Functionalized and metal-doped biomass-derived activated carbons for energy storage application

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ABSTRACT

The development of a viable hydrogen storage system is one of the key challenges which must be solved prior to the establishment of a hydrogen economy. One of the envisaged options to store hydrogen is adsorption on high surface area porous materials such as activated carbons (ACs). The aim of the present study is to develop a low cost hydrogen storage material and to improve its uptake capacity at room temperature. First, an activated carbon has been prepared from olive pomace through chemical activation procedure. Then, the carbon surface has been decorated with oxygen functional groups and with metal nanoparticles. A careful textural characterizations show that, in contrast to other gases, oxygenated groups hindered H_2 access to active adsorption sites. Hence acid activation should be avoided for hydrogen adsorbent preparation. While, the insertion of metal nanoparticles improve the H_2 adsorption performance of AC via spillover mechanism at room temperature, unless the metal content and the catalyst preparation method were optimized.

1. Introduction

Hydrogen is a very attractive alternative energy vector for replacing fossil fuel-based economy. The future Hydrogen Economy offers a potential solution to satisfying the global energy requirements while reducing (and eventually eliminating) carbon dioxide and other greenhouse gas emissions and improving energy security. It stores the highest energy per mass and can be produced directly from sunlight. Therefore, hydrogen economy is one of the major initiatives for many countries [1]. In 2003, US President George W. Bush announced a $ 1.2 billion Hydrogen Fuel Initiative to reserve America's growing dependence on foreign oil by developing the technology needed for commercially viable hydrogen-powered fuel cells.

Among many hurdles that face the implementation of hydrogen economy is the hydrogen storage for its transportation and onboard use. Two different storage technologies are conventionally used, i.e. hydrogen gas in high pressure tanks made of steel or composite material, and liquid hydrogen in cryogenic vessels. Both technologies possess severe important drawbacks. Indeed,

hydrogen gas occupies large volumes at room temperature, and high pressures of several hundred bar are necessary to reach high storage capacities. Liquid hydrogen is successfully used for space shuttles propulsion, however the low condensation temperature of about 20 K, the related hydrogen boil-off and the sophisticated isolation technique, which is necessary at these temperatures, are big disadvantages for vehicles. In addition the energy required for liquefaction corresponds to more than 30% of the energy content of hydrogen [2].

Adsorptive storage on nanoporous materials is a rapidly maturing alternative hydrogen storage technology that offers comparable storage densities at much lower pressures compared to compressed composite tanks. Hydrogen molecules are simply trapped in the voids called "micropores" thanks to the Van der Waals forces and they are released by a depression. This technique guarantees a rapid kinetic and a full reversibility which are of major concern for mobile hydrogen storage. Therefore, a lot of attention has been focused during last few decades on developing microporous adsorbents for automotive hydrogen storage application. These include, metal organic frameworks (MOFs) [3],[4], zeolites [5], and carbon-based materials [6]. In particular, carbon-based materials seem to be more advantageous than the structured crystallographic adsorbents MOFs and zeolites in terms of low cost, good chemical, and thermos-mechanical stability, easier

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regeneration, low densities, and wide diversity of bulk and pore structure.

However, the maximum obtained isosteric heat of adsorption on carbons was only 6 kJmol^{-1} [7] due to the weak Van de Waals dispersive energy. This value is well below the 20–30 kJ mol^{-1} fixed by the US Department of Energy (DOE) as a goal for hydrogen storage systems to be used for automotive applications. Hence, typically temperatures of about 80 K are necessary to reach high storage capacities in physisorption. In contrast, room temperature hydrogen storage technologies are more desirable in vehicles. Thus, one should explore other mechanisms improving H$_2$ storage capacity of porous materials.

A way for increasing hydrogen storage capacity at ambient conditions is by adding transition metals (TM) atoms to carbon structures, thus obtaining composite materials that combine physical and chemical adsorption processes. This activation may be explained through the spillover mechanism which involves the dissociative chemisorptions of H$_2$ molecules on TM particles and the migration of the resulting H atoms to remote surface sites, otherwise inaccessible to molecular hydrogen. Hydrogen spillover was first used to describe the improvement in hydrogen storage materials by Leuking and Yang [8]. They found that the residual NiMgO catalyst used in the production of multi walled carbon nanotubes (MWCNTs) also acted as a spillover source. Consequently these MWCNTs had a higher hydrogen uptake than those which had the catalyst completely removed by acid reflux. Importantly it was also noted that the process was reversible at moderate temperatures giving a distinct advantage over metal hydrides and cryogenic porous materials. In general, the process of hydrogen spillover involves three primary steps: (i) chemisorptive dissociation of gaseous hydrogen molecules on a transition metal catalyst; (ii) migration of hydrogen atoms from the catalyst to the substrate; and (iii) diffusion of hydrogen atoms onto substrate surfaces [9–11].

All these favorable observations have encouraged several experimental investigations, which are grouped in Table 1 with a particular focus on activated carbon metal doping.

Oxygen is by far the most conventional heteroelement present on carbon surface. It is spontaneously present, even at room temperature, and forms different types of organic functionalities, regardless of the nature of the carbon. Oxygen groups modify the polarity of carbon surface and therefore might affect its interaction with hydrogen molecules. Published theoretical and experimental studies concerning the effect of oxygen functional groups on hydrogen storage capacities are contradictory. Agarwal et al. [23] reported that hydrogen storage capacity increased with the amount of acidic groups present on carbon surface. Bleda-Martinez et al. [24] studied the importance of dangling carbon bonds in hydrogen adsorption, and concluded that unsaturated oxygen sites

were responsible of high hydrogen uptakes. Huang et al. [25] evaluated the textural characteristics of ACs before and after an oxidation

process, and found that hydrogen capacity was lowered when the amount of oxygen-containing functional groups increased. Zhao et al. [26] showed that the presence of functional groups has a negative effect on hydrogen adsorption on activated carbons due to repulsive interactions between hydrogen molecules and functional groups. Therefore, the effect of oxygen content on hydrogen storage capacity is still debated and, most of times, it is difficult to separate the combined effects of surface area and surface chemistry.

In the present study we examined the effect of the introduction of metal nanoparticles as well as the addiction of oxygen functional groups; on the strength of the interaction hydrogen-carbon surface.

To achieve these goals a typical Mediterranean biomass residue was used to prepare a chemically activated carbon. Subsequently, it surface was altered with insertion of oxygen functional groups via simple HNO$_3$ wet oxidation. In parallel, we inserted Pd, Pt, Ni, Cu, Co and Ag nanoparticles at different preparation stage and at different contents. The raw and modified carbons were characterized using different sophisticated techniques such as: N$_2$ and CO$_2$ sorption analyses, TPD-MS, XRD, and TEM. Finally, their H$_2$ storage performance was measured using three volumetric devices in three international laboratories for insuring high reproducibility.

2. Materials and methods

2.1. Activated carbons preparation

The plain activated carbon was prepared from olive pomace. First, the raw precursor was washed abundantly with hot distilled water to obtain grains of olive stones sized to about 1–3 mm. Then, dried olive stones were activated through chemical process using the orthophosphoric acid as activating agent. The preparation protocol was optimized by Gharib and Ouederni [27]. The obtained sample was granular and labeled as **AC**.

Wet oxidation about 30 g of AC was mixed with 250 mL of 1 M nitric acid aqueous solution under a reflux at boiling for 36 h. The resulting materials were filtered and extensively washed with distilled water until the cleaning water pH was approximately 7. The sample so prepared was nominated as **AC-ox**.

Metal decoration The plain sample **AC** was doped with noble metals (Pd, Pt) and with transition metals (Ni, Cu, Co, Ag). For Pd and Pt-doped samples the decoration procedure was the classical excess wet impregnation method. Thus, a mass of **AC** was dispersed in acetone solution containing either Pd acetyl acetonate Pd(C$_5$H$_7$O$_2$)$_2$ or Pt acetyl acetonate Pt(C$_5$H$_7$O$_2$)$_2$, and left on a rotary evaporator for 24 h at 50 °C. After filtration the impregnated carbon

Table 1
Spillover hydrogen uptake enhancements for a wide range of doped activated carbon materials.

Support	Catalyst	T(K)	P(MPa)	Uptake without dopant	Uptake with dopant	Enhancement	References
AX-21(AC)	10wt%Pd	298	10	0.6 wt%	1.8 wt%	3	[12]
AX-21(AC)	5.6wt%Pt	298	10	0.6 wt%	1.2 wt%	2	[13]
AC (1200m^2/g)	3wt%Pt	298	10	0.3 wt%	0.9 wt%	3	[14]
AC (1617m^2/g)	50wt%Cu	298	–	–	1.22 wt%	significant	[15]
AC(1073m^2/g)	1wt%Ni	298	3	0.15 wt%	0.53 wt%	3	[16]
Carbon xerogel (1803 m^2/g)	9.7wt%Ni	298	20	Very low	1	significant	[17]
AC(3400 m^2/g)	10wt%Pd	303	6	0.41 wt%	0.53 wt%	1.3	[18]
Template carbon (3798m^2/g)	6wt%Pt	298	10	0.84 wt%	1.34 wt%	1.6	[19]
AC (3089 m^2/g)	10wt%Ni	303	5	0.82 wt%	1.6 wt%	2	[20]
AC (3168 m^2/g)	2.5wt%Pd/Pt	298	18	1 wt%	1.65 wt%	1.65	[21]
AC(3197 m^2/g)	1.86 wt% Pd	298	25	0.6 wt%	1.4 wt%	2.3	[22]