

USING OF METAL HYDRIDES FOR PREPARATION OF NANOSCALED POWDERED METALS AND ALLOYS IN DIFFERENT MEDIA

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Introduction

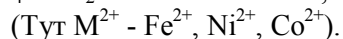
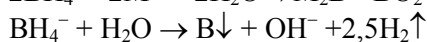
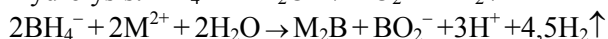
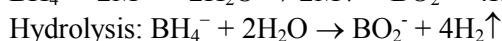
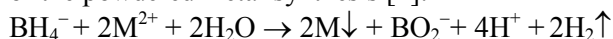
Methods for synthesis of nanoscaled powdered metals and alloys continue to excite ever growing interest, which is caused by unique properties of the said materials making possible their application as catalysts, magnetic solids and magnetic liquids [1, 2, 3].

Results and Discussion

Powders were synthesized in a glass reactor in the argon atmosphere, through reduction of the relevant metal salt (mixture of salts) by sodium borohydride in an aqueous solution. The pH-meter was used for keeping watch on acidity of the reaction mixture. The synthesis was carried out at 10 - 25 °C.

The aqueous solutions of sodium borohydrate are known to show an alkaline reaction. Addition of sodium borohydrate to a cobalt (II) salt solution increases pH of the water medium.

The following reactions take place in the course of the powdered metal synthesis [4]:



The accompanying side reactions result in the excessive tetrahydroborate consumption and in formation of the admixtures of boron and borides. The reductive efficiency of a tetrahydroborate solution increases with solution acidity increase. This effect is related to acceleration of the process of BH_4^- hydrolysis and formation of both molecular [B_2H_6 , BH_2OH , $\text{BH}(\text{OH})_2$] and ionic [BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$, $\text{BH}(\text{OH})_3^-$] intermediate particles. Such particles are even more potent reducing agents than BH_4^- ions. A material increase of the pH value is observed in the point where the metal ion reduction process (spectrophotometric method of control) comes to the end. Thus, the pH control of solution in process of synthesis of a powdered metal allows

to achieve the complete metal extraction from the solution and to avoid excessive consumption of sodium borohydride.

The powders were separated from solution either by centrifugation, or by decantation (magnet was used for holding the cobalt or iron powders inside reactor) and were rinsed 2-3 times first by water and then by isopropanol or methanol, and dried over KOH in a dessicator, in the atmosphere of argon.

It was shown that reduction of cobalt (II), nickel (II), iron (II) or neodymium (II) compounds by sodium borohydride allows attaining high yields of amorphous powders containing relevant metals or their boron and/or oxygen compounds, which are promising as starting materials for magnetic Fe-Nd-B systems.

Resistance of the synthesized powders to air oxygen oxidation and hydrolysis was studied. The crystalline phases arising on heating amorphous powders within 300 - 1000 °C were described using the X-ray phase analysis technique.

Sodium borohydride reduces efficiently Ni^{2+} ions preliminary adsorbed from an aqueous nickel salt solution by mesoporous titania suspension. As a rule, a 2 – 6 –fold excess of the reducing agent was applied in this case. This synthesis was carried out at 20 °C. The powdered mesoporous titania covered by metallic nickel coating was separated from solution through its decanting, washed till the neutral reaction of the rinse water and than used in photochemical experiments. As far as only Ni^{2+} ions were identifiable in the decanted solution, it evidences that Ni^{2+} ions were practically quantitatively bound by TiO_2 .

The photochemical activity measurements were carried out with the degassed ethanol suspension samples of the product (0.05 g of TiO_2 covered by nickel coating in 10 ml of ethanol and water content of 2 mol/l). The samples were irradiated at 40 °C by light emitted from DRS-1000 lamp and passed through the colour-filter UFS-2 ($\lambda = 365$ nm, and light intensity $I = 2,6 \cdot 10^{-6}$ N q/min.). The system

was stirred by a magnetic stirrer during irradiation. Irradiation of the said suspension caused bluish coloration resulting from Ti^{3+} formation ($Ti^{4+} \xrightarrow{h\nu} Ti^{3+}$); and, also, molecular hydrogen release with a constant rate was observed. The yield of hydrogen was measured using chromatographic technique. The system was working steadily and was evolving hydrogen with quantum yield $\gamma(H_2) = 0,1 - 0,5$.

The effect of nickel concentration in a coating, as well as of temperature, water content and method of metal application, on hydrogen quantum yield was studied.

The resulting metallic nickel containing TiO_2 samples have shown the catalytic activity in the model photochemical reaction of hydrogen release from water-ethanol solution (water content of 2 mole/l), which was comparable with catalytic potency of the starting nickel-free TiO_2 exhibited in the presence of metallic palladium/silica (Pd/SiO_2) catalyst, which is well known as a catalyst of the dark step of molecular hydrogen formation (0.02 g of Pd/SiO_2 , Pd content making 0.2 % w/w from SiO_2).

Such systems are promising as photocatalysts of decomposition of the organic environmental pollutants [5].

Conclusions

Metal hydrides are shown to be promising for preparation of the nanoscaled powdered metals and alloys, including those used as photocatalysts of organic matter oxidation.

References

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