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Materials Syntheses

A Practical Guide

 SpringerWienNewYork

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© 2008 Springer-Verlag/Wien
Printed in Germany

SpringerWienNewYork is part of
Springer Science+Business Media
springer.at

Typesetting: Camera ready by the editors
Printing: Strauss GmbH, 69509 Mörlenbach, Germany

Printed on acid-free and chlorine-free bleached paper
SPIN: 12123858

With numerous Figures

Library of Congress Control Number: 2008926905

ISBN 978-3-211-75124-4 SpringerWienNewYork

Controlling Size and Morphology of Zeolite L

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Abstract The synthesis of zeolite L crystals of high purity and well-defined morphology is described. Four procedures are detailed, leading to (a) large elongated cylindrical crystals, (b) medium-sized disc-shaped crystals, (c) nano-sized crystals, and (d) medium-sized cylindrical-shaped crystals.

Classification

form:	crystalline powder
function:	molecular sieve, host material for supramolecular organization of organic molecules
preparation:	hydrothermal synthesis
composition:	$M_n[A_{16}Si_{27}O_{72}] \cdot n H_2O$ ($M = K^+$ or Na^+)

Introduction

Zeolites are crystalline aluminosilicates featuring defined channels and cavities.[1] The ability to accommodate various organic and inorganic species while being transparent in the UV-Vis-NIR makes zeolites ideal host materials for supramolecular organization.[2] In many cases, the confinement of molecules in zeolites and the catalytic activity of surface adsorption sites lead to interesting photochemical phenomena not observed in solution.[3]

Zeolite L possesses one-dimensional channels arranged in a hexagonal pattern. The free diameter of the main channels varies from 7.1 Å (narrowest part) to 12.6 Å (widest part). The morphology of the crystals can be approximated by a cylinder, with the channel entrances located at the base planes. A crystal with a diameter of 550 nm typically consists of about 80'000 parallel channels. High-resolution electron microscopy has been used to image the surface structures of zeolite L and to advance the understanding of growth processes and defects.[4] Materials obtained by the inclusion of organic dye molecules into the channels of zeolite L feature a variety of intriguing properties, ranging from increased dye stability to photonic antenna functions and optical anisotropy.[5]

In most procedures for zeolite synthesis, the gel composition is given as a ratio of oxides. In order to correctly calculate the required amounts of starting material from this ratio, one has to take into account that hydroxides can be considered oxides plus water (KOH = ½ K₂O and ½ H₂O, for example). The purity of the starting materials should also be considered, bearing in mind that the water content of the hydroxides can be quite significant. Our procedure to calculate the amounts of starting material for a given molar composition



is as follows. The required amounts of KOH, NaOH, Al(OH)₃, SiO₂, and H₂O are:

$$\text{Weight}_{\text{KOH}} = \frac{\text{Mol}_{\text{KOH}} \cdot \text{MW}_{\text{KOH}}}{P_{\text{KOH}}} \quad \text{with} \quad \text{Mol}_{\text{KOH}} = 2a$$

$$\text{Weight}_{\text{NaOH}} = \frac{\text{Mol}_{\text{NaOH}} \cdot \text{MW}_{\text{NaOH}}}{P_{\text{NaOH}}} \quad \text{with} \quad \text{Mol}_{\text{NaOH}} = 2b$$

$$\text{Weight}_{\text{Al(OH)}_3} = \frac{\text{Mol}_{\text{Al(OH)}_3} \cdot \text{MW}_{\text{Al(OH)}_3}}{P_{\text{Al(OH)}_3}} \quad \text{with} \quad \text{Mol}_{\text{Al(OH)}_3} = 2c$$

$$\text{Weight}_{\text{SiO}_2} = \text{Mol}_{\text{SiO}_2} \cdot \text{MW}_{\text{SiO}_2} \quad \text{with} \quad \text{Mol}_{\text{SiO}_2} = d$$

$$\text{Weight}_{\text{TotH}_2\text{O}} = \text{Mol}_{\text{H}_2\text{O}} \cdot \text{MW}_{\text{H}_2\text{O}} \quad \text{with} \quad \text{Mol}_{\text{TotH}_2\text{O}} = e$$

MW designates the respective molecular weights, whereas P represents the purities. This means that 98 % pure KOH has a P_{KOH} = 0.98. The total amount of water is distributed among the silica suspension and the aluminate solution as follows:

$$\text{Weight}_{\text{H}_2\text{O SiO}_2\text{ susp.}} = \frac{\text{Weight}_{\text{SiO}_2} (1 - P_{\text{SiO}_2})}{P_{\text{SiO}_2}}$$

$$\begin{aligned} \text{Weight}_{\text{H}_2\text{O Al}_2\text{O}_3\text{ sol.}} = \text{Weight}_{\text{TotH}_2\text{O}} - & \left[\text{Weight}_{\text{H}_2\text{O SiO}_2\text{ susp.}} + \text{Weight}_{\text{KOH}} (1 - P_{\text{KOH}}) \right. \\ & + \text{Weight}_{\text{NaOH}} (1 - P_{\text{NaOH}}) + \text{Weight}_{\text{Al(OH)}_3} (1 - P_{\text{Al(OH)}_3}) \\ & + \frac{1}{2} \cdot \text{Mol}_{\text{KOH}} \cdot \text{MW}_{\text{H}_2\text{O}} + \frac{1}{2} \cdot \text{Mol}_{\text{NaOH}} \cdot \text{MW}_{\text{H}_2\text{O}} \\ & \left. + \frac{3}{2} \cdot \text{Mol}_{\text{Al(OH)}_3} \cdot \text{MW}_{\text{H}_2\text{O}} \right] \end{aligned}$$

P_{SiO₂} specifically refers to the SiO₂ content of the silica suspension.

Materials

- Ludox HS-40 (40 wt.% SiO₂), purchased from Aldrich, used as received.

- Aerosil OX-50 (silica powder), purchased from Degussa, used as received.
- Aerodisp W 1226 (26 wt.% SiO₂), purchased from Degussa, used as received.
- Aluminum hydroxide, purchased from Fluka, purity >99 %, used as received.
- Aluminum powder, purchased from Fluka, purity >99 %, used as received.
- Potassium hydroxide pellets, purchased from Fluka, purity ≥86 %, used as received.
- Sodium hydroxide pellets, purchased from Merck, purity >99 %, used as received.
- Doubly distilled water (used throughout the synthesis).
- Pressure-tight poly(tetrafluoroethylene) (PTFE) vessel (see ref. 6 for an example).

Safety and Disposal

Safety and handling instructions for the chemicals are found in the corresponding materials safety data sheets (MSDS). The pressure-tight PTFE vessel should be designed to well withstand the vapor pressure of water at the employed temperatures (at least 175 °C which corresponds to approximately 890 kPa).

Procedures

A. Large Zeolite L Crystals (Fig. 1)

An amount of 3.11 g of potassium hydroxide is added to 22.00 g of doubly distilled water and stirred at 0 °C (on ice) for 5 min. Next, 0.58 g of metallic aluminum powder is added under nitrogen flow, and the mixture is stirred at 0 °C for 15 min. After letting the solution warm to room temperature, stirring is continued for 1.5 h under nitrogen flow. The resulting solution is filtered to remove Fe(OH)₃, which is due to Fe as an impurity in aluminum, until a clear solution is obtained. This solution is added to 14.34 g of Ludox under vigorous stirring, the latter having been stirred between 5 and 10 min beforehand. After 3 to 6 min of further stirring, the opaque gel is transferred to the PTFE vessel for crystallization at 175 °C for 72 h under static conditions. The composition of the gel is 2.24 K₂O–1.00 Al₂O₃–8.98 SiO₂–164.40 H₂O.

After crystallization, the pressure vessel is cooled in ice for 1 h before opening. The product is centrifuged (4000 rpm, 8 min) and washed with boiling doubly distilled water until the pH of the supernatant becomes neutral. The crystals are dried for approximately 16 h at 80 °C in air, yielding about 5 g of material. Subsequent ion exchange is performed by suspending the material in 70 ml of doubly distilled water and adding 4.0 g of potassium nitrate. After stirring this suspension for 5 h

at about 50 °C, the zeolite is centrifuged (4000 rpm, 8 min) and washed until the pH of the supernatant becomes neutral. Finally, the crystals are dried in air for 16 h at 80 °C.

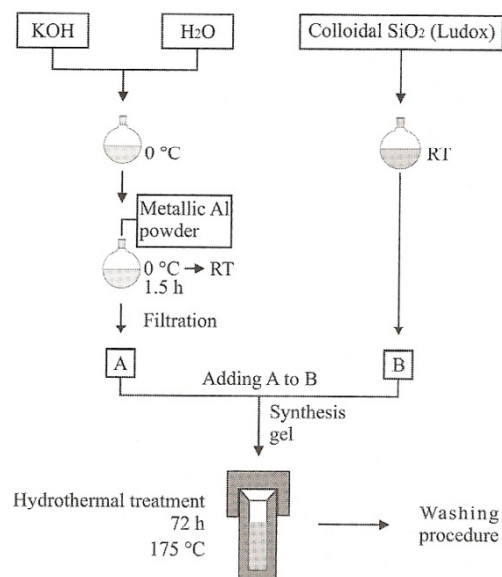


Fig. 1. Scheme of the synthesis procedure for large zeolite L crystals.

Characterization

The following experiment was performed to conveniently check the success of the synthesis. When zeolite L is added to an aqueous solution of thionine, aggregates of the dye immediately form on the external zeolite surface. Upon boiling the sample for about 1 min, a sudden color change from violet to blue is observed. This effect is due to the insertion of the dye molecules into the zeolite L channels where they can exist as monomers only. The blue color remains after cooling to room temperature. If the test is negative (no color change), the additional characterization methods are unnecessary.[7]

The products were analyzed by X-ray powder diffraction (using a Guinier camera de Wolff Mk.IV, CuK_α radiation, ENRAF-NONIUS and also a Stoe STADIP powder diffractometer in transmission, CuK_α radiation, focusing Ge(III) monochromator) for phase identification (Fig. 2). The patterns were compared to a standard pattern of commercial zeolite L (Union Carbide or UOP). Reference XRD

patterns are also available from ref. 8. The morphology of the crystals was examined by means of scanning electron microscopy (JEOL JSM 840 and Hitachi S-3000N). A homogeneous distribution of cylindrical crystals with hexagonal cross-section and smooth surfaces is obtained. The average length of the crystals is 6 μm with an average diameter of 2 μm .

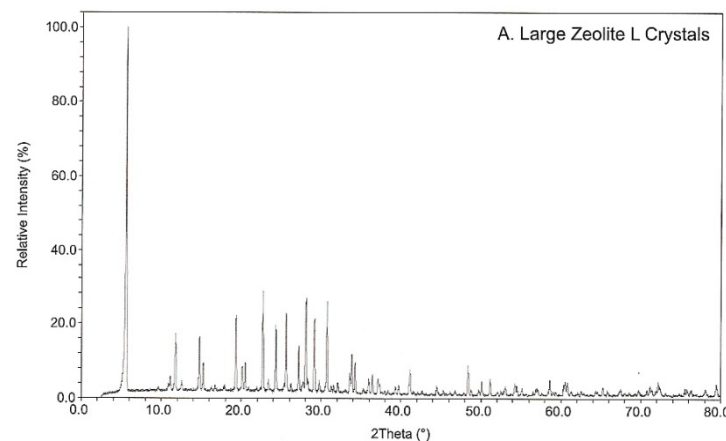


Fig. 2. X-ray powder diffractogram for large zeolite L crystals measured in transmission.

Comments

The reason for ion exchange is to have only potassium ions as exchangeable cations. The final composition is obtained after the ion exchange.

B. Medium-sized Disc-shaped Zeolite L Crystals (Fig. 3)

An amount of 2.76 g of potassium hydroxide, 1.74 g of sodium hydroxide, and 0.62 g of aluminum hydroxide are added to 17.40 g of doubly distilled water and refluxed for 3 h in an oil bath at 120 °C resulting in a clear solution. After letting this solution cool to room temperature, it is added under stirring to 17.67 g of Ludox, the latter having been stirred between 5 and 10 min beforehand. After 3 to 6 min of further stirring, the opaque gel is transferred to the PTFE vessel for crystallization at 160 °C for 48 h under dynamic conditions (rotation at 40 rpm). The composition of the gel is 5.40 K_2O –5.50 Na_2O –1.00 Al_2O_3 –30.00 SiO_2 –416.08 H_2O . For the application of dynamic crystallization conditions, an oven equipped

with a device enabling rotation of the PTFE vessels at various speeds is used (see ref. 6 for details).

After crystallization, the pressure vessel is cooled in ice for 1 h before opening. The product is centrifuged (4000 rpm, 8 min) and washed with boiling doubly distilled water until the pH of the supernatant becomes neutral. The crystals are dried for approximately 16 h at 80 °C in air, yielding about 2 g of material. Ion exchange is performed as outlined in procedure A.

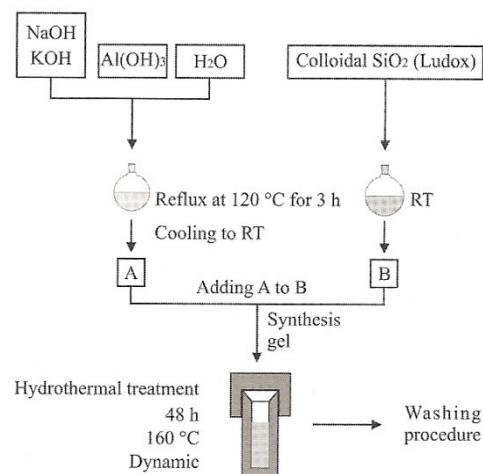


Fig. 3. Scheme of the synthesis procedure for medium-sized disc-shaped zeolite L crystals.

Characterization

Characterization was performed as described for Synthesis A. The X-ray powder diffractogram is shown in Fig. 4. A homogeneous distribution of disc-shaped zeolite L crystals with an average length of 0.35 μm and an average diameter of 1 μm is obtained.

Comments

Partial addition of sodium hydroxide yields disc-shaped crystals of higher quality by reducing intergrowth. Aging the final gel in the closed PTFE vessel for 15 h at room temperature before crystallization leads to crystals with an average length of 0.065 μm and an average diameter of 0.4 μm .

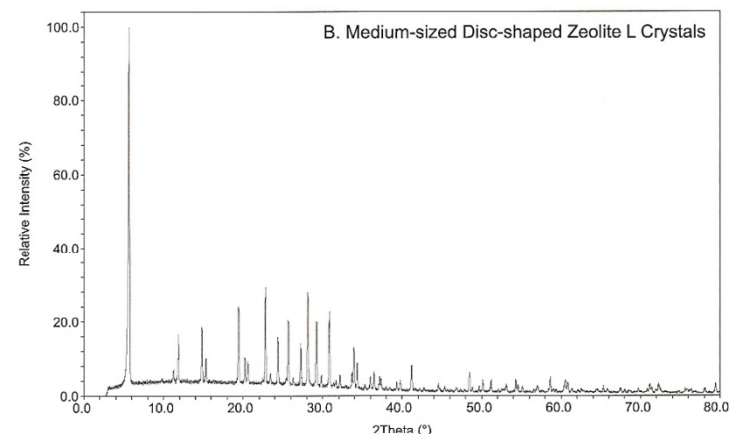


Fig. 4. X-ray powder diffractogram for medium-sized disc-shaped zeolite L crystals measured in transmission.

C. Nano-sized Zeolite L Crystals (Fig. 5)

An amount of 4.84 g of potassium hydroxide and 1.56 g of aluminum hydroxide is added to 20.00 g of doubly distilled water and refluxed for 15 h in an oil bath at a temperature of 115 °C resulting in a clear solution. A silica suspension is prepared separately as follows: 28.04 g of doubly distilled water are added to 12.02 g of silica powder and suspended for 15 min at 18000 rpm (Ultra Turrax mixer, IKA T18 Basic). This suspension is left between 30 min and 1 h, and mixed for 10 min at 18000 rpm before use.

An amount of 7.23 g of potassium hydroxide and 21.68 g of doubly distilled water is added to the silica suspension and refluxed for 15 h in an oil bath at 115 °C. After letting the potassium aluminate solution and the potassium silica suspension cool to room temperature, the potassium aluminate solution is added to the potassium silica suspension under vigorous stirring. After stirring for 3 to 6 min, the opaque gel is transferred to the PTFE vessel for crystallization at 170 °C for 6 h under dynamic conditions (rotation at 16 rpm). The composition of the gel is 9.34 K_2O –1.00 Al_2O_3 –20.20 SiO_2 –412.84 H_2O .

After crystallization, the pressure vessel is cooled in ice for 1 h before opening. The product is centrifuged (5000 rpm, 40 min) and washed with boiling doubly distilled water until the pH of the supernatant becomes neutral. The crystals are dried for approximately 16 h at 80 °C in air yielding about 1.5 g of material. Ion exchange is performed as outlined in procedure A.

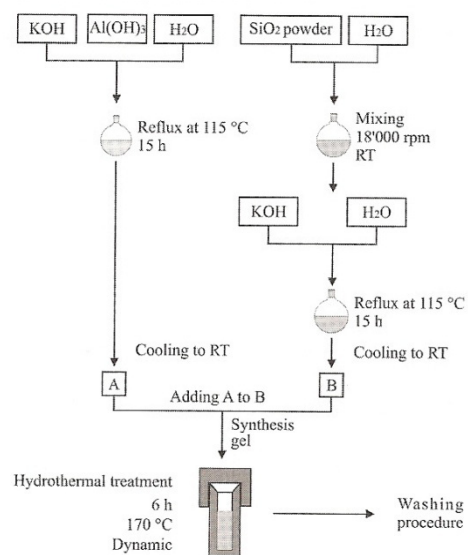


Fig. 5. Scheme of the synthesis procedure for nano-sized zeolite L crystals.

Characterization

The products were analyzed by XRD (Fig. 6) and transmission electron microscopy (Hitachi H-600-2 and Philips XL30 ESEM-FEG). Zeolite L crystals with dimensions in the order of 30 nm are obtained, featuring a tendency to agglomerate into larger clusters of 80–100 nm. The XRD pattern shows the line broadening expected for such small crystallites.

D. Medium-sized Cylindrical-shaped Zeolite L Crystals (Fig. 7)

An amount of 3.18 g potassium hydroxide, 1.60 g of sodium hydroxide, and 2.21 g of aluminum hydroxide is added to 9.40 g of doubly distilled water and refluxed for 3 h in an oil bath at 120 °C resulting in a clear solution. A silica suspension is prepared separately as follows: 35.07 g of colloidal silica (Aerodisp W1226, Degussa, 26 wt.% of SiO₂) and 6.39 g of doubly distilled water are mixed and kept in an ultrasonic bath for about 10 min. After letting the potassium sodium aluminate solution cool to room temperature, it is added to the colloidal silica suspension under vigorous stirring. After further stirring for 3 min, the opaque gel is trans-

ferred to the PTFE vessel for crystallization at 160 °C for 144 h under static conditions. The composition of the gel is 1.73 K₂O–1.41 Na₂O–1.00 Al₂O₃–10.81 SiO₂–173.00 H₂O.

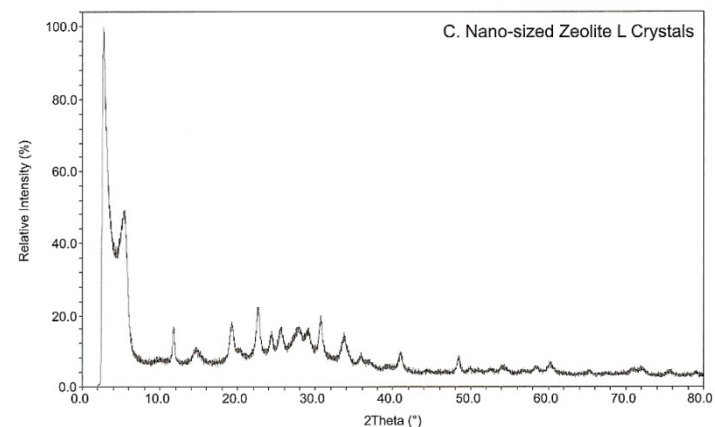


Fig. 6. X-ray powder diffractogram for nano-sized zeolite L crystals measured in transmission.

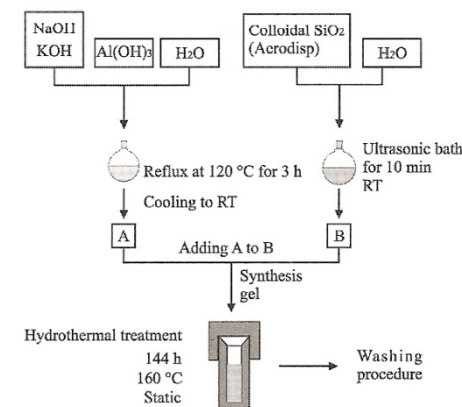


Fig. 7. Scheme of the synthesis procedure for medium-sized cylindrical-shaped zeolite L crystals.

After crystallization, the pressure vessel is cooled in ice for 1 h before opening. The product is centrifuged (4000 rpm, 8 min) and washed with boiling doubly distilled water until the pH of the supernatant becomes neutral. The crystals are

dried for approximately 16 h at 80 °C in air yielding about 6 g of material. Ion exchange is performed as outlined in procedure A.

Characterization

Characterization was performed as described for Synthesis A. The X-ray diffractogram is shown in Fig. 8. A homogeneous distribution of medium-sized zeolite L crystals with smooth surfaces and an average length of 0.9 μm and an average diameter of 0.7 μm is obtained.

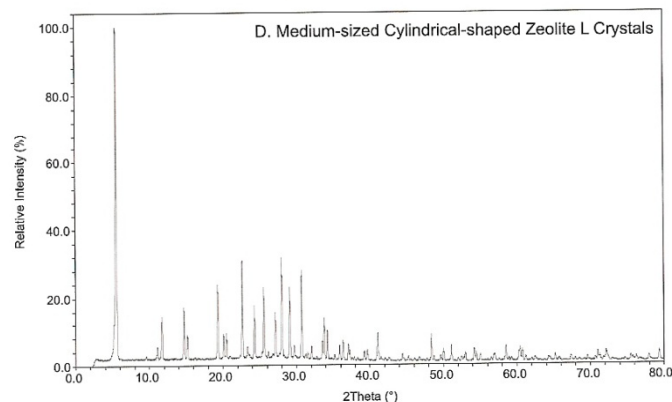


Fig. 8. X-ray powder diffractogram for medium-sized cylindrical-shaped zeolite L crystals measured in transmission.

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