Sorption reactions in Reactive Hydride Composites (RHC) and partially fluorine substituted composites

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Hydrogen storage in solid materials is a decisive factor in the application of fuel cell technologies. Fast kinetics and dehydrogenation enthalpies around 25-50 kJ mol^{-1} H_2 (P_{eq}= 1bar) are needed for compatibility with PEM fuel cells. An approach to improve reaction kinetics and thermodynamics is the destabilization by use of combined systems; especially those consisted of combination of two hydrides. The two hydrides react with each other to form a new compound during dehydrogenation reaction. This formation is exothermic and thus the overall dehydrogenation enthalpy is lowered [1]. These kinds of mixtures are called reactive hydride composites (RHC). The $Ca(BH_4)_2+MgH_2 \rightarrow CaH_2+MgB_2+4H_2$ as RHC is a promising material for hydrogen storage [2], however kinetics constrains impede their practical application. With the addition of F atoms in the form of a suitable compound a destabilization of the system is expected. The present work study the effect of adding an related F-compound directly to the charged form $Ca(BH_4)_2$ + MgH_2 or the uncharged form CaH_2+MgB_2.

The following Ca-based reactive hydride composites (RHC) were prepared by ball milling: 1) $9CaH_2+10MgB_2+CaF_2$ and 2) $10Ca(BH_4)_2+9MgH_2+MgF_2$. The as-milled non-hydrogenated (uncharged) composite was heated at 350°C and exposed to hydrogen atmosphere at 130 bar in a PCTPro-2000 (SETARAM Instrumentation) manometric instrument. Dehydrogenation reaction was followed by in situ SR-PXD. Figure 1 presents the in situ SR-PXD characterization of the dehydrogenation behavior of $9CaH_2+10MgB_2+CaF_2$ – 1ab composite. After hydrogenation, the formation of $Ca(BH_4)_2$, MgH_2 and $Ca_4Mg_3H_{14}$ can be observed (bottom of Figure 1). Additionally to the peaks of unreacted CaF_2 and MgB_2 several unidentified peaks are present. As the heating process, at around 160°C, the α- to β-$Ca(BH_4)_2$ phase transformation is observed. The formation of CaH_2 stared at 325°C, the intensities of CaF_2 and MgB_2 peaks increase. Simultaneously, the peak intensity of hydrogenated phases $Ca(BH_4)_2$ and MgH_2 decrease. The peaks of $Ca_4Mg_3H_{14}$ and mostly of the original unidentified phases disappear after some time in isothermal conditions. After the dehydrogenation reaction, the presence of CaF_2, MgB_2, CaH_2, Mg and unidentified peaks at 2.8 and 3.0 $Å^{-1}$ are observed. The presence of Mg and unidentified phases is not desired, because this can reduce the overall reversibility after several cycles. The dehydrogenation of $3CaH_2+4MgB_2+CaF_2$ – 1ab was studied elsewhere [3]. In the $3CaH_2+4MgB_2+CaF_2$ composite was not evidence of formation of $Ca_4Mg_3H_{14}$ after hydrogenation. An unidentified peak at 1.6 $Å^{-1}$ was also observed in this material.

The dehydrogenation of $10Ca(BH_4)_2+9MgH_2+MgF_2$ monitored by in situ SR-PXD is presented in Figure 2. The as milled material present peaks corresponding to $Ca(BH_4)_2$, MgH_2 and MgF_2. In addition to the intense broadening of peaks as a result of ball milling, there is the presence of several unidentified peaks. Most of these peaks disappear at the α- to β- $Ca(BH_4)_2$ phase transition temperature. At 350°C, the peaks

corresponding to $Ca(BH_4)_2$ and MgH_2 species vanishes and emerge peaks of CaF_2, CaH_2 and Mg. CaF_2 was not present in the initial mixture, it was formed under dehydrogenation reaction; this indicates a mobility of F atoms during the solid-gas reactions. The formation of CaF_2 is favored thermodynamically, ΔH_{298} = -1229.3 kJ mol^{-1}, vs MgF_2 ΔH_{298} =-1124 kJ mol^{-1} [4].

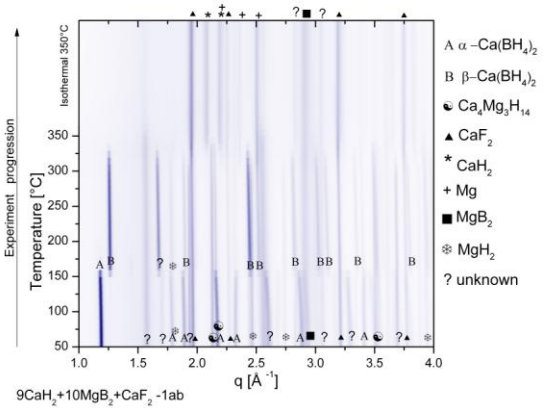

Figure 1. In situ SR-PXD dehydrogenation of $9CaH_2+10MgB_2+CaF_2$–1ab RHC. (5°C min^{-1}, λ= 0.7 Å)

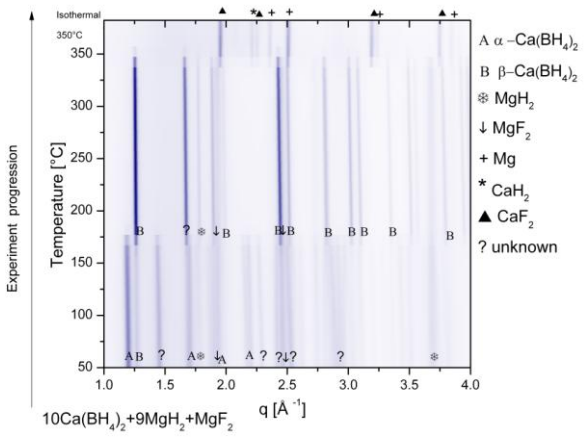

Figure 3. In situ SR-PXD first dehydrogenation of $10Ca(BH_4)_2+9MgH_2+MgF_2$ RHC. (5°C min^{-1}, λ= 0.7 Å)

Conclusions

The formation of CaF_2 is observed after dehydrogenation of $10Ca(BH_4)_2+9MgH_2+MgF_2$. The function of CaF_2 in the RHC is as a doping agent, no formation of fluorine substituted $Ca(BH_4)_2$ is evident. In the long term, the reversibility of the RHC is compromised by the formation of ternary hydride $Ca_4Mg_3H_{14}$ during hydrogenation and by the formation of Mg instead of MgB_2 during dehydrogenation.

References

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