Hydrolysis of $Mg(BH_4)_2$ and its coordination compounds as a way to obtain hydrogen

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HIGHLIGHTS

- $Mg(BH_4)_2 \times 0.5Et_2O$ and $Mg(BH_4)_2 \times$ diglyme are synthesized and characterized.
- $Mg(BH_4)_2$ and its analogs coordinated with ligands are hydrolyzed.
- The byproduct of hydrolysis reaction is B_2H_6.
- $Mg(BH_4)_2 \times$ diglyme produces diborane-free hydrogen with acceptable rate.
- Quantum-chemical calculations for solid state hydrolysis mechanisms are performed.

ARTICLE INFO

ABSTRACT

Three ligand-stabilized $Mg(BH_4)_2$–based complexes have been synthesized and evaluated as potential hydrogen storage media for portable fuel cell applications. The new borohydrides: $Mg(BH_4)_2 \times 0.5Et_2O$ and $Mg(BH_4)_2 \times$ diglyme (diglyme – $CH_3O(CH_2)_2O(CH_2)_2OCH_3$) have been synthesized and examined by X-ray single crystal diffraction method. Hydrolysis reactions of the compounds liberate hydrogen in quantities ranging from 46 to 96% of the theoretical yield. The hydrolysis of $Mg(BH_4)_2$ and other borohydrides is also accompanied by the diborane formation. The amount of liberated diborane depends on the Mg-coordination environment. To explain this fact quantum-chemical calculations have been performed. It is shown that formation of Mg-O-Mg-bridges enables the side process of diborane generation. It means that the size and denticity of the ligand directly affects the amount of released diborane. In general, the larger the ligand and the higher its denticity, the smaller is amount of diborane produced. The new compound $Mg(BH_4)_2 \times$ diglyme decomposes without diborane formation that allows one to be considered as a new promising chemical hydrogen storage compound for the practical usage.

1. Introduction

Magnesium borohydride $Mg(BH_4)_2$, having a high gravimetric (14.9 wt %) and volumetric (up to 147-145 g H_2 L^{-1}) density of hydrogen, is considered to be one of the most promising materials for hydrogen storage applications [1,2]. Due to its lowest decomposition temperature and mildest conditions for partial re-hydrogenation demonstrated experimentally magnesium borohydride is an attractive material for the reversible hydrogen storage.

Up to date a lot of research has been done to investigate thermal decomposition and reversible dehydrogenation of pure magnesium

borohydride as well as its mixtures with catalysts and other additives. Despite more than a hundred published research papers on $Mg(BH_4)_2$ no practically acceptable results have been obtained so far. In most cases the hydrogen re-absorption needs impractically high hydrogen pressures, temperatures and reaction durations. A partial reversibility and cycling of H_2 under relatively mild conditions was demonstrated but the amount of recharged hydrogen did not exceed about 2.5 wt%. Moreover, the kinetics of hydrogen desorption from $Mg(BH_4)_2$ was too low for practical applications [3]. A direct decomposition of magnesium borohydride to release all hydrogen stored requires temperature higher than 400 °C [4] and additional energy supply to keep the reaction going

on since this process is endothermic [5].

There is another way to obtain hydrogen from $Mg(BH_4)_2$, viz., hydrolysis. The hydrolysis procedure is a widely used way to obtain hydrogen from Mg hydrides as well as other hydrides and borohydrides [6–18]. It is known that magnesium borohydride, similar to other I and II group metal borohydrides, can be hydrolyzed [19], thereby available information on that process is hardly sufficient. According to the ideal equation (1) and (12.7) wt% of hydrogen could be released in the stoichiometric reaction of magnesium borohydride with water that looks promising for the practical usage. Moreover, $Mg(BH_4)_2$ hydrolysis reaction proceeds spontaneously even without external energy supply.

$$Mg(BH_4)_2 + 4H_2O \rightarrow Mg(BO_2)_2 + 8H_2 \ (12{,}7w\%) + Q \qquad (1)$$
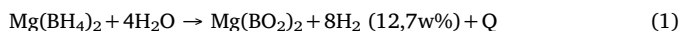
Despite the fact that the hydrolytic way to obtain hydrogen from Mg $(BH_4)_2$ looks attractive the process can be complicated by the diborane formation. This possibility was pointed out by Konoplev et al. as Mg $(BH_4)_2$ hydrolysis in a moist atmosphere is accompanied by the diborane-like smell [20]. Diborane as an admixture in the hydrogen flow causes problems in the practical usage of this reaction. One of the problems is that diborane is highly toxic so it becomes dangerous to purge PEM FC to atmosphere. Moreover, diborane reduces the fuel cell performance by 39% [21].

The best-studied borohydride hydrolysis process relates to the hydrolysis of $NaBH_4$ in dilute water or water-alkaline solutions [22]. It was found that borane is formed in the course of the reaction as an intermediate (this was experimentally confirmed by Davis at al. by adding aqueous trimethylamine to the solutions [23,24]). Nevertheless, diborane as an admixture in hydrogen was found niether in the spontaneous nor catalyzed hydrolysis reaction [25]. It is known that in dilute sodium borohydride solutions, the species being actually hydrolyzed is a free solvated BH_4^- ion [26] and all numerous mechanistic researches have been done for this ion. Unfortunately, gravimetric and volumetric hydrogen densities of dilute solutions are too low to be used widely. In the case of concentrated solutions and melts, the hydrolysis probably proceeds according to a different mechanism.

Earlier [27], was performed quantum-chemical calculations for the hydrogen elimination process from sodium borohydride dihydrate with no free solvated BH_4-groups. It was shown that H_2 elimination barrier can be significantly decreased by extra stabilization of the OH^- anion by neighboring metal cations. Moreover, the elimination of a water molecule from the $[B(OH)_4]^-$ anion (the main product of the sodium borohydride hydrolysis at water deficiency [28]) through the transformation of $>B(OH)_2$ into $>B=O + H_2O$ also requires to overcome an energy barrier, but the barrier is lower than that for H_2 elimination. This process requires small energy inputs, which are abundantly compensated by the energy released during the hydrogen elimination. It means that studies of borohydride hydrolysis process at water deficiency and hydrolysis proceeding at the liquid-solid interface become important for the practical usage, particularly for $Mg(BH_4)_2$ having one of the highest gravimetric hydrogen density.

It is known that hydrolysis reactions of classical hydrides often proceed violently releasing large amounts of heat [29], which make them impractical for portable application. Moreover, these compounds are moisture sensitive and thus difficult-to-handle. The new type of borohydrides stabilized with organic ligands may help to overcome these drawbacks. The use of organic ligands to stabilize $LiBH_4$ results in its lower sensitivity to moisture in the air than the initial borohydride [30]. In addition, Stearns et al. [31]. has shown that the reaction enthalpies (ΔHr) related to the hydrolysis of coordination compounds are lower than that for parent $LiBH_4$. In the case of $Mg(BH_4)_2 \times 3THF$ the effects are the same as for $LiBH_4$ coordination compounds [32].

In this work, we present hydrolytic behavior investigation of Mg $(BH4)_2$ and its coordination analogs: hydrolytic properties as a function of the magnesium atoms' coordination environment.

2. Experimental

2.1. Materials

All operations were carried out in an inert atmosphere using a Schlenk line or an argon filled glove box. $MgCl_2$ (99.9% purity, Aldrich), $NaBH_4$ (99.995% purity, Aldrich) were used as received. The solvents were distilled and dried by conventional methods before use. Specimens for the elemental analysis were prepared by dissolving solid samples in dilute hydrochloric acid.

2.2. Characterization methods

Hydrogen content was determined volumetrically *via* sample hydrolysis in 1 M hydrochloric acid. Hydrolyzed solutions were used for the magnesium content measurements by atomic absorption spectroscopy on an AAS 3 Carl Zeiss Jena apparatus.

Infrared (IR) spectra were measured on a FT-IR Bruker Vertex 70 V spectrophotometer. For solid substances, the ATR mode in vacuum was used. For gases, a cylindrical cuvette with KBr flat sides was applied. For liquids, a drop of a substance was placed on one KBr disc and pressed against another one inside the glove box.

Single-crystal X-ray diffraction data were collected at the 'Belok' beamline (λ = 0.96990 Å) of the Kurchatov Synchrotron Radiation Source (NRC Kurchatov Institute, Moscow, Russian Federation) using Rayonix SX165 CCD detector. A total of 360 images for each compound were collected using an oscillation range of 1.0° and φ scan mode, and corrected for absorption using the *Scala* program. The data were indexed, integrated and scaled using the utility *iMOSFLM* implemented in the CCP4 software suite. Structures were determined by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and their position was refined within the riding model with fixed isotropic displacement parameters $[U_{iso}(H) = 1.5U_{eq}(C)$ for the CH_3-groups and $1.2U_{eq}(C)$ for other groups]. All calculations were carried out using the SHELXTL program.

Crystallographic data for $Mg(BH_4)_2 \times 0.5Et_2O$ and Mg $(BH_4)_2 \times$ diglyme have been deposited with the Cambridge Crystallographic Data Center, CCDC 1545435 and CCDC 1545436. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac. uk).

All operations have been carried out under an inert atmosphere either in a glove box or using the Schlenk technique.

2.3. Synthetic procedures

$Mg(BH_4)_2$ have been prepared according to a ball-milling procedure of $MgCl_2$ and $NaBH_4$ in diethyl ether [33,34]. ZrO_2 (4 kg, inner volume 500 ml) vial was loaded with $MgCl_2$ and $NaBH_4$ (in a weight ratio of 1:3), 100 ml of dried Et_2O and ZrO_2 (Ø 10 and Ø 19 mm) in a glove box. The balls/powder mass ratio was 20:1. The synthesis was performed in a Fritsch P6 planetary ball mill at 200 rpm during 8 h in total. After completion of the reaction, the grinding bowl was opened and the reaction mixture was transferred to a glass filter. The mixture was filtered and the residue was washed with diethyl ether. A combined clear colorless filtrate was evaporated under reduced pressure at room temperature for 2 h resulting in a viscous liquid. Subsequent heating up to 80 °C yielded a white solid. The solid was heated in an oil bath to 220–230 °C for 2 h. The residue was ground with pestle and mortar in a glove box and reheated to the same temperature for additional 2 h yielding 3.66 g (35.7%) of unsolvated $Mg(BH_4)_2$. Elemental analysis (average of 3 runs), %: Mg 45.8, H 14.4; calculated for MgB_2H_8, %: Mg 45.2, H 14.8. IR: 1127 cm^{-1}, 1259 cm^{-1}, 2272 cm^{-1}, 2387 cm^{-1} and 2659 cm^{-1}. Powder XRD pattern of the sample obtained was in a good