Adsorption and reaction of formaldehyde on thin-film cerium oxide

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Abstract

Formaldehyde adsorption and reaction have been studied on cerium oxide thin films that were vapor deposited on Ru(0001). The formaldehyde behavior was examined as a function of temperature, exposure and Ce oxidation state. Formaldehyde chemisorbs on fully oxidized CeO_2 as dioxymethylene, CH_2O_2. The dioxymethylene decomposes and desorbs as formaldehyde between 200 K and 400 K. No other products are formed. On reduced ceria, formaldehyde also adsorbs as dioxymethylene. In addition to the formaldehyde desorption between 200 K and 400 K, a more strongly bound form of dioxymethylene is formed that produces formaldehyde at 440 K. Above 400 K, some of the dioxymethylene reacts to form formate and methoxy on the surface. These species decompose to produce H_2, CO and CH_2O above 500 K.
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1. Introduction

Cerium oxide is commonly used in three-way auto exhaust catalysts as well as in water–gas-shift catalysts due to its oxygen storage capacity [1,2]. Cerium oxide catalysts are also of interest in other chemical processes such as the production of functionalized hydrocarbons. Many of these processes involve the production and interconversion of simple C_1 molecules such as methane, methanol, formaldehyde and formic acid [3]. Investigations of adsorption, decomposition and production of these C_1 molecules on well-defined cerium oxides provide insights for the understanding of the mechanisms in the actual industrial reactions.

On metal surfaces, submonolayer coverages of formaldehyde generally dehydrogenate to form CO [4–7]. Various intermediates such as formyl, methoxy and formate have been identified during formaldehyde decomposition. High doses of formaldehyde on metal surfaces may result in polymerization of formaldehyde to paraformaldehyde at low temperatures [6–8]. Pre-adsorbed oxygen may also induce the polymerization of formaldehyde [9–11].

The adsorption and reaction of formaldehyde have been studied on ZnO [12], MgO [13], Cr_2O_3 [14] and TiO_2 [15] single-crystal surfaces as well as on silica, pure and fluorided alumina, magnesia, titania, thoria, zirconia, iron oxide, $ZnAl_2O_4$ [16,17] and ceria powders [18]. Formaldehyde decomposition is greatly dependent on the nature of the oxides. Various intermediate species and reactivity have been observed. For example, the $(000\bar{1}) - O$ polar face of ZnO is not active toward formaldehyde decomposition. Only gaseous formaldehyde was detected between 160 K and 500 K. However, on the (0001)-Zn polar face, formaldehyde decomposes to CO, CO_2 and H_2 via a formate intermediate [12]. On both a MgO film and a MgO(100) single crystal surface, simultaneous formation of methoxy and formate were observed upon formaldehyde adsorption [13]. These species are the result of a Cannizzaro-type disproportionation reaction at the surface base sites. The study of formaldehyde adsorption on TiO_2(001) demonstrates that the decomposition is sensitive to the oxidation

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state of the Ti and the presence of O vacancies [15]. Formaldehyde reacts with the reduced titania surface containing O vacancies and lower oxidation states of Ti to produce methanol both at 370 K and 550 K. However, the high temperature methanol desorption is suppressed on the fully oxidized surface. This is because the higher temperature methanol is suggested to result from formaldehyde reduction on the reduced, oxophilic Ti^{x+} ($x < 4$) sites. Lorenzelli's group studied the adsorption and transformation of formaldehyde on oxide powders such as silica, alumina, magnesia, titania, thoria, zirconia and iron oxide [16,17]. They found that either polyoxymethylene or dioxymethylene were formed on the oxides. Heating the surface above room temperature resulted in the disproportionation of dioxymethylene to formate and methoxy species. This process competes with the direct oxidation of dioxymethylene to formate on oxides.

Formaldehyde decomposition on cerium oxide powder was investigated by Li et al. [18]. Formation of dioxymethylene and polyoxymethylene species were observed on both oxidized CeO_2 and on the partially reduced CeO_2 powder. The dioxymethylene can either decompose to methoxy and formate via a Cannizzaro reaction mechanism above 373 K or to formate directly via the oxidation of dioxymethylene. These formate species further decompose above 573 K and leave carbonate and isolated OH groups on the surface. Li et al. concluded that the Cannizzaro reaction was more favorable on the partially reduced cerium oxide powder.

In this paper, the gaseous products formed following the adsorption and decomposition of formaldehyde on highly oriented cerium oxide films were investigated with temperature-programmed desorption. Surface intermediates were characterized by core-level soft X-ray photoelectron spectroscopy (SXPS) and near edge X-ray absorption spectroscopy (NEXAFS). Various ceria films with different oxidation states were prepared and X-ray photoelectron spectroscopy was used to characterize their oxidation states. The effects of the oxidation states of the cerium oxide films and the formaldehyde coverage were examined.

2. Experimental

The experiments were performed in two different UHV chambers. The temperature programmed desorption (TPD) experiments were performed in a chamber at ORNL. The temperature was ramped at 3 K/s and the sample was biased -70 V to prevent electrons generated by the mass spectrometer ionizer from stimulating reactions at the surface. The chamber was also equipped with a cylindrical mirror analyzer and a Mg anode X-ray source. Ce 3d, 4d or valence band photoemission spectra were used to determine the Ce oxidation state [19]. Soft X-ray photoelectron spectroscopy (SXPS) and Near-edge X-ray absorption fine structure (NEXAFS) were performed in a chamber at the National Synchrotron Light Source. Experiments were conducted on beamline U12A. C 1s SXPS spectra were recorded using 410 eV excitation. The binding

energies were referenced relative to the Ru(0 0 0 1) Fermi edge. Other extrinsic factors that could influence peak position, such as charging or band bending, were checked by recording the Ce 4d spectrum at a given photon energy.[1]

NEXAFS was performed at the C k-edge. The energy resolution was less than 0.5 eV and the photon energy was calibrated using the dip in the photon flux at 284.7 eV [20]. The reported spectra were recorded at normal photon incidence although the spectra were unchanged at grazing incidence. The X-ray absorption was recorded using a partial yield electron detector. The high-pass retarding grid was set at -215 V. Third order X-ray excitation of the Ce M_{IV} and M_V edges created apparent absorption peaks at 295 eV and 301 eV. The absorption due to only higher order radiation was determined by recording spectra with a retarding grid voltage of -315 V, i.e., greater than the first-order wavelength. The background resulting from the higher order excitation was subtracted from the NEXAFS spectra. The spectra with adsorbate were then normalized to spectra taken without adsorbate.

$CeO_2(1 1 1)$ films were grown in situ on Ru(0 0 0 1) as has been described previously [21]. Briefly, $CeO_2(1 1 1)$ was produced by depositing Ce metal in an $^{16}O_2$ ambient of 2×10^{-7} Torr while the Ru was at 700 K. In one series of experiments $^{18}O_2$ (Cambridge Isotopes, >95 at% ^{18}O) was used in order to study the incorporation of lattice oxygen into the reaction products. The Ce flux was monitored by a mass spectrometer during deposition to ensure reproducible results. After deposition the sample was annealed to 900 K. The ceria films were estimated to be ≈5 nm thick based on the attenuation of the Ru AES or Ru 3d XPS intensities. In general, the films used in the SXPS and NEXAFS experiments may have been slightly thicker than those used in the TPD experiments. Reduced cerium oxide films were produced by growing a film at a lower oxygen pressure or by exposing a $CeO_2(1 1 1)$ film to methanol as described previously [22].

Gaseous formaldehyde was produced by heating paraformaldehyde powder (Aldrich) to 90 °C in a glass tube attached to the gas manifold. Prior to use, formaldehyde was purified by continuous pumping on the paraformaldehyde powder with periodic heating. The gas manifold was pumped out and refilled before each dose and the purity of formaldehyde was checked with the mass spectrometer. Water, methanol and methyl formate have been reported as possible impurities following the decomposition of paraformaldehyde [4,5]. There were no impurities found in formaldehyde except a trace amount of methanol at very high H_2CO exposures. The relative intensities of cracking fragments from CH_2O were determined by comparing the intensities in the desorption of a formaldehyde multilayer at 105 K. Formaldehyde produces cracking fragments at

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[1] The Ce 4d X''' peak position is 122.3 eV when referenced against the Ru Fermi edge. In Ref. [19] the Ce 4d X''' peak position was reported as 122.8 eV. Similarly, the O 1s and valence band peak positions are 0.5 eV lower than reported in Ref. [19].