Catalytic generation of hydrogen by applying fluorinated-metal hydrides as catalysts

S. Suda*, Y.-M. Sun, B.-H. Liu, Y. Zhou, S. Morimitsu, K. Arai, N. Tsukamoto, M. Uchida, Y. Candra, Z.-P. Li

Chemical Energy Laboratory, Department of Environmental and Chemical Engineering, Kogakuin University, 2665-1, Nakano-machi, Hachioji-shi, Tokyo 192-0015, Japan

Received: 13 November 2000/Accepted: 14 November 2000/Published online: 9 February 2001 - © Springer-Verlag 2001

Abstract. Metal–hydrogen complexes such as NaAlH₄, KBH₄, and NaBH₄ are known as high H-content materials. The highly reactive natures of these materials against moist air and water can be easily stabilized in aqueous KOH and NaOH solutions. Accordingly, it is required to develop catalysts suitable for generating hydrogen from the stabilized metal–hydrogen complexes in alkaline solutions.

This work is aimed at developing catalysts that can generate hydrogen from such solutions with considerably high kinetics under moderate temperature and pressure conditions.

We have found that Mg_2Ni , a typical high-temperature hydriding alloy, exhibits excellent functions as a catalyst for the hydrolysis of BH_4^- -ion-containing solutions. The fluorination-treatment (F-treatment) effects on granular particles of Mg_2Ni and Mg_2NiH_4 are reported in this paper.

Metal hydrides that contain more than 3 wt. % have been targeted in the WE-NET Project of MITI, Japan [1]. An international cooperative project under IEA Task-12 has been conducted to develop hydrogen storage materials that store more than 5 wt. % [2]. An academic group organized by about 50 universities and research institutes has been conducting a project named "New Protium Function" for developing high H-capacity metal hydrides since 1998 for four years, funded by the Ministry of Education, Science, Sports and Culture [3]. Despite countless efforts in the past aimed at developing high H-capacity materials, the level targeted earlier has not been reached.

These materials have been attracting strong interest for use in the fuelling systems for fuel-cell (FC) cars such as liquid hydrogen, high-pressure hydrogen, metal hydrides, methanol, gasoline, and carbons. However, the hydrogenstorage (H-storage) system applicable to FC cars has not been established. Moreover, H-storage systems as have been developed, do not necessarily fulfil the practical requirements of FC cars with regard to H-generation rates under severe operating conditions, energy density per weight and volume, and other technical problems as well as their cost-effectiveness.

On the other hand, sodium aluminum hydrides have been developed as H-storage material by applying their gassolid decomposition reactions. Ti-catalyzed NaAlH₄ and Na₃AlH₆ have been studied by Bogdanovic [4] and the cyclic H-capacity up to 200 °C is reported as 4.2 wt. %. Ti-doped and Ti/Zr-doped NaAlH₄ have been extensively studied by Jensen and others [5, 6]. H-capacity is reported as 4.0 wt. % by an advanced Ti-doped NaAlH₄ at 100 °C, and 4.5 wt. % at 100 °C by Ti/Zr-doped NaAlH₄. The theoretical H-capacity obtained by 3-stepwise reactions is 7.4 wt. % under wide temperature ranges between 50 °C and 250 °C. A series of recent research activities performed by Jensen and others was reported elsewhere [7]. Reproduction, namely, recombination of NaAlH₄ reactions from "used fuel" after decomposition to generate hydrogen has been developed by Gross and others [8]. Cyclic durability, capacity, and kinetic should be icluded in the future studies for engineering applications of this material as suggested by Sandrock and others [9].

An alkaline metal-hydrogen complex compound, NaBH₄, has been studied as a high H-storage material by many researchers [10–14]. In [15–19], the engineering feasibility of NaBH₄ as the H-generation resource has been suggested. A US patent was published in 1975 for recycling "used fuel" as borates to NaBH₄ [20].

The basic reaction of NaBH₄ is listed as NaBH₄ + 2H₂O \rightarrow 4H₂ + NaBO₂ as can be seen in many chemical handbooks and textbooks in which H-generation is accounted as 10.8 mass %. However, it does not happen in practice from the experimental fact that the concentration of NaBH₄ given as the stoichiometric relation, exceeds the solubility limit in an aqueous solution.

In alkaline-stabilized solutions, materials such as KBH_4 and $NaBH_4$ exist as the form of BH_4^- -complex ions. It is not reasonable to compute the H-content of this material simply as 10.8 mass %, which seems to be extreme high compared to other conventional H-containing materials. It is necessary to take account of the solubility limit, density, and viscosity as well as the formation of crystalline materials.

^{*}Corresponding author. (E-mail: bt73093@ns.kogakuin.ac.jp)

The present work is aimed at developing a new Hstorage system based on the metal-hydrogen complex ions such as BH_4^- in an aqueous KOH or NaOH solution. It is our final goal to establish an H-supply system based on the oxidation/reduction process by using metal oxides such as KBO₂ (potassium metaborate), NaBO₂ (sodium metaborate), and NaB₄O₇ (sodium tetraborate), which can be obtained easily as natural resouces in the form of crystalline materials.

In this paper, the catalytic function of Mg_2Ni treated by an F-treatment and the reaction kinetics during hydrogen generation from BH_4^- complex ion-containing KOH and NaOH solutions are reported.

1 Experimental results

A series of metals, Mg, Mg₂Ni, MgH₂, and Mg₂NiH₄ used as catalysts were fluorinated by an F-treatment procedure. F-solution was prepared by mixing 0.6 ml of HF and 6g of KF in 1 l of water. F-treatment was performed for 5g of each of the metals and Mg₂Ni in 200 ml of HF/KF solution by agitating at 500 rpm for 30 min at 30 °C. The samples after F-treatment were washed by water several times and were dried under evacuated condition after removing water by a centrifuge [21]. The F-treatment is applied in order to remove oxides, to form fluoride, and to create hydride layers at the extreme surface of granular particles. The F-treatment reported by Sun [22] is found to be (a few tens of times) more effective for generating a larger specific surface than the untreated particle.

The metal-hydrogen complex ion, BH_4^- , was prepared as 10 wt. % KOH and NaOH solutions, individually. The concentration of those complex ions was varied up to the solubility limits in those alkaline solutions at 25 °C. In Fig. 1,

Table 1. Fluorinated metals and MgNi used for catalytic hydrolysis

Fluorinated catalyst	Specific surface area (m^2/g)	Weight (g) w	Surface area (m ²) $a \times w$
Ni	2.65	0.72	1.91
Co	4.22	0.45	1.91
Cu	2.45	0.78	1.91
Fe	0.96	2.00	1.91
Ru	14.57	0.13	1.91
Zn	1.14	1.68	1.91
Mn	1.03	1.85	1.91
Ti	0.19	10.05	1.91
Mg	0.46	4.15	1.91
Mg ₂ Ni	6.50	0.29	1.91

the solubility limit of BH_4^- -complex ion solution is illustrated as a function of its concentration under several alkaline concentration conditions. The samples used as catalysts are listed in Table 1. All samples used in this experiment were weighted to have the same surface area (= $1.91 \text{ m}^2/\text{g}$) in order to evaluate the hydrolysis kinetics under the same conditions. H-generated by the catalytic hydrolysis was measured by a *P*-v-*T* method at room temperature. Reaction kinetics during H-generation was determined under isothermal conditions by the amount of H-generated as a function of time elapsed.

The experimental results on the untreated and F-treated Mg_2Ni are shown in Fig. 2. The kinetics of the hydrogenated Mg_2Ni after F-treatment (F-treated Mg_2NiH_4) is shown in Fig. 3. Catalytic hydrolysis by several metals is illustrated in Fig. 4 for comparison. F-treated Mg_2Ni was hydrogenated in a conventional Sievert apparatus to prepare the F-treated Mg_2NiH_4 . From an XRD analysis, Mg_2NiH_4 peaks were confirmed with peaks of MgF_2 .



Fig. 1. Solubility of BH_4^- in NaOH solution



Fig. 2. H-generated by F-treated- and untreated MgNi



Fig. 3. H-generated by hydrogenated MgNi after F-treatment (F-Mg2NiH4)



Fig. 4. Rates of H-generation by various F-treated metals and MgNi

2 Discussions

Catalytic effects of F-treated Mg_2Ni were found apparently more effective than those of untreated Mg_2Ni . Between F-treated Mg_2Ni and F-treated Mg_2NiH_4 , there was little difference in the rates of H-generation. From these experiments, hydrogenation after F-treatment of Mg_2Ni to form Mg_2NiH_4 was demonstrated to be not effective in the improvement of catalytic hydrolysis of F-treated Mg_2Ni .

In the previous works summarized in [23], it has been proved that the surface oxides are removed by F-treatment to produce the fluoride layer, which exhibits extremely high affinity to H-uptakes. In addition, it has been known that the hydride phase is formed at the extreme surface of particles during F-treatment [24]. The hydride phase in Mg₂Ni, differently from other metal hydrides, forms hydride phase gradually from the surface towards the center of the particle [25]. The depth of hydride phase is dependent on the particle size as well as on the hydrogen pressure and time elapsed during hydrogenation process.

The fluoride layer is known as MgF_2 both in pure-Mg and Mg_2Ni particle surfaces. These fluoride layers were reported to improve the hydriding kinetics considerably under lower temperature and pressure conditions [24, 26–28]. However, pure-Mg did not exhibit a trace of catalytic function in this experiment even after F-treatment as can be seen in Fig. 5.

The hydride layer formed during F-treatment at the extreme surface of Mg₂Ni was found to work as the active site for hydrolysis. The Mg₂Ni particle at the extreme surface is estimated to disproportionate to $xMgF_2$ and Mg_{2-x}NiH₄ during F-treatment and to provide NiH₄⁻-enriched, S. Suda phase combining with Mg non-stoichiometrically. The NiH₄⁻-enriched phase should act as the active catalytic site for hydrolysis judging from those experimental data. Hydrogen existing as the negative ion in NiH₄⁻ does not participate in the hydrolysis. It is the authors' understanding that the NiH₄⁻ acts as catalyst but not as H-donor in hydrolysis.

Noreus and others have extensively studied bonding state and strength of NiH_4^- in Mg_2NiH_4 [29–34]. The high temperature-level requirement for the releasing of hydrogen from Mg_2NiH_4 is explained well by the tight bonding between Ni and H.

Meanwhile, hydrogenation of F-treated Mg₂Ni did not exhibit noticeable catalytic functions when compared with the F-treated/unhydrided Mg₂Ni. It is explained by the stoichiometric disproportionation of Mg_{2-x}Ni to Mg₂NiH₄ and Nio as illustrated in the following equation: $2Mg_{2-x}Ni$ $+2(2-x)H_2 \rightarrow (2-x)Mg_2NiH_4 + xNi^\circ$. Metallic Ni° is estimated to exhibit catalytic functions that are comparable with



Fig. 5. Catalytic effects of pure Mg and MgNi in hydrolysis

the role of pure Ni and F-treated Ni. The NiH₄-complex ion that combined stoichiometrically with Mg does not work as the catalyst as shown in Fig. 2.

It is, however, preferable from practical engineering and cost-effectiveness viewpoints that no further chemical processing such as hydrogenation is required other than F-treatment process.

3 Conclusions

Catalytic functions of pure Mg and Mg₂Ni were evaluated in accordance with the studies on the fluorination effects on catalytic hydrolysis of BH_4^- -complex ion solutions.

F-treatment effects on Mg_2Ni were found prominent for improving the H-generation kinetics. The increased specific area by F-treatment enhanced the catalytic function of Mg_2Ni .

Hydrogenation effects on the F-treated Mg_2Ni , i.e. $F-Mg_2NiH_4$, were not observed clearly in this work.

Hydrogenation during F-treatment was estimated to result in the disproportionation of Mg₂Ni to xMgF₂ and Mg_{2-x}NiH₄ at the extreme surface. And the NiH₄⁻-enriched surface is considered to contribute to the improved kinetics. Disproportionation effects on the catalytic activity should be subjected to further detailed studies.

Acknowledgements. This work has been funded by NEDO (The New Energy & Industrial Technology Development Organization) for "The Development of Metal–Hydrogen Complex Solutions as the H-Storage System". It has also been supported in part by grant-in-aid for Scientific Research on Priority Area A of the "New Protium Function" from the Ministry of Education, Science, Sports and Culture. The authors wish to express their special thanks to these two governmental organizations for their funding and support.

References

- K. Fukuda: Proc. WE-NET Hydrogen Energy Symposium, Tokyo (1999) pp. 1–26; M. Yoshikawa: Proc. WE-NET Hydrogen Energy Symposium, Tokyo (1999) pp. 27–34; NEDO, Booklet of the International Clean Energy Network Using Hydrogen (WE-NET) (2000)
- 1996–1998 Annual Report: International Energy Agency (IEA) Agreement on the Production and Utilization of Hydrogen
- 1998–1999 Annual Progress Report (available in Japanese): Grantin-aid Project for Scientific Research on Priority Area A of "New Protium Function in Sub-nano Matters" (Ministry of Education: Science, Sports and Culture)
- 4. B. Bogdanovic, M. Schwickardi: J. Alloys Comp. 253/254, 1 (1997)
- C.M. Jensen, R. Zidan, N. Mariels, A. Hee, C. Hagen: Int. J. Hydrogen Energy 24, 461 (1999)

- R.A. Zidan, S. Takara, A.G. Hee, C.M. Jensen: J. Alloys Comp. 285, 119 (1999)
- B. Lewandowski, T. Seidl, S. Takara, D. Sun, C.M. Jensen: Proc. Int. Symp. Metal-Hydrogen Systems (Noosa, Queensland, Australia 2000) p. 288
- K.J. Gross, C. Jensen, S. Takara, G.J. Thomas: Proc. Int. Symp. Metal-Hydrogen Systems (Noosa, Queensland, Australia 2000) p. 287
- G. Sandrock, K. Gross, G.J. Thomas, C. Jensen, S. Takara: Proc. Int. Symp. Metal-Hydrogen Systems (Noosa, Queensland, Australia 2000) p. 278
- H.I. Schlesinger, H.C. Brown, A.B. Finholt, J.R. Gilbreath, H.R. Hockstra, E.K. Hydo: J. Am. Chem. Soc. 75, 215 (1953)
- 11. A. Levy, J.B. Brown, C.J. Lyons: Ind. Eng. Chem. 52, 211 (1960)
- 12. H.C. Brown, C.A. Brown: J. Am. Chem. Soc. 84, 1493 (1962)
- 13. J.A. Gardiner, J.W. Collat: J. Am. Chem. Soc. 87, 1692 (1965)
- K.A. Holbrook, P.J. Twist: "Hydrolysis of the Brohydride Ion Catalyzed by Motal-Boron Alloys", J. Chem. Soc. (A), 890 (1971)
- 15. M.M. Krccvoy, R.W. Jacobson: Ventron Alembic 15, 2 (1979)
- C.M. Kaufinan, B. Sen: "Hydrogen Generation by Hydrolysis of Sodium Tetrahydroborate: Effects of Acids and Transition Metals and Their Salts", J. Chem. Soc., Dalton Trans. 307 (1985)
- V.C.Y. Kong, F.R. Foulkes, D.W. Kirk, J.T. Hinatsu: Int. J. Hydrogen Energy 24, 665 (1999)
- S.C. Amendola, S.L. Sharp-Goldman, M. Saleem Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder: Int. J. Hydrogen Energy 25, 969 (2000)
- S.C. Amendola, M. Binder, M.T. Kelly, P.J. Petillo, S.L. Sharp-Goldman: "A Novel Catalytic Process for generating Hydrogen Gas from Aqueous borohydride Solutions", Adv. in Hydrogen Energy 36 (2000)
- H.B.H. Cooper, Electrolytic Process for the Production of Alkali Metal Borohydrides, US Patent 3734842 (22 May 1973); C.H. Hale, Production of Metal Borohydrides and Organic Onium Borohydrides, US Patent 4931154 (5 June 1990); S. Amendola, Electroconversion Cell, US Patent 5804329 (8 September 1998)
- Y.-M. Sun, K. Iwata, S. Chiba, Y. Matsuyama, S. Suda: J. Alloys Comp. 253/254, 520 (1997)
- Y.-M. Sun, X.-P. Gao, N. Araya, E. Higuchi, S. Suda: J. Alloys Comp. 293–295, 364 (1999); Y.-M. Sun, S. Suda: Proc. Int. Symp. Metal-Hydrogen Systems (Noosa, Queensland, Australia 2000) p. 288
- Z.-P. Li, Y.-M. Sun, B.-H. Liu, X.-P. Gao, S. Suda: Mater. Res. Soc. Symp. Proc. 513, 25 (1998)
- 24. F.-J. Liu, G. Sandrock, S. Suda: Z. Phys. Chem. 183, 163 (1994)
- 25. X.-L. Wang, N. Haraikawa, S. Suda: J. Alloys Comp. 231, 397 (1995)
- 26. F.-J. Liu, G. Sandrock, S. Suda: Trans. Mater. Res. Soc. Jpn. 18B, 1229
- (1994)
- 27. F.-J. Liu, S. Suda: J. Alloys Comp. 230, 58 (1995)
- 28. F.-J. Liu, S. Suda: J. Alloys Comp. **232**, 212 (1996)
- D. Noreus, K. Jansson, M. Nygren: Z. Phys. Chem. NF 146, 191 (1985)
- 30. D. Noreus, L. Kihlborg: J. Less-Common Metals 123, 233 (1986)
- 31. D. Noreus, L.G. Olsson: J. Chem. Phys. 78, 2419 (1983)
- 32. D. Noreus: Z. Phys. Chem. NF 163, 575 (1989)
- M. Olofsson-Martensson, M. Kritikos, D. Noreus: J. Am. Chem. Soc. 122, 6960 (1999)
- M. Olofsson-Martensson, U. Haussermann, J. Tomkinson, D. Noreus: J. Am. Chem. Soc. 121, 10908 (1999)