

**THE REMOVAL OF TEMPLATE FROM MeAPO<sub>4</sub>-5 AND MeAPSO<sub>4</sub>-5 BY  
CALCINATION AND TREATMENT WITH METHANOLIC  
HYDROCHLORIC ACID: STRUCTURAL EFFECT AND MECHANISM**

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**Abstract**

This paper reports on the removal of tripropylamine template from MeAPO<sub>4</sub>-5 and MeAPSO<sub>4</sub>-5 by calcination and treatment with methanolic HCl. Structural effect upon the removal of template on MeAPO<sub>4</sub>-5 and MeAPSO<sub>4</sub>-5 and the possible mechanism of the reaction are discussed. Treatment with methanolic HCl refer as 'demetalation', effectively removes organic template from MeAPO<sub>4</sub>-5 and MeAPSO<sub>4</sub>-5 as Me-amine complexes.

**Introduction**

Since catalysts are activated by calcination in air at high temperatures, an important requirement of aluminophosphates molecular sieves as catalyst is its thermal stability. Calcination removes hydrocarbon reactants and residues, brings about redispersion of the metal cations in aluminophosphates which facilitates their removal by subsequent ion exchange. This process usually leads to the deposition of carbonaceous material which blocks the acid sites that consequently renders the solid catalytically inactive. Several alternative means of chemical activation have been studied, the most successful being the interaction with dilute methanolic hydrochloric acid. (Gelsthorpe and Theocharis, 1988, Malla and Komarneni, 1995). Malla and Komarneni observed that aluminophosphate and silicoaluminophosphate molecular sieves treated with methanolic HCl is an effective alternative route for the removal of organic template molecules from molecular sieves, specifically when the pore size of the molecular sieves  $\geq 6$  Å. Following their success, the effect of the removal organic template by calcination and treatment with methanolic HCl of metal-containing AlPO<sub>4</sub>-5 (MeAPO<sub>4</sub>-5) and metal-containing SAPO<sub>4</sub>-5 (MeAPSO<sub>4</sub>-5) was carried out.

**Experimental**

Synthesis and characterization.

The AlPO<sub>4</sub>-5, SAPO<sub>4</sub>-5, MeAPO<sub>4</sub>-5 and MeAPSO<sub>4</sub>-5 samples were synthesized with modification according to established procedure (Wilson and Flanigen, 1982). Composition of the gel mixture is 1.2 Al<sub>2</sub>O<sub>3</sub> : 1.0 P<sub>2</sub>O<sub>5</sub> : 0.25 MeO : 0.4 SiO<sub>2</sub> (for SAPO<sub>4</sub>-5) :  $\gamma$  Pr<sub>3</sub>N : 40 H<sub>2</sub>O. The Pr<sub>3</sub>N was added dropwise into the mixture until pH 4.9 was achieved. The AlPO<sub>4</sub>-5/SAPO<sub>4</sub>-5 containing magnesium, manganese, cobalt,

and zinc are labelled as MAPO<sub>4</sub>-5/MAPSO<sub>4</sub>-5, MnAPO<sub>4</sub>-5/MnAPSO<sub>4</sub>-5, CoAPO<sub>4</sub>-5/CoAPSO<sub>4</sub>-5, and ZAPO<sub>4</sub>-5/ZAPSO<sub>4</sub>-5 respectively. X-ray diffractograms of samples were obtained by using XRD Siemens D5000 Diffractometer in the scanning range of 2θ between 2 and 40° using Kα (λ = 0.1542 nm) as source. Chemical analysis data were collected by X-ray fluorescence analysis using Siemens SRS 303. The crystalline compounds were further examined with infrared (IR) spectroscopy using the KBr pellet technique. Differential Thermogravimetry Analysis (DTG) were performed in air using a Mettler TG50 with a scan rate of 10 °C/min. The MAS NMR experiments were performed using Varian Unity INOVA 400 MHz 9.4T spectrometer. The <sup>27</sup>Al MAS NMR spectra were recorded at 104.26 MHz using 0.1 μs radiofrequency pulses, a recycle delay of 0.5 s and spinning rate of 5 kHz. The <sup>31</sup>P MAS NMR spectra were recorded at 161.87 MHz using 2.0 μs radiofrequency pulses, a recycle delay of 1.0 s and spinning rate of 4.5 kHz.

#### Removal of template molecules.

The washed and dried crystalline samples were calcined at 500-600 °C in air for 5-20 hours to remove the entrapped organic molecules.

#### Treatment with methanolic HCl.

One gram sample was treated with 50 mL of 1 M methanolic HCl in a teflon-lined 125 mL stainless steel vessel (Parr bomb) at 110-150 °C for 20 hours followed by quenching of the the bottom half of the vessel in cold water to room temperature. Sample was first washed with methanol followed with deionized water using centrifugation and dried at 110 °C.

### Results and Discussion

Differential Thermogravimetric diagrams in Figures 1 and 2 show a template-lattice interaction in MeAPO<sub>4</sub>-5 and MeAPSO<sub>4</sub>-5. The samples showed three distinct weight losses: A low temperature weight loss attributed to physisorbed water and tripropylamine (~7 wt%), a weight loss of ~5 wt%, in the range of 380-500 °C which corresponds to the desorption of tripropylamine and cracking of the occluded tripropylamine molecules to smaller molecules. Since the channels of AlPO<sub>4</sub>-5 are polar (Uytterhoeven et al., 1989), the tripropylamine molecules, which are also highly polar, are strongly held in the channels at lower temperatures. However, at higher temperatures, the desorption of tripropylamine is expected to be prolonged. Thus, in the overall removal of the tripropylamine molecules, the physical (desorption of tripropylamine) and chemical (the cracking of tripropylamine) processes occur simultaneously. In the third stage (500 - 700 °C), a weight loss of ~6 wt% is due to the very slow desorption of ammonia and/or tripropylamine which was adsorbed strongly on the high energy sites of MeAPO<sub>4</sub>-5/ MeAPSO<sub>4</sub>-5 due to the release of trapped gaseous products after the complete collapse of the structure (Akolekar, 1996).

After calcination,  $\text{MnAPO}_4\text{-5}$  and  $\text{CoAPO}_4\text{-5}$  are pink and blue solids respectively. Visually, it is difficult to determine whether carbon residue still remain after calcination. However, upon calcination at 550 °C for 5 hours, the colour change of  $\text{AlPO}_4\text{-5}$ ,  $\text{SAPO}_4\text{-5}$  and  $\text{MAPO}_4\text{-5}$  from white to gray confirmed the absence of carbon residue. The samples turned white after they were calcined at 550 °C for 20 h.

When  $\text{CoAPO}_4\text{-5}$  was refluxed with methanolic HCl, the concentration of cobalt calculated from XRF data shows a decrease in concentration of 58.3% from the original weight. Elemental analysis using XRF shows that  $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$  ratio is 1.09. XRD and IR data show that the framework of  $\text{CoAPO}_4\text{-5}$  did not collapse after refluxing with methanolic HCl at 110 °C for 20 hours, suggesting that Al-O-P bonds remain intact and is not affected by HCl. Although the template was removed together with the incorporated metal in the framework, the structure did not collapse. This suggests that the amount of framework Co and non-framework Co (if any) bonded to the template must be small. It is observed that there is no loss in the crystallinity of the sample after it was calcined and a slight decrease in crystallinity after  $\text{CoAPO}_4\text{-5}$  was refluxed with methanolic HCl. This result is in agreement with the chemical analysis by XRF as shown in Figure 5.

Infrared spectrum of the treated samples in Figure 3 shows that calcination of  $\text{CoAPO}_4\text{-5}$  at 550 °C for 20 hours (Sample A) decreases the intensity of the peak at 560  $\text{cm}^{-1}$  compared to the calcination at 550 °C for 5 hours (Sample B). When  $\text{CoAPO}_4\text{-5}$  was refluxed with methanolic HCl at 110 °C for 20 hours (Sample C), the intensity at 560  $\text{cm}^{-1}$  also decreases compared to refluxing at room temperature in the same time period (sample D). However, XRD data showed an increase in the relative crystallinity after  $\text{CoAPO}_4\text{-5}$  was calcined, and a decrease after the sample was refluxed with methanolic HCl (see Table 1). The presence of the peak at (001) indicates that the quality of the large pore of the sample remains unaltered (see Figure 4).

Increasing the reflux temperature to 150 °C for 20 hours, did not change the blue colour, confirming the presence of cobalt in the sample. The ions were leached into solutions during hydrothermal crystallization and reflux with methanolic HCl.

The  $^{27}\text{Al}$  MAS-NMR spectrum in Figure 6(a) consists of a main peak at 36.67 ppm and other peaks at 9.69 ppm. The first peak is assigned to tetrahedral  $\text{Al}(\text{PO})_4$  while the peak shift at 9.69 ppm is assigned to the  $\text{AlO}(\text{OH})$  of the unconverted starting material (Kismojohadi, 1995). This form of Al was attributed to either the template, water molecules in the channels, or basic aluminium-phosphate reaction intermediate. The presence of octahedral Al is not observed in  $\text{CoAPO}_4\text{-5}$  sample. This result eliminates the possibility of non-framework aluminium bonded with the template. This finding is also supported by  $^{31}\text{P}$  MAS-NMR spectra as shown in Figure 6(b). A

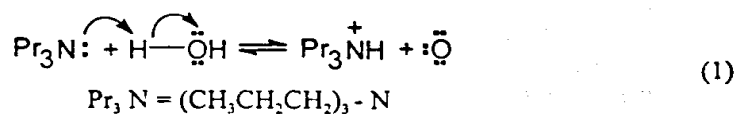
symmetrical peak occurring at 19 to -30 ppm (relative to external  $H_3PO_4$ ) is assigned to tetrahedral  $PO_4$  units in the framework.

Proposed mechanism.

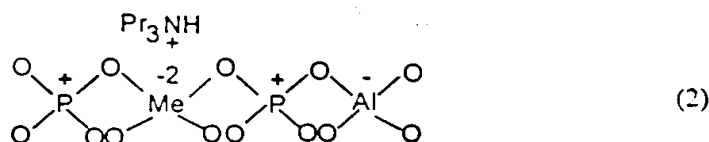
From the results obtained, we proposed the following mechanism of removal of template by calcination and reflux with methanolic HCl.

**Mechanism for the removal of template by calcination.**

During synthesis, tripropylamine acts as a weak base and accepts one proton from water in a reversible acid-base reaction.



The template which fills the channel in  $MeAPO_4-5$ 's can be bonded with the metals in two ways, firstly,

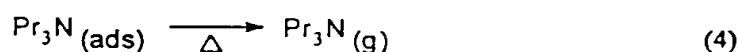


and secondly, with non-framework metal to form metal-template complexes,

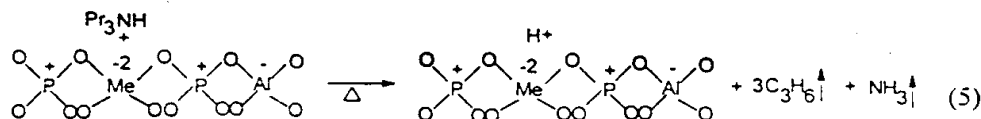


Removal of  $C_3H_6$  and  $NH_3$  from the framework of  $MeAPO_4-5$  during calcination occur in two steps:

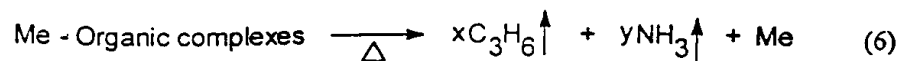
(i) the release of template first as free amine at low temperature,



(ii) followed by degradation of the proton or metal-complexed amine at high temperature.

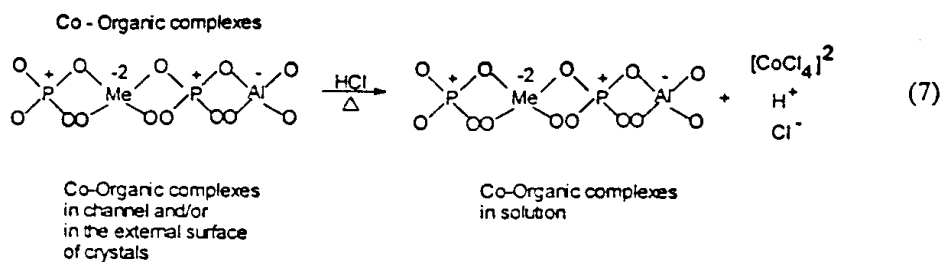


and/or



Mechanism of the removal of template by methanolic HCl.

The most possible mechanism for the removal of template by methanolic HCl is as follows:



A blue solution was obtained after the sample was refluxed with methanolic HCl. This indicates that Co-amine is occluded as organo-metallic complexes  $[\text{CoCl}_4]^{2-}$ . (Moore, 1982).

### Conclusions

Decomposition of  $\text{Pr}_3\text{N}$  in  $\text{MeAPO}_4\text{-5}$  and  $\text{MeAPSO}_4\text{-5}$  samples is significantly different from those of  $\text{AlPO}_4\text{-5}$  and  $\text{SAPO}_4\text{-5}$  samples. Refluxing with methanolic HCl at low temperature effectively removes occluded organic template molecules from metal substituted  $\text{AlPO}_4\text{-5}$  samples. Based on the proposed mechanism of removal, we refer the reaction as 'demetalation'.

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Table 1 Relative crystallinity of treated CoAPO<sub>4</sub>-5 sample.

Sample	Treatment	Relative crystallinity (%)
CoAPO <sub>4</sub> -5	as synthesized	77
A	calcination at 550 °C for 20 h	100
B	calcination at 550 °C for 5 h	85
C	reflux with methanolic HCl at 110 °C for 20 h	51
D	reflux with methanolic HCl at room temperature for 20 h	60

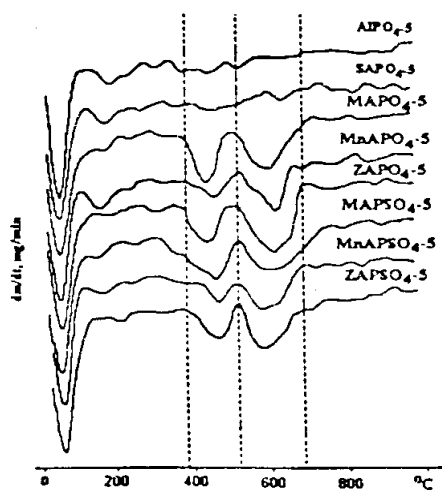


Figure 1 DTG curves of AlPO<sub>4</sub>-5, SAPO<sub>4</sub>-5, MeAPO<sub>4</sub>-5 and MeAPSO<sub>4</sub>-5.

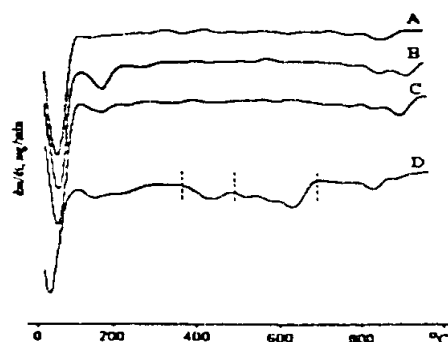
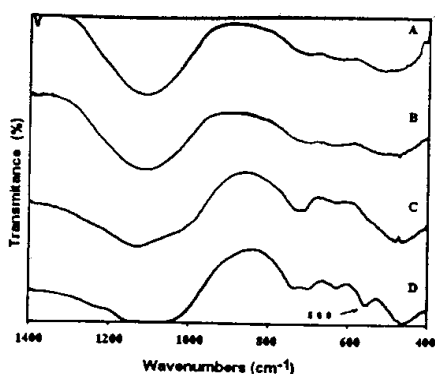
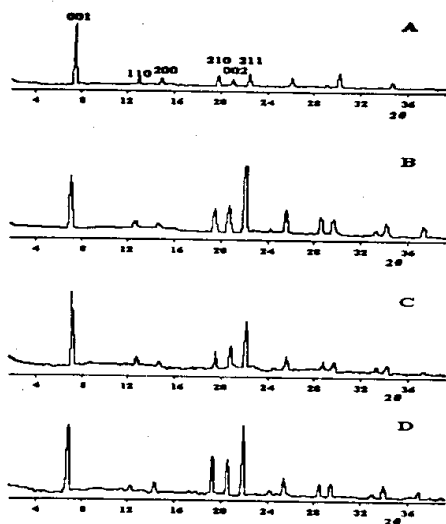


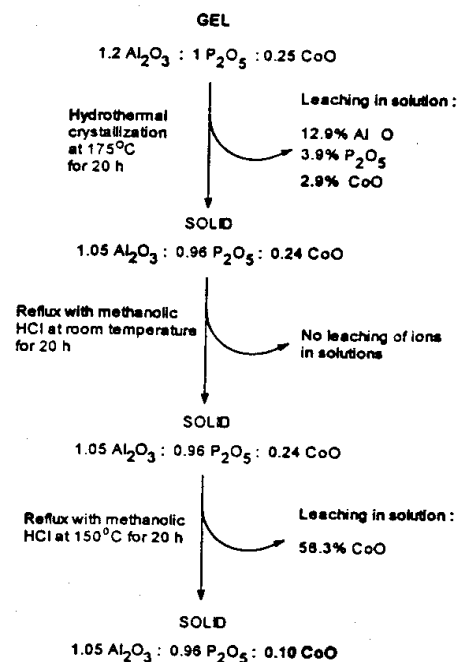
Figure 2 DTG curves of CoAPO<sub>4</sub>-5: A - after calcination at 550 °C for 20 h; B - after calcination at 550 °C for 5 h; C - after reflux with methanolic HCl at 110 °C for 20 h; D - after reflux with methanolic HCl at room temperature for 20 h.



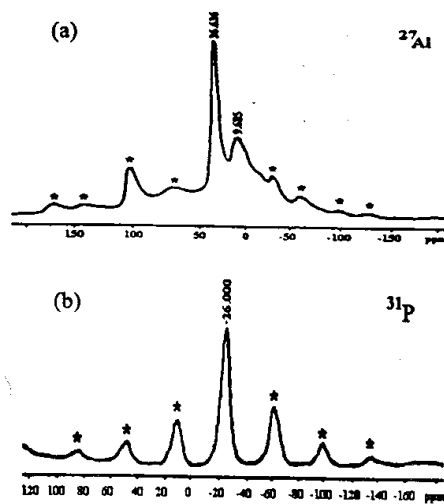
**Figure 3** IR spectrum of  $\text{CoAPO}_4\text{-5}$  :  
 A - after calcination at  $550^\circ\text{C}$  for 20 h;  
 B - after calcination at  $550^\circ\text{C}$  for 5 h;  
 C - after reflux with methanolic HCl at  $110^\circ\text{C}$  for 20 h; D - after reflux with methanolic HCl at room temperature for 20 h.



**Figure 4** XRD spectrum of  $\text{CoAPO}_4\text{-5}$   
 A - after calcination at  $550^\circ\text{C}$  for 20 h;  
 B - after calcination at  $550^\circ\text{C}$  for 5 h;  
 C - after reflux with methanolic HCl at  $110^\circ\text{C}$  for 20 h; D - after reflux with methanolic HCl at room temperature for 20 h.



**Figure 5** Leaching of ions (aluminium, phosphorous and cobalt) of  $\text{CoAPO}_4\text{-5}$  during hydrothermal crystallization and reflux with methanolic HCl.



**Figure 6**  $^{27}\text{Al}$  and  $^{31}\text{P}$  MAS spectrum of  $\text{CoAPO}_4\text{-5}$ , with spinning sidebands indicated by asterisks (\*).