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Ambient Pressure Dry-Gel Conversion Method for Zeolite MFI Synthesis Using Ionic Liquid and Microwave Heating

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Abstract: We report an ambient pressure synthesis method for silicate zeolite. This method combines the advantages of ionothermal synthesis, dry-gel conversion, and microwave radiation, making it a promising, safe, fast, and continuous process for industrial application.

Zeolites are a class of crystalline oxides that have uniform and molecular-sized pores (0.3−1.2 nm in diameter). Zeolites have been widely used in catalysis, ion exchange, and separation.[1,2] Recently, other applications of zeolites in their film forms have emerged ranging from computer chips to space stations.[3] Zeolites are normally prepared using a hydrothermal synthesis method,[1,4] which takes place in sealed vessels and involves a significant amount of autogenous pressure. The required high pressure is not convenient for a large-scale and continuous production process, especially for certain applications of zeolite thin films where the current technologies are dominated by ambient pressure processes.

Recently, a new ionothermal method was introduced to the synthesis of zeolites under ambient pressure in open vessels, in which ionic liquids were used as solvents instead of water or other organic solvents.[5−10] An ionic liquid is a liquid that essentially consists only of ions with a melting temperature below 100 °C. One of the most interesting properties of ionic liquids is their negligible vapor pressure even at relatively high temperatures, allowing zeolites to be prepared at ambient pressure. Aluminophosphate zeolites have been successfully synthesized using an ionothermal method, in both powder[8,10] and film forms.[11] However, there are few successful reports for aluminosilicate- or silicate-based zeolite synthesis using ionic liquids.[7] The main problem is the very limited solubility of silica precursor materials in the commonly used ionic liquids.[7]

Besides the solution-mediated hydrothermal/ionothermal methods, the dry-gel conversion (DGC) method has been used for converting a dry gel to zeolites in the presence of steam, sometimes, with structure-directing agents (SDA) in the vapor phase.[12,13] This method can separate the nucleation and crystallization processes of zeolite synthesis, beneficial for preparing nanocrystals and thin films. The DGC method has been used for producing both aluminophosphate and aluminosilicate zeolites.[12,14] However, sealed reactor and autogenous pressure are still necessary since water is essential in the DGC method.

Herein, we report an ambient pressure method for silicate-based zeolite synthesis, which combines the advantages of ionothermal synthesis, the dry-gel conversion method, and microwave heating.

Many ionic liquids are highly hygroscopic, and these include 1-ethyl-3-methyl imidazolium bromide ([Emim]Br) and 1-butyl-3-methylimidazolium bromide ([Bmim]Br) that are the most commonly used ionic liquids in zeolite ionothermal synthesis.[9,15] The hygroscopic nature of ion liquids means a small amount of water is always present in them, even at high temperatures over 100 °C at ambient pressure. Will the small amount of water in ionic liquid be able to provide the necessary solvation to the dry gel for crystallization? If yes, the DGC method using ionic liquids can be an overall ambient pressure process since nucleation (dry gel preparation) can be realized at temperatures less than 100 °C.[16]

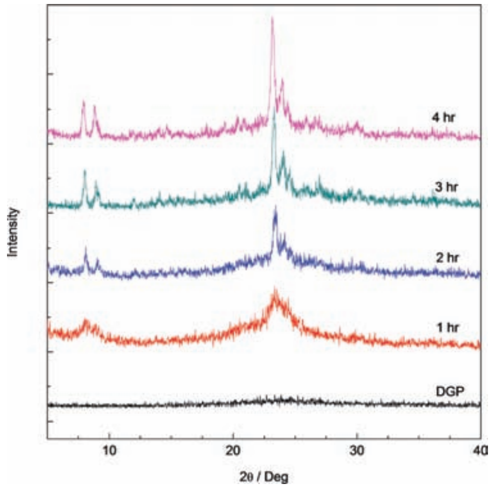

Figure 1. XRD patterns of synthesized MFI crystals from DGP under microwave radiation for different times.

Our first trial was just adding [Bmim]Br to a dry gel precursor (DGP) in a beaker and putting the beaker into a convection oven to see if it is possible to crystallize the DGP. The DGP was prepared from the synthesis solution with the following molar composition: 1:3:52.4:25.1 TPAOH/SiO_2/H_2O/EtOH.[17] The solution was aged at 60 °C for 11 days under stirring and then dried via lyophilization to obtain the DGP. Then, 10 g of [Bmim]Br were added to 0.2 g of DGP in a beaker. After 24 h of heating at 175 °C, no crystalline phase was detected by X-ray diffraction (XRD), suggesting that the small amount of water naturally contained in [Bmim]Br was not enough to crystallize the DGP. Then different amounts of water (up to 2 g) were added to [Bmim]Br before mixing with the DGP, but the DGP remained amorphous after 24 h of synthesis likely because the excess amount of water could not be retained in an open vessel even before the temperature of [Bmim]Br reached 175 °C.

Ionic liquids consist entirely of ions and therefore absorb microwave irradiation extremely efficiently. The application of microwave heating to ionothermal synthesis dramatically decreases the synthesis time of AEL zeolite.[6,10] Hence, we used microwave heating instead of conventional heating to convert the DGP to zeolite at ambient pressure. The DGP was successfully converted to MFI crystals after 2 h microwave radiation at 175 °C at ambient pressure in the presence of excess water (Figure 1). The product

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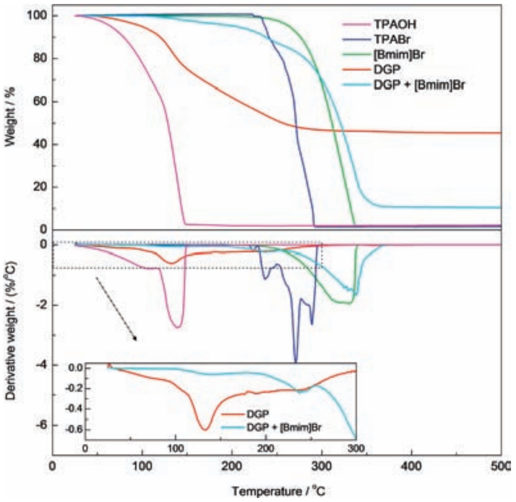

Figure 2. TGA-DTG (TGA derivative) plots of TPAOH, TPABr, [Bmim]Br, DGP, and DGP mixed with [Bmim]Br.

crystallinity increased with microwave radiation time for the first 3 h but remained the same after that.

However, the DGP stayed amorphous without adding extra water to [Bmim]Br even after 3 h of microwave synthesis. Now the question is why does the excess amount of water work for microwave radiation but not for convection heating. It is noted that a significant number of water drops were found on the wall of the synthesis vessel even after 4 h at 175 °C under microwave radiation. At the beginning, the temperature of the synthesis mixture was rapidly increased to 175 °C within a couple of minutes; excess water evaporated from the ionic liquid and then condensed when encountering the cold atmosphere and the vessel wall since a temperature gradient was created in the vessel while microwave radiation heated [Bmim]Br directly and selectively. Ideally, it can be described as a reflux process under microwave radiation. Water can be supplied back to [Bmim]Br for zeolite crystallization. This expectation was confirmed by monitoring the pressure of the [Bmim]Br−H_2O system in a sealed vessel at 175 °C under microwave radiation (Figure S1). There is no autogenous pressure for a mixture of 0.2 g of H_2O/5 g of [Bmim]Br in a 10 mL sealed vessel.

Another concern for DGC method is the SDA decomposition in dry gel.[12] It is known that quaternary ammonium ions are subject to the β-H (Hofmann) elimination and α-C substitution in the presence of OH^-.[18] From Figure 2, it can be clearly seen that TPABr is more stable than TPAOH. The decomposition peak of TPA^+ in the DGP is at 130 °C, the same as that for TPAOH, while in the presence of [Bmim]Br, the decomposition peak of TPA^+ is at 240 °C, corresponding to the decomposition of TPABr. As a result, there is another advantage of using [Bmim]Br in dry-gel conversion: stabilizing the SDA, because an ion exchange process between OH^- and Br^- should take place easily considering the much greater amount of Br^- than OH^- in the [Bmim]Br−H_2O−DGP system.

In conclusion, an MFI zeolite has been successfully synthesized at ambient pressure via a dry-gel conversion method using ionic liquid and microwave heating. The most important function of the ionic liquid is its ability to retain a sufficient amount of water at high temperature and ambient pressure for the gel crystallization. Ionic liquid fulfils this function by being hygroscopic, nonvolatile, and efficient in absorbing microwave energy that can lead to a superheated fluid due to inversed heating.[19] It also helps the stabilization of the SDA by an ion exchange process. This method is expected to have a significant impact on zeolite film synthesis, as a safe, fast, and continuous process for industrial applications.

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Supporting Information Available: Experimental details and Figure S1 for pressure measurement of [Bmim]Br/H_2O system in a sealed vessel at 175 °C under microwave radiation. This material is available free of charge via the Internet at http://pubs.acs.org.

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