Ionothermal Synthesis

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Ionic Liquids and Microwaves—Making Zeolites for Emerging Applications**

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Zeolites are extremely well known porous materials with "traditional" applications in catalysis, ion exchange, and gas separation. Over the last 10 years or so there has, however, been an increasing interest in developing these porous solids into new areas—what Davis calls "emerging" applications.[1] The range of potential applications of zeolites now encompasses new medical/biological technologies,[2] microelectronics,[3] and hosts for lasers.[4] Getting the materials in the right form to be useful in an application is, of course, a major requirement before they can be used. Processing zeolites as thin films and coatings opens up many potential applications, and they have been used as sensor materials,[5] low-*k* dielectric films,[6] and antimicrobial surface coatings.[7] Over the last few years Yan and co-workers[8] have developed corrosion-resistant coatings based on zeolites that are promising alternatives to currently used technologies. Zeolite coatings have good mechanical and thermal properties, and are effective at protecting against corrosion on various metals including aluminum and stainless steel. Significantly, non-fibrous zeolites have well-known toxicology and are generally recognized as safe—some compositions are even classified as such by several countries' food and drug standards agencies. They are used on a large scale as water softeners in detergent washing powders, and several zeolites now have approved applications in medicine, including as MRI contrast agents[9] and as proclotting agents in traumatic bleeding.[10] In contrast, commonly used chromate-based anticorrosion coatings are toxic and carcinogenic. Obviously, replacing these highly regulated chemicals with safer alternatives is very attractive, and perhaps zeolites offer one such "environment-friendly" alternative. Unfortunately, the traditional methods of synthesizing zeolites involve hydrothermal treatment of the starting materials in sealed containers, which takes place under significant amounts of autogenous pressure. The requirement for high pressure is, at the very least, inconvenient when it comes to coating surfaces. In this issue of *Angewandte Chemie*, however, Yan and co-workers[11] have reported a relatively new method of zeolite synthesis that uses ionic liquids instead of water as the solvent. One of the properties of ionic liquids is that they have little or no volatility, which means that even at elevated temperatures they produce no autogenous pressure,[12] thus allowing zeolites to be prepared at ambient pressure.

Ionic liquids (ILs) have several important properties that make them good solvents for the synthesis of inorganic materials.[13] Being ionic, they can be relatively polar solvents suitable for the dissolution of many different types of inorganic salts, although this does depend significantly on the composition of the particular IL chosen. Many ILs, especially those based on imidazolium and quaternary ammonium salts, are chemically very similar to the types of organic cations that are commonly used as structure-directing agents or templates in the preparation of zeolites using the hydrothermal method. Replacing the solvent and the organic template with a single ionic liquid is the basis of the ionothermal method of zeolite synthesis (Figure 1), which has been developed over the last couple of years.[14] This relatively new method of synthesis has shown some interesting effects in the preparation of zeolites[15] and other porous solids such as metal coordination polymers.[16] These include unusual anion control properties of the IL, where changing the nature of the anion in the IL leads to different product phases.

Perhaps the most interesting property of ILs is their relatively low vapor pressure. As ILs are composed entirely of ions, the enthalpy of vaporization, ΔH_{vap}, is considerably greater than for water and organic solvents. This means that while it is possible to distil ILs under certain conditions,[17] they can be regarded as if they have negligible vapor pressure. This property is the main reason why ILs have been proclaimed as green alternatives to volatile organic solvents for many fine-chemical transformations. In ionothermal synthesis, however, the main impact of the very low vapor pressure of ILs is that there is no longer the same requirement for sealed reaction vessels to retain the solvent as there is in hydrothermal synthesis. Zeolites can be ionothermally prepared in open vessels on the bench top rather than in sealed teflon-lined autoclaves, as is normally the case in traditional zeolite preparations (Figure 1).

In the first examples of ionothermal synthesis, conventional heating was used, but Xu et al. extended this technique to show that microwave heating could be used to an equal

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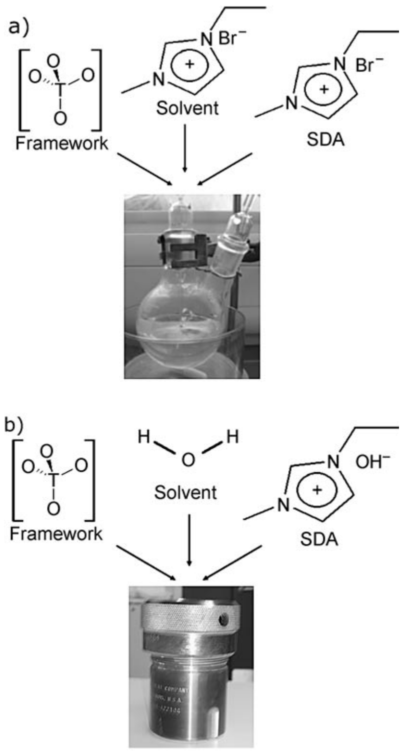

Figure 1. A comparison of ionothermal and hydrothermal synthesis of zeolites. In ionothermal synthesis (a) the solvent and the structure-directing agent (SDA) are the same chemical species—the ionic liquid 1-methyl 3-ethyl imidazolium bromide. The lack of vapor pressure from the ionic liquid allows synthesis at ambient pressure in normal laboratory flasks. In contrast, hydrothermal synthesis (b) uses water as a solvent, which produces autogenous pressure at high temperature, thus requiring the use of high-pressure reaction vessels. $T = 100$–$200\,°C$.

effect.[18] ILs are good microwave absorbers, and combining this with the low pressure evolution at high temperature opens up many possibilities for the use of microwaves in zeolite synthesis. Microwave-assisted organic synthesis (MAOS) has been well developed over recent years, and the microwave-assisted hydrothermal synthesis of zeolites has also been reasonably well studied.[19] The great advantage of microwave heating is the very short reaction times that occur. However, use of volatile solvents still causes problems with excessive pressure production, especially from hot spots. Scientific microwave heating setups therefore require pressure-release mechanisms to ensure safe operation. Microwave heating of ILs, however, produces no such pressure increases (unless there is breakdown of the IL into volatile components). Such simple practical advantages offer a bright future for microwave synthesis in ILs.

Yan and co-workers have used microwave heating under ionothermal conditions to prepare extremely well-oriented zeolite coatings on copper-containing aluminum alloys—materials that are used extensively in the aerospace industries but that do suffer from corrosion problems. During the course of the research they produced two different types of zeolite coating. One was a pure aluminophosphate (AlPO) with the AEL framework structure type. The other coating, while having the same AEL framework topology, has silicon substituting for some of the framework atoms to make a silicoaluminophosphate (SAPO). Remarkably, the small change in composition has a profound impact on the nature of the coating. The AlPO coating crystallizes quickly under microwave conditions and leads to an almost randomly oriented coating that protects the underlying aluminum metal only slightly. In contrast, the SAPO coating crystallizes more slowly and is highly aligned to the surface of the metal (Figure 2). The coatings adhere well to the metal surface and DC polarization results indicate that the coatings make excellent anticorrosion barriers, especially when sealed with a bis(triethoxysilyl)methane/nanoparticulate zeolite composite.

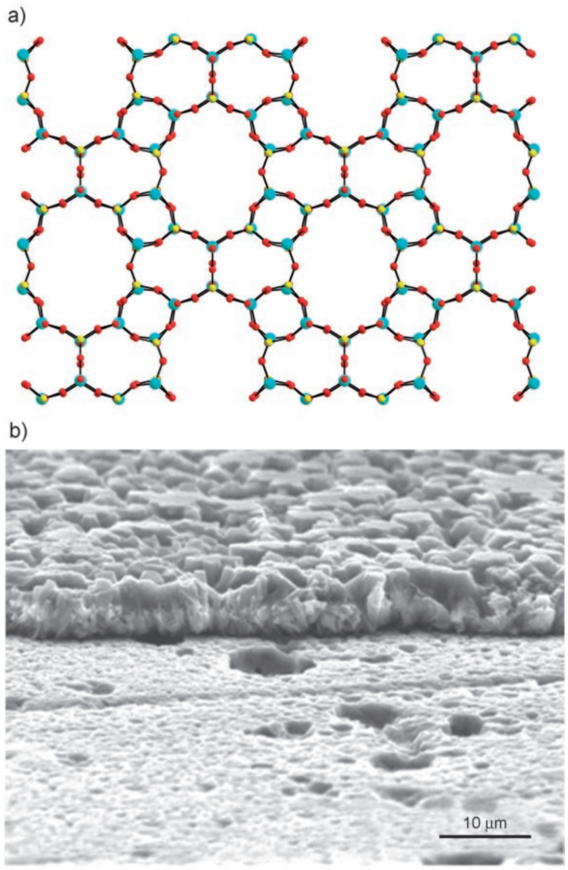

Figure 2. a) The AEL zeolite framework topology (O red, Al blue, P yellow) and b) a scanning electron micrograph showing a cross section of the SAPO-11 (AEL) coating on aluminum alloy (taken from reference [11]).

The work reported by Yan and co-workers gets around one of the practical disadvantages of the hydrothermal synthesis of zeolites for the preparation of high-quality films and coatings, and is an important development in its own right. However, perhaps the most interesting, and potentially most important, feature of ionothermal synthesis is that it is not limited to zeolites, but is potentially applicable to any material that can be prepared using solution-state "soft chemical" approaches. Ionic liquids are often called "designer solvents", and the range of properties that can be engineered into the ILs means that they can be used to replace water or organic solvents in many different systems. This ionothermal/microwave method for preparing high-quality coatings may therefore have a much wider impact than simply in anti-corrosion technology.

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[1] M. E. Davis, *Nature* **2002**, *417*, 813.

[2] P. S. Wheatley, A. R. Butler, M. S. Crane, S. Fox, B. Xiao, A. G. Rossi, I. L. Megson, R. E. Morris, *J. Am. Chem. Soc.* **2006**, *128*, 502.

[3] S. Li, Z. J. Li, Y. S. Yan, *Adv. Mater.* **2003**, *15*, 1528.

[4] U. Vietze, O. Krauss, F. Laeri, G. Ihlein, F. Schüth, B. Limburg, M. Abraham, *Phys. Rev. Lett.* **1998**, *81*, 4628.

[5] S. Mintova, T. Bein, *Microporous Mesoporous Mater.* **2001**, *50*, 159.

[6] Z. J. Li, M. C. Johnson, M. W. Sun, E. T. Ryan, D. J. Earl, W. Maichen, J. I. Martin, S. Li, C. M. Lew, J. Wang, M. W. Deem, M. E. Davis, Y. S. Yan, *Angew. Chem.* **2006**, *118*, 6477; *Angew. Chem. Int. Ed.* **2006**, *45*, 6329.

[7] A. M. P. McDonnell, D. Beving, A. J. Wang, W. Chen, Y. S. Yan, *Adv. Funct. Mater.* **2005**, *15*, 336.

[8] a) D. E. Beving, A. M. P. McDonnell, W. S. Yang, Y. S. Yan, *J. Electrochem. Soc.* **2006**, *153*, B325; b) A. Mitra, Z. B. Wang, T. G. Cao, H. T. Wang, L. M. Huang, Y. S. Yan, *J. Electrochem. Soc.* **2002**, *149*, B472; c) X. L. Cheng, Z. B. Wang, Y. S. Yan, *Electrochem. Solid-State Lett.* **2001**, *4*, B23.

[9] D. L. Rubin, K. L. Falk, M. J. Sperling, M. Ross, S. Saini, B. Rothman, F. Shellock, E. Zerhouni, D. Stark, E. K. Outwater, U. Schmiedl, L. C. Kirby, J. Chezmar, T. Coates, M. Chang, J. M. Silverman, N. Rofsky, K. Burnett, J. Engel, S. W. Young, *JMRI-J. Mag. Res. Imag.* **1997**, *7*, 865.

[10] A. Mahajna, M. Hirsh, M. M. Krausz, *Eur. Surg. Res.* **2007**, *39*, 251.

[11] R. Cai, M. Sun, Z. Chen, R. Munoz, C. O'Neill, D. Beving, Y. Yan, *Angew. Chem.* **2008**, *120*, 535; *Angew. Chem. Int. Ed.* **2008**, *47*, 525.

[12] R. Ludwig, U. Kragl, *Angew. Chem.* **2007**, *119*, 6702; *Angew. Chem. Int. Ed.* **2007**, *46*, 6582.

[13] M. Antonietti, D. B. Kuang, B. Smarsly, Z. Yong, *Angew. Chem.* **2004**, *116*, 5096; *Angew. Chem. Int. Ed.* **2004**, *43*, 4988.

[14] a) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* **2004**, *430*, 1012; b) E. R. Parnham, R. E. Morris, *Acc. Chem. Res.* **2007**, *40*, 1005.

[15] a) A. Taubert, Z. Li, *Dalton Trans.* **2007**, 723; b) E. R. Parnham, R. E. Morris, *J. Mater. Chem.* **2006**, *16*, 3682; c) E. R. Parnham, R. E. Morris, *Chem. Mater.* **2006**, *18*, 4882; d) E. R. Parnham, R. E. Morris, *J. Am. Chem. Soc.* **2006**, *128*, 2204; e) E. R. Parnham, P. S. Wheatley, R. E. Morris, *Chem. Commun.* **2006**, 380; f) E. A. Drylie, D. S. Wragg, E. R. Parnham, P. S. Wheatley, A. M. Z. Slawin, J. E. Warren, R. E. Morris, *Angew. Chem.* **2007**, *119*, 7985; *Angew. Chem. Int. Ed.* **2007**, *46*, 7839.

[16] a) Z. J. Lin, A. M. Z. Slawin, R. E. Morris, *J. Am. Chem. Soc.* **2007**, *129*, 4880; b) Z. J. Lin, D. S. Wragg, R. E. Morris, *Chem. Commun.* **2006**, 2021; c) Z. J. Lin, D. S. Wragg, J. E. Warren, R. E. Morris, *J. Am. Chem. Soc.* **2007**, *129*, 10334.

[17] M. J. Earle, J. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, J. A. Widegren, *Nature* **2006**, *439*, 831.

[18] Y. P. Xu, Z. J. Tian, S. J. Wang, Y. Hu, L. Wang, B. C. Wang, Y. C. Ma, L. Hou, J. Y. Yu, L. W. Lin, *Angew. Chem.* **2006**, *118*, 4069; *Angew. Chem. Int. Ed.* **2006**, *45*, 3965.

[19] S. H. Jhung, T. H. Jin, Y. K. Hwang, J. S. Chang, *Chem. Eur. J.* **2007**, *13*, 4410.

