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Mesoporous Carbon Prepared from Carbohydrate as Hard Template for Hierarchical Zeolites

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A mesoporous carbon prepared from sucrose was successfully employed as a hard template to produce hierarchical silicalite-1, thus providing a very simple and inexpensive route to desirable zeolite catalysts from widely available raw materials. The porous carbon was prepared by hydrothermal treatment of a mixture of sucrose and ammonia followed by carbonization of the mixture in N_2 at high temperatures. The porous carbon produced by this method was subsequently applied as a hard template in the synthesis of mesoporous silicalite-1 and removed by combustion after synthesis. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAD), thermal gravimetry (TG), differential scanning calorimetry (DSC), N_2 physisorption measurements, Hg porosimetry and CHN elemental analysis techniques were applied to investigate the porous carbon template as well as the mesoporous zeolite single-crystal material.

Introduction

Zeolites constitute an important class of crystalline microporous solids due to their widespread application in adsorption, separation and catalysis. Their importance stems from their unique pore structures, which make them highly selective to adsorbed molecules for separation purposes, or towards product molecules in catalysis. Moreover, they exhibit good thermal and hydrothermal stabilities during heterogeneous catalytic reactions.[1,2] However, the pore sizes of zeolites or zeolite-type materials, which are smaller than 1.5 nm, often restrict their applications due to diffusion limitations.[3]

Many strategies have been developed to overcome this problem, e.g. synthesizing larger-pore zeolite structures[4] and mesoporous molecular sieves,[5] reducing the size of the individual zeolite crystals,[6] subjecting the prepared zeolite to post-treatments like dealumination[7] and desilication,[8] as well as various hard template routes, where the template is removed after synthesis.[9] Naturally, pores created by post synthesis chemical treatments are highly dependant on the composition and structure of the original material, and a zeolite material consisting of nanosized crystals causes problems with handling during its applications. On the other hand, hard-template methods produce mesoporous zeolites with controlled porosity independent of their composition and structure, and have thus provided a general approach to solve this problem. So far, carbon blacks,[10] multiwalled carbon nanotubes,[11] carbon nanofibers,[12] carbon mesoporous molecular sieves,[13] carbon aerogels,[14–15] polymer aerogels,[16] and very recently mesoscale cationic polymers[17] have been utilized to fabricate zeolite materials which have a hierarchical pore system of intracrystalline mesopores interconnected with the conventional micropores.

Recently, mesoporous carbons have found application as hard templates for the production of very porous metal oxides such as Al_2O_3[18] and MgO.[19] Furthermore, also binary metal oxides like $MgAl_2O_4$ have been successfully prepared by this strategy.[20] More importantly, mesoporous carbons can also be employed to cast hierarchical-porous zeolites with tailored mesoporosities.[14–16] Mesoporous carbons are conventionally prepared by carbonization of a carbon precursor on a mesoporous silica template such as MCM-48,[21] SBA-15,[22] or amorphous silica,[23,24] which is subsequently removed by dissolving it in either HF or NaOH. Another category of mesoporous carbons are the carbon aerogels, which are prepared by pyrolysis of resorcinol/formaldehyde aerogels in an inert gas at high temperatures.[25–27] These methods are very costly and/or tedious. Preparation of an aerogel, for instance, entails supercritical fluid treatments making it both expensive and complex in preparation. In this paper, we report a simple and convenient way to prepare a mesoporous carbon template and its application in the synthesis of mesoporous silicalite-1. Contrary to the previously reported methods that typically rely on the availability of special and often expensive mesoporous carbons obtained from only a few suppliers, the present method only involves chemicals that are widely

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available. The starting materials used here, sucrose and ammonia, are very inexpensive in comparison with aerogel precursors, and no sacrificial silica is needed. As carbon blacks are normally 100 times more expensive than sucrose, the outstanding features of the reported method are its simplicity, convenience and inexpensiveness.

Results and Discussion

Mesoporous Carbon Template

After hydrothermal treatment of a mixture of sucrose and ammonia for 2 d, a brown solid was obtained. N_2 physisorption measurements of this brown solid showed that it has a surface area of 34 m^2/g. In Figure 1 is shown a photographic image of the brown solid. It can be seen, that the brown solid retains the shape of the Teflon beaker in which it was produced and this allows for formation of larger zeolite objects though controlled templating.

Figure 1. Photographic image of the brown solid obtained after hydrothermal treatment of a mixture of sucrose and ammonia in a Teflon beaker. The porous carbon maintains the shape of the beaker.

From the TG and DSC measurements of the brown solid, shown in Figure 2, it can be seen that a major weight loss occurs between 400 and 500 °C. This is due to dehydration of the sucrose during decomposition. Above 500 °C, several endothermic peaks appear in the DSC profile. These are due to carbonization of the decomposed sucrose, since carbonization is an endothermic process. Hydrothermal treatment of the sucrose and ammonia mixture is necessary to obtain a porous carbon, because heating of sucrose directly causes melting and more complex decomposition, which results in non-porous carbon after thermal decomposition.

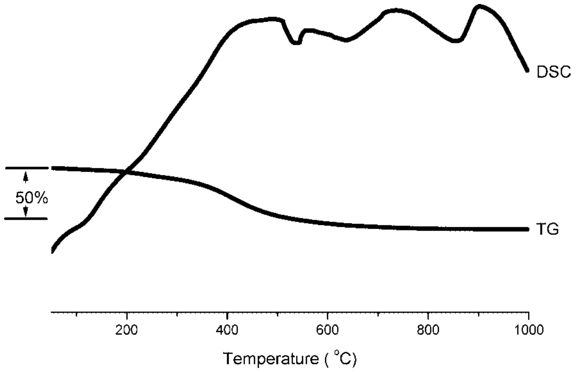

Figure 2. TG and DSC profiles of the solid obtained after hydrothermal treatment of a mixture of sucrose and ammonia.

Thermal decomposition of the brown solid at 850 °C in N_2 resulted in a porous black solid. This solid contained (by weight) 86.5% C, 1.17% N and 1.25% H, as examined by CHN elemental analysis. Thus, even after carbonization, minor amounts of nitrogen and hydrogen are present in the carbonaceous material. The remaining mass of the sample is most likely oxygen, which is not detected by this technique. Oxygen could easily be present in the carbonaceous material in the form of hydroxy groups.

N_2 adsorption and desorption isotherms of the porous black solid are shown in Figure 3. It can be seen that the isotherm contains a hysteresis loop which starts at a relative pressure of 0.8 and then rises dramatically with increasing pressure. According to the IUPAC classification of physisorption isotherms, isotherms featuring this type of hysteresis loops are classified as type IV isotherms, and are characteristic of mesoporous materials. From Figure 3 it is also evident, that the pore size distribution of the porous carbon is quite broad beginning at 10 nm and ending at more than 100 nm. Since the BET surface area of the carbon material presented here is only 416 m^2/g (further results from the physisorption analyses are listed in Table 1), the material is not superior to the known carbon aerogels, which possess surface areas above 1000 m^2/g and narrow pore size distributions.[27]

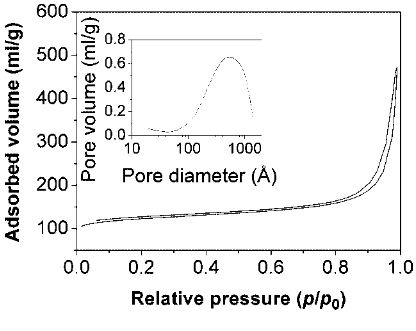

Figure 3. Nitrogen adsorption/desorption isotherms of the porous carbon obtained by carbonizing sucrose. The inset shows the pore size distribution obtained from the desorption branch of the isotherm using the BJH method.

Table 1. Surface area and porosity analyses of the mesoporous carbon template and the mesoporous silicalite-1 material obtained from it.[a]

	S_{BET} [m^2/g]	Micropore vol. [cm^3/g]	Meso- + macropore vol. [cm^3/g]	Mesopore size [nm]
Carbon	416	0.13	0.60	ca. 53
Meso silicalite-1	403	0.09	0.37	ca. 31

[a] The micropore volume is estimated from a *t* plot (DeBoer) and total pore volumes were calculated based on volume adsorbed at a relative pressure of p/p_o = 0.99, volumes of mesoporosity and macroporosity are calculated accordingly.[15]

However, given that the mesoporous carbon prepared in this way works well as a template in the synthesis of hierarchical zeolites, as will be shown later, the specific porosity properties of the material are not important.

Mesoporous Silicalite-1

After crystallization of a zeolite gel mixture adsorbed on the porous carbon and subsequent calcination of the crude product in air, a white powder was obtained. The XRD pattern obtained for this powder is shown in Figure 4: the material contains exclusively highly crystalline MFI-structured material, since no peaks from other crystalline materials are observed in the pattern and there is no amorphous background. Thus, the prepared sample is a phase-pure silicalite-1 material. The peaks in the XRD diagram shown in Figure 4 are broader than the peaks observed in XRD patterns of conventional microporous ZSM-5 samples (also of MFI framework structure). This appears to be a general phenomenon in all XRD patterns of mesoporous zeolites produced by carbon templating. Even though the overall crystal sizes are similar in conventional and mesoporous samples, the XRD line width of the mesoporous samples always shows significant broadening. Thus, it is not possible to differentiate between nanosized and mesoporous zeolite samples from XRD analyses alone. However, the line broadening is still indicative of the porous carbon functioning as a chemically inert hard template during the crystallization of the zeolite.

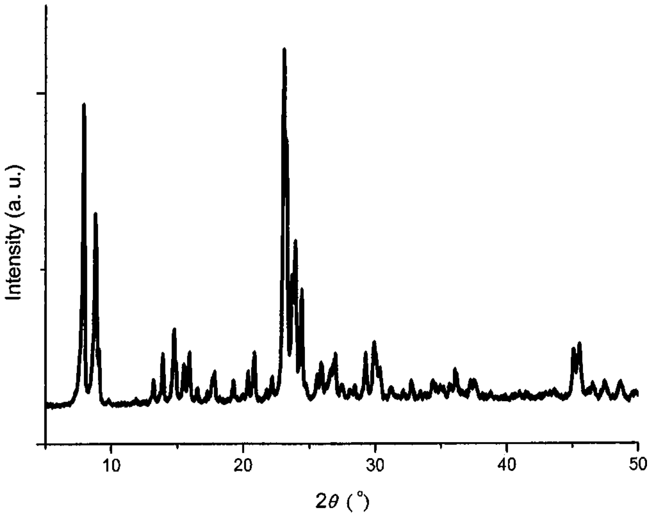

Figure 4. XRD pattern of the prepared silicalite-1 material.

In Figure 5 is shown the nitrogen physisorption isotherms of the mesoporous silicalite-1 material. It can be seen, that the isotherms contain two hysteresis loops, one at relative pressure below 0.4 and one starting at relative pressure 0.9. The hysteresis loop at a low relative pressure is commonly observed for microporous silicalite-1 and results from a phase transformation of dinitrogen inside the micropores of the pure silica MFI structure.[9] The hysteresis loop starting at a relative pressure of 0.9 is a type IV isotherm, which indicates that the material contains mesoporosity. Besides a micropore volume of 0.09 mL/g, the material contains an additional pore volume of 0.37 mL/g, attributable to mesopores and macropores. This is calculated from the total volume of N_2 adsorbed by the material at a relative pressure of P/P_o = 0.99. The pore size distribution of the mesoporous silicalite-1 is relatively narrow and centered at 31 nm, which is comparable to mesoporous zeolites prepared from other carbon templates.[10,14–16] The findings from nitrogen physisorption are completely verified by Hg intrusion data, which also reveal that some larger macropores, which cannot be seen efficiently by physisorption, are present. They are attributed to intercrystal voids in the material. The similarity of the physisorption data and the Hg porosimetry data confirms what has been found before: the pore system of the zeolite consists of an interconnected and homogeneously distributed system of intracrystalline mesopores that completely penetrate the crystals. Thus, since the newly developed procedure presented here clearly produces a hierarchical microporous/mesoporous material, which exhibits porosity similar to that of mesoporous silicalite-1 materials prepared using carbon blacks[10] and carbon aerogels as templates,[14–16] it is preferable when considering the complex nature of the carbon aerogel preparation and its high cost.

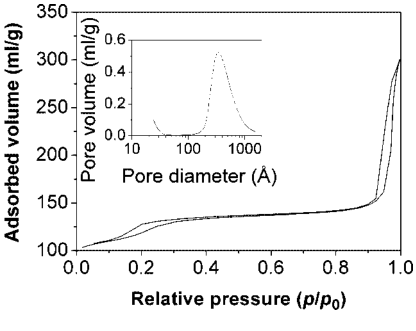

Figure 5. Nitrogen adsorption/desorption isotherms of the mesoporous zeolite silicalite-1 material after combustion of the carbon and organic templates. The inset shows the pore-size distribution obtained from the desorption branch of the isotherm using the BJH method.

A comparison of the pore-size distributions of the porous carbon and the silicalite-1 material (Figures 3 and 5) clearly points out that a mesoporous zeolite with a relatively narrow pore size distribution can be produced from a porous carbon having a much more broad pore size distribution. This suggests that the mesoporous silicalite-1 crystals start to grow inside the pores of the carbon matrix and during crystallization gradually encapsulate the carbon. Thus, since the porosity of the zeolite is a negative replica of the carbon template, the specific pore size distribution of this template is less important. This tendency has also been observed for mesoporous zeolites templated from different carbon blacks, since not all carbon blacks are able to efficiently produce mesoporous zeolites.[12] In this light, the route to mesoporous zeolites presented here is superior to carbon-black-based methods because, using the method reported here, it is not possible to alter the porosity of the carbon matrix by pushing aside the carbon particles during zeolite growth.

Figure 6 shows the results of SEM analyses of the prepared mesoporous silicalite-1 after combustion of the carbon and organic templates. Figure 6a shows a low-magnification SEM image of the prepared material: the sample contains only impressively homogeneously sized single crystals, which can be seen all over the sample. From the higher resolution images, shown in Figure 6b–d, it can easily be seen that the single crystals are all sponge-like in appearance, which is a characteristic feature of mesoporous zeolites. Moreover, the coffin-like morphology exhibited by the mesoporous single crystals is typical of MFI-structured crystals. Furthermore, this mesoporous silicalite-1 material is quite similar to the one reported by Jacobsen using commercially available carbon black as hard template,[10] and it is different from carbon-aerogel-templated mesoporous silicalite-1 which contains a mixture of nanosized crystals and larger mesoporous monocrystals.[14] However, in the carbon-aerogel-templated systems the zeolite properties can be influenced by the crystallizations conditions.[14–16] This can probably be ascribed to different crystallization kinetics in the various carbon matrix materials. Thus, zeolite crystallization in the confined space of the carbons leads to nanosized crystals instead of the mesoporous crystals obtained when the zeolite encapsulates the carbon particles. From the SEM analyses of the prepared zeolite material it is concluded that the present sample contains exclusively mesoporous silicalite-1 single crystals. Here, we only show the use of a specific carbon produced by carbohydrate decomposition. However, it can be envisaged that a wide range of different carbons can be produced with this approach, and that could lead to possibilities for tuning the zeolite mesopore size just as it is possible with different carbon black materials.

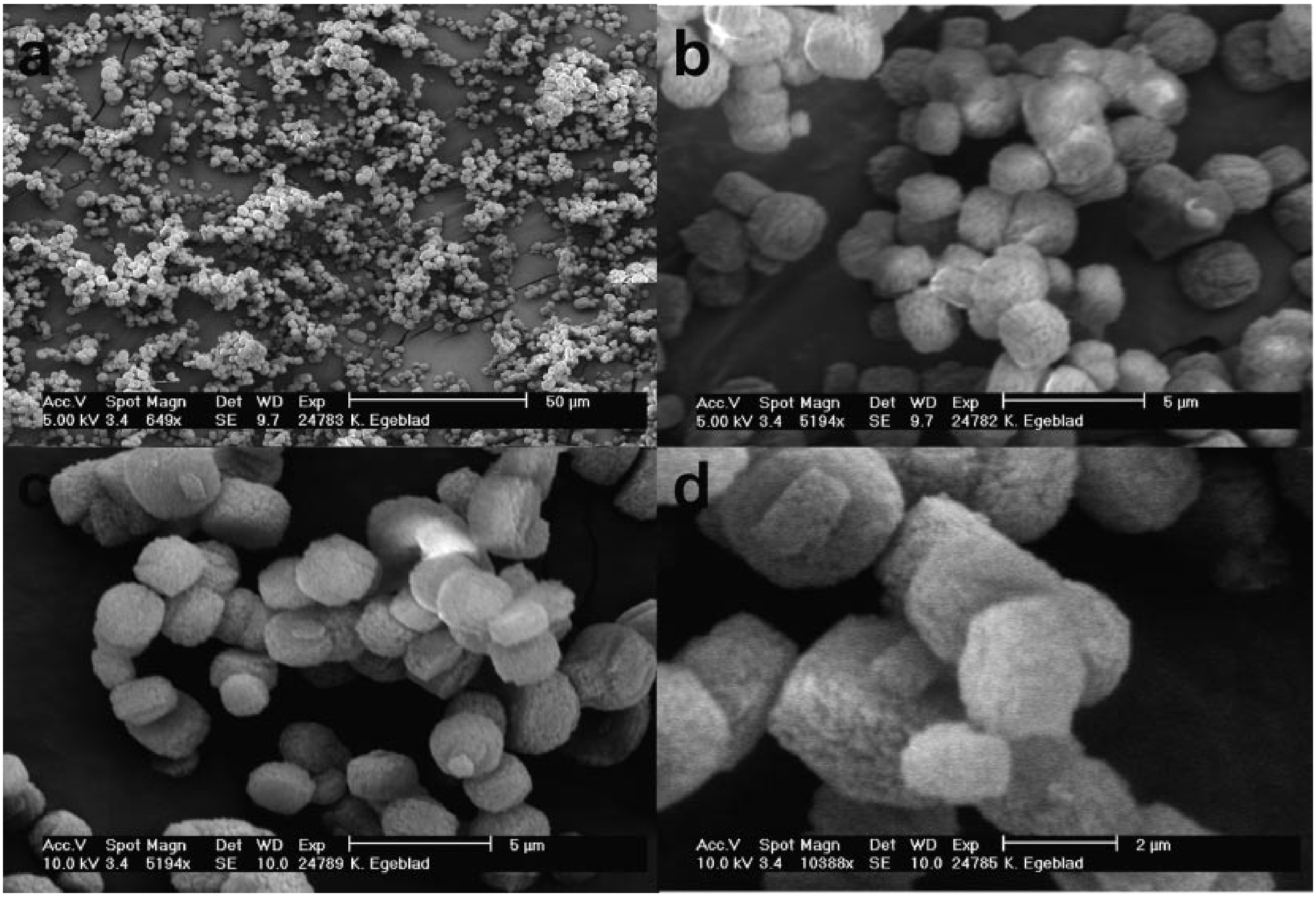

Figure 6. SEM images of the mesoporous silicalite-1 single crystals at different magnifications.

From the TEM images of the prepared mesoporous silicalite-1 material shown in Figure 7 it is evident, that the material does indeed consist of mesoporous single crystals as the sponge-like coffin shape is readily identifiable in these images. The close-up TEM image shown in Figure 7b along with the SAD pattern shown in its inset unambiguously confirms the single-crystalline nature of the materials.

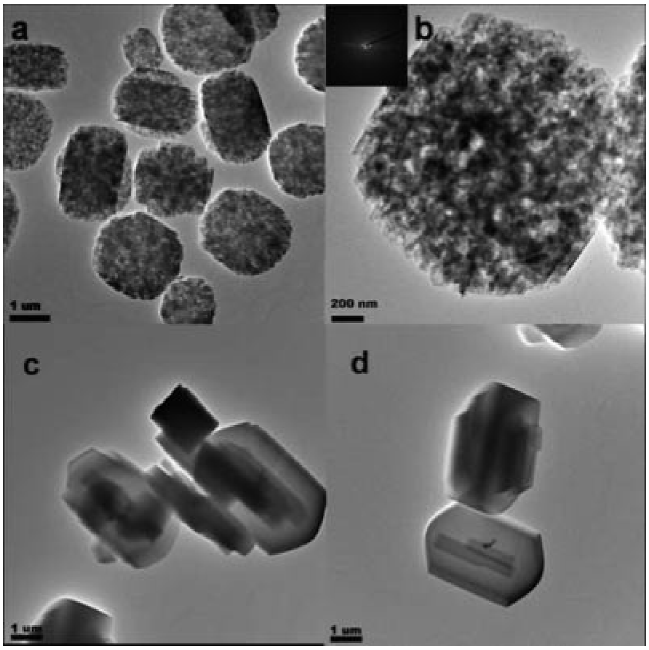

Figure 7. TEM images of the mesoporous silicalite-1 single crystals. The inset in (b) shows the SAD pattern of the area marked by a circle in the image, c) and d) show images of analogously prepared zeolite without the carbon template.

Conclusions

Mesoporous zeolite single crystals of MFI structure were synthesized from cheap and readily available starting materials using a newly developed and very simple procedure in which an in-situ prepared mesoporous carbon is used as a mesopore template during synthesis and subsequently removed by combustion. XRD, SEM, TEM, SAD and N_2 physisorption measurements of the prepared zeolite material showed that the material contained exclusively mesoporous silicalite-1 single crystals, which are very similar to those obtained using much more expensive carbon black as the mesopore template. N_2 physisorption measurements of the carbon template showed that this material was in fact mesoporous, although not as porous as carbon aerogels. However, since the carbon template can obviously be used for the synthesis of mesoporous zeolite single crystals, the specific porosity of the carbon template is perhaps not so important. Nevertheless, understanding the mechanisms leading to the mesoporous carbon as well as its specific role in templating mesoporous zeolites might lead to mesoporous zeolites with even better properties. In all, the simple procedure presented here, combined with the comparatively cheap carbon matrix, make this method attractive for the synthesis of other zeolite or zeolite-type structures or perhaps even other oxide materials.

Experimental Section

Hierarchical microporous/mesoporous silicalite-1 single crystals were obtained after combustion of a zeolite/carbon composite material, prepared by first producing a mesoporous carbon template material onto which the necessary zeolite gel components were impregnated and subjected to hydrothermal conditions.

The porous carbon template was prepared by dissolving 13.1 g of sucrose (98 %, Aldrich) in a mixture of 9.6 mL of EtOH (absolute), 7.5 mL of H_2O (deionized) and 1.0 mL of ammonia (25 wt.-%, Fluka) whilst stirring at 50 °C for 1.5 h. The material was transferred to a Teflon beaker and hydrothermally treated at 180 °C for 2 d, producing a brown solid which retained the shape of the beaker. The brown solid was crushed in a mortar and transferred to a horizontal tube furnace and heated to 850 °C in a flow of N_2 for 5 h to afford a porous black carbonaceous solid.

Mesoporous silicalite-1 single crystals were prepared by sequentially impregnating the necessary zeolite gel components onto the porous black carbonaceous solid. First, a mixture of 3.4 g of TPAOH (tetrapropylammonium hydroxide, 40 wt.-%, Aldrich) and 2.0 mL of EtOH was impregnated onto 2.5 g of porous black solid and the mixture was dried in air under ambient conditions overnight. Then, the material was impregnated with 3.0 mL of TEOS (tetraethyl orthosilicate, 98 %, Aldrich) which was allowed to hydrolyze in air for 1 d. After aging, the material was transferred to a Teflon beaker which was placed inside a Teflon-lined autoclave with 10.0 mL of H_2O added outside the beaker. The autoclave was hydrothermally treated at 180 °C for 3 d before the carbon and organic templates were removed by combustion at 550 °C for 24 h.

XRD was performed with a Philips PW 3710 X-ray diffractometer using Cu-K_α radiation (λ = 0.154 nm) in the 2θ range between 5 and 50° at a scanning speed of 0.6°/min.

Nitrogen adsorption/desorption isotherms were collected at liquid-nitrogen temperature (–196 °C) with a Micromeritics ASAP 2020. All samples were outgassed under vacuum at 200 °C overnight prior to measurement. The total surface area was calculated according to the BET method. Mesopore volumes were determined by the BJH method from the desorption branch of the isotherms, while micropore volumes and external surface areas were determined by using a *t*-plot analysis.

Hg porosimetry was measured by intrusion using a Quantachrome equipment.

SEM was performed with a Philips XL20 FEG. The calcined zeolite samples were placed on a carbon film and Pt was evaporated onto the sample for approximately 20 min to achieve sufficient conductivity.

TEM was performed with a JEM 2000FX using an accelerating voltage of 300 kV. SAD was used to obtain electron diffraction patterns from individual grains of powder. A few mg of the powdered samples were suspended in 2 mL of ethanol, and the suspension was sonicated for 1 h. Then, the suspension was allowed to settle for 15 min, before a drop was taken and dispersed on a 300 mesh copper grid coated with holey carbon film.

TG and DSC were conducted with NETZSCH STA 409 PC/PG equipment with a ramp of 20 °C/min under a nitrogen flow of 20 mL/min.

CHN elemental analysis was performed with a CE Instruments FLASH 1112 Series EA.

Acknowledgments

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