SUPPLEMENTARY INFORMATION

Hydrogen Cycling in γ-$Mg(BH_4)_2$ with Cobalt-based Additives

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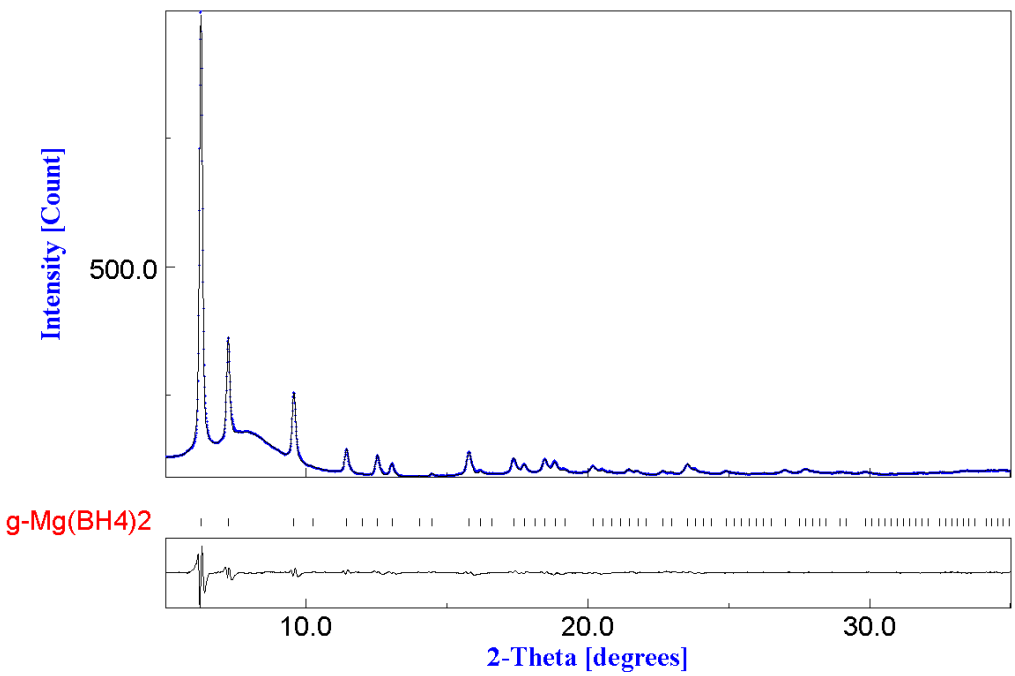

Fig. S1. SR-PXD (λ = 0.70135 Å) pattern of the commercial milled $Mg(BH_4)_2$ (S1) showing only γ-phase and a small amount of amorphous phase(s).

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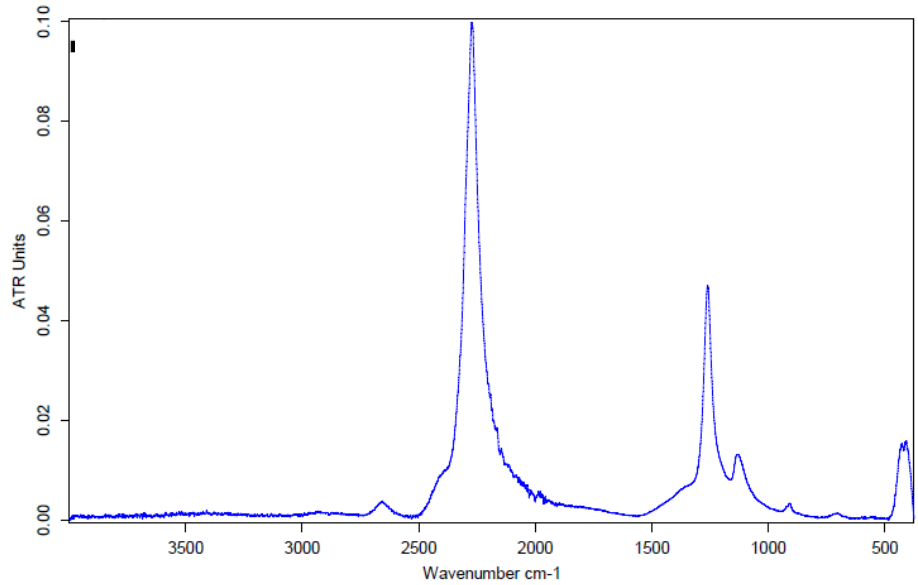

Fig. S2. IR-ATR spectrum of commercial γ-$Mg(BH_4)_2$ used for sample preparation (S0).

Table S1. Solid-state reaction models[1] (general equation and the equation for y=0.5 at $t=t_{0.5}$) used for comparison with the experimental desorption and absorption curves (Fig. 2). The curves shown on Fig. 2 were plotted according to the numerical data for y and $t/t_{0.5}$ reported in ref. S1 (ref.33).

Short name	Equation	Description
D1	$D_1(y) = y^2 = \frac{k}{x^2}t; D_1(0.5) = 0.2500\left(\frac{t}{t_{0.5}}\right)$	1-dimentional diffusion-controlled reaction with constant diffusion coefficient, where $2x$ is the thickness of the reacting layer
D2	$D_2(y) = (1-y)\ln(1-y) + y = \frac{k}{r^2}t = 0.1534\left(\frac{t}{t_{0.5}}\right)$	2-dimentional diffusion-controlled reaction into a cylinder of radius r
D3	$D_3(y) = (1-(1-y)^{1/3})^2 = \frac{k}{r^2}t = 0.0426\left(\frac{t}{t_{0.5}}\right)$	3-dimentional diffusion-controlled reaction in a sphere of radius r
D4	$D_4(y) = \left(1-\frac{2y}{3}\right) - (1-y)^{2/3} = \frac{k}{r^2}t = 0.0367\left(\frac{t}{t_{0.5}}\right)$	Diffusion-controlled reaction starting on the exterior of a spherical particle of radius r
R2	$R_2(y) = 1-(1-y)^{1/2} = \frac{u}{r}t = 0.2929\left(\frac{t}{t_{0.5}}\right)$	Phase-boundary controlled reaction at the interface, for a circular disk reacting form the edge inwards, or for a cylinder, where u is a constant velocity of the interface

R3	$R_3(y) = 1 - (1-y)^{1/3} = \frac{u}{r}t = 0.2063\left(\frac{t}{t_{0.5}}\right)$	Phase-boundary controlled reaction at the interface, for a sphere of radius *r*, reacting from the surface inward, where *u* is a constant velocity of the interface
A2	$A_2(y) = (-\ln(1-y))^{\frac{1}{2}} = kt = 0.8326t/t_{0.5}$	Avrami-Erove'ev equation for two dimensional growth of random nuclei with constant interface velocity
A3	$A_3(y) = (-\ln(1-y))^{\frac{1}{3}} = kt = 0.8850(t/t_{0.5})$	Avrami-Erove'ev equations for three dimensional growth of random nuclei with constant interface velocity

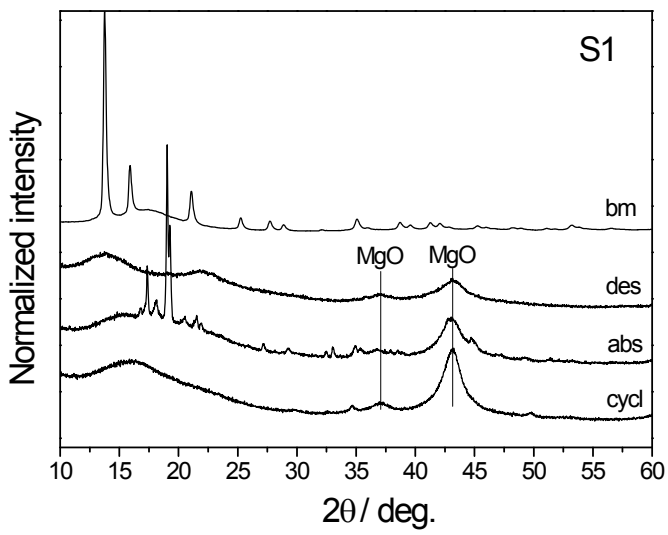

Fig. S3. PXD patterns of the S1 before (*bm*) and after desorption (*des*), after the 1st absorption (*abs*), and the 3rd absorption (*cycl*). (λ = 1.5418 Å).

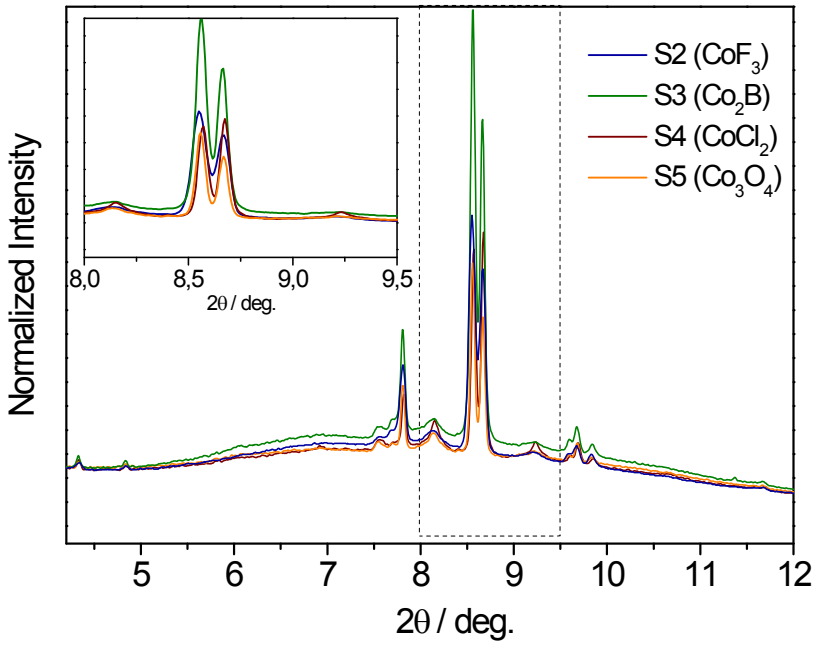

Fig. S4. SR-PXD patterns of samples S2-S5 after the 1st absorption. The inset shows the expanded view of the $Mg(BH_4)_2$ peaks in the 8.0 - 9.5° region. (λ = 0.70135 Å).

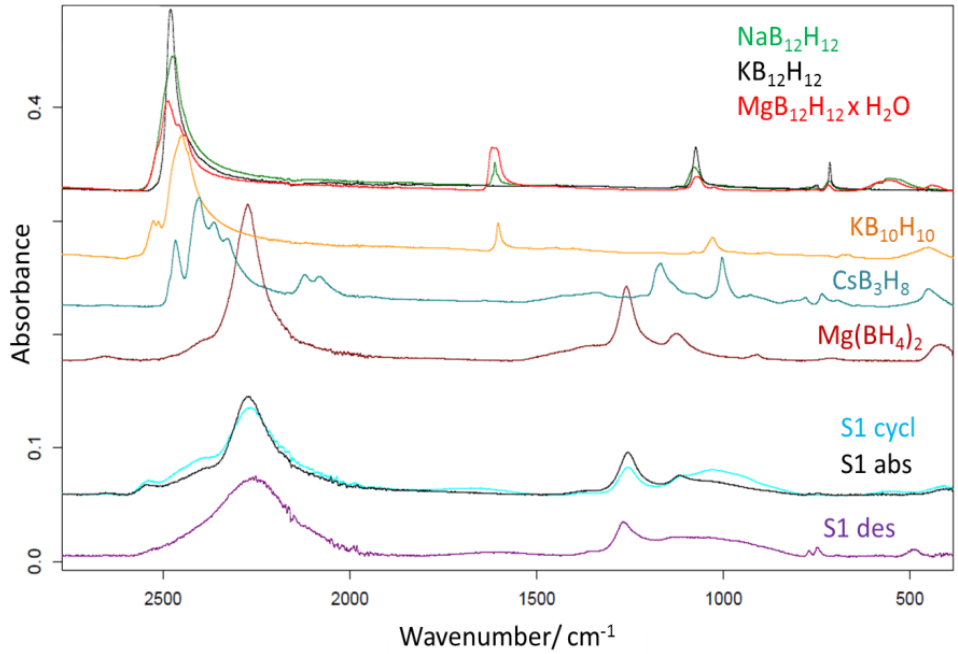

Fig. S5. ATR-IR spectra of S1 after the first desorption, 1st absorption, and cycling compared to the spectra of some reference compounds. The peaks at ν_{max}/cm^{-1} 1630 in the spectra of $MB_{12}H_{12}$ (M = Mg,Na) and $KB_{10}H_{10}$ are due to water.

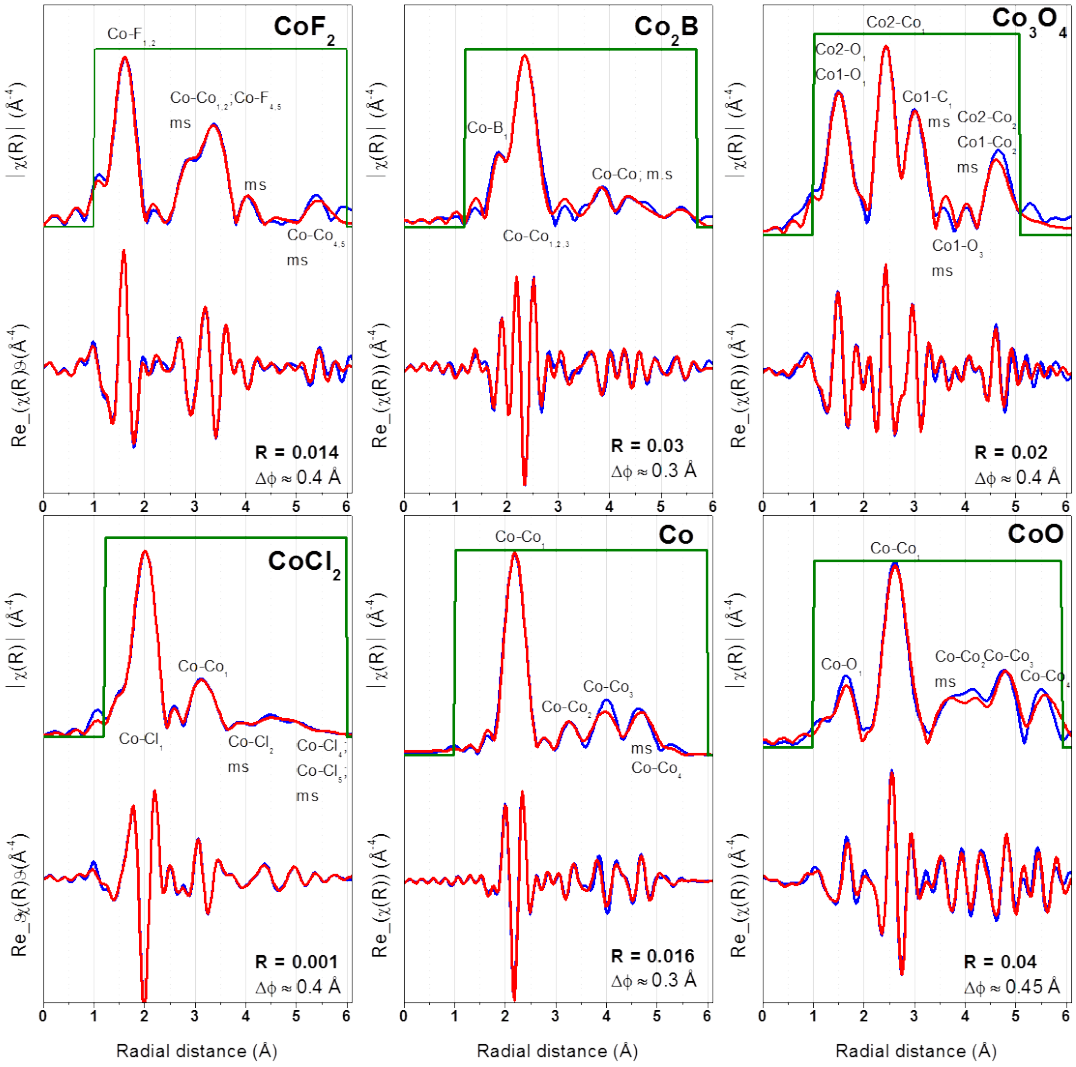

Fig. S6. Amplitude (up) and real part (bottom) of the k^3-weighted FT of the EXAFS spectra of the commercial additives that were used as references, and peak assignment. Fit quality **R** and phase shift $\Delta\varphi$ are reported on the figures. Experimental data are plotted in blue, fit – in red, and fitting window – in green. **CoF_2:** The assignment was based on the fit to the 25 theoretical single scattering (ss) and multiple scattering (ms) paths. Only the largest contributing backscattering neighbors are indicated on the figure. Several less significant multiple scattering paths at the larger *R* (4.5 – 6 Å) were omitted, which is the reason of the somewhat worse fit in this region. The parameters of the fit were: passive electron reduction factor S_0^2, shift in the edge energy ΔE_0, mean square displacement σ^2, and changes in the lattice parameters. σ^2 for the multiple scattering paths was expressed through the respective values for the single scattering

paths involving the same scatters.[2] ΔR was expressed through the lattice parameters minus R_{eff}, where the latter is the initial interatomic distance. **Co_2B:** Fit of the 13 theoretical ss and ms paths in the range 1.17-5.7 Å. Due to the complexity of the structure, several less significant multiple scattering paths were omitted which is the reason of larger errors. This fit however still satisfies our purposes of peak assignment. The parameters of the fit were: passive electron reduction factor S_0^2, shift in the edge energy ΔE_0, mean square displacement σ^2, and changes in the lattice parameters. σ^2 for the multiple scattering paths was expressed through the respective values for the single scattering paths involving the same scatters. ΔR was expressed through the lattice parameters minus R_{eff}, where the latter is the initial interatomic distance. **$CoCl_2$:** fit of 10 ss and ms pathways with parameters S_0^2, ΔE_0, σ^2, ΔR. **Co_3O_4:** fit of 17 ss and ms pathways with parameters S_0^2, ΔE_0, σ^2, *alpha, deltaa*. The fit was performed based on two FEFF calculations for the Co1 (Co^{2+}, tetrahedral coordination, ⅓ 1/3 of atoms) and Co2 (Co^{3+}, octahedral coordination, ⅔ atoms). S_0^2 for Co2 was expressed as $S_0^2(1)*2$. ΔR was expressed through R_{eff}*alpha* for multiple scattering pathways and through the cell parameter a ($a = a_0 + deltaa$) for the single scattering pathways. The misfit results from the omitting of some less significant ms pathways and also probably from some slight differences between the crystallographic structure and the Co_3O_4 sample used in this work. **CoO:** fit of 25 ss and ms pathways with parameters S_0^2, ΔE_0, σ^2, *alpha*. ΔR was expressed through R_{eff}*alpha*. The misfit results from the omitting of some less significant ms pathways and also probably from some slight disorder in the CoO sample. The latter is especially true for the fit of the first two peaks where all theoretical pathways are included in the model. **Co:** fit of 28 ss and ms pathways with parameters S_0^2, ΔE_0, σ^2, *alpha*. ΔR was expressed through R_{eff}*alpha*.

References

S1. J. H. Sharp, G. W. Brindely and B. N. Narahari Achar, *J. Am. Ceram. Soc.*, 1966, **49**, 379-382.

S2. E. A. Hadson, P. G. Allen, L. J. Terminello, M. A. Denecke and T. Reich, *Phys. Rev. B: Condens. Matter*, 1996, 156-165.