JOURNAL OF CATALYSIS 77, 289–292 (1982)

NOTES

Improved Hydrogen Absorption of $SmMg_3$ and Mg_2Ni Intermetallics upon Complexation with Large Aromatic Molecules

In earlier papers (*1, 2*) we reported the first study on the rare earth intermetallic compound $SmMg_3$ modified with condensed ring compounds. The material formed when $SmMg_3$ was treated with anthracene readily absorbed hydrogen at room temperature, although there was no indication of hydrogen uptake by $SmMg_3$ alone under similar conditions. We speculated that the treatment with aromatic materials provided a novel way of improving the characteristics of hydrogen absorption by the intermetallics as a hydrogen storage medium.

It has been shown that Mg_2Ni can absorb hydrogen to produce the hydride to an extent exceeding the capacity of liquid hydrogen by up to a factor of 1.3 on a per unit volume basis (*3*). The hydrogen density of Mg_2NiH_n is comparable to that of $LaNi_5H_n$ (*4, 5*) considered an excellent hydrogen host. However, the pressure and temperature applied in the H_2 absorption process are too high to be practical.

In light of the information just described, we were interested in the general behavior of the intermetallic compounds ($SmMg_3$ and Mg_2Ni) treated with aromatic compounds in terms of hydrogen storage materials. Characterization of the present materials was also conducted using NMR and ESR.

The intermetallic compounds used in this work were $SmMg_3$ and Mg_2Ni. Details regarding the preparation of $SmMg_3$ are described in earlier publications (*1, 2*). Mg_2Ni was commercially available from Nippon Yttrium Company. Confirmation of the desired structure in these samples was obtained by X-ray diffraction analysis. The condensed ring compounds (anthracene, phenanthrene, chrysene, and perylene) obtained from Tokyo Kasei Company were used without further purification. Hydrogen as an absorbate was purified by passage through a molecular sieve and liquid nitrogen trap. In a typical preparation of the samples based on the alloys and the aromatic compounds the intermetallic compounds were crushed to a fine powder before being placed in a 50-ml Schlenk reactor flushed thoroughly with dry N_2. The reaction of equimolar amounts of the alloys and the aromatic materials was carried out in the presence of trace amounts of C_2H_5Br[1] in a 10-ml anhydrous tetrahydrofuran (THF) solvent (freshly distilled over sodium wire) at room temperature. The suspended mixture was stirred for a week, followed by evacuation to provide dark-green products. The mixture thus prepared was transferred to the sample chamber, connected to a high-vacuum system, and evacuated to ca. 10^{-5} Torr prior to each run. The products were sensitive to air turning into nonreactive materials by oxidation. Thus, these operations were carried out under dry N_2. Hydrogen uptake measurements were made using volumetric equipment (212 cm^3) and the quantity of hydrogen absorbed was calculated from the change in pressure of a mercury manometer. ESR studies of the aromatic additives were carried out at room

---

[1] Although precise reasons for the addition of C_2H_5Br are not clear, it is possible to see similar experiences elsewhere (B. Bogdanovic *et al.*, *Angew. Chem. Int. Ed. Engl.* **19**, 818 (1980).

0021-9517/82/090289-04$02.00/0

temperature with a JEOL-JES-ME X-band spectrometer under 100-kHz modulation and the field was calibrated with Mn^{2+} ion doped in magnesium oxide powder.

The materials derived from the intermetallics ($SmMg_3$ and Mg_2Ni) and different aromatic compounds instantaneously absorbed hydrogen at room temperature when exposed to high-purity hydrogen at 630 Torr. For various systems the variation of hydrogen uptake with time is illustrated in Fig. 1. The intermetallic compounds employed gave rise to a capability of absorbing copious quantities of hydrogen under mild conditions upon complexing. For comparison it is informative to note that $SmMg_3$ or Mg_2Ni alone hardly showed any indication of hydrogen uptake under similar conditions: below atmospheric pressure at room temperature. Preliminary kinetic studies showed that the rate of hydrogen uptake was almost proportional to the hydrogen pressure under initial conditions. Regarding the $SmMg_3$–anthracene and Mg_2Ni–anthracene systems, apparent activation energies for the initial absorption process were found to be 8.6 and 7.3 kcal/mol in the range of 0 to 40°C, respectively.

Few studies have been reported for the hydrogenation of $SmMg_3$, but it is clear by X-ray analysis that $SmMg_3$ is decomposed to SmH_n and Mg when contacted with hydrogen (*6*). With regard to Mg_2Ni, there has been a valuable report by Reilly and Wiswall (*3*) in regard to the hydrogen storage capacity of Mg_2Ni. It was shown that Mg_2Ni reacted readily with hydrogen at about 21 atm and 325°C. Desorption isotherms were determined, from which pressure–composition isotherms (Fig. 2) were obtained for the Mg_2Ni–H system in the range of 1.77 to 9.71 atm and 298 to 349°C. One plateau pressure region was found. This indicates the existence of two crystallographically distinguishable hydrides which can be designated as α and β. On the basis of thermodynamic considerations they represented the relationship between the dissociation pressure P (atm) and temperature T (K)

$$\log P_{\beta \rightarrow \alpha} = -3360/T + 6.389. \quad (1)$$

According to simple arithmetic using eq. (1), the Mg_2Ni–H system without the aromatic materials possesses a plateau pressure of ($\alpha + \beta$) 1.3×10^{-5} atm (9.9×10^{-2} Torr) at 25°C. Consequently, even taking into account hysteresis between absorption and desorption processes, it seems that hydrogen absorption by Mg_2Ni itself is possible at a low pressure and temperature applied in this study, which is not possible with observable rates without the aromatic compounds. It is apparent that the treat-

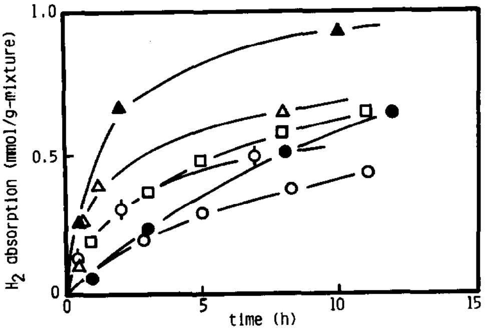

FIG. 1. Time courses of hydrogen absorption by $SmMg_3$ and Mg_2Ni combined with various aromatic compounds. Open symbols: Mg_2Ni; solid symbols: $SmMg_3$. ○: Anthracene; ⌽: phenanthrene; □: chrysene; △: perylene.

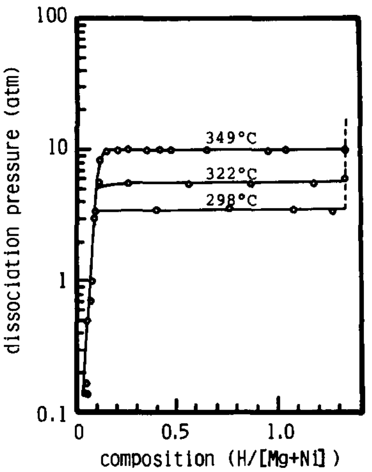

FIG. 2. Desorption isotherms for the Mg_2Ni–H system (*3*).

ment of $SmMg_3$ and Mg_2Ni with the aromatic materials led to superior properties as a hydrogen container, indicating a lowering of the pressure and temperature for hydrogen absorption.

The ability of hydrogen absorption varied considerably among the complexing systems with change in the partner materials. The nature of the aromatic compounds with which Mg_2Ni or $SmMg_3$ is combined is important in determination of this capability. We believe that the difference is a consequence of variation of electronic interaction between the intermetallic compound and the aromatic materials. For the THF-soluble part of the $SmMg_3$–anthracene system, for example, attempts have been made to perform electronic spectrum measurements (*2*) which showed that an additional electron donor–acceptor complex is formed and appears at 598 nm. Figure 3 shows an ESR signal of the powdery sample obtained when perylene was added for complexation with Mg_2Ni. The resulting material developed a yellowish-green color and gave an unresolved spectrum of perylene anion radicals with a *g* value of 2.0036 (perylene anion radical in solution, 2.0026 (*7*)) and overall width of ~40 G. These imply the occurrence of charge transfer to form aromatic anion radicals to some extent and production of materials similar to complexes (*8*) formed when alkali metals are combined with condensed ring compounds. Accepting that the electron donor–acceptor complexes derived from alkali metal–aromatic adducts possess the ability to activate specifically hydrogen (*8*) in the present system the complexes formed on the alloy surface are likely involved in breaking of the hydrogen bond, followed by entry of hydrogen into the alloys by spillover. Hence, the roles of the complexes might be similar to those of elemental Ni generated in the surface to dissociate molecular hydrogen into atomic hydrogen in the model which Wallace *et al.* (*9, 10*) proposed concerning hydrogen absorption by $LaNi_5$.

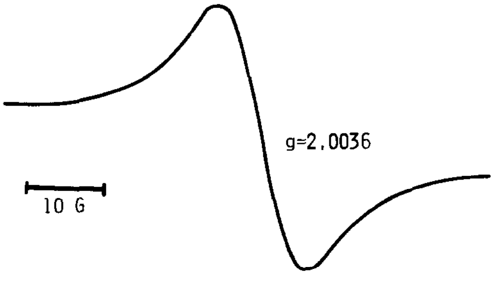

FIG. 3. ESR signal of organic radicals obtained by addition of perylene to Mg_2Ni.

To establish the action of hydrogen occluded in the material NMR studies were conducted. NMR measurements using a JEOL MH-100 model were made on the sample after hydriding and dehydriding without exposure to air, although all the samples were not very soluble in a C_6D_6 solvent. The hydriding samples showed small proton peaks corresponding to hydrogenated aromatic compounds. For example, the Mg_2Ni (or $SmMg_3$)–anthracene–H system yielded a complex containing 9-monohydroanthracene (9-H NMR absorption at 3.68 ppm). This finding is in accord with that obtained from the Na–anthracene–H system (*8*). Quantitative details are not available at present, but it is deduced that most of the hydrogen reacts with Mg_2Ni or $SmMg_3$ to produce its hydride (*11*). Moreover, it was also confirmed by NMR analysis that the reacting hydrogen was readily detached from the aromatic materials after brief evacuation.

To use the present materials as an effective means of storing hydrogen, reversible hydriding and dehydriding are required under favorable conditions. The samples after hydrogenation were subjected to degassing to ca. 10^{-5} Torr for 2 h at room temperature, followed by rehydrogenation by introducing hydrogen (630 Torr). In a series of experiments, the Mg_2Ni–anthracene system exhibited the best recovery of hydrogen with good reproducibility (Fig. 4). Reversibility of other systems was not as efficient as that for the Mg_2Ni–anthracene. Considering that the obtainable pressure ($<10^{-5}$ Torr) *in vacuo* is much lower than the pla-

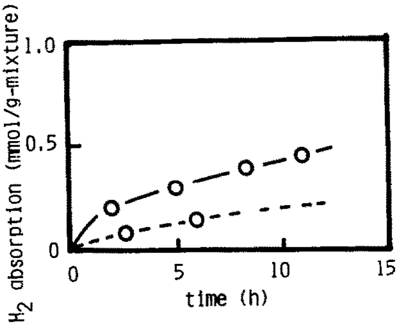

FIG. 4. Recovery of hydrogen for the Mg_2Ni–anthracene system. The solid line represents the time course of the first absorption and the broken line the second absorption after evacuation.

teau pressure (at 25°C) for Mg_2NiH_n and the NMR results, it is presumed that dehydriding of Mg_2NiH_n at room temperature is kinetically difficult and that its behavior is ultimately dependent upon the type of interaction of the intermetallics and the aromatic materials.

ACKNOWLEDGMENTS

We would like to express our sincere appreciation to Professor W. E. Wallace, University of Pittsburgh, for cooperation in preparing the intermetallic compound $SmMg_3$. This work was supported by a grant from the Ministry of Education, Japan.

REFERENCES

1. Imamura, H., and Tsuchiya, S., *Chem. Commun.* 567 (1981).
2. Imamura, H., and Tsuchiya, S., *J. Catal.* **72,** 383 (1981).
3. Reilly, J. J., and Wiswall, R. H., Jr., *Inorg. Chem.* **7,** 2254 (1968).
4. van Vucht, J. H. N., Kuijpers, F. A., and Bruning, H. C. A. M., *Phillips Res. Rep.* **25,** 133 (1970).
5. Kuijpers, F. A., *Phillips Res. Rep. Suppl.* **2,** (1973).
6. Beck, R. L., Summary Report on Contract No. AT (33-3)-3 to the U.S. Atomic Energy Commission from the University of Denver, October 15, 1962. Available from the Office of Technical Services, Department of Commerce, Washington, D.C.
7. Alger, R. S., "Electron Paramagnetic Resonance: Techniques and Applications." Interscience, New York, 1968.
8. Tamaru, K., and Ichikawa, M., "Catalysis by Electron Donor-Acceptor Complexes." Kodansha Ltd., Tokyo, 1975.
9. Wallace, W. E., Karlicek, R. F., Jr., and Imamura, H., *J. Phys. Chem.* **83,** 1708 (1979).
10. Wallace, W. E., Elattar, A., Imamura, H., Craig, R. S., and Moldovan, A. G., *in* "The Science and Technology of Rare Earth Materials" (W. E. Wallace and E. C. Subbarao, Eds.) p. 329. Academic Press, New York, 1980.
11. Imamura, H., Takahashi, T., Galleguillos, R. I., and Tsuchiya, S., submitted for publication.

HAYAO IMAMURA[2]
TOSHIO TAKAHASHI
SUSUMU TSUCHIYA

Department of Industrial Chemistry
Faculty of Engineering
Yamaguchi University
Tokiwadai, Ube 755
Japan

Received November 19, 1981; revised March 19, 1982

---

[2] Author to whom correspondence should be addressed.