Interaction of RT_3 (R = Ce, Y; T = Ni, Co) intermetallic compounds with alkaline solutions of MBH_4 (M = Na, K, Rb, and Cs)

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The interaction of RT_3 (R = Ce, Y; T = Ni, Co) intermetallic compounds (IMC) with alkaline solutions of MBH_4 (M = Na, K, Rb, and Cs) was studied in the temperature range of 298—318 K. For all intermetallic compounds, the reaction of catalytic hydrolysis of $NaBH_4$ is zero order with respect to MBH_4 and first order with respect to RT_3. The reaction rate decreases and the activation energy of the catalytic hydrolysis of MBH_4 increases in the following order: $NaBH_4$, KBH_4, $RbBH_4$, and $CsBH_4$. The hydride phases RT_3H_x (x = 2.3—3.9) were synthesized by the interaction of RT_3 IMC with alkaline solutions of MBH_4. They are similar in composition to the products formed in the reaction of RT_3 with gaseous hydrogen at high pressure. The rate of hydrogenation of RT_3 in alkaline solutions of MBH_4 decreases on going from sodium to cesium.

Key words: alkali metal borohydrides, catalytic hydrolysis, reaction order; intermetallic compounds, hydride phases.

Reactions of hydride-forming intermetallic compounds (IMC) with alkaline solutions of alkali metal borohydrides are of interest both as a fundamentally new route to the synthesis of hydride phases of IMC and as a new catalytic process of hydrogen generation.

In a study of the interaction of $LaNi_5$ type IMC with alkaline solutions of MBH_4 (M = Na, K, Rb, and Cs), we established[1—3] the dependences of the reaction rate on the nature of M in MBH_4 and on the concentration of a solution of MOH, which were previously unknown for the homogeneous and catalytic (occurring in the presence of individual metals such as Ni and Co)[4,5] hydrolyses of MBH_4.

The reactions of RT_3 IMC with gaseous hydrogen have been studied in detail.[6—8] Therefore, it is possible to compare the chemical composition of the hydride phases formed in the interaction of IMC with hydrogen under pressure and in solutions of alkali metal borohydrides.

The present work is aimed at elucidation of general regularities of the chemical processes that occur in the interaction of hydrogen-sorbing IMC with inorganic hydrides. RT_3 type (R = Ce, Y; T = Ni, Co) IMC, which differ from $LaNi_5$ compounds by their higher content of the rare-earth element and by the fact that they contain alkali metal borohydrides with different size cations (from Na^+ to Cs^+), were chosen as the subjects of the study. The kinetics of the catalytic hydrolysis of borohydrides MBH_4 (M = Na, K, Rb, and Cs) in the presence of the IMC indicated was studied, and the conditions and composition of the products of the hydrogenation of RT_3 in alkali solutions of MBH_4 were determined.

Experimental

Metals of the following purity were used for obtaining RT_3 IMC (R = Ce, Y; T = Ni, Co): Ce, 99.6%; Y, 99.6%; Ni, 99.99%; and Co, 99.95%. The blend was melted in an electric-arc furnace under an argon pressure of 0.2 MPa. The melts were annealed at 873 K for 250 h and then hardened. The phase composition of the melts was monitored by X-ray diffraction using a DRON UM-1 diffractometer. Prior to analysis, assay buttons of the melts were dispersed in a ball mill filled with argon.

Sodium borohydride was purified by double recrystallization of the technical product from a 1 *M* solution of NaOH. The $NaBH_4$ obtained contained 98.5% of the main substance. Potassium borohydride was synthesized by the exchange reaction of $NaBH_4$ with KOH in water according to a known procedure.[9] The KBH_4 formed contained 98.8% of the main substance. Rubidium and cesium borohydrides were obtained by the exchange reaction of $NaBH_4$ with the hydroxide of the corresponding metal in an aqueous-alcoholic solution according to a procedure described previously.[10] $RbBH_4$ and $CsBH_4$ contained 99% of the main substance.

The behavior of RT_3 in alkaline (1.0 and 4.0 mol L^{-1} MOH) solutions of MBH_4 at 298, 308, and 318 K was studied by the tensieudiometric method using a previously described[11] setup with a calibrated volume. This setup made it possible to monitor the amount of the gas yielded in hydrolysis and the amount of hydrogen absorbed by IMC. In some cases, the method of vacuum extraction of hydrogen was used along with tensieudiometric measurements for the determination of hydrogen in the hydride phases obtained by the reactions of RT_3

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 921—923, May, 1997.

1066-5285/97/4605-0881 $18.00

with alkaline solutions of MBH_4. The accuracy of determination of the hydrogen content in samples was ±0.1 atom H_2 per mole RT_3 (H/RT_3).

The specific catalytic activity of IMC in the hydrolysis of alkaline solutions of MBH_4 was calculated as the ratio of the rate constant of the hydrolysis of MBH_4 (k/mol min^{-1}) to the weight of IMC (m/g).

Results and Discussion

The study of the interaction of RT_3 with alkaline solutions of MBH_4 revealed several general regularities in the catalytic hydrolysis of alkali metal borohydrides in the presence of $LaNi_5$ (see Refs. 1—3) and RT_3 type IMC. As in the case of $LaNi_5$ compounds, the rate of the hydrolysis of MBH_4 in the presence of RT_3 becomes maximum and constant after performing five to ten experiments with the same IMC sample. The study of the dependences of the reaction rate of the catalytic hydrolysis of MBH_4 on the initial concentration of MBH_4 (0.05—0.30 mol L^{-1}), the weight of RT_3 (0.1—1.0 g), the temperature of the process, and the concentration of alkali in a solution for all RT_3 IMC studied and alkali metal borohydrides showed that the reaction is first order with respect to RT_3 IMC and zero order with respect to MBH_4, which is similar to the hydrolysis of MBH_4 in the presence of $LaNi_5$ type IMC.

Analyzing the results of the determination of the catalytic activity of RT_3 in the hydrolysis of alkaline solutions of MBH_4 (Table 1), we can observe a considerable decrease in the hydrolysis rate on going from $NaBH_4$ to $CsBH_4$ for all intermetallides studied.

This unexpected fact was first observed experimentally[3] for the hydrolysis of MBH_4 in the presence of $LaNi_5$ type IMC. To explain this phenomenon, it was proposed that the size of the alkali cation affects the rate of the catalytic hydrolysis of MBH_4. It is known that the chemical activity of alkali metal borohydrides increases as the polarizing effect of the alkali cation on the borohydride ion increases. This results in a distortion of its symmetry and redistribution of the electron density on the H atoms. In the series of cations Na^+, K^+, Rb^+, and Cs^+, with radii of 0.98, 1.33, 1.49, and 1.69 Å, respectively, Na^+ (with the smallest radius) has the strongest polarizing effect on BH_4^-. This explains the fact that $NaBH_4$ had the highest chemical activity in the studied series of borohydrides. It has been previously shown[12] that in an aqueous medium the difference between the electronegativities of metals decreases sharply as the ionicity of the bonds in the molecules increases, which cancels out the polarizing effect of the cations. This assertion has been used[13] to explain why the experimental rates of the homogeneous hydrolysis of borohydrides of different alkali metals are almost the same. The results of our study suggest that the polarizing effect of alkali cations on the BH_4^- anion takes place in the interaction of MBH_4 with the surface of the IMC particles in the heterogeneous hydrolysis of MBH_4 in the presence of RT_3 as well as in the presence of the $LaNi_5$ type IMC studied previously.[5]

Table 1. Specific catalytic activity (k/m) of RT_3 IMC in the hydrolysis of MBH_4 in 1 M and 4 M solutions of MOH (298 K)

RT_3	$k/m \cdot 10^5$/mol min^{-1} g^{-1}							
	$NaBH_4$		KBH_4		$RbBH_4$		$CsBH_4$	
	1 M	4 M	1 M	4 M	1 M	4 M	1 M	4 M
$CeNi_3$	5.25	7.88	4.65	6.40	3.52	3.68	0.72	0.08
$CeCo_3$	1.65	2.10	1.42	1.85	1.11	1.00	0.26	0.04
YNi_3	3.50	4.72	3.00	3.75	2.42	2.58	0.55	0.06
YCo_3	1.00	1.30	0.78	1.10	0.62	0.62	0.18	0.02

The values of the apparent activation energies of the catalytic hydrolysis of MBH_4 in the presence of RT_3 IMC were calculated from the temperature dependences of the reaction rates. These values range from 53—60 kJ mol^{-1} (for $NaBH_4$) to 65—70 kJ mol^{-1} (for $CsBH_4$) and almost coincide (within the experimental error) with the apparent activation energies of the catalytic hydrolysis of MBH_4 in the presence of the $LaNi_5$ type IMC determined by us. This result agrees with the assumption that the considerable decrease in the reaction rate of the hydrolysis of MBH_4 in the presence of IMC is independent of the composition of the latter and is related primarily to the nature of M in MBH_4.

The results presented in Table 1 show that the ratios between the catalytic activities of RT_3 IMC in the reaction of the same alkali metal borohydride are retained for all MBH_4 studied; in addition, some correlations between the chemical composition of RT_3 IMC and their catalytic activity can be revealed. For the same R, the catalytic activity of RT_3 containing Ni as the transition metal is higher than that of Co-based IMC. IMC with R = Ce have higher catalytic activity than IMC containing Y with the same T. Based on the suggested[1] model of the formation of catalytic layers on the surface of $LaNi_5$ type IMC (related to the subsequent formation of the oxide and hydroxide forms of the rare-earth metal and highly catalytically active Ni crystallites due to the irreversible chemical interaction of IMC with an alkaline solution of $NaBH_4$), the fact that the activity of the RCo_3 catalysts is lower than that of RNi_3 catalysts can be explained by the existence of Co crystallites, which have lower catalytic activity than Ni crystallites, in the surface layers. This was experimentally proved in the study of the hydrolysis of $NaBH_4$ using the individual Ni and Co catalysts.[4,5] The fact that the catalytic activity of CeT_3 is higher than that of YT_3 can be associated with the fact that Ce is less stable to oxidation than Y. Therefore, in the interaction of RT_3 IMC with alkali solutions of MBH_4, the surface layers of the CeT_3 particles have more Ni or Co crystallites, which determine their catalytic activity, to a greater extent than the layers of YT_3 particles.

In the case of $NaBH_4$ and KBH_4, for all RT_3 IMC increasing the concentration of alkali in a solution from 1.0 to 4.0 mol L^{-1} results in an increase in the hydrolysis rate; for $RbBH_4$, the rate remains almost unchanged, and only for $CsBH_4$ is the reaction substantially retarded. A qualitatively similar effect of the alkalinity of the solution was observed by us[3] for the hydrolysis of MBH_4 in the presence of the $LaNi_5$ type IMC. An increase in the concentration of alkali in the catalytic hydrolysis of MBH_4 in the presence of IMC can favor, on the one hand, an increase in the catalytic activity of IMC due to its further segregation in more concentrated alkaline solutions and, on the other hand, an increase in the stability of the borohydride solutions. Probably, the first factor predominates for $NaBH_4$ and KBH_4, while $CsBH_4$, which is more stable with respect to catalytic hydrolysis, becomes more stable as the concentration of CsOH increases.

The tensieudiometric study of the interaction of the RT_3 compounds with alkaline solutions of MBH_4 showed that along with the process of catalytic hydrolysis, the formation of hydride phases of RT_3 IMC occurs and the absorption of hydrogen continues until the maximum composition of the RT_3H_x phases, which exist at pressures not greater than 0.1 MPa, is observed in the first cycle. When the next portions of MBH_4 are added to the solution with the hydride phase, they undergo complete hydrolysis without the subsequent absorption of hydrogen. The composition of the hydride phases, $CeNi_3H_{2.8}$, $CeCo_3H_{3.5}$, $YNi_3H_{2.3}$, and $YCo_3H_{3.9}$, obtained by the interaction of RT_3 IMC with alkaline solutions of MBH_4 (M = Na, K, Rb, and Cs) is almost the same for all MBH_4 within the experimental error of the method used for determining the hydrogen content, but the rate of the hydrogenation of RT_3 depends directly on the reaction rate of the catalytic hydrolysis of MBH_4 and decreases on going from $NaBH_4$ to $CsBH_4$. A similar interrelation between the rates of the hydrogenation of IMC and the catalytic hydrolysis of MBH_4 was observed for the interaction of $LaNi_5$ type IMC with alkali metal borohydrides.[3] This indicates the existence of a common mechanism for the hydrogenation of RT_3 and $LaNi_5$ in alkaline solutions of MBH_4, which suggests that atomic hydrogen generated in the hydrolysis of MBH_4 on the surface of the IMC particles participates in the hydrogenation of IMC.

Unlike the hydrogenation of RT_3 IMC by gaseous H_2, which requires elevated pressures (0.2—5.0 MPa),[6—8] the interaction of RT_3 with alkaline solutions of MBH_4 occurs at hydrogen pressures <0.1 MPa, which is an additional argument in favor of the assertion that atomic hydrogen is involved in the reactions of hydrogenation of IMC in alkaline solutions of MBH_4.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09615a).

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Received December 25, 1996