

Note

Preparation of Lanthanide Hydrides of Nanometric Size by the Catalytic Method[†]

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Rare-earth metals were hydrogenated in the presence of TiCl₄ catalyst in tetrahydrofuran (THF) at 45 °C under normal pressure. Transmission electron micrographs showed that the resulting lanthanide hydrides were in the form of nanoparticles. The rate of hydrogenation decreased with increasing atomic number of the rare-earth elements.

Keywords lanthanide hydrides, nanoparticles, catalytic hydrogenation

Introduction

Lanthanide hydride can be prepared by direct hydrogenation of the metal provided that it is first activated by heating to 300 °C in hydrogen, followed by cooling under hydrogen.¹ Using this method to prepare lanthanum hydride, the product has an average diameter around 50 μm, and its specific surface area is too small to be measured by BET method. In recent years, particles of nanometric size have been attracting intensive interest because of their outstanding properties and potential applications. They exhibit much higher chemical reactivity than their conventional counterpart.²⁻⁴ It is obvious that lanthanide hydrides in the form of nanometric size may find new applications in many fields. To our knowledge, there is no report on the preparation of lanthanide hydride of nano-

metric size. In this paper we report the preparation of nanoparticles of five lanthanide hydrides ranging from light lanthanide to heavy lanthanide.

Experimental

Lanthanide hydrides are sensitive to air and moisture, therefore, all reactions and operations were carried out strictly under dry argon atmosphere using Schlenk technique. Gases and reagents were treated under oxygen-free and water-free conditions using argon as an inert gas. Reagents and solutions were placed in a Schlenk flask under an argon atmosphere.

Catalytic synthesis of lanthanide hydrides

The nanometric lanthanum hydride was prepared by adding 3.47 g (25 mmol) of metallic lanthanum (>99%) from the General Research Institute for Nonferrous Metals (cut into metal filings with a hacksaw) to an already evacuated dry reaction vessel, which was then filled with argon. This vessel was evacuated at 1.3 Pa for 30 min to remove volatile impurities from the lanthanum metal surface and filled with argon again. THF (15 mL) and TiCl₄ (0.015 mL) were then added under argon. The argon

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Received June 17, 2002; revised September 3, 2002; accepted September 19, 2002.

Project supported by the National Natural Science Foundation of China (No. 50071025) and the Research Foundation of Liaoning Provincial Educational Committee (No. 20042095).

[†]Dedicated to Professor HUANG Yao-Zeng on the occasion of his 90th birthday.

was evacuated, and hydrogen (>99.99%) was passed into the reaction vessel. The uptake of hydrogen was measured with a constant-pressure gas burette. The reaction was maintained at 45 °C in an oil bath, and the reaction mixture was stirred magnetically. The prepared hydride slurry was centrifuged for 10 min, and the solid was washed twice with THF (8 mL each) and then evacuated to dryness at 80 °C for 1 h. The black powder of lanthanum hydride was obtained. Similar method was used for the preparation of other lanthanide hydrides (M = Nd, Sm, Dy, Yb).

Characterization

Transmission electron micrographs (TEM) were recorded on a JEM-1200EX electron microscope operated at 100 kV. X-Ray powder diffraction (XRD) was carried out on a Rigaku D/max-rB diffractometer, Cu target, graphite monochromator, tube voltage 40 kV, and tube current 50 mA. The specific surface areas of the nanopowders were measured by means of low-temperature adsorption and calculated according to the BET equation.

Results and discussion

In our preliminary experiments, it was found that rare-earth metals did not react directly with hydrogen in solution. Extremely slow reaction occurred only after the metal had been activated in hydrogen at 300 °C. The idea of catalytic preparation of nanometric lanthanide hydrides in solution was originated from our previous research in which Li, Na and K were hydrogenated using TiCl_4 -naphthalene as a catalyst.⁵ Experiments showed that this catalyst did work for the hydrogenation of lanthanides. Lanthanides could react slowly with naphthalene forming a dark blue solution in the presence of TiCl_4 . Therefore, it was once believed that the formation of lanthanide naphthalenide might be an intermediate for this catalytic reaction. Later experiments showed that the hydrogenation could proceed in the presence of TiCl_4 alone without substantially effecting the reaction rate. In the following experiments, La, Nd, Sm, Dy and Yb were hydrogenated at 45 °C using a small amount of TiCl_4 as catalyst. The uptake of hydrogen stopped before MH_3 was formed. The time for complete hydrogenation of the five lanthanides was shown in Table 1. The rate of hydrogenation decreases remarkably with increasing atomic number of the rare-

Table 1 Time for complete hydrogenation of five lanthanides^a

Lanthanide	Time (h) for complete hydrogenation
La	58
Nd	68
Sm	120
Dy	173
Yb	262

^aReaction conditions for catalytic hydrogenation: 45 °C, normal pressure, THF (15 mL), TiCl_4 (0.015 mL), ($n_{\text{La}} : n_{\text{TiCl}_4} = 1000:5$).

earth elements except Nd. The difference in rate between La and Nd is relatively small. Fig. 1 shows the kinetic curves for the hydrogenation of three lanthanides. From the product compositions, it seems that there are nonstoichiometric phases of MH_2 and MH_3 . This is in agreement with the lanthanide hydrides prepared in the gas-solid phase.^{1,6} According to the amount of hydrogen uptake, the compositions of the catalytically prepared lanthanide hydrides are as follows: $\text{LaH}_{2.84}$, $\text{NdH}_{2.80}$, $\text{SmH}_{2.72}$, $\text{DyH}_{2.82}$ and $\text{YbH}_{2.55}$. Elemental analysis of the products is required in further experiments. These hydrides are black pyrophoric solids, easily react with oxygen and water. Transmission electron micrographs show that the powders of the five lanthanide hydrides obtained are in the

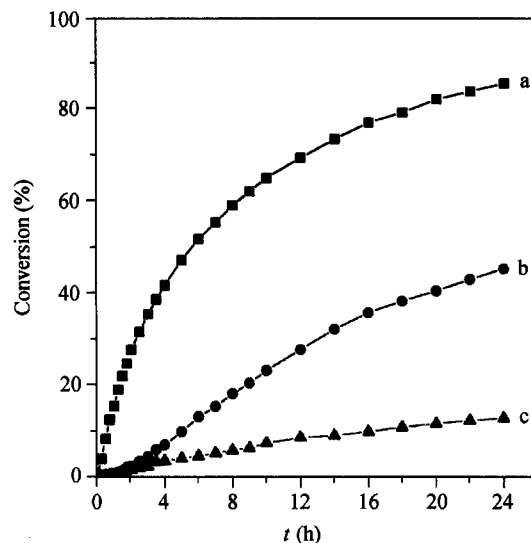


Fig. 1 Kinetic curves of the hydrogenation of rare-earth metals as a function of reaction time catalyzed by TiCl_4 in the first 24 h (reaction conditions are the same as those in Table 1 except reaction time), a: lanthanum hydride; b: samarium hydride; c: ytterbium hydride.

form of nanoparticles. The primary particle sizes of these five hydrides are quite similar. Most of the particles lie in the range of 20–30 nm. Fig. 2 shows the TEM images of lanthanum hydride and samarium hydride as examples. In comparison with the hydrogenation in the gas-solid phase, the hydrogenation of rare-earth metals in THF gives much smaller particle size which suggests that THF might bind to the surface of the nanoparticles and prevent them from growing bigger. The BET surface area of lanthanum hydride is 9.2 m²/g. Although this value is large, it seems to be not so large in comparison with those of the nanometric alkali metal hydrides⁵ which have comparable particle sizes with that of the lanthanum hydride. This is because the lanthanum hydride has much higher density than those of the alkali metal hydrides, while the specific surface area is based on unit weight of the material measured. X-Ray diffraction pattern of nanoparticles of lanthanum hydride is shown in Fig. 3. The crystal structure of nanometric lanthanum hydride is cubic in nature.⁷

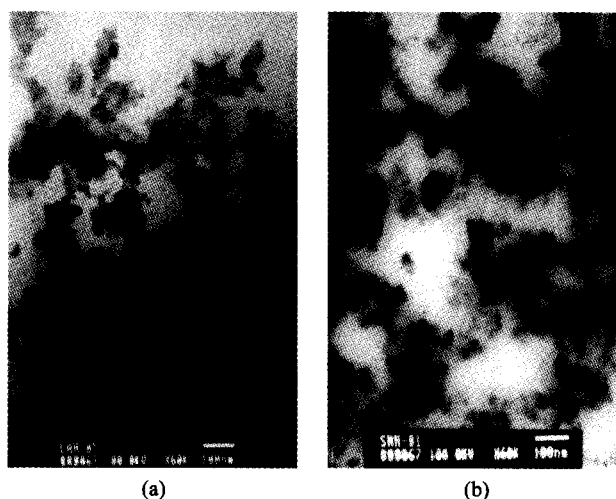


Fig. 2 TEM images of nanoparticles of lanthanum hydride (a) and samarium hydride (b).

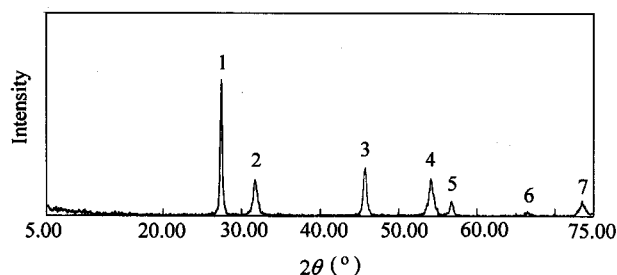


Fig. 3 XRD pattern of lanthanum hydride by the catalytic method.

Particles of nanometric size give rise to advantages in chemical reactions over conventional ones in many respects. In our previous research we found that the activities of nanometric LiH, NaH, KH and Mg powders were two to four orders of magnitude higher than their conventional counterparts in organic, inorganic and organometallic reactions.^{8–11} Besides, the particle size of the product prepared from these nanometric powders was also of nanometric size.^{12,13} The difference in activity between nano and non-nano particles was even more tremendous when nano-particles were used as an active component in catalyst.⁴ It is expected that nanometric lanthanide hydrides will find applications both in synthetic chemistry as well as in catalysis.

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