Gas–Solid Exchange

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Isotopic Exchange in Porous and Dense Magnesium Borohydride**

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Abstract: *Magnesium borohydride ($Mg(BH_4)_2$) is one of the most promising complex hydrides presently studied for energy-related applications. Many of its properties depend on the stability of the BH_4^- anion. The BH_4^- stability was investigated with respect to H→D exchange. In situ Raman measurements on high-surface-area porous $Mg(BH_4)_2$ in 0.3 MPa D_2 have shown that the isotopic exchange at appreciable rates occurs already at 373 K. This is the lowest exchange temperature observed in stable borohydrides. Gas–solid isotopic exchange follows the $BH_4^- + D^\bullet \rightarrow BH_3D^- + H^\bullet$ mechanism at least at the initial reaction steps. Ex situ deuteration of porous $Mg(BH_4)_2$ and its dense-phase polymorph indicates that the intrinsic porosity of the hydride is the key behind the high isotopic exchange rates. It implies that the solid-state H(D) diffusion is considerably slower than the gas–solid H→D exchange reaction at the surface and it is a rate-limiting steps for hydrogen desorption and absorption in $Mg(BH_4)_2$.*

Metal borohydrides (MBHs) are complex hydrides containing hydrogen-rich molecular BH_4^- anions counterbalanced by metal cations. Alkali or alkaline-earth MBHs (but Be) are ionic stable compounds, decomposing above 473 K with release of mostly H_2.[1] Their stability is related to the strong B−H bonds in BH_4^-, which are only slightly perturbed by weak interactions with the cations.[2] Owing to the high hydrogen density, MBHs have been extensively studied for solid-state hydrogen-storage applications.[1] The compounds with the highest hydrogen content, lowest stability, and those releasing mostly H_2 are most attractive. $Mg(BH_4)_2$ has one of the highest hydrogen capacities (14.8 wt % H),[3] and DFT calculations predicted an exceptional, compared to other stable MBHs, thermodynamics with decomposition and H_2 release below 373 K.[4] However, in practice $Mg(BH_4)_2$ decomposes above 473 K.[5] These inconsistencies have been partially attributed to high kinetic barriers.[6]

$Mg(BH_4)_2$ has a number of polymorphs, among them the γ-phase, which is the first example of a nanoporous hydride with high specific surface area (SSA, $> 1000\,m^2\,g^{-1}$[7]). The pores have a diameter of about 7 Å and are accessible to guest molecules. Other polymorphs of $Mg(BH_4)_2$, α-, β-, β′-, ε-, δ-, ζ-$Mg(BH_4)_2$,[5a,7,8] and amorphous,[8c] do not possess this unique high SSA. At about 423–473 K both α-, and γ-$Mg(BH_4)_2$ irreversibly transform through several high-temperature polymorphs to β-$Mg(BH_4)_2$, which decomposes above 473 K.[5a,b]

Herein the stability of BH_4^- with respect to H→D substitution in γ-, β-, and (ε + β)-$Mg(BH_4)_2$ was studied by vibrational spectroscopy. Raman and IR spectroscopy is particularly useful for characterization of the BH_4^- structure and the environment in MBHs.[9] Free molecular BH_4^- ions have T_d symmetry and four normal modes of vibrations: symmetric stretching and bending, $\nu_1(A_1$, Raman-active (R)) and $\nu_2(E$, R); asymmetric stretching and bending, $\nu_3(F_2$, IR-active, R) and $\nu_4(F_2$, IR, R), respectively. The E mode is doubly degenerate, and F mode is triply degenerate. When BH_4^- is embedded in a crystalline lattice, the symmetry of BH_4^- is lowered owing to site-symmetry and crystal-field effects. This can cause splitting of degenerate and activation of inactive vibrations,[10] as is also seen in the IR spectra of γ-$Mg(BH_4)_2$ (Supporting Information, Figure S1). H→D substitution causes further changes in the spectra, which is firstly due to the symmetry-lowering: $BH_4(T_d) \rightarrow BH_3D(C_{3v}) \rightarrow BH_2D_2(C_{2v})$, and because of the new modes of B−D-containing groups. Owing to the large mass difference of the isotopes, vibrational spectra of the molecular groups with H and D are easily distinguished and can be used to study various intermolecular processes in complex hydrides.[11] Previous studies of H→D substitution in alkali borohydrides (Li, Na, K) were carried out at high T (> 473 K) for many hours confirming the stability of BH_4^-.[12a–c] Lower exchange temperatures (405–445 K) were found by ex situ deuteration of dense α-$Mg(BH_4)_2$ and $Ca(BH_4)_2$,[12d] and thus correlating with the lower T_{dec} compared to alkali MBHs.[1] Herein we study the isotopic exchange in nanoporous γ-$Mg(BH_4)_2$ and show that the H→D substitution occurs as low as 373 K at only 0.3 MPa D_2. We suggest that the higher exchange T, p, or reaction time is required primarily to overcome the D bulk diffusion kinetic barriers.

Upon heating γ-$Mg(BH_4)_2$ in 0.3 MPa of D_2, the first evidence of H→D exchange appeared in the Raman spectrum (Figure 1) as a peak at 1717 cm^{-1} corresponding to the B−D stretching frequency region in borohydrides[13] and assigned to the ν(B−D) in BDH_3^- (see the Supporting

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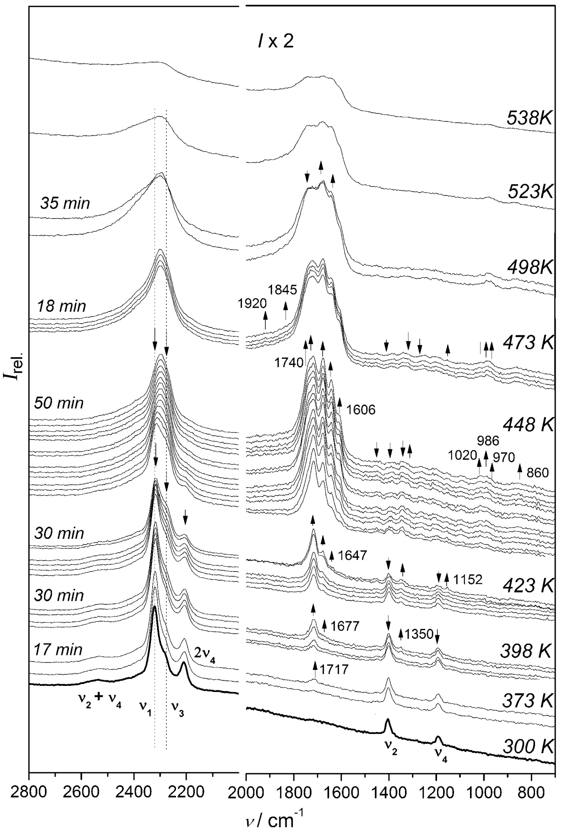

Figure 1. Selected in situ Raman spectra of H → D exchange in γ-$Mg(BH_4)_2$ at different isothermal steps. The intensity in the 2000–700 cm^{-1} region is multiplied by two.

Information). It is expected that the exchange reaction had started at even lower T but was not detected owing to the insufficient concentration of the substituted species. With further heating up to 398, 423, 448 K and isothermally at those steps, the peak at 1717 cm^{-1} grew in intensity and developed shoulders at 1677, 1647, and 1606 cm^{-1}, which was attributed to the symmetric B–D stretching (ν_s) in $BD_2H_2^-$, BD_3H^-, and BD_4^-, respectively. Simultaneously, the intensity of $\nu_1(BH_4)$ and $\nu_2(BH_4)$ modes at 2320 and 1404 cm^{-1} decreased indicating destruction of the BH_4^- groups. The symmetric bending mode ν_2 of tetrahedral molecules can only be observed in isotopically pure BX_4^- ions. By the end of the 473 K isotherm, the $\nu_2(BH_4)$ had disappeared indicating that in most BH_4^- at least one H was substituted with D. Instead, multiple weak peaks developed in the 1600–1100 cm^{-1} region owing to the transformation of $\nu_2(BH_4)$ into the bending modes of various newly formed $BH_xD_{4-x}^-$. The D–B–D bending modes of these deuterated ions appeared at 1050–700 cm^{-1}.[13] Above 498 K the exchange reaction rates slowed down significantly. The intensity of the 1677–1647–1606 cm^{-1} peaks increased at the expense of the 1717 cm^{-1} peak, as expected from gradual substitution. Above 473 K the spectra started to show fluorescent background, leading to complete disappearance of the $Mg(BH_4)_2$ vibrational features at 538 K. We relate this to the sample decomposition[5,14a] and formation of reaction product(s) that are fluorescent with 532 nm excitation laser wavelength.

The in situ observation of the $BDH_3 \rightarrow BD_2H_2 \rightarrow BD_3H \rightarrow BD_4$ formation demonstrates that the isotopic substitution occurs via the exchange reaction between a single D atom of a D_2 molecule and one H atom from $BH_xD_{4-x}^-$ but not via the $BH_4 + D_2 \rightarrow BH_2D_2$ mechanism, at least at the initial steps. The exchange reaction may follow $BH_4^- + D_2 \rightarrow BH_3D^- + HD$ or $2BH_4^- + D_2 \rightarrow 2BH_3D^- + H_2$ pathway. In the gas phase, only D_2 was observed (Supporting Information, Figure S2), which is most probably because of the low concentration of the exchanged gas. Both exchange mechanisms imply that the B–H bonds in $Mg(BH_4)_2$ break in the very mild conditions, which is in agreement with the low thermodynamic stability of $Mg(BH_4)_2$ predicted by the DFT calculations.[4] Note also that $Mg(BH_4)_2$ was shown to undergo the reactions with B_2H_6/H_2 and metal hydrides in the solid state with the formation of higher boranes at the comparably low temperatures.[14b,c] The H → D exchange can follow similar reaction mechanisms.

The intensity of the BH_xD_{4-x} peaks can be related to the concentration of the respective species.[12c] Figure 2 shows the 448 K isotherm, where the integrated intensity of each peak (normalized by the sum of ν(B–H) + ν(B–D) intensity[12c]) is plotted. This graph also shows that the total intensity of the B–D peaks increases with the same reaction constant as the intensity of B–H stretching peaks declines. This confirms H → D substitution reaction and not decomposition.

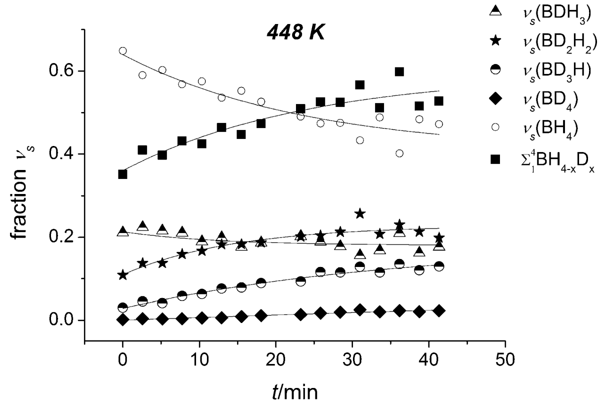

Figure 2. Integrated intensity of the peaks at 2321 cm^{-1} ($\nu_s(BH_4)$) and the peaks at 1717, 1677, 1647, 1606 cm^{-1} assigned to the symmetric B–D stretching, ν_s, in various BH_xD_{4-x} at 448 K. Total intensity (Σ) of the B–D stretching peaks is also plotted for comparison with the $\nu_s(BH_4)$. The lines are merely to guide the eye.

The highest H → D exchange rates were observed in the phase-transition temperature region of γ-$Mg(BH_4)_2$ at 448 K.[5a] After heating to 548 K (at the end of the experiment), γ-$Mg(BH_4)_2$ was transformed to β-$Mg(BH_4)_2$ (Supporting Information, Figure S3). To understand if there is a relation between H → D exchange and the phase transitions, we deuterated three different polymorphs of $Mg(BH_4)_2$: as-received porous γ-$Mg(BH_4)_2$, a mixture of (ε + β)-, and dense β-$Mg(BH_4)_2$. ε-$Mg(BH_4)_2$ in the (ε + β)-sample was identified from comparison with published PXD pattern (Supporting Information, Figure S4b,d).[5a] The IR spectra of the deuterated samples, obtained ex situ (Figure 3), indicate that the most hydrogen was substituted in the porous γ-$Mg(BH_4)_2$, and

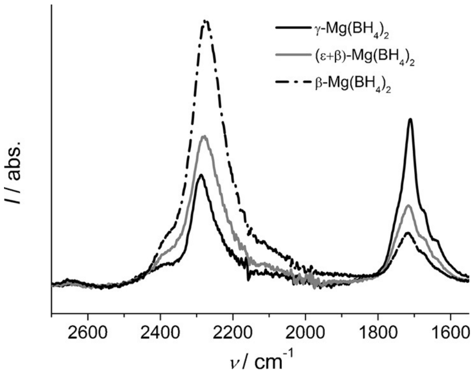

Figure 3. IR spectra of the three $Mg(BH_4)_2$ phase polymorphs after 2 h deuteration under 0.3 MPa D_2 at 440 K.

the least in the dense β-$Mg(BH_4)_2$. To obtain approximately similar to γ-$Mg(BH_4)_2$ exchange in α-$Mg(BH_4)_2$, 23 h and 4.2 MPa D_2 at 435 K was required.[12d] Comparing the vibrational spectra of the four polymorphs (Supporting Information, Figure S5),[11a] it can be seen that the B–H and B–D vibrations are found in the same energy ranges. This implies that the BH_4^- in all phases have similar environment and therefore similar stability of B–H bonds. Thus it appears that the H→D exchange rates in $Mg(BH_4)_2$ depend on the porosity and the surface area of the borohydride. The intermediate exchange rates in (ε+β)-$Mg(BH_4)_2$ between those of the γ- and β-polymorphs suggest that the ε phase should have some porosity.

Isotopic exchange comprises two major phenomena: gas–solid exchange and solid-state diffusion of D into the bulk between different BH_xD_{4-x} ions. In the porous high SSA γ-$Mg(BH_4)_2$ the concentration of the deuterated species on and near the surface after gas–solid reaction is already sufficient to be measured in situ on a timescale of minutes. Indeed this corresponds to the timescale for the gas–solid exchange, as shown by our in situ measurements. In the dense polymorphs (α and β), this reaction occurs probably with the rates similar to those of porous γ-$Mg(BH_4)_2$. However, owing to the very low SSA, the concentration of the deuterated species on the surface is too low to be detected after short deuteration time and low T, p. A representation of the isotopic-exchange reaction in the porous and dense $Mg(BH_4)_2$ is shown in the Supporting Information, Figure S6. A similar relation between the surface area of an adsorbent and the IR intensity of the physisorbed molecules is known from surface studies by vibrational spectroscopy.[15] Increase in T, p, and/or reaction time, enhances D diffusion into the bulk of dense $Mg(BH_4)_2$, and thus the concentration of the deuterated species becomes sufficient to measure. We suggest therefore that bulk D diffusion is the rate-limiting step in the isotope exchange reactions, and likely in dehydrogenation and re-hydrogenation reactions in $Mg(BH_4)_2$. This justifies increasing the SSA of a borohydride by, for example ball-milling or dispersing it in the porous matrix, as a good method to improve the kinetics of the diffusion-related reactions. It also implies that the activation energy E_a of $51 \pm 15\,kJ\,mol^{-1}$ for the isotope-exchange reaction, reported by Hagemann et al.[12d] for α-$Mg(BH_4)_2$, should be related mostly to bulk D diffusion. The in situ studies on high-surface-area metal hydrides will allow separating the two processes and determining E_a of the gas–solid reactions. This approach can be applied not only to H-sorption reactions but also to other processes such as, for example, oxidation, hydrolysis, and reduction of CO_2.

Experimental Section

All sample handling was performed in an Ar-filled glove box with O_2 and H_2O levels kept under 0.1 ppm. Commercial γ-$Mg(BH_4)_2$ (Sigma–Aldrich, 95%) was used as received. β-$Mg(BH_4)_2$ and (ε+β)-$Mg(BH_4)_2$ were prepared from γ-$Mg(BH_4)_2$ (see the Supporting Information). For the Raman measurements, circa 10 mg of γ-$Mg(BH_4)_2$ was pressed into pellet and loaded into a cell with a sapphire window designed for in situ studies at variable T and p. After a prolonged pumping in vacuum, the cell was filled with 0.3 MPa D_2 and heated at $5\,K\,min^{-1}$. The heating was paused at various temperatures to record Raman spectra. For the ex situ deuteration, γ-, (ε+β)-, and β-$Mg(BH_4)_2$ (ca. 20–30 mg) were heated at 440 ± 4 K in 0.34 ± 0.06 MPa D_2 for 2 h. Powder X-ray Diffraction (PXD) patterns were obtained before and after deuteration (Supporting Information, Figure S4). Attenuated total reflection IR (ATR-IR) measurements were performed on the pure samples without dilution before and after deuteration in the Ar-filled glove box at room temperature. More experimental details can be found in the Supporting Information.

Keywords: gas–solid exchange · hydrogen isotope exchange · magnesium borohydride · Raman spectroscopy

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