

Magnesium/Carbon Composite Nano-Material for Hydrogen Storage and Sulfocompound Hydrogenation

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Abstract: Magnesium/carbon composite hydrogen storage material was prepared by reactive ball-milling under hydrogen atmosphere. The material was tested by TEM, XRD, DSC, FT-IR, and dehydrogenation device so as to clarify its microscopic structure, crystal phase, dehydrogenation temperature, functional groups and hydrogen capacity. It was shown that crystallitic carbon from anthracite carbonization was an effective milling aid for magnesium. Dispersive nano-particles about 20 to 60 nm were prepared from the mixture of 65 wt.% of magnesium and 35 wt.% of crystallitic carbon by milling for 3 h under 1 MPa of hydrogen atmosphere. The magnesium hydrided into MgH₂ and the crystallitic carbon was endowed with C=CH₂ functional group during milling. The hydrogen capacity of the composite material is 5.81 wt.%. The initial dehydrogenation temperature of the material is 275.8 °C, which is much lower than that of pure MgH₂. The hydrogen and magnesium in the material can react with CS₂ or thiophene and result in H₂S and MgS.

Keywords: hydrogen storage material; magnesium; crystallitic carbon; reactive milling; sulfocompound

1. Introduction

Hydrogen storage materials have attracted intensive attention for future hydrogen economy. Magnesium is emerging as the most promising candidate of hydrogen storage material for automotive application due to its low cost, light weight and high hydrogen capacity (theoretically 7.6 wt.%). However, magnesium is primarily limited by its high temperature and low rate of hydriding and dehydriding ^[1-3]. Recent studies involving creating nano-composites and doping catalysts have succeeded in improving its kinetic performance ^[4-5].

In liquid fuel and synthetic gas, sulfocompounds, such as CS_2 , thiophene, sulfoether, etc., are usually deleterious. Traditionally, to remove the organic sulfur has been achieved by hydrodesulfurization (HDS) process using alumina-supported CoMoS catalyst. However, to satisfy new, more stringent environmental restrictions on the sulfur content of fuels, more active HDS catalysts are being requested by the industry ^[6-8]. Magnesium/carbon composite hydrogen storage material with active hydrogen can act as hydrogen provider as well as catalyst for sulfocompound hydrogenation.

2. Experimental

2.1. Preparation of the Hydrogen Storage Material

The reactive milling to prepare hydrogen storage material from the mixture of 65 wt.% of magnesium and 35 wt.% of crystallitic carbon was carried out on a planetary ball-mill. The crystallitic carbon was prepared from anthracite coal by demineralization and carboniza-

tion. The demineralization process was combined by alkaline melting and acid rinsing treatments to remove most mineral matter inherent to the coal to an extent of ash content 0.05 wt.%. The carbonization was carried out in an electric resistance furnace at 1500 °C for 1 h. For milling, the milling vessels were charged with 1 MPa of hydrogen and the work revolution of the main axis of the mill was set at 270 r/min. Each vessel was charged with 10 g of the mixture of magnesium and crystallitic carbon in the designed ratio, and the weight ratio of milling balls to raw material was about 45:1. Then the vessels were purged by hydrogen, and charged with 1 MPa of hydrogen. During milling, the vessels were recharged with hydrogen every other 0.5 h in order to maintain the hydrogen pressure at about 1 MPa. After milled for 3 h, the material was displaced in a glovebox with argon atmosphere so as to prevent it being oxidized and the hydrogen storage material was prepared.

The observation of the material particles was performed on a Hitachi H-800 transmission electron microscope (TEM) operated at 150 kV and 20 μ A with point resolution of 4.5 Å and lattice resolution of 2.04 Å. The functional groups of the material were determined by a Nicolet 380 Fourier transform infrared spectroscopy (FT-IR). The dehydrogenation temperature of the material was determined by a Netzsch STA 449C differential scanning calorimeter (DSC) with a heating rate of 10 °C/min in argon flow at a rate of 60 mL/min. The crystal phase of the material was determined by a Rigaku D/Max-rB X-ray diffraction instrument (XRD). A dehydrogenation test device designed according to water displacement principle was used to measure the volume of 2010 The Second China Energy Scientist Forum

hydrogen released from the material heated at 400 °C and then the hydrogen capacity was calculated from the weight of the material and the released hydrogen.

2.2. Hydrogenation of Sulfocompounds

The hydrogenation of CS_2 was carried out in a tube reactor. The hydrogen storage material was charged into the reactor, and argon with CS_2 continuously flowed through the reactor, and then the reactor was installed up to the heating furnace. When heated at 200 °C, the hydrogen storage material released hydrogen, and the hydrogen reacted with CS_2 into H_2S . The resulted H_2S was carried out of the reactor by argon and absorbed by Pb(NO₃)₂ solution into PbS.

The hydrogenation of thiophene was carried out in an autoclave reactor. After the hydrogen storage material and thiophene were charged into the reactor, the reactor was purged by argon and heated up to 350 °C, and the hydrogen released from the hydrogen storage material reacted with thiophene. The resulted H_2S was carried out of the reactor by argon and absorbed by $Pb(NO_3)_2$ solution into PbS.

3. Results and Discussion

3.1. Characterization of the Hydrogen Storage Material

The particle size of the hydrogen storage material is about from 20 to 60 nm as the TEM image shown (Figure 1). Magnesium is a kind of soft, malleable and aggregatable metal, so it is difficult to make magnesium into nanoparticles by milling without aids because of serious aggregation of magnesium particles. Crystallitic carbon from anthracite is not aggregatable, and therefore it can play a role of dispersive agent for magnesium particles, which can protect magnesium particles from "cold welding". In addition, the carbon particles with sharp and hard edges can play a role of milling medium for magnesium. Moreover, hydrogen in the milling atmosphere can make magnesium particles expanded and become brittle by penetrating into magnesium crystal lattice in the form of hydrogen atoms, and it is helpful for the magnesium particles to be milled into smaller ones. Dispersive nanoparticles were prepared in 3 h of ball-milling with 35 wt.% of the carbon additive into magnesium.

XRD pattern (Figure 2) of the hydrogen storage material showed that the diffraction peaks of magnesium almost disappeared, and the diffraction peaks of MgH_2 was obvious. It suggested that most magnesium in the depth of X-ray detection hydrided into MgH_2 after milling under hydrogen atmosphere. In addition, MgO was detected, which was from the oxidation of magnesium when the sample was exposed into air, and iron appeared, which was from the inner wall of the milling vessel.





Figure 1. TEM image of the hydrogen storage material



Figure 2. XRD pattern of the hydrogen storage material

The DSC curve of the hydrogen storage material (Figure 3) showed that the initial dehydrogenation temperature is 275.8 °C, and the main peak temperature is 344.2 °C, which are much lower than those of pure MgH₂, 350 °C and 390 °C, respectively. The dehydrogenation of the material is endothermic. With the increase of temperature, the dehydrogenation of the hydrogen storage material became faster. Low temperature and high rate of hydrogen release are desired for hydrogen storage material ^[9, 10]. The release of hydrogen from magnesium and carbon composites is expressed by the following equations:



Figure 3. DSC curve of the hydrogen storage material



The hydrogen capacity of the hydrogen storage material was 5.81 wt.% measured by the device of water displacement. The theoretical hydrogen capacity of pure MgH₂ is 7.6 wt.%. The magnesium content in the composite hydrogen storage material is 65 wt.%. If the hydrogen was all stored in magnesium, the hydrogen capacity of magnesium would be 8.67 wt.%, above its theoretical value. It suggested the crystallitic carbon stored at least 3.39 wt.% of hydrogen (carbon basis). Both magnesium and crystallitic carbon played the role of hydrogen storage.

The FT-IR spectra of the hydrogen storage material after heated at certain temperatures (Figure 4) showed the changes of C=C and C-H functional groups in the material. When the temperature increased from 100 °C to 240 °C, the spectra of the material did not change obviously. With the increase of temperature from 240 °C to 300 °C, the absorption peaks of C-H in C=CH₂ group at 1143.8 cm⁻¹ became weak and moved 1019.9 cm⁻¹, and the absorption peaks of C=C in the range of 1248.6 to 1637.9 cm⁻¹ became strong. When the temperature increased from 330 °C to 500 °C, no obvious changes were observed in the spectra. It suggested that C=CH₂ actively released hydrogen in the temperature range of 240 °C to 300 °C.

The particle of crystallitic carbon from anthracite carbonization was composed of graphenes. It combined with hydrogen during milling. The carbon atoms at the edge of graphenes were hydrogenated into C=CH₂, and C=CH₂ released hydrogen and became C=CH even C=C. Just like activated carbon, carbon nanotubes and carbon nanofibers ^[11, 12], the cryatallitic carbon can also store hydrogen, but in different mechanism.



Figure 4. FT-IR spectra of the hydrogen storage material

3.2. Characterization of the Hydrogenation **Products**

The gasous product from CS_2 and thiophene hydrogenation by the hydrogen storage material was rinsed by $Pb(NO_3)_2$ solution and black precipitate appeared from the solution. The XRD pattern of the precipitate was showed in Figure 5. It suggested that the precipitate is PbS, and CS_2 and thiophene were hydrogenated by the hydrogen from the hydrogen storage material and consequently H_2S yielded.



Figure 5. XRD pattern of the precipitation from Pb(NO₃)₂ solution

The XRD pattern of the hydrogen storage material after reaction with CS₂ at 200 °C was shown in Figure 6 (a). It showed that diffraction peaks of MgH₂ were still strong and peaks of magnesium and MgS appeared by comparing with the XRD pattern of the original material. It suggested that some MgH₂ released hydrogen and became into magnesium, and part of the magnesium sulfurized into MgS. Peaks of MgO and iron remained.

Yegiazarov et al discovered that the products from CS_2 hydrogenation changed with the reaction conditions as the following ^[13]:

$$CS_{2} + H_{2} \begin{cases} \xrightarrow{\Lambda} H_{2}S + CH_{4} \\ \xrightarrow{Ni} CH_{2}(SH)_{2} \\ \xrightarrow{Co} CH_{3}SH + H_{2}S \end{cases}$$

When the hydrogen storage material was used as hydrogen provider, CS_2 was hydrogenated into H_2S at temperature as low as 200 °C, which is much lower than the initial dehydrogenation temperature, 275.8 °C (Figure 3). It suggested that the hydrogen in crystal magnesium lattice and C=CH₂ group was active for the reductive reaction. The reaction between MgH₂ and CS₂ could be expressed by the following equation:

$$MgH_2 + CS_2 \rightarrow MgS + H_2S + CH_4$$

When the temperature was lower than 300 °C, no obvious reaction between thiophene and the hydrogen storage material happened. At 350 °C, the XRD pattern of the hydrogen storage material after reaction with thiophene was shown in Figure 6 (b). It showed that diffraction peaks of MgH₂ disappeared and peaks of MgS dominated. It suggested that almost all of the MgH₂ dehydrided into magnesium at a temperature higher than its dehydrogenation temperature, and the magnesium easily combined with sulfur. The reaction equation is as following:

 $MgH_2 + C_4H_4S \rightarrow MgS + H_2S + C_4H_r$

The composition of the resulted C_4H_x needs to be further studied in the later work. According to some reports, the hydrogenation products of thiophene changed



with the reaction conditions, such as temperature, pressure and catalyst ^[14].



Figure 6. XRD patterns of the hydrogen storage material after reaction with CS₂ (a) and thiophene (b)

4. Summary and Conclusions

The crystallitic carbon from anthracite carbonization is an effective milling aid for magnesium powder. Dispersive particulate material of particle size from about 20 to 60 nm was prepared from the mixture of 65 wt.% of magnesium and 35 wt.% of crystallitic carbon by milling for 3 h under 1 MPa of hydrogen atmosphere. In the composite material, magnesium was hydrided into MgH₂, and the crystallitic carbon endowed with C=CH₂ functional group. Both types of hydrogen in magnesium and carbon released when the material was heated. The hydrogen capacity of the composite material is 5.81 wt.%. The initial dehydrogenation temperature of the material is 275.8 °C, which is much lower than that of pure MgH₂.

 CS_2 was hydrogenated by the hydrogen released from the hydrogen storage material at 200 °C, and thio-

phene was hydrogenated at 350 °C. Both reactions resulted in H_2S and some magnesium in the material was sulfurized into MgS.

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