

Synthesis of Large ZSM-5 Crystals under High Pressure

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ABSTRACT

The synthesis temperature for silicalite-I (MFI) can be raised to 300 °C by applying high pressure to stabilize the structure-directing organic template. The elevated temperature and pressure favor the formation of crystals with improved quality. Prismatic silicalite-I crystals with a uniform size of about 0.7 x 0.2 x 0.2 mm have been obtained by heating a gel prepared from TMA-silicate solution, TPABr and sodium hexafluorosilicate at 250 °C under a pressure of 80 MPa. The influence of synthesis conditions on the crystal sizes has been studied by systematically changing temperature, pressure and gel compositions. Under the specific conditions of 250 °C and 80 MPa, a strong correlation was found between the crystal size and the F/Si mole ratio of the starting gel, which enables the preparation of uniform crystals of silicalite-I with preset dimensions.

INTRODUCTION

Large uniform zeolite crystals are highly desired for many uses that range from crystal structure analysis, adsorption and diffusion studies to zeolite functional materials. Synthetic zeolites obtained from hydrothermal reactions are usually in the form of microcrystalline powders. Considerable progress has been made in the growth of large zeolite crystals by carefully adjusting the solvents and starting materials. [1-4] We have been investigating the possibility of improving the size and crystal quality of microporous materials by using synthesis temperatures and pressures that are higher than those usually employed (220-400 °C, 50-200 MPa). By using this approach, we obtained crystals of the microporous titanosilicate ETS-10 suitable for single crystal X-ray structure analysis. [5] Similar experimental conditions were used to mimic the natural growth conditions of zeolite minerals. [6]

It is a general rule that high pressures and high temperatures favor the formation of dense phases rather than microporous metastable phases such as zeolites. Many synthetic zeolites are stabilized by organic templates that act as space fillers in the crystal structure or as structure-directing agents. Decomposition of the templates often determines the upper temperature limit of the zeolite synthesis. However, most organic templates can be stabilized to high temperatures by applying a high pressure. Therefore, under high pressure the synthesis temperatures of many zeolites may be substantially raised, which favors formation of large crystals because of higher crystal growth rates.

We have chosen the silica form of the synthetic zeolite ZSM-5 (silicalite-I, MFI) to test this synthesis strategy because the synthesis of silicalite-I below 200 °C has been thoroughly

investigated, and it is known that the presence of organic templates is crucial for its formation. [7,8] In addition, silicalite-I is one of the most important synthetic molecular sieves and is the only one having a hydrophobic framework with 10-ring channels. The natural counterpart of ZSM-5 called mutinaite was recently discovered in cavities of ancient magmatic rocks [9], indicating that it might be formed at quite high temperatures.

EXPERIMENTAL

Synthesis

An aqueous solution of tetramethylammonium silicate ($\text{TMAOH} \cdot 2\text{SiO}_2$) (Aldrich, 99.99+%) was used as the silica source, and tetrapropylammonium bromide (TPABr) (Aldrich, 98%) as the templating agent. Other materials used were: Na_2SiF_6 (Aldrich, 98%), $(\text{NH}_4)_2\text{SiF}_6$ (Aldrich, 98%), and deionized water.

In a typical synthesis experiment, TMA-silicate solution and TPABr solution were added to a flexible Teflon tube ($\sim 5 \times 50$ mm). After adding the proper amount of hexafluorosilicate the tube was sealed in air and then inserted into a high pressure vessel. The tube was heated using a LECO HR-1B-2 high pressure - high temperature system for 4 days. The reaction vessel was then removed from the oven and cooled to room temperature in air. The product was washed with water, filtered and dried in air.

Characterizations

The products were examined with an optical microscope and with X-ray powder diffraction on a Scintag-2000 diffractometer using CuK_α radiation. Infrared spectra were measured using a Galaxy FTIR 5000 spectrometer with the KBr pellet method. Scanning electron microscope images were recorded on a JEOL JSM 6400 microscope. Single crystal X-ray diffraction data were measured on a Siemens SMART diffractometer equipped with a CCD area detector using MoK_α radiation at 293 K. The crystal structure refinements were performed using the program SHELXTL. [10]

RESULTS AND DISCUSSION

The effects of temperature and pressure

Starting with reaction mixtures of the following mole ratio 1.0 $\text{TMAOH} \cdot 2\text{SiO}_2$: 0.25 Na_2SiF_6 : 0.39 TPABr : $\sim 100\text{H}_2\text{O}$, single phase silicalite-I crystals were obtained in the temperature range 230-300 °C and pressure range 50-100 MPa (Fig.1). A reaction at 330 °C and 100 MPa resulted in only quartz. The best crystals of silicalite-I with a maximum dimension of ca. 0.45 mm were obtained from reactions at 250 °C. As the synthesis temperature deviates from 250 °C the crystal sizes decrease.

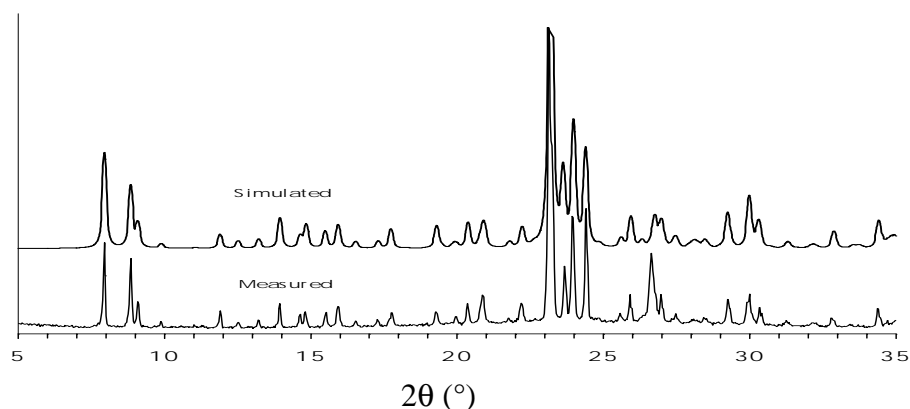
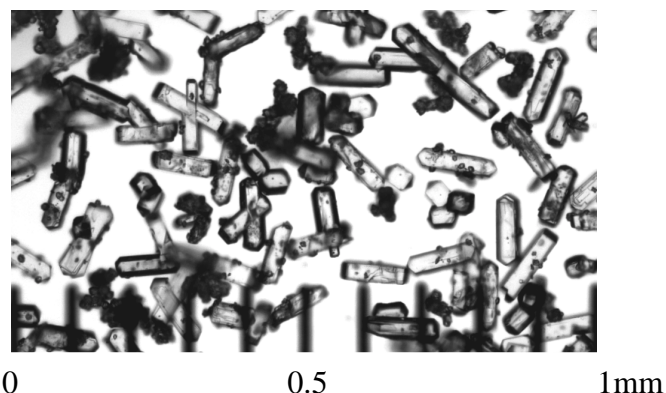


Fig.1 X-ray powder diagram of a silicalite-I sample synthesized at 300 °C and 100 MPa (bottom). The top diagram is simulated with structure data from single crystal X-ray diffraction.

Fig.2 Optical micrograph of silicalite-I crystals synthesized at 300 °C and 100 MPa.



Reactions at 300 °C and 100 MPa produced crystals with sizes of ca. 0.1 mm (Fig.2). According to Fleming and Crerar the solubility of quartz at high pH has a maximum around 230 °C. [11] This may also be true for other forms of silica and may account for our observation that the largest crystals were obtained near this temperature. The high solubility might lead to a low oversaturation and formation of fewer nucleation centers, thus favoring growth of large crystals.

Pressure has no substantial influence on the products in the range mentioned above. Reactions performed at 230-250 °C under autogenous pressures (< 4 MPa) lead to the formation of the dense phase cristobalite instead of silicalite-I, which is in agreement with previous observations [7], and probably is because of the decomposition of the template.

The infrared spectrum of a sample synthesized at 300 °C and 100 MPa is shown in Fig.3. In addition to the characteristic bands of the silicalite-I framework between 1300 - 400 cm^{-1} , typical bands for the TPA cations are clearly observed (1384, 1475, 2984 cm^{-1}). Therefore, the applied pressure does stabilize the organic template at synthesis temperatures as high as 300 °C.

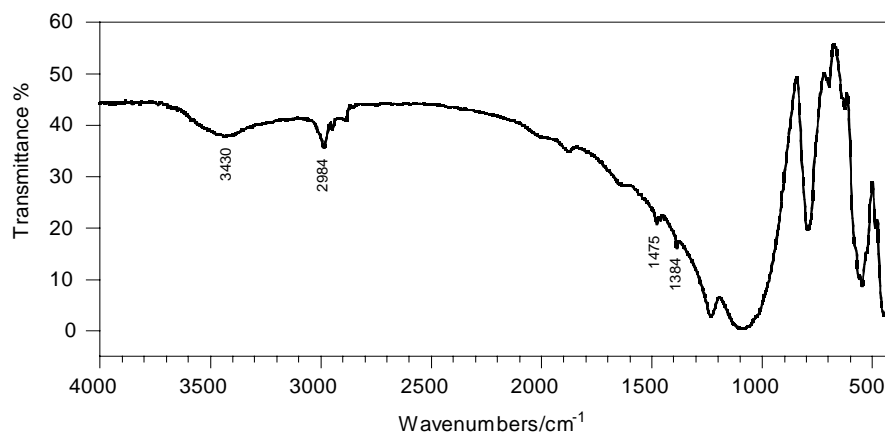
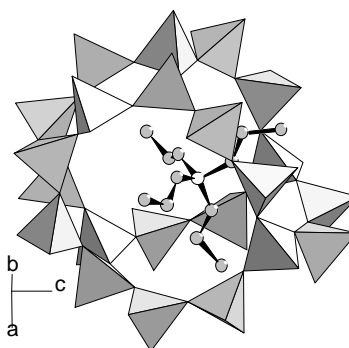


Fig.3 IR spectrum of silicalite-I synthesized at 300 °C and 100 MPa.

Fig.4 The structure of silicalite-I refined from single crystal X-ray data, showing TPA cations located inside the channels.



The encapsulation of the TPA template is also confirmed by crystal structure refinements with X-ray diffraction data measured on a single crystal synthesized at 250 °C and 80 MPa (Fig.4). The structure has a space group symmetry $Pnma$ with cell dimensions $a = 19.999(2)$ Å, $b = 20.007(2)$ Å, $c = 13.398(1)$ Å. TPA molecules are located at intersections between the [010] and [100] 10-ring channels with each of the N-C-C-C arms pointing to a 10-ring, similar to that previously reported in the literature. [12]

The effect of fluorine

The effect of Na_2SiF_6 was investigated by varying its concentration in the reaction mixtures. At the specific conditions of 250 °C and 80 MPa, a strong correlation between the F/Si ratio of the starting mixture and the size of the synthesized silicalite-I crystals was observed (Fig.5). In the absence of Na_2SiF_6 , elongated prisms of silicalite-I with uniform sizes of about 0.2 x 0.03 x 0.03 mm were formed. As the content of Na_2SiF_6 increases the prisms became thicker in addition to increasing in overall size. The largest crystals of ca. 0.7 x 0.2 x 0.2 mm were synthesized with a F/Si ratio of 1.5 (Fig.6). In reactions with F/Si ratios higher than 1.8, Na_2SiF_6 recrystallized and no silicalite-I was formed. With other conditions unchanged, Na_2SiF_6 was

replaced by $(\text{NH}_4)_2\text{SiF}_6$ which has a much higher solubility. However, the sizes of silicalite-I crystals (ca. $0.3 \times 0.06 \times 0.06$ mm) obtained did not change as the $(\text{NH}_4)_2\text{SiF}_6$ content varied. Therefore, F and Na are probably both responsible for the crystal size changes.

The majority of the silicalite-I crystals obtained in our experiments are well separated crystals with a good uniformity in size. However, when carefully examined it is found that most of them are twinned by a 90° rotation around the c axis. Such twinning is often observed in ZSM-5 crystals synthesized by other methods. A small amount of cross-intergrowing crystals were also observed in our samples. The crystal surfaces show large variations even between different crystals from the same synthesis experiment. In particular, small cavities and sometimes satellite crystallites are observed on the surfaces of crystals prepared at high F/Si ratios (Fig.7). In the final stage of crystal growth the F content in the solution increases thus increasing the solubility of silica. Fluctuations of the reaction conditions might cause dissolution of the growing crystals and formation of secondary nucleation centers.

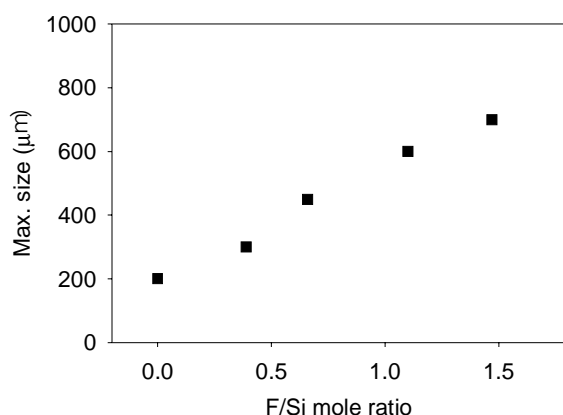


Fig.5 Correlation between silicalite-I crystal size and the reagent F/Si ratio adjusted by using Na_2SiF_6 for syntheses at 250°C and 80 MPa .

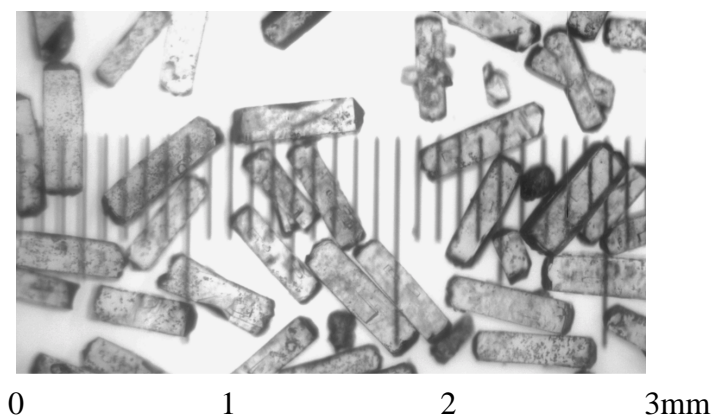


Fig.6 Optical micrograph of silicalite-I crystals synthesized at 250°C and 80 MPa .

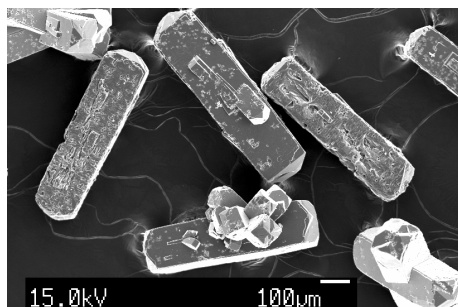


Fig.7 SEM image of silicalite-I crystals synthesized at 250 °C and 80 MPa.

CONCLUSIONS

Large silicalite-I crystals can be prepared by using temperatures and pressures that are substantially higher than usually employed. Organic templates can be stabilized at high temperatures by applying high pressures. We anticipate that the synthesis temperatures of many other zeolite materials can be substantially raised under high pressures.

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