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Low-Temperature Decomposition of Some Halogenated Hydrocarbons Using Metal Oxide/Porous Carbon Catalysts

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Abstract: Catalysts comprising metal oxides dispersed on porous carbon supports are shown to be very effective in the decomposition of halogenated hydrocarbons by air at and below 250 °C. A wide range of substrates, including methylene chloride, 1,2-dichloroethane, 1,2,4-trichlorobenzene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, and carbon tetrachloride, are converted selectively to CO_2, CO, and HCl. The carbon supports also show significant activity in the absence of metal species. Trends in reactivity with catalyst variation suggest that the carbon micropore content and acidity are determining factors in the catalytic activity. Mechanistic studies with a porous, highly active CrO_3/Ambersorb[1] (Ambersorb is a registered trademark of the Rohm and Haas Company) resin illustrate that the components operate through two discrete pathways: the carbon functions oxidatively as a catalytic agent itself while the chromium species functions to decompose the chlorinated hydrocarbon anaerobically. Kinetic studies of methylene chloride decomposition over an undoped Ambersorb resin show a first-order dependence on CH_2Cl_2 concentration and an activation energy of 11.0 kcal/mol. In further examination of the catalytic decomposition process, it was found that a source of hydrogen, either as a component of the chlorinated hydrocarbon or as an added reagent, is necessary to regenerate the catalyst. Water was found to serve this function but not to saturate the active site for adsorption and destruction of the organic reactant. This finding gives the carbon catalysts a clear advantage over zeolite based catalysts for aqueous hazardous waste remediation processes.[1]

Introduction

Halogenated hydrocarbons have widespread application as solvents in the chemical industry due to their relative inertness and ability to dissolve organic compounds. Investigations regarding the toxicity and carcinogenic properties of halogenated organics have raised industry awareness on the matter of proper disposal of these hazardous materials.[1] Incineration is presently the preferred method, but temperatures exceeding 1000 K are required to obtain complete decomposition.[2,3] Highly toxic materials such as dioxin are often formed as byproducts. In cases of low concentration of contaminant in the gas phase, the process becomes exceedingly inefficient as the entire sample must be heated to the combustion temperature. For a typical incinerator,[4] the cost of the fuel alone can reach about 40% of the total operating cost. Consequently, development of low-temperature processes for halogenated waste disposal can offer significant improvement over present methods.

Spivey[5] presents an exhaustive review (to 1987) of low-temperature oxidative decomposition catalysts for application in environmental remediation. The majority of the catalysts can be put into two categories: transition metal oxides (either unsupported or adsorbed onto an inorganic oxide support) and supported noble metals. The noble metal catalysts (Pd, Pt, Rh, Ru) are poor choices for oxidation of halogenated hydrocarbons because of the high expense and the poisoning of the catalysts by the Cl_2 and HCl produced in the reaction.[6,7] A number of patents have been issued for destroying halogenated hydrocarbons with metal oxide catalysts,[8] but optimum temperatures for these systems are usually >300 °C, and the halogenated hydrocarbon concentration is typically limited to less than 10 000 ppm.

The purpose of this study is to examine porous carbon materials as catalysts for the catalytic combustion of halogenated hydrocarbons at low temperature (<300 °C). Analysis of the factors influencing reactivity, such as temperature, atmosphere, and pore structure of the carbon, provides insight into the reaction mechanism.

Experimental Section

Reagents. A number of porous carbon adsorbents are utilized in this study, and their surface areas and pore volumes are listed in Table I. Ambersorb adsorbents were donated by the Rohm and Haas Co. The materials (denoted as A563 and A572 or 563 and 572) are prepared by the patented pyrolysis of sulfonated ion-exchange resins[9] and have very reproducible surface areas and pore volumes. The sample ER42-30 (also obtained from Rohm and Haas) is a noncommercial, experimental carbon adsorbent designed to provide the specific pore characteristics as shown in Table I. The Kureha carbon sample is manufactured by the Kureha Chemical Industry Company, Ltd., Japan. An ultrahigh-surface-area powdered carbon, termed AX21, was obtained from Anderson Development Co. This support is produced by the reaction of petroleum coke with KOH and subsequent pyrolysis. Washing the salt out of the carbon matrix after pyrolysis gives pores of molecular dimensions; the high surface area of AX21 is attributed to these micropores.[10] AX21 was dried at 100 °C under vacuum before use. The zeolite sample is LZ-Y52 (produced by Union Carbide), and it was dried in vacuo at 100 °C for 12 h prior to use. The silica support, Davison grade 62, was obtained from W. R.

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Table I. Surface Area and Pore Volumes of the Carbonaceous Adsorbents Used in This Study

carbon sample	surface area (m^2/g)	micropore vol (mL/g)	mesopore vol (mL/g)	macropore vol (mL/g)
A563	604	0.22	0.16	0.24
A572	1200	0.49	0.26	0.41
ER42-30[a]	1200	0.45	0.29	0.02
Kureha	1000	0.53	0.02	0.02
AX21[b]	2000+	1.7	0.70	

[a] Proprietary carbon (polymer-based). [b] Organic-based carbon.

Grace Co. and has a surface area of 340 m^2/g. Activation of the silica was achieved by washing with 1 M HCl(aq), rinsing with water, and drying in vacuo at 80 °C for 72 h.

The chlorinated reactants were purchased from Aldrich Chemical Co. Methylene chloride and carbon tetrachloride were distilled over P_2O_5 prior to use. All other halogenated hydrocarbons were used as received. The metal salts were all purchased from Aldrich and used without further treatment unless otherwise specified. Air, hydrogen, helium, argon, and nitrogen were supplied by Liquid Air Co. All gases were used without further purification.

Instrumentation. Reaction products were analyzed on a Varian 3700 gas chromatograph equipped with a 3 m × $^1/_8$ in. stainless steel Porapak Q (100/120 mesh) column and a thermal conductivity detector. Light gases (CO_2, CO, N_2, O_2, H_2O) were analyzed on a 15 × $^1/_8$ in. Carboxen[2] 1000 (Carboxen is a registered trademark of Supelco) (60/80 mesh) column on the same detector. GCMS was accomplished on a Varian 3400 GC linked to a Finnegan 700 ion-trap mass spectrometer. Magnetic susceptibility was performed on a Johnson-Matthey JME balance. The porosimetry method used was single-point BET, which was performed at Rohm and Haas on a Micromeritics 2300 porosimeter. X-ray photoelectron spectroscopy was performed on a Kratos XSAM-800 spectrometer using Mg Kα radiation (nonmonochromatic) operating[2] at 15 kV and 12 mA, with the sample at 5×10^{-9} Torr. Scanning electron microscopy was performed on a Jeol JSM 35C electron microscope using an electron acceleration voltage of 15 kV. The micrographs were taken at 6000X and 30000X.

Reactor. A packed-bed, glass, 10-mm-diameter flow reactor was used for all catalytic experiments. A course glass frit supports the catalyst. The reaction tube is heated either with a commercially available Thermolyne Briskheat flexible electric heat tape or a resistance oven consisting of nichrome wire wrapped around a 4 in. Pyrex tube with quartz wool packing material for even heating. The heating element is controlled by a digital temperature controller Model CN-2041 (Omega Engineering) equipped with a J-type thermocouple and once equilibrated provided temperature control to ±2 °C.

A 2.0-g sample of catalyst (48 mm bed height) is used unless noted otherwise in the catalytic experiments, and this sample is covered with a 15-cm length of glass beads for mixing and heating the reactants prior to catalyst contact. A Model FL-320 rotameter (Omega Engineering) is used to obtain flow control of gas feeds from 0.2 up to 50 mL/min. A soap bubble meter in the post-catalyst zone is used to determine overall flow rates of the gases. The halogenated reactants are delivered with an air stream either by passing the gas through a reservoir or by pumping a liquid feed to the top of the heated zone with a custom-built motorized syringe pump. The vapor pressure of the hydrocarbon and the temperature of the reservoir determine the substrate concentration in the air stream for the reservoir delivery method; the rate of the constant delivery volume sets the concentration for the syringe method. The typical hydrocarbon concentration is 60 000 ppm for optimum decomposition efficiency at 1.0 mL/min air flow. The liquid volume feed rate for the halogenated reactants is 0.01–0.05 mL/h for the reservoir method and 0.05–0.10 mL/h for the syringe pump method.

Gas samples taken before and after the catalyst bed are compared to determine conversions. A halogen mass balance is performed by collecting the HX produced in an aqueous NaOH bubbler placed at the reactor outlet and back-titrating to quantify the HX produced. The mass of the catalyst is checked after most reactions to determine if loss of carbon occurs; for all experiments at 250 °C there is no weight loss of the catalyst, even after 150 h of reaction.

Catalyst Preparation. All catalysts are prepared by a pore-filling method (incipient wetness) whereby only enough solvent is used to fill the void space of the carbon; this procedure ensures intimate contact of the dopant solution with the interior support surface. The soluble precursor species CrO_3, $TiCl_4$, $KMnO_4$, $Ce(NO_3)_3$, $SbCl_5$, NH_4VO_3, H_2SO_4, $Co(NO_3)_2$, and $FeCl_3$ are utilized in the catalyst preparations. The solvent is water in all cases except for $TiCl_4$ where CH_2Cl_2 is used. Once impregnated, the catalysts are converted to the hydrated oxide or oxychloro forms in a number of different ways. Titanium tetrachloride is hydrolyzed in moist air whereas iron and antimony chlorides are treated with base to obtain the oxides. In all other cases, heating of the impregnated support to the reaction temperature of 250 °C under air leads to oxide formation. The catalysts are all 14% metal oxide by mass unless otherwise noted.

Table II. Activity of Various Carbon Catalysts in the Catalytic Combustion of Methylene Chloride[a]

catalyst	conversion (%)[b]	catalyst	conversion (%)[b]
CrO_3/563	99.9(±0.1)	A572	78(±3)
CrO_3/572	99.9(±0.1)	A563	69(±3)
TiO_2/572	93(±1)	A563, CrO_3[d]	48(±3)
$KMnO_4$/ $Ce(No_3)_3$/572	95(±1)	A563(NaOH)	32(±4)
Sb_2O_5/572[c]	52(±3)	A563(NH_4OH wash)	52(±4)
V_2O_5/572	82(±3)	ER 42-30	73(±3)
H_2SO_4/572	83(±3)	Kureha	94(±2)
cobalt oxide/572	75(±4)	AX21	23(±4)
iron oxide/572[c]	65(±4)		

[a] Conditions: 250 °C, 1 mL/min air flow, 2.0 g of catalyst, [CH_2Cl_2] = 60 000 ppm, 72 h reaction time. [b] Conversions based on GC analysis and HCl product quantification. [c] Metal chloride-doped carbon support treated with base to obtain hydrated metal oxide species. [d] A layer of 563 over a layer of CrO_3, separated by a plug of glass wool.

Results and Discussion

Catalytic Combustion Reactivity Studies. Methylene chloride was chosen to begin study of the catalytic combustion of halogenated hydrocarbons because of its high vapor pressure and the hydrogen balance:

$$CH_2Cl_2 + O_2 \rightarrow CO_2 + 2HCl \qquad (1)$$

The reaction is more complicated than shown in eq 1 because carbon monoxide is also observed in the exit stream. Regardless of the final carbon product the chloride–hydrogen balance is the same. The activities of the metal oxide/carbon adsorbent catalysts for the above reaction at 250 °C are presented in Table II. Unexpectedly, the blank experiments with the untreated A572 and A563 supports lead to substantial oxidation of CH_2Cl_2. This is consistent with detailed studies of oxidative dehydrogenation reactions over oxide catalysts which show[11–14] that oxygen-containing carbon species in the coke formed from hydrocarbon reacting at acid sites play an important role in the redox chemistry.[15]

Four of the supported metal oxide catalysts in Table II stand out as being superior to the others. The catalysts CrO_3/563, CrO_3/572, $KMnO_4$/$Ce(NO_3)_3$/572, and TiO_2/572 all show conversions higher than 90%, and in the case of the chromium catalysts, the conversion is essentially 100%. These results demonstrate the ability of the metal oxide/porous carbon catalysts to completely destroy chlorinated hydrocarbons from a contaminated air stream. Alumina-supported Cr_2O_3 is reported to be effective in the catalytic decomposition of methylene chloride[4] and chloroform[16] at temperatures ranging from 350 to 550 °C. However, a rapid drop in activity of this catalyst occurred by loss of the metal as volatile CrO_3Cl_2. No volatilization of the metal species occurs with the Ambersorb resin catalysts even after 150 h of reaction. This observation will be discussed in more detail in the characterization section. A blank experiment was per-

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Table III. Reactivity of Carbon Catalysts with Varous Halogenated Hydrocarbons[a]

substrate	catalyst	air flow rate (mL/min)[b]	substrate feed rate (mL/min)[c]	water feed rate (mL/h)[d]	reaction time (h)[e]	conversion (%)
methylene chloride	CrO_3/563	1.0	0.05	0		99.9+
methylene chloride	CrO_3/563	5.0	0.05	0		32
1,2,4-trichlorobenzene	CrO_3/563	6.0	0.06	0		19
tetrachloroethylene	CrO_3/563	1.0	0.05	~0.01		16
1,1,2,2-tetrachloroethane	CrO_3/563	1.0	0.05	~0.01		63
methylene bromide	CrO_3/563	1.0	0.005	0		93
1,2-dichloroethane	TiO_2/572	1.0	0.05	0		99.7
1,2-dichloroethane	TiO_2/572	1.0	0.05	0.12		94
1,2-dichloropethane	572	1.0	0.05	0		97
1,2-dichloroethane	572	1.0	0.05	0.12		97
1,2-dichloroethane	LZ-Y52	1.0	0.05	0		23
1,2-dichloroethane	LZ-Y52	1.0	0.05	0.12		4
carbon tetrachloride	563	1.0	0.014	0	5	73
carbon tetrachloride	563	1.0	0.014	0	48	47
carbon tetrachloride	563	1.0	0.014	0	120	5
carbon tetrachloride	563	1.0	0.014	0.06	140	15
carbon tetrachloride	563	1.0	0.014	0.60	170	47

[a] Conditions: 250 °C, 2.0 g of catalyst, 72 h reaction time (unless otherwise mentioned). [b] Air flow rate is dicated by reaction stoichiometry and substrate feed rate. [c] Substrate feed rate is dependent on volatility and method of delivery. [d] Water is used either as a source of protons or to demonstrate adsorption competition. [e] Time refers to CCl_4 reaction which is presented as a function of time as well as water feed rate. For ala other reactions a steady-state conversion is listed, which is not a function of the reaction time.

formed using CrO_3 doped into silica by the same procedure as that used for the Ambersorb resin catalyst. Methylene chloride decomposition occurs at 250 °C with an initial conversion of 90% which gradually drops to 25% after 24 h. Concurrent with this loss in activity was the appearance of a residue on the walls of the reactor in the post-catalyst zone which appeared to be a mixture of red CrO_2Cl_2 and green chromium(III) oxide.

Iron and antimony oxides supported on carbon give conversions which were lower than that for the support itself. The preparation of both of these catalysts involves treatment of the chloride precursor with sodium hydroxide to obtain the hydrated oxide. This would neutralize any acid sites on the carbon and suggests that the catalytic combustion reaction is influenced by acidity as reported for the decomposition of 1,2-dichloroethane over TiO_2/SiO_2.[17] To further investigate the importance of acid centers, a 5-g sample of A563 was washed with 8.3×10^{-2} mol of aqueous ammonia. A measurable drop in activity of about 10–15% is observed with these catalysts. Addition of 8.8×10^{-3} mol of sodium hydroxide to 5 g of A563 produces an even larger drop in activity of ~30 to 40%. Acidity influences the catalytic activity of the unmetalated carbon catalysts in the deep oxidation reaction.

Pore structure of the carbons is a determining factor in adsorption efficiency[9] and therefore has a significant impact on the catalytic efficiency of the low-temperature decomposition process. Table I also lists the pore volumes and surface areas for various unmodified carbon samples and their respective activities in the decomposition of methylene chloride. Similar conversions are obtained with ER42-30, a non-commercial polymer-based carbon adsorbent, and A572. The structural character of the two samples is similar except the macro- and mesopore volumes differ. The observed similarity in reactivity implies that under our conditions the larger pores do not contribute to the rates of this reaction. The importance of microporosity is shown by A563, with less micropore volume, showing less reactivity than A572 and the all-micropore Kureha sample giving very high conversion.

Surface area is often quoted to be a decisive factor in the activity of inorganic oxide catalysts. Previous work on carbon-supported molybdenum catalysts[18] has shown greater complexity on carbon systems. As seen in Table II, AX21 has very low activity in this reaction despite its extremely high surface area. Since AX21 is derived from KOH treated petroleum coke, acid character is absent, and this is shown to be unfavorable for deep oxidation activity. Treatment of AX21 with concentrated HCl(aq) does not generate activity in this support. Absence of acid functionality on the surface or different pore characteristics are probable causes of the different reactivity of this material.

Another explanation for the lack of activity of AX21 would require that a minimum percent of the total pore volume be meso- or macroporous to facilitate efficient adsorption kinetics by the micropores. Since AX21 does not possess an appropriate amount of these larger pores, its kinetic reactivity is low. The observation that Kureha carbon, despite its very low meso- and macropore volume, is extremely active in the catalytic combustion reaction argues against this proposal.

Substrate Variation. In addition to methylene chloride, a number of other halogenated compounds were employed in the catalytic combustion reaction, and the results are presented in Table III. The CrO_3/563 catalyst is used and flow rates as well as reactant feed rates are varied to show that optimization of these variables can lead to effective oxidation of a wide range of substrates. An aromatic reactant, 1,2,4-trichlorobenzene, was utilized as a model for polychlorinated biphenyls (PCBs), and it is observed that the reactivity is comparable to that seen for methylene chloride at a similar feed rate (entry two of the table). Complete decomposition of trichlorobenzene is expected with longer residence times. The substrate 1,1,2,2-tetrachloroethane is hydrogen deficient, but it can be decomposed if an external hydrogen source is provided. In this instance, water performs this function. Better conversions are anticipated once the amount of water added is optimized. Methylene bromide serves to show that brominated organics can be oxidized.

Experiments with 1,2-dichloroethane (DCE) are interesting from the standpoint of the influence of water on catalyst reactivity (Table III). For the DCE reaction, the substrate contains sufficient hydrogen for the complete oxidation to HCl with the remainder forming water according to the following equation:

$$Cl\text{-}CH_2\text{-}CH_2\text{-}Cl + {}^5/{}_2O_2 \rightarrow 2HCl + 2CO_2 + H_2O \qquad (2)$$

Reactivity of DCE under standard reaction conditions with TiO_2/572 is impressive with 99.7% conversion. Upon addition of water to the reaction at a feed rate about 10 times that of DCE, the activity is still high at 94% conversion. With the unmodified support, the conversion with water and without water is identical

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at 97(±2)% within the error limits. These results are in stark contrast to literature reports for the reaction catalyzed by zeolites[19] where a drop of between 10 and 60% was observed with water addition. Indeed, use of LZ-Y52 zeolite in our system showed a significant water sensitivity as seen in Table III. These observations with the carbon catalysts indicate that competitive adsorption of water, which is known to occur with aluminosilicates, is not a major factor on these carbon surfaces. The hydrophobic nature of some Ambersorb adsorbents will deter water adsorption.

Carbon tetrachloride is a model compound for the general category of fully chlorinated, non-olefinic hydrocarbons. Table III shows the results of the catalytic destruction of carbon tetrachloride using A563 (undoped). The conversion after 5 h is 73% compared to a conversion of 55% for methylene chloride under identical conditions. Energies for C–Cl bonds in chlorinated methane derivatives are typically on the order of 20–25 kcal/mol lower than the corresponding C–H bond energies, indicating thermodynamic favorability of C–Cl bond cleavage over C–H bond cleavage. This coupled with a 2:1 ratio of C–Cl bonds in CCl_4 versus CH_2Cl_2 accounts for the increased reactivity. The decline of activity after 120 h shows that a reactant is being depleted; in this case it is most likely the hydrogen necessary to form the HCl product. Addition of water at 0.06 mL/h increases conversion from 5% to 15%. At 0.60 mL/h the conversion rises to 47%, indicating that water can provide the hydrogen needed for conversion to CO_2. The reaction is in effect a hydrolysis reaction. The excess water required over the stoichiometric amount shows that water is not used efficiently in this reaction. This is consistent with the greater affinity of A563 for chlorinated hydrocarbons than for water.

The reactions discussed thus far were performed at 250 °C. Increasing the temperature to 300 or 350 °C results in oxidation of the carbon support, and decreasing the temperature to 200 °C leads to condensation of the organic into the carbon pores, thus causing the reaction to stop because of oxygen deficiency at the active sites. In a typical experiment there is a threshold point at ca. 215 °C where condensation of the organic material results in a sudden drop in activity to 0%. Upon heating the Ambersorb to 225 °C or higher, release of substantial amounts of methylene chloride is observed. This is expected if liquid condensed in the carbon pores at the lower temperature.

It is desirable to attain lower temperatures for the deep oxidation reaction in order to apply the technology to existing adsorbent regeneration methods which operate at 140–170 °C.[9] Ambersorb adsorbents, utilized commercially in wastewater purification, are regenerated with superheated steam to remove the organic contaminant. Catalytic oxidation at these lower temperatures simultaneously would remove and destroy the organic. The catalytic oxidation of CH_2Cl_2 was performed at lower temperature in the presence of water vapor. The results of this experiment are presented in Figure 1. The catalyst used in this experiment is A563, and the water is introduced by saturating the air stream in a water bubbler before contacting the reactor. With a water-saturated air flow, a fairly smooth decline in activity is observed down to 150 °C where 15% conversion is still maintained. At 140 °C, the post-catalyst concentration of methylene chloride was observed to drop from the condensation of CH_2Cl_2 in the pores. Water is apparently ineffective at preventing condensation of methylene chloride at temperatures lower than 150 °C.

Mechanism Studies. Data for the methylene chloride reaction at 250 °C, with A563 as the catalyst, were fit to a plug-flow model[20] for a reaction that is first order or pseudo-first order in CH_2Cl_2. An assumption is made in this model that the oxygen concentration is large enough to remain essentially unchanged through the course of the reaction, thereby allowing for determination of the rate constants with respect to methylene chloride concentration. The k values were determined over a range of flow rates of 1 to 10 mL/min; the average value (not including 1 mL/min) for k is 5.3(±0.4) × 10^{-3} s^{-1}. The rate constants obtained are consistent throughout the rate, with the exception of the value of 3.5 × 10^{-3} for a flow rate of 1 mL/min. This slow air flow can lead to back pressure or allow larger amounts of methylene chloride to form in the vapor phase of the reservoir decreasing the O_2 to CH_2Cl_2 ratio. At 1 mL/min the molar ratio of oxygen to methylene chloride is calculated to be 2.3. The ratio appears to be low enough that oxygen is not in large excess throughout the reactor and enters into the rate equation. Thus, oxygen has a non-zero order in the catalytic combustion reaction. This observation is in contrast to the study done by Weldon and Senkan[16] where it was determined that the catalytic oxidation of chloroform using Cr_2O_3/Al_2O_3 was zero order in oxygen. The comparison implies that adsorption of oxygen onto the carbon is an integral part of the mechanism whereas nonporous inorganic oxides are less able to absorb oxygen.

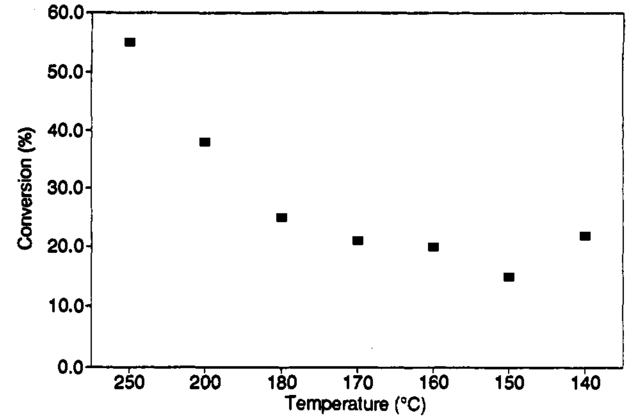

Figure 1. Activity of Ambersorb 563 in the deep oxidation of methylene chloride as a function of decreasing temperature in the presence of water (ca. 0.01 mL/h).

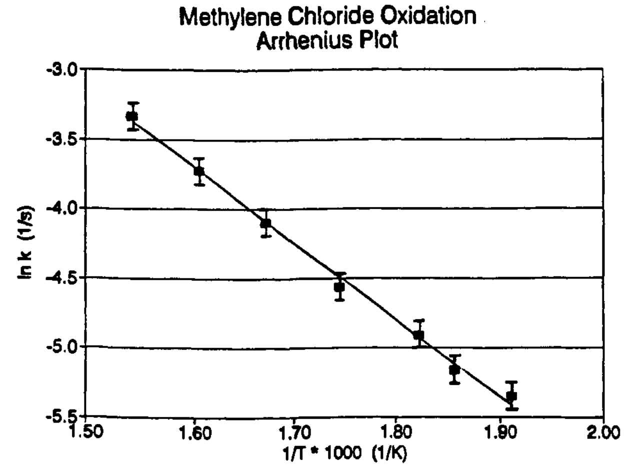

Figure 2. Arrhenius plot (first order, ln k vs temperature^{-1}) for the deep oxidation of methylene chloride at 3 mL/min (air flow and 2.0 g catalyst sample). Linear regression gives a best-fit line of ln k = (−5.543 × 10^3)(1/T) + 5.179. These values give E_a = 11.0 kcal/mol and the Arrhenius constant = 177.5 s^{-1}.

An Arrhenius plot for the temperature range of 250 to 375 °C is shown in Figure 2 for a flow rate of 3 mL/min. The activation energy (E_a) derived from a least-squares treatment on this plot is 11.0 kcal/mol (A = 177.5 s^{-1}), which is comparable to that observed for the same reaction over cerium and chromium oxides supported on zeolites.[19] The low value of the activation energy compared to even the weaker C–Cl bond dissociation energy (73 kcal mol^{-1} in CCl_4) indicates substantial interaction of species formed in the transition state with the catalyst.

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Isotope effects were examined by utilizing CD_2Cl_2 as the reactant. Conditions for comparing the deuterated to the undeuterated reactant were kept as similar as possible by using the same catalyst sample (A563) and the same flow rates. A smaller bed height was employed than for the reactions presented in Table II. Here 35(±2)% of CD_2Cl_2 was oxidized as compared to 49(±2)% for CH_2Cl_2. This implies a $k_H/k_D = 1.4$, which is slightly higher than the estimated value of 1.2 for typical secondary isotope effects at 250 °C. This suggests that C–H bond clevage may be involved in the rate-determining step for this substrate. The reported ability of carbon materials to function as both hydride and hydrogen atom abstractors[21,22] and investigations of alcohol reactivity in terms of C–H bond cleavage[23] over carbon catalysts offer precedence for this type of reactivity. The catalytic cycle for the combustion reaction requires that oxygen regenerate reduced surface species back to the active oxidized state. The effectiveness of the oxygen regeneration step determines the projected lifetime of the catalyst as it is subjected to repeated oxidation/reduction cycles.

A deep oxidation of CH_2Cl_2 at 250 °C was carried out using $CrO_3/563$ as the catalyst where air and nitrogen were alternated through the reactor. The initial air stage showed a high activity (85%), but upon changing to N_2, activity decreased to <10% over the next 10 h of reaction. Upon reintroducing air into the system, activity resumed within an hour to a level of 85%. These results show that the catalyst is reversibly reduced by the organic reactant with oxygen completing the catalytic cycle by reoxidizing the catalyst to the active state. The observation that the catalyst continues to operate even 8 h after air is removed from the system shows that there is a significant concentration of oxygen and catalytically active sites on the carbon which are used effectively in the reaction. The reduced catalyst is rapidly oxidized back to full activity upon contact with air, demonstrating the effectiveness of the catalyst oxidation step. The ability of the Ambersorb catalysts to rapidly attain their original activity after complete reduction illustrates their potential for long lifetimes in industrial applications.

Magnetic susceptibility measurements were utilized to determine the chromium oxidation state in the catalyst and to follow changes during reaction. The magnetic susceptibility, χ_g (magnetic susceptibility per gram, cgs units), for A563 is 3.15×10^{-6}. A fresh catalyst sample of $CrO_3/563$ gives a χ_g value of 5.51×10^{-6}. Correcting the result obtained with $CrO_3/563$ to remove the carbon contribution results in $\chi_g = 2.80 \times 10^{-6}$ for 0.14 g of Cr species; this translates into a susceptibility of 2.00×10^{-5} per gram of Cr species present on the catalyst. Assuming a formula weight of 100 g/mol (based on CrO_3), one obtains a χ_m of 2.00×10^{-3} mol^{-1} and a μ_{eff} ($\mu_{eff} = 2.828(\chi_m T)^{1/2}$) of approximately 2.18 μ_B. The spin-only formula, $\mu_{eff} = [(n + 2)n]^{1/2}$, gives an estimate of $n = 1.4$ for the number of unpaired electrons per Cr atom. This number indicates the presence of mixed oxidation states for the catalyst. Determination of the oxidation states involved is difficult because of complications arising from antiferromagnetic coupling and a multitude of possible oxidation states. The values obtained in this experiment for χ_g (2.0×10^{-5} mol^{-1}) can be compared to literature values of 2.5–3.0×10^{-5} mol^{-1} for Cr_2O_3[24] and suggest appreciable amounts of reduced chromium. A sample of the same catalyst utilized in the catalytic combustion experiment resulted in a value of $n = 1.5$. The slight increase in paramagnetism after reaction is also consistent with the XPS analysis (vide infra).

The chromium oxidation state distribution was examined further in catalytic experiments. An attempt was made to isolate the reduced species formed in the catalytic combustion of CH_2Cl_2 at 250 °C by replacing the oxygen reactant with nitrogen and examining the catalyst once the reaction had stopped. In contrast to A563 alone where conversion dropped to 5% in 10 h, for $CrO_3/563$, a stable conversion level of 30% was maintained for ~100 h in the absence of oxygen. Minimal amounts of carbon oxides and organic products were observed in the post-catalyst stream. Magnetic susceptibility of this catalyst sample showed no change from the fresh catalyst ($n = 1.4$). The reaction was repeated using helium with identical results, showing that the reactivity was not due to an oxygen impurity in the nitrogen.

The possibility exists for a stoichiometric reaction of methylene chloride with Cr(VI) and subsequent reduction to Cr(III) by sequential electron transfer processes, proceeding through intermediate oxidation states Cr(V) and Cr(IV). However, the amount of methylene chloride reacted in the experiment (10.1 mmol) is more than the oxidation equivalents available from the chromium even if all the chromium is Cr(VI) initially, which is not the case. Furthermore, the magnetic susceptibility shows no change in the paramagnetism.

The results for the CrO_3/SiO_2 catalyst are different. Magnetic susceptibility on the catalyst after reaction, at the conditions listed in Table II, shows a significant amount of reduced chromiums formed in the reaction ($n = 1.46$ for the after reaction catalyst in contrast to $n = 0$ for the fresh material; XPS studies also show this result, vide infra). The reactivity of the catalyst also decreases over time, reaching a level of just 20% after 24 h, regardless of the atmosphere. The catalyst changes to an intense black color, indicating a large amount of coking. Loss of the metal from the silica as evidenced by discoloration, and the reduction of chromium(VI) demonstrate that the silica catalyst is very different than the carbon analogs in terms of metal/support interactions.

A blank sample consisting of a physical mixture of A563 and pure CrO_3 was studied by magnetic susceptibility. The χ_g obtained for this sample was 5.21×10^{-7}, which is lower than that for untreated Ambersorb resin. This indicates pure CrO_3 makes only a diamagnetic contribution to the sample susceptibility. If this experiment is compared to the results for the prepared catalyst, it can be inferred that the carbon acts as a reducing agent upon preparation of the catalyst to form lower valent chromium species which are not formed in the physical mixture.

The question remains as to whether or not Cr_2O_3 or a higher oxidation state is the active oxidation state for catalytic decomposition. To study this, 0.5 g of $CrO_3/563$, which gives 93% conversion in the CH_2Cl_2 experiment under these conditions, was pretreated with H_2 for 1 h in order to reduce the chromium species present. Activity of this reduced catalyst in the methylene chloride reaction gave 59(±2)% conversion. This value is within the error limit for the reactivity of the blank support, at 55(±3)% when 0.5 g of catalyst is used. Magnetic susceptibility measurements on the reduced catalyst gave $n = 3.1$ unpaired electrons per Cr atom, which is consistent with the full reduction to Cr(III). Thus, a high oxidation state chromium species, most likely Cr(VI), is the active metal oxidation state for low-temperature oxidative decomposition. It can also be stated that the Cr(III) is not regenerated to Cr(VI) under the conditions of the experiment.

The results presented above lead to a number of suggestions about the reaction mechanism. As far as the net reaction is concerned, chromium is functioning non-oxidatively. Precedence for CrO_3 functioning as a Lewis acid in a non-oxidative process is seen in the reaction of CrO_3 with HCl to form $HOCrO_2Cl$ and CrO_2Cl_2.[25] The first step of this reaction can be viewed as involving a weakly bound HCl adduct that transfers a proton to an oxygen forming a Cr–Cl bond. In the case of CH_2Cl_2, chlorine atom abstraction in the rate-determining step followed by rapid or concerted hydrogen atom transfer would generate $HOCrO_2$-

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Table IV. Summary of XPS Data for Chromium Catalysts

sample	peak max (eV)	inten	assign
	$CrO_3/563$		
before reaction, θ = 0°	579.3	100	Cr(VI)
before reaction, θ = 90°	576.4	17.2	Cr(III)
	579.1	85.7	Cr(VI)
after reaction, θ = 0°	579.7	95.1	Cr(VI)
after reaction, θ = 90°	576.7	20.0	Cr(III)
	579.2	71.9	Cr(VI)
	CrO_3/SiO_2		
before reaction	582.0	89.8	Cr(VI)
after reaction	581.7	67.0	Cr(VI)
	578.4	28.0	Cr(III)

Cl. This process is consistent with the observed secondary kinetic isotope effect. The carbon support and possibly chromium are involved in the oxidation of the resulting carbon fragment to CO_2.

$$CrO_3 + CH_2Cl_2 \rightarrow HOCrO_2Cl\ [HCCl]$$

$$[HCCl] + O_2 \xrightarrow[\text{[Cr?]}]{\text{[C]}} HCl + CO_2$$

Hydrolysis of $HCrO_3Cl$ is catalytic in water ($HOCrO_2Cl + H_2O \rightarrow CrO_2(OH)_2 + HCl \rightarrow CrO_3 + H_2O$).

Catalyst Characterization. The materials examined in X-ray photoelectron experiments were CrO_3 supported on 563, both before and after the catalytic combustion of methylene chloride, and CrO_3 supported on silica gel before and after reaction. Because the carbon catalysts are in bead form and have a fairly smooth surface, the effect of takeoff angle, θ, on XPS response was studied as a way of determining if the chromium oxidation state changes as a function of depth. The angle is defined as 0° for detected photoelectrons exiting parallel to the surface plane and 90° for detected photoelectrons exiting perpendicular to the surface plane. Table IV shows a summary of the XPS data. The intensity values given are in arbitrary units and not percentages. There appear to be two different peaks for chromium on the carbon at the 90° takeoff angle, in contrast to one peak for 0° that is attributed to Cr(VI). This observation suggests that Cr(III) is present on the catalyst and may exist at the interface between carbon and Cr(VI). The binding energies found for both Cr(VI) and Cr(III) correlate almost perfectly with those reported in the literature for Cr(VI) and Cr(III) oxo-compounds.[26-29] When the results are compared for the used catalyst versus the fresh catalyst, the Cr(VI) to Cr(III) ratio decreases from 5 to 3.5 after reaction. The indication is that chromium is in a slightly more reduced state after the reaction, which is consistent with the aforementioned magnetic susceptibility results.

In the case of a silica-supported CrO_3 catalyst, before reaction there is only one signal observed. Because the silica is amorphous, changing the takeoff angle offers no change in the spectrum. The binding energies are slightly higher. After reaction there is a considerable amount of Cr(III) formed with the Cr(VI) to Cr(III) ratio of 2.1. The reduction of chromium in this example indicates that chromium is more easily reduced on the silica catalyst than the carbon analogs. This is consistent with the catalytic results which showed an initial 97% conversion which gradually drops to 20% after 24 h. We have previously mentioned that Cr(III) is not active. This reduction, coupled with the loss of chromium from the support by formation of volatile oxychlorides and coking of the silica during the reaction, leads to catalyst deactivation.

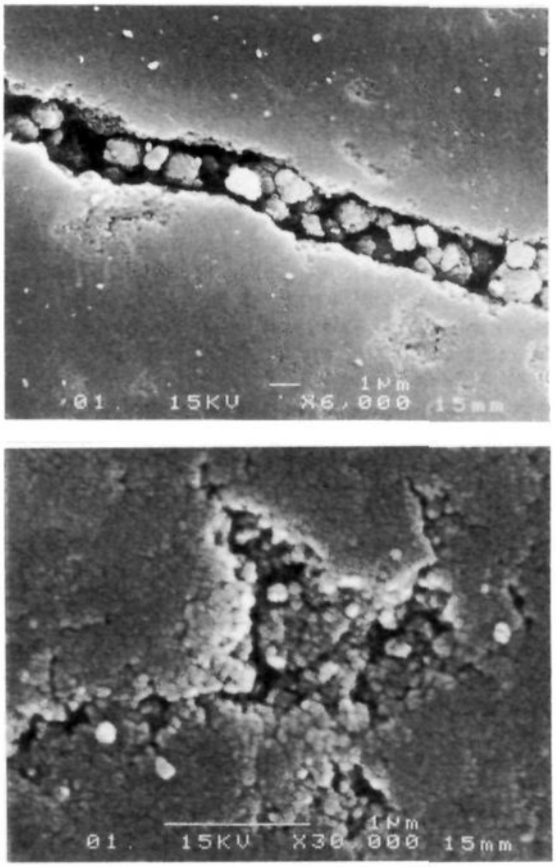

Figure 3. Scanning Electron Micrographs of Ambersorb 563 at (a) 6000 and (b) 30000 magnification.

As mentioned previously, porous carbon catalysts have been found to possess high metal dispersion, and this effect has been observed by scanning electron microscopy.[26] Scanning electron micrographs of A563 are presented in Figure 3 (6000 magnification and 30000 magnification). At 6000 magnification, there is a large fault in the sample which provides a view of the interior pore structure arising from the copolymer precursor. The micrograph at 30000x illustrates the detail for a pore of macroporous dimensions with mesopores observed as small cracks in the surrounding surface. Micropores on the surface of the carbon bead, which in these figures are too small to see, are often cited to be the defining character which accounts for the molecular sieving action observed for certain carbon materials.[30-32]

The micrographs in Figure 4 are of $CrO_3/563$ at 6000 and 30000 magnification, respectively, and they reveal some qualitative information about catalyst structure. This sample has been heated to 250 °C and used in a catalytic reaction for an extended period of time. One would expect that CrO_3, which has a melting point of 195 °C, would melt and recrystallize upon cooling into aggregates, or large crystallites, unless it was highly dispersed and anchored to the surface. The lack of large crystallites observed in Figure 4 is strong evidence that dispersion and adhesion to the surface has occurred as demonstrated with MoO_3 supported on high surface area carbon materials.[26] The synergistic activity of $CrO_3/563$ presented in Table II is also indicative of this high level of dispersion and attachment of CrO_3 to the carbon surface.

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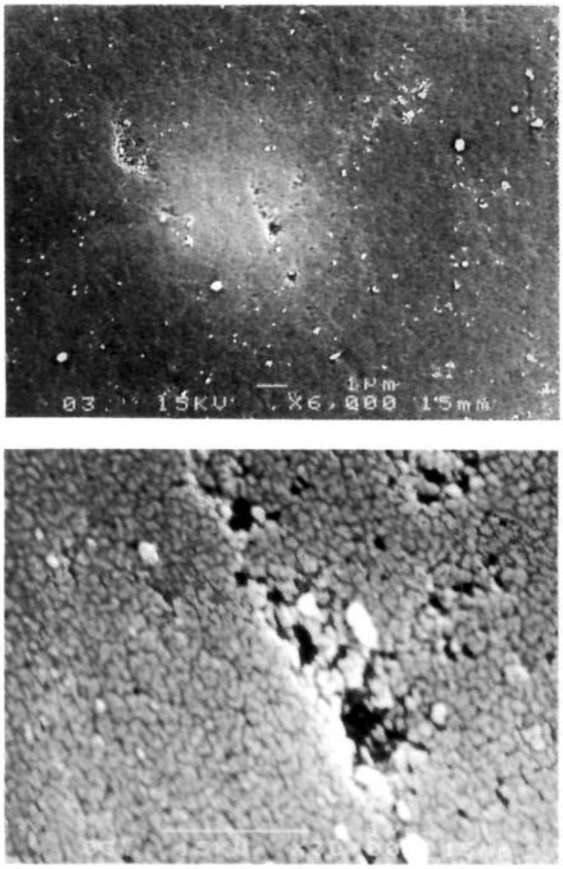

Figure 4. Scanning electron micrographs of $CrO_3/563$ at (a) 6000 and (b) 30000 magnification.

A vital aspect of catalyst structure is the physical placement of the metal on the support; for porous catalysts this can be studied by porosimetry. The single-point BET porosimetry method was used to determine the changes in A563 upon addition of CrO_3. The surface area for the CrO_3 doped carbon is determined to be 682 m^2/g, which is identical to that of the untreated carbon (680 m^2/g). The micropore volumes likewise are the same (0.25 mL/g for $CrO_3/563$ vs 0.26 mL/g for 563). A significant difference is observed in the total pore volume, which is 0.60 mL/g for the chromium catalyst whereas untreated 563 has 0.79 mL/g total pore volume. The lack of significant change in the total surface area and the micropore volume upon adding CrO_3 indicates that the oxide does not penetrate or cover the openings to the micropores. The CrO_3 enters the pores of the carbon bead and is contained in the meso- and macropores rather than the micropores. It is expected that the micropores would not be penetrated by the impregnation solution due to the fact that A563 is very hydrophobic and water was the solvent used to prepare the catalyst. Furthermore, H_2CrO_4 and its polymer aggregates ($H_2Cr_2O_7$, for example) are too large to enter the micropores. The unique properties of the carbon supported catalysts arise because the CrO_3 does not obstruct the penetration of the organic reactants into the carbon micropores and there is a high level of dispersion for the metal on the support.

Conclusions

Certain carbon-based catalysts are shown to be very effective for the low-temperature catalytic combustion of halogenated hydrocarbons. A number of metal oxides supported on porous carbon adsorbents, as well as the carbon supports themselves, have shown remarkable ability to decompose chlorinated and brominated organic compounds to CO_2, CO, and HX.

In the case of chromium(VI) oxide on carbon, an unusually stable and active catalyst was developed which was found to consist of mixed-valent chromium species, most likely Cr(VI) and Cr(III). Susceptibility and spectroscopic studies of this material indicate that the reduced chromium preferentially resides at the carbon/chromium interface, which may be related to the exceptionable stability observed for this catalyst (oxidative stability and inhibition of volatilization) relative to a silica analog or a physical mixture of the two pure components. Reducing the chromium oxidation state with hydrogen was found to destroy the catalytic activity from the chromium; however, the activity observed in an inert atmosphere suggests that the Cr(VI) species functions via a non-oxidative pathway. Structural examination of the chromium catalysts revealed that the metal is present mostly in the meso- and macropore region of the carbon and does not hinder penetration of the micropore region; in addition, there appears to be significant dispersion of the metal as viewed by electron microscopy.

In contrast to the chromium activity, the carbon itself functions in a net oxidative manner in the catalytic combustion reaction; kinetic studies show a non-zero order for oxygen in the rate equation. Methylene chloride was found to exhibit first-order behavior, with an activation energy of 11 kcal/mol. The presence of hydrogen, either as part of the reactant molecule (as in CH_2Cl_2) or as part of an additive such as water, was determined to be important for efficient decomposition of the organic to carbon oxides and HCl. Excess water in the reaction stream did not inhibit the reaction in any way and even promoted the reaction at lower temperature.

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