

Synthesis and Their Catalytic Performance on Microporous Materials(CHA, ERI and MTT types)

Misook Kang, Jong-Yul Park* and Myeong-Heon Um**

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-Ku, Kyoto 606-01, Japan

*Department of Chemistry, Pusan National University, Pusan 609-735, Korea

**Department of Industrial Chemistry, Cheonan National Technical College, Cheonan 330-240, Korea

마이크로다공성재료의 합성과 촉매적성능(CHA, ERI, and MTT types)

강미숙 · 박종열* · 엄명현**

일본 경도대학교 물질에너지학과

*부산대학교 화학과

**국립천안공업대학 공업화학과

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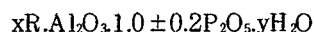
초 특 삼차원적 골격구조를 가지며 세공의 크기와 산성도가 유사한 SAPO-44, SAPO-34(CHA type), SAPO-17(ERI type), 그리고 1차원적 골격구조를 가진 ZSM-23(MTT type) 촉매재료를 합성하고, 메탄올 전환반응에 있어서의 촉매적 성능을 비교 검토하였다. 이들의 산성도 세기는 SAPO-44 > SAPO-34 > SAPO-17 > ZSM-23 순으로 나타났다. 메탄올 전환성능을 비교한 결과, 삼차원적 골격구조를 가지고 있는 SAPO-34와 SAPO-44에서 높은 에틸렌 선택성이 얻어졌으며, 특히 Ni를 골격내에 도입시켰을 때 그 선택성은 더욱 증가하였다. 반면에 1차원적 골격구조를 가지고 있는 ZSM-23에서는 입체적 형상선택성의 감소로 올레핀보다는 파라핀의 선택성이 우세하였다.

Abstract This work was focused on the synthesis and their catalytic performance on microporous materials having various pore types and dimensions in structures, such as the SAPO-34 and the SAPO-44 with CHA type, the SAPO-17 with ERI type of three dimensional structures, and the ZSM-23 with MTT type of one dimensional structure. Synthesized materials exhibited various acidities and the selectivities to olefin in methanol conversion. As a result, the order of their acid strength was as follows; SAPO-44 > SAPO-34 > SAPO-17 > ZSM-5. On the other hand, the CHA type materials, such as SAPO-34 and SAPO-44, had high selectivity to light olefins(ethylene or propylene), and ZSM-23 with MTT type of one dimensional structure showed high selectivity to paraffins over C₅~. This result is a proof that the structure in material had strong influence on catalytic performance. In addition, a surprising result is that the catalytic selectivity to ethylene enhanced on Ni-corporated materials compared with the non-corporated.

1. Introduction

The aluminophosphate molecular sieves (A₂PO₅) are new class microporous crystalline materials with which have potential use for catalysts.^{1~4)} Aluminophosphates possess many structural similarities to silicates: (a) A₂PO₅ is isoelectronic to SiO₂, (b) the average of the ionic radii of Al³⁺ (0.39 Å) and P⁵⁺ (0.17 Å) is 0.28 Å, which is very close to ionic radius of Si⁴⁺ (0.26 Å), and (c) dense phases of A₂PO₅ are isomorphous to several structural forms of SiO₂, i.e., α- and β-quartz; α-, β-, and γ-tridymite; and α- and β-cristobalite,^{1,2)} in which two Si atoms are replaced with a pair of Al and P atoms. The synthesis of aluminophosphate molecular sieves is carried out hydrothermally at a temperature in a range of 125-250 °C from reactive aqueous gels con-

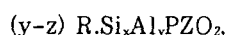
taining alumina, phosphate, and quaternary ammonium hydroxide is used. The product has the following general formular:



where the quantities x and y represent the amounts required to fill the microporous voids within the neutral A₂PO₅ framework.

Silicoaluminophosphate molecular sieves (SAPO-n)^{5~10)} were proposed for the extension of the aluminophosphate materials. The incorporation of silicon into framework sites was aimed to generate family of silicoaluminophosphate materials exhibits structural diversity, in which have three-dimensional crystal structure. SAPO-40, SAPO-41, and SAPO-44 have novel structures; SAPO-5, SAPO-11, SAPO-16, and

SAPO-31 have the structures topologically related to the aluminophosphates, while SAPO-17 (erionite type) and SAPO-20 (sodalite type) have the structures topologically related to both zeolites and aluminophosphates. The SAPO molecular sieves materials are also synthesized hydrothermally at 100~200°C from reactive mixtures containing organic amine or quaternary ammonium templates. The anhydrous form of crystal SAPO-34 has a wide compositional range of :



where x, y, and z represent the mole fractions of silicon, aluminum, and phosphorous ranging from 0.01-0.98, 0.01-0.60, and 0.01-0.52, respectively, with $x+y+z=1$ while R is a monovalent organic cation.

Although the physical properties of various SAPO's have been reported frequently, their catalytic performance in methanol conversion reaction have not yet been fully explored. Especially, these have been used in the synthesis of light olefins using this route in petroleum chemistry.^{11~13)}

In this work, therefore, various silicoaluminophosphates possessing different pore sizes were synthesized by adopting the rapid crystallization method developed by T. Inui,¹⁴⁾ The SAPO-34 and SAPO-44 with chabazite type (CHA), SAPO-17 with erionite type (ERI) having 8-membered oxygen ring, and then ZSM-23 (MTT) having one-dimensional structure and 10-membered ring were synthesized. In addition, their catalytic performance in methanol conversion reaction was investigated, and their structure and acidity were discussed.

2. Experimental

Preparation of catalysts

Reagents

Reagents used in preparation of catalysts were introduced as follows ; tetraethyl ammonium hydroxide (TEAOH, 35wt% aqueous solution, Aldrich Chemical Company LTD.), cyclohexylamine (CHA, Wako pure Chem. Industries LTD.), and pyrrolidine (Nacalai tesque. Inc.) were used as the template. Aluminum isopropoxide (AIP, Wako pure Chem. Industries LTD.), sodium aluminates ($NaAlO_2$, Nacalai tesque. Inc.), and sodium hydroxide (NaOH, Nacalai tesque INC.) were used as aluminium source. Cataloid-30 (30wt% SiO_2 , Kasei Tesque.), phosphoric acid (85wt% H_3PO_4 , Nacalai Tesque. Inc.), and nickel nitrate ($(Ni(NO_3)_2 \cdot 6H_2O)$, Nacalai Tesque. Inc.) were used as starting materials of

Si, P, and Ni, respectively.

Hydrogels preparation

In Fig. 1, the typical preparation procedure of these catalysts is shown. The preparations were followed to synthesis method printed by B.M. Lok, etc.⁵⁾ with applying to the rapid crystallization method developed in Inui Lab.¹⁴⁾ In case of Ni-incorporated materials, the ratio of Si/Ni was 40. These preparations are described as nexts ;

NiAPSO-34 ; 30.640g of AIP was added to 63.110g of TEAOH in a 500 ml beaker, and then stirred vigorously with a homogenizer. The stirring was continued for 10 min. Solution of 0.173g of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in 10ml of H_2O was added to the previous mixture. The mixture was stirred for 10min with a homogenizer. SiO_2 of 4.506g was added to the mixture and was stirred for 20min. H_3PO_4 of 17.294g dissolved in 10ml of H_2O was added to the previous mixture and was stirred until homogeneous gel condition.

NiAPSO-44 ; 20.425g of AIP was added to CHA aqueous solution of 4.950g was diluted to 25g of H_2O . The solution was stirred with homogenizer for 10min. Solution of 0.218g of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in 5ml of H_2O was added to the previous mixture, and then the mixture was stirred for 10min. SiO_2 of 6.000g was added to the mixture and was stirred for 20min. H_3PO_4 of 11.518g was added to the previous mixture and was

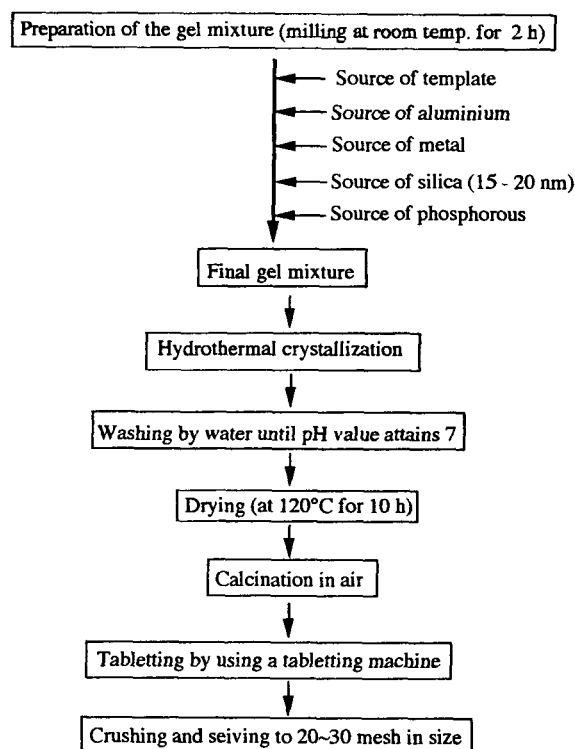


Fig. 1. Preparation procedure for materials.

stirred until homogeneous gel condition.

NiAPSO-17 ; 20.425g of AIP was added to CHA aqueous solution of 4.950g was diluted to 25g of H₂O. The solution was stirred with homogenizer for 10min. Solution of 0.036g of Ni(NO₃)₂·6H₂O dissolved in 5ml of H₂O was added to the previous mixture, and then the mixture was stirred for 10min. SiO₂ of 1.000g was added to the mixture and was stirred for 20min. H₃PO₄ of 11.527g was added to the previous mixture and was stirred until homogeneous gel condition.

NiZSM-23 ; 1.193g of NaAlO₂ was added to pyrrolidine aqueous solution of 4.950g was diluted to 5g of H₂O. The solution was stirred with homogenizer for 10min. Solution of 2.153g of Ni(NO₃)₂·6H₂O dissolved in 5.905ml of H₂O was added to the previous mixture, and then the mixture was stirred for 10min. SiO₂ of 59.566g was added to the previous mixture and was stirred until homogeneous gel condition.

Hydrothermal crystallization

Each precursor gel was put in Teflon tube, and all materials were crystallized hydrothermally together adopting the rapid crystallization method.¹⁴ The vessel contained reactive hydrogel was put in a stainless steel autoclave. Atmosphere in the autoclave was in air. The autoclave was transferred into a dry oven, and the temperature was kept at 200°C for 10h, 48h, 48h, and 24h for NiAPSO-34, NiAPSO-44, NiAPSO-17, and NiZSM-23, respectively. Synthesized crystals were washed by repeated cycles of centrifugation until pH 7 and were dried at 120°C for 10h, and were calcined at 600°C for 3h in air. Prepared materials as catalysts were tabulated and crushed up with 20-24 mesh to provide the reaction.

Characterization of catalysts

Synthesized crystals were identified by powder X-ray diffraction analysis (XRD), Shimadzu XD-D1 with Nickel filtered Cu K α radiation at an angle of 2 θ range from 5 to 50 degree.

BET surface areas of materials 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.

Size and shape of materials were observed by scanning electron microscope (SEM) with Hitachi-Akashi.

Acidity of material was estimated by TPD profiles of pre-absorbed NH₃, determined by a Rigaku micro thermo gravimetric analyzer thermoflex TG 8110 equipped with thermal analysis station TAS 100. The

preparation was explained as follows ; A 150mg portion of sample with powder form was placed in sample pan. It was heated up 500°C at a constant heating rate of 20°C/min in a flow of nitrogen at a flow rate of 50ml/min to remove absorbed water. The sample was cooled down to 50°C and N₂ was replaced as mixed gas containing 5% NH₃ balanced with N₂. After the NH₃ was adsorbed on whole available acid sites of sample at that temperature, which was recognized as no further increase in the sample weight, the mixing gas was replaced as N₂, again. This sample was heated up from 50°C to 80°C at a heating rate of 1°C/min, and then kept at the temperature until significant decrease in the sample weight was observed. The sample was heated up from 80°C to 600°C at a heating rate of 10°C/min to desorb the almost adsorbed NH₃.

Reaction method on methanol conversion

The methanol conversion reaction to hydrocarbon using microporous materials as catalysts was carried out by a continuous flow apparatus as shown in Fig. 2, under the following conditions ; catalyst weight : 0.325g, GHSV : 2000/h, gas compositions : 20mol% methanol (saturator temp : 34°C) - 80mol% N₂ (flow rate : 15ml/sec), reaction temperature : 450°C, reaction time : 1h, crushed catalyst size : 20-24mesh, reaction column : inner size 0.5cm, temperature of connected heating tape : above 50°C

Reaction preparation

A 0.325g of a catalyst crushed up with 20-24mesh form was placed in the reaction column and packed up

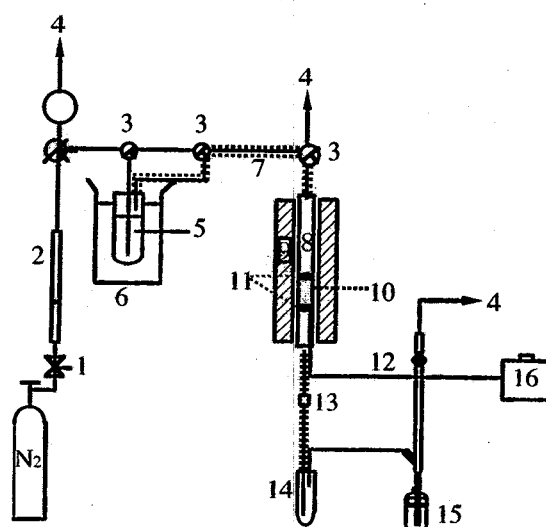


Fig. 2. Schematic diagram of fixed-bed flow-type reaction apparatus. 1. Needle valve; 2. Flow meter; 3. Three-way stopcock; 4. Purge; 5. MeOH; 6. Water bath; 7. Ribbon heater; 8. Tubular reactor; 9. Electric furnace; 10. Catalyst; 11. Quartz wool; 12. Thermocouple; 13. Sampling port; 14. Trap; 15. Soap-film flow meter; 16. Temperature controller.

the top and bottom with quartz wool. The N_2 gas as balance gas was flowed to the reaction column with catalyst. The catalyst was heated up to $500^\circ C$ at constant heating rate of $15^\circ C/min$ to remove the adsorbed water. The temperature was kept for 10min. It was cooled down to reaction temperature with cooling rate $10^\circ C/min$. The temperature of reaction was kept for 30min. And then the N_2 gas was changed to mixing gas, N_2 gas of 80mol% and methanol gas saturated of 20mol% at the reaction temperature for 1h. After 1h, the reaction products were ejected with a 1ml injector and were determined by three FID-type gas chromatography and one TCD-type. The columns of VZ-10 for analysis of gaseous hydrocarbons, SILICON-OV-101 for analysis of gasoline range hydrocarbons, and Porapark T for analysis of methanol and dimethylether were used.

Preparation of coke analysis

The produced coke was investigated using DTG techniques with DT-40 of Shimadzu, detailed as follows: A weighed amount (ca.20mg) of a sample was placed in a sample pan and heated from $300^\circ C$ to $700^\circ C$ at a heating rate of $10^\circ C/min$ in a 40ml/min air flow. The reference sample was 20mg of α -alumina. The data was acquired from the decrease of weight.

3. Results and Discussion

Physical properties of materials

Their pore structures are summarized in Table 1. The SAPO-34 and 44, are the CHA type with 8-oxygen membered ring in three dimensional structure, and SAPO-17 is ERI type also with three dimensional structure, on the other hand, ZSM-23 has 10-oxygen membered ring in one dimensional structure.

The XRD patterns of all the materials synthesized are shown in Fig. 3. The peak patterns of all the materials accorded well to those mentioned in patents. Their surface areas were 580, 490, 400 and $230 m^2/g$ for SAPO-34, SAPO-44, SAPO-17, and ZSM-23,

Table 1. Physical properties of materials

Materials	Al_2O_3/SiO_2 ratios	Pore systems
SAPO-34	3.03	8 3.8 × 3.8 ***
SAPO-44	2.13	8 3.8 × 3.8 ***
SAPO-17	14.30	8 3.6 × 5.1 ***
ZSM-23	0.02	10 4.5 × 5.2 *

*Pore system; bold face numerals are number of tetrahedra defining a channel; light face numerals designate channel dimensions(A); asterisks indicate whether 1-, 2-, or 3-dimensional (for example, *indicates one-dimension)

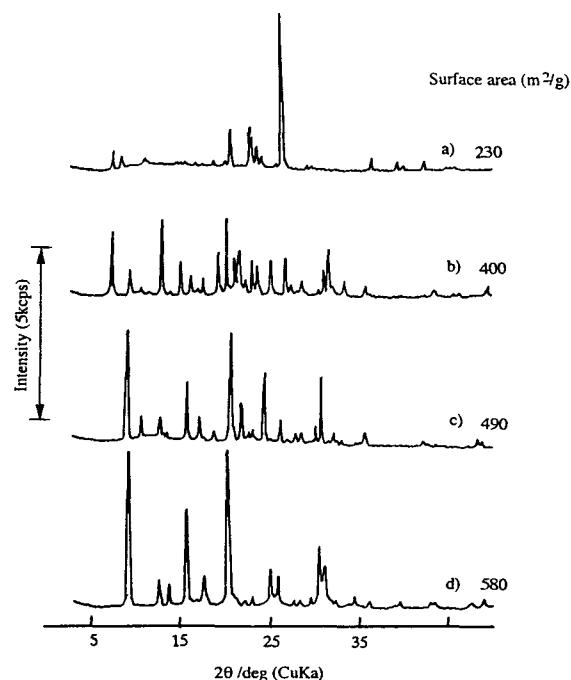


Fig. 3. XRD pattern for as-synthesized materials. (a) SAPO-34, (b) SAPO-44, (c) SAPO-17, and (d) ZSM-23

respectively. These results show that three dimensional structure has larger surface areas than that in one dimensional structure.

In Fig. 4, the shapes of materials are shown. The SAPO-34 and 44 had same shape as cubic types, however the size was larger in SAPO-44 than the SAPO-34. On the other hand, SAPO-17 and ZSM-23 have a cylinder and round type, respectively

Acidity for materials

The NH_3 -profiles of all the materials are shown in Fig. 5. These profiles consist of two peaks: one appears at a low temperature range $150 \sim 180^\circ C$ and the other appears at a high temperature range $420 \sim 470^\circ C$. These low and high desorption peaks correspond to the weak and strong acid sites, respectively. As shown, SAPO-17 showed only one peak for desorption of NH_3 at around $150 \sim 180^\circ C$, and ZSM-23 also exhibited one broad peak at around $200 \sim 300^\circ C$. For the SAPO-34 and SAPO-44, two desorption peaks at a low temperature range around $150 \sim 180^\circ C$ and at a high temperature range around $400 \sim 450^\circ C$ were observed. It is generally accepted that the low and high temperature desorption peaks correspond to the weak and strong acid sites, respectively, and therefore, the order of acid strength was increased as follows; $ZSM-23 < SAPO-17 < SAPO-34 < SAPO-44$. However the acid amounts in SAPO-34 was much than that in SAPO-44.

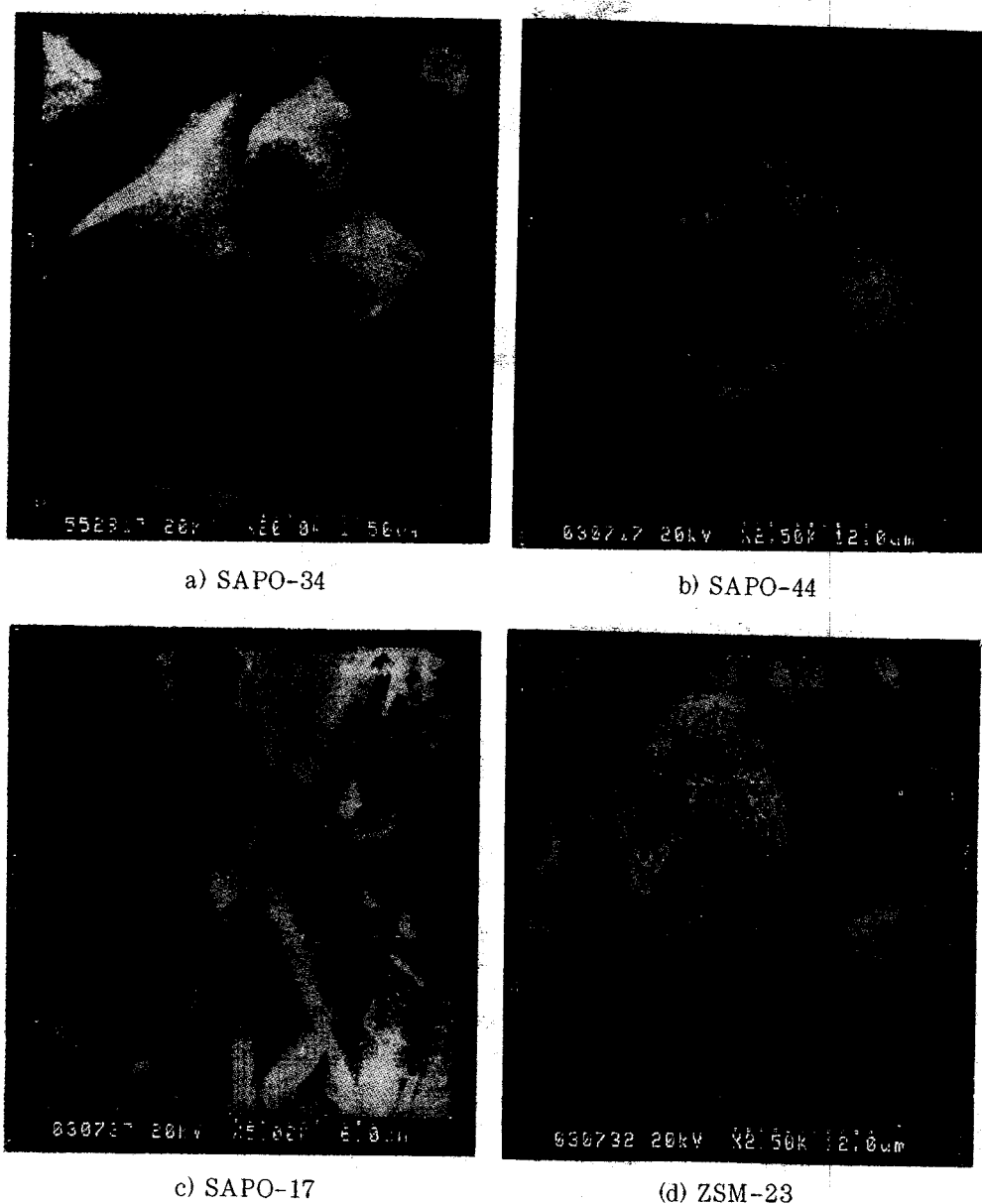


Fig. 4. SEM photographs for materials.

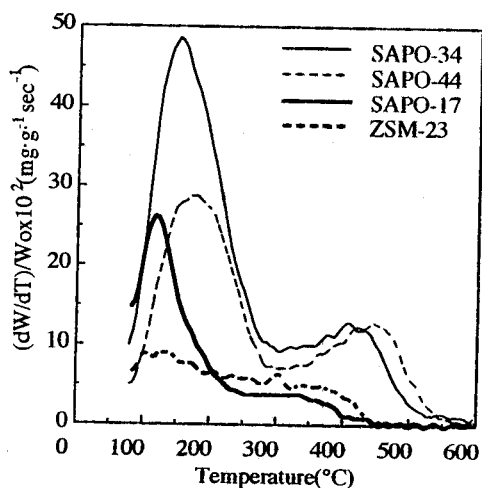


Fig. 5. NH₃-TPD profiles for various microporous materials.

Catalytic performances on methanol conversion reaction

Fig. 6 shows the result for methanol conversion reaction on prepared catalysts. The products were determined after methanol conversion reaction at 450°C for 1h. On SAPO-44 and SAPO-17 with the 8 oxygen membered ring, the selectivities to olefins were high. In general, with an increase in particle size and acid strength, the selectivity to light olefins has been decreased.¹³⁾ In spite of having the stronger acid strength and the larger particle size in SAPO-44 compared with SAPO-34, the selectivity to ethylene was more increased. This was attributed that the acid amount of SAPO-34 (9.06 μmol/m²) was much than that of SAPO-44 (7.99 μmol/m²). From this result, it was confirmed

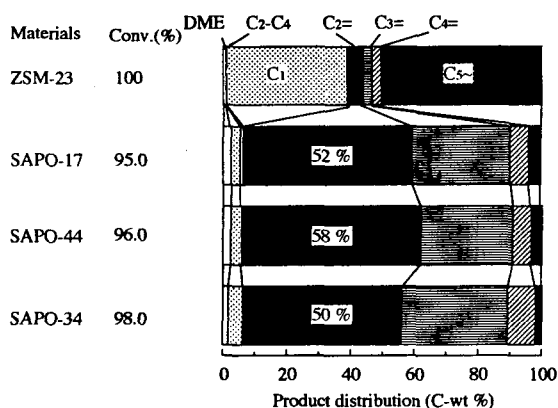


Fig. 6. Product distribution for methanol conversion on various microporous materials. Reaction conditions: GHSV 2000/h, Temperature 450°C, Time on stream 1h, MeOH 20mol% diluted by N₂.

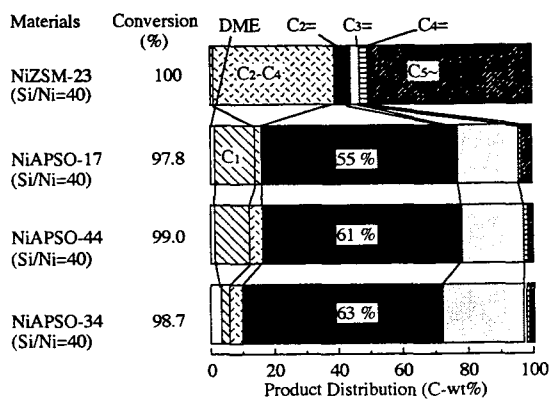


Fig. 7. Product distribution for methanol conversion on Ni-incorporated microporous materials. Reaction conditions: GHSV 2000/h, Temperature 450°C, Time on stream 1h, MeOH 20mol% diluted by N₂.

that the acid amount has more strongly influence on catalytic selectivity than acid strength. On the other hand, ZSM-23 was rather exhibited higher selectivity to paraffins over C₅~. This result attributed to low shape selectivity resulted from one dimensional structure in ZSM-23. The methanol conversion for all catalysts obtained as above 95%.

Effect of metal incorporated to framework

In general, zeolitic materials possess lots of acid sites and certain acidic strengths, attributed to their high Al contents and tetrahedral Al sites, respectively. However, as the addition of silica (SAPO) and/or other metal ions to the structure, it was introduced changes in both of catalytic performance and acidity. Therefore, if the Si was substituted by other transition metals, the acid sites should be decreased. For the enhance of ethylene selectivity, we tried to decrease in acidity as incorporated metal to framework. As a result, Ni-incorporated materials were successively synthesized.

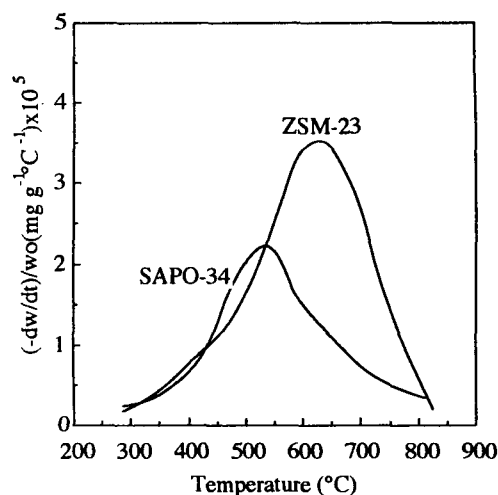


Fig. 8. TPO profiles for coke deposited on microporous materials. Reaction conditions: GHSV 2000/h, Temperature 450°C, Time on stream 1h, MeOH 20mol% diluted by N₂.

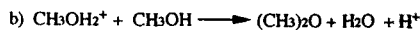
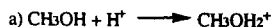
The distribution of products after methanol conversion reaction for nickel-incorporated materials at 450 °C for 1h are shown in Fig. 7. The selectivities to ethylene in all catalysts were enhanced in comparison that of non-metal incorporated materials. This is the result of decrease in acidity of Ni-incorporated materials. In particular, on NiAPSO-34, the selectivity to ethylene increased above 15% compared with SAPO-34.

After the reaction for 1h, the amounts of coke deposited on the materials were analyzed by TPO and the profiles are shown in Fig. 8. Compared with ZSM-23, the amount of coke deposited on SAPO-34 with three dimensional structure decreased. This is a result that the steric effect was weakened in ZSM-23 with one dimensional, and therefore, the coke formation was progressed continually compared with in three dimensional structure.

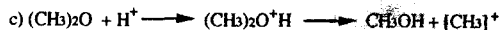
Mechanism on methanol conversion

The reaction mechanism, in which methanol conversion to hydrocarbon can be considered as follows scheme 1; it is generally accepted that the methanol conversion reactions go on by the formation of ethylene as the initial alkene product. Various mechanisms^{12,15)} have been proposed for the initial formation of ethylene from methanol and carbenoid species, carbonium ion or oxonium ion/oxonium ylide were suspected as the intermediate. However, once ethylene is formed, the reactions are continued by a completely different mechanism. Ethylene is methylated with methyl cation from methanol or dimethylether yielding propylene and step-wise methylation of alkenes take place. On the NiAPSO-34 materials, methylation of alkenes goes on much faster than the initial formation of ethylene. It is facts

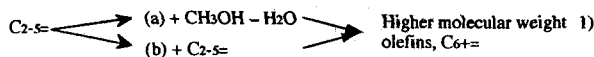
1) Dimethyl ether formation



2) First C-C bond formation - - Carbene, Oxonium, Methyl cation mechanism



3) Oligomerization



Scheme 1. Reaction mechanism expected for the methanol conversion on microporous materials.

that the addition of alkenes having lower carbon chain was grown up to alkenes having higher carbon chain in materials with larger size and stronger acidity, promptly. However, smaller size materials could prevent that oligomerization generated continually, as having fast diffusion rate, or shorter station time in material.

4. Conclusion

This work was focused on the synthesis and their catalytic activity on microporous materials having various pore types and dimensions, such as SAPO-34, SAPO-44, and SAPO-17. These results were exhibited as follows ;

1) The selectivity to olefin was increased on CHA type such as SAPO-34 and SAPO-44, and the selectivity to paraffins over $\text{C}_5\sim$ was increased on ZSM-23 with one dimensional structure.

2) On Ni-incorporated materials, the selectivity to light olefins (ethylene or propylene) was enhanced compared with non-metal incorporated materials.

3) After the reaction for 1h, the amounts of coke de-

posited on SAPO-34 with three dimensional structures decreased compared with ZSM-23 with one dimensional structure.

References

1. D.W. Breck, Zeolite Molecular Sieves, *Structure, Chemistry and use*, John Wiley & Sons, New York (1974)
2. R. Szostak, Molecular Sieves, *Principle of synthesis and identification*, Van Nostrand Reinhold, New York (1989)
3. S. Bhatia, Zeolite Catalysis, *Principle and applications*, CRC press, Florida (1990)
4. E.M. Flanigen, Stud. Surf. Sci. Catal., **58**, 13 (1991)
5. B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan, and E.M. Flanigen, U.S. Pat., 4440871 (1984)
6. S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannon, and E.M. Flanigen, J. Am. Chem. Soc., **104**, 1146 (1982)
7. S.T. Wilson, B.M. Lok, C.A. Messina, and E.M. Flanigen, Proc. 6th. Intern. Zeol. Conf., Reno, 1983, Butterworths, London, pp.97 ~ 109 (1984)
8. B.M. Lok, C.A. Messina, R.L. Patten, R.T. Gajek, T.R. Cannan, and E.M. Flanigen, J. Am. Chem. Soc., **106**, 6092 (1984)
9. E.M. Flanigen, B.M. Lok, R.L. Patton, and S.T. Wilson, Stud. Surf. Sci. Catal., **28**, 103 (1986)
10. S.T. Wilson, Stud. Surf. Sci. Catal., **58**, 137 (1991)
11. J.M. Thomas, Y. Xu, C.R.A. Catkow, and J.W. Coaves, Chem. Mater., **3**, 667 (1991)
12. T. Inui, S. Phatanasri, and H. Matsuda, J. Chem. Soc., Chem. Commun., 205 (1990)
13. T. Inui and M. Kang, Appl. Catal., A : General, **164**, 211 (1997)
14. T. Inui, ACS Symp. Series, **398**, 479 (1989)
15. C.D. Chang, Catal. Rev.-Sci. Eng., **25**, 1 (1983)