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MAS-NMR study

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# Structural distortion in *MeAPO*–5 molecular sieves : a $^{31}\text{P}$ MAS-NMR study

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**ABSTRACT** : Solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) was used for characterization of a series of metal containing microporous aluminophosphate of AFI type (*MeAPO*–5 with *Me* : *Mg*, *Co*, *Zn* and *Mn*). The position of *Me* atoms, whether in the framework or extraframework have been examined using  $^{31}\text{P}$  MAS NMR and bulk chemical analysis. It was found that  $^{31}\text{P}$  chemical shift values carried information about the distortion of *MeAPO*–5 structures by *Me* atoms which was correlated to the ionic size of *Me* atoms incorporated into their framework.

**KEYWORDS** : Microporous materials; Nuclear resonance

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## 1 INTRODUCTION

Crystalline microporous aluminophosphates of AFI type (*AlPO*<sub>4</sub>–5) is a large pore molecular sieve consisting of a unidirectional, 12-ring channel system [1,2]. *AlPO*<sub>4</sub>–5 contains frameworks of alternating *AlO*<sub>2</sub>– and *PO*<sub>2</sub>+ tetrahedra which are electrically neutral; showing no Brønsted acidity. In order to produce Brnsted acidity, an anionic framework has to be generated by substituting an n-valent tetrahedral framework cation, with an (*n* – 1) valent tetrahedral cation. In *AlPO*<sub>4</sub>–5, this can be done either by replacing the pentavalent phosphorus with Si, or by replacing the trivalent aluminium with a divalent ion. This class of materials is potentially important acid catalyst materials [3]. Although the influence of divalent metal atoms to the catalytic properties of *MeAPO*–5 (*Me* : *Mg*, *Co*, *Zn* and *Mn*) was reported [4], it has been experimentally difficult to verify that the transition metal ion (*Me*) incorporated by hydrothermal synthesis is actually in the framework. These heteroatom-substituted AlPO are very difficult to characterize because of the variety of possible locations, coordinations and oxidation state of the metals ions. Despite several characterization techniques used, important questions still remain which include the following: Are the metals incorporated into tetrahedral framework positions ? What is the effect of incorporated metal atoms to the local structure? What is the

maximum loading of metal ions? Although no single methods is available to answer all these questions up to know, in this paper we demonstrated that these questions could be answered only by interpretation of  $^{31}\text{P}$  MAS NMR spectra and chemical analysis of a series of *MeAPO*–5.

## 2 EXPERIMENTAL

The synthesis of divalent metal substituted *AlPO*<sub>4</sub>–5 are described in [1]. *MeAPO*–5 was synthesized with a gel composition of 1.0 Al<sub>2</sub>O<sub>3</sub>:1.0 P<sub>2</sub>O<sub>5</sub>:0.25 MeO:1.0 Pr<sub>3</sub>N:40 H<sub>2</sub>O. The samples resulted from the incorporation of manganese, cobalt, zinc and magnesium in the synthesis of *AlPO*<sub>4</sub>–5 are labeled as *MnAPO*–5, *CoAPO*–5, *ZAPO*–5 and *MAPO*–5 respectively. *AlPO*<sub>4</sub>–5 was used as a reference material for all measurements and calculations discussed hereafter. The MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The  $^{31}\text{P}$  MAS NMR spectra were recorded at 161.87 MHz using 0.5 ms radio frequency pulses, a recycle delay of 1.0 s and spinning rate of 7.0 kHz. Chemical shifts for  $^{31}\text{P}$  was referred to 85% *H*<sub>3</sub>*P*O<sub>4</sub>. The *MeAPO*–5 samples were characterized by x-ray diffraction (XRD) analysis using Bruker D8 Diffractometer in the scanning range of 2θ between 2 and 40° using copper *K*α (θ = 0.1542 nm at 35 kV and 35 mA) as the source of radiation. Silicon powder was

TABLE 1: Relative peak areas from the measured and related  $^{31}\text{P}$  MAS NMR spectra of  $\text{AlPO}_4-5$  and  $\text{MeAPO}-5$ .

Sample	Normalized peak areas for the different P environment			
	P (3Me, Al)	P (2Me, 2Al)	P (Me, 3Al)	P (4Al)
<i>MAPO</i> -5	-	-	15.35% (-24.1 ppm)	84.65% (-31.6 ppm)
<i>ZAPO</i> -5	-	14.19% (-22.4 ppm)	8.06% (-26.2 ppm)	77.75% (-32.1 ppm)
<i>MnAPO</i> -5	-	-	-	100% (-33.0 ppm)
<i>CoAPO</i> -5	-	-	-	100% (-31.8 ppm)
<i>AlPO</i> <sub>4</sub> -5	-	-	-	100% (-29.1 ppm)

TABLE 2: The fraction of T sites occupied by Me in framework and extra framework of  $\text{MeAPO}$  determined by  $^{31}\text{P}$  MAS NMR and chemical analysis. Here, the bulk chemical analysis using X-Ray Fluorescence (XRF) spectrometer.

Sample	Determination method		
	MAS NMR (Me in the framework)	Chemical Analysis (Me total)	Me in the extraframework (%)
<i>MAPO</i> -5	0.03	0.06	50
<i>ZAPO</i> -5	0.03	0.06	50

used as an internal standard in the measurement of unit cell parameters in order to correct for any instrumental error which might occur. In all cases the peak at  $2\theta = 28.4^\circ$  of silicon ( $hkl = 111$ ) was taken as a reference. Unit cell parameters were calculated from peak position  $2\theta > 8^\circ$  in order to minimize errors at low diffraction angle, using the least square refinement techniques. Chemical analysis data were collected by X-ray fluorescence (XRF) analysis using Siemens SRS 303.

### 3 RESULTS AND DISCUSSIONS

The  $^{31}\text{P}$  MAS NMR spectra of  $\text{AlPO}_4-5$  and  $\text{MeAPO}-5$  are shown in Fig. 1. Generally the spectra are broad with the main peak centred around -30 ppm corresponding to P(4Al) tetrahedra and shoulders around -24 ppm and -22 ppm assigned to P(Me, 3Al) and P(2Me, Al) respectively. Detail assignments of signals in each sample are given in Tab. 1. Comparatively, the distribution of peaks varies for each sample. The results of the deconvolution of *MAPO*-5 and *ZAPO*-5  $^{31}\text{P}$  are presented in Tab. 1.

$^{31}\text{P}$  is a spin  $I = 1/2$  nucleus (with no quadrupole moment), and  $^{31}\text{P}$  MAS NMR can distinguish between different environment. However, spectral sig-

nals are broadened by the presence of transition metals. The degree of broadening of the spectral signals due to the presence of  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  are expected to be less than  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  in *MeAPO*-5. Due to the fact that  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  are paramagnetic, their unpaired electron(s) can produce very efficient relaxation of the neighbouring nucleus and cause broadening of the spectral signals [5].  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  occur in high abundance and possess high magnetogyric ratios. Because of that, the resolution of the signals of the Mn- and Co-containing  $\text{AlPO}_4-5$  are lower, hindering the elucidation of their  $^{31}\text{P}$  MAS NMR spectra. In addition, the broadening of the  $^{31}\text{P}$  MAS NMR peak of *MnAPO*-5 can be correlated with the distortion of the structure. This is explained by the influence of the size (ionic radii) of Me atom; a larger Me atom distorts the structure of *MeAPO*-5. The structure of *MnAPO*-5 is more distorted than *CoAPO*-5 because the ionic radius of  $\text{Mn}^{2+}$  (0.80) is larger than  $\text{Co}^{2+}$  (0.72).

As shown in Fig. 1, the  $^{31}\text{P}$  chemical shift around -30 ppm assigned to the P(4Al) environment for *MeAPO*-5 is different. The shift is due to the increase in  $T\text{-O-P}$  ( $T : \text{Me}$  or  $\text{Al}$ ) bond angle of the framework [6]. The average  $T\text{-O-P}$  angle around the P(4Al) tetrahedral site was calculated based on the

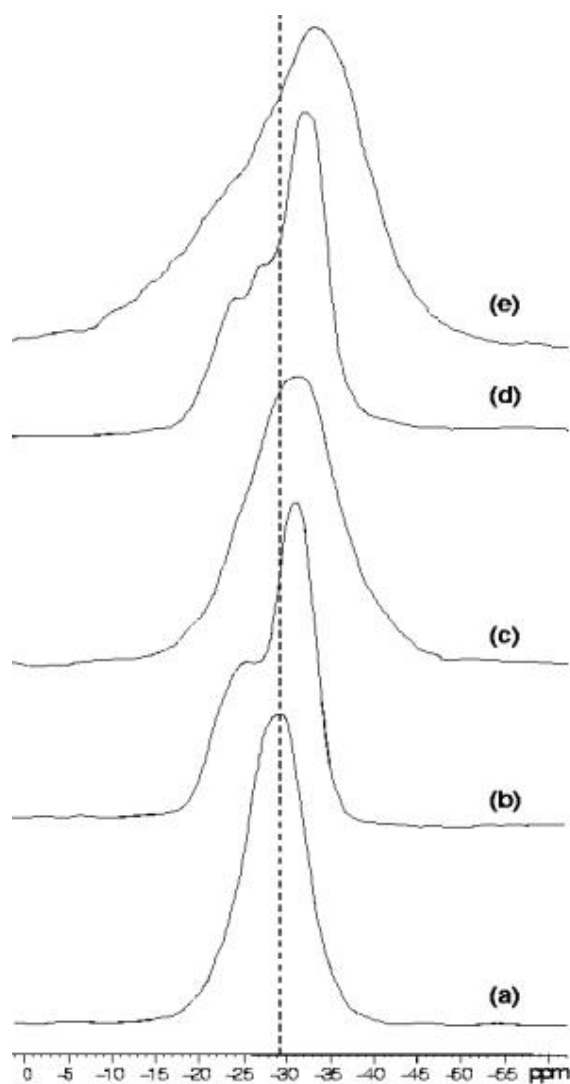


FIGURE 1:  $^{31}\text{P}$  MAS NMR spectra of  $\text{AlPO}_4\text{-5}$  and  $\text{MeAPO-5}$  (ppm from  $\text{H}_3\text{PO}_4$ ); (a)  $\text{AlPO}_4\text{-5}$ , (b)  $\text{MAPO-5}$ , (c)  $\text{CoAPO-5}$ , (d)  $\text{ZAPO-5}$ , (e)  $\text{MnAPO-5}$ .

empirical correlation [6]. The dependence of the  $^{31}\text{P}$  chemical shift on the  $T\text{-O-P}$  angle is according to the relation :

$$\text{mean } T - O - P \text{ angle/degree} = \frac{47 - \alpha}{0.51}, \quad (1)$$

where  $\alpha$  is chemical shifts ppm.

Fig. 2 shows the relationship between the mean  $T\text{-O-P}$  angle and the ionic radii of metal atom in  $\text{AlPO}_4\text{-5}$  and  $\text{MeAPO-5}$ . The atom with the largest ionic radii showing the largest mean  $T\text{-O-P}$  angle is Mn and the lowest ionic radii size showing the lowest angle is Al. Calculation of the unit cell of  $\text{MeAPO-5}$  using their XRD patterns showed that manganese having the largest ionic radius (0.81), imposes the largest effect to the increase of the  $T\text{-O-P}$  angle, fol-

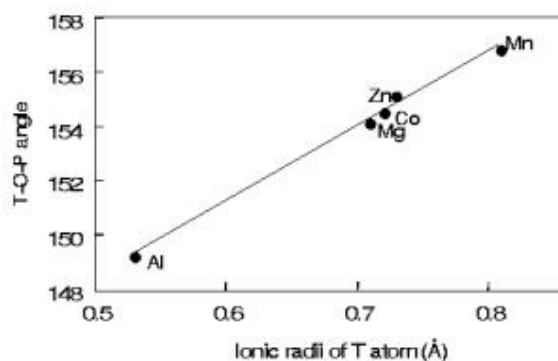


FIGURE 2: Relationship between mean  $T\text{-O-P}$  angle and ionic radii of metal atom in  $\text{AlPO}_4\text{-5}$  and  $\text{MeAPO-5}$ .

lowed by zinc (0.73), cobalt (0.72), magnesium (0.71) and aluminum (0.53) respectively. This suggests that the ionic size of the incorporated divalent metal influences the  $T\text{-O-P}$  angle in the structure of  $\text{AlPO}_4\text{-5}$ . One expects that the higher is the  $T\text{-O-P}$  angle, the bigger is the unit cell volume. Calculation of the unit cell volume of  $\text{AlPO}_4\text{-5}$  (1384),  $\text{MAPO-5}$  (1388),  $\text{CoAPO-5}$  (1387),  $\text{ZAPO-5}$  (1382) and  $\text{MnAPO-5}$  (1387) show that the unit cell volumes do not follow the trend in the  $T\text{-O-P}$  because the unit cell volume is not solely affected by the  $T\text{-O-P}$  angle but by other factors such as the T-O and/or P-O bond lengths, the hydrogen bond and the cation coordination [7,8]. The result obtained, indicates that the incorporation of the Me atoms distorts the structure of  $\text{MeAPO-5}$  in the long-range. Short-range order of  $^{31}\text{P}$  in  $\text{MeAPO-5}$  suggests that the distortion of  $\text{MeAPO-5}$  crystals is correlated with the  $T\text{-O-P}$  angle.

Although the relationship between  $^{31}\text{P}$  chemical shift with  $T\text{-O-P}$  angle is only based on the empirical evidence, several authors have attempted to create a unified theoretical foundation for  $^{31}\text{P}$  chemical shift in all classes of phosphorus compounds [6,9-14], but success here depends on the fact that we are dealing with only limited structural variation. The other influencing factor on the  $^{31}\text{P}$  chemical shift is that, the extraframework divalent metal molecules causes further distortion to the tetrahedral P which corresponds to  $P(4Al)$  site. The presence of the larger extraframework divalent metal molecules may cause steric strain on the  $T\text{-O-P}$  ( $T$ : Me or Al) bond angle. In order to release the strain and accommodate the larger extraframework Me molecules, the bond angle has to be readjusted. To exclude this possibility, the extraframework divalent metals were removed by treatment with methanolic HCl [15]. It was observed that no significant difference in the chemical shifts and linewidth of  $^{31}\text{P}$  MAS NMR peaks between AlPOs

treated with methanolic *HCl* compared to those as synthesized. This proves that the distortion of *T-O-P* angle is not caused by the extraframework divalent metals. From this result, it can be suggested that the size of the incorporated divalent metal can change the *T-O-P* angle in the  $AlPO_4-5$  based materials structure.

The following relationship was used to estimate the quantity of divalent metals in the framework position from the  $^{31}P$  MAS NMR which is assigned to  $P(4Al)$  sites [16] :

$$Me = \frac{\sum_{n=0}^4 (4-n) I_{P(nAl)}}{8 \sum_{n=0}^4 I_{P(nAl)}} . \quad (2)$$

The observation of the peak area in the spectrum relates to the amount of phosphorus atom in these samples. Tab. 2 shows the percentage of substitution of *Me* for *Al* in the samples; calculated by deconvolution of NMR peaks. The results show little agreement with the chemical analysis results. This implies that some portion of *Me* occupy the extraframework position in the samples. This result is in agreement with result reported by Blasco et.al. for *Mg*-containing AFI aluminophosphates [17].

#### 4 CONCLUSIONS

$^{31}P$  MAS NMR spectra of  $AlPO_4-5$  and  $MeAPO-5$  prove that their corresponding framework structure is distorted by the incorporation of divalent metal. It is shown that the *T-O-P* (*T* : *Mn*, *Zn*, *Co* and *Mg*) angle is different from that of *Al-O-P* angle from  $AlPO_4-5$ . Calculation of the amount of incorporated divalent metals is only possible for  $MAPO-5$ , and  $ZAPO-5$  because broadening of signal occurs in the presence of *Mn* and *Co* in  $MnAPO-5$ , and  $CoAPO-5$ . Although deconvolution of  $^{31}P$  MAS NMR spectra shows that incorporation of divalent metal occurs, by comparison with the chemical analysis data, it shows that a portion of the divalent metals also occupy the extraframework position.

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