Unique Organic−Inorganic Interactions Leading to a Structure-Directed Microporous Aluminophosphate Crystallization as Observed with in situ Raman Spectroscopy

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Microporous aluminophosphates represent an important family of molecular sieves known to possess intriguing physicochemical and catalytic properties. In particular, when Al^{3+} or P^{5+} frameworks are partially replaced with metal ions, such as Co^{2+}, Ni^{2+}, or Zn^{2+}, shape-selective catalysts are produced, active for a number of potentially industrially important reactions, including selective alkane oxidation and conversion of methanol to olefin (MTO).[1]

For the synthesis of most (Me)APOs an organic "template" is critical for the formation of microporosity.[2] However, the way in which the template achieves this microporosity is still unclear. Lobo and Davis[3] attempted to rationalize the function of the template by proposing three possible roles: (i) space filling, where packing occurs and is nonspecific to a particular structure; (ii) structure direction, where the template affects the nucleation process, leading to specific structures from specific templates; and (iii) true templating, where enhanced guest−host interactions occur during crystalline ordering. Various experiments have also provided insight into how templates enable such microporous structures to form. For example, NMR has highlighted the importance of weak, noncovalent intermolecular forces in precrystalline phases during zeolite formation, whereas Raman spectroscopy has suggested that encapsulation of the template in precrystalline amorphous solid occurs and also undergoes protonation.[4] Combined experimental and computational studies demonstrated the importance of conformation and template−template interactions in both the gel and the formation products.[5] Understanding these types of inorganic−organic interactions and the template role in microporosity generation is therefore of importance not only for a rational design of such materials but also could lead to a greater understanding into organic−inorganic molecular interactions within the microporous frameworks.

Single-phase, crystalline AlPO-34 can only be synthesized in the presence of F^-, Si^{4+}, or divalent metal ions.[6] Previous studies indicated that a close interaction between the template and the framework occurs due to the presence of induced charges via the formation of a $F-Al^{3+}$ bridge or by substitution of P^{5+} for Si^{4+}. It has also been postulated that a similar interaction might occur for divalent metal substitution of Al^{3+}, suggesting a cooperative framework−template role may be important for specific phase formation.[7] Naudin et al. have demonstrated that a common template used in microporous material preparation (tetraethylammonium hydroxide (TEAOH)) exists in two conformations, tt.tt and tg.tg, when in solution.[8] Yet in crystalline SAPO-34, only one conformation was found (similar to the tg.tg conformer[9]), indicating that the template conformation may play a role in specific phase formation. To understand this phenomenon, we have performed in this work

time-resolved in situ Raman spectroscopy to study the formation of MeAPO-34 using TEAOH as a template and to probe key organic−inorganic interactions necessary for the formation of MeAPO-34. We demonstrate that the role of the template was more complex than previously envisaged since we propose that both the location and conformation of the template molecule were critical for the formation of MeAPO-34, while AlPO-5 formation appears to be controlled by the conformation of the template molecule alone.

Examples of time-resolved in situ Raman spectra are given in Figure 1. The plotted region is dominated by two bands known to give an indication of the relative amounts of each template conformational state.[8] Critically, we observed changes in the relative intensities of these bands for the 30% Zn^{2+}-substituted gel during crystallization, which were not seen in the unsubstituted systems which did not crystallize. These data are more clearly illustrated in Figure 2, where we show a time-resolved analysis of these ratios for both systems. Most significantly, we observed a substantial increase in the relative amount of the tg.tg conformer for 30% ZnAPO gels at 80 and 100 °C. The changes were both sigmoidal and temperature dependent and only occurred in the 30% of the systems, which formed the crystalline ZnAPO-34 material. To prove the generality of the observations, we also obtained similar results for the formation of CoAPO-34 and MnAPO-34 materials. A comparative ex situ XRD study on the crystallization of the ZnAPO gel at 80 °C suggested that the change in conformer occurred prior to the onset of Bragg peak formation, indicating that the conformational changes coincided with the formation of a prephase or microcrystallites.

From these studies, it appeared that an intimate relationship between the Zn^{2+} substituted into an Al^{3+} site of the microporous framework and the template occurred, which was critical for the formation of the MeAPO-34 structure. This interaction is likely to be induced by the resulting framework charge produced by the substitution since such changes were not observed in samples that did not crystallize. This induced charge appeared to cause one of the conformers (the tg.tg) to locate at specific positions within the framework, which appeared to be a necessary step to enable the MeAPO-34 framework to form.

In a separate XRD study, it was observed that increasing the amount of Zn^{2+} used in the synthesis gel increased the amount of crystalline product formed, indicating its role was more than that of a nucleation center. However, we did not observe changes in the in situ Raman data with gels containing ≤20% Zn^{2+} since we rationalize that there was a sufficient reservoir of tg.tg conformer already in the system at the beginning to allow the MeAPO-34 structure to form. However, at higher Zn^{2+} loadings, some template must convert from the tt.tt to the tg.tg conformer (as seen in Figure 1) in order to occupy the increased number of Zn^{2+} sites.

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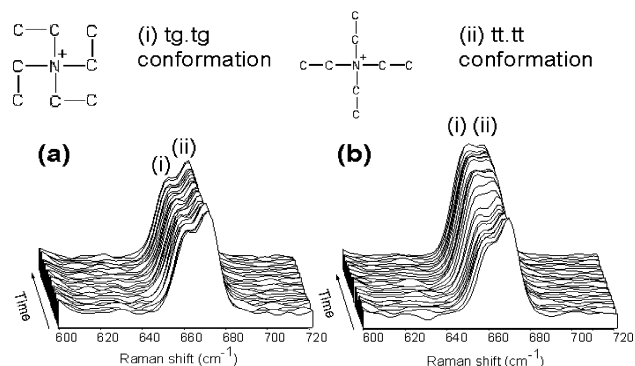[‡] Utrecht University.

Figure 1. Time-resolved in situ Raman spectra for synthesis gels with (a) no framework substitution and (b) 30% substituted Zn^{2+}. The structures of the two TEAOH conformations are also indicated.
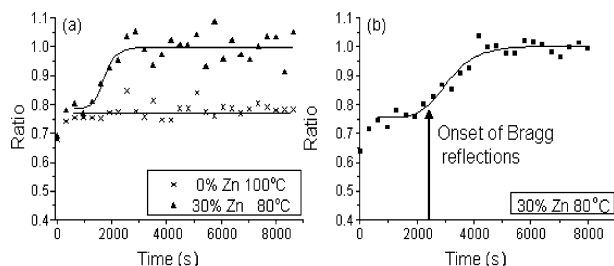

Figure 2. (a) Time-resolved analysis of the ratio of tg.tg to tt.tt conformers. (b) Combined in situ Raman and ex situ XRD analysis. The arrow marks the onset of crystallization.
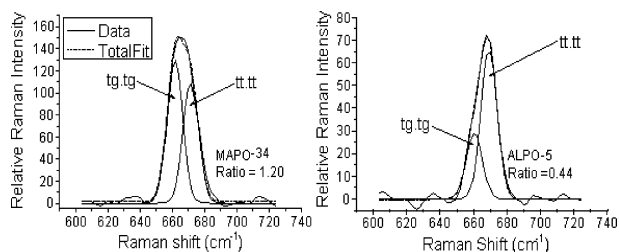

Figure 3. Raman bands at 645−685 cm^{-1} for the crystalline ZnAPO-34 and AlPO-5 samples after treatment. The bands have been profiled in order to determine the ratio of each conformer in the crystalline product.

Ex situ measurements of the ZnAPO-34 final gels and crystalline powders showed that a high proportion of the tg.tg conformer was maintained in the framework. Upon washing, the relative amount of loosely bound tt.tt conformer was reduced. The final ratio of tg.tg:tt.tt (Figure 3) was 1.20, which was significantly greater than the starting ratio of 0.7. The remaining tt.tt conformer was probably randomly encapsulated during the formation of the $AlPO_4$ framework. Significantly, for the final AlPO-5 material, an opposite trend was seen, where the tt.tt conformer dominated the structure and a final conformer ratio of ~0.44 was obtained. Thus, it appeared that, since no specific template location from metal-substituted charge induction occurred, the organic conformation appeared to be the sole driving force for AlPO-5 formation. These observations are summarized in Figure 4, where we present a scheme for MeAPO-34 or AlPO-5 formation depending on the synthesis conditions.

We observed that significant interactions between the template and the inorganic species indicated a "true templating"[3] interaction occurring in MeAPO-34 synthesis, but this effect was caused primarily by the substituted metal directing the position of the template. The template acted additionally as either a space filler or structure directing agent around which the final structure formed. The formation of AlPO-5 specifically from the tt.tt conformer and MeAPO-34 from the tg.tg conformer indicated that the template's
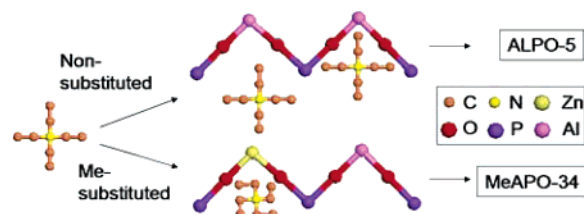

Figure 4. Scheme representing the formation of both AlPO-5 and MeAPO-34 using TEAOH as template.

role was somewhat more than space filling, but as both MeAPO-34 and AlPO-5 are known to form from other templates, it is difficult to classify its role as specific structure directing.[3] Clearly, classical theories concerning the role of the template tend to oversimplify its role since there are complex metal−organic interactions which appear to favor the formation of one structure over another. This suggested that a better understanding of these effects would be necessary if a greater experimental control over hydrothermal synthesis of molecular sieves is to be realized.

In conclusion, we have demonstrated that MeAPO-34 formation is governed by a complex relationship between the metal ion and the conformation of the organic component, while AlPO-5's formation is determined only by the template conformation. It is likely that such organic−inorganic interactions play a more general role in the formation of many other microporous materials. Therefore, this study provides new insights into their formation mechanisms; moreover, it also suggests that one must consider mixed conformer template formation processes since potentially the different conformers could favor the formation of different microporous structures.

Supporting Information Available: Further details on the experimental setup, sample preparation, in situ Raman experiments with Co^{2+} and Mn^{2+}, ex situ XRD experiments, and the temperature dependence of TEAOH. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Thomas, J. M.; Raja, R.; Sankar, G.; Bell, R. G. *Acc. Chem. Res.* **2001**, *34*, 191. (b) Haw, J. F.; Song, W. G.; Marcus, D. M.; Nicholas, J. B. *Acc. Chem. Res.* **2003**, *36*, 317. (c) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. *Acc. Chem. Res.* **1998**, *31*, 485.

(2) (a) Karge, H. G., Weitkamp, J., Eds. *Molecular Sieves Science and Technology*; Springer: Berlin, 1988; Vol. 1. (b) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.

(3) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.

(4) (a) Burkett, S. L.; Davis, M. E. *J. Phys. Chem.* **1994**, *98*, 4647. (b) Dutta, P. K.; Puri, M. *J. Phys. Chem.* **1987**, *91*, 4329. (c) Grandjean, D.; Beale, A. M.; Petukhov, A. V.; Weckhuysen, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 14454.

(5) (a) Paik, W. C.; Shin, C. H.; Lee, J. M.; Ahn, B. J.; Hong, S. B. *J. Phys. Chem. B* **2001**, *105*, 9994. (b) Han, B.; Lee, S. H.; Shin, C. H.; Cox, P. A.; Hong, S. B. *Chem. Mater.* **2005**, *17*, 477. (c) Gomez-Hortiguela, L.; Cora, F.; Catlow, C. R. A.; Perez-Pariente, J. *J. Am. Chem. Soc.* **2004**, *126*, 12097.

(6) (a) Pastore, H. O.; Coluccia, S.; Marchese, L. *Annu. Rev. Mater. Res.* **2005**, *25*, 351. (b) Marchese, L.; Frache, A.; Gianotti, E.; Martra, G.; Causa, M.; Coluccia, S. *Microporous Mesoporous Mater.* **1999**, *30*, 145.

(7) Lewis, D. W.; Catlow, C. R. A.; Thomas, J. M. *Chem. Mater.* **1996**, *8*, 1112.

(8) Naudin, C.; Bonhomme, F.; Bruneel, J. L.; Ducasse, L.; Grondin, J.; Lassegues, J. C.; Servant, L. *J. Raman Spectrosc.* **2000**, *31*, 979.

(9) Brand, H. V.; Curtiss, L. A.; Iton, L. E.; Trouw, F. R.; Brun, T. O. *J. Phys. Chem.* **1994**, *98*, 1293.

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