

POSTER

INFLUENCE OF THE SURFACE CHARACTERISTICS OF ACTIVATED-CARBON SUPPORTS ON THE DISPERSION OF DEPOSITED PALLADIUM AND PLATINUM

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INTRODUCTION

Activated carbons are widely used as a support for precious-metal catalysts. A high dispersion of the deposited metal is desirable for an economic use of the metal. The pore structure of the support is a very important characteristic as well, depending on the intended application of the catalyst. There have been many studies on the influence of the nature of the precursor and the preparation conditions on the dispersion of the reduced metal; functional groups on the carbon surface are important, too. Surprisingly, quite different, even contradictory, results have been published on the effect of surface oxides on the dispersion, as cited in ref. [1]. In this study a few results on the dispersion of carbon-supported Pd and Pt are described.

Oxidized carbon surfaces have acidic character and cation exchange properties due to the formation of carboxylic groups on the surface [2]. The surfaces of carbons heat-treated at ca. 1000°C are basic and have anion exchange properties, because surface groups of basic character are formed upon exposure to O₂ at room temperature [2]. Aromatic basal planes can bind protons, too. Usually, the concentration of basic sites is much smaller than that of acidic surface groups in oxidized carbons, but there are always basic groups present, too, in acidic carbons.

EXPERIMENTAL

The activated carbons were extracted with boiling HCl solution and washed [3]. The following carbons are characterized in Table 1: (1) AR2, from coconut shells (Sutcliffe), (2) Norit SGM, from peat (Norit NV), (3) Anthralur, from peat (Lurgi).

TABLE 1 - Characterization of the carbons

Carbon	(1)	(2)	(3)
apparent surf. area, m ² /g	1675	1250	618
micropore volume, cm ³ /g	0.66	0.45	0.24
mesopore volume cm ³ /g	0.13	0.13	0.07

The metals were deposited on the carbons either by the incipient wetness method or by adsorption from solution. The dried materials were reduced with H₂ at 150°C (1 hr.), followed by 1 hr. at 250°C with Pt. The dispersions were measured by CO chemisorption from an H₂ stream (pulse method) using a Micro-metrics Chemisorb 2700 in-strument [3].

RESULTS AND DISCUSSION

Table 2 shows the effect of pretreatment of an activated carbon (Anthralur) on the dispersion obtained with different Pd precursors. With H₂PdCl₄, the dis-

TABLE 2 - Dispersion of Pd as function of precursor and surface treatment
(Anthralur, 100 µmol Pd/g, reduction at 150°C).

Surface treatment	H ₂ PdCl ₂		Pd acetate	[Pd(NH ₃) ₄](NO ₃) ₂
	incipient wetness	adsorption	incipient wetness	incipient wetness
no treatment	0.58	-	0.30	0.30
N ₂ at 900°C	0.64	-	0.38	0.38
H ₂ at 900°C	0.34	0.15	0.28	0.47
NH ₃ at 900°C	0.35	-	0.32	0.52
O ₂ at 380°C	0.73	0.65	0.27	0.27

TABLE 3 - Dispersion of Pt as function of loading and preparation conditions
(adsorption of H_2PtCl_6 , normally 30 mins. contact time)

Support	Reduction at 150°C		Reduction at 250°C	
	1 % Pt	4 % Pt	1 % Pt	4 % Pt
Anthralur	0.51	0.27	0.25	0.19
AR2	0.33	0.86	0.20	0.76
AR2, HCl added (see text)	0.80	-	0.25	-
Norit, 15 min.adsn.	-	-	0.32	0.72
Norit, 20 hrs.adsn.	-	-	0.60	0.68
Norit, 20 hrs.adsn. 30 x HCl excess (see text)	-	-	-	0.40

persion was highest with the acidic surface of the oxidized carbon, whereas much lower dispersions were found with carbons with basic surface properties. This was unexpected because it was assumed that basic carbons with anion exchange properties should bind PdCl_4^{2-} ions resulting in a high dispersion after reduction. The reason was apparently that an excess of hydrochloric acid had been used to dissolve PdCl_2 . The solution had a lower pH than corresponded to the IEP of the oxidized carbon (ca. pH 3), and protons adsorbed on the surface created a positive surface charge. In addition, bidentate carboxyl groups seem to be good anchoring sites for chloro complexes. EXAFS data indicate a ligand exchange for oxygen on oxidized surfaces [1]. In the case of the reduced, basic carbon surfaces, competition by other anions, e.g. excess Cl^- ions, might interfere with PdCl_4^{2-} adsorption.

This explanation is confirmed by the effect of added HCl shown in Table 3. One would expect a lower dispersion with increased metal loading. However, with the carbon AR2 the opposite effect was observed. This is due to an increased acidity with increased H_2PtCl_6 concentration. When the H^+ concentration of the 1% Pt solution was quadrupled by addition of the calculated quantity of HCl, the dispersion increased considerably. Higher HCl additions (30 times the original H^+ concentration) resulted in a decrease of the dispersion.

Palladium acetate, a water-insoluble trimer, was adsorbed from solution in acetone. Table 1 shows that surface treatment of the carbon had practically no effect on the dispersion. With the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ complex, the dispersion increased with increasing basicity of the surface. This is difficult to explain. The solution of $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$ was nearly neutral.

Other factors that influence dispersion are time of adsorption (Table 3) and the H_2 flow rate during re-

duction. For 1% Pt, reduced at 250°C, increasing the flow from 20 to 60 cm^3/min resulted in an increase of dispersion from 0.26 to 0.38 for Anthralur, and from 0.62 to 0.74 for Norit.

A further complication is that Pd and Pt compounds are able to oxidize the carbon surface with concomitant reduction to the metallic state [1,2,4]. Presumably, this reaction is slow, and the creation of additional metal nuclei may explain the effects of adsorption time on dispersion shown in Table 3.

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