Sorption and Separation of CO_2 via Nanoscale AlO(OH) Hollow Spheres

Sara Simonato, Henriette Gröger, Jens Möllmer, Reiner Staudt, Angela Puls, Frieder Dreisbach, and Claus Feldmann*

Supporting Information

Synthesis of nanoscale AlO(OH) hollow spheres

The synthesis of nanoscale AlO(OH) hollow spheres was performed as described elsewhere (cf. [11]). In general, the micellar system was established by *n*-hexane as the non-polar dispersant phase, a mixture of methanol and water (1:1) as the polar phase, cetyltrimethylammonium bromide (CTAB) as surfactant and *1*-hexanol as cosurfactant. At ambient temperature, Al(*sec*-OC$_4$H$_9$)$_3$ was added to the dispersant phase of the equilibrated, transparent *w/o*-microemulsion and left to react for 12 h. The as-prepared hollow spheres were collected as a colorless solid by centrifugation and purified by sequential resuspension/ centrifugation in/from isopropanol. Finally, the as-prepared AlO(OH) hollow spheres were dried for 12 h while concurrently increasing the temperature ($293 \rightarrow 333$ K) and reducing the pressure ($1 \rightarrow 10^{-3}$ mbar) to remove all water/methanol inside of the inner cavity.

Transmission electron microscopy (TEM) of the as-prepared AlO(OH) hollow spheres was performed on a Philips CM 200 FEG/ST microscope, operating at 200 kV. TEM samples were prepared by ultrasonic nebulisation of γ-AlO(OH) suspensions in pentane on a holey carbon-film copper grid.

X-ray powder diffraction (XRD) and selective area electron diffraction (SAED) of nanoscale AlO(OH) hollow spheres

Chemical composition and crystallinity of the as-prepared γ-AlO(OH) hollow spheres are confirmed by X-ray powder diffraction pattern as well as by selective area electron diffraction (Figure S1). Both are in agreement to the expected Bragg peaks as reported for reference data. With regard to the XRD pattern the following aspects have to be considered. First, the scattering power is comparably weak due to the very thin crystalline sphere wall. Therefore, the Bragg peaks are broad and observed with low intensity. Second, the crystalline sphere wall does definitely not represent an isotropic bulk-crystal. As a consequence, the intensity as

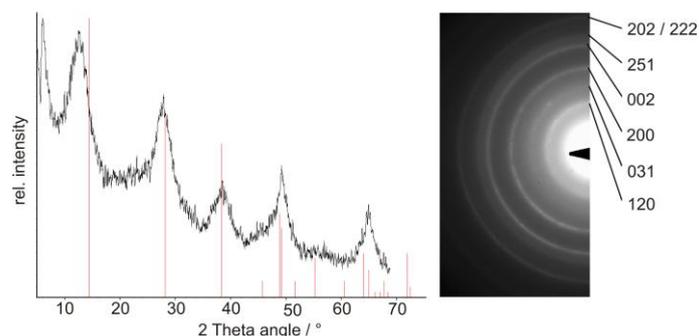well as the position of the Bragg peaks to a certain extent is different from what is given as reference data.

Figure S1. X-ray powder diffraction (XRD) and selective area electron diffraction (SAED) of as-prepared γ-AlO(OH) hollow spheres indicating its crystallinity and chemical composition (ICDD-No. 21-1307, γ-AlO(OH) – boehmite).

Thermogravimetry (TG) of nanoscale AlO(OH) hollow spheres

The thermal properties of the as-prepared AlO(OH) hollow spheres were studied based on thermogravimetry. Since the hollow spheres were synthesized at the water-to-oil phase boundary of water/methanol-filled micelles, the as-prepared nanomaterial contains large quantities of water and methanol. To this concern, TG shows a continuous weight loss of up to 31% at temperatures below 200 °C due to the evaporation of water/methanol located inside of the inner cavity of the hollow spheres (Figure S2). Careful drying is required to remove this amount of water and methanol without destructing the hollow sphere structure (cf. results and discussion section). At even higher temperatures (200−500 °C) the TG of the AlO(OH) hollow spheres shows an additional weight loss of 14% due to the transformation of AlO(OH) to Al_2O_3 (calc. 15%).
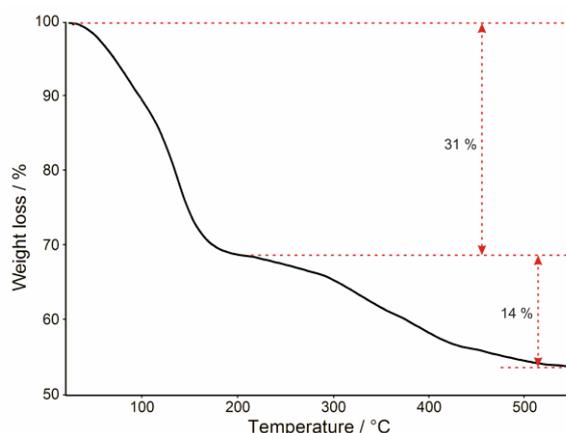

Figure S2. Thermogravimetry (TG) of as-prepared AlO(OH) hollow spheres (total sample weight: 49 mg).

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Comparison of as-prepared nanoscale AlO(OH) hollow spheres and massive AlO(OH) nanoparticles as a reference

In order to verify the unique properties of the as-prepared nanoscale AlO(OH) hollow spheres, massive AlO(OH) nanoparticles with similar particle diameter and chemical composition – but without an inner cavity – have been applied and compared as a reference. Aiming at a reliable reference material that is independently available from our research activities, we have purchased AlO(OH) nanoparticles with a diameter of 10–20 nm from SkySpring Nanomaterials Inc., Houston, Texas. This reference material was treated and investigated similarly as the as-prepared hollow spheres.
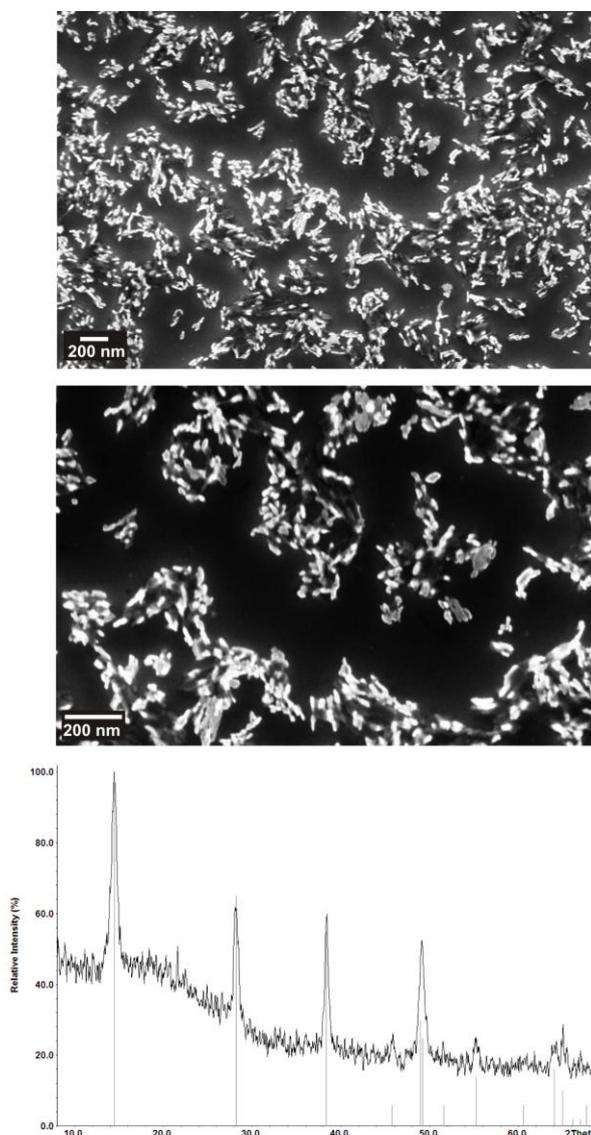

Figure S3. Particle size, composition and crystallinity of massive AlO(OH) nanoparticles (reference material: SkySpring Nanomaterials Inc.) according to electron microscope (SEM) and X-ray powder diffraction (ICDD-No. 21-1307, γ-AlO(OH) – boehmite).

Electron microscopy and X-ray powder diffraction analysis confirm the specifications as given by the supplier. Thus, the massive AlO(OH) nanoparticles exhibit uniform size and shape with particle diameters ranging from 10 to 30 nm (Figure S3). The reference sample was identified as crystalline boehmite with a mean crystallite diameter of 23 nm deduced via the Scherrer equation. While these characteristics are very similar to the as-prepared nanoscale hollow spheres (cf. Figures 1 and S1), the massive AlO(OH) nanoparticles are indeed well suited as a reference material. Fourier-transformed infrared spectra confirm the similarity of the hollow spheres as well as of the massive AlO(OH) nanoparticles (Figure S4). The more narrow shape of the vibrations in case of the massive nanoparticles is in accordance to the larger crystallite size as compared to the hollow spheres exhibiting an inner cavity.
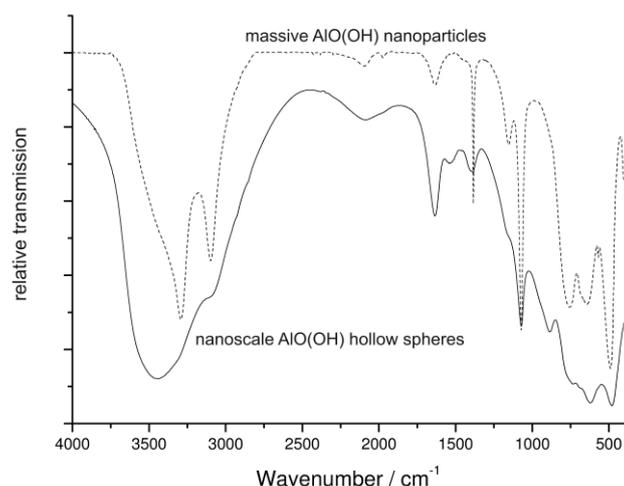

Figure S4. FT-IR spectra of as-prepared nanoscale AlO(OH) hollow spheres and massive AlO(OH) nanoparticles (reference material: SkySpring Nanomaterials Inc.).

Based on the similarity of size and composition of the as-prepared nanoscale AlO(OH) hollow spheres and the massive AlO(OH) nanoparticles, gas sorption and specific surface of both nanomaterials were compared. Already nitrogen sorption of the reference material turned out as significantly different as compared to the hollow spheres (Figure S5). In contrast to the hollow spheres (cf. Figure 2) only a minor hysteresis between N_2 adsorption and N_2 desorption is observed. Moreover, the specific surface as deduced via the Brunauer-Emmett-Teller formalism with 117 m^2g^{-1} is much lower. This finding is in accordance with the absence of an inner cavity in case of the massive AlO(OH) nanoparticles. With regard to CO_2 sorption, massive AlO(OH) nanoparticles were similarly pre-treated as the hollow spheres (Figure S6). The maximal CO_2 uptake of the reference material (80 mg g^{-1}) is again much lower as compared to the hollow spheres (260 mg g^{-1}). A CO_2 uptake being more than three-

times as high as for massive AlO(OH) nanoparticles again points to the special properties of the as-prepared nanoscale AlO(OH) hollow spheres.
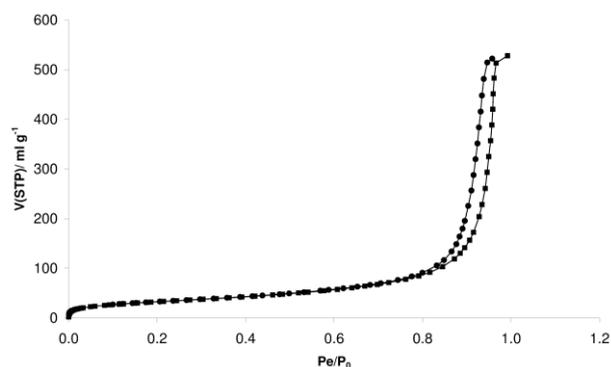

Figure S5. N_2 sorption of massive AlO(OH) nanoparticles at 77 K (reference material: SkySpring Nanomaterials Inc.).
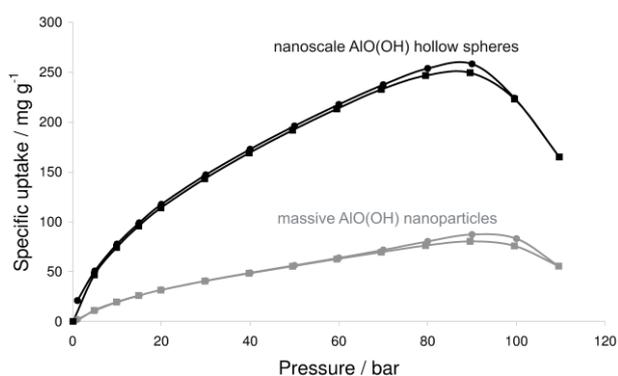

Figure S6. Comparison of CO_2 sorption isotherms of as-prepared nanoscale AlO(OH) hollow spheres and of massive AlO(OH) nanoparticles (reference material: SkySpring Nanomaterials Inc.): pretreatment (i.e. removing all water from the nanoparticles) at 423 K and CO_2 sorption analysis at 373 K.