

Solid-state nuclear magnetic resonance characterization of the second generation of the UEC family of molecular sieves

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Abstract

This work reports the characterization using solid-state NMR of the second generation of the UEC family of molecular sieves, such generation is composed by two tridimensional silicoaluminophosphates synthesized from a layered aluminophosphate (AIPO-CJ70). The 3D structures are analogous to SAPO-5 (UEC-4) and SAPO-15 (UEC-5), both were characterized using multinuclear solid-state NMR, ^{27}Al -MQ-MAS and $^{29}\text{Si}\{^{27}\text{Al}\}$ TRAPDOR.

Key words: UEC family, Solid-state NMR, TRAPDOR

Introduction

Aluminophosphates and silicoaluminophosphates can have structures analogous to the zeolites, a 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. 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 a precursor, it was possible to synthesise CHA and LEV structures named CAL-1 to -5.¹ Using AIPO-CJ70 as a precursor in the synthesis made it possible to obtain SAPO-5 (UEC-4) and SAPO-15 (UEC-5) analogues. Both structures have the insertion of Si atom in the AIPO framework, such insertion can create Brønsted acid sites or islands rich in Si, those situations and the effects in near Al sites can be studied with multinuclear solid-state NMR, ^{27}Al -MQ-MAS and $^{29}\text{Si}\{^{27}\text{Al}\}$ TRAPDOR.²

Results and Discussion

Both UEC-4 and -5 syntheses were monitored by powder XRD, the first one has a direct transformation in the AFI-type structure, with the best crystallinity with 72 h of reaction time. In the early steps of the UEC-5 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 insertion of Si in the UEC-5 was studied by ^{27}Al -MQ-MAS NMR and $^{29}\text{Si}\{^{27}\text{Al}\}$ TRAPDOR. Using the NMR parameters found in the MQ experiment, the 1D spectrum could not be simulated with only two sites, indicating one or more minor sites create from the insertion of Si in comparison with the pure aluminophosphate, to confirm such idea a $^{29}\text{Si}\{^{27}\text{Al}\}$ TRAPDOR was made (Fig. 1) and the disappearance of the signal at -92.5 ppm confirm the presence of Si-O-Al bonds. 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, ^{29}Si NMR decoupled from proton and with ^1H - ^{29}Si cross polarization was made. The increase of intensity in the $\text{Si}(\text{OAl})_4$ site shows the presence of the Brønsted acid site.

In the ^{13}C 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. Moreover, in the UEC-5, the organics SDAs are

fragmented during the synthesis process, resulting in small amines in the final material.

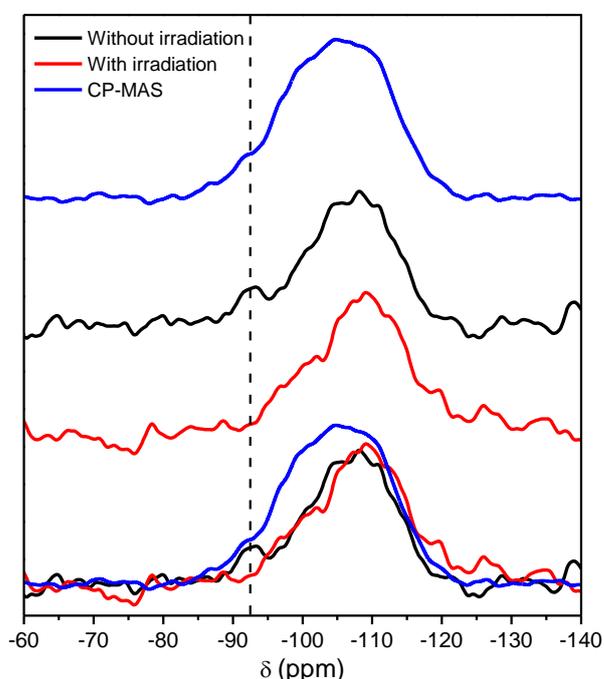


Image 1. $^{29}\text{Si}\{^{27}\text{Al}\}$ TRAPDOR of the UEC-5, the curve in black indicate a spin-echo experiment without the irradiation in the ^{27}Al , the red line indicates the same experiment with the irradiation and the blue line indicates a ^1H - ^{29}Si CP-MAS experiment.

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 ^{29}Si MAS NMR, while in UEC-5, the presence of Si inserted in the structure was observed using ^{27}Al -MQ-MAS and $^{29}\text{Si}\{^{27}\text{Al}\}$ TRAPDOR. In UEC-4, both organics work together to build the AFI-type structure, and in the UEC-5 the organic are fragmented.

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¹ Pastore, H. O., et al. *Microporous Mesoporous Mater.* **2008**, 107, 81–89.

² Greiser, S., et al. *Solid State Nucl. Magn. Reson.* **2016**, 79, 6–10.