

REMOVAL OF SPENT Cr-Cu CATALYST FROM SURFACE OF CHEMICAL MODIFIED CARBON CARRIER

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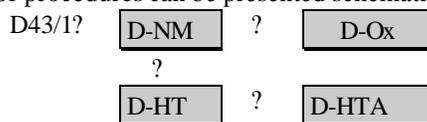
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Introduction

For many years Cr-Cu impregnated active carbon has been used to remove toxic agents (e.g. CNCl, HCN) from a stream of gas. However, under extreme conditions of operation, or as it is consumed, it quickly loses its efficacy. Despite a number of studies [1-4], the nature and changes of the active phase at the surface of fresh and aged sorbents have still not been fully explained. Here we report the results of an investigation into recovery of active carbon support by removal of spent Cr-Cu catalyst (after cyanogen chloride action).

Experimental

The supports used in this experiment were prepared from carbon D-43/1 (CarboTech, Essen) by ash removal (below 0.2%) (D-NM) and surface modification by oxidation with nitric acid (D-Ox), heating under vacuum (D-HT) and in an ammonia atmosphere (D-HTA). The details of the modification procedures was reported elsewhere [5]. The sequence of procedures can be presented schematically:



The chemical surface structure of the carbon samples thus obtained was characterized by the determination of the total oxygen and nitrogen content (accurate 0.2%) and the neutralization of surface acidic and basic functional groups with sodium hydroxide and hydrochloric acid (both 0.1 M) respectively. The Cr-Cu sorbents were then obtained by impregnating modified carbon samples with an ammoniacal solution of copper and chromium salts in the manner reported in [3].

The sorbents obtained were tested with respect to their protective features, and the time of their protective action against cyanogen chloride (t_{PA} , min) under standard conditions [4] were determined.

The chromium and copper salts were removed from deactivated sorbent samples by repeated washing in hot (boiling) hydrochloric acid (0.1 M) until the metal species in solution could no longer be detected. The degree of

demetalization (quantity of remaining metal) (Me^r , %) was estimated by ash analysis for fresh (a) and washed (e) sorbent samples.

The XPS spectra were recorded on an EscaLab 210 (V. G. Scientific Ltd.) photoelectron spectrometer using non-monochromatised Al K_{α} radiation (1486.6 eV). Prior to XPS measurement the carbon samples were dried for 2 h at 100°C. The vacuum in the analysis chamber was always better than 5×10^{-10} Pa. High-resolution scans were performed over the 574-583 eV (Cr $2p_{3/2}$) and 930-948 eV (Cu $2p$) ranges [6]. This peak-fitting was repeated until an acceptable fit was obtained (error $\approx 5\%$). For calibration purposes, the carbon 1s electron bond energy corresponding to graphitic carbon was referenced at 284.5 eV [6].

Results and Discussion

The surface modification procedures applied to de-ashed active carbon yield carbon samples of a very different chemical nature and a similar porous structure [5]. Oxidation with nitric acid leads to a greater number of acidic surface structures. Annealing, however, especially in ammonia enhances the basic properties of the carbons at the expense of their acidic properties (Table 1). In this way the carbon carriers bound various amounts of oxygen and/or nitrogen surface functional groups.

The sorption of heavy metal cations and their interaction with the carbon surface both depend strongly on the chemical nature of the adsorbent. It is assumed that sorption passes through ion-exchange or complex formation; however, this may also be due to other processes, e.g. charge-transfer reactions, physical adsorption of aqua-, amina- and hydroxy-complexes, interactions between metal ions and the π -electrons of aromatic structures (π -d complexes) [7,8].

Impregnated carbon samples were placed in stream of chlorocyanide gas in a standard test procedure: the times of their protective actions are set out in Table 1. The protective capacity of the tested sorbents depends on the surface chemistry of the carrier materials and decreases rapidly for oxidized active carbon sample. In contrast, heat treatment of the carbon carrier under vacuum or in an

ammonia atmosphere enhanced the protection capacity of the Cu-Cr sorbent.

The spent catalytic phase (impregnated salts) was removed from the surface of the tested sorbents a by washing with hot dilute inorganic acid (0.1 M HCl). The efficiency of elution is shown in Table 1. The amounts of residual metals depend on the surface chemistry of the support materials, and is the highest for D-HTA and D-Ox carbon samples. Table 2 shows the XPS results obtained by curve-fitting the Cr 2p_{3/2} and Cu 2p spectra of metals sorbed on the D-Ox carbon before (a) and after washing procedure (e). The binding energy (B.E.) and the relative peak area (r.p.a.) for separate peaks were estimated and collected. Analysis of XPS studies (Table 2) indicates that the washing procedure applied here removed copper species completely. The metallic remains detected on the carbon surface can be ascribed to strongly sorbed (physically or chemically) chromium species.

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Table 1. Surface chemical properties, time of protective action and efficiency of metal removal for tested carbon carriers

Carbon	O/N (%)	0.1 M NaOH up-take (mM/g)	0.1 M HCl up-take (mM/g)	t _{PA} (min)	Me ^F (%)
D-43/1	-	-	-	62	88.1
D-NM	2.9	0.373	0.295	60	88.5
D-Ox	10.8	1.663	0.131	46	84.8
D-HT	0.6	0.134	0.420	67	89.9
D-HTA	0.4/1.9	0.100	0.632	64	81.4

Table 2. Selected XPS results for oxidized carbon sample (fresh Cr-Cu sorbent -a, recovered material -e)

Sorbent ? ? XPS ?	D-Ox-CrCu/a		D-Ox-CrCu/e		Possible surface structures
	B.E. (eV)	r.p.a. (%)	B.E. (eV)	r.p.a. (%)	
Cr 2p _{3/2}	576.3	12.4	-	-	CuCrO ₂ , CrO ₂ ⁻ [CrCl _x] ^{(3-x)+} [Cr(NH ₃) ₃] ³⁺ -O-CrO ₂ , Cr(NH ₃)Cl ₃ , CrO ₄ ²⁻
	-	-	576.9	72.0	
	577.4	64.0	-	-	
	-	-	578.6	28.0	
	579.1	23.6	-	-	
Cu 2p	935.0	100	-	-	[Cu(NH ₃) ₄] ²⁺ , CuO, Cu(OH) ₂ shake up satellites --
	941.5	-	-	-	
	944.1	-	-	-	