FINAL REPORT
U. S. Department of Energy

THE ADSORPTION AND REACTIONS OF HALOGENATED VOLATILE ORGANIC COMPOUNDS (VOCs) ON METAL OXIDES

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Grant Number: DE-FG07-96ER14724
Project Duration: September 15, 1996 - September 14, 2000

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Executive Summary

One of the most common environmental problems in the United States and the DOE complexes is the contamination of soils and ground water by toxic volatile organic compounds such as carbon tetrachloride (CCl_4). At the Hanford site, for example, the disposal of an estimated 360-580 cubic meters of CCl_4 has resulted in a 7 mile underground plume. The purpose of this research was to provide a fundamental understanding of the adsorption and catalytic reactions of CCl_4 on metal oxide surfaces with a view to developing strategies for its remediation.

Emphasis was placed on the alkaline earth metal oxides; *i.e.*, MgO, CaO, SrO and BaO because it had previously been demonstrated that MgO and CaO reacted with CCl_4 to form the corresponding metal chloride and carbon dioxide. This process was named Adestructive adsorption,@ although one should recognize that the surface-initiated dechlorination reactions often result in the partial or complete conversion of the metal oxide to the metal chloride. The disposal of the metal chloride then becomes a problem.

In the initial phase of this program, the destructive adsorption of CCl_4 on the alkaline earth oxides listed above was studied as a function of the reaction temperature and the amount of CCl_4 injected. The reaction was followed using *in situ* Raman spectroscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, and ^{13}C magic angle spinning nuclear magnetic resonance spectroscopy. It was found that the activity toward CCl_4 parallels the basicity of the alkaline earth metal oxide; *i.e.*, the activity decreased in the order BaO>SrO>CaO>MgO. Barium oxide readily reacted with CCl_4 at 200-300EC, and, at these low temperatures, CO_2 was the only gas-phase product that evolved from the surface. At higher reaction temperatures, other alkaline earth metal oxides, such as CaO and MgO, also became active, and phosgene ($COCl_2$) was found to be a reactive

intermediate in the destruction of CCl_4. Barium oxide could be regenerated by dissolving the chloride in water, followed by precipitation of barium carbonate, and subsequent calcination. Thus, the challenge of disposal of barium chloride could be avoided.

Based on the results obtained with the alkaline earth oxides, the research was extended to two members of the lanthanide oxide series, La_2O_3 and CeO_2. The first of these, La_2O_3, is a strongly basic metal oxide and the other, CeO_2, is an example of a reducible metal oxide. In the latter case, one might expect that Cl_2 would be formed along with CO_2. Over La_2O_3, the reaction of CCl_4 began at about 300EC with the rapid formation of LaOCl and the release of CO_2 into the gas phase. The complete transformation of LaOCl into $LaCl_3$ was much more difficult, and required high reaction temperatures and large amounts of CCl_4. In the case of CeO_2, CCl_4 destruction started at around 450EC, and was accompanied by the reduction of Ce(IV) to Ce(III) and the formation of CeOCl as an intermediate product.

Although the destructive adsorption of CCl_4 may be used in certain strategies for remediation, a catalytic reaction of CCl_4 with H_2O would generally be more useful since in many cases the hydrocarbon is present in an aqueous phase. The reaction cycle that was observed for BaO suggested that a catalytic reaction might be possible. It was found that MgO is active as a catalyst for the reaction of CCl_4 with H_2O to form CO_2 and HCl. The HCl could be neutralized in aqueous NaOH, and the resulting dilute salt solution could be easily disposed of. Among the alkaline earth oxides, MgO is the only active catalyst at moderate temperatures. Over 1.72 g MgO at 525EC, a conversion $> 99\%$ (no remaining CCl_4 was detected) was achieved for 72 h. The CCl_4 and H_2O pressures were 2 Torr and 4 Torr, respectively. Thus, nearly complete removal of CCl_4 can be achieved over a long period. The favorable catalytic activity of MgO relative to the other alkaline earth oxides is attributed to two factors; first, MgO is not as readily converted to $MgCl_2$, and, second, the decomposition temperature of $MgCO_3$ (-430EC) is substantially less than that of the other carbonates. As a consequence, chloride and carbonate phases do not substantially inhibit the catalytic activity.

The scientific knowledge generated by this project should enable environmental engineers to evaluate the potential of destructive adsorption of CCl_4 and the catalytic reaction of CCl_4 with H_2O as an alternative for the remediation of carbon tetrachloride. A paper describing destructive adsorption was presented at the 1998 American Chemical Society Meeting and papers on this subject and the catalytic conversion of CCl_4 have been published in the *Journal of Physical Chemistry*, *Physical Chemistry Chemical Physics* and *Chemical Communications*.

Research Objectives

One of the most common environmental problems in the United States and in the DOE complex is the contamination of soils and ground water by volatile organic compound (VOCs). For example, leakage of solvents (trichloroethylene and tetrachloroethylene) has produced a plume larger than three square miles of contaminated soils and underlying ground water at the Savannah River site. At the Hanford site, the disposal of 360-580 cubic meters of carbon tetrachloride has resulted in a 7 mile underground plume. Hundreds of sites within the DOE complex with similar contamination have been identified.

Vacuum (vapor) extraction, a well-developed and demonstrated technology for treatment of the vadose zone (the region between the surface and ground water), generates a waste stream containing VOCs. In fact, all *in situ* remediation systems currently being demonstrated include a vapor extraction component. Because the Clean Air Act now requires treatment of all vapor streams, there is a pressing need for innovative technologies that destroy chlorinated VOCs in a safe and economical manner.

The objective of this study was to provide fundamental information on the manner in which carbon tetrachloride reacts with basic metal oxides. The research focused on two aspects of this problem: (1) the destructive adsorption of CCl_4, which results in the formation of a metal chloride or oxychloride, along with CO_2, and (2) the catalytic reaction of CCl_4 with H_2O over a metal oxide to produce HCl and CO_2. It was of interest to determine the relative activities of a series of oxides, both for destructive adsorption and the catalytic reaction. In the destructive adsorption process, regeneration of the metal chloride or oxychloride was investigated because of potential problems that would be associated with disposal of a solid waste. For the catalytic reaction, the conversions that could be achieved, the lifetime of the catalysts, the kinetics of the reaction and the possible formation of phosgene as a highly undesirable side product were explored in some detail.

Methods and Results

Destructive Adsorption of Carbon Tetrachloride

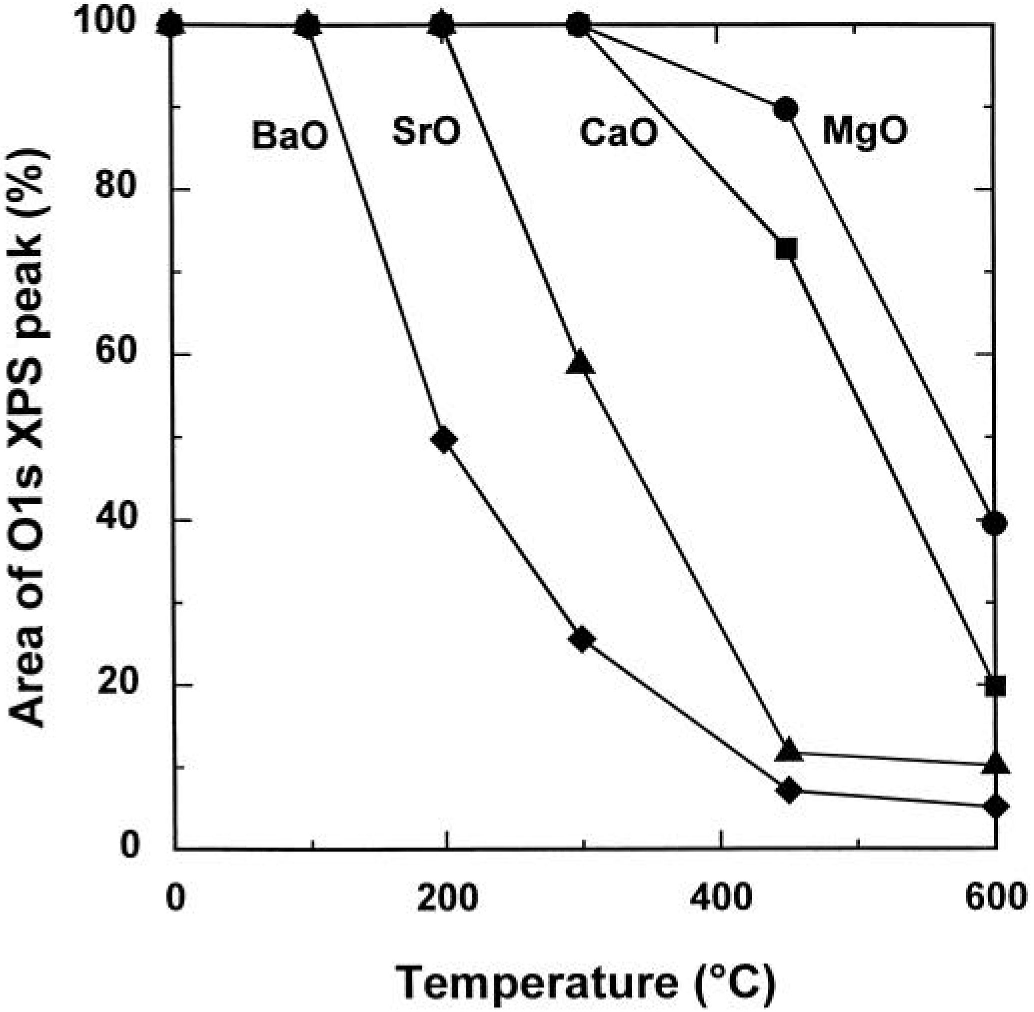
Introduction. Klabunde and co-workers [1] have shown that CaO and MgO are able to destroy chlorinated hydrocarbons, yielding CO_2, traces of $COCl_2$, and the corresponding metal chlorides. Operating temperatures were relatively high, but complete transformation of the oxide into the chloride was possible by depositing transition-metal oxides (*e.g.*, Fe_2O_3) onto the oxide. Although the process has been named Adestructive adsorption,@ one should recognize that the surface initiated dechlorination reactions often result in the partial or complete conversion of the metal oxide to the chloride.

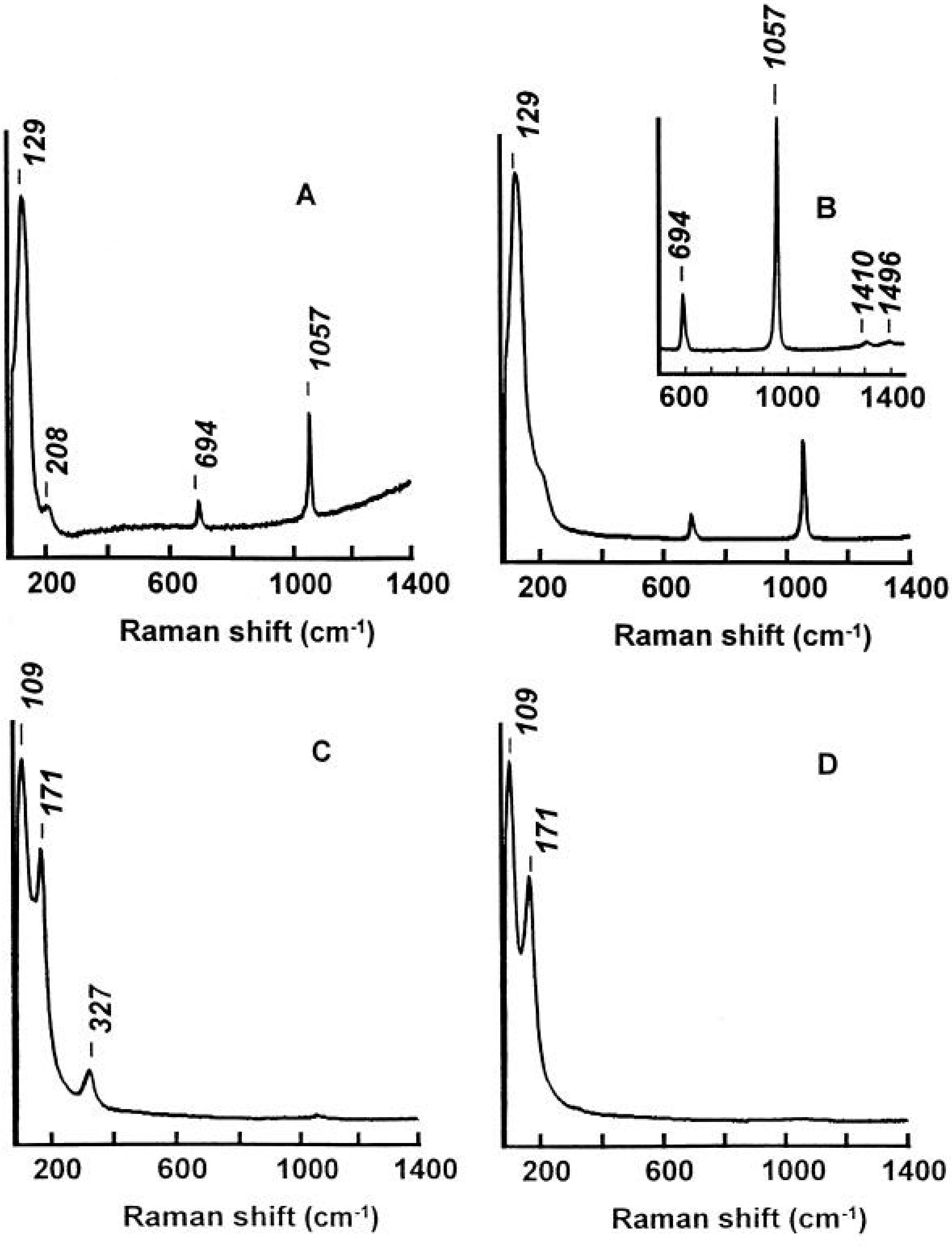
As part of this project, the destructive adsorption of CCl_4 on a series of alkaline earth metal oxides was studied in detail. It will be shown that the activity parallels the ionicity/basicity of the alkaline earth metal oxide; *i.e.*, BaO>SrO>CaO>MgO. At lower temperatures (200-300EC), only CO_2 was observed as a gas phase product, but at higher temperatures (450-600EC), a small amount of $COCl_2$ was also detected. In addition, at the higher temperatures an unusual metal oxide chloride, *viz*., M_4OCl_6 (M=Ba, Sr, or Ca) was also detected in the solid phase. Additional experiments were carried out to determine the reactions of CCl_4 with two lanthanide oxides, La_2O_3 and CeO_2.

Methods. All metal oxides were obtained from commercial sources and were treated at 600EC in oxygen overnight prior to reaction with CCl_4. Carbon tetrachloride normally was introduced into a stream of helium as a pulse, with a time period between pulses of about 2 h. The extent of reaction between CCl_4 and the metal oxide was followed by x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, infrared spectroscopy and nuclear magnetic resonance spectroscopy.

Results. Near-surface reactions of the metal oxides with CCl_4 were followed by XPS. When CCl_4 was introduced, chlorination of the first several layers of the oxide was evident by an increase in intensity of the Cl p. XPS peak and a decrease in intensity of the O ls XPS peak of the metal oxide. The extent of the reaction at the surface of BaO, SrO, CaO and MgO as a function of the reaction temperature is compared in Fig. 1. It is clear that BaO, the most active material for CCl_4 destruction, readily reacted with CCl_4 at 200EC, and the transformation to the chloride, as indicated by XPS, was almost complete at 450EC. X-ray diffraction results confirmed that the bulk, as well as the surface, was extensively converted into $BaCl_2$; thus, oxygen atoms must readily diffuse from the bulk to the surface to undergo O^{2-}/Cl^{-} exchange. The decrease in reactivity toward CCl_4 is consistent with the heats of reaction for $2MO + CCl_4$ 6 $2MCl_2 + CO_2$.

The reactions that occur in the solid phase were followed at elevated temperatures with *in situ* Raman spectroscopy. Because the sampling depth is about 0.3 Fm, one is primarily measuring the state of the bulk phase. As an example, the chlorination process of BaO with CCl_4 at 600EC will be discussed in detail. The Raman spectrum of calcined BaO contained bands at 129 and 208 cm^{-1}, which are shown in Fig. 2A. These bands are typical of defect lattice modes. In addition, bands at 694 and 1057 cm^{-1} were detected, indicating the presence of surface carbonates. After injecting 10 FL of CCl_4 at 600EC (spectrum 2B), the amount of surface carbonate increased, and two additional bands at 1410 and 1496 cm^{-1} due to monodentate surface carbonates became clearly visible. Additional doses of CCl_4 resulted in an overall decrease in the amount of surface carbonates.


100
80
60
40
20
0
Area of O1s XPS peak (%)
0
200
400
600
Temperature (°C)
BaO
SrO
CaO
MgO

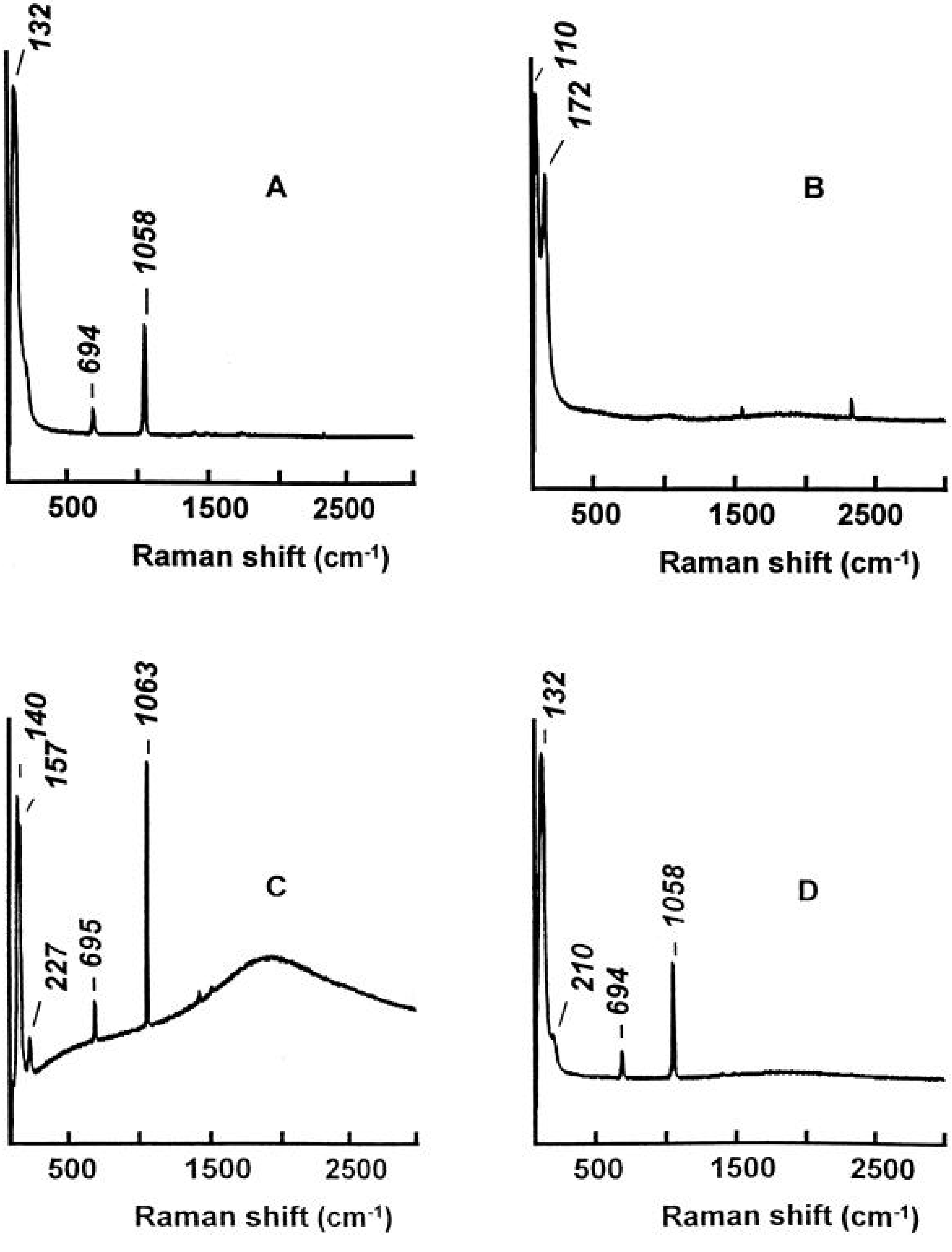


Furthermore, new Raman bands at 109 and 171 cm^{-1} became apparent, which resulted from the Ba-Cl lattice modes in $BaCl_2$. An additional band centered around 327 cm^{-1} (spectrum 2C) reached a maximum after injecting 20 FL of CCl_4. This band is due to the formation of a metal oxide chloride, *viz*., Ba_4OCl_6, which may be envisaged as a structure in which three out of four oxygen atoms are replaced by chlorine atoms.

As illustrated in the Raman spectra of Fig. 3, the original BaO can be regenerated by first dissolving the $BaCl_2$, which is highly hygroscopic, in deionized water at room temperature. Precipitation of the Ba^{2+} ions as $BaCO_3$ was then accomplished either by adding ammonium carbonate to the solution or by passing CO_2 through the solution for several hours at 25EC. After filtration, the formation of $BaCO_3$ was spectroscopically verified (spectrum 3C). In a final step, $BaCO_3$ was extensively transformed into BaO by calcination in O_2 at 600EC (spectrum 3D). This potential for recycling the BaO/$BaCl_2$ has an important practical advantage in that no solid waste would have to be disposed of.

Gas phase products that evolved from the oxide surfaces during the chlorination process were monitored by infrared spectroscopy, and the results obtained over BaO are presented in Fig. 4. At 200 and 300EC, the only detectable gas-phase product was CO_2, but at higher reaction temperatures, a small amount of $COCl_2$ was also observed. This suggests that $COCl_2$ is an intermediate product in the decomposition of CCl_4. Over CaO, Klabunde and co-workers [1f] showed that $COCl_2$ formed during destructive adsorption of CCl_4 could be eliminated by using an excess of the metal oxide.

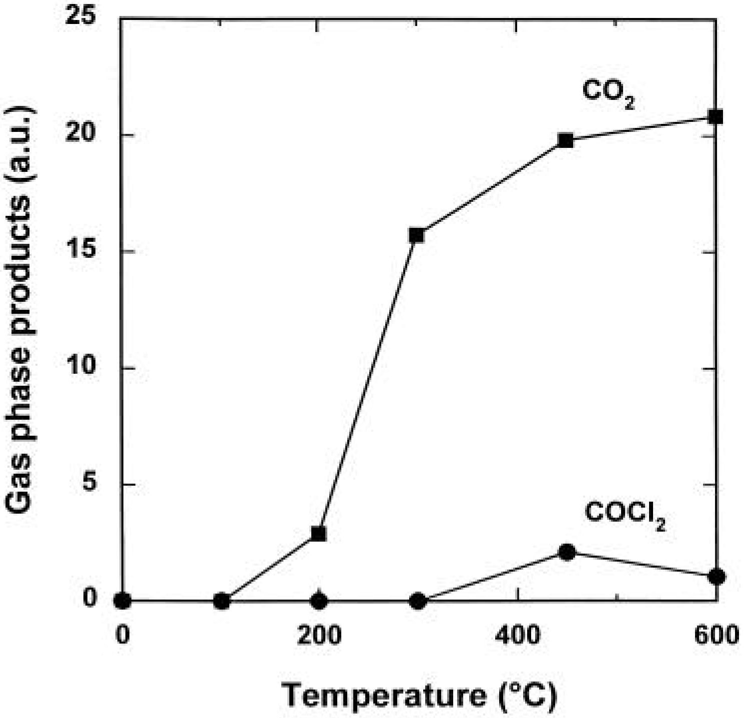
Further information about the chlorination process came from ^{13}C magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. When $^{13}CCl_4$ was added to BaO at 25EC,

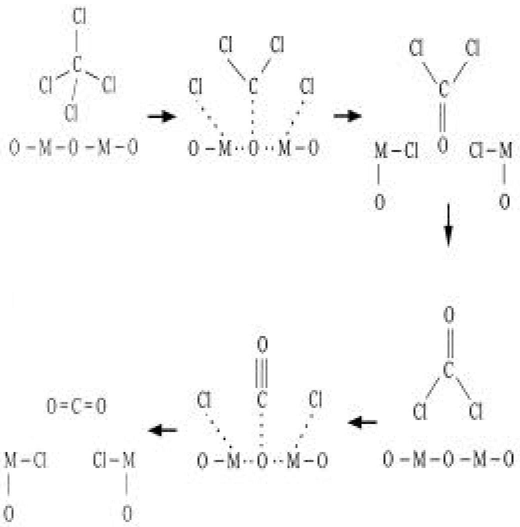


two peaks were observed at 97 and 95 ppm, which are assigned to physisorbed and gas phase tetrachloride. After heating the sample to 300EC and cooling it to 25EC, both $^{13}CCl_4$ resonances decreased in intensity, and another peak at 126 ppm, due to $^{13}CO_2$, was observed. No other species was observed, which is consistent with the IR results shown in Fig. 4.

Similar results were obtained during the destructive adsorption of CCl_4 over the lanthanide oxides, La_2O_3 and CeO_2, only with these materials the extent of reaction was smaller than that found for BaO and SrO, but comparable with that observed for MgO and CaO. With La_2O_3, the destructive adsorption to form LaOCl and CO_2 was rapid, but the complete reaction to $LaCl_3$ was much slower. With CeO_2, there was a change in oxidation state from Ce(IV) to Ce(III) as CCl_3 was formed. The results obtained by several spectroscopic methods suggest a possible reaction pathway for the destructive adsorption of CCl_4 as shown in Scheme 1. This is the same pathway as that proposed previously by Hooker and Klabunde [1d]. The first step involves the physisorption of CCl_4 on the oxide surface. The covalent C-Cl bond is then polarized and broken by the ionic MO lattice. The polarization of the C-Cl bond is more pronounced on the highly ionic surfaces; thus, the

destruction activity parallels the ionicity of the alkaline earth metal oxides. The overall result of this process is the formation of $COCl_2$ and a partially chlorinated MO surface, which becomes much less reactive. In the second step, $COCl_2$ is readsorbed, and further reacts with the surface to form CO_2, which readsorbs onto the metal oxide surface to form a monodentate surface carbonate. Further chlorination results in the formation of a fully chlorinated material, and CO_2 is released into the gas phase. Except for MgO, M_4OCl_6 phases occur as intermediates when the reaction temperature is high. Apparently, at lower temperatures the chloride ions introduced into the lattice are disordered, and the formation of the metal chloride occurs without the generation of a M_4OCl_2 phase.


Gas phase products (a.u.)
Temperature (°C)
25
20
15
10
5
0
0
200
400
600
CO_2
$COCl_2$


Cl
C
O−M−O−M−O
O−M··O··M−O
M−Cl
Cl−M
O
O=C=O

The Catalytic Hydrolysis of CCl_4 over Magnesium Oxide

Introduction. The results described above for the destructive adsorption of CCl_4 suggested that it may be possible to achieve a catalytic cycle involving the reaction of CCl_4 with H_2O to form HCl and CO_2; *i.e.*,

$$CCl_4 + 2H_2O \; 6 \; 4HCl + CO_2, \tag{1}$$

which has ÄGE $_{500EC}$ = !390 kJ mol^{-1}. This catalytic reaction was only briefly described in the patent literature [2]; although, the uncatalyzed reaction occurs slowly in water [3]. Reaction 1 does not occur over BaO, but, unexpectedly, it was found that MgO is a catalyst for the reaction.

Methods. The catalyst was prepared by the decomposition of $Mg(OH)_2$ obtained by stirring an aqueous slurry of MgO (Fisher, light) at 80EC for 24 h. The $Mg(OH)_2$ (20-40 Mesh size) was decomposed at 400EC in flowing O_2. The reaction of CCl_4 with H_2O was carried out in a plug-flow reactor at a total flow rate of 80 mL min^{-1} with He as the diluent. Gas chromatography was used to analyze for CCl_4, CO_2 and H_2O, while HCl was trapped in water and subsequently titrated with aqueous $AgNO_3$.

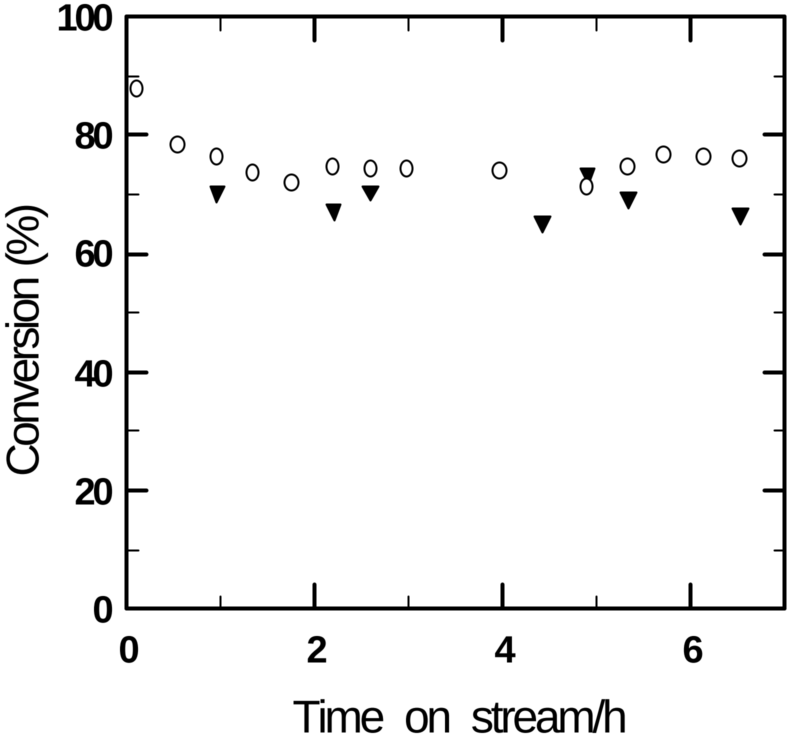
Results. The conversions of CCl_4 and H_2O are shown in Fig. 5 for the reaction carried out at 500EC over 0.40 g MgO with $P(CCl_4) = 2$ Torr and $P(H_2O) = 4$ Torr. Under these conditions, the initial conversion of 88% decreased to *ca*. 74% during the first hour, but thereafter the conversion remained nearly constant. After 24 h on stream, the conversion was 68%. The surface area of the catalyst decreased from 130 to 55 $m^2 g^{-1}$, with most of the decrease occurring during the first hour. At the same partial pressures of CCl_4 and H_2O, but with 1.19 g MgO at 525EC, the conversion was

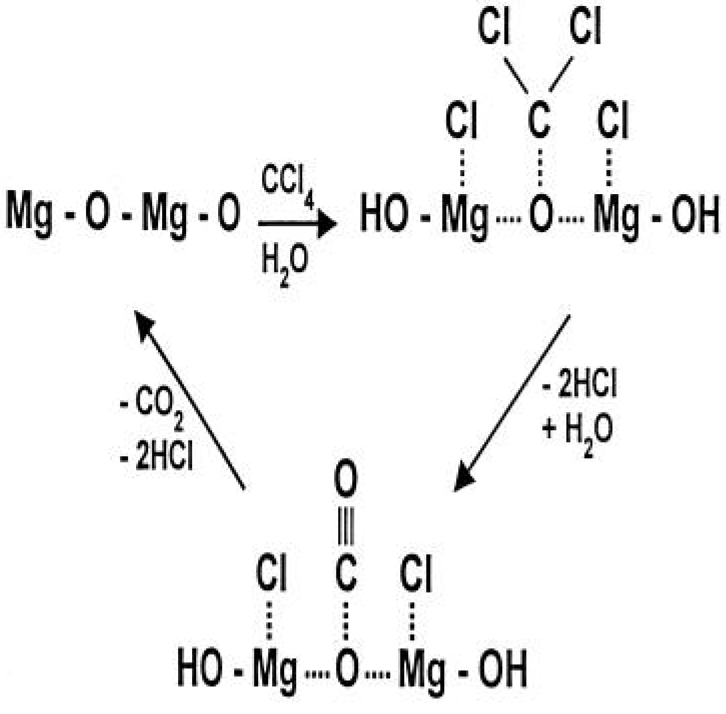
>99% (no remaining CCl_4 was detected) for 72 h. Thus, nearly complete removal of CCl_4 can be achieved over a long period.

Kinetic results were obtained under differential reaction conditions, which were achieved either by using a smaller amount of catalyst or by operating at lower temperatures. Over the temperature range 400-500EC with 2 Torr CCl_4 and 4 Torr H_2O, the apparent activation energy was 85 kJ mol^{-1}. At the same initial pressures and at 450EC, the specific activity was 0.24 Fmol $g^{-1}s^{-1}$ or 4.1 nmol $m^{-2}s^{-1}$ for a catalyst having a surface area of 55 m^2. The reaction orders with respect to CCl_4 and H_2O were 0.68 and !0.02 to !0.36, respectively. The order with respect to H_2O became more negative as the temperature decreased.

The amount of chloride in the sample after reaction was 4 wt%, which corresponds to a Cl/Mg ratio of 0.047. This value may be compared with a near surface Cl/Mg ratio of 0.12 (as determined from XPS), which was nearly the same for samples that had been on stream for 1 h at 500EC or for 70 h at 525EC. After steady state was attained, there was nearly a 100% chlorine balance between surface carbonates on MgO.

The results are consistent with the mechanism described in Scheme 2, which is adapted from Scheme 1 for the destructive adsorption of CCl_4. Although phosgene is a potential intermediate, none was detected in the gas phase by IR spectroscopy. The rate limiting step is believed to be the dissociative adsorption of CCl_4, although this is inhibited by the presence of chloride ions on the surface, which is consistent with the fact that the reaction order with respect to CCl_4 is less than unity. The dissociative adsorption of H_2O to form hydroxide ions is very rapid at the reaction temperatures used. One might expect that the formation of carbonate ions, derived from CO_2, would inhibit the reaction, but this is not the case since the addition of CO_2 to the feed, in a 30-fold excess of that


Conversion (%)
Time on stream/h
0
20
40
60
80
100
0
2
4
6


Mg - O - Mg - O
CCl4
H2O
HO - Mg ···· O ···· Mg - OH
Cl
C
Cl
Cl
Cl
- 2HCl
+ H2O
O
C
Cl
Cl
HO - Mg ···· O ···· Mg - OH
- CO2
- 2HCl

produced during the reaction, did not influence the reaction rate. The presence of chloride ions may decrease the basicity of the surface and thereby minimize the formation of surface carbonates on MgO.

The results described to this point were obtained using Fisher MgO (Ca < 1%, Fe < 0.05%); however, one experiment was carried out with Puratronic MgO (99.998%), and at comparable conditions the activity was the same, indicating that impurities such as iron do not play a role. By contrast, CaO and, as noted above, BaO were not active as catalysts. Both of these oxides are more effective than MgO for the activation of CCl_4 to form the metal chloride at 425EC (Fig. 1); therefore, the first step in the reaction mechanism would readily occur. Moreover, the replacement of $Cl^{!}$ ions by $CO_3^{2!}$ ions on $BaO/BaCl_2$ can even take place at 25EC, albeit slowly. It appears that the formation of stable carbonates on CaO and BaO inhibits the catalytic reaction over the temperature range employed in this study. At a pressure of 2 Torr CO_2, the decomposition temperatures of $CaCO_3$ and $BaCO_3$ are 430, 600 and 970EC, respectively [4].

Preliminary experiments were carried out on MgO that had been impregnated with either iron or vanadium ions. The addition of Fe to the MgO had relatively little effect on the catalytic activity for reaction 1, but the addition of V significantly increased the activity. For example, the conversion at 400EC for a 124 mg sample of pure MgO was 8% after 1 h on stream, but for a 62 mg sample of 5 mol% V/MgO it was 57%. Over 830 mg of the V/MgO sample at 400EC the conversion was 100% for nearly 18 h, but thereafter the conversion decreased as a result of the loss of vanadium from the catalyst. Vanadium chloride is a relatively volatile salt. The loss of vanadium under the reaction conditions would be a serious impediment to the practical utilization of a V/MgO catalyst.

Relevance, Impact and Technology Transfer

As noted in the previous section, the removal of chlorinated hydrocarbons from contaminated ground water is a critical DOE environmental management problem, and the removal of carbon tetrachloride from water is one of the more challenging aspects of this problem. The fundamental studies carried out under this project demonstrate two possible strategies for the removal of carbon tetrachloride; namely, (1) destructive adsorption on the alkaline earth oxides and certain lanthanide metal oxides and (2) the catalytic hydrolysis of CCl_4 over magnesium oxide. Obviously, engineering and economic studies will have to be carried out to evaluate the advantages of these methods with respect to other approaches.

The research has shown that BaO is the most suitable oxide, among those studied, for the destructive adsorption of CCl_4, both with respect to its activity at moderate temperatures and its potential for regeneration. The catalytic properties of MgO for the hydrolysis of CCl_4 have been demonstrated for the first time.

Project Productivity

Within the financial resources that were provided, the goals of the project were accomplished and exceeded. At the outset, the prospect of having a catalyst for the hydrolysis reaction was not anticipated.

Personnel Supported

Faculty: Professors Wayne Goodman, James Haw and Jack Lunsford
Postdoctoral Associates: Drs. Gerhard Mestl, Bert Weckhuysen and Ulrike Weiss
Graduate Student: Mr. Thomas Krawietz

Publications

1. ADestructive Adsorption of Carbon Tetrachloride on Alkaline Earth Metal Oxides,@ B. M. Weckhuysen, G. Mestl, M. P. Rosynek, T. R. Krawietz, J. F. Haw and J. H. Lunsford, *J. Phys. Chem. B*, **1998**, *102*, 3773.

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3. AThe Catalytic Hydrolysis of CCl_4 to HCl and CO_2 over Magnesium Oxide,@ U. Weiss, M. P. Rosynek and J. H. Lunsford, *Chem. Commun.*, **2000**, 405.

Interactions

1. AThe Adsorption and Reactions of Halogenated Volatile Organic Compounds on Metal Oxides,@ presented by J. H. Lunsford as a poster at the EMSP Workshop, Chicago, 1998.

2. ALow-Temperature Destructive Adsorption of Chlorinated Hydrocarbons on Basic Oxides,@ B. M. Weckhuysen, G. Mestl, M. P. Rosynek, T. R. Krawietz, J. F. Haw and J. H. Lunsford, Spring National American Chemical Society Meeting, Dallas, 1998. This work was highlighted in the April 20, 1998 issue of *Chemical and Engineering News*, p. 71.

Patents

None

Future Work

Although the project will not be continued in this laboratory, there is a need for further research on the catalytic hydrolysis of CCl_4.

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