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Improved hydrogen storage properties of MgH2 doped with chlorides of transition metals Hf and Fe

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Keywords
storage, hydrogen, mgh2, doped, fe, improved, properties, chlorides, transition, metals, hf

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Improved hydrogen storage properties of MgH₂ doped with chlorides of transition metals Hf and Fe

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Abstract

The effects of HfCl₄ and FeCl₃ addition on the de/rehydrogenation properties of MgH₂ were investigated. Both HfCl₄ and FeCl₃-doped MgH₂ samples started to released hydrogen at about 270 °C, a decreased of about 70 °C and about 140 °C compared to as-milled and as-received MgH₂, respectively. In terms of the desorption kinetics, the HfCl₄-doped MgH₂ sample showed significant improvement, with 6.0 wt.% hydrogen released within 10 min at 300 °C, while the FeCl₃-doped MgH₂ and undoped MgH₂ samples released 3.5 and 0.2 wt.% hydrogen, respectively, under the same conditions. In terms of the absorption kinetics, 5.5 wt.% hydrogen was charged at 300 °C under 3.0 MPa hydrogen in 1 minute for the HfCl₄-doped MgH₂ sample, while 4.8 wt.% was absorbed by the FeCl₃-doped MgH₂ sample, compared to just 3.0 wt.% hydrogen for the undoped MgH₂ sample under the same conditions. From the Arrhenius plot based on isothermal dehydrogenation kinetics at different temperatures, the apparent activation energy of as-milled MgH₂ is calculated to be 166 kJ/mol, and this value is reduced by 64 and 36 kJ/mol after doping with HfCl₄ and FeCl₃, respectively. A cycling study of dehydrogenation at 300 °C shows that the hydrogen capacity of the HfCl₄-doped MgH₂ sample was maintained at about 6 wt.% after 10 cycles. Based on the X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy examinations, we believe that the significant improvement of MgH₂ sorption properties in the doped samples is due to the catalytic effects of in-situ generated metal species and MgCl₂ that were formed during the dehydrogenation process.

Keywords: MgH₂; HfCl₄; FeCl₃; Catalytic effect

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1. Introduction

Safety and cost are the two major technical challenges for the commercialization of hydrogen storage in pressurized gas and cryogenic liquid forms. Apart from the two forms mentioned above, solid-state hydrogen storage has been an attractive option due to its high gravimetric hydrogen capacity and favourable safety considerations. Solid-state hydrogen storage materials can be divided into two categories, which is physically bound hydrogen; where the hydrogen gas is physisorbed to a high surface area substrate (exterior or interior) such as carbon nanotubes [1, 2], and chemically bound hydrogen; where the hydrogen has formed a chemical compounds with the substrate (e.g. metal hydrides [3,4] and complex hydrides [4-7]) and the hydrogen is desorbed through a thermal decomposition. Among them, metal hydride, especially MgH2, exhibits promising potential as an energy carrier due to the high energy density (7.6 wt.% for MgH2), with the added advantages of low cost and superior reversibility [8-13]. Nevertheless, its high decomposition temperature and slow desorption/absorption kinetics are two problems that limit the use of MgH2 as a hydrogen storage material [14, 15]. Extensive efforts have been made to overcome these problems, including the introduction of catalysts into MgH2. Various catalysts have been doped into MgH2 by mechanical milling. These include metals [16-18], metal oxides [19, 20], transition metal halides [21-26], carbon materials [27, 28], nanosized alloys [29, 30], and combinations of carbon materials and transition metals, transition metal halides, and Ti0.4Mn0.22Cr0.1V0.28, with this last combination termed BCC composite because of its body centred cubic structure [31-33].

Many studies have shown that the transition-metal compounds showed high effective catalysis due to the high affinity of transition-metal cations toward hydrogen [17, 34-36]. In addition, transition metal fluorides, such as TiF3 and NbF5, have been introduced into MgH2 to enhance its kinetics [21, 22, 25, 37]. It was claimed that both metal and fluorine anions contribute to the kinetic enhancement of MgH2. As a source of both transition metal and halogen anions, transition metal halides are attractive for use as an additive to prepare an Mg-based hydrogen storage system.

In this work, FeCl3 and HfCl4, with the aim of combining the functions of both transition metal cations and chlorine anions, will be introduced to prepare a MgH2–metal chloride system. Samples were analysed by Sieverts type pressure-composition-temperature (PCT) apparatus, differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The possible catalysis mechanism of the two dopants is then discussed.

2. Experimental details

Pure MgH2 (hydrogen storage grade), HfCl4 (98% purity), FeCl3 (reagent grade, 97%), and MgCl2 (anhydrous, ≥ 98%) were purchased from Sigma-Aldrich. Hafnium powder (-325 mesh, 99.6%) and Iron powder (-200 mesh, 99+% (metal basis)) were purchased from Alfa Aesar. All materials were used as received with no further purification. The MgH2 and additives were respectively loaded into a sealed stainless steel vial together with hardened stainless steel balls in an argon atmosphere MBrAun Unilab glove box. The ratio of the weight of the balls to the weight of powder was 40:1. The samples were then milled in a planetary ball mill (QM-3SP2) for 1 h, by first milling for 0.5 h, resting for 6 min, and then milling for another 0.5 h in a different direction at the rate of 400 rpm.
The experiments on de/re-hydrogenation were performed in a Sieverts-type pressure-composition-temperature (PCT) apparatus (Advanced Materials Corporation). The sample was loaded into a sample vessel in the glove box. For the temperature programmed desorption (TPD) measurements, all the samples were heated in a vacuum chamber, and the amount of desorbed hydrogen was measured to determine the lowest decomposition temperature. The heating rate for the TPD experiment was 5 °C/min, and samples were heated from room temperature to 450°C. The de/re-hydrogenation kinetics measurements were conducted at the desired temperature with initial hydrogen pressures of 0.001 MPa and 3.0 MPa, respectively.

XRD analysis was performed using a GBC MMA X-ray diffractometer with Cu Kα radiation. θ-2θ scans were carried out over diffraction angles from 20° to 80° with a speed of 2.00 °/min. Before the measurement, a small amount of sample was spread uniformly on the sample holder, which was wrapped with plastic wrap to prevent oxidation.

Differential scanning calorimetry (DSC) analysis of the dehydrogenation process was carried out on a Mettler Toledo TGA/DSC 1. The sample was loaded into an alumina crucible in the glove box. The crucible was then placed in a sealed glass bottle in order to prevent oxidation during transportation from the glove box to the DSC apparatus. An empty alumina crucible was used for reference. The samples were heated from room temperature to 500 °C under an argon flow of 30 ml/min, and the heating rate was 15 °C/min.

Fourier transformation infrared (FTIR) spectroscopy analyses were carried out using a Shimadzu IRPrestige-21 model equipped with a KBr beamsplitter and a deuterated L-alanine triglycine sulfide (DLATGS) detector. Samples were mixed uniformly with potassium bromide (KBr) powder with an agate mortar and pestle, and then put into the sample holder. KBr background spectra were recorded before analysis of the samples. 40 scans were carried out between 400 and 1600 cm⁻¹, with a spectral resolution of 4 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) were obtained using a SPECS PHOIBOS 100 analyser installed in a high-vacuum chamber with the base pressure below 10⁻⁸ mbar; X-ray excitation was provided by Al Kα radiation with photon energy \( h\nu = 1486.6 \text{ eV} \) at a high voltage of 12 kV and a power of 120 W. The XPS binding energy spectra were recorded at the pass energy of 20 eV in the fixed analyser transmission mode, and the XPS spectra of the doped samples were collected after bombardment of the sample using an Ar ion source with ion energy of 5 keV. Samples were prepared inside an Ar glove box, by dusting powders onto an adhesive carbon tape. The samples were then placed in a sealed container in order to reduce oxidation during transportation from the glove box to the XPS apparatus. Analysis of the XPS data was carried out using a commercial CasaXPS2.3.15 software package. The background was corrected using the linear approximation.

3. Results and discussion

Fig. 1 shows the temperature-programmed desorption (TPD) patterns for the dehydrogenation of as-received MgH₂, as-milled MgH₂, MgH₂ + 10 wt.% HfCl₄, and MgH₂ + 10 wt.% FeCl₃. The as-received MgH₂ starts to release hydrogen at about 410 °C, with a total dehydrogenation capacity of 7.0 wt.% H₂ by 430 °C. After milling, the onset desorption temperature of MgH₂ was reduced to about 340 °C, indicating that the milling process also influences the onset desorption temperature of MgH₂, as reported by Huot et al. [38]. After doping with HfCl₄ and FeCl₃, the onset desorption temperature of MgH₂ decreased dramatically. Both of the doped samples start to release hydrogen at about 270 °C, a decrease of about 70 °C and about 140 °C compared with the
as-milled and as-received MgH₂, respectively. However, the HfCl₄-doped MgH₂ sample showed faster desorption rates than the FeCl₃-doped MgH₂ sample.

Fig. 1. Temperature-programmed desorption (TPD) patterns for the dehydrogenation of as-received MgH₂, as-milled MgH₂, MgH₂ + 10 wt.% FeCl₃, and MgH₂ + 10 wt.% HfCl₄.

The thermal properties of the as-milled MgH₂, and the HfCl₄- and FeCl₃-doped MgH₂ samples were further investigated by DSC, as shown in Fig. 2. The as-milled MgH₂ starts to release hydrogen at about 380 °C. After doping with HfCl₄ or FeCl₃, MgH₂ starts to release hydrogen at about 310 °C, which represents a reduction of about 70 °C compared to the as-milled MgH₂. This result is comparable with the results of the PCT measurements (Fig. 1). Furthermore, it can be seen that the onset decomposition temperatures of the samples in DSC are slightly higher than in the TPD (Fig. 1). These differences may result from the fact that the dehydrogenation was conducted under different heating rates and different heating atmospheres in the two types of measurements.

Fig. 2. DSC traces of (a) as-milled MgH₂, (b) MgH₂ + 10 wt.% FeCl₃, and (c) MgH₂ + 10 wt.% HfCl₄. Heating rate: 15 °C min⁻¹, argon flow: 30 ml/min.
In order to investigate the performance of the hydrogen desorption kinetics, the hydrogen desorption capacity at constant temperature was measured. Fig. 3a and 3b presents typical hydrogen desorption curves at 300 °C and 280 °C. It is clear that doping MgH₂ with HfCl₄ significantly improves the desorption kinetics. The HfCl₄-doped MgH₂ sample can release about 5.2 wt.% hydrogen in 5 min at 300 °C, while the FeCl₃-doped MgH₂ and the undoped MgH₂ samples released about 1.5 wt.% and 0.2 wt.% hydrogen, respectively, under the same conditions. A further desorption kinetics study at 280 °C shows that the HfCl₄-doped MgH₂ sample released about 4.3 wt.% hydrogen within 20 min and the FeCl₃-doped MgH₂ sample released about 2.7 wt.%, but no hydrogen release from the pure MgH₂ was observed. This result indicates that doping with HfCl₄ results in significant improvement in desorption kinetics for MgH₂ compared with FeCl₃ doping. This kinetic enhancement is related to the energy barrier for H₂ release from MgH₂. In order to determine the effects of FeCl₃ and HfCl₄ addition on the activation energy of MgH₂, the Arrhenius equation was employed. From the Arrhenius equation, the isothermal kinetics depends on the heating temperature and can be expressed as

\[ \ln \left( \frac{\text{rate}}{T^2} \right) = \ln A - \frac{E_a}{RT} \]

Fig. 3. Desorption kinetics measurements of MgH₂, MgH₂ + 10 wt.% FeCl₃, and MgH₂ + 10 wt.% HfCl₄ at (a) 300 °C and (b) 280 °C under vacuum.
\[ k = k_0 \exp (-E_A/RT) \]  

(1)

where \( k \) is the rate of dehydrogenation, \( k_0 \) is a temperature-independent coefficient, \( E_A \) is the apparent activation energy for hydride decomposition, \( R \) is the gas constant, and \( T \) is the absolute temperature. As shown in Fig. 4, by plotting \( \ln(k) \) vs. \( 1/T \), the apparent activation energy, \( E_A \), for \( \text{H}_2 \) release from the as-milled \( \text{MgH}_2 \) sample, the \( \text{FeCl}_3 \)-doped \( \text{MgH}_2 \) sample, and the \( \text{HfCl}_4 \)-doped \( \text{MgH}_2 \) sample can be estimated. From the calculation, the apparent activation energy, \( E_A \), for the as-milled \( \text{MgH}_2 \) is 166 kJ/mol, which is comparable to the values of 168 kJ/mol and 162 kJ/mol obtained by DSC (Kissinger method), as reported in our previous papers [39,40]. This value can be lowered by 36 kJ/mol and 62 kJ/mol after doping with \( \text{FeCl}_3 \) and \( \text{HfCl}_4 \). (\( E_A = 130 \) kJ/mol for the \( \text{FeCl}_3 \)-doped \( \text{MgH}_2 \), and \( E_A = 102 \) kJ/mol for the \( \text{HfCl}_4 \)-doped \( \text{MgH}_2 \).) Thus, the decreased activation energy indicates that the desorption kinetics of the \( \text{MgH}_2 \) is significantly improved.

![Arrhenius plot](image)

Fig. 4. Arrhenius plots of \( \ln(k) \) vs. \( 1/T \) for as-milled \( \text{MgH}_2 \), \( \text{MgH}_2 + 10 \) wt.% \( \text{FeCl}_3 \), and \( \text{MgH}_2 + 10 \) wt.% \( \text{HfCl}_4 \).

Fig. 5(a) and (b) shows the absorption kinetics measurements at two different temperatures for the \( \text{HfCl}_4 \) and the \( \text{FeCl}_3 \)-doped \( \text{MgH}_2 \). For comparison, the \( \text{MgH}_2 \) is also included in this figure. The samples were soaked at two constant temperatures (280 and 300 °C) under 3 MPa hydrogen pressure. The doped samples show a significant improvement with respect to absorption kinetics. The hydrogen absorbed by the \( \text{HfCl}_4 \)-doped \( \text{MgH}_2 \) sample at 300 °C reached 5.3 wt.% within 1 min, and a hydrogen absorption capacity of 4.6 wt.% was reached by the \( \text{FeCl}_3 \)-doped \( \text{MgH}_2 \) sample at the same time. In contrast, the undoped \( \text{MgH}_2 \) sample just absorbed 2.8 wt.% hydrogen over the same time. Furthermore, the \( \text{HfCl}_4 \) and \( \text{FeCl}_3 \)-doped \( \text{MgH}_2 \) samples can absorb 4.5 and 4.0 wt.% hydrogen at 280°C within 1 min, respectively, which is higher than for the \( \text{MgH}_2 \) at 300 °C.
Fig. 5. Absorption kinetics measurement of MgH$_2$, MgH$_2$ + 10 wt.% FeCl$_3$, and MgH$_2$ + 10 wt.% HfCl$_4$ at (a) 300 °C and (b) 280 °C under 3 MPa hydrogen pressure.

Since HfCl$_4$ shows the best catalytic effects on the hydrogen absorption/desorption kinetics of MgH$_2$, the cycling performance of the HfCl$_4$-doped MgH$_2$ sample was further characterized. The cycling performance of the MgH$_2$ + 10 wt.% HfCl$_4$ sample at 300 °C after rehydrogenation at 300 °C under 3 MPa hydrogen pressure is shown in Fig. 6. The desorption kinetics persisted well, even after the 10$^{th}$ cycle, indicating that HfCl$_4$ is a good catalyst for the cycle life of MgH$_2$. The hydrogen storage capacity after 30 min desorption shows almost no decrease with cycling, being maintained at 6 wt.%, as shown in the inset of Fig. 6.
Fig. 6. The cycling performance of MgH$_2$ + 10 wt.% HfCl$_4$ at 300 °C under vacuum after rehydrogenation at 300 °C under 3 MPa hydrogen pressure. The main figure shows the hydrogen released in the 1$^{st}$, 5$^{th}$, and 10$^{th}$ cycles, while the inset shows the hydrogen capacity vs. cycle number.

Figs. 7 and 8 show XRD spectra for the FeCl$_3$ and HfCl$_4$-doped MgH$_2$ samples after milling, after dehydrogenation at 450 °C, and after rehydrogenation at 300 °C under 3 MPa hydrogen pressure. The results show that neither FeCl$_3$ nor HfCl$_4$, nor any secondary FeCl or HfCl-containing phase, was detected in either doped sample after milling, which is probably due to the

![X-ray diffraction patterns](image)

Fig. 7. X-ray diffraction patterns of the FeCl$_3$-doped MgH$_2$ (a) after milling, (b) after dehydrogenation, and (c) after rehydrogenation.
fact that the FeCl₃ and HfCl₄ grains are too small to be detectable in the MgH₂ matrix by XRD, or because the FeCl and HfCl-containing phases may exist in an amorphous state directly after ball milling. Theoretically, the reaction between MgH₂ and HfCl₄ or FeCl₃ may also occur during milling but they should not be easily detected in XRD due to fine crystalline or near-amorphous state incurred by high energy ball milling. In the dehydrogenation spectra for both samples, there are distinct peaks of Mg, which indicates that the reactions were completed. A small amount of MgO was also detected in the dehydrogenation spectra due to slight oxygen contamination. In addition, some peaks of MgCl₂ appear after dehydrogenation, suggesting that the reactions of MgH₂ + 10 wt.% FeCl₃ and MgH₂ + 10 wt.% HfCl₄ may occur as follows:

\[
\begin{align*}
3\text{MgH}_2 + 2\text{FeCl}_3 & \rightarrow 3\text{MgCl}_2 + 2\text{Fe} + 3\text{H}_2 \quad (2) \\
2\text{MgH}_2 + \text{HfCl}_4 & \rightarrow 2\text{MgCl}_2 + \text{Hf} + 2\text{H}_2 \quad (3a) \\
or \\
2\text{MgH}_2 + \text{HfCl}_4 & \rightarrow 2\text{MgCl}_2 + \text{HfH}_2 + \text{H}_2 \quad (3b)
\end{align*}
\]

For the FeCl₃-doped MgH₂ sample (Fig. 7b), peaks assigned to Fe are present, but no evidence of Hf-containing phase is observed for the HfCl₄-doped MgH₂ sample (Fig. 8b) after dehydrogenation. For the rehydrogenated sample, it can be seen that Mg is largely transformed into MgH₂. Peaks of MgCl₂ still remain, together with a small amount of MgO. For the FeCl₃-doped MgH₂ sample (Fig. 7c), Fe species still remain unchanged after rehydrogenation.

The effect of FeCl₃ and HfCl₄ addition on the MgH₂ bonding was investigated by FTIR measurements. The FTIR spectra for the as-milled MgH₂, the as-milled MgH₂ + 10 wt.% FeCl₃ and the as-milled MgH₂ + 10 wt.% HfCl₄ are shown in Fig. 9. According to Wang et al. [41], there are two main regions with active infrared vibrations of the Mg – H bonds, in which the spectra in the 400-800 cm⁻¹ region correspond to the Mg – H bending bands and the spectra in the 900 – 1300 cm⁻¹ region correspond to the Mg – H stretching bands. In our study, the stretching and bending bands for the as-milled MgH₂ are centred at about 1234 cm⁻¹ and about 704 cm⁻¹, respectively. After doping with FeCl₃ and HfCl₄, hardly any difference was found in the FTIR spectra, indicating that the MgH₂ lattice is essentially unaffected by the presence of HfCl₄ and FeCl₃. Or, the changes are too small to be detected since the mole fraction of HfCl₄ and FeCl₃ are much smaller than that of MgH₂ and therefore the majority of MgH₂ just appears chemically intact in the FTIR results.
As discussed above, the formation of MgCl₂ is probably due to the reaction between MgH₂ and HfCl₄ during the dehydrogenation process (Eq. 3(a) or (b)). The XRD spectra for the dehydrogenated and rehydrogenated samples show no detection of Hf-containing phases, due to their low concentration or amorphous structure. In order to investigate the nature of the Hf-containing species after dehydrogenation and after rehydrogenation in more detail, XPS measurements were conducted. Fig. 10 shows the Hf 4f spectra for pure HfCl₄ and for the HfCl₄-doped MgH₂ samples after dehydrogenation and after rehydrogenation. The pure HfCl₄ sample shows the characteristic peaks of Hf⁴⁺, situated at 20.3663 eV for 4f⁵/₂ and 18.6500 eV for 4f⁷/₂, as shown in Fig. 10a.
Fig. 10. XPS Hf 4f spectra with fitting results for pure HfCl₄ (a) and for MgH₂ + 10 wt.% HfCl₄ after (b) dehydrogenation and (c) rehydrogenation.

The Hf 4f transition was less pronounced in the HfCl₄-added MgH₂ samples than in the pure HfCl₄. In order to better identify the response from Hf in the spectra recorded for the HfCl₄-added MgH₂ sample after dehydrogenation and after rehydrogenation, in situ ion milling (for 10 min) using an Ar ion source with ion energy of 5 keV, as described in a previous paper [42], was employed. This resulted in a better signal-to-noise value for the Hf 4f peak as compared with that recorded for the same sample before the ion etching, although the noise level was still comparable with the signal.

Deconvolution of the peak structure using the CasaXPS2.3.15 software package was performed for the fitting of the peak structure obtained for the HfCl₄-added MgH₂ samples; Fig. 10b and 10c show the fitting results for the samples after dehydrogenation and after rehydrogenation. It is found that the dehydrogenation and rehydrogenation processes result in the shift of the Hf 4f₅/₂ and Hf 4f₇/₂ peaks from HfCl₄. For the sample after dehydrogenation, the position of the Hf 4f₅/₂ peak and of the Hf 4f₇/₂ peak is 19.0670 eV and 17.4215 eV, respectively. After rehydrogenation, there was no significant change in the Hf 4f transition that could be observed in our XPS measurements. (The positions of the Hf 4f₅/₂ and the Hf 4f₇/₂ peaks were 19.3793 eV and 17.9525 eV, respectively.) Due to the lack of evidence of local structure, we attribute these signals of intermediate valence states to Hfₓ⁺⁺-containing compounds (0 < x < 4).

In order to investigate the Hf-containing phase after dehydrogenation and after rehydrogenation in more detail, we prepared a MgH₂ sample with 50 wt.% HfCl₄, since it is not easy to analyse the phase composition of the sample with 10 wt.% HfCl₄ by XRD. Fig. 11 displays the XRD patterns of the MgH₂ sample with 50 wt.% HfCl₄ after 1 h of milling, after dehydrogenation at 450 °C, and after rehydrogenation at 300 °C under 3 MPa hydrogen pressure. After 1 h ball milling, only MgH₂ phase was detected, indicating that the HfCl₄ phase is in an amorphous state directly after ball milling. After dehydrogenation at 450 °C, as compared with the dehydrogenated MgH₂ + 10 wt.% HfCl₄ sample (Fig. 8(b)), a new diffraction peaks was formed, which is indexed as HfH₂. From the results, we assume that reaction 3(b) occurred during the dehydrogenation process in MgH₂ + 50 wt.% HfCl₄. According to Barraud et al. [43], grinding of hydrated hafnium tetrachloride, ph-HfCl₄ + Mg, leads to the formation of hafnium hydride, and this hydride starts to decompose at about 500 °C. After rehydrogenation, this diffraction peaks still remain unchanged. Based on this result, it is likely that HfH₂ was also formed during the dehydrogenation process in the 10 wt.% HfCl₄-doped MgH₂ sample.
Fig. 11. X-ray diffraction patterns of the 50 wt.% HfCl₄-doped MgH₂ (a) after milling, (b) after dehydrogenation and (c) after rehydrogenation.

XRD examination of the dehydrogenated FeCl₃ and HfCl₄-doped MgH₂ samples identifies the formation of MgCl₂, and this product still remains after rehydrogenation. The formation of MgCl₂ encourages us to speculate that MgCl₂ may be acting as a real catalyst. In addition, we assume that Hf exist as a reaction product from reaction 3(a) during the dehydrogenation process. So, to examine the effects of MgCl₂ and Hf on MgH₂, samples of MgH₂ doped with 10 wt.% MgCl₂, Hf, and (MgCl₂ + Hf) were prepared, as shown in Fig. 12. For comparison, the as-milled MgH₂ and the MgH₂ + 10 wt.% HfCl₄ are also included in this figure. It is clear that the dehydrogenation temperature of MgH₂ was improved by doping with MgCl₂, (MgCl₂+Hf), and Hf compared to as-milled MgH₂.

Fig. 12 shows that MgCl₂, Hf, and (MgCl₂ + Hf) also have a positive influence on the hydrogenation behaviour of MgH₂, but it is not as good as that of MgH₂ + 10 wt.% HfCl₄. Therefore, Hf⁺⁺ containing compound may act as the actual catalyst in the HfCl₄-doped MgH₂ system. Many studies have shown that transition metals act as catalysts in the dissociation of hydrogen molecules and the recombination of hydrogen atoms in the molecular state. A theoretical study of Nobuhara et al. [44] shows that, as hydrogen molecules reach the catalyst surface, charge is donated from the hydrogen s-orbitals to the surface s- and d-states, accompanied by a back donation from the surface s- and d-states to the hydrogen anti-bonding states. The interaction of the surface s- and d-electrons with hydrogen molecular orbitals enhances the hydrogen dissociation on the surfaces. During the desorption process, the Mg-H bond of MgH₂ is activated by the catalyst, so that the electrons of the bonding orbitals of MgH₂ are donated to the unoccupied orbitals of the catalyst, and subsequently, the electrons of the
occupied orbitals of the catalyst are back donated to the antibonding orbitals of the MgH2 (back-donation) [45]. The electronic exchange reactions result in easier Mg-H dissociation, thus favouring the recombination of hydrogen atoms into hydrogen molecules. In this study, the valence electron configurations of Hfx+ are 6s25d2-x, compared with 6s25d2 for Hf. Clearly, the lower 5d orbital occupancy of Hfx+ allows an increased electron exchange with hydrogen molecules and Mg-H bonds of MgH2. As a result, Hfx+-species may have a more pronounced catalytic effect than metallic Hf, as supported by the TPD measurements presented in Fig. 12. Based on the XRD results of de/rehydrogenation of MgH2 + 50 wt.% HfCl4 (Fig. 11b and 11c), we speculate that the enhancement of sorption properties of the HfCl4-doped MgH2 sample may be due to the HfH2 species. This speculation is in agreement with Kyoi et al. [46], who reported that a mixture of MgH2 and HfH2 heated up to 600°C under 4 – 8 GPa hydrogen in a multi-anvil cell showed an improved desorption temperature of MgH2. In the case of the FeCl3-doped MgH2 sample, the formation of Fe during the dehydrogenation process may play an important role in enhancement of MgH2 sorption, since it is well known that Fe is a good catalyst for MgH2 [17, 47]. The presence of Fe metal may interact with hydrogen molecules, which may lead to the dissociation of hydrogen molecules and the improvement of the desorption/absorption rate.

Apart from the speculated catalytic effects of Fe and Hf species, the function of Cl− may also introduce an extra catalytic effect on MgH2 sorption properties. As shown in Fig. 12, MgCl2 also has a positive influence on the dehydrogenation behaviour of MgH2. The catalytic effect of MgCl2 may further combine with the catalytic function of Fe or Hf species to generate a synergetic effect. However, further work is still required to clarify more details on the exact role of HfCl4 and FeCl3 addition in MgH2.

4. Conclusion

This study shows that HfCl4 and FeCl3 are both effective additives for improving the dehydrogenation temperature and sorption kinetics of MgH2. Both of the doped samples start to release hydrogen at about 270 °C, a decrease of about 70 °C and about 140 °C compared to the as-milled and as-received MgH2, respectively. A hydrogen desorption capacity of 6.0 wt.% can be reached within 10 min at 300 °C for the HfCl4-doped MgH2 sample and 3.5 wt.% for the FeCl3-doped MgH2 sample, while only 0.2 wt.% hydrogen was desorbed by MgH2. Meanwhile, 5.5 wt.% hydrogen was absorbed at 300 °C under 3 MPa hydrogen in 60 s for the HfCl4-doped MgH2 sample and 4.8 wt.% for the FeCl3-doped MgH2 sample, while the MgH2 sample only absorbed 3.0 wt.% hydrogen under the same conditions. The apparent activation energy, $E_A$, for hydrogen desorption was estimated to be 102 kJ/mol and 130 kJ/mol for the HfCl4-doped MgH2 and the FeCl3-doped MgH2 samples, a decrease of 64 and 36 kJ/mol, respectively compared to the as-milled MgH2 (166 kJ/mol). In addition, a cycling study of dehydrogenation at 300 °C showed that the hydrogen capacity of the HfCl4-doped MgH2 sample was maintained at about 6.0 wt.% after 10 cycles. From the XRD and XPS results, we suggest that the significant improvement in the MgH2 sorption properties was due to the catalytic effect of Fe and Hf species that formed during the dehydrogenation process. In addition, the formation of MgCl2 may also play a critical role, and it is very likely that there are synergetic effects, when MgCl2 is combined with Fe and Hf species.

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