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# The ionic size of metal atoms in correlation with acidity by the conversion of cyclohexanol over MeAPO-5

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## Abstract

The conversion of cyclohexanol was investigated over MeAPO-5 [Me = Mg, Co, Mn and Zn]. The acidity of the catalysts was correlated with the ionic radii of Me atoms incorporated into the structure of the catalysts. Based on this correlation, it is suggested that the distortion of structure by the larger Me atoms was associated with the T–O–P angle and hence the acid strength. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* A. Microporous materials; D. Catalytic properties

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## 1. Introduction

Crystalline microporous aluminophosphates (AlPO<sub>4</sub>-5) [1] contain frameworks of alternating AlO<sub>2</sub><sup>-</sup> and PO<sub>2</sub><sup>+</sup> tetrahedra which are electrically neutral; showing no Brønsted acidity. In order to produce Brønsted acidity, an anionic framework has to be generated by substituting an *n*-valent tetrahedral framework cation, with an (*n*-1) valent tetrahedral cation. In our previous paper [2], it was shown that the conversion of cyclohexanol is a good pointer to evaluate the Brønsted acidity and basicity of metal-substituted AlPO<sub>4</sub>-5 (MeAPO-5). Despite the numerous reports on the correlations between structure and activity of AIPO by theoretical calculations [3–5], experimental evidence of the correlation has never been reported. Furthermore, reports on the incorporation of the various divalent metals into AIPO

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framework are often varied and inconsistent. Previously, it was demonstrated that metal-substituted  $\text{AlPO}_4\text{-5}$  is a potential catalyst for dehydration of alcohol [6]. In this work, the conversion of cyclohexanol over  $\text{MeAPO-5}$  [ $\text{Me} = \text{Mg, Co, Mn and Zn}$ ] was studied in order to correlate the structure, ionic size of  $\text{Me}$  atoms with acidity of  $\text{MeAPO-5}$  by XRD, solid-state  $^{31}\text{P}$  MAS NMR, XRF and  $\text{NH}_3\text{-TPD}$ .

## 2. Experimental

$\text{AlPO}_4\text{-5}$  and all  $\text{MeAPO-5}$  [ $\text{Me} = \text{Mg, Co, Mn and Zn}$ ] prepared as described in [1] were characterized after chemical treatment with methanolic  $\text{HCl}$  in order to remove the template molecules and the extraframework  $\text{Me}$  [7].  $\text{MeAPO-5}$  was synthesized with a gel composition of 1.0  $\text{Al}_2\text{O}_3$ :1.0  $\text{P}_2\text{O}_5$ :0.25  $\text{MeO}$ :1.0  $\text{Pr}_3\text{N}$ :40  $\text{H}_2\text{O}$ . The samples resulted from the incorporation of manganese, cobalt, zinc and magnesium in the synthesis of  $\text{AlPO}_4\text{-5}$  are labeled as  $\text{MnAPO-5}$ ,  $\text{CoAPO-5}$ ,  $\text{ZAPO-5}$ , and  $\text{MAPO-5}$  respectively.  $\text{AlPO}_4\text{-5}$  was used as a reference material for all measurements and calculations discussed hereafter.

The  $\text{MeAPO-5}$  samples were characterized by  $x$ -ray diffraction (XRD) analysis using Siemens D5000 Diffractometer in the scanning range of  $2\theta$  between 2 and  $40^\circ$  using copper  $\text{K}\alpha$  ( $\theta = 0.1542$  nm at 35 kV and 35 mA) as the source of radiation. Silicon powder was 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 ( $\text{hkl}=111$ ) 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. The MAS NMR experiments were performed using Varian  $^{\text{Unity}}$ I-NOVA 400 MHz 9.4T spectrometer. The  $^{31}\text{P}$  MAS NMR spectra were recorded at 161.87 MHz using 2.0  $\mu\text{s}$  radio frequency pulses, a recycle delay of 1.0 s and a spinning rate of 4.5 kHz. Chemical shifts for  $^{31}\text{P}$  was referred to 85%  $\text{H}_3\text{PO}_4$ . The samples were characterized after calcination at  $400^\circ\text{C}$  overnight by MAS NMR and XRD.

Ammonia was used as the sorbed molecule in  $\text{NH}_3\text{-TPD}$  experiment. TPD data was acquired from Micromeritics 2900 TPD/TPR. The sample was heated at  $500^\circ\text{C}$  for 40 minutes and cooled down to  $100^\circ\text{C}$  before passing ammonia. After saturating with  $\text{NH}_3$ , the sample was flushed with  $\text{N}_2$  in order to remove the physically adsorbed  $\text{NH}_3$ . Temperature for adsorption was increased at a rate of  $5^\circ\text{C}/\text{min}$ .

The dehydration and dehydrogenation of cyclohexanol over  $\text{AlPO}_4\text{-5}$  and  $\text{MeAPO-5}$  and characterization of their products were carried out as described in [2].

## 3. Results and discussion

### 3.1. Physical properties

XRD patterns of  $\text{AlPO}_4\text{-5}$ ,  $\text{MnAPO-5}$ ,  $\text{CoAPO-5}$ ,  $\text{ZAPO-5}$  and  $\text{MAPO-5}$  show that the samples are pure and highly crystalline as reported [6]. The framework of  $\text{MeAPO-5}$  by bulk

Table 1

Framework composition of MeAPO-5 and AlPO<sub>4</sub>-5 by bulk chemical analysis

Sample	Normalized elemental ratio		
	Me	Al	P
AlPO <sub>4</sub> -5	-	0.50	0.50
MAPO-5	0.03	0.47	0.50
MnAPO-5	0.04	0.46	0.50
ZAPO-5	0.03	0.47	0.50
CoAPO-5	0.03	0.47	0.50

chemical analysis as tabulated in Table 1 shows a strong evidence of isomorphous substitution of Me atoms by Al into the framework of MeAPO-5. Figure 1 shows the trend in the unit cell parameters of the *a*-axis and *c*-axis of the hexagonal lattice of AFI structure of MeAPO-5 samples respectively. It shows that an increase in parameter *a* and a decrease in parameter *c* with the incorporation of divalent metals into the framework. The decrease in parameter *c* was due to the influence of the size and amount of Me atoms that was incorporated into the framework of AlPO<sub>4</sub>-5 structure.

Figure 2 shows the relationship between the mean T–O–P angle and ionic radii of metal atom in AlPO<sub>4</sub>-5 and MeAPO-5 as calculated from the <sup>31</sup>P MAS NMR spectra. The T–O–P angle was calculated using the following relation [8]:

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

where  $\alpha$  = chemical shift ppm. It is evident that manganese having the largest ionic radius (0.81Å), imposes the largest effect to the increase of the T–O–P angle, followed by zinc (0.73Å), cobalt (0.72Å), magnesium (0.71Å) and aluminum (0.53Å) respectively. This suggests that the ionic size of the incorporated divalent metal influences the T–O–P angle in the structure of AlPO<sub>4</sub>-5.

One expects that the higher is the T–O–P angle, the bigger is the unit cell volume. Calculation of the unit cell volume of AlPO<sub>4</sub>-5 (1384Å<sup>3</sup>), MAPO-5 (1388Å<sup>3</sup>), CoAPO-5 (1387Å<sup>3</sup>), ZAPO-5 (1382Å<sup>3</sup>) and MnAPO-5 (1387Å<sup>3</sup>) show that the unit cell volumes do not follow the trend in the T–O–P because the unit cell volume is not solely affected by the T–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 [9,10].

If a large divalent Pb atom (covalent radii = 1.54Å and ionic radii = 1.20Å [11]) is incorporated into the framework of AlPO<sub>4</sub>-5, the *a*-axis of the unit cell of Pb-AlPO<sub>4</sub>-5 is smaller than in MeAPO-5 and its *c*-axis is larger than in MeAPO-5. It is calculated from the AlPO<sub>4</sub>-5 phase that the lattice parameters of Pb-AlPO<sub>4</sub>-5 are, *a* = 13.704Å and *c* = 8.509Å. Attempt to incorporate a larger atom such as Pb (1.20Å) atom into AlPO<sub>4</sub>-5 was not successful as pure product could not be obtained. Successful incorporation may be achieved only if the microporous framework is flexible. Referring to the ideal radius ratio for tetrahedral coordination of 0.225–0.414 as suggested by Flanigen *et al.* [12], the radius ratio for Pb<sup>2+</sup> is obviously not ideal for tetrahedral coordination in AlPO<sub>4</sub>-5. This result reinforces our previous observation that the distortion of the structure of MeAPO-5 is caused by the size of the divalent metal atom.

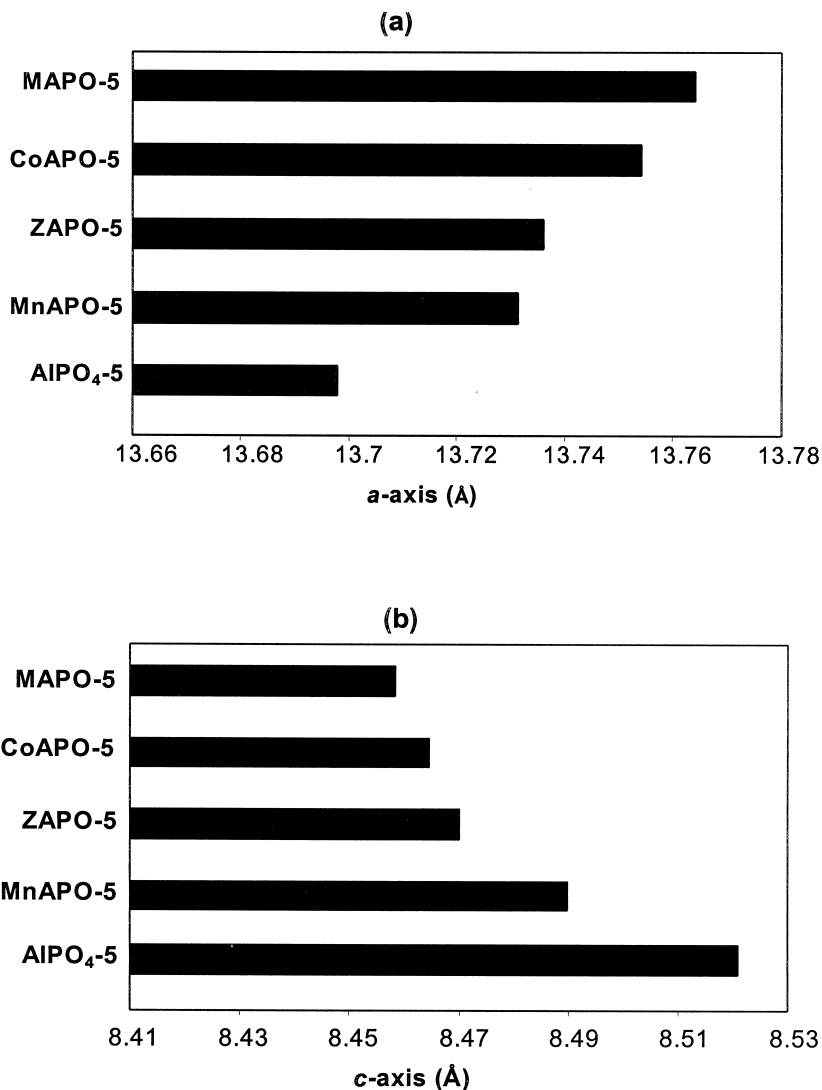


Fig. 1. The *a*-axis and *c*-axis unit cell parameters of AlPO<sub>4</sub>-5 and MeAPO-5.

The result obtained, indicates that the incorporation of the Me atoms distorts the structure of MeAPO-5 in the long-range. Short-range order of <sup>31</sup>P in MeAPO-5 suggests that the distortion of MeAPO-5 crystals is correlated with the T–O–P angle.

### 3.2. Catalytic activity of MeAPO-5

It was observed that cyclohexene and cyclohexanone were the major products in the conversion of cyclohexanol over MeAPO-5. Cyclohexene was the product from the reaction of cyclohexanol in the presence of Brønsted acid sites and cyclohexanone from the reaction of cyclohexanol in the presence of the base sites [2,13,14]. The role of the acid and base sites



Table 2

The hypothetical concentration of H atom as Brönsted acid in  $\text{AlPO}_4\text{-5}$  and  $\text{MeAPO-5}$  molecular sieves and the conversion of cyclohexanol over these catalysts

Sample <sup>a</sup>	Composition		Amount of acid sites (mmol/g) <sup>d</sup>	Conversion of cyclohexanol (%) <sup>e</sup>
	Me <sup>b</sup>	H <sup>c</sup>		
$\text{AlPO}_4\text{-5}$	-	-	0.04	Trace
$\text{MAPO-5}$	0.03	0.03	0.41	18
$\text{CoAPO-5}$	0.03	0.03	0.40	18
$\text{ZAPO-5}$	0.03	0.03	0.43	22
$\text{MnAPO-5}$	0.04	0.04	0.42	33

<sup>a</sup> After treatment with methanolic HCl at 110°C for 10 h.

<sup>b</sup> Bulk chemical analysis using XRF spectrometer.

<sup>c</sup> Assume that (i) Me occupy the framework position, (ii) one Me atom generates one Brönsted acid site (=  $\text{AlO}_3\text{P.HOMeO}_3\text{P}$ ).

<sup>d</sup> The number of acid site was correlated with the amount of ammonia chemisorbed.

<sup>e</sup> Temperature = 400°C, contact time = 2 h.

case of  $\text{MnAPO}$  the T–O–P angle contributes to the highest conversion of cyclohexanol to cyclohexene.

The only credible, though complex, relationship between activity and acidity of the  $\text{MeAPO-5}$  was found when we considered the acid strength.  $\text{MnAPO-5}$ , being the strongest acid in the group studied, gave the highest conversion of cyclohexanol and is therefore considered as the most reactive catalyst. However, in our view, acid strength itself is not the only cause of the high activity; the number of acid sites also affects the activity.

Counting of acid sites seems to be more difficult. Prior studies have shown that there is a good correlation between the catalytic activity of a solid in certain reaction with the variation in the number of acid centers. The correlation between the amount of ammonia desorbed from the TPD curves with the number of acid sites from the overall composition of  $\text{MeAPO-5}$  is shown in Table 2. It shows that the amount of ammonia desorbed among the  $\text{MeAPO-5}$  samples is almost the same and is in agreement with the hypothetical concentration of H atom as Brönsted acid. It should be noted that the expected concentrations of the acid sites are estimated from the overall composition. The calculation is based on the assumption that Me atoms occupy the framework position.

The results in Table 2 indicates that the activity of the  $\text{MeAPO-5}$  increase in the following order:  $\text{MnAPO-5} > \text{ZAPO-5} > \text{CoAPO-5} > \text{MAPO-5}$ . Since the ionic radii of Me atom affects the acid strength, it is considered as a measure of activity of the  $\text{MeAPO-5}$ . The effect of the acid strength of catalyst is clearly observed in Figure 4. From this result, the synergy effect of acid strength and number of acid sites to activity is clearly demonstrated.

The rank of the acidity obtained above contradicts the result observed by Pozas *et al.* [17]. They observed that the dehydration of ethanol increases over catalysts in the following order  $\text{CoAPO-5} > \text{ZAPO-5} > \text{MnAPO-5}$ . Calculation of lattice parameter by Pozas *et al.* shows that the incorporation of Mn, Co and Zn into  $\text{AlPO}_4\text{-5}$  implies a lattice expansion compared to the original  $\text{AlPO}_4\text{-5}$ . However, they observed that the cell parameters of the hexagonal lattice of AFI structure type of  $\text{CoAPO-5}$ ,  $\text{ZAPO-5}$  and  $\text{MnAPO-5}$  are similar. Our observations are different because the distortion of  $\text{MeAPO-5}$

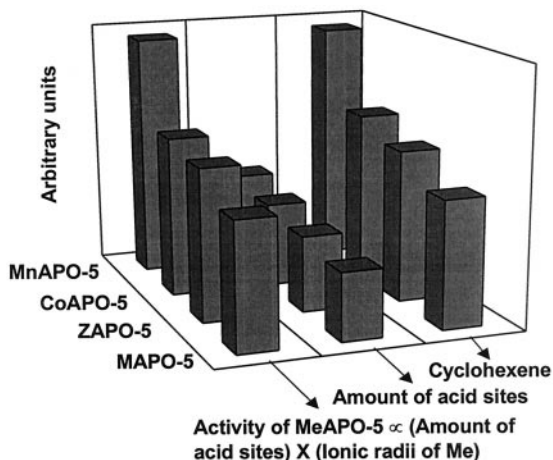


Fig. 4. Comparing the trend of percentage of cyclohexene with the amount of acid sites and activity of MeAPO-5.

follow the trend of the ionic radii of Mn, Co and Zn. The Me concentration used by us in the synthesis of MeAPO-5 differs from those used by Pozas *et al.* Elemental ratio of Me reported by Pozas *et al.* was 0.010–0.014. Instead we increased the Me content threefold. Clearly these changes influence the distortion of the hexagonal lattice of the AFI structure.

A possible explanation for the difference between our results and that of Pozas *et al.* is that, the incorporation of a large amount of Me atom into the framework of  $\text{AlPO}_4\text{-5}$  not only cause distortion of the hexagonal lattice of the AFI structure, but also demonstrates the effect of ionic radii of Me atom on the structure. This effect was not clearly observed for a lower concentration of Me atom. The order of activity for MeAPO-5 with the lower concentration of Me atom was in agreement with the effective charge on oxygen atom calculated using Pauling's third rule as reported earlier [2].

#### 4. Conclusions

The correlation between the ionic radii of divalent metals incorporated into the framework with the acidity of MeAPO-5 catalysts was observed in the conversion of cyclohexanol. The acidity of catalysts was correlated with the ionic size of Me atom in MeAPO-5 according to the following order:  $\text{Mn} > \text{Zn} > \text{Co} > \text{Mg}$ . The metal-substituted  $\text{AlPO}_4\text{-5}$  influences the acid strength and number of acid sites. The number of acid sites is the controlling factor in cyclohexanol conversion. Both structural (T–O–P angle) and chemical formula are factors that affect the acidity of MeAPO-5.

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