Hard-Templating Pathway To Create Mesoporous Magnesium Oxide

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Mesoporous magnesium oxide has been prepared through a hard-templating pathway using mesoporous carbon aerogel as template and magnesium nitrate solution as MgO precursor. The used carbon aerogel can be synthesized by drying a resorcinol/formaldehyde polymer under ambient pressure conditions instead of the usually employed supercritical drying method. After removal of the carbon template by a simple combustion at 600 °C for 8 h in air, the obtained MgO primary particles have close to spherical shapes, which are connected to form a three-dimensional network structure. The surface area and pore volume can reach up to 150 $m^2 \cdot g^{-1}$ and 0.73 $cm^3 \cdot g^{-1}$, respectively. A carbon aerogel template with larger pore diameter also leads to MgO with an increasing pore diameter. Such a tunable mesopore structure of MgO with high surface area, large pore volume, and tunable pore size could be advantageous for practical applications, for instance in catalysis.

Introduction

Magnesium oxide (MgO) has been extensively used in catalysis, toxic waste remediation, or as an additive in refractory materials, paints, and superconductor products based on its versatile properties.[1,2] In the field of catalysis, MgO shows strongly basic property that can be exploited for base catalysis in many organic reactions, such as alcohol dehydrogenation.[3] It can also be used as catalyst support; e.g. nickel-supported MgO catalyst shows interesting anticoking ability in the re-forming reaction of methane with CO_2, in which two main green house gases are converted into desirable syngas to produce fuels or chemicals.[4] It has been demonstrated that nanocrystalline MgO shows excellent adsorbent properties due to both enhanced surface areas and intrinsically higher surface reactivity.[5,6] Hence, it is very desirable to develop alternative synthesis methods to produce in a controllable manner highly porous MgO with high specific surface area.

MgO is usually synthesized by thermal decomposition of magnesium hydroxide or carbonate.[7] A simple hydrothermal treatment for commercial bulk magnesium oxide crystals results in platelike porous magnesium hydroxide and oxide with a surface area of nearly 100 $m^2 \cdot g^{-1}$.[8] Nanocrystals of MgO can be synthesized by an alkoxide hydrolysis process, using $Mg(OCH_3)_2$ as precursor.[6] Particulates based on these small MgO nanocrystals exhibit unexpectedly high surface chemical reactivity that allowed successful utilization as high-capacity destructive adsorbents for toxic chemicals[9] or use as a selective benzylation catalyst.[2] However, this alkoxide hydrolysis approach appears to be rather expensive for conventional catalytic applications. The adsorption of magnesium nitrate in a copolymer derived from hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) leads to nanoporous MgO after calcination. Density of the copolymer directly affects the porosity of the obtained MgO materials.[10] In this case, the copolymer plays a templating role. As an alternative method, hard-templating pathways attract considerable attention due to the rather simple procedure.[11−13] In a hard-templating route, the voids of a preformed template, normally porous silica or carbon, are impregnated with solutions or liquid precursors of desired composition. The subsequent solidification and removal of the template may lead to the negative replicas. Mesoporous carbon as hard template is advantageous for the formation of porous binary or multinary metal oxides, since the template can be easily removed by combustion.[14,15] Moreover, the pore systems of many mesoporous carbons can be controlled to some extent

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by varying the synthetic conditions. This could provide a chance for synthesis of porous oxides with controllable size and desired chemical composition. In the present investigation, we are interested in the possibility of using carbon aerogel as hard template and concentrated magnesium nitrate solution as precursor to synthesize mesoporous MgO, since the carbon aerogel has a three-dimensional network consisting of spherical particles with high surface area, large pore volume, and controllable pore size distribution in the mesopore range. Repeated nanocasting[14,16] has recently been used to produce ordered mesoporous MgO from a CMK-3 template.[17]

A universal method to synthesize carbon aerogel is based upon an aqueous polycondensation of resorcinol with formaldehyde and subsequent supercritical drying with carbon dioxide, with subsequent carbonization of the polymer. However, the complexity of the supercritical drying limits extensive application of carbon aerogels. Hence, in the present work supercritical drying is replaced by ambient pressure drying to synthesize porous carbon aerogel, which is used in turn as template for magnesium oxide synthesis. The textural parameters of the carbon aerogel can be flexibly tuned at the nanoscale by changing the synthetic conditions,[18−22] which could have an effect on the porous structure of the corresponding MgO products.

Experimental Section

Preparation of Carbon Aerogel and Mesoporous MgO. Carbon aerogels were synthesized through polycondensation of resorcinol with formaldehyde catalyzed by sodium carbonate. Resorcinol (Fluka 99%), formaldehyde (Fluka 36.5% in water, methanol-stabilized), and sodium carbonate (Fluka 99.5%) were dissolved in deionized water under stirring with a magnetic stir bar to get a homogeneous solution. After thermal curing (1 day at room temperature, 1 day at 50 °C, and 3 days at 90 °C), the wet gels were introduced into acetone to exchange the water inside the pores, then dried at room temperature under ambient pressure, and further pyrolyzed at temperatures of up to 800 °C under argon atmosphere and thus transformed into carbon aerogels. By varying the catalyst concentration and reactant content, a series of carbon aerogels with different structural parameters could be obtained. The detailed synthetic conditions are listed in Table 1.

Magnesium nitrate hexahydrate (Fluka 98%) was dissolved in deionized water to form the MgO precursor solution at a concentration of 3.83 M. By immersion of carbon aerogels in magnesium nitrate solution at room temperature, MgO precursors were introduced into the pore system of the carbon aerogels. After removal of the remaining solution and a subsequent drying step at 50 °C, white MgO products were generated by calcination at 600 °C for 8 h in a quartz tube under a flow of dry air to remove the carbon aerogel templates.

Characterization. X-ray diffraction patterns of the samples were recorded with a Stoe STADI P diffractometer in transmission geometry. Nitrogen adsorption isotherms were recorded with an ASAP2010 adsorption analyzer (Micromeritics) at 77 K. Before the sorption measurements, all samples were degassed at a temperature of 250 °C for at least 6 h. Pore sizes and pore size distributions were calculated by the BJH method from the desorption branches. Total pore volume was estimated from the amount adsorbed at $p/p_0 = 0.99$. Total surface areas were determined by the BET method. Mesopore surface areas and micropore volume of carbon aerogels were calculated by the *t*-plot method. Scanning electron microscopy (SEM) investigations were carried out with a Hitachi S-3500N instrument. For transmission electron microscopy (TEM) a Hitachi HF2000 microscope equipped with a cold field emission gun at a beam energy of 200 kV was used. The MgO sample was prepared on a lacey film in a glovebox.

Table 1. Synthetic Conditions and Texture Parameters of the Carbon Aerogel Templates

sample	C_{syn}[a]	S_{BET} ($m^2 \cdot g^{-1}$)	S_{meso} ($m^2 \cdot g^{-1}$)	V_{total} ($cm^3 \cdot g^{-1}$)	V_{mic} ($cm^2 \cdot g^{-1}$)	D_{max} (nm)
CA-1	20/200	578	249	0.41	0.15	5.8
CA-2	50/500	660	303	0.72	0.16	7.3
CA-3	50/1000	620	249	0.71	0.17	10
CA-4	30/500	697	299	1.14	0.18	12.9
CA-5	40/500	722	360	1.35	0.17	15.2

[a] C_{syn}: synthetic conditions of carbon aerogels. For example, 20/200 means the percentage of resorcinol and formaldehyde is 20% and molar ratio of resorcinol/sodium carbonate is 200; others represent the same meaning. S_{BET}: specific surface area calculated on the basis of the BET theory. S_{meso} and V_{mic}: mesopore surface area and micropore volume calculated with the *t*-plot method. V_{total}: single-point total pore volume. D_{max}: pore size with a maximum in the pore size distribution (desoption branch; CA-1 using adsorption branch).

Results and Discussion

The textural properties of the as-synthesized carbon aerogels were analyzed by nitrogen sorption. The isotherms of the carbon templates show pronounced type IV characteristics with well-developed H1 type hysteresis loops except for CA-1 (Figure 1a). The step gradually increases in size, and the closure points of the hysteresis loops clearly shift to higher relative pressures of 0.60−0.75 in the isotherms of sample CA-2 to CA-5. This indicates an enhanced volume adsorbed during capillary condensation and an increase of the corresponding pore size of the samples. Sample CA-1 shows a type IV feature but with H2 type loop in the relative pressure range of 0.40−0.80 (Figure 1a, insert), indicating the existence of ink-bottle-like pores with a narrow entrance and a large cavity. At relative pressures below 0.1, the high uptake for all carbon aerogels implies the presence of a large amount of micropores in all of the carbon aerogel templates, which should be a result of the carbonization process.[20,21]

The pore size distributions (PSDs) of the carbon templates were determined by the BJH model from the desorption branches except for sample CA-1. In the case of CA-1, its pore size calculated from the desorption branch is only related to a "neck effect" that normally leads to a very narrow PSD curve, which is not the true reflection of PSD of samples. This is due to the closure of the hysteresis around $p/p_0 = 0.42$ due to instability of the meniscus. The desorption branch was thus not used in order to avoid errors,[23] but instead the adsorp-

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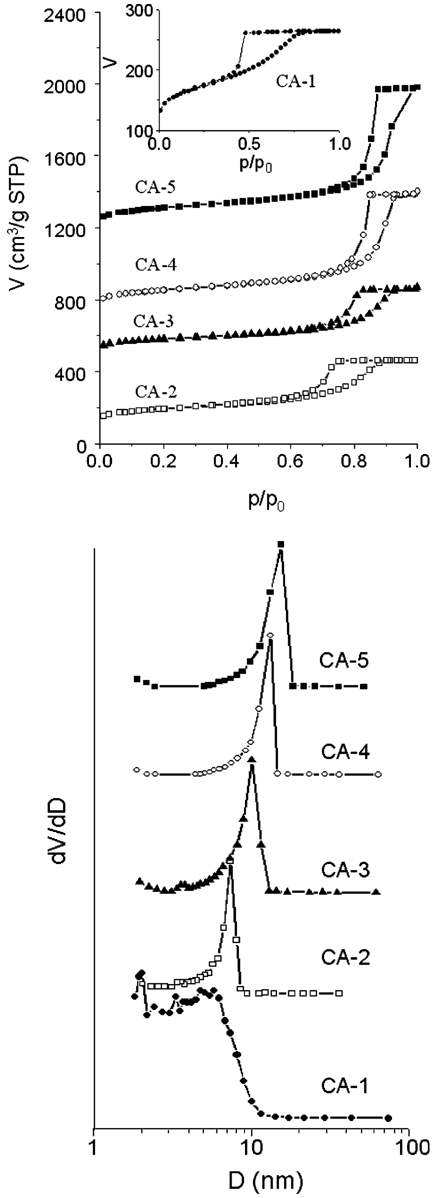

Figure 1. Nitrogen sorption isotherms of the carbon aerogels (insert isotherm is of CA-1) (a); the corresponding pore size distributions (b). The isotherms of CA-3, CA-4, and CA-5 were offset vertically by 400, 700, and 1100 $cm^3(STP)\cdot g^{-1}$, respectively.

tion branch has to be used to analyze the PSD of CA-1.[24] As shown in Figure 1b, the carbon templates basically have narrow PSDs, and the pore size with a maximum of the PSD curves shifts to larger values from sample CA-1 to sample CA-5. One should keep in mind, though, that the curve for sample CA-1 cannot be directly compared to the other curves, since use of the adsorption branch will lead to an overestimation of the pore size. The textural parameters as well as the synthetic conditions are compiled in Table 1. As can be seen, a series of carbon aerogels with a gradually increasing pore size from 5.8 to 15.2 nm can be produced by changing the synthetic conditions. The as-synthesized carbon aerogels have a high BET surface area of around 600−700 $m^2\cdot g^{-1}$, of which about half can be attributed to mesopore surface area.

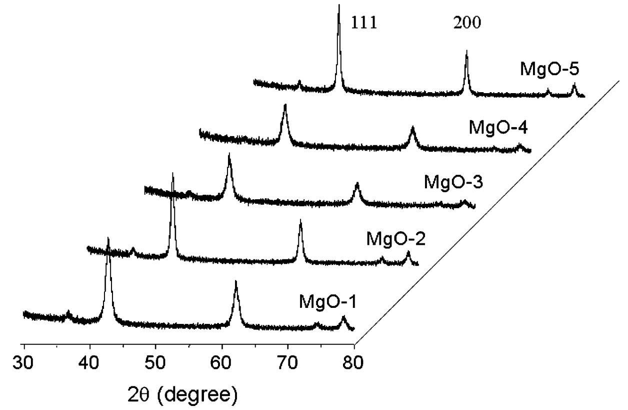

Figure 2. XRD patterns of the mesoporous magnesium oxides.

Table 2. Texture Parameters of the Mesoporous Magnesium Oxides

sample	CS[a] (nm)	S_{BET} ($m^2\cdot g^{-1}$)	S_{meso} ($m^2\cdot g^{-1}$)	V_{total} ($cm^3\cdot g^{-1}$)	V_{mic} ($cm^3\cdot g^{-1}$)	D_{max} (nm)
MgO-1	19	127	111	0.42	0.005	7.2
MgO-2	13	153	130	0.65	0.01	10.9
MgO-3	12	154	128	0.66	0.01	12.6
MgO-4	10	151	119	0.73	0.01	13.2
MgO-5	19	86	72	0.42	0.006	17.8

[a] CS: mean crystallite size determined by application of Scherrer equation from powder data in the 2θ range of 30−80°.

The above-synthesized carbon aerogels as templates were soaked in the concentrated magnesium nitrate solution. After drying and calcination, the magnesium oxides were obtained, which are further referred to as MgO-1, MgO-2, ..., MgO-5, respectively, where the number represents the relation between the carbon aerogel templates and the obtained magnesium oxides. The obtained MgO products were analyzed by wide-angle X-ray diffraction (XRD) measurement, and the XRD patterns are shown in Figure 2. All of the peaks can be readily assigned to a pure phase of periclase MgO [JCPDS 71-1176], which basically proves the formation of a homogeneous compound with rock salt structure.[8] The mean sizes of the crystalline domains calculated from the Scherrer equation are listed in Table 2. As can be seen, the MgO products consist of nanocrystals with an average size of 10−20 nm. The typical morphologies of the carbon template parent (for the example of CA-4) and its corresponding MgO product (MgO-4) were visualized by SEM measurement. The image shows that it is not easy to identify the particle feature of the carbon aerogel in SEM due to the small size of individual carbon particles. The morphology is monolithic on the micrometer scale, with the particles having a coarse surface (Figure 3). On the other hand, the MgO sample exhibits a somewhat different morphology compared to its original carbon template. Many irregular particles with macropores between them can be easily found in the MgO product (Figure 3). This is probably due to fragmentation during carbon combustion due to the lower volume of the MgO formed.

More information about the pore structure of the carbon template and the resulting MgO are revealed by transmission electron microscopic. As seen in Figure 4, the carbon aerogel exhibits a uniform structure with a

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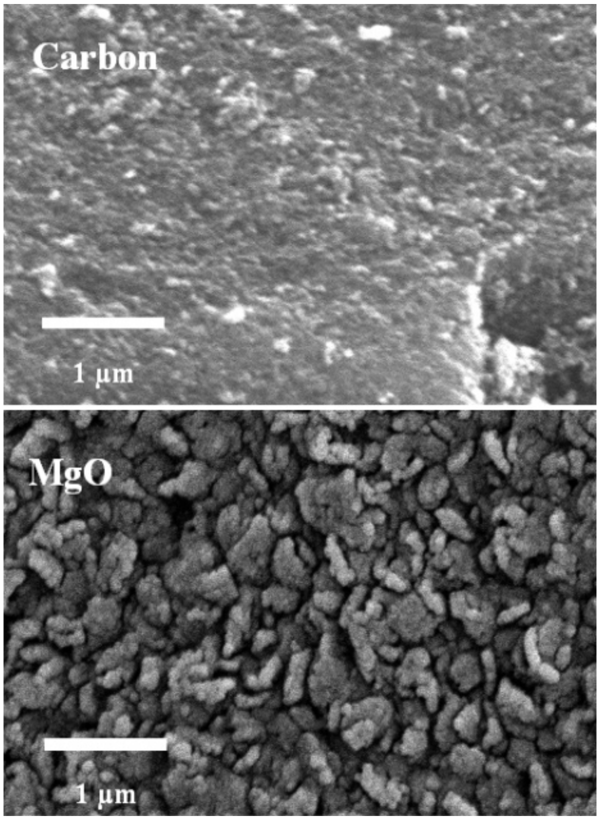

Figure 3. SEM images of carbon aerogel template (CA-4) and the corresponding mesoporous magnesium oxide (MgO-4).

well-defined three-dimensional network consisting of roughly spherical carbon particles. The estimated diameters of the spherical particles are around 10−15 nm. These primary particles are cross-linked with each other to form the abundant textural mesopores in the carbon aerogels.[19] In Figure 4, the TEM image of the MgO shows that also the MgO has a three-dimensional network consisting of well-developed, also roughly spherical particles. The estimated particle sizes are around 8−10 nm on the basis of the high-resolution TEM (Figure 4 insert). This value is in good agreement with the results provided by XRD, which gave a domain size of 10 nm (Table 2). Comparing Table 1 and Table 2, one can see that the pore sizes of the carbon aerogel templates roughly correspond to the particle sizes of the MgO formed, as would be expected for a nanocasting process. Additionally, EDX measurements with TEM show that the obtained MgO consists of Mg and O with an atomic ratio of 1:1. Elemental analysis confirmed that the residue of carbon in the final MgO product was below 0.4 %. This demonstrates that nearly complete removal of the carbon template from MgO by calcination at 600 °C for 8 h can be achieved.

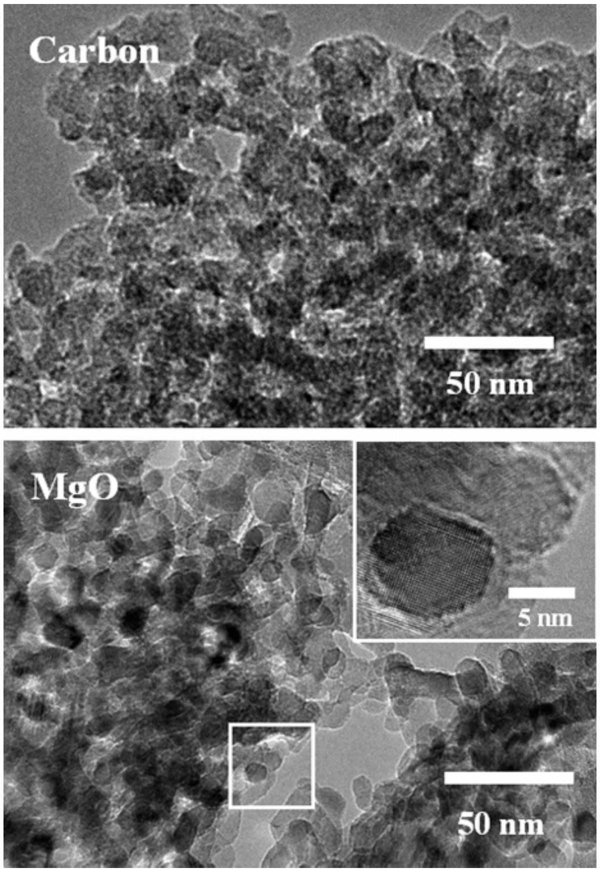

Figure 4. TEM images of the carbon aerogel template (CA-4) and the corresponding mesoporous magnesium oxide (MgO-4).

Figure 5 shows the nitrogen sorption isotherms and the corresponding pore size distributions of the obtained MgO samples. The isotherms of MgO exhibit type III characteristics with a significant type H3 loop (Figure 5a). The type H3 loop, which does not clearly exhibit any adsorption plateau at relative pressures close to unity, is usually related to existence of slit-shape pores in materials.[25] It is also indicative of a pore size distribution extending into the macropore range, a fact which is also clear from the SEM image in Figure 3. Obviously, TEM, SEM, and nitrogen sorption measurements are consistent with each other.

The results presented above reveal that the textural characteristics of MgO are different from those of the parent carbons. The amount adsorbed at low pressure of the nitrogen adsorption isotherms is nearly negligible, which basically indicates the MgO products have essentially mesoporous character. This can be attributed to the formation of dense crystalline material in the pores of the carbon template from the nitrate precursor. Either the micropores of the carbon are therefore not filled by the precursor solution or the very small MgO particles which form in the micropores coalesce during thermal treatment.

Additional microporosity could possibly be created, if the precursor in the pores is first transformed to brucite, which is topotactically converted to periclase.[26] The textural parameters of the obtained MgO samples determined by nitrogen adsorption analysis are listed in Table 2. Despite the calcination at 600 °C for 8 h, the MgO still has BET surface area up to of 150 m^2/g, which is comparable or even higher than those of other MgO products synthesized by surfactant-assisted methods,[6] thermal decomposition,[7] or gel−template method.[10] The mesopore surface area of the MgO estimated by the *t*-plot method is essentially equal to the total BET

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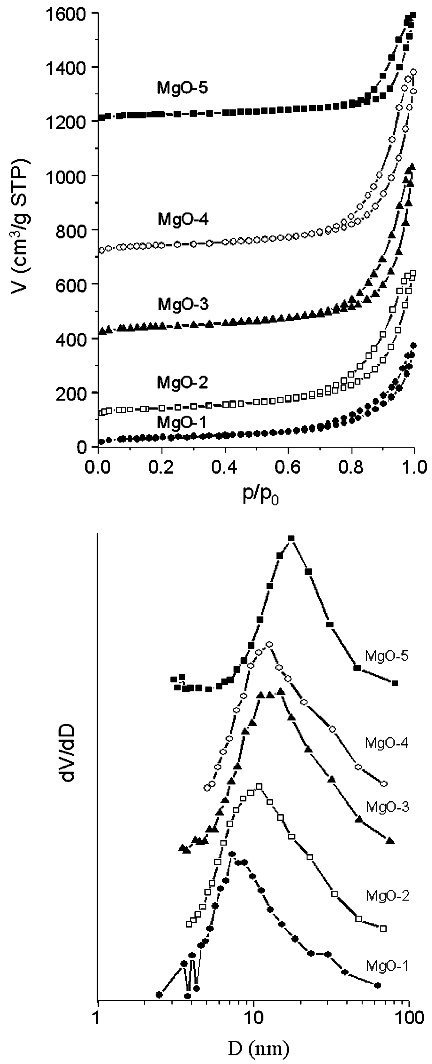

Figure 5. Nitrogen sorption isotherms of the magnesium oxides (a) and the corresponding PSDs (b). The isotherms of MgO-2, MgO-3, MgO-4, and MgO-5 were offset vertically by 200, 400, 600, and 1100 $cm^3(STP) \cdot g^{-1}$, respectively.

surface area. This further verified that the porosity of the MgO mainly due to the contribution of mesopores. The micropore volumes calculated from the *t*-plot method are extremely low compared to those of the carbon templates. Since no proper reference isotherm for MgO was available, a standard isotherm for silica was used as reference. The values determined should therefore not be taken at face value but rather as indicative to recognize the trends. The pore size distributions of the MgO exhibit a single peak shape, but they are substantially broadened as compared to the carbon templates. They cover the range of 5−40 nm and even extend with a small contribution into the macropore regime (Figure 5b). The pore sizes sequentially increase from 7.2 to 17.8 nm for samples MgO-1 to MgO-5, with pore size of the corresponding carbon template from 5.8 to 15.2 nm. That is, the larger the pore size of carbon templates, the larger the pore sizes of the resultant MgO products by this hard-templating pathway. One would expect a direct relationship between the pore size of the MgO and the carbon particle sizes of the carbon aerogels. However, these carbon particle sizes are difficult to assess. Generally, it can be stated that larger carbon particle sizes correspond to large pore sizes in the aerogels, so that a trend in pore size also reflects a trend in particle size.

The larger mesopores in MgO would be very efficient for mass transfer of reactants in catalytic reactions, especially in liquid-phase processes, and reactant molecules can easily access the active sites present in the materials.[27] Comparing the textural parameters of the carbon template and the MgO products in Table 1 and Table 2, one can conclude that the specific surface area (S_{BET}), mesopore surface area (S_{meso}), and total pore volume (V_{total}) of the carbon aerogels increase continuously from CA-1 to CA-5. As expected for a nanocasting process, the corresponding MgO products retain this sequentially increasing trend from MgO-1 to MgO-4 except for sample MgO-5, which has a relatively low surface area of only 86 $m^2 \cdot g^{-1}$. As seen in the TEM (Figure 4), the mesopores of MgO predominantly result from the aggregation of MgO nanoparticles. In Table 2, the results of the XRD measurement show that MgO-5 consists on average of 19-nm-sized crystallites. Such relatively larger particles lead to materials with an obvious large pore size compared with the other MgO products. This causes the decrease of the surface area as well as of the pore volume. MgO-1 also has a domain size of 19 nm, but a higher surface area at identical pore volume as MgO-5, which indicates smaller average pore sizes, as also seen in the PSD. This is probably due to a different packing of the particles, which are templated by the much smaller pores of CA-1. The results of all analyses give clear evidence that the carbon aerogel has the function of a hard template to create the mesoporous MgO.

Other mesoporous oxides, such as aluminas,[28] and possibly even spinels also can be prepared by the proposed pathway, just as it was possible to create a multitude of different oxides by the activated carbon pathway.[15] Carbon aerogel templating might thus be generalized to other mesoporous materials. The presently employed templates, carbon aerogels based on the polycondensation of resorcinol with formaldehyde, can be synthesized using ambient pressure drying instead of the traditional supercritical fluid drying. Compared to activated carbon templating, the pathway using carbon aerogels has several advantages, such as the high purity of the aerogel template and thus of the resulting oxide and the possibility to tailor the textural properties of aerogel and thus the oxide formed. Carbon aerogels are still more expensive than activated carbons, and therefore, the resulting materials have to be a benefit compared to the activated carbon derived ones for practical applications.

Conclusion

The present study demonstrates that mesostructured MgO materials can be synthesized by a hard-templating pathway using carbon aerogel as template and concentrated magnesium nitrate solution as MgO precursor. The morphology of the MgO product with three-

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dimensional network basically reflects the framework of the carbon template. Increase of the pore size of the carbon template essentially leads to MgO with an increased pore size. That provides a possibility to control the porous structure of MgO and possibly also that of other metallic oxides. The simplicity of the proposed method and relatively easy availability of both carbon template and magnesium precursor could be beneficial for a scale-up of the synthetic pathway.

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