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Adsorption and reaction of methanethiol on thin-film cerium oxide

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Abstract

The adsorption and reaction of methanethiol, CH_3SH, have been studied on cerium oxide thin films that were vapor deposited on Ru(0001). The behavior of the CH_3SH was examined as a function of the Ce oxidation state. CH_3SH weakly interacts with fully oxidized $CeO_2(111)$ forming both chemisorbed CH_3SH and $CH_3S + OH$. OH forms through the reaction of the sulfhydrol H with the surface O. These species recombine and desorb near 180 K leaving the surface virtually clean. When the ceria is ca. 50% reduced, the chemisorbed CH_3SH desorbs near 150 K while the $CH_3S + OH$ are stable to 400 K. These species react above 450 K to produce predominantly CH_4 and CH_3SH. A small amount of CH_2O and water are also formed through reaction with the O in the ceria. Atomic S is left on the surface. S 2p, C 1s and O 1s soft X-ray photoelectron spectroscopy were used to identify the nature of the chemisorbed species and the adsorption site of the CH_3S or S.
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Keywords: Cerium; Thermal desorption spectroscopy; Soft X-ray photoelectron spectroscopy; Methanethiol

1. Introduction

Cerium oxide has been identified as a possible material for use as a sorbent or catalyst for desulfurization processes [1]. Since ceria is also an active component in automotive exhaust catalysts, it is potentially susceptible to S-poisoning from S-containing molecules in the exhaust stream. In order to obtain a fundamental understanding of the interactions between S-containing molecules and cerium oxide, we are investigating the adsorption and reaction of selected molecules on well characterized $CeO_X(111)$ thin films.

The S-containing molecules in fossil fuels are mostly complex polyaromatic species. However, the study of the interaction of simple S-containing molecules with model catalytic surfaces provides the building blocks for understanding the interactions of more complex chemical species. A number of studies have investigated the interaction of H_2S with different oxide surfaces [2–8], and we have previously reported on the interaction of H_2S on $CeO_X(111)$ [9]. The examination of CH_3SH has been more limited with results on $TiO_2(111)$ [10], ZnO(0001) and ZnO$(000\bar{1})$ [11] having been reported. The general observation is that these thiols (SH containing species) interact with the cations in the oxide. Depending on the strength of the adsorption, dissociation can occur as the sample is heated. The interaction of the thiols with the cations is in contrast to SO_2 which interacts with the O centers [12–18].

There are obvious similarities between CH_3SH and CH_3OH or H_2S, and methanethiol's reactivity could possibly be predicted based on the behavior of these other molecules on cerium oxide. We have shown that CH_3OH [19] and H_2S [9] are able to adsorb on fully oxidized $CeO_2(111)$ and form CH_3O– and HS– intermediates that are stable to elevated temperatures. Although the $CeO_2(111)$ surface is terminated by an O layer, this layer is relatively open and adsorbates can bind to the Ce^{4+} ions in the second layer because Ce cations are not fully coordinated to eight O anions. The results in this paper indicate that CH_3SH interacts much more weakly with the fully oxidized surface compared to H_2S or CH_3OH.

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When the ceria is partially reduced to $CeO_X(111)$, CH_3OH and H_2S interact more strongly with the Ce cations by adsorbing in the O vacancies. CH_3SH also interacts more strongly with reduced ceria and readily dissociates into $CH_3S + H$ which are stable to 500 K. Above 500 K these surface fragments react to produce predominantly CH_3SH and CH_4. This differs from methanol where there is no indication of C–O bond cleavage to produce methane. Methanethiol also produces very little H_2O or H_2 whereas these are the primary decomposition products from hydrogen sulfide.

2. Experimental

The experiments were performed in two different UHV chambers. The temperature programmed desorption (TPD) experiments were performed in a chamber at Oak Ridge National Laboratory. 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 to record Ce 3d photoemission spectra that were used to determine the Ce oxidation state [20]. Soft X-ray photoelectron spectroscopy (sXPS) was performed on beamline U12A at the National Synchrotron Light Source. S 2p and C 1s core-levels were recorded using 410 eV excitation, and O 1s spectra were recorded using 600 eV excitation. 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 [19]. In the sXPS experiments, Ce 4d and valence band spectra were used to determine the Ce oxidation state [20].

$CeO_2(111)$ films were grown *in situ* on Ru(0001) as has been described previously [21,22]. Briefly, $CeO_2(111)$ was produced by depositing Ce metal in an O_2 ambient of 2×10^{-7} torr while the Ru was at 700 K. 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 ca. 5 nm thick based on the attenuation of the Ru AES or Ru 3d XPS intensities. Reduced cerium oxide films were produced by growing a film at a lower oxygen pressure or by exposing a $CeO_2(111)$ film to methanol as described previously [19].

In the TPD experiments, exposures of CH_3SH (Matheson, 99.5%) were performed through a directed doser to enhance the gas flux on the CeO_2 surface, to minimize exposure to the sample holder and to the back of the Ru(0001) substrate, and to minimize the background signal during TPD [23]. A typical 200 s exposure was approximately equal to 20 L ($1\ L = 1 \times 10^{-6}$ torr s). Exposures in the sXPS experiments were performed by backfilling the chamber through a leak valve.

3. Results

3.1. Temperature programmed desorption

CH_3SH was adsorbed on fully oxidized ceria at 100 K, and the resulting temperature programmed desorption (TPD) spectra are shown in Fig. 1. The only desorption products were CH_3SH (Mass 48), CH_4 (Mass 16) and a small amount of H_2 (Mass 2) and H_2O (Mass 18). No SO_X, S_X, $(CH_3S)_2$, $(CH_3)_2S$ or CH_2O were detected. A pronounced CH_3SH peak is observed at 180 K. This is associated with chemisorbed or recombinant methanethiol. Physisorbed/multilayer desorption occurs below 120 K [10,24,25]. Methane desorption occurs over a broad range from 250 to 450 K. The Mass 2 and Mass 18 peaks below 200 K are probably associated with methanethiol interaction with the mass spectrometer. The intensity of the water peak near 280 K was weak and is consistent with the amount of water anticipated from the background based on the TPD from CH_3SH on Ru(0001) run just prior to growing the ceria film in these experiments.

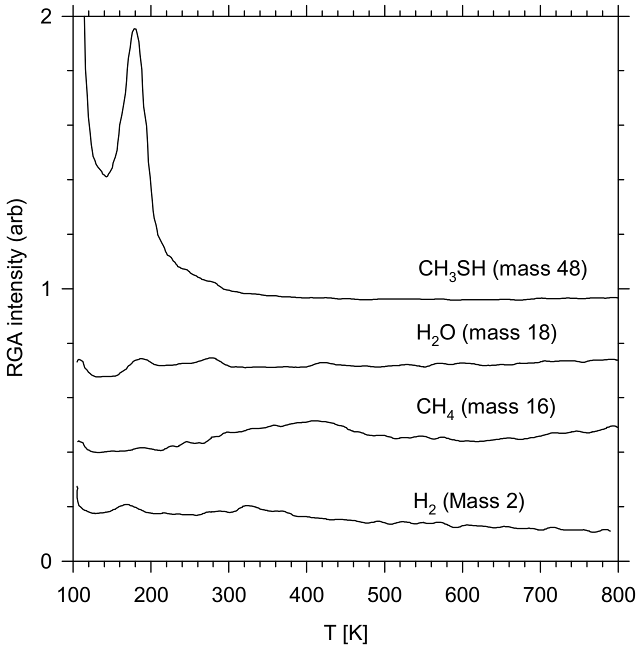

Fig. 1. Temperature programmed desorption following CH_3SH exposure on $CeO_2(111)$ at 100 K.

CH_3SH was also adsorbed on a partially reduced $CeO_{1.75}(111)$ film at 100 K (Fig. 2). The predominant product is methane at 600 K. CH_3SH also desorbs at higher temperatures with a primary peak near 610 K and a smaller, broader feature centered near 520 K. The weakly chemisorbed CH_3SH shifts to a lower desorption temperature near 150 K. In addition to the products noted above, we also monitored CO, CO_2, OCS and hydrocarbon fragments. None of these products were observed. The only additional desorption products compared to the fully oxidized films are a small amount of CH_2O (Mass 29, the most