

NMR SPECTROSCOPY ON SAPO AND MnSAPO THIN FILMS

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INTRODUCTION

Transition-metal (Me) functionalized mesoporous aluminophosphate (AlPO) and silicoaluminophosphate materials (SAPO) have been widely investigated as heterogeneous catalysts due to their hydrothermal stability and high catalytic activity [1]. So far, they were mostly prepared in form of powders and as such they have attracted attention as acid, base and redox heterogeneous catalysts. As thin films, these materials could have potential in optics and electronics.

Recently, the detailed preparation and structural characterisation of thermally stable mesoporous cubic AlPO thin film was reported [2]. In this contribution we extend the work in this field and present solid-state NMR spectroscopy studies of SAPO and MnSAPO thin films.

EXPERIMENTAL

We prepared mesoporous aluminophosphate thin films with ordered cubic pore arrangement, functionalized by silicon (SAPO) or silicon and manganese (MnSAPO). Thin films were prepared on a glass substrate by evaporation-induced self-assembly under controlled temperature and relative humidity using dip-coating method. Initial sol was prepared by mixing $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$, tertaethyl orthosilicate (TEOS) and phosphoric acid. MnSAPO was prepared by adding manganese acetate to the sol prior to the addition of phosphoric acid. The solution was stirred for 2 hours and subsequently block copolymer Pluronic F127 was added to the mixture under stirring. Clear solution, with molar ratio of 1 $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$: 1 H_3PO_4 : 0.2 TEOS : 0,005 F127 : 50 EtOH : 0.05 $\text{Mn}(\text{CH}_3\text{COO}) \cdot 4 \text{H}_2\text{O}$, was obtained after 2 hours of vigorous stirring. Thin films were deposited on clean glass substrate by dip-coating method at a constant withdrawal speed at ambient temperature and humidity. As-prepared films were left at the above described conditions for 24 hours, then at 60°C for 24 hours and at 130 °C for 24 hours. Finally the films were calcined at 400 °C for 6 hours.

^{31}P , ^{27}Al and ^{29}Si MAS NMR spectra of SAPO thin films scratched from glass substrates were recorded on 600 MHz Varian NMR system equipped with a Varian 3.2 mm MAS probe. Larmor frequencies for phosphorus, aluminium and silicon at 14.1 T are 242.89, 156.35 and 119.15 MHz, respectively. Chemical shifts are reported relative to the signal of ^{31}P in 85% H_3PO_4 , ^{27}Al in 1M solution of $\text{Al}(\text{NO}_3)_3$ and ^{29}Si in tetramethylsilane. Samples of SAPO were in all experiments spun at 10 kHz, while samples of MnSAPO were spun at frequencies of up to 20 kHz.

An Agilent 5500 atomic force microscope (AFM) was used for the topographic characterization of the calcined SAPO and MnSAPO thin films on a glass substrate. NCHR-SuperSharpSilicon probes made by NanoSensors with a tip radius of 2 nm, 330 kHz resonance frequency and a spring constant of 42 N/m were used. The imaging was performed in non-contact mode (NC-mode), at room humidity and temperature conditions. The average scan size was 1 μm \times 1 μm . Scans were made with scan rate of 1.4 lines/s and 512 line resolution.

RESULTS AND DISCUSSION

Morphology of the thin film surface was investigated using atomic force microscopy (Figure 1). Ordered mesopore structure can be seen in an AFM image of calcined SAPO and MnSAPO thin films. The observed pore arrangement is consistent with (110) surface of the body centred cubic pore structure. FFT performed on AFM images reveal that MnSAPO thin films exhibit pore structure that is not as highly ordered as in SAPO films.

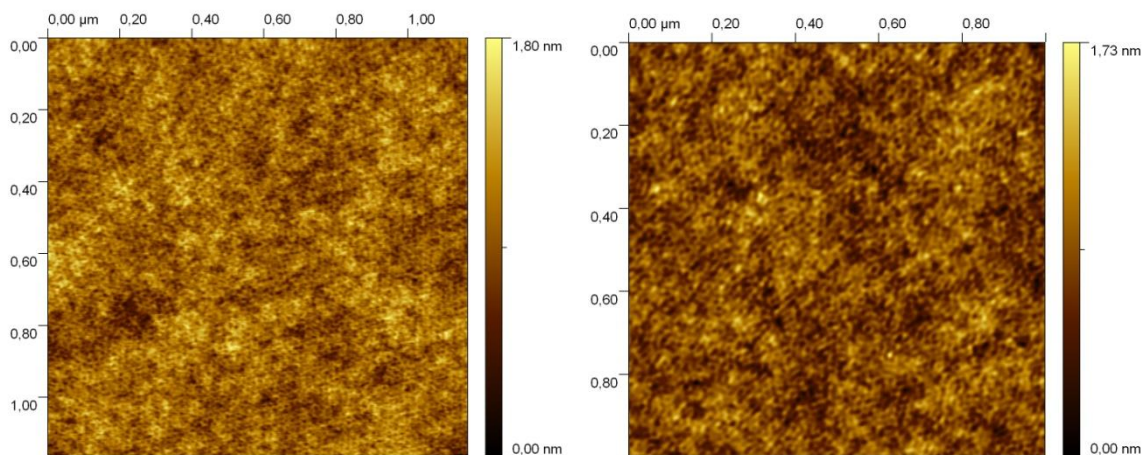


Figure 1. On the left hand side is an AFM image of SAPO thin film and on the right hand side a FFT (Fast Fourier Transform) filtered AFM image. In both cases pores are clearly visible.

Composition of the framework of SAPO and MnSAPO thin films on the atomic scale was investigated by solid-state NMR spectroscopy. ^{27}Al MAS NMR spectra of cubic mesoporous SAPO thin films (Figure 2) are very similar to NMR spectra obtained on the related cubic mesoporous AIPO thin films [2,3]. From ^{27}Al MAS NMR spectrum of as-synthesised SAPO thin film it is evident that almost all aluminum is hexa-coordinated. After the calcination approximately one third of Al atoms become tetra- and about 10 % penta-coordinated. This, on one hand, suggests that the structure becomes more condensed. On the other hand the amount of octahedrally coordinated Al still present after calcination is unusually high for powdered AIPO materials, which means that the number of water molecules or hydroxyl groups still present in the framework is much higher than in related bulk material [4,5]. Such behaviour in aluminum seems to be unique to thin films [2].

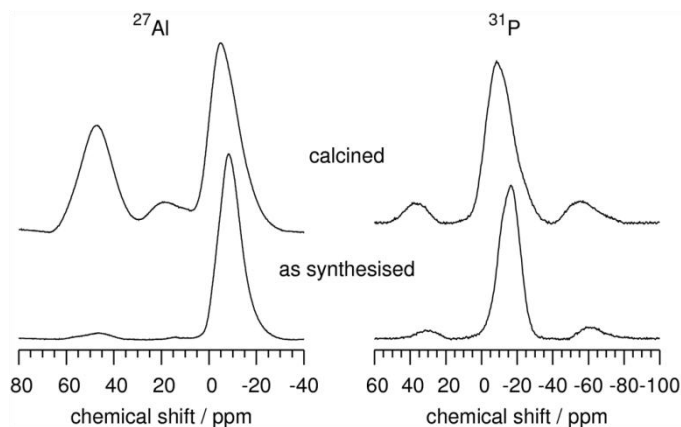


Figure 2. ^{27}Al and ^{31}P MAS NMR spectra of as-synthesised and calcined SAPO thin films.

³¹P MAS NMR spectra of SAPO thin films exhibit relatively broad signals composed of several contributions with the chemical shifts between -10 and -20 ppm. This also indicates that the framework is not fully condensed neither in the as-prepared nor in the calcined thin film. Contributions to the signal with the chemical shift of about -10 ppm can be assigned to phosphorus nuclei with less than four aluminum atoms in the first cation coordination sphere and are more pronounced in the calcined film than in the as-prepared one. This suggests that the framework of SAPO thin film is quite sensitive to the removal of the template molecules.

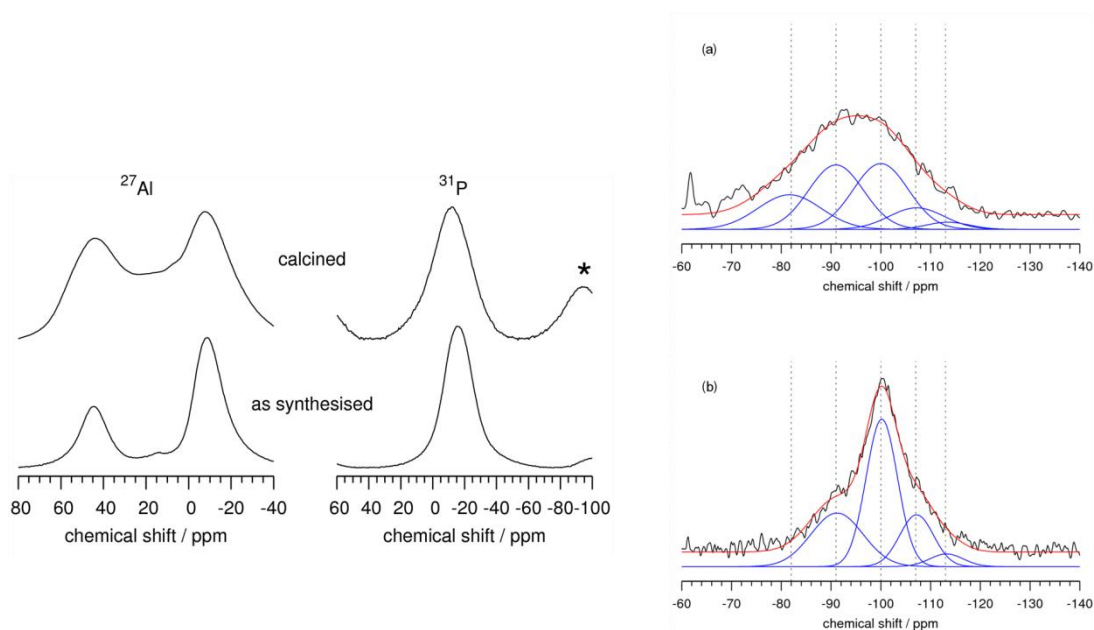


Figure 3. ²⁷Al and ³¹P solid-state MAS NMR spectra of as-synthesized and calcined MnSAPO thin films are presented on the left hand side. Asterisk marks the spinning sideband. On the right: recorded ²⁹Si MAS NMR spectra of as-synthesized (a) and calcined (b) MnSAPO thin film and their decomposition into individual contributions.

In MnSAPO thin films (Figure 3) ²⁷Al NMR reveals that in as-synthesized film about 30% of Al is already tetrahedrally coordinated. After the calcination the ratio of tetra- and hexa-coordinated aluminum atoms stays almost the same. Broadening of the peaks in the ²⁷Al NMR spectra after the calcination of MnSAPO films suggests that calcined thin films have more defects. Increased number of defects in the framework is likely a consequence of a less ordered pore arrangement, as seen in the AFM image in Figure 1.

³¹P NMR spectra of MnSAPO thin films, similarly as in SAPO samples, show a shift of the resonance peak to the higher frequencies after the sample was calcined. This means that the majority of phosphorous atoms in calcined thin films have less than four Al neighbours.

Because of the very small amount of silicon in the framework and low sensitivity of ²⁹Si nuclei, we were not able to detect ²⁹Si MAS NMR spectra of the SAPO thin films. In MnSAPO samples NMR-active nuclei had much shorter relaxation times and we were therefore able to accumulate more scans while recording the spectra. ²⁹Si NMR spectra in MnSAPO thin films (Figure 3) show strong contributions at -91 and -82 ppm. Taking into account that the framework of the film is poorly condensed, the two contributions could be assigned to Si(OSi)₂(OH)₂ and Si(OSi)(OH)₃ species, respectively. However, the spectra of MnSAPO thin films also exhibit signals at -107 and -113 ppm, which can be assigned to Si(OSi)₃(OAl) and Si(OSi)₄ units. A large fraction of the last two units indicates that the Si is incorporated in the walls of mesoporous material in form of silicon rich domains.

CONCLUSION

²⁷Al, ³¹P and ²⁹Si MAS NMR spectra revealed changes in the structure after the samples were calcined. In both, SAPO and MnSAPO thin films, the fraction of tetra-coordinated aluminium increases after the calcination, while the intensity of a peak belonging to hexa-coordinated alumina slightly reduces. ²⁷Al and ³¹P NMR spectra reveal that MnSAPO mesoporous thin films contain more defect sites and are therefore less condensed than SAPO thin films. AFM image shows that the mesopore structure is nevertheless sustained. From ²⁹Si NMR spectra it can be deduced that Si is incorporated in the structure of the mesoporous material in form of areas rich in silicon.

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