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Low-Temperature Generation of Basic Carbon Surfaces by Hydrogen Spillover

J. Angel Menéndez and Ljubisa R. Radovic

Fuel Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

Bo Xia and Jonathan Phillips*

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

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It is demonstrated that stable basic carbons, which will not adsorb oxygen in ambient laboratory conditions, can be created via a relatively low-temperature process. These highly basic carbons are created by treating mixtures of carbons and platinum (in the form of particles supported on a high surface area material) in hydrogen at 500 °C, or even at lower temperatures in some cases. In the absence of platinum, creation of highly basic and stable surfaces with the same starting material requires hydrogen treatments at far higher temperatures (ca. 900 °C). Evidence is presented to support the hypothesis that the role played by platinum (or any noble metal) is to produce atomic hydrogen, which spills over onto the carbon surface. This atomic hydrogen hydrogasifies the most reactive, unsaturated carbon atoms at far lower temperatures than molecular hydrogen, thus leading to surface stabilization at relatively low temperatures.

Introduction

Modern industry requires activated carbons with not only optimum physical properties (e.g., surface area, porosity, pore size distribution, hardness, etc.) but also specified chemical properties. By use of different treatments, the chemical properties of a carbon can be tailored^{1,2} for specific applications. For example, there are a variety of oxidative treatments designed to produce acidic activated carbons with different distributions of oxygen-containing acidic groups.^{2–7} In contrast, methods for creating activated carbons with basic properties, which are stable in ambient conditions, are still under investigation. Such carbons are of great interest in numerous applications.^{8–13}

Recently, we demonstrated one method for creating a stable basic carbon.¹⁴ Activated carbons treated in hydrogen at high temperature (only 900 °C or higher) were found to be basic in character and stable in ambient laboratory conditions for periods of months. This treatment was effective in removing oxygen in the form of CO and CO₂, thus removing the acidic functional groups (e.g., carboxyl, lactone, phenol) from the surface. Moreover, the most reactive carbon atoms, which were left behind by oxygen removal (as carbon oxides), were subsequently removed by hydrogen, thus greatly diminishing the tendency of the carbon to readsorb oxygen and reacidify.

The focus of the present work is on testing a new hypothesis regarding the creation of stable, basic carbon surfaces. To wit: In the presence of hydrogen atoms, stable basic carbon surfaces can be created at far lower temperatures than is possible in the presence of molecular hydrogen. Experimentally, it was shown that in the presence of noble metals, capable of creating and “spilling over” hydrogen atoms, stable basic carbon surfaces could be created at 500 °C or higher. That is, in the presence of noble metals, stable basic carbons can be created at temperatures at least 400 °C lower than is possible in their absence.

Experimental Section

Sample Preparation. Two different carbons were employed in the experiments described below. One material is a commercial activated carbon, Norit C-Granular (Nc), prepared from a wood precursor by phosphoric acid activation. It is of very high purity and has a high BET surface area (1378 m²/g). This material was in some cases mixed with a commercially available carbon (Alfa Aesar, Johnson-Matthey, Stk#38343, 1% Pt) containing 1 wt % platinum in highly dispersed form (PtC). The particle sizes of the carbons were very different (PtC: 4 × 8 mesh, Nc < 70 mesh), allowing them to be separated by sieving at the completion of all treatments and prior to any measurements.

Samples were prepared in quartz boats placed within a quartz reactor (5 cm, i.d.). In all cases, samples were prepared in 2 g batches. Table 1 is a list of all samples treated, giving the treatment conditions used (gaseous atmosphere, time, and temperature) as well as the values for the point of zero charge (PZC), which are discussed in detail below. The nitrogen-treated sample (N950) was first conditioned in flowing nitrogen (150 mL/min) for 1 h at ambient temperature. Next, the sample temperature was raised to 950 °C at a rate of 25 °C/min. The sample was held in flowing nitrogen for 3 h at 950 °C, then rapidly cooled to room temperature and held at that temperature for another hour. The sample was then removed from the reactor and a fraction (0.3 g) prepared immediately for the determination of PZC. Thus, the PZC was determined after a very brief exposure (<5 min) to ambient laboratory atmosphere.

All other samples were treated in a similar fashion. The hydrogen-treated samples (H150–H950) were treated in the same way except that (i) hydrogen was substituted for nitrogen, (ii) the maximum treatment temperatures ranged from 150 to 950 °C, and (iii) once cooled to room temperature, nitrogen was flowed over the samples for 1 h before the samples were removed and exposed to ambient atmosphere. The third step was performed to ensure that all hydrogen was flushed from the chamber/sample prior to oxygen exposure.

In one group of experiments, the commercial PtC was pretreated in an acid solution (PtC–Ox). That is, the material

* To whom correspondence should be addressed.

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TABLE 1: Summary of Treatments and PZC of As-Received and Treated Carbons

sample code	treatment	PZC
Raw Materials		
PtC	none	9.8
Nc	none	2.5
PtC-Ox	HNO ₃ (18%), 60 °C, 64 h	3.6
Treatments Using PtC-Ox as Starting Material		
PtC-Ox-H150	H ₂ , 3 h, 150 °C	4.8
PtC-Ox-H250	H ₂ , 3 h, 250 °C	6.2
PtC-Ox-H350	H ₂ , 3 h, 350 °C	9.6
Treatments Using Nc as Starting Material		
N500	N ₂ , 3 h, 500 °C	3.8
N950	N ₂ , 3 h, 950 °C	5.2
H150	H ₂ , 3 h, 150 °C	2.5
H350	H ₂ , 3 h, 350 °C	2.7
H425	H ₂ , 3 h, 425 °C	3.3
H500	H ₂ , 3 h, 500 °C	5.6
H650	H ₂ , 3 h, 650 °C	6.3
H800	H ₂ , 3 h, 800 °C	7.5
H950	H ₂ , 3 h, 950 °C	9.0
Nc Mixed with PtC during the Treatment and then Separated by Sieving		
H150/PtC	H ₂ , 3 h, 150 °C	2.6
H350/PtC	H ₂ , 3 h, 350 °C	3.6
H425/PtC	H ₂ , 3 h, 425 °C	7.0
H500/PtC	H ₂ , 3 h, 500 °C	9.0
H500/PtC ^a	H ₂ , 3 h, 500 °C	8.5
H500/PtC ^b	H ₂ , 3 h, 500 °C	8.5
H500/PtC ^c	H ₂ , 3 h, 500 °C	8.8

^a With PtC reused twice. ^b With PtC reused three times. ^c PtC:Nc = 1:2 by mass.

was treated in a weakly acidic solution of HNO₃ (18%) at 60 °C for 64 h. This pretreatment was employed to convert the surface into an acidic state (PZC = 3.6) prior to treatment with hydrogen at 150, 250, and 350 °C. Indeed, the PZC of the surface of this carbon as it arrived from the supplier showed it to be alkaline (basic), with a value of 9.8.

It should be noted that the last seven samples listed in Table 1 are mixtures. In each case (except when indicated) the mixtures consisted of 1 part Nc and 2 parts (by mass) of the commercial PtC. The mixtures were treated in H₂ at 150, 350, 425, and 500 °C as noted. After treatment the two carbons were separated by sieving in all cases.

There was also one study conducted ("unmixed") in which the two carbons were present in the furnace together, but not all were intimately mixed. Three quartz boats, each 4 cm long, were used. The furthest upstream contained only Nc, the middle boat contained a 2:1 mixture of PtC and Nc, and the third boat also contained only Nc. Each boat was separated from the others by a 5 mm "air" gap. These carbons were treated at 500 °C in flowing hydrogen (approximately 100 cm³/min, equivalent to a velocity of about 5 cm/min) using the usual procedure.

Physical Surface Characterization. Micropore volumes, apparent surface areas, and porosities of selected samples were determined from physical adsorption measurements with N₂ at 77 K and CO₂ at 273 K using the Autosorb-6 volumetric system (Quantachrome Corp.). The surface areas were obtained from N₂ adsorption data using the BET equation. The micropore volumes were calculated from CO₂ isotherms using the Dubinin-Radushkevich (DR) equation. The mesopore volumes were determined using the standard t-method applied to the N₂ adsorption data. Table 2 summarizes the textural properties of representative carbon samples.

Chemical Surface Characterization. Elemental analysis of all samples was determined using a LECO CHN-600 instrument.

TABLE 2: Textural Properties of Selected Carbons

carbon	BET surface area (m ² /g)	DR-CO ₂ pore volume (cm ³ /g)	mesopore volume (cm ³ /g)
PtC	1000	<i>a</i>	<i>a</i>
Nc	1378	0.31	0.55
N950	1257	0.37	0.50
H500	1224	0.30	0.55
H950	1241	0.34	0.49

^a Not determined.

The oxygen content was estimated by difference. In ancillary experiments, agreement with oxygen content obtained from temperature-programmed desorption experiments was found to be within $\pm 5\%$.¹⁵ Table 3 contains the data on elemental analysis and mass loss for the as-received and representative chemically treated carbon samples.

The point of zero charge (PZC) of each sample was determined using a modified version of a simple method proposed by Noh and Schwarz,^{15,16} referred to as reverse mass titration.¹⁵ Slurries of 10 wt % were prepared by mixing particles of carbon (<0.21 mm) with distilled-deionized (DD) water in a plastic bottle sealed under N₂. The pH of the slurry was measured after shaking it for 24 h. Some DD water was subsequently added, and the previous procedure was repeated for slurries of 8, 6, 4, 2, and 1 wt %. A plot of equilibrium pH vs solid weight fraction yields a curve and the equilibrium pH at the plateau of the curve corresponds to the PZC.

Microcalorimetric measurements were carried out in a Calvet-type apparatus that allows *in situ* sample pretreatment. Details of the apparatus and procedures are provided elsewhere.¹⁷ Using Nc as the starting material, the different samples were prepared *in situ* following the same procedures described earlier, using N₂ at 950 (N950) and 500 °C (N500), H₂ at 950 (H950) and 500 °C (H500), as well as a physical mixture of 7 parts (by mass) of Nc and 1 part of PtC in H₂ at 500 °C. As a reference, the sample PtC was also treated in H₂ at 500 °C.

After treatment the samples were gravity-transferred (avoiding all air exposure) to the adsorption cell and evacuated for 24 h at 0.05 Torr. Known microdoses of O₂ were then introduced sequentially, and oxygen adsorption isotherms were obtained by plotting the micromoles of O₂ adsorbed per gram of carbon vs the equilibrium pressure after each dose. Sample and dose sizes were adjusted (whenever possible) such that 15 or more doses were required to saturate the surface. Thus, the heats evolved as a result of each oxygen microdose, measured using thermopiles,¹⁸ were essentially "differential".

Each dose yields a ballistic curve (heat output vs time). From these ballistic curves a quasi-differential heat of adsorption is obtained by integrating the area under the curve and dividing by the amount of gas adsorbed. A parameter related to the differential rate of adsorption, the normalized width of the curve (in time units) at half-peak-height-maximum (NCWHM), was used as a qualitative measure of relative adsorption rates.

Results

A battery of experimental techniques were employed to study the surface chemistry of three types of samples: nitrogen-treated pure carbons, hydrogen-treated pure carbons, and mixtures with carbons containing some platinum particles, as described above. Treating pure carbon samples in H₂ rather than N₂ had significant consequences. As demonstrated below, and in earlier work,¹⁴ N₂ treatment removes oxygen-containing functional groups, creating a more basic surface. However, these surfaces quickly readsorb oxygen at ambient laboratory conditions,

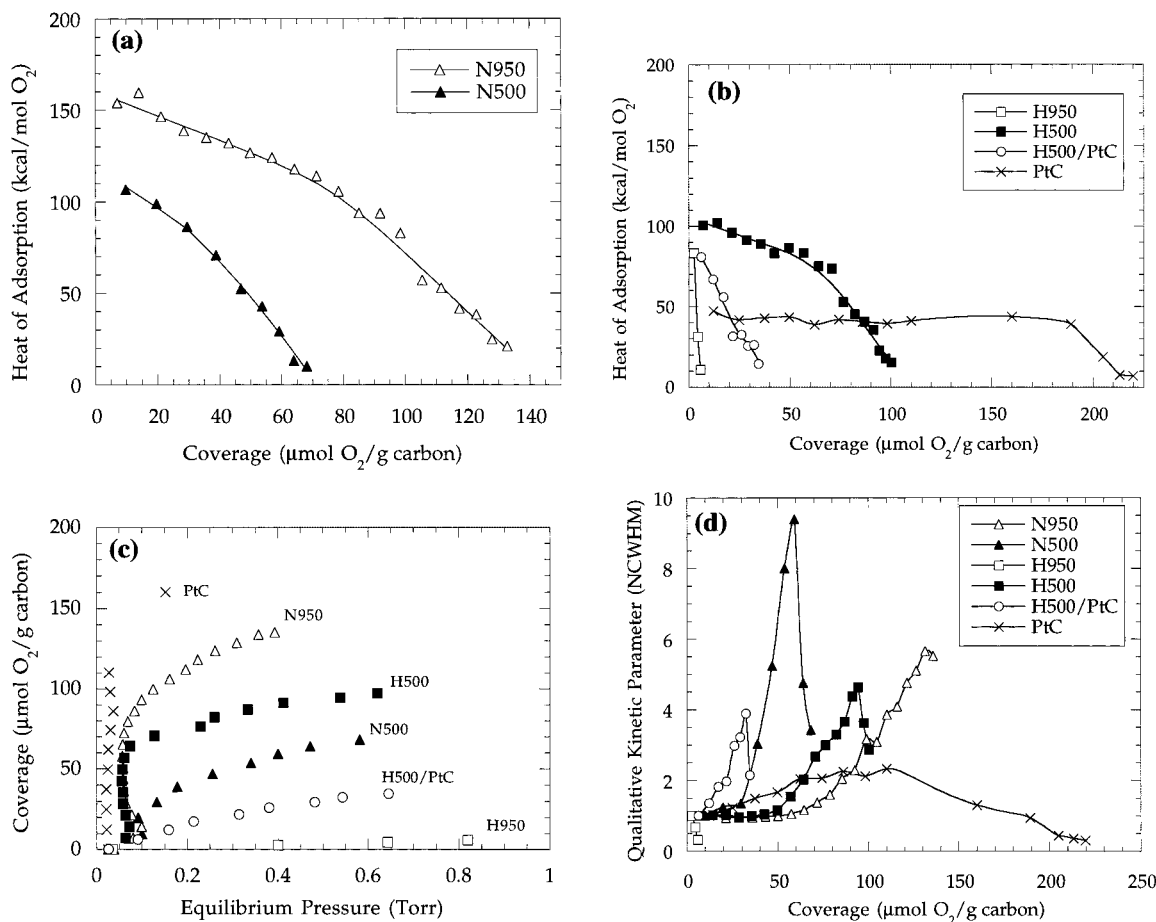


Figure 1. Results of oxygen microcalorimetric studies at 298 K: (a) differential heats and amounts of oxygen adsorbed on two nitrogen-treated pure Nc samples; (b) heats and amounts adsorbed on PtC, and a mixture of PtC and Nc, after treatments at 500 °C in hydrogen (H500 and H950 curves also shown for comparison); (c) isotherms plotted for all samples (data were collected in microcalorimeter concomitantly with heat data); (d) kinetic data on oxygen adsorption at 298 K for treated activated carbons.

TABLE 3: Chemical Analysis of As-Received and Surface-Treated Carbon

carbon	wt %				molar ratio		wt % loss ^b
	C	H	N	O ^a	H/C	O/C	
Nc	82.3	2.3	0.3	15.1	0.335	0.138	
PtC	94.0	0.4	0.6	5.0	0.051	0.040	
N950	94.2	0.6	0.6	4.6	0.076	0.037	8.3
N500	90.0	2.3	0.4	7.3	0.301	0.061	6.7
H950	99.0	0.4	0.3	0.3	0.048	0.002	20.2
H500	91.8	2.3	0.6	5.3	0.301	0.043	11.2
H500/PtC	95.5	2.2	0.6	1.7	0.276	0.013	15.5

^a Calculated by difference. ^b Dry basis.

regaining their acidity. In contrast, hydrogen-treated surfaces contain much less oxygen and remain that way even following air exposure. Novel to the present study is the finding that samples prepared from mixtures under hydrogen had characteristics similar to that of pure samples prepared in hydrogen, but these characteristics were produced following treatment at far lower temperature. For example, such a sample prepared in hydrogen at 500 °C had the same resistance to oxygen adsorption, and virtually the same stabilized PZC value, as a pure sample prepared at 950 °C.

Nitrogen-Treated Nc. The finding that the BET and DR surface areas are virtually unchanged (Table 2) suggests that high-temperature nitrogen treatment caused few changes in the physical structure of the carbon. In contrast, use of a variety of techniques led to the conclusion that treatment in nitrogen (N950) changed the surface chemistry dramatically. In particular it is clear that this treatment led to the desorption of

oxygen-containing groups from the surface (Table 3) and to the formation of a surface less acidic than the untreated material (Table 1). However, the surface formed is not as basic or as stable as that found after hydrogen treatments.

The calorimetric data provide evidence that the surfaces were not passivated by nitrogen treatment. That is, as shown in Figure 1a, significant quantities of oxygen were adsorbed at room temperature following treatment at both 950 and 500 °C. This suggests both that oxygen was removed, creating fresh carbon active sites, and that these new active sites are not completely stable against oxygen readsorption at low temperatures (25 °C). The calorimetric data also show that the amount of oxygen readsorbed declines with decreasing treatment temperature. Still, it is clear from Figure 1c that the amount of oxygen adsorbed following nitrogen treatment at 950 °C is far higher than the amount adsorbed by the same material treated

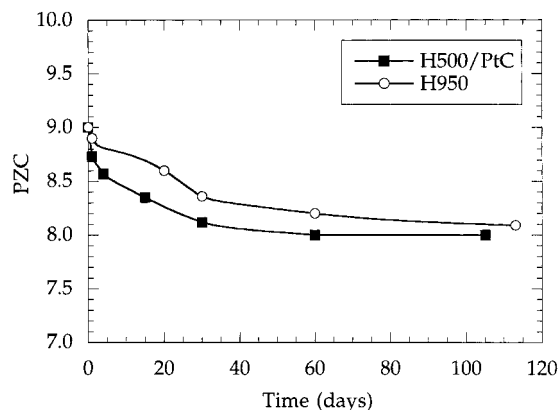


Figure 2. Changes in the point of zero charge of H950 and H500/PtC upon exposure to ambient air.

in hydrogen at 950 °C or by the mixture material treated in hydrogen at 500 °C.

The strong oxygen adsorption measured with the calorimeter helps to explain the finding that the PZC values following nitrogen treatment are always lower than those found after equivalent hydrogen treatment or for the mixture samples treated in hydrogen (Table 1). That is, the calorimetric studies suggest that the brief air exposure of the sample prior to the PZC measurement (<5 min) resulted in a significant readsorption of oxygen and concomitant acid center generation. It is also notable that the low-coverage heats of adsorption on N950 are far higher than those reported commonly for carbon materials. Indeed, the highest heats for oxygen adsorption on carbon previously reported were on the order of 100 kcal/mol O₂.^{18–20} In contrast, the heats of adsorption recorded for the N500 sample (Figure 1a) are similar to those reported in earlier studies.^{14,18}

Hydrogen-Treated Nc. All experimental measures, except measures of surface area and porosity (Table 2), show that the Nc treated at 950 °C in H₂ was far different from the same material treated at the same temperature in N₂. For example, the nitrogen-treated sample clearly contained significant oxygen, whereas the hydrogen-treated sample had virtually none (Table 3). This indicates that the hydrogen-treated samples resist reoxidation, at least at ambient conditions. The chemical analysis indicates another apparent anomaly: H950 has an even lower hydrogen/carbon ratio than the N950 sample. In fact, as the severity of H₂ treatment increases, the H/C ratio in the carbon decreases.¹⁴ A related observation had been made previously: hydrogen does not adsorb on high-temperature hydrogen-treated carbon.²¹

The calorimetric studies also indicate that H950 does not readsorb a significant amount of oxygen at 298 K. Indeed, under the conditions at which the calorimetric experiments were conducted N950 adsorbed about 20 times as much oxygen as H950 (Figure 1).

The PZC values of the hydrogen-treated samples (Table 1) clearly indicate that these treatments result in the creation of a stable basic surface. Measurements of PZC as a function of time (Figure 2) confirm this finding. It is evident that the PZC value of H950 decreases marginally over a period of 30 days and then is virtually unchanged over the next 150 days.

Hydrogen-Treated Oxidized PtC. It is evident from all the data that the PZC of oxidized PtC samples (PtC–Ox) is higher than the PZC of equivalently treated Nc samples. As shown in Figure 3 the PZC of the oxidized PtC sample treated at 350 °C in H₂ was 9.8, whereas the Nc sample treated in the same fashion had a value of only 2.7. As shown in the figure, even oxidized PtC samples treated at lower temperatures had significant

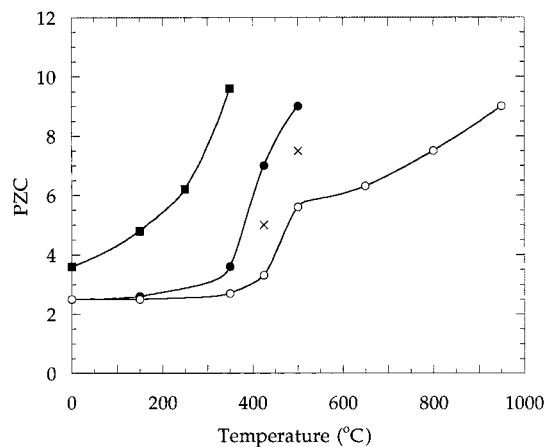


Figure 3. Variations in the point of zero charge (PZC) with treatment temperature (in H₂) for as-received Norit C carbon (○) and for surface-modified carbon samples in the presence of a Pt catalyst: ●, Norit C mixed with commercial activated carbon containing 1% Pt catalyst (in a ratio of 1:2); ×, Norit C treated in a different boat downstream; ■, commercial activated carbon containing 1% Pt, previously exposed to concentrated nitric acid at 60 °C for 64 h.

increases in PZC values, whereas the Nc samples showed no effect of hydrogen treatment at these temperatures.

Calorimetric data collected from a PtC sample treated at 500 °C in H₂ are shown in Figure 1b. As discussed below, much of the oxygen adsorption is attributed to the platinum and not to sites on the carbon surface.

Hydrogen-Treated Mixtures. It was found that the chemical character of the treated Nc samples was profoundly impacted by the mixing process. That is, the surfaces of Nc treated in a mixture were far more basic than those of pure Nc samples treated in equivalent fashion.

The PZC values of Nc separated from the mixture by sieving are remarkable. After treatment at 500 °C the PZC was 9.0 (Figure 3). This value is as high as that for sample H950 and far higher than that of H500 (5.6). Even after reducing the relative fraction of PtC, from 2 PtC:1 Nc to 1 PtC:2 Nc, a virtually identical PZC value (8.8) was obtained. As illustrated in Figure 3, treatments of the mixtures at lower temperature also dramatically increased the PZC of the Nc component.

Stability tests indicate that the surfaces of Nc treated in the mixtures are stable. As shown in Figure 2, there was very little change in the PZC of the Nc removed from the Nc/PtC mix and exposed to ambient laboratory conditions for months. In fact, it is virtually as stable as the H950 sample.

A calorimetric study of a mixture (1 PtC:7 Nc) was performed after treatment in hydrogen at 500 °C. As shown in Figure 1b, this sample adsorbed far less oxygen (per gram of Nc) than the H500 sample. Moreover, approximately 50% of the oxygen that was adsorbed probably adsorbed on the platinum surface. (The PZC and other measures of Nc properties from mixed samples were performed after separation by sieving. In contrast, this was not feasible for calorimetric experiments.) Once the adsorption on the platinum component was subtracted, it was found that the amount of oxygen adsorbed, on a gram carbon basis, was virtually identical with the amount adsorbed on the H950 sample. Thus, the calorimetric study verified that the Nc prepared in a mix is stable and adsorbs far less oxygen than H500.

Hydrogen-Treated Unmixed PtC and Nc. The PZC values of each of the batches of Nc carbon from the unmixed experiment were also measured. The Nc carbon in the upstream boat had a PZC value of 7.0, while the PZC value of the Nc in the downstream boat was 7.5 (Figure 2) and the PZC of the Nc

in the middle boat (after separation from PtC) was 9.0. For comparison, the PZC of Nc treated at the same position as the middle boat (with no platinum present at all) was 5.6. It is clear that the presence of the platinum increases the PZC value even if the metal is not intimately mixed with the carbon.

Discussion

Observations. Perhaps the most significant result of the present work is the empirical finding that stable basic carbons can be produced at far lower temperatures in the presence of platinum than in its absence. The PZC studies demonstrated that the basicity of the Nc carbon treated in a mixture with platinum-containing carbon (PtC) is always higher than that of the Nc carbon treated at the same temperature in the absence of noble metal. In fact, the PZC values of the Nc carbon treated in the mixtures were found to be equivalent to that of the Nc carbon treated at temperatures at least 400 °C higher in the absence of platinum. Also, microcalorimetric and long-term PZC studies showed that Nc carbon gains stability against readsorption of oxygen at far lower temperatures when some platinum is present in the mixture.

Other findings are consistent with the suggestion that platinum (or another noble metal) is a key ingredient required to lower the temperature at which stable basic carbons are formed. First, PtC carbon, a high-surface-area carbon material containing platinum particles dispersed on its surface, becomes basic and stable after hydrogen treatments at remarkably low temperatures. Second, even the Nc carbon that is not in intimate contact with platinum-containing carbon becomes basic at lower temperatures than Nc carbon treated neat.

Finally, as discussed in our earlier report,¹⁴ it is important to note the difference between carbons treated in hydrogen and those treated in nitrogen. The latter treatment is never found to produce basic and stable surfaces. This is clearly shown by PZC measurements, which indicate acidic surfaces even following high-temperature treatment in nitrogen, and by calorimetric studies, in which oxygen was found to adsorb rapidly at room temperature on nitrogen-treated carbon. Also, as noted previously,¹⁴ both nitrogen-treated and low-temperature hydrogen-treated (H 500) samples have a slight "knee" in the isotherm at very low pressures (Figure 1c). This was shown to coincide with a very small amount of CO evolution. Presumably, this gas-phase CO is generated by interaction between "adsorbing" O₂ and very loosely bound carbon atoms. Hypothetically, high-temperature hydrogen treatment or low-temperature hydrogen treatment in mixtures containing platinum removes "dangling" carbon (see below), hence, no CO evolution and no isotherm "knee" are expected (none found!) for these samples.

Model. Earlier work suggests an explanation for the action of the platinum.^{22–24} It is postulated that platinum particles dissociate hydrogen molecules, creating hydrogen atoms that "spill over" to the carbon surface, both via surface and gas-phase diffusion, hydrogasifying the most reactive surface carbon atoms. That is, the hydrogen atoms remove carbon atoms (probably as methane) that are left in a highly unsaturated state^{14,25} due to the thermal removal of neighboring carbon atoms, as CO₂ or CO. The following two-step process is thus hypothesized to take place during the hydrogen treatment of Nc carbon mixed with PtC at 500 °C. First, the Nc carbon loses most of its oxygen as CO₂ (and some CO) owing to thermal decomposition of the surface oxygen groups (a process possibly accelerated in the presence of hydrogen atoms). Subsequently, hydrogen atoms generated by the platinum "hydrogasify" the highly unsaturated carbon atoms that are left behind by this thermal process.

The above model suggests that the difference between Nc treated neat in hydrogen at 500 °C and Nc treated in the presence of platinum at the same temperature is solely the number of residual highly reactive carbon atoms on the surface. The Nc sample treated in H₂ in the presence of platinum will have very few such sites, while Nc treated without platinum present will have a significant number of highly unsaturated carbon atoms. These sites in the sample treated neat quickly adsorb oxygen upon air exposure at room temperature, returning the surface to an acidic condition. In contrast, on Nc treated with platinum present all unsaturated carbon atoms that remain are capable of adsorbing oxygen only at elevated temperatures. Indeed, it has long been known that on some carbon active sites oxygen will not adsorb at temperatures of less than 300 °C.²⁶

There are other possible hypotheses that might explain the role of H atoms in stabilizing the surface. Indeed, it has been shown previously¹⁴ that high-temperature H₂ treatment (e.g., H950) accomplishes three tasks: (i) it removes surface oxygen; (ii) it stabilizes some of the reactive carbon sites by forming stable C–H bonds; (iii) it hydrogasifies the most reactive carbon atoms. Data in Table 3 and Figures 1 and 3 indicate that the third process is the most significant when hydrotreating in the presence of platinum, as postulated. First, sample H500/PtC exhibits initial heats of O₂ adsorption that are comparable to those of sample H950 and lower than those of sample H500 (Figure 1b), suggesting that oxygen adsorbs on sites similar to those found on the former. There is no evidence of adsorption on highly reactive sites. Second, the extent of room-temperature O₂ adsorption of sample H500/PtC is much lower than that of samples H500 and N500 (Figure 1c). Third, the weight loss during treatment of sample H500/PtC is higher than that of samples N500 and H500 and consistent with gasification. All these observations are consistent with the postulate that at 500 °C H atoms generated by spillover are effective at removing highly reactive carbon atoms. It is concluded that experimental evidence supports the postulate that low-temperature stabilization in the presence of platinum occurs primarily by the hydrogasification of the most reactive carbon atoms ("dangling" carbon atoms).

It remains unclear, however, whether a secondary action of hydrogen atoms is to increase the rate of decomposition of oxygen-containing surface groups. The results are not conclusive. As noted above, sample H500/PtC has a basicity and stability very similar to that of H950, yet its oxygen content is significant. This result does not support an acceleration of oxygen removal by hydrogen atoms. In contrast, the oxygen content of H500/PtC is significantly lower (by a factor of 3) than that of H500. This latter observation could be interpreted as evidence that hydrogen atoms enhance surface oxygen removal. Nevertheless, it is possible that the difference in oxygen content between H500 and H500/PtC can be traced to the fact that only the former sample had a significant number of highly reactive carbon atoms following treatment and that subsequent air exposure resulted in higher oxygen uptake prior to elemental analysis. This interpretation is certainly supported by the calorimetric results, which show that H500 adsorbs significant amounts of oxygen whereas H500/PtC does not.

Spillover. There is a voluminous literature on hydrogen spillover and its effects in catalysis.^{27–36} Of particular significance to the present work is the finding that the rate of hydrogen atom diffusion across carbon surfaces is particularly high.^{21,30} It has also been shown that on carbon surfaces chemical effects are apparent in some cases even at 30 °C.³⁶ Thus, it is reasonable to postulate that hydrogen atoms are present on all carbon surfaces that are in intimate contact with the platinum,

even at the lowest temperatures employed in the present work. Although this is not "proof" that the hydrogen atoms hydrogasify highly unsaturated (dangling) carbons (or accelerate oxygen removal), it is a plausible explanation for the observation that stable basic carbons form at lower temperatures in the presence of platinum. Indeed, dissociative H₂ chemisorption on the carbon surface is known to be the rate-determining step in carbon hydrogasification.³⁷ Finally, it must be noted that methane formation during activated carbon–hydrogen reactions is known to be accelerated by noble metals. This was attributed to the action of hydrogen atoms generated by the noble metal.³⁸

A second finding is also consistent with earlier observations of hydrogen spillover. That is, in the present results there is evidence that gas-phase hydrogen atom "spillover" occurs at temperatures of 350 °C or higher. Indeed, it was found that above 350 °C the PZC value of Nc carbon increased even when there was no direct contact between the Nc and PtC particles. That is, several experiments were conducted in which quartz boats containing only Nc were surrounded by quartz boats containing PtC and treated in hydrogen. In those cases in which PtC was present in adjacent boats the PZC values of Nc carbon showed dramatic increases (Figure 3) relative to control cases (no PtC anywhere in the system) as long as the temperature was above 350 °C. Earlier workers also report observations consistent with the onset of gas-phase transport of hydrogen atoms at temperatures above 350 °C.^{21,22,28,32} Although the contribution of secondary reactions at carbon sites physically separated from platinum (e.g., gasification of dangling carbons by steam produced by removal of oxygen functionalities) cannot be ruled out on the basis of the present data, they are considered unlikely at the low temperatures of interest for the present discussion.

There is also evidence that the proximity of platinum determines the temperature at which stable basic carbon will form. Specifically, the data show that true basic surfaces (PZC > 7) were found on Nc carbon after treatment in hydrogen at (i) ~750 °C with no platinum in the system, (ii) ~500 °C with platinum present but not in direct contact with Nc surfaces, (iii) ~400 °C for intimate mixtures with platinum-bearing surfaces, and (iv) ~300 °C with platinum particles present on the carbon surface.

Summary

Our earlier studies indicated that hydrogen treatments must be carried out at high temperatures (>900 °C) to produce highly basic (PZC > 9.0) and stable carbon surfaces. The present study shows that in the presence of platinum-bearing surfaces (and most likely other noble metals), stable and highly basic surfaces can be produced at temperatures of 500 °C or less. There is strong evidence to support the hypothesis that the role of the platinum is to produce hydrogen atoms, which subsequently spill over onto the carbon surface. The temperature at which hydrogen atoms gasify unsaturated carbon atoms is postulated to be far lower than that required for gasification by molecular hydrogen. Thus, in the presence of platinum (and hence hydrogen atoms) carbon surfaces are stabilized at far lower temperatures.

There is also evidence provided that suggests that hydrogen atoms are transported through the gas phase at temperatures of 350 °C or higher.

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