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Dimethyl methylphosphonate decomposition on fully oxidized and partially reduced ceria thin films

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ABSTRACT

The thermal decomposition of dimethyl methylphosphonate (DMMP) on crystalline ceria thin films grown on Ru(0 0 0 1) was studied by temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and infrared absorption reflection spectroscopy (IRAS). TPD experiments show that methanol and formaldehyde desorb as the two main products at 575 K, while water, formaldehyde and CO are produced above 800 K. IRAS studies demonstrate that DMMP adsorbs via the phosphoryl oxygen at 200 K, but the P═O bond converts to a bridging O—P—O species at 300 K. DMMP decomposition initially occurs via P—OCH_3 bond scission to form methyl methylphosphonate (MMP) and methyl phosphonate (MP) between 300 and 500 K; XPS and IRAS data are consistent with a methoxy intermediate on the surface at these temperatures. The more stable P—CH_3 bonds remain intact up to 700 K, and the only surface intermediate at higher temperatures is believed to be PO_x. Although the presence of PO_x decreases activity for DMMP decomposition, some activity on the ceria surface remains even after 7 cycles of adsorption and reaction. The ceria films become reduced by multiple DMMP adsorption-reaction cycles, with the Ce^{+4} content dropping to 30% after seven cycles. Investigations of DMMP reaction on reduced ceria surfaces show that CO and H_2 are produced in addition to methanol and formaldehyde. Furthermore, DMMP decomposition activity on the reduced ceria films is almost completely inhibited after only 3 adsorption-reaction cycles. Similarities between DMMP and methanol chemistry on the ceria films suggest that methoxy is a key surface intermediate in both reactions.

1. Introduction

The development of materials for the catalytic decomposition of organophosphorus nerve agents, such as VX, Sarin and Soman, is a research area of critical importance for national security. While carbon adsorbents have been employed in filtration devices for decontamination in the field, the adsorption is reversible and has limited capacity. Dimethyl methylphosphonate (DMMP, $(CH_3O)_2PO(CH_3)$) is frequently used as a simulant molecule for understanding the activity of the organophosphorus nerve agents because DMMP is nontoxic but has structural similarities to the nerve agents. Despite excellent activity for breaking C—H, C—P and P—O bonds, transition metal surfaces are poor catalysts for organophosphorus decomposition due to poisoning of active sites by phosphorus byproducts [1–5]. More recently, MgO and CaO nanoparticles have been used as reactive adsorbents for organophosphorus compounds, but the surface reactions are stoichiometric rather than catalytic, ultimately limiting the capacity for decomposition of the chemical agents [6–10]. The metal oxide surfaces are believed to be passivated by the formation of PO_x or metal phosphates [9,11–13]. However, there is evidence that highly reducible metal oxides like ceria and titania are less susceptible to phosphorus poisoning from DMMP decomposition. For example, ceria powders have been reported to be highly active for DMMP decomposition, and this unusual activity was attributed to the ability of lattice oxygen to participate in the reaction [14]. In a previous study, it was reported that the TiO_2(1 1 0) surface maintains some activity for DMMP decomposition after multiple cycles of adsorption and reaction [15]. Moreover, phosphorus from DMMP decomposition could be removed from titania by heating in oxygen.

In this work, we are investigating the thermal chemistry of DMMP on crystalline ceria thin films under ultrahigh vacuum conditions in order to develop a fundamental understanding of the decomposition of organophosphorus compounds on ceria. Ceria is known as a good catalytic material, particularly for reactions requiring a medium for oxygen storage [16]. Ordered ceria thin films grown on Ru(0 0 0 1) are ~2–5 nm thick [17–19] and exhibit

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high reflectivity associated with the metal support, providing high signal intensity in the infrared reflection absorption spectroscopy (IRAS) experiments; these ultrathin films are also sufficiently conductive for X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). The ceria thin films have been extensively studied and characterized by the Mullins group [17,20,21]. Another advantage of working with the ceria films is that the oxidation states of ceria can be controlled. For the fully oxidized CeO_2 films, low energy ion scattering studies indicate that the surface is predominantly oxygen-terminated, and the films exhibit sharp LEED patterns characteristic of the (1 1 1) surface of the fluorite structure [20]. STM studies show that the ceria films are atomically flat with single-layer high steps and terraces of 50–100 nm, and the films can be imaged with atomic scale resolution [17]. However, Lu et al. have demonstrated that the film growth conditions can influence the quality of the film [22]; morphological differences in the film are evident in STM but not in LEED. For the reduced CeO_x films grown in a lower pressure of O_2, ion scattering indicates that a significant amount of Ce is exposed due to numerous oxygen vacancies [20].

2. Experimental

CeO_2(1 1 1) and partially reduced CeO_x(1 1 1) films were grown *in situ* by vapor deposition of cerium onto a Ru(0 0 0 1) surface held at 700 K under an oxygen atmosphere. This procedure has been described in detail in several previous publications [19,20,23]. The reduced ceria films were prepared by decreasing the oxygen background pressure from 10^{-7} Torr to 10^{-8} Torr unless otherwise specified. Growth of labeled $Ce^{18}O_2$(1 1 1) films was achieved by substituting $^{16}O_2$ with labeled $^{18}O_2$ obtained from Cambridge Isotopes (>95% isotopic purity). The Ce oxidation states were determined from XPS data for the Ce 3d and Ce 4d regions by fitting the spectra with a linear combination of pure Ce^{+3} and Ce^{+4} spectra [21,24].

Before all experiments, DMMP was purified by multiple freeze–pump-thaw cycles. In some cases, the DMMP sample was found to be contaminated by methyl bromide, which was removed by immersing the DMMP bottle in a water–ice bath and pumping on it for 10 h. Molecular sieves were also placed in the DMMP bottle to eliminate water, and IRAS data for DMMP multilayers did not indicate any impurities.

Temperature programmed desorption (TPD), conventional XPS and IRAS experiments were performed in two different chambers at Oak Ridge National Laboratory (ORNL). The base pressure in the TPD/XPS system was 2×10^{-10} Torr. TPD spectra were recorded by a UTI 100C mass spectrometer, and the temperature was ramped at a rate of 2 K/s using an RHK TM310 temperature programmer. During heating in front of the mass spectrometer, the sample was biased at −70 V to prevent surface damage due to electrons from the mass spectrometer ionizer. DMMP was dosed at 150 K through an effusive gas doser [25,26] to minimize desorption from the sample holder, and the crystal was flashed to >600 K prior to DMMP exposure to remove ambient water adsorbates. XPS experiments were carried out with a MgKα anode and a Physical Electronics double pass cylindrical mirror analyzer [24]. The reduced ceria films in the TPD experiments were ∼65% Ce^{+4}.

For the IRAS experiments, the near-stoichiometric films were >99.5% Ce^{+4} and 85% Ce^{+4} according to XPS, while the CeO_x films were highly reduced with ∼30% Ce^{+4}, corresponding to $CeO_{1.65}$. IRAS data were collected with a Mattson Infinity infrared spectrometer by passing the light through a ZnSe wire grid p-polarizer, reflecting off of the sample at a ∼85° angle and focusing onto a liquid nitrogen-cooled MCT detector. All spectra were acquired at 4 cm^{-1} resolution and summed over 1000 scans. The spectrum of the ceria film prior to DMMP exposure was used as the background. Dry air-purged bags enclosed the entire beam path, but some minor water interference was removed from the spectra by manually subtracting reference water spectra collected with the experimental setup. The crystal was initially cooled to 100 K and transferred into a turbomolecularly-pumped IR cell. Heating to the various temperatures was performed at a rate of ∼1 K/s, and the sample was re-cooled to 100 K during collection of IR spectra. DMMP was introduced into the IR cell at $\sim 10^{-5}$ Torr above the base pressure; this exposure was sufficient to produce condensed DMMP multilayers on the surface.

Soft X-ray photoelectron spectroscopy (sXPS) was conducted using synchrotron radiation on beamline U12a at the National Synchrotron Light Source (NSLS), and the associated UHV system has been described elsewhere [23,24]. The base pressure in this system was $<4 \times 10^{-10}$ Torr. The sXPS data were collected with a VSW 125 hemispherical analyzer using a photon incident angle of 35° and electron emission angle of 30° with respect to the surface normal. Binding energies were referenced to the position of a satellite peak at 122.3 eV in the Ce(4d) spectrum [19]. C(1s), O(1s) and P(2p) spectra were collected at beam energies of 400 eV, 600 eV and 340 eV, respectively, and the instrumental resolution was roughly 0.5 eV. The CeO_2 films were reduced by exposure to acetone at 600 K for 20 min at a pressure of 2×10^{-6} Torr above the base pressure. Previous studies show acetone is an effective reductant for CeO_2 [25], and an analysis of the XPS Ce(4d) region indicated that the reduced CeO_x films were ∼50% Ce^{+4}.

3. Results

3.1. TPD and conventional XPS studies

3.1.1. On stoichiometeric ceria (CeO_2)

The reaction of DMMP on fully oxidized ceria produces formaldehyde (30 amu, CH_2O) and methanol (31 amu, CH_3O) as the major gaseous products (Fig. 1a). The main desorption peaks for both products occur at 575 K, but small desorption features are also observed at 440 K; trace amounts of H_2O desorption are detected at 575 K. Furthermore, a smaller high temperature peak for formaldehyde appears at 800 K and is accompanied by H_2O desorption (18 amu) at the same temperature. The evolution of DMMP itself is monitored at 79 amu (PO_3) since this is one of the more intense large fragments of DMMP observed in the mass spectrum. DMMP evolution occurs at ∼200 K in a sharp peak that is attributed to multilayer desorption, but there are also smaller desorption features at 240 K and 420 K. Masses other than those corresponding to the cracking fragments of the identified products are not observed. Specifically, there is no H_2 (2 amu), methane (16 amu), CO_2 (44 amu), PO (47 amu) and PO_2 (63 amu) beyond the intensities expected from DMMP cracking. Dimethyl ether production was monitored at mass 46 amu, as further discussed in the next paragraph. All of the 28 amu signal at 575 K can be accounted for by cracking of formaldehyde and methanol, demonstrating that the production of CO does not occur; however, the 28 amu signal at 800 K most likely has some contribution from CO. The assignment of the 31 amu peak to methanol is confirmed by the 31:32 amu ratio, which is the same as for pure methanol. The assignment of the 79 amu peak at 420 K to DMMP rather than PO_3 or some other fragment is based on a comparison of the 47:63:79:94:124 amu ratios for the desorbing product with those of DMMP itself. Similarly, identification of the 30 amu desorption species as formaldehyde is based on the 29:30 amu ratio after both of these signals are corrected for methanol fragmentation. Given that the 30:31 amu ratio for pure methanol leaked into the cham-