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# Interaction between $\text{Li}_2\text{Mg}(\text{NH})_2$ and CO: Effect on the hydrogen storage behavior of the $\text{Li}_4(\text{NH}_2)_3\text{BH}_4$ doped $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ composite

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## ABSTRACT

Metal hydrides have been studied as a promising solution for the hydrogen recovery from gas mixtures of industrial processes. However, scarce information is available about the behavior of amides as hydrogen purification material. In this work, the tolerance against CO, hydrogen sorption kinetics and the thermodynamics of the  $\text{Li}_4(\text{NH}_2)_3\text{BH}_4$  doped  $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$  composite after repetitive dehydrogenation and rehydrogenation cycles with 0.1 mol% of  $\text{CO-H}_2$  mixture were investigated. A progressive degradation of the hydrogen storage capacity of the material and an improvement in the dehydrogenation rate (50%) was observed for the composite after 20 cycles of the CO containing gas mixture. The formation of  $\text{Li}_2\text{CN}_2$  and  $\text{MgO}$ , which are the main responsible for the deterioration of the hydrogen storage properties, was confirmed by Fourier transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRPD). For the first time, the reaction between pure CO and the dehydrogenated product  $\text{Li}_2\text{Mg}(\text{NH})_2$  was demonstrated. This reaction is fast and produces mainly  $\text{Li}_2\text{CN}_2$  and  $\text{MgO}$  as solid products. When a high CO pressure was diluted with  $\text{H}_2$  (mol ratio 1:8), the reactivity of  $\text{Li}_2\text{Mg}(\text{NH})_2$  with CO was notably reduced and mainly  $\text{MgO}$  formation was detected. No clear reaction of CO with  $\text{Mg}(\text{NH}_2)_2$  was detected by FTIR, XRPD and volumetric measurements. Evaluation of the reactivity of CO with  $\text{LiNH}_2\text{-LiH}$ ,  $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$  and  $\text{LiBH}_4$  systems provides the following decreasing ranking of reactivity:  $[\text{NH}]^{2-} > [\text{NH}_2]^- > [\text{BH}_4]^-$ .

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## Introduction

Different processes are used to produce hydrogen, such as steam reforming from hydrocarbons, partial oxidation of methane and coal gasification among others. Unfortunately,

the hydrogen obtained is usually accompanied by other gases, such as  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and CO. Thus, an intermediate step is generally required for its separation and purification in order to obtain high purity hydrogen, both for its storage as well as for its usage in different applications. Within the available options, metal hydrides can be used for hydrogen

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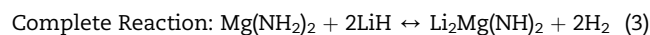
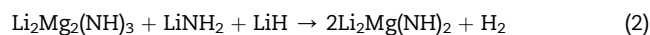
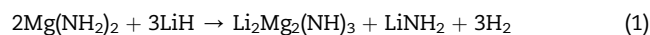
purification due to its capacity to absorb selectively hydrogen from a gas mixture [1,2]. Various studies have been carried out using these materials to purify hydrogen mainly from gas mixtures containing CO impurities. As a general behaviour, it was found that hydride forming alloys severely decrease their hydrogen storage capacity with increasing CO concentration [3–6]. The studies involving hydrogen purification and storage by metal hydrides are mostly related to AB<sub>5</sub>-type materials such as LaNi<sub>5</sub> or modified LaNi<sub>5</sub> by partial substitution (Sn, Co, Mn, Al) [2,6–9]. Han et al. investigated the cyclic stability of the LaNi<sub>5</sub> alloy with hydrogen containing CO as impurity. They found that the CO molecule can be easily adsorbed on the alloy surface, producing poisoning and depressing its hydrogen storage capacity [6]. To avoid or reduce poisoning by CO, several methods have been proposed which involve changes in the alloy composition and/or surface modifications, such as the plating method, the fluorination treatment and oxidation-reduction method [2,7]. Lototsky has shown that AB<sub>5</sub>-type materials modified by surface treatment are feasible candidates for hydrogen separation from a gas containing a CO<sub>2</sub> and CO mixture [7,8]. More recently, the LaNi<sub>4.73</sub>Sn<sub>0.27</sub> alloy has shown a deterioration in the kinetics with cycling in presence of CO (10 and 100 ppm), without loss of hydrogen storage capacity [9]. However, the CO separation ability of the AB<sub>5</sub> is dependent of the temperature and CO concentration in the gas mixture.

On the other hand, there are few studies on hydrogen purification using MgH<sub>2</sub>-based materials. Dehouche et al. showed the effect of CO impurity (110 ppm) on hydrogen storage properties after cycling of the MgH<sub>2</sub>-V composite. Furthermore, the effect of other impurities such as N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> in the same composite was evaluated [3]. The presence of CO as impurity deteriorates the advantageous hydrogen dissociative chemisorption properties of vanadium. The kinetics deterioration and the capacity loss of the composite due to the MgO<sub>x</sub> formation was demonstrated [2].

Moreover, studies of the hydrogen sorption properties of amides as well as their tolerance to cycling using hydrogen-rich gas mixtures with impurities are limited. The CO<sub>2</sub>-H<sub>2</sub> mixture, consisting of 20% CO<sub>2</sub> and 80% H<sub>2</sub> as a product of the steam reforming of natural gas, was used for hydrogen storage in Li<sub>3</sub>N [10,11] and LiNH<sub>2</sub>-Li<sub>3</sub>N [12]. These authors observed that the hydrogen storage properties of the Li-N-H system were unaltered by the presence of CO<sub>2</sub>. Recently, Sun et al. investigated a series of contaminants such as N<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub> [13] and CO [14,15] using 2LiNH<sub>2</sub>-MgH<sub>2</sub> as storage system. These authors reported that the hydrogen desorption properties and the phase structure were unaffected by N<sub>2</sub> and CH<sub>4</sub> impurities. However, when a mixture of O<sub>2</sub> (0.1 mol %)-H<sub>2</sub> was employed, LiNH<sub>2</sub> and MgO were identified on the surface of the material with the consequent irreversible loss in the hydrogen storage capacity. Additionally, the negative effect of CO (1 mol %) impurity on the hydrogen storage properties of 2LiNH<sub>2</sub>-MgH<sub>2</sub> was shown. In fact, a reduction in the dehydrogenation rate and a loss in the storage capacity were noted after 6 cycles. This is mainly due to the formation of Li<sub>2</sub>CN<sub>2</sub> and MgO phases. The authors propose a possible reaction, but no additional investigations to prove this statement were performed.

The Li-Mg-N-H system is considered as a promising material for hydrogen storage. The hydrogen desorption

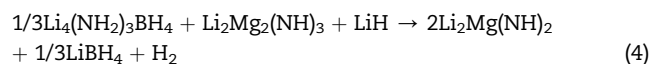
reaction of the Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH composite occurs in two-steps, reactions (1) and (2), with the Li<sub>2</sub>Mg<sub>2</sub>(NH)<sub>3</sub> phase as intermediate. The complete dehydrogenation process leads to the Li<sub>2</sub>Mg(NH)<sub>2</sub> phase, according to reaction (3).



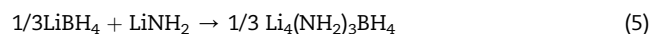
However, this system has some kinetic constraints and for this reason catalysts are required to increase the sorption rates and obtain lower desorption temperatures. Several studies were done using different additives to improve the hydrogen storage properties of the Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH system. Catalysts, such as metal hydrides (CsH, CaH<sub>2</sub>, RbH, KH) [16,17], borohydrides (LiBH<sub>4</sub>, Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub>, Ca(BH<sub>4</sub>)<sub>2</sub>, Mg(BH<sub>4</sub>)<sub>2</sub>) [18–21], halides (CaBr<sub>2</sub>, LiBr, LiI, RbF, KF, TiCl<sub>3</sub>, VCl<sub>3</sub>) [22] and other compounds were employed. These catalysts reduced the activation energy barrier and improved the thermodynamics properties of the system.

In particular, we selected the Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> as dopant of the Li-Mg-N-H system because the presence of Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> improves the hydrogen sorption properties as was evaluated in a previous work of the group [19]. The Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> doped sample increases the dehydrogenation and hydrogenation rates twice and twenty times, respectively, at 200 °C. The function of Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> was catalytic, decreasing the activation energy of hydrogen desorption with respect to the undoped sample.

The role of the additive in the reaction mechanism of the system was shown according to the following reaction [19]:



Then, the LiBH<sub>4</sub> obtained by reaction (4) reacts with LiNH<sub>2</sub> produced by reaction (1) to form Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> again:



Considering the participation of Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> in the dehydrogenation mechanism the difference observed in the PCI curve at 200 °C for LM and LMB sample was explained [19].

In view of the fast sorption kinetics of the Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> doped Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH composite, this material was selected to further studies. The aim of the present work is to analyze the effect of CO as impurity on the dehydrogenation kinetics and hydrogen storage capacity, as well as studying the cycle durability of the Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> doped Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH composite with CO (0.1 mol %) -containing H<sub>2</sub>. Furthermore, the possible interaction mechanisms of the CO molecule with the composite with and without Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub>, during CO (0.1 mol %)-H<sub>2</sub> cycling, are discussed.

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