

THE POTENTIAL FOR INCREASING THE USE OF CATALYTIC CARBONS IN COMMERCIAL APPLICATIONS

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Keywords: Catalysis, oxidized activated carbon, elimination reactions

ABSTRACT

A carbon catalyst, prepared either by oxidizing activated carbon with air at 500-700°C or by oxidizing activated carbon with boiling nitric acid followed by heating it to 500-700°C, is the subject of this paper. This catalyst, designated OAC₅₀₀₋₇₀₀, catalyzes the removal of hydrogen chloride from alkyl halides. Because OAC₅₀₀₋₇₀₀ retains adsorptive properties of an activated carbon it can be used both to adsorb pollutants from liquid or gaseous streams and to convert them to recyclable products. A highly-developed micropore structure is not required for all uses of activated carbon or a catalyst produced from it. A comparatively inexpensive (\$325/ton projected) low surface area (<300 m²/g) carbon has been developed at the Illinois State Geological Survey (ISGS) for cleaning incinerator flue gas. This grade of activated carbon is widely used in Europe for flue gas cleaning and for other applications. Activated carbon adsorbents of some type are required by recently passed U.S. Environmental Protection Agency (EPA) regulations for municipal waste combustors to control emission of cadmium, mercury, lead, dioxins, furans and acid gases (U.S. EPA, 1995). Similar regulations are expected for hospital and hazardous waste incinerators. The marketing of less costly activated carbons of the type used widely in Europe is expected in the United States. Low cost OAC₅₀₀₋₇₀₀ made from less expensive grades of activated carbon may become available for large scale adsorbent/catalyst systems designed to both remove and decompose toxic pollutants found in liquid and gaseous streams, chlorinated organic compounds in particular.

INTRODUCTION

OAC₅₀₀₋₇₀₀ has the potential to solve a number of environmental problems associated with misplaced organic chlorides. Chlorinated compounds in drinking waters and aquatic environments have become a significant topic for study by scientists concerned about effects of direct toxicity and/or carcinogenicity on human and aquatic life (Hanson, 1994). A correlation between surface water chlorination and cancer mortality rates in humans has been shown to be statistically significant (Kalmaz and Kalmaz, 1981). The chlorination of surface waters has been shown to produce high levels of trihalomethanes (THMs) (Bellar et al., 1974). Roughly 98% of this nation's drinking water systems use chlorination. More than 300 chlorinated organic compounds have been identified in chlorinated potable waters, cooling waters, and sanitary effluents (U.S. Environmental Protection Agency (EPA), 1975). Activated carbons are needed to capture, concentrate, and decompose pesticides and THMs that are formed when the water is chlorinated (Graham and Ramaratnam, 1993). Regeneration with steam or superheated steam in the field is practical with low molecular weight volatile organic compounds (VOCs), but less volatile organics may require high temperatures (750-850°C) if regeneration of the expensive types of activated char now available is required.

The destruction of halogenated organics in wastes is another potential use of OAC₅₀₀₋₇₀₀. Halogenated organic compounds account for a major portion of toxic and persistent hazardous wastes. In Illinois, the General Assembly in 1981 passed a bill which prohibits landfill disposal of hazardous wastes effective January 1, 1987, unless the generator and disposal site operator can demonstrate that no reasonable alternative is available. In 1983, this schedule was accelerated for liquid hazardous wastes; P.A. 83-1078 prohibits landfill disposal of liquid hazardous wastes unless there is no reasonable alternative. A November 7, 1986, rule on solvents and dioxins began the phasing out of all landfill disposal of halogenated solvents. Methods which will convert some of this hazardous waste into recyclable chemical compounds are high priorities for the Illinois Hazardous Waste Research and Information Center (Miller, 1990).

The destruction of halogenated waste compounds is also a goal of the US EPA. A US EPA report describes an experimental project at Radian Corporation, Research Triangle Park, North Carolina, to validate the effectiveness of a treatment of halogenated waste compounds with a reagent composed of potassium hydroxide in a relatively small quantity of polyethylene glycol (Harden & Ramsey, 1986). It was effective in destroying the organic compounds chosen as being representative of low molecular weight compounds encountered in hazardous wastes including CCl₄, CHCl₃, CH₂Cl₂, C₂H₄Br₂, and CCl₃NO₂.

Potential uses of OAC₅₀₀₋₇₀₀ go beyond the problem of chlorinated organics. OAC₅₀₀₋₇₀₀ has recently been shown to catalyze other elimination reactions including the dehydration of alcohols, the deamination of amines and the dehydrosulfurization of mercaptans (Kruse et al., 1991).

BACKGROUND

Oxygen complexes control many of the properties of activated carbons (Boehm and Bewer, 1976; Leon y Leon D. and Radovic, 1994). An oxidized carbon catalyst of a type first described in the patent literature (Kruse and Ray, 1966) is the focus of this paper. It was initially produced by air oxidation of carbon blacks and activated carbons in the 500-700°C temperature range and is now designated OAC₅₀₀₋₇₀₀. It was effective for the dehydrochlorination of alkyl halides and promoted polymerization of chloromethyl aromatics (Kruse, 1969a). Incorporating potassium salts into the catalyst inhibited skeletal rearrangements of olefins produced from monochloro n-alkanes (Mahan et al., 1967). Continuous vapor phase dehydrochlorination of mixed linear C₁₃-C₁₄ monochlorides gave >95% conversion for 690 hours (73.5 g of alkyl chlorides/gram catalyst) with OAC₅₀₀₋₇₀₀ produced from Darco activated charcoal (Kruse, 1969b). Engineers advising the inventors of this catalyst believed the costs would be too high for one-time use in a commercial plant. Regeneration was achieved with a steam-nitrogen mixture at 750°C but predicting the time needed to attain the desired precise amount of burn-off was difficult. Too much gasification shortened catalyst life. The regeneration method and the projected catalyst cost were among the factors that frustrated commercial development in the late 1960s. The commercial price of activated carbons marketed in the United States remains high today, at approximately \$0.40 to dollars/pound (one to a few dollars/kg) and OAC₅₀₀₋₇₀₀ manufactured from them will bear the same high cost liability of the 1960s.

Not all processes require the expensive, high surface area adsorbents that dominate the U.S. domestic market. STEAG's a/c/tTM process is one of the processes being offered for licensing in the United States to clean incinerator flue gas. It does not require a sorbent with a N₂, BET surface area greater than 300 m²/g (Bruggendick, 1993). The spent sorbent from STEAG's process is not regenerated, and regeneration may not be necessary with other processes using lower cost, lower surface area activated carbon. The state of Illinois through its Illinois Clean Coal Institute has demonstrated that an activated carbon satisfactory for use in STEAG's process can be produced from Illinois coal (Kruse et al., 1995b). The projected price by the ISGS for this sorbent, if produced in a dedicated plant having an 80,000 tons/year capacity, is \$325/ton (\$0.35/kg).

The price of the adsorbent (herdofenkoks) used by STEAG's European licensees is about \$0.15/lb (\$0.33/kg). This less costly activated carbon adsorbent has been available in Europe for several decades. Adsorbents of this type, made from brown coal, are known in Germany as F-coal and in Russia as S-coal (Smisek, 1970). They are used in technical applications for which cost and not adsorption capacity is the primary concern. This is the case when the active life of the material is for some reason low and replacement is not dictated by inadequate adsorption capacity. For example, the desulfurization of industrial gases using activated carbon is effective because activated carbon catalyzes the reaction



The sulfur, deposited in the pores of the active carbon, is extracted when the hydrogen sulfide in the gas exceeds a prescribed limit. Gas-adsorption active carbons are not suitable for this purpose. For this use, the important factor is not a highly developed microporous structure, but the number of macropores. The best results are obtained with F-coal.

DISCUSSION

A two step method for producing OAC₅₀₀₋₇₀₀ is a recent development (Kruse, 1995). The discovery that the oxidation of an activated carbon with boiling nitric acid followed by desorption of most of the CO₂-forming oxygen complexes in an inert atmosphere produces OAC₅₀₀₋₇₀₀ was a by-product of other research. During a study to determine the effect of oxygen complexes on the selective adsorption of targeted compounds from water, a series of carbons having differing levels of oxygen complexes was prepared by thermally desorbing CO₂ and CO from oxygen complexes introduced by nitric acid oxidation (Feizoulof et al., 1993). Adsorption isotherms for p-nitrophenol (PNP) were determined for the series of carbons and plots were made of the data using the Freundlich equation. The slope of the line generated in these plots is a measure of the strength of adsorption. The strength of the adsorption of PNP went through an unexpected maximum between desorption temperatures of 425°C and 725°C; material desorbed at 525°C had the highest slope (figure 1a). The adsorption tests were then repeated with carbons produced by desorption at 475°C, 525°C, 575°C and 625°C. The strongest adsorption was at 575°C (figure 1b).

Initial catalyst work by the author in the 1960s showed that the oxygen complexes put on below about 300-400°C did not produce dehydrohalogenation catalysts. Heating to 800°C destroyed the catalyst properties. A temperature of 600°C was an ideal mid range temperature for producing the active catalyst. Because temperature programmed desorption (TPD) in the recent studies showed the oxygen complexes on materials produced by the two methods, i.e., air (or dilute oxygen) oxidation (figure 2 e,f) and the two step oxidation/desorption method (figure 2 b,c) were similar and the strength of the adsorption of PNP went through a maximum at the preferred temperature (600°C) for producing the catalyst with air, comparisons of catalyst

activity were made. The percent conversion in a vapor phase dehydrochlorination of 1,1,2,2-tetrachloroethane at 450°C over a bed of the test material was the measure of catalyst activity (Fatemi et al., 1993). The material produced by desorption of oxygen complexes at 500-700°C was indeed a good catalyst (Kruse et al., 1995a). It appears that CO-producing oxygen complexes are essential and that the CO₂-producing complexes that are desorbed by heating to 500°C reduce catalyst activity. A similar effect for catalyzing oxidation reactions was stated by Boehm et al. (1984), "enhancement could sometimes also be observed after chemisorption of oxygen. There was no clear-cut picture in this case, however, the general impression is that catalytic activity is enhanced by basic surface oxides, whilst acidic surface oxides are inhibitory".

The adsorption properties of the starting activated carbon are modified but not lost by making it a catalyst. Most of the initial carbon's adsorption capacity is available to remove a variety of pollutants from liquid and gas streams and, in addition, OAC₅₀₀₋₇₀₀ has the potential to convert many classes of pollutants to recyclable compounds (Kruse et al., 1992; Beaulieu et al., 1992; Fatemi et al., 1993; Feizoulof et al., 1993).

COMMERCIALIZATION

Important factors for future commercial development of OAC₅₀₀₋₇₀₀ include (1) how it ranks in competing tests with other catalysts, (2) comparative disposal costs and (3) availability and pricing. Porous glass (unglazed porcelain) (Lycourghiotis, 1976), silica gel, (Misono, 1973, Lycourghiotis et al., 1981; Mochida et al., 1981; Suarez and Mazzieri, 1987), B-18 crown ether-potassium chloride on silica gel (Fujitsu et al., 1985), alcoholic potassium hydroxide, and the new Calgon carbon catalyst, Centaur, are among its rivals. Extensive comparative tests of OAC₅₀₀₋₇₀₀ and other catalysts will be necessary to determine the strengths and weaknesses for specific applications. The disposal costs must be weighed against regeneration costs. Incineration appears an option for OAC₅₀₀₋₇₀₀ and Centaur not available to other catalysts. It remains to be seen how much the price of Centaur (about \$2.50/pound today) will decrease with large scale production.

The estimated production capacity of activated carbon in the United States, which currently has N₂ BET surface areas from 500-2500 m²/g, was estimated in 1990 to be 146,000 metric tons (Baker et al., 1992). Retrofitting only a fraction of the existing incinerators with carbon-based systems would create a demand greater than exists today for all types of activated carbon. Because of the number of grades of activated carbon marketed today, the prices reflect fine chemicals prices, often in dollars per pound. With the arrival of dedicated facilities for producing 80,000 ton/year or more of one type of activated carbon, the prices can be expected to decline, whatever the grade of activated carbon marketed. The future cost of OAC₅₀₀₋₇₀₀ should parallel the decreasing prices of activated carbon marketed in the United States.

CONCLUSIONS

The high cost of many technically feasible systems for protecting the environment prevents serious consideration of their use. Providing the data base on lower cost adsorbents and catalysts will promote their commercial availability in the future. A low temperature oxidation/desorption sequence has been developed; this process is not only more readily managed than air oxidation at 500-700°C for producing OAC₅₀₀₋₇₀₀ dehydrochlorination catalyst but may also be adaptable to regenerating the catalyst activity of fixed beds in place. The projected availability of lower cost activated carbons means lower cost OAC₅₀₀₋₇₀₀ produced from them. There are many areas where organic halide capture and destruction can be tested for addressing environmental pollution problems. The recycling of hydrocarbons that are produced by removing hydrogen chloride, water and hydrogen sulfide from a host of organic compounds would support the growing emphasis on recycling misplaced and spent materials.

ACKNOWLEDGEMENT & DISCLAIMER

This report was prepared by Carl Kruse and the ISGS with support, in part, by grants made possible by U.S. Department of Energy (DOE) Cooperative Agreement Number DE-FC22-92PC92521 and the Illinois Coal Development Board (ICDB) and the Illinois Clean Coal Institute (ICCI) and managed by F.I. Honea, D.D. Banerjee, and H. Feldmann. Neither Carl Kruse and the ISGS nor any of its subcontractors nor the U.S. DOE, Illinois Department of Energy & Natural Resources, ICDB, ICCI, nor any person acting on behalf of either assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report. Contributions by A.A. Lizzio, C.A. Feizoulof, J.A. DeBar, M. Fatemi, M.M.M. Chou, I. Demir, S. Carlson, G. Zajac and R.T. Lagman are acknowledged. The views and opinions of author expressed herein do not necessarily state or reflect those of the U.S. Department of Energy. I also acknowledge the in-kind contribution of funds by the Alternative Feedstock Development program of Amoco Corporation.

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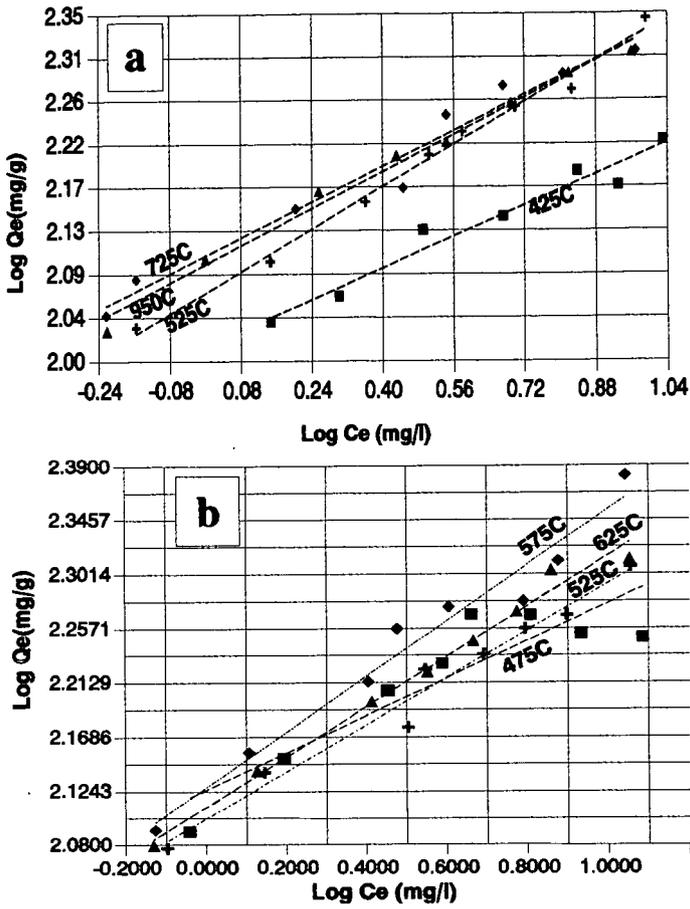


Figure 1. Freundlich equation plots for p-nitrophenol on HNO₃-oxidized activated carbon desorbed to the temperature shown.

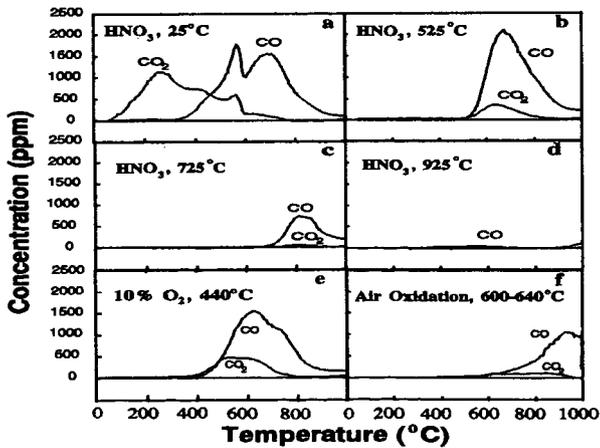


Figure 2. TPD profiles of HNO₃-oxidized chars desorbed at 25°C to 925°C and oxygen oxidized samples.