

Polyol-mediated synthesis of nanoscale $\text{Mg}(\text{OH})_2$ and MgO

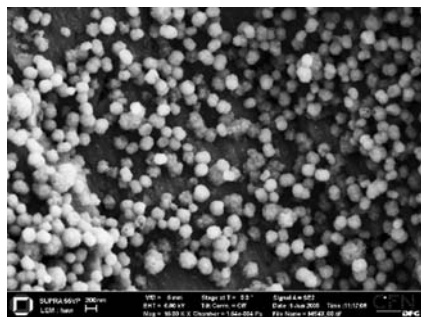
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Abstract Nanoscale $\text{Mg}(\text{OH})_2$ and MgO is prepared via a polyol-mediated synthesis. With concern to the experimental conditions, spherical particles, 20 and 100 nm in size are realized. Dynamic light scattering proves the presence of non-agglomerated and monodispersed $\text{Mg}(\text{OH})_2$ in as-prepared suspensions of diethylene glycol. Based on the results of infrared spectroscopy, thermal analysis and X-ray powder diffraction, as-prepared $\text{Mg}(\text{OH})_2$ can be dehydrated at a surprisingly low temperature (300 °C) to form MgO with almost similar particle size and shape.

Graphical abstract Polyol-mediated Synthesis of Nanoscale $\text{Mg}(\text{OH})_2$ and MgO

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Introduction

Nanoscale $\text{Mg}(\text{OH})_2$ and MgO are of significant importance for different types of technical application. This includes heterogeneous catalysis, transparent fillers, various aspects of surface conditioning (e.g., hardening, UV-stabilization, flame protection), protective layers (e.g., in AC-plasma display panels), waste remediation as well as biomedical applications (e.g., as bactericide) [1–5]. The synthesis of nanoscale $\text{Mg}(\text{OH})_2$ and MgO so far has been predominately performed via gas-phase methods [6–9]. Especially thin compact layers of crystalline MgO have been successfully deposited on flat substrates (e.g., glass, ceramics, metal) by these measures. Since gas-phase methods entail non-protected surfaces, agglomeration of nanoparticles is normally observed. Agglomerated particles, however, are less suited for several of the above-mentioned applications.

In a liquid-type synthesis, particle agglomeration can be diminished upon addition of surface-active stabilizers. However, little is known with concern to the synthesis of nanoscale $\text{Mg}(\text{OH})_2$ or MgO in liquid media. On the one hand, precipitation from aqueous solution, and on the other hand, Mg -alcoholate based sol–gel synthesis have been described [4, 10–13]. In general, liquid-phase synthesis till now has resulted in $\text{Mg}(\text{OH})_2$ exhibiting a comparably broad size distribution. Moreover, adequate studies with concern to colloidal stability and particle agglomeration are lacking. Aiming at an alternative access to nanoscale $\text{Mg}(\text{OH})_2$ and MgO , here, a polyol-mediated synthesis is presented. Focus of this investigation is on the one hand the degree of agglomeration, and on the other hand on an application of low cost and less harmful chemicals. The latter is aimed to establish a process, which is in principle suited for industrial scale-up [14].

Experimental

Synthesis

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Aldrich), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (99%, Aldrich), NaOH (97%, Aldrich) and diethylene glycol (DEG, 99%, Acros) were used as starting materials. To realize nanoscale $\text{Mg}(\text{OH})_2$, 0.50 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (2.46 mmol) were dissolved in 25 ml of diethylene glycol (solution A). Second, 1.50 g NaOH (37.50 mmol) were dissolved in 3 ml of water and mixed with 25 ml of diethylene glycol (solution B). Under intense stirring and nitrogen flow, solution A was added to solution B, with the latter previously heated to 50 °C. A temperature of 50 °C was maintained for additional 30 min, thereafter increased to 240 °C, and again maintained for 10 min. During heating volatile compounds were distilled off. When cooled to room temperature, an opalescent suspension with nanoscale $\text{Mg}(\text{OH})_2$ in DEG was realized. This suspension was colloidally stable, containing spherical particles with a diameter of 100 nm. With a suited washing process, viz. three times performing centrifugation and resuspension from/in ethanol, nanoscale $\text{Mg}(\text{OH})_2$ was separated as a colorless powder. Finally, this powder was dried in air for 30 min at 80 °C in a drying oven.

$\text{Mg}(\text{OH})_2$, 20 nm in diameter was prepared similarly, however, with a reduced NaOH concentration of 0.78 g NaOH (19.50 mmol). Furthermore, solution A was added to solution B at a temperature of 100 °C, which was maintained for 30 min. Thereafter, the resulting dispersion was directly left to cool to room temperature.

Characterization

Dynamic Light Scattering (DLS) was conducted in polystyrene cuvettes with a Nanosizer ZS from Malvern Instruments. A Zeiss Supra 40 VP equipped with a field emission gun (samples sputtered with Pt, acceleration voltage of 10 kV, working distance of 3–5 mm) was used for *Scanning Electron Microscopy (SEM)*. *X-ray Powder Diffraction (XRD)* measurements were conducted with a Stadi-P diffractometer (Stoe) with germanium monochromatized CuK_α radiation. *Thermal Gravimetry (DTA-TG)* was performed on a Netzsch STA 409 device (samples in Al_2O_3 crucibles, N_2 atmosphere). A Bruker Vertex 70 FT-IR was used for performing *Infrared Spectroscopy (IR)*. All samples were measured in KBr pellets with a resolution of 4 cm^{-1} . *BET analysis* (BET = Brunauer–Emmett–Teller) was performed by nitrogen adsorption with a Belsorp-mini apparatus.

Results

Particle morphology and size distribution

Nanoparticle formation by hydrolysis of suited metal precursors in a multidentate, high-boiling alcohol at elevated temperature (150–300 °C) has been previously described for various metals and metal compounds [15–17]. In general, this so-called polyol-mediated synthesis is characterized by the chelating properties of the polyol, which limits the particle growth and which stabilizes the particle surface with concern to agglomeration. As a consequence of the comparably high temperatures of synthesis, crystalline nanomaterials can often be realized.

Aiming at a polyol-mediated synthesis of nanoscale $\text{Mg}(\text{OH})_2$ and MgO , however, decomposition of the liquid phase due to both, strongly alkaline conditions and elevated temperatures, has to be considered. To tackle both limitations, nucleation of $\text{Mg}(\text{OH})_2$ is initiated here between 50 and 100 °C. With the $[\text{OH}^-]$ concentration being reduced thereafter, particle growth is performed up to a temperature of 240 °C. With this sequence of synthesis, a $[\text{Mg}^{2+}]:[\text{OH}^-]$ ratio of 1:4 up to 1:8 turned out to be most suited in order to avoid decomposition of DEG, but to initiate the formation of uniform $\text{Mg}(\text{OH})_2$ nanoparticles. With concern to a potential industrial application, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was exclusively used as a low cost and less harmful precursor.

Two different suspensions of as-prepared $\text{Mg}(\text{OH})_2$ in DEG are pictured in Fig. 1. Depending on the relevant



Fig. 1 Suspensions of nanoscale $\text{Mg}(\text{OH})_2$ in DEG: $\varnothing = 20 \text{ nm}$, 2.9 mg/ml (left); $\varnothing = 100 \text{ nm}$, 2.9 mg/ml (right)

particle diameter, the suspensions are with transparent appearance in daylight (diameter below about 40 nm) or translucent (above about 40 nm in diameter). Dynamic light scattering is used to quantify particle diameter and size distribution (Fig. 2). As-prepared suspensions exhibit particle diameters of 20 and 100 nm with a narrow size distribution. SEM/TEM micrographs (Fig. 2) display a spherical morphology and confirm the particle size. Taking the primary particle size deduced from SEM and the size distribution from DLS analysis into account, $\text{Mg}(\text{OH})_2$ particles in as-prepared DEG suspensions are indeed non-agglomerated.

Thermal behavior and formation of nanoscale MgO

With concern to X-ray powder diffraction patterns, as-prepared $\text{Mg}(\text{OH})_2$ is non-crystalline. IR spectra elucidate the chemical composition of the nanoscale solid (Fig. 3). Vibrational bands at $3,500\text{--}3,250\text{ cm}^{-1}$: $\nu(\text{O-H})$, $3,000\text{--}2,800\text{ cm}^{-1}$: $\nu(\text{C-H})$, $1,350\text{--}1,250\text{ cm}^{-1}$: $\delta(\text{CH}_2)$ and $1,200\text{--}1,000\text{ cm}^{-1}$: $\nu(\text{C-O})$ indicate the presence of diethylene glycol. This correlation is verified by comparing the spectra of as-prepared $\text{Mg}(\text{OH})_2$ and DEG as a pure solvent. It is also in accordance with former investigations evidencing DEG to be adhered on the surface of nanoscale oxide particles [16, 17]. In addition, a strong absorption at $3,700\text{--}3,600\text{ cm}^{-1}$ has to be attributed to predominantly ionic (O-H)-groups and corresponds to $\text{Mg}(\text{OH})_2$ as a solid compound [18]. Two additional vibrational bands are visible at $1,750\text{--}1,650\text{ cm}^{-1}$ and at $1,400\text{--}1,300\text{ cm}^{-1}$. Both have to be ascribed to carbonyl groups ($\nu(\text{C=O})$) stemming, on the one hand, from $[\text{CO}_3]^{2-}$ anions ($1,400\text{--}1,300\text{ cm}^{-1}$) and, on the other hand, from a carbonic acid ($1,750\text{--}1,650\text{ cm}^{-1}$) [19]. This finding originates from the drying

Fig. 2 Size and morphology of nanoscale $\text{Mg}(\text{OH})_2$: SEM/TEM micrographs of powders and DLS analysis of as-prepared DEG-suspensions

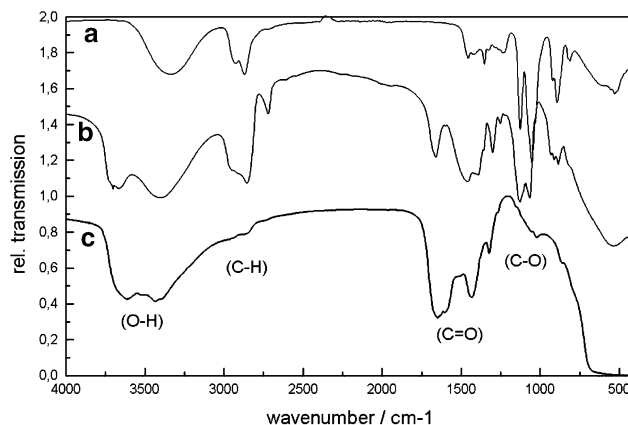
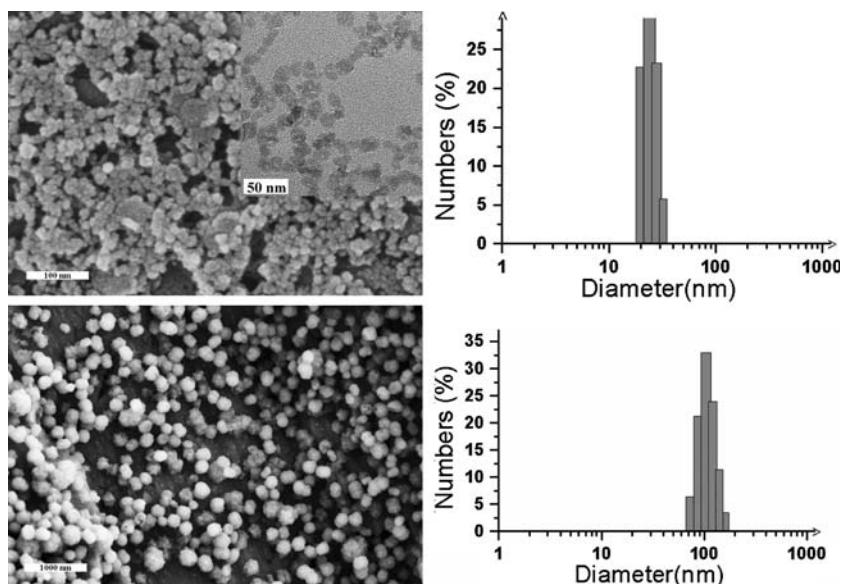


Fig. 3 IR spectra: (a) pure DEG; (b) as-prepared nanoscale $\text{Mg}(\text{OH})_2$; (c) nanoscale MgO subsequent to annealing at $300\text{ }^\circ\text{C}$ for 30 min

process of as-prepared nanoscale $\text{Mg}(\text{OH})_2$ in air (30 min at $80\text{ }^\circ\text{C}$), which results in a certain absorption of CO_2 as well as in a partial oxidation of DEG to the corresponding diglycolic acid.

Thermal analysis (DTA-TG) indicates a weight loss of as-prepared $\text{Mg}(\text{OH})_2$ in two steps (Fig. 4). In a first step ($50\text{--}300\text{ }^\circ\text{C}$) a weight loss of 32% (5.4 mg) is observed. This value matches well with the expectation of losing one molecule of water per formula unit (31%, 5.1 mg). Consequently, this first decomposition step has to be attributed to the dehydration of $\text{Mg}(\text{OH})_2$ to MgO . In contrast to literature data ($T_{\text{decomp}} > 250\text{ }^\circ\text{C}$) [10–13], dehydration is observed here at a surprisingly low temperature. A second weight loss (31%, 5.1 mg) occurs between 300 and $450\text{ }^\circ\text{C}$. Considering the boiling point of DEG ($254\text{ }^\circ\text{C}$) [20], this second step is in accordance with the evaporation of DEG being adhered on the particle

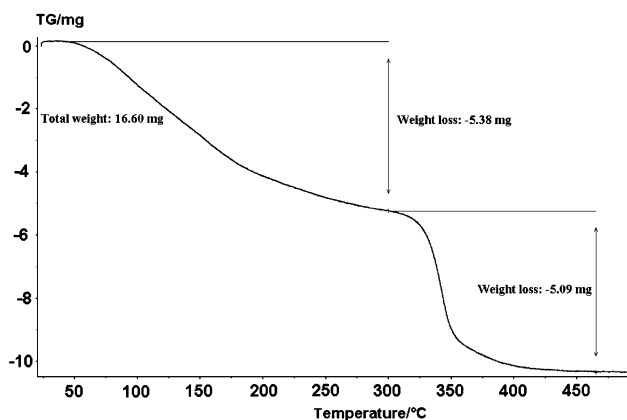


Fig. 4 Thermal gravimetry (TG) of nanoscale $\text{Mg}(\text{OH})_2$

surface. In fact, temperature range and amount of weight loss also corresponds to former findings deduced from other oxides [16, 17].

While measuring the specific surface of as-prepared $\text{Mg}(\text{OH})_2$, the surface load on the nanoparticles can be verified. For particles, 20 nm in size, BET-analysis (BET: Brunauer–Emmett–Teller) results in a specific surface (A_{BET}) of $210 \text{ m}^2/\text{g}$. Considering the density of bulk $\text{Mg}(\text{OH})_2$ (2.360 g cm^{-3}) [20], this value is in accordance with both, the observed particle diameter as well as the presence of non-agglomerated particles. The surface load can be deduced qualitatively when considering the thermal decomposition and the specific surface. First, the weight loss ascribed to the decomposition of DEG (31%) has to be considered. Based on 1 g of as-prepared $\text{Mg}(\text{OH})_2$ a weight loss of 310 mg results, which corresponds to 1.76×10^{21} molecules (molecular weight of DEG: 106 g/mol). Second, BET-analysis evidences a specific surface of $210 \text{ m}^2/\text{g}$ or $2.10 \times 10^{26} \text{ pm}^2$. Dividing the number of molecules by the specific surface estimates the free area per absorbed DEG molecule, which is $119,318 \text{ pm}^2$. This value is in sufficient agreement with the area of one DEG molecule, which is deduced from Van-der-Waals radii, which is $316,008 \text{ pm}^2$ [21, 22]. Although, this calculation is surely a qualitative estimation, the order of magnitude can be interpreted as a type of monomolecular layer of DEG on as-prepared nanoscale $\text{Mg}(\text{OH})_2$.

Dehydration of $\text{Mg}(\text{OH})_2$ below a temperature of $300 \text{ }^\circ\text{C}$ is further confirmed by X-ray powder diffraction (Fig. 5). Annealing of as-prepared, amorphous $\text{Mg}(\text{OH})_2$ for 30 min at $300 \text{ }^\circ\text{C}$ obviously yields crystalline MgO. According to IR spectra (Fig. 3), surface coordinating DEG is now completely oxidized to the corresponding dicarbonic acid with the relevant vibrational bands at $3,700\text{--}3,350 \text{ cm}^{-1}$: $\nu(\text{O-H})$, $3,000\text{--}2,800 \text{ cm}^{-1}$: $\nu(\text{C-H})$, $1,750\text{--}1,650 \text{ cm}^{-1}$: $\nu(\text{C=O})$ and $1,100\text{--}1,000 \text{ cm}^{-1}$: $\nu(\text{C-O})$. Due to its absorption strength, the spectrum is now

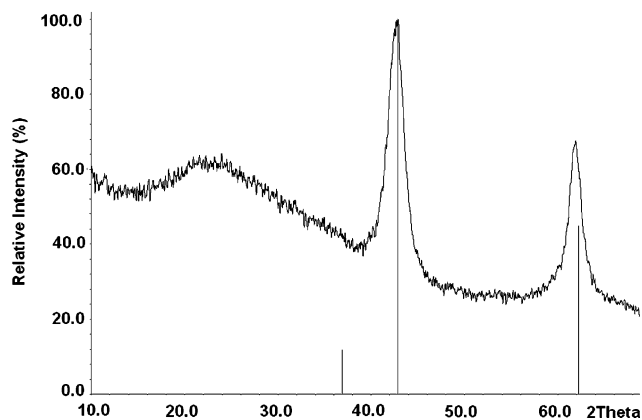


Fig. 5 XRD pattern of MgO after annealing of as-prepared $\text{Mg}(\text{OH})_2$ powder (30 min at $300 \text{ }^\circ\text{C}$, reference: ICDD-No. 74-447)

dominated by $\nu(\text{C=O})$. On the contrary, $\nu(\text{C-H})$ and $\nu(\text{C-O})$ are observed as comparably weak absorptions as it is also found in case of comparable examples [18, 19]. With the useful assumption that the dicarbonic acid is adhered to the nanoparticle surface due to attractive interaction between oxygen atoms and surface-bound Mg^{2+} , a comparably high energy of the (O-H)-vibration is expected ($>3,400 \text{ cm}^{-1}$) and indeed confirmed (Fig. 3). Due to annealing in air, CO_2 adsorption is increased resulting in an intensified absorption at $1,400\text{--}1,300 \text{ cm}^{-1}$. Since the surface stabilizer of as-prepared nanoscale $\text{Mg}(\text{OH})_2$ —although in its oxidized form—is still present as a surface determination on the annealed MgO particles, in principle, temperature-driven particle growth and agglomeration should be suppressed. SEM micrographs confirm this view. Comparing as-prepared, 20 nm sized $\text{Mg}(\text{OH})_2$ particles (Fig. 2) and the identical sample after dehydration to MgO (Fig. 6), it turned out that both are almost similar in size and shape.

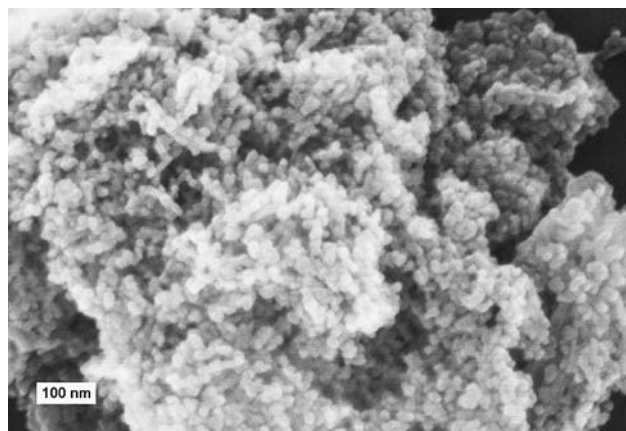


Fig. 6 Size and morphology of nanoscale MgO after annealing of as-prepared $\text{Mg}(\text{OH})_2$ (30 min at $300 \text{ }^\circ\text{C}$)

Conclusions

Nanoscale $\text{Mg}(\text{OH})_2$ particles with a spherical shape are firstly prepared via a polyol-mediated synthesis. A special feature of the synthesis is a particle diameter, which can be adjusted between about 20 nm and 100 nm. The resulting suspensions of $\text{Mg}(\text{OH})_2$ in DEG contain non-agglomerated particles. Herein, DEG acts as the liquid phase and as a surface-active component stabilizing the nanoparticles. With concern to the specific surface and the thermal behavior, a monomolecular coverage of DEG on as-prepared $\text{Mg}(\text{OH})_2$ can be deduced. Subsequent to centrifugation and washing, as-prepared nanoscale $\text{Mg}(\text{OH})_2$ can be dehydrated to form crystalline MgO with almost similar size and shape. With 300 °C, altogether, dehydration to MgO occurs at a surprisingly low temperature. Since the thermal treatment is carried out in air, DEG is oxidized to diglycolic acid during annealing. With a further increase in temperature (450 °C) it is also possible to remove the surface stabilizer completely.

Altogether, the size-selective formation of nanoscale and non-agglomerated $\text{Mg}(\text{OH})_2$ as well as the low-temperature dehydration to nanoscale MgO might gain interest with concern to $\text{Mg}(\text{OH})_2$ or MgO layer deposition on, for instance, glass, metal or plastics. In principle, the sequence of reaction seems to be suited also for an industrial up-scale, since low-cost and less harmful solids and solvents have been applied throughout.

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