

## Synthesis, characterization, and MTO performance of MeAPSO-34 molecular sieves

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### ABSTRACT

MeAPSO-34 molecular sieves were synthesized successfully with metal ions of Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mg, Ca, Sr, and Ba ( $Me/Al_2O_3=0.05$ ). IR,  $NH_3$ -TPD measurements and fixed bed MTO performances of all the samples were carried out in comparison with SAPO-34. The results illustrated that the incorporation of metal ions had great effects on structure and acidity of the molecular sieves. It was interesting that most MeAPSO-34 molecular sieves exhibited effective enhancement of the MTO performance. Especially, the incorporation of  $Co^{2+}$ ,  $Zn^{2+}$  and  $Mg^{2+}$  ions showed promising modification effect for the MTO catalysts.

### 1. INTRODUCTION

Methanol to olefins (MTO) is a well known important reaction for non-oil route synthesis of light olefins from natural gas or coal [1]. Small pore silicoaluminophosphate (SAPO) molecular sieve was demonstrated to be effective catalysts, in which SAPO-34 has been proven to be the most attractive candidate for practical catalyst development [2]. The SAPO-34 molecular sieve after incorporating metals into the framework had been found exhibiting high selectivity to form ethylene in the MTO reaction [3-6]. The higher selectivity could be attributed to the modifications of the acidic strength, the acid distribution and the pore or channel size of SAPO-34 molecular sieve with the incorporation of metals.

The present work was to synthesize MeAPSO-34 molecular sieves with a large variety of metal ions, to research the modification effect of metal ions on physical and chemical properties of SAPO-34 and to comparatively investigate MTO performance of the synthesized samples. This would be helpful for understanding the relationship among synthesis, property and performance of the catalyst and the reaction.

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## 2. EXPERIMENTAL

### 2.1. Synthesis

All the syntheses were carried out hydrothermally. Pseudoboehmite (72.2 wt%  $\text{Al}_2\text{O}_3$ , purissimum grade), ortho-phosphate (85 wt%, analytical grade) and silica sol (25.0 wt%  $\text{SiO}_2$ ) were used as the starting materials to get aluminum, phosphorous and silicon respectively. Triethylamine (TEA) was used as templating agent.

SAPO-34 molecular sieve was synthesized by the batch composition: 3TEA:  $0.2\text{SiO}_2$ :  $\text{Al}_2\text{O}_3$ :  $\text{P}_2\text{O}_5$ :  $50\text{H}_2\text{O}$ , and MeAPSO-34 samples were synthesized under the same condition as that for SAPO-34 apart from further addition of metal salts into the synthesis system with Me/ $\text{Al}_2\text{O}_3$  (Me denotes metal ions) ratio equaled 0.05. The metal ions used were Cr, Fe, Ni, Cu, Ca, Sr, Ba ions (as metallic nitrate), Mn, Co, Zn, Mg ions (as metallic acetate) and Ti ion (as  $\text{Ti}(\text{SO}_4)_2$ ).

### 2.2. Characterization and catalytic tests

The structure type and crystallinity of all the samples were checked by powder X-ray diffraction (XRD) on a D/max-rb diffractometer.

Chemical composition of all the samples was determined by X-ray fluorescence analysis on a Philips Magix spectrometer.

The IR spectra were recorded on a Perkin 983G infrared spectrophotometer. The framework vibrations of the molecular sieves were examined by using 5% sample in KBr.

The measurement of acidity of all samples was performed on a homemade ammonia-TPD apparatus.

The MTO reactions were carried out on a fixed bed reactor. Reaction conditions were as follows: temperature=450°C, WHSV(MeOH)= $2\text{h}^{-1}$ . On-line GC with Porapak-QS column and FID detector was used in product analysis.

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis of MeAPSO-34 molecular sieves

MeAPSO-34 molecular sieves could be synthesized successfully with Me/ $\text{Al}_2\text{O}_3$ =0.05, in which Me were Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mg, Ca, Sr, and Ba respectively. The relative crystallinity of all samples was calculated by the peak intensities of  $2\theta \sim 9.430$ ,  $15.940$  and  $20.510$  in the XRD pattern on the basis of taking that of SAPO-34 as 100%. The results indicated that the relative crystallinities of most samples were higher than 85% except the cases of TAPSO-34 and CaAPSO-34 (lower than 70% without impurity). ZnAPSO-34 gave the highest relative crystallinity up to 124%, indicating that the synthesis system was favorable for the formation of CHA structure.

### 3.2. Chemical composition of products

The composition of the corresponding as-synthesized MeAPSO-34 samples with different metals was given in Table 1.

In case of SAPO molecular sieve, it had been concluded that there was no direct linkage between Si and P via oxygen-bridge. It was proposed that Si atoms incorporate into  $AlPO_4$  structure by two different substitution mechanisms [7-8]: the first one, the Si substitution for phosphorus formed  $Si(4Al)$  structure; the second mechanism was the double substitution of neighboring aluminum and phosphorus by two silicon atoms forming  $Si(nAl)(n=3-0)$ . So the ratio of  $(Si+P)/Al$  should be equal to 1 if there were no Si-O-Si (or no Si-O island) in the structure. In MeAPSO system, the formation of MeAPSO molecular sieve could be taken as the replacement of P and/or Al of the  $AlPO_4$  framework by silicon and/or metal. If the ratio of  $(Si+P)/(Al+Me)$  ratio were equal to or more than 1, the incorporation should be taken as a partial replacement of Al by Me ions. If the ratio of  $(Si+P)/(Al+Me)$  ratio were less than 1, metal ions could be incorporated into the framework by replacing silicon. This could be an evidence for the incorporation of metal ions into framework structure.

In Table 1, for most samples except CuAPSO-34 and SrAPSO-34, the  $(Si+P)/(Al+Me)$  ratios were more than or equal to 1, indicating that tetrahedrally coordinated aluminum was partially replaced by Me ions. It was possible that there was also no Me-O-Al and lack of Si-O-Si linkage in the most MeAPSO-34 samples.

Table 1

Molar composition of the crystalline products of as-synthesized MeAPSO-34

Products	Molar composition of the crystalline products		
	Al: Si: P: Me	$(Si+P)/(Al+Me)$	Molar oxide composition
SAPO-34	1.000:0.124:0.871	0.995	$(Al_{0.501}Si_{0.062}P_{0.437})O_2$
TAPSO-34	1.000:0.152:0.873:0.018	1.007	$(Al_{0.490}Si_{0.074}P_{0.427}Ti_{0.009})O_2$
CrAPSO-34	1.000:0.150:0.881:0.004	1.027	$(Al_{0.492}Si_{0.074}P_{0.433}Cr_{0.002})O_2$
MnAPSO-34	1.000:0.135:0.912:0.031	1.016	$(Al_{0.481}Si_{0.065}P_{0.439}Mn_{0.015})O_2$
FAPSO-34	1.000:0.132:0.905:0.032	1.005	$(Al_{0.483}Si_{0.064}P_{0.438}Fe_{0.015})O_2$
CoAPSO-34	1.000:0.133:0.917:0.032	1.017	$(Al_{0.480}Si_{0.064}P_{0.440}Co_{0.016})O_2$
NiAPSO-34	1.000:0.139:0.884:0.023	1.000	$(Al_{0.489}Si_{0.068}P_{0.432}Ni_{0.011})O_2$
CuAPSO-34	1.000:0.136:0.869:0.032	0.974	$(Al_{0.491}Si_{0.067}P_{0.427}Cu_{0.015})O_2$
ZnAPSO-34	1.000:0.141:0.902:0.041	1.002	$(Al_{0.480}Si_{0.068}P_{0.433}Zn_{0.020})O_2$
MgAPSO-34	1.000:0.146:0.904:0.016	1.033	$(Al_{0.484}Si_{0.070}P_{0.438}Mg_{0.008})O_2$
CaAPSO-34	1.000:0.149:0.888:0.005	1.032	$(Al_{0.490}Si_{0.073}P_{0.435}Ca_{0.003})O_2$
SrAPSO-34	1.000:0.135:0.883:0.031	0.987	$(Al_{0.488}Si_{0.066}P_{0.431}Sr_{0.015})O_2$
BaAPSO-34	1.000:0.146:0.875:0.008	1.013	$(Al_{0.495}Si_{0.072}P_{0.431}Ba_{0.004})O_2$

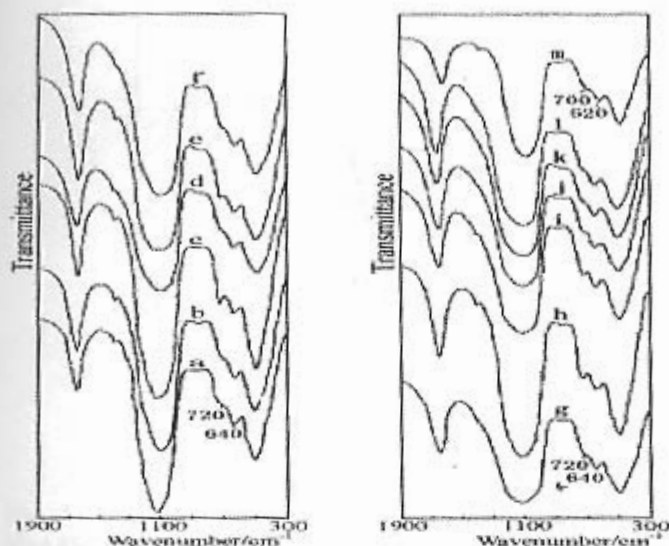


Fig. 1. IR spectra of TAPSO-34(a), CrAPSO-34(b), MnAPSO-34(c), FAPSO-34(d), CoAPSO-34(e), NiAPSO-34(f), CuAPSO-34(g), ZnAPSO-34(h), MgAPSO-34(j), CaAPSO-34(g), SrAPSO-34(k), BaAPSO-34(l), SAPO-34(m) in the framework region

### 3.3. IR studies in the framework region

The IR spectra of the framework vibration of as-synthesized SAPO-34, MeAPSO-34 samples were presented in Fig. 1. For SAPO-34, the bands around  $1100\text{cm}^{-1}$ ,  $620\text{cm}^{-1}$  and  $700\text{cm}^{-1}$  could be observed. The bands around  $1100\text{cm}^{-1}$  had been assigned to the asymmetric stretching of the  $\text{TO}_4$  tetrahedra, the  $620\text{cm}^{-1}$  was due to vibrations of the double-ring, and the  $700\text{cm}^{-1}$  could be related to T-O-T symmetric stretching. For MeAPSO-34, the framework vibration bands of all samples were similar to that of SAPO-34, but a shift of the peak positions of structure-sensitive bands could be found. For example, when metal ions were incorporated into the framework, the bands at  $620, 700\text{cm}^{-1}$  in MeAPSO-34 were shifted to around  $640, 720\text{cm}^{-1}$ . Moreover, the change in the intensity of some absorption peaks could be found. For MnAPSO-34, CoAPSO-34, ZnAPSO-34 and MgAPSO-34, the intensity of peaks around  $720\text{cm}^{-1}$  increased. This demonstrated that metal ions could be incorporated into the framework of SAPO-34 to form Me-O-T bond, which brought the shift of peaks and variety of intensity in the framework vibration bands.

### 3.4. $\text{NH}_3$ -TPD studies

The acidity properties of the MeAPSO-34 samples were measured by  $\text{NH}_3$ -TPD technique in comparison with that of SAPO-34. TPD profiles of  $\text{NH}_3$

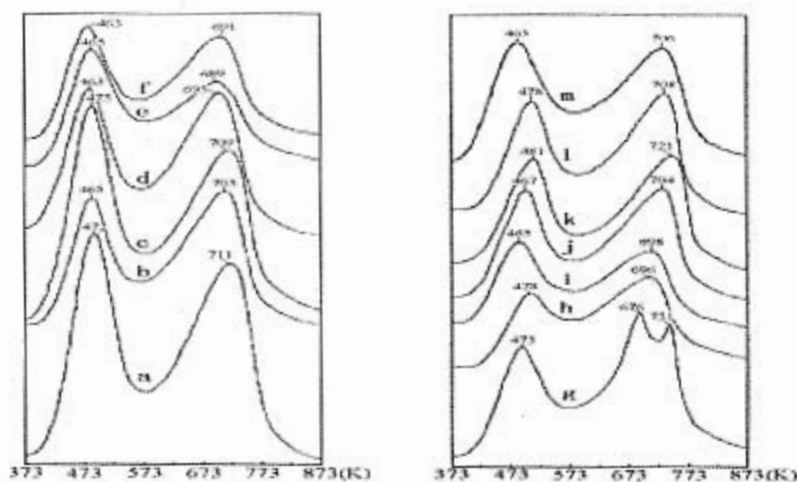


Fig. 2. TPD profiles of ammonia desorption from TAPSO-34(a), CrAPSO-34(b), MnAPSO-34(c), FAPSO-34(d), CoAPSO-34(e), NiAPSO-34(f), CuAPSO-34(g), ZnAPSO-34(h), MgAPSO-34(i), CaAPSO-34(j), SrAPSO-34(k), BaAPSO-34(l) and SAPO-34(m)

desorption from SAPO-34 and MeAPSO-34 are given in Fig. 2. For SAPO-34, in addition to the low temperature peak at 465K that was due to the acidity of external surface hydroxy groups, second peak is observed at 706K, which could be assigned to structure acidity. The  $\text{NH}_3$  desorption temperatures of MeAPSO-34 molecular sieves were quite different, which was associated with the variety of intensities of both weak and strong acid sites. It was interesting that CuAPSO-34 gave two peaks of strong acid sites, and the  $\text{NH}_3$  desorption temperatures were 676K and 731K, respectively. For FeAPSO-34, CoAPSO-34, NiAPSO-34, ZnAPSO-34 and MgAPSO-34, the amount of strong acid sites decreased. These results demonstrated that the incorporation of metal ions could adjust the acid intensity and the number of weak and strong acid sites.

### 3.5. MTO results of MeAPSO-34

Table 2 listed the activity and the optimum selectivities of methole to  $\text{C}_2 + \text{C}_3$  of MTO reaction over the SAPO-34 and MeAPSO-34 samples. It could be seen that for all MeAPSO-34 samples the initial conversion of methanol can reach 100%, which is similar to that of SAPO-34. The life-time (denoting the time on stream when conversion is lower than 100%) could be used to represent the activities of the samples, and the sequence of the life-time for the samples were: SrAPSO-34 > CaAPSO-34 > MnAPSO-34 > BaAPSO-34 > CrAPSO-34 > CuAPSO-34 > MgAPSO-34 > FAPSO-34 > TAPSO-34 > SAPO-34 > ZnAPSO-34 > CoAPSO-34 > NiAPSO-34. This indicates that the incorporation of certain metal

Table 2  
Optimum product distribution in MTO over SAPO-34 and MeAPSO-34 catalysts

Samples	SAPO-34	Ti-	Cr-	Mn-	Fe-	Co-	Ni-	Cu-	Zn-	Mg-	Ca-	Sr-	Ba-
TOS (min.)	120	136	164	170	135	90	60	159	119	160	177	192	142
Products (wt%)													
CH <sub>4</sub>	1.8	1.6	1.7	1.4	1.9	1.8	3.9	1.1	1.2	1.1	1.1	1.5	1.1
C <sub>2</sub> H <sub>4</sub>	53.3	50.0	54.3	56.2	58.6	60.4	55.7	52.0	59.5	54.1	52.2	53.3	50.9
C <sub>2</sub> H <sub>6</sub>	0.8	0.5	0.6	0.3	0.5	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.3
C <sub>3</sub> H <sub>6</sub>	28.9	36.7	33.8	32.1	29.8	32.5	31.5	36.4	32.1	37.5	37.7	36.6	38.5
C <sub>3</sub> H <sub>8</sub>	1.9	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C <sub>4</sub> H <sub>8</sub>	7.4	7.6	6.5	5.6	5.0	3.2	4.6	6.3	4.4	4.5	5.5	5.4	6.1
C <sub>4</sub> H <sub>10</sub>	1.4	1.4	1.2	1.0	0.9	0.6	0.9	1.2	0.8	0.8	1.0	1.0	1.1
C <sub>5</sub> <sup>+</sup>	4.6	2.3	2.0	3.4	2.7	1.4	3.2	2.8	1.6	1.8	2.2	1.8	2.0
C <sub>2</sub> -C <sub>3</sub> <sup>+</sup> (wt%)	82.2	86.7	88.1	88.3	88.4	92.9	87.2	88.4	91.6	91.6	89.9	89.9	89.4

ions could yield a modification effect on activity. For example, the incorporation of four kinds of alkali-earth ions into SAPO-34 prolonged the life-time of the catalysts. It was also observed that the selectivities to form C<sub>2</sub>+C<sub>3</sub> olefins of all MeAPSO-34 catalysts were superior to that of SAPO-34. Especially, the selectivities to C<sub>2</sub>+C<sub>3</sub> olefins of CoAPSO-34, ZnAPSO-34 and MgAPSO-34 were more than 90%.

#### 4. CONCLUSION

MeAPSO-34 molecular sieves had been synthesized successfully with Me/Al<sub>2</sub>O<sub>3</sub>=0.05. The results indicated that the incorporation of metal ions had great effects on structure and acidity of the molecular sieves. It was interesting that most MeAPSO-34 molecular sieves exhibited effective enhancement of the MTO performance. Especially, the incorporation of Co<sup>2+</sup>, Zn<sup>2+</sup> and Mg<sup>2+</sup> ions shows promising modification effect for the MTO catalysts.

#### REFERENCES

- [1] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan, E.M. Flanigen, *J. Am. Chem. Soc.*, 106 (1984) 6092.
- [2] S. Nawaz, S. Kolboe, S. Kvisle, K.P. Lillerud, M. Stocker, H.M. Oren, *Stud. Surf. Sci. Catal.*, 61 (1991) 421.
- [3] M.A. Djieugoue, A.M. Prakash, L. Kevan, *J. Phys. Chem. B*, 104 (2002) 10726
- [4] T. Inui, S. Phatanasri, H. Mutsuda, *J. Chem. Soc., Chem. Commun.*, (1990) 205
- [5] J. M. Thomas, Y. Xu, C.R.A. Catlow, J.W. Couves, *Chem. Mater.*, 3 (1991) 661
- [6] M. Kang, *J. Mol. Catal., A Chem.*, 150 (1999) 205
- [7] S. Ashtekar, S.V.V. Chilukuri and D.K. Chakrabarty, *J. Phys. Chem. B*, 98 (1994) 4878.
- [8] G. Sastre, D.W. Lewis, C. Richard and A. Catlow, *J. Phys. Chem. B*, 101 (1997) 5249.