to be of great value in the clarification of fundamental assignments in the rather complex spectra of a molecule of moderate size and low symmetry. Further vibrational studies of methyldiborane are recommended to identify some low-frequency fundamentals that are presently unassigned but are predicted by the force field presented here.

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Preparation and Hydriding Behavior of Magnesium Metal Clusters Formed in Low-Temperature Cocondensation: Application of Magnesium for Hydrogen Storage

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Magnesium metal clusters formed in low-temperature matrices were investigated with a view to forming the metal hydride. In practice, magnesium readily absorbed large amounts of hydrogen under more moderate conditions (P_{H_2} = 460 torr, T = 200–250 °C) when it had been transformed into tetrahydrofuran- (THF-) solvated small particles formed by the cocondensation reaction of magnesium atoms with THF molecules at −196 °C. To elucidate the characteristics of hydrogen sorption of Mg–THF, a comparative study with pure magnesium powder was carried out. It is believed from the H_2–D_2 isotope scrambling measurements that the high activity of the present Mg–THF system for hydrogen absorption is due to a rapid surface process in comparison with the case of the pure magnesium. This identification is reinforced by the employment of surface modification techniques.

Introduction

Hydrogen is a very versatile fuel. It can replace petroleum products as a fuel in almost all, if not all, uses. However, there is a containment problem with regard to obtaining a high energy density. Recently, a great deal of attention has been devoted to metal hydrides as a means of containing hydrogen safely and efficiently. It is known that magnesium can react with hydrogen to form the hydride to an extent exceeding the capacity of liquid hydrogen by up to a factor of 1.6 on a per unit volume basis, which satisfies a practical energy density. This property arouses considerable interest in its application for hydrogen storage. In practice, however, some improvement of hydrogen sorption properties is often required. The changes in the sorption properties of magnesium have been investigated by alloying with other metals[1–6] or plating nickel,[7] because magnesium itself is poor as a hydrogen host due to the slow kinetics of hydriding and dehydriding.

We have recently found[8] that magnesium metal clusters, which have been formed by the reaction of metal atoms with organic media in low-temperature matrices, are able to absorb hydrogen readily under mild conditions and, moreover, without the "activation treatment" consisting of repeated cycles of evacuating, heating to ca. 400 °C, and then pressurizing at 70–200 atm of hydrogen. In organic chemistry this low-temperature codeposition method has been known to afford very effective reagents in which the active metal particles are utilized in slurry form.[9]

Studies of the changes in the properties of hydrogen sorption are of fundamental interest. Accordintly, to establish the nature of the magnesium formed by clustering of metal atoms in tetrahydrofuran (THF) vapor, the characteristics of hydrogen sorption were examined in comparison with the results obtained by using pure magnesium activated by the conventional method.

Experimental Section

The active magnesium metal clusters were prepared from the best grade (>99.95%) of elemental magnesium obtainable commercially (Furukawa Magnesium Co. Ltd.). Tetrahydrofuran (THF), which was reagent grade, was thoroughly dehydrated by sodium wire before cocondensing with the high-temperature magnesium species. The apparatus used to prepare the Mg–THF matrix was a reaction vessel containing a THF inlet system and fitted with a heating part consisting of a spiral-shaped tungsten filament (o.d. = 1 mm; The Japan Lamp Industrial Co. Ltd.) connected between tungsten rod electrodes (2.0 × 500).

In a standard procedure for the preparation of Mg–THF the reaction zone was evacuated to a pressure of ca. 10^{-6} torr and then cooled with liquid nitrogen (−196 °C). The tungsten wire heater was gradually energized to vaporize magnesium atoms, and simultaneously the inlet needle valve was slowly opened to introduce THF vapor (ca. 10^{-2} torr) into the system. During the vaporization of 1 g of magnesium, about 5 mL of THF was codeposited on the inner cooled surface of the reactor over a period of 15 min. After completion of the reaction, a dark gray matrix was present and the vessel was allowed to warm to room temperature under vacuum. The excess THF was pumped off, leaving a dry active Mg–THF powder.

The activated magnesium in the form of a fine powder was produced by repeated procedures of hydrogenation at 80 atm and dehydrogenation at 400 °C under vacuum.

Hydrogen absorption measurements were made by using conventional volumetric equipment. Prior to every run the sample was outgassed at 200 °C to ca. 10^{-5} torr for 2 h and then exposed to hydrogen at pressures of up to ca. 460 torr at the prescribed temperatures. The quantity of hydrogen absorbed was calculated from

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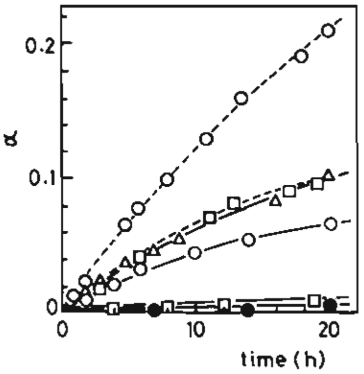

Figure 1. Variation of hydrogen absorption with time. Measurements were made in the presence of hydrogen at 460 torr at 200 °C (solid line) and 250 °C (dotted line). Prior to each run Mg–THF was outgassed for 2 h at 25 (●), 100 (□), 200 (○) and 300 °C (△).

the change in pressure of a mercury manometer.

Results and Discussion

The Mg–THF powder prepared in this way was extremely reactive and instantaneously absorbed hydrogen at 200–250 °C without the conventional "activation processing" when exposed to hydrogen at 460 torr. The development with time of hydrogen uptake is illustrated in Figure 1, where α is the fraction of the material reacted to time t. For comparison it is informative to note that magnesium powder is itself incapable of absorbing hydrogen at measurable rates under similar conditions even after being subjected to adequate activation. Direct comparison of the activities of Mg–THF and pure magnesium metal grains reported to date is not possible because the hydriding conditions employed are too different. We tried to compare our data with those extrapolated to the present conditions (P_{H_2} = 460 torr, T = 200 °C) on the basis of the dependence of hydriding of magnesium on temperatures and pressures, which has been studied by Stander,[10] by assuming an approximately linear relationship. There was no marked difference between the two,[8] but it seems quite certain that the Mg–THF powder is exceptionally active for hydrogen absorption without the "activation". In addition, preliminary kinetic studies of Mg–THF yielded an apparent activation energy for the absorption process of 9.9 kcal/mol,[8] whereas pure magnesium samples have been known to yield much higher values such as 23.1 kcal/mol,[10] 27.6 kcal/mol,[11] or above.[12] On the basis of these observations we can speculate that magnesium possesses the capability of absorbing copious quantities of hydrogen under milder conditions upon clustering of magnesium atoms in organic media. The results strongly imply that the cocondensation reaction in low-temperature matrices constitutes a novel approach to the improvement of the sorption properties of magnesium as a hydrogen container, indicating a pronounced enhancement of the hydriding rate under mild conditions.

Precise reasons for these properties are unknown; however, of particular interest are the morphology of the magnesium particles, the form of the surface magnesium, and the changes in these properties after codeposition with THF molecules on a cold surface. According to scanning electron microscope (SEM) studies the activated pure magnesium had a block appearance with a smooth surface (Figure 2a), whereas the as-codeposited magnesium was made up of layer-type flakes resulting from the dispersion of magnesium atoms in THF vapor and subsequent cocondensation (Figure 2b). In both cases the particles were widely distributed in size and shape, but it seems that the THF-solvated magnesium had relatively smaller sizes than the activated one. This is consistent with the evaluation of the average magnesium diameter (d_{av}) calculated by assuming homogeneous spherical particles and taking into account the results obtained from the BET gas adsorption: $d_{av} = 6V/S$, where S and V are the total surface area and the volume of a metal, respectively. The average particle size was estimated at <2.1 μm for Mg–THF and <9.0 μm for the pure magnesium (Table I). However, it is unlikely that the exceptional activity of Mg–THF can be fully interpreted in terms of geometrical discussions of the magnesium particles, although for this mean value of the equivalent spherical particle diameter, our discussion assumes that the particles are nonporous, so that the surface area refers only to the external surface.

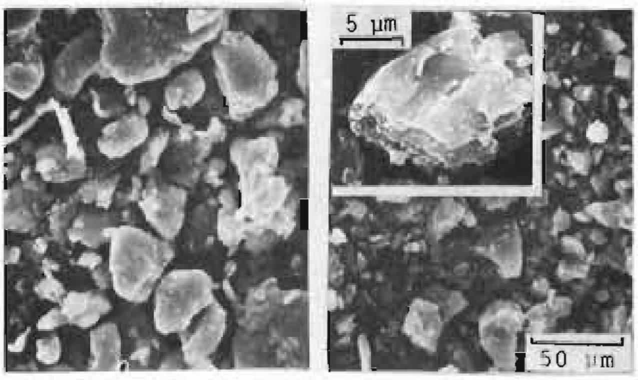

Figure 2. Scanning electron micrographs of magnesium particles: (a) left, activated magnesium; (b) right, Mg–THF (as prepared).

Table I. Characterization of Magnesium Samples

	BET surface area,[a] m²/g	d_{av},[b] μm	compn[c]
Mg-THF	1.64	2.1	$Mg(C_xH_yO_z)_{\sim 0.0274}$; $y/x \simeq 3.0$
activated Mg	0.38	9.0	Mg

[a] Adsorption measurements were made at −196 °C with nitrogen as an adsorbate by means of the BET method. [b] $d_{av} = 6V/S$ (see text). [c] The magnesium sample used contained Zn, Mn, Al, Fe, and Cu impurities. The composition was determined by elemental analysis and atomic absorption spectroscopy.

It should be noted that the quite active Mg–THF particles were those in which large amounts of organic materials were solvated on the magnesium clusters. This sample was molecularly defined by compositional analyses, summarized in Table I. Mg–THF was the material with the component ratio of $Mg(C_xH_yO_z)_{\sim 0.0274}$; $y/x \simeq 3.0$. This reflects partially irreversible decomposition of THF upon the cocondensation reaction with the high-temperature species on a cold surface. The organic molecules attached to the magnesium aggregates were cleaved upon pyrolysis with an increase in the evacuation temperature. Heating at 200 °C resulted in the formation of $Mg(C_xH_yO_z)_{\sim 0.0270}$; $y/x \simeq 4.3$. The organics evolved upon pyrolysis were identified as THF and small amounts of organic fragments (C_nH_{2n+2} ($1 \leq n \leq 4$) and aldehydes) by mass spectrometry. The absorption rate of hydrogen by Mg–THF markedly varied with the evacuation temperature before the run (Figure 1) and increased by over 2 orders of magnitude with a change in temperature from 25 to 300 °C. This is probably responsible for the extent of exposure of the active sites on the metal clusters by evolution of these adsorbed organics.

A sequence of events of considerable complexity is involved in the sorption process: hydrogen transport up to the surface

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(step 1), chemisorption onto the surface (step 2), surface migration (step 3), chemisorption–absorption transition (step 4), solid diffusion (step 5), and phase transformation (step 6). The present investigation might be construed in part as a study of changes in surface properties of the magnesium particles caused by dispersing metal atoms into organic media, because it was confirmed from X-ray diffraction studies of Mg–THF that the hexagonal structure of magnesium was maintained in the bulk after cocondensation reaction. In view of the appearance of the specific activity of transition-metal clusters formed in such a way for catalytic gas-phase reaction,[13–15] it is further deduced for the present system that the surface process involved in steps 2–4 is concerned with acceleration of the reaction of magnesium with hydrogen. To check this, attempts were made to perform H_2–D_2 equilibrium reactions, because the isotopic-exchange reaction is available as an index of metal surface activity for dissociative adsorption. When Mg–THF was outgassed at 200 °C and was brought into contact with equimolar amounts of H_2 and D_2 (each 39 torr), rapid formation of HD occurred even at 0 °C and its rate was 1.35×10^{19} molecules·s^{-1}·g^{-1}. On the other hand, the activated pure magnesium was inactive under these conditions and exhibited only a slight activity at 240 °C. In the course of our study on the improvement of sorption properties of metal hydrides using the modification techniques,[16–19] it has been shown that surface-treating the Mg–THF particles with aromatic molecules enhances the hydrogen uptake rate of magnesium as a result of the formation of electron donor–acceptor complexes on the particle surface.[8] Accordingly, the marked effect of aromatics would appear to eliminate internal steps as rate controlling, i.e., steps 5 and 6, and we can conclude that the surface processes are important in Mg–THF.

Registry No. Magnesium, 7439-95-4; hydrogen, 1333-74-0.

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Electrochemical and Spectroscopic Studies of Polypyridine Complexes of Fe(II/III) and Ru(II/III) in the Aluminum Chloride-*N*-1-Butylpyridinium Chloride Molten Salt

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The electrochemical and spectroscopic behavior of $Fe(bpy)_3^{2+}$, $Fe(phen)_3^{2+}$, and $Ru(bpy)_3^{2+}$ in an ambient-temperature molten salt system, aluminum chloride–*N*-1-butylpyridinium chloride (BuPyCl), has been studied as a function of melt composition. The complexes show a single one-electron reversible oxidation wave from melt compositions of 1:1 to 2:1 ($AlCl_3$:BuPyCl mole ratio). Visible spectroscopic and electrochemical data indicate that these compounds are stable in the neutral (1:1) and acid (mole ratio >1) melts, while $Ru(bpy)_3^{2+}$ is stable in basic melts (mole ratio <1), but $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ decompose to $FeCl_4^{2-}$. Comparison of the formal potentials for M(III/II)–polypyridine couples studied in this melt and in other solvents indicates that the redox properties of these complexes are relatively insensitive to the nature of the solvent. It was shown that oxygen acts as an oxidant in the acid melts to oxidize $Fe(bpy)_3^{2+}$, $Fe(phen)_3^{2+}$, and $Ru(bpy)_3^{2+}$ to their corresponding 3+ forms. The 3+ form of each complex was stable in acid melts for several weeks. Perchlorate is also shown to function as an oxidant in acidic melts.

Introduction

The molten salt system composed of aluminum chloride and *N*-1-butylpyridinium chloride (BuPyCl) is liquid at ambient temperatures (~30 °C) over a wide compositional range varying from ~0.7:1 to 2:1 (mole ratio ot $AlCl_3$ to BuPyCl).[1,2] The Lewis acid–base properties of these melts change as the mole ratio of $AlCl_3$ to BuPyCl changes. The melts can be characterized as acidic, basic, or neutral depending on the mole ratio of $AlCl_3$ to BuPyCl being greater than, less than, or equal to unity.[3] In the acidic melts, anionic species are $Al_2Cl_7^-$ and $AlCl_4^-$, in basic melts $AlCl_4^-$ and Cl^-, and in neutral melts $AlCl_4^-$. It has been shown that equilibrium 1 with $\log K = -16.9 \pm 2$[4] provides an adequate description of the system throughout the entire range of melt composition.[2]

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \tag{1}$$

In view of their nonlability and extreme stability in the absence of direct illumination, low-spin complexes of $Ru(bpy)_3^{2+}$, $Fe(bpy)_3^{2+}$, and $Fe(phen)_3^{2+}$ (where bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline) were chosen to study in $AlCl_3$–BuPyCl melts. These complexes were selected for several reasons. Initially we were interested to know whether these compounds are stable in this molten salt media, i.e. whether the reactant's coordination sphere remains intact while the Lewis acid–base properties of the melts are varied. A second aspect of this work was the examination of the possible use of these complexes as internal reference couples. In addition, the use of these melts as solvents for modified-electrode studies, which includes Ru(II)/Ru(III) polymers, suggested such studies.[5]

Spontaneous oxidation of hydrocarbons in highly acidic $AlCl_3$–BuPyCl melts has been observed by Robinson and Osteryoung.[1] The slow chemical oxidation of iodide in acidic $AlCl_3$–BuPyCl melts has been suggested to be due to a reaction

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