INVESTIGATION OF CARBON DEPOSITION OF METHANE DECOMPOSITION ON HIGHLY ACTIVE MAGNESIUM POWDER OF NANOMETRIC SIZE

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Introduction

Highly active magnesium powder of nanometric size (Mg\textsuperscript{*}) doped with transition metal compounds, can be obtained from the dehydrogenation of the magnesium hydride (MgH\textsubscript{2}) prepared catalytically according to references [1, 2]. At 723 K the NiCl\textsubscript{2}-doped Mg\textsuperscript{*} can react fairly rapidly with nitrogen to form magnesium nitride of nanometric size [2-5]. In this work we investigated the reactions of NiCl\textsubscript{2}-doped and undoped Mg\textsuperscript{*} with CH\textsubscript{4} by in-situ thermogravimetric balance and the morphology of carbon deposits on Mg\textsuperscript{*} by transmission electron microscopy (TEM) measurement.

Experimental

The undoped and doped MgH\textsubscript{2} were prepared catalytically according to references [1, 2]. The prepared MgH\textsubscript{2} (4-6 mg) was transferred under Ar atmosphere to a quartz basket (8 mm id. and 5 mm high). The basket was then hung in the middle of the vertical quartz tube reactor (14 mm id. and 8 cm long) which was heated by a furnace. CH\textsubscript{4} flow rate was 40 ml min\textsuperscript{-1} and heating rate 10 K min\textsuperscript{-1}. The weight changes of the Mg\textsuperscript{*} samples were recorded by an in-situ thermogravimetric balance. CH\textsubscript{4} (99.99\%) and Ar (99.99\%) were used without further purification. TEM measurements were performed using JEOL JEM-100C X II operated at 100 kV. The samples were treated in an ultrasonic bath of dehydrated organic solvent and then dispersed on a carbon TEM grid with holes.

Results and Discussion

Table 1 shows four different Mg\textsuperscript{*} systems, which were doped with different amount of NiCl\textsubscript{2} and Ni powder, respectively. The in-situ thermogravimetric curves of four different Mg\textsuperscript{*} samples are shown in Figure 1. The first part of weight loss of the curves expresses the process of dehydrogenation of the samples and Mg\textsuperscript{*} is formed in-situ. The part of weight gain of the curves is that of carbon deposition of CH\textsubscript{4} decomposition on Mg\textsuperscript{*}. The second part of weight loss of the curves may be due to the carbon elimination. The weight gain of S1 sample (undoped Mg\textsuperscript{*}) begins from 683 K and continues to 1013 K, the total weight gain is 9 wt\% of the original weight of S1. S1 begins losing weight when the temperature is higher than 1013 K. The weight gain of S2 (2.5 mol\% NiCl\textsubscript{2}-doped Mg\textsuperscript{*}) begins from 573 K and continues to 868 K, the total weight gain is 30 wt\% of S2, but the weight loss is serious with increasing the temperature further (weight loss 23 wt\%). The weight gain of S3 (20 mol\% NiCl\textsubscript{2}-doped Mg\textsuperscript{*}) begins from 948 K and no tendency of weight loss is observed until to 1073 K, the total weight gain is 9 wt\% of S3. The weight gain of S4 (2.5 mol\% Ni-doped Mg\textsuperscript{*}) begins from 653 K and continues to 984 K, the total weight gain is 10 wt\% of S4, then the weight loss is obvious with increasing the temperature further (weight loss 4 wt\%). It was reported that the temperature of the commercial Mg powder reacting with CH\textsubscript{4} was ca. 923 K [6].

TEM measurements show that the morphology of carbon deposits on four different Mg\textsuperscript{*} samples are very distinct (Figures 2a-2d). In Figure 2a, a kind of coral-like morphology produced on the undoped Mg\textsuperscript{*} is observed. In Figures 2b and 2c, the morphology of carbon deposits formed on the NiCl\textsubscript{2}-doped Mg\textsuperscript{*} are irregular. A sand-like morphology formed on the Ni-doped Mg\textsuperscript{*} is observed in Figure 2d.

Conclusions

The temperature of Mg\textsuperscript{*} reacting with CH\textsubscript{4} reduces greatly. Doping NiCl\textsubscript{2} and Ni powder remarkably affects not only the activity of Mg\textsuperscript{*} reacting with CH\textsubscript{4}, but also the stabilities and morphology of carbon deposits formed on Mg\textsuperscript{*}. The 2.5 mol\% NiCl\textsubscript{2}-doped Mg\textsuperscript{*} can react with CH\textsubscript{4} at temperature as low as 573 K. A kind of coral-like carbon deposits formed on the undoped Mg\textsuperscript{*} is observed.

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References


<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Dopant</th>
<th>Doping amount (mol%)</th>
<th>Preparation methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>none</td>
<td>0</td>
<td>refs. [1, 2]</td>
</tr>
<tr>
<td>S2</td>
<td>NiCl₂</td>
<td>2.5</td>
<td>Ibid.</td>
</tr>
<tr>
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<td>NiCl₂</td>
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<td>Ibid.</td>
</tr>
<tr>
<td>S4</td>
<td>Ni²</td>
<td>2.5</td>
<td>Ibid.</td>
</tr>
</tbody>
</table>

* powder.

**Table 1. Composition and preparation of Mg systems**

Figure 1. In-situ thermogravimetric curves of the Mg samples. S1-S4 are the same as those shown in Table 1. CH₄ flow rate: 40 ml min⁻¹. Heating rate: 10 K min⁻¹.

Figure 2. TEM micrographs of carbon deposits formed on S1 (a), S2 (b), S3 (c) and S4(d), respectively.