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Synthesis of a new functionalized surface precursor of lithium–magnesium–urea solid blend ball milled with tracers from ordered-mesoporous-γ-alumina for high-performance hydrogen storage

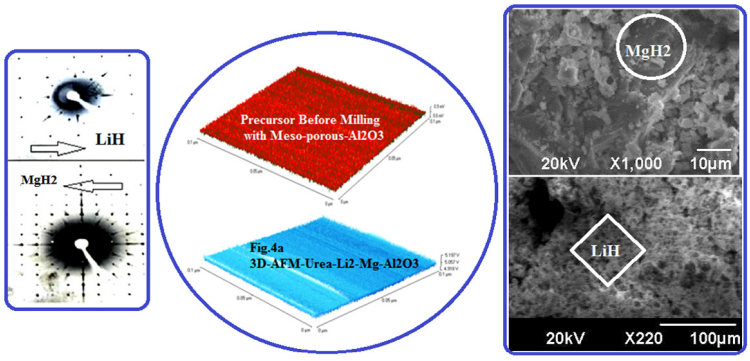
Khaled M. Elsabawy [a,b,*], Ahmed M. Fallatah [b]

[a] Chemistry Department, Materials Unit, Faculty of Science, Tanta University, Tanta, 31725, Egypt
[b] Chemistry Department, Faculty of Science, Nano-Structured Materials Gp., Taif University, 888, Alhawya, Taif City, Saudi Arabia

HIGHLIGHTS

- The present investigations are successfully introduced a new functionalized surface precursor of urea/Li–Mg powders/γ-Al_2O_3 as new potential candidate for hydrogen storage with powerful ultra high H_2-release capacity ~6.91 wt% at 340 °C.
- Hydrogen release capacity was enhanced by eliminating defects and lake of surface area caused by released ammonia bi-products.
- Incorporating of mesoporous-γ-Al_2O_3 trace additions were successful acting as acidic sorbent material for ammonia capture.
- Amidation process (amide forming) via action of urea on Li_2 – Mg-alloy which stabilized on surface's of precursor as M-N-H with releasing protons, accompanied with forming MNH_2 (where M=Li and Mg) exhibits high desorption (H_2-release) capacity of 6.91 wt% at 340 °C which is higher and better than individual Li_2Mg-alloy as hydrogen storage matter.

GRAPHICAL ABSTRACT



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ABSTRACT

A functionalized active surface solid mixtures blend of urea/Li_2 – Mg alloy powders/mesoporous-γ-Al_2O_3 precursor was applied for the first time as a promising material for hydrogen storage. Li_2/Mg-alloy powders were interfacially formed amide which stabilize on the surface as M-N-H with releasing proton under action of urea at desorption temperatures. For eliminating lake of surface area caused by released ammonia bi-product, ordered mesoporous-γ-Al_2O_3 was added in tracers to act as acidic sorbent material at higher temperatures for ammonia capture. Generally, hydrogen release from this system

* Corresponding author at: Chemistry Department, Materials Unit, Faculty of Science, Tanta University, Tanta 31725, Egypt.
E-mail addresses: khaledelsabawy@yahoo.com, ksabawy@yahoo.com (K.M. Elsabawy).

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occurred via the deprotonation of the protic N-H moieties by the hydridic metal. So hydrogen release velocities will be enhanced and promoted over produced hydrides by incorporating lithium/Mg ions in the proposed hydrogen storage system. The synthesized precursor was well characterized by both of scanning electron microscope (SEM) and 3D-atomic force microscope (3D-AFM) by additional to X-ray diffraction analyses to prove structure. Pressure-Composition (P-H_2-C) isotherms of desorption for the new precursor urea/Li_2Mg-Alloy/γ-Al_2O_3 were measured giving a promising results with maximum desorption (H_2-released) capacity of 6.91 wt% at 340 °C.

1. Introduction

There are numerous techniques and methodology for storing hydrogen; each method has its own advantages and disadvantages, Züttel [1] reported a typical six main categories for hydrogen storage. The conventional first two techniques are high pressure and liquification at cryogenic temperatures. The rest hydrogen storage techniques are hydrogen generation through chemical reactions processes (chemical storage) and solid-state hydrogen storage techniques.

Since application of magnesium as a relatively high hydrogen storage in the form of non-metallic MgH_2 with capacity of 7.6 wt%.

Many researchers attempted to develop hydrogen storage features as reactivity, capacities and rate of hydrogen release [2–15]. The most common applicable techniques for enhancing H2-storage features as capacity of MgH_2 was ball milling with additions of a small amount of transition metal powders as (Ti, V, Mn, Fe, Ni, Nb, Pd, etc., and their oxides or fluorides) and ball-milled cycles for appropriate time periods. It was notified that mechanically milled powders of doped MgH2 exhibits an excellent reactivity towards hydrogen absorption [16–20].

One of applied new approach is contributing of H-sources as amides or imides in the hydrogen release process depending up on advanced model of thermodynamically stabilized metal-N-H [21–26].

Recently, materials with unique mesoporous structure are expected to apply widely as catalyst supports, adsorbents, ceramics, and abrasives. Alumina is good candidate model for those materials. A great deal of recent effort has been devoted to synthesis and tailor mesoporous alumina with a high specific surface area and large pore volume by using various templates, including surfactants [27–33].

The main target of present investigations are introducing a solid mixture blend of urea/Li–Mg powders/mesoporous-γ-Al_2O_3 precursor with an active surface centers as a new potential candidate for hydrogen storage anticipating by its powerful ultra high capacity for hydrogen release depending on interfacial M–N–H formation. γ-Al_2O_3 additions act as acidic sorbent material at higher temperatures for NH_3 capture.

2. Experimental procedures

The kinetic investigations were performed via fully automated Sievert-type Apparatus. The curves of pressure composition isotherm (PCI) were performed inside gas reaction controller (GRC) with two PCI modes PCI desorption Mode (PCId) and PCI Absorption Mode (PCIa).

2.1. Synthesis and characterization of precursor

New precursor consists of 5 gm of urea (99% Sigma-Aldrich), 5 gm of Li–Mg alloy powders (supplied from Metallurgy Central lab-MCL-Egypt with purity of ∼98%) were ball milled with 0.25 gm of well characterized mesoporous-nano-γ-alumina with molar ratios (20:1).

The weight ratios was (ball-to-powder weight ratio = 50:1). The powder was ball milled in argon atmosphere by a (Retsch PM100 planetary mill for 24 h at 200 rounds min^{-1}).

The synthesis of urea precursor was divided into three steps, the first one is mixing of urea and Li–Mg alloy by ratios (1:1) and grinding till complete homogeneity, while the second step is addition of meso porous alumina and milling as mentioned above, finally the third step is activation process by gentil heating (+2° /3 min) till 50 °C and fixation step for 25 min.

The components of the synthesized precursor system was characterized via X-ray diffraction (XRD) measurements which carried out at room temperature on the ground samples using Cu-K_α radiation source and a computerized Shimadzu (Japan) diffractometer with two theta scan technique. High-resolution Atomic Force microscopy (AFM) (Veeco-di Innova Model-2009-AFM-USA) and Scanning Electron Microscopy (SEM-Philips-USA) were applied on powders for testing morphological features including grain sizes and topological map using a computerized elemental analyzer unit.

2.2. Surface area calculations (BET) of γ-alumina

Brunauer–Emmet–Teller (BET) specific surface areas (SSA) were obtained with an automatic system (Model 2200A, Micro-meritics Instrument Co., Norcross, GA), using nitrogen gas as an adsorbate at liquid nitrogen temperature. The pore size distribution calculated from the desorption branch of the nitrogen isotherm by the BJH (Barrett–Joyner–Halenda) model.

2.3. Characterization of ordered mesoporous-nano-γ-alumina

The structure of the applied γ-alumina was carefully investigated via BET-calculations measurements, XRD, SEM and 3D-AFM.

The BET surface area of γ-alumina was measured and found ∼342 m^2 g^{-1} with average pore diameter of ∼13 nm according to BJH (Barrett–Joyner–Halenda) desorption model which is fully consistent with literatures [27,28,30].

SE-micrographs Fig. 1(a,b) confirmed that the applied gamma-alumina is an ordered mesoporous spheres as clear in Fig. 1(a) with grains sizes averaged in between 1.43 and 3.9 μm.

The analyses of most intense reflection peaks of XRD pattern measured for the applied gamma-alumina as shown in Fig. 1(c) indicated that the crystalline structure of the applied γ-alumina is mainly belongs to a single cubic phase with *Fd-3m* space group.

Fig. 1(d) shows 2D- and 3D-AFM images captured for mesoporous alumina which indicated that, the synthesized alumina is a homogeneous mixture and arranged in a regular arrays without violation with minimum heights average of 1.61 μm and maximum of 2.43 μm respectively.

An AFM-grain size analyzer indicated that the grains sizes were in average of 1.56–4.32 μm which is fully consistent with those data estimated from SEM analyses mentioned before.