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Versatile Route to Zeolite Single Crystals with Controlled Mesoporosity: in situ Sugar Decomposition for Templating of Hierarchical Zeolites

Marina Kustova, Kresten Egeblad, Kake Zhu, and
Claus H. Christensen*

Center for Sustainable and Green Chemistry, Department of Chemistry, Technical University of Denmark, Kemitorvet, Building 206, DK-2800 Lyngby, Denmark

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Zeolites are among the most widely used industrial catalysts.[1] Their superior performance can often be attributed to the existence of a well-defined system of micropores (size below 2 nm diameter) with uniform shape and size, typically of molecular dimensions. However, for some applications, the sole presence of such micropores can also result in an unacceptably slow diffusion of reactants and products to and from the active sites located inside the zeolite crystals. In such cases, a diffusion limitation is imposed on the reaction rate.[2] To overcome this limitation, researchers have pursued several different preparative strategies. One possibility is to minimize the size of the zeolite crystals,[3−6] which is often in the range of 0.5−50 μm, and thereby shorten the diffusion path. Another possibility is to increase the pore size of the zeolite, and this approach has led to the discovery of novel zeolites with larger pores[7−10] and ordered mesoporous materials.[11,12] The most common and successful approach so far is to introduce an additional system of mesopores (sizes between 2 and 50 nm) into each individual zeolite crystal. This is typically done by suitable posttreatments such as dealumination,[13,14] and desilication.[15−17] Recently, it was shown that mesopores can be introduced directly into the zeolite crystals, without a partially destructive posttreatment, simply by conducting the crystallization in the presence of a mesoporous carbon material.[18] The carbon particles are encapsulated by the zeolite crystals during growth. After complete crystallization, the carbon is easily removed by combustion to produce highly mesoporous zeolite single crystals that combine some of the most desirable catalytic properties of zeolites and mesoporous molecular sieves.[19]

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* Corresponding author. E-mail: chc@kemi.dtu.dk.

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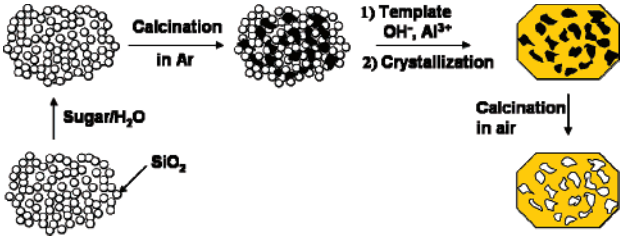

Figure 1. New route for the preparation of mesoporous zeolite single crystals using sucrose as the carbon template.

Here, we demonstrate a simple, new, and versatile method for the preparation of mesoporous zeolites. This new method applies in situ generation of the required carbon template by decomposition of a carbohydrate directly onto the silica raw material used for the zeolite synthesis. This method significantly extends the scope of the carbon-templating approach. Most importantly, it allows careful control of the porosity of the mesoporous zeolite in a very simple manner and it does not depend on the availability of specialized carbon templates. The mesoporous zeolite single crystals resulting from the carbon-templating method have already shown promising catalytic properties in several reactions.[19−24] So far, these hierarchical zeolite structures have been reported for the MFI,[25] MEL,[20] and MTW[26] framework types and most recently also for BEA, AFI, and CHA.[27] Other synthesis schemes for preparing hierarchical zeolites have been presented as well, such as assembling zeolite seeds with organic structure directors present,[28] resin macrotemplating,[29] using carbon aerogels,[30,31] recrystallization,[32] and templating mesoporous zeolites from a mixture of small organic alkylammonium salts and mesoscale cationic polymers.[33]

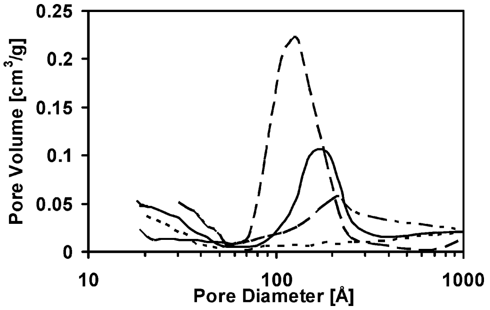

Figure 2. Controlled mesoporosity of zeolites prepared simply by varying the amount of sugar in the silica (from top C/Si = 1.75; 0.87; 0.58; 0.0).

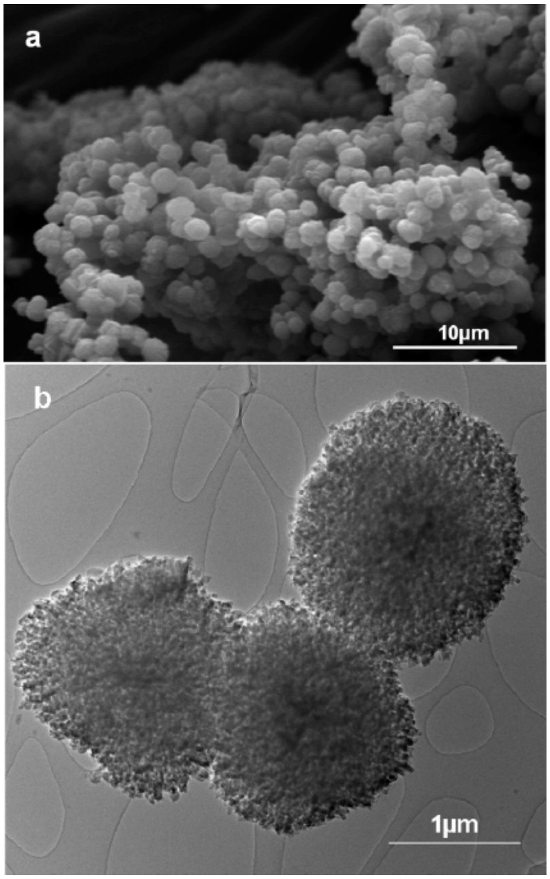

Figure 3. Representative (a) SEM and (b) TEM images of mesoporous ZSM-5 zeolite single crystals prepared by in situ carbon templating.

Figure 1 shows a schematic illustration of the new route for preparation of mesoporous zeolites. In the first step, silica gel is impregnated to incipient wetness with a concentrated solution of sucrose. During calcination in an inert gas (Ar), the auxiliary carbon particles are then formed by decomposition of sucrose inside the silica gel. After that, a zeolite synthesis gel is formed from the resulting carbon−silica composite by addition of the base and a suitable template. Upon complete crystallization, the carbon is removed by combustion and the mesoporous zeolite is formed.

The X-ray powder diffraction patterns for the mesoporous ZSM-5 and ZSM-11 zeolites are shown in Figures S1 and S2 of the Supporting Information. It is clearly seen that the samples exclusively contain highly crystalline MFI- and MEL-structured material, respectively.[34] The mesopore size distribution of the ZSM-5 zeolite after combustion of the carbon is shown in Figure 2 and the effect of changing the

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carbon/silica ratio in the recipe is evident. Surface areas as well as micro- and mesopore volumes are summarized in Table S1 of the Supporting Information. Thus, it is clear that by introduction of more or less concentrated solutions of sucrose during impregnation of the silica, the mesopore volume can be tuned without altering the micropore volume.

Hg intrusion experiments gives essentially mesopore volumes identical to those obtained from nitrogen physisorption. This shows that the mesopores are actually accessible and distributed over the interior volume of the zeolite crystals. This is also supported by the representative images from scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for the mesoporous ZSM-5 zeolite shown in Figure 3. From the SEM image (a), it can be seen that the sample is highly crystalline and that crystals of a quite uniform size are obtained. From the TEM image (b), it is easily possible to see the individual mesoporous zeolite crystals, which clearly features some brighter areas distributed all over. These brighter areas are the mesopores created by removal of the carbon introduced as sucrose. The vast majority of the crystals are mesoporous zeolite single crystals, but some less mesoporous zeolite crystals can sometimes also be formed. The average crystal size determined from SEM and TEM for the mesoporous zeolite crystals is about 1 μm, and the typical shape of MFI-type crystals is observed.

The mesoporous zeolite crystals are unique in the sense that they contain interconnected micropores and mesopores inside each individual single crystal. So far, the present method for the preparation of mesoporous zeolites is demonstrated as a new, very simple route to these hierarchical zeolites. The method applies in situ generation of the carbon template from sucrose impregnated onto silica gel, and therefore the resulting material is readily available at low cost. The method does not rely on the availability of special and expensive mesoporous carbons, only on the mesoporous silicas that are used widely and can be obtained easily by precipitation. However, the most important attribute of the present approach is that is allows careful design of the porosity. This is essential for catalytic applications, because this is the way that efficient mass transport can be tuned to maximize catalyst performance. With this simple method, it is possible that mesoporous zeolites could be so easily and inexpensively available that they will find use in industrial applications.

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Supporting Information Available: Detailed synthesis procedures, X-ray diffraction, and pore analysis (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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