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Fast carbon dioxide recycling by reaction with γ -Mg(BH₄)₂

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S1. Experimental Section.

Samples. γ -Mg(BH₄)₂ was purchased from Sigma Aldrich (95% purity, 54978-1G, batch #MKBK0970V). α -Mg(BH₄)₂ was synthesized by direct wet chemical synthesis from pre-milled MgH₂ (98%, Alfa-Aesar) and Et₃N · BH₃ (97%,Sigma Aldrich).¹ The materials have been handled in inert atmosphere (M Braun Lab Star Glove Box supplied with pure 5.5 grade Nitrogen, <0.5 ppm O₂, <0.5 ppm H₂O). CO₂ (4.8 N purity, dry bone) was supplied by Rivoira. MgO material has been obtained by decomposition under dynamic vacuum up to 400°C for 2 days of Mg(NO₃)₂ · 6 H₂O (Sigma-Aldrich) and handled in inert atmosphere in order to avoid hydration and carbonatation reactions.

Powder XRD measurements. Powder X-Ray Diffraction measurements were performed in the 2θ range 2° – 90° (step size of 0.017°, time per step 200 s) using a laboratory diffractometer (Panalytical X'Pert Pro Multipurpose Diffractometer) equipped with Ni filtered Cu source in Debye-Scherrer geometry. Samples before and after reaction with CO₂ were sealed into boron silica glass capillaries of internal diameter 0.8 mm in a protected atmosphere.

Carbon dioxide adsorption measurements. An intelligent gravimetric analyzer (IGA-002, supplied by Hiden Analytical Ltd, UK) was used, equipped with a circulating thermostatic bath for the temperature control and an ultrahigh vacuum system (10⁻⁶ mbar). The mass uptake was measured as a function of time, and each point of the isotherm was recorded after 4 h: in any case the equilibration was reached after this time. Before each measurement and between the first and second isotherms, the sample was degassed for 12 h at RT.

Buoyancy corrections were carried out using the weights and densities of all the components of the sample and counterweight sides of the balance and the measured temperature. The density of the samples has been determined by helium isotherms conducted on the samples at 293 K in the 0-20 bar range. The isotherms obtained show absence of gas interaction phenomena.

Nitrogen adsorption isotherms were measured on a commercial volumetric apparatus (*Micromeritics ASAP2020*) at 77 K. Prior measurement, the powders were degassed at RT for 24 h on a vacuum line equipped with a turbomolecular pump and then the samples were transferred in the measurement cell in a glove box. The specific surface area was obtained by using the BET, Brunauer–Emmett–Teller (Brunauer et al., 1938), and Langmuir (Gregg and Sing, 1982; Langmuir, 1916) approximations in the standard pressure range ($0.05 < p/p_0 < 0.20$). Because of the well known diffusion problems of nitrogen in the pores of γ -Mg(BH₄)₂,^{4,5} only 5 points measurements have been carried out by allowing very long equilibration times for each dose (45 s).

FTIR spectroscopy. Attenuated Total Reflection (ATR-IR) spectra (2 cm⁻¹ resolution, average on 256 scans) were collected on loose powder on a Bruker Alpha spectrophotometer, equipped with an internal reflection element in diamond and placed in the glove box. In situ FTIR spectra in transmission mode (2 cm⁻¹ resolution, average on 32 scans) were collected on a Bruker Vertex70 spectrophotometer. The samples were measured in the form of self-supporting pellets inside a quartz cell in controlled atmosphere. The gas phase reaction products were analyzed by using an *ad hoc* cell with an optical path length of 10 cm.

¹³C NMR spectroscopy. ¹³C solid state CP MAS NMR (cross polarization magic-angle spinning nuclear magnetic resonance) spectra were recorded on a Bruker AVANCE II 400 instrument operating at 100.65 MHz. A 4 mm outer diameter zirconia rotor (sample volume= 80 μL), filled inside a glow-box, was employed and spun at 12 kHz. A ramp cross-polarization pulse sequence was used (contact time= 4.5 ms, recycle delays= 5 s, scans= 4096). The ¹³C scale was calibrated with glycine (¹³C methylene signal at 43.86 ppm) as external secondary reference.

S2. In situ FTIR in transmission of CO₂ reaction with Mg(BH₄)₂ samples. Insight on the reaction mechanisms of CO₂ with γ -Mg(BH₄)₂ and α -Mg(BH₄)₂ have been obtained by performing *in situ* infrared spectroscopy measurements. The spectra recorded at increasing time on γ -Mg(BH₄)₂ after dosing 100 bar of CO₂ are reported in *Figure S1*. The results obtained for the same experiment conducted on α -Mg(BH₄)₂ are reported in *Figure S2*. At difference from what reported e.g. for ammonia borane,² in this case the products are all formed simultaneously and do not evolve further hydrogenating the C atom. In fact, the absorption bands associated to the products grow in intensity in a parallel way as a function of time, indicating that allowing longer contact of CO₂ with the borohydride, causes the only the increase of the concentration of the products without further modifications.

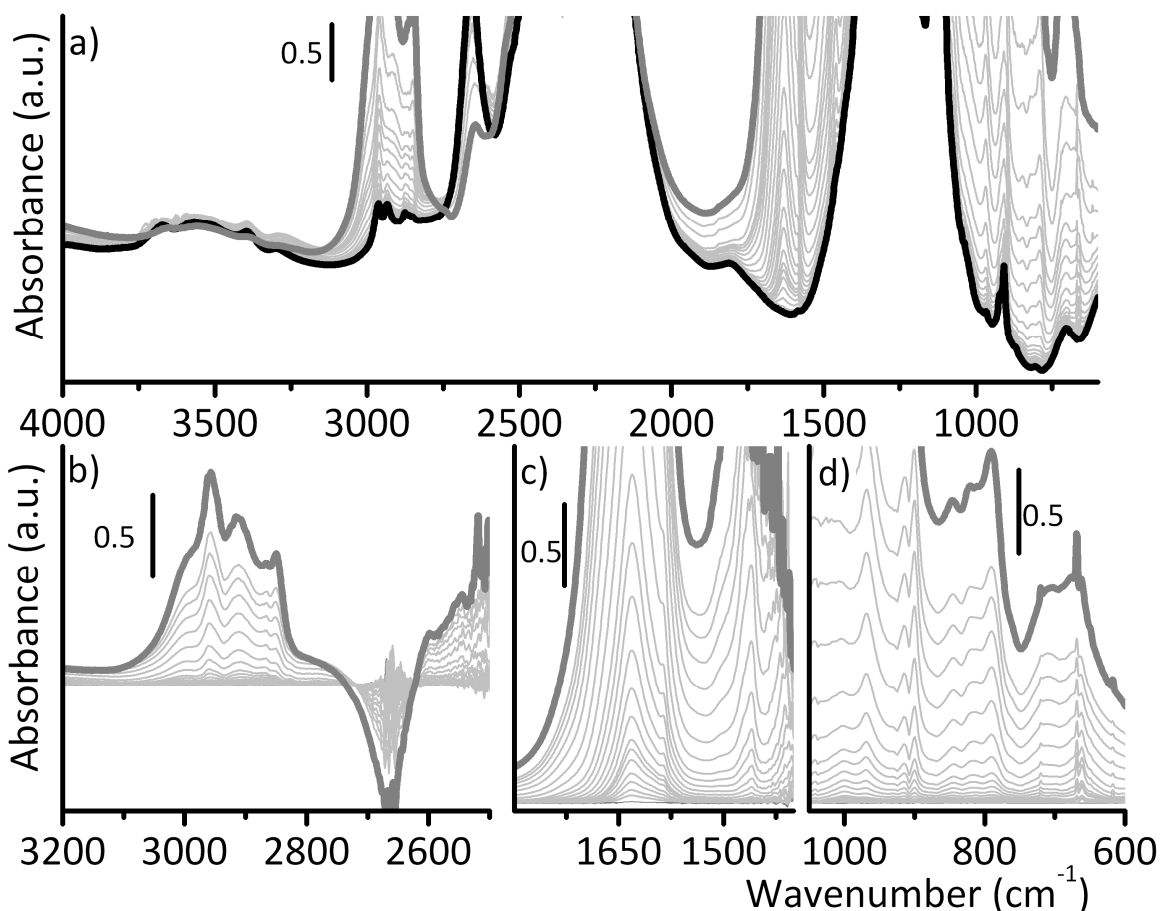


Figure S1. Part a): In situ FT-IR spectra collected during reaction of γ -Mg(BH₄)₂ with 100 mbar of CO₂ at room temperature. Black spectrum: γ -Mg(BH₄)₂ before reaction; dark grey spectrum: after 12 hours of reaction. Parts b)-d): same as part a) after subtraction of the spectrum of γ -Mg(BH₄)₂ (black).

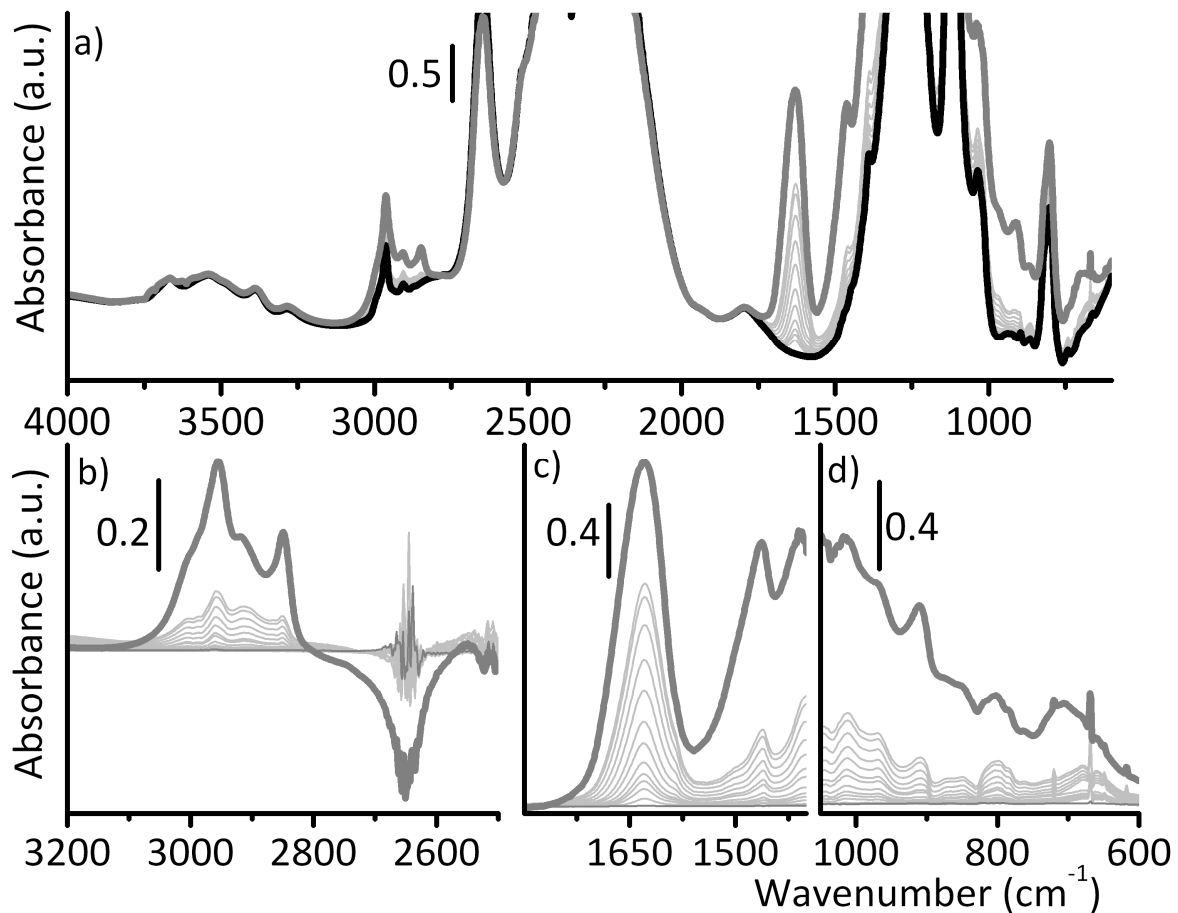


Figure S2. Part a): In situ FT-IR spectra collected during reaction of α -Mg(BH₄)₂ with 100 mbar of CO₂ at room temperature. Black spectrum: α -Mg(BH₄)₂ before reaction; dark grey spectrum: after 24 hours of reaction. Parts b)-d): same as part a) after subtraction of the spectrum of α -Mg(BH₄)₂ (black).

S3. Rietveld refinement of $\text{Mg}(\text{BH}_4)_2$ samples. The purity of the samples as received has been verified by performing a Rietveld refinement on the patterns with MAUD software.³ The analysis confirmed the purity of the α - $\text{Mg}(\text{BH}_4)_2$ sample (see *Figure S3a*), whereas the γ - $\text{Mg}(\text{BH}_4)_2$ sample resulted to be composed by 84% of γ - $\text{Mg}(\text{BH}_4)_2$ and 16% of α - $\text{Mg}(\text{BH}_4)_2$ (proportion on volume, equivalent to 78 to 22% in mass, see *Figure S3b*).

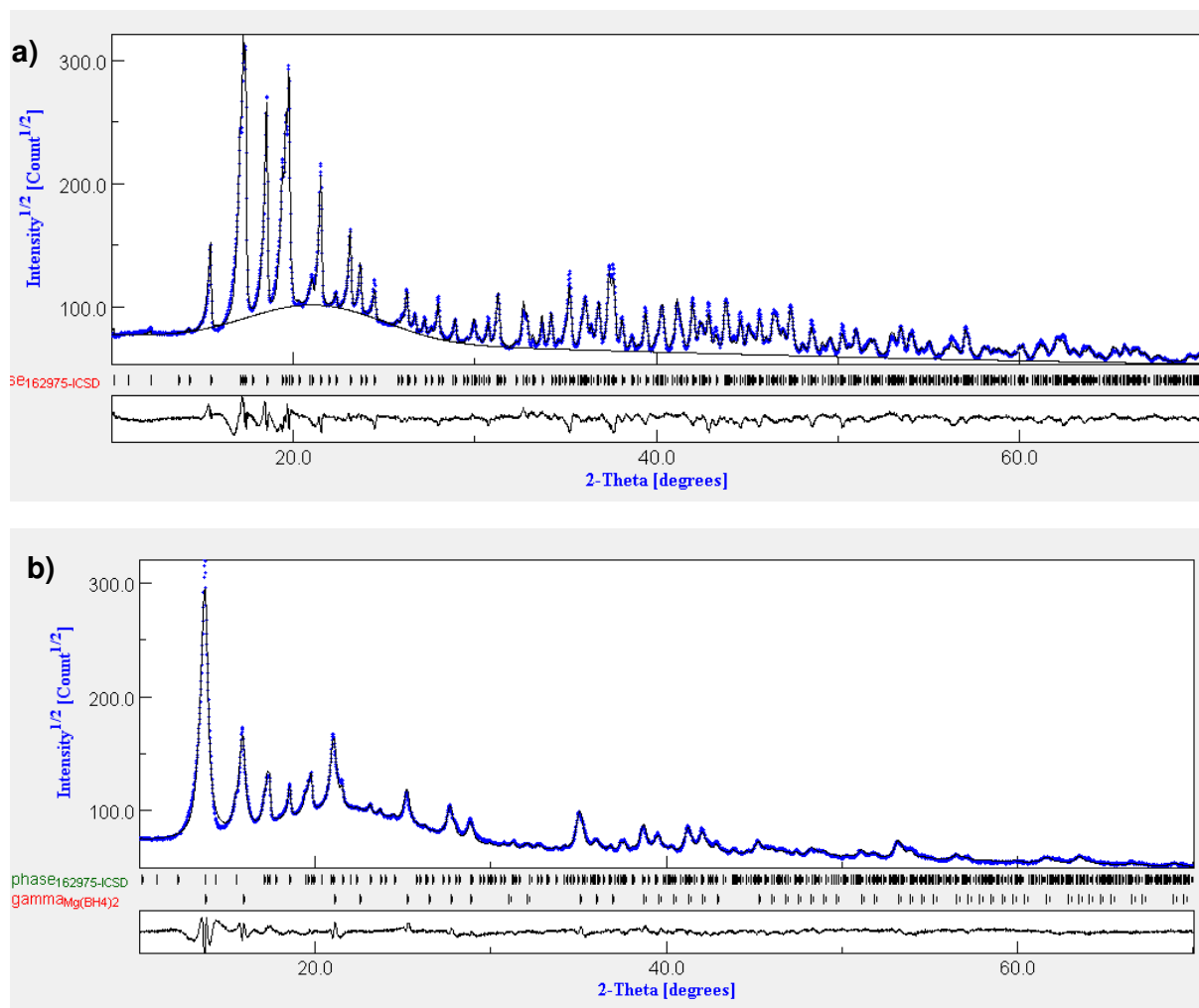


Figure S3. Rietveld refinement output for the a) α - $\text{Mg}(\text{BH}_4)_2$ and b) γ - $\text{Mg}(\text{BH}_4)_2$ patterns recorded on the as received samples.

S4. Rietveld refinement of $\text{Mg}(\text{BH}_4)_2$ samples after reaction with CO_2 . The patterns of γ - $\text{Mg}(\text{BH}_4)_2$ and α - $\text{Mg}(\text{BH}_4)_2$ have been recorded after contact with 1 bar of CO_2 at 30°C for 3 days,

followed by a short degassing procedure; the powder were then sealed in capillaries in N₂ atmosphere. The refinement confirms the qualitative analysis of the patters, that is the very small effect on the peaks of α -Mg(BH₄)₂ phase both if pure (*Figure S4a*) or present as impurity in the γ -Mg(BH₄)₂ sample (*Figure S4b*). the peaks relative to the γ phase are totally missing after the reaction with CO₂. An extra opeak at about 13° remains unidentified.

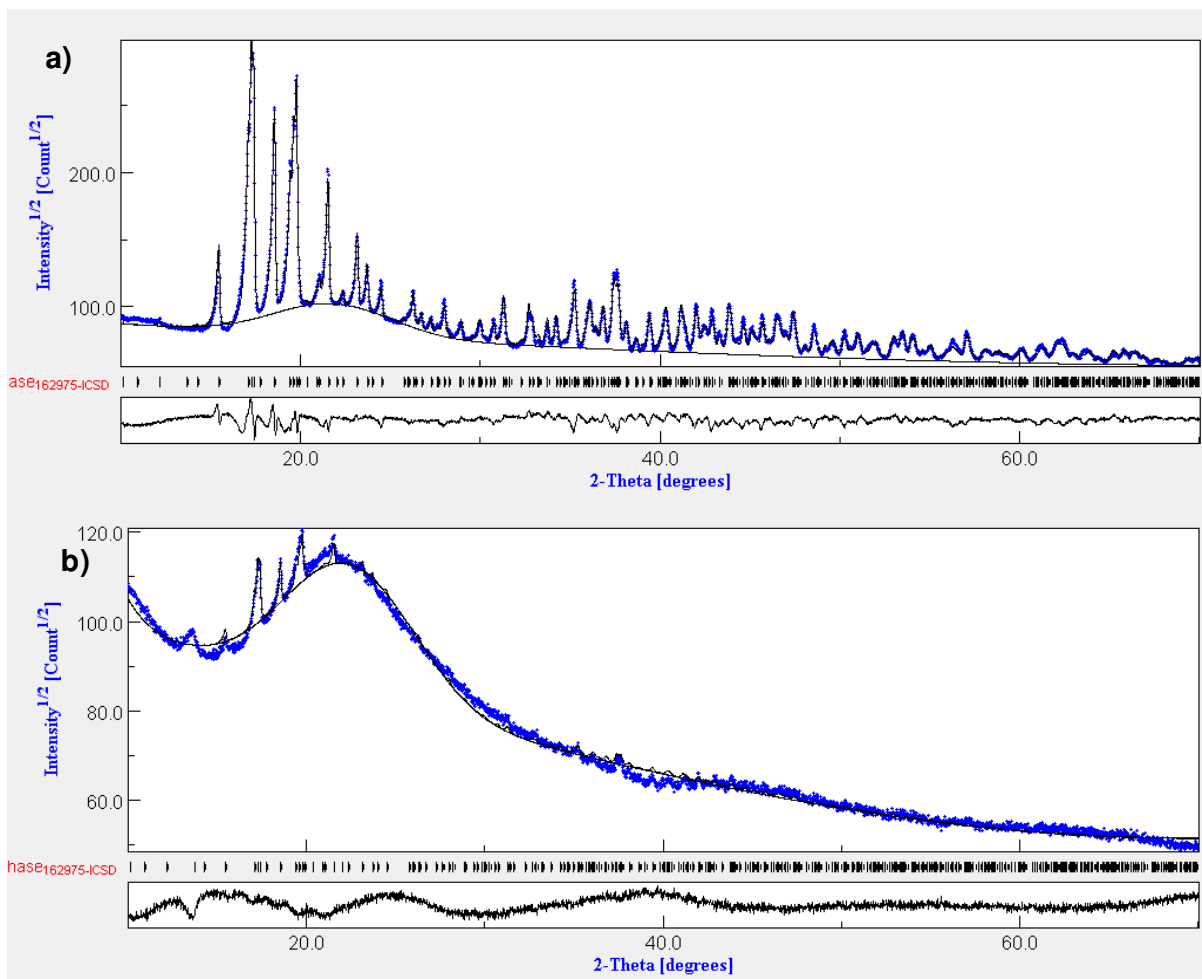


Figure S4. Rietveld refinement output for the a) α -Mg(BH₄)₂ and b) γ -Mg(BH₄)₂ patterns recorded after contact with 1 bar of CO₂ for 3 days.

S5. Surface area of Mg(BH₄)₂ samples before and after reaction with CO₂.

The surface areas obtained for the SA value obtained for γ -Mg(BH₄)₂ and α -Mg(BH₄)₂ before and after contact with 1 bar of CO₂ at 25°C for 3 days are reported in Table S1. Also by considering the fraction of α -Mg(BH₄)₂ phase in the studied γ material (22% in mass), the measured surface area of the single γ phase would amount to 586 m² g⁻¹, that is about 50% of the theoretical one (1160 m² g⁻¹), although the long equilibration times adopted in the analysis. This underestimation is due to the very slow diffusion of nitrogen in the pores of this materials, as evidenced in previous studies.^{4,5} Nevertheless, the measured surface area of γ -Mg(BH₄)₂ material (458 m² g⁻¹) resulted to be more than two order of magnitude larger than the α -Mg(BH₄)₂ one (4 m² g⁻¹).

This difference is strongly reduced after contact with 1 bar of CO₂ at 30°C for 3 days, being the surface area of γ -Mg(BH₄)₂ of only 18 m² g⁻¹ because of the collapse of its porous structure. Interestingly, also the surface area of α -Mg(BH₄)₂ was slightly reduced (0.5 m² g⁻¹).

Table S1. Surface area (m² g⁻¹) of γ -Mg(BH₄)₂ and α -Mg(BH₄)₂ before and after contact with 1 bar of CO₂ at 30°C for 3 days. In italics is indicated the value obtained with the higher correlation coefficient for each material.

	S _{BET}	S _{Langmuir}
γ -Mg(BH ₄) ₂	325	458
γ -Mg(BH ₄) ₂ /CO ₂	<i>18</i>	24
α -Mg(BH ₄) ₂	4	10
α -Mg(BH ₄) ₂ /CO ₂	<i>0.5</i>	0.8

S6. IR spectrum of the gas phase composition after CO₂ reaction with γ -Mg(BH₄)₂ for 3 days.

The comparison of the spectral features reported in Figure S5 with the data present in NIST Standard Reference Database⁶ allowed to identify all the gas phase components as unreacted CO₂ and B₂H₆, liberated from the pores after the collapse of the structure. No gaseous organic products from the CO₂ reaction with γ -Mg(BH₄)₂ are observed at RT and 1 bar.

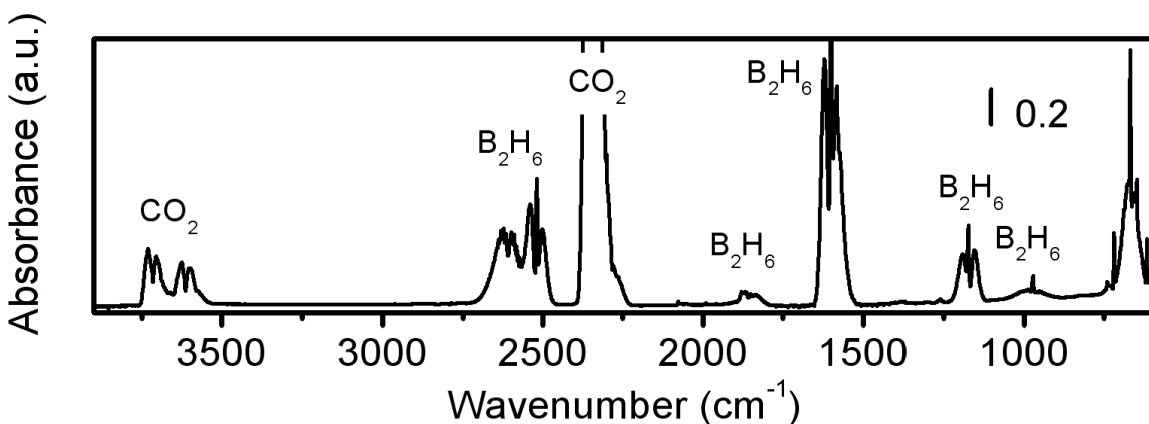


Figure S5. IR spectrum of the gas phase environment after 3 days of reaction of γ -Mg(BH₄)₂ with 1 bar of CO₂

1 K. Chlopek, C. Frommen, A. Leon, O. Zabara, M. Fichtner, *J. Mater. Chem.* **2007**, *17*, 3496.

2 R. Xiong, J. S. Zhang, J. W. Lee, *J. Phys. Chem. C* **2013**, *117*, 3799.

3 L. Lutterotti, S. Matthies, H.-R. Wenk, "MAUD: a friendly Java program for material analysis using diffraction", *IUCr: Newsletter of the CPD*, *21* (1999), 14.

⁴ N. P. Stadie, E. Callini, B. Richter, T. R. Jensen, A. Borgschulte and A. Züttel, *J. Am. Chem. Soc.*, **2014**, *136*, 8181-8184.

⁵ Y. Filinchuk, B. Richter, T. R. Jensen, V. Dmitriev, D. Chernyshov and H. Hagemann, *Angew. Chem. Int. Ed.*, **2011**, *50*, 11162–11166.

⁶ NIST Standard Reference Database 69: NIST Chemistry WebBook, <http://webbook.nist.gov/>.