Development of new composite materials for hydrogen storage. The AB$_5$ type hydride alloy with silica glass support.

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Abstract. Use of the spill-over effect to enhance catalytic activity and the amount of absorbed hydrogen in a new composite material is reported. An AB$_5$ lanthanum nickel alloy with a small number of additives serves as the catalyst and the bulk material for hydrogen storage and a silica glass powder with a developed surface serves as the support material. The amount of absorbed hydrogen in the alloy and composite is determined from thermo-gravimetric data. Structural changes in the developed composite during hydrogenation are found to confirm the synergy between the alloy and the support material.

1. Introduction
The amount of hydrogen sorbed in a solid state material can be increased in several ways. Adapting nanostructuring of the host material and/or enhancing its surface absorption capability are two of the recently employed options [1]. A classical AB$_5$ alloy is LaNi$_5$, which has a high hydrogen capacity and is easily activated. However, due to a high plateau pressure and short life cycle, this binary compound is not very suitable for applications [2]. The physical and chemical properties of LaNi$_5$ may be improved by substituting lanthanum atoms with rare earth metals (e.g. Ce, Pr, Nd) and/or nickel by transition metals (e.g. Al, Mn, Co, Cr). These alloys are presently known to provide fast hydrogenation kinetics and better life cycle behaviour.

The diffusion of active species on the surface may play an important role in multi-functional catalyst transport reactions. Specifically, the migration of hydrogen atoms from metal to oxide or carbon surface is important because no dissociative activity is necessary for hydrogen adsorption. This property, referred to as the spill-over effect, is widely exploited in catalysis [3]. The spill-over of hydrogen involves electron transfer to acceptors within the support, modifying the chemical nature of the support. It may also activate a previously inactive material and/or induce subsequent hydrogen physisorption (Figure 1). The dissociation of hydrogen molecules on a catalyst and subsequent spill-over of atomic hydrogen to the support are highly dependent on the chemical bridges formed at the interface [4]. The hydrogen spill-over can be assessed by calculating the ratio of the number of hydrogen atoms to the total number of metal atoms. When spill-over occurs, the hydrogen/metal ratio will typically exceed the stoichiometric value. In the case of materials that form hydrides, this relationship will exceed the stoichiometric ratio of the hydride [5].

In this report, the use of a metal alloy, together with a lighter support material, is suggested to produce a composite from a hydride alloy and borosilicate glass. The glass in this new composite serves as a support material that does not interact with hydrogen molecules directly, but can adsorb spill-over hydrogen from a catalyst, such as an AB$_5$ metal alloy.
2. Experimental

An AB₅ alloy (trade name 7-10) of Metal Rare Earth Limited of China was chosen for the experiments. The scanning electron microscope studies of the material were performed on a Carl Zeiss EVO 50 XVP instrument equipped with an energy dispersive X-ray detector.

Sample structural properties were studied on a X-STOE Theta/theta X-ray diffractometer system using Cu Kα radiation and STOE software.

Tungsten – carbide crucibles with balls of the same material and a Retsch ® MM200 ball mill were used to grind the raw 7-10 material and prepare the glass powder and composite materials. The composite reported in this research consisted of 3.7 weight parts of 7-10 alloy and 1 part of Pyrex glass.

Hydrogen sorption on prepared samples was studied by thermo-gravimetric techniques. The measurements were performed on equipment based on a Sartorius high pressure balance combined with systems to control pressure, temperature, and gas supply. The sample was placed in an airtight steel container under a vacuum or controlled gas atmosphere. The pressure was varied from 10⁻³ to 30 bar, and the temperature was varied from room temperature to 300°C. The sample (340±2 mg) was initially degassed at ambient temperature in a vacuum of 10⁻³ bars, flushed with helium gas, and filled with hydrogen gas up to 10 bars. Before evacuating hydrogen from the container (to 10⁻³ bar), the sample in was heated to 260°C and cooled. The heating and cooling steps were repeated twice and terminated by evacuation of the system. After that, the pressure inside the measuring device was increased in a stepwise manner. The sample weight was measured as a function of time following each increase in pressure. The same procedures were applied to the composite.
3. Results
The scanning electron microscope results (Figure 2) and energy dispersive X-ray detector measurements (Table 1) demonstrate that the composition of 7-10 alloy is close to the stoichiometric AB₅ : A₀.9₆B₅.₀₄ (A=La, Ce, Nd, Pr; B=Ni, Co, Mn, Al, Cr). The calculated molecular mass of the sample was 435.74 g/mol. To determine the molecular mass of the alloy and to make additional calculations, we assumed that metal hydride contained a minimal amount of oxygen after the pretreatment procedure.

![Figure 2: Scanning electron microscope images of the 7-10 alloy. A) untreated, grain size < 50 μm, magnification 11 000. B) ball-milled, grain size < 2 μm, magnification 10 000. Note that the alloy agglomerates in clusters after milling.](image)

| Element | Weight% | Atomic% |
|---------|---------|---------|
| La      | 17,51   | 8,24    |
| Ce      | 9,88    | 4,61    |
| Nd      | 3,07    | 1,39    |
| Pr      | 0,98    | 0,45    |
| Ni      | 52,89   | 58,89   |
| Co      | 6,23    | 6,91    |
| Mn      | 5,08    | 6,05    |
| Al      | 1,93    | 4,67    |
| Cr      | 0,39    | 0,49    |
| O       | 2,03    | 8,30    |

The thermo-gravimetric analysis demonstrated that hydrogen is easily absorbed and desorbed in pure LaNi₅, as the pressure of hydrogen gas is increased and decreased. A minimal amount of hydrogen (0.26 w. %) remained in the pure LaNi₅ sample at atmospheric pressure. In contrast, a different response was observed by the high-pressure balance plot for the 7-10 alloy. The amount of hydrogen absorbed at elevated pressures slightly decreased after the pressure returned to one
atmosphere (Figure 3). Thus, after hydrogenation, the material retained a significant amount of hydrogen under ambient conditions.

Figure 3: High pressure balance data plot for a raw 7-10 sample at room temperature.

For composite samples prepared with the Retsch® MM200 ball mill, significant hydrogen absorption of 1.4 – 1.5 wt% was achieved (Table 2). Comparing the high pressure balance plots of the composite materials made from the 7-10 alloy and LaNi₅, we observed that the glass/7-10 alloy composite absorbed more hydrogen relative to the glass/LaNi₅ composite under similar conditions (Figure 4).

The maximum amount of absorbed hydrogen in raw 7-10 alloy and its composite was calculated as $x$ in $\text{AB}_2\text{H}_x$ and expressed in weight % in three different ways. Table 2 shows the total ($\Delta m_{\text{total}}$) and average ($\Delta m_{\text{av}}$) change in weight after several absorption/desorption cycles and weight of the compounds at the end of the hydrogen treatment, when samples returned to ambient conditions ($\Delta m$). Composites of glass/7-10 alloy contained a larger amount of absorbed hydrogen, as compared to pure 7-10 alloy, which could be explained by spill-over hydrogen from the catalyst (7-10 alloy) to the glass support.
Figure 4: Amount of hydrogen absorbed by LaNi5/glass (solid line) and 7-10 alloy/glass (dashed line) composites at hydrogen pressure 10 bars.

Table 2: Weight variations and stoichiometric values of alloy and its composite

|                  | 7-10       | Δm, mg  | w%    | x    |
|------------------|------------|---------|-------|------|
| Δm_{total}       | 5,507      | 1,582   | 6,966 |      |
| Δm_{av}          | 5,138      | 1,477   | 6,499 |      |
| Δm(1atm)         | 4,883      | 1,405   | 6,177 |      |
| 7-10+glass       |            |         |       |      |
| Δm_{total}       | 5,048      | 1,643   | 7,242 |      |
| Δm_{av}          | 4,616      | 1,504   | 6,621 |      |
| Δm(1atm)         | 4,393      | 1,433   | 6,302 |      |

The X-ray diffractometer results showed that the diffraction peaks of hydrogenated 7-10 alloy were significantly displaced toward smaller angles compared to the raw alloy, indicating that hydride had been formed throughout the α and β-phases. We observed that the β phase of the alloy hydride in ball-milled composites formed sooner relative to the raw alloy. The shift in alloy peaks in the X-ray diffractometer plot observed after the hydrogenation of composite (Figure 5) was an unexpected result. Lattice parameters and cell volume of the hexagonal P6/mmm symmetry of the alloy in hydrogenated composite corresponds to that of the hydride gamma (γ) phase, which was never reached with the hydrogenation of pure 7-10 alloy (Figure 5, Table 3). The more extensive hydrogenation of catalyst AB5 particles in the presence of the glass phase could be explained by synergy between the alloy and support.
Figure 5: X-ray diffractometer plot of raw (7-10raw), hydrogenated 7-10 alloy (7-10H), and hydrogenated 7-10 alloy in composite (7-10gl-H). For clarity, the last two curves are displaced by 100 and 200 intensity units.

Table 3: Structural parameters of raw and hydrogenated samples of alloy 7-10 and composite

| Sample                  | a, Å  | c, Å  | V, Å³ |
|-------------------------|-------|-------|-------|
| 7-10                    | 5,008 | 4,057 | 88,12 |
| 7-10 hydrogenated       | 5,326 | 4,234 | 104,0 |
| 7-10+glass hydrogenated | 5,369 | 4,275 | 108,78|

Conclusions

As shown by the thermo-gravimetric data, the composite synthesized from the 7-10 alloy and borosilicate glass absorbed more hydrogen per unit weight than each of the components separately. We believe this occurred as a result of the spill-over phenomenon. It can be deduced that hydrogen molecules are chemisorbed and dissociated at catalyst surface (mostly Ni) sites such as the AB₅ alloy. Bridges between the catalyst and glass particles facilitate migration of the chemisorbed hydrogen atoms onto the glass surface. Desorption occurs directly from glass sites of relatively lower energy without migration back to the catalyst. The hydrogen spill-over depends on the glass-catalyst contact. The contact changes with the quality of mixing and milling.

From the X-ray diffraction patterns, the β-phase of hydrogenation occurs sooner in ball-milled composite samples, as compared to pure alloy samples. Formation of the hydride γ-phase observed in the hydrogenated composite has never been detected upon hydrogenation of the 7-10 alloy.

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