Communication

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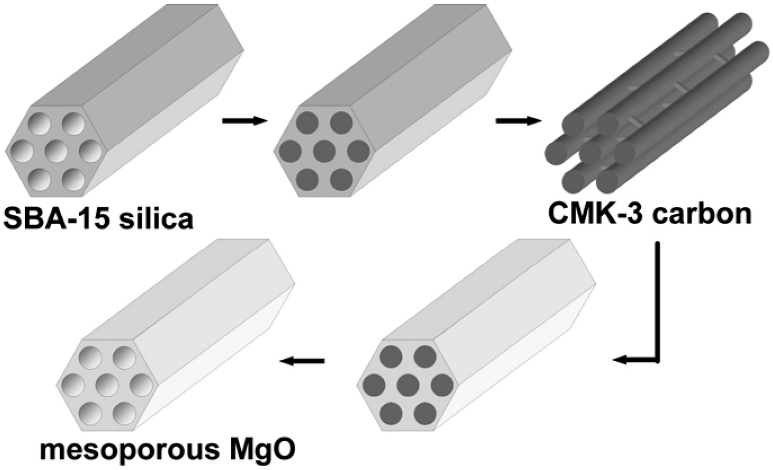

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Ordered Mesoporous Magnesium Oxide with High Thermal Stability Synthesized by Exotemplating Using CMK-3 Carbon

Jan Roggenbuck and Michael Tiemann*

Institute of Inorganic and Analytical Chemistry, Justus Liebig University, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany

Received October 21, 2004; E-mail: michael.tiemann@anorg.chemie.uni-giessen.de

One of the great potential applications of porous materials with narrow pore size distribution is as heterogeneous catalysts, since they provide a combination of large specific surface area and a certain degree of size- and shape-selectivity (molecular sieve properties). Most of the common materials, from crystalline microporous (zeolitic) to periodically ordered mesoporous, are either acidic (e.g. aluminosilicates) or neutral (e.g. silicas, aluminum phosphates). Porous catalysts with basic properties, on the other hand, usually have to be prepared by postsynthetic doping of host materials with basic guest species, such as zeolites with alkali (earth) metal oxides[1−3] or mesoporous silica (MCM-41, SBA-15) with magnesium oxide.[4,5] However, porous materials which intrinsically possess strong basicity without the need of postfunctionalization are rare. Since bulk magnesium oxide shows excellent basic catalytic properties, e.g. for selective dehydrogenation/dehydration[6] or aldol addition,[7,8] the demand for ordered mesoporous magnesium oxides is obvious. Here we describe the first synthesis of mesoporous magnesium oxide with a periodically ordered uniform pore system, narrow pore size distribution, and high thermal stability.

The conventional synthesis of periodically ordered mesoporous materials, i.e. the utilization of self-assembled aggregates of amphiphiles (such as surfactants or block copolymers) as structure-directors,[9,10] has its limitations when it comes to non-siliceous products.[11] A promising alternative is the utilization of mesoporous solid materials as "hard" templates, which cast their structures faithfully to the final products. To distinguish between "soft" and "hard" templates, the terms *endo*- and *exotemplate* have been suggested.[12] In the field of ordered mesoporous materials, the exotemplating concept is frequently used in the synthesis of CMK-type carbons, for which mesoporous silicas serve as exotemplates.[13] It has recently been shown that these mesoporous carbons can themselves be employed for further exotemplating,[14−16] yielding new mesoporous materials which may not be accessible by conventional endotemplating.

Mesoporous SBA-15 silica[10] and CMK-3 carbon[17] were prepared according to the literature procedures. In a typical synthesis of mesoporous magnesium oxide, 5 g of CMK-3 was dispersed in 100 mL of an aqueous solution (0.25 mol L^{-1}) of magnesium nitrate (Merck) and stirred for 2 h to impregnate the mesopores with magnesium nitrate. After filtration and drying in a vacuum, the sample was heated under air atmosphere to 300 °C at a constant rate of 2.5 °C/min, to convert magnesium nitrate to magnesium oxide within the pores. This procedure was repeated three times. Finally, the carbon was removed by heating to 800 °C at a constant rate of 2 °C/min; thermal analysis (see Supporting Information) shows that this involves a mass loss of ca. 55%, revealing that a substantial part of the CMK-3 pores has been filled with MgO.

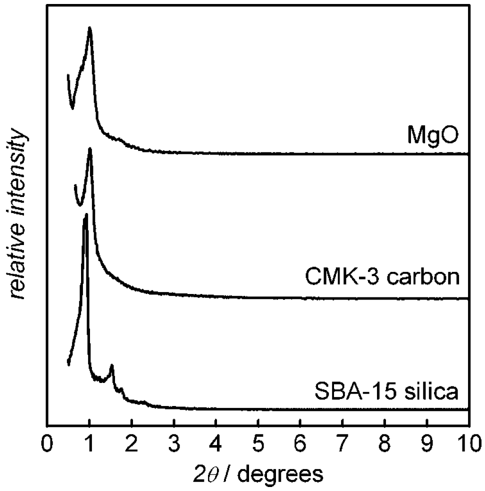

Figure 1. Powder X-ray diffraction diagrams of mesoporous magnesium oxide and "parent" CMK-3 carbon/SBA-15 silica materials (recorded on a Bruker AXS D8, using Cu Kα radiation, 40 kV, 40 mA; counting time: 2 s; steps: 0.01° (2θ).

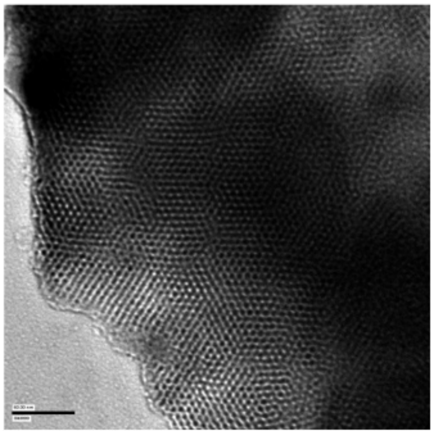

Figure 2. TEM image of mesoporous magnesium oxide; the scale bar corresponds to 60 nm (recorded on a Philips CM30-ST).

Figure 1 shows the powder X-ray diffraction diagram of a mesoporous magnesium oxide as well as those of the "parent" SBA-15 and CMK-3 materials which consecutively served as exotemplates. The broadening of the 100 reflection reveals some decrease in structural order; in the final product only the 100 and 110 reflections are distinguishable. Nonetheless, transmission electron microscopy (TEM) still shows an intact long-range periodic order with hexagonal symmetry in the resultant mesoporous MgO material (Figure 2). No reflections are observed in the wide-angle XRD region (not shown), and no atomic-scale periodicity is detected by TEM/SEAD, which indicates that the material is not crystalline over extended regions. EDX analysis confirms the Mg:O stoichiometry of 1:1.

The mesoporous nature of the product is confirmed by nitrogen physisorption. Figure 3 shows the sorption isotherm and pore size

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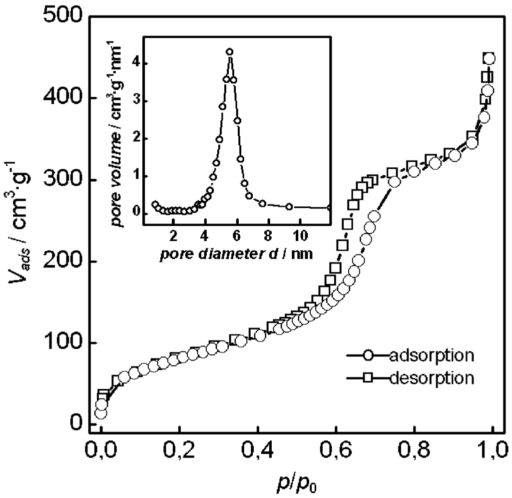

Figure 3. Nitrogen physisorption isotherms (○, adsorption; □, desorption) and BJH pore diameter distribution (inset, from the desorption branch) of mesoporous magnesium oxide (measured on a Quantachrome Autosorb 6 at 77 K).

Table 1. Powder X-ray Diffraction and Nitrogen Physisorption Data of the Three Samples from a Consecutive Series of Exotemplating

sample	d_{100} (nm)	surface area[a] (m^2 g^{-1})	pore diameter[b] (nm)	pore volume (cm^3 g^{-1})
SBA-15	9.7	524	8.4	1.26
CMK-3	8.8	833	3.9	0.67
MgO	8.7	306	5.6	0.51

[a] Calculated by the BET method. [b] Calculated by the BJH method from the desorption isotherm.

distribution of the same mesoporous MgO as in Figure 1; the isotherm has the characteristic type IV shape, comparable to those of the "parent" SBA-15 and CMK-3 materials (not shown). The BJH pore diameters and the specific BET surface areas and pore volumes, as well as the d_{100} values (from the powder X-ray diagrams) of all three materials, SBA-15, CMK-3, and MgO, are shown in Table 1. The substantial differences in the specific surface areas and total pore volumes are consistent with the fact that the densities of the respective materials increase in the order $C < SiO_2 < MgO$; for the bulk phases the densities are 1.8−2.1 g cm^{-3} (amorphous carbon), 2.26 g cm^{-3} (tridymite SiO_2), and 3.6 g cm^{-3} (periclase MgO).[18] However, the above-mentioned partial loss of structural order also accounts for the lower surface area of mesoporous MgO as compared to that of SBA-15. The smaller pore diameter in the MgO implies that it has thicker pore walls than the SBA-15; this is possible because the wall thickness in CMK-3 is always lower than the pore diameter in the parent SBA-15.[17]

For potential application in basic heterogeneous catalysis, it is necessary that the mesoporous MgO samples possess a high degree of thermal stability. The basic properties of the catalysts need to be "activated" by calcination at ca. 700 °C (removal of chemisorbed species, such as OH, H, CO_2). Our products do not show any significant loss of structural order after repeated heating to 800 °C, as confirmed by powder XRD. Figure 4 shows a temperature-programmed CO_2 desorption (TPD) curve which characterizes the basic strength of mesoporous MgO. Before the measurement, the sample was calcined for 2 h at 700 °C in a vacuum and then exposed to a CO_2 flow for 1 h at room temperature, followed by removal of physisorbed CO_2 by flushing in a helium flow at room temperature. The desorption of chemisorbed CO_2 (heating rate: 10 K min^{-1} in flowing helium) takes place over a temperature range up to 300 °C, which confirms a degree of basicity comparable to that recently reported for SBA-15 silica coated with MgO.[5]

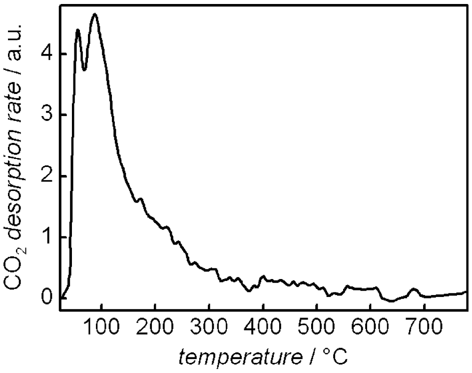

Figure 4. Temperature-programmed desorption (TPD) of CO_2 from mesoporous MgO (measured on a Quantachrome ChemBET 3000, equipped with a thermal conductivity detector).

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Supporting Information Available: Thermal analysis of MgO/CMK-3. This material is available free of charge via the Internet at http://pubs.acs.org.

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