Nanostructured carbons modified with nickel as potential novel reversible hydrogen storage materials: Effects of nickel particle size

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ABSTRACT

In this study, ordered mesoporous carbons CMK-3 were prepared by a nanocasting method using SBA-15 silica as template and sucrose as carbon source. The pure CMK-3 was modified with nickel by wet impregnation method and the effects on hydrogen storage capacity were studied at different pressures and temperatures. The structural, textural and chemical properties were evaluated in order to investigate their correlation with hydrogen adsorption properties. Also, computational methods (DFT) contributed to the understanding of hydrogen storage interactions in the Ni/C samples.

Two different behaviors on the hydrogen adsorption were obtained after reduction treatment under H_2 atmosphere. For the unreduced samples at 77 K, the textural properties were the determining factor in the H_2 storage capacity. On the other hand, for the reduced samples at room temperatures, the presence of nickel nanoparticles increased the hydrogen adsorption, with a possible dependence of the particle size.

1. Introduction

Since the 1970s, hydrogen has been considered as an attractive energy carrier for the storage of renewable energy [1]. The physical and chemical properties of hydrogen are in many cases unique despite the fact that hydrogen appears to be the simplest element. For on-board use, the issue is the amount of hydrogen that can be safely stored in a vehicle and delivered as required under operational conditions. In addition, hydrogen storage must be reversible at or near room temperature. Thus, the major scientific challenge is to design low-cost, lightweight materials that can reversibly and rapidly store hydrogen near ambient conditions at a density equal to or greater than liquid hydrogen [2]. An interesting alternative is the physisorption, which provides fast adsorption/desorption kinetics and almost instantaneous equilibrium between adsorbed hydrogen and hydrogen in the gas phase. Thus, materials with large surface areas and low densities, such as nanostructured carbons, are attractive for hydrogen storage applications, which is the main bottleneck for the realization of on-board hydrogen fuel cell vehicles. In the last years, numerous synthesis methods have been studied for obtaining porous carbon materials with interesting textural properties. Among them, carbons mesostructured from Korea (CMK) have gained important attention. The high control of the specific surface, significant flexibility in the pore size and structural diversity of ordered mesoporous carbonaceous materials, make them good candidates for diverse applications [3,4]. Moreover, the metal incorporation into carbon materials promotes the presence of active sites, contributing to improve hydrogen storage [5]. The use of noble metals is often economically non-viable. Therefore, recent studies have been geared towards substituting noble with transition metals. Thus, promising results were obtained by means of "spillover" effect by employing various carbon, zeolites, MOFs materials, doped with Pt, Ni, Pd, Ru [5]. Spillover of atomic hydrogen is a well-documented mechanism in heterogeneous catalysis [6,7] however, the details of spillover based hydrogen storage processes have not yet been well understood since it is difficult to obtain direct evidence of the mechanism [8].

Another possible route for improving the hydrogen storage is via Kubas-type interaction [9], due to empty d-orbitals of transition metal centers [10]. The Kubas interaction strength stands midway between hydrides and physisorption in binding strength. Thus, Anbia et al. [11] have studied the effect of mesoporous carbon CMK-3 as support on Pt

catalytic activities, dissociation of hydrogen molecules and enhanced hydrogen absorption on modified MIL-101 (MIL, Matérial Institut Lavoisier) at room temperature. At the same time, Giasafaki et al. [5] have presented a significant enhancement of the hydrogen storage capacity upon (Pd) metal-doping at room temperature. Meanwhile, Huang et al. [12] have found that cobalt-embedded ordered mesoporous carbon (OMC) materials present higher hydrogen adsorption capacity than the OMC pure, due to the Kubas-type interaction between Co and H_2. Also, the hydrogen spillover effect might occur in parallel. Among transition metals for enhancing hydrogen storage capacity, nickel is particularly promising because it is abundant, inexpensive compared to other metals, and is able to enhance hydrogen storage properties. Juárez et al. [13] studied the introduction of Ni into CMK-1, displaying improved results in hydrogen at 77 K and high pressure (10 bars) that at low pressure.

Despite the different properties of these materials that can influence the storage capacity, like specific area, composition and pore size, it is necessary to understand the mechanism of hydrogen uptake to improve these materials for hydrogen storage. Several authors have attributed to the enhance of hydrogen storage capacity of different carbon materials to a spillover effect. However, spillover effect remains controversial, and understanding and more information about this phenomenon are still needed [14].

Thereby, in previous reports [15], we have shown the hydrogen adsorption behavior at 77 K and ambient temperature of Ni/SiO_2 system indicated a different mechanism of sorption at those temperatures. In addition, Density Functional Theory (DFT) calculations showed that the spillover effect was energetically unfavorable. Thus, we considered a possible hydride formation at room temperature.

In this sense, this work aims to examine hydrogen storage capacity of ordered mesoporous carbon CMK-3 modified with nickel. The textural and chemical properties were evaluated and discussed regarding the hydrogen adsorption. Based on DFT calculations, the focus of the work is to find key factors in hydrogen storage to understand the H_2 adsorption mechanism and direct the design of carbon-based hydrogen adsorbents systems.

2. Material and methods

2.1. Synthesis of mesoporous carbon

The synthesis of the ordered mesoporous carbon CMK-3 was carried out using SBA-15 silica as template and sucrose as carbon source, following the synthesis procedure described by Barrera et al. [16]. The synthesis procedure of ordered mesoporous silica SBA-15 is reported by Carraro et al. [17].

The CMK-3 was synthesized via a two-step impregnation of the mesoporous SBA-15, with a solution of sucrose dissolved in sulfuric acid and water in a mass ratio of 1:1.3:0.14:5 (SBA-15:Sucrose:H_2SO_4:H_2O). The mixture was stirred at room temperature for 1 h and then it was dried at 373 K for 6 h and subsequently at 433 K for 6 h. A second impregnation with a mixture of sucrose aqueous solution, sulfuric acid and water with a mass ratio of 0.8:0.09:5 was performed to ensure the template pore filling. This mixture was treated again at the same drying conditions to complete the polymerization step. Then, the resultant dark brown colored composite was heated from room temperature (RT) up to 1173 K for 6 h under a N_2 flow of 180 mL/min with a heating rate of 3 K/min to complete carbonization.

The silica template was dissolved in a 5 wt.% hydrofluoric acid solution at RT for 24 h. The template-free carbon obtained was filtered, washed with deionized water and ethanol (50:50% v/v) until the conductivity value was smaller than 10 μS/cm. Finally, the nanostructured carbon was dried overnight at 353 K.

2.2. Synthesis of Ni/CMK-3 mesoporous carbon

The ordered mesoporous carbon CMK-3 was modified with Ni by wet impregnation method using nickel nitrate (Ni(NO_3)$_2$·$6H_2O$, Merck) as the source of nickel. The mesoporous carbon CMK-3 was mixed with a solution of Ni(NO_3)$_2$·$6H_2O$ in ethanol with a concentration corresponding to the desired metallic loading (2.5 and 10 wt.%) and a rotary evaporator was used to remove excess of ethanol at about 323 K. The solution was held in a flask, which was partially submerged in the water bath, and powered by a motor which slowly rotates the flask for an even heat distribution. The impregnated samples were dried at 333 K overnight and were thermally treated in a N_2 flow (25 mL/min) at 473 K for 5 h. Subsequently, the temperature was increased to 773 K with a heating rate of 4 K/min and kept during 5 more hours. The synthesized samples are denoted as Ni/CMK-3(x), where x indicates the expected metal loading percentage (nominal loading).

2.3. Characterization

The textural characterization was carried out by N_2 adsorption-desorption isotherms at 77 K (N_2 with 99.999% purity) in an ASAP 2000 equipment (Micromeritics Instrument Corporation, USA). Adsorption isotherms were acquired in a scale of relative pressures of p/p_0: from 0.001 to about 0.985 (adsorption branch) and from 0.985 to 0.3 (desorption branch). The total number of adsorption/desorption data points was 105 (adsorption: 68 and desorption 37). Free-space calibration using He and the interval equilibrium time was 25 s. Before the measurements, the samples were degassed at 523 K for 12 h under vacuum. The specific surface area (S_{BET}) was calculated by the Brunauer-Emmett-Teller (BET) method using the adsorption data, in the pressure range of p/p_0: 0.05–0.25, where the conditions of linearity and considerations regarding the method were fulfilled. The total pore volume (V_{TP}) was calculated at a relative pressure of 0.98 [18], and the micropore volume ($V_{μP}$) and primary mesopore volume (V_{MP}) were calculated by αS-plot method using the standard isotherm GCB-1. The pore size distributions of the samples were determined by *QSDFT* method (Quenched Solid State Functional Theory) using the Quantachrome software, with the kernel N_2 at 77 K on carbon, slit/cylindrical pores, adsorption branch.

The samples were also analyzed by X-ray diffraction (XRD) using a PANanalytical Empyrean diffractometer with Cu Kα radiation (λ = 1.5418 Å) in the range of *2θ* from 0.7 to 7° and from 10 to 80°. The scan step was 0.05° with a step time of 8 s for the analysis.

Transmission electron microscopy (TEM) images were collected using a Philips CM200UT transmission electron microscope. Samples were dispersed in ethyl alcohol 99.5% and a drop of the suspension was deposited on a lacey carbon copper grid.

Scanning electron microscopy (SEM) images of the materials were obtained on a SEM-FEG Nova NANO-SEM 230. Gold coverage was applied to make samples conductive. The acceleration voltage was 20 kV.

Fourier Transform Infrared Spectroscopy (FTIR) was measured in a System 2000–Perkin Elmer spectrometer in an optical range of 400–3000 cm^{-1} at a resolution of 4 cm^{-1}.

Temperature-Programmed Reduction (TPR) was performed on a ChemiSorb 2720 apparatus (Micromeritics Instrument Corporation, USA), in a temperature range from room temperature to 1073 K with a heating rate of 10 K/min in a binary gas flow (5 vol % H_2/N_2) of 20 mL/min STP, and the reduction reaction was monitored by the H_2 consumption with a thermal conductivity detector (TCD).

X-ray photoelectron spectra (XPS) were obtained in a VG Microtech ESCA apparatus equipped with an Al anode (Al Kα radiation, 1486.6 eV) and VG100AX spherical analyzer.

Hydrogen adsorption measurements at 77 K and pressures up to 10 bar were performed in a static volumetric system (Micromeritics Instrument Corporation, USA, ASAP, 2050), appropriately calibrated. High-pressure adsorption isotherms of hydrogen were measured at