Synthesis of an Ionic Liquid and Its Application as Template for the Preparation of Mesoporous Material MCM-41: A Comprehensive Experiment for Undergraduate Students

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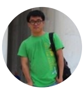

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Synthesis of an Ionic Liquid and Its Application as Template for the Preparation of Mesoporous Material MCM-41: A Comprehensive Experiment for Undergraduate Students

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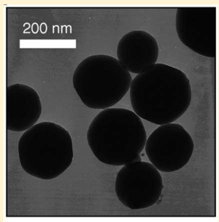
Supporting Information

ABSTRACT: A new solvent-free microwave experiment to synthesize the ionic liquid 1-hexadecyl-3-methylimidazolium bromide (HDMIm-Br) in high yield is presented. The structure is confirmed by IR and ^{1}H NMR spectra. HDMIm-Br is then used to prepare an organic−inorganic mesoporous material MCM-41. The microscopic arrangements of mesoporous materials MCM-41 are studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM). This experiment is a modification of previously reported methods for synthesizing the ionic liquid. More importantly, the comprehensive experiment helps the students design and deal with reactions reasonably and highlights the difference between basic experiments and academic research, which is useful to develop a student's reasoning and experimental skills.



MCM 41

KEYWORDS: Upper-Division Undergraduate, Analytical Chemistry, Laboratory Instruction, Organic Chemistry, Hands-On Learning/Manipulatives, Materials Science, Surface Science, Synthesis, Undergraduate Research

A new solvent-free microwave experiment to synthesize the ionic liquid 1-hexadecyl-3-methylimidazolium bromide (HDMIm-Br) in high yield is presented. The structure is confirmed by IR and ^{1}H NMR spectra. HDMIm-Br is then used to prepare an organic−inorganic mesoporous material MCM-41.[1] The microscopic arrangements of mesoporous materials MCM-41 are studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

This laboratory experiment is used as an introduction for third-year undergraduate students wishing to pursue research. The experiment functions as a bridge to understand the difference between basic laboratory courses and academic research. This comprehensive experiment is divided into three parts. First, a discussion forum is held where the students present their original experimental design. Then, the students individually discuss the experimental design with the teacher to determined the final procedure. Second, as the course is scheduled from 8 p.m. to 10 a.m. for about two weeks, the laboratory schedules for the students, teachers, and teaching assistants need to be determined and the laboratory work completed. Finally, after the laboratory work is finished, another discussion forum is held. The experimental setup requires the students to search the literature, design a reaction route, discover and solve problems, explain and discuss the relationship between properties and structures, and draw conclusions. The students are required to design a synthetic procedure considering the limitations of reagents and equipment in teaching laboratory.

The primary goal of this experiment is to synthesize an organic−inorganic mesoporous material MCM-41[2] and characterize the microscopic arrangements. This experiment is suitable for the students who have taken a full year of organic chemistry. The ionic liquid used for the synthesis of mesoporous material, MCM-41, is prepared through a free-solvent microwave reaction. Although this technique is rare in traditional organic experiments, it has many advantages, such as minimizing solvents and time, improving the yield, and reducing pollution to the environment. The characterization of the mesoporous material MCM-41 by X-ray diffraction (XRD) and transmission electron microscopy (TEM) benefits the students by exposing them to instruments that might be used in the future research.

■ EXPERIMENTAL OVERVIEW

An ionic liquid (HDMIm-Br) was prepared from 1-methylimidazole and hexadecane bromide via a microwave reaction (Scheme 1).[3,4] This is classified as a green reaction due to its efficiency and low pollution to the environment. The crude product was recrystallized from tetrahydrofuran, filtered, and dried at 50 °C to afford a white solid with 100% yield. HDMIm-Br was characterized by IR and ^{1}H NMR. The ionic liquid was added to a solution of sodium hydroxide, reacted with expanding agents (mesitylene/*n*-decane, 1:1 (v:v)) and tetraethyl orthosilicate at 80 °C. The crude product was heated in an autoclave at 80 °C for 24 h, washed with water and ethanol, and dried for 4 h. Finally, MCM-41 was obtained after calcining at 540 °C in a muffle furnace. The microscopic arrangement of MCM-41 was characterized by XRD and TEM. The total time required for the experiment is about 2−3 days. (The lab is open for two weeks from 8:00 p.m. to 10:00 a.m., and the students could use their free time to arrange their own experiments.) All chemicals are of analytical grade and are commercially

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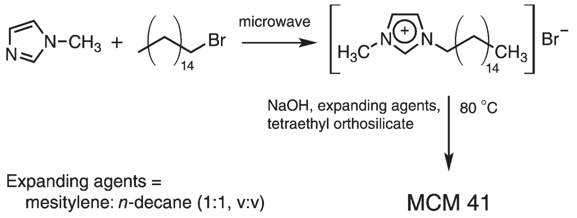
Scheme 1. Synthesis of MCM 41



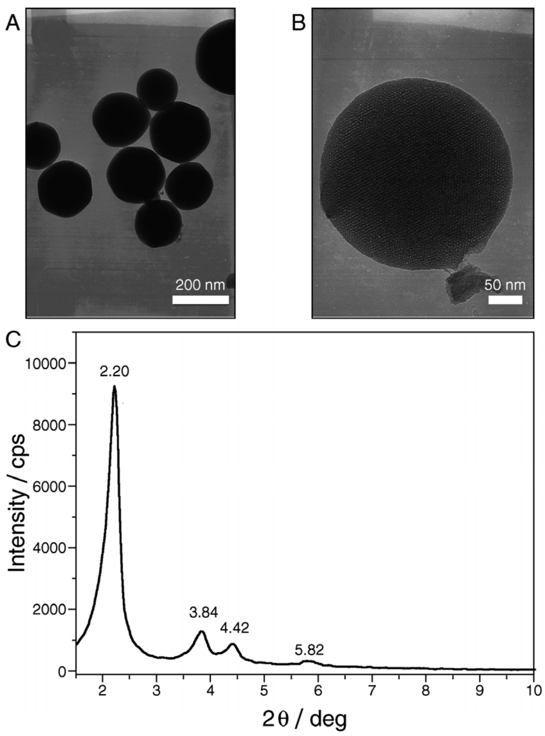


Figure 1. (A and B) TEM images of MCM-41 and (C) XRD of MCM-41.

available. The detailed experimental procedures are available in the Supporting Information.

■ HAZARDS

1-Methylimidazole causes eye, skin, digestive, and respiratory tract burns. 1-Methylimidazole and bromohexadecane are combustible. Bromohexadecane may cause irritation to skin, eyes, and respiratory tract and may be harmful if swallowed or inhaled. Tetraethyl orthosilicate is a skin and eye irritant, long-term exposure may cause kidney or liver damage, and it is flammable. Mesitylene, THF, and *n*-decane may cause irritation to skin, eyes, and respiratory tract, may be harmful if swallowed or inhaled, and are flammable. Sodium hydroxide is caustic; it causes burns to any area of contact. Environmental regulations should be followed for the disposal of waste.

■ RESULTS AND DISCUSSION

Students characterize the target ionic liquid and the resulting mesostructured material by ^{1}H NMR, IR, XRD, and TEM. Typical results from one group of students are discussed. The IR peaks at 2850 cm^{-1} (stretching frequency for methylene), 1583, 1473 cm^{-1} (stretching frequency for imidazole ring), and 1380 cm^{-1} (antisymmetric bending frequency of methyl linking to imiazole ring) revealed that the ionic liquid was obtained, and the ^{1}H NMR spectra further confirmed it was obtained with high purity (both spectra are shown in the Supporting Information).

The TEM images of MCM-41 (Figure 1A,B) showed that the diameters of spherical particles of MCM-41 were mainly 200−300 nm with uniform hexagonal pore structures. The calculated pore diameter (including single-wall thickness) was about 4.6 nm, which was in the range of mesoporous materials. The mesoporous structure could also be further confirmed by the sharp peaks at 2.20°, 3.84°, 4.42°, and 5.82° shown in the XRD (Figure 1C). These data indicated that the molecular sieve MCM-41 had been obtained from the synthesized ionic liquid and it had an ordered and regular arrangement.

■ CONCLUSION

This experiment clearly demonstrates that the solvent-free microwave reaction plays an important role for the synthesis of ionic liquid used to obtain mesoporous materials MCM-41. The students become aware of the opportunity to find new efficient methods to obtain the traditional target compounds with less pollution. The IR, NMR, XRD, and TEM measurements further help the students confirm the purity of target compounds and its assembly properties. More importantly, the comprehensive experiment helps the students learn how to design and deal with reactions reasonably and also highlights the difference between basic experiments and academic research, which is useful to develop a student's reasoning and experimental skills.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experiment procedure, notes for the instructor, chemicals, equipment, and questions. This material is available via the Internet at http://pubs.acs.org.

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