



# Tetraalkylammonium salt/alcohol mixtures as deep eutectic solvents for syntheses of high-silica zeolites



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## ABSTRACT

Molecular sieves such as zeolites and aluminophosphates are industrially important materials that are usually prepared under hydrothermal conditions. Recent years have seen the development of a new ionothermal synthetic method, where an ionic liquid or a deep eutectic mixture is used as the medium for synthesizing these microporous materials. Although many ionothermal syntheses of aluminophosphate based molecular sieves have recently been described, the ionothermal preparation of highly siliceous or completely siliceous zeolites is rare. The present work focuses on the ionothermal synthesis of zeolites using several tetraalkylammonium salt/alcohol-based deep eutectic solvents (DESs). ZSM-5 can be synthesized using a mixture containing tetrapropylammonium bromide or tetraethylammonium chloride and pentaerythritol. The effects of many variables have been studied, including the silica source, seeding, mineralizing agent, and aluminum additives, along with the structure directing role of tetraalkylammonium ions and the amount of water present in the reaction. In the tetramethylammonium chloride and 1,6-hexanediol DES, the mineralizing agent plays an important role in the type of framework being formed. Sodalite was produced when NaOH was used as the mineralizing agent, while ZSM-39 was synthesized when  $\text{NH}_4\text{F}$  was present instead. These results demonstrate that tetraalkylammonium salt/alcohol-based DESs can be used to prepare highly siliceous and aluminosilicate zeolites. The use of DES enables control over zeolite morphology. A proper choice of DES can also lead to enhanced local ordering around Si in a siliceous zeolite. For some DESs, changing the mineralizing agent can yield different zeolite frameworks. The potential of this approach is to produce zeolites with new framework topologies.

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## 1. Introduction

Zeolites are a group of silicate and aluminosilicate microporous materials that are often used in ion-exchange, catalysis, and adsorption processes. These applications are made possible due to the presence of regular internal cavities and channels of discrete sizes and shapes, which are unique for each type of zeolite [1]. Many zeolites are synthesized in a hydrothermal manner at temperatures of ca. 150–200 °C by mixing a base, silica, and an organic structure-directing agent (SDA) in water, which serves as the solvent [2]. Recently, a new synthetic method known as ionothermal synthesis was developed for the preparation of aluminophosphates ( $\text{AlPO}_4\text{s}$ ), metal-organic frameworks (MOFs) and coordination polymers [3–19]. The ionothermal synthesis approach involves

using an ionic liquid or a deep eutectic mixture as a solvent rather than water.

An ionic liquid (IL) is usually defined as a salt that is fluidic at ambient temperature (<100 °C) [20]. However, since the reactions to make zeolites are usually conducted at temperatures higher than 100 °C, an ionic liquid in this context can be defined as any salt with a melting point below the range of 150–200 °C [3]. A deep eutectic mixture is composed of two different salts exhibiting a melting point depression, and this mixture is also known as a deep eutectic solvent (DES). For the preparation of zeolite and zeolitic materials, the melting point of such DESs needs to be below 130 °C. The first reported work in this area was for the preparation of aluminophosphate materials, and involved the use of an IL (1-ethyl-3-methylimidazolium bromide,  $[\text{emim}]\text{Br}$ ) and a DES consisting of a urea and choline chloride mixture [3]. There are several advantages of using an IL in syntheses. For example, the IL can serve as both the organic SDA and the solvent, which means the competition between solvent and the SDA for growing crystalline materials is

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minimized. Also, by using ILs or DESs as the solvents, the vapor pressure is reduced significantly [21]. One type of DESs that have been employed to prepare microporous materials is a quaternary ammonium salt/alcohol mixture [22]. The organic SDA plays an important role in the formation of the zeolite framework [22]. In this mixture, the quaternary ammonium ion can also act as the SDA. Dong's group was able to prepare different types of  $\text{AlPO}_4$ s by varying the quaternary ammonium salts present in the reaction mixture containing pentaerythritol [22]. This work has shown that  $\text{AlPO}_4$  structures can be formed in the presence of alcohol.

While much attention has been put into making new framework structures using ILs or DESs, there is also interest in improving the synthetic strategies used in zeolite preparation. In the past few decades, there have been examples of preparing silicates and aluminosilicates in a non-aqueous environment. Bibby and Dale first reported that sodalite (SOD) could be synthesized in ethylene glycol [23]. Reports have shown that zeolite ZSM-5 (MFI) can be prepared in the presence of ethanol [24], glycerol [25], and in a mixture of ethylenediamine and triethylamine [26]. The ZSM-39 (MTN) zeolite, which is isostructural with the 17 Å cubic gas hydrate, has also been synthesized in non-aqueous conditions; specifically, it was synthesized in a morpholine and pyrrolidine/mepiquat mixture in the presence of HF [27–29]. These examples have shown that zeolites can be made in a reaction mixture containing alcohol or amine species.

Although much effort has been made towards the preparation of zeolites through non-aqueous routes, the number of studies remains quite limited. As for ionothermal synthesis, there have been few reports on the study of high-silica zeolites, despite the fact that much work has been devoted to the syntheses of zeolite-like materials. This relative paucity of reports is probably due to the poor solubility of silica in the reaction mixture when the water content is low, since water is essential for the hydrolysis of silica and the polycondensation of silicate species [30]. Another problem is that many syntheses of zeolites are carried at high pH in the presence of hydroxide ions such as NaOH or KOH [1], which exhibit significantly reduced solubilities when water is scarce or absent.

To the best of our knowledge, there are only five reported syntheses of zeolites under ionothermal synthesis conditions. Sodalite was synthesized in 1-ethyl-3-methylimidazolium bromide ([emim] Br) in the presence of  $\text{OH}^-$  at high pH [31,32]. Yan's group synthesized ZSM-5 by microwave-heating a mixture formed from 1-butyl-3-methylimidazolium [Bmim] bromide and a dry-gel precursor containing the ZSM-5 organic SDA, TPAOH [33]. Morris's group reported the synthesis of several siliceous zeolites in a fluoride medium by using the [Bmim] bromide/hydroxide IL. The products of Morris' synthesis could be either phase-pure silicalite-1 (MFI) or a mixture of Theta-1 (TON) and MFI [34], suggesting that the presence of  $\text{TPA}^+$  is important for the formation of phase-pure ZSM-5. Recently, Zeolite Y, ZSM-5, and ZSM-22 have been prepared in imidazolium halide ionic liquids [35–37]. MER type zeolites have been prepared using hydrated alkali silicate ionic liquids (HSIL) made from the hydrolysis of tetraethoxysilane (TEOS) in alkali hydroxide–water mixtures [38]. For all of the cases just described, a small amount of water must be present to ensure the successful production of zeolite materials, indicating that water is crucial for the formation of silicate and aluminosilicate materials in either IL or DES. Furthermore, these examples also indicate that in order to have consistency among the final products, the presence of an organic SDA that is specific for the desired final framework is extremely important.

The main difficulties in generating silicate and aluminosilicate frameworks in ILs or DESs are the poor solubility of starting materials and the lack of reproducible results. In this report, we have overcome these problems through the use of colloidal silica and various organic SDAs as part of the DESs. Under our experimental

conditions, no additional water was required beyond the water contained in the reactants since the amount of water in colloidal silica is sufficient. We demonstrate the successful syntheses of three zeolite types: ZSM-5 (MFI), sodalite (SOD), and ZSM-39 (MTN). The silicalite-1 (siliceous form of ZSM-5) syntheses were performed in both fluoride and hydroxide media, using colloidal silica as the silica source and a deep eutectic mixture composed of tetrapropylammonium bromide (TPABr) or tetraethylammonium chloride (TEACl), along with pentaerythritol (PE) (Fig. 1a). The aluminosilicate ZSM-5 was prepared in a NaOH environment. SOD and MTN type zeolite were produced in a tetramethylammonium chloride (TMACl) and 1,6-hexanediol mixture in the presence of NaOH and  $\text{NH}_4\text{F}$ , respectively (Fig. 1b).

## 2. Experimental

### 2.1. Synthesis of silicalite-1 (MFI) using TPABr/PE

A typical procedure is as follows: Ammonium fluoride ( $\geq 98\%$ , Alfa Aesar), pentaerythritol (98+%, Alfa Aesar), tetrapropylammonium bromide (98%, Sigma–Aldrich), and calcined ZSM-5 (from the hydrothermal synthesis using TPABr) were mixed quantitatively and ground using a mortar and pestle. The ground solid mixture was then transferred to a 40 mL Teflon container. To this mixture, a source of colloidal silica (Ludox HS-40, Ludox CL-X, or Ludox TM-50, Sigma–Aldrich) was then added. The silica contents in Ludox HS-40, Ludox CL-X, and Ludox TM-50 are 40 weight (wt.%), 45 wt.%, and 50 wt.%, respectively, in a  $\text{H}_2\text{O}$  suspension. The components were hand-mixed using a spatula until a sticky white paste was formed inside the Teflon cup. The Teflon container was then placed inside a stainless steel autoclave and the reaction mixture was heated at 170 °C for 19–24 days. For instance, in one of the syntheses, 2.5 g TPABr, 3.0 g PE, 1.0 g  $\text{NH}_4\text{F}$ , and 0.05 g as-made ZSM-5 seeds were mixed and ground. 2.5 g Ludox HS-40 was then added to the ground mixture. For every 2.5 g of Ludox HS-40, there is 1.5 g of  $\text{H}_2\text{O}$ . The typical molar composition of the initial batch is: 1  $\text{SiO}_2$ : 1.6  $\text{NH}_4\text{F}$ : 1.3–1.7 pentaerythritol: 0.25–0.56 TPABr: 3–5  $\text{H}_2\text{O}$ .

### 2.2. Synthesis of the aluminosilicate ZSM-5 (MFI) using TPABr/PE

The preparation of aluminosilicate ZSM-5 is similar to the procedures described in the previous section, except that the  $\text{NH}_4\text{F}$  was replaced by NaOH (99%, Caledon), and a source of aluminum was also added. The sources of aluminum were alumina (~8%  $\text{H}_2\text{O}$ , Strem Chemicals), aluminum isopropoxide (98+%, Sigma–Aldrich), or aluminum sulfate hydrate (98%, Sigma–Aldrich). Tetrapropylammonium bromide, pentaerythritol, sodium hydroxide, an aluminum source, and 5% ZSM-5 seeds were mixed and ground using a mortar and pestle. The ground mixture was then transferred to a Teflon container, where Ludox HS-40 was added. The ingredients were hand-mixed using a spatula until a semi-transparent, mobile liquid gel was formed, and then the Teflon container was put inside a stainless steel autoclave. The gel was reacted for 21–28 days at 170 °C. The typical molar composition of the initial batch is: 1  $\text{SiO}_2$ : 0.1 NaOH: 1.3–1.7 pentaerythritol: 0.56 TPABr: 0.02 Al: 5  $\text{H}_2\text{O}$ . For instance, in a synthesis that uses  $\text{Al}(\text{O}-i\text{Pr})_3$  as the Al source, 5.0 g Ludox HS-40 was added to a ground mixture of 5.0 g TPABr, 6.0 g PE, 0.2 g NaOH, 0.14 g  $\text{Al}(\text{O}-i\text{Pr})_3$ , and 0.1 g as-synthesized ZSM-5 seeds. The reagents were hand-mixed and the reaction time for this batch was 25 days at 170 °C.

### 2.3. Synthesis of silicalite-1 using TEACl/PE

The synthesis of silicalite-1 using tetraethylammonium chloride monohydrate ( $\geq 98.0\%$ , Sigma Aldrich) as the template followed

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