Magnesium Aminoethyl Phosphonate ($Mg(AEP)(H_2O)$): An Inorganic-organic Hybrid Nanomaterial with High CO_2:N_2 Sorption Selectivity

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SUPPORTING INFORMATION

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ANALYTICAL TOOLS

Scanning electron microscopy (SEM) was conducted on a Zeiss Supra 40 VP, using an acceleration voltage of 4 kV and a working distance of 4 mm. SEM samples were prepared by evaporation of an ethanolic suspension of the as-prepared powder. The mean particle diameter was calculated by statistical evaluation of at least 500 particles.

Low-energy scanning transmission electron microscopy (STEM) was performed on a Zeiss Supra 40 VP, using an acceleration voltage of 20 kV and a working distance of 4 mm to analyze the size distribution and shape of the nanoparticles. Samples for low-energy STEM were prepared by evaporating dispersions of particles in dodecane on an amorphous carbon (Lacey-)film copper grid.

X-ray powder diffraction (XRD) was carried out with a Stoe Stadi-P diffractometer using Ge-monochromatized Cu-$K_{\alpha1}$ radiation.

Fourier-transformed infrared spectroscopy (FT-IR) was performed on a Bruker Vertex 70. Samples were prepared by pestling of 2 mg of Mg(AEP)(H_2O) with 300 mg of dried KBr in a glove-box.

Thermogravimetry (TG) was performed with a Netzsch STA 409C instrument, applying α-Al_2O_3 as crucible material as well as reference sample. The samples were heated in air up to 1300 °C with a heating rate of 1 K min^{-1}. The total sample weight was 30 mg.

Thermogravimetry with coupled mass spectrometry (TG-MS) was performed with a Setaram Sensys Evo instrument (α-Al_2O_3 crucibles; helium atmosphere; maximal temperature: 600 °C; heating rate: 5 K min^{-1}; total sample weight: 30 mg), coupled with an Pfeiffer OmniStar mass spectrometer (electron spray at 70 eV).

Elementary analysis (C, H, N) was performed with an Elementar Vario EL device (Elementar, Hanau, Germany).

SYNTHESIS

All experimental work was performed in vacuum or under nitrogen utilizing Schlenk-techniques or glove-boxes. H_2AEP (Aldrich, 99%), 0.5 *M* Mg(n-C_4H_9)$_2$ solution in *n*-hexane (Sigma, >99%), cetyltrimethylammonium bromide (CTAB, Sigma, 99%) and all further chemicals were applied as received.

Mg(AEP)(H_2O): First, a transparent microemulsion was prepared as follows: 70 ml of toluene as the non-polar phase, 3 mL of a 0.27 M H_2AEP solution as the polar phase, 1.82 g of cetyltrimethylammonium bromide (CTAB) as the surfactant and 5 ml of *n*-hexanol as the co-surfactant were stirred vigorously for 30 minutes at 35 °C (heating via oil bath).

Subsequently, 1.6 mL of a 0.5 M $MgBu_2$ solution in *n*-hexane was injected. The light yellow precipitate was washed three times with ethanol and carefully dried for 2 hours at 10^{-3} mbar at 60 °C. Mg(AEP)(H_2O) was obtained as a white powder with a yield of 99% (130 mg).

CHEMICAL COMPOSITION AND THERMAL BEHAVIOUR OF Mg(AEP)(H_2O)

While the as-prepared Mg(AEP)(H_2O) turned out as non-crystalline, Fourier-transformed infrared spectroscopy (FT-IR), thermogravimetry (TG), thermogravimetry coupled with mass spectrometry (TG-MS) and elementary analysis were involved to validate its chemical composition.

FT-IR spectra validate all characteristic vibrations as related to aminoethyl phosphonate (ν(O–H): 3300–2900 cm^{-1}; ν(C–H): 2950–2850 cm^{-1}; ν(C–N)/δ(C–H): 1600–1200 cm^{-1}; $\nu(PO_3)$: 1200–850 cm^{-1}, $\delta(PO_3)$: 750–400 cm^{-1}) (Figure S1). The much sharper/splitted vibrations of H_2AEP can be ascribed to the fact that the starting material is highly crystalline whereas the as-prepared nanomaterial is non-crystalline. FT-IR spectra of Mg(AEP)(H_2O) are also very comparable to bulk-Mg$(HAEP)_2(H_2O)_5$ as reported by *Menke et al.*[1]

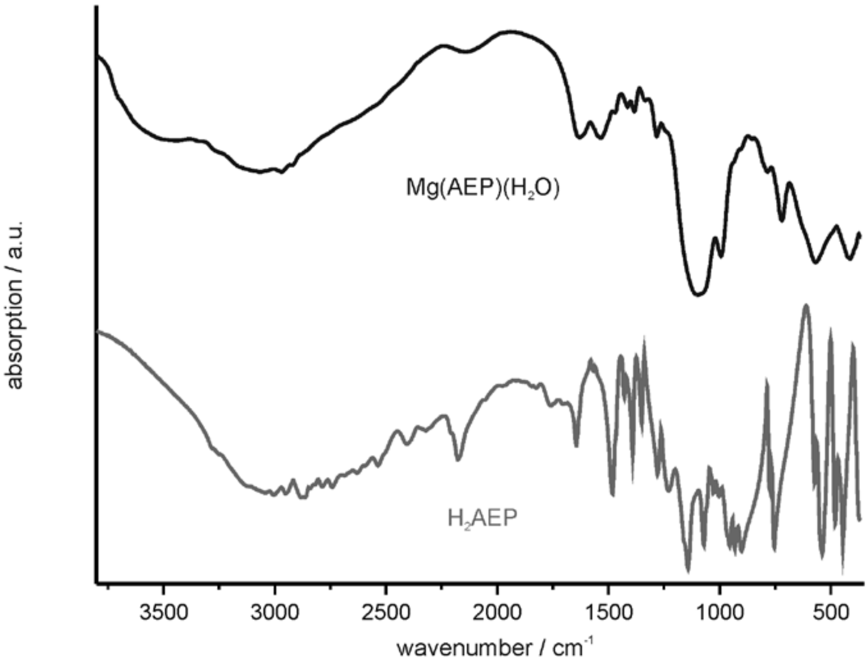

Figure S1. FT-IR spectra of as-prepared Mg(AEP)(H_2O) nanoparticles in comparison to aminoethyl phosphonic acid (H_2AEP) as the starting material.

TG of Mg(AEP)(H_2O) shows four-step decomposition with a total weight loss of 43.5% in steps of: (*1.*) 11.0% (90–250 °C); (*2.*+*3.*) 27.0% (250–600 °C) and (*4.*) 5.5% (600–700 °C) (Figure S2). These steps are not well separated, but show significant overlap. Especially, step

(*3.*) and (*4.*) are fused together and therefore taken as one decomposition step in the following. The observed thermal decomposition of Mg(AEP)(H_2O), in sum, can be rationalized according to the following reactions:

(*1.*) $Mg(O_3P(CH_2)_2NH_2)(H_2O) \rightarrow Mg(O_3P(CH_2)_2NH_2) + H_2O\uparrow$ (calculated: 10.9%)

(*2.*+*3.*) $Mg(O_3P(CH_2)_2NH_2) \rightarrow$ "$MgPO_3$" $+ CH_2{=}CH_2\uparrow + NH_3\uparrow$ (calculated: 27.2%)

(*4.*) 12"$MgPO_3$" $+ 3O_2 \rightarrow 4Mg_3(PO_4)_2 + P_4O_{10}\uparrow$ (calculated: 14.3%)

P_4O_{10} as a decomposition product starts to react with the crucible material at temperatures of 600–700 °C and is therefore not evaporated completely. X-ray powder diffraction, finally, proves the presence of farringtonite, $Mg_3(PO_4)_2$ as the thermal remnant (Figure S3).

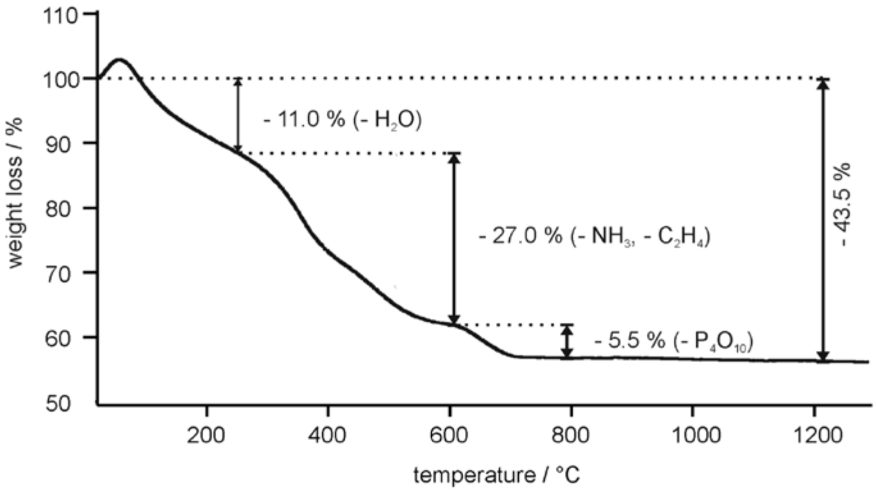

Figure S2. TG analysis of as-prepared Mg(AEP)(H_2O) nanoparticles indicating the thermal decomposition (total sample weight: 30 mg; atmosphere: air; heating rate: 1 K min^{-1}).

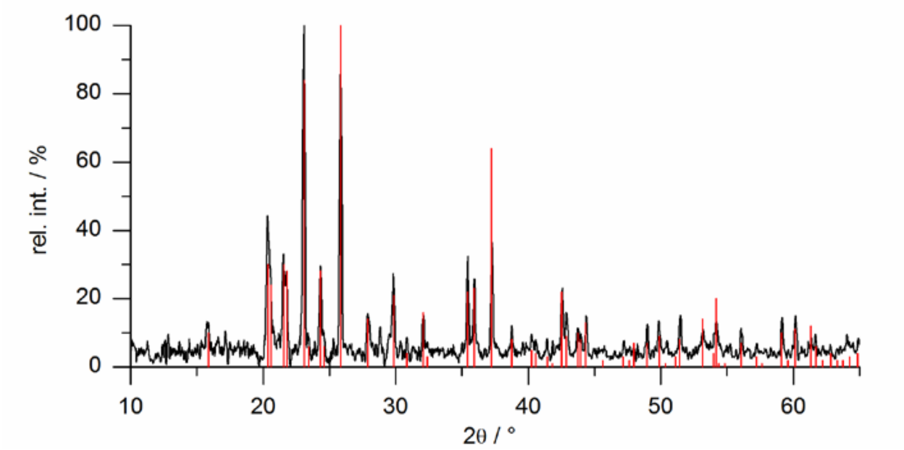

Figure S3. X-ray powder diffraction pattern of the thermal remnant after the TG analysis of Mg(AEP)(H_2O) with temperatures up to 1300 °C (reference: ICDD-No. 33-876, farringtonite syn, $Mg_3(PO_4)_3$).

Thermogravimetry coupled with mass spectrometry (TG-MS) was performed up to a temperature of 600 °C to verify the above decomposition products (Figure S4). Accordingly, H_2O^+ at 90–200 °C ($m/z = 18$, indicating water), NH_2^+ at 320–600 °C ($m/z = 16$, indicating primary amines), and $C_2H_5^+$ 250–600 °C ($m/z = 29$, indicating ethyl derivatives) were observed. Note that the evaporation of H_2O is accompanied by minor amounts of OH^+ ($m/z = 17$, not shown) and O^+ ($m/z = 16$, similar to NH_2^+). In addition, evaporation of NH_3 is accompanied by minor amounts of NH_4^+ ($m/z = 18$, similar to H_2O^+) and NH_3^+ ($m/z = 17$, not shown). Moreover, evaporation of $C_2H_5^+$ is accompanied by additional fragments, too (*i.e.*, $C_2H_3^+$: $m/z = 27$, $C_2H_4^+$: $m/z = 28$). Based on mass spectrometry, evaporation of NH_3 and C_2H_4 can indeed be detected for the overlapping decomposition steps (*2.*) and (*3.*).

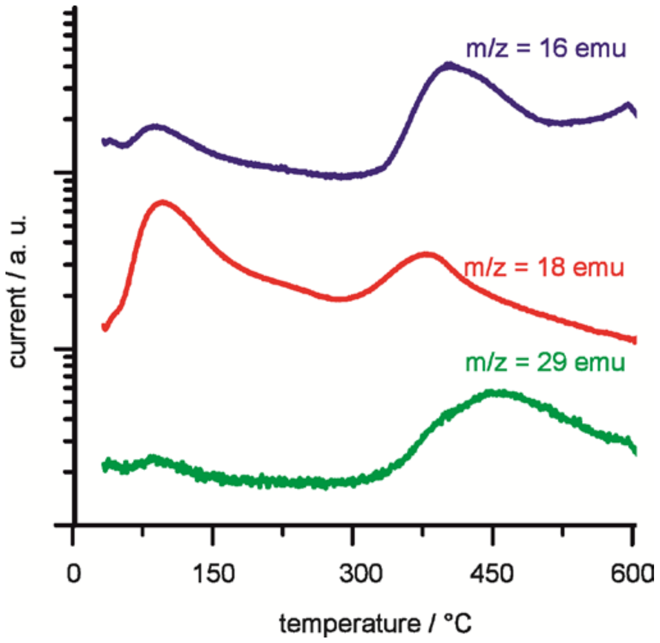

Figure S4. TG-MS of Mg(AEP)(H_2O) nanoparticles indicating NH_2^+ ($m/z = 16$), H_2O^+ ($m/z = 18$) and $C_2H_5^+$ ($m/z = 29$) as thermal decomposition products (total sample weight: 30 mg; atmosphere: helium; heating rate: 5 K min^{-1}).

Elementary analysis (*i.e.*, C, H, N) finally confirms the composition of Mg(AEP)(H_2O) with experimental values of $m(C)_{obs} = 14.2(1)\%$, $m(H)_{obs} = 4.3(1)\%$ and $m(N)_{obs} = 6.0(1)\%$. These data are well in accordance to the calculated amounts $m(C)_{calc} = 14.5\%$, $m(H)_{calc} = 4.8\%$ and $m(N)_{calc} = 8.5\%$. In sum, the results from FT-IR, TG and elementary analysis reliably validate the chemical composition of the as-prepared nanomaterial as Mg(AEP)(H_2O).

SORPTION ANALYSIS

Volumetric N_2 sorption analysis of as-prepared Mg(AEP)(H_2O) was carried out with a Belsorp mini II. Specific surface and pore volume were determined according to the formalisms given by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH). This standard nitrogen sorption analysis resulted in a type IV isotherms (Figure S5). According to the Brunauer-Emmett-Teller (BET) formalism, a specific surface of 322 $m^2\ g^{-1}$ was obtained. The pore volume was calculated based on a Barrett-Joyner-Halenda (BJH) analysis and resulted in a value of 0.9 $cm^3\ g^{-1}$.

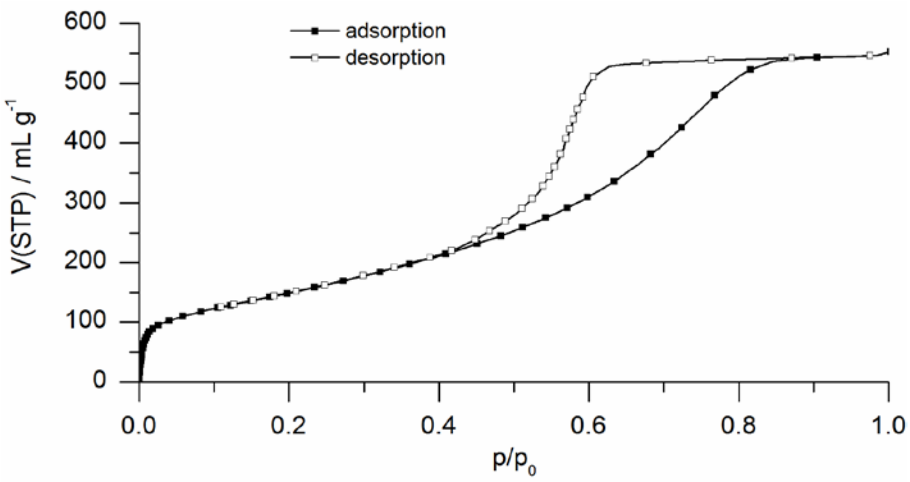

Figure S5. Nitrogen sorption as obtained by volumetric analysis.

The large specific surface of the Mg(AEP)(H_2O) nanoparticles is in accordance with its small particle diameter (20 nm). In addition, certain porosity is related to pores/fissures between different nanoparticles in a powder and very typical for high-surface nanomaterials. Moreover, Mg(AEP)(H_2O) was prepared by using techniques that were also applied for obtaining hollow spheres.[2,3] Thus, in a microemulsion approach one reactant ($MgBu_2$) was added to the non-polar phase (*n*-hexane) while a second reactant (H_2AEP) was added to the polar phase (water). If the reactants meet first at the hexane-to-water phase boundary, a certain inner cavity might remain after synthesis and subsequent to drying of the nanoparticles. For Mg(AEP)(H_2O), the far most of the nanoparticles are definitely not hollow but massive. At least for some nanoparticles, however, STEM images indicate an inner cavity that also contributes to the porosity of the sample (Figure S6).

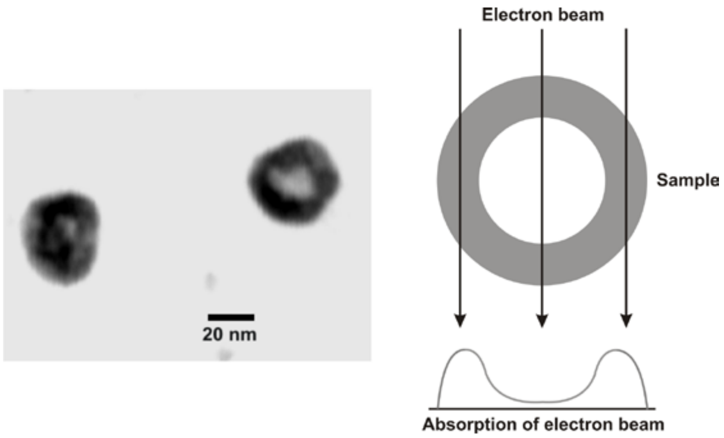

Figure S6. STEM images of Mg(AEP)(H_2O) nanoparticles indicating an inner cavity at least for some nanoparticles and scheme showing the absorption of the electron beam for nanoparticles with an inner cavity.

Gravimetric CO_2 and N_2 sorption analysis were carried out with a magnetic suspension balance (Rubotherm) that can be operated up to 200 bar. The significance of the balance is ≤0.1 mg. Thus, a stainless steel sample holder was filled with the as-prepared powder sample and the balance was evacuated for 6 h at 333 K and 10^{-3} mbar until constant mass was achieved. Afterwards, the gas was dosed into the balance chamber to elevated pressures. Equilibrium was achieved within 30 min to 2 h and identified by constant weight and pressure. The temperature was kept constant with an accuracy of ±0.5 K for each measurement. Additionally, a helium buoyancy correction was used to calculate the surface excess mass from the measured values. A detailed description of this procedure can be found elsewhere.[4] A general problem, however, is that the buoyancy correction becomes less precise at very high pressure. This is a well-known and partly still unsolved problem.[4,5] While Mg(AEP)H_2O is close to saturation above 100 bar, the CO_2 uptake appears like being reduced at even higher pressure due to the less precise buoyancy correction at this pressure (cf. Figure 2). In fact, the “real” maximal CO_2 uptake of Mg(AEP)H_2O is even slightly higher as 152 mg g^{-1}.

CO_2 remaining on the Mg(AEP)(H_2O) nanoparticles after the 1st sorption cycle was validated based on gravimetric sorption analysis (*cf.* Figure 2) as well as based on infrared spectra (FT-IR) spectra (Figure S7). Hence, the intensity of ν(C=O) (1650–1500 cm^{-1}) is significantly increased after the 1st sorption cycle as compared to the as-prepared Mg(AEP)(H_2O) nanoparticles (Figure S9). Note that the spectra were normalized on the phosphonate valence vibration with its maximal absorption at 1099 cm^{-1}. While the intensity of *ν*(PO_3) is identical for Mg(AEP)(H_2O) samples before and after CO_2 sorption, this measure allows comparing the intensity of *ν*(C=O), which is indicative for the amount of CO_2 remaining on the nanoparticles subsequent to the 1st sorption cycle.

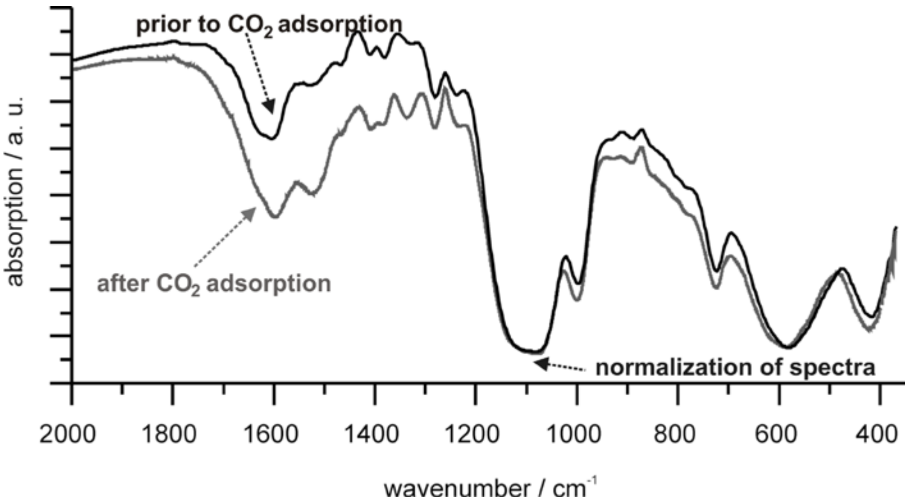

Figure S7. FT-IR spectra of Mg(AEP)(H_2O) nanoparticles before and after performing the CO_2 sorption experiments (spectra normalized on *ν*(PO_3) at 1099 cm^{-1}).

The stability of the Mg(AEP)(H_2O) nanoparticles under the conditions of CO_2 sorption experiments (*i.e.*, 293–353 K, 10^{-7}–120 bar) is validated by thermogravimetry (Figure S8). Thus, thermal analysis is shown for Mg(AEP)(H_2O) samples before and after performing the sorption experiments. The fact that both samples show identical behaviour (within the limits of experimental significance) shows that no decomposition of the Mg(AEP)(H_2O) occurred during the sorption experiments. In fact, not even a noticeable amount of intrinsic water was evaporated. Slight differences occur right at the onset of the TG curves (≤50 °C) that are attributed to buoyancy when heating the atmosphere inside of the TG device.

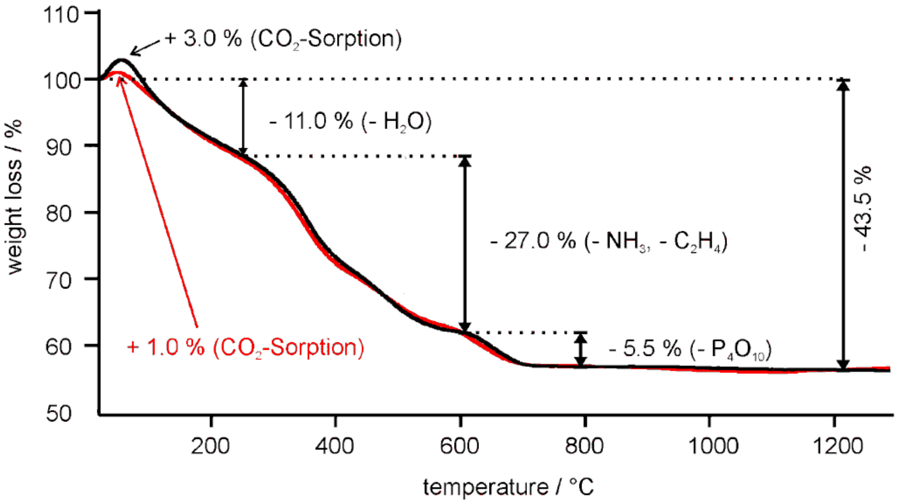

Figure S8. Thermogravimetric analysis indicating the thermal decomposition of Mg(AEP)(H_2O) before and after performing the CO_2 sorption experiments (total sample weight: 30 mg; atmosphere: air; heating rate: 1 K min^{-1}).

Sorption-desorption isotherms (*cf.* Figure 2) indicate that a certain amount of CO_2 (19 mg g^{-1}) remains adsorbed on the Mg(AEP)(H_2O) nanoparticles even after expansion of the pressure from 110 to 1 bar of CO_2. This CO_2 remaining on the sample after desorption is also validated by infrared spectra (Figure S7) and attributed to a follow-up reaction of the carbamate $[RNHCOO]^-$ and intrinsically available water according to *Eq.* 2 (*cf.* main text):

$$(Eq. 2) \qquad [RNHCOO]^- + H_2O \leftrightarrows [HCO_3]^- + RNH_2$$

Largely all CO_2 remaining on Mg(AEP)(H_2O) nanoparticles can be desorbed by evacuation as well as by heating in an atmosphere, not containing CO_2. Accordingly, evacuation of the Mg(AEP)(H_2O) sample was performed at elevated temperature (*i.e.*, 10^{-3} mbar, 333 K, 6 h) subsequent to the sorption-desorption cycle (Figure S9). Alternatively, the Mg(AEP)(H_2O) sample was flushed with Helium after performing the sorption-desorption cycle to remove the CO_2 atmosphere. Thereafter, the sample was heated in Helium atmosphere (1 bar He atmosphere, 353 K, 12 h) (Figure S10). With both these measures, 13 mg g^{-1} of CO_2 (evacuation) and 16 mg g^{-1} of CO_2 (heating in He atmosphere) can be removed. Note that pressure reduction to evacuation was conducted very slow (within 30 min) in order to avoid any dusting inside of the suspension balance. Altogether, 96–98% of CO_2 (*i.e.* 146 to 149 mg g^{-1} of 152 mg g^{-1}) adsorbed on the Mg(AEP)(H_2O) nanoparticles can be reversibly desorbed when including an evacuation or heating step. At least 88% of CO_2 (*i.e.* 133 mg g^{-1} of 152 mg g^{-1}) can be reversibly desorbed just by pressure swing between 110 bar and 1 bar.

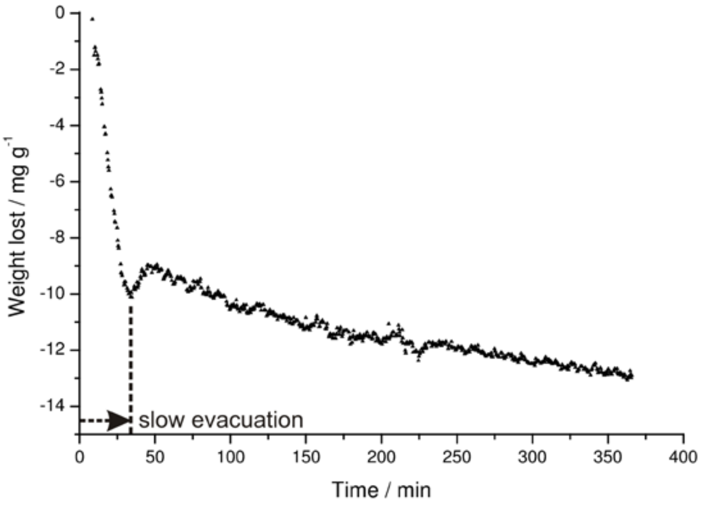

Figure S9. Release of CO_2 remaining after sorption-desorption cycle on Mg(AEP)(H_2O) nanoparticles via evacuation (*i.e.*, 10^{-3} mbar, 333 K, 6 h, total sample weight: 92.4 mg).

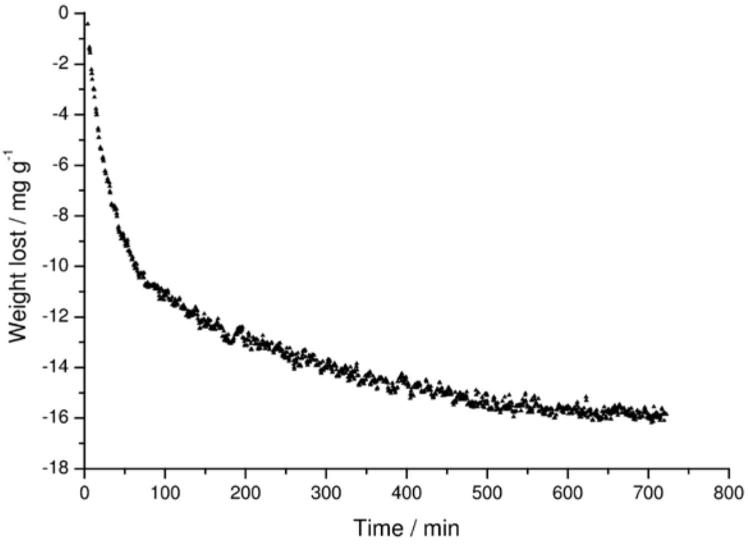

Figure S10. Release of CO_2 remaining after sorption-desorption cycle on Mg(AEP)(H_2O) nanoparticles via heating in atmosphere, not containing CO_2 (1 bar He atmosphere, 353 K, 12 h, total sample weight: 100.8 mg).

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