The Adsorption and Reaction of Halogenated Volatile Organic Compounds (VOC's) on Metal Oxides

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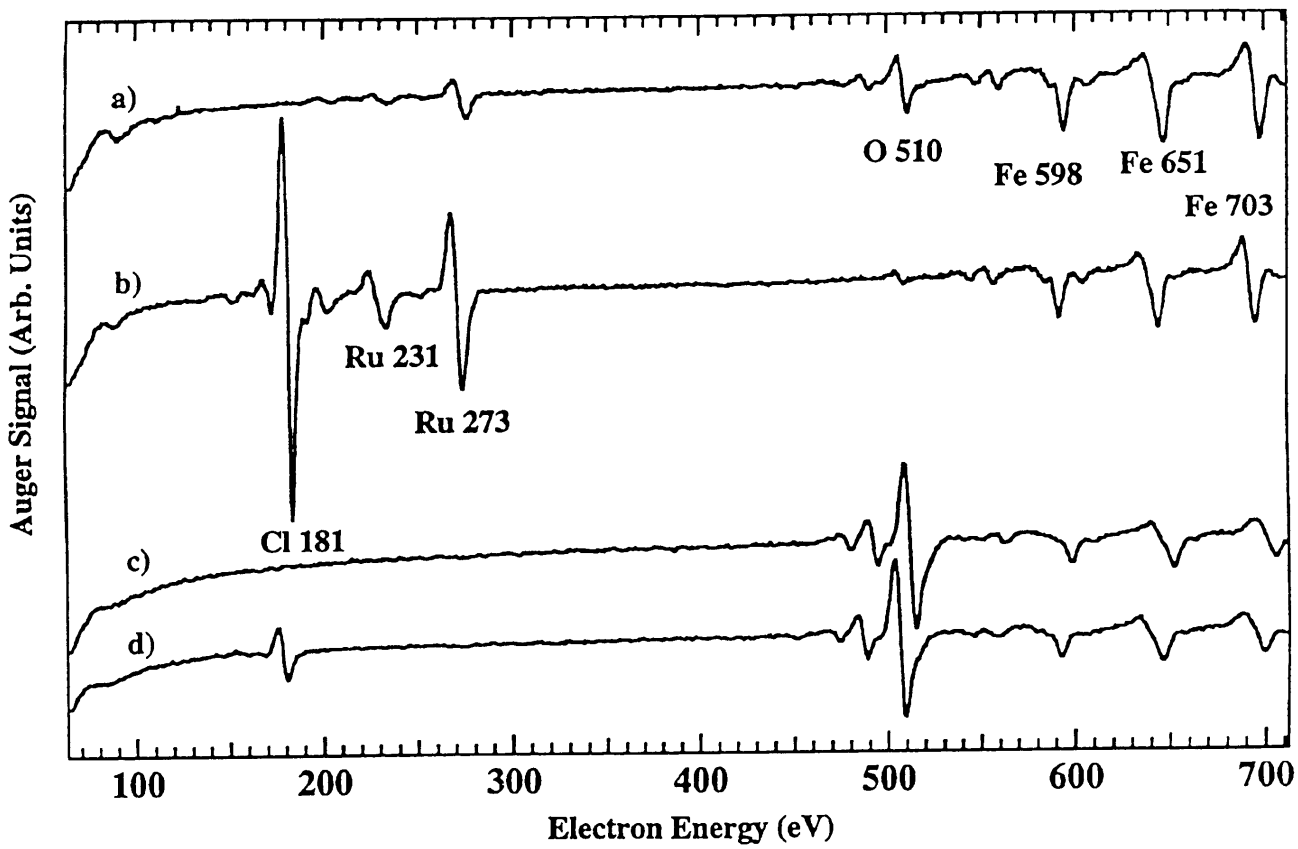
Introduction

The goal of this research is to elucidate the properties of metal oxides responsible for the activation of halocarbons and the nature of the intermediates formed in the dissociative adsorption of this general class of compounds.

This information is essential for interpreting and predicting stoichiometric and catalytic pathways for the safe destruction of halocarbon pollutants.

Surface Spectroscopic Studies

Adsorption and Reaction of TCE with Fe_2O_3 and FeO Surfaces



(a) Auger spectrum for an Fe + FeO film grown on a Ru(0001) single crystal surface.

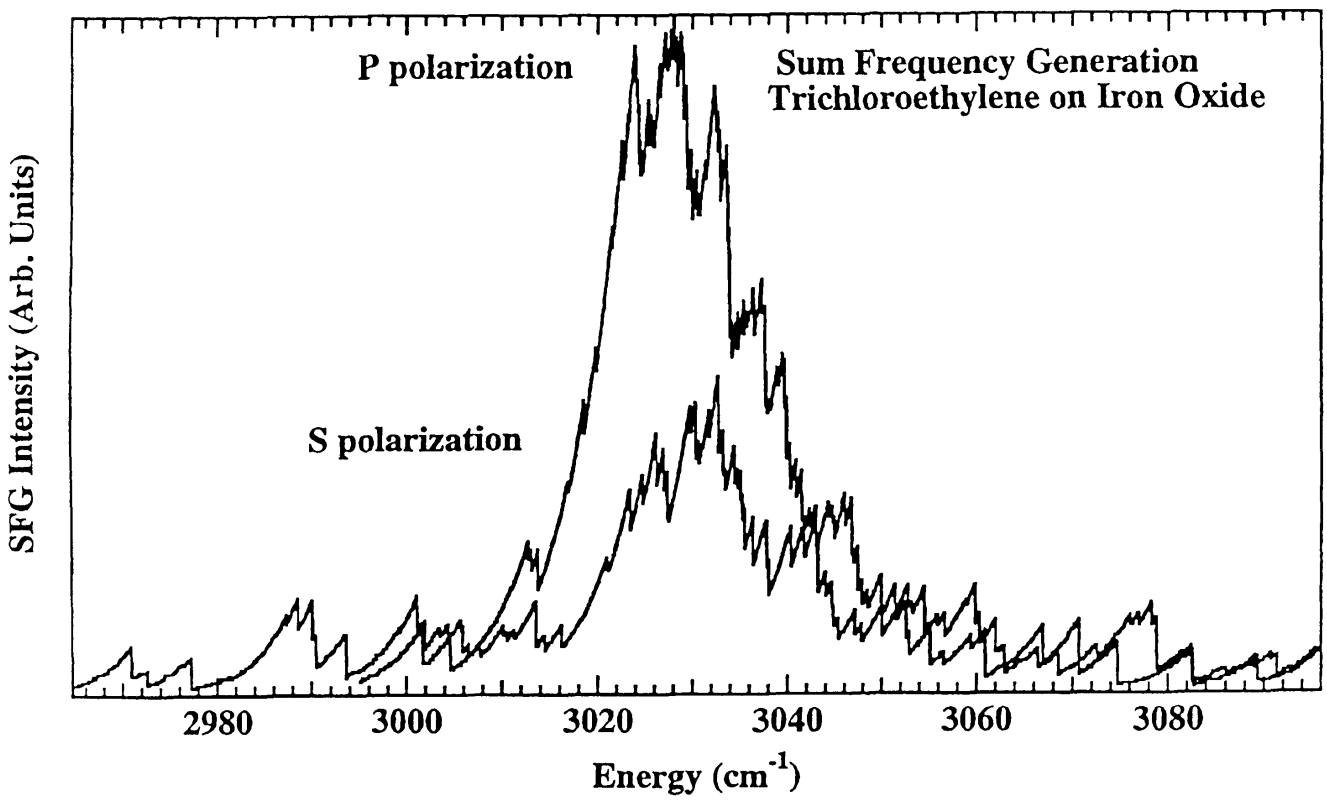
(b) Auger spectrum of surface in (a) at 120K exposed to TCE then heated to 710K.

(c) Auger spectrum of an Fe_2O_3 film prepared on a Ru(0001) surface.

(d) Auger spectrum of surface in (c) at 120K exposed to TCE then heated to 300K.

- FeO is much more reactive to trichloroethylene (TCE) than Fe_2O_3.
- Reaction mechanism involves oxygen abstraction from the surface leaving a Cl bound to Fe.

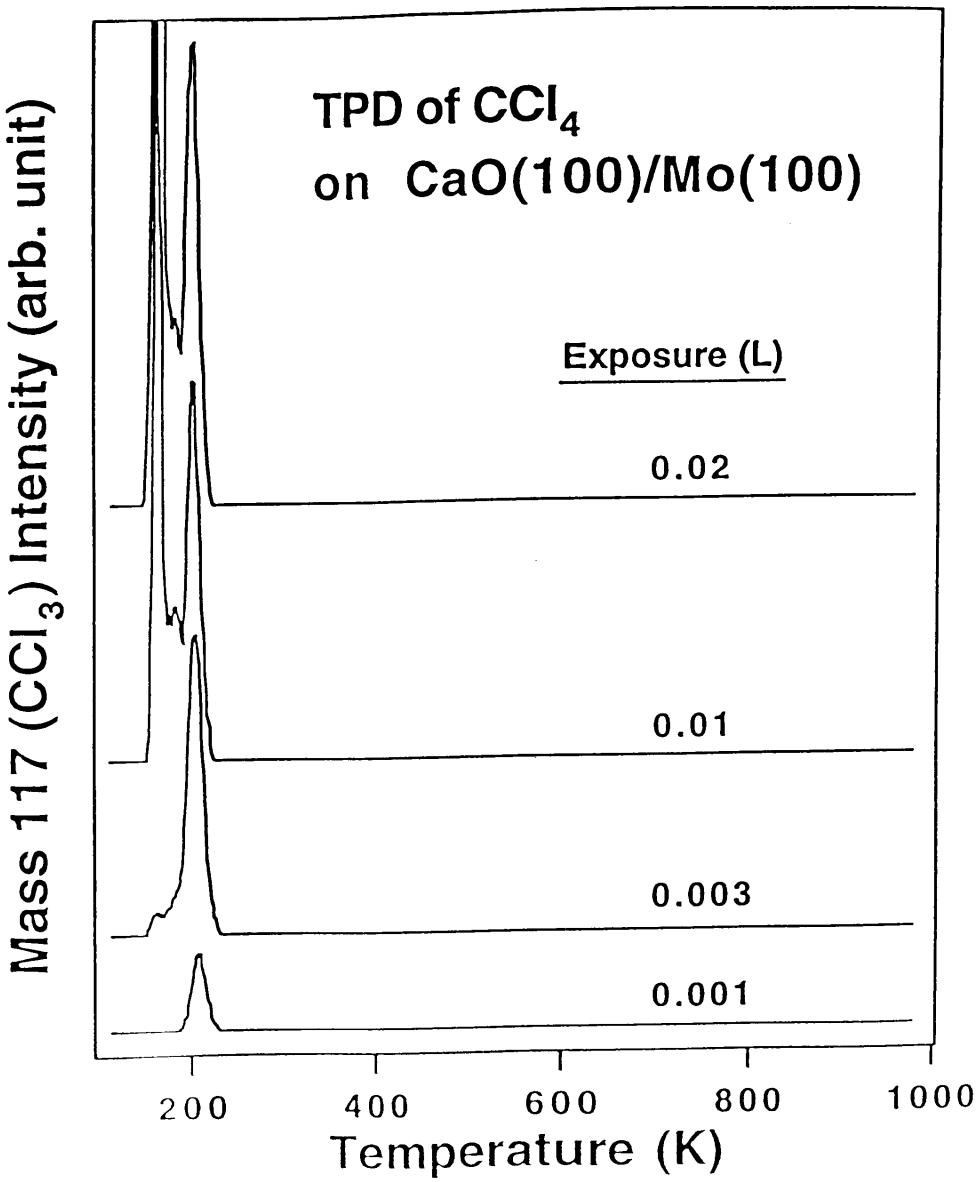
In-situ Spectroscopy Using Sum Frequency Generation (SFG)



Sum frequency generation spectra of an Fe + FeO film grown on Ru(0001) exposed to TCE at 120K.

- Fe_2O_3 surface shows no detectable signal; TCE believed to be less ordered on this surface compared with FeO.
- Reduced activity of Fe_2O_3 surface compared with FeO related to less strongly bound and less ordered TCE.

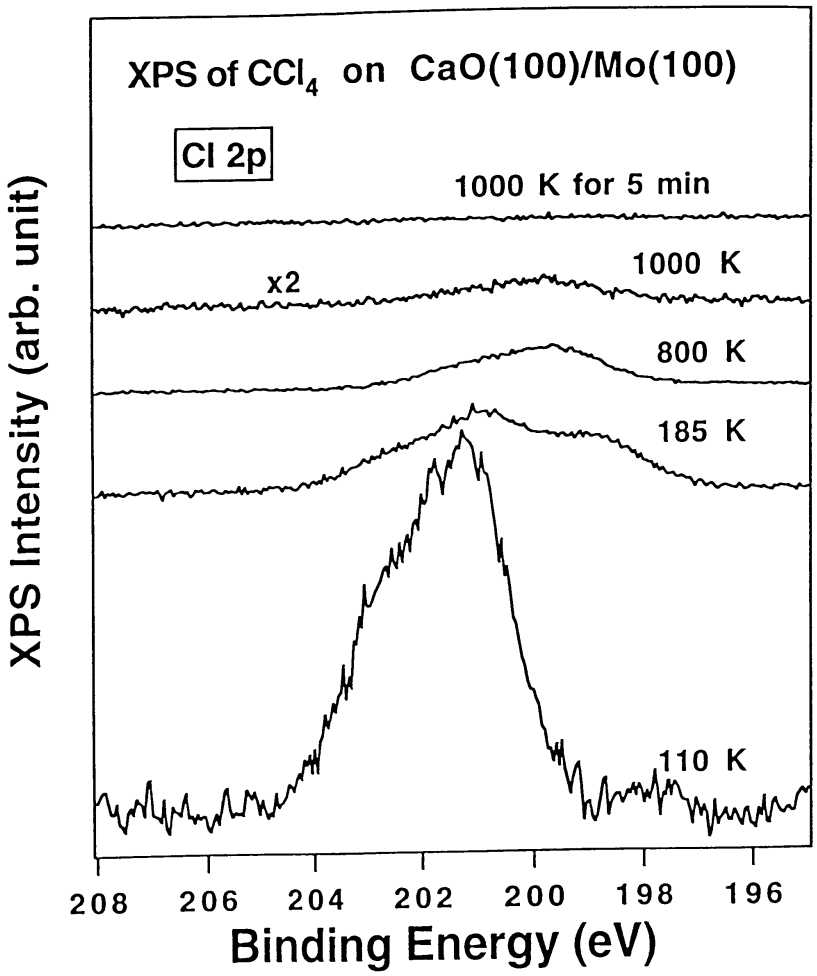
Adsorption of CCl_4 on CaO(100)



TPD spectra for undissociated CCl_4 species adsorbed on CaO(100) at 110K as a function of CCl_4 exposure

- CCl_4 desorbs primarily molecularly with only minor amounts decomposing to surface C_{ads} and Cl_{ads}.
- The activation energy for desorption of multilayer CCl_4 is 9.3kcal/mol.

Reactivity of CCl_4 on CaO(100)



Cl $2p_{2/3}$ XPS spectra for 0.01 L CCl_4 on CaO(100) as a function of annealing temperature

- Most of the adsorbed CCl_4 desorbs from CaO(100) surface by 185K.
- Annealing to 800 K eliminates carbon from the surface; however, chlorine remains.
- Ca-Cl bond still remains after a brief anneal to 1000K.
- Sustained heating at 1000K breaks the Ca-Cl bond with the desorption of chlorine.

Destructive Adsorption of Carbon Tetrachloride on Alkaline Earth Metal Oxides

- Klabunde et al.* showed that specially prepared ultrafine particles of CaO or MgO are able to destroy chlorinated hydrocarbons, with formation of CO_2 and the simultaneous transformation of the solid into the corresponding metal chloride (destructive adsorption).

$$2\ MeO + CCl_4 \rightarrow 2\ MeCl_2 + CO_2$$

Note: maximum of $n_{CCl_4,conv} / n_{MeO}$ and $n_{CO_2,form} / n_{MeO}$ equals 0.5.

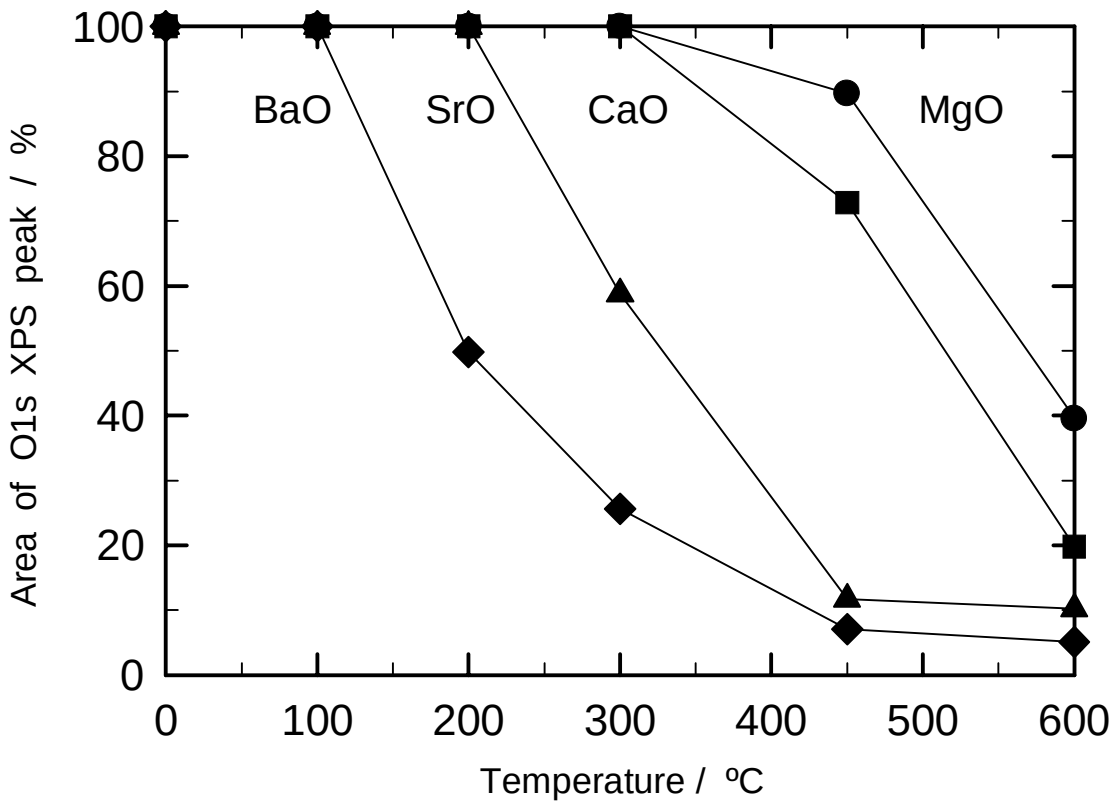
- We have studied this reaction on a series of commercially available alkaline earth metal oxides in a flow-type reactor and followed the transformation of the solid by *in situ* Raman and X-ray photoelectron spectroscopy.

* K.J. Klabunde, J. Stark, O. Koper, C. Mohs, D.G. Park, S. Decker, Y. Jiang, I. Lagadic and D. Zhang, J. Phys. Chem. 100 (1996) 12142-12153.

Experimental

- Before reaction, MgO, CaO, SrO and BaC_2O_4 (≥ 99.5 %) were treated overnight at 600 ºC in flowing oxygen.
- Surface areas (after calcination, using the BET-method): MgO: 38 m^2/g, CaO and SrO: 3 m^2/g, BaO: 2 m^2/g.
- Continuous flow reactor: feeding carbon tetrachloride (p = 6-30 Torr) diluted in helium under atmospheric pressure, effluent was analyzed by GC.
- Raman spectroscopy: continuous gas flow through the metal oxide (50 mg) in the cell, CCl_4 was injected in pulses of 10 µl liquid volume.
- XPS: CCl_4 was injected in one pulse (ratio CCl_4 : metal oxide of 20:1).

Activity of the Oxides at Various Temperatures



- X-ray photoelectron spectroscopy was used to monitor the chlorination of the metal oxides during the reaction with CCl_4 at temperatures of 200 to 600 ºC.
- The Cl2p XPS peak increases in intensity ($MeCl_2$) while the intensity of the O1s XPS peak of the metal oxide decreases.
- The activity of the alkaline earth metal oxides for the destructive adsorption of CCl_4 parallels the basicity and ionicity: BaO > SrO > CaO > MgO

Cyclic process for the regeneration of BaO

- In a cyclic process, the barium oxide (reacted with carbon tetrachloride into the chloride) can be regenerated.
- The hydrolysis of the chloride is followed by the precipitation of the carbonate and a final high-temperature treatment.

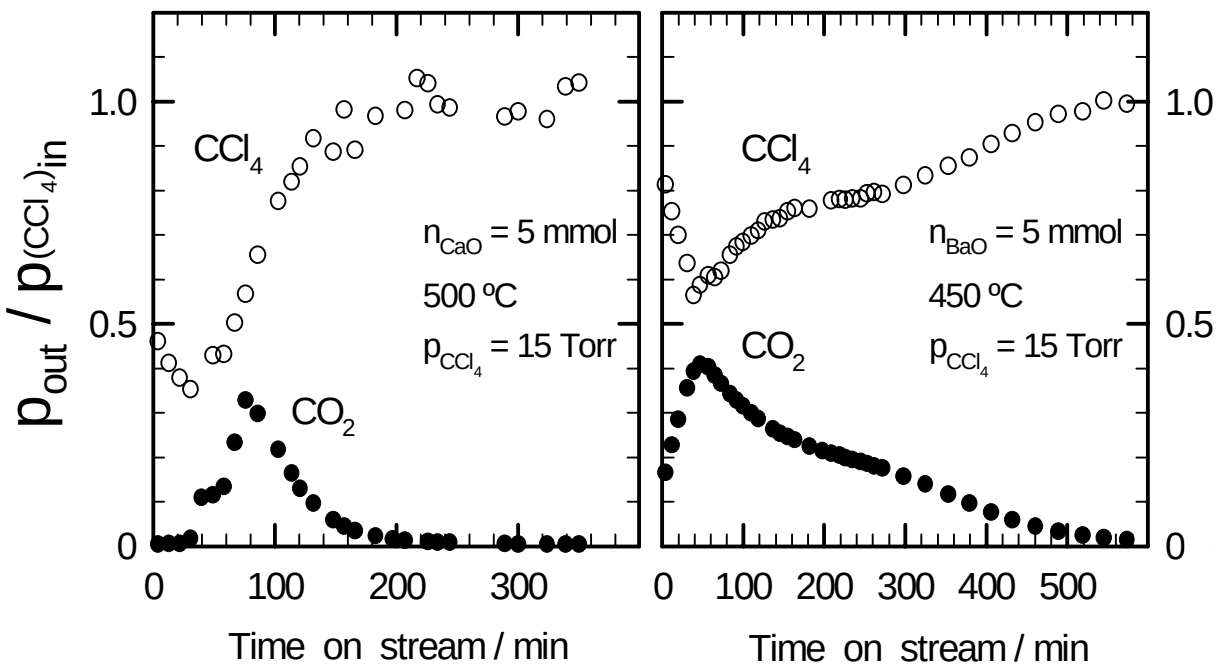
$$2\ BaO + CCl_4 \rightarrow 2\ BaCl_2 + CO_2$$

$$BaCl_2 + 2\ H_2O \rightarrow Ba(OH)_2 + 2\ HCl$$

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$

$$BaCO_3 \rightarrow BaO + CO_2$$

Conversion of CCl_4 and Formation of CO_2

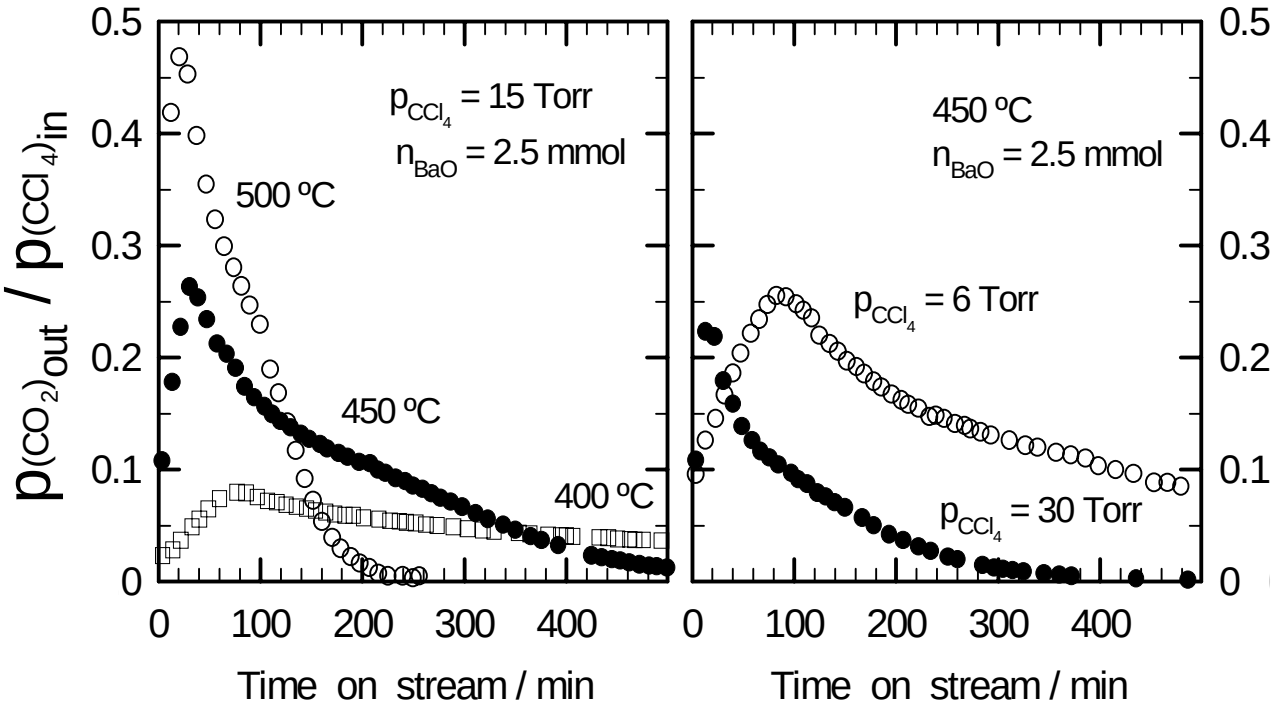


$\int n_{CCl_4,conv} / n_{CaO} = 0.2$ $\int n_{CCl_4,conv} / n_{BaO} = 0.5$

$\int n_{CO_2,form} / n_{CaO} = 0.1$ $\int n_{CO_2,form} / n_{BaO} = 0.5$

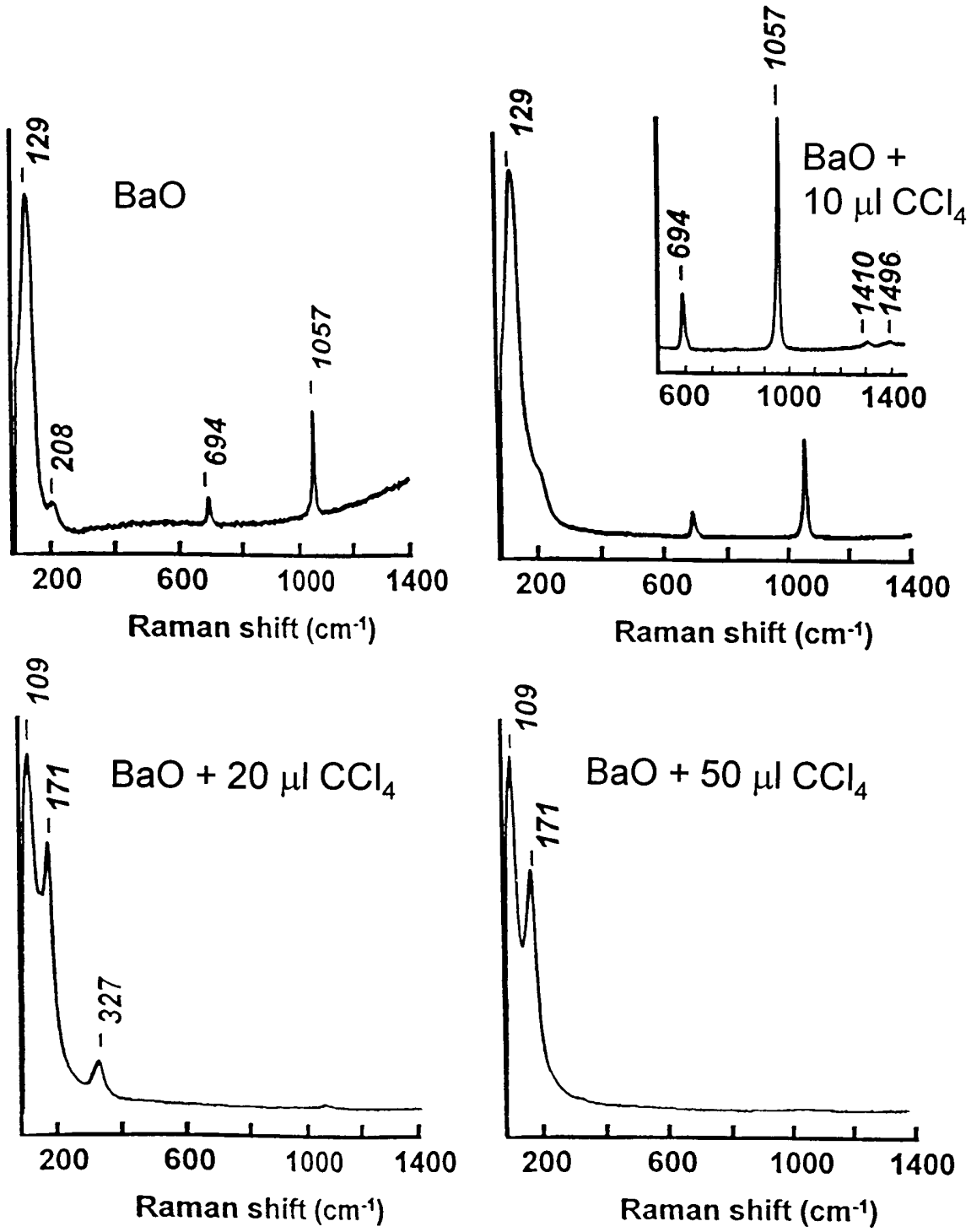
- In the reaction of CCl_4 below 500 ºC, CO_2 is the only detected gas phase product.
- On BaO at 500 ºC, small amounts of condensed products are formed.
- The amounts of converted CCl_4 and CO_2 produced reveal that BaO can be completely transformed into the chloride at 450 ºC.
- on CaO, part of the CO_2 product remains adsorbed on the mixed calcium oxide/chloride.

Influence of Temperature and CCl_4-Partial Pressure

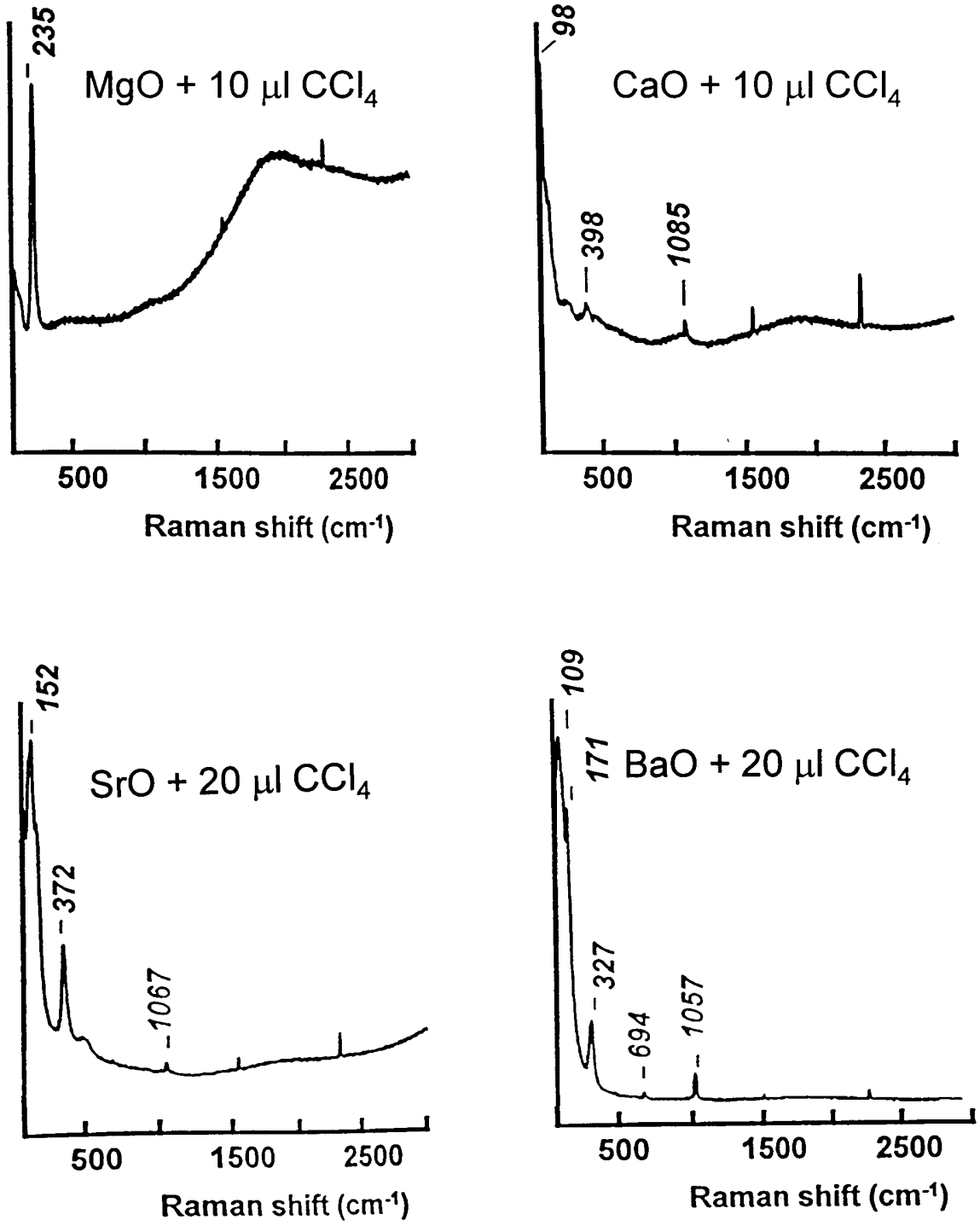


- At temperatures above 400 ºC, BaO can completely be converted into the chloride by the reaction with CCl_4.
- Increasing both the reaction temperature and the partial pressure of CCl_4 shortens the time until the transformation of the solid is completed.

Transformation of Barium Oxide at 600 °C



Reaction on Different Oxides at 600 °C

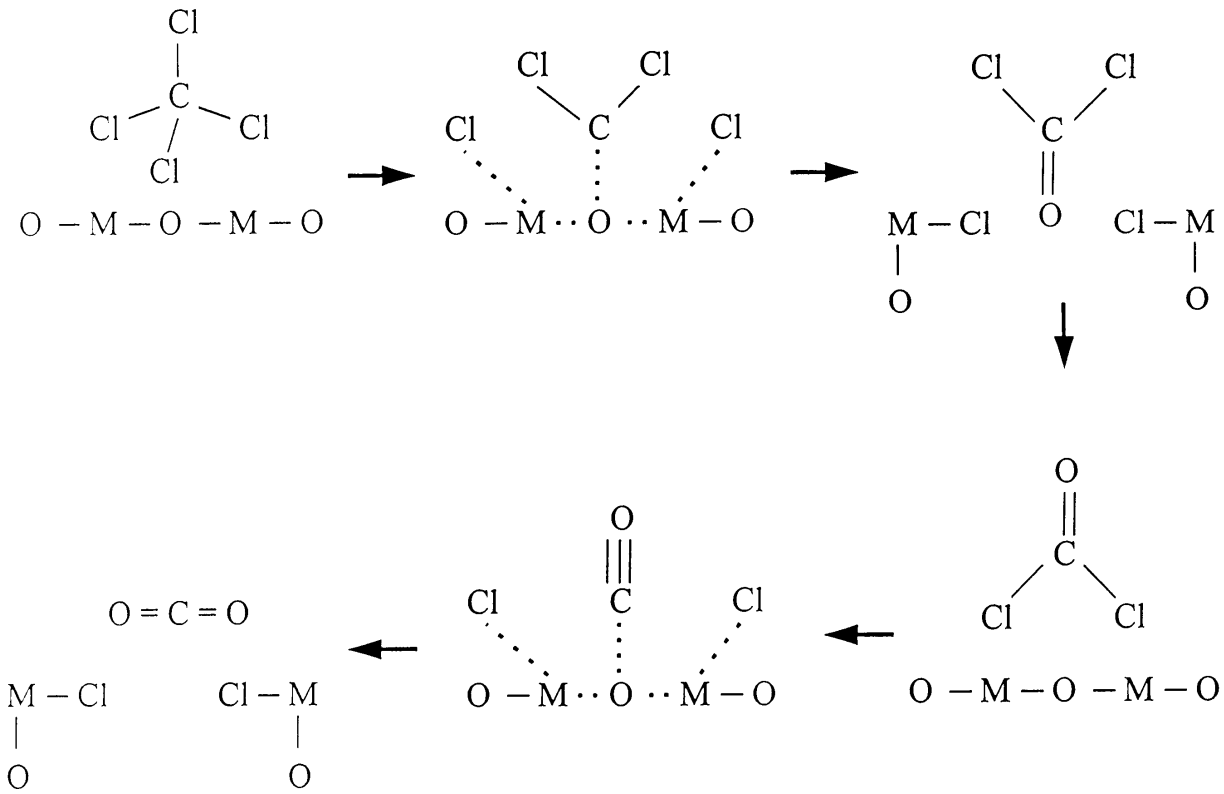


- After injection of CCl_4, new Raman bands arise which can be attributed to the corresponding $MeCl_2$.
- These bands increase with the amount of CCl_4 injected.
- At 600 ºC on BaO, SrO and CaO, with increasing amount of CCl_4, the bands of surface carbonates first increase and then completely disappear.
- On MgO, formation of a carbonate does not occur since $MgCO_3$ decomposes around 450 ºC.
- At 600 ºC, CCl_4 destruction also results in the formation of an unusual metal oxide chloride Me_4OCl_6 (Me = Ba, Sr or Ca).

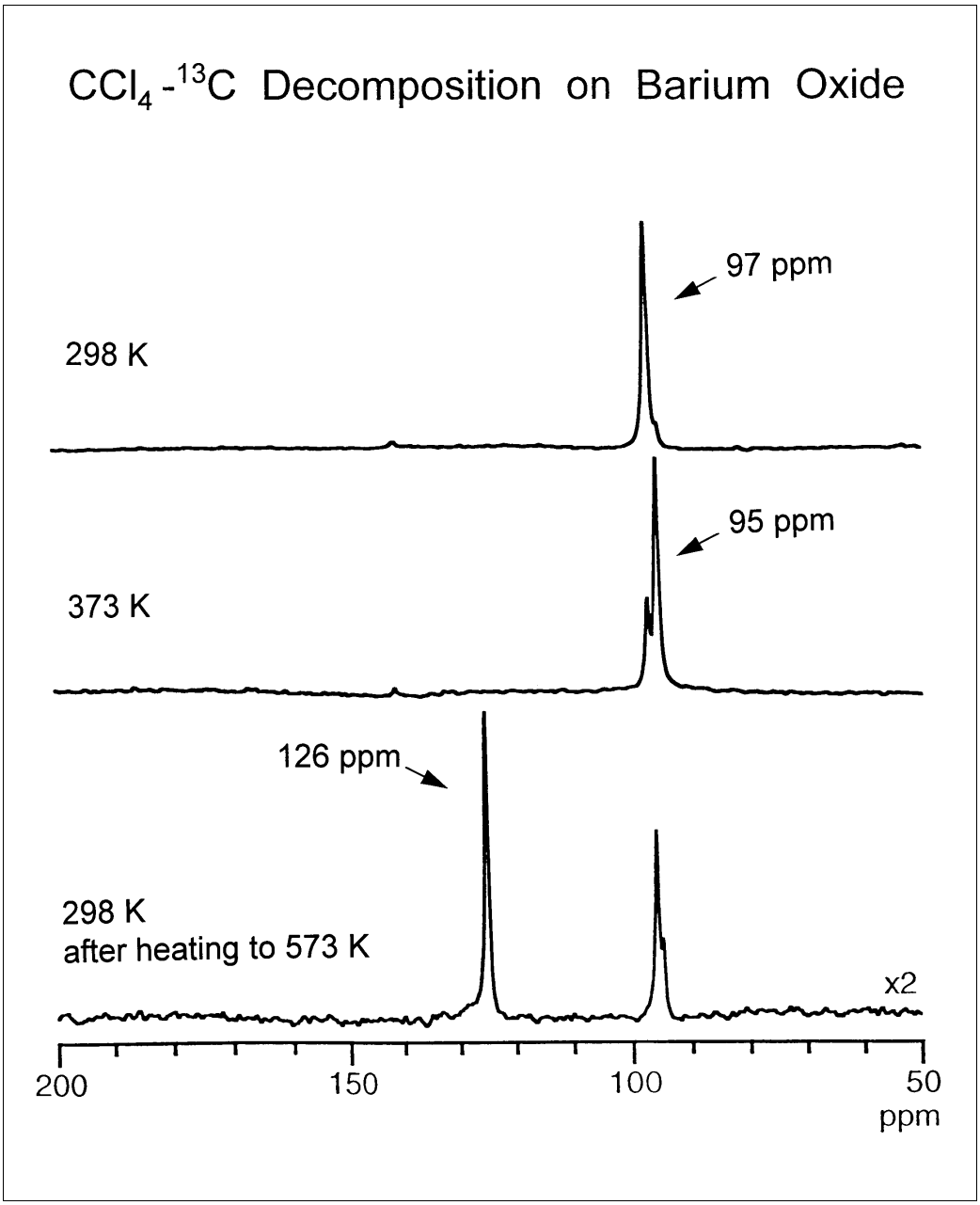
Raman Bands of Different Compounds

Material	Raman Frequencies / cm^{-1}
MgO	none
CaO	95; 109
SrO	98; 152
BaO	129; 208
$MgCl_2$	143; 235
$CaCl_2$	109; 120; 142; 193; 235
$SrCl_2$	183
$BaCl_2$	109; 171
$MgCO_3$ (surface)	1085
$CaCO_3$ (surface)	1083
$SrCO_3$ (surface)	710; 1067
$BaCO_3$ (surface)	689; 1057; 1410; 1496
Ca_4OCl_6	398
Sr_4OCl_6	372
Ba_4OCl_6	327

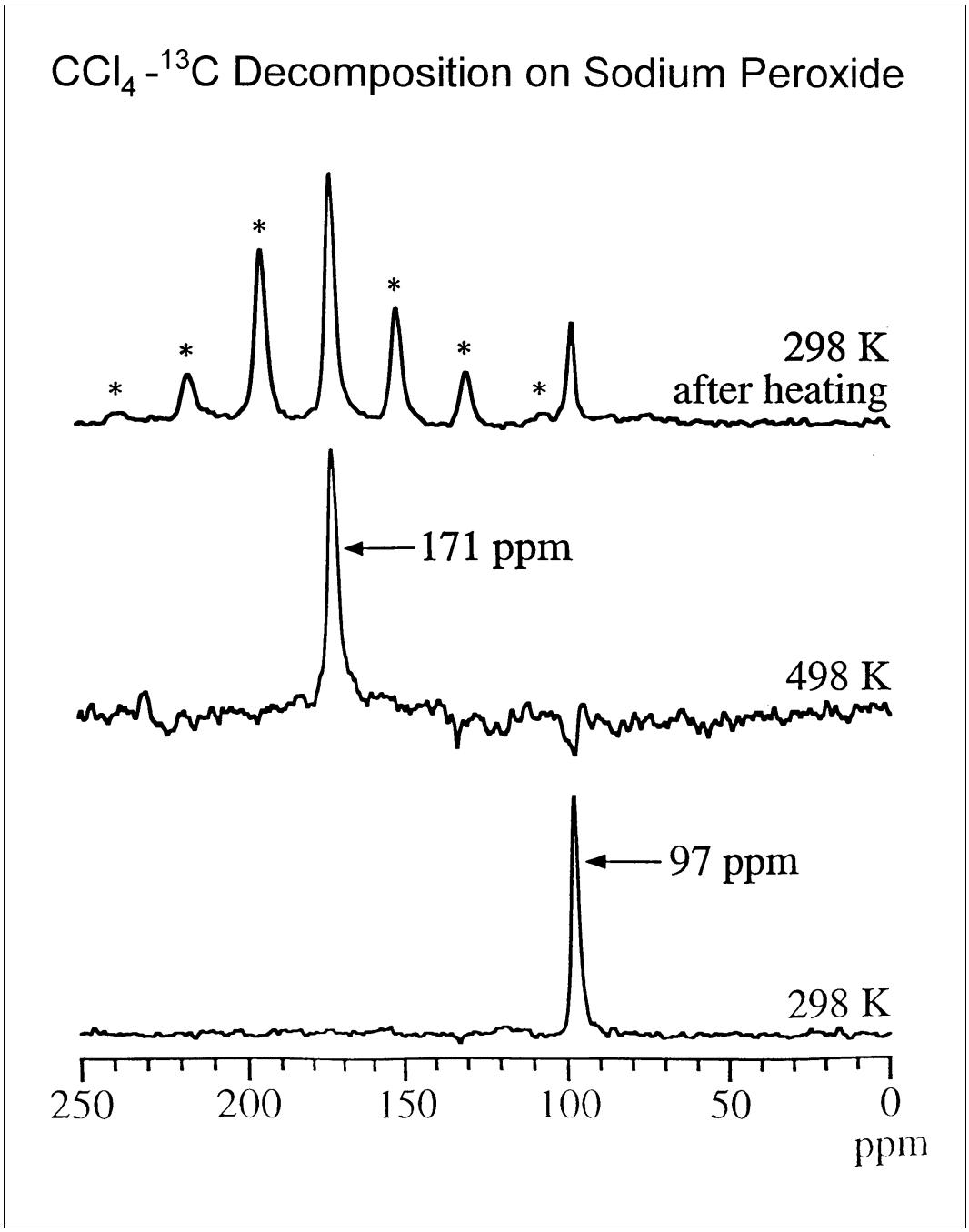
Mechanistic Scheme



Solid State NMR Spectroscopy



- At room temperature, CCl_4 is unreactive on BaO.
- At 373K, the amount of physisorbed species decreases; most of the CCl_4 is observed in the gas phase.
- After reaction at 573 K, a new signal at 126 ppm appears which is due to the formation of CO_2.



- At room temperature, CCl_4 is unreactive on Na_2O_2.
- It is converted completely to a carbonate species at 498K.
- The carbonate is likely in equlibrium with free CO_2 at this temperature.
- Upon returning the sample to room temperature, a static carbonate is observed.

Conclusions

The reactions of carbon tetrachloride, and to a lesser extent trichloroethylene, with metal oxides have been investigated. Emphasis has been placed on understanding the surface phase, as well as the bulk phases, that are present during these transformations. The results obtained lead to the following conclusions:

- Carbon tetrachloride is weakly adsorbed on a CaO(100) surface, primarily in the molecular form. A small amount of Cl remains on the surface at temperatures up to 1000 K, but sustained heating at 1000 K breaks the Ca-Cl bond, with the desorption of chlorine.

- Trichloroethylene reacts with FeO via an oxygen atom abstraction reaction, leaving Cl bound to Fe.

- Alkaline earth metal oxides are active materials for the destructive adsorption of CCl_4. The activity parallels the basicity of the oxide; i.e., BaO > SrO > CaO > MgO.

- The destruction process is essentially a bulk reaction that requires the continuous renewal of the metal oxide surface by O^{2-}/Cl^{-} exchange.

- In the case of barium, the resulting $BaCl_2$ can be recycled by dissolving it in water, followed by precipitation and calcination.

- Carbon tetrachloride completely reacts with Na_2O_2 at 498 K, forming a surface carbonate that is in equilibrium with gas phase CO_2. The Na_2O_2 appears to be considerably more reactive than BaO.

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