

## CUBIC MESOPOROUS ALUMINOPHOSPHATE THIN FILMS: STRUCTURAL CHARACTERIZATION AND APPLICATION OPPORTUNITIES

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### ABSTRACT

Mesoporous aluminophosphate thin films templated by nonionic copolymer surfactant (Pluronic-F108 and -F127) were prepared by the dip-coating method. Self-assembly of copolymer surfactants with different sizes and hydrophilic properties into cubic symmetry causes the formation of thin films with different pore dimensions. Symmetry of pore arrangement was determined by SAXS and TEM measurements. It has been shown that these films are stable to thermal treatment, and that there is an evolution of the inorganic framework, according to <sup>27</sup>Al and <sup>31</sup>P NMR spectra. Silicon and manganese were effectively incorporated within aluminophosphate framework which was confirmed by NMR and XANES/EXAFS analysis. Acidity and hydrophilic properties of metal-modified (SAPO and MnSAPO) aluminophosphate frameworks of thin films make these materials applicable for membranes, energy storage and catalytic applications.

Keywords: thin films, mesoporous aluminophosphate, SAXS

### INTRODUCTION

Important feature of mesostructured solids, based on various metal oxides, is their ability to form thin films with thickness on a nanometric scale, where the contribution of surface is much higher than in powder (xerogel) analogues. Investigations in this type of materials are rapidly uprising due to their potential applications as chemical and optical sensors, shape-selective membranes separation and energy-storage devices [1,2]. Mesoporous thin films based on silica are thoroughly investigated and with the proper chemical treatment they show numerous applicative properties such as catalytic activity [3], templating ability for production of nanowires [4], photovoltaic properties [5], moisture sensing [6], etc. Similar properties can also be expected for aluminophosphate thin films, however mesoporous AIPO materials are known only as powders. Majority of these materials are templated by cationic surfactant molecules, which are strongly bonded with aluminophosphate framework by electrostatic interactions. This usually causes partial or total collapse of the mesostructure upon removal of surfactant. Tian et al. [7] produced mesoporous AIPO material templated by nonionic copolymer surfactants for the first time. This material is thermally stable and ordered mesostructure is preserved after the surfactant removal due to the weaker surfactant-inorganic framework interactions in comparison with cationic surfactant molecules.

Here we report on the synthesis, structural characterization and application opportunities of new mesoporous aluminophosphate thin films with cubic (*Im $\bar{3}m$* ) pore arrangement. Cubic (F127-templated) aluminophosphate thin films were also successfully modified by silicon (SAPO) and additionally by manganese (MnSAPO).

### EXPERIMENTAL

Aluminophosphate solutions were prepared by mixing AlCl<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> prior to the addition of Pluronic copolymers F127 and F108 in ethanolic medium. Al / P and Al / S (S =

copolymer surfactants) molar ratios in solutions were 1 and 200 respectively. Thin films were deposited on a glass substrate by dip-coating method at room temperature, constant humidity and controlled speed. Surfactant was removed from inorganic framework by calcination at 673 K in air flow. Synthetic procedure for the synthesis of SAPO and MnSAPO thin films were identical, only TEOS and manganese acetate were added into initial solution with Si/Al and Mn/Al molar ratios of 0.2 and 0.01-0.05, respectively.

Mesostructure symmetry was determined by small angle X-ray scattering (SAXS) measured at Elettra synchrotron facility (Trieste, Italy) and by transmission electron microscopy (TEM) on JEOL JEM 2100 microscope. Local environment of aluminium and phosphorus atoms were investigated by NMR spectra recorded on 600 MHz Varian system. Local environment of manganese cations was determined by X-ray absorption spectroscopy (XANES/EXAFS) in HASYLAB synchrotron facility at DESY (Hamburg, Germany).

## RESULTS AND DISCUSSION

### *F127-, F108-templated aluminophosphate thin films*

Deposition of AlPO thin films by dip-coating from the above described solutions resulted in the formation of smooth and homogenous surface of (a) F127- and (b) F108-templated mesoporous aluminophosphate thin films with a thickness of 500 nm. Figure 1a shows a GISAXS pattern of as-deposited F127-templated aluminophosphate thin film, typically assigned to a cubic body-centered spherical pore arrangement with  $Im\bar{3}m$  symmetry with the (110) plane oriented perpendicular to the substrate. Figure 1c shows GISAXS pattern of as-deposited F108-templated aluminophosphate thin film with similar pore symmetry than in the case of F127-templated sample. Cell parameter dimensions  $a$  of 17.5 nm and 18.5 nm for as-deposited F127- and F108-templated samples respectively were determined. Thin films retain their ordered mesostructure up to 673 K, however unit cell parameter  $a$  contracts to 8.9 and 9.5 nm for F127- and F-108 templated films, respectively, as indicated from GISAXS patterns of calcined F127- and F108-templated samples (Figures 1b and 1d respectively).

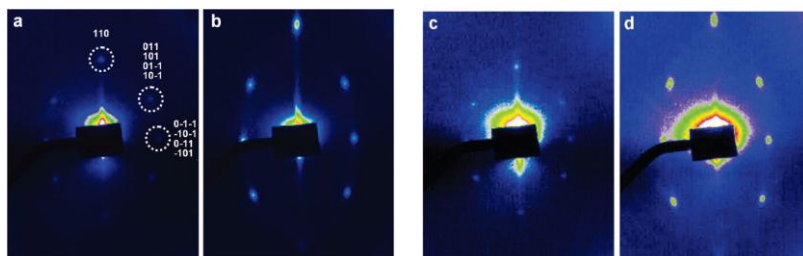


Figure 1. GISAXS patterns of the as-deposited mesoporous aluminophosphate thin films templated with Pluronic F127 (a) and F108 (c). Thermally treated F127-templated (b) and F108-templated (d); templated films at 673 K.

Highly-ordered cubic pore arrangement of the template-free thin film samples thermally treated at 673 K was investigated by TEM. Micrographs shown on Figures 2a and 2b represents pore arrangement of template-free F127-templated thin film along [111] and [110] pore direction respectively, whereas Figures 2c and 2d show F08-templated mesoporous aluminophosphate thin film sample along [111] and [110] pore direction respectively.

Local environment of Al and P atoms during thermal treatment of F127- and F108-templated AlPO thin films was investigated by NMR. Figure 3 show  $^{31}\text{P}$  and  $^{27}\text{Al}$  NMR spectra of thin film samples treated at different temperatures.  $^{31}\text{P}$  NMR spectra of as-deposited and thermally treated samples suggest the presence of four coordinated phosphorous that does not change significantly during the thermal treatment.  $^{27}\text{Al}$  NMR spectra of as-deposited AlPO thin films indicate that most of the aluminium atoms are octahedrally coordinated Al species bonded to three or four P atoms. By increasing the

treatment temperature, aluminium environment is almost completely transformed to tetrahedral coordination, due to the loss of coordinated water and OH groups.

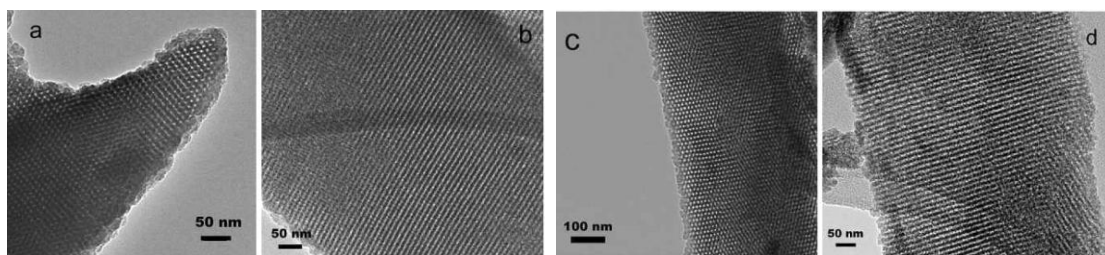


Figure 2. TEM images of calcined aluminophosphate thin film samples: F-127 templated along (a) [111] and (b) [110] pore directions; F108-templated along (c) [111] and (d) [110] pore directions.

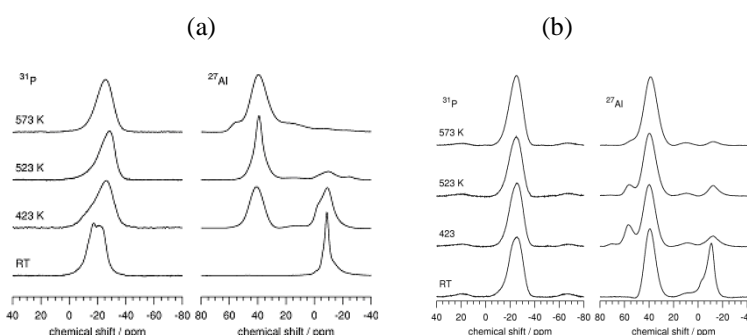


Figure 3. <sup>31</sup>P and <sup>27</sup>Al NMR spectra of (a) F127- and (b) F108-templated mesoporous aluminophosphate thin films treated at specified temperatures.

### F127-templated SAPO and MnSAPO thin films

Incorporation of silicon and manganese into F127-templated aluminophosphate thin film frameworks did not affect symmetry of mesostructure (cubic,  $Im\bar{3}m$ ), however the unit cell parameter  $a$  in SAPO and MnSAPO films is somewhat bigger in comparison with pure aluminophosphate thin films (19.5 nm in both cases). Upon thermal treatment contraction for about 50 % occurs, which was already observed in pure AIPO thin films.

<sup>27</sup>Al MAS NMR spectra of mesoporous SAPO thin films are very similar to NMR spectra obtained on the related cubic mesoporous AIPO thin films. In the as-prepared SAPO film nearly all aluminium atoms are hexa-coordinated. After calcination, part of aluminium transforms to tetra- (30 %) or penta- coordinated species (10 %). <sup>31</sup>P MAS NMR spectra suggest that the SAPO framework is not fully condensed, either in the as-prepared film or in the calcined film.

Oxidation state and local environment of manganese in MnSAPO thin films was studied by X-ray absorption spectroscopy using XANES and EXAFS methods. From XANES spectra shown on Figure 4a, the average valence state of 2.3 for as-deposited and 2.4 for calcined film was deduced. Mn EXAFS spectra of as-synthesized and calcined MnSAPO thin films, together with best-fit EXAFS models, are shown in Figure 4b. Manganese cations of as-deposited MnSAPO thin film are coordinated to four oxygen atoms in the first coordination shell, but two of them are at a shorter distance of 2.10 Å and two of them at a longer distance of 2.27 Å. Coordination number of manganese does not change upon calcination. Two oxygen atoms are at the distances 2.07 Å and two at 1.82 Å, which is consistent with the average tetrahedral Mn<sup>+3</sup>-O distance of 1.93 Å.

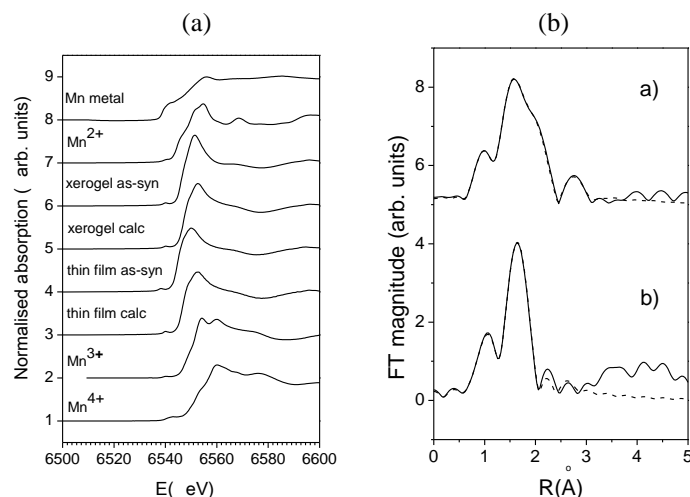


Figure 4. (a) Normalized Mn K-edge XANES spectra of as-synthesized and template-free MnSAPO xerogels and thin films and of Mn reference samples (Mn metal, Mn<sup>2+</sup>O, K<sub>3</sub>[Mn<sup>3+</sup>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>].3H<sub>2</sub>O, and Mn<sup>4+</sup>O<sub>2</sub>); (b) Fourier transform magnitude of the k<sup>3</sup>-weighted Mn EXAFS spectra of the a) as-synthesized and b) calcined MnSAPO thin films. (solid line – experiment, dashed line - EXAFS model).

## CONCLUSION

New cubic mesoporous aluminophosphate thin films, templated by nonionic copolymer surfactants were synthesized by dip-coating method. Highly ordered mesostructures ( $Im\bar{3}m$ ) were determined by SAXS and TEM analysis. It has been shown that these films remain stable during thermal treatment, and that there is an evolution in the inorganic framework, according to <sup>27</sup>Al and <sup>31</sup>P NMR spectra. The contribution of tetrahedrally coordinated aluminium in AlPO samples increases when raising the temperature of sample treatment. Cubic mesostructures are particularly interesting due to the three-dimensional nature of the pores. In these materials, accessibility and diffusivity of the host molecules is expected to be improved comparing with familiar materials with the hexagonal pore arrangement. Large pore dimensions of the AlPO thin films could enable hosting for metal oxides and pure metal nanoclusters. With incorporation of silicon (SAPO) and additionally manganese (MnSAPO) within aluminophosphate framework hydrophilic, and acidic properties are expected to be enhanced. This could enable applications in the fields of catalysis, electronics, chemical sensing and energy storage.

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