

Synthesis of magnesium hydrides with carbonic nanocomposite catalyst

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A wide application of hydrogen as an ecologically pure fuel is limited by the absence of safe and effective systems of its storage and transportation. The well-known hydrogen storage systems are divided into three groups: compressed gas balloons, cryogenic reservoir with liquid hydrogen and metal, alloy or compound hydrides. Hydrogen storage in metal hydrides is the most secure and makes it possible to attain higher weight hydrogen density than in high-pressure cylinders or cryogenic systems with liquid hydrogen. An ideal material for hydrogen storage must contain as much hydrogen per weight unit of material as possible. Moreover, hydrogen absorption and desorption must occur fairly fast at low temperatures and pressures.

Among metal hydrogen storages one of the most promising is magnesium. Hydride MgH_2 contains 7.6 wt.% of hydrogen, which exceeds the capacity of other well-known metal systems. However, metallic magnesium is characterized by a very low hydrogenation rate. The primary hydrogenation is especially complicated. The metal surface is normally covered by a thin oxide layer that hinders hydrogen penetration into the metal. Therefore, it is necessary to destroy the surface oxide layer during the first hydrogenation (material activation) after which the subsequent hydrogen absorption occurs faster.

A well-known surface activation method of magnesium and other metals is their vacuum or hydrogen exposure at high temperatures. However, as a rule, high temperatures (over 400° C) and hydrogen pressure (over 60 bar) for a long period of time is required for magnesium surface activation [1].

A breakthrough in the creation of solid-state hydrogen storages is related to the application of mechanical activation (MA) processes. Surface activation of metal hydrogen storage can be reached by its treatment in a vibratory or a planetary mill in hydrogen atmosphere at room T and atmospheric pressure. In spite of the efficiency of such method, complete hydrogenation requires prolonged treatment because of high dissociation energy of hydrogen molecules and a slow diffusion rate of hydrogen deep into material [2]. Besides, the dehydrogenation and the subsequent hydrogenation at elevated temperatures occur very slowly.

Catalysts can considerably accelerate the process of magnesium hydrogenation during its mechanoactivation in hydrogen atmosphere. Such 3d-transition metals as manganese, iron, cobalt, nickel [3] as well as metal oxides and some other compounds [4] are well-known catalysts. A positive effect is observed when graphite and carbon nanotubes [6] are introduced. Using such catalysts as graphite and vanadium, hydrogenation kinetics was considerably increased, whereas the hydrogen pressure was decreased to 4 bar and milling temperature of magnesium was reduced to 300° C [7]. Thus, up to date magnesium hydrogenation synthesis at MA requires a long period of time, high T and hydrogen pressure even in the presence of catalysts.

In this paper new carbon-encapsulated catalysts based on 3d-metals are proposed [8]. Two different types of carbonic Ni-based nanocomposites were synthesized by a gas condensation method and a method of joint milling of nickel and ultradispersed diamonds obtained by the explosion synthesis.

In the gas condensation (GC) method metal evaporation and condensation were carried out in an inert gas atmosphere containing butane. The particles size was controlled using the inert gas pressure and the gas flow rate close to the evaporation zone. Carbon coating thickness was determined by hydrocarbon concentration introduced into the inert gas flow. Thus, we managed to obtain stable Ni-based

nanocomposites with an average metal particle size in the region of 2–5 nm having 2–3 nm carbon coating.

A technique of catalyst preparation by MA method consists in the joint milling of nanodiamonds and nickel with a different initial component concentration during different time in the vibratory mill.

The catalytic activity of mechanothesized catalysts depends both on the milling time, nickel and diamond concentration and on the type of milling equipment (steel or bronze mortar). Milling in a bronze mortar impaired catalytic properties of a mixture (nickel+diamond). Best catalysts were obtained by the nickel and diamond milling for 8 hrs in a steel mortar. Contamination as a result of steel mortar wear did not lead to a degradation of the catalytic properties of nanocomposites. Efficiencies of optimized catalysts obtained by different methods at early milling stages are close to each other. Discrepancies are evident at treatment time over 2 hrs. It should be mentioned that hydrogen capacity of magnesium at room T for different catalysts is almost the same (about 80%), however, the time of its attainment for GC catalyst is considerably more (over 20 hrs).

For an increase of hydrogen capacity and a decrease of hydrogenation time, the milling temperature was raised to 140° C.

For GC Ni-based carbon encapsulated nanocomposite, complete hydrogen capacity and fast kinetics are already attained at 100° C.

The study of kinetics of thermal hydrogenation of this material at 300° C (three cycles) shows that the complete hydrogenation occurs during less than 5 minutes already after the 2-nd cycle of dehydrogenation/ hydrogenation for the Mg composite with MA catalyst.

Thus, new unique catalysts of magnesium hydrogenation based on nanocomposites containing nickel with carbon coating or nickel+nanodiamonds obtained by explosion synthesis were synthesized. The catalytic activity depends on the catalyst composition (nickel/ diamond ratio) and preliminary treatment time at mechanical activation of the catalyst. Milling equipment material composition (bronze or steel) also affects catalytic properties. Mechanical activation of the catalyst in the steel mortars does not reduce its catalytic properties.

Complete magnesium hydrogen capacity is attained during 2 hour- treatment (hydrogen pressure 1 bar, T about 100 °C) of the Mg powder with the Ni-based carbon-encapsulated nanocomposite or MA catalyst (nickel+ 30% weight diamond) preliminary milled for 8 hrs in the steel mortar.

Acknowledgments

We are greatly acknowledge N. N. Schegoleva for characterization of the samples by TEM.

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