

Structural selectivity by molecular control in porous solid formation

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Introduction

Understanding how porous crystalline materials (e.g. zeolites and their polymorphs) are formed under hydrothermal conditions from a precursor gel, is of considerable fundamental interest since it could lead to a more rational approach towards the design and synthesis of new molecular sieves. A very powerful but relatively unexplored way of probing these processes is to perform in situ studies during crystallization, in real time. However the application of one or two techniques to study this process means that the characterization is often partial. Therefore to overcome these limitations it is beneficial to perform either multiple in situ measurements using a variety of analytical techniques or to combine complementary techniques into one experimental setup; an approach which often yields new insight.[1] We show how both approaches have been used for a greater understanding into the self-assembly processes of microporous aluminophosphate (AlPO) phases.

Materials and Methods

For these experiments gels with the following molar ratios were used:

1.0 – 1.5 P:1-x Al: x (Me) acetate:0.8 – 1.5 Template: 17 – 26 H₂O

Where the chemical sources used were H₃PO₄ (phosphorus), Al(OH)₃ or pseudoboehmite (aluminum), triethylamine or tetraethylammonium hydroxide (template) and where x = transition metal (Me = Cobalt, Chromium or Zinc) and was varied between 0.00 and 0.3. In situ hydrothermal crystallization studies of (Me)APO-5 formation, starting from the precursor gel, were performed using scattering techniques such as SAXS/WAXS as well as spectroscopic methods such as UV-Vis, Raman and XAFS at the Al and substituent metal K-edges. In addition a combined SAXS/WAXS/XAFS setup was developed to study zinc substitution in order to correlate the changes that occurred during crystallization at the molecular, nanoscopic and crystalline level in one experiment. Separate in situ Raman measurements were also performed on the zinc-substituted systems to follow the behaviour of the templating species.

Results and Discussion

Our use of scattering and spectroscopic techniques has allowed us to obtain new insight into the formation of these molecular sieves from a macroscopic and an atomic perspective. For example, spectroscopic methods such as Al K-edge XAFS and Raman revealed that the precursor gels reacted to yield tetrahedral Al³⁺ containing Al-O-P aggregates, which the scattering (SAXS) data suggested were, on average, between 8 – 11 nm in size. During the hydrothermal treatment these were observed to gradually grow in size to ca. 35 nm, before the formation of pure and metal (Co²⁺ or Cr³⁺) substituted AlPO-5 began at ca. 160°C.[2,3] When Zn²⁺ was used in the system, crystallization began when the aggregates reached a size of ca. 12 nm before the ZnAPO-34 framework formed at the relatively low

temperature of 90°C.[4,5] Perhaps most interestingly we also observed when the loading of Zn²⁺ was increased to ca. 30% (for Al³⁺), changes in the relative intensity of two bands in the Raman spectra (due to different conformers (tt.tt) and (tg.tg) of the TEOAH template) accompanied the crystallization of ZnAPO-34. This was not seen in the un-substituted systems that formed AlPO₄-5.

Significance

From these studies it appears that an important molecular relationship occurred between the heteroatom in the microporous framework and the template, which is critical for the formation of MeAPO-34. In addition, it appeared that the formation of the final crystalline materials occurred via a solid amorphous-solid crystalline reaction. We discuss these results in an attempt to rationalize the growth of these porous materials.

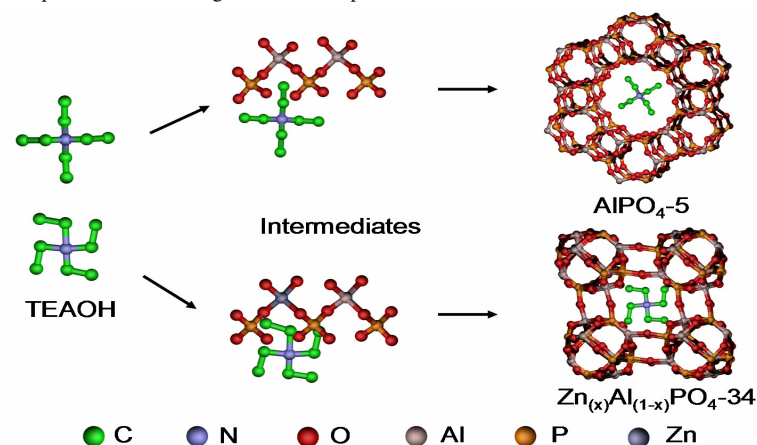


Figure 1. On synthesis, aluminophosphate crystallizes as a porous solid known as AlPO₄-5, which contains regular arrays of microscopic channels. This process is directed by an organic base (tetraethylammonium hydroxide; TEOAH) in the reaction mixture. Raman data suggest that TEOAH forms a complex with the aluminophosphate molecules that acts as a template for constructing the AlPO₄-5 lattice. When zinc is incorporated into some of the aluminophosphate molecules, TEOAH adopts an alternative conformation. This yields a different intermediate complex that acts as a template for the formation of a structure known as ZnAPO-34.

References

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