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

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Research Objective

The goal of the research is to elucidate the properties of the materials responsible for the activation of halocarbons and the nature of the intermediates formed in the dissociative adsorption of this class of compounds. This information is essential for interpreting and predicting stoichiometric and catalytic pathways for the safe destruction of halocarbon pollutants. The specific objectives are: (1) to study the adsorption and reactivity of chloromethanes and chloroethanes on metal oxides; (2) to identify the reaction intermediates using spectroscopic methods; and (3) to develop kinetic models for the reaction of these halocarbons with oxide surfaces.

Research Progress and Implications

This report summarizes work after 20 months of a 36-month project. Emphasis has been placed understanding the surfaces phases, as well as the bulk phases that are present during the reactions of chlorinated hydrocarbons with strongly basic metal oxides. Most of the research has been carried out with carbon tetrachloride.

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. The CaO films were grown at 400 K followed by annealing to 1000 K in an oxygen background to improve their crystalline quality. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) did not reveal the presence of any impurities, including carbonate ions, on the surface. The ratio of the Ca to O XPS peaks was found to be nearly 1, indicating a nearly stoichiometric CaO film.

Temperature-programmed desorption (TPD) desorption spectra were acquired for CCl_4 subsequent to increasing CCl_4 exposures on Ca/Mo(100) at 110 K. A single desorption feature was observed at 207 K. This feature shifted to 203 K and new desorption features developed at 167 K and 183 K as a function of the CCl_4 exposure. The desorption feature at 167 K shows characteristic zero-order behavior, indicating desorption from multilayer CCl_4 . No desorption peaks associated with CO, CO_2 , OCl, CaCl or CaCl_2 were observed. Furthermore, neither carbon nor chlorine was detected with AES and XPS after thermal desorption at 1000 K.

The Cl XPS spectra were obtained after CCl_4 adsorption at 110 K with increasing annealing temperature. XPS and AES measurements showed no carbon or chlorine signals after direct heating of the sample to 280 K, demonstrating that all CCl_4 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 CCl_4 occurred. Annealing the sample to 1000 K for 5 min apparently breaks the Ca-Cl bond followed by desorption of the chlorine ion or CaClx .

Destructive Adsorption of CCl_4 on Alkaline Earth Oxides: Destructive adsorption in this context involves the reaction of CCl_4 with a metal oxide to form the corresponding metal chloride and CO_2 . The reaction has been followed over the alkaline earth oxides as a function of the amount of CCl_4 injected and the reaction temperature. By using XPS and Raman spectroscopy, it was found that the activity toward CCl_4 parallels the basicity of the oxide; i.e., the activity decreased in the order $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$. Barium oxide begins to react with CCl_4 at 200-300° C, and, at these low

temperatures, CO₂ was the only gas phase product that evolved from the surface. At higher reaction temperatures, other oxides such as CaO and MgO also become active, and COCl₂ was found to be an intermediate. Although the destruction process is initiated at the surface, the continuous O₂²⁻/Cl⁻ exchange results in the bulk transformation of the metal oxide to the metal chloride. At higher temperatures, these solid state reactions involve an unusual alkaline earth metal oxide chloride; viz., M₄OC₁₆ (M=Ba, Sr or Ca).

With BaO it is possible to go through a reaction cycle by dissolving the chloride in water, followed by precipitation of the barium carbonate. Subsequent calcination of the carbonate results in the formation of the original oxide. Based on favorable thermodynamics, one can conceive of several catalytic cycles involving BaO. For example, the addition of H₂O to CCl₄ should result in the continuous formation of HCl and CO₂ as reaction products.

NMR Studies of the Reaction of CCl₄ with strongly Basic Oxides: Nuclear magnetic resonance (NMR) evidence suggests that sodium oxide and sodium peroxide may be superior to even barium oxide for the stoichiometric destruction of CCl₄ and C₂H₃Cl₃. The reaction occurs at temperatures as low as 275° C. Cesium hydroxide also was surprisingly active, but solid sodium hydroxide was unreactive under similar conditions. The reaction of ¹³CCl₄ with BaO was followed in a rotor at temperatures between 25° C and 300° C. Heating the sample to 300 C caused the desorption of physisorbed CCl₄ and the formation of CO₂, which is consistent with results obtained by FT-IR spectroscopy and gas chromatography. No other carbon-containing species were detected by NMR.

Planned Activities

Research will continue on the reactions of CCl₄ with thin films of well characterized oxides. On conventional oxides, emphasis will be placed on the catalytic destruction of CCl₄, either by reaction with H₂O or O₂. Elementary steps in the reaction cycle will be followed using in-situ FT-IR and Raman spectroscopies. NMR spectroscopy will be used to examine both the gas phase and the solid phase during stoichiometric reactions over alkali metal oxides, peroxides and superoxides.