ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2008, Vol. 53, No. 6, pp. 858–860. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.D. Makhaev, L.A. Petrova, B.P. Tarasov, 2008, published in Zhurnal Neorganicheskoi Khimii, 2008, Vol. 53, No. 6, pp. 928–931.

SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

Hydrolysis of Magnesium Hydride in the Presence of Ammonium Salts

V. D. Makhaev, L. A. Petrova, and B. P. Tarasov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

Received May 4, 2007

Abstract—The influence of the nature of ammonium salts (NH_4Cl, $(NH_4)_2SO_4$, $(NH_4)HSO_4$, $[(CH_3)NH_3]Cl$) and their concentration in aqueous solutions on the hydrolysis of magnesium hydride has been studied. The highest degree and fastest rate of hydrolysis are observed at an ammonium salt concentration of ~7.5%. The most efficient activator among the ammonium salts under consideration is $(NH_4)HSO_4$.

DOI: 10.1134/S0036023608060077

Light metal hydrides contain the largest amount of active hydrogen (12.7% in LiH, 4,2% in NaH, 7.66% in MgH_2) and are thought of as good candidates for production of hydrogen, which can be released by various methods, including thermolysis or hydrolysis [1]. The use of alkali-metal hydrides in hydrolytic processes of hydrogen generation is hindered by their extremely high reactivity [2]. At the same time, the chemical activity of magnesium hydride varies in a wide range depending on the method of preparation [3–5]. Magnesium hydride obtained as a fine powder by pyrolysis of organomagnesium compounds is an extremely reactive substance igniting when brought in contact with water and rapidly decomposing or self-igniting in air [3, 4]. Magnesium hydride obtained by direct hydrogenation of metallic magnesium at high temperature and pressure is stable in air, is slowly hydrolyzed by water, and is rapidly hydrolyzed by acids [5]. The hydrolysis of MgH_2 theoretically yields more than 15 wt % of hydrogen in terms of the magnesium hydride used:

$$MgH_2 + 2H_2O = Mg(OH)_2 + 2H_2. \quad (1)$$

Magnesium is an inexpensive and readily available metal, and the synthesis of magnesium hydride from elements is an efficient and effective method. The low activity of magnesium hydride synthesized from elements in air ensures its safe use. Inasmuch as the use of acids in processes of hydrolytic hydrogen generation is often undesirable, it is of interest to search for neutral reagents that promote the hydrolysis of nonactivated air-stable magnesium hydride obtained from elements. As shown in [5], a 5% solution of ammonium chloride rapidly and quantitatively hydrolyses magnesium hydride obtained from elements. At the same time, it is worth noting that the hydrolysis parameters have not been studied as a function of the ammonium chloride concentration and the nature of ammonium salt [5]. The present work is aimed at studying the rate and degree of hydrolysis of MgH_2 as a function of the nature and concentration of ammonium salts.

EXPERIMENTAL

A magnesium hydride powder was obtained by hydrogenation of magnesium with hydrogen in the presence of 4 wt % Fe and 4 wt % V_2O_5 upon mechanical activation in a ball mill. The sample under consideration contained ~75% MgH_2 and 17% Mg. Commercially available acids and ammonium salts of chemically pure and pure for analysis grades were used as received. Solutions of HCl, H_2SO_4, H_3PO_4, NH_4Cl, $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and $[(CH_3)NH_3]Cl$ were prepared in distilled water.

Hydrolysis of magnesium hydride was carried out in a setup for volumetric analysis by treating a weighed sample of MgH_2 (25–30 mg) with a definite amount of a solution of one of the above reagents (20 mL). The volume of released hydrogen was determined volumetrically [1].

RESULTS AND DISCUSSION

Treatment of the sample with a 10% solution of phosphoric, hydrochloric, or acetic acid led to rapid release of hydrogen. The conversion (α) in the reactions of hydrolysis caused by the action of other reagents was assessed as the ratio of the amount of hydrogen released in the reaction with an aqueous solution of a reagent to the above amount of hydrogen. It is worth noting that the reaction is highly exothermic and that, when MgH_2 is decomposed by a small excess of a solution (MgH_2 : solution = 1 : 10, 1 : 20), the reaction mixture is strongly heated. Therefore, in all experiments described below, a large excess of an aqueous solution was used: 20 mL of a solution per ~30 mg of hydride.

For comparison with earlier results [5], we studied the hydrolysis of magnesium hydride by distilled water

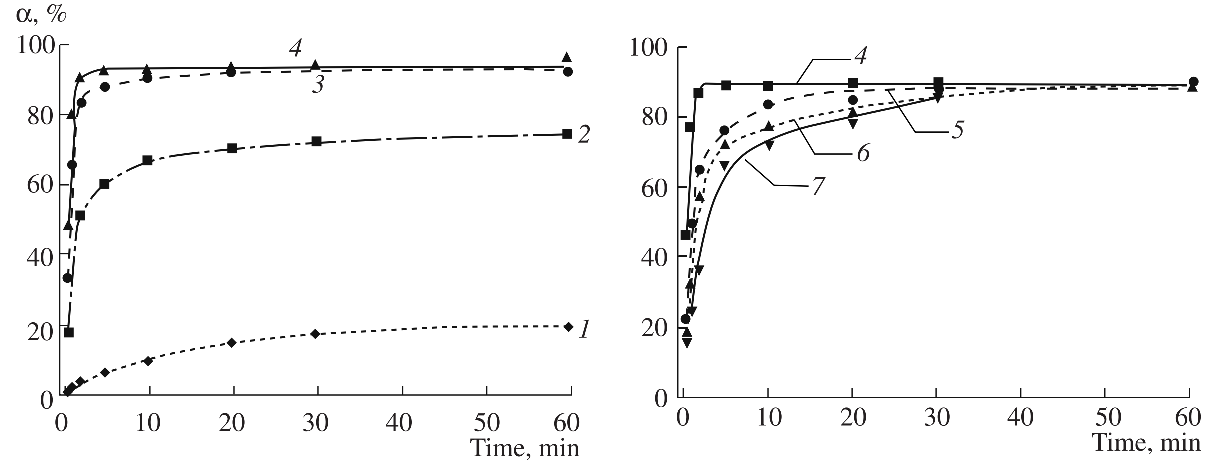

Fig. 1. Degree of hydrolysis of MgH_2 by NH_4Cl solutions of various concentration vs. process duration: (*1*) distilled water (0% NH_4Cl); (*2*) 0.5, (*3*) 2.5, (*4*) 7.5, (*5*) 10, (*6*) 15, and (*7*) 20% NH_4Cl.

without ammonium salt additions. We found that within 30 min the degree of hydrolysis is ~18% and within 24 h 57% of hydrogen contained in the sample is removed. This is noticeably larger than the percentage described for pure magnesium hydride (14.8% in 24 h [5]) and can be explained by the presence of V_2O_5 impurities and a smaller grain size of the sample used. An increase in the reactivity of MgH_2 with a decrease in the particle size has been repeatedly found [6, 7]. Nevertheless the sample under consideration was rather stable and contained, after a month of storage in air, ~85% of the initial hydrogen content. Thus, hydrolysis of magnesium hydride with distilled water proceeds slowly and cannot be used for realization of a rapid and controlled process of hydrogen generation.

We tried to accelerate hydrolysis by binding of the nascent magnesium ions by Trilon B introduced into water; however, no acceleration of hydrolysis was observed.

Study of the hydrolysis of magnesium hydride by solutions of ammonium chloride with different concentrations showed that the presence of even a small amount of NH_4Cl (0.5% solution) considerably promotes the hydrolysis (Fig. 1, curve *2*): the amount of hydrogen released in 5 min exceeds the amount of hydrogen released within 24 h of hydrolysis in pure water (60 and 57%, respectively). As the concentration of ammonium chloride increases from 0.5 to 7.5%, the hydrolysis rate increases and the conversion in the latter case is as large as 92% in 5 min. In this solution, the degree of hydrolysis achieved within 24 h (α_{24}) is also the highest one, 95.4% (Fig. 2). A further increase in the concentration of an NH_4Cl solution leads to some decrease in the hydrolysis rate and α_{24}.

The influence of the nature of ammonium salts was studied for $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and $[(CH_3)NH_3]Cl$. Comparison of Figs. 1 and 3 shows that the $(NH_4)_2SO_4$ concentration has approximately the same effect on the hydrolysis rate as the NH_4Cl concentration. Therefore,

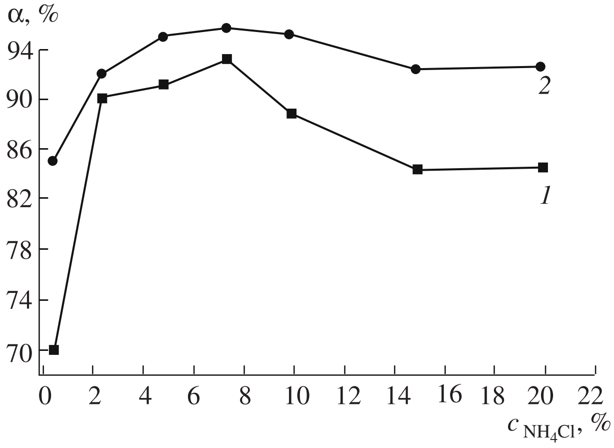

Fig. 2. Degree of hydrolysis of MgH_2 vs. the concentration of ammonium chloride achieved within (*1*) 20 min and (*2*) 24 h.

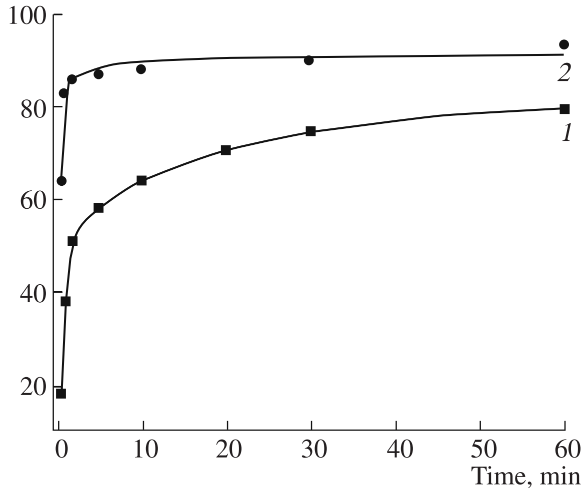

Fig. 3. Time dependence of the degree of hydrolysis of MgH_2 by $(NH_4)_2SO_4$ solutions of various concentration: (*1*) 0.5 and (*2*) 7.5%.

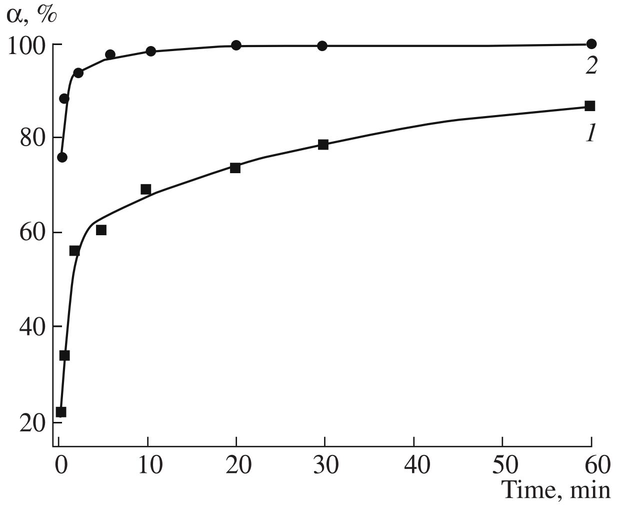

Fig. 4. Time dependence of the degree of hydrolysis of MgH_2 by $(NH_4)HSO_4$ solutions of various concentration: (*1*) 0.5 and (*2*) 7.5%.

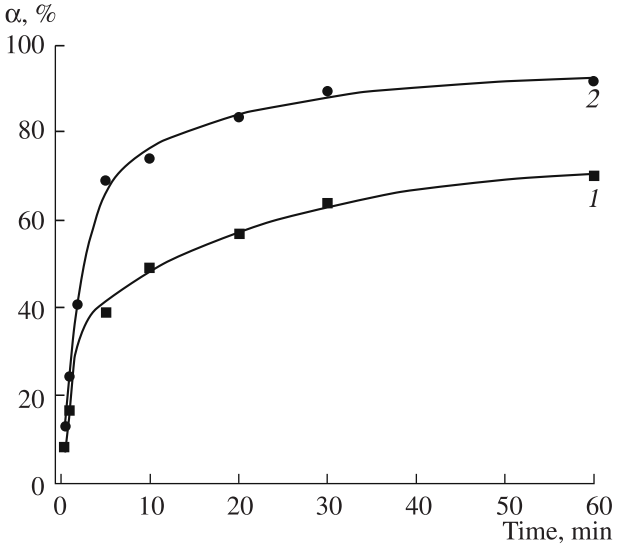

Fig. 5. Time dependence of the degree of hydrolysis of MgH_2 by $(CH_3)NH_3Cl$ solutions of various concentration: (*1*) 0.5 and (*2*) 7.5%.

we suggested that it would be more interesting to study the reaction with $(NH_4)HSO_4$, an acid ammonium salt. It can be assumed that a stoichiometric amount of $(NH_4)HSO_4$ will suffice for the complete hydrolysis of magnesium hydride, since the HSO_4^- anion will neutralize the hydroxyl ion produced in hydrolysis and thus promote the hydrolysis process. Indeed, hydrolysis in the presence of $(NH_4)HSO_4$ proceeds somewhat more vigorously and is more profound than in the presence of neutral ammonium salts (Fig. 4); however, in this case as well, a large excess of an ammonium salt is required to ensure rapid and complete hydrolysis. As distinct from the experiments with ammonium chloride and sulfate in which the highest degree of hydrolysis was 95%, the reaction with $(NH_4)HSO_4$, like those with acids, rapidly leads to the complete hydrolysis of the sample (100%). We may assume that the reaction with the above reagents involves not only magnesium hydride but also the impurities of iron and metallic magnesium contained in the sample. It is likely that the reaction with ammonium chloride or sulfate does not involve these impurities or its depth is insignificant.

Study of the hydrolysis of MgH_2 in the presence of methylammonium chloride $[(CH_3)NH_3]Cl$ showed that the process is promoted not only by inorganic ammonium salts but also by organic amine salts. However, in the latter case, the promotion effect is considerably weaker (Fig. 5).

Thus, our findings show that different ammonium salts promote the hydrolysis of magnesium hydride. The maximal acceleration of the reaction is observed at a salt concentration of ~7.5%. $(NH_4)HSO_4$ is the best activator of the reaction.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 05-03-0827).

REFERENCES

1. S. D. Kushch, A. A. Poletaev, and B. P. Tarasov, Altern. Energ. Ekol., No. 2(34), 26 (2006).
2. A. F. Zhigach and D. F. Stasinevich, *The Chemistry of Hydrides* (Khimiya, Leningrad, 1969) [in Russian].
3. M. P. Jolibois, Compt. Rend. **155** (3), 353 (1912).
4. E. Wiberg and R. Bauer, Z. Naturforsch., B: Chem. Sci. **5** (4), 396 (1950).
5. T. N. Dymova, Z. K. Sterlyadkina, and N. G. Eliseeva, Zh. Neorg. Khim. **6** (4), 769 (1961).
6. M-H. Grosjean, M. Zidoune, J-Y. Huot, and L. Roue, Int. J. Hydrogen Energ. **31**, 1159 (2006).
7. M-H. Grosjean, M. Zidoune, and L. Roue, J. Alloys Comp. **404**, 712 (2005).