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

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Ultrafine particles of CaO react with CCl_4 to yield $CaCl_2$ and CO_2. Phosgene is an intermediate product but can be avoided if excess CaO is employed. The reaction with $CHCl_3$ yields $CaCl_2$, CO, and H_2O, while C_2Cl_4 yields $CaCl_2$, carbon, and $CaCO_3$. Thermodynamically these are all favorable reactions, but kinetic parameters demand that high surface area CaO be used. However, under the right conditions multiple layers of the CaO particles can be converted to $CaCl_2$. An aerogel/autoclave method for the preparation of high surface area CaO is described.

Introduction

The increasing amounts of chlorocarbons in our environment causes the need to find easy and effective ways to destroy them without producing toxic byproducts (hopefully the byproducts will be useful). The most widespread groups of chlorinated compounds include polychlorinated biphenyls (PCBs), which have extremely high thermal stabilities and are used as lubricants, heat-transfer fluids, plasticizers, transformer fluids, and cleaning solvents such as CCl_4, $CHCl_3$, and C_2Cl_4.[1]

Several reports on the decomposition of chlorocarbons by catalytic oxidation to yield mainly HCl and CO_2 as products are available. For example, supported and unsupported Pt, V_2O_3, and Cr_2O_3,[2-5] zeolites,[6] and other commercially available catalysts[7-9] have been employed with some success.

Our approach to destroying various toxic chemicals is noncatalytic and depends on surface active reagents that strip heteroatoms from the toxic material and allow only the release of nontoxic hydrocarbons or carbon oxides. For example the "destructive adsorption" of organophosphorus compounds on MgO caused the phosphorus atom to be immobilized as a strongly bound residue, and the only volatile products were CH_3OH and HCOOH.[10]

In principle, similar chemistry can be applied for the destructive adsorption of chlorocarbons. For adsorbents/reactants such as MgO or CaO, the desirable products would be $MgCl_2$/$CaCl_2$ and carbon oxides. Thermodynamically such reactions are favorable. Table I shows that the standard heats of formation of $MgCl_2$/$CaCl_2$ exceed those of MgO/CaO, and hydrated forms have extremely favorable $\Delta H_f°$. These differences can be put to good use in chlorocarbon reactions, as further demonstrated in the anticipated reactions shown in (1) and (2) and it can be predicted that CaO would be the most energetically favorable destructive adsorbent to use. However, since these are solid/gas or solid/liquid reactions, and $CaCl_2$ is not continually removed from the CaO surface, surface area and reactivity became crucial factors, which has been clearly demonstrated in earlier work with MgO-organophosphorus compound reactions.[11] Thus, we have spent

$$2CaO + CCl_4 \rightarrow 2CaCl_2 + CO_2 \qquad (1)$$

$$\Delta H°_{rxn} = -573 \text{ kJ/mol}$$

$$2MgO + CCl_4 \rightarrow 2MgCl_2 + CO_2 \qquad (2)$$

$$\Delta H°_{rxn} = -334 \text{ kJ/mol}$$

considerable time on developing the best methods of preparation of the high surface area CaO. We have had some success with a modified aerogel procedure[12-17] that was used earlier for preparation of nanoscale MgO particles.[18] The aerogel prepared material (AP-CaO) had a surface area of 120 m^2/g (average crystallite size = 7.4 nm) compared with commercial powdered CaO of 5–10 m^2/g (average crystallite size = 28 nm).

Table I. Standard Heats of Formation

compound	$\Delta H°_f$ [kJ/mol]	compound	$\Delta H°_f$ [kJ/mol]
CaO	−636	$CaCl_2$	−795
MgO	−598	$MgCl_2$	−642
Fe_2O_3	−822	$FeCl_3$	−405
		$CaCl_2 \cdot 2H_2O$	−1400
		$MgCl_2 \cdot 2H_2O$	−967

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(12) The hypercritical drying approach was first developed by Kistler[13] in 1932 for preparation of high surface area silica. However, the drying step, when water is the solvent, can still be a problem because of the high surface tension of water then tends to trap water in the small pores, which eventually rupture. Therefore, Teichner and co-workers,[14,15] Zarzycki,[16] and others[17] started to use organic solvents instead of water, and even better results were obtained. The metal oxide products—aerogels—are very porous materials with low densities, large numbers of defect sites, and extremely high surface areas. Depending on the material, these surface areas can range as high as 1200 m^2/g. The materials are also relatively free from impurities and no additional washing or cleaning is necessary.

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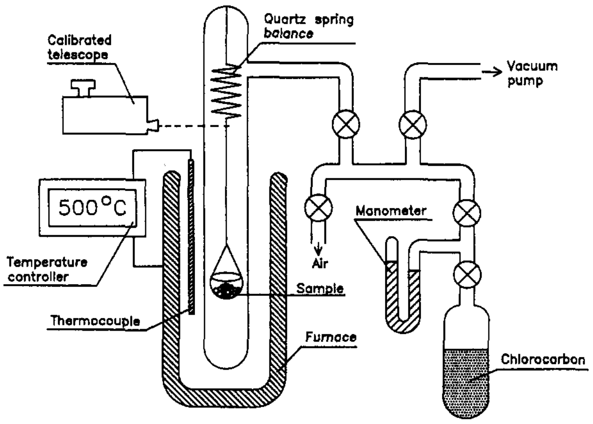

Figure 1. Vacuum line with quartz spring balance.

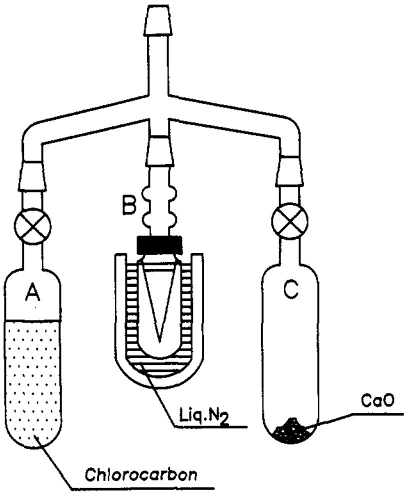

Figure 2. Apparatus used for reaction of excess CaO with chlorocarbons and collection of solid and gaseous products.

Experimental Section

General Description of Apparatus and Instruments Used. (*1*) *Quartz Spring Balance and Vacuum Line.* The set up that was used in these experiments is shown in Figure 1. The apparatus was composed of three main parts: the vacuum line, the spring balance part with a system to introduce vapor of chlorocarbons, and the calibrated scope to observe the changes in the length of the spring. A minibasket with the sample (about 0.05 g) was attached to the quartz spring balance. The sample was heated to a desired temperature using the furnace. The temperature was regulated using a temperature controller with a thermocouple. The differences in a weight of the sample, during the adsorption, caused changes in the length of the spring which allowed determination, by comparing to a calibration curve, the percent of conversion of calcium oxide into calcium chloride. The chlorocarbons were introduced as a vapor and the vapor pressure was measured using the Hg manometer. This system allowed measurement of changes in weight of ±0.1 mg.

(*2*) *X-ray Powder Diffraction.* The instrument used was a Scintag-XDS-2000 spectrometer. The sample, directly before the measurement, was taken out of the sample tube, ground, and loaded, as a powder, onto the XRD sample cell. The time of exposure to the atmosphere was about 5 min. The spectrometer was set at a voltage of 40 kV and a current 40 mA. The scans were from 20° to 85° with the scanning rate of 2°/min.

(*3*) *IR Experiments.* A sample of calcium hydroxide (calculated amount to keep the ratio CaO:chlorocarbon 5:1 or 10:1) was placed in a glass tube equipped with a stopcock and vacuum port, and heat treated under vacuum (10^{-3} Torr) at 500 °C. After the activation, a certain amount of chlorocarbon (0.2 mL) was introduced using the assembly shown in Figure 2. First 0.1 mL of chlorocarbon from tube A was transferred under vacuum, using liquid N_2, to the calibrated vial, B. Then, this amount was transferred, in the same way, to a 250-mL Schlenk tube (C) that contained activated CaO. This procedure was repeated so that the final volume of chlorocarbon was 0.2 mL in tube C. Finally, the tube was closed, and the sample was slowly heated (2 h) to the desired temperature. After 9 h of adsorption/reaction, at this temperature, the tube was allowed to cool, and the gases were transferred under vacuum, using liquid N_2, into a homemade IR gas cell with the KBr windows. Infrared spectra of the gas products were recorded from 4000 to 600 cm^{-1} with a Perkin-Elmer Model 1310 spectrophotometer.

Preparation of AP–CaO. (*1*) *Preparation of 10% Calcium Methoxide in Methanol Solution.* $Ca(OCH_3)_2$ was obtained from calcium and methanol. First calcium metal was cut into slices with an electric saw, rubbed with sandpaper, cleaned with acetone, and cut into small pieces (5 mm) directly before the reaction. Then, to a 500-mL round-bottom flask 8 g (0.2 mol) of calcium and 230 mL (182 g, 5.68 mol) of spectroanalyzed grade methanol were introduced:

$$Ca + 2CH_3OH \rightarrow Ca(OCH_3)_2 + H_2$$

The reactants were stirred at room temperature for 16 h. To prevent the calcium methoxide from atmospheric moisture, the reaction was carried out under a slow flow of nitrogen gas. When the reaction started, formation of bubbles of hydrogen, on the calcium surface, was observed. After all metal reacted the product resembled a milkshake. Calcium methoxide was stored under nitrogen in the flask for future use.

(*2*) *Hydrolysis of Calcium Methoxide.* A solution of calcium methoxide in organic solvent was hydrolyzed at room temperature overnight, by stirring 20 g (0.2 mol) of 10 wt % $Ca(OCH_3)_2$, 180 mL (156 g, 1.7 mol) of toluene, and 1.2 mL (0.07 mol) of triply distilled, deionized water in a 400-mL beaker:

$$Ca(OCH_3) + 2H_2O \rightarrow Ca(OH)_2 + 2CH_3OH$$

When the water was added, drop by drop, using the syringe, a white solid was formed in the solution, that slowly transformed to a clear gel. To prevent the mixture from evaporation the beaker was covered with aluminum foil. After an hour an additional drop of water was added to make sure that all the methoxide reacted. If a white solid was still formed, more water was added. After overnight stirring at room temperature the methoxide was completely transformed into hydroxide.

(*3*) *The Autoclave Treatment Procedure.* The autoclave treatment caused calcium hydroxide to be dried, under hypercritical conditions, while maintaining high surface area. The hydroxide gel solution was transferred into the glass liner of the Parr mini reactor. The mixture was first flushed with nitrogen and the reaction was carried out under nitrogen, with an initial pressure of 100 psi. The reactor was slowly heated from room temperature to 265 °C at 1 °C/min. Time of the heating was about 4 h. After reaching the desired temperature, the reactor was kept at 265 °C for 10 min. During heating the pressure inside the minireactor increased from 100 to 600 psi. When the autoclave procedure was finished, the system was immediately vented to the atmosphere, the furnace was taken off, and the calcium hydroxide was flushed with nitrogen gas for 10 min to remove the remaining organic solvents. The reactor was then allowed to cool to room temperature for approximately 2 h. The autoclave procedure was followed by a careful drying in the oven at 120 °C and then thermal conversion of calcium hydroxide.

(*4*) *Thermal Conversion of Calcium Hydroxide into Calcium Oxide.* Before each experiment $Ca(OH)_2$ was activated under dynamic vacuum (10^{-3} Torr) at the desired temperature, usually 500 °C. The sample was placed in a Schlenk tube and evacuated at room temperature for 30 min. Later it was slowly heated (6 h) from room temperature to 500 °C and then kept under these conditions for 15 h. Most of the water came off at 350 °C; therefore, the sample was kept at this temperature for 1.5–2 h. The slow heating prevented rapid outgassing of the sample and sintering. After the heat treatment, the Schlenk tube was closed and the sample was stored under vacuum for future use. Calcium oxide obtained by this method had a surface area of 120 m^2/g.

(*5*) *Surface Area Measurement.* Surface area of the calcium oxide and hydroxide was determined using the BET method. The instrument used was a Micrometrics FlowSorb II 2300 with

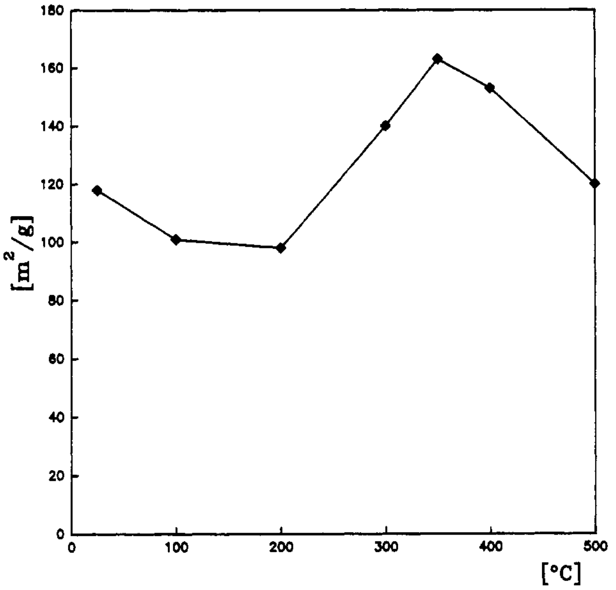

Figure 3. Surface area of the autoclave prepared calcium hydroxide activated under vacuum at different temperatures ($Ca(OH)_2 \rightarrow CaO$).

a Dual Channel System (900 Series, Sierra Instruments). The sample was exposed to N_2 gas and the quantity of a nitrogen that adsorbed on the sample as a single layer, was measured. From the number of adsorbed molecules and the area occupied by each the surface area was directly calculated. The preferred gas mixture for a monolayer formation was 30% volume of N_2 and 70% of He. The adsorption was done at the boiling point of nitrogen.

Preparation of CP–CaO. Conventionally prepared CaO was made from commercial calcium oxide by boiling it with distilled water, activating it under vacuum, and drying it in the oven overnight at 120 °C. To a 400-mL beaker, 10 g of CaO and 150 mL of water were added, and the beaker was covered with a watch glass to avoid quick evaporation of the water. The slurry was heated to 80 °C and then kept at this temperature for 2 h (when the water was almost completely evaporated). The calcium hydroxide obtained was dried in the oven overnight at 120 °C. Before each experiment CP–CaO was activated under dynamic vacuum (10^{-3} Torr) at the desired temperature in a manner similar to that described for AP–CaO.

Adsorbates/Reactants. Chloroform (Fisher Science), carbon tetrachloride (Fisher Science), and tetrachloroethylene (Aldrich) before the experiments were freeze–pump–thaw degassed seven times and stored under vacuum in glass cylinders.

Quartz Spring Balance Experiment Using the Example of Adsorption/Decomposition of CCl_4. Calcium hydroxide was dried in the oven at 120 °C and pressed into pellets, which were crushed and sieved to obtain a grain size between 1.2–0.07 mm. Into a minibasket of the spring balance 0.05 g of the calcium hydroxide was introduced. The sample was first outgassed at room temperature for 30 min and then activated under a dynamic vacuum at 500 °C for 15 h—the procedure was similar to the thermal conversion of calcium hydroxide into calcium oxide for AP–CaO and CP–CaO. The amount of evaporated water, usually about 25% of the total mass, and the weight of the calcium oxide were determined. After the heat treatment, vapors of carbon tetrachloride, under static vacuum, at desired temperature, were introduced. The initial pressure was about 150 Torr and increased with time—the stopcock between the tube with CCl_4 and the spring balance was open during the whole time of adsorption/decomposition. The readings of the changes in the length of the balance spring were taken every 10 min for the first hour and then every 30 min for the next 3 h. When the adsorption/decomposition was finished, 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 the XRD results, that calcium oxide was transformed into calcium chloride, the percent of conversion of CaO into $CaCl_2$ was calculated.[19] The solid product was later studied using X-ray powder diffraction.

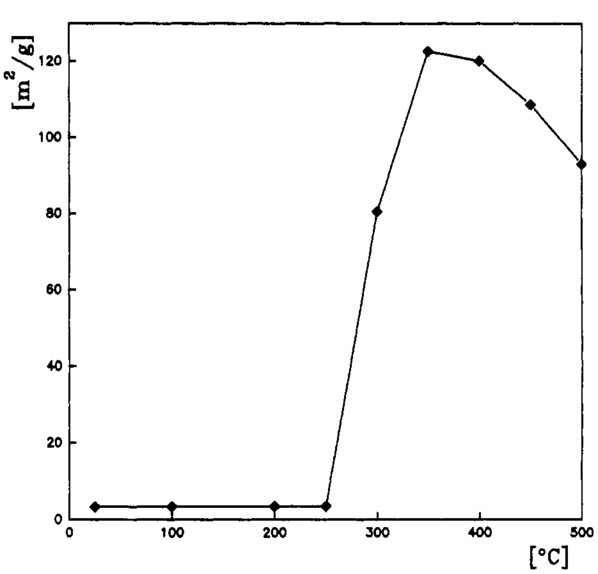

Figure 4. Surface area of the conventionally prepared calcium hydroxide activated under vacuum at different temperatures ($Ca(OH)_2 \rightarrow CaO$).

Results

Surface Areas of AP–CaO and CP–CaO. The surface areas of the conventionally and the autoclave prepared calcium oxides were studied using the BET method, after thermal activation of the samples under vacuum at different temperatures (Figures 3 and 4). Interestingly, the surface area of the autoclave prepared calcium oxide AP–CaO decreased upon activation, while that of the conventionally prepared CP–CaO increased. Upon activation at 500 °C the surface areas for conventionally and autoclave prepared calcium oxides were similar, about 120 m^2/g. The highest surface area, in both cases, was obtained after activation of calcium hydroxide at 350 °C. At this temperature most of the water came off, and the hydroxide was converted into calcium oxide, which was confirmed by X-ray powder diffraction spectroscopy. After thermal activation at 100 and 200 °C, no peaks of calcium oxide in the XRD spectra were observed; at 300 °C the product was a mixture of calcium oxide and hydroxide; at 350 °C mainly the peaks of CaO were observed; at 400 and 500 °C the only product was calcium oxide.

Determination of the Amount of Converted Calcium Oxide into Calcium Chloride. Solid and Gaseous Products of Decomposition of Chlorocarbons Carbon Tetrachloride. Plots of the conversion of CaO into $CaCl_2$ after adsorption/decomposition of CCl_4 per mole of AP or CP–CaO at different temperatures of reaction are shown in Figures 5 and 6. In Table II are presented the percentage conversions of conventionally prepared CaO into $CaCl_2$ for each of the chlorocarbons studied after 4 h and after overnight reaction time. At 200 °C almost no conversion was observed for both types of oxides. With increasing temperature of the reaction, the percent of conversion increased and was the highest, about 70%, at 400 °C. After overnight adsorption/decomposition the

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(19) At the highest temperature (500 °C) along with $CaCl_2$ formation we observed graphite formation. We are currently attempting to obtain a complete carbon balance including graphite, CO, CO_2, and $CaCO_3$.

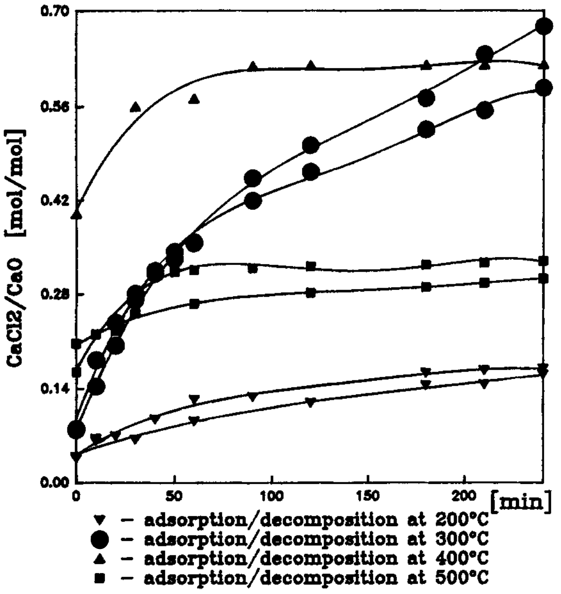

Figure 5. Adsorption/decomposition of carbon tetrachloride/mol of AP-CaO versus the time of exposure at different temperatures.

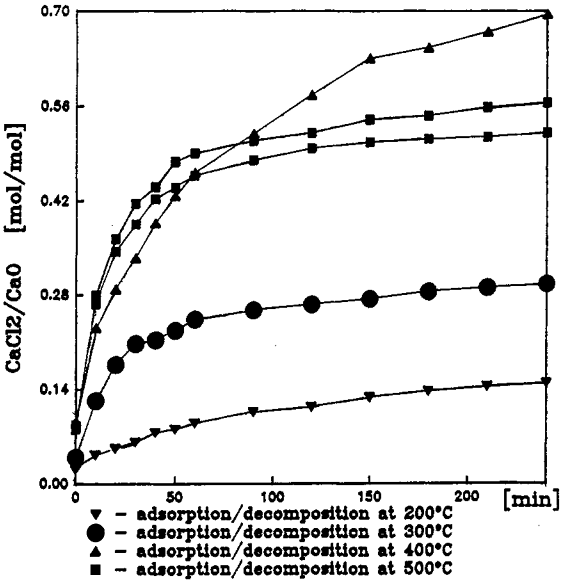

Figure 6. Adsorption/decomposition of carbon tetrachloride/mol of CP–CaO versus the time of exposure at different temperatures.

Table II. Conversion of CaO into $CaCl_2$ at Different Temperatures of Adsorption of Chlorocarbons

		$CaCl_2/CaO$ [mol/mol]	
chlorocarbon	temp [°C]	4h	overnight
$CHCl_3$	200	0.19	0.27
	300	0.29	0.37
	400	0.38	0.52
	500	0.31	0.43
CCl_4	200	0.15	0.23
	300	0.27	0.31
	400	0.63	0.81
	500	0.54	0.62
C_2Cl_4	200	0.03	0.05
	300	0.06	0.10
	400	0.30	0.50
	500	0.80	0.97

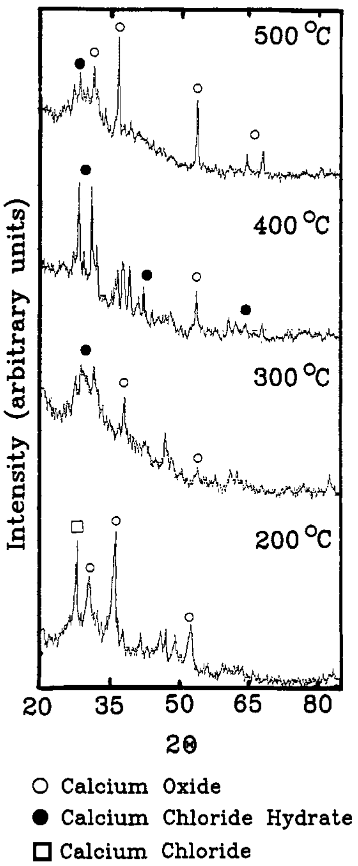

Figure 7. XRD spectra of AP–CaO after adsorption/decomposition of carbon tetrachloride at different temperatures.

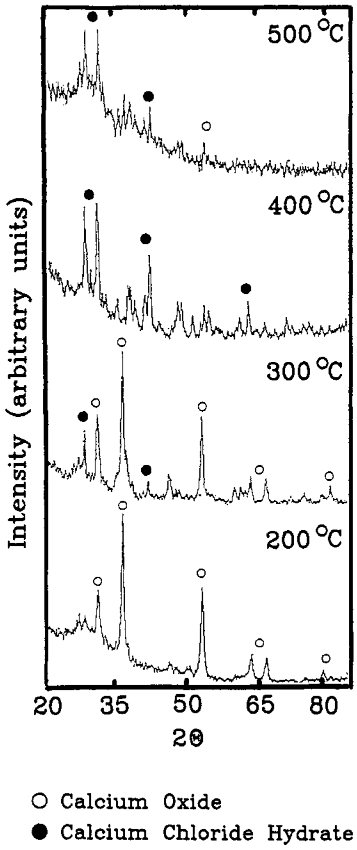

Figure 8. XRD spectra of CP–CaO after adsorption/decomposition of carbon tetrachloride at different temperatures.

maximum conversion was 80%. These surprisingly high conversions indicate that not only surface CaO species were reacting. As the surface of CaO reacted to form $CaCl_2$, this layer was obviously permeable to more CCl_4 and further reaction. However, there is a limit to this

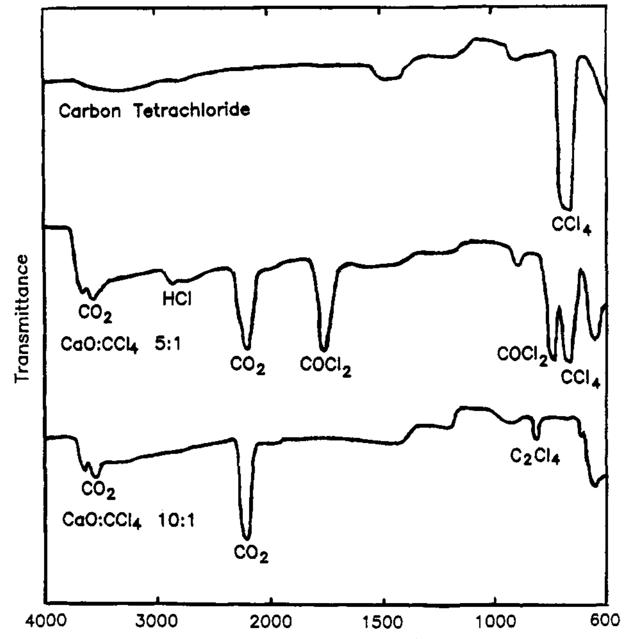

Figure 9. IR spectra of the gaseous products after decomposition of carbon tetrachloride on CP–CaO at 400 °C.

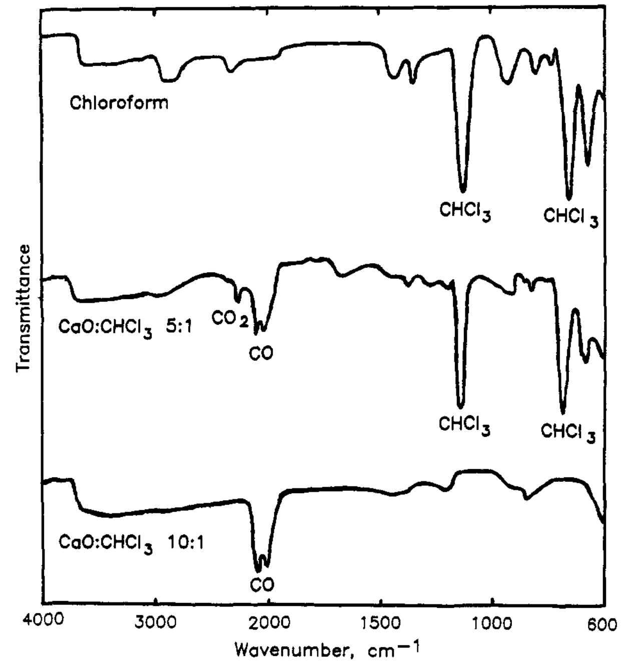

Figure 10. IR spectra of the gaseous products after decomposition of chloroform on CP–CaO at 400 °C.

permeability as multiple layers form, as it is evident from the fact that complete conversion was not possible.[20]

Interestingly when the temperature of reaction was increased from 400 to 500 °C, conversions decreased. It was noted that the CaO was covered with a black substance, most probably graphite. It appears that a new decomposition pathway, that of pyrolysis to form graphite on the CaO surface was possible, and this graphite coating may have inhibited further conversion of CaO to $CaCl_2$ (since the carbon did not tend to migrate into the CaO particles).

The solid products were analyzed by XRD (Figures 7 and 8). The progressive conversion of CaO to $CaCl_2$ is evident and agrees with the quartz spring balance studies; when the conversion was below 20% the main solid component was still CaO, while at higher conversions $CaCl_2$ became progressively more evident at the expense of CaO. It should be noted that usually the hydrate was observed $CaCl_2 \cdot 2H_2O$. The hygroscopic nature of $CaCl_2$ evidently is responsible, and during workup and analysis H_2O was adsorbed. Also, if any H_2O was formed during the formation of $CaCl_2$, this would be another source.

To help in the identification of gaseous products, GC and IR studies were used. Different ratios of CaO:CCl_4 were employed, and 400 °C was chosen as the optimum temperature. Figure 9 presents IR spectra of gas phase products. When the ratio of CaO:CCl_4 was 5:1, the products observed were CO_2, Cl_2CO, HCl, and remaining CCl_4. (The HCl formed we believe came from residual surface-OH groups on the CaO providing the necessary hydrogen.) When the ratio of CaO:CCl_4 was 10:1, the major product was CO_2 along with a small amount of C_2Cl_4. No Cl_2CO was present. These results suggest that a two-step process may be operating where phosgene is an intermediate (*warning*: phosgene is toxic and must be handled and analyzed with care):

$$CaO + CCl_4 \rightarrow CaCl_2 + Cl_2CO \qquad \Delta H^\circ_{rxn} = -242 \text{ kJ/mol}$$

$$CaO + Cl_2CO \rightarrow CaCl_2 + CO_2 \qquad \Delta H^\circ_{rxn} = -335 \text{ kJ/mol}$$

From the heats of formation it can be concluded that both reactions are likely, and we found the same behavior for both AP- and CP-CaO.

Chloroform. Similar studies were carried out for $CHCl_3$. It was found that $CHCl_3$ was more sensitive to reaction temperature. At 500 °C a graphitization pathway was very favorable yielding a coating on the remaining CaO that inhibited further reaction. For the autoclave prepared CaO the highest conversion after 4 h occurred at 300 °C, where about 50% of CaO was converted to $CaCl_2$. The lowest conversion, about 10%, was found at 200 °C. For CP–CaO the highest conversion occurred at 400 °C, and the lowest at 200 °C. The gaseous products from a 400 °C reaction over CP–CaO (CaO:$CHCl_3$ = 5:1) were CO, H_2O, and a small amount of CO_2. At a ratio of 10:1 only CO and H_2O were detected (Figure 10). Thus, the main reaction pathway at 300–400 °C appears to be CO and H_2O formation:

$$3CaO + 2CHCl_3 \rightarrow 3CaCl_2 + 2CO + H_2O$$

$$\Delta H^\circ_{rxn} = -700 \text{ kJ/mol}$$

Tetrachloroethylene. This compound is very stable thermally, even up to 500 °C. However, in the presence of excess CaO fine particles at about 500 °C, a graphitization pathway was observed. Besides carbon, the other major products were $CaCl_2$ and $CaCO_3$. For CP–CaO the percent conversion of CaO to $CaCl_2$ was 80% over a 4-h period, and 97% overnight (at 500 °C). For the AP–CaO this ratio was somewhat lower. However, it must be noted that several solid products were formed in this system including $CaCl_2$, $CaCO_3$, and CaClOH.

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(20) For greatly increased reaction times, for example 16 h instead of 4 h, even more CaO was converted, but never 100%.

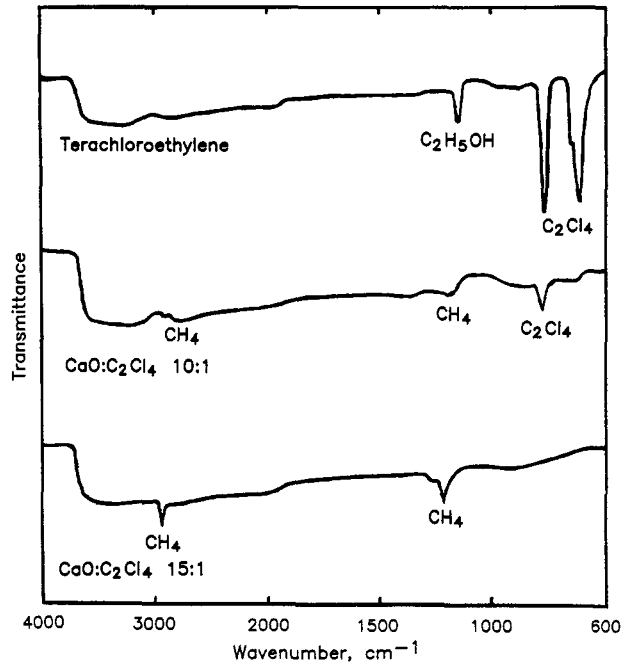

Figure 11. IR spectra of the gaseous products after decomposition of tetrachloroethylene on CP–CaO at 500 °C.

Complete destruction of C_2Cl_4 was possible when the mole ratio of CaO:C_2Cl_4 was about 15. The only gaseous product detected was a trace of CH_4. We believe the sources of hydrogen for the production of traces of CH_4 was the ethanol stabilizer present in commercial C_2Cl_4. Even with high-purity samples, that were freshly distilled, small amounts of ethanol and C_2HCl_3 or similar hydrochlorocarbons were present as impurities.

Elemental analysis of the solid residue of this CaO/C_2Cl_4 reaction showed that the percent of carbon (as graphite plus $CaCO_3$) was 4.02% with hydrogen >0.5% and chloride as 21.78%. Indeed, graphite formation was prevalent in the C_2Cl_4 case, and we believe this is a major reaction pathway.[19]

Although the CaO/C_2Cl_4 system is complex and further work is needed in order to elucidate material balances there are two important conclusions: (1) C_2Cl_4 can be completely decomposed over excess CaO; (2) the major reaction pathway is carbon and $CaCO_3$ formation, not CO or CO_2 gas formation. In a simplified form, the dominant reaction seems to be

$$3CaO + C_2Cl_4 \rightarrow 2CaCl_2 + CaCO_3 + C$$

$$\Delta H^\circ_{rxn} = -838 \text{ kJ/mol}$$

Discussion

These reactions show that CaO may be used as a destructive adsorbent for chlorocarbons. However, gas–solid reactions are sensitive to surface effects and coatings, and kinetic as well as thermodynamic parameters are important. Therefore, maximizing the surface area of the CaO is important. In the case of AP–CaO a very high surface area material was prepared and behaved best 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 $Ca(OH)_2$, as shown in Figure 4. This "blossoming" behavior has been observed before for $MgCO_3$[21] and $Mg(OH)_2$[22] and is quite striking in the case of calcium. Apparently during $Ca(OH)_2$ dehydration under vacuum, where the hot steam is removed very quickly, the forming CaO particles break off in very small sizes and without a chance for sintering. This unique behavior seems to be very dependent on the conditions of heat treatment (rate of heating, pumping speed, etc.).

Further work is certainly needed in order to understand this interesting CaO–chlorocarbon chemistry. Aromatic chlorocarbons are currently being investigated, and more details about the effects of flow gases He, air, or H_2 are being clarified.

At this time we can conclude that CaO is an effective solid reagent for destruction of chlorocarbons. The 300–400 °C temperature range is best and a mole ratio of CaO:chlorocarbon of about 10:1 is often necessary. Of course, this can be dependent on the surface area of the CaO and on the experimental conditions. The main products from these reactions are innocuous materials such as $CaCl_2$ and CO_2 and in some cases $CaCO_3$ and graphite.

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Registry No. $CHCl_3$, 67-66-3; CCl_4, 56-23-5; C_2Cl_4, 127-18-4; CaO, 1305-78-8.

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