correlationship between the acid sites on crystals and the selectivity to ethylene. Reaction condition: GHSV 1000 h^{-1}, 425°C, time on stream 1 h. Gas composition: MeOH 15 mol%–N_2 85 mol%.

Fig. 5. Effect of GHSV on selectivity to ethylene and methanol conversion. Reaction condition: temperature 425°C, time 1 h, 20–24 mesh. Gas condition: MeOH 15 mol%–N_2 85 mol%.
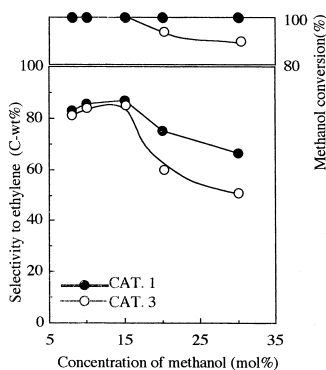
Fig. 6. Effect of concentration of methanol on selectivity to ethylene and methanol conversion. Reaction condition: temperature 425°C, time 1 h, 20–24 mesh. GHSV: 1000 h^{-1}, valence gas: N$_2$.

Fig. 8. Effect of methanol concentration on deposited coke amount. Reaction condition: temperature 425°C, time on stream 1 h, 20–24 mesh, GHSV 500 h^{-1}. Gas composition: valence gas — N$_2$.

nal surface decreased. In particular, the coke amount was exhibited as the smallest value for CAT.3.

3.4. Effect of reaction condition on methanol conversion

The relationship between the selectivity to ethylene and GHSV on CAT.1 and CAT.3 is compared in Fig. 5. With an increase in the GHSV, the methanol conversion and selectivity to ethylene decreased on both catalysts; however, the decreased rate was slow on CAT.3. In particular, the selectivity to ethylene and methanol conversion were about 78 wt.% and

100% on CAT.3 at the GHSV of 500 h^{-1}; however, these decreased abruptly when the GHSV increased up to 1500 h^{-1}.

The changes of the selectivity to ethylene and methanol conversion under various methanol concentrations on CAT.1 and CAT.3 are shown in Fig. 6. The selectivity to ethylene and methanol conversion exhibited the best yield in both catalysts when the concentration of methanol was 15 mol% with GHSV of 500 h^{-1}. However, the more the methanol concentration increased, the more the selectivity to ethylene decreased. The decreased rate was slower in CAT.3 than CAT.1.
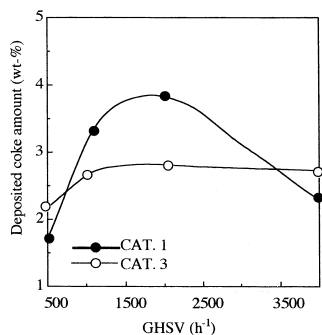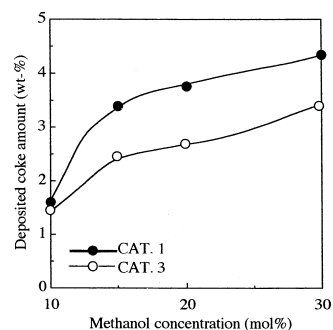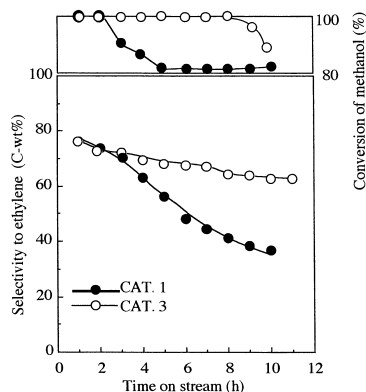

Fig. 7. Effect of GHSV on deposited coke amount. Reaction condition: temperature 425°C, time on stream 1 h, 20–24 mesh. Gas composition: MeOH 15 mol%–N$_2$ 85 mol%.

Fig. 9. Effect of time on stream on selectivity to ethylene and methanol conversion. Reaction condition: temperature 425°C; GHSV 1000 h^{-1}. Gas composition: MeOH 10 mol%–N$_2$ 90 mol%.

Table 4

Comparison of product distribution on new CAT.3 and the revived CAT.3 by re-calcination at 600°C for 3 h

Treatment	Conversion (%)	Temperature (°C)	DME	Product distribution (C-wt.%)					
				C_1	C_2–C_4	C_2=	C_3=	C_4=	C_5~
New CAT.3	100	425	0.00	7.09	1.31	78.0	9.86	2.0	1.74
Used CAT.3 for three times	100	425	0.00	7.52	1.50	76.5	10.4	2.5	1.61
Used CAT.3 for five times	100	425	0.00	7.60	1.53	77.0	9.96	3.0	1.07

3.5. Analysis of deposited coke

Fig. 7 shows the changes of deposited coke amount under the various GHSV on CAT.1 and CAT.3. With an increase in the GHSV, the deposited coke amount in CAT.3 increased until $1000 \ h^{-1}$ and it was kept constantly. However, the deposited coke amount decreased in CAT.1, on the contrary, when the GHSV was transferred to above $4000 \ h^{-1}$. It is ascribed that the methanol is flowed very fast into the cavity and then the staying time of produced intermediates from methanol in cavity is shorter — in consequence, the intermediates are not transferred to longer chain carbons.

Changes of deposited coke amount under various methanol concentrations on CAT.1 and CAT.3 are shown in Fig. 8. From this result, it was reconfirmed that when the methanol concentration increased, the deposited coke amount increased in both catalysts proportionally. However, it was retarded on CAT.3.

3.6. Lifetime on CAT.3

Fig. 9 shows the change of the selectivity to ethylene under change of reaction time. As shown, the selectivity to ethylene was above 70 wt.% and it was kept on until 10 h on CAT.3. For the CAT.1, the beginning displayed high ethylene selectivity. However, the selectivity decreased abruptly when the reaction time increased.

Table 4 illustrates the result for methanol conversion reaction on revived CAT.3 by treatment at 600°C for 3 h. Surprisingly, when the revived frequency increased, the methane selectivity increased. From this result, it could be supposed that the incorporated nickel component was extruded by repeated thermal treatment and then in consequence, it led to the catalytic deactivation. However, the deactivation was not appeared until revival with five times.

4. Conclusion

In the correlationship between the catalytic performance and acid properties, it was elucidated that the acid density was related closely to the selectivity to ethylene and methanol conversion. In particular, the selectivity to ethylene was related to the acidic density located on internal surface and the coke formation was related to the acid density located on external surface.

In general, the catalytic performance on methanol conversion has influence on reaction condition. In particular, it was well-known that the activity was at its best value at a higher GHSV and lower methanol concentration. However, the selectivity to ethylene and methanol conversion had the best yield under mild conditions, such as GHSV of $500 \ h^{-1}$ and a methanol concentration of 15 mol% for almost all catalysts in this study, surprisingly.

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