Study of Adsorption Properties on Lithium Doped Activated Carbon Materials

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A volumetric method was applied to study an adsorption coefficient of hydrogen molecules in a gas phase on super activated carbon surface. The investigations were focused on getting the best possible materials for the energy storage. Several treatments on raw samples were used to improve adsorption properties. The biggest capacities were obtained after high temperature treatment at reduced atmosphere. The adsorption coefficient at 77 K and 2 MPa amounts to 3.158 wt%. The charge transfer between lithium and carbon surface groups via the doping reaction enhanced the energy of adsorption. It was also found that there is a gradual decrease in the adsorbed amount of H_2 molecules due to occupation active sites by lithium ions.

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1. Introduction

Hydrogen is a clean fuel which could directly deliver energy, particularly as used in fuel cells. Hydrogen may be a major energy source by 2030, if and only if viable infrastructure develops for its storage and transportation. In automotive transportation, the difficulties of H_2 storage are due to a large space required as well as the security of passengers. Up to now, no technology can assume the constraint imposed on the automotive application.

In the seventies, several studies on intercalation compounds of graphite (with Li or K) have shown that these compounds can store hydrogen by either chemisorp-

tion (at 200 K) or physisorption (at lower temperature 77 K and 100 K). Adsorption capacities of these compounds were found to be small [1]. For example, the second stage compound MC_{24} (M = K, Rb, Cs) can physisorb 1.15% weight of H_2 at 77 K [2]. The hydrogen molecules are then inserted in between the intercalated graphite planes. Activated carbons are capable of having very high surface area for hydrogen adsorption; relatively high pressures and low temperature are required e.g. 80 K. The recent study on an activated carbon, known as super-activated (microporous) carbon, reports an adsorption capacity of 0.3% at 295 K and 3 MPa, and 5 weight% at 77 K and the same pressure [3]. This result is in agreement with the very high specific surface area of this carbon and shows that a microporosity (pore diameter lower than 2 nm) is required to obtain high specific adsorption capacity of hydrogen. Very high storage capacities were claimed for carbon nanotubes and nanomaterials. However, it was found that the values of H_2 sorption on graphite nanofibers are rather 1% [4] than 65% at room temperature [5]. Despite they are macroporous, the carbon deposits including single walled nanotubes are considered as interesting materials for hydrogen sorption. Indeed, this material contains high energy adsorption sites [6]. Many recent papers report the use of nanostructured carbons for hydrogen storage [7].

From the recent literature, it appears clearly that the most promising materials for hydrogen adsorption are microporous materials (diameter of pores smaller than 2 nm) for which the energy of sorption at the sites are higher. In this work we have focused on activated carbons (AC), especially super-activated carbon for which a typical surface area obtained from Brunauer–Emmett–Teller (BET) method is 2500 m^2/g. The charge transfer, by doping reaction is supposed to charge the carbon matrix and then to enhance the energy of adsorption [8].

2. Experimental

We have studied AC materials of specific surface area of 1600 m^2/g determined by BET method. In order to obtain the capacity of hydrogen adsorption, a volumetric method was applied to determine the isotherm of adsorption. Before each experiment a volume of adsorption bench was characterized by helium gas and was corrected after a weighted amount of the sample was introduced in the sorption cell. Before hydrogen adsorption measurements the samples were vacuumed at 10^{-4} Torr for a few hours. The experiment was performed at 77 K and at room temperature (RT) on each pristine sample.

In order to remove sorbed water from the micropores, samples were heated to 473 K under secondary vacuum (10^{-4} mbar) for 10 hours. This first treatment consists of simply degassing the sample. The amount of sorbed water varies from sample to sample; it is strongly dependent on contamination of oxygen surface groups which make carbon surface hydrophilic. The second treatment is so-called high temperature treatment (HTT) in reduced atmosphere (H_2/N_2 mixture). First

hydrogen/nitrogen mixture (with flow rate 20/80 vol/vol respectively) was purged through the sample whereas the temperature of furnace was gradually increased in 3 hours to the final temperature, then this temperature was stabilized for a period of 2 hours. After that the furnace was cooled down also in 3 hours. All HTT procedures were performed at 973 K.

Such prepared samples were doped with electron donors. The aim was to obtain an energy of adsorption high enough (i.e. –20 kJ mol^{-1}) to make use of the porosity of these microporous materials at room temperature and ambient pressure (10 bar), so that these materials could be useful for an application in the automotive conditions. In order to increase the energy of adsorption of carbon nanoporous materials, the idea is to charge the carbon matrix by doping reactions using electron donor elements such as lithium metal. The doping was performed by reaction in the Li vapor phase. The activated carbon was first mixed with a weighted amount of liquid Li at $T > 473$ K. Then, the mixture was annealed at $T = 563$ K in a sealed stainless steel container evacuated at 10^{-5} mbar. Each step of doping procedure was controlled by X-ray for checking the structure of product reaction, by nuclear magnetic resonance (NMR) on ^{7}Li which monitored a contamination level of metallic lithium, by electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) to show if there is a change in electronic properties on carbon surface. Using this procedure the samples of LiC_6 and LiC_{18} were obtained to study. The average mass of the samples was 1 g.

3. Results and discussion

The adsorption properties of treated and not treated samples are reported in Table. The highest adsorption capacity for these materials is obtained for the sample of HTT treated at 973 K. The coefficient is 3.16 wt% at 2 MPa and 77 K. The other samples have smaller adsorption capacity. The samples doped by Li ions have had the lowest absorption capacity; there is a negative correlation between the abundance of lithium ions and adsorption coefficient at the final pressure. The amount of adsorbed hydrogen (H_2) as a function of pressure at 77 K is shown in Fig. 1. At room temperature the results obtained in the same range of pressure are ten times lower for doped samples. The isotherm has a linear characteristic.

In order to understand the effect of HTT on the material electronic structure, and to correlate it to adsorption properties of pristine, treated and doped samples, the EPR measurements were performed in 10–300 K temperature range.

At room temperature EPR signals of pristine carbons consist of an asymmetric line with $\Delta H_{pp} = 1.7$ mT line width. A shape of it is not Dysonian due to conducting electrons as observed for example for pure graphite. Temperature and microwave power dependences of spectra were studied. It has been well known that in many carbon materials the line width of ESR signals depends strongly on temperature. Usually decreasing temperature results in line narrowing and the

Adsorption capacities at 2 MPa of raw and modified activated carbons (degassed samples were heated at 473 K in 10^{-5} mbar vacuum).

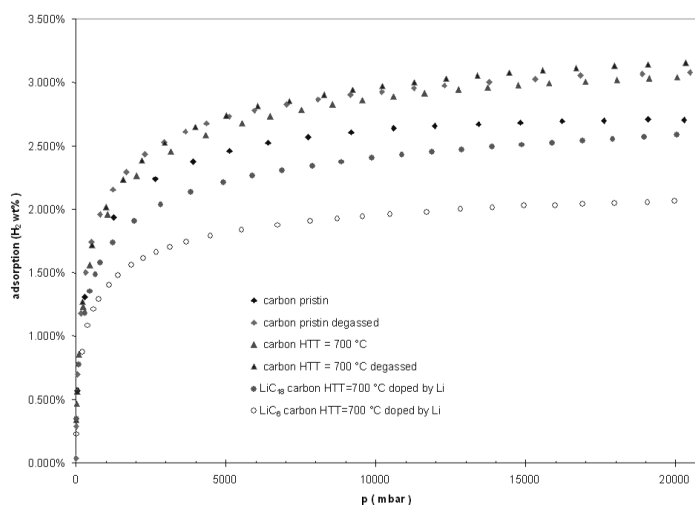| No.	Samples	Adsorption coefficient at 2 MPa [wt%]
1	raw sample	2.711
2	raw degassed	3.129
3	HTT=973 K, H_2	3.044
4	HTT=973 K, H_2 degassed	3.158
5	HTT=973 K, H_2 LiC_{18}	2.589
6	HTT=973 K, H_2 LiC_6	2.098

Fig. 1.   Isotherms of activated carbons at 77 K (H_2 wt% versus pressure).

asymmetry of the line diminishes. In our case the spectra are narrowing but we also observe important changes in the line shape. This asymmetry and the change of the line shape on microwave power suggest an inhomogeneous broadening. The analysis of the line shape allows experimental spectra to be deconvoluted into three different lines, distinguished by their g-factor, width, and amplitude. The results of the deconvolution are shown in Fig. 2. This implicates that the observed spectra result from different paramagnetic centers. Taking into account the g-factor and the line width, each line can be assigned to a different electron state.

The g-values of these two lines do not differ much (2.0031 and 2.0028). They can be distinguished only by their 0.102 mT and 0.408 mT widths. We found that these two lines are observed in all samples studied. The g-value does not depend
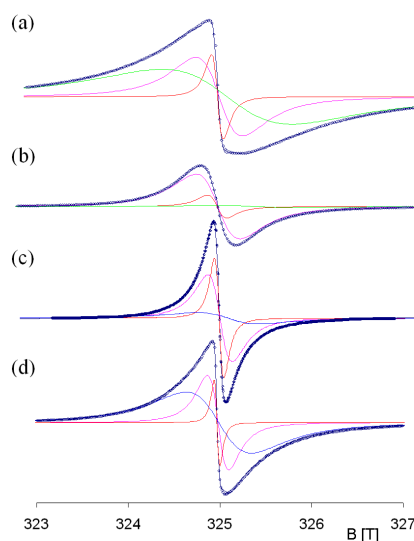
Fig. 2. Evolution of the line shape of AC against HTT and process of doping at temperature 10 K: (a) raw degassed sample, (b) sample treated at 973 K, (c) HTT sample at 973 K doped to LiC_{18}, (d) HTT sample at 973 K doped to LiC_6. Solid lines represent components of the deconvolution procedure.

on temperature and each sample has a different line width. The ratio between the double integrals of the narrowest and the wider lines is almost 2% and depends on the sample. However, an evidence of the occurrence of the narrowest line is clear at low temperature where the shape of the spectra is very sharp and the contribution of this line is obvious from spectra recorded at different microwave powers. Many experimental data performed on carbon materials: graphite [9] and fullerenes, have attributed g-value, very close to $g_\perp = 2.0027$ (perpendicular to $\boldsymbol{c}$ axis in graphite) to the resonance of electrons on the surface on carbon plane. Deconvolution of the spectra suggests that the signal comes from two different states of electrons localized and delocalized which differ in the line width. Localized states formed by hetero atom bonded to the carbon on the surface should exhibit narrow line. Such paramagnetic state should have shorter relaxation time than delocalized state thus the EPR line is broad. From transmission electron microscope (TEM) analysis of these materials, we have found that the average particle contains about 50 carbon atoms arranged in hexagonal plane. Such small particles give partial increase in total paramagnetic susceptibility from localized states. On the other hand, the broader line can be attributed to resonance of delocalized electron spin on the surface, well known in graphite materials.

The widest line has g-factor close to 2.0024 at 10 K. The g-value depends on temperature and at RT has the value of 2.0015. The line width at 10 K is 1.135 mT and increases to 2.575 mT at RT. In high surface area carbon black sample in the

presence of oxygen or after an intensive acidic oxidization (HNO_3), a similar wide EPR line was attributed to hole carriers, as reported by Liu et al. [10]. In our materials the contribution of this line in the spin susceptibility is very high. It is over 80% for raw carbon at 4.2 K. This shows that carbon materials are rather p-type conductors. The contribution of this line is dependent on temperature of the treatment and on doping process. There is a negligible contribution for sample HTT at 973 K and significant one for doped samples (Fig. 2). XPS experiments performed on our materials have shown that the absence of oxygen in groups on the surface is important for treated samples. Thermal treatment with reduced gas (H_2/N_2) leads to decrease in the contamination of oxygen in AC and in the contribution in paramagnetic susceptibility of the line responsible for hole centers. In our opinion this broad line can be like a fingerprint of oxygen and holes presence in AC materials. Impurities of oxygen were not possible to avoid in doped samples despite a great care to have oxygen free atmosphere. Thus, EPR signal was observed. The holes can be related to the grafting of species at the surface of carbon materials which can localize the electron on the surface, thus creating holes in carbon layers. In the case of AC, the basic surface groups (as pyrones) can be the origin of the hole type carriers.

The doping process can introduce the additional amount of electron density on carbon groups on the surface. It was shown by NMR experiment that at the beginning of the process samples contained almost only metallic lithium with chemical shift $\delta = 240$ ppm. After annealing at temperature 653 K the charge transfer process takes place, hence metals are transformed to ionic state with $\delta = 1.5$ ppm. X-ray study performed on the same samples showed a small amount of impurities due to formation of lithium carbons (LiC). Taking into account these impurities and contaminations of oxygen we have expected that doped samples would have better adsorption properties than pristine samples. The raw material has blocked porosity by adsorbing water or another molecule. The degassing process and HTT remove all adsorbed molecules from the surface. As a result these samples are characterized by higher adsorption coefficient. The simulation implies that higher electron density on the surface improves adsorption properties due to stronger interaction between the carbon plane and condensed gas state. Therefore the final adsorption properties are significantly lower than of pristine sample. The process of doping introduces an electron density by charge transfer on the surface. It was shown that EPR signal becomes stronger. This implicates higher energy of adsorption. Doped samples of LiC_{18} and LiC_6 at much lower pressure have higher content of adsorbed H_2 molecules. Increased pressure results in lowering the adsorption coefficient because lithium ions occupy active sites on which the gas molecules of H_2 can be adsorbed.

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