

Symbiotic CeH_{2.73}/CeO₂ Catalyst: a Novel Hydrogen Pump

A novel symbiotic CeH_{2.73}/CeO₂ catalyst was *in situ* induced in Mg-based hydrides, leading to remarkably reduced hydrogen desorption temperatures. More importantly, we reveal a spontaneous hydrogen release effect at the CeH_{2.73}/CeO₂ interface using *in situ* High-Resolution Transmission Electron Microscope (HRTEM) and *ab-initio* calculations.

Using additives/catalysts to destabilize hydrides of high hydrogen storage density, e.g. MgH₂ with 7.6 wt.%-H and desorption temperature as high as 300-400 °C, is one of the most important strategies to overcome the hurdle of applying hydrogen storage materials in technologies related to hydrogen energy. Despite tremendous efforts, the development of additives/catalysts with high catalytic activity and easy doping remains a great challenge. In this work, we report a simple method to induce a novel symbiotic CeH_{2.73}/CeO₂ catalyst in Mg-based hydrides, which is capable of being mass produced. The first step is to hydrogenate the amorphous Mg-Ce-Ni alloy to get a multiphase composite of MgH₂, Mg₂NiH₄ and CeH_{2.73}, and the second step is to oxidize the hydrogenated sample to generate CeO₂ from CeH_{2.73}. Moreover, we reveal a spontaneous hydrogen release effect at the CeH_{2.73}/CeO₂ interface, which leads to a dramatic increase of catalytic activity compared with either the CeH_{2.73} or CeO₂ catalyst alone. TPD-MS analysis was performed on a **Hidden QIC-20** mass spectrometer (Figure 1a). With the increase of the CeH_{2.73} to CeO₂ ratio, the hydrogen desorption temperature decreases at first and then increases after reaching the trough at the molar ratio of 1:1. The catalytic activity of the symbiotic CeH_{2.73}/CeO₂ might have a close relationship with their interface density, which reaches the maximum when molar ratio of CeH_{2.73} to CeO₂ is 1:1, however, the mechanism is not well understood. The lowest dehydrogenation onset temperature is only ~210 °C in the presence of the symbiotic CeH_{2.73}/CeO₂, which is ~210 °C lower than that of conventional MgH₂.

The dynamic boundary evolution during hydrogen desorption was observed in the symbiotic CeH_{2.73}/CeO₂ at atomic resolution using *in situ* High-Resolution Transmission Electron Microscope (HRTEM) Figure 1 (b)).

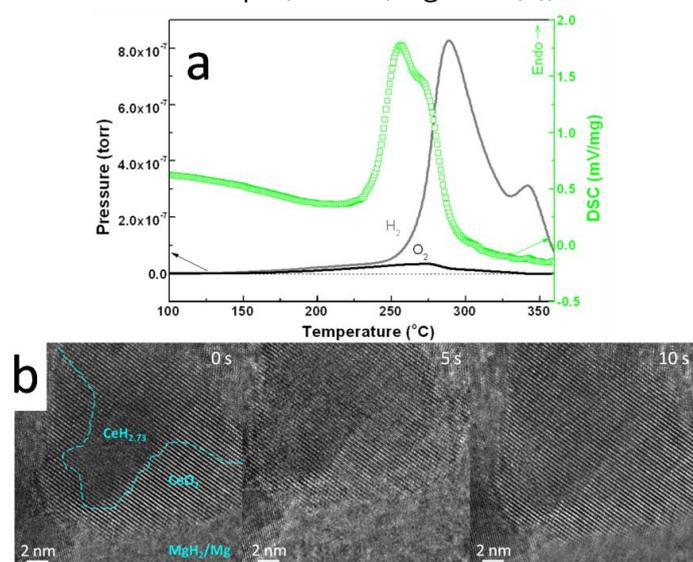


Figure 1. (a) DSC and TPD-MS curves of the symbiotic CeH_{2.73}/CeO₂ doped MgH₂, heating rate of 2 K/min. (b) *In situ* HRTEM images of the dehydrogenation process, boundary between CeH_{2.73} and CeO₂ is roughly drawn with a dash line at the beginning of hydrogen desorption

The boundary region suffers severe distortions and the distorted areas fluctuates wave-like during hydrogen desorption, suggesting that the interface region of the symbiotic nanocrystals undergo structural evolution at the atomic scale, which presumably plays a prominent role for the release of hydrogen in dehydrogenation. Combining the *ab-initio* calculations, which show significant reduction of the formation energy of hydrogen vacancy in the $\text{CeH}_{2.73}/\text{CeO}_2$ boundary region in comparison to those in the bulk MgH_2 and $\text{CeH}_{2.73}$, we demonstrate that the outstanding catalytic activity can be attributed to the spontaneous hydrogen release effect at the $\text{CeH}_{2.73}/\text{CeO}_2$ interface.

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Hidden Product:

[QGA](#) Atmospheric Gas Analysis System (was QIC-20)