Destructive Adsorption of Chlorinated Hydrocarbons on Ultrafine (Nanoscale) Particles of Calcium Oxide. 2

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As a one-step approach to the safe destruction of chlorocarbons, the reaction of carbon tetrachloride with ultrafine particles of calcium oxide to give calcium chloride and carbon dioxide ($CCl_4(g) + 2CaO(s) \rightarrow CO_2(g) + 2CaCl_2(s)$) has been studied in detail. Calcium oxide prepared by an aerogel/hypercrytical drying method (AP−CaO) is superior to a conventionally prepared (CP−CaO) sample, and both are vastly superior to commercial CaO (CM−CaO). Optimum temperature for this gas−solid reaction is 450 °C, although AP−CaO reacted with reasonably high capacity as low as 300 °C. The effects of surface −OH, added water, CCl_4 pressure, and a wide range of temperatures are discussed. Conditions for the suppression of byproducts C_2Cl_4 and Cl_2CO are presented. Morphological changes in the particles after CCl_4 reaction were studied by atomic force microscopy. A wide range of other techniques have been applied toward complete characterization of the process and products, including FT-IR, pulsed U-tube reaction studies, gravimetric adsorption, X-ray diffraction, and GC-MS.

Introduction

The problems associated with proper use, disposal and destruction of chlorinated compounds are of great interest and are controversial. Some people have called for a “chlorine-free economy” as was proposed in 1993. However, it was calculated that complete elimination of chlorinated compounds would cost the U.S. and Canada $102 billion/year.[1,2]

The most extensively used method to destroy unwanted chlorocarbons is by incineration. Toxic chlorinated compounds appear to be completely destroyed by high-temperature thermal oxidation;[3] however, there is a concern about the production of toxic byproducts, products of incomplete combustion (PICs) such as chlorine-containing furans and dioxins.[4,5] To minimize the formation of PICs, catalytically stabilized thermal combustors are employed.[6] Other methods of decomposition are focusing on decreasing the temperature necessary for decomposition. They include the following:

(1) Oxidative catalysis over metal oxides and noble metals to yield mainly HCl and CO_2 as products. Recently, a very good review by Spivey about catalytic oxidation[7] was published. For example, supported and unsupported Pt, V_2O_3, and Cr_2O_3,[8−11] zeolites,[12,13] and other commercially available catalysts[14,15] have been employed with some success. The decomposition of carbon tetrachloride on Pt/γ-Al_2O_3 occurs according to the reaction[16]

$$2CCl_4(g) + C_3H_8(g) + 5O_2 \rightarrow 5CO_2(g) + 8HCl(g) \quad (1)$$

The decomposition was about 95%, and the optimum temperature was between 420 and 500 °C. This method, however, requires a use of an expensive catalyst, which with time gets poisoned.

(2) Metal oxide/porous carbon catalysts described by Drago and co-workers.[17] This decomposition is also based on an oxidative catalysis; however, because porous carbon is used, the presence of a noble metal is not required.

(3) Catalytic decomposition of hydrochlorocarbons over high surface area γ-alumina.[18,19] The primary pathway for decomposition of 1,1,1-trichloroethane proceeded via α,β-HCl elimination around 130 °C. At higher temperature, 430 °C, the resulting 1,1-dichloroethene decomposed to produce HCl and carbon:

$$CH_3CCl_3(g) \rightarrow CH_2{=}CCl_2(g) + HCl(g) \quad (2)$$

$$CH_2{=}CCl_2(g) \rightarrow 2HCl(g) + 2C(s) \quad (3)$$

(4) The reaction of sodium oxalate to yield NaCl (or NaF with Freons), CO_2, and carbon, as described by

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Crabtree and co-workers,[20] for example

$$\mathrm{CF_2Cl_2(g) + 2Na_2C_2O_4(s) \xrightarrow{270-290\ ^\circ C} 2NaCl(s) + 2NaF(s) + 4CO_2(g) + C(s)} \quad (4)$$

Recently we reported an additional promising method that at relatively low temperatures (400−500 °C) converts halocarbons to CO_x and calcium halides in one step.[21] The process is based on X^-/O^{2-} exchange on the surface of CaO (or MgO or Fe_2O_3); thus, oxidizing conditions are not needed. Since the chemistry is based on a surface−gas reaction, high surface areas and intrinsic reactivities are beneficial, and so we have synthesized and studied nanoscale particles, which have proven to exhibit unexpectedly high surface reactivities:[22−25]

$$\mathrm{2CaO(s) + CCl_4(g) \rightarrow 2CaCl_2(s) + CO_2(g)} \qquad \Delta H_{\mathrm{rxn}}^\circ = -573\ \mathrm{kJ} \quad (5)$$

Herein are reported details of these investigations for CaO with CCl_4. The results point out an additional useful feature of aerogel-prepared nanophase materials.[26−28]

To further place this study in the proper context, the work of Michael and co-workers[29] on thermal decomposition should be mentioned. It was discovered that the dissociation $CCl_4 \rightarrow CCl_3 + Cl$ is a second-order reaction and that at low pressures two Cl were produced from CCl_4, indicating that the reaction $CCl_3 \rightarrow CCl_2 + Cl$ is also an important process. This thermal decomposition sequence required temperatures in excess of 800 °C.

Experimental Section

A. Preparations of Calcium Oxide Samples. Three types of CaO samples were used:

(1) Commercial (CM−CaO). Nonactivated calcium oxide (Fisher Scientific) was used without any further treatment. The surface area was around 10 m^2/g.

(2) Conventionally Prepared (CP−CaO). Conventionally prepared CaO was made from commercial calcium oxide (Fisher Scientific) by boiling it with distilled water to homogeneously convert it to calcium hydroxide and activating the hydroxide under vacuum.[22] The surface area of such an oxide was around 100 m^2/g.

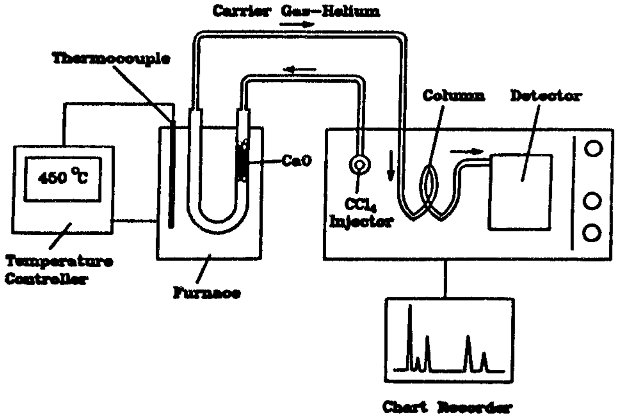

Figure 1. Schematic of minireactor−GC setup used for chlorocarbon decomposition studies.

(3) Aerogel/Autoclave Prepared (AP−CaO). Autoclave-prepared calcium oxide was made starting from calcium metal and methanol. The obtained calcium methoxide was hydrolyzed in toluene−methanol, and the resulting sol−gel was dried in an autoclave. High surface area calcium hydroxide was activated under vacuum at 500 °C. The surface area of the final CaO was around 120 m^2/g. The detailed procedure for this process is described in ref 22.

B. GC Studies. These studies were conducted in order to find the best conditions for decomposition of the halocarbons (for example, CCl_4) as well as to compare the destructive abilities of various types of calcium oxide. A stainless steel minireactor was connected to a GC instrument (GOW-MAC Instrument Corp.). The schematic of the setup is shown in Figure 1. The reactor was heated to a desired temperature and 1 μL portions of liquid CCl_4 (ACS grade) were injected. The injector temperature was 200 °C. The decomposition products (gaseous effluent) were carried out by helium (flow rate 30 cm^3/min) to the column (5% OV 101 Chromosorb P, 100 °C), where they were separated. Then the products were detected by a thermal conductivity detector, kept at 180 °C, and recorded.

(1) Thermal Decomposition. For the thermal decomposition studies only aluminum silicate wool was placed in the reactor, which was heated to a desired temperature. The efficiency of the decomposition of carbon tetrachloride was determined, based on the areas of CCl_4 peaks in the chromatogram.

(2) Decomposition on Calcium Oxide. To study the decomposition on calcium oxide, 0.1 g amounts of CaO (previously activated at 500 °C) were placed in the reactor and supported with aluminum silicate wool. The best temperature for the decomposition of CCl_4 was found to be 450 °C.

The results are shown as the relationship between the gaseous effluent and the number of injections made. To obtain the percentage of the gaseous effluent, first calibration curves were obtained for each product in the empty reactor, keeping the same conditions (temperature, flow rate) as used during the decomposition experiment with calcium oxide. Then the percentage was calculated as if that compound were exclusively formed. For example, for tetrachloroethylene formation the reaction $2CCl_4 \rightarrow C_2Cl_4 + Cl_2$ was assumed, and the amount of eluted C_2Cl_4 was calculated assuming that for every 2 mol of carbon tetrachloride injected one more of tetrachloroethylene was produced.

C. GC-MS. To the mass spectrometer a stainless steel reactor was attached, which was heated to the required temperature. This setup was very similar to the GC system, only here after separation on the column, the products were introduced to a mass spectrometer (Perkin-Elmer Q-Mass 910). For carbon tetrachloride decomposition, 0.1 g of calcium oxide was used and 1 μL injections were made. Usually, about 70 injections were made. To study water influence, the same amount of CaO was used, but in each pulse a liquid mixture of 1 μL of chlorocarbon and 0.5 μL of water was injected. In these experiments, 21 injections were made for CP−CaO and 40 for AP−CaO.

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(26) They are used in Cerenkov radiators as detectors to identify the charge of high-energy particles and to measure their velocity. Transparent silica aerogels cover the range of refractive indices between 1.01 (gases) and 1.2 (liquids), and this is difficult to achieve using other materials.[27] This finding in 1974 has led to a renewed interest in aerogels and to extensive studies in the past two decades.[28] Other applications are as gellifying rocket propellants, insulators in dual-pane windows, or even insecticides that are not harmful to humans. The most widely studied, in recent years, application of aerogels is in catalysis. For example, in Fischer-Tropsch catalysis, catalytic hydrogenation of carbon monoxide, Fe_2O_3/SiO_2 and Fe_2O_3/Al_2O_3 exhibit higher activity, by 2 or 3 orders of magnitude, than the conventional reduced iron catalysts.[27]

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D. Gravimetric Adsorption Studies. This technique was used to determine the extent of destructive adsorption of carbon tetrachloride on calcium oxide at various temperatures and pressures. Calcium hydroxide was placed in a basket attached to a quartz spring and heated under vacuum at 500 °C overnight, to convert it to calcium oxide.[22] The typical weight loss was about 25%. Then, vapors of carbon tetrachloride (under static pressure) were introduced, at desired temperatures and pressures. In a typical experiment the reading of the spring length was taken every 5 min for the first hour and then every 30 min for the next 3 h. The final reading was taken after overnight exposure of sample to the chlorocarbon. When adsorption/decomposition was completed, the system was evacuated for 1 h. On the basis of a calibration curve, the sample weight changes were determined. Assuming, on the basis of X-ray diffraction (XRD) that calcium oxide transformed into calcium chloride, the percent conversion of CaO into $CaCl_2$ was calculated. In other experiments before CCl_4 adsorption, water or carbon dioxide preadsorption was carried out.

E. Powder X-ray diffraction (XRD) was used to characterize the solid starting material and products. The temperature studies were conducted to find the best conditions for the decomposition. In these experiments the reaction temperatures were changed, and the solid products studied to determine the percent of conversion of calcium oxide into calcium chloride. During the XRD measurement on the reacted samples, most of the solid samples turned liquid, because of the high hygroscopicity of the calcium chloride formed. X-ray diffraction patterns were recorded using Scintiag-XDS-2000 instrument. The spectrometer was set at a voltage of 40 kV and current 40 mA. The scans were from 20 to 85° with a scanning rate of 2°/min.

F. Infrared spectroscopy (FT-IR) was used to observe changes of the calcium oxide surface during carbon tetrachloride adsorption/decomposition as well as the gases produced during the reaction. Calcium hydroxide powder was pressed into a tungsten grid[25] and heat-treated under vacuum at 500 or 800 °C. Then, CCl_4 vapors, under various pressures, were introduced, and the IR spectra were taken without moving the sample out of the IR beam; therefore, the intensities shown are corresponding to the same place on the sample. The instrument used was a Mattson R/S-1 infrared spectrometer with an MCT liquid nitrogen cooled detector.

G. AFM Studies. Atomic force microscopy was used to observe changes in topology of the surface upon chlorocarbon adsorption. The CCl_4 adsorption was performed at 450 °C. The CCl_4 vapors were introduced under different pressures: 10, 20, 50, and 100 Torr. The sample was allowed to react with CCl_4 for 5 or 15 min and then was outgassed at 450 °C for 2 h before cooling to room temperature. Imaging the sample surface was carried out using a commercial AFM (SPM 30 from Wyko Inc.) in a contact mode. A 100 mm long and rectangular cantilever with a spring constant of 0.37 N/m and a Si_3N_4 integrated pyramidal tip were used. All pictures were obtained in air at room temperature. The AFM experiments were carried out on different parts of the surface to ensure that the observed structure was representative and reproducible.

Results

A. Carbon Tetrachloride Decomposition with and without CaO. *(1) Thermal Decomposition without CaO.* Gas chromatography (GC) and gas chromatography with mass spectrometry (GC-MS) were used to study the thermal decomposition of carbon tetrachloride in the stainless steel reactor. Up to 450 °C no decomposition was seen, while at 500 °C small amounts of C_2Cl_2 ($m/e = 94$) and C_2Cl_5 ($m/e = 201$) were observed:

$$CCl_4 \rightarrow Cl{-}C{\equiv}C{-}Cl + Cl_2C{=}CCl_2 \qquad (6)$$

At 600 °C a complete conversion of carbon tetrachloride into tetrachloroethylene took place. During fragmenting of CCl_4, the following reactions may have taken place:

$$Cl + CCl_4 \rightarrow CCl_3 + Cl_2 \qquad (7)$$

$$2CCl_3 \rightarrow C_2Cl_5 + Cl \rightarrow C_2Cl_4 + 2Cl \qquad (8)$$

$$2CCl_2 \rightarrow C_2Cl_3 + Cl \rightarrow C_2Cl_2 + 2Cl \qquad (9)$$

Table 1. Number of Moles of Calcium Oxide Necessary for Complete Decomposition of CCl_4 (Surface Areas of Oxides in Parentheses)

temp [°C]	CM−CaO (10) [mol/mol][a]	CP−CaO (110) [mol/mol]	AP−CaO (80) [mol/mol]	AP−CaO (108) [mol/mol]
350				4.6
400	>275	275	5.4	3.9
450	16	14	3.6	3.2
500	11	6.0	2.5	2.9

[a] Moles of CaO necessary to destroy 1 mol of CCl_4.

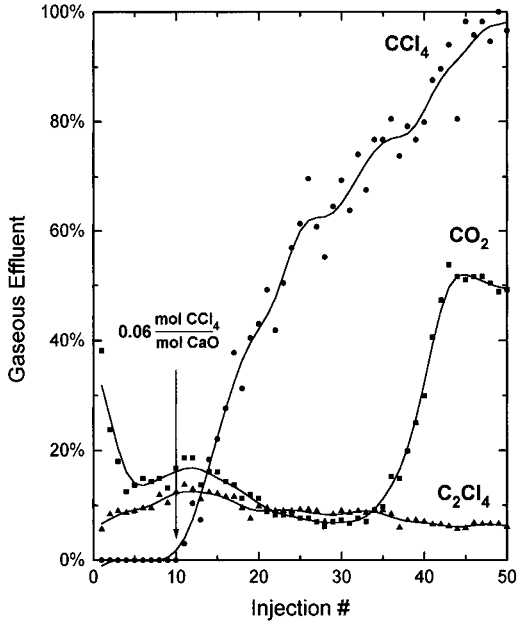

Figure 2. Products of decomposition of CCl_4 on CP−CaO at 450 °C. Each injection was 1 μL of CCl_4; 0.1 g of CaO was in the bed.

(2) Dependence of the Temperature, Surface Area, and Type of Calcium Oxide. In Table 1 the number of moles of commercial (CM−CaO), conventionally prepared (CP−CaO) and autoclave prepared (AP−CaO) calcium oxide that are necessary for *complete* decomposition of carbon tetrachloride are given. These data were obtained from minireactor-GC studies, based on the number of injections that could be made before the CCl_4 peak appeared in the chromatogram. For CP and CM−CaO the temperature for decomposition had to be at least 450 °C, whereas for AP−CaO 350 °C was sufficient.

In the case of AP−CaO, surface area had an effect on the decomposition ability of the oxide. With the higher surface area (108 m^2/g) more chlorocarbon could be decomposed than in the sample with the surface area of 80 m^2/g. If the reaction $2CaO + CCl_4 \rightarrow 2CaCl_2 + CO_2$ was stoichiometric, 2 mol of calcium oxide would be necessary to decompose 1 mol of carbon tetrachloride.

Figures 2 and 3 show the percentage of the gaseous effluent versus the number of injections for CP−CaO

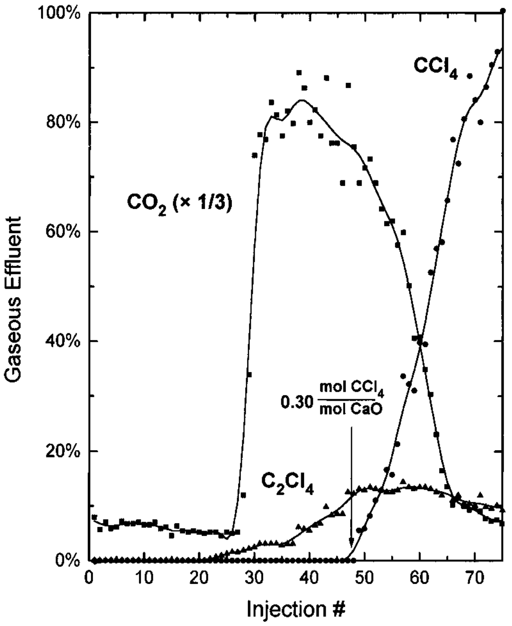

Figure 3. Products of decomposition of CCl_4 on AP−CaO at 450 °C. Each injection was 1 μL of CCl_4; 0.1 g of CaO was in bed.

and AP−CaO, respectively. The "breakthrough" number, indicated with an arrow, corresponds to the end of complete destruction of CCl_4. The major gaseous product was carbon dioxide. Tetrachloroethylene was also formed as a minor side product. The amount of C_2Cl_4 produced was much smaller in the case of AP−CaO, compared to conventionally prepared. It appears that CO_2 is back adsorbed on the remaining calcium oxide; therefore, in the beginning not much is evolved. When the oxide is completely used up, to form either calcium chloride or calcium carbonate, then the carbonate starts to react with carbon tetrachloride. This reaction is also thermodynamically favorable ($\Delta H_{rxn}° = -217$ kJ/mol), however, not as favorable as the reaction with calcium oxide ($\Delta H_{rxn}° = -573$ kJ/mol).

The reaction between commercial calcium carbonate and carbon tetrachloride was carried out, and it was found that $CaCO_3$ is able to decompose CCl_4 with production of carbon dioxide and calcium chloride. This reaction, however, was not as efficient as for CaO and a much larger amount of tetrachloroethylene as a side product was formed. After the breakthrough point, formation of a small amount of phosgene was also observed. The amount of decomposed carbon tetrachloride was largest for the autoclave prepared calcium oxide (108 m^2/g), and at 500 °C the decomposition was approaching stoichiometric. CP−CaO completely decomposed 0.06 mol of CCl_4/mol of calcium oxide. Tetrachloroethylene formation was largest for CM−CaO and smallest for AP−CaO, and it was strongly dependent on the temperature (at higher temperature, more C_2Cl_4 was produced). This system is very sensitive to temperature, type of reactor, and flow rate. Also time between injections is a crucial factor. If this time was prolonged, more CCl_4 was decomposed. Presumably, chloride ion is first adsorbed on the surface, and if enough time is allowed it migrates to the bulk and O^{2-} migrates to the surface, exposing fresh oxide surface for reaction.

B. Conversion of Calcium Oxide into Calcium Chloride. Plots of the conversion of CaO into $CaCl_2$ after adsorption/decomposition of CCl_4 per mole of CP or AP−CaO were reported earlier.[22] The most striking feature was the immediate reaction of the chlorocarbon with AP−CaO, and the longer reaction time for CP−CaO. For the same amount of chlorocarbon to be adsorbed/decomposed on CaO only minutes are necessary for AP−CaO, and about 1 h on CP−CaO; within 10 min the conversion on AP−CaO was about 0.5 while for CP−CaO, 0.2. Thus, it is clear that the AP-samples have a much higher initial surface reactivity.

C. Low-Temperature Adsorption of Carbon Tetrachloride on CaO. *(1) Adsorption at Room Temperature and 200 °C.* Carbon tetrachloride mainly physisorbs on the calcium oxide surface at room temperature. By increasing the pressure of CCl_4, the amount of physisorbed material increased, but upon evacuation essentially all of the CCl_4 could be removed. When the adsorption temperature was increased to 200 °C (50 Torr pressure of CCl_4), carbon tetrachloride could not be removed by evacuation. Possibly chemisorption and/or chemical reaction (to produce calcium chloride) took place. The adsorption was slightly higher on AP−CaO (2.7×10^{-4} mol of CCl_4/1 g of CaO) than on CP−CaO (2.5×10^{-4} mol of CCl_4/1 g of CaO).

The adsorption at room temperature and 200 °C was also studied by infrared spectroscopy.[30−34] Figure 4 shows the IR spectra taken at various pressures of CCl_4. First, it should be noted that there are strong interactions between −OH groups and the chlorocarbon, as is evident by the loss of intensity of the −OH band at 3714 cm^{-1} corresponding to isolated hydroxyl groups. The peak broadened, and a broad band around 3500 cm^{-1} appeared that is assigned to the associated (hydrogen bonding) hydroxyl groups. By increasing the pressure of carbon tetrachloride these interactions became more visible.

When the pressure was 20 Torr or higher, a peak around 2950 cm^{-1} with a smaller shoulder around 2876 cm^{-1} was observed that can be assigned to linearly bound CO_2.[33] (At this wavenumber also bidentate formate, HCOO, occurs; however, its formation on the

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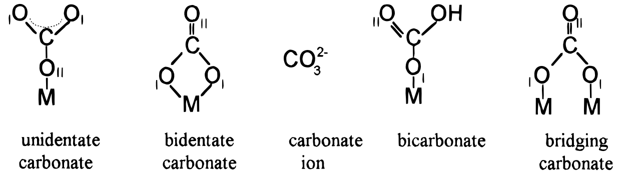
(30) After heating calcium hydroxide to 500 °C (bottom spectrum, Figure 4), two different species can be observed in the infrared spectrum. First, isolated hydroxyl groups give a band around 3714 cm^{-1}. The second region is due to various types of carbonate species on the surface. These bands are not clearly resolved, but based on the literature the carbonate species are as follows: The peak at 1560 cm^{-1} is due to O_ICO_I antisymmetric stretching of unidentate carbonate. A very broad feature between 1360 and 1560 cm^{-1} is due to a mixture of O_ICO_I symmetric stretching of unidentate carbonate and O_ICO_{II} symmetric stretching of bicarbonate. The very sharp band at 1300 cm^{-1} is attributed to CO_{II} antisymmetric stretching of bidentate carbonate. A small shoulder at 1069 is due to CO_{II} stretching of unidentate carbonate.[31−33] Around 879 cm^{-1}, antisymmetric stretching of calcium carbonate (calcite) occurs. Additional peaks for $CaCO_3$ are 1429−1492 cm^{-1} (symmetric stretching) and at 706 cm^{-1}, bending:[34]



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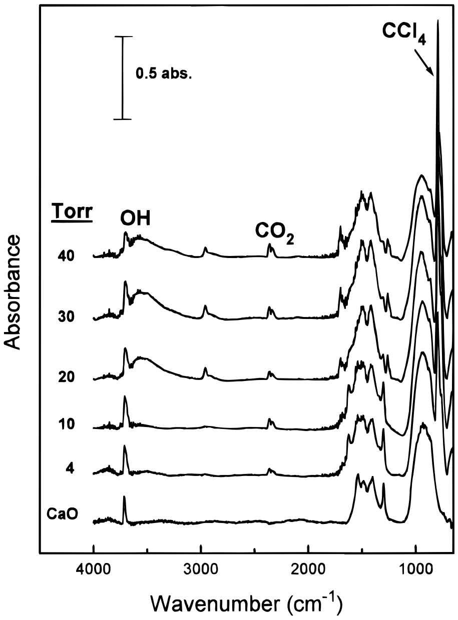

Figure 4. IR spectra of the solid after carbon tetrachloride adsorption on CP−CaO under various pressures at room temperature.

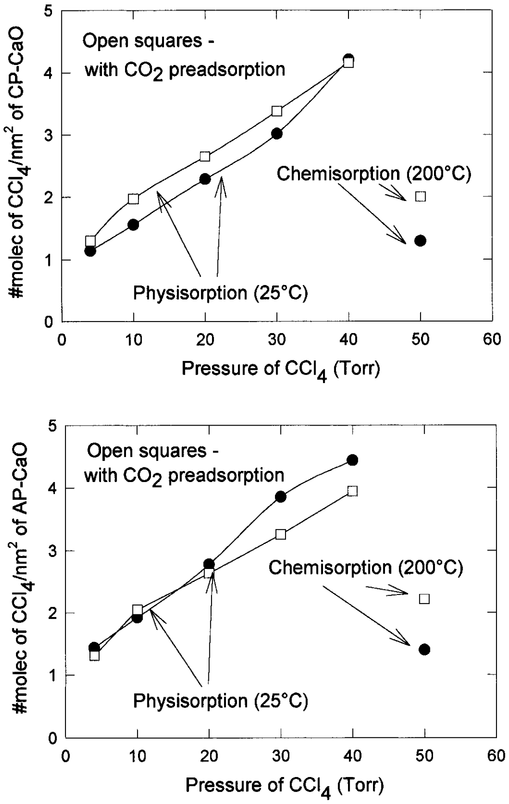

Figure 5. Adsorption of various pressures of carbon tetrachloride on CP−CaO (upper) and AP−CaO (lower) at room temperature (and at 200 °C at 50 Torr) with and without CO_2 preadsorption.

surface is not very probable.) It is apparent that even at room temperature there is reaction between CCl_4 and CaO producing some CO_2. This is not surprising in view of our earlier report of the appearance of CCl_x on the surface even as low as −160 °C.[25] However, in the case of CO_2 appearance at room temperature, we cannot be sure if this is due to the $CCl_4 + 2CaO \rightarrow CO_2 + 2CaCl_2$ reaction (that is efficient at elevated temperatures) or reconstruction of surface $CaCO_3$ species due to the influence of CCl_4.

When the same study was carried out at 200 °C, similar spectra were obtained. Strong interaction with −OH was evident, as at 200 °C the isolated −OH band completely disappeared, and linearly bound adsorbed CO_2 appeared. In 1960 Peri and Hannan studied room-temperature adsorption of CCl_4 on the surface of γ-alumina and also observed broadening and decrease in intensity of OH bands.[35] They proposed the following interactions:

$$Al_s{-}OH + CCl_4 \rightarrow Al_s{-}O{-}CCl_3 + HCl \qquad (10)$$

In our studies the formation of HCl was not observed upon room-temperature adsorption; however, it could be very quickly back adsorbed on the oxide to restore the hydroxyl and to form Ca−Cl bonds, which could not be monitored by this experiment. In 1971 Goodsel and co-workers[36] observed that when carbon tetrachloride was adsorbed on CaO (reactivated at 450 °C) the sharp band at 3704 cm^{-1} shifted to 3699 cm^{-1} without an appreciable loss in intensity, while the band at 3500 cm^{-1} remained unaffected.

(2) Effect of Carbon Dioxide Preadsorption. At room temperature carbon dioxide preadsorption slightly increased the amount of CCl_4 adsorption on CP−CaO (Figure 5). For AP−CaO a slight decrease at higher pressures was observed. Upon evacuation all carbon tetrachloride was removed. When the same experiment was conducted at 200 °C, the amount of chemisorbed (or reacted) carbon tetrachloride was larger when carbon dioxide was present on the surface for both types of oxides.

(3) Effect of Water Preadsorption on CCl_4 Decomposition. The effect of water preadsorption on CCl_4 decomposition was studied by gravimetric adsorption studies. After CaO activation at 500 °C the sample was cooled to room temperature, and water vapors were introduced under a pressure of 20 Torr and allowed to adsorb for 1 and 15 min (two different experiments). The amount of adsorbed water was strongly dependent on the pressure and time of adsorption reaching as high as 20 molecules of H_2O/1 nm^2 of calcium oxide, therefore implying that the adsorption was not only confined to the surface. After evacuation of the sample at room-temperature no weight change was observed, indicating that no chemisorbed water was lost. Subsequently, carbon tetrachloride was adsorbed on the oxide, under different pressures at room temperature. The amount of adsorbed CCl_4 was much smaller compared to the sample without water preadsorption (0.42 molecule of CCl_4/nm^2 compared to 1.92 molecules of CCl_4/nm^2, for an AP−CaO sample using a pressure of 10 Torr, and adsorption time of 15 min). After evacuation, all physisorbed CCl_4 was removed. The sample was then heated to 200 °C (still no weight change was noticed, implying that the adsorbed water was very strongly adsorbed in the form of $Ca(OH)_2$, and CCl_4 vapors were introduced under a pressure of 50 Torr. However, no CCl_4 adsorption was observed on all samples with water preadsorption. This experiment was conducted for both types of calcium oxide, conventionally prepared and autoclave

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(35) Peri, J. B.; Hannan, R. B. *J. Phys. Chem.* **1960**, *64*, 1526.

(36) Low, M. J. D.; Takezawa, N.; Goodsel, A. J. *J. Colloid Interface Sci.* **1971**, *37*, 422.

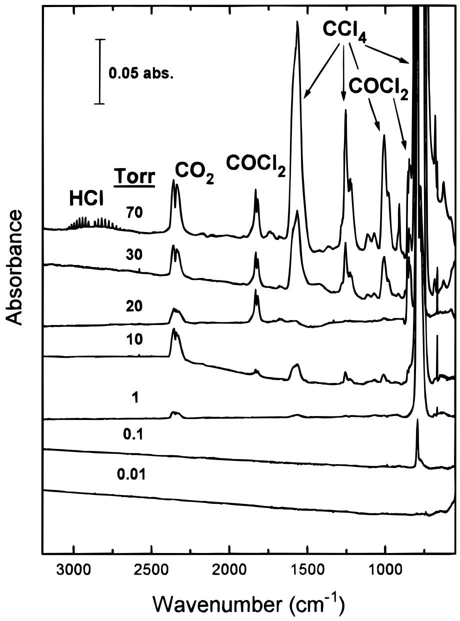


Figure 6. IR spectra of the gaseous products after CCl_4 decomposition, at 500 °C, under various pressures on AP−CaO (preactivated at 800 °C).

prepared, and the results were very similar in both cases.

D. Gaseous Products of Decomposition of CCl_4 or CaO. The gaseous products of decomposition at different ratios of CCl_4 to CaO were reported earlier. It had been concluded that a two-step process probably occurred when a limited amount of CaO was present; in this case phosgene (Cl_2CO) was an intermediate.[22] Herein are reported additional data at various CCl_4 pressures.

AP−CaO, preactivated at 800 °C, was exposed to various static pressures of carbon tetrachloride at 450 °C as is shown in Figure 6. At low pressures (0.01−0.1 Torr), the only gaseous species observed was carbon tetrachloride. When the pressure was 1 Torr, carbon dioxide was the only product. At 10 Torr a small amount of phosgene was observed, together with CO_2. At the highest pressure, 70 Torr, a band corresponding to HCl appeared in the IR spectrum (hydrogen coming from surface −OH). The solid products formed during the adsorption were studied by IR as described in section E.

Mass spectrometry aided in identification of these gaseous products. Using the pulsed U-tube reactor apparatus, 1 μL injections of CCl_4 were passed over CaO samples at 450 °C. On the 48th injection mass spectra were collected and shown in Figure 7. For the AP−CaO sample the product mixture is much cleaner and devoid of phosgene. In fact, the CO_2 and C_2Cl_4 peaks coming off were at least 100 times less intense than for CP−CaO, indicating that CO_2 product was still being adsorbed on remaining CaO.

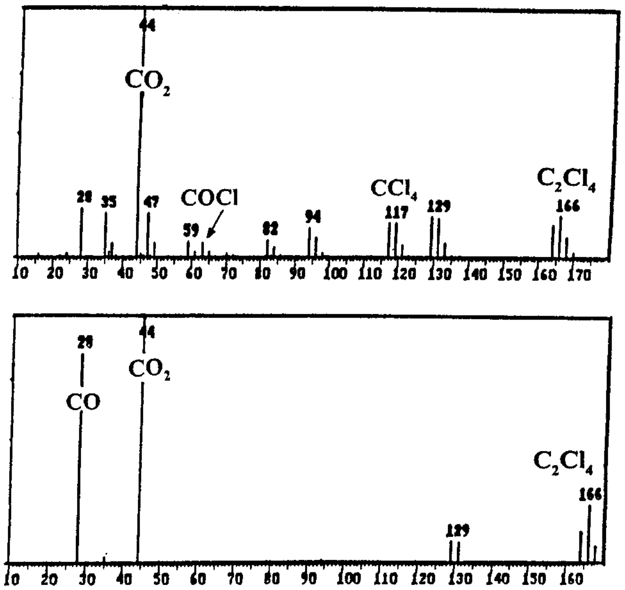


Figure 7. Mass spectra of the gaseous products after injecting 48 μL of CCl_4 on CP−CaO (upper) and AP−CaO (lower) at 450 °C.

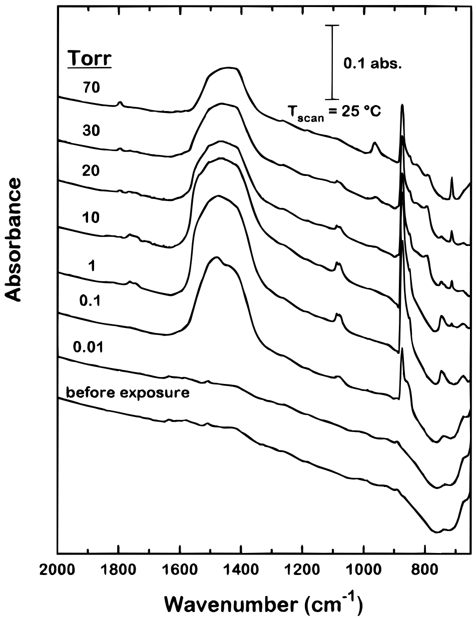


Figure 8. IR spectra of the solid products after CCl_4 decomposition under various pressures on AP−CaO (preactivated at 800 °C).

E. Solid Products of Decomposition. Solid products were studied, using infrared spectroscopy, in the 2000−650 cm^{-1} range. After activation at 800 °C calcium oxide does not have any bands in this region. Upon adsorption of CCl_4 at 500 °C the formation of bands corresponding to calcium carbonate were observed, as shown in Figure 8. With increasing pressure of carbon tetrachloride, $CaCO_3$ bands became more prominent (1078, 1436, and 1481 cm^{-1}), but when the sample was exposed to 20 Torr of chlorocarbon, their intensities decreased. It can be concluded that carbon tetrachloride reacted with calcium oxide to produce CO_2, that was subsequently adsorbed on calcium oxide to produce $CaCO_3$. However, upon introduction of larger amounts of CCl_4, calcium carbonate reacted with incoming carbon tetrachloride to produce $CaCl_2$ and CO_2. After addition of 4, 8, 12, and 14 μL of CCl_4/0.1 g of AP−CaO, the solid product was calcium carbonate; after addition of 16 μL calcium chloride became visible in the XRD spectrum and progressively increased until it became the only product after an excess of chlorocarbon had been added. The surface area of calcium oxide after reaction with an excess of carbon tetrachloride decreased very significantly: from 120 to below 10 m^2/g.

Complete elemental analyses of these solid products were obtained, and are given in Table 2 (after 75 μL of

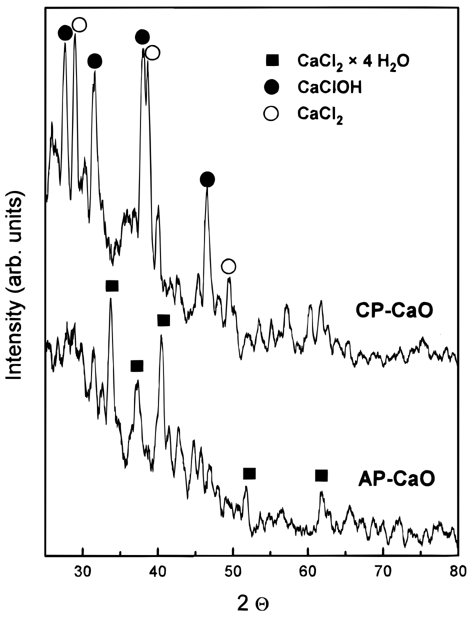


Figure 9. XRD spectra of the solid after decomposition of 50 μL of CCl_4 on AP and CP−CaO at 450 °C.

Table 2. Elemental Analysis of CaO before and after CCl_4 Decomposition

sample	calcium [%]	oxygen [%]	carbon [%]	hydrogen [%]	chloride [%]
CP−CaO (before)	51.48	44.67	1.40	2.45	
CP−CaO (after)	30.85	31.70	0.92	2.47	34.06
AP−CaO (before)	44.56	50.68	2.90	1.86	
AP−CaO (after)	18.41	41.39	0.13	4.96	35.11
CaO	*71.41*	*28.59*			
$Ca(OH)_2$	*54.05*	*43.24*		*2.7*	
$CaCO_3$	*40*	*48*	*12*		
$CaCl_2$	*36.07*				*63.93*
$CaCl_2$ 2 H_2O	*27.23*	*21.78*		*2.72*	*48.27*
$CaCl_2$ 4 H_2O	*21.87*	*34.99*		*4.37*	*38.77*
CaClOH	*43.27*	*17.31*		*1.08*	*38.34*

CCl_4 were passed through a 0.1 g bed of calcium oxide at 450 °C). In italics the theoretical data for possible decomposition compounds are shown.

Before reaction, AP−CaO possessed twice as much carbon as CP−CaO. This is most likely due to residual methoxy groups that are on the surface. The relatively large amount of hydrogen on CP−CaO implies the presence of calcium hydroxide. After the decomposition AP−CaO has much less carbon, which agrees with the higher reactivity of oxide and carbonate species on AP−CaO, to form more $CaCl_2$ and CO_2. The AP sample after reaction resembles mostly $CaCl_2{\cdot}4H_2O$, whereas CP after reaction appears to be a mixture of calcium chloride, calcium chloride hydrate, and $CaCO_3$. These data agree with the XRD spectra shown in Figure 9. The major peak for calcium carbonate overlaps with the peak of calcium chloride.

F. Effect of Water on CCl_4 Decomposition. GC-MS was used to study water influence (in each injection 1 μL of CCl_4 and 0.5 μL of H_2O), and Table 3 compares the decomposition products for samples with and without water present. The gaseous products and their distribution were different in each case.

Table 3. Water Effect on Carbon Tetrachloride Decomposition at 450 °C[a]

products	CP−CaO + CCl_4 + H_2O [μL]	AP−CaO + CCl_4 + H_2O [μL]
CO	1 (1)	1 (1)
CO_2	1 (1)	1 (1)
$COCl_2$	9 (none)	23 (none)
CCl_2OH_2	4 (none)	21 (none)
C_2Cl_4	2 (1)	9 (21)
CCl_4	6 (11)	30 (48)

[a] The numbers of milliliters correspond to the amount of CCl_4 injected after which the certain compound appeared in the mass spectrum. In parentheses, data for reaction without water presence are given.

It can be seen that large amounts of water have a detrimental effect on the carbon tetrachloride decomposition. The amount of CCl_4 that can be completely decomposed is smaller, and undesired byproducts such as dichloromethanol and phosgene are produced. For conventionally prepared calcium oxide after the first injection of a $CCl_4{-}H_2O$ mixture, carbon monoxide and a small amount of carbon dioxide were detected. After injection of 7 μL of CCl_4, carbon dioxide became the major decomposition product. In the second injection tetrachloroethylene was observed, which quickly grew with increasing the amount of CCl_4 injected. Dichloromethanol appeared after 4 μL of carbon tetrachloride (with 2 μL of water). The breakthrough number for carbon tetrachloride was 6 μL. Phosgene appeared on the 10th injection, and by the 14th injection it became larger than the carbon dioxide peak. Autoclave prepared oxide, AP−CaO behaved better, compared to the CP−CaO, but the behavior is not as good as in the absence of water. In the beginning the major product was carbon monoxide; however, more carbon dioxide was produced during the first injection than on CP−CaO. After 9 μL of $CCl_4{-}H_2O$, tetrachloroethylene appeared as a byproduct and slowly grew. However, its amount was much smaller, than with CP−CaO. Interestingly, with autoclave-prepared CaO more carbon monoxide was formed than with CP−CaO. Dichloromethanol and phosgene appeared almost at the same point, 21st and 23rd injection, respectively. The phosgene peak became larger than the carbon dioxide peak after injecting 37 μL of CCl_4.

Representative GC-MS data were obtained on the 10th injection (each injection 1 μL of CCl_4 plus 0.5 μL of H_2O; 450 °C reaction temperature). For CP−CaO, three GC peaks were observed and analyzed and corresponded to a mixture of (1) $N_2/CO/CO_2/Cl_2CO/Cl_2CH_2O$; (2) CCl_4, and (3) C_2Cl_4. In the case of AP−CaO, only two GC peaks were observed, and these corresponded to (1) $N_2/CO/CO_2$ and (2) C_2Cl_4. Again, it is clear that the AP−CaO enabled more complete reaction and a simpler mix of products. Solid products were analyzed by IR and XRD and mixtures of $CaCO_3$, $CaCl_2{\cdot}4H_2O$, and $CaOCl_2{\cdot}4H_2O$ (or $Ca(OCl)_2{\cdot}H_2O$) were observed.

G. Surface Morphology Changes. *(1) CM−CaO.* The reaction with CCl_4 was performed on a powdered CM−CaO sample (not pressed) as described in the Experimental Section. After reaction the powder was lightly packed down on adhesive tape prior to AFM observation. To prove that the observed structure was reproducible, the sample was investigated on different places and with different samples from the same batch. After reaction at 450 °C for 5 min with CCl_4 (pressures of 10 and 50 Torr), the CM−CaO sample still exhibited a surface made of small particles, varying in size from 35 to 60 nm and forming aggregates. Among these aggregates flat areas can be seen that are assumed to

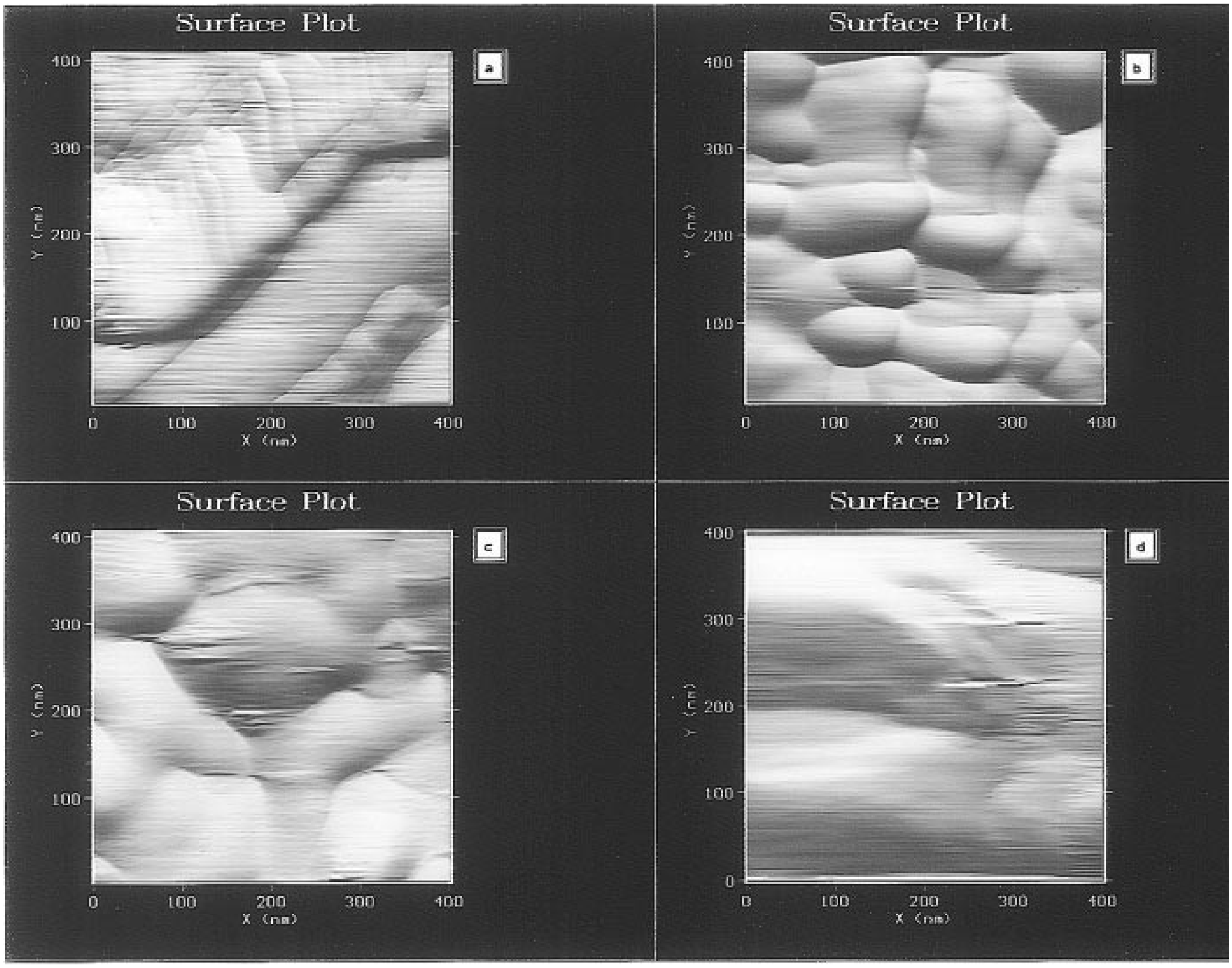


Figure 10. AFM images of pressed conventionally prepared CaO (CP−CaO) after CCl_4 adsorption at 450 °C for 5 min at (a) 10, (b) 20, (c) 50, and (d) 100 Torr.

be $CaCl_2 \cdot H_2O$ layers resulting from the CCl_4 decomposition. These layers do not cover the whole surface which is in many ways very similar to the surface before reaction. Also, no major differences have been noticed between samples exposed to 10 and 50 Torr of CCl_4 vapors. When the CCl_4 pressure reached 100 Torr, with the same conditions of temperature and of reaction time, stacking of layers was observed and no singular particles could be seen.

(2) CP−CaO. After CCl_4 adsorption on CP−CaO, the sample was very hygroscopic and a few minutes after exposure to air, a water layer formed on the surface. Probably, calcium chloride, that is very hygroscopic, transformed into $CaCl_2 \cdot 2H_2O$ during the reaction with the moisture in the atmosphere.

On a CP−CaO sample exposed to a low pressure of CCl_4 (10 Torr), at 450 °C for 5 min, three different types of surfaces were observed, which can be seen on the same picture (Figure 10a). They probably correspond to different coverage rates of the surface by a $CaCl_2 \cdot 2H_2O$ layers. In some places, the surface displays unreacted areas where small particles (around 35 nm in size) can be seen. Other places show a layered overlapping platelet structure. The individual particles cannot be distinguished any longer, which might be described as a “partial” coverage of the surface by $CaCl_2 \cdot 2H_2O$. When the surface was fully covered by $CaCl_2 \cdot 2H_2O$, no particles were observed. The surface exhibits wide flat areas. So the reaction with CP−CaO is not uniform over the whole surface because unreacted areas can be found. It seems that there are some places on the surface more favorable than others for this reaction.

When the CCl_4 pressure reached 20 Torr (Figure 10b), the coverage rate of the surface by $CaCl_2 \cdot 2H_2O$ was still partial since some particles can be observed; other places showed the $CaCl_2 \cdot 2H_2O$ layer deposition.

After exposing the CP−CaO surface to a CCl_4 pressure of 50 Torr, under the same conditions of temperature and of reaction time (Figure 10c), more or less flat areas can be observed, but the whole surface is not uniform, but with a CCl_4 pressure of 100 Torr (Figure 10d) the flat surface is almost uniform.

(3) AP−CaO. After exposure to CCl_4 pressure of 20 Torr for 5 min at 450 °C, the AP−CaO surface is not as hygroscopic as CP−CaO, and the color of the sample is the same as before the reaction, white. The surface still displays some small particles (20 nm, Figure 11b) but larger particles which look like clusters (60−100 nm) growing on the surface can also be observed, suggesting that the reaction starts on some particular sites but not in a uniform way.

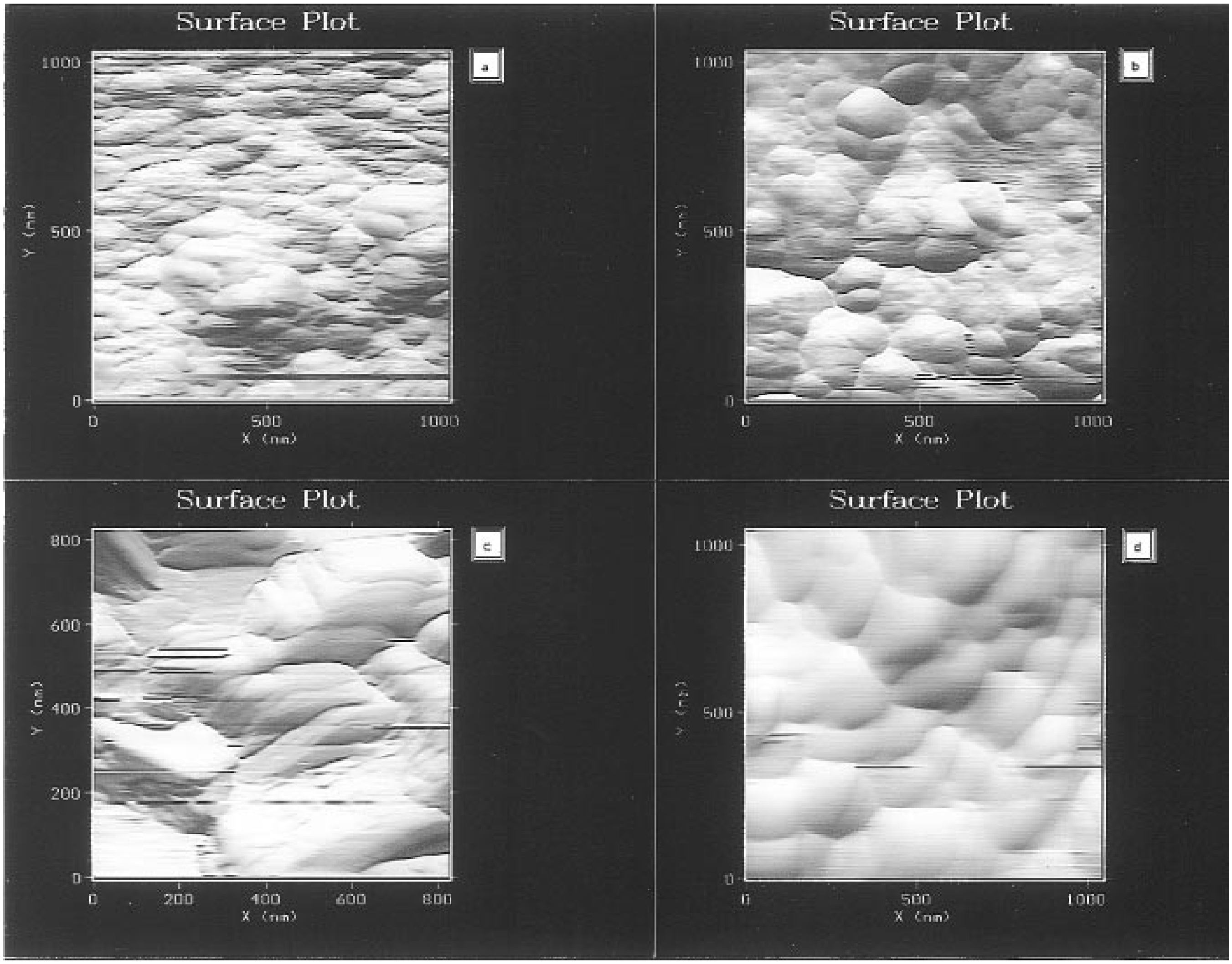


Figure 11. AFM images of pressed autoclave prepared CaO (AP−CaO) after CCl_4 adsorption at 450 °C for 5 min at (a) 10, (b) 20, (c) 50, and (d) 100 Torr.

When the CCl_4 pressure reached a higher value (100 Torr) for 5 min at 450 °C, the AP−CaO sample surface was completely black and turned into a thick liquid after long exposure to air. Unlike CP−CaO, the surface is not flat but is still made of particles which are much larger and could correspond to aggregates covered by $CaCl_2 \cdot 2H_2O$ layers. Further reaction caused more smoothing and $CaCl_2$ coverage progressively (Figures 11b−d).

Discussion

Gas−solid reactions are sensitive to surface effects, coatings, and kinetic and thermodynamic parameters. Therefore, maximizing surface area of the adsorbent is important. Calcium oxide has proven to work well as a destructive adsorbent for carbon tetrachloride. In the case of AP−CaO a very high surface area material was prepared and behaved better at lower temperatures. However, CP−CaO was also effective at elevated temperatures because of a rather unique phenomena—the development of ultrafine (nanoscale) particles upon careful dehydration of $Ca(OH)_2$.

For the thermal decomposition of CCl_4 in the stainless steel reactor, a temperature above 650 °C was necessary. With the use of calcium oxide the best temperature for decomposition was found to be 450 °C. Increasing the surface area of the oxide increased the decomposition ability. Also, when the time between injections were prolonged, the decomposing ability of CaO increased, that could be connected with allowing enough time for the chloride ion migration to the bulk and renewing the surface for decomposition.

During decomposition the major gaseous product was carbon dioxide, and the solid product was calcium chloride. Traces of other gaseous byproducts, such as phosgene and tetrachloroethylene were also formed. *However, if an excess of the oxide was used, the phosgene production could be completely eliminated.* The formation of phosgene and tetrachloroethylene was smaller on AP−CaO and further decreased with increasing the surface area of the oxide and decreasing the temperature of the decomposition. Based on the data, the following three-step pathway is proposed for the process:

$$2CaO + CCl_4 \rightarrow 2CaCl_2 + CO_2 \qquad \Delta H = -573\ \text{kJ} \tag{11}$$

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \Delta H = -178\ \text{kJ} \tag{12}$$

$$2CaCO_3 + CCl_4 \rightarrow 2CaCl_2 + 3CO_2 \qquad \Delta H = -217\ \text{kJ} \tag{13}$$

All these reactions are thermodynamically favorable, and this model agrees with the induction time observed for CO_2 release, followed by a large and rapid production of carbon dioxide. From the pressure studies, it was determined that by increasing pressure of chlorocarbon the amount of produced carbon dioxide increased; however, when a large excess of chlorocarbon was employed, the formation of phosgene increased as well. At 70 Torr, a small amount of hydrogen chloride was also formed, with hydrogen coming from the residual hydroxyl groups on the surface. Upon reaction of carbon tetrachloride with a "clean" CaO surface (pretreated at 800 °C) the formation of carbonate species was observed (mainly unidentate carbonates). With an excess of carbon tetrachloride the intensities of these peaks decreased, which confirms the reaction between $CaCO_3$ and CCl_4.

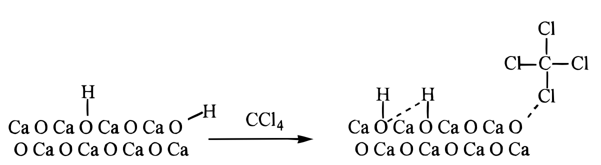
According to the model, first carbon tetrachloride reacts with calcium oxide to produce carbon dioxide and calcium chloride. Carbon dioxide very quickly back adsorbs on the remaining oxide to produce calcium carbonate. When an excess of CCl_4 is added, calcium carbonate reacts with it to produce calcium chloride and more carbon dioxide. The last reaction is not as favorable, as the direct reaction with calcium oxide.

Conventionally prepared calcium oxide (CP−CaO) did not evolve as much carbon dioxide, as the autoclave-prepared CaO. It can be concluded that the produced carbonate species on AP−CaO are much more reactive than on CP−CaO.

The mechanism of the reaction $CCl_4 + 2CaO \rightarrow CO_2 + 2CaCl_2$, which must be quite complex, cannot be known from the present data. However, some insight has been gained.

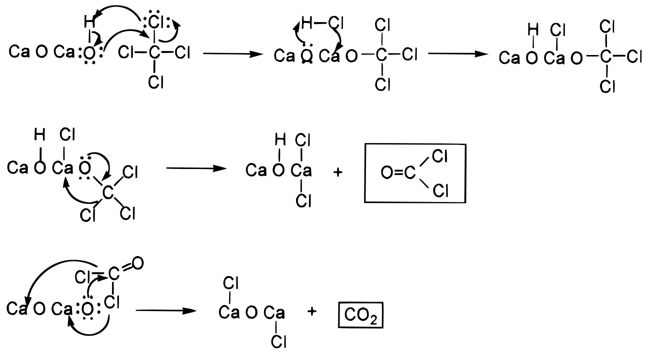
The first question might deal with whether the initial interaction is radical-like or resembles an ionic reaction.[37] Products that would be expected if a radical process were involved would include C_2Cl_6 and perhaps Cl_2, and these were never observed. However, the intermediacy of $:CCl_2$ seems likely since small amounts of C_2Cl_4 and Cl_2CO were observed, when excess of CaO was not present, and a CCl_x species (probably $:CCl_2$) was observed during low-temperature IR studies.[25]

The effect of surface −OH groups was also studied. It was determined that upon room-temperature adsorption of CCl_4, the ν_{O-H} band for isolated −OH decreased with increasing CCl_4 pressure, and a new band for associated −OH grew in. This suggests that CCl_4 physisorbed by displacing H^+ such that they are able to hydrogen bond with each other on another part of the oxide surface:

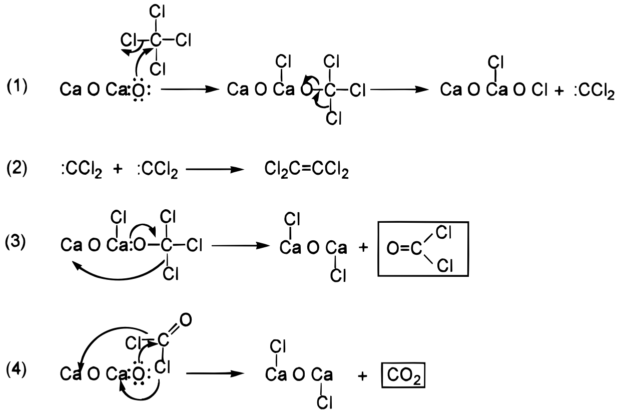


It was also found that an increased number of surface −OH did not aid the high-temperature $CCl_4 \rightarrow CO_2$ conversion and that the presence of large amounts of water had a detrimental effect. In addition, an expected product of a direct CCl_4/surface −OH reaction would be HCl. Although it would be expected that HCl would quickly react with the CaO surface ($CaO + 2HCl \rightarrow CaCl_2 + H_2O$), a trace of HCl in the gas was observed when higher pressures of CCl_4 were employed. (The OH must have come from the interior of the CaO particles since surface −OH was not observed by IR before the reaction started.) Furthermore, a CaO that was devoid of surface −OH (after an 800 °C preheat treatment) functioned relatively well in the $CCl_4 \rightarrow CO_2$ reaction.

Scheme 1. Possible Steps in CCl_4 Conversion to CO_2 on Ultrafine CaO with the Involvement of Surface OH Groups

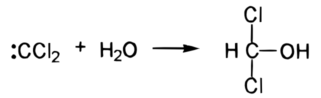


Scheme 2. Possible Steps in CCl_4 Conversion to CO_2 on Ultrafine CaO



We conclude from these data that surface −OH groups serve as a initial adsorption sites for CCl_4 (probably because they preferably locate at coordinately unsaturated oxides on edges/defects, which the CCl_4 molecules also prefer) but that surface −OH sites are not necessary to initiate the $CCl_4 \rightarrow CO_2$ reaction, but they do react and could lead to final products as shown in Scheme 1.

A similar scheme can be drawn for the reaction with Lewis acid/base sites as shown in Scheme 2. The formation of $:CCl_2$ could lead through dimerization to C_2Cl_4, or in the presence of large amounts of water to $CHCl_2OH$, a minor product only found when sufficient water was available:



$$:CCl_2 + H_2O \longrightarrow H\overset{Cl}{\underset{Cl}{C}}-OH$$

Interestingly, large amounts of water also caused an increase in phosgene formation, and this may be due to the competition of water for Lewis acid sites, discouraging step 4 of Scheme 2.[38]

When CO_2 is formed, and sufficient Lewis base sites still exist, it is adsorbed as well, and can exist on the

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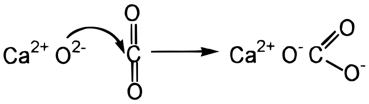
(37) For a discussion of radical reactions on metal oxide surfaces see: Xu, M.; Ballinger, T. H.; Lunsford, J. H. *J. Phys. Chem.* **1995**, *99*, 14494.

surface in mono- or bidentate forms.



On the basis of the gravimetric adsorption studies and the pulsed GC studies, it was found that AP−CaO exhibited more capacity for $CCl_4 \rightarrow CO_2$ conversion and lower temperatures could be used. For example the gravimetric experiments showed that AP−CaO reacted well at both 300 and 400 °C. Using CP−CaO higher temperatures were necessary. In addition AP−CaO reacted much faster with CCl_4. Such findings must be due to the presence of more active surface sites on AP−CaO, and on a more facile ability for Cl^-/O^{2-} exchange. It seems certain that these differences cannot be explained based on surface area alone, and other factors are obviously involved. In fact, detailed morphological data is necessary, and we hope to report such data soon.[39]

It should be noted, however that even though AP−CaO is superior to CP−CaO, both are vastly superior to normal commercially available CaO for this CCl_4 chemistry. This conclusion was based on pulsed U-tube reaction studies, as well as examination of surface changes during CCl_4 reaction by atomic force microscopy (AFM); CM−CaO appeared almost unaffected by CCl_4. However, for CP−CaO a striking surface smoothing was observed which increased with higher CCl_4 pressures. Interestingly, AP−CaO also showed similar smoothing, but individual particles remained visible longer. On the basis of an accumulation of data, we believe this can be rationalized by faster Cl^-/O^{2-} migration from the surface toward the bulk on AP−CaO, and so the buildup of a complete coverage by $CaCl_2$ takes longer than on CP−CaO.

Summary of Results

High surface area calcium oxide works well as a destructive adsorbent for carbon tetrachloride decomposition.

The final decomposition products are carbon dioxide and calcium chloride. The byproducts such as phosgene and tetrachloroethylene can be eliminated if an excess of oxide is used.

Aerogel/autoclave prepared CaO (AP−CaO) is the better choice for decomposition, because the reaction is faster, can be carried out at lower temperatures, and decomposition capacity is considerably higher compared to CP−CaO, and much higher than commercial CaO.

When carbon tetrachloride reacts the morphology of the surface changes and appears smoother. The extent of smoothing depends on CCl_4 pressure used as well as on the type of oxide.

Acknowledgment. The support of the Army Research Office and the Hazardous Substance Research Center (administered by Kansas State University for the Environmental Protection Agency and the Department of Energy) is acknowledged with gratitude.

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(38) Zhou and Cowin (Zhou, X. L.; Cowin, J. P. *J. Phys. Chem.* **1996**, *100*, 1055) have discussed photodestruction of CCl_4 on MgO films in the presence and absence of water.

(39) Koper, O.; Lagadic, I.; Klabunde, K. J., manuscript in preparation.