Crystallization mechanism of AlMepO-β

Yue Qi, Gongwei Wang and Zhongmin Liu

Natural Gas Utilization & Applied Catalysis Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P. O. Box 110, Dalian 116023, China

A microporous aluminum methylphosphonate, AlMepO-β, was prepared by hydrothermal method. The crystallization process was studied using XRD, PC-NMR, IR and SEM. It was found that a transform of phases occurred in the crystallization process. An intermediate phase between starting gel and AlMepO-β was first reported.

1. INTRODUCTION

Microporous aluminum methylphosphonate AlMepO-β, first reported by Maeda and co-workers[1], is an organic-inorganic composite molecular sieve, which is stable against heating up to 673K. Its structure is composed of the Al-O-P network and the channels (with a diameter of ca.7.0Å) lined with the -CH_3 group, which are covalently bonded with P atoms and arranged along the *c*-axis. The present study investigated the phase transforming process in the crystallization process of AlMepO-β by using XRD, MAS NMR and IR.

2. EXPERIMENTAL

Pseudo-boehmite (74.4wt% Al_2O_3, 25.6wt% water) and methylphosphoric acid (98.5%) were used as aluminum and phosphate source respectively. AlMepO-β was prepared based on a hydrothermal method described in the literature [2] from a gel composed of Al_2O_3: $1.5CH_3PO_3H_2$: $40H_2O$: 0.5 1,4-dioxane. To form the starting gel, pseudo-boehmite and methylphosphoric acid were dispersed in water and then 1,4-dioxane was added. The mixture was stirred at ambient temperature for 1 hour and then removed to a 100ml Teflon-lined stainless-steel autoclave. The initial gel was heated and crystallized at 423K under autogenic pressure for 0~144 hours. Samples of different crystallization time were filtered, thoroughly washed and air-dried.

X-ray power diffraction patterns were recorded on a RIGAKU D/max-rb instrument using Cu Kα radiation with a nickel filter. SEM photographs were obtained on a HITACHI S-3200N scanning electron microscope. IR spectra of the samples in the region of the framework stretching vibrations (300-1600cm^{-1}) were measured using KBr containing pellets on a Perkin-Elmer 983G IR spectrophotometer. ^{31}P, ^{27}Al CP/MAS and MAS NMR spectra were carried out on a Bruker DRX-400 spectrometer. The spinning speeds were 4k, and 8kHz for ^{31}P and ^{27}Al, respectively, and chemical shifts are quoted respectively from 85% phosphoric acid, and $Al(H_2O)_6^{3+}$. Short radio-frequency pulse 1/20 was used for the ^{27}Al spectra to ensure that the measurements were quantitatively reliable.

3. RESULTS AND DISCUSSION

The XRD patterns of the samples of different crystallization times were shown in Figure 1. The starting material (0h sample) gives no apparent diffraction peak, suggesting that the gel is amorphous. The 24h sample gives a strong peak at $2\theta = 9.48$, which has not been reported in the existing literatures. This peak disappears when the crystallization time is 60hours, while appear the characteristic diffraction peaks for AlMepO-β (strongest peak at $2\theta=7.18$)[2]. The weak peak at $2\theta=11.65$ in the pattern of 60h sample is ascribed to a layered aluminum methylphosphonate AlMepO-ζ [4]. When the crystallization time is 144 hour, the diffraction peaks attributed to AlMepO-β weaken greatly, while the peaks for AlMepO-ζ become strong. The intensities of the peaks at $2\theta=9.48$, 7.18, 11.65, respectively, are plotted against crystallization time in Figure 2. In the initial stage of crystallization, only the peak at $2\theta=9.48$ appears. The intensity of this peak increases with crystallization time and reaches the maximum at 32 hour and then lowers down till the peak disappears at 48 hour. The peak for AlMepO-β (at $2\theta=7.18$) appears at 32 hour and its intensity increases as the peak at $2\theta=9.48$ lowers. The intensity of this peak reaches the maximum at 60 hour and then begins

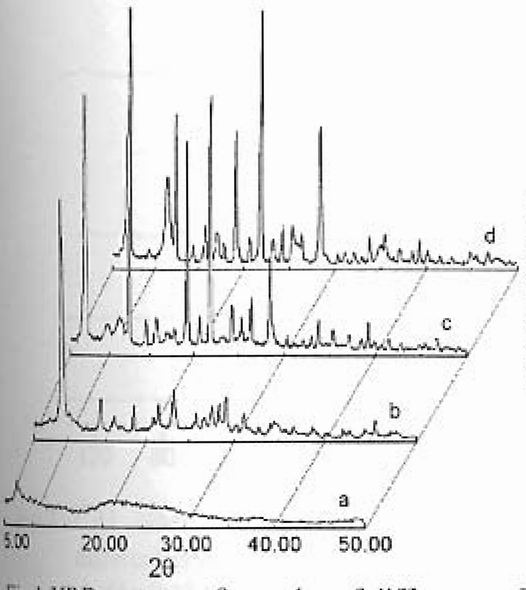


Fig.1 XRD patterns of samples of different crystallization time

(a)0h; (b)24h; (c)60h; (d)144h

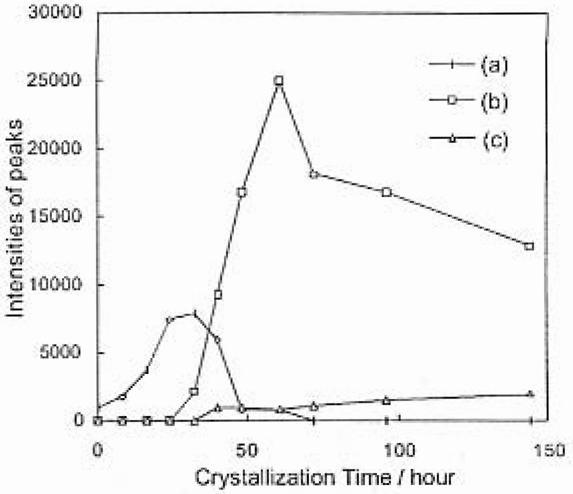


Fig.2 Relative Intensities of peaks against crystallization time

(a)$2\theta=9.48$; (b) $2\theta=7.18$; (c) $2\theta=11.65$

to lower with increasing crystallization time. Meanwhile, the intensity of the peak of $2\theta=11.65$, for AlMepO-ζ, gradually increases. This change of the peak intensities with increasing crystallization time suggests a transform of phases in the whole crystallization process. The amorphous starting gel first converted to the phase characterized by $2\theta = 9.48$ (nominated phase A), and then the latter to AlMepO-β. It seems that this phase A is the precursor to AlMepO-β. In the later stage of the crystallization, AlMepO-β partly converted to AlMepO-ζ. This means that AlMepO-β is not stable in the crystallization condition, and apt to be converted to a more stable layered product - AlMepO-ζ.

Figure 3 shows the ^{27}Al MAS NMR spectra of the samples of different crystallization times. The starting material (0h sample) gives four peaks ascribed to Al_{Th} (46.5ppm) and Al_{Oh} (12.4, -4.5 and -10.0ppm), respectively. This relatively complicated coordinate circumstance of Al sites is owing to the existence of many coordinates, such as H_2O, $CH_3PO_3H_2$, $CH_3PO_3H^-$ and $CH_3PO_3^{2-}$, in the starting synthesis gel [3]. The broad and irregular shapes of these peaks suggest the amorphous nature of the sample. The 24h sample gives only one peak (-3.4ppm) for Al_{Oh}, while the peaks for Al_{Th} almost disappears. The simpler coordinate circumstance of Al sites suggests the forming of more regular structure via certain rearrangement. This result agrees with the conclusion from the above XRD study: The starting material converts to

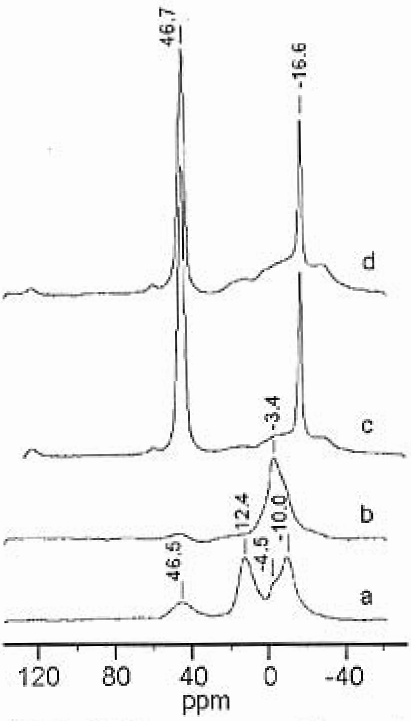


Fig.3 ^{27}Al NMR spectra of samples of different crystallization time
(a)0h; (b)24h; (c)60h; (d)144h

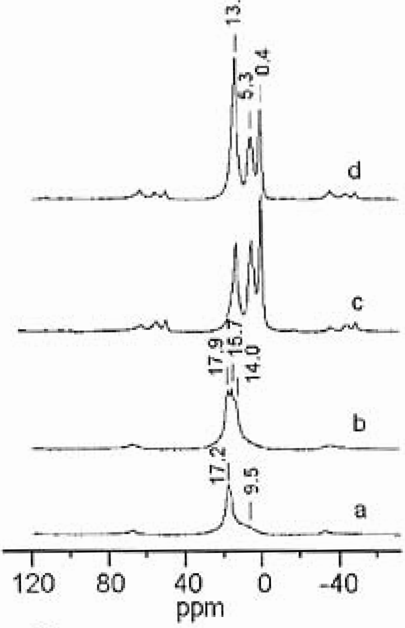


Fig.4 ^{31}P NMR spectra of samples of different crystallization time
(a)0h; (b)24h; (c)60h; (d)144h

a new phase with more regular structure. This phase should be the above-mentioned phase A. In the spectrum of 60h sample, the two sharp peaks for Al_{Th} (46.7ppm) and Al_{Oh} (-16.6ppm), with an intensity ratio of 3:1, are characteristic for AlMepO-β, in which exist two kinds of Al sites, i.e. Al_{Th} and Al_{Oh} with a atom ratio of 3:1[2]. When the crystallization time is 144 hour, the peak for Al_{Oh} (-16.6ppm) becomes stronger. This can be explained by the forming of AlMepO-ζ, in which the Al sites are six-coordinated [4]. The signals assigned to AlMepO-β and AlMepO-ζ overlap at -16.4ppm so increas the intense of peak. Besides, a broad peak from 20ppm to -30ppm was observed in this spectrum. It seems that an amorphous phase forms in the mean time.

The ^{31}P MAS NMR spectra of the samples of different crystallization times (Figure 4) show that the P sites in all samples are four coordinated. The ^{31}P chemical shifts here are different from those of AlPOs molecular sieves, owing to the presence of the bonded $-CH_3$ [2]. The 60h sample (AlMepO-β) gives three resonance peaks at 13.5, 5.3, and 0.4ppm, respectively. In the study of Maeda and coworkers [2], five ^{31}P MNR resonance peaks for (14.4, 12.6, 9.9, 6. 5 and 1.1) were reported. We assigned this difference to the disparity in sample preparation and instrumentation. Some peaks here could be overlapped. With comparison of the spectrum of AlMepO-β (60h sample), the peaks for the 0h sample (17.2 and 9.5ppm) the 24h sample (17.9, 15.7 and 14.0ppm) are located in higher field. Maeda and coworkers reported the liner correlation between the mean P-O-Al angles of AlMepOs and the ^{31}P MAS NMR chemical shifts of assigned signals [2,4]. According to this correlation, smaller chemical shifts correspond to larger mean P-O-Al angles. Thus the fact that the mean Al-O-P angles in the 0h and 24h samples are smaller than those in AlMepO-β suggests that the mean Al-O-P angle increased gradually, passing through an intermediate phase (phase A), to fit the request to form the structure of AlMepO-β. When crystallization time is 144 hour,

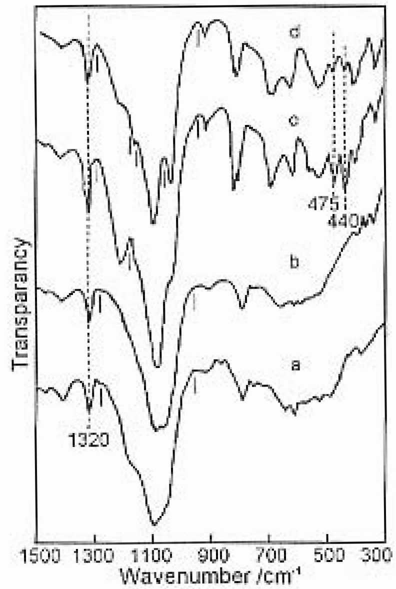
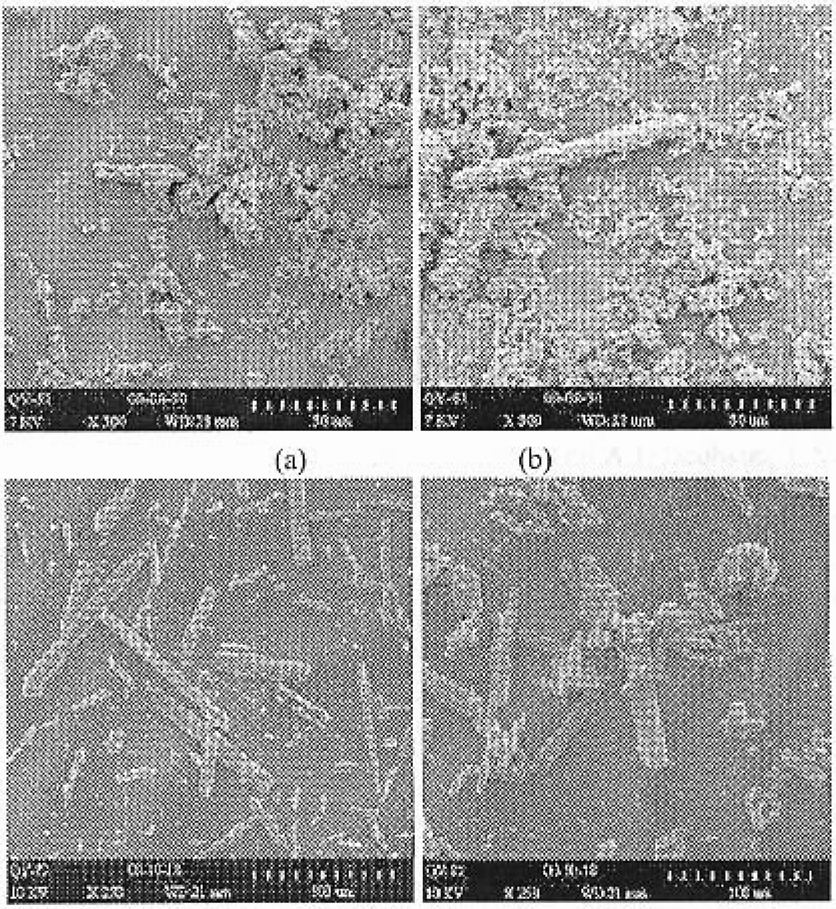


Fig 5 IR spectra of the structural region for AlMepO-β samples of different crystallization times (a)0h; (b)24h; (c)60h; (d)144h

sample gives a more intense peak at 13.5ppm because of the forming of AlMepO-ζ[4].

The IR spectra of the samples (Figure 5) give similar C-H stretching and bending, resulting from the presence of methyl group. The band at 1320cm^{-1} is characteristic for phosphaonates with P-C bond [5,6]. The bands from 1200 to 1000cm^{-1}, derived from T-O stretches [7-9], are overlapped in the spectra of the 0h and 24h samples, while separated into two clusters (1230~1170cm^{-1} for P-O stretches and 1150~1050cm^{-1} for Al-O stretches [2]) in the spectrum of the 60h sample. This difference corresponds to change of Al-O and P-O bond lengths in the crystallization process.



(a) (b)

(c) (d)

Fig. 6 SEM images of samples
(a) 24h; (b) 32h; (c) 60h; (d) 144h

The results from XRD and solid MAS NMR revealed a new phase with relatively regular structure (phase A) at 24 hour. This phase does not show regular form in the SEM view (Figure 6a). When crystallization time is 32 hour, diffraction peaks for AlMepO-β have just appear, but no complete AlMepO-β crystals were observed in the SEM view (Figure 6b).

There appear some needle-like objects without distinct crystal face. These objects should be the intermediate forms from Phase A to AlMepO-β. When crystallization time is 60 hour, complete AlMepO-β crystals are observed (Figure 6c). In the latter stage of crystallization (144 hour), stacked AlMepO-ζ tablet-like crystals appear (Figure 6d). Besides, the crystals of AlMepO-β become worn, because of long time leaving with acid solution, and some amorphous substance appeared.

4. CONCLUSIONS

The crystallization of AlMepO-β is a phase transforming process. In this process, the coordinate numbers of Al sites, the mean Al-O-P angles and the bond lengths of Al-O and P-O change with increasing crystallization time. There is an intermediate phase (nominated Phase A) between the starting gel and AlMepO-β. The scheme for the crystallization process is suggested as: staring material (amorphous) → Phase A → AlMepO-β → AlMepO-ζ + amorphous phase.

REFERENCES

1.K. Maeda; Y. Kiyozumi and F. Mizukami; European Patent Application, 0671 403 A1
2.K. Maeda; Y. Kiyozumi and F. Mizukami; J. Phys. Chem. B, 101 (1997) 4402-4412
3.C.S. Blackwell and R.L. Patton; J. Phys. Chem., 88 (1984) 6135-6139
4.K. Maeda; Y. HashiGushi, Y. Kiyozumi and F. Mizukami; Bull. Chem. Soc. Jpn., 70 (1997) 345-349
5.W.T.A. Harrison, L.L. Dussack, J.T. Vaughey, T. Vogt, and A.J. Jacobson, J. Mater. Chem. 6 (1996) 81.
6.W.T.A. Harrison, L.L. Dussack and A. J. Jacobson, Inorg. Chem. 35 (1996) 1461.
7.R.A. Van Nordstrand, D.S. Santilli and S.I. Zones ACS Symp. Ser. 368 (1988) 236
8.M.E. Davis, C. Montes, P.E. Hathaway, J.P. Arhancet, D.L. Hasha and J.M. Garces, J. Am. Chem. Soc. 111 (1989) 3919
9.L. Sierra de Saldarriaga, C. Saldarriaga and M.E. Davis, J. Am. Chem. Soc. 109 (1987) 2686