Hydrogen Capacity of Palladium-Loaded Carbon Materials

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Several samples of palladium-loaded single-wall carbon nanotubes and palladium-loaded MAXSORB activated carbon were prepared by means of the reaction of the raw carbon support with $Pd_2(dba)_3 \cdot CHCl_3$. When carbon nanotubes were used as the support, the palladium content in the samples reached 13−31 wt % and fine particles of 5−7 nm average size were obtained. In the case of the samples with MAXSORB as the support, the palladium content was higher (30−50 wt %) and the particle size larger (32−42 nm) than in the nanotube samples. At 1 atm and room temperature, the hydrogen capacity of the palladium-loaded samples exceeds 0.1 wt % and is much higher than the capacity of the raw carbon supports (less than 0.01 wt %). The maximum hydrogen capacity at 1 atm and room temperature was found to be 0.5 wt %. A maximum hydrogen capacity of 0.7 wt % was obtained at 90 bar in a palladium-loaded MAXSORB sample, while the capacities for the raw carbon nanotubes and MAXSORB at the same pressure were 0.21 and 0.42 wt %, respectively. At low pressure, it was observed that the H/Pd atomic ratios in the palladium-loaded samples were always higher than in the bulk Pd. The spillover effect is considered as a possible cause of the high H/Pd atomic ratios. On the other hand, the effect of the pressure increase on the spillover was observed to be very low at high pressure and room temperature.

Introduction

The catalytic activity of palladium in hydrogenation reactions has been known for many years. H_2 molecules can be dissolved and dissociated in the crystalline network of bulk Pd to form low-stability palladium hydrides, and then hydrogen in the palladium structure can react with other species that are otherwise inert. To maximize the active surface of the metal and get a better efficiency of the catalyst, Pd is usually supported on porous materials (high-surface-area oxides or carbons) in the form of very small particles. The activity of such a catalytic system is usually much higher than the separated activity of the palladium and the support. This fact is explained by the interaction of the hydrogen atoms from the palladium structure with the support. In this way, hydrogen spreads from the palladium structure to the support, and this phenomenon, which has been proved with distinct metals and supports, is known as hydrogen spillover.[1]

From the viewpoint of hydrogen storage technology, the spillover seems to be a way of increasing the absolute hydrogen capacity of the carbon materials. Similarly to the increase in the catalytic activity of the system Pd + C support, one can think of an enhancement of the hydrogen capacity. In fact, when hydrogen moves from the palladium hydride to the support, some empty sites appear in the palladium structure. These sites can be occupied by other H_2 molecules from the gas phase, so the total hydrogen that is absorbed in the system Pd + C support is more than expected if there were no interaction between the palladium structure and the carbon support. Recent studies have proved experimentally that the hydrogen capacity (wt %) of several metal + C support systems is higher than the capacity of the raw carbon materials.[2−6] However, the capacity is never higher than 1.5 wt % at high pressure and room temperature, and the contribution of the spillover is not clear. On the other hand, it has been observed that the spillover effect at low pressure (up to 1 atm) does not present a simple dependence on pressure, but it presents a maximum at less than 100 Torr and a non clearly defined tendency.[7]

In this work, we study hydrogen sorption at room temperature in samples of palladium-loaded carbon nanotubes and MAX-ORB activated carbon. Low- and high-pressure hydrogen isotherms were measured for the raw carbon materials and for palladium-loaded samples. We report data of hydrogen sorption and study the desorption process. We finally try to evaluate the spillover effect at high pressure by means of secondary spillover experiments. The study is completed with the characterization of the samples by transmission electron microscopy, X-ray diffraction, determination of the palladium content, hydrogen isotherms at −196 °C, and nitrogen adsorption at −196 °C.

Experimental Methods

Single-wall carbon nanotubes (SWNTs) were prepared by the electric-arc-discharge method using Ni/Y (2/0.5 atom %) as the catalyst in the graphite precursor. The material was used without further treatment, and some of its adsorption properties have already been reported.[8] MAXSORB is a high-surface-area activated carbon that is obtained from petroleum coke by means of chemical activation with KOH. Production and adsorption characteristics of MAXSORB have been previously described.[9]

SWNTs and MAXSORB were loaded with palladium particles by reaction between the carbon support and the palladium

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organometallic complex Pd$_2$(dba)$_3$·CHCl$_3$ [tris(dibenzylidene-acetone)dipalladium(0)].[10] The palladium compound and the carbon support were added to distilled toluene under an inert atmosphere and stirred at room temperature until the solution changed from red to yellow. Then, the resulting suspension was vacuum filtered through a 3 μm pore polycarbonate filter membrane, and the solid part was dried at 125 °C and ground with a mortar. In this way, two samples with different Pd contents were prepared with each carbon support. The loaded samples are labeled as SWNTs:Pd 1:1 and 1:2 and MAXSORB: Pd 1:1 and 1:2, indicating the weight ratio of the reactants. The efficiency of the particle preparation method was examined by transmission electron microscopy (TEM), induction-coupled plasma spectrometry (ICPS), and X-ray diffraction (XRD). The palladium content was determined by ICPS, and the crystallite size was calculated from the X-ray diffractograms using the software TOPAS P.

The volumetric system Autosorb-1 from Quantachrome Instruments was used to obtain the nitrogen adsorption isotherms at −196 °C for all the samples. The BET specific surface area and the micropore volume were calculated from the nitrogen adsorption data.

Low-pressure hydrogen isotherms (5−800 Torr) at liquid nitrogen temperature (−196 °C) and room temperature (23 °C) were also obtained in the Autosorb-1. Before all the measurements in Autosorb-1, the materials were degassed at 250 °C under a vacuum of better than 10^{-6} mbar for more than 12 h. Desorption isotherms (800−5 Torr) were also measured at room temperature to study the reversibility of the hydrogen sorption. Following the customary practice, the hydrogen capacity obtained in the volumetric system is here expressed as the volume per gram of sample. The volume of hydrogen (cm^3) is given at standard temperature and pressure (STP) conditions. For the low-pressure isotherms, hydrogen was considered as an ideal gas because the error committed is negligible.

High-pressure hydrogen isotherms up to approximately 90 bar were carried out at 25 °C in a VTI system provided with a Rubotherm magnetic balance. The samples were pretreated at 250 °C under a vacuum of better than 10^{-6} mbar until a constant weight was achieved. The nonideality of hydrogen was taken into account by means of the Peng−Robinson equation of state. Hydrogen sorption data obtained in the gravimetric system are expressed as the weight percent change:

$$\text{wt \% change} = \frac{\text{mass of hydrogen}}{\text{mass of dry sample}} \times 100$$

where the mass of hydrogen is the hydrogen capacity at each pressure and the mass of dry sample was taken after the pretreatment at 250 °C, just before the sorption process was started. Conversion between units of wt % change and V(STP)/g is straightforward.

Palladium Particle Size and Porous Structure of the Materials

In general, when metallic particles are settled on a substrate, the size of the particles is proportional to the amount of loaded metal. By means of the palladium loading method that is described above, it was possible to get particles of quite small size and in high concentration (Table 1). For the samples SWNTs:Pd 1:1 and SWNTs:Pd 1:2, the calculated average particle size was 5 and 7 nm, respectively. A much larger average size was obtained in the palladium-loaded MAXSORB samples (32 nm for MAXSORB:Pd 1:1 and 42 nm for MAXSORB:Pd 1:2). The average crystallite size was calculated

TABLE 1: Palladium Content (wt %) Determined by ICPS, Crystallite Size Calculated from XRD Data, and Porosity Characteristics of the Samples[a]

	[Pd] (wt %)	crystallite size (nm)	S_{BET} (m²/g⁻¹)	V_{mi} (cm³/g⁻¹)
SWNTs:Pd 1:1	13.20	4.8	334	0.07
SWNTs:Pd 1:2	31.52	7.1	232	0.05
MAXSORB:Pd 1:1	29.90	31.8	508	0.16
MAXSORB:Pd 1:2	49.07	41.8	199	0.06
SWNTs			262	0.05
MAXSORB			2112	0.63

[a] S_{BET} = BET specific surface area, V_{mi} = Dubinin−Radushkevich micropore volume.
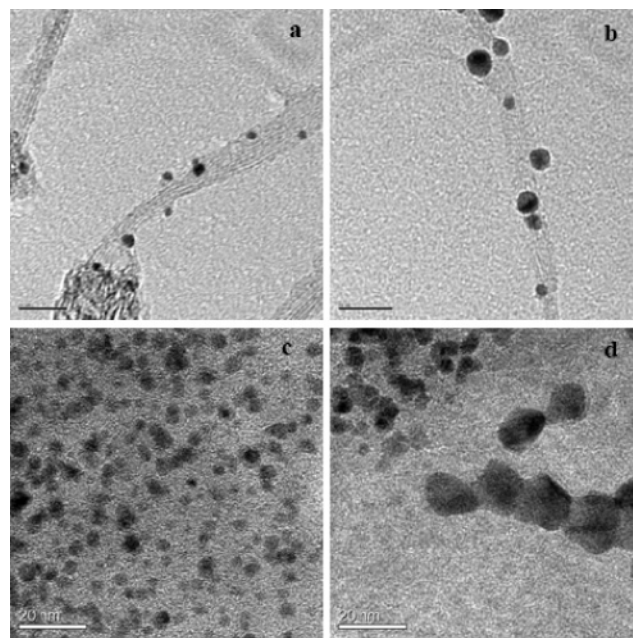

Figure 1. TEM images of the four Pd-loaded samples described in this project: Pd-loaded bundle of nanotubes in SWNTs:Pd 1:1 (a), Pd-loaded bundle of nanotubes in SWNTs:Pd 1:2 (b), MAXSORB:Pd 1:1 (c), and MAXSORB:Pd 1:2 (d). Scale bars correspond to 20 nm in all cases.

from the XRD data and shows good agreement with the particle size observed in the TEM images (Figure 1). In the sample SWNTs:Pd 1:1, particles with diameters of approximately 2−7 nm were observed on the bundles of SWNTs. The particles are regularly spherical and sparse. In SWNTs:Pd 1:2, palladium particles had diameters of 2−15 nm, although many of them were around 5 nm. Particles were slightly larger than in the sample SWNTs:Pd 1:1, but still sparse. In MAXSORB:Pd 1:1, TEM images showed particles of 2−14 nm and even larger, with many at about 3−6 nm. Particles were not as perfectly spherical as in the samples of SWNTs. Palladium aggregates were densely distributed on the carbon surface and occasionally reached sizes as large as 50−100 nm. In MAXSORB:Pd 1:2, palladium particles were clearly larger than in the other samples. Particles of 5−20 nm, larger aggregates of different shapes, and particles of about 30 nm with nearly spherical shape could be observed. From the XRD data (not shown), it was concluded that most of the loaded palladium was Pd(0), although some PdO was also detected.

The amount of palladium that was loaded on MAXSORB activated carbon was higher than on SWNTs, although equivalent proportions of the reactants were used (Table 1). Since nucleation and growth of metallic particles are processes occurring at the surface of the carbon substrates, variations in
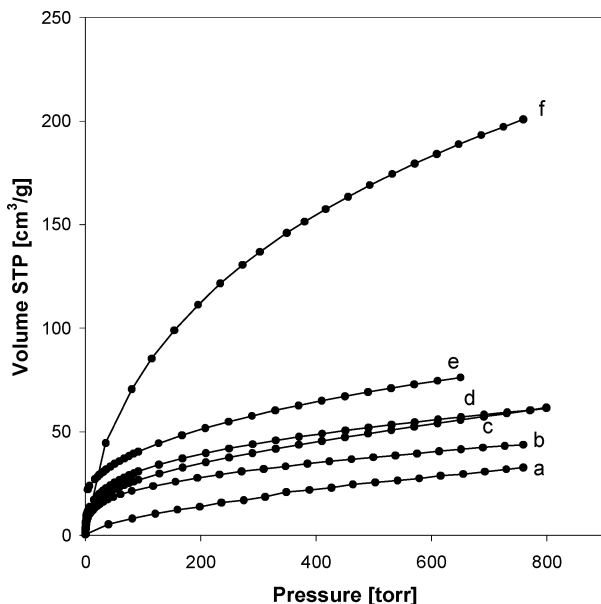
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Figure 2. Low-pressure hydrogen isotherms at −196 °C of MAX-SORB:Pd 1:2 (a), raw SWNTs (b), SWNTs:Pd 1:2 (c), SWNTs:Pd 1:1 (d), MAXSORB:Pd 1:1 (e), and raw MAXSORB (f).

Figure 3. Low-pressure hydrogen isotherms at room temperature of raw SWNTs (a), SWNTs:Pd 1:1 (b), SWNTs:Pd 1:2 (c), MAXSORB:Pd 1:1 (d), and MAXSORB:Pd 1:2 (e).

Pd loading may be related to the wide differences in surface area and pore volume. The BET specific surface area of MAXSORB is about 8 times higher than that of SWNTs, and the micropore volume is about 12 times higher (Table 1). Although SWNTs are light carbon structures with a large specific surface, the BET area of a raw arc-discharge sample of SWNTs is not very high due to the presence of impurities (disordered carbon forms, graphite, graphite-covered catalytic particles). Therefore, MAXSORB provides more nucleation sites than SWNTs. Moreover, the adsorption sites of MAXSORB are weak (wide micropores) and very close to each other, so particles join to form aggregates, thus leading to higher particle size.

On the other hand, the particle loading reaction led to a slight increase in the surface area of the SWNTs but to a big decrease in that of MAXSORB (Table 1). In fact, palladium particles probably occupied the surface adsorption sites of MAXSORB and blocked the entrance for N_2 molecules, and thus, the BET surface area of the loaded samples decreased. However, the surface development in the samples of SWNTs is not clear and could be due to the opening of the nanotubes during the loading reaction in toluene.

Hydrogen Isotherms and Reversibility

Hydrogen isotherms at −196 °C (Figure 2) show that capacities at very low temperature are associated with the surface area of the materials. The activity of the palladium at −196 °C is very weak because the kinetics of the absorption process is extremely slow, and thus, the total capacity is mainly due to the physical absorption. The absorption of hydrogen in the palladium structure is a quite complicated process that involves, first, dissolution of hydrogen in palladium and, second, formation of the palladium hydride (the so-called α and β phases, respectively). As the temperature increases, physical adsorption becomes weaker and the activity of palladium increases because the accommodation of hydrogen in the palladium crystalline network becomes faster. Therefore, the hydrogen capacity at room temperature is not directly controlled by the porosity characteristics.
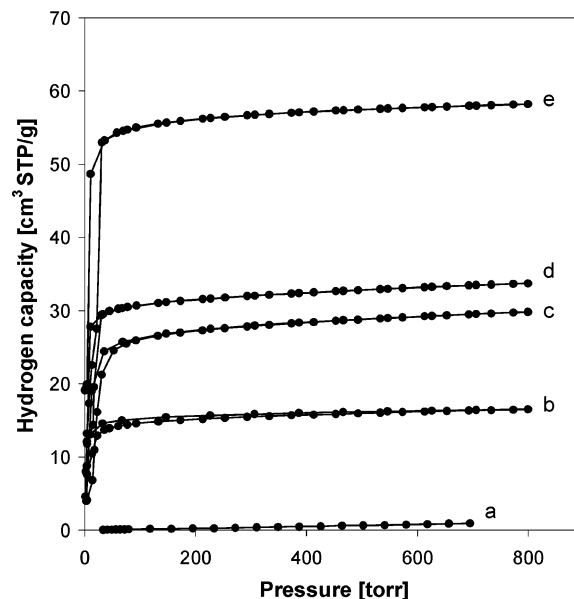
At low pressure, room temperature hydrogen isotherms of the palladium-loaded carbon materials show type I profiles with a very steep initial increase (Figure 3) and their hydrogen capacity is much higher than that of the raw carbon materials, which present linear isotherms. In fact, the hydrogen capacity of all of the loaded samples at atmospheric pressure exceeds 10 cm³ (STP)/g (0.1 wt %), while the capacity of the raw carbon materials is less than 1 cm³ (STP)/g (0.01 wt %) (Table 2). A maximum hydrogen capacity of 58 cm³ (STP)/g at 1 atm was found in the sample MAXSORB:Pd 1:2, which also has the highest palladium content.

Nevertheless, the desorption process in the palladium-loaded samples is more difficult than in the raw materials. The hydrogen isotherms present a low-pressure hysteresis (5−35 Torr), which is typical of Pd and Pd alloys,[11] and there is an important fraction of the absorbed hydrogen that needs pressures lower than 5 Torr or high temperatures to be released (Table 2). Therefore, it can be said that hydrogen sorption in the palladium-loaded samples is in part irreversible at room temperature.

In the high pressure range, the room temperature isotherms of the loaded samples present the same initial step increase that is observed in the low pressure range. However, the hydrogen capacity increases very slowly after that (Figures 4 and 5). A maximum capacity of 0.70 wt % at 90 bar was found in the sample MAXSORB:Pd 1:2 (Table 2). It can also be seen that the difference between the hydrogen capacity of loaded and raw materials is at 90 bar much smaller than at low pressure.

To check the reproducibility of the high-pressure isotherms, the sample cell was pumped out after the measurement and degassed at 250 °C and a second isotherm was carried out at the same conditions. The second isotherm shows almost the same capacity as the first one in the sample SWNTs:Pd 1:1, slightly less capacity in the samples SWNTs:Pd 1:2 and MAXSORB:Pd 1:1, and much lower capacity in the sample MAXSORB:Pd 1:2 (Figures 4 and 5). Some of the absorbed hydrogen is thus very strongly stuck, and needs a temperature higher than 250 °C to be released.

TABLE 2: Room Temperature Hydrogen Capacity of the Materials at 1 atm, Zero Pressure (Origin), 5 Torr (Desorption Branch), and 90 bar[a]

| | H (1 atm) | | | H (origin) | | | | H (90 bar) | | |
| | | wt % | | | wt % | | H_{des} (5 Torr) | | wt % | |
	V(STP)	change	H/Pd	V(STP)	change	H/Pd	V(STP)	V(STP)	change	H/Pd
SWNTs:Pd 1:1	16.48	0.15	1.21	14.84	0.13	1.05	9.62	17.78	0.16	1.29
SWNTs:Pd 1:2	29.72	0.27	0.91	26.65	0.24	0.81	7.37	56.67	0.51	1.73
MAXSORB:Pd 1:1	33.64	0.30	1.07	30.94	0.28	1.00	14.72	44.45	0.40	1.43
MAXSORB:Pd 1:2	58.14	0.52	1.13	55.75	0.50	1.09	24.39	77.78	0.70	1.53
SWNTs	0.99	<0.01		0	0			23.33	0.21	
MAXSORB	0.82	<0.01		0	0			46.67	0.42	

[a] The hydrogen capacity is expressed as the volume at standard temperature and pressure [V(STP)] (cm³/g), weight percent change [(mass of hydrogen × 100)/mass of sample], and H/Pd atomic ratio.
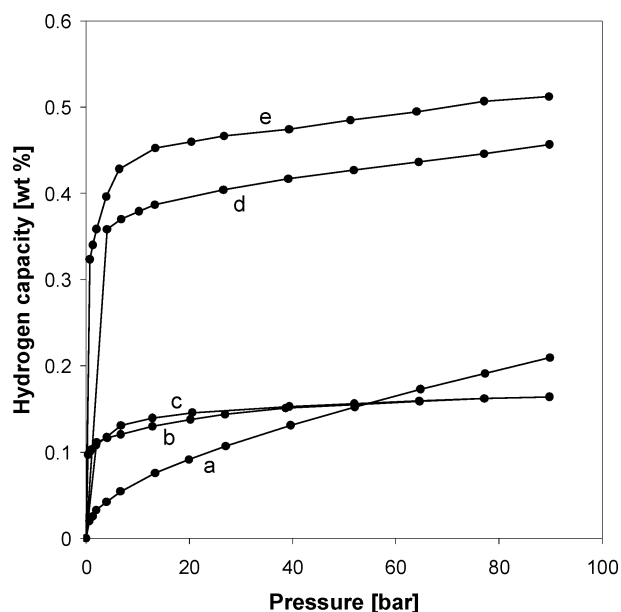

Figure 4. High-pressure hydrogen isotherms at room temperature of raw SWNTs (a), SWNTs:Pd 1:1 second cycle (b), SWNTs:Pd 1:1 first cycle (c), SWNTs:Pd 1:2 second cycle (d), and SWNTs:Pd 1:2 first cycle (e). The hydrogen capacity is expressed as the weight percent change [(mass of hydrogen × 100)/mass of sample].

Figure 5. High-pressure hydrogen isotherms at room temperature of raw MAXSORB (a), MAXSORB:Pd 1:1 second cycle (b), MAXSORB: Pd 1:1 first cycle (c), MAXSORB:Pd 1:2 second cycle (d), and MAXSORB:Pd 1:2 first cycle (e). The hydrogen capacity is expressed as the weight percent change [(mass of hydrogen × 100)/mass of sample].

Spillover Effect

At room temperature and 1 atm of H₂, bulk Pd shows a hydrogen capacity of approximately 0.56 wt %, which equals a palladium hydride with a stoichiometry of 0.6 H/Pd.[11,12] In the palladium-loaded samples, the atomic ratio H/Pd was higher than 0.9 at 1 atm (Table 2). As the pressure increases, the atomic ratio H/Pd also increases in the loaded samples, and it becomes higher than 1.2 at 90 bar (Table 2). However, the increase at high pressure is mainly due to the physical adsorption of hydrogen and not to the palladium activity.

It has been previously commented that physical adsorption of H₂ on the raw carbon materials is very weak at low pressure, and thus, the isotherms are linear, so if the linear region above 200 Torr in the low-pressure isotherms (Figure 3) is linearly fitted, the intercept with the origin gives a value of hydrogen capacity that is free of physical adsorption effects (the Benson–Boudart approximation, which is widely used in chemisorption analysis). In the palladium-loaded samples, the value of the intercept ranges from 14 cm³ (STP)/g for SWNTs:Pd 1:1 to 55 cm³ (STP)/g for MAXSORB:Pd 1:2 (Table 2). Such values of hydrogen capacity at zero pressure lead to H/Pd atomic ratios between 0.8 and 1.1 (Table 2), which are still higher than that of bulk palladium.
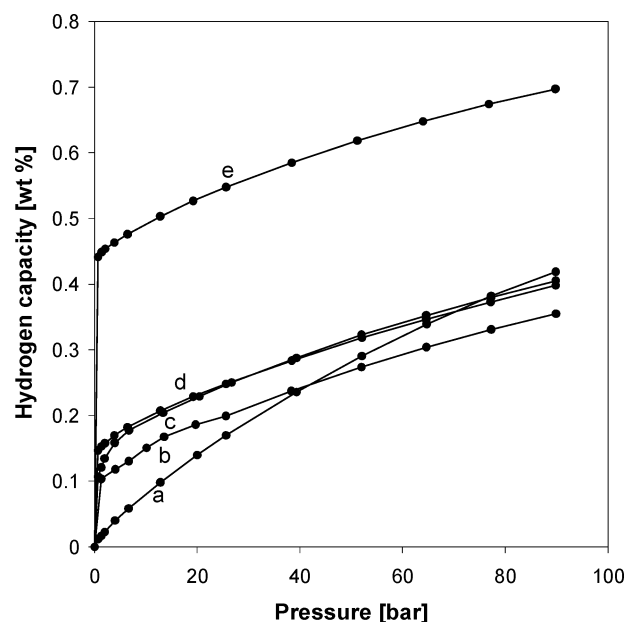
Two different factors have been described in the literature as possible causes of H/Pd ratios higher than 0.6. The first one is the spillover effect, and the second one is joined to the very small size of the palladium particles. In Pd clusters of small size (1 or several nm) the H/Pd ratio is usually found to be higher than 0.6.[13] The H/Pd ratio is expected to increase as the particle size diminishes, due to the increase in the number of surface and subsurface sites in Pd. However, for our palladium-loaded samples there is not a clear correlation between the XRD crystallite size and the H/Pd ratio (Table 1), so the effect of the particle size is not clear. Let us see now how the spillover effect can explain the H/Pd ratios at the intercept with the origin. It must be remembered that most of the hydrogen is captured at pressures lower than 200 Torr, while at pressures between 200 Torr and 1 atm, the increase in the hydrogen capacity is very low and similar to that observed in the raw carbon materials (~0.02 wt %). Also the difference between the H/Pd ratio at 800 Torr and that at the origin is small (Table 1), so the spillover in the range 200–800 Torr is very weak. Therefore, to explain the high H/Pd ratios at the origin, an enhanced spillover effect at pressures less than 200 Torr must be taken into account. The enhanced spillover effect at very low pressure has been recently described in a similar way.[7]
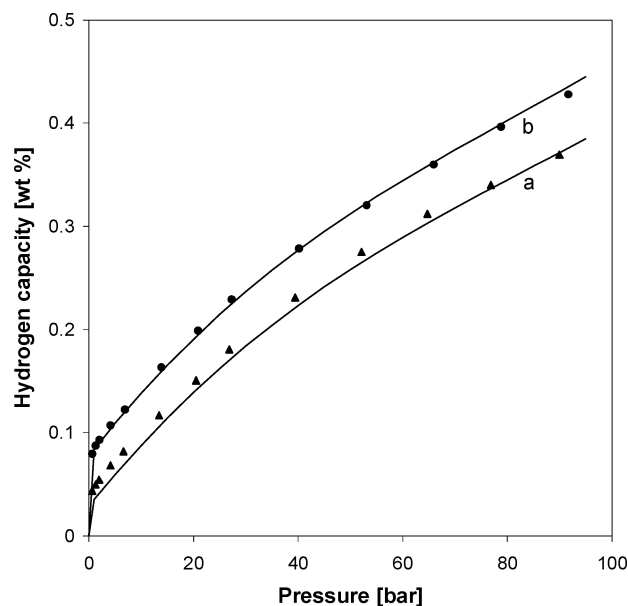
Figure 6. Scattered points represent the experimental hydrogen isotherms at room temperature of the mixtures SWNTs:Pd 1:1 + MAXSORB (20/80) (a) and SWNTs:Pd 1:2 + MAXSORB (20/80) (b). Solid lines represent the isotherms that were calculated as a linear combination of the isotherms of the components of the mixtures. The hydrogen capacity is expressed as the weight percent change [(mass of hydrogen × 100)/mass of sample].

Figure 7. Scattered points represent the experimental hydrogen isotherms at room temperature of the mixtures MAXSORB:Pd 1:1 + MAXSORB (20/80) (a) and MAXSORB:Pd 1:2 + MAXSORB (20/80) (b). Solid lines represent the isotherms that were calculated as a linear combination of the isotherms of the components of the mixtures. The hydrogen capacity is expressed as the weight percent change [(mass of hydrogen × 100)/mass of sample].

The same trend was also observed at pressures above 1 atm. In fact, the hydrogen capacity of the loaded samples in the range 1−90 bar increases only in a way similar to that of the raw substrates (Figures 4 and 5). The weakness of the spillover at high pressures was also seen in several experiments of secondary spillover. A secondary spillover acceptor is a raw substrate that is put in contact with the primary catalytic system metal + substrate, and hydrogen is spilled over first from the metal to the primary substrate and then to the secondary substrate. In this project, the MAXSORB activated carbon was chosen as the secondary substrate because it presented a higher hydrogen capacity than SWNTs. Several mixtures of the palladium-loaded samples with the raw MAXSORB were prepared and their high-pressure isotherms measured. All the mixtures had 20 wt % of one of the palladium-loaded samples and 80 wt % of the raw MAXSORB. The palladium-loaded samples were used for the mixtures after the measurement of the two subsequent hydrogen isotherms that are shown in Figures 4 and 5. In a secondary spillover process, if the spillover were operative at high pressure, it would be expected to achieve hydrogen capacities for the mixtures higher than the weighted average of the components. Nevertheless, the predicted average isotherms and the experimental data are very close to each other (Figures 6 and 7). The wider difference was found in the case of the mixture MAX-SORB:Pd 1:1 + MAXSORB, for which the experimental data were slightly higher than the predicted isotherm by about 0.05 wt % at 90 bar.

Now the question arises of why the hydrogen spillover can produce a great increase in the activity of a catalyst and thus in the reaction rate but cannot increase significantly the hydrogen capacity at high pressure. Maybe the answer is because in a hydrogenation reaction, hydrogen goes out of the substrate fast and reacts, leaving the sites in the substrate free for other hydrogen atoms. However, in a storage experiment, hydrogen remains in the substrate and soon saturates it. Indeed, if the hydrogen pressure is increased in the reactor, the transference of hydrogen to the substrate and then to the reactant becomes
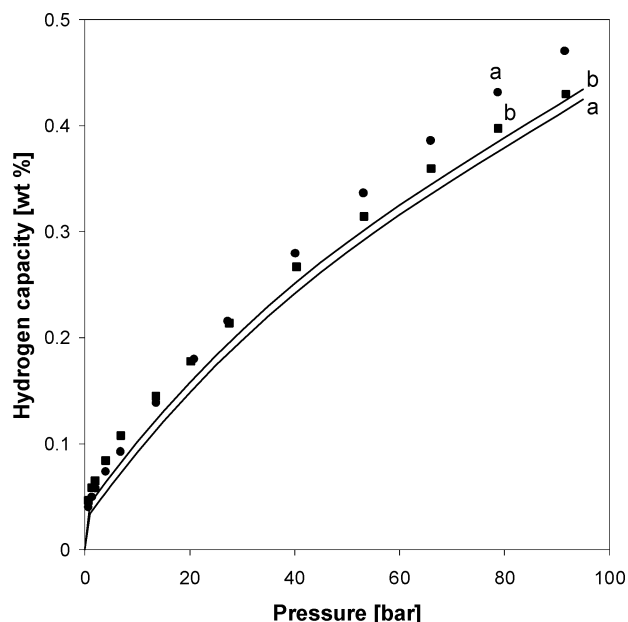
faster, increasing the reaction rate. However, in the storage experiments, most of the sites on the substrate are saturated at low pressure, so the increase in the hydrogen pressure does not lead to much higher hydrogen capacities.

Finally, it must be said that, although hydrogen spillover can explain the high H/Pd atomic ratios, the results presented here are not a direct proof of the existence of the spillover effect in this case. However, the spillover effect is specially considered because it is a well-documented phenomenon in the literature.

Conclusions

Palladium-loaded carbon materials have higher hydrogen capacity at low and intermediate pressures than the raw materials. At 1 atm, the capacity of the loaded samples was found to be more than 1 order of magnitude greater than that of the raw materials and reached a maximum of 0.5 wt %. However, at 90 bar, the difference in the hydrogen capacity between the loaded and the raw materials decreases. The maximum capacity at 90 bar in a palladium-loaded sample was found to be 0.7 wt %, while the capacity of MAXSORB activated carbon exceeds 0.4 wt %. Moreover, hydrogen isotherms of the palladium-loaded samples do not show complete reversibility at room temperature, so the difference from the raw materials is even smaller in a second sorption process.

At pressures lower than 200 Torr, the H/Pd atomic ratio was found to be higher than 0.8 and thus higher than the H/Pd ratio of pure palladium hydride, which is 0.6 at about 1 atm. The high H/Pd ratios could be explained by a low-pressure (<200 Torr) spillover effect. On the other hand, the spillover effect was found to have a very small contribution to the total hydrogen capacity at high pressure and room temperature.

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