카본 담지 **Pt** 촉매의 산소 흡착능에 대한 금속 불순물의 영향

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Effect of Metal Impurities on Oxygen Adsorption Capability of Activated Carbons and Their Supported Pt

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Introduction

Carbon-supported noble metals have been widely used in industrial chemical processes including liquid-phase hydrogenation and organic synthesis [1]. 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 [2]. 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 [3]. When an activated carbon-supported Pt catalyst was pretreated in flowing pure H_2 at 950^oC or at temperatures lower than 500^oC, the activated carbon adsorbs very little oxygen at room temperature. However, this carbon material following such pretreatment in a flow of pure N_2 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.

Experimental

An activated carbon, Norit SX1, was used as received for a support to prepare a monometallic Pt catalyst using H_2PtCl_6 xH_2O (Aldrich, 99.995%) as the metal precursor. Carbon-supported Pt was obtained by impregnating a certain amount of the activated carbon with the desired amount of Pt in an aqueous solution (0.67 cm^3/g) and drying overnight in an oven at 383K, designated Pt/C-N. 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 H_2, O_2, CO and CO_2 on those carbon-based samples was measured, typically at 300K, using a conventional volumetric stainless steel vacuum system with a high vacuum below 10^{-7} Torr. Gas pressure and temperature during the adsorption measurements of probe molecules are measured using a differential pressure gauge and a temperature indicator, respectively. Details of this volumetric system have been described elsewhere [4]. 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 O_2, as described previously [4].   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 H_2 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 cm^3/min with a Tylan Model FC 260 mass flow controller

Results and Discussion

There was no capability of the SA30 carbon reduced at 673K for both H_2 and CO adsorptions at 300 K, as listed in Table 1 with uptake values for other samples used.   Unlike the behavior of the carbon for H_2 and CO adsorption at 300K, it showed significant O_2 adsorption capability and the oxygen irreversibly adsorbed on the pure carbon was 27.5 µmol/g at 300 K.   Total and irreversible H_2 uptakes on the 3% Pt/C-W reduced at 673K were observed to be about 31.8 and 19.1 µmol/g, respectively.   This total uptake at 300K corresponds to a Pt dispersion of 41% on the activated carbon, assuming H_2 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 H_2 uptake on the catalyst surface. Adsorption behavior of O_2 on the catalyst at 300 K was examined and this sample possessed total and irreversible O_2 adsorption capacity of 203.1 and 192.9 µmol/g, respectively.   The O_2 uptake of the catalyst corresponds to a surface Pt exposure of ca. 2.5 even using the irreversible adsorption amount, assuming oxygen molecules were dissociatively accommodated onto the Pt surface at a ratio of $O : Pt_s$ = 1 as in the case of H_2 adsorption.   If the total H_2 uptake value provides a Pt dispersion for the catalyst after reduction at 673K, the value from the irreversible O_2 uptake was about 6 times greater than that based on the H_2 adsorption at 300K.   This uptake corresponds to 165.4 µmol Pt_s/g, assuming oxygen molecules were nondissociatively adsorbed on surface Pt sites and correcting the O_2 adsorption amount by the pure carbon itself.   The value is close to total Pt sites (153.9 µmol/g) presented in the 3% Pt/C-W, giving a Pt dispersion by 100%; however, this behavior for the O_2 adsorption at 300K will be further discussed later.

Table 1. Adsorption of O_2, H_2, CO and CO_2 at 300 K on pure activated carbons and their supported Pt

Catalyst	Pretreatment	Gas uptake (µmol/g)				
		O_2 Irr	H_2 Tot	CO Irr	H_2-O_2 Titr	CO_2 Irr
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
SX1	LTHT	15.8	-	0.0	-	-
	HTHT	15.5	0.0	0.0	-	-
3% Pt/C-N	LTHT	55.8	11.5	33.3	100.3	-
	HTHT	45.7	26.9	40.0	91.9	-

The total CO uptake was observed to be about 58.8 µmol/g, while the value was 24.0 µmol/g after evacuating followed by reintroducing CO onto the surface at the temperature.   This indicates that 34.8 µmol/g of CO was irreversibly accommodated on the catalyst surface, which corresponds to a CO_{irrev}/Pt_{total} = 0.23 if CO molecules were adsorbed on surface Pt atoms with a stoichiometry of CO_{irrev}/Pt_{total} = 1.   Compared to the surface Pt fraction (H_{total}/Pt_{total} = 0.41) by the H_2 chemisorption at

300K, the value based on irreversible CO uptake on the catalyst was significantly lower. 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 µmol/g of irreversible uptake was observed for the Pt/C-W catalyst after reduction at 673K. The H_2 titration of O atoms after the O_2 adsorption at 300K exhibited total H_2 uptake of 95.7 µmol/g; therefore, the surface Pt fraction of the catalyst based on this total H_2 uptake appeared to be about 63.8 µmol/g, if an adsorption stoichiometry of unity exists between surface Pt sites and adsorbed O atoms. This value was close to that revealed from the H_2 chemisorption.

Adsorption behavior of H_2, O_2 and CO at 300K was examined for the 3% Pt/C-W after hydrogen pretreatment at 473K. Total H_2 uptake of 12.0 µmol/g was obtained for the catalyst upon H_2 adsorption with an irreversible value of ca. 3.2 µmol/g. This indicates that about 24.0 µmol Pt_s/g based on the total uptake value was present in the catalyst, which corresponds to a $H_{total}/Pt_{total} = 0.16$, assuming a stoichiometry of $H/Pt_s = 1$. Compared to the surface Pt fraction ($H_{total}/Pt_{total} = 0.41$) by the H_2 chemisorption for the catalyst reduced at 673K, the Pt exposure value was significantly lower. The O_2 irreversibly adsorbed on the catalyst reduced at 473K was quite close to that for the high temperature reduction catalyst. When hydrogen was introduced to the LTHT Pt/C-W at 300K, about 167.8 µmol/g of total H_2 uptake was observed from the titration with 136.7 µmol/g irreversibly adsorbed on the catalyst. These two values were much higher than those obtained by the H_2 titration on the HTHT Pt/C-W at 300K.

The SA30 activated carbon has exhibited an irreversible O_2 uptake of 27.5 µmol/g at 300K with a total adsorption amount of 32.3 µmol O_2/g volumetrically, while 203.1 and 192.9 µmol O_2/g of total and irreversible uptakes, respectively. If this catalyst has a total O_2 uptake on Pt similar to that (ca. 31.8 µmol/g) for H_2 adsorption at 300K, assuming an adsorption stoichiometry of $O/Pt_s = 1$, it indicates that an additional O_2 adsorption of 134 µmol/g at 300K occurred on this Pt/C-W catalyst even after correcting the irreversible oxygen adsorption capability of the pure carbon itself, as mentioned above. Therefore, it was necessary to see if oxygen-sensitive metals could be quantitatively verified in the two materials. 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 detection limit was 0.02 wt%. When metal contents were compared between SA30 and 3% Pt/C-W, a difference in the sodium content was revealed. The sodium content of 1.4% may exist on the catalyst surface after reduction at 673K, as sodium oxide (Na_2O), which may react with O_2 to produce Na peroxide according to the following reaction at room temperature: $2Na_2O + O_2 \rightarrow 2Na_2O_2$. If the Na oxides are completely dispersed on the catalyst surface, ca. 150 µmol/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 µmol/g), the carbon support itself (ca. 32.3 µmol/g), and the Na_2O (ca. 150 µmol/g), the total O_2 uptake on MONPTC01 of 213 µmol O_2/g is surprisingly close to that measured volumetrically in the previous work, *i.e.*, 203.1 µmol O_2/g. Therefore, this elemental analysis gives one plausible explanation for the unusually large O_2 adsorption on Pt/C-W at 300K, even though this does not readily explain all adsorption characteristics of this catalyst, particularly for O_2/H_2 titration after reduction at 473K.

The adsorption capability of the pure Norit SX1 carbon was volumetrically measured by adsorbing H_2, CO and O_2 at 300K, as also listed in Table 1. There was no capability of the pure carbon for irreversible H_2 adsorption after reduction at 673K. It is anticipated that H_2 should not be irreversibly accommodated on the carbon at 300K after reduction at 473K, even though it was not measured. The carbon reduced at 673K exhibited about 9.7 µmol/g of CO adsorption ability with respect to pressure, but no irreversible uptake on the activated carbon was obtained. Similar uptake values for total and reversible CO adsorption at 300K were revealed for the carbon after reduction at 473K. Unlike the behavior of the Norit carbon for H_2 and CO adsorption at 300K, significant irreversible O_2 adsorption was shown for the carbon, irrespective of reduction temperature used. As

shown in Fig. 2, the amount of irreversibly adsorbed oxygen on the pure carbon was 15.5 μmol/g at 300K after reduction at 673K. A similar irreversible uptake (15.8 μmol O_2/g) was found for the carbon reduced at 473K.

After the 3% Pt/C-N catalyst underwent LTHT, H_2, O_2 and CO adsorption at 300K was measured to obtain surface Pt exposure. Total H_2 uptake on the Pt catalyst reduced at 473K was about 11.5 μmol/g (23.0 μmol Pt_s/g). Carbon monoxide was used to estimate surface Pt atoms in 3% Pt/C-N at 300K. The total CO uptake was about 50.1 μmol/g, while the reversible value was ca. 16.8 μmol/g for the catalyst. This presents 33.3 μmol CO/g that was irreversibly retained on the catalyst surface after evacuation for 1 h at 300K, which corresponds to a $CO_{irrev}/Pt_{total} = 0.22$. Compared to the surface Pt fraction ($H_{total}/Pt_{total} = 0.15$) from H_2 chemisorption at 300 K for 3% Pt/C-N pretreated at 473 K, the value based on irreversible CO uptake was somewhat higher. The higher surface Pt concentration for Pt/C-N reduced at 473K may suggest blocking of surface Pt atoms by mobile carbon atoms, or a large fraction of the CO may be bridged-bonded. The catalyst showed total and irreversible O_2 adsorption capacities of 55.7 and 52.7 μmol O_2/g, respectively. The irreversible O_2 uptake value corresponds to a surface Pt exposure of 48% ($O_{irrev}/Pt_{total} = 0.48$), after subtracting the adsorption on pure Norit carbon from the uptake value and assuming oxygen molecules were dissociatively accommodated onto the Pt surface at a ratio of $O : Pt_s = 1$, as in the case of H_2 chemisorption. Note that the pure carbon after reduction at 473K gave an irreversible value of only 15.8 μmol O_2/g, as discussed above. If the total H_2 uptake value is used to obtain a Pt dispersion for the catalyst reduced at 473K, the value from the irreversible O_2 uptake after correcting for the irreversible O_2 uptake on the carbon was about 3 times greater than that based on the H_2 adsorption at 300K. The H_2 titration of O-covered Pt atoms after O_2 adsorption at 300K exhibited total H_2 uptake of 100.3 μmol/g. Therefore, the surface Pt fraction of the catalyst, pretreated by LTHT, based on this total H_2 uptake was about 66.9 μmol/g, if an adsorption stoichiometry of unity exists between surface Pt sites and adsorbed O atoms. This value was significantly higher than that (23.0 μmol Pt_s/g) obtained from the H_2 chemisorption, as discussed above. It was assumed that O_2 molecules adsorbed on the pure carbon at 300K are not titratable.

Conclusions

Elemental analysis of the Pt/C-W and the SA30 suggests that sodium atoms included in the catalyst might be causing a large amount of untitratable O_2 adsorption on the catalyst at 300K, since the pure carbon exhibited relatively a little amount of irreversible oxygen adsorption at 300K. Carbon-supported Pt using a Norit SX1 activated carbon was well behaved for H_2, O_2 and CO adsorption at 300K. However, adsorption behavior was significantly dependent on the pretreatment procedure used, although the Pt dispersion for the 3% Pt/C-N after undergoing LTHT was relatively consistent.

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