Carbon scaffold modified by metal (Ni) or non-metal (N) to enhance hydrogen storage of MgH₂ through nanoconfinement

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Abstract

This work focuses on improving the kinetics of de/hydrogenation of nanoconfined MgH_2 by using functionalized ordered mesoporous carbon scaffolds (N doped and Ni decorated). The microstructure characterization demonstrates that $x\text{Ni-CMK-3}$ ($x=1$ and 5 wt%) and N-CMK-3 are suitable as scaffolds to load nano MgH_2 . Interestingly, the thermal analysis (TPD-MS measurement) and hydrogen absorption/desorption isotherms reveal that Ni-decorating or N-doping into CMK-3 structure can significantly promote both the hydrogen storage capacity and kinetics. This work suggests that the strategy of combining metal/non-metal doping and nano-confinement is promising, which may open a new avenue for enhancing the hydrogen sorption performance of MgH_2 under mild operational conditions.

Key words: Hydrogen storage; nanoconfinement; nanoparticles; mesoporous carbon; MgH_2

1 Introduction

A significant challenge for the widespread use of hydrogen as a practical alternative to fossil fuels is the development of safe and efficient hydrogen storage materials.^[1] Light metal hydride, such as MgH_2 , is a promising candidate due to its high gravimetric and volumetric hydrogen storage density (e.g., 7.6 wt% H_2 and $110 \text{ kg H}_2 \text{ m}^{-3}$ for MgH_2).^[2-4] However, practical use of MgH_2 has been hampered by the slow kinetics and high temperatures required for hydrogen absorption/desorption, especially hydrogen release from MgH_2 .^[5]

In general, chemically the decomposition of a compound is actually to break the bonding network between constituent elements, which is essentially determined by the electron overlapping between neighbouring atoms. Therefore, removing electrons associated with a specific bond can make the bond breakage easier. This simple strategy has been widely employed to improve the kinetics and thermodynamics of chemical reactions, such as the decomposition of MgH_2 for the application of hydrogen storage.^[6] In the last decade, several approaches such as adding catalytic oxides/compounds,^[7-9] multi-component nano-catalysts,^[10-13] Mg alloying^[14-19], and chemically destabilizing MgH_2 with the addition of reactive compounds (borohydrides, alanates and amides)^[20-23] have been widely used to weaken the strong Mg-H bonding and improve the hydrogen storage properties. Recently, Ouyang et al. developed a plasma-assisted milling technique to realize the dual tuning of thermodynamic and kinetic properties, as such a process can realize the simultaneous rapid formation of a Mg-based solid solution and the *in-situ* induced catalyst.^[24,25] For further scalable commercialization, Pistidda et al. developed a cost-effective method for cycling the industrial waste Mg alloys to produce cheap Mg based hydrogen storage systems.^[26] On the other hand, preparing nanoscale Mg/ MgH_2 particles from “bottom-up” approach has also been proved by both theoretically and experimentally feasible to enhance the kinetics and thermodynamics of hydrogen storage.^[27-32] In our previous work,^[33] we reported that low temperature hydrogen release (from 50°C) was realized by inserting nano MgH_2 into ordered mesoporous carbon scaffold, e.g. CMK-3, with a relative high loading of 37.5 wt%. Furthermore, through the computational calculations, we found that the charge transfer from MgH_2 to the carbon scaffold plays a critical role for the significant reduction of thermodynamics of MgH_2 dehydrogenation. However, it is noteworthy that hydrogen sorption kinetics is still slow in such Mg-CMK-3 confined system, underlining the need to further improve.

Accordingly, we functionalized the CMK-3 carbon scaffold by two different ways that include metal decorating and non-metal doping. Nickel (Ni) as one of the effective catalysts which was selected to decorate on the CMK-3 surface due to its high catalytic activity for enhancing hydrogen storage in Mg/MgH₂ system.^[34,35] Alternatively, incorporation of heteroatoms (e.g., N, B, and S) onto the carbon materials to modify their surface physicochemical properties have been widely studied.^[36] Among them, N-containing carbons have already received considerable attentions for enhanced hydrogen uptake in physisorption,^[37, 38] however, there are rare experimental studies on the effect of N-doped carbon as a scaffold for nanoconfined Mg/MgH₂.

In this work, we have investigated on the effects of the carbon scaffold modified by metal (Ni) and non-metal (N) on nanoconfined MgH₂ for hydrogen sorption. A plausible catalytic mechanism will be also discussed. Our findings provide more solid evidence to effect of combining size and interfacial confinement as well as the catalytic effect of Ni or N on hydrogen storage of Mg/MgH₂ system.

2. Experiment Details

2.1 Ni-CMK-3 synthesis

Firstly, CMK-3 was prepared by a nanocasting method using ordered mesoporous silica (SBA-15) as template reported in previous studies.^[39, 40] Successive two-step impregnation procedure and high temperature calcination at 900 °C under argon atmosphere were employed. The silica template was removed by 10% HF leaching at room temperature and the carbon sample was washed with distilled water before drying in air at room temperature for 24 h. Secondly, to obtain different amounts of the Ni decorated in CMK-3 scaffolds (denoted as xNi-CMK-3, x represents the weight percentage which are 1, 5, and 10 wt%, respectively), the matched (by calculation) amounts of Ni(NO₃)₂·6H₂O (Sigma-Aldrich) was dissolved in ethanol and the CMK-3 was added to the solution by stirring for 48 h, and then the mixture was dried at 50 °C in the oven. Finally, the dried samples were reduced in 5 % H₂/N₂ gas mixture at 500 °C for 2 h.

2.2 N-CMK-3 synthesis

The N-doped CMK-3 (denoted as N-CMK-3) was prepared by heat treatment of the pristine CMK-3 loaded in a ceramic boat in a SiC tube furnace at 600 °C for 4 h under a pure NH₃ gas atmosphere with a total flow rate of 100 mL min⁻¹.

2.3 Loading of MgH₂ into Ni-CMK-3 or N-CMK-3

A new modified approach was developed in order to incorporate magnesium hydride into as-prepared nanoporous Ni-CMK-3 or N-CMK-3 scaffolds. Before impregnation procedure, selected Ni-CMK-3 or N-CMK-3 was first dried under vacuum at 140 °C for 12 h in order to remove moisture and gaseous impurities from the porous structure. Afterwards, 0.2 g dried Ni-CMK-3 or N-CMK-3 was impregnated with 1.5 ml dibutylmagnesium MgBu_2 (1.0 M solution in heptane, Sigma-Aldrich) in Ar filled glove box. The Ni-CMK-3 or N-CMK-3 in MgBu_2 solution were left to dry for several days until the solvent heptane was completely evaporated and solid MgBu_2 was embedded into the pores, and then the dried composites were transferred to PCT reactor for further hydrogenation, which reacted with hydrogen to form magnesium hydride (0.04 g) and butane under a temperature of 200 °C and a hydrogen pressure of 8 MPa, denoting as $0.2\text{MgH}_2@\text{Ni-CMK-3}$ or $0.2\text{MgH}_2@\text{N-CMK-3}$ (weight ratio of MgH_2 and Ni-CMK-3 or N-CMK-3 is 1:5). Afterwards, the impregnation and hydrogenation procedure was repeated two more times and the final composite was denoted as $0.6\text{MgH}_2@\text{Ni-CMK-3}$ or $0.6\text{MgH}_2@\text{N-CMK-3}$ (weight ratio of MgH_2 and Ni-CMK-3 or N-CMK-3 is 3:5, ca. 37.5 wt% MgH_2 loading). This method has been confirmed to be effective for the synthesis.^[33] All the sample handling was performed in an Ar-filled glovebox (MBraun), in which the water/oxygen levels were below 1ppm.

2.4 Materials characterization

The composition and microstructure of Ni-CNK-3 or N-CMK-3 were characterized by X-ray diffraction (XRD, Rigaku Miliflex) with $\text{Co K}\alpha$ radiation, N_2 adsorption (Quadratorb SI, Quantachrome) at 77 K, X-ray photoelectron spectrometer (XPS, Kratos Axis ULTRA) with $\text{Mg K}\alpha$ radiation, scanning electron microscopy (SEM, JEOL 6300), and transmission electron microscope (TEM, FEI Tecnai 20) with an accelerating voltage of 200 kV. The samples for TEM measurements were dispersed in heptane by ultrasonication and then deposited onto a holey carbon film on a copper grid.

2.5 Hydrogen storage measurements

Hydrogen sorption properties of the nanocomposites ($\text{MgH}_2@\text{Ni-CMK-3}$ or $\text{MgH}_2@\text{N-CMK-3}$) were measured by temperature program control desorption with mass spectrometry (TPD-MS) performed by Brooks 5850E mass flow controllers, which is attached with a quartz reactor in a tube furnace.^[41] The temperature was raised from room temperature to 500 °C at the rate of 5 °C min^{-1} , with ultra pure helium (99.999%) as carrier gas at a rate of 50 mL min^{-1} . Furthermore, the hydrogen isothermal kinetic curves of $\text{MgH}_2@\text{Ni-CMK-3}$ or $\text{MgH}_2@\text{N-CMK-3}$ have been measured by an automated Sieverts' apparatus (Suzuki Shokan PCT H_2 Absorption Rig). Before absorption, the system was degassed for 2 h within the

sample cell being heated at 350 °C. Absorption/desorption measurements were performed at various temperatures with an initial pressure of 2 MPa for hydrogenation and 1 KPa for dehydrogenation, respectively. The content of gaseous ab/desorbed hydrogen capacities were calculated from the loaded MgH_2 .

3. Results and discussion

3.1 Characterization of xNi-CMK-3 scaffolds

Figure 1 Power XRD patterns of pristine CMK-3 and xNi-CMK-3 samples (x=1, 5 and 10 wt%).

To characterize the change of the microstructure and porosity of the prepared xNi-CMK-3 scaffolds (x=1, 5, and 10 wt%), X-ray diffraction (XRD) and N_2 physisorption techniques were employed. Figure 1 depicts the nickel crystals in CMK-3 with increasing sizes as the

nickel contents increased. The mean grain sizes of Ni in xNi-CMK-3 scaffolds are 4.5 nm for 1Ni-CMK-3, 9.6 nm for 5Ni-CMK-3, and 10.7 nm for 10Ni-CMK-3, respectively, calculated by using the Scherrer equation. In addition, it was associated with a deterioration of the graphitic structure with high Ni loading. For instance, between CMK-3 and 10Ni-CMK-3, at an angle of 22° , the Bragg peak was clearly reduced in amplitude and broadened, but the structure of carbon remains undamaged in low Ni loading of 1% and 5%. The CMK-3 structure change was due to the destruction of the carbon surface surrounding the catalyst (Ni) nanoparticles. Moreover, the N_2 physisorption analysis (Figure 2a) shows representative type IV isotherm and a hysteresis loop in the relative pressure (P/P_0) range of 0.3-0.75 for CMK-3, 1Ni-CMK-3 and 5Ni-CMK-3 whose Brunauer-Emmett-Teller (BET) surface areas are $1487 \text{ m}^2 \text{ g}^{-1}$, $1360 \text{ m}^2 \text{ g}^{-1}$ and $1288 \text{ m}^2 \text{ g}^{-1}$ respectively, indicating a high uniformity of mesopores that provides the accessibility of guest materials, in this case, MgBu_2 solution. More importantly, such high BET surface areas may provide high density of Mg-Ni interface, leading to enhance the hydrogenation/dehydrogenation along interface region due to the change of interfacial energy.^[42] However, it was noteworthy that the hysteresis loop disappeared in 10Ni-CMK-3 with low BET surface area of $468 \text{ m}^2 \text{ g}^{-1}$, implying the pore blocking or structure damage appears with increasing Ni loading. On the other hand, calculation from the adsorption branch by Barrett-Joyner-Halenda (BJH) model for CMK-3 (Figure 2b) confirms a narrow pore size distribution (4 nm) and the mesopore pore volume of xNi-CMK-3 decreases with increased Ni adding amount, further demonstrating that the Ni nanoparticles were formed inside the mesopores. The connected channels of ordered mesoporous carbon is helpful for MgBu_2 solution penetration as illustrated by the reduction of the mesopore volume.

Figure 2 Nitrogen sorption isotherms (a) and pore size distribution curves (b) of the pristine CMK-3 and xNi-CMK-3 samples (x=1, 5 and 10 wt%).

To further verify the Ni dispersion and accessibility of xNi-CMK-3 scaffolds, transmission electron microscopy (TEM) has been used to observe their structure and morphology. As shown in Figure 3, while 1Ni-CMK-3 and 5Ni-CMK-3 samples both exhibited an ordered array of mesoporous carbon nanorods dispersed with uniform Ni nanoparticles with a size distribution of *ca.* 2-3 nm in the pores and *ca.* 8-10 nm outside the pores, no obvious mesoporous framework was observed for the 10Ni-CMK-3, showing that its ordered structure may be destroyed. This indicated that the mesoporous accessibility of xNi-CMK-3 scaffolds decreases with increased Ni adding amount, which agrees well with N₂ physisorption results.

Figure 3 TEM images of (a) 1Ni-CMK-3, (b) 5Ni-CMK-3 and (c) 10Ni-CMK-3 samples, respectively.

In summary, it is suggested that 1Ni-CMK-3 and 5Ni-CMK-3 scaffolds are available to host loading MgBu₂ solution due to their unchanged ordered structure.

3.2 Characterization of N-CMK-3 scaffold

Scanning and transmission electron microscopy images (Figure 4a-c) show that the nitrogen doped CMK-3 (N-CMK-3) carbon nanorods maintain the ordered array of mesoporous structure, but exhibit more surface roughness than the pristine CMK-3 which may be attributed to slight etching or collapse of ultrafine nanostructures of the carbon during nitrogen doping process.^[43] Moreover, the chemical composition of N-CMK-3 is determined by X-ray photoelectron spectroscopy (XPS) analysis. The “surface” N information is of particular importance, as it gives direct indication of the amount and types of N present on the carbon surface that interact with hydrogen or Mg-H bond for hydrogen absorption/desorption. XPS analysis reveals that N doping level is 1.2 at% (atomic

percentage) in N-CMK-3. Due to the low doping temperature, there is no quaternary N formed.^[44] As shown in Figure 4d, the asymmetric N1s XPS peak of N-CMK-3 was fitted to two main peaks of pyridinic N (398.5 eV) and pyrrolic N (400.0 eV).^[45] The pyridinic N that contributes to the π conjugation with one p electron corresponds to a tetrahedral nitrogen phase bonded to a sp^3 -hybridized carbon atom (N sp^3 C).^[46] The pyrrolic N atoms with two p electrons in the π conjugation corresponds to a trigonal nitrogen phase bonded to a sp^2 -coordinated carbon atom (N sp^2 C).^[46]

Figure 4 SEM images of N-CMK-3 (a) from low magnification to (b) high magnification, (c) TEM image and (d) N1s XPS spectrum of the N-CMK-3.

3.3 Hydrogen storage of Mg/MgH₂ confined by Ni-CMK-3 and N-CMK-3 and its mechanism

When the scaffolds loading Mg/MgH₂, the Mg/MgH₂ particles formed both inside and outside the pores. Nickel (Ni) is a classical and effective de/hydrogenation catalyst, and hence it is interested in its catalytic behaviour on the hydrogen desorption from nanoconfined MgH₂@xNi-CMK-3 (x=1 and 5) systems. The hydrogen release was firstly investigated using temperature programmed desorption mass spectrometry (TPD-MS). Not surprisingly, The TPD-MS file (Figure 5a) shows the distinguished hydrogen release of MgH₂@xNi-CMK-3 and MgH₂@CMK-3 in two different temperature zones. In high temperature range (zone 1, 250-500 °C), it is obvious that the peak temperature of the H₂ desorption shifted down from 430 °C for MgH₂@CMK-3 to 370 °C for MgH₂@1Ni-CMK-3, and further to 350 °C for MgH₂@5Ni-CMK-3, indicating Ni plays an catalytic role in dehydrogenation of MgH₂ outside the pores. On the contrary, it is also noticed that in low temperature range (zone 2, 25-250 °C) from MgH₂ inside the pores, the hydrogen release was suppressed with increasing Ni content as compared to MgH₂@CMK-3, although the onset temperature of hydrogen release still started from 50 °C (Figure 5a inset). Based on our previous study on MgH₂@CMK-3 system, as the low temperature hydrogen release is mainly from the Mg-C interface confinement due to electron transfer from MgH₂ particles to the CMK-3 substrate; as a consequence, the Mg-H bonding is weakened.^[33] Recently, such a Mg-C bonding catalytic mechanism at nanoscale interface has also been evidenced in Mg-graphene wrapped systems.^[47,48] It is speculated that partial deterioration of the carbon surface surrounding the Ni catalyst nanoparticles in xNi@CMK-3 scaffolds may lead to decreasing the number of unsaturated carbons on CMK-3 surface (evidenced by XRD results, Figure 1), and thus decrease the Mg-C bonding sites. However, the presence of Ni has a significant positive impact on the main dehydrogenation peak of nanoconfined MgH₂, indicating that Ni catalysts promote the release of hydrogen, which may be attributed to the strong capacity to catch hydrogen and form H₂ molecules at the surface. To understand the physical mechanism, more theoretical work, particularly computational modelling, is desirable.

Figure 5 TPD-MS spectra by recording the mass spectrometer intensity of H_2^+ ions ($m/e=2$), measuring from room temperature to 500 °C (heating rate 5° min^{-1}). (a) The thermal dehydrogenation behaviours of $\text{MgH}_2@5\text{Ni-CMK-3}$, $\text{MgH}_2@1\text{Ni-CMK-3}$ and $\text{MgH}_2@CMK-3$ with inset enlarged curves at low temperature (25-250 °C); (b) the thermal dehydrogenation behaviours of $\text{MgH}_2@N\text{-CMK-3}$ and $\text{MgH}_2@CMK-3$ with inset enlarged curves at low temperature (25-250 °C).

With respect to thermal dehydrogenation behaviour of $\text{MgH}_2@N\text{-CMK-3}$, it is interestingly found that non-metal (N) doped CMK-3 also exhibits a significant catalytic enhancement in dehydrogenation of nanoconfined MgH_2 . As shown in Figure 5b, the major peak for H_2 release shifts down from 430 °C for $\text{MgH}_2@CMK-3$ to 350 °C for $\text{MgH}_2@N\text{-CMK-3}$. To our best knowledge, this is the first observation on such significant improvement by non-metal (N) catalyst in the dehydrogenation of MgH_2 . Similar to Ni-catalyst, modification by nitrogen has no improvement for the dehydrogenation in the low temperature range (25-250 °C) (Figure 5b inset). Accordingly, it is speculated that the observed improvement by the addition of N may come from the stabilization effect with the formation of N-Mg bonds, which has been supported by computational calculations.^[49] Simultaneously, the introduced N atoms cover a part of unsaturated carbons (evidenced by XPS result, Figure 4d); as a result, Mg atoms bonded with unsaturated carbon are reduced as well and hydrogen released from Mg-C interface at low temperature becomes less.

Figure 6 Hydrogenation kinetics of MgH₂@5Ni-CMK-3, MgH₂@1Ni-CMK-3, MgH₂@N-CMK-3 and MgH₂@CMK-3 composites at two different temperatures (a) 300 °C and (b) 200 °C under a pressure of 2MPa. Before absorption, the system was degassed for 2 h within the sample cell being heated at 350 °C.

To gain further insight into the roles of metal (Ni) and non-metal (N) in catalytic effects, we investigated the de/hydrogenation kinetics of MgH₂@5Ni-CMK-3, MgH₂@1Ni-CMK-3 and MgH₂@N-CMK-3 composites at varied temperatures under a hydrogen pressure of 2 MPa for hydrogen absorption and 1 KPa for dehydrogenation. As presented in Figure 6a, it can be clearly observed that MgH₂@5Ni-CMK-3, MgH₂@1Ni-CMK-3 and MgH₂@N-CMK-3 exhibit better hydrogen absorption properties than that of MgH₂@CMK-3 at 300 °C, which can absorb about 6 wt% hydrogen within 10 min and reach ~6.5 wt% in 2 h. Moreover, MgH₂@1Ni-CMK-3 and MgH₂@N-CMK-3 can also absorb 6.5 wt% hydrogen at 200 °C within 2 h, and MgH₂@5Ni-CMK-3 can even absorb 7.5 wt% hydrogen at 200 °C within 2h

which is superior to the absorbed capacity (6.5 wt%) at 200 °C within the same duration (Figure 6b), implying that the higher temperature may inhibit the catalytic role of Ni in facilitating the dissociation of molecular H_2 for further combination with Mg.

Figure 7 Hydrogen desorption profiles of the as-prepared composites ($MgH_2@CMK-3$, $MgH_2@N-CMK-3$, $MgH_2@1Ni-CMK-3$, and $MgH_2@5Ni-CMK-3$) at (a) 300 °C, (b) 280 °C and (c) 250 °C in a vacuum of < 1 KPa, and (d) the comparison of the capacities of dehydrogenation within 2 h of the composites at 300 °C and relevant activation energies for dehydrogenation.

Figure 7a-c show the desorption kinetics of $MgH_2@CMK-3$, $MgH_2@N-CMK-3$, $MgH_2@1Ni-CMK-3$, and $MgH_2@5Ni-CMK-3$ at 300 °C, 280 °C and 250 °C, respectively. From Figure 7a, the confined MgH_2 by N-CMK-3 can desorb about 5 wt% hydrogen within 1 h and 7.5 wt% in 10 h at 300 °C which is 1.5 times faster than that of $MgH_2@CMK-3$. The confined MgH_2 by xNi-CMK-3 (x=1 and 5) exhibits better desorption performance, which can release about 7.5 wt% hydrogen in only 2 h at 300 °C. Figure 7b-c show Ni or N can

catalyze hydrogen release at lower temperatures. To further study the catalytic effect of varying functionalized scaffolds in MgH_2/Mg heterogeneous phase transformation, the desorption data (Figure 7a-c) are analysed by using Johnson-Mehl-Avrami (JMA) theory,^[50] 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). A linear interpolation of the plots, $\ln(-\ln(1-\beta))$ vs $\ln(t)$, could yield the values of n and k . The values of the exponent were close to 1 for all nanoconfined samples by the best fit of our data, indicating that the phase transformation of MgH_2 to Mg occurs by instantaneously numerous nucleation and growth along one-dimensional (1D) lines,^[51] which may be ascribed to the tubular nanostructure in CMK-3 based frameworks. Furthermore, the activation energies (E_a) for dehydrogenation were determined by the slope of the fitted line via plotting $\ln(k)$ versus $1/T$ and then calculating the values via Arrhenius equation ($E_a = -RT \ln(k/k_0)$ with k derived from above JMA analysis). The changing trend of E_a and the capacities of dehydrogenation within 10 h of $\text{MgH}_2@\text{CMK-3}$, $\text{MgH}_2@\text{N-CMK-3}$, $\text{MgH}_2@1\text{Ni-CMK-3}$, and $\text{MgH}_2@5\text{Ni-CMK-3}$ at 300 °C are summarized in Figure 7d, which clearly shows: (1) nanoconfined MgH_2 by Ni or N modified CMK-3 can significantly enhance the hydrogen releasing capacity from 5 wt % to 7.5 wt%, which is close to the theoretical value of MgH_2 (7.6 wt%); (2) of particular interest, it was found that the desorption kinetics of $\text{MgH}_2@\text{N-CMK-3}$ was considerably improved comparing with $\text{MgH}_2@\text{CMK-3}$ (E_a decreased from $125.3 \pm 2.1 \text{ kJ mol}^{-1}$ to $116.2 \pm 1.8 \text{ kJ mol}^{-1}$), and further reduced to $109.2 \pm 1.3 \text{ kJ mol}^{-1}$ for $\text{MgH}_2@1\text{Ni-CMK-3}$ and $107.6 \pm 1.2 \text{ kJ mol}^{-1}$ for $\text{MgH}_2@5\text{Ni-CMK-3}$, respectively, indicating addition of Ni or N-doping into CMK-3 can significantly enhance the hydrogen release kinetics of nanoconfined MgH_2 .

4. Conclusion

In conclusion, we have functionalized the CMK-3 by metal (Ni) or non-metal (N) doping, and investigated their catalytic effects on hydrogen storage of nanoconfined Mg/MgH_2 . The microstructure characterization demonstrates that 1Ni-CMK-3, 5Ni-CMK-3 and N-CMK-3 are suitable for MgH_2 loading due to the remained ordered channels of CMK-3. The thermal analysis by TPD-MS and hydrogen sorption kinetics reveal that Ni or N-doping can significantly promote the hydrogen storage capacity and increase the kinetics. The hydrogen release was suppressed with the presence of Ni or N decorated on CMK-3 at low temperatures (25-250 °C), which may be ascribed to the decrease of Mg-C bonding sites. Although the confined MgH_2 can release hydrogen at such a low temperature, the capacity is

too low due to only very small fraction of MgH_2 can accommodate inside the pores. How to synthesize all MgH_2 inside the pores of porous frameworks without any particles on the out surface is a big challenge.

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