On the hydrogen desorption entropy change of modified MgH₂Jie Cui^{1,2}, Liuzhang Ouyang², Hui Wang², Xiangdong Yao^{3,4,*}, Min Zhu^{2,4,*}¹ *Analysis and Test Center, South China University of Technology, Guangzhou, 510640, P. R. China.*² *School of Material Science and Engineering, South China University of Technology, Guangzhou, 510640, P. R. China.*³ *School of Natural Sciences, Griffith University, Nathan, QLD 4111, Australia.*⁴ *Australia-China Joint Laboratory for Energy & Environmental Materials, Griffith University, Nathan, QLD 4111, Australia***Abstract:**

Reducing hydrogen desorption temperature (T_d) is a current challenge for application of Mg-based hydrogen storage alloys. The equilibrium T_d is directly determined by the thermodynamics, characterized by the enthalpy (ΔH) and the entropy (ΔS), of hydrogen desorption reaction of MgH₂. While the change of ΔH has been proved due to the size effect and alloying effect, the ΔS is customary considered as entropy of H₂, being a constant of 130.5 Jmol⁻¹·K⁻¹. Very recently, however, the ΔS is experimentally reported to change in some cases as well. In this work, for the first time, we proposed a model to illustrate theoretically that the vary of ΔS , which significantly influences the T_d , of MgH₂ with the changing particle/grain size, covering catalyst on surface and forming solid solution of MgH₂ that facilitates the hydrogen molecule dissociation. The model is supported by the experimental results.

Key words: MgH₂; desorption; entropy; size effect; catalysis**1. Introduction**

The difficulty in hydrogen storage is heavily hindering the hydrogen energy application that is an important strategy to solve the critical problems such as fossil fuel depletion, environmental pollution and global climate change^[1]. Over the tremendous efforts devoted in

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the last decades, hydrides of high hydrogen storage capacity have been developed, however, they are generally difficult to release hydrogen in a fast rate under moderate conditions ^[2]. In a particular example, MgH₂ requires a temperature of 300°C to desorb H₂ although it has significant merits of high hydrogen capacity, excellent reversibility and low cost. Nevertheless, substantial progress has been achieved in improving dehydrogenation kinetics of Mg-based hydrides through various strategies and fast hydrogen absorption at an ambient temperature can be realized in recent years ^[3].

However, hydrogen desorption of MgH₂ still requires high temperature or low H₂ pressure, which is determined by the dehydrogenation thermodynamics ^[4] expressed in the following equation according to van't Hoff plot ^[5]:

$$T_d = \Delta H / \Delta S \quad (1)$$

Where T_d is hydrogen desorption temperature, ΔH and ΔS are the enthalpy and entropy of hydrogen desorption, respectively. Typically, the ΔH and ΔS are about 75 kJ mol⁻¹ and 130.5 Jmol⁻¹·K⁻¹ for a bulk MgH₂ system, respectively ^[3]. Accordingly, the T_d is calculated to be 289°C under 1 atm H₂ pressure, which is too high for Mg to be used practically, in particular for mobile applications. Thus, it is of great interesting to develop new strategies to tune the thermodynamics by destabilizing MgH₂ ^[6].

Theoretically, it is predicted that the ΔH can be reduced obviously when the size of MgH₂ is reduced to several nanometer, ^[7] for example, to 63 kJmol⁻¹ at the size of 0.9 nm ^[8] and the corresponding T_d can be remarkably reduced to ~200 °C if the ΔS is considered as a constant of ~130.5 Jmol⁻¹·K⁻¹. These predictions triggered intensive experimental investigations. For example, Paskevicius et al. produced Mg/MgH₂ nano-particles with a size of 15~40 nm by the mechanochemical method, and the ΔH and the ΔS are measured to be 74.75±0.42 kJ mol⁻¹ H₂ and 129.6J mol⁻¹ H₂, respectively ^[9].

Almost all the theoretical and experimental studies about the thermodynamics of hydrogen desorption are based on a general regarding of a constant ΔS . However, there are a few examples shown that the ΔS is variable in recent research ^[7,10]. For instance, a significant decrease of the ΔH (63.8 ± 0.5 kJ mol⁻¹) and the ΔS (117.2 ± 0.8 Jmol⁻¹K⁻¹) was reported in MgH₂ nanoparticles with a size of less than 3 nm by hydrogenation of Bu₂Mg inside the pores of a carbon scaffold ^[7]. Although the ΔH is greatly decreased, the decrease of the T_d was only

11 °C because of the counter effect of the decreased ΔS . Buckley et al ^[9] synthesized MgH_2 nanoparticles embedded in a LiCl salt matrix by a mechanochemical method. They found the ΔH decreased from $74.06 \pm 0.42 \text{ kJ mol}^{-1}$ for the bulk MgH_2 to $71.22 \pm 0.49 \text{ kJ mol}^{-1}$ for the MgH_2 nanoparticles of about 7 nm. However, the ΔS also decreased from $133.4 \pm 0.7 \text{ Jmol}^{-1}\text{K}^{-1}$ to $129.6 \pm 0.8 \text{ Jmol}^{-1}\text{K}^{-1}$. Similarly, due to the decrease in the ΔS , the decrease of T_d is much less than that calculated from the sole ΔH change. In our previous work, it was firstly observed that, the ΔS could be increased to $136.3 \text{ Jmol}^{-1}\text{K}^{-1}$ in a core-shell structured Mg with Ti-based catalyst as the shell ^[11]. Besides that, in $\text{Mg}_{90}\text{In}_5\text{Cd}_5$ ternary solid solution alloy, ΔS is $154.8 \text{ Jmol}^{-1} \text{ H}_2 \text{ K}^{-1}$, which is much higher than the values for pure Mg $138.9 \text{ Jmol}^{-1} \text{ H}_2 \text{ K}^{-1}$ in Lu's report ^[12]. The above results indicate that it is possible to alter ΔS in both directions, i.e. either larger or smaller. However, the ΔS was regarded as constant in general and the physical nature is still unclear for the ΔS changes in those situation. Although it was reported that the decrease of ΔS in nano Mg system may originate from statistical errors in Van 't Hoff plots ^[13,14]. The fact of the desorption/absorption pressure increasing during the size reduction can not be neglected which state the ΔS may altered in the modified Mg/ MgH_2 system. Hence, it is very significant to figure out the nature for the ΔS change by establishing theoretical models, and this is also important for exploring strategy to tuning thermodynamics of hydrogen storage reaction.

In this paper, we develop a model for the dehydrogenation entropy ΔS of MgH_2 modified in particle/grain size, composition by forming solid solutions, and surface by coating catalyst. It can be predicted, from this model, that the dehydrogenation entropy would change, e.g. be less than $120.1 \text{ Jmol}^{-1}\text{H}_2\text{K}^{-1}$ at the particle/grain size of 3 nm. The theoretical calculations from this model are consistent with the experimental results.

2. Statistical concept in dehydrogenation entropy of MgH_2

According to the Boltzmann entropy expansion, the system's entropy (S) can be expressed as the Eq (2) ^[15].

$$S = k \ln W_B = Nk \ln \frac{Z}{N} + \frac{U}{T} + Nk \quad (2)$$

Where k is Boltzmann constant, W_B is the number of the most probable microstates, N is number of the atoms in the system, Z is the partition function, U is the internal energy and T is

the temperature. Indeed, the system's entropy is the sum of various independence movements (translation, rotation, vibration, electronic movement and electronic anti-nuclear movement) of particles. In our case, the contribution of electronic movement and electronic anti-nuclear movement to the system's entropy can be ignored because they are in ground state under general temperatures. Hence, the S can be comprised of three contributions (S_t , S_r and S_v) as indicated in supporting information I, where S_t , S_r and S_v stands for the entropy of translation, rotation and vibration, respectively.

According to the equation for S_t , S_r and S_v as shown in supporting information I, it can be found the number of atoms in the system is one of the key factor, and the number of the atoms should be 1 and 3 mol for a system of 1 mol Mg and MgH₂, respectively. Hence, S_{Mg} and S_{MgH_2} can be expressed as Eq (3) and (4), respectively, where N_A is Avogadro's constant, h is the Planck constant, Θ_r stands for rotational factor, σ is the symmetry number, Θ_v stands for vibrational factor, V is the volume, m is the mass.

$$S_{Mg} = N_A k \ln \frac{V_{Mg} (2\pi m_{Mg} kT)^{3/2}}{N_A h^3} + \frac{11}{2} N_A k + N_A k \ln (T / \Theta_{r_{Mg}} \cdot \sigma) + N_A k \ln \left[\left(1 - e^{-\Theta_{v_{Mg}}/T} \right) / N_A \right] + N_A k \Theta_{v_{Mg}} T^{-1} (e^{\Theta_{v_{Mg}}/T} - 1)^{-1} \quad (3)$$

$$S_{MgH_2} = 3N_A k \ln \frac{V_{MgH_2} (2\pi m_{MgH_2} kT)^{3/2}}{N_A h^3} + \frac{33}{2} N_A k + 3N_A k \ln (T / \Theta_{r_{MgH_2}} \cdot \sigma) + 3N_A k \ln \left[\left(1 - e^{-\Theta_{v_{MgH_2}}/T} \right) / 3N_A \right] + 3N_A k \Theta_{v_{MgH_2}} T^{-1} (e^{\Theta_{v_{MgH_2}}/T} - 1)^{-1} \quad (4)$$

3. The effect of nanosizing on the dehydrogenation entropy of MgH₂

Obviously, one of the most remarkable structural features in nano materials is that there are huge interfaces and higher specific surface area. Thus, there is an excess volume (ΔV) in nano materials in comparison with the volume of perfect crystal in bulk materials (V_0). The volume in nanomaterials can be described as $V' = V_0 (1 + \Delta V)$. According to the model of excess volume in Song's work^[16], the volume ratio of the nano to bulk material can be expressed as Eq (5), where d is the diameter of the equivalent spherical volume of nanoparticles or nano-crystals and δ is thickness of the grain boundary.

$$\frac{V'}{V_0} = \frac{0.8[d^3 - (d-\delta)^3] + d^3}{d^3} \quad (5)$$

Hence, as shown in supporting information I, S_t of Mg and MgH₂ are both increased due to

the increase of V' in nano-size Mg/MgH₂. $\Delta S_{t_{Mg}}$ and $\Delta S_{t_{MgH_2}}$ can be expressed as Eq (6) and Eq (7), respectively, where R is molar gas constant.

$$\Delta S_{t_{Mg}} = R \ln \frac{V'_{Mg}}{V_{0Mg}} \quad (6)$$

$$\Delta S_{t_{MgH_2}} = 3R \ln \frac{V'_{MgH_2}}{V_{0MgH_2}} \quad (7)$$

S_r is not affected by the change of volume, thus the $\Delta S_{r_{Mg}}$ and $\Delta S_{r_{MgH_2}}$ can be neglected. Besides, the average interatomic distance is increased from r_0 in bulk material to r' in nano material (corresponding to the volume change), which can affect the S_v both in Mg and MgH₂. To simplify the calculations, the volume expansion is supposed to be equivalently as the interatomic distance increase as shown in supporting information II. Hence, $\Delta S_{t_{Mg}}$ and $\Delta S_{t_{MgH_2}}$ can be expressed as Eq (7) and Eq (8), respectively.

$$\Delta S_{v_{Mg}} = R \ln \frac{r'_{Mg}}{r_{0Mg}} \quad (7)$$

$$\Delta S_{v_{MgH_2}} = 3R \ln \frac{r'_{MgH_2}}{r_{0MgH_2}} \quad (8)$$

The entropy of the dehydriding reaction of MgH₂ can be short standed as ΔS , it can be described as Eq (9)

$$\Delta S = S_{Mg} + S_{H_2} - S_{MgH_2} \quad (9)$$

For the bulk Mg/MgH₂, ΔS_{bulk} can be calculated as,

$$\Delta S_{bulk} = S_{Mg}^{\theta} + S_{H_2}^{\theta} - S_{MgH_2}^{\theta} \quad (10)$$

When considering nano-size Mg and MgH₂, the excess volume and change of average interatomic distance should be taken account. Hence, ΔS_{nano} can be described as Eq (11),

$$\Delta S_{nano} = (S_{Mg}^{\theta} + S_{H_2}^{\theta} - S_{MgH_2}^{\theta}) + \left(R \ln \frac{V'_{Mg}}{V_{0Mg}} + R \ln \frac{r'_{Mg}}{r_{0Mg}} - 3R \ln \frac{V'_{MgH_2}}{V_{0MgH_2}} - 3R \ln \frac{r'_{MgH_2}}{r_{0MgH_2}} \right) \quad (11)$$

For the convenience of calculations, the same ratio of excess volume is considered in Mg and MgH₂ ($\frac{V'_{Mg}}{V_{0Mg}} = \frac{V'_{MgH_2}}{V_{0MgH_2}} = \frac{V'}{V_0}$). Accordingly, the same increase of average inter atomic distance

($\frac{r'_{Mg}}{r_{0Mg}} = \frac{r'_{MgH_2}}{r_{0MgH_2}} = \frac{r'}{r_0} = \sqrt[3]{\frac{V'}{V_0}}$) was taken into account. Hence, ΔS_{nano} can be derived as Eq(12).

$$\Delta S_{nano} = \Delta S_{bulk} - \frac{8}{3} R \ln \frac{0.8[d^3 - (d-\delta)^3] + d^3}{d^3} \quad (12)$$

It can be found that ΔS_{nano} is decreased with the partilce/grain size as indicated in surpporting information III. This can also explain the nature of the enthalpy entropy

correlations as mentioned again several times recently in ‘compensation effects’ which were reported in other systems^[17,18]. And it can be easily understand a weakening of intermolecular bonds (related to the enthalpy) which leads to an increase of the configurational freedom and hence a smaller degree of ordering in the system (related to the entropy). The reduction of the entropy significantly increases the T_d , although the size effect can lower desorption ΔH significantly and decreases T_d as reported in Dresselhaus’s work^[19]. Thus, the T_d change is much less due to the effect of size reduction on the entropy. As shown in the supporting information III, combining the size effect on both ΔH and ΔS , the $T_{p_{eq}=1 \text{ atm}}$ is predicted to only lower to 160 °C when d is 3 nm, while it is 124 °C by ignoring the effect of ΔS .

4. The effect of solid solution formation on dehydrogenation entropy of MgH_2

The formation of Mg-based solid solution, can probably alter the dehydrogenation enthalpy and entropy change of the systems with an acceptable loss of capacity^[20,21]. Usually, the change of the enthalpy is highly recognized in Mg based solid solution, such as Mg-In^[18], Mg-Al^[22] and Mg-Al-Li system^[19]. Lately, the negligible change of the entropy is also noticed. The ΔS are 140.0 and 138.6 $\text{Jmol}^{-1}\text{H}_2\text{K}^{-1}$ in 5 at. % and 10 at. % Al supersaturated Mg-Al solid solutions, respectively^[23]. Thus, the configurationally entropy contributed to dehydrogenation entropy can no longer be ignored.

For solid solution constituted of A and B elements, suppose the atom concentration of A and B are x_A and x_B mol, respectively, and the sum of x_A and x_B is 1 mol. Hence, the combination of atom B in A-B solid solution should be $C_{(x_A+x_B) \cdot N_A}^{x_B \cdot N_A}$ as shown in Eq (13).

$$C_{(x_A+x_B) \cdot N_A}^{x_B \cdot N_A} = \frac{[(x_A+x_B) \cdot N_A]!}{[(x_A \cdot N_A)!] \cdot [(x_B \cdot N_A)!]} \quad (13)$$

Hence, the increase of configuration entropy (ΔS_{AB}) contributed by the solid solution can be derived as Eq (14).

$$\Delta S_{AB} = -R(x_A \cdot \ln x_A + x_B \cdot \ln x_B) \quad (14)$$

For the Mg-based Mg-B binary solid solution, supposing it completely reversible during hydriding/dehydriding and the amount of solution element x_B being between 0 and 0.5 ($0 \leq x_B \leq 0.5$), the hydriding/dehydriding reaction can be described as Eq(15).

Here, the dehydriding entropy (ΔS) for per mol H_2 should be modified as Eq(16).

$$\Delta S = \left[S_{\text{Mg}_{(1-x_B)}\text{B}_{x_B}} + (1 - x_B)S_{\text{H}_2} - (1 - x_B)S_{\text{MgH}_2} - x_B S_B \right] / (1 - x_B) \quad (16)$$

Hence, as indicated in supporting information IV, the ΔS can be derived as Eq (17). It can be found ΔS increases with the solubility in Mg-based solid solution alloys as shown in Fig. 2. The entropy increasing significantly decreases the Td .

$$\Delta S = \Delta S_{\text{bulk}} - R \left[\frac{x_B}{(1-x_B)} \cdot \ln x_B + \ln(1 - x_B) \right] \quad (17)$$

5. The effect of coating catalyst on dehydrogenation entropy of MgH₂

When MgH₂ desorbs hydrogen, the H atoms will occupied surface of the Mg/MgH₂ particles. These H atoms would change the surface status and contribute to the ΔS , depending on the H concentration. Besides that, Mulder et al reported that a surprising result that substantial amounts of H dissolve in the Mg α -phase by neutron diffraction.^[24] And that also prompted them to reanalyze previously obtained data on Nb- and V-catalyzed MgH₂ reported earlier. They also find the amounts of H dissolve is much larger than the un-catalyzed Mg/MgH₂ system which lead to the deviations in the entropy of catalyzed Mg/MgH₂ system. Hence, in the catalyzed Mg/MgH₂ system, the effect of catalyst cannot be ignored any more. Fig. 4 is the schematic of dissociated H atom in different modified MgH₂ systems, being with non-catalyst, doping catalyst and covered catalyst. As shown in Fig. 4a, due to the high activation energy (E_A) of H₂ dissociation in pure Mg/MgH₂, the amount of dissociated H is very few at ambient temperature. With the catalysts doping, as shown in Fig. 4b, due to the low E_A of H₂ dissociation on the surface of catalysts, the amount of dissociated H is higher than that in pure Mg/MgH₂. Especially, in the catalyst covered core-shell structured system, as schematically shown in Fig. 4c, the covered catalyst enables high concentration of dissociated H on the surface layer as reported in Mg-Ti systems^[11], which is supposed to change the ΔS .

Here, taking C as catalyst for short, x_C and x_H mol as the amount of catalyst and dissociated H, respectively, the dehydrating ΔS for per mol H₂ in Eq (9) should be modified as

$$\Delta S = S_{\text{Mg-C-H}} + \left(1 - x_C - \frac{x_H}{2} \right) \cdot S_{\text{H}_2} - S_{\text{MgH}_2-\text{C}} / \left(1 - x_C - \frac{x_H}{2} \right) \quad (18)$$

For the core-shell structured Mg-C system, $S_{\text{Mg-C-H}}$ and $S_{\text{MgH}_2-\text{C}}$ can be affected by the covered catalyst and dissociated H. And this is depended much on the structure of the catalyst and its activation energy during H₂ dissociation. As indicated in Supporting information V in

detail, ΔS can be obtained as shown in Eq(19).

$$\Delta S = \frac{(1-x_C) \cdot S_{Mg}^\theta + x_H \cdot S_H^\theta - R \left[\frac{x_H}{x_C} \ln \frac{x_H}{x_C} + \left(1 - \frac{x_H}{x_C} \right) \ln \left(1 - \frac{x_H}{x_C} \right) \right] + \left(1 - x_C - \frac{x_H}{2} \right) \cdot S_{H_2}^\theta - (1-x_C) \cdot S_{MgH_2}^\theta}{\left(1 - x_C - \frac{x_H}{2} \right)} \quad (19)$$

Taking Mg-Ti system in our reported work^[11] as an example, the x_C of Ti catalyst is about 0.1 mol and the covered layer of Ti is about 5~10 nm. Here, we assume the average thickness (ε) of Ti is 7.5 nm. We suppose every Ti atom on the extreme surface act as the catalytic active center which can induce one hydrogen molecule dissociated. Hence, x_H can be obtained by getting the amount of Ti atom on the extreme surface. As shown in Supporting information V, the value of x_H in Mg-Ti system is 0.00311 mol. Taking the corresponding values into Eq (19), the value calculated in Mg-Ti system is $132.3 \text{ Jmol}^{-1} \text{H}_2 \text{K}^{-1}$ which is $1.8 \text{ Jmol}^{-1} \text{H}_2 \text{K}^{-1}$ larger than the pure Mg/MgH₂. This entropy increasing can lower the T_d .

6. Validate the model using existing experimental data

In short, ΔS decreases with the particle size of Mg/MgH₂, and increases with the solubility in Mg-based solid solution alloy. It also increases with the concentration of dissociated H on the surface of Mg/MgH₂ particles which depends on the activity of catalyst on H₂ dissociation.

The dehydriding ΔS data derived from our experimental nano-size Mg and many nano-size Mg-based systems from other groups^[7, 9, 25] are given in Table 1. As shown in Fig.1, our experimental data marked as filled circle and other groups data marked as hollow circular, pentacle and box are consistent with the calculated result. The results of the dehydriding ΔS reduced with the particle size (ranging from 15-100nm)^[26] also match with our calculation model. Anyway, as discussed above, the ΔS decreases substantially with the particle size due to the size effect only when the particle size reduces to very small. Thus, the decrease of T_d is not significantly which is in conformity with the reported works.

Taking Mg-Al (Mg_{0.95}Al_{0.5} and Mg_{0.9}Al_{0.1}) as example for solid solutions^[19], calculated ΔS of Mg_{0.95}Al_{0.5} and Mg_{0.9}Al_{0.1} are 132.2 and $133.5 \text{ Jmol}^{-1} \text{H}_2 \text{K}^{-1}$ which are 1.7 and $3.0 \text{ Jmol}^{-1} \text{H}_2 \text{K}^{-1}$ higher than pure MgH₂, respectively. The reported experimental ΔS of Mg-Al (Mg_{0.95}Al_{0.5} and Mg_{0.9}Al_{0.1}) are 2.1 and $3.5 \text{ Jmol}^{-1} \text{H}_2 \text{K}^{-1}$ higher than pure MgH₂, respectively. This also supports our computational model applicable.

According to Eq (19), dehydriding ΔS increases with the concentration of dissociated H on the surface of Mg/MgH₂, and hence, increase with the decrease of activation energy for H₂

dissociation. This is in agreement with our experimental work on transition metals catalyst covered core-shelled structured Mg-TM systems^[11,27]. The ΔS for Mg-Ti, Mg-V, Mg-Nb and Mg-Ni system varies in the order of their activation energy for H₂ dissociation theoretical calculating in Pozzo's work^[28].

7. Conclusion

The effect of modifying MgH₂, in terms of nanosizing, forming solid solution and doping catalysts, on dehydrogenation entropy are calculated by establishing theoretical model. It can be found that the nanosizing results in the decreasing of dehydrogenation ΔS while forming solid solution and doping catalyst leads to the increase of it. It is predicted that the ΔS will be less than 120.1 Jmol⁻¹K⁻¹ when the particle/grain size is reduced to 3 nm. Besides that, the ΔS would increase along with the increase of solubility of the Mg-based hydrogen storage solid solution alloy. And it also increase with the content of dissociative H on the hydrides surface, which is affected by catalyzing effect of doped catalysts. The results of present theoretical model are consistent with the experimental results both from our research and others' report.

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Table 1 Dehydrogenation equilibrium pressure under different temperature, particle size, reaction ΔH and ΔS for the reactions of $\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$ from different system

Fig. 1 The curve of Grain size/particle size effect on dehydrogenation entropy

Fig. 2 The curve of solid solubility effect on dehydrogenation entropy

Fig. 3 The curve of solid solubility effected on dehydrogenation entropy

Fig. 4 The schematic diagram of dissociated H atom in different Mg-based systems. a: Pure Mg; b: Ball-milled Mg/MgH₂ with TM-based catalyst; c: core-shell structured Mg-TM

Table 1 Dehydrogenation equilibrium pressure under different temperature, particle size, reaction ΔH and ΔS for the reactions of $\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$ from different systems

Sample ID	T (°C)						Particle size	$\Delta H/\Delta S$
	P_{eq} (bar)	250	275	300	325	350	(nm)	(kJmol ⁻¹ H ₂ / Jmol ⁻¹ K ⁻¹)
Mg-Ti	0.4160	0.9141	1.8642				~800	75.1/136.3
Mg-Nb	0.3777	0.8305	1.7049	—	—		~800	75.1/135.5
Mg-V	0.4109	0.9035	1.8546	—	—			75.1/136.2
Mg-Co	0.2599	0.5708	1.1706	—	—			75.0/132.2
Mg-Ni	0.4311	0.9480	1.9461	—	—			75.1/136.6
Mg-Mo	0.2144	0.4709	0.9657	—	—			75.0/130.6
N-Mg	—	—	0.8235	1.5888	2.9081		~40	74.9/129.1
B-MgH ₂	—	—	0.8798	1.7006	3.1179		~1000	75.1/130.8
Refer [7]	—	—	—	—	—		~7	71.2/129.6
Refer [9]	—	—	—	—	—		<3	63.85/117.2
Refer [25]	—	—	—	—	—		17	72/125

Fig. 1 The curve of Grain size/particle size effect on dehydrogenation entropy

Fig. 2 The curve of dehydrogenation temperature under 1atm depended on grain size/particle size

Fig. 3 The effect of solubility on dehydrogenation entropy of Mg based solid solution

Fig. 4 The schematic diagram of dissociated H atom in different Mg-based systems. a: Pure Mg; b: Ball-milled Mg/MgH₂ with TM-based catalyst; c: core-shell structured Mg-TM

Highlights

- A theoretical model is proposed to explain ΔS change in dehydriding of MgH_2 .
- The ΔS value is decreased with the reduction of particle size.
- The ΔS value is increased with the increased solid solubility of the Mg-based
- The ΔS value is increased with dissociative H caused by the doped catalysts.
- The present theoretical model of ΔS are consistent with the experimental results.

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On the hydrogen desorption entropy change of modified MgH_2

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