Thermochimica Acta 312 (1998) 87–93

thermochimica
acta

Calorimetric study of oxygen adsorption on activated carbon

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Abstract

Microcalorimetry was employed to study the surface chemistry of activated carbon. The chemistry of active sites was found to be a function of the pretreatment procedure. Following treatment at high temperature (950°C) in nitrogen, the carbon adsorbed a great deal of oxygen at 25°C with a remarkably high heat of adsorption (approx. 125 kcal/gmol O_2), whereas after treatment at high temperature in hydrogen the same carbon adsorbed virtually no oxygen at 25°C. It was found, however, that the hydrogen treated carbon did adsorb oxygen at an elevated temperature (150°C). Changes in the character of oxygen interaction with the carbon surface can be related to the nature of unsaturated sites on the carbon surface. Specifically, after treatment in nitrogen the surface contains a high concentration of highly unsaturated ('dangling') carbon atoms which interact rapidly and strongly with oxygen. All these sites are removed by the hydrogen treatment leaving only partially unsaturated sites, which only interact with oxygen at elevated temperature. © 1998 Elsevier Science B.V.

Keywords: Oxygen adsorption; Activated carbon; Microcalorimetry

1. Introduction

It is increasingly clear that microcalorimetry provides unprecedented insight into the structure and surface chemistry of high surface area materials, such as acid catalysts [1,2], supported metal catalysts [3–6] and carbons [7–12]. That is, calorimetry can provide significant information regarding the 'chemistry' of the outermost layer of a solid. It is the chemistry of this layer which controls processes such as adsorption and heterogeneous catalysis. Other techniques, in particular electron spectroscopies (e.g. Auger, XPS), only provide average composition, and limited chemical, information regarding the top few atomic layers of a solid. Moreover, these techniques are generally not amenable to the study of powders, nor to distinguishing small quantities of active material on a heterogeneous surface (e.g. supported metal catalyst), nor to distinguishing special sites on the surface of a nearly homogeneous material (e.g. carbon, alumina). Even methods which probe the outermost layer, such as isotherm determination, are of limited value. For example, adsorption isotherms cannot distinguish which metal dominates the surface of a bimetallic catalyst particle, nor provide information on the distribution of active sites on an adsorbent such as carbon.

In the present work, a novel microcalorimeter was employed to study the impact of treatment gas on the character of adsorption sites on an activated carbon. The technique readily revealed that treatment at high temperature in nitrogen leaves a surface with a high concentration of both 'dangling carbon' sites and lower energy sites requiring activation to adsorb oxygen, whereas the same material treated in hydrogen has only the lower energy sites on the surface.

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PII S0040-6031(97)00442-5

2. Experimental

2.1. Instrument

Possibly the greatest impediment to increased application of the calorimetric technique is the lack of instrumentation which is inexpensive and relatively easy to employ. In earlier work, we described an instrument which can be built with readily available equipment [13]. The instrument described earlier suffered several limitations. In particular, it can only be operated near room temperature. Thus, we developed a new design which enabled operation at temperatures as high as 200°C. This permits the study of activated adsorption and insures, in many cases, that the adsorbed phase is in equilibrium with the gas phase [14,15].

The instrument described not only is far less expensive than commercial systems, it also has some features which are not found in those systems. For example, the dose volume is at the same temperature as the sample-cell/thermopile sandwich. There is no need for concern regarding possible consequences of adding 'cold' gas to a 'hot' sample. Also, the dose volume consists of two precision baratron pressure gauges. Thus, pressure readings are available at every instant of time. This provides information regarding the kinetics of adsorption. Such information is not available in other systems in which pressure readings are only taken at the beginning and end of each adsorption step.

The instrument is designed to allow for: (i) sample preparation in vacuum or flowing gas at temperatures as high as 1100°C; (ii) transfer of powder samples (as much as 8 cm^3) under vacuum to the sample cell; (iii) adsorption with thoroughly equilibrated gas; (iv) precise determination of the amount of gas adsorbed; and (v) precise determination of the heat released at temperatures ranging 25–200°C.

Samples are prepared in a quartz tube, placed in a tube furnace located outside the precisely temperature-controlled convection oven (Despatch, LND 1-42-3) containing a microcalorimeter. Gas from the gas handling system can be passed through the microcalorimeter and then over the sample, or the sample can be treated under a vacuum of 1×10^{-6} torr. Following completion of the pre-treatment, the sample is transferred to the sample cell simply by tilting the convection oven to an angle of about 30° relative to horizontal. The cradle holding the oven is so designed that the tilting and transfer process can be done by a single individual (Fig. 1).

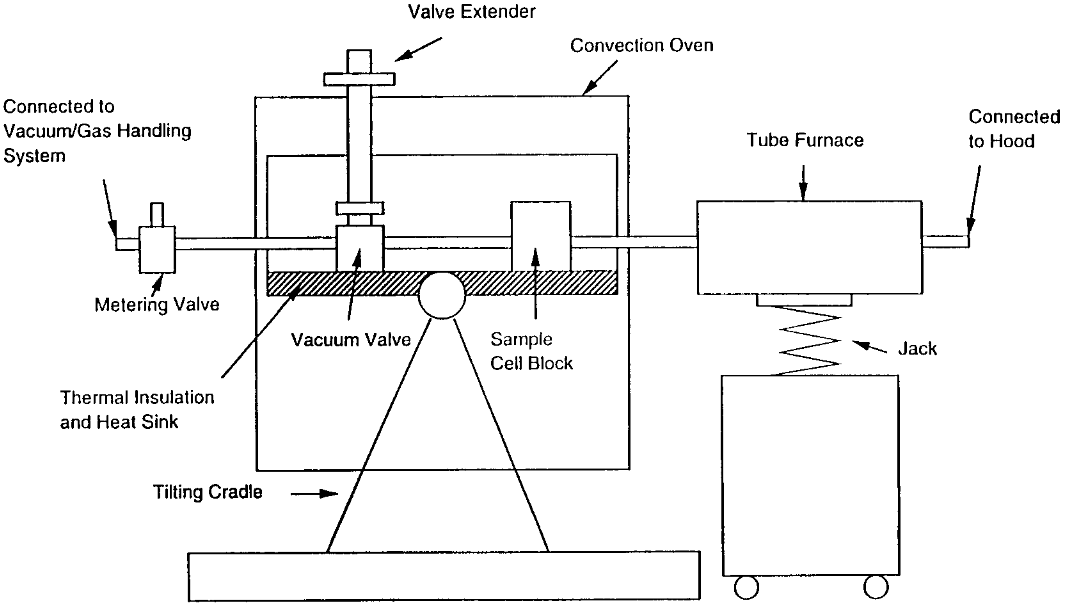

Fig. 1. Cut-away side-view of microcalorimeter system.

Gas is introduced to the sample in two steps. First, it is metered into the dose volume from the gas handling/vacuum system using a needle valve. The dose volume which is entirely at the predetermined operating temperature, consists of two high temperature baratron gauge heads (Model 615AD-MKS Instruments) and the tubing which connects them to (i) the vacuum/gas system and (ii) the sample cell. The tubing is of stainless steel, and all joints are weld joints. After a brief period of time (ca. 2 min), during which the gas equilibrates to the system, the second step is performed; gas is allowed into the sample chamber. It should be noted that the valves (Nupro 4BKT series, rated to 482°C) are turned using extenders which reach outside the oven. The process as described is not very different from that employed to collect standard isotherms. The only significant change is that the gas sample temperature is allowed to equilibrate with the system prior to its admission to the cell. Also, it should be noted that precision pressure gauges provide information regarding adsorption kinetics.

The four thermopiles are arranged to provide maximum signal and minimal drift (Fig. 2). The two (S1 and S2) surrounding the sample cell are electrically opposite to the two others (R1 and R2). This arrangement was shown to be effective in near-ambient systems, and the theory is discussed elsewhere [9,13,14]. The calorimeter is insulated with about 5 cm double-shell enclosure of high temperature insulating material on all sides. In general, it is understood that thick insulation improves calorimeter thermal stability [14]. However, this thick insulation does slow down the achievement of equilibrium. In this system, it takes approximately 6 h to achieve a stable thermal baseline following sample transfer.

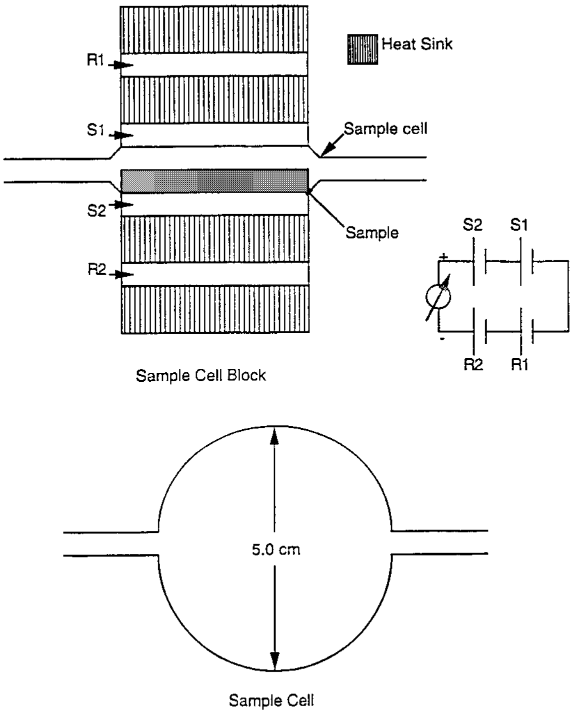

Fig. 2. Cross section of sample cell block.

Calibration of the instrument was carried out electrically [14,16,17]. A precision high-temperature resistor (about 500 Ω) was inserted into the cell and constant current applied. Total power input was then correlated to output signal to determine a calibration constant. A range of heat inputs were employed to ensure that the calibration constant was valid at all input power rates and at all total power inputs (Table 1).

Table 1
Results form electrical heating calibration (resistor: R=482 Ω) [a]

Voltage (V)	Time of heat input (s)	Total heat input (J)	Heat from output peak (J)	Calibration constant
1.54	80.29	0.395	0.239	1.653
2.18	70.24	0.693	0.440	1.574
3.08	65.32	1.286	0.789	1.630
4.87	35.36	1.740	1.049	1.659
4.87	41.54	2.044	1.243	1.644
4.87	47.44	2.334	1.459	1.600
4.87	75.08	3.694	2.303	1.604

[a] Mean=1.623, Standard deviation=2.922×10^{-2}.

The electrical calibration method is superior to the use of 'standard' chemical heats for several reasons. First, unlike the chemical method, it permits testing over a whole range of total input heat values and rates of heat input. Linearity of response need not be assumed. Second, the chemical test is not a true absolute standard. Errors made in other laboratories are propagated. Also, accurate information regarding the impact of temperature on these standards is not necessarily available. In contrast, resistance and current are easily measured with high accuracy with simple laboratory instruments at all temperatures. Thus, an electrical calibration is a true absolute calibration.

Typical heat output curves are shown in Fig. 3(a), and it is clear that baseline drift is not an issue with this instrument. Typical pressure curves are shown in Fig. 3(b). From these curves relative rates of adsorption can be determined. There is no significant lag time between the actual and measured pressure. Thus, the relative differential adsorption rates are more accurately obtained from the pressure readings than from heat curves, as the latter are convoluted with a rather slow instrument transfer function.

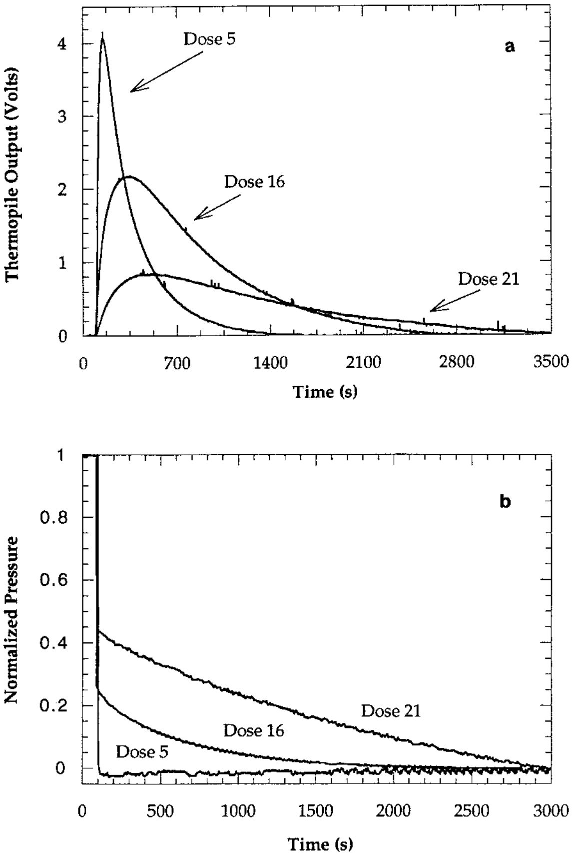

Fig. 3. (a) Characteristic thermograms for oxygen adsorption at 150°C on sample treated in N_2. (b) Characteristic pressure curves for oxygen adsorption at 150°C on sample treated in N_2.

2.2. Samples

High temperature hydrogen- and nitrogen-treated samples were made from a commercial activated carbon Norit C granular (Nc), which possesses a relatively high concentration of oxygen-containing surface groups [12]. Nitrogen-treated samples (ca. 0.5 gm) were made from powdered Nc (ca. <0.210 mm) heated to 950°C in the preparation tube in a flow (150 ml/min) of ultra-high-purity N_2 at 25°C/min. After holding this temperature for 3 h, the samples were allowed to cool down and then gravity-transferred to the sample cell. They were subsequently evacuated for 24 h at 1×10^{-6} torr. This time was enough to equilibrate the system to the temperature (25 or 150°C) at which gas adsorption was carried out. High temperature hydrogen-treated samples were prepared in the same fashion except that the hydrogen was substituted for nitrogen.

3. Results

Plots of the observed differential heats of adsorption vs. the carbon surface covered by oxygen are shown in Fig. 4(a) for adsorption at 25°C and in Fig. 5(a) for adsorption at 150°C. Using the pressure data collected during the experiments, typical isotherms of adsorption can also be plotted (Fig. 4(b) and Fig. 5(b)).

A number of features should be noted. First, all the samples treated in N_2 adsorb more oxygen and with higher initial heats of adsorption than samples treated in H_2 under similar conditions. The initial heats of adsorption on N950 samples are, in fact, significantly higher than the known heat of carbon combustion (94 kcal/g mol oxygen) to form CO_2 [18]. Second, at 25°C H950 adsorbs virtually no oxygen, although at 150°C it adsorbs a significant amount of O_2. Third, more oxygen adsorbs on N950 at 150°C than at

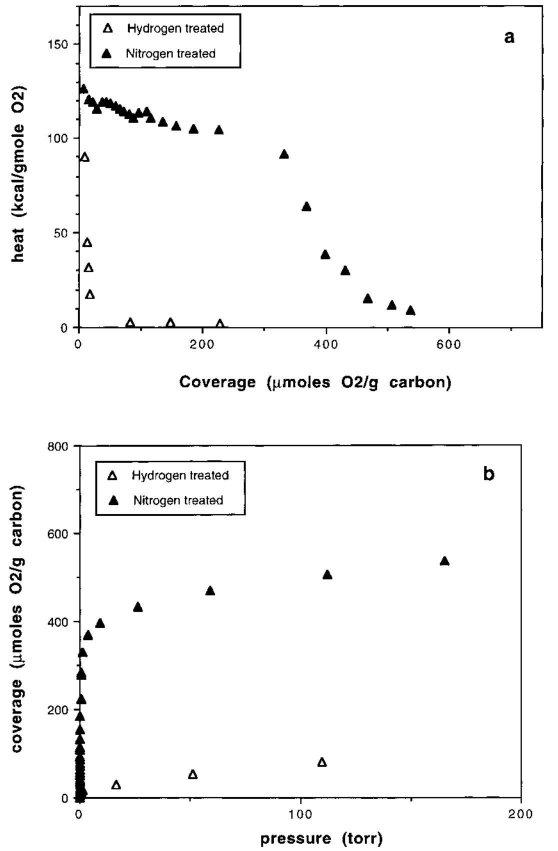

Fig. 4. Results of oxygen microcalorimetric studies at 25°C for surface-treated activated carbons: (a) differential heats as a function of surface coverage; (b) adsorption isotherms.

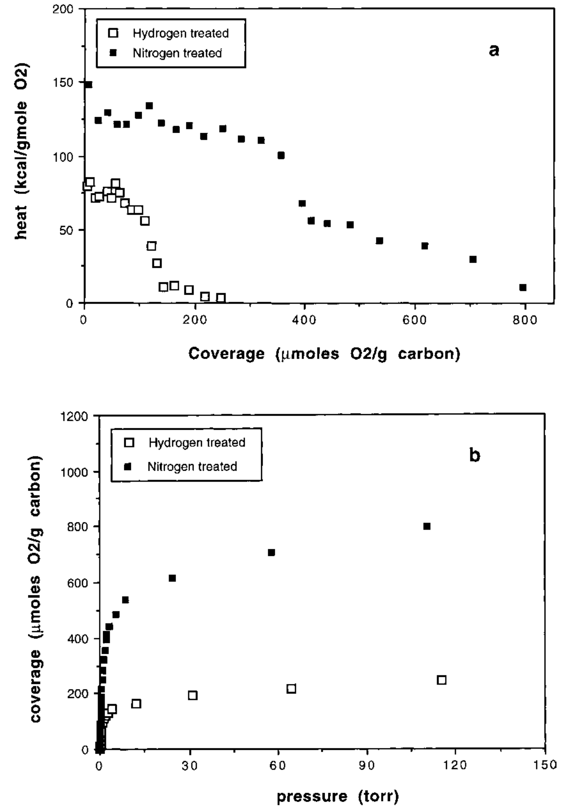

Fig. 5. Results of oxygen microcalorimetric studies at 150°C for surface-treated activated carbons: (a) differential heats as a function of surface coverage; (b) adsorption isotherms.

25°C. The 'extra' adsorption noted on N950 at 150°C has a heat profile similar to that seen for the H950 at 150°C.

As a means to obtain 'relative rate data' from the pressure curves, it is a standard practice in our laboratory to 'normalize' kinetic data obtained from the pressure gauge. First, all pressures curves are normalized to read between one (the initial dose pressure) and zero (the final/equilibrium pressure reached). The normalized adsorption time is the amount of time it takes for the pressure to drop to 0.1 on the normalized scale. Finally, the normalized adsorption parameter (NAP) for each dose is computed by dividing the normalized adsorption time for each dose by the normalized adsorption time of the first dose.

It is believed that a plot of NAP vs. Dose yields a reasonable model of gradual changes in adsorption kinetics, reflecting both chemisorption and mass-transfer processes. As an example of the use of NAP values to obtain qualitative kinetics, it is instructive to consider the data obtained for adsorption on the nitrogen-treated sample measured at 25°C (Fig. 6(a)). To begin the analysis examine the final adsorption processes. These are clearly physical adsorption (see final low heats, Fig. 4(a)). Physical adsorption is known to be a very rapid process [19]. Thus, the time for pressure to equilibrate, only in post-chemisorption/physical adsorption doses, reflects the time it takes for mass transfer to produce equilibrium throughout the bed, including within pores. Next, examination of the first 21 doses reveals NAP values which are much larger than those for the physical adsorption process. This suggests that chemisorption is far slower than physical adsorption. Qualitatively, for these doses,

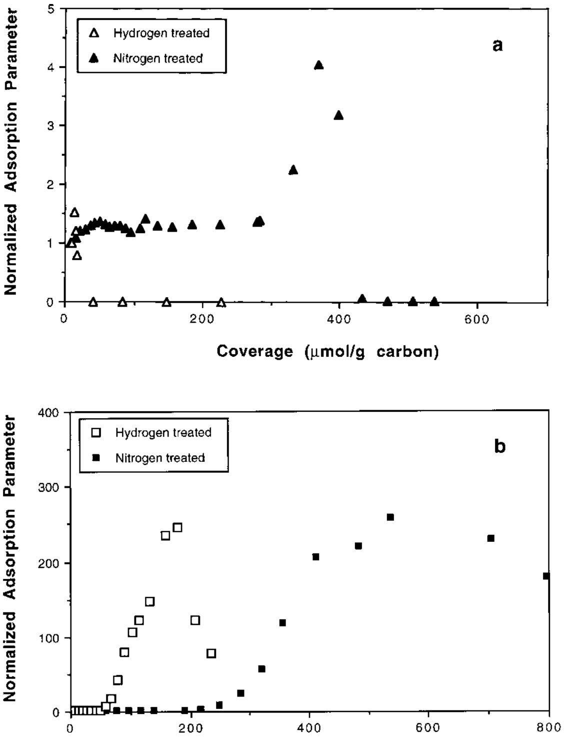

Fig. 6. Plots of the normalized adsorption parameter vs. sample coverage for surface treated activated carbons (a) adsorption at 25°C, (b) adsorption at 150°C.

kinetics is clearly dominated by adsorption rates and not by mass transfer.

The increased NAP values for doses 22–24 indicate that adsorption for these doses occurred much more slowly than it did for the first 21 doses. This is not surprising. Rapidly adsorbing sites are used first. The remaining sites have higher activation energy, causing the rate of adsorption to slow down. Clearly, adsorption rate is controlled by the kinetics of chemisorption at less 'active' sites. Similar considerations can explain the NAP pattern seen on all other samples.

4. Discussion

A significant body of work indicates that the temperature at which both treatments were conducted (ca. 950°C) is essentially enough to remove all the oxygen-containing groups from the surface of the carbon [12,20,21]. Yet, earlier studies clearly indicate that only the sample treated in nitrogen is expected to re-adsorb a significant amount of oxygen at 25°C. It is known that on the hydrogen-treated sample, little oxygen re-adsorption takes place at 25°C. Indeed, the findings of the present study confirm earlier observations [12,20].

It was previously postulated that although H950 does not adsorb oxygen at 25°C, it is not because the surface is saturated. Rather, adsorption on sites of H950 requires activation [12]. Thus, significant adsorption is anticipated at a sufficiently high temperature. It can be clearly seen that considerable adsorption does take place on the hydrogen-treated sample when adsorption is carried out at 150°C. This is consistent with many studies of carbon. It is known that the total activated surface area of a carbon (ASA) can only be measured, using chemisorption, at 300°C [22,23]. Moreover, the heat of adsorption is relatively low. The observed behavior is consistent with earlier models of the structure of these sites. They are postulated to be atoms at the edge of basal planes with two nearest-neighbor basal planes. All basal-plane atoms with one nearest neighbor have been removed as methane during the hydrogen treatment.

The results of oxygen adsorption on N950 suggests that these surfaces have two very different sites. One site type is like that described above for H950. The 'extra' (low-energy) adsorption at 150°C is assumed to take place at such sites. The high energy sites on the N950 surface (adsorb O_2 with heats >100 kcal/gm mol O_2) are postulated to be very different in structure. These sites have only one nearest-neighbor basal plane. They remain during the nitrogen treatment because the temperature employed is too low to anneal the surface and there is no hydrogen available to convert them to methane.

'Dangling' carbon atoms have already broken two basal-plane bonds and are in a 'higher' energy state than the normal edge atoms with only one broken basal-plane bond. Therefore, they can more strongly bond with oxygen (higher heats) than the edge atoms with two nearest-neighbor basal planes, thus accounting for the high heats of adsorption observed. The formation of CO like surface species is not considered likely as the heats evolved from such processes are too low.

It is also instructive to contrast adsorption on the nitrogen-treated samples at the two temperatures. More gas adsorbs at 150°C than at 25°C. Clearly, the initial adsorption at 150°C takes place on sites much like those which adsorb oxygen at 25°C. However, at 150°C adsorption also takes place on sites which do not adsorb oxygen at 25°C. This indicates that there are sites on nitrogen treated carbon, like on hydrogen treated carbon, which require activation for adsorption to occur. The heat of adsorption profile of the 'activated adsorption' sites on the nitrogen-treated sample is very similar to that observed on the hydrogen-treated sample studied at 150°C. This suggests that the nitrogen-treated samples contain both high energy sites requiring no activation to adsorb oxygen, and sites requiring activation, which are similar in character to those found on the hydrogen-treated sample. The suggestion that two categories of sites exist on a single carbon surface is consistent with the general understanding of carbon surfaces [24,25].

In sum, the availability of a high-temperature calorimetry data provided unique, and previously unexpected, insight into the surface chemistry of nitrogen and hydrogen treated activated carbons. These results are of potential value in catalysis. For example, the use of carbon as a catalyst support is hindered to some extent by the weak bonding, generally found between carbon and metals (WMSI), thus metal particles on carbon tend to rapidly sinter [26,27]. It is possible that dangling carbon atoms can interact strongly with metal atoms, providing a link between metal and support. Also, there is interest in employing carbons as NO_x reducing agent. Carbon will reduce NO, but it is generally found to be non-selective, thus will also interact with oxygen. Possibly H950, which does not interact with oxygen at low temperatures, can selectively reduce NO in the exhaust streams of lean burn power plants.

Acknowledgements

This work was made possible by financial support from the National Science Foundation (NSF-CTS-9423094). Also, a postdoctoral grant to JAM (Spanish Scientific Council, CSIC) is gratefully acknowledged.

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