

THE ADSORPTION AND REACTION OF HALOGENATED
VOLATILE ORGANIC COMPOUNDS (VOC'S) ON METAL OXIDES

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Introduction

The interactions of carbon tetrachloride with strongly basic oxides and hydroxides have been studied by several techniques in order to understand the surface reactions and the subsequent bulk reactions that result in the destruction of the chlorinated hydrocarbon. Emphasis has been placed on understanding the surface phases, as well as the bulk phases, that are present during these transformations. As a result of the study with barium oxide, a reaction cycle has been demonstrated that may have practical significance in the removal of chlorinated hydrocarbons.

Surface Science Studies: The adsorption/reaction of CCl_4 with CaO

Ultra-thin CaO films were synthesized under ultrahigh vacuum (UHV) conditions by evaporating calcium onto a Mo(100) surface in a 5×10^{-7} Torr O_2 background. The CaO films were grown at 400 K followed by annealing to 1000 K for 10 min in an oxygen background to improve their crystalline quality. The rate of Ca evaporation and thus the growth rate of the CaO was determined by temperature programmed desorption (TPD) by acquiring TPD spectra as a function of the Ca deposition time. Well-defined features for monolayer and multilayer desorption were observed, the monolayer corresponding to a feature with a shoulder at ~930 K, which shifts to ~905 K, and the multilayer to a second feature at ~595 K, which appears and becomes more intense as the deposition time is increased. This second feature at ~595 K is characteristic of zero order desorption, indicating multilayer desorption of Ca from Mo(100). Using the leading edge analysis method, the heat of desorption of multilayer Ca was determined to be 34.5 kcal/mol. The TPD spectrum of Ca from Mo(100) shows complex desorption features above ~700 K, attributable to strong repulsive interactions between the Ca atoms in the submonolayer regime.

A (1×1) square LEED pattern for a 30 ML CaO film on Mo(100) was observed. The LEED spots of the 30 ML CaO/Mo(100) preparation are very diffuse, suggesting poor long-range order of the CaO film and is possibly due to the large lattice mismatch (8.1%) between CaO(100) and Mo(100). This large mismatch could lead to significant strain at the CaO/Mo(100) interface. Auger electron spectroscopy (AES) of a 30 ML CaO film grown on Mo(100) shows Ca(LVV) and O(KLL) transitions at 290 eV and 510 eV, respectively; no other transitions corresponding to impurities were observed. X-ray photoelectron spectroscopy (XPS) measurements also show no C 1s peak related to CaCO₃. The binding energy of the Ca 2p_{3/2} is 346.0 eV, in good agreement with that of bulk CaO(100) [1]. No extra feature on the high binding energy side (possibly due to CaCO₃) was observed. The O 1s XPS features appear at 529.4 eV with a very small shoulder at ~531.0 eV and are attributable to the oxide and peroxide, respectively. The ratio of the Ca to O XPS peaks was found to be 1±0.1, indicating a nearly stoichiometric CaO film.

TPD spectra were acquired for CCl₄ subsequent to its adsorption with increasing CCl₄ exposures on CaO/Mo(100) at 110 K. The parent peak was monitored using the fragment, CCl₃⁺, since the CCl₄⁺ fragment is unstable and dissociates to CCl₃⁺. A single desorption feature for CCl₄ is observed at 207 K. This feature shifts to 203 K and new desorption features develop at 167 K and 183 K as a function of the CCl₄ exposure. The intensity of the desorption feature at 167 K increases continuously as the exposure increases. This new desorption feature shows characteristic zero-order behavior, indicating desorption from multilayer CCl₄. The activation energy for desorption was measured to be 9.94 kcal/mol using the Redhead peak analysis method, a value that agrees well with the CCl₄ sublimation enthalpy of 9.28 kcal/mol [2]. Parent and fragment ions from CCl₄:m/q = 35 (Cl⁺), 47 (CCl⁺), 82 (CCl₂⁺) and 117 (CCl₃⁺) have the same desorption temperatures with identical

lineshapes, demonstrating that all ions are made in the same desorption process. No desorption peaks associated with CO, CO₂, OCl, CaCl, CaCl₂ were observed. Furthermore, neither carbon nor chlorine was detected with AES and XPS after thermal desorption to 1000 K.

The Cl 2p_{3/2} XPS spectra were obtained for 0.01 L CCl₄ adsorbed on 30 ML CaO/Mo(100) at 110 K with increasing annealing temperature. For a sample temperature of 110 K, three XPS peaks for Cl 2p appear at 201.3 eV and 203.1 eV, corresponding to the doublet of the chlorine 2p peak, and at 197.9 eV, possibly due to Cl⁻. After annealing to 185 K, the peak intensity for the Cl 2p feature is greatly reduced, and the peak positions shift to 200.9 eV, 202.7 and 198.9 eV, respectively. After annealing to 1000 K, the peak intensity for Cl 2p is reduced without any change in peak positions; however, this peak eventually disappears after annealing the sample to 1000 K for 5 min. Furthermore, XPS and AES measurements show no carbon or chlorine signal for a 0.01 L exposure of CCl₄ adsorbed on CaO after direct heating of the sample to 280 K, demonstrating that all CCl₄ and its fragments desorb from the CaO surface. The appearance of Cl peaks in the XPS spectra taken after annealing the sample to 800 K indicates that some irreversible photon induced decomposition or reaction of CCl₄ has occurred. Annealing the sample to 1000 K for 5 min apparently breaks the Ca-Cl bond followed by desorption of the chlorine ion or CaCl_x.

Nuclear Magnetic Resonance Studies: Reactions of CCl₄ with Strongly Basic Oxides and Hydroxides

High-resolution solid state MAS, NMR and complementary flow reactor studies have been used to investigate halocarbon decomposition over several alkaline earth metal oxides and alkali metal oxides, peroxides, and anhydrous hydroxides.

Klabunde and co-workers [3] have previously reported that “destructive adsorption” of CCl_4 occurs on the alkaline earth metal oxides MgO and CaO in a stoichiometric reaction to generate CO_2 and alkaline earth metal chlorides. Similarly, we used ^{13}C MAS NMR to probe the reaction of CCl_4 on MgO and BaO . CCl_4 - ^{13}C (Cambridge Isotopes, 99% ^{13}C) adsorbed on MgO at 298 K shows a single resonance of 97 ppm corresponding to a weakly physisorbed species. Heating to 348 K causes partitioning of CCl_4 between the physisorbed complex and the gas phase CCl_4 (95 ppm). Cycling of the temperature shows that this process is indeed completely reversible. Further heating to 573 K is required to begin the “destructive adsorption” described by Klabunde. BaO showed similar results at 573 K, but with better conversion of CCl_4 . In subsequent investigations CCl_3CH_3 - $^{13}\text{C}_2$ (Cambridge Isotopes, 99% $^{13}\text{C}_2$) adsorbed on both MgO and BaO was found to be unreactive even at temperatures as high as 573 K with contact times in excess of 1 hour. Furthermore, these temperatures are approaching the upper temperature limit of conventional high-resolution MAS NMR probes.

Obviously, if solid state *in situ* MAS NMR is to be used to investigate these types of reactions, stronger base and/or oxidizing substrates need to be implemented in order to reduce the temperature at which the reactions occur. Following this line of reasoning, we shifted from the alkaline earth metal oxides to the alkali metal oxides and peroxides.

^{13}C MAS NMR investigations of CCl_4 adsorbed on sodium oxide, Na_2O (Aldrich 99%), and sodium peroxide, Na_2O_2 (Aldrich 99%), showed chemistry nearly identical to that of the alkaline earth metal oxides but with the onset of reaction occurring at reduced temperature. Complete conversion of CCl_4 occurred by 498 K for both Na_2O and Na_2O_2 , indicating a negligible effect of the oxidizing property of the substrate upon CCl_4 destruction. In each system, the CO_2 product was

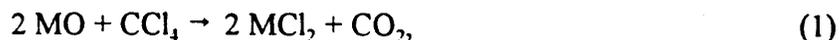
bound to the basic surface as a carbonate (^{13}C resonance at 171 ppm) as opposed to the gas phase CO, present for the alkaline earth metal oxides. X-ray powder diffraction of the reagent bed following CCl_4 destruction showed the presence of large amounts of NaCl.

Perhaps the most dramatic result of these preliminary investigations involving basic alkali metal compounds is the reaction of CCl_4 on anhydrous CsOH. ^{13}C MAS NMR studies of this system showed that complete conversion of CCl_4 to surface carbonate can be accomplished at temperatures as **low** as 373 K (200 K below the onset of reaction on MgO).

The strong influence of basicity of the substrate upon the temperature necessary for CCl_4 destruction has led us to consider the most basic of metal oxides, Cs_2O , for the destruction of halocarbon stocks. However, our preliminary investigations into the cesium oxide system has shown that commercially available materials sold as “Cesium Oxide” are in fact a mixture of cesium superoxide, CsO_2 , cesium peroxide, Cs_2O_2 ; and cesium hydroxides. Significant progress has been made in understanding the cesium/oxygen system with the use of ^{13}Cs MAS NMR. Currently, materials with purity greater than 95% have been prepared in useful quantities for CsO_2 , Cs_2O_2 , and at lower purity for Cs_2O . Investigations of halocarbon destruction on these materials is in progress.

Destructive Adsorption of CCl_4 on Alkaline Earth and Lanthanide Metal Oxides

The destructive adsorption of CCl_4 on basic metal oxides (MO), which may be described by the reaction



was studied on MgO, CaO, SrO and BaO 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 decreases in the order $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$, which also is consistent with the heats of reaction for eq. 1.

Barium oxide readily reacted with CCl_4 at 475-573 K and, at these low temperatures, CO, was the only gas-phase product that evolved from the surface. At higher temperatures, other alkaline earth oxides, such as CaO and MgO, also became active, and COCl_2 was found to be a gas phase reaction intermediate in the destruction of CCl_4 . Although the destruction process is initiated at the surface, the continuous $\text{O}^{2-}/\text{Cl}^-$ exchange results in the bulk transformation of the metal oxide to the metal chloride. MgO and CaO were only partially transformed into MgCl_2 and CaCl_2 , respectively, at temperatures up to 873 K, which is consistent with earlier findings of Klabunde and co-workers [1], but BaO was extensively converted into BaCl_2 . During the reaction of CaO, SrO and BaO with CCl_4 at 873 K a Raman band was observed at 300-400 cm^{-1} , which is attributed to a metal oxide chloride having the composition M_4OCl_6 . This material is believed to be an intermediate phase in the formation of MCl_2 . A mechanism is proposed in which a weakly bound form of CCl_4 (detected by NMR) reacts with the oxide to form gas phase COCl_2 (detected by IR) and a partially chlorided surface (detected by XPS). The phosgene further reacts to produce the final chlorided material (detected by XPS and Raman) and CO, (detected by IR and NMR).

For practical considerations, it was significant to observe that BaO could be regenerated by dissolving the chloride in water, followed by precipitation as barium carbonate and subsequent calcination.

Preliminary studies on the destructive adsorption of CCl_4 on La_2O_3 and CeO_2 have been carried out. La_2O_3 is much more active than CeO_2 , and CCl_4 destruction started at around 573 K with the rapid formation of LaOCl and the release of CO_2 into the gas phase. The complete transformation of LaOCl into LaCl_3 is much more difficult to obtain, and requires high reaction temperatures and large amounts of CCl_4 . In the case of $\text{CeO}_2/\text{CCl}_4$ destruction starts at around 723 K and is accompanied by the reduction of Ce(IV) to Ce(III). CeOCl is detected as an intermediate product, and complete transformation of CeO_2 into CeCl_3 is only observed at 873 K.

References

1. M. I. Sosulnikov and Yu A. Teterin, *J. Electron Spectros. Related Phenom.* 59 (1992) 111.
2. CRC Handbook of Chemistry and Physics, 68th ed. (CRC Press, Boca Raton, Florida, 1987-88) C-664.
3. K. J. Klabunde, J. Stark, O. Koper, C. Mohs, G. D. Park, S. Decker, Y. Jiang, I. Lagadic and D. Zhang, *J. Phys. Chem.* 100 (1996) 12142; O. Koper, I. Lagadic and K. J. Klabunde, *Chem. Mater.* 9 (1997) 838.