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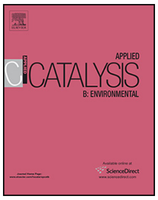

Supported Co catalysts prepared as thin films by magnetron sputtering for sodium borohydride and ammonia borane hydrolysis

M. Paladini, G.M. Arzac*, V. Godinho, M.C. Jiménez De Haro, A. Fernández

Instituto de Ciencia de Materiales de Sevilla, CSIC-Univ. Sevilla, Américo Vespucio 49, Isla de la Cartuja, Seville, Spain

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ABSTRACT

Supported Co catalysts were prepared for sodium borohydride and ammonia borane hydrolysis by magnetron sputtering for the first time under different conditions. Ni foam was selected as support. Deposition conditions (time, pressure, and power) were varied to improve catalytic activity. A decrease in deposition power from 200 to 50 W, leads to a decrease in crystallite and column size and a higher activity of catalysts. The increase in deposition pressure from 1.5×10^{-2} to 4.5×10^{-2} mbar produces same effect but in this case the enhancement in activity is higher because amorphous materials were obtained. The highest activity for SB hydrolysis was 2650 ml min^{-1} $g_{cat}{}^{-1}$ for the 50 W Co 4.5 (4 h) sample ($E_a = 60 \pm 2$ kJ mol^{-1}). For AB hydrolysis activity for the 50 W Co 3.2 (4 h) sample was similar. Durability of the thin films was tested for both reactions upon cycling (14 cycles). Diluted acid washing was effective to recover the activity for sodium borohydride reaction but not for ammonia borane hydrolysis. The strong Co–NH_3 interactions explain the non-efficiency of the acid washing.

1. Introduction

Nowadays, hydrogen is considered as a potential future energy carrier owing to its high energy content, renewability and non-polluting energy release (reaction with oxygen produces water as only by-product). However, one bottleneck for the development of a hydrogen economy is the issue of hydrogen storage. Over the last decade hydrolysis of chemical hydrogen storage materials such as sodium borohydride (SB) and ammonia borane (AB) have proven to be an efficient approach for hydrogen generation [1–4]. Both hydrides are stable in dry air and easy to handle and combine low molecular weight (37.8 and 30.7 g mol^{-1} for SB and AB, respectively) with high gravimetric hydrogen content, making them very attractive. Catalyzed sodium borohydride and ammonia borane hydrolysis are safe exothermic reactions that produce hydrogen according to (1) and (2), respectively [1–4].

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 \quad (1)$$

$$NH_3BH_3 + 2H_2O \rightarrow NH_4{}^+ + BO_2{}^- + 3H_2 \quad (2)$$

Both spontaneous reactions are slow and need catalysts to occur at appreciable rates. One of the main obstacles for the practical application of the catalytic hydrolysis of these (SB and AB) chemical hydrogen storage materials is the need to develop efficient, economical and durable catalysts to accelerate reactions (1) and (2) [1–4]. Co based catalysts have demonstrated in the past decade to be the most advantageous and cost effective for reaction (1) [1–3,5–7] and also for reaction (2) [4–7].

From a technological and operational point of view, i.e. system and reactor design, it is highly desirable to have Co catalysts in a supported form [2,3]. Supported catalysts do not aggregate as powder catalysts and can be recovered from the reaction medium, to be reused in multi-use applications. Traditionally, Co supported catalysts have been mainly prepared by the impregnation-chemical reduction method [1–14]. In most cases, sodium borohydride is employed as reducing agent leading to the formation of Co–B materials [15–18].

Electrodeposition has also been presented as a convenient method for scale-up the production of supported Co catalysts [19,20]. However for non-conducting substrates an intermediate step for the deposition of a conductive layer is need.

Pulsed laser deposition is a PVD (physical vapor deposition) technique that has been employed for the preparation of catalysts for SB and AB hydrolysis. Co–B thin films and more recently, Co nanoparticles on a B film have been prepared by this method [21–24]. This technique allows to deposit high density granular films of different roughness with the target stoichiometry [21–25].

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* Corresponding author. Tel.: +34 954489552; fax: +34 954460665.
E-mail address: gisela@icmse.csic.es (G.M. Arzac).

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Magnetron sputtering is a PVD technique that allows the deposition of thin films with precise controlled thickness over a wide variety of substrates due to the low deposition temperature of the process. It can be easily scaled to industrial processes and is a low cost process without the need of precursors avoiding emissions of toxic by-products. The control of the deposition conditions allows controlling the microstructure of the coatings and sputtering conditions can be readily reproduced from run-to-run. This technique has proven before to be a versatile tool to prepare nanostructured and porous materials in our group [26–28]. To our knowledge, magnetron sputtering has not been reported as preparation technique for supported Co catalysts for sodium borohydride or ammonia borane hydrolysis before [29].

In this paper, Ni foam supported nanostructured Co coatings (Co/Ni foam) were prepared as thin films by magnetron sputtering in a wide range of conditions as catalysts for reactions (1) and (2). As a proof of concept, PTFE membranes were also used as thin film support.

Catalytic activity of the Co/Ni foam materials was tested for reactions (1) and (2) in 4.5 wt% NaOH and pure water, respectively. Activity is correlated to deposition conditions, crystallinity and nanostructure. Durability was also tested for both reactions upon cycling (14 cycles) and compared. A reactivation step consisting in dilute acid washing was also employed and the results discussed.

2. Experimental

2.1. Catalysts preparation

To investigate the influence of the different deposition parameters on the activity of the supported catalyst, Co nanostructured coatings were deposited under different pressure and dc power. Table 1 summarizes the deposition conditions employed.

The coatings were deposited using a 2″ magnetron from AJA in magnetic target configuration, from a pure cobalt target (Kurt J. Lesker 99.95% pure, 1 mm thick) under pure argon atmosphere. The base pressure before deposition was 10^{-6} mbar, and working pressures from 1.5×10^{-2} to 4.5×10^{-2} mbar of Ar were employed to prepare the coatings.

The influence of the deposition power on the microstructure and consequently on activity was investigated by changing the dc power supplied from 50 to 200 W.

The coatings were deposited directly on commercial Ni foam (Goodfellow 1.6 mm thick, 95% porosity, 20 pores cm^{-1}) and PTFE (polytetrafluoroethylene) membranes (Whatman 0.2 μm pore size, polypropylene backed). Before deposition, Ni foam or PTFE membranes were cut into $0.5 \times 0.5\ \text{cm}^2$ pieces and grouped to be used in a small reactor (see Section 2.3). Each group was weighted before and after each deposition to obtain the total mass of catalyst deposited. Depositions times of 2 and 4 h allowed to obtain different catalyst mass under similar deposition conditions.

Ni foam was washed first with ethanol and then with HCl 0.1 M in an ultrasonic bath before each synthesis. No previous treatment was done on PTFE membranes. As a reference for characterization (specially electron microscopy), in each deposition Si (1 0 0) substrates were included. The Si substrates were cleaned with acetone and dried in a nitrogen flow.

Catalysts are named by their deposition/synthesis conditions and the support. As an example, 200 W Co 1.5 (2 h) catalyst is the Ni foam supported catalyst prepared by magnetron sputtering at 200 W power and 1.5×10^{-2} mbar Ar pressure during 2 h. To avoid confusion, Table 1S (included as Supporting information) correlates catalyst name and preparation conditions. In those cases in which the support is different from Ni foam, it will be clearly indicated in the text.

2.2. Catalysts characterization

Scanning electron microscopy (SEM) was performed to study the morphology of the coatings on the different substrates and the thickness of samples deposited on Si (1 0 0) in a high resolution FEG microscope, HITACHI S4800 operating at 2 kV equipped with an EDX detector (Bruker X-Flash 4010). The microstructure of the coatings was investigated by transmission electron microscopy (TEM), performed using a Philips CM 200 microscope with 2.4 Å resolution. Cross-sectional transmission electron microscope (XTEM) specimens were prepared in the conventional way by mechanical polishing followed by Ar^+ ion milling to electron transparency of coatings deposited on Si substrates. Surface topography was investigated by atomic force microscopy (AFM) Nanotec system working in tapping mode, with Si tips of 150 kHz resonant frequency and $20\ \text{N m}^{-1}$ spring constant. 3D surface images of $5 \times 5\ \mu$m were acquired and analyzed with the WSxM free available software from Nanotec [30].

X-ray diffraction measurements were performed using Cu $K\alpha$ radiation in a Siemens D5000 diffractometer in a Bragg-Brentano configuration in the 2θ angle range of 20–90 degrees. The surface chemical composition of the catalyst before and after test was investigated by XPS. XPS spectra were recorded with a Leybold Heraus LH electron spectrometer using Al Ka radiation with 40 eV pass energy at normal emission take off angle. The spectra were calibrated with the position C (1s) (from contamination) signal at 284.9 eV.

2.3. Hydrogen generation (HG) test

Ni foam supported Co catalysts were tested as following: a certain amount of supported catalyst (1–8 mg) was placed at the bottom of a three necked heart-shaped flask. The flask was immersed in a water bath maintained at 23 ± 0.5 °C and connected to a 100 ml gas burette. The reactions (1) and (2) started by injecting 38 mg of SBH dissolved in 1 ml of 4.5 wt% NaOH solution or 40 mg of AB dissolved in 1 ml of MilliQ® water, respectively. The amount of generated hydrogen was measured by reading the displacement of the piston in the gas burette (gas-tight by a mercury o-ring) as a function of time. For AB hydrolysis experiments the produced gas was passed through a flask with 0.1 M H_2SO_4 solution to remove ammonia, before directing to the gas burette. No stirring was used for the experiments, except for the stirring effect of the evolved hydrogen. The HGR (Hydrogen Generation Rate, ml min^{-1}) was obtained from the slope of the plot of the volume of hydrogen evolved vs time in linear regime. Experiments were done in duplicate, and showed to be reproducible. In this paper, catalytic activity (expressed in $\text{ml min}^{-1}\ \text{g}_{\text{cat}}{}^{-1}$) is obtained as the slope from the plot of HGR (ml min^{-1}) as a function of the mass of supported catalyst.

To test durability, the above mentioned tests for reaction (1) and (2) were repeated for 14 times. After each test, catalyst was extracted from the reaction medium and washed with distilled water and ethanol then it was dried under a N_2 flow. When indicated, the used catalyst was washed with 10^{-4} M HCl. This acid washing is intended to eliminate the adsorbed $\text{BO}_2{}^-$ ions which produce catalyst deactivation [20,31]. Catalyst loss was evaluated after each test by weighting.

3. Results and discussion

3.1. The supported catalyst

By choosing the adequate deposition conditions, magnetron sputtered highly columnar coatings, with high surface area to be used as catalysts, can be obtained. Fig. 1 shows the morphology