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Al–Ga doped nanostructured carbon as a novel material for hydrogen production in water

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1. Introduction

The availability of cheap energy sources has enabled an extraordinary growth of population, as well as significant improvement in the life standards of a part of the world during the last centuries. However, foreseeable reductions in the availability of fossil energy sources combined with significant environmental issues require to move towards and intensive and efficient use of renewable energies [1]. This is the reason why the interest in H_2 energy increased sharply at the end of the 20th century, boosted by the growing global concerns about emissions of CO₂, main responsible for the current climate change [2]. Hydrogen may be one of the leading contenders as an alternative to current fuels, since it can be cleanly burned instead of conventional fossil fuels, but it can also be electrochemically oxidized in fuel cells to generate electric power with higher efficiencies [3]. Furthermore, it is theoretically appropriate for stationary, mobile and portable applications [4,5]. However, nowadays the development of a H₂ economy seems far to be attained because effective methods for H₂ production, as well as its storage and distribution, are still needed to fulfill expectations [4–6]. For instance, the generation of H₂ from suitable starting materials, such as water, at relatively low temperature is critical [7]. Moreover, up to now none of the alternative studied methods for H₂ storage has reached enough maturity for applications [8,9] since none of them has yet taken all the technical challenges up [5,10].

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ABSTRACT

Production of hydrogen using Al–Ga doped nanostructured carbon in pure water is studied. The XRD and BET techniques were used for sample analyses. Dehydrogenation data of aluminum on the ordered mesoporous carbon were collected at 353 K. In the present work the oxidation rate of activated aluminum and water is investigated depending on eutectic composition and reaction temperature. The H₂ generation rate increases with the rise of temperature. Incorporated Al–Ga–OMC nanocomposite had faster (hydrogen production rate was 112 ml H₂ min⁻¹ g⁻¹) and more efficient (hydrogen production yield was 100%) dehydrogenation kinetics than incorporated Al–OMC nanocomposite and ball-miled active aluminum. @ 2011 Elsevier B.V. All rights reserved.

Hydrogen is recognized as an environment-friendly fuel. A lot of researchers have recently focused their interests on the generation of hydrogen by the hydrolysis of metal or metal hydrides [11–19]. Among these chemicals, Al is a very potential material for hydrogen generation as it is a safe, simple and compact source of high-purity hydrogen. Theoretically, the hydrolysis of 1 g Al produces 1.245 L of H₂, so it is possibly used as hydrogen generator for fuel cells.

However, a passive thin layer of oxide produced on aluminum and aluminum alloys protects surface against further oxidation and corrosion. Some suggestions have been proposed for removing the oxide layer and increasing the activation of aluminum. One is immersing aluminum in alkaline environment such as NaOH; but NaOH is extremely corrosive, corroding apparatus as well [20–23]. The idea of using Al (or Al alloys) as an energy source to obtain H₂ has been evaluated in the last years giving a significant number of publications that have been reviewed recently [24]. The other suggestion is amalgamation, i.e. moistening aluminum surface using mercury or eutectic gallium-indium which are toxic and/or expensive [25]. It is considered that gallium acts on aluminum just as mercury, i.e. it covers its surface by a liquid metal film penetrating the metal and leading to embrittlement of aluminum. Such an action is explained by the effect of adsorptive decrease in solid strength under the physical-chemical influence of medium. As a result, the metal is being destroyed. The considered effect is called the Rebinder's effect.

Another way to facilitate continuous generation of hydrogen is to break particles into smaller particles to increase specific area surface and, consequently, to increase chemical activity of aluminum [26,27]. Recently, carbon materials, in particular carbon nanotubes,

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have been demonstrated to have an excellent catalytic effect on hydrogen storage in metal based alloys by enhancing the hydrogen diffusion in M–C systems [28,29].

In this work, we prepared novel high-specific-surface area Al–Ga modified mesoporous carbon from highly ordered mesoporous carbon host, and demonstrated Al–Ga–OMC system that exhibit ultrafast hydrogenation kinetics with very high capacity.

2. Experimental

2.1. Materials

The reactants used in this study were tetraethoxysilane (TEOS, 98%, Acros) as a silica source, non-ionic oligomeric alkyl-ethylene oxide surfactant (Pluronic 123) as a surfactant, HCl (35 wt%), ethanol and deionized water for synthesis of mesoporous silica (SBA-15), sucrose as a carbon source, sulfuric acid as a catalyst for synthesis of mesoporous carbon, $Al_2(SO_4)_3$ and gallium as fictionalization agents. All chemicals were of analytical grade from Merck.

2.2. Nanomaterials preparation

2.2.1. Mesoporous silica and unmodified mesoporous carbon samples

SBA-15 silica was prepared according to the procedure reported by Zhao et al. [30] by using a non-ionic oligomeric alkyl-ethylene oxide surfactant (Pluronic 123) as a structure directing agent, after that template removal by means of calcinations at 773 K in flowing air. Ordered porous carbon was synthesized via a two step impregnation of the mesopores of SBA-15 with a solution of sucrose using an incipient wetness method [31]. Briefly, 1.0 g of the as-prepared SBA-15 was impregnated with an aqueous solution obtained by dissolving 1.1 g of sucrose and 0.14 g of H_2SO_4 in 5.0 g of deionized water. The mixture was then dried at 373 K for 6 h, and subsequently at 433 K for 6 h. The silica sample, containing partially polymerized and carbonized sucrose, was treated again at 373 and 433 K after the addition of 0.65 g of sucrose, 90 mg of H_2SO_4 and 5.0 g of deionized water. The sucrose-silica composite was then heated at 1173 K for 4 h under nitrogen to complete the carbonization. The silica template-free carbon product thus obtained was filtered, washed with deionized water and ethanol, and dried.

2.2.2. Aluminum modified mesoporous carbon

Aluminum was loaded on mesoporous carbon surface according to the procedure reported by Oh and Park [32]. The mesoporous carbon was heated first at 773 K for burn-off, then physically activated with water vapor in 1323 K. For treatment, $Al_2(SO_4)_3$ used as received. For pretreatment with acid, 5 g of activated carbon was dipped into 100 mL of 0.01 M phosphoric acid solution and stirred for 24 h at room temperature. Air and bubbles in the solutions were removed under a pressure of ca. 1.33 Pa for 20 min, and then the solution was discarded. The samples were dried at 383 K for 48 h in an air atmosphere. For metal treatment, 5 g of activated carbons were dipped into 100 mL of 0.05–0.1 M aqueous aluminum sulfate and stirred for 12 h at room temperature. After removal of the liquid, samples treated with aluminum were dried completely in an oven.

2.2.3. Aluminum-gallium alloy preparation

Alloys in amounts of up to 1 g were melted in glassy graphite crucibles under a layer of a fluxing agent consisting of cryolite with additives of calcium and aluminum fluorides in a gradientless tubular furnace [33]. The starting mixture containing Al–OMC of reagent grade and gallium was heated to 1173 K under N₂ gas flow (10 ml/min) and kept at this temperature for 15 min, after which the crucible was rapidly (3–5 min) cooled to 303–313 K under an inert atmosphere. After cooling, a weighed sample of the alloy (0.1–0.2 g) was treated with distilled water in a temperature-controlled flask attached to a gas burette graduated in 0.1 mL increments.

2.2.4. Textural and structural studies

The porous structure of the surface modified samples was estimated by powder XRD (Philips 1830 diffractometer) using graphite monochromated Cu K α radiation. Adsorption isotherms of the mesoporous carbon samples were obtained using a N₂ gas microporosimeter (micromeritics model ASAP 2010 sorptometer) at 77 K. Pore size distribution and specific surface area were calculated by Dollimore–Heal [34] and BET [35] methods. Pore volume was estimated from the amount of adsorbed N₂ gas at 0.963 in relative pressure, which derives from 25 nm radii pores. Micropore volume was calculated by *t*-plot.

2.3. H₂ measurement

The kinetics of interactions between aluminum and water was investigated by a volumetric method. The measurements of hydrogen volumes at room temperature were accomplished with tenfold stoichiometric surplus of water to minimize the influence of the temperature factor. To carry out the reaction at a high temperature, the reactor was located in water bath. To quantify the evolving hydrogen



Fig. 1. Adsorption-desorption isotherms of nitrogen at $77\,\mathrm{K}$ on OMC and Al–Ga–OMC.

the measuring experimental set-up was used. It consisted of a temperature controlled glass reactor connected with a water-filled burette for hydrogen collection. The aluminum powder (0.07–0.4g) was added in a glass reactor (100 cm³) with water (50 ml) heated to a predetermined temperature. Hydrogen evolving reaction started when aluminum powder came into contact with water. Hydrogen was cooled to the ambient temperature by bubbling through water in a filled burette. Evolving hydrogen was collected in a water burette to measure the quantity of hydrogen.

3. Results and discussion

3.1. Textural characterization

Pore textural properties of the pure ordered mesoporous carbon and aluminum–gallium modified mesoporous carbon were calculated from the nitrogen adsorption and desorption isotherms shown in Fig. 1., it can be seen that after modification the obtained carbons still have type IV isotherms, indicating that mesoporosity is still preserved. However, the modification leads to a decrease in the total uptake of the mesoporous carbon, which reflects the decrease of the total pore volume resulting from Al–Ga alloy modifications. Interestingly, the modified nanoporous carbon essentially keeps the bimodal pore size distribution, which is characteristic of the parent mesoporous carbon. The textural parameters of porous materials listed in Table 1 clearly confirm the structural changes of OMC to Al–Ga–OMC. Especially, the variations of the surface area and pore volume are significant by Al–Ga alloy loading.

In order to check the structural degradation, XRD data of carbonaceous samples were obtained on Philips 1830 diffractometer using Cu K α radiation of wavelength 0.154 nm. Fig. 2 reports low angle XRD patterns of the parent mesoporous silica and of samples OMC and Al–Ga–OMC. With SBA-15, three well-resolved peaks are observed, corresponding to the (100), (110) and (200) reflections typical of the 2D hexagonal space group *p*6*mm*. With all replicas, the main reflection peak is well maintained, indicating that rather ordered mesoporous materials with hexagonal structures were obtained. With respect to the parent silica, a shift of the d100 peak towards higher 2 θ values is observed, in agreement with the literature [30].

Fable 1	
Fextural parameters of the OMC and Al-Ga-OMC employed in this study.	

Adsorbent	d spacing (nm)	$A_{\rm BET} ({ m m}^2{ m g}^{-1})$	$V_{\rm p}~({\rm cm^3~g^{-1}})$
OMC	3.7	1530	0.73
Al-Ga-OMC	3.43	1362.4	0.58



Fig. 2. Low angle XRD patterns of the parent SBA-15 and of carbonaceous mesoporous adsorbents (OMC and Al-Ga-OMC).



Fig. 3. Effect of Al quantity on maximum rate of H₂ production.

3.2. Hydrogen production study

3.2.1. Effect of Al mass

The relationship of the H₂ release and the added Al–Ga–OMC sample quantity was studied added Al–Ga–OMC mass in the reactor between 0.07 and 0.4 g. As the Al–Ga–OMC quantity increased, the hydrolysis rate became faster (Fig. 3). Concretely, the maximum H₂ reaction rate followed a linear relationship with the initially added Al–Ga–OMC mass. The highest H₂ production rate obtained in this set of experiments has been ca. 112 ml min⁻¹ g⁻¹ Al powder with a 100% yield. A comparison of these results with other results found in the literature showed that H₂ production rate using Al–Ga–OMC is much higher than the other similar systems.

3.2.2. Effect of temperature

The effect of temperature on the reaction rate was also examined. Prior and also during to the experiments, Al–Ga–OMC containing solutions were initially heated to selected temperatures between 293 K and 353 K and the results has been showed



Fig. 4. Temprature effect on H₂ generation rate by Al–Ga–OMC.

Table 2

Exprimental results of hydrogen production yield and rate.

Experiment name	Yield (%)	Stop time (min)	Maximum rate (ml H ₂ min ⁻¹ gr ⁻¹)	Reference
Al-OMC	95	20	97	Current work
Al-Ga-OMC	100	20	112	Current work
Bal-miled activate Al	100	40	75	[37]

in Fig. 4. Once the desired temperature was attained, the experiment was fulfilled by adding 0.4g of Al–Ga–OMC to the heated samples. As expected, the H₂ generation rate increases with the rise of temperature (Fig. 4). To quantify this effect, we calculated the activation energy of H₂ generation by means of an Arrhenius plot by using the rate constant k from the maximum H₂ flow rates obtained at different temperatures. Activation energy was found to be 93.6 kJ mol⁻¹ (standard error with 95% confidence interval), which is clearly higher than 40 kJ mol⁻¹, so that the process is controlled by a chemical step rather than by mass transfer.

3.2.3. Effect of Al composition

The concurrence of best composition with aluminum could enhance hydrogen generation rates and prevent aluminum surface passivation [36]. Thus, Al–Ga–OMC alloy was tested in order to study variations in hydrogen evolution rates and yields. Al–Ga–OMC, Al–OMC and activated ball-miled Al [36] experiments were performed using a mixture of approximately 0.4g of which one of Al powders. The obtained hydrogen production curves are compared in Table 2. The best yield and the faster maximum rate were achieved using Al–Ga–OMC alloy powder. Concretely, Al–Ga–OMC system exhibits ultrafast hydrogenation kinetics (gallium catalytic effect) with very high capacity (mesoporous carbon high surface area and loading capacity).

4. Conclusions

In summary, in this work the behavior of incorporated Al–Ga–OMC and Al–OMC nanocomposites and also ball-miled active aluminum corrosion has been investigated. Preliminary experiments with water showed a synergistic effect of base Al mass and temperature to increase hydrogen production rate. Besides, it has been observed that transition metals significantly enhance the hydrogen kinetics while mesoporous structure remarkably increases the capacity.

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