Catalytically enhanced dehydrogenation of MgH_2 by activated carbon supported Pd- VO_x ($x=2.38$) nanocatalyst

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Abstract

In this paper, we reported that a new multi-component catalyst of activated carbon supported nanosized Pd and VO_x (Pd-VO_x/AC, x=2.38) prepared by wet impregnation method exhibited significant catalytic effect on hydrogen desorption of MgH₂. It is demonstrated that the nanocomposites of MgH₂+Pd-VO_x/AC prepared by ball milling could reduce the desorption temperature, e.g. differential scanning calorimetry (DSC) measurement indicated that the peak desorption temperature decreased ~40°C, and also improve the desorption kinetics of MgH₂, e.g. desorbed 6.5 wt% hydrogen within 30 min at 300°C under an initial pressure of 1 KPa. A significant decrease of activation energy (E_a) indicated that Pd-VO_x/AC catalyst is highly efficient for MgH₂ dehydrogenation, which may be ascribed to the synergistic effect of nanometric bimetals (metal oxides) and nanocarbon.

Keywords: Hydrogen storage, Magnesium-based nanocomposites, Pd-VO_x/AC, multi-component catalyst, synergistic effect

1. Introduction

The challenges of global warming and finite fossil fuel-based energy resources have made hydrogen a promising alternative candidate for the next generation of renewable and sustainable energy carrier. Realization of this perspective requires a practical hydrogen storage material. Hydrogen compression which is considered as the simplest way to store hydrogen, many of the prototype and demonstration vehicles have used compressed gas cylinders in the past decade [1, 2]. However, thus far, this technique is still unlikely to meet the ultimate hydrogen gravimetric capacity target of 7.5 wt% set by DOE due to low energy density [3, 4]. Therefore, the development of efficient, safe, and light weight storage materials for hydrogen applications is a key technological objective within the drive toward the hydrogen economy such as fuel-cell-based electric vehicles [5]. Magnesium hydride, MgH_2 , has high theoretical hydrogen capacity (7.6 wt%) and low cost, making magnesium and its alloys have been considered among the most promising candidates for hydrogen storage [1, 5]. However, the material has two main shortcomings for such applications [6]: The dehydriding reaction is strongly endothermic (about 74 kJ/mol), so that the desorption temperature requires above 300°C, which is too high for many envisioned uses such as on-board storage of hydrogen in fuel cell powered automobiles. In addition, the kinetics of absorption/desorption of MgH_2 is notoriously slow.

Experimentally, many efforts have been devoted to overcome these two barriers, e.g. lowering the desorption temperature and improving the kinetics, which has involved the modification both on structure of the main material (magnesium) and its composition such as catalysts. A good example is the use of magnesium compound such as Mg_2NiH_4 to reduce the large reaction enthalpy, which lowers the hydrogen sorption temperature to about 200°C, albeit at the expense of the theoretical storage

capacity which is decreased to 3.6 wt% [7, 8]. The second issue, reaction kinetics, impacted by several factors such as the diffusion of atomic H through material matrix and surface dissociation/recombination reactivity for the H₂ molecules. So far, the desorption kinetics of MgH₂ has been greatly improved by preparation of nanostructure materials via physical/chemical synthesis or high energy ball milling with various catalytic additives [9-11]. The main contribution to the substantial improvement on hydrogen sorption properties is that the magnesium and catalysts are nanostructured, which leads to the increase of the specific surface area and the decrease of diffusion path lengths due to the reduction of grain and particle sizes. Additionally, the doped catalytic additives, which are distributed uniformly on the magnesium surface in form of nanoparticles, are proved to facilitate the dissociation/recombination of hydrogen on magnesium surface. Among the different catalysts studies, micrometric Pd [12] and V₂O₅ [13] have attracted considerable attention. Hanada et al. [11, 14] investigated the catalytic effect of 3d-transition metal and some metal oxides in form of nanoparticles on the hydrogen storage properties of MgH₂. They suggested that the reason why using nanoparticle size additives is to make the catalysts distribute homogeneously on the surface of MgH₂ and reduce the milling time to avoid severe internal strains. Most recently, Lillo-Rodríguez et al. and Wu et al. [15, 16] reported that the effect of carbon supported nickel catalyst enhanced in MgH₂ decomposition comparing with direct doping the identical catalysts and further clarified the importance of nickel particle size or the carbon-nickel interaction for its catalytic properties.

In this paper, we report the synthesis of co-doped Pd and VO_x on activated carbon (denoted as Pd-VO_x/AC) by wet impregnation approach, and its catalytic effects on MgH₂ desorption that contribute to the ultrafast kinetics with a high capacity at relative low temperatures. A possible

dehydrogenation mechanism is proposed in terms of synergistic catalytic effects of Pd^{nano} and $\text{VO}_x^{\text{nano}}$, especially highlighting the carbon supported catalyst plays an important role.

2. Experimental details

2.1. *Synthesis of Pd-VO_x/AC catalyst*

The microporous activated carbon (AC, 99% purity) was obtained from Calgon Carbon Company as the initial carbon support. Ammonium metavanadate (NH_4VO_3 , $\geq 99\%$ purity, Sigma-Aldrich) was chosen as the vanadium pentoxide (V_2O_5) precursor. The $\text{V}_2\text{O}_5/\text{AC}$ was firstly prepared by wet impregnation method [17]. The well dried AC was impregnated in an aqueous solution of VO^{2+} prepared from the required amount of ammonium metavanadate and oxalic acid as described by Economidis et al. [18]. The VO^{2+}/AC solution was continued to stir for 24 h at room temperature until most of solvent evaporated, followed by drying at 120°C overnight and subsequently calcified at 350°C for 2 h with a heating rate of $5^\circ\text{C}/\text{min}$ under air [19]. Pd nanoparticles were synthesized using palladium diacetate ($\text{Pd}(\text{OAc})_2$, 98% purity, Sigma-Aldrich) as Pd precursor in $\text{V}_2\text{O}_5/\text{AC}$ template, the $\text{V}_2\text{O}_5/\text{AC}$ template (0.8 g) was mixed with 20 ml $\text{Pd}(\text{OAc})_2$ (0.09 M) solution and stirred for 48 h, followed by drying the slurry at 120°C overnight and subsequently reduced in 5% H_2/N_2 gas mixture at 500°C for 2 h with $5^\circ\text{C}/\text{min}$ ramping rate. The nominal composition of the as-prepared catalyst (Pd-VO_x/AC) is 20 wt% Pd, 5 wt% VO_x and 75 wt% AC.

2.2. *Synthesis of nano-catalyzed MgH₂ composites*

Before being mixed with any catalysts, MgH_2 powder (hydrogen storage grade, Sigma-Aldrich) was premilled under 5.5 bar H_2 for 2 h in a high energy SPEX 8000 vibration ball mill (60 Hz model) in the

sealed vial with ball-to-powder weight ratio 40:1. And then as prepared Pd-VO_x/AC, Pd/AC and AC were mixed respectively with the premilled MgH₂ in the presence of 5 wt% and milled for 2 h. (Leading to a Palladium content of 1 wt%, a VO_x content of 0.25 wt% and a carbon content of 3.75 wt% in the final MgH₂ based composites, respectively.) All the sample handling was performed in an Ar-filled glovebox (MBraun), in which the water/oxygen levels were below 1ppm.

The porosity and structure of the catalysts were characterized by nitrogen adsorption (Quantachrome, USA), X-ray diffraction (XRD, Rigaku Miliflex) with Co K α radiation, and X-ray photoelectron spectrometer (XPS, Kratos Axis ULTRA). In addition, the metallic content of the as-prepared catalysts were quantified by using a Varian Vista Pro inductively coupled plasma optical emission spectrometry (ICP-OES) instrument on samples digested with HNO₃ and HF acids. Moreover, the microstructure of the carbon supported Pd-VO_x catalysts was analyzed by transmission electron microscope (TEM, FEI Tecnai 20) equipped with an energy dispersive X-ray spectroscopy (EDXs) analysis unit (AMETEK).

The effect of carbon supported catalysts on the decomposition temperature of MgH₂ was determined by differential scanning calorimetry (DSC, Mettler Toledo). A heating rate of 5°C/min was used and experiments were performed under an Ar flow rate of 50 ml/min (BOC gases, 99.999% purity). Furthermore, hydrogen isothermal desorption profiles of the composites were measured by an automated Sieverts' apparatus (Suzuki shokan PCT H₂ Absorption Rig). Before measuring, the system was degassed for 2 h within the sample cell being heated to 350°C and then rehydrogenated for 2 h at 300°C with an initial pressure of 2 MPa. Desorption measurements were performed at various temperatures with an initial pressure of 1 KPa.

3. Results and Discussion

3.1. Microstructure Characterization of Pd-VO_x/AC catalyst

It is well recognized that the performance of carbon supported catalyst depends on the textual properties of the support (surface area, porosity). Thus, in order to obtain a well dispersed metal catalyst, the surface of the activated carbon (AC) support must be accessible. Table S1 shows the results for the porous texture characterization of such sample obtained by physical adsorption of N₂ gas at 77K, and the surface area is calculated by BET (Brunauer-Emmett-Teller) method. The Table shows that the AC as support with 1174 m²·g⁻¹ BET specific surface area and 0.52 cm³·g⁻¹ total pore volume, which decreases to 887 m²·g⁻¹ and 0.39 cm³·g⁻¹ after Pd-VO_x loading due to pore filling and pore blocking, suggesting both the Pd and VO_x are loaded on the AC surface.

To characterize the microstructure of the synthesized Pd-VO_x/AC catalyst, X-ray diffraction (XRD) and X-ray photoelectron spectrometer (XPS) techniques are employed. Fig. 1 presents the XRD pattern of the samples of AC supported (a) 20wt%Pd-5wt%VO_x, (b) 20wt%Pd, and (c) 20wt%V₂O₅, respectively. It is clear to see that the metallic palladium (Pd) peaks existing in the 20wt%Pd-5wt%VO_x/AC (Fig. 1a) are consistent with the Pd characteristic peaks in 20wt%Pd/AC (Fig. 1b), indicative of the successful reduction of Pd catalyst in the 20wt%Pd-5wt%VO_x/AC. The mean grain size of Pd in Pd-VO_x/AC is 11.2 nm calculated by using the Scherrer equation. As the Pd particles are synthesized by reduction of Pd(OAc)₂ at a temperature of 500°C, partial V₂O₅ on the template of 5wt%V₂O₅/AC will be reduced to low valence oxides. Accordingly, we denote the vanadium oxides as VO_x. From Fig. 1a, XRD pattern indicates that there are no obvious VO_x characteristic peaks in the 20wt%Pd-5wt%VO_x/AC sample, suggesting that VO_x particles could be homogenously dispersed in the activated carbon support but the small loading amount makes them

undetectable by this technique. XPS is used to further determine the surface chemical composition and valence states of VO_x in $\text{Pd-VO}_x/\text{AC}$ (Fig. 1 inset). The $\text{V}2\text{p}_{3/2}$ peak at binding energy of 517.6 eV corresponds to $\text{V}_2\text{O}_5 (\text{V}^{5+})$ with a small peak at lower binding energy of 516.1 eV corresponds to $\text{VO}_2 (\text{V}^{4+})$ [20], and the molar ratio of $\text{V}^{5+}/\text{V}^{4+}$ determined from XPS is 3.13, corresponding to the composition of VO_x ($x=2.38$) in $\text{Pd-VO}_x/\text{AC}$. In addition, to further confirm the bulk phase metallic contents in the nominal 20wt%Pd-5wt% VO_x/AC , 20wt%Pd/AC, and 20wt% $\text{V}_2\text{O}_5/\text{AC}$ catalysts, inductively coupled plasma optical emission spectrometry (ICP-OES) is applied and the results are summarized in the Table S2. It is shown that the amount of Pd in $\text{Pd-VO}_x/\text{AC}$ and Pd/AC is around 20wt%, VO_x and V_2O_5 are also coincided with the nominal amount in $\text{Pd-VO}_x/\text{AC}$ and $\text{V}_2\text{O}_5/\text{AC}$, respectively, indicating the real composition is closed to the pre-calculated values.

In order to further investigate the microstructure of this $\text{Pd-VO}_x/\text{AC}$ catalyst, transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDXs) techniques are used. Fig. 2a shows the TEM bright field image of the microstructure of $\text{Pd-VO}_x/\text{AC}$ sample, which clearly indicates a homogeneous dispersion of small and uniform particles with a size of 8~10 nm on AC support. Furthermore, the composition of nanoparticles on activated carbon support is also indentified by EDXs in Fig. 2b, which shows both Pd and V elements existing in different selected spots in the AC matrix, suggesting that the Pd-VO_x nanoparticles are well distributed on the anchoring sites on the surface of activated carbon matrix.

3.2. Microstructure Characterization of $\text{MgH}_2+\text{Pd-VO}_x/\text{AC}$ nanocomposties

Fig. 3 presents the X-ray diffraction patterns of the as milled $\text{MgH}_2+\text{Pd-VO}_x/\text{AC}$ sample as well as those of the dehydrogenated and hydrogenated states after cycling at 300°C. In Fig. 3a, we found that

the reflection peaks attributed to any Pd, VO_x or AC catalyst phases are absent after ball milling, which is most likely a combination of the low concentration of the catalyst phases and the lack of long range order for a highly dispersed nanoparticulate catalysts. Moreover, it was observed that the most intense Bragg peaks are identified as tetragonal β -MgH₂, and partial high-pressure metastable orthorhombic phase γ -MgH₂ due to intensive milling. The grain size of β -MgH₂ has been estimated by modified Scherrer formula [21] by considering both crystallite size and lattice strain after ball milling, which is around 12.5 nm. Additionally, Fig. 3b and Fig. 3c showed that the most intense peaks from Mg in the dehydrogenated state of MgH₂+Pd-VO_x/AC which transforms into β -MgH₂ after hydrogenation, together with some small amount of Fe and MgO phase, which is inevitable from long period ball mill and sample transferring.

A TEM bright field image of the MgH₂+Pd-VO_x/AC nanocomposite ball milled for 2h is shown in Fig. 4a, and the corresponding selected area electron diffraction pattern (SAED) is shown in Fig. 4c. It is demonstrated that all the diffraction rings correspond to the MgH₂ phase. As observed in the dark field image (Fig. 4b), the average grain of the Mg is around 10 nm, which agrees well with the estimated results based on the XRD measurement.

3.3. Hydrogen Storage Properties

To explore the changes of thermodynamics in MgH₂+Pd-VO_x/AC system, the dehydrogenation curves of the nanocomposites are measured by thermal analysis. Fig. 5 gives the DSC profiles of the various composites after rehydrogenation with a heating rate of 5°C/min. The peak temperature of hydrogen desorption is observed to shift downward from 365°C for pure MgH₂, to 346°C for MgH₂+AC, and further to 336°C for MgH₂+Pd/AC, eventually to 324°C for MgH₂+Pd-VO_x/AC. It is suggested that the

result agrees well with previous hypothesis that the synergetic effect of Pd-VO_x instead of Pd on carbon support mainly contributes to the desorption of MgH₂. Moreover, it also gives the experimental evidence to support the prediction of V₂O₅ on MgH₂ desorption studied by Du et al. which suggested that the Mg-H bond length becomes elongated when MgH₂ clusters are positioned on the V₂O₅ (001) surface [22].

Hydrogen desorption kinetics is further investigated for rehydrogenated MgH₂+Pd-VO_x/AC sample by isothermal dehydrogenation rate measurement at varied temperatures from 300°C to 350°C. As shown in Fig. 6a, it can be clearly observed that the sample desorbed about 6.5 wt% hydrogen at 350°C within only 4 min and can desorb 6.5 wt% hydrogen in 30 min and reach almost 7 wt% after 1 h at 300°C, which is clearly superior to that of MgH₂+Pd/AC, MgH₂+VO_x/AC, MgH₂+AC and MgH₂ systems (Fig. 6b), indicating that V₂O₅ is effective for desorption as the theoretical calculation predicted [22].

In our study, the hydrogen desorption from metal hydrides involves a synergistic effect of three basic steps: (a) the nucleation and growth of the metal phase at special nucleation sites in the parent hydride phase that could be adjacent to Pd-VO_x nanocatalyst sites; (b) the atomic diffusion of H, dissociated from the hydride phase, is obviously enhanced by the increase of grain boundaries corresponding to small magnesium hydrides grains, the interface of dislocation sites formed by intensive ball milling, and unblocked micropore diffusion paths introduced by activated carbon support, towards to the sample surface; (c) the surface atomic recombination into H₂.

As we know, hydrogen desorption in a crystalline solid can either occurs as random nucleations or preferential nucleations along certain favourable “routes” due to defects or catalytic sites. [23, 24] So further understanding the physical mechanism of nucleation of MgH₂/Mg will help us to optimise the

hydrogen storage performance of these materials. In order to elucidate the nucleation mechanism of MgH_2/Mg and $\text{Pd-VO}_x/\text{AC}$ catalytic effect in metal hydride heterogeneous phase transformation, the desorption data are analyzed by using Johnson-Mehl-Avrami (JMA) theory [25]: upon a first-order phase transition, the reacted fraction is given as function of time by $\beta = 1 - \exp[-(kt)^n]$, where β is the reacted fraction, t is the desorption time, $k=k(T)$ is the temperature dependent kinetic constant, and n is the JMA exponent (reaction order) that is related to the transformation mechanism. A linear interpolation of the plots, $\ln(-\ln(1-\beta))$ vs $\ln(t)$, could yield the value of n and k . The value of the exponent was ~ 1 for $\text{MgH}_2+\text{Pd-VO}_x/\text{AC}$ sample by a best fit of our data and its effective activation energy (E_a) is evaluated through the Arrhenius plot of rate constant k (see the inset in Figure 6a), given 114.2 kJ/mol H_2 , which is lower than that of the pure MgH_2 (161.8 kJ/mol H_2).

The different values of the JMA exponent and activation energy suggest different dimensionalities and mechanisms of $\text{MgH}_2(\text{Mg})$ phase formation for the H_2 desorption in various catalysts doped MgH_2 composites. Generally, the increased rate of hydrogen desorption of MgH_2 can be partially understood on the basis of the nanosize effect. However, it is found that, after the identical ball milling process, various n is obtained for different systems. As shown in Table 1, for $\text{MgH}_2+\text{Pd-VO}_x/\text{AC}$ and $\text{MgH}_2+\text{VO}_x/\text{AC}$ samples, the values of n are close to 1, indicating that the phase transformation of MgH_2 to Mg occurs by instantaneously numerous nucleation and growth including along one-dimensional (1D) dislocation lines and thickening of needles, cylinders and plates [26,27], while $n=1.5$ for $\text{MgH}_2+\text{Pd}/\text{AC}$ and MgH_2+AC , and $n=1.6$ for MgH_2 , respectively, which implies that the phase transformation of MgH_2 to Mg has a zero nucleation rate (i.e., negligible initial dimensions) and it is a diffusion-limited growth reaction [26,28]. Accordingly, it is demonstrated that $\text{MgH}_2/\text{Pd-VO}_x$ interface could be the “catalytic sites” for $\text{MgH}_2(\text{Mg})$ preferential nucleation transformation. Additionally, as shown in Fig.

6b, we found that the average desorption rate of AC doped MgH_2 is 3.8 folds higher than that of the pure MgH_2 within 30 min at 300°C , suggesting that the existence of carbon facilitates the diffusion of H atoms (dissociated from MgH_2 matrix) to the surface. The difference (22.6 kJ/mol H_2) of E_a between $\text{MgH}_2+\text{Pd/AC}$ (126.8 kJ/mol H_2) and MgH_2+AC (149.4 kJ/mol H_2) indicates that the small amount of nano Pd catalyst (1 wt%) addition can significantly improve the dehydrogenation kinetics. More interestingly, it is noteworthy that introducing only 0.25 wt% VO_x through $\text{Pd-VO}_x/\text{AC}$ into MgH_2 further improves both the desorption capacity (7 wt%) comparing with that of VO_x/AC doped MgH_2 system (5 wt%) and kinetics (6.5 wt% within 30 min), suggesting the coupling of Pd and VO_x is more effective than Pd or VO_x alone. Accordingly, the E_a of $\text{MgH}_2+\text{Pd-VO}_x/\text{AC}$ (114.2 kJ/mol H_2) is further reduced. Furthermore, the presence of homogenously dispersed nanoscale Pd-VO_x particles in MgH_2 matrix enables a significant increase of intimate contacts between the catalyst particles and MgH_2 that provides much more activated sites for the hydride dissociation and Mg formation, which allows a instantaneous nucleation as indicated previously ($n \sim 1$).

4. Conclusions

In conclusion, we successfully synthesized a new catalyst of activated carbon supported nanosized Pd and VO_x ($x=2.38$) through impregnation method. Microstructure characterization demonstrates that the size of Pd and VO_x is at nanoscale (8-10 nm). It is expected that these nanoparticles will increase significantly the intimate contacts between the catalyst and MgH_2 when milled with MgH_2 , therefore, improve the desorption kinetics and reduce the desorption temperature of MgH_2 . Experimental investigations confirm that the peak desorption temperature of catalyzed MgH_2 can be lowered $\sim 40^\circ\text{C}$.

And the desorption kinetics can be increased in a few folds (PCT measurement), which may attribute to the significant reduction of the activated energy.

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Table 1 – JMA exponent and activation energy of the dehydrogenation of different Mg based systems

Systems	JMA exponent	Activation Energy
	n	E_a (kJ·mol ⁻¹ H ₂)
MgH ₂ +5wt%(20%Pd-5% VO _x /AC)	1	114.2
MgH ₂ +5wt%(20%Pd/AC)	1.5	126.8
MgH ₂ +5wt%(5% VO _x /AC)	1	117.6
MgH ₂ +5wt%AC	1.5	149.4
MgH ₂	1.6	161.8

FIGURE LEGEND

Fig. 1 – X-ray diffraction pattern of the AC-supported (a) 20wt%Pd-5wt%VO_x, (b) 20wt%Pd, and (c) 20wt% V₂O₅. The high resolution XPS spectrum of V 2p_{3/2} measured on the pristine surface of 20wt%Pd-5wt%VO_x/AC is presented in the inset.

Fig. 2 – TEM image of (a) activated carbon supported Pd-VO_x and (b) with EDXs analysis.

Fig. 3 – X-ray diffraction patterns of the MgH₂+Pd-VO_x/AC nanocomposites (a) as milled (b) after dehydrogenation (c) after rehydrogenation.

Fig. 4 – TEM micrographs of the MgH₂+Pd-VO_x/AC nanocomposite as milled. (a) Bright field image, (b) dark field image, and (c) SAED pattern.

Fig. 5 – DSC profiles of the rehydrogenated sample of pure MgH₂, MgH₂+AC, MgH₂+Pd/AC, MgH₂+Pd-VO_x/AC mechanically milled for 2h. The heating rate is 5°C/min.

Fig. 6 – Isothermal desorption kinetics of rehydrogenated MgH₂+Pd-VO_x/AC sample milled for 2h under initial hydrogen pressure 1 KPa: (a) at the temperatures of 350°C, 330°C and 300°C, Arrhenius plot of rehydrogenated MgH₂+Pd-VO_x/AC sample is presented in the inset; (b) comparisons with MgH₂+Pd/AC, MgH₂+VO_x/AC, MgH₂+AC, and MgH₂ systems at 300°C.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6