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Destructive Adsorption of Carbon Tetrachloride on Alkaline Earth Metal Oxides

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The destructive adsorption of CCl_4 on MgO, CaO, SrO, and BaO has been 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, Fourier transform 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 200−300 °C, 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 $COCl_2$ was found to be a reaction intermediate in the destruction of CCl_4. Although the destruction process is initiated at the surface, the continuous O^{2-}/Cl^- exchange results in the bulk transformation of the metal oxide to the metal chloride. Barium oxide could be regenerated by dissolving the chloride in water, followed by precipitation as barium carbonate and subsequent calcination. In addition, carbon tetrachloride destruction at around 600 °C resulted in the formation of an unusual alkaline earth metal oxide chloride, viz., M_4OCl_6 (M = Ba, Sr, or Ca).

Introduction

Chlorinated hydrocarbons (CHC's) have widespread industrial applications as lubricants, heat-transfer fluids, plasticizers, transformer fluids, and cleaning solvents due to their relative inertness and ability to dissolve organic compounds.[1] The increasing amounts of CHC's released in the environment, together with their suspected toxicity and carcinogenic properties, have prompted researchers worldwide to find clean and effective methods for destroying them.[2,3] Incineration is presently the most widely used method;[4,5] however, high temperatures are required, and toxic byproducts, such as dioxins and furans, are often formed. Several alternative and cleaner destruction methods, such as oxidative catalysis over transition-metal oxides and noble metals, are proposed in the literature.[6−9] Recently, Klabunde and co-workers[10−15] 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.[10,11] Although the process has been named "destructive 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.

In this paper we present a detailed study of the destructive adsorption of CCl_4 on a series of alkaline earth metal oxides. It will be shown that the activity parallels the ionicity/basicity of the alkaline earth metal oxide; i.e., BaO > SrO > CaO > MgO. Thus, BaO and SrO were the most active materials, and reacted

with CCl_4 at temperatures as low as 200−300 °C. At these temperatures, the only gas-phase product that evolved from the surface was CO_2, whereas at 450−600 °C, $COCl_2$ was also detected. Furthermore, the mineralization process is essentially a bulk reaction, which proceeds at higher temperatures with the formation of an unusual metal oxide chloride, viz., M_4OCl_6 (M = Ba, Sr, or Ca).

Experimental Section

Reagents. Alkaline earth metal oxides and chlorides were purchased from Alfa Aesar: MgO (puratronic, 99.998%); CaO (puratronic, 99.95%); SrO (puratronic, 99.5%) and BaO (obtained by heating barium oxalate in oxygen at 600 °C; barium oxalate (puratronic, 99.999%); $MgCl_2 \cdot 6H_2O$ (puratronic, 99.999%); $CaCl_2 \cdot 4−6H_2O$ (puratronic, 99.9965%); $SrCl_2 \cdot 6H_2O$ (puratronic, 99.9965%); and $BaCl_2 \cdot 2H_2O$ (puratronic, 99.999%). All metal oxides were treated at 600 °C in oxygen overnight prior to reaction with carbon tetrachloride. $BaCO_3$ (certified A.C.S.) was obtained from Fisher Scientific Co. CCl_4 (99.9%) and $^{13}CCl_4$ (99.9%) were purchased from Aldrich and Cambridge Isotopes, respectively. All gases used in this study were of UHP grade, and were obtained from Matheson.

X-ray Powder Diffraction. X-ray powder diffraction data were obtained with a Guinier camera using Cu Kα radiation with 2θ range of 5°−85°. The samples were kept under vacuum during measurements to avoid rehydration.

Surface Area Measurements. Surface areas of the alkaline earth metal oxides, calcined in air at 600 °C, were determined using the BET method. A Quantasorb instrument was used to measure the amount of N_2 adsorbed at 77 K. The following surface areas were obtained: MgO (38 m^2/g), CaO (3 m^2/g), SrO (3 m^2/g), and BaO (2 m^2/g).

X-ray Photoelectron Spectroscopy. X-ray photoelectron (XPS) spectra were acquired using a Perkin-Elmer (PHI) model

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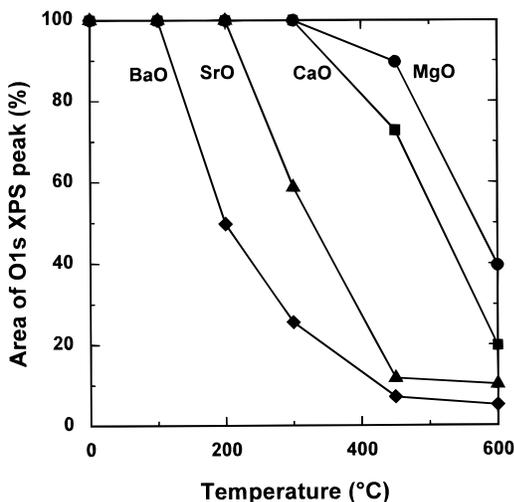
Figure 1. XPS results on the chlorination reaction of BaO, SrO, CaO, and MgO as a function of reaction temperature.

5500 spectrometer. The metal oxides in the form of pressed wafers were treated in a specially designed fused-quartz reactor system with an O-ring-sealed port that allowed in situ transfer of the ceramic holder containing the treated sample into a stainless steel vacuum transport vessel (PHI model 609217). The removable vessel was transferred to a similar port on the inlet system of the spectrometer. XPS spectra were typically recorded using a pass energy of 29.25 eV, a step increment of 0.125 eV, and a Mg anode power of 400 W.

Raman Spectroscopy. In situ Raman spectra were recorded using a Holoprobe spectrometer from Kaiser Optical, equipped with a high-performance holographic notch filter and an electrically cooled CCD camera with 256 × 1022 pixels. The exciting light source was a Nd:YAG laser, which was frequency doubled to 532 nm. The laser power employed was 2.5 mW. The Raman cell, described elsewhere,[16] was designed such that the gases flowed through the bed of the metal oxide.

Infrared Spectroscopy. FT-IR spectra were obtained using a Perkin-Elmer 2000 FT-IR spectrometer. Self-supporting wafers of the metal oxide were mounted on a fused-quartz bracket that was placed in an IR cell constructed of fused quartz. This cell was equipped with KBr windows and a heating region into which the wafer was raised.

Nuclear Magnetic Resonance. In situ ^{13}C MAS NMR spectra were acquired with a CMX-360 spectrometer at 90.5 MHz. $^{13}CCl_4$ was adsorbed onto the metal oxide using a shallow bed CAVERN cell, described in detail elsewhere.[17]

Results and Discussion

1. Near-Surface Reactions of CCl₄ with the Metal Oxides. X-ray photoelectron spectroscopy (XPS) was used to monitor the chlorination process as a function of the amount CCl_4 injected, the reaction temperature, and the type of alkaline earth metal oxide.[18] CCl_4 was introduced into a stream of helium as a pulse, and the time period between the pulses was about 2 h. Chlorination in the first several layers of the oxide was evident by an increase in intensity of the Cl 2p XPS peak and a decrease in intensity of the O 1s 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 Figure 1. It is clear that BaO, the most active material for CCl_4 destruction, readily reacted with CCl_4 at 200 °C, and the transformation process to the chloride, as indicated by XPS, was almost complete at 450 °C.
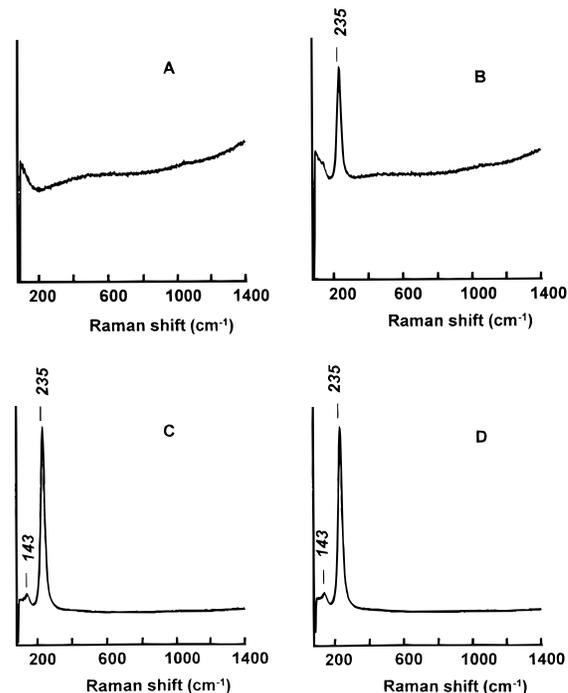

Figure 2. In situ Raman spectra of MgO measured at 600 °C in He as a function of the amount of CCl_4 injected: (A) 0 μL of CCl_4, (B) 10 μL of CCl_4, (C) 20 μL of CCl_4, and (D) 50 μL of CCl_4. About 20 μL of CCl_4 is sufficient to convert MgO into $MgCl_2$, assuming that 2 mol of MgO would be necessary to decompose 1 mol of CCl_4. The collection time was 60 s.

X-ray diffraction (XRD) results confirmed that the bulk, as well as the surface, was extensively converted into $BaCl_2$. Thus, the decomposition process is a bulk reaction in nature, and oxygen atoms readily diffuse from the bulk to the surface to undergo O^{2-}/Cl^- exchange. The reactivity toward CCl_4 decreased in the order BaO > SrO > CaO > MgO, which also is consistent with heats of reaction for $2MO + CCl_4 \rightarrow 2MCl_2 + CO_2$.[19] Furthermore, MgO and CaO were only partially transformed into $MgCl_2$ and $CaCl_2$, respectively, at temperatures up to 600 °C, which is consistent with earlier findings of Klabunde and co-workers.[11,12]

2. In Situ Characterization of the Reaction by Raman Spectroscopy. 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 μm, one is measuring the state of the material primarily in the bulk. CCl_4 was introduced into a stream of helium as a pulse, and the time period between the pulses was again about 2 h. The residence time of CCl_4 in the bed was approximately 0.5 s.

As an example, the chlorination process of MgO and BaO with CCl_4 at 600 °C will be discussed in detail. The respective Raman spectra are given in Figures 2 and 3. Calcined MgO has a rock salt structure, and as a consequence, first-order Raman scattering is symmetry-forbidden. No Raman bands were observed in the MgO sample after treatment in He at 600 °C (spectrum 2a). After injecting 10 μL of CCl_4 at 600 °C (spectrum 2b), a Raman vibration at 235 cm^{-1} became apparent, and the intensity of this band gradually increased with increasing amount of CCl_4 injected (spectra 2c and 2d). At higher CCl_4 loadings, a weaker band at 143 cm^{-1} became visible. Both Raman bands are typical of $MgCl_2$ (Table 1).

By contrast, the Raman spectrum of calcined BaO contained absorptions at 129 and 208 cm^{-1} (spectrum 3a), which are typical of defect lattice modes. Although BaO also has a rock

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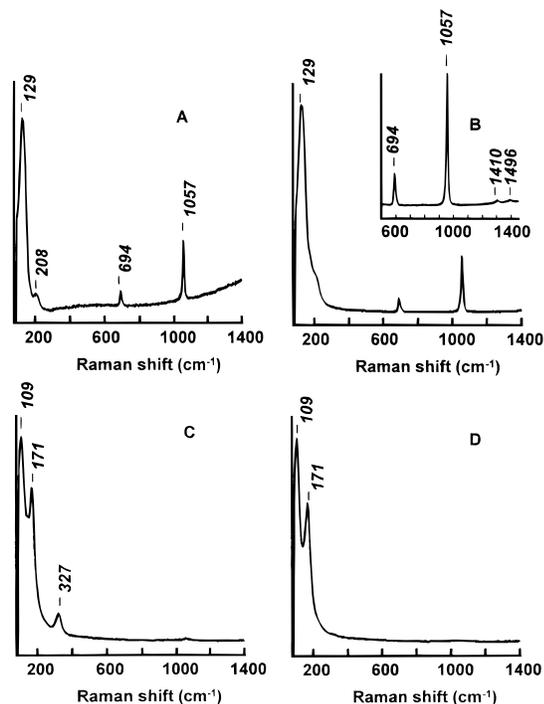*J. Phys. Chem. B, Vol. 102, No. 19, 1998* **3775**

Figure 3. In situ Raman spectra of BaO measured at 600 °C in He as a function of the amount of CCl₄ injected: (A) 0 μL of CCl₄, (B) 10 μL of CCl₄, (C) 20 μL of CCl₄, and (D) 50 μL of CCl₄. About 15 μL of CCl₄ is sufficient to convert BaO into BaCl₂, assuming that 2 mol of BaO would be necessary to decompose 1 mol of CCl₄. The collection time was 60 s.

TABLE 1: Raman-Active Lattice Modes of Alkaline Earth Metal Oxides, Chlorides, and Carbonates

material	Raman freq (cm⁻¹)[a]	material	Raman freq (cm⁻¹)[a]
MgO	none	CaCl₂	109; 120; 142; 193; 235
CaO	95; 109	SrCl₂	183
SrO	98; 152	BaCl₂	109; 171
BaO	129;[b] 208	BaCO₃	140; 157; 227
MgCl₂	143; 235		

[a] The Raman frequencies at 600 °C were obtained for the pure materials after heating in oxygen and/or helium at 600 °C, with the exception of BaCO₃, which was measured at 25 °C. [b] This Raman band splits into two components at temperatures below 300 °C, and at 25 °C the two bands are located at 140 and 157 cm⁻¹.

TABLE 2: Raman Frequencies (cm⁻¹) of Unidentate Surface Carbonates and Oxide Chlorides for Different Alkaline Earth Metal Oxides[a,b]

material	Raman frequencies of surface carbonates (cm⁻¹)				Raman frequency of metal oxide chloride (cm⁻¹)
	ν_1	ν_2	ν_3	ν_4	
MgO	nd	1085 (vw)	nd		nd
CaO	nd	1083 (w)	nd	nd	398 (m)
SrO	nd	1067 (m)	710 (w)	nd	372 (s)
BaO	1410 (w)	1057 (s)	689 (m)	1496 (w)	327 (s)

[a] nd, not detected; vw, very weak; w, weak; m, medium; s, strong. [b] For reference spectra and assignments of monodentate surface carbonates, see refs 23–26.

salt structure, the spectroscopic exclusion rule may be weakened due to the presence of such lattice defects. In addition, vibrations at 694 and 1057 cm⁻¹ were detected, indicating the presence of surface carbonates (Table 2). After injecting 10 μL of CCl₄ at 600 °C (spectrum 3b), the amount of surface carbonates increased, and two additional bands at 1410 and 1496 cm⁻¹ due to monodentate surface carbonates became clearly visible. This suggests that CO₂ formed during CCl₄ destruction
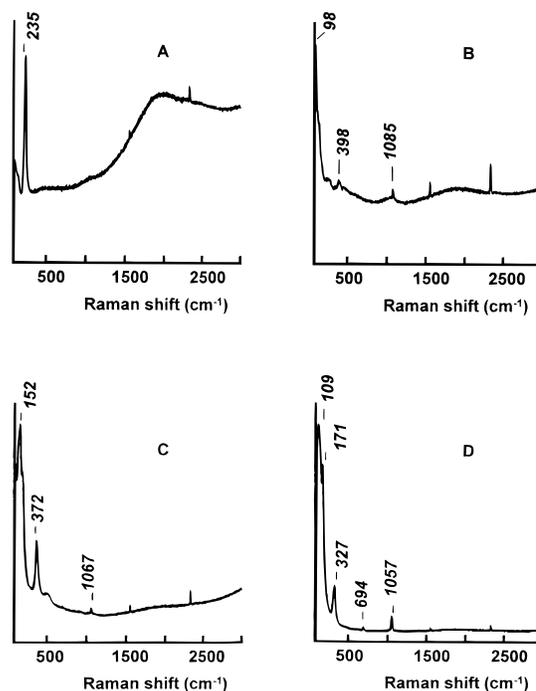

Figure 4. In situ Raman spectra of partially chlorinated alkaline earth metal oxides measured at 600 °C in He: (A) MgO after injecting 10 μL of CCl₄, (B) CaO after injecting 10 μL of CCl₄, (C) SrO after injecting 20 μL of CCl₄, and (D) BaO after injecting 20 μL of CCl₄. The collection time was 60 s. The Raman bands at 1559 and 2333 cm⁻¹ are due to O₂ and N₂, respectively, which are present in the gas phase between the detector and the in situ Raman cell.

is readsorbed onto the metal oxide surface. Additional doses of CCl₄ resulted in an overall decrease in the amount of surface carbonates. Furthermore, new Raman bands at 109 and 171 cm⁻¹ became apparent, which are due to Ba−Cl lattice modes (Table 1). The formation of BaCl₂ was confirmed by XRD. An additional band centered at around 327 cm⁻¹ was also observed, and its intensity reached a maximum after injecting 20 μL of CCl₄. It is also important to note that this band was not observed at 450 °C. The band is due to the formation of a metal oxide chloride, viz., Ba₄OCl₆, which can be envisaged as a structure in which three out of four oxygen atoms are replaced by chlorine atoms.[20]

The Raman spectra of partially chlorinated materials after reacting the alkaline earth metal oxide with CCl₄ at 600 °C are compared in Figure 4. It is clear that bands due to monodentate surface carbonates could not be detected on MgO but were apparent on CaO, SrO, and BaO. The frequencies obtained, together with the band assignments, are summarized in Table 2. The Raman frequency of the weak ν_2 (symmetric stretch) vibration of monodentate surface carbonates on MgO was observed at 450 °C. The differences observed among the metal oxides are related to the comparative stabilities of their surface carbonates. Indeed, it is known that the stability of surface carbonates is a function of the basicity or ionicity of the metal oxide, i.e., BaCO₃ > SrCO₃ > CaCO₃ > MgCO₃ .[21] Thus, gas-phase CO₂ , formed during CCl₄ decomposition, readily readsorbs on BaO, whereas on MgO, the readsorption process does not occur because of the instability of surface MgCO₃, which has a decomposition temperature of about 450 °C.[21] Finally, it is important to note that both CaO and SrO could be transformed into the corresponding chloride by adding more CCl₄ as evidenced by the presence of the metal chloride bands (Table 1).
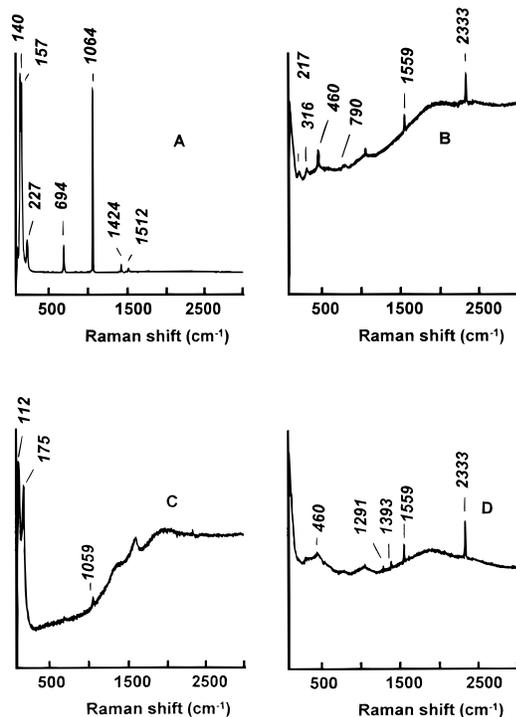
Figure 5. In situ Raman spectrum (A) of calcined BaO measured at 25 °C after introducing CCl_4, (B) with focus on gas phase above the BaO surface at 25 °C, (C) of $BaCl_2$ measured at 300 °C, and (D) with focus on the gas phase above the $BaCl_2$ surface, measured at 300 °C. The collection times for the Raman spectra with the focus on the solid and gas phase were 60 s, and 240 s, respectively.

Another difference among the metal oxides is the absence or presence of a Raman band in the range $300-400$ cm^{-1}. This Raman band, as mentioned above, is due to the formation of an unusual metal oxide chloride, viz., M_4OCl_6. This assignment was confirmed by preparing the barium oxide chloride in the in situ Raman cell at 700 °C for 17 h according to a modified literature procedure, and its presence was verified by XRD.[20] The Raman vibration at around $300-400$ cm^{-1} could not be detected on MgO (Figure 4A), and was only clearly visible for CaO, SrO, and BaO at CCl_4 destruction temperatures as high as 600 °C, and for extended time periods between the CCl_4 pulses (approximately 4 h) (Figure 4B−D). The intensity of this Raman vibration was also a function of the amount of CCl_4 injected; the intensity was greatest after $10-20$ μL of CCl_4. Finally, it is important to note that the Raman frequency of the metal oxide chloride is a function of the type of metal ion, i.e., 326 cm^{-1} for Ba_4OCl_6, 372 cm^{-1} for Sr_4OCl_6, and 398 cm^{-1} for Ca_4OCl_6.

In a series of static experiments, CCl_4 was introduced into the in situ Raman cell at room temperature after treating the calcined metal oxide in vacuo at 600 °C. The result is illustrated in Figure 5 for BaO. By focusing the laser beam on the gas phase above the BaO surface, the four allowed Raman bands due to gas-phase CCl_4 at 220, 318, 462, and 790 cm^{-1} became visible (Figure 5B). The bands at 1559 and 2333 cm^{-1} are due to O_2 and N_2, respectively, that are in the air between the cell and the optics of the Raman spectrometer. Heating the sample to 300 °C resulted in the rapid formation of $BaCl_2$ (Figure 5C), and the Raman bands of gas-phase CO_2 at 1291 and 1393 cm^{-1} became apparent (Figure 5D). In addition, the bands due to gas-phase CCl_4, above the solid sample, were greatly reduced in intensity. Comparable results were obtained by flowing a CCl_4-saturated helium stream through the in situ Raman cell,
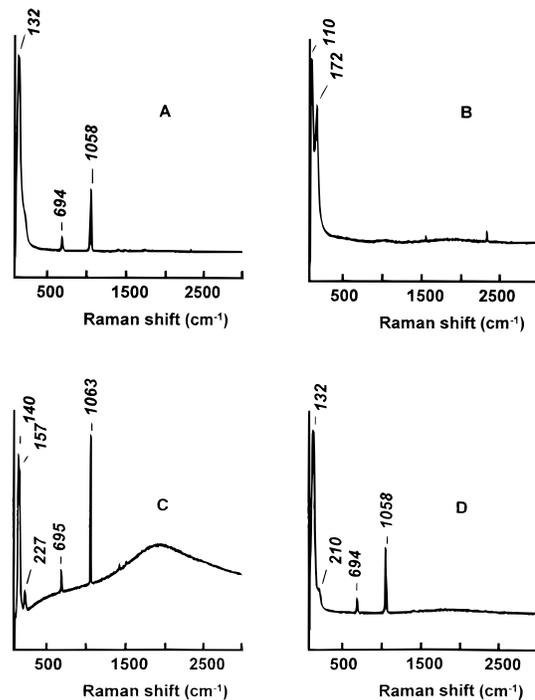

Figure 6. In situ Raman spectrum (A) of BaO measured at 600 °C in He, (B) of BaO measured at 600 °C in He after injecting 50 μL of CCl_4, (C) of $BaCO_3$ measured at 25 °C in He, and (D) of regenerated BaO measured at 600 °C in He. The collection time was 60 s.

in which case the conversion of BaO into $BaCl_2$ was observed at around $200-300$ °C.

Finally, it is important to note that barium chloride, as the final product of the destructive adsorption of CCl_4, can be recycled as illustrated in Figure 6 for BaO. In a first step, BaO was converted into $BaCl_2$ by dosing BaO with 50 μL of CCl_4 at 600 °C (Figure 6A, and B). The $BaCl_2$, which is highly hygroscopic, was dissolved in deionized water at room temperature. Precipitation of $BaCO_3$ was then accomplished either by adding ammonium carbonate to the solution or by passing CO_2 through the solution for several hours at 25 °C. After filtration, the formation of $BaCO_3$ was spectroscopically verified as shown in Figure 6C (Table 1). In a final step, $BaCO_3$ was extensively transformed into BaO by calcination in O_2 at 600 °C (Figure 6D). Thus, alkaline earth metal chlorides can be easily recycled into their corresponding oxides. This is an important practical advantage, which makes the process a promising alternative for the cleanup of CHC's contaminants.

3. Characterization of Gas-Phase Intermediates and Products by Infrared Spectroscopy. Gas-phase molecules evolving from the oxide surface during the chlorination process were also monitored by Fourier transform infrared (FT-IR) spectroscopy, and CCl_4 was added in one batch instead of pulses.[22] Results obtained over BaO are presented in Figure 7, and similar results were obtained for SrO. At 200 and 300 °C, the only detectable gas-phase molecule was CO_2, as indicated by the $\nu_{C=O}$ vibration at 2348 cm^{-1}. At these temperatures, the amount of CO_2 gradually increased with increasing reaction temperature. At higher reaction temperatures, $COCl_2$, with a $\nu_{C=O}$ vibration at 1829 cm^{-1}, was also observed. The amount of $COCl_2$ reached a maximum at 450 °C after about 30 min. This suggests that $COCl_2$ is an intermediate product in the decomposition of CCl_4. In the case of MgO and CaO, CO_2 and a small amount of $COCl_2$ were always present together, which is in agreement with the observations of Klabunde and co-workers.[11,12,15] Very recently, the same authors discussed
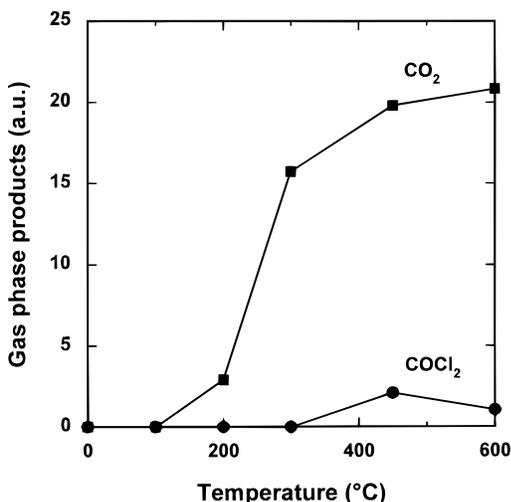
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Figure 7. Gas-phase CO_2 and $COCl_2$ produced during the decomposition of CCl_4 on BaO as a function of the reaction temperature.

TABLE 3: Raman and Infrared Frequencies of Several Organic Compounds[a]

compound	frequencies (cm^{-1})[b]
CCl_4	218 (R); 314 (IR, R); 459 (R); 790 (IR, R)
CO_2	667 (IR); 1286 (R); 1388 (R); 2348 (IR)
$COCl_2$	285 (IR, R); 440 (IR, R); 569 (IR, R); 580 (IR, R); 849 (IR, R); 1827 (IR, R)
HCl	2884 (IR, R)
C_2Cl_4	335 (IR); 920 (IR)

[a] From refs 27−29. [b] IR, infrared active mode; R, Raman active mode.

TABLE 4: Conversion of Metal Oxide to the Metal Chloride

time (min)	conversion of MgO to $MgCl_2$ (%)				conversion of BaO to $BaCl_2$ (%)			
	200 °C[a]	300 °C	450 °C	600 °C	200 °C	300 °C	450 °C	600 °C
0	0	0	0	0	0	0	0	0
15	0	0	5.5	21.2	11.2	20.2	36.4	67.4
30	0	0	8.2	46.4	25.0	56.7	73.0	100.0
45	0	0	15.0	59.1	37.0	69.1	100.0	100.0
60	0	0	17.0	62.6	38.6	71.7	100.0	100.0

[a] Temperature of reaction.

the conditions for the suppression of $COCl_2$ formation during CCl_4 decomposition.[15] It was shown that $COCl_2$ formation could be eliminated if an excess of CaO was used. In this respect, our experiments were conducted with a molar ratio of CCl_4:metal oxide of 5:1.

By monitoring the amount of CCl_4 reacted, and assuming that 2 mol of MO would be necessary to decompose 1 mol of CCl_4, it was possible to calculate the percentage of MO converted into MCl_2. The results are given in Table 4 for MgO and BaO after different reaction temperatures and times. It is evident that MgO and BaO were gradually converted into the corresponding chloride with increasing reaction temperature and time. The transformation into the metal chloride was complete in 45 min at 400 °C for BaO, whereas for MgO incomplete conversion was observed, even after 60 min at 600 °C. These results are consistent with those derived from X-ray photoelectron spectroscopy (vide supra), and confirms the important role of O^{2-}/Cl^- exchange in continuously renewing the metal oxide surface. Klabunde and co-workers[10,11] recently found that the addition of transition-metal oxides, such as Fe_2O_3, onto CaO or MgO resulted in a complete transformation into the chloride. The supported transition-metal oxide was believed to enhance the O^{2-}/Cl^- exchange at the metal oxide surface.
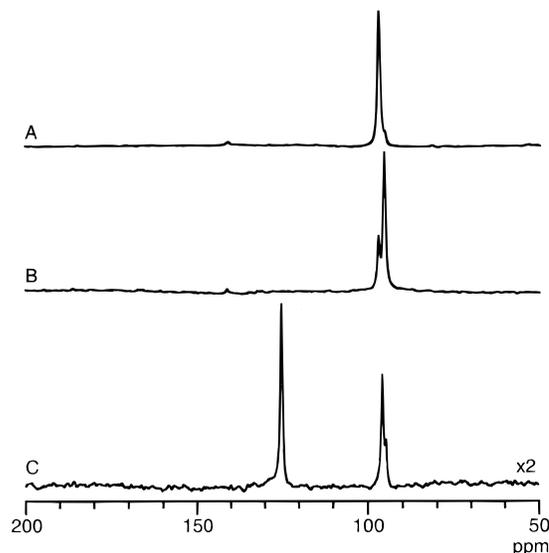

Figure 8. The 90.5 MHz ¹³C MAS NMR spectra of ¹³CCl₄ on BaO: (A) measured at 25 °C immediately following adsorption, (B) measured at 100 °C, and (C) measured at 25 °C after reaction at 300 °C. The spectra are a result of 512 transients utilizing a 4 s recycle delay. The spinning speed was 4 kHz. The molar ratio of ¹³CCl₄:BaO was 1:21.

SCHEME 1: Reaction Pathway for the Destructive Adsorption of CCl₄ on Alkaline Earth Metal Oxides
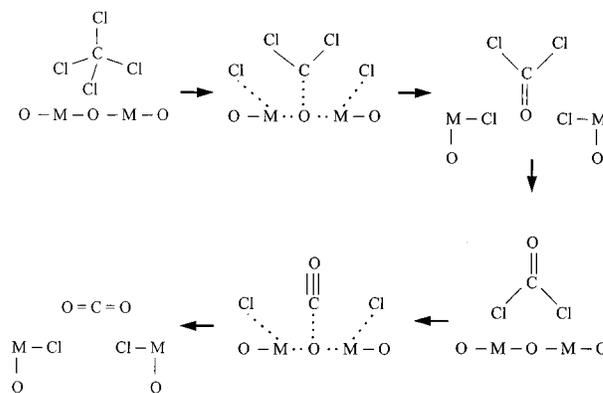
4. Evidence from ¹³C Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy. Further information about the chlorination process came from ¹³C magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. As illustrated in Figure 8 for BaO, before reaction, two peaks were observed at 97 and 95 ppm and assigned to physisorbed and gas-phase ¹³CCl₄, respectively.[30] Heating BaO to 100 °C caused desorption of the physisorbed ¹³CCl₄, increasing the relative intensity of the 95 ppm resonance. After heating to 300 °C, both ¹³CCl₄ resonances decreased in intensity, and a new peak at 126 ppm was observed. This peak is due to the formation of ¹³CO₂.[30] No other species were observed, and thus, consistent with the FT-IR results, CO_2 is the only gas-phase product formed during the CCl_4 decomposition on BaO at 300 °C.

5. Reaction Pathway for Destructive Adsorption of Carbon Tetrachloride. The results obtained using several spectroscopic methods suggest a possible reaction pathway (Scheme 1) for the destructive adsorption of CCl_4 on alkaline earth metal oxides, which is the same as that proposed previously by Hooker and Klabunde.[13] The first step involves the physisorption of CCl_4 on the alkaline earth metal oxide surface. The covalent C−Cl bond is then polarized/broken by the ionic MO lattice. This step must be fast since no surface reaction intermediates could be detected by in situ spectroscopies. The polarization

of the C−Cl bond is more pronounced on ionic surfaces. Thus, the destruction activity parallels the ionicity of the alkaline earth metal oxides; i.e., the activity decreases in the order: BaO > SrO > CaO > MgO. 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 finally released into the atmosphere. Except with 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_6 phase.

Conclusions

1. Alkaline earth metal oxides are active materials for the destructive adsorption of carbon tetrachloride. The destruction activity parallels the basicity of the alkaline earth metal oxide; i.e., the activity toward CCl_4 decreases in the order: BaO > SrO > CaO > MgO.

2. The major gas-phase product formed during CCl_4 destruction is CO_2, although some $COCl_2$ is also observed, especially at higher reaction temperatures and short contact times. $COCl_2$ may be an intermediate in the destructive adsorption of CCl_4.

3. The destruction process is essentially a bulk reaction that requires the continuous renewing of the metal oxide surface by O^{2-}/Cl^- exchange. Thus, mobility of oxygen and chlorine atoms in the bulk of the material becomes important.

4. Destruction of CCl_4 at high reaction temperatures is accompanied by the formation of unusual alkaline earth metal oxide chlorides, viz., M_4OCl_6 with M = Ba, Sr, or Ca.

5. The resulting barium chloride can easily be recycled by dissolving it in water, followed by precipitation and calcination. Thus, a promising alternative emerges for the cleanup of CHC's in the environment.

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(18) The molar ratio of CCl_4:metal oxide was 20:1, and XPS spectra were recorded 2 h after the CCl_4 was introduced. The O 1s XPS peak of the metal oxide was integrated using the standard software package of the Perkin-Elmer XPS instrument.

(19) The heat of reaction, ΔH_{react} (kcal/mol), for the conversion of the metal oxide to the metal chloride, at 400 °C increases in the order: BaO $(-216.0) <$ SrO $(-182.2) <$ CaO $(-146.3) <$ MgO (-87.9). These data were calculated using the software package *HSC* (Outokumpu Research Oy, Pori, Finland).

(20) Barium oxide chloride, Ba_4OCl_6, has a hexagonal structure and is isostructural with Ca_4OCl_6 and Sr_4OCl_6. Magnesium oxide chloride does not exist, probably because of the small ionic radius of magnesium ions. Ba_4OCl_6 can be prepared by heating stoichiometric amounts of $BaCl_2$ and BaO at high temperatures (Frit, B.; Holmberg, B.; Galy, J. *Acta Crystallogr.* **1970**, *B26*, 16). Similar synthesis procedures exist in the literature for the preparation of Ca_4OCl_6 and Sr_4OCl_6 (Frit, B.; Chbany, M. M.; Tanguy, B.; Hagenmuller, P. *Bull. Soc. Chim. Fr.* **1968**, *1*, 127; Meyer, H. J.; Meyer, G.; Simon, M. *Z. Anorg. Allg. Chem.* **1991**, *596*, 89; Reckeweg, O.; Meyer, H. J. *Z. Kristallogr.* **1997**, *212*, 235).

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