

SEPARATION USING ENCAPSULATED METAL HYDRIDE

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Abstract

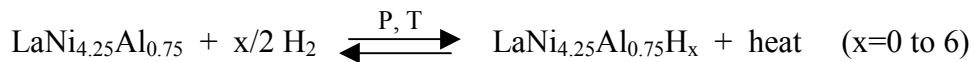
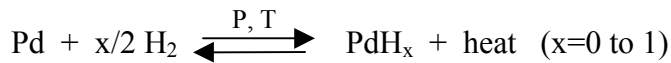
Metal hydride particles were encapsulated in a porous silica matrix. The encapsulation process successfully converted the small metal hydride particles into large granules suitable for packing gas separation columns. The granules absorbed hydrogen readily and withstood many hydrogen absorption cycles without producing fines. The porosity of the silica matrix was optimized so that the pores were large enough to allow hydrogen to easily move within the matrix and react with the metal hydride particles, but small enough to act as a filter to prevent passage of larger molecules including harmful impurities. An experimental apparatus has been installed to test the granules for hydrogen separation from other gases using a thermal absorption process.

Introduction

Metal hydrides can absorb hydrogen selectively and reversibly. They are ideal for use in hydrogen separation if not for some practical problems. Metal hydrides can be “poisoned” by reactive impurities such as carbon monoxide and thereby become inactive. Their particles break up to fines after repeated reaction with hydrogen. The fines can plug up columns and stop gas flow. Therefore, before they can be used for hydrogen separation applications, the above problems must be solved. In this work, a sol-gel encapsulation method was developed that can overcome these two problems. The plan is to produce encapsulated metal hydride material for packing experimental columns. The columns will be tested for hydrogen separation with synthetic gas feeds using a temperature swing absorption process. The goal is to develop an efficient hydrogen separation process for hydrogen production, and for hydrogen recovery from waste streams.

Metal Hydride Basics

A special group of metals and metal alloys can react with hydrogen reversibly under moderate conditions, like room temperature and atmospheric hydrogen pressure. The reaction product is a metal hydride. The term metal hydride has been used loosely to mean both the metal and the product. Examples are palladium and La-Ni-Al alloys. Their reactions may be expressed as follows:



These metal hydrides can be used for hydrogen storage and for hydrogen separation.

Metal Hydride for Hydrogen Separation

For hydrogen separation, metal hydrides can be applied in a temperature swing absorption (TSA) process. In a typical TSA process, the metal hydride is packed in a jacketed column. The jacket can be heated and cooled to swing the column temperature. During the absorption phase of a cycle, the column is cooled and the mixture to be separated is fed into one end of the column. Hydrogen in the mixture is absorbed by the metal hydride. The other gases simply pass through the column and can be discharged as waste. When the metal hydride in the column is saturated with hydrogen, the feed is stopped, and the column is heated to discharge the hydrogen. High purity hydrogen can be produced. Cooling and heating can be achieved with low quality or waste heat sources. A low cost separation process can be developed. Figure 1 illustrates the schematic of a separation column.

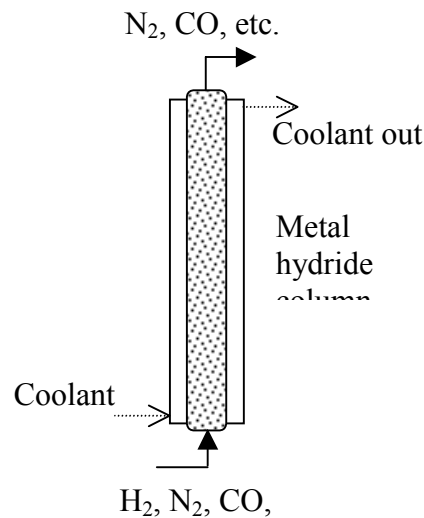


Figure 1. Hydrogen separation column

However, before we can put such a process into practical use, we must overcome two technical problems. First, metal hydride particles break up to fines in micron size. The fines can compact themselves and plug up gas flow paths. Second, reactive impurities, such as carbon monoxide, can “poison” the surface of the metal hydride particles and render them inactive to hydrogen. The metal hydride fines must be converted to stable granules, and must be protected from active impurities.

Sol-Gel Encapsulation of Metal Hydrides

It is well known that highly porous silica gels can be made via the sol-gel process (Thomas 1988). The pore size of the dried gels can be varied from less than 30 Å to larger than 100 Å (0.01 micron) depending on fabrication conditions. It is also known that similar highly porous silica material can also be produced from fumed silica products. The pores in this type of porous silica can be 10 or more times smaller than the smallest metal hydride particles. It appears that silica gel is an excellent porous matrix to encapsulate and trap the metal hydride fines. The high porosity of these gels provides many paths for hydrogen gas to reach the encapsulated metal hydride particles. The pore size can also be controlled to screen out impurities other than hydrogen. These possibilities have been studied in an earlier project. Findings of that work have been published (Heung, 1999). The steps to produce encapsulated metal hydride are described below.

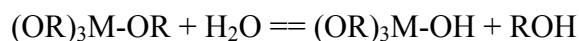
Preparing metal hydride powders

Commercially produced $\text{LaNi}_{4.25}\text{Al}_{0.75}$ in the form of millimeter size particles is first activated by exposing to 5 atm hydrogen gas at room temperature, and then subjected to repeated hydriding and dehydriding. After about 20 cycles, most of the particles will break up to powders small enough to go through a 45 micron sieve. These fresh metal powders must not be exposed to air in a single step because air exposure will cause too much oxidation, rendering the material useless. They must be exposed to air gradually over several days, so that a thin layer of oxide can slowly form on the surface of the metal particles. This thin oxide layer protects the metal particle from further oxidation. The particles are then stable and can be handled in open air. After being sieved through a 45-micron sieve, the metal hydride powders are saved for encapsulation.

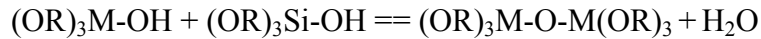
Porous Silica Formation

Porous silica may be produced using a sol-gel process. The process starts with the hydrolysis of an organo metallic compound. The hydrolyzed compound is polymerized via water and alcohol condensation. A dry product is produced after the water and alcohol are removed. Thermal treatment following the drying step is sometimes used to further modify the structure of the final product. The reactions involved are described as follows:

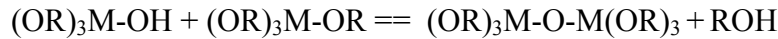
Hydrolysis:



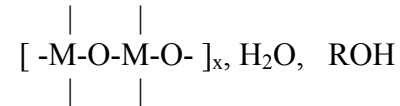
Water condensation:



Alcohol condensation:



Final products:



where M is an element such as Si, Al and Ti, and R is an alkyl group ($-C_xH_{(2x+1)}$).

In addition to the above sol-gel approach, porous silica can also be produced using fumed silica. Commercially available fumed silica is produced by the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen. In the combustion process, molten spheres of silica are formed. The diameters of these spheres are in the order of nanometers. They collide and fuse with one another to form branched, three-dimensional, chain-like aggregates. Fumed silica can polymerize via the hydrolysis process when blended with water, to form a highly porous product.

Encapsulating metal hydride

Metal hydride powders are encapsulated in a porous silica matrix by using two different methods. The first uses a sol-gel to produce the matrix and the second uses fumed silica. Both methods can encapsulate metal hydride particles at ambient or low temperatures, which have no adverse effect on the integrity or properties of the particles.

Sol-Gel Method

The sol-gel method to encapsulate the metal hydride particles involves the following steps. Solution A is prepared by adding ethanol to water while stirring. The ethanol to water ratio is two to five parts water to one part water. The acidity of the solution is adjusted by adding HCl until the pH value is in the range of 1 to 2.5. Solution B is prepared by mixing ethanol into tetraethyl orthosilicate (TEOS) in the ratio of one part ethanol to two parts TEOS. Solution A is added to solution B slowly while stirring continuously to form a sol. To the sol a measured amount of the metal hydride powders prepared earlier is added. The mixture is stirred to keep the metal hydride particles dispersed uniformly throughout the sol. The mixing is maintained until the sol turns into gel and the metal hydride particles become suspended in the gel. The gel is then allowed to mature for several days. When the polymerization is complete, the gel becomes a solid phase submerged in the liquid water and ethanol. The liquid is evaporated at room temperature, followed by evacuation at temperature of up to about 600 °C. After drying, large pieces of silica encapsulated metal hydride are formed. The large pieces are mechanically broken up into granules of 1-5 mm size for testing. Refer to Figure 2 for encapsulation steps.

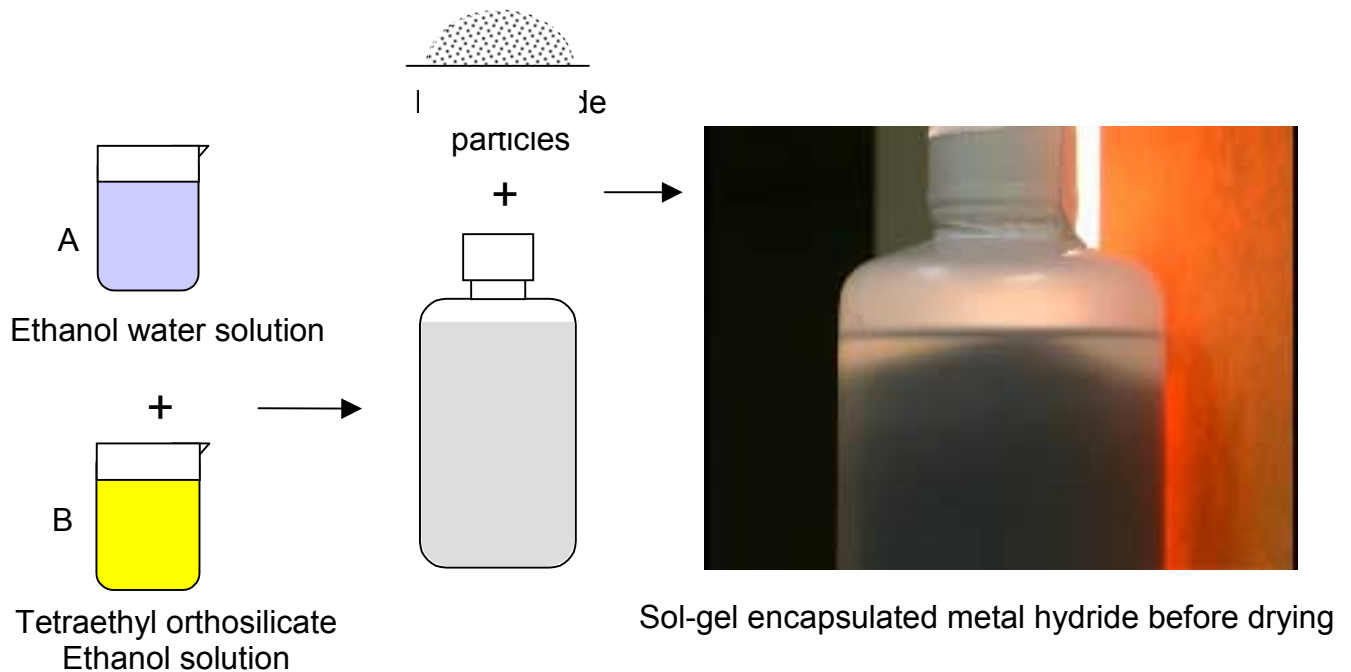


Figure 2. Encapsulation process

Fumed Silica Method

In this method, commercially available CAB-O-SIL[®] fumed silica from Cabot Corporation is used to embed the metal hydride particles. The fumed silica, in the form of a light and fluffy powder, is added and blended into water a little at a time. A water-like sol is formed. The mole ratio of water to fumed silica is between 10 to 30. While stirring continuously, a measured amount of metal hydride powders is added, also in small steps. In the end, a uniform, thick, watery mixture is formed. The mixture is poured quickly into a tray and spread out to solidify. The solid is dried in air and then broken into granules of 1-5 mm size for testing.

Hydrogen Separation Test

The encapsulated metal hydride as shown in Figure 3 will be tested for hydrogen separation from synthetic gas mixtures in a small laboratory scale.

A small test column and a gas manifold have been fabricated and installed for the testing. The column is a U-shape stainless steel tube, 3/4" diameter and 6" long. The manifold is built from 1/8" stainless steel tubing to minimize the gas holdup of the system. The feed mixture will be synthesized by metering the component gas with mass flow controllers. The gas mixture, after passing through the column, will be sampled with thermal conductivity device. See Figures 4 and 5. A breakthrough in hydrogen concentration will be detected when the column is saturated with hydrogen. The synthetic feeds planned for the tests include mixtures of hydrogen, nitrogen, methane, carbon monoxide and moisture. The performance of the material will be evaluated on the amount of hydrogen it can remove in each cycle under different conditions that include feed

composition, flow rate and number of cycles. Initial test is expected to begin in about two months.



Figure 3. Silica encapsulated metal hydride



Figure 4. Separation test column



Figure 5. Separation test manifold

Acknowledgments

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