Synthesis of Large Single Crystals of Pentasil-type Silica Zeolites from Non-alkaline Medium

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Large single crystals of pentasil-type silica zeolites (Silicalite-I and ZSM-39) have been synthesized with choline cation, 1,4-diazabicyclo[2.2.2]octane, and tetramethylammonium cation as templates from non-alkaline medium.

The morphology of zeolite crystals is an important factor in many studies and industrial applications.[1,2] Great effort has been devoted to the synthesis of large crystals of zeolite ZSM-5,[3—5] but the products are often contaminated with gel or other unwanted substances. However, previous authors reported the synthesis of large crystals of ZSM-5 using TPA^+ (tetrapropylammonium cation) as a template. There is no report in the literature on the synthesis of large single crystals of ZSM-5 with other organic templates. A new route to prepare pentasil-type zeolites was developed by Guth,[5] using

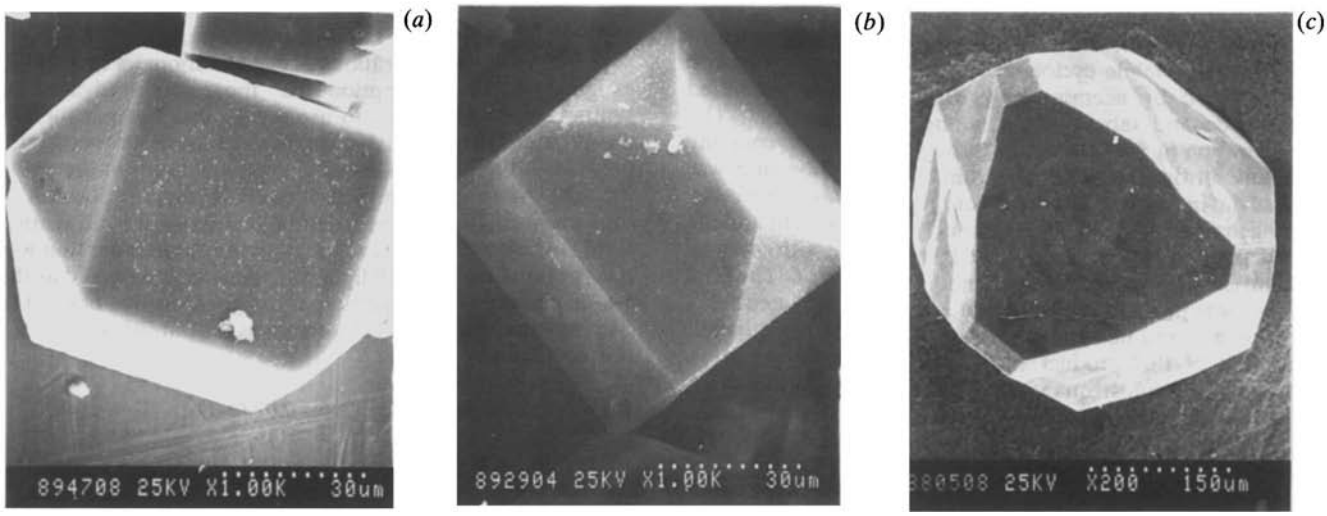

Figure 1. Scanning electron micrographs of (a) Choline-silicalite-I (sample A), (b) DO-silicalite-I (sample B), and (c) Silica ZSM-39 (sample C).

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

Sample	SiO_2	Template[a]	NH_4F	HF	H_2O	Crystallization time (days)	Temperature /°C	Products
A	1.0	0.5	1.0	—	50	21	190	ZSM-5
B	1.0	0.5	—	1.5	40	52	150	ZSM-5
C	1.0	1.1	1.8	—	40	7	190	ZSM-39

[a] The template of sample A, B and C is CH^+, DO and TMA^+, respectively.

a non-alkaline medium in the presence of fluoride ions. In this way, large single crystals of Silicalite-I were obtained with TPA^+ cation. Here we report the synthesis of large single crystals of Silicalite-I with choline cation (CH^+) and 1,4-diazabicyclo[2.2.2]octane (DO), and silica ZSM-39 with tetramethylammonium cation (TMA^+). The samples were characterized by means of *X*-ray powder diffraction, scanning-electron microscopy, composition and thermal analysis.

A typical synthesis began with the combination of water and templates. A solution was formed, to which fumed silica and NH_4F or HF(40%) were added with stirring. The crystallization of the reaction mixture was carried out in a stainless steel autoclave under autogenous pressure at 150—190 °C. The crystalline product was filtered, washed, and dried at ambient temperature. The typical reactant compositions, crystallization conditions, and products are listed in Table 1.

The Silicalite-I was synthesized with CH^+ and DO respectively, and silica ZSM-39 was prepared using TMA as a template. The experiments were successful in obtaining fully crystalline and pure phases. No contamination with other zeolites or species was observed under *X*-ray powder diffraction examination. The scanning electron microscopy analysis (Figure 1) shows that both the single crystals of sample A and B have the same shape and the same size, *ca.* 100 μm in length. The crystal of sample C has the typical octahedral shape, but is considerably larger (400 μm).

DTA-TG (differential thermal analysis-thermogravimetric) analysis shows that the sample A and B lost organic species at 408 and 420 °C, respectively. Thermal analysis of sample C shows that the organic template could not be completely removed from the silica framework by heating in air at 1200 °C for 9 h. The compositions of samples A, B, and C obtained from chemical analysis are $(CHF)_{9.4}\cdot(SiO_2)_{96}$, $(DOHF)_{4.8}\cdot(SiO_2)_{96}$, and $(TMAF)_{9.4}\cdot(SiO_2)_{136}$, respectively.

In summary, large single crystals of Silicalite-I and silica ZSM-39 have been produced for the first time hydrothermally from $R\text{-}SiO_2\text{-}H_2O\text{-}F^-$ (R = choline cation, 1,4-diazabicyclo[2.2.2]octane and tetramethylammonium cation, respectively) systems.

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