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CHARACTERIZATION OF $AlPO_4$-BASED MOLECULAR SIEVES AND METHANOL CONVERSION TO LIGHT OLEFINS

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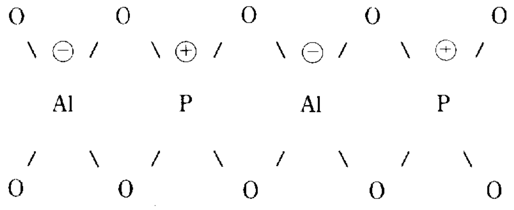
Abstract—Of the $AlPO_4$-based molecular sieves, $AlPO_4$, SAPOs, and MeAPOs of different pore sizes were prepared at 100-200℃ by a hydrothermal crystallization method. This study was purposed to maximize the yield of light olefins through methanol conversion. Crystal structure was confirmed by means of XRD and SEM, and acidity was examined by TPD and IR of adsorbed ammonia on the catalysts. It was found that SAPO-34 exhibited more than 90% selectivity for light olefins such as ethylene, propylene, and butylene due to shape selectivity through small pores, although it had a strong acidity. MeAPO-34 exhibited slightly lower selectivity for light olefins than SAPO-34 and different product distribution, depending on the electronegativity of the metal in its framework. SAPO-17 and SAPO-44, which have the same pore size with SAPO-34 but different pore structure from SAPO-34, showed less selectivity for light olefins than SAPO-34.

INTRODUCTION

Many studies for methanol conversion reactions over zeolites including ZSM-5 have been carried out since the end of the 1970s. Methanol to gasoline process (MTG) utilizing ZSM-5 exhibited an excellent selectivity for high octane gasoline or aromatic compounds, due to its shape-selective characteristics. Recently, studies on methanol to olefin process (MTO) rather than MTG have been focused on. In general, it has been known that conditions such as high reaction temperatures, short contact time, weak acidity, and low pressure are required for the synthesis of light olefins from methanol [1]. In the conversion of methanol to light olefins employing ZSM-5, propylene is a main product formed by the consecutive reaction of methanol and ethylene formed. On the other hand, zeolites having a small pore size like that of an erionite give a high selectivity for ethylene but exhibit severe deactivation. Accordingly, recent works concentrated on the development of new catalysts for the maximization of light olefins from methanol conversion.

$AlPO_4$-based molecular sieves [2, 3] developed in Union Carbide since 1982 have particular acidic properties and various pore structures [4, 5], since its framework is composed of Al and P instead of Si, differing from the conventional zeolites. In $AlPO_4$, the mole ratio of Al and P is strictly 1, as shown in the following figure. Therefore, $AlPO_4$ has electrically neutral framework since it is composed of same number of AlO_4^- and PO_4^+ tetrahedra.



In spite of its neutral framework, its surface selectivity is mildly hydrophilic due to the electronegativity difference between Al (1.61) and P (2.19). Therefore, $AlPO_4$ shows very weak acidity (4). If part of Al or P in $AlPO_4$ is replaced by Si or other metals, the framework becomes electrically negative so that it has acidic properties [4, 6]. Since $AlPO_4$-based molecular sieves have manifold characteristics in their composition, structure, and acidic properties, they can be applied to new catalytic processes and also to the modification of the conventional processes [7, 8].

In this study, $AlPO_4$, SAPOs, Mg-, Mn-, Co-, Zn-substituted MAPO, MnAPO, CoAPO, ZAPO, and TiAPSO, Ti- and Si-substituted together, were prepared and their reaction characteristics in methanol conversion to light olefins were investigated.

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Table 1. Prepared catalysts

Pore size	
Large pore	$AlPO_4$-5
(0.8 nm)	SAPO-5
Intermediate pore	$AlPO_4$-11
(0.6 nm)	SAPO-11
Small pore	SAPO-34
(0.43 nm)	MAPO-34
	CoAPO-34
	MnAPO-34 (Mn substituted)
	ZAPO-34 (Zn substituted)
	TiAPSO-34 (Ti, Si substituted)
	SAPO-17
	SAPO-44

EXPERIMENTAL

1. Preparation of the Catalysts

Catalysts were prepared according to the reports [9-11]. The catalysts used in this work are listed in Table 1. The catalysts include three component catalysts such as SAPO and MeAPO as well as four component catalyst such as TiAPSO. For the synthesis of TiAPSO, Si and Ti sources were simultaneously introduced. The reagent composition and organic templating agents used for the preparation of the catalysts are represented in Table 2. The preparation conditions and calcination temperature of the catalysts are summarized in Table 3.

2. Characterization of the Catalysts

The crystallinity and structure of the catalysts were confirmed by X-ray diffractometer (Rigaku, D/MAX II-A). XRD patterns of the catalysts are represented together with the data in the literatures in Fig. 1-3. The position and intensity of typical peaks of the catalysts prepared are found to be identical with those in the literatures.

The crystal shape and size of the prepared catalysts were examined by means of SEM (JEOL, JSM-35). As shown in Fig. 4 and 5, SAPO-5 is a hexagonal-shaped crystal and SAPO-34 is of cubic crystal.

In order to investigate the acidic characteristics of the catalysts, TPD experiments of adsorbed ammonia were conducted. 0.2 g of the catalyst was charged in a quartz tube of 10 mm o.d., pretreated at 400℃ for 30 min in He stream, cooled to room temperature, and then adsorbed with ammonia, in pulse, up to saturation. The catalyst temperature was raised to 110℃ and was kept for 30 min under He stream to remove the physisorbed ammonia. Subsequently, the temperature of the catalyst bed was increased to 600℃ at the heating rate of 12℃/min under He stream of 50 cc /min. Desorbed ammonia was detected by TCD of GC (Yanaco, G-1800).

Table 2. Molar ratio of reaction mixtures

Catalysts	Molar ratio
$AlPO_4$-5	$Pr_3N : Al_2O_3 : P_2O_5 : 40\ H_2O$
SAPO-5	$TPAOH : 0.1\ SiO_2 : Al_2O_3 : P_2O_5 : 57\ H_2O$
$AlPO_4$-11	$Pr_2N : Al_2O_3 : P_2O_5 : 40\ H_2O$
SAPO-11	$Pr_2NH : 0.3\ SiO_2 : Al_2O_3 : P_2O_5 : 57\ H_2O$
SAPO-34	$TEAOH : 0.6\ SiO_2 : Al_2O_3 : P_2O_5 : 52\ H_2O$
MAPO-34	$TEAOH : 0.4\ MgO : 0.8\ Al_2O_3 : P_2O_5$ $: 40\ H_2O$
CoAPO-34'	$TEAOH : 0.4\ CoO : 0.8\ Al_2O_3 : P_2O_5$ $: 40\ H_2O$
MnAPO-34	$TEAOH : 0.4\ MnO : 0.8\ Al_2O_3 : P_2O_5$ $: 40\ H_2O$
ZAPO-34	$TEAOH : 0.4\ MgO : 0.8\ Al_2O_3 : P_2O_5$ $: 40\ H_2O$
TiAPSO-34	$TEAOH : 0.1\ TiO_2 : 0.5\ SiO_2 : Al_2O_3 : P_2O_5$ $: 52\ H_2O$
SAPO-17	$CHA : 0.1\ SiO_2 : Al_2O_3 : P_2O_5 : 50\ H_2O$
SAPO-44	$CHA : 0.6\ SiO_2 : Al_2O_3 : P_2O_5 : 50\ H_2O$

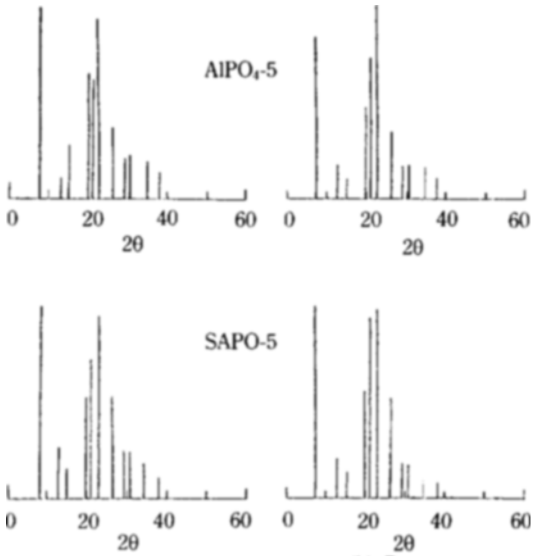
*Pr_3N: Tripropylamine
TPAOH: Tetrapropylammonium hydroxide
TEAOH: Tetraethylammonium hydroxide
Pr_2NH: Di-n-propylamine
CHA: Cyclohexylamine

Table 3. Synthetic condition of the catalysts

Catalysts	Al source	Temp.(℃)	Time(hr)	Cal. temp.(℃)
$AlPO_4$-5	AB	150	70	550
SAPO-5	AI	200	48	550
$AlPO_4$-11	AB	200	24	550
SAPO-11	AI	200	48	600
SAPO-34	AI	200	48	550
MAPO-34	AB	200	72	500
CoAPO-34	AI	100	66	500
MnAPO-34	AI	150	120	500
ZAPO-34	AI	100	68	500
TiAPSO-34	AI	200	48	550
SAPO-17	AI	200	50	550
SAPO-44	AI	200	52	550

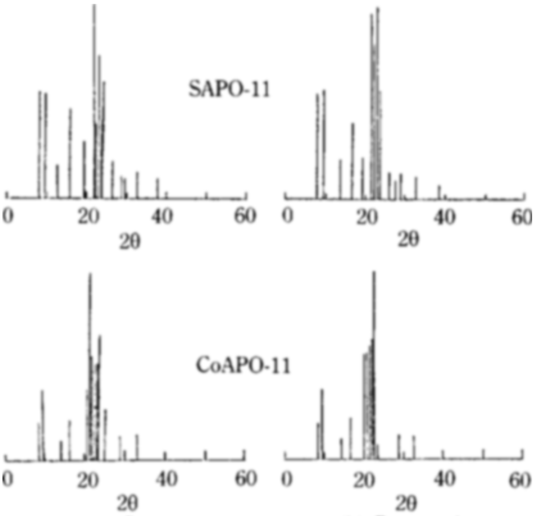
*AB: Boehmite-phase alumina
AI: Aluminium isopropoxide

TPD spectra for $AlPO_4$-5 and SAPO-5 are represented in Fig. 6. Since the framework of $AlPO_4$-5 is electrically neutral, it exhibits very weak acidity, whereas SAPO-5 has stronger and greater Brönsted acid sites, since it is composed of an electrically negative framework. TPD results of SAPO-5, SAPO-11, and SAPO-



(a) Patent (b) Prepared

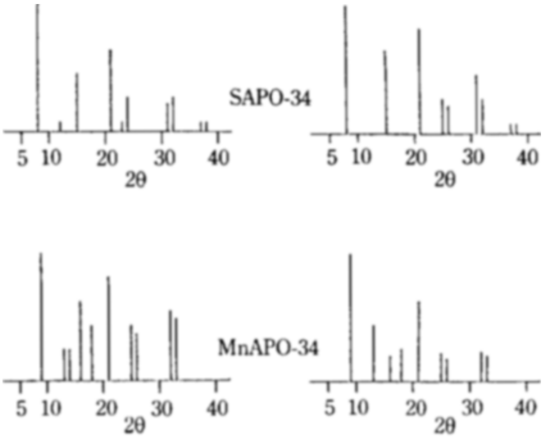
Fig. 1. XRD patterns of -5 structure.



(a) Patent (b) Prepared

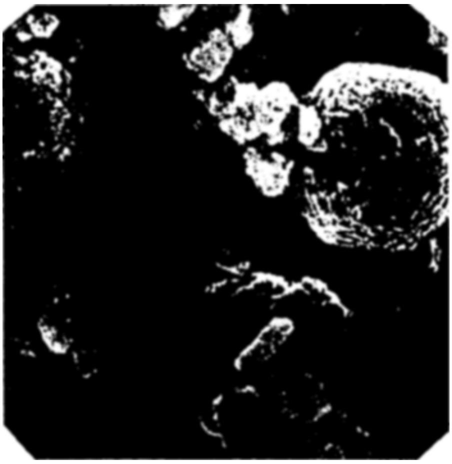
Fig. 2. XRD patterns of -11 structure.

34 were compared with that of HZSM-5 in Fig. 7. SAPO-34 shows distinctive weak and strong acid sites as in HZSM-5. The desorption temperature of ammonia from a weak acid site on SAPO-34 is lower than that on HZSM-5, but the strong acidity on SAPO-34 is found to be nearly equivalent to that on HZSM-5. The order of the amount and the strength of a weak acid among SAPOs is as follows; SAPO-34>SAPO-11 >SAPO-5. Strong acid sites were not observed on SAPO-5 and SAPO-11, as on SAPO-34 or HZSM-5.



(a) Patent (b) Prepared

Fig. 3. XRD patterns of -34 structure.



AlPO$_4$-5

SAPO-5

Fig. 4. SEM of AlPO$_4$-5 and SAPO-5.

SAPO-34

MnAPO-34

Fig. 5. SEM of SAPO-34 and MnAPO-34.

Fig. 8 shows the TPD spectra of adsorbed ammonia on SAPO-34, MnAPO-34, and ZAPO-34. The position of weak acid of each catalyst is about the same, but the peaks of the strong acid sites are much smaller and positioned at a higher temperature than SAPO-34.

The structure of the catalysts and their acidic characteristics were examined by means of FT-IR (Bomem DA3-02). A sample wafer, of which the diameter and thickness were 15 mm and 0.1 mm, respectively, was composed of 2 mg catalyst and 20 mg KBr. A sample wafer was placed in an IR cell, evacuated for 30 min at 300°C, and its IR spectrum was measured at the specified temperatures. For the ammonia adsorption experiments, sufficient dosage of ammonia was added to the catalyst wafer in an IR cell at a room temperature, and excessively adsorbed ammonia was removed under evacuation for 1 hr. Then, we measured the change of the IR spectrum of adsorbed ammonia with respect to the temperature change. The IR spectra of adsorbed ammonia on SAPO-34 are represented in Fig. 9. According to a previous study on adsorbed ammonia on silica-alumina [12], a NH_4^+ peak representing a Brönsted acid was positioned at 1400-1420 cm^{-1} and a Lewis acid peak appeared at 1600-1620 cm^{-1}. In Fig. 9 we observed adsorbed ammonia peaks at 1410 cm^{-1} and 1620 cm^{-1}, respectively. Accordingly, it was found that SAPO-34 has both Brönsted and Lewis acids. It has been known that a Lewis

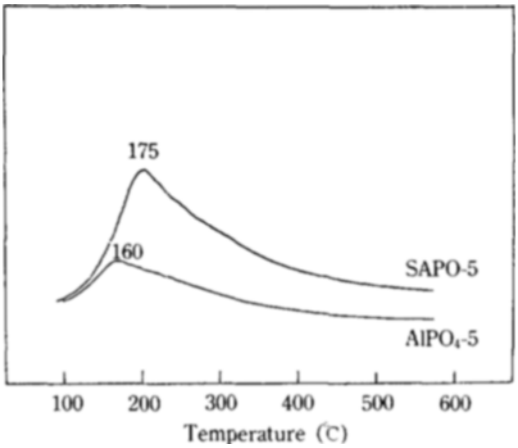


Fig. 6. NH$_3$ TPD of AlPO$_4$-5 and SAPO-5.

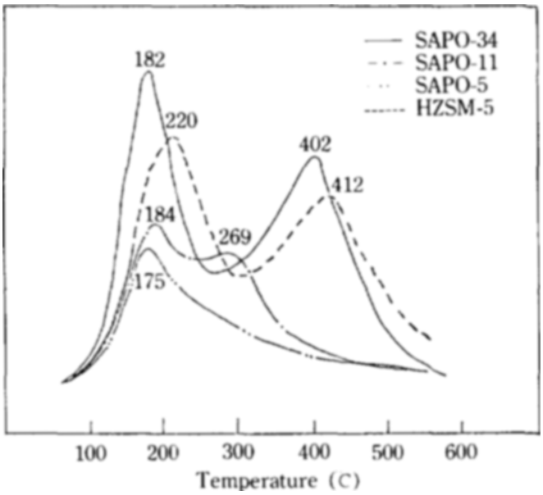


Fig. 7. NH$_3$ TPD of SAPO-5, -11 and HZSM-5.

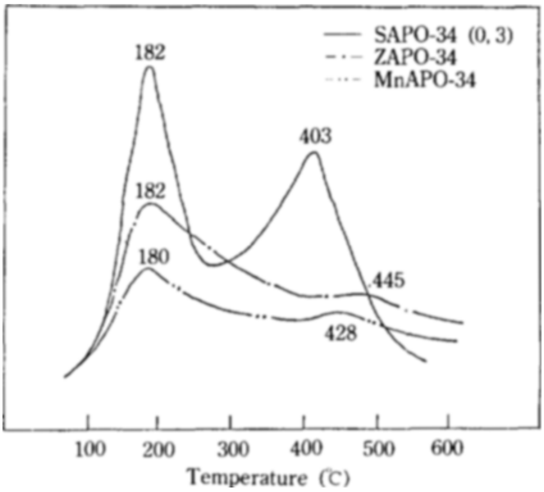


Fig. 8. NH$_3$ TPD of SAPO-34, MnAPO-34 and ZAPO-34.

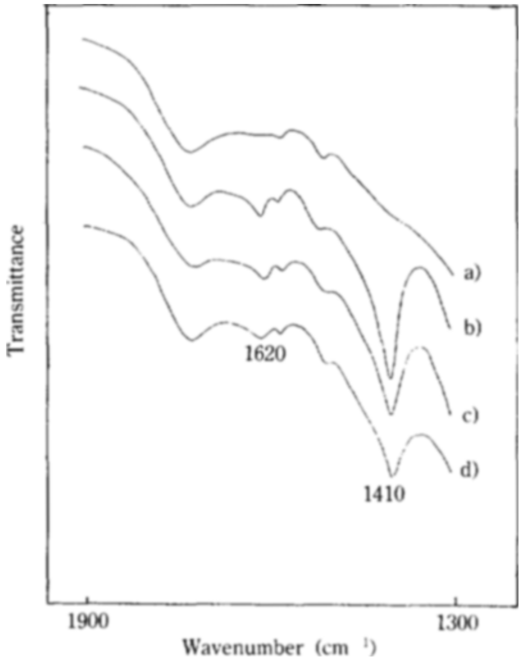


Fig. 9. IR spectra of NH$_3$ adsorbed on SAPO-34.

a) fresh catalyst, after NH$_3$ adsorption at room temperature, desorbed at b) 100℃, c) 200℃, d) 300℃.

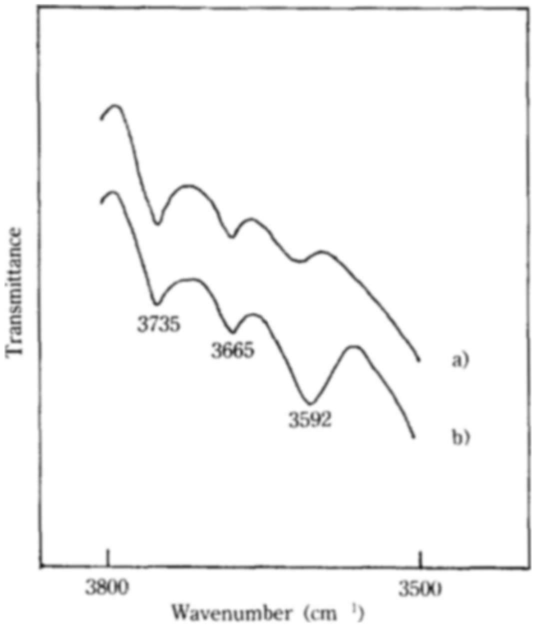


Fig. 10. IR spectra of SAPO-34.

a) fresh catalyst, b) after NH$_3$ adsorption at room temperature, desorbed at 100℃.

acid on SAPO-34 can be formed by binding a part of Al with O in the framework of an octahedral, not of a tetrahedral [13]. The hydroxyl groups on SAPO-34 were observed at 3735, 3665, and 3592 cm^{-1} in Fig. 10. However, when adsorbed with ammonia, only the peak at 3592 cm^{-1} was remarkably reduced. From this result, it is revealed that this hydroxyl group is responsible for the acid site.

3. Methanol Conversion Reaction

Methanol conversion reaction was carried out in a conventional fixed bed flow reactor. 0.2 g of the catalyst was charged in a stainless steel tubular reactor with a 1/4 inch outside diameter. The reactant, consisting of 30 wt% methanol and 70 wt% water, was introduced through a syringe pump with helium as a carrier gas. The products were analyzed with a 2 m Porapak Q column and a 2 m Carbowax column connected in series. The oven temperature in gas chromatography was programmed to range from 80℃ to 200℃ with a heating rate of 7.5℃/min.

RESULTS AND DISCUSSION

The product distributions and methanol conversion over AlPO$_4$-5, SAPO-5, SAPO-11, SAPO-34, and HZSM-5 are represented in Table 5. Because of the low acidity on AlPO$_4$-5, methanol conversion on it is much lower than on the other catalysts. Comparing SAPOs with HZSM-5, SAPOs exhibit higher selectivity for light olefins such as ethylene and propylene than HZSM-5. It was observed in TPD analysis that the acid strength of SAPO-5 and SAPO-11 was markedly

Table 4. Product distribution of methanol conversion over various catalysts

Catalysts	$AlPO_4$-5	SAPO-5	SAPO-11	SAPO-34	HZSM-5
Temp.(℃)	450	450	450	450	450
Conv.(%)	5.6	34.7	65.8	100	100
Selectivity					
C_1	33.0	1.1	2.2	2.3	2.5
$C_{2=}$	19.2	2.5	16.6	57.2	1.3
C_2	1.4	–	0.5	0.5	1.5
$C_{3=}$	30.1	18.3	26.4	32.9	5.9
C_3	–	–	3.5	–	16.0
$C_{4=}$	3.5	36.4	22.0	1.7	17.5
C_4	4.2	8.6	2.5	4.1	6.8
C_{5^-}	9.6	33.1	26.3	1.2	48.3
$C_{2=}$, $C_{3=}$, $C_{4=}$	52.8	57.2	65.0	91.8	24.7

*Feed: MeOH 30 wt% + H_2O 70 wt%
WHSV: 1.2 hr^{-1} (MeOH)

Table 5. Product distribution of methanol conversion over SAPO-34 and MeAPO-34

Catalysts	SAPO-34	ZAPO-34	MnAPO-34	CoAPO-34	MAPO-34
Conv.(%)	100	100	100	100	100
Selectivity					
C_1	2.3	2.0	3.2	3.9	6.0
$C_{2=}$	57.2	50.5	54.4	53.5	44.6
C_2	0.5	0.8	1.3	2.1	1.6
$C_{3=}$	32.9	34.3	30.4	30.0	30.9
C_3	–	1.3	1.8	2.0	7.2
$C_{4=}$	1.7	2.4	2.2	2.0	2.9
C_4	4.1	6.6	5.1	4.9	4.8
C_{5+}	1.2	2.1	1.6	1.6	2.0
$C_{2=}$, $C_{3=}$, C_4	91.8	87.2	87.0	85.5	78.4

*Rxn temp. = 450℃
Feed: MeOH 30 wt% + H_2O 70 wt%
WHSV: 1.2 hr^{-1} (MeOH)

low in comparison with that of SAPO-34 or HZSM-5. It was known that in methanol conversion over zeolites the conversion of light olefins, formed at the beginning of the reaction, into aromatics or paraffins took place in the strong acid sites. Since SAPO-5 and SAPO-11 have weak acidity, methanol conversion is low and further reaction of light olefins into higher paraffins is suppressed. Thus, reactions over SAPO-5 and SAPO-11 lead to higher selectivity for light olefins. SAPO-34 exhibited more than 90% selectivity for light olefins including ethylene, propylene, and butylenes. In particular, the selectivity for ethylene was amounted to 60%. As shown in the TPD spectra, acid strength and acid amount of SAPO-34 were about the same as those of HZSM-5. Nevertheless, the selectivity for light olefins over SAPO-34 is exceedingly higher than that of HZSM-5. This is not because further reaction of light olefins into higher hydrocarbons is suppressed, but because the higher hydrocarbons formed from light olefins can not pass through the narrow pore (4.3Å) and are secondarily cracked into light olefins.

Examining the product distribution according to the pore sizes of SAPOs, SAPO-5 (8Å), with the largest pore, exhibits the highest selectivity for C_4 olefins and SAPO-11, with the intermediate pore, shows the highest selectivity for propylene. The experimental results of methanol conversion over SAPO-34 and MeAPO-34 were listed in Table 6. The selectivity for light olefins over MeAPO-34 is slightly lower than that on SAPO-34 but is much higher than those over SAPO-5, SAPO-11, and HZSM-5. Although SAPO-34 and MeAPO-34 have the same structure, they show different product distribution. This is because SAPO is

Table 6. Product distribution of methanol conversion over SAPO-34, SAPO-17 and SAPO-44

Catalysts	SAPO-34	SAPO-17	SAPO-44
Conv.(%)	100	100	100
Selectivity			
C_1	2.3	4.1	6.3
$C_{2=}$	57.2	38.0	28.4
C_2	0.5	0.7	2.1
$C_{3=}$	32.9	30.9	39.2
C_3	–	1.2	2.4
$C_{4=}$	1.7	11.8	12.0
C_4	4.1	7.9	5.7
C_{5+}	1.2	5.4	3.9
$C_{2=}$, $C_{3=}$, $C_{4=}$	91.8	80.7	79.6

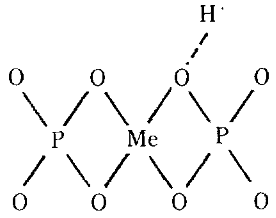
*Rxn temp. = 450℃
Feed: MeOH 30 wt% + H_2O 70 wt%
WHSV: 1.2 hr^{-1} (MeOH)

Table 7. Product distribution of methanol conversion over SAPO-34 and TiAPSO-34

Catalysts	SAPO-34	TiAPSO-34
Conv.(%)	100	100
Selectivity		
C_1	2.3	2.2
$C_{2=}$	57.2	53.3
C_2	0.5	1.4
$C_{3=}$	32.9	30.5
C_3	–	5.7
$C_{4=}$	1.7	1.4
C_4	4.1	4.4
C_{5+}	1.2	1.1
$C_{1=}$, $C_{2=}$, $C_{3=}$	91.8	85.2

*Rxn temp. = 450℃
Feed: MeOH 30 wt% + H_2O 70 wt%
WHSV: 1.2 hr^{-1} (MeOH)

synthesized by substituting P in the framework of $AlPO_4$ for Si, while in MeAPO Al is substituted by each metal. This different substituting target element in the framework of $AlPO_4$ leads to the different Brönsted acidity [4]. The different product distribution among MeAPOs also results from the differing acid strengths due to the electronegativity difference of each substituting metal [14, 15]. Brönsted acid strength in an acid catalyst depends on how easily it gives up a proton. The proton kept on MeAPO is bonded with oxygen in the framework, as shown in the following figure.



If the bonding strength between Me and O is increased, that between O and H^+ is relatively weakened. In this case, H^+ is easily separated from O. Accordingly, if the electronegativity difference between Me and O becomes great, the bonding strength of Me-O is increased so that the Brönsted acidity becomes strong. Since the electronegativity of Mg, Mn, Zn, and Co is 1.2, 1.5, 1.6, and 1.8, respectively and that of O is 3.5, MAPO-34 has the greatest bonding strength of Me-O, and therefore has the strongest Brönsted acidity. As shown in Table 6, MAPO-34, compared to other MeAPOs, exhibits low selectivity for light olefins and high selectivity for light paraffins such as ethane and propane. This is because hydrogen transfer reactions easily take place, due to its strong Brönsted acidity.

SAPO-34 and MeAPO-34 have the same structure as chabazite. Methanol conversion results using SAPO-17 and SAPO-44, which have the same pore size but different structure from SAPO-34, are summarized in Table 7, in comparison with that using SAPO-34. SAPO-17 has the same structure as erionite, while the structure of SAPO-44 is not consistent with but similar to that of chabazite. The olefin selectivity over SAPO-17 and SAPO-44 is about 80%, lower than that over SAPO-34. It is found from this result that among the zeolites with small pore sizes, SAPO-34 is compatible for the high selectivity of the light olefins.

The substitution mechanism of Si and Ti into the framework of $AlPO_4$ to form TiAPSO-34 is the same with Si substitution into the framework of $AlPO_4$ to form SAPO-34, except that a part of Si in SAPO-34 is replaced by Ti. The product distribution of methanol conversion over TiAPSO-34, compared with that over SAPO-34, is represented in Table 8. The selectivity for ethylene and propylene over TiAPSO-34 is slightly lower than that over SAPO-34, whereas the selectivity for ethane and propane is high. This is because hydrogen transfer reactions over TiAPSO-34 is faster than that over SAPO-34, due to the strong Brönsted acidity of TiAPSO-34. Brönsted acidity of TiAPSO-34 is higher than that of SAPO-34, because the electronegativity of Ti (1.5) is smaller than that of Si (1.8).

CONCLUSION

It was observed from the TPD analysis of adsorbed ammonia that the acid strength of SAPO-34 was almost equivalent to that of HZSM-5 and that MeAPO-34 had only a small amount of acid, but strong acidity in comparison strength of SAPO-34 was almost equivalent to that of HZSM-5 and that MeAPO-34 had only a small amount of acid, but strong acidity in comparison with SAPO-34. It was also found from the IR study that SAPO-34 had both Lewis and Brönsted acidities. In the methanol conversion reaction, SAPO-34 exhibited over 90% selectivity for light olefins such as ethylene, propylene, and butylene. This was found to be due to the influence of shape selectivity, owing to the small pore size. The product distribution over MeAPOs was dependent on the electronegativity of metals in the framework of MeAPOs. Among the MeAPOs tested, MAPO-34 had the strongest acidity, resulting in a high selectivity for paraffins, but a low selectivity for light olefins.

ACKNOWLEDGEMENT

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