

# Effect of Carbon Surface Oxidation on the Catalytic Properties of Carbon-Supported Metals

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## Introduction

Recently, there has been growing interest in the use of carbons as catalyst supports, particularly in applications involving heavy petroleum or coal-derived feedstocks. Various formulations involving Co and Co-Mo supported on carbon have shown superior activity for the hydrogenation and hydrodesulfurization of model compounds, compared to equivalent alumina supported catalysts (1). In addition, cracking and polymerization reactions which deposit coke (carbon) and lead to deactivation of the catalyst have been shown to be less prevalent on carbon than on alumina-based formulations (1).

The available evidence indicates that the nature of the carbon surface, particularly the presence of functional groups can have an important influence upon the catalytic properties of carbon supported metals (1,2). In order to study the influence of surface properties more closely, a carbon support was treated in a controlled manner so as to modify the concentration and type of surface functional groups prior to metal addition. The modified supports were then loaded with 3 wt% molybdenum and the activity of the catalysts determined for the hydroconversion of high boiling coal liquids.

## Support Selection

The results of previous studies have emphasized the difficulties of attempting to derive fundamental relationships between catalyst properties and activities when using different carbon supports (2). Accordingly, a single carbon, Ambersorb XE-340, which can be made with reproducible chemical and physical characteristics was employed in the current research.

Ambersorb XE-340 is hard and durable carbon (crush strength > 3.0 kg/particle) with a pore size distribution appropriate for the hydrogenation of high-boiling coal liquids, since it contains virtually no micropores and almost 70% of the total pore volume is contained in pores of diameter 100-300 Å. It has a surface area of 400 m<sup>2</sup>/g (N<sub>2</sub> at 77 K) and a pore volume of 0.34 cm<sup>3</sup>/g.

## Support Treatment

Samples of Ambersorb XE-340 were subjected to a number of treatments intended to introduce oxygen or nitrogen functionalities to the carbon surface. The treatments and their effects upon the elemental composition of Ambersorb XE-340 are summarized in Table 1. Following each treatment, the carbons were repeatedly washed with copious quantities of distilled, deionized water. It can be seen that the various treatments produced quite different results. The HNO<sub>3</sub> treatment effected an increase in nitrogen content as well as greatly increasing the oxygen content. Reaction with sulfuric acid also raised the oxygen content and, in addition increased the sulfur content.

The treatments with potassium permanganate and potassium dichromate served principally to oxidize the carbon, potassium permanganate being the more effective oxidant of the two. In both cases, despite the extensive post-treatment washing, residual potassium was left on the carbon. The reactions with ammonia increased the nitrogen content, the extent of nitrogen addition increasing with reaction temperature.

The samples treated with acids and with potassium permanganate and potassium dichromate were subjected to analysis by Fourier Transform Infrared Spectroscopy (FTIR) in diffuse reflectance (Digilab, Model FTS-15E) in order to provide further detail on the functional groups which were introduced by the pretreatment. Treatment with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> caused comparatively little change to the spectrum of the parent carbon; the KMnO<sub>4</sub> treatment may have introduced some etheric groups; HNO<sub>3</sub> treatment introduced NO<sub>2</sub>, possibly NO<sub>3</sub> and carbonyl groups; cold sulfuric acid treatment introduced SO<sub>2</sub> and carbonyl groups while the hot sulfuric acid treatment increased the intensity of the carbonyl and SO<sub>2</sub> bands and introduced absorptions which may correspond to SO<sub>3</sub> or SO<sub>3</sub>H and C-S and S=O.

## Catalyst Preparation

Impregnation of the support with an active metal involved directly introducing MoS<sub>2</sub> onto the support by the thermal decomposition of a tetra-

Table 1. Elemental Analyses of Functionalized Ambersorb XE-340 Support

Treatment	C	H	Analysis (% wt)		S	K
			O	N		
None	90.22	3.26	1.42	<0.05	3.83	N.D.
Boiling conc. $\text{HNO}_3$ , 2 h	64.90	2.26	25.32	4.61	N.D.	N.D.
Conc. $\text{H}_2\text{SO}_4$ , 2 h at room temp.	84.44	3.28	6.26	N.D.	5.74	N.D.
Boiling conc. $\text{H}_2\text{SO}_4$ , 2 h	68.21	2.79	20.10	N.D.	9.13	N.D.
Boiling saturated $\text{KMnO}_4$ sol <sup>n</sup> , 2 h	75.73	3.07	7.71	N.D.	N.D.	2.14
Boiling saturated $\text{K}_2\text{Cr}_2\text{O}_7$ sol <sup>n</sup> , 2 h	90.00	3.80	1.90	N.D.	N.D.	0.046
$\text{NH}_3$ at 400°C, 1.5 h*	89.16	3.45	2.05	0.53	3.85	N.D.
$\text{NH}_3$ at 600°C, 1.5 h*	91.68	2.63	1.79	0.87	3.33	N.D.

N.D. = not determined; \* After the method of Boehm, et al. (3)

thiomolybdate salt. An aqueous solution of ammonium heptamolybdate was converted to one of ammonium tetrathiomolybdate by bubbling through  $\text{H}_2\text{S}$  at room temperature. The catalyst was then impregnated with the solution of the thiosalt. In the reaction described below the catalysts were dried at 110°C in vacuum.

#### Activity of Catalysts for Coal Asphaltene Conversion

The activities of the prepared catalysts were determined using tube bomb reactors for the hydroconversion of coal-derived liquids. The feed was the 850°F recycle solvent fraction produced on the Lummus Integrated Two Stage Liquefaction unit when operating on Wyodak Coal. The experiments were conducted under the following conditions: 5.0 g feed, 0.5 g catalyst, 7 MPa  $\text{H}_2$  (cold), 450°C, 1 h. Carbon disulfide was added to the reaction mixture in sufficient quantity (0.2 ml) to maintain the catalyst in the sulfided form.

The data in Table 2 indicate that the nitrated supports show the highest activity for asphaltene conversion with relatively low gas make and carbon deposition on the catalyst. The acid treated samples show either a reduction ( $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{HNO}_3$ ) or only slight increase ( $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$ ) in activity over the

untreated support. The data imply that additional hydrocracking and hydrogenation activity can be conferred to the catalyst by treatment of the support with ammonia.

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Table 2. Activity of Ambersorb XE-340 for Hydroconversion of Coal Derived Asphaltenes

Support Treatment	% Asphaltenes (Hexane Insolubles)	% Asphaltene Conversion	% $\text{C}_{1-4}$ * Yield	% Increase In Catalyst Weight
None	25.7	23.7	4.0	3.0
$\text{K}_2\text{Cr}_2\text{O}_7$	31.4	17.8	2.6	23.0
$\text{KMnO}_4$	27.6	27.7	N.D.	6.4
$\text{HNO}_3$	33.7	11.8	9.6	N.D.
cold $\text{H}_2\text{SO}_4$	28.6	25.1	2.4	11.1
hot $\text{H}_2\text{SO}_4$	27.6	27.7	3.1	5.1
$\text{NH}_3$ , 400°C	22.0	42.4	6.9	4.3
$\text{NH}_3$ , 600°C	16.2	57.6	5.9	5.0

N.D. = not determined; \* hydrocarbons only