

POSTER

DEACTIVATION OF ASC CARBON UPON ADSORPTION OF CYANOGEN CHLORIDE

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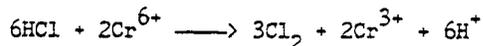
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INTRODUCTION

The removal of cyanogen chloride from streams of polluted air by ASC carbon, includes physical adsorption followed by chemical reactions in the presence of copper(2+) and chromium(6+) additives[1]. The efficiency of chemisorption depends on the Cr(6+) and Cu(2+) content of the activated carbon. Changes in the oxidation state of these ions are associated with carbon deactivation[2], a process which is accelerated upon exposure to high humidities at elevated temperatures[3].

It was suggested[4] that HCl evolved during the chemisorption destroys the active species by reduction of chromium(6+):



This is an attempt to explain the deactivation of an impregnated carbon in the course of chemisorption of cyanogen chloride. Since physical adsorption precedes the chemical reactions, deactivation may not be solely due to changes in chromium oxidation state but also to low availability of active sites.

The conversion of CNCl into strongly adsorbed higher molecules is proposed as a possible route of surface deactivation.

EXPERIMENTAL

Dry samples of activated carbon were packed into 24 mm diameter cylindrical columns. CNCl was taken directly from a cylinder at a flow rate of 4 cc/min and diluted with dried air (R.H.=20%) to a concentration of 3 mg/l. CNCl in the effluent air was determined electrochemically as a chloride ion after trapping in a 2N NaOH solution. Breakthrough time was determined visually by a color reaction with pyridine-dimedone reagent (limit of detection: 2-3µg/l).

The tests were carried out using 4 cm deep columns (10g carbon) through which the flow rate was 2 l/min. Different exposure times were taken, at the end of which each carbon bed was heated up to 50°C for 16 hours under reduced

pressure. Then it was subjected to another experiment under otherwise the same conditions.

RESULTS AND DISCUSSION

Figure 1 shows breakthrough times of carbon beds, pre-exposed to cyanogen chloride and treated at 50°C under reduced pressure, as a function of exposure time. The point designated as 2nd breakthrough refers to a bed pre-exposed up to its full adsorption capacity. The point at the lower right represents a bed after two full adsorption cycles. It can be seen from the figure that the additive time of two successive exposures, exceeds the breakthrough time (117 min) obtained in one continuous run. This means that partial regeneration takes place during the desorption stage.

Cyanogen chloride uptake on Cu-Cr impregnated carbon is accompanied with precipitation of products which retain on the surface after the regeneration process. Surface compositions of as received ASC and CNCl-treated (PCK) carbon samples, as determined by XPS, is summarized in Table 1. There is an increase in carbon content and parallel decrease in oxygen content of PCK charcoal, which can be attributed to products precipitation. Moreover, the appearance of nitrogen and chlorine species in equivalent amounts on the PCK surface, shows clearly that these precipitates originate from CNCl monomer. An aromatic trimer, C₃N₃Cl₃, was already mentioned as one possible product[5].

Since it has been established that the active centers for cyanogen chloride destruction contain Cr(6+) associated with copper(2+)[6], and aged carbon loses its effectiveness due to reduction of Cr(6+) to Cr(3+) species, the question which arises is whether the adsorption process stopped when the conversion of Cr(6+) is completed? There could be at least one more reason for carbon deactivation, i.e. an accumulation of strongly adsorbed products of cyanogen chloride. These products result in surface coverage which diminishes the availability of adsorption sites.

XPS spectra of Cr and Cu species before and

after the exposure were also recorded. Cr(2P_{3/2}) spectrum was resolved into Cr(3+) peaks at binding energies of 576.50 and 577.64 eV, and Cr(6+) component, at binding energy of 579.09 eV. Both species are present in approximately equal amounts on the basis of peak area, for the two types of carbons. These results show that upon chemisorption of cyanogen chloride, chromium impregnants, which are considered the active sites, do not undergo significant change in their oxidation state. The Cu(2P_{3/2}) XPS spectrum shows no significant change in the composition of copper species upon exposure to CNCl, as well.

The conclusion is inevitable that deactivation is at least partially due to blockage of active sites by products deposition. This situation is analogous to catalyst deactivation by coke formation, where large product molecules cover the active centers and slow down the reaction. Breakthrough time is therefore an indication to the efficiency of carbon catalyst as a CNCl neutralizer.

In many cases of catalyst deactivation, a complete regeneration can be achieved by air oxidation under elevated temperatures. A partial regeneration of active carbon was also shown to be possible, resulting in cumulative service time longer than breakthrough time, as can be seen from Figure 1. However, regeneration of active carbon is limited to low temperatures at which removal of high reaction products from the surface is not efficient. It is believed that a complete removal of these compounds could restore the adsorption capacity to a larger extent.

CONCLUSIONS

Cu(2+) and Cr(6+) species, the active centers, retain in significant amounts after adsorption of CNCl has been completed. However, these sites are not available for further reaction when covered by adsorbed product molecules.

A partial surface regeneration, the extent of which is inversely proportional to the exposure time, can be achieved by moderate heating.

REFERENCES

1. L.A.Jonas, Carbon, 16 115 (1978).
2. J.L.Hammarstrom and A.Sacco,Jr., J.Catal., 112 267 (1988).
3. P.Ehrburger, J.Lahaye, P.Dziedzinl and R. Fangeat, Carbon, 29 297 (1991).
4. E.J.Poziomek, R.A.McKay and R.P.Barrett, Carbon, 13 259 (1975).
5. F.Wolf and P.Renger, Z.Chem., 12 293 (1972).
6. P.N.Krishnan, S.A.Katz, A.Birenzvige and H. Salem, Carbon, 26 914 (1988).

TABLE 1 - Elemental concentrations (atomic%) as determined by XPS

Carbon type	C	O	Cr	Cu	N	Cl
ASC	78.1	18.7	1.5	1.7	0.2	-
PCK*	82.3	11.8	1.7	1.3	*2	*2

*ASC carbon, exposed to CNCl.

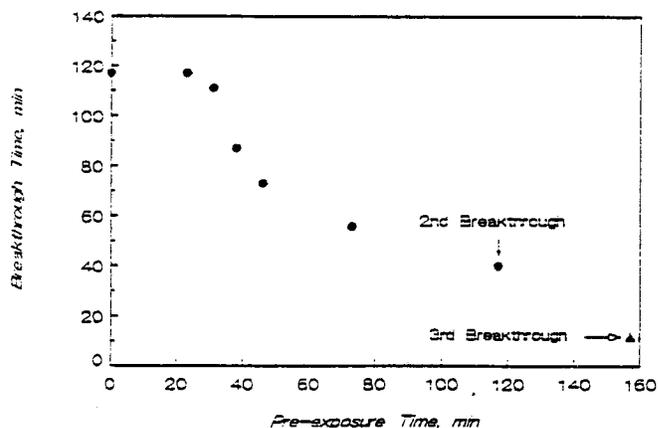


Figure 1 - Breakthrough time as a function of pre-treatment period with CNCl.