Adsorption and reaction of methanol on thin-film cerium oxide

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Abstract

Methanol adsorption and reaction has been studied on cerium oxide thin films that were vapor deposited on Ru(0 0 0 1). The methanol behavior was examined as a function of temperature and Ce oxidation state. Methanol reacts at low temperatures with fully oxidized CeO_2 to produce water at 200 K while formaldehyde and methanol desorb near 560 K. This leads to the reduction of the ceria. On reduced ceria, more methanol can be adsorbed and it undergoes more extensive decomposition producing CO and H_2 near 640 K in addition to formaldehyde and water. As the degree of ceria reduction increases, more H_2 and less H_2O are produced. TPD experiments using isotopically labeled CH_3OD show that deuterated water is produced from the oxidized surface at low temperatures, whereas the deuterium is stabilized on the reduced surface and is incorporated into the dihydrogen that desorbs near 600 K. High resolution C 1s and O 1s XPS and C k-edge NEXAFS measurements were performed to quantify the amount of methanol adsorbed and to identify the adsorbed species.
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1. Introduction

Cerium oxide is a principal component in automotive exhaust catalysts [1]. Its primary function is as an oxygen storage medium. In this regard, reactive gases may either lose oxygen to oxygen deficient ceria or remove oxygen from the ceria. These processes aid in reduction and oxidation reactions.

It has generally been observed that in a UHV environment, most adsorbates require oxygen vacancies on the ceria surface in order to adsorb and therefore most gases do not strongly interact with the fully oxidized surface [2–6]. We are investigating a series of molecules in which a reactive atom, such as O or S, may provide a means for a molecule to attach to the surface.

There are many cases on both metals and oxide surfaces where methanol adsorbs by breaking the O–H bond form-

ing a methoxy on the surface [7–12]. The fate of the surface methoxy is typically quite different on metals and oxides, however. On metals the methyl group rapidly dehygrogenates leaving CO and adsorbed H [7–9]. These eventually desorb as gaseous CO and H_2 and temperature programmed desorption is similar to a coadsorbed layer of CO and H_2. On oxides the rupture of the C–H bonds is more selective leading to methanol recombination or formaldehyde as products [10–12]. On TiO_2 and Cr_2O_3 surfaces C–O bond cleavage has been observed leading to CH_4 formation [11,12]. In cases where the C–O bond is broken, or where O can be removed from the substrate, CO_2 and H_2O may also be reaction products [12–14].

Two previous studies have examined the adsorption of methanol on cerium oxide surfaces. Siokou and Nix adsorbed CH_3OH at 300 K on ceria films grown on Cu(1 1 1) [13]. The primary desorption products were CO and H_2 that desorbed near 580 K with smaller amounts of H_2O, CH_2O, CH_3OH and CO_2 desorbing at a similar temperature. Ferrizz et al studied CH_3OH adsorption on single crystal $CeO_2(1 1 1)$, CeO_2 grown on yttria-stabilized

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zirconia (YSZ) and ceria films on $Al_2O_3(0001)$ [14]. Only a small amount of methanol reacted with the fully oxidized $CeO_2(111)$ surface and this produced formaldehyde at 680 K. More methanol adsorbed on a sputtered $CeO_2(111)$ surface however the reaction products and desorption temperatures were unchanged. In particular, CO and H_2 were not observed. The $CeO_2/YSZ(100)$ surface demonstrated more methanol adsorption than the single crystal as well as CO, H_2O and H_2 desorption in addition to H_2CO and CH_3OH. The authors conducted a series of methanol adsorption/desorption cycles and with each cycle the amount of CO and H_2 increased while the amounts of the other products decreased. An intermediate behavior was observed for methanol on CeO_2/Al_2O_3. Initially only a small amount of methanol adsorbed producing CH_2O and CH_3OH in a manner similar to the $CeO_2(111)$ single crystal. Following successive adsorption/desorption cycles, the amount of methanol adsorbed, and the amount of formaldehyde produced, increased after each cycle. After several cycles, CO production was observed. Ferriz et al. concluded that the methanol was adsorbing at surface oxygen vacancies and that the product distribution progressed from CH_2O to CO as the number of oxygen vacancies increased. They proposed that their results were consistent with those of Siokou and Nix if the films grown on Cu(111) were not fully oxidized.

Siokou and Nix also studied the intermediates formed after methanol adsorption by infrared vibrational spectroscopy [13]. They concluded that CH_3O-species were formed and they were able to distinguish methoxy in different adsorption sites. They did not detect any OH species on the oxide. Under certain conditions, such as pre-oxidizing an annealed film before CH_3OH adsorption, they detected HCOO intermediates that decomposed forming CO_2. Methoxy intermediates in multiple adsorption sites were also observed by Namai et al. on $CeO_2(111)$ by non-contact atomic force microscopy [15].

The current work expands on these previous studies in a number of significant ways. We observe formaldehyde and water desorption following methanol adsorption on a fully oxidized $CeO_2(111)$ film grown on Ru(0001). CO and H_2 desorption are only seen when the ceria surface is reduced. In this regard we concur with the proposal of Ferriz et al. that the surfaces studied by Siokou and Nix were not fully oxidized. However, we see substantially more methanol chemisorption than was reported by Ferriz et al. on the oxidized surface. Further, the methanol adsorption only doubles on the reduced surface which is a substantially smaller increase than was reported by Ferriz et al. Therefore we conclude that while O vacancies will facilitate methanol adsorption, they are not a necessary condition for methanol adsorption.

Methanol is a powerful reductant for the ceria films. For this to occur, O atoms have to be removed from the ceria lattice. The earlier studies reported weak water desorption at elevated temperatures that did not appear to account for a significant amount of ceria reduction. In the present study we have observed water desorption at 200 K that was not observed in either of the previous studies because they conducted their adsorptions at room temperature. Isotopic labeling using CH_3OD and $Ce^{18}O_2$ indicated that this low temperature water resulted from a reaction between the deuterium in the alcohol and ^{18}O in the ceria. On a reduced surface, water formation is suppressed and hydroxyls are formed on the surface that recombine and desorb as H_2 at elevated temperatures. Isotopic labeling and O 1s SXPS provide direct evidence of the hydroxyl formation on the reduced surface.

We have used SXPS and NEXAFS to identify the surface intermediates. The SXPS also enabled us to quantify the concentrations of the surface intermediates. CH_3O and OH were the only surface species detected. We did not observe formate as was reported by Siokou and Nix on some of their surfaces, nor did the SXPS provide direct evidence for methoxy adsorption in different types of adsorption sites [13]. In particular, while we observed binding energy differences between methoxy absorbed on oxidized and reduced surfaces, we did not see multiple types of species coexisting on any given surface. Based on their IR spectra, Siokou and Nix reported methoxy species adsorbed simultaneously in top, bridge and hollow sites on the Ce cations.

A unique aspect of this study was the use of $^{18}O_2$ to grow the cerium oxide film. The appearance of the ^{18}O label in the desorption products provides new insights into the interaction between the methanol adsorbate and the ceria substrate.

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. 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 on beamline U12A. C 1s and O 1s SXPS spectra were recorded using 410 eV and 600 eV excitation, respectively. The binding energies were referenced relative to the Ru(0001) 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 [16].[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 [17]. The X-ray absorption was recorded using a

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[1] The Ce 4d X''' peak position is 122.3 eV when referenced against the Ru Fermi edge. In Ref. [16] 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. [16].