Hydrogen Uptake and Hydrogenation Activity of the Rare Earth Intermetallic Compound $SmMg_3$ treated with Anthracene

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Summary The material formed when the rare earth intermetallic compound $SmMg_3$ was treated with anthracene readily absorbs hydrogen at room temperature and catalyses the hydrogenation of ethene.

It has been shown that many rare earth intermetallic compounds reversibly absorb copious quantities of hydrogen, which is occluded dissociatively,[1-4] the intermetallic $LaNi_5$ being an excellent hydrogen storage medium, for example. Recently, because of their large absorption capacity and their rapid hydriding or dehydriding rates much attention has been directed to these intermetallic compounds as hydrogen hosts. Alkali metal-treated polynuclear aromatic compounds such as naphthalene, anthracene, *etc.*, in which formation of electron donor–acceptor complexes as a result of charge-transfer between the substrates has been established, can activate hydrogen and absorb considerable quantities to form the metal hydride.[5] In view of this it is of interest to investigate the action of hydrogen on rare earth intermetallic–polynuclear aromatic compound systems.

The compound $SmMg_3$ used was prepared by the induction melting method.[6] The $SmMg_3$ sample was crushed to a fine powder before being placed in a 50 ml Schlenk reactor flushed thoroughly with dry N_2.

The $SmMg_3$–anthracene complex was prepared by the reaction of $SmMg_3$ (1 mmol) with anthracene (0·4—2 mmol) in anhydrous tetrahydrofuran (10 cm^3) at room temperature for several days followed by evacuation to provide dark green products. The complex thus obtained was transferred to the sample holder, connected to a high-vacuum system, without exposure to air and evacuated at *ca.* 10^{-5} Torr prior to each run. Hydrogen absorption measurements and olefin hydrogenations were carried out using conventional volumetric equipment and a gas-recirculation reactor, respectively. The extent of conversion was established by collecting the reactant gas, followed by gas chromatography with an active alumina-treated squalane column.

The present product derived from $SmMg_3$ and anthracene instantaneously absorbed hydrogen at room temperature when exposed to high-purity hydrogen at about 400 mmHg pressure. The amount of hydrogen taken up was calculated from the change in pressure, and the variation of hydrogen uptake with time is illustrated in the Figure. Preliminary kinetic experiments showed that the rate of hydrogen uptake was almost proportional to the hydrogen pressure under the initial conditions, the rate increasing with increasing anthracene : $SmMg_3$ ratio. Hydrogen is absorbed by $SmMg_3$ alone, in a decomposed form SmH_n and Mg as shown by *X*-ray analysis,[7] only after activation by evacuation at elevated temperatures, but there have been few detailed studies on the hydrogenation of $SmMg_3$.

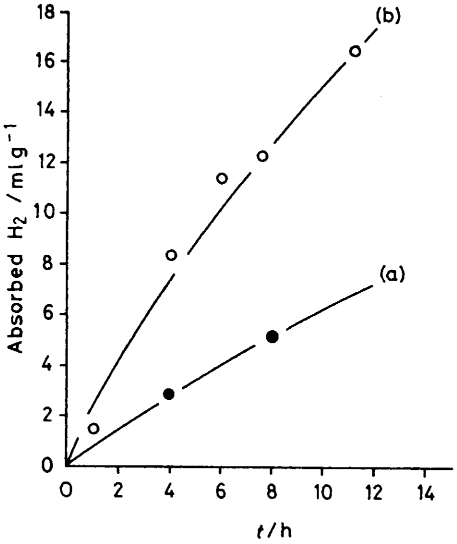

Figure. Variation of hydrogen uptake with time at room temperature, with 1 g of complex and hydrogen at 400 mmHg pressure: (a) $SmMg_3$: anthracene = 1 : 0·4; (b) $SmMg_3$: anthracene = 1 : 2.

To examine the ability of the $SmMg_3$–anthracene complex to catalyse hydrogenation reactions the hydrogenation of ethene was studied at 293 or 323 K with a mixture of C_2H_4 (40 mm Hg) and H_2 (100 mmHg). The reaction progressed readily at 293 K to form ethane, whereas at 323 K hydrogen uptake by the complex also occurred simultaneously to some extent. The hydrogenation was first order in hydrogen pressure with a rate at 293 K of $3·7 \times 10^{-2}$ mmol of C_2H_6 h^{-1} (g cat)$^{-1}$. However, the anthracene-free system, $SmMg_3$ alone, showed hardly any catalytic activity as a hydrogenation catalyst, even under severe conditions. The results obtained are in reasonable accord with the concept that complexing $SmMg_3$ with anthracene gives rise to sites available for hydrogen activation as in the alkali metal–anthracene systems.[5]

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[1] J. H. N. Van Vucht, F. A. Kuijpers, and H. C. A. N. Bruning, *Philips Res. Rep.*, 1970, **25**, 133.

[2] T. Takeshita, W. E. Wallace, and R. S. Craig, *Inorg. Chem.*, 1974, **13**, 2282.

[3] F. A. Kuijpers, *Philips Res. Rep.*, 1973, Suppl. 2.

[4] H. H. van Mal, *Philips Res. Rep.*, 1970, Suppl. 1.

[5] K. Tamaru and M. Ichikawa, 'Catalysis by Electron Donor-Acceptor Complexes,' Kodansha Ltd., Tokyo, 1975.

[6] H. Imamura and W. E. Wallace, *J. Catal.*, 1980, **65**, 127.

[7] R. L. Beck, Summary Report on Contract No. AT(33-3)-3 to the U.S. Atomic Energy Commission from the University of Denver, October 15th, 1962. Available from the Office of Technical Services, Department of Commerce, Washington D.C.