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Zeolite Synthesis

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Solventless Synthesis of Zeolites**

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In chemistry, the age-old question "*Which solvent should I use?*" is gradually being replaced with "*Do I actually need a solvent at all?*" It is of course very timely to develop solvent-free approaches to synthesis because of the great scope for improving upon the environmental impact, safety, energy consumption, and economic cost associated with traditional solvent-intensive chemical processes. Of these, the cost associated with recycling waste solvent provides a very strong driver for increasing the product to solvent ratio, with the eventual goal of removing the need for solvents altogether. Of course, this driver is strongest when the solvent itself is expensive or toxic (as is the case with most organic solvents) but even when the solvent is water the treatment and recycling costs can be significant. For these reasons we are currently witnessing the accelerated development of solvent-free synthesis.

Of course solventless synthesis is not new. It has long been applied to the synthesis of inherently insoluble inorganic materials, and the synthesis of many ceramic oxides, hydrides, and nitrides is carried out in the solid state routinely. However, these synthetic procedures often require very high temperatures and repeat firings to ensure that the bond-making/-breaking and organization processes have enough energy for the formation of crystalline phases.

An alternative method of adding energy into the system is through grinding, in what is commonly called mechanochemical synthesis.[1] This involves simply grinding, either by hand using a pestle and mortar or nonmanually using a ball mill or other apparatus. Although still counterintuitive to many chemists, this simple method can often provide quantitative reactions within a few minutes. We aren't (yet) taught this in university courses! Strikingly, in addition to generating less waste, there are often practical benefits of ease, simplicity, and rate compared to traditional solvent-based methods. Although this method has traditionally been applied to inherently insoluble inorganic materials such as alloys, oxides, nitrides, and hydrides, it is now being extended very effectively into the molecular domain. It has been found to be highly efficient for a wide range of organic C−C and C−X bond-forming reactions, for the formation of pharmaceutical cocrystals, and for the synthesis of metal complexes including porous metal organic frameworks (MOFs). Encouragingly, we are also seeing increased patent activity and industrial application of "molecular mechanochemistry", even performed at scales of several tens of kilograms, such as in the synthesis of certain drug–carrier composites.[2] Further unconventional but effective approaches to solventless molecular synthesis include the use of melt phases[3] and the exploitation of reactions between solids and gases.[4,5] The relationships between the various types of synthetic techniques are shown in Figure 1.

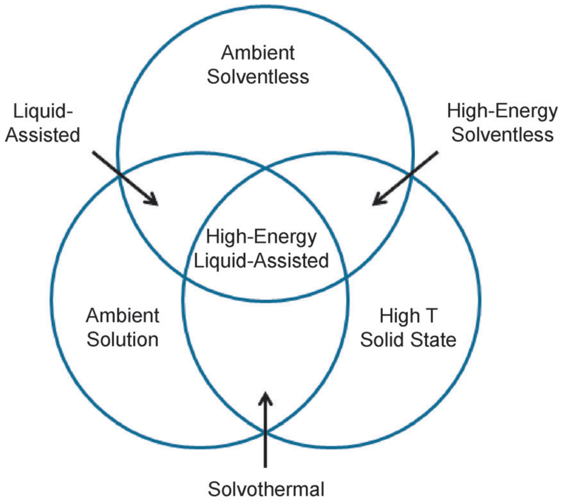

Figure 1. The relationships between the common types of reaction conditions. Adapted from reference [12].

In a recent paper, Ren and co-workers[6] reported the solventless synthesis of various zeolites (Figure 2). The method involved grinding of dry raw materials followed by heating to 180 °C.

Zeolites are among some of the most important industrial inorganic solids. These highly porous aluminosilicate frameworks have found extensive applications across a wide range of industries. They are well known as water softeners in

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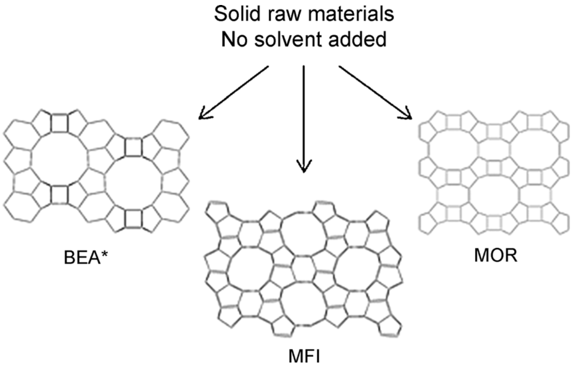

Figure 2. The solventless synthesis can produce some of the most important industrial zeolites, including zeolite beta (BEA*), ZSM-5 (MFI), and mordenite (MOR).

detergents, as catalysts in the oil and fine-chemicals industries, and as adsorbents and delivery agents in medicine/healthcare.

Zeolites are commonly prepared using solvothermal techniques,[7] usually employing water as the solvent but sometimes organic solvents or ionic liquids.[8] The temperature of the synthesis is usually less than 200 °C. The synthesis mixture can also contain an organic "structure-directing agent" (SDA), around which the inorganic framework forms. In industry, the solvent used is invariably water and the procedures rarely employ organic SDAs, as these add to the costs of the synthesis and are calcined out of the inorganic solids at the end of the manufacture.

The paper by Ren and co-workers is striking in that there have been quite a large number of attempts to prepare zeolites using solvent-free processes in the past. A significant number of these used a mechanochemical approach utilizing grinding of the raw materials, yet most have required some sort of hydrothermal processing step at the end to ensure high crystallinity of the products. There are many reports on what is called the dry gel conversion (DGC) process, where the starting materials are formed into a gel using solvent processing. The gel is then dried by evaporating any solvent before heating to produce the final crystalline product, but this cannot be regarded as a true solvent-free synthetic method.[9] However, the DGC process has been of great interest as a method of preparing shaped particles, which is especially important for applications, by extruding or forming particular shapes of the gel prior to the crystallization step.

Ren and co-workers used a hybrid of these two approaches. The raw materials (hydrated sodium silicate and fumed silica, plus any organic SDA and sources of heteroatoms such as Al and Fe) were first ground manually for 10–20 min, and then crystallization occurred when the solids were heated at 180 °C for 24–48 h. At no stage was any solvent added to the mixture. Using this approach Ren and co-workers managed to prepare a variety of some of the most industrially important zeolites, those with the MFI, SOD, MOR, BEA*, and FAU framework types. In addition the process also allowed the incorporation of several different heteroatoms (Al, Fe, B, Ga) into the structures, opening up potential uses of the zeolites in catalysis.

These are surprising results given the number of attempts to prepare zeolites by solvent-free methods in the past. The work raises many questions about the mechanism. Firstly, is there any mechanochemical reaction, in other words, is the initial grinding itself important in inducing the reaction? Powder X-ray diffraction (XRD) of the ground raw materials doesn't show any change in the phases present so it seems unlikely that there is a great deal of reaction simply during grinding, although some reaction may occur on the surfaces of the particles and go undetected by XRD. The bulk of the energy needed for the crystallization therefore seems to come from the heating step and the grinding, if it is necessary at all, may be primarily to get the solid raw materials in close contact.

A potential clue to the mechanism of synthesis is given by the fact that the starting materials must be hydrated. This is not actually all that uncommon, and other "nonaqueous" solvent systems, such as that in ionothermal synthesis,[10] often require a small amount of water to be present. It is also the case that solvent-free mechanochemical synthesis is sometimes improved by the addition of small amounts of solvent.[11,12] Such a situation is often called liquid-assisted grinding (LAG) and can accelerate reactions significantly. Other nominally dry syntheses are also improved by exposure to humid air in so-called vapor-assisted processes. Therefore it seems that at least some hydration processes are required during the crystallization phase, at the very least to provide kinetically accessible pathways for the reaction. Given that the major reaction occurring in zeolite synthesis is silicate condensation, it is not surprising that the presence of some water could lead to an alternative energetic pathway for the process. Perhaps this synthesis is not quite *mechanistically* solvent-free, even if no solvent is actually deliberately added?[1]

Another important question in all zeolite synthesis is how the organic SDA interacts with the silica in order to direct the synthesis towards one particular product. The research by the Ren group different SDAs lead to the different structures, which matches well with the results of traditional hydrothermal synthesis. However, closer inspection of the amorphous intermediates formed during the process indicates that before crystallization takes place there is already well-developed microporosity. The authors contend that this is completely different to hydrothermal synthesis where at a similar stage of the process there is no porosity in the intermediate materials. This is an intriguing difference, and begs the question as to whether there is anything fundamentally different about the SDA–framework interactions in the two methods. At present we don't have enough mechanistic information to understand fully what is going on.

What is clear from the recent literature, including the paper by Ren et al., is that there is a move towards the reduction or removal of solvent from synthetic procedures. But can such processes be scaled up so that they have commercial significance? Any new process has challenges associated with scale-up, but the solvent-free synthesis of zeolites looks to have many advantages that could be exploited. In addition to the obvious reduction in raw materials and recycling/waste costs, there is also the advantage that separation of the solvent from the product is not required. In addition, as Ren and co-workers point out, there are volume savings on going solvent-free (as the synthesis will take up significantly less volume), as well as potential capital savings from a reduction in the need for pressure vessels, as solvent heated to high temperature produces significant autogenous pressure. Given that the yields of the process seem very competitive with hydrothermal synthesis, the potential for scale-up and application seems clear.

Of course, what hasn't been yet demonstrated is that the properties of these materials are at least as good as those of the hydrothermally synthesized zeolites. If it turns out they perform as well their hydrothermal counterparts, and if the drive towards decreased waste and cost continues as we expect it to, there is a strong likelihood that solventless synthesis could be of great interest to industry. A particularly good target might be the BEA* structure as this can be prepared without the use of organic SDA (although it does require seeding) and is an excellent catalyst for many processes.

The fact that such examples of efficient solvent-free synthesis throw up so many questions emphasizes that in addition to the potential for large-scale applications, synthetic chemistry under solvent-free (or minimal-solvent) conditions is also a fertile ground for fundamental studies of reactivity.

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