

OXIDATION/DESORPTION TREATMENT OF CARBON TO ENHANCE ITS ADSORPTIVE/CATALYTIC PROPERTIES

Carl W. Kruse, Anthony A. Lizzio, Cuneyt A. Feizoulof,
Joseph A. DeBarr and Mohammad Fatemi²

Illinois State Geological Survey (IGSS), 615 E. Peabody, Champaign, IL 61820

¹ Camp Dresser & McKee Inc., The Sears Tower, Suite 450, 233 S. Wacker Dr., Chicago, IL 60606-6306

²Amoco Corporation, Amoco Research Center, P.O. Box 3011, Naperville, IL 60566

INTRODUCTION

The goal was to understand how pore size distribution is narrowed to improve adsorption selectivity for gases, how capacity for SO₂ is increased, how adsorption of organics from water solution is enhanced and how catalyst activity is facilitated. Surface oxygen was applied to coal char or activated coal char by boiling nitric acid, and several series of carbons were produced by progressively desorbing oxygen from these modified chars at successively higher temperatures. The remaining oxygen was characterized by determining the amount of oxygen evolved as CO₂ and CO during temperature programmed desorption (TPD). The properties of these desorbed oxidized chars, depending on what fraction of the oxygen is desorbed, were those useful as molecular sieves [1,2], SO₂ adsorbers [3,4], liquid phase adsorbers of p-nitrophenol (PNP) [5], and dehydrochlorination catalysts of a type patented in the 1960s [6]. These applications are believed to depend on the size of pores or the openings them, the pore volume, and catalyst sites. The question arises "by what mechanism does this uncomplicated treatment enhance the desired properties for these diverse uses that appear to require different properties?"

EXPERIMENTAL PROCEDURES

Preparation of oxidized/partially desorbed carbons: A 65x100 mesh fraction of IBC-102, a Colchester (Illinois No. 2) coal from the Illinois Basin Coal Sample Program (IBCSP) [7], heated in N₂ at 700°C for 1/2 hr (the control in Table 1), was treated for 2.5 hr with 10 M nitric acid. to the temperatures shown. For the desorption step the temperature was ramped quickly to the target temperature and held there for 2 hours while purging with an inert gas. Where indicated, the char was activated by steam gasification before the nitric acid oxidation. **SO₂ adsorption capacity:** The capacity after 6 hours using 2500 ppmv SO₂, 7% H₂O, and 5% O₂ was measured using a Cahn TG-131 thermogravimetric analyzer (TGA) system.

Table 1. Effect of nitric acid treatment on CMS properties (IBC-102, 700°C)

Sample	Outgas Temp. (°C)	Adsorbed		O ₂ /N ₂
		O ₂ (cm ³ /g)	N ₂ (cm ³ /g)	
Control	130	5.12	3.71	1.38
HNO ₃ , 80°C	25	0.30	0.03	10.00
HNO ₃ , 80°C	130	2.22	0.31	7.16
HNO ₃ , 80°C	160	2.91	0.48	6.06
HNO ₃ , 80°C	180	4.72	1.83	2.58

Table 2. Variation of SO₂ capacity with oxygen content (IBC-102, 900°C; H₂O; 860°C)

Sample	Outgas Temp. °C	SO ₂ Capacity (mg/g)	Oxygen (wt %)
Control		176	1.1
45% HNO ₃ , 2.5 hr	120	26	16.4
45% HNO ₃ , 2.5 hr	525	91	5.9
45% HNO ₃ , 2.5 hr	725	241	1.6
45% HNO ₃ , 2.5 hr	925	287	0.5

TPD: A 0.5 g sample was heated in flowing nitrogen (0.5 L/min) at 5°C/min to a final temperature of 1000°C where it was held for 1 hour.

Dehydrochlorination catalyst preparation and testing: The procedures described previously were applied to Calgon F-400 and to activated char made from IBC-109, a Herrin (Illinois No. 6) coal from the IBCSP [8,9,10].

PNP adsorption capacity: These procedures are those described in a previous paper [11].

DISCUSSION OF RESULTS

The adsorption of both oxygen and nitrogen, kinetic diameters 3.46 Å and 3.68 Å, respectively, is markedly diminished by nitric acid oxidation (Table 1). The adsorption capacity is restored in proportion to the amount of the oxygen functionalities removed at successive desorption temperatures; not at the same rate for the two gases, however. The restoration takes place faster for oxygen, the smaller of the two, resulting in the high selectivity (higher ratio) needed for pressure swing gas separation processes. Adsorption of SO₂ follows a similar pattern of a restored capacity that increases as oxygen-containing groups are desorbed; the increase is most pronounced between 525 and 725°C (Table 2).

PNP was most strongly adsorbed (higher slope) on oxidized activated char desorbed to 525°C in this four-sample series (Figure 1). The strongest adsorption was at 575°C when the tests were repeated on material spanning temperatures from 475°C to 625°C in 50 degree increments. This is the temperature range in which air oxidation of carbons was shown in the 1960s to produce an excellent dehydrochlorination catalysts [6]. Dehydrohalogenation tests confirmed that the nitric acid-oxidized carbons desorbed to the 475°C to 625°C temperature range have the catalyst properties of the material produced by air oxidation in the same temperature range. Heating to the 800-900°C is known to destroy these catalysts. Because suitably-prepared oxidized carbon dehydro-

halogenates monochlorinated n-paraffins without appreciable rearrangement of the linear carbon skeleton, and the catalyst activity has not correlated with the concentration of oxygen functional groups determined by XPS, the site at which the reaction occurs has been postulated to be in pores of suitable dimensions [12]. Sites on opposing walls providing a concerted removal of hydrogen and chlorine atoms on molecules adsorbed between them could produce the linear olefin without a carbonium ion intermediate. An increase in the proportion of pores having the correct dimensions and the desired opposing functional groups could also increase the strength of adsorption of molecules held in such positions and the ability to "fine tune" pore dimensions would then be as important in the catalytic process as it is known to be in making molecular sieves for specific applications.

TPD profiles show that catalyst produced by desorbing to 525°C and material produced by air oxidation are alike in that neither has a high proportion of CO₂-forming oxygen groups believe to be predominantly carboxyl groups (Figure 2). These are the groups that produce a high degree of hydrogen bonding as well as covalently bonded anhydrides. Removing the carboxyl groups from a structure having them in sufficient numbers and proximity to be cross-linked should relax the structure and promote movement of some structural segments.

CONCLUSION

The changes observed in the adsorption/catalysis properties of oxidized/desorbed chars and activated chars may reflect (1) a change in the internal pore volume that is available due to a partial filling of fixed pore volume with oxygen containing groups, or (2) a restricted access to the fixed internal pore volume by restrictions at the mouth of pores and/or (3) a shrinking of the structure due to interaction of functional groups on opposing pore walls that decrease pore volume. This postulated, unproven pore shrinking mechanism visualizes an effect analogous but opposite to the swelling of coal by pyridine and other Lewis bases.

ACKNOWLEDGEMENT & DISCLAIMER

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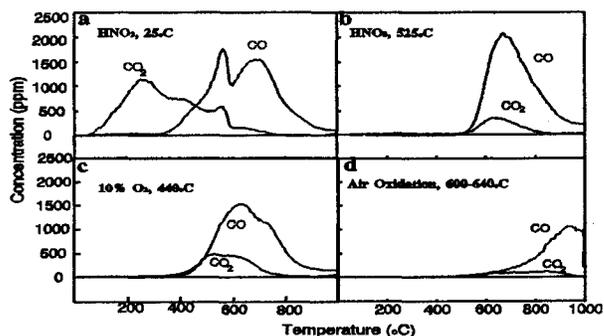


Figure 1. TPD profiles: a & b HNO₃ treated, c & d air oxidized

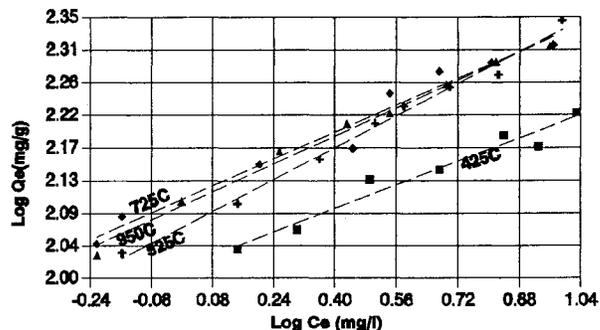


Figure 2. Freundlich equation plots for PNP adsorption on HNO₃-oxidized AC/desorbed to temperature shown