First Syntheses of Pentasil-type Silica Zeolites from Non-aqueous Systems

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Several pentasil-type silica zeolites (silicalite-1, ZSM-39, and ZSM-48) have been synthesized from non-aqueous systems in the presence of specific templating agents and characterized by means of composition analysis and *X*-ray powder diffraction.

Hydrothermal techniques are the typical methods of synthesis employed for molecular sieve zeolites. Barrer and Denny's pioneering work[1] demonstrated that organic bases could be used as whole or part replacements for the inorganic base component. The syntheses using organic bases have yielded many new materials, including the commercially important ZSM-5(MFI). Organic templating agents were also important in the development of the aluminophosphate family of molecular sieves.[2] Reports on zeolite syntheses from organic solvents, or mixed solvent systems in which water is a minor component, are scarce. Recently, Bibby and Dale[3] reported the synthesis of silica-sodalite and aluminosilicate sodalites with a wide range of Si/Al ratios from ethylene glycol and propanol solvents, which was followed by a study on the rapid synthesis and *X*-ray structure determination of silica-sodalite from non-aqueous systems.[4] More recently, van Erp and his coworkers[5] synthesized BaT, hydroxysodalite, and kaliophilite using many organic solvents, such as glycol, glycerol, sulpholane, Me_2SO, ethanol, pyridine, and C_6-C_7 alcohols. It has been known that the zeolites containing 4- and 6-rings can be synthesized in non-aqueous systems, but so far the syntheses of pentasil-type zeolites in organic solvents have not been reported. Here we report the syntheses of silicalite-1, ZSM-39, and ZSM-48 from non-aqueous systems in the presence of effective templating agents.

A typical synthesis began with the combination of NaOH and solvent or mixed solvents. A solution was formed, to which the fumed silica and templating agent or crystal seed (silica-sodalite) were added with stirring. The crystallization of the reaction mixture was carried out in a stainless steel autoclave under autogenous pressure at 180 °C. The crystalline product was filtered, washed with distilled water and dried at ambient temperature. The products were characterized by means of *X*-ray powder diffraction, and thermal and composition analysis. The typical reactant compositions, crystallization conditions and products are listed in Table 1.

The silicalite-1 was synthesized (run 3) and its *X*-ray powder diffraction pattern was very similar to that for orthorhombic tetrapropylammonium-silicalite-1. Thermal analysis in flowing N_2 showed that most of the ethylene glycol (EG) and tetrapropylammonium bromide (TPABr) molecules were lost from the framework over the temperature range of 100—600 °C. The total weight loss above 100 °C corresponded to a unit cell composition of $(TPABr)_{2.2}\ (EG)_x\ (SiO_2)_{96}$ (x = 0—10). The formation of silicate-1 is critically dependent on the amounts of NaOH and TPABr present. We noted that by decreasing the amount of NaOH from 1.5 to 1.0 mole, we could obtain silicalite-1 and silica-sodalite in turn. Without the templating agent TPABr (*c.f.* run 2) we only obtained a crystalline phase B with unknown structure which contained ethylene glycol as the inclusion molecule. In addition, the base/silica molar ratio for the initial reaction mixture has only a small influence on the formation of silicalite-1.

The ZSM-48 was obtained from runs 5 and 6, both of which use ethylene glycol and butyl alcohol as mixed solvents. The butyl alcohol can be replaced by amyl alcohol or hexyl alcohol. Without TMABr or silica-sodalite crystal seeds no crystalline products were formed. The role of silica-sodalite crystal seeds introduced into the synthesis system is probably that of nucleation of ZSM-48, but further investigations are being made. The ZSM-48 obtained from run 5 has the unit cell composition $(BuOH)_{3.8}(SiO_2)_{48}$.

The ZSM-39 was prepared from a non-aqueous mixture with the range of reactant mole composition being: (1—10)

Table 1. The typical reactant compositions, crystallization conditions, and products.

Run	Reactants[a] moles NaOH	SiO_2	Solvent	Template	Crystallization time[b]/days	Product
1	1.0	2.0	40 EG		3	SS
2	1.5	2.0	40 EG		10	B
3	1.5	2.0	40 EG	0.3 TPABr	25	silicalite-1
4	1.0	4.0	15 GE + 35 BuOH	5.0 $PrNH_2$	50	ZSM-39
5[c]	1.0	2.0	20 EG + 12 BuOH		50	ZSM-48
6	1.0	2.0	20 EG + 12 BuOH	0.1 TMABr	25	ZSM-48

[a] EG = ethylene glycol, GE = glycerol, BuOH = butyl alcohol, SS = silica-sodalite, TMABr = tetramethylammonium bromide, TPABr = tetrapropylammonium bromide. [b] Crystallization temperature 180 °C. [c] Silica-sodalite seeds added.

$PrNH_2$, NaOH, (2—6) SiO_2, (10—20) glycerol (GE), (20—50) BuOH at 150—180 °C for 30—70 days. The chemical composition of the crystalline product from run 4 was $(PrNH_2)_{11.2}(SiO_2)_{136}$.

The organic templating agent used in non-aqueous systems has the same effect, *i.e.* structure-directing, as in aqueous systems. Not all templating agents which are effective in aqueous solution can be used in non-aqueous systems. The problem is probably the proper matching between templating agents and solvents. The particular effect of silica-sodalite crystal seeds on the formation of ZSM-48 was observed. The crystallization of the pentasil-type silica zeolites in non-aqueous systems requires more time than in aqueous systems under the same temperature conditions.

Increasing the content of NaOH in the initial mixture from which the silica-sodalite crystallized and the introduction of specific templating agents lead to the formation of silicalite-1. silica, ZSM-39, and ZSM-48 can be synthesized in the presence of effective templating agents or crystal seeds from non-aqueous systems. The present results showed that not only zeolites containing 4- and 6-membered rings but also zeolites containing 5-membered rings can be obtained from non-aqueous systems.

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