

OA19) Oxygen Adsorption Capability of An
Activated Carbon and Its Supported Pt
Catalyst

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1. Introduction

Carbon-supported noble metals have been widely used in industrial chemical processes including liquid-phase hydrogenation and organic synthesis [Puri, 1970]. Activated carbons are frequently used to prepare supported metal catalysts, since they have, in general, specific properties such as high surface area and porosity, plus relatively low intrinsic chemical activity and they are not easily destroyed by acids and bases. Modification of the surface of activated carbons is an increasingly attractive method for novel applications of these materials not only as catalysts and their supports, but also as adsorbents for both gas and liquid separations [Radovic. and Rodriguez-Reinoso, 1997]. It is known that thermal treatments of activated carbons at high temperatures readily remove oxygen from the active sites at the edges of graphite-like crystallites. Recent studies have reported that the character of the residual carbon active sites depends significantly on the gaseous atmosphere in which such treatment is carried out [Menendez et al., 1996]. When an activated carbon-supported Pt catalyst was pretreated in flowing pure H₂ at 1223 K or at temperatures lower than 773 K, the activated carbon adsorbs very little oxygen at room temperature. However, this carbon material following such pretreatment in a flow of pure N₂ adsorbs as much as 20 times more oxygen under the same conditions. In this paper, we demonstrate that such oxygen adsorption capability of activated carbons with nanosized Pt particles after different pretreatments could also depend significantly on metal impurities in the carbon supports

2. Experimental

A sample of an activated carbon, Westvaco SA30, was used as received to investigate the oxygen adsorption behavior with different pretreatments. The present study also used the 3% Pt/C catalyst, referred to Pt/C-W, which had been provided by Pharmacia and prepared using the wet impregnation of a Westvaco SA30 carbon. An elemental analysis of the samples was quantitatively determined by atomic absorption spectroscopy (AAS).

Adsorption of H₂, O₂, CO and CO₂ on those carbon-based samples was measured, typically at 300 K, using a conventional volumetric stainless steel vacuum system with a high vacuum below 10⁻⁷ Torr. Details of this volumetric system have been described elsewhere [Kim et al., 2001]. Before introducing the gas required for sample pretreatment and adsorption measurements into the volumetric system, it was further purified by passing it through commercial moisture traps and Oxytraps (Alltech Associates), except for O₂. Prior to the adsorption measurement, each catalyst sample was pretreated in situ in a laboratory-designed adsorption cell, and pretreatment at 473 K in a flow of pure H₂ is designated LTHT (low-temperature hydrogen treatment) to distinguish it from a high temperature hydrogen treatment (HTHT) at 673 K. The flow rate of each gas during the sample pretreatment was controlled at 32 cm³/min with a Tylan Model FC 260 mass flow controller. In addition, an oxidized surface of 3% Pt/C-W has been characterized to clarify the reason this catalyst possesses a huge amount of oxygen uptakes at 300 K.

3. Results and Discussion

No capability for both H₂ and CO adsorptions at 300 K on the SA30 carbon reduced at 673 K was revealed, as listed in Table 1 with uptake values for other samples used, but the carbon had significant O₂ adsorption capability and the oxygen irreversibly adsorbed on the pure carbon was 27.5 μmol/g at 300 K. Total and irreversible H₂ uptakes on the 3% Pt/C-W reduced at 673 K were observed to be about 31.8 and 19.1 μmol/g, respectively. This total uptake at 300 K corresponds to a Pt dispersion of 41% on the activated carbon, assuming H₂ molecules were atomically adsorbed on Pt surfaces and a H/Pt_s adsorption stoichiometry of 1 occurs. Note that the dispersion was obtained based on total H₂ uptake on the catalyst surface. Adsorption behavior of O₂ on the catalyst at 300 K was examined and this sample possessed total and irreversible O₂ adsorption capacity of 203.1 and 192.9 μmol/g, respectively. If the total H₂ uptake value provides a Pt dispersion for the catalyst after reduction at 673 K, the value from the irreversible O₂ uptake was about 6 times greater than that based on the H₂ adsorption at 300 K. This uptake corresponds to 165.4 μmol Pt_s/g, assuming molecular adsorption on surface Pt sites. It should be noted that the 3% Pt/C-W catalyst has total Pt sites of 153.9 μmol/g.

Table 1. Adsorption of O₂, H₂, CO and CO₂ at 300 K on 3% Pt/C-W catalyst

Catalyst	Pretreatment	Gas uptake (μmol/g)				
		O ₂ Irr	H ₂ Tot	CO Irr	H ₂ -O ₂ Titr	CO ₂ Irr
Westvaco SA30	HTHT	27.5	0.0	0.0	-	-
3% Pt/C-W	LTHT	190.7	11.9	36.2	167.8	-
	HTHT	192.9	31.8	34.8	95.7	19.1

The total CO uptake at 300 K was observed to be ca. 58.8 $\mu\text{mol/g}$ with an irreversible uptake of 34.8 $\mu\text{mol/g}$ on the catalyst surface. The adsorption behavior of CO_2 on the carbon-supported Pt needs to be examined because carbon supports usually have a variety of surface functional groups with microporosity. About 19.1 $\mu\text{mol/g}$ of irreversible uptake was observed for the Pt/C-W catalyst after reduction at 673 K. The H_2 titration of O atoms after the O_2 adsorption at 300 K exhibited total H_2 uptake of 95.7 $\mu\text{mol/g}$. The extent of the adsorption behavior of H_2 , O_2 and CO at 300 K on 3% Pt/C-W after hydrogen pretreatment at 473 K is also listed in Table 1. The O_2 irreversibly adsorbed on the catalyst reduced at 473 K was quite close to that for the high temperature reduction catalyst. When hydrogen was subsequently introduced to the LTHT Pt/C-W at 300 K, about 167.8 $\mu\text{mol/g}$ of total H_2 uptake was observed from the titration with 136.7 $\mu\text{mol/g}$ irreversibly adsorbed on the catalyst. The SA30 activated carbon has exhibited an irreversible O_2 uptake of 27.5 $\mu\text{mol/g}$ at 300 K with a total adsorption amount of 32.3 $\mu\text{mol O}_2/\text{g}$ volumetrically.

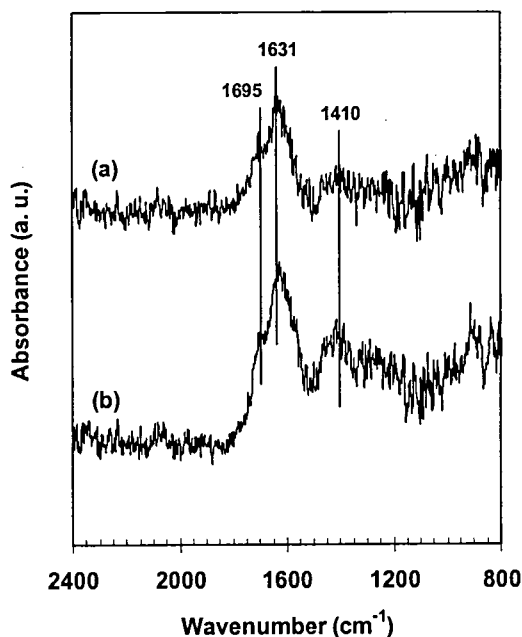
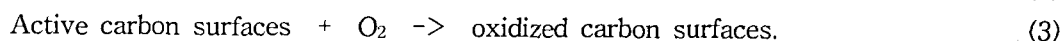


Fig. 1. IR spectra for 3% Pt/C-W: (a) after O_2 adsorption at 300 K for 30 min (b) after cyclic H_2 and O_2 adsorptions at 300 K.

The IR study of O_2 adsorption on the 3% Pt/C-W catalyst was conducted after it had undergone Procedure HTHT to see if the carbon support could react with O_2 at 300 K, thereby giving larger uptake values for the adsorption on the catalyst. Figure 1 shows the IR spectra of the catalyst after O_2 adsorption at 300 K. An intense band at 1631 cm^{-1}

developed with a shoulder and broad peak at 1695 and 1410 cm^{-1} , respectively, as oxygen was adsorbed on the catalyst after reduction at 673 K. The band frequencies were basically similar after cyclic H_2 and O_2 adsorption at 300 K, and they could be assigned to carbonate species [Taylor and Amberg, 1961; Liotta et. al., 1996]. Therefore, during O_2 adsorption on the catalyst carbonates can be produced from the reaction between O_2 and the carbon support. This indicates that the large oxygen uptakes on the catalyst at 300 K can be attributed to adsorption on the carbon support, although sodium species (1.4% Na) could give an additional O_2 uptake at 300 K, as discussed earlier. It was also consistent with the behavior of O_2 adsorption on pure SA30 carbon as a function of reduction temperature.

Metals possibly causing a large O_2 adsorption amount on the Pt/C-W catalyst as observed volumetrically were screened and then quantitatively determined. The weight detection limit was 0.02% upon the analysis. When metal contents were compared between SA30 and 3% Pt/C-W, a significant difference in the sodium content was revealed. The 1.4% sodium as sodium oxide (Na_2O) existed in the catalyst, which may react with O_2 to produce Na peroxide even at room temperature. If the Na oxides are completely dispersed on the catalyst surface, ca. 150 $\mu\text{mol/g}$ of O_2 may additionally adsorbed on the catalyst by the possible reaction above because 1.4% Na in the Pt/C-W catalyst corresponds to slightly over 600 μmol Na. Considering each possible contribution from the Pt atoms (ca. 31.8 $\mu\text{mol/g}$), the carbon support itself (ca. 32.3 $\mu\text{mol/g}$), and the Na_2O (ca. 150 $\mu\text{mol/g}$), the total O_2 uptake on 3% Pt/C-W (213 $\mu\text{mol O}_2/\text{g}$) is surprisingly close to that measured volumetrically, i.e., 203.1 $\mu\text{mol O}_2/\text{g}$. Therefore, this elemental determination gives one of plausible explanations for the unusually large O_2 adsorption on 3% Pt/C-W at 300 K, even though this does not readily explain all adsorption characteristics of this catalyst, particularly for O_2/H_2 titration after reduction at 473 K. Based on these IR results and the previous discussion for the oxygen adsorption on the pure carbon and 3% Pt/C-W containing 1.4% Na as a metal impurity, the adsorption behavior of the catalyst after different pretreatments can be adequately described through the following surface reactions:



4. Conclusions

A huge amount of the oxygen adsorption at 300 K on the 3% Pt/C-W catalyst after different pretreatment procedures may be due to the oxygen uptakes on Pt_s sites as well

as to the surface reactions of O₂ with Na₂O and active surface carbons. This is very consistent with the results acquired by the volumetric O₂ adsorption, elemental analysis and IR spectra for 3% Pt/C-W and SA30 after different pretreatments.

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