



Synthesis and characterization of the second generation of the UEC family of molecular sieves

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Abstract

This work reports the transformation of a layered aluminophosphate (AIPO-CJ70) with N,N-dimethylbenzylamine as SDA and inorganic layers containing two different Al sites and three P sites, where two of them are $\equiv\text{P}=\text{O}$ sites and the other is a $=\text{P}(\text{OH})=\text{O}$ group, in three dimensional silicoaluminophosphates with structures analogous to SAPO-5 and SAPO-15. The synthetic process of the 3D materials are different. The SAPO-5 analogue, called UEC-4, was synthesized in an aqueous media in the presence of TEABr and silica, and the SAPO-15 analogue, UEC-5, was synthesised by a dry-gel conversion method in the presence of n-butylamine and silica. Both materials were characterized with powder X-rays diffraction, solid state nuclear magnetic resonance, infrared spectroscopy, scanning electron microscopy and termogravimetry.

Key words: Silicoaluminophosphate, 2D-3D transformation, Zeotypes

Introduction

Aluminophosphates and silicoaluminophosphates have structures analogous to the zeolites, an usual synthesis method is the mixture of single sources of Si, Al and P together with an agent capable to direct the desired structure, generally an amine or a quaternary ammonium cation. Recent works show the existence of a layered intermediate during the synthetic process, this layered material interacts with the SDA to generate the three-dimensional structures.¹

Starting from a layered structure instead of single sources of T atoms (T = Si, Al, P), the CAL family of molecular sieves was created, using the AIPO-Kanemite as precursor, it was possible to synthesise CHA and LEV structures named CAL-1 to -5.² Using AIPO-CJ70³ as precursor in the synthesis made it possible to obtain SAPO-5 (UEC-4) and SAPO-15 (UEC-5) analogues. This AIPO has a layered structure with N,N-dimethylbenzylammonium as SDA, the inorganic layer is compose by two $[\text{AlO}_4]^-$ groups, two $\equiv\text{P}=\text{O}$ groups and a $=\text{P}(\text{OH})=\text{O}$ group.

Results and Discussion

The synthesis was monitored by powder XRD, the effect of variation in the synthesis time is shown in Image 1 for the UEC-5. In the early steps of the synthesis, the layered precursor expands the interlayer space, giving origin to at least three intermediates and, after 120 h, a pure SAPO-15 phase appears, the best crystallinity was observed after 168 h of synthesis time.

The existence of Si-O-Al bonds in the UEC-5 was determined using ²⁷Al Multiple Quantum MAS NMR. Using the NMR parameters found in the MQ experiment, the 1D spectrum could not be simulated, which indicates the presence of Si-O-Al bond.

In relation to UEC-4, with the insertion of silica in the synthesis the substitution of P sites for Si atoms gel is expected, giving origin to Brønsted acid sites. To observe this substitution, ²⁹Si NMR decoupled from proton and with ¹H-²⁹Si cross polarization was made. The increase of intensity in the Si(OAl)₄ site shows the presence of the Brønsted acid site.

In the ¹³C MAS NMR of UEC-4, peaks from tetraethylammonium and N,N-dimethylbenzylamine were observed. Their simultaneous presence means that both

SDAs are working together to build the AFI-type structure of UEC-4.

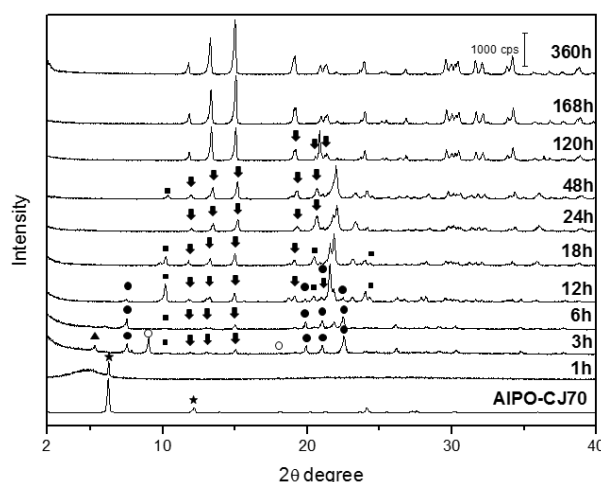


Image 1. XRD patterns from UEC-5 in different times of synthesis.

Conclusions

AFI-type and SAPO-15 structures were prepared from a single source of Al and P in layered form.

The results suggest that both materials have the Si-O-Al bond. Brønsted acid sites were observed in UEC-4 by ²⁹Si MAS NMR, while in UEC-5, the presence of Si inserted in the structure was observed using ²⁷Al-MQ-MAS.

In UEC-4, both organics work together to build the AFI-type structure.

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