



Application of surface-modified metal hydrides for hydrogen separation from gas mixtures containing carbon dioxide and monoxide



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ABSTRACT

Application of surface-modified MH material for H_2 separation using temperature/pressure swing absorption–desorption was studied. The substrate alloy had the following composition $LaNi_{3.55}Co_{0.75}Al_{0.4}Mn_{0.3}$, and the surface modification was carried out through fluorination followed by aminosilane functionalization and electroless deposition of Pd. The material was found to have good poisoning tolerance towards surface adsorbates, even for the large (~ 1.5 kg) batches. Feasibility of its application for H_2 separation from gas mixtures (up to 30% CO_2 and 100 ppm CO) was demonstrated by testing of a prototype H_2 separation system (~ 280 g of MH in two reactors), and H_2 separation reactor (0.75 kg of MH). The H_2 separation was characterized by stable performances in the duration of 250 absorption/desorption cycles. However, the total process productivity was found to be limited by the sluggish H_2 absorption (partial H_2 pressure ≤ 2.5 bar, temperature below 100 °C). In the presence of CO_2 and CO, additional deceleration of H_2 absorption was observed at space velocities of the feed gas below 5000 h^{-1} .

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1. Introduction

Selectivity of reversible hydrogen interaction with hydride-forming materials allows for the development of simple and efficient pressure/temperature swing absorption–desorption systems for hydrogen separation from complex gas mixtures and its fine purification [1,2]. However, so far, this approach was successfully implemented only for hydrogen-rich feed gases (vent streams in the ammonia synthesis loop, $H_2 > 50\%$) which contain relatively innocuous admixtures, mainly nitrogen and argon [3,4]. At the same time, the gases associated with processing of coal, petrol, natural gas and other carbonaceous/fossil fuels feedstock, in addition to hydrogen, may contain significant amounts of other components, mainly carbon dioxide and monoxide, which in most cases cause the deterioration of hydrogen sorption performances of metal hydrides (MHs) [5,6].

Earlier the authors reported on the improvement of activation performances and poisoning tolerance of AB_5 -type hydride-forming materials surface-modified by fluorination and/or electroless deposition of metals (including Pd), possessing high catalytic activity towards the dissociative H_2 chemisorptive process [7]. The development of a prototype H_2 separation and purification system based on the advanced MH materials [8] successfully demon-

strated its feasibility for H_2 separation from gas mixtures containing CO_2 and CO.

This investigation presents results of further feasibility studies focused on the integration of the materials in H_2 separation and purification systems. Special attention and care was paid to the upscaling effect in the implementation of MH for H_2 separation.

2. Experimental

Selection of the substrate MH materials and applied operation conditions (pressure, temperature, and feed gas composition) was based upon typical application requirements (processing of a carbonaceous feedstock including desulphurization, steam reforming and water–gas shift reaction). The experimental conditions assumed operation in the temperature range 50–80 °C (selective H_2 absorption at its partial pressure in the mixture up to 2.5 bar) to 200 °C (H_2 desorption at ~ 1 bar).

The substrate material used in this study was an AB_5 -type battery alloy ($A = La$; $B = Ni_{0.71}Co_{0.15}Mn_{0.06}Al_{0.08}$) purchased from Guangzhou Research Institute of Non-Ferrous Metals (China). According to XRD (Bruker AXS D8 Advance, Cu $K\alpha$, $\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5444$ Å, $\lambda_2/\lambda_1 = 0.5$, $2\theta = 10$ – 90°), the material contained single AB_5 phase with lattice parameters $a = 5.06750(7)$ Å, $c = 4.0382(1)$ Å.

The equilibrium hydrogen absorption/desorption performances (PCTs) of the substrate were studied using a PCT Pro–2000 gas

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sorption analyzer (Hy-Energy LLC) in the ranges $T = 50\text{--}200\text{ }^{\circ}\text{C}$ and $P = 0\text{--}50\text{ bar}$. The collected data were further processed by the model of phase equilibria in metal–hydrogen systems [9] facilitating the calculation of the equilibrium hydrogen concentrations in the MH (C) at any given hydrogen pressure (P) and temperature (T). The material was found to have a maximum hydrogen storage capacity of $\sim 6.6\text{ H/AB}_5$ ($175\text{ cm}^3/\text{g STP}$) at $T = 20\text{ }^{\circ}\text{C}$ and $P_{\text{H}_2} = 100\text{ bar}$. The reversible H capacity of the material (absorption at $2.5\text{ bar}/80\text{ }^{\circ}\text{C}$; desorption at $1\text{ bar}/200\text{ }^{\circ}\text{C}$) was determined as $127.5\text{ cm}^3/\text{g STP}$, which is higher than the corresponding value of $89.5\text{ cm}^3/\text{g STP}$ for the previously studied *Mischmetal*-based AB_5 [7].

Surface modification of the AB_5 substrate (powder 200 mesh/ $74\text{ }\mu\text{m}$) was carried out by fluorination, followed by aminosilane functionalization and electroless deposition of Pd, according to the procedure described in [10,11]. Distinct from the previous studies, where small quantities ($\sim 5\text{ g}$) of the sample were prepared, the present work attempted to upscale the surface modification procedure. The design of the surface modification reactors (100 g to 10 kg of the substrate powder per load) was based upon the following considerations: (i) chemical stability towards acidic/alkaline media; (ii) sufficient agitation of the material; and (iii) effective mixing of reagents. Two reactors based on “impeller” (0.1–1.5 kg MH) and “tumble/drum” (1–10 kg MH; see inset in Fig. 1) mixing of the reagents were developed and tested in the course of this activity.

The activation performances of the surface-modified materials were evaluated by measurement of H_2 absorption kinetics ($P_{\text{H}_2} = 5\text{ bar}$; $T = 20\text{ }^{\circ}\text{C}$) in a Sieverts-type volumetric installation, without activation by vacuum heating, after the materials were exposed to air (no less than two weeks) prior to the experiment.

In addition, rates of selective absorption of H_2 (25%) from feed gas, containing up to 30% CO_2 and up to 0.33% CO (balance – N_2 ; gas mixtures of specified compositions supplied by Air Liquide South Africa), were measured. The experiments were carried out in a running flow mode with a space velocity up to $40,000\text{ h}^{-1}$. MH powder ($m \sim 4\text{ g}$) was loaded in a tubular reactor with internal diameter of 10 mm. Activation of the MH sample and determination of amount of H_2 absorbed from the feed gas (C_H) for the specified period of time (t_{MAX}) was carried out using a Sieverts-type volumetric installation attached to the experimental setup. Hydrogen absorption rates, r , in the running-flow mode were estimated using simplified thermal calculations according to formula:

$$r = C_H \frac{\Delta T}{\int_0^{t_{\text{MAX}}} \Delta T dt}, \quad (1)$$

where ΔT is the difference between actual (T) and starting (T_0) sample temperature, t is time.

Despite Eq. (1) is a rough simplification which results in a lagging of the calculated reaction rates behind real ones, for the applied experimental conditions the deviations were found to be quite small (see [Supplementary information](#)). Thus Eq. (1) can be used for the comparison of hydrogenation rates at different feed gas compositions.

Further experimental details can be found in [7].

The first prototype of the experimental H_2 separation system included two running-flow reactors (140 g of the surface-modified MH material per reactor) equipped with electric heaters and air coolers whose operation was synchronized with switching gas flows by motorized valves. The reactors were operated in opposite phases, i.e. H_2 absorption from the feed gas in a cooled reactor with the simultaneous desorption of pure H_2 from the heated reactor.

The second prototype running-flow MH reactor for H_2 separation was made as a stainless steel cylinder; the internal space of the reactor, $\varnothing 45 \times 150\text{ mm}$. The reactor comprised a water-cooled heat exchanger and was filled with 750 g of the surface-modified MH material. Heating of the reactor was carried out by a bracket electric heater.

Both prototypes were tested using a specially designed test rig (supply pressure – 10 bar; output pressure of pure H_2 – 1–1.5 bar; feed gas flow rate – 1–10 L/min; maximum heating temperature – $200\text{ }^{\circ}\text{C}$). The gas composition (mixture input, mixture output, H_2 output) was monitored using a QMC200 mass spectrometer (Stanford Research Systems Inc.) equipped with a capillary for sampling atmospheric pressure gas. The details on design and operation of the H_2 separation system (first prototype) and the test rig are presented in [8].

3. Results and discussion

Express screening of the activation performances of the prepared batches of the surface-modified AB_5 -type material (kinetics of hydrogen absorption at mild conditions, see Fig. 1) showed that

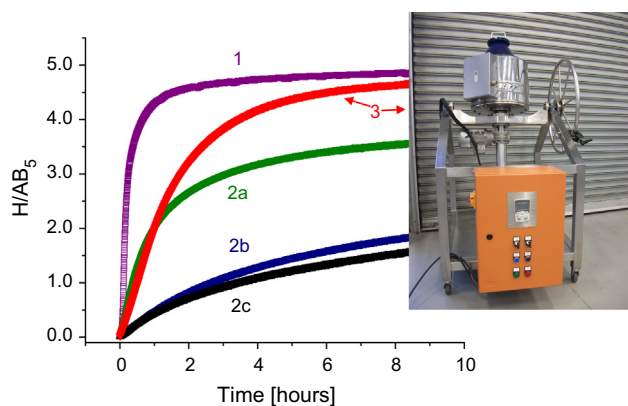


Fig. 1. H absorption in non-activated $\text{La}(\text{Ni},\text{Co},\text{Al},\text{Mn})_5$ (5 bar $\text{H}_2/20\text{ }^{\circ}\text{C}$) surface modified by fluorination – aminosilane functionalization – Pd electroless deposition using various batch sizes of the substrate: (1) Laboratory sample: $m = 5\text{ g}$; (2) “Impeller” mixing: $m = 100\text{ g}$ (a), 300 g (b), and 1 kg (c); and (3) “tumble/drum” mixing: $m = 1.5\text{ kg}$. The inset shows reactor realizing “tumble/drum” mixing (option 3; up to 10 kg MH load).

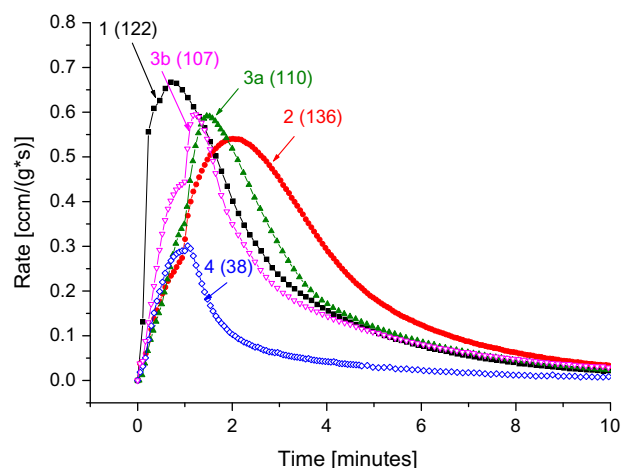


Fig. 2. Dynamics of H_2 absorption by the surface-modified $\text{La}(\text{Ni},\text{Co},\text{Al},\text{Mn})_5$ alloy in running-flow mode at $T_0 = 20\text{ }^{\circ}\text{C}$. The partial H_2 pressure and flow rate are 2 bar and 0.25 L/min, respectively. The values in brackets correspond to maximum hydrogen absorption capacity [$\text{cm}^3/\text{g STP}$]: (1) Pure H_2 ; (2) 25% $\text{H}_2 + 10\% \text{CO}_2 + \text{N}_2$ (balance); (3) 25% $\text{H}_2 + 10\% \text{CO}_2 + 100\text{ ppm CO} + \text{N}_2$ (balance); (a) cycle # 1, and (b) cycle #16; and (4) 25% $\text{H}_2 + 28\% \text{CO}_2 + 0.33\% \text{CO} + \text{N}_2$ (balance).

when increasing the batch size, the hydrogen absorption kinetics deteriorated significantly as compared to the 5 g laboratory sample prepared using magnetic stirring (curve 1). The deterioration was more pronounced for the samples prepared using the “impeller” mixing system (curves 2 a–c), and was associated with insufficient agitation of the alloy powder (density about 8 g/cm³) and the solution used in surface modification (~ 1 g/cm³). Improved results were obtained using the “tumble/drum” mixing system which provided more intensive agitation, which resulted in a uniform distribution of the coating on the surface of the substrate (confirmed by SEM) and subsequent rapid kinetics of hydrogen charging (curve 3), which compared well to the laboratory sample.

Fig. 2 presents the experimental data on selective H₂ absorption by the surface-modified material (from 1.5 kg batch) at room temperature and various feed gas compositions. No significant deterioration of H₂ absorption rate from the feed gas containing up to 10% CO₂ and up to 100 ppm CO was observed. Deterioration occurred only where mixtures containing 0.33% CO and 28% CO₂ (curve 4) were used. The effect of slow reaction rates, in this case, resulted in the decrease of the hydrogen absorption capacity

achieved in 10–15 min to 25–30 cm³/g within 3 cycles, and remained approximately the same in the subsequent cycles. Note that for the unmodified materials hydrogen absorption capacity dropped to almost zero in ~ 5 cycles when operating on feed gas containing ~ 40 ppm CO.

Fig. 3 summarizes test results of the first prototype H₂ separation system. The gas separation process is characterized by ‘stable’ performances when operating on feed gases containing 25% of H₂, up to 30% of CO₂, and up to 100 ppm of CO. Introduction of CO₂ and CO into the feed gas resulted in a slight ($\sim 20\%$) decrease of the average output productivity as compared to that observed upon introduction of the H₂ + N₂ mixture. However, no further decreases in the productivity were observed within the first 500 operation cycles (250 absorption/desorption cycles for each reactor), in the absence of regeneration (re-activation by the vacuum heating). The main impurities in the output hydrogen (MS analysis) when operating in the feed gas mixture 25% H₂ + 30% CO₂ + 100 ppm CO + N₂ (balance) were N₂ + CO (estimated concentration about 1%), CO₂ ($\sim 0.5\%$), water vapour ($\sim 0.5\%$) and light hydrocarbons ($\sim 0.3\%$).

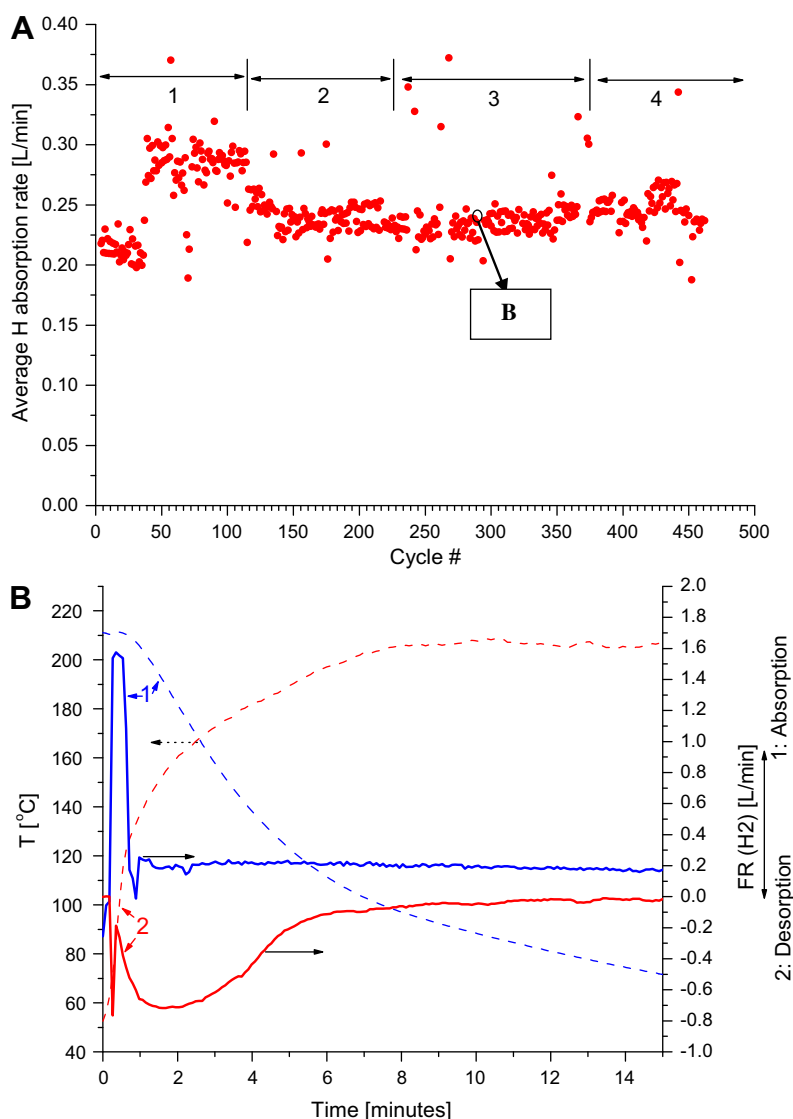


Fig. 3. (A) Average H₂ absorption rates during the operation of the first prototype (H₂ separation system). Feed gas pressure 10 bar, output of pure H₂ at 1 bar. Most of the cycles were carried out at the flow rate of feed gas = 1.5 L/min; deviations of the data from the general trend are mainly caused by the variations of this parameter (1...5 L/min). The ranges 1–4 correspond to the following compositions of the feed gas: (1) 25% H₂ + N₂; (2) 25% H₂ + 10% CO₂ + 100 ppm CO + N₂; (3) 25% H₂ + 20% CO₂ + 100 ppm CO + N₂; and (4) 25% H₂ + 30% CO₂ + 100 ppm CO + N₂. (B) Typical operation cyclogram of the system (cycle # 300).

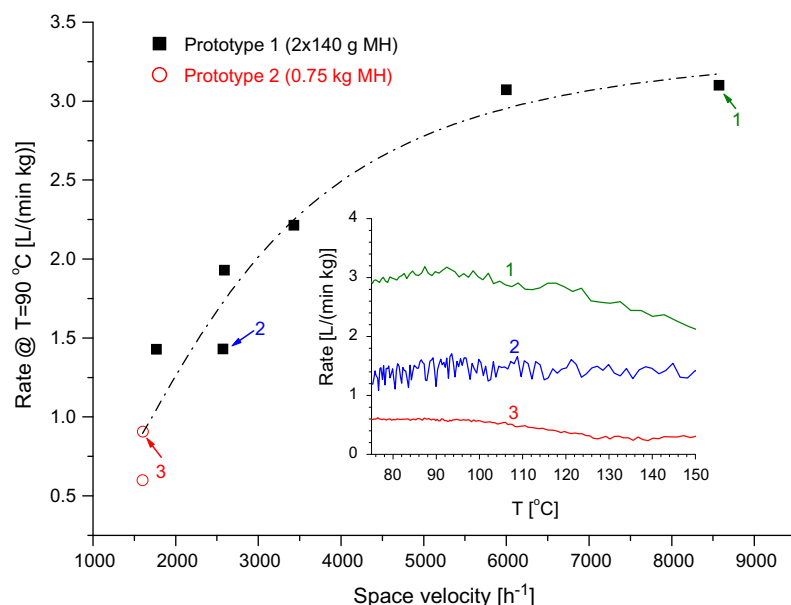


Fig. 4. Dependencies of H_2 absorption rates on the space velocity of the feed gas (25% $H_2 + N_2$). The inset shows typical dependencies of the H_2 absorption rates on the reactor temperature.

At the same time, the average productivity per cycle was only about 0.2 L H_2 /min, and was limited by slow hydrogen absorption in the material (see Fig. 3B). The main origin for this observation seems to be in the limitation of mass transfer in the gas phase at high (75%) total concentration of the impurities in the feed gas and relatively low H_2 partial pressure (2.5 bar), resulting in low driving force of H_2 absorption.

As it can be observed from Fig. 4, summarizing results on H_2 absorption rates at $T = 90^\circ\text{C}$ for the MH H_2 separation system (prototype 1) and the MH H_2 separation reactor (prototype 2), the rate of selective H_2 absorption significantly depends upon the space velocity (v) of the feed gas. When the space velocity decreases below $3000\text{--}5000\text{ h}^{-1}$, the decrease of H_2 absorption rate becomes very pronounced. This finding can be explained by the decrease of H_2 concentration in the proximity to the surface of MH material and the necessity to supply “fresh” volumes of the feed gas with higher H_2 concentration to maintain higher absorption rates. Accordingly, the concentration of active impurities (CO_2 and CO) at low space velocities becomes higher resulting in further deterioration of H absorption performances of the MH material. At $v < 2000\text{ h}^{-1}$ the observed H_2 absorption rate for 25% $H_2 + 30\%$ $CO_2 + 100\text{ ppm CO} + N_2$ mixture was about 60% of the corresponding value for 25% $H_2 + N_2$.

4. Conclusions

The feasibility of the application of AB_5 -type hydride-forming alloy materials surface-modified by fluorination and electroless deposition of Pd, for H_2 separation from gas mixtures (25% H_2 , up to 30% CO_2 and 100 ppm CO), was demonstrated by the testing of prototype H_2 separation system ($\sim 280\text{ g}$ of MH in two reactors), and H_2 separation reactor (0.75 kg of MH). The H_2 separation was characterized by stable performances within 250 absorption/desorption cycles.

At the same time, the total process productivity was found to be limited by the slow selective H_2 absorption under the process conditions. The H_2 absorption was shown to be hindered by mass transfer in the gas phase at space velocities of feed gas below 5000 h^{-1} . Special engineering solutions providing sufficient space

velocities (e.g., by operation in flowing-circulation mode) are thus necessary for efficient application of MH to separate hydrogen from mixtures which contain high ($\times 10\%$) concentrations of accompanying gases.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jallcom.2013.02.096>.

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