

Final Draft
of the original manuscript:

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**Nanoconfined $2\text{LiBH}_4\text{-MgH}_2\text{-TiCl}_3$ in carbon aerogel scaffold
for reversible hydrogen storage**
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[14]. Not only metal hydrides, but also complex hydrides have been infiltrated in nanoporous carbon aerogels, and they presented superior kinetics as compared with ball-milled materials. Nanoconfined NaAlH₄ prepared by melt infiltration showed a single-step dehydrogenation at low temperatures as well as rehydrogenation at mild condition (e.g., 24 bar H₂ at 150 °C) [17]. Besides, a lot of attention has been focused on the confinement of LiBH₄ in nanoporous carbon aerogel scaffold, due to its high gravimetric H₂ storage capacity (18.5 wt. %) [5]. Simultaneously, nanoconfinements of reactive hydride composites (e.g., 2LiBH₄-MgH₂ [4, 18-19], 2NaBH₄-MgH₂ [20], and LiBH₄-Ca(BH₄)₂ [21]) have also been carried out. All of them showed a considerable improvement in hydrogen sorption kinetics. For example, nanoconfined 2LiBH₄-MgH₂ in resorcinol-formaldehyde carbon aerogel released hydrogen ten times faster than the bulk sample during the 1st dehydrogenation [4]. Moreover, instead of a normal two-step dehydrogenation, a single-step reaction was obtained from 2LiBH₄-MgH₂ after nanoconfinement, suggesting that the thermodynamics had changed [4, 18]. Furthermore, catalytic doping in the nanoconfined hydride sample was performed to improve its kinetic properties. Nielsen et al. [22] reported that nanoconfinement of NaAlH₄ in carbon aerogel catalyzed with 3.0 wt. % TiCl₃ showed superior dehydrogenation kinetics over both nanoconfined NaAlH₄ (without catalyst) and bulk NaAlH₄-TiCl₃.

On the basis of 2LiBH₄-MgH₂ composite, it is well known that various additives, such as TiCl₃, ZrCl₄, VCl₃ [12, 23], TiO₂ [24], and Nb₂O₅ [25] have been loaded to optimize the reaction performance during de-/rehydrogenation. In the present study, we extend our previous research by focusing on kinetic improvement of the nanoconfined 2LiBH₄-MgH₂ in carbon aerogel scaffold by catalytic doping. Prior to melt infiltration of 2LiBH₄-MgH₂, titanium trichloride (TiCl₃) is impregnated in carbon aerogel scaffold prepared from resorcinol-formaldehyde (RF) aerogel. Nanoconfinements of both hydride composite and catalyst are confirmed by N₂ adsorption-desorption measurements, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). Dehydrogenation, reversibility, reaction mechanisms, and kinetics of both nanoconfined samples (with and without TiCl₃) are determined by *in situ* synchrotron radiation powder X-ray diffraction (SR-PXD), Fourier transform infrared spectroscopy (FTIR), coupled manometric-calorimetric measurements, and titration experiments.

Figure 1

Figure 2

Figure 3

Figure 4

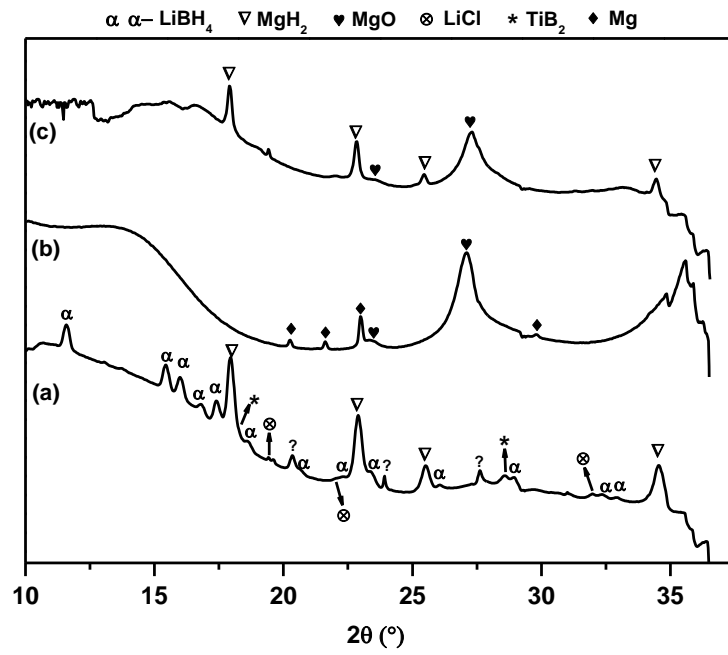


Figure 5

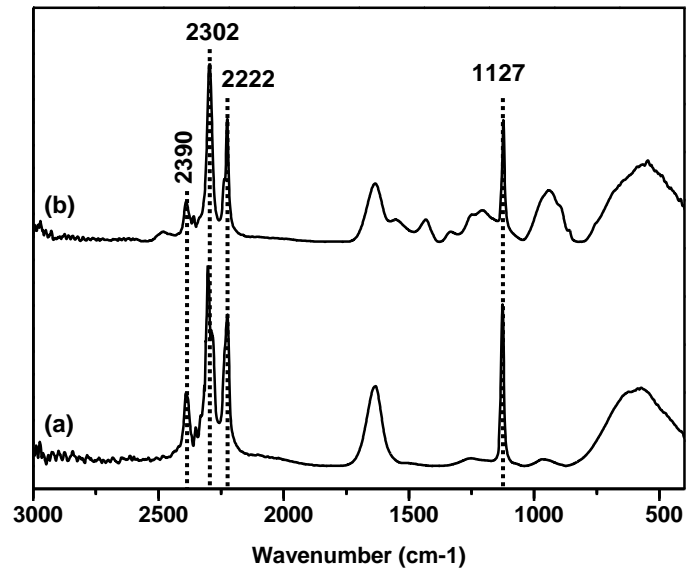


Figure 6