

Adsorption and reaction of hydrogen sulfide on thin-film cerium oxide [☆]

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Abstract

The adsorption and reaction of hydrogen sulfide, H₂S, have been studied on cerium oxide thin films that were vapor deposited on Ru(0001). The behavior of the H₂S was examined as a function of Ce oxidation state. H₂S weakly chemisorbs on fully oxidized CeO₂ desorbing near 155 K. Hydrogen from the H₂S reacts with the surface O to desorb as water between 200 K and 450 K. When ca. 20% of the Ce⁴⁺ is reduced to Ce³⁺ more H₂S dissociates to –OH and –SH and water is produced near 580 K. When the ceria is ca. 70% reduced, water formation is suppressed and H₂ desorbs near 580 K. S 2p photoelectron spectroscopy indicates the decomposition of H₂S into –SH and then –S as the sample is annealed from 100 K to 600 K. O 1s photoemission indicated the presence of H₂O and –OH.

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1. Introduction

Sulfur is a pervasive environmental pollutant. Trace amounts of sulfur in fossil fuels such as coal and gasoline can be oxidized to SO_x during combustion. SO_x species are toxic in their own right but also produce acid rain when combined with moisture in the upper atmosphere. S is also known to poison automotive three-way catalysts and NO_x storage materials.

Cerium oxide is a key component in automotive exhaust catalysts. Its primary function is an O storage medium, releasing O under fuel rich conditions and absorbing O during lean fuel conditions. The facile removal of O from the ceria lattice produces an accommodating site for

adsorption of S in the O vacancy. The replacement of O by S reduces the O storage capacity of the ceria.

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.

H₂S adsorption has been studied on MgO(100) [1], Al₂O₃ [2], Cr₃O₄/Cr₂O₃ [3], Cu₂O [4], UO₂ [5], TiO₂ [6,7] and ZnO [8]. The general observation is that the S interacts with the cationic centers and H₂S deprotonates to produce adsorbed HS and S. There is no tendency to produce SO_x species. This is in contrast to the adsorption of SO₂ on oxide surfaces [9–12], including ceria [13–15], where the S interacts with the O anions to produce surface sulfate and sulfite.

The results in this paper suggest similar results specifically that H₂S decomposes on ceria to produce adsorbed SH and S. There is no evidence of SO_x species. There is a clear indication of water desorption following H₂S exposure which suggests that S replaces O in the lattice.

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The adsorption and decomposition of H₂S can be compared with O-containing adsorbates such as H₂O [16,17], CH₃OH [18–20] and CH₂O [21]. These molecules bind to the surface through the O atom. The adsorption is facilitated by O vacancies on the surface but they are also capable of adsorbing on a fully oxidized surface. This suggests that adsorption occurs in both atop sites and threefold hollow site on the Ce cations. In this study it is shown that much less S adsorbs compared to O species indicating that adsorption in the low coordination sites is not as favorable for S.

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 an Mg anode X-ray source. Ce 3d, 4d or valence band photoemission spectra were used to determine the Ce oxidation state [22]. Soft X-ray photoelectron spectroscopy (sXPS) was performed in a chamber at the National Synchrotron Light Source. Experiments were conducted on beamline U12A. S 2p 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 [20].

CeO₂(111) films were grown *in situ* on Ru(0001) as has been described previously [23,24]. Briefly, CeO₂(111) was produced by depositing Ce metal in an ¹⁶O₂ ambient of 2×10^{-7} Torr while the Ru was at 700 K. In one series of experiments ¹⁸O₂ (Cambridge Isotopes, >95% ¹⁸O) 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 ca. 5 nm thick based on the attenuation of the Ru AES or Ru 3d XPS intensities. In general, the films used in the sXPS 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 CeO₂(111) film to methanol as described previously [20].

In the TPD experiments, exposures of H₂S (Matheson, 99.5%) were performed through a directed doser to enhance the gas flux on the CeO₂ 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 [17]. A typical 200 second exposure was approximately equal to 20 L (1 L = 1×10^{-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

H₂S was adsorbed on fully oxidized and partially reduced ceria at 100 K. The only desorption products were H₂S, H₂O and H₂. In particular, no S_X (monitored by fragments at Mass 32 or 64) or SO_X products were observed. The temperature programmed desorption was studied as a function of the Ce oxidation state. The desorption of H₂S (Mass 34), H₂O (Mass 18) and H₂ (Mass 2) are shown in Figs. 1–3, respectively. The top spectra from the oxidized CeO₂ surface in each figure were recorded after modifications had been made to improve the chamber vacuum. Hence the baselines are flatter and the H₂ and H₂O spectra have less noise.

Weakly chemisorbed H₂S desorbs at 155 K on oxidized CeO₂ (Fig. 1, top). As the surface becomes more reduced, the desorption energy of the H₂S decreases nearly linearly with the Ce oxidation state. When the surface is ca. 90% Ce³⁺ the H₂S desorption temperature is 115 K. There are no H₂S desorption states at higher temperatures from any of the ceria surfaces.

Two prominent water desorption features are observed from oxidized CeO₂ at 155 K and 220 K (Fig. 2, top). Desorption also occurs in a broad, structureless decay that extends to above 400 K. Note that the top spectrum has been magnified by a factor of three to help visualize the desorption relative to the background. The intensity of

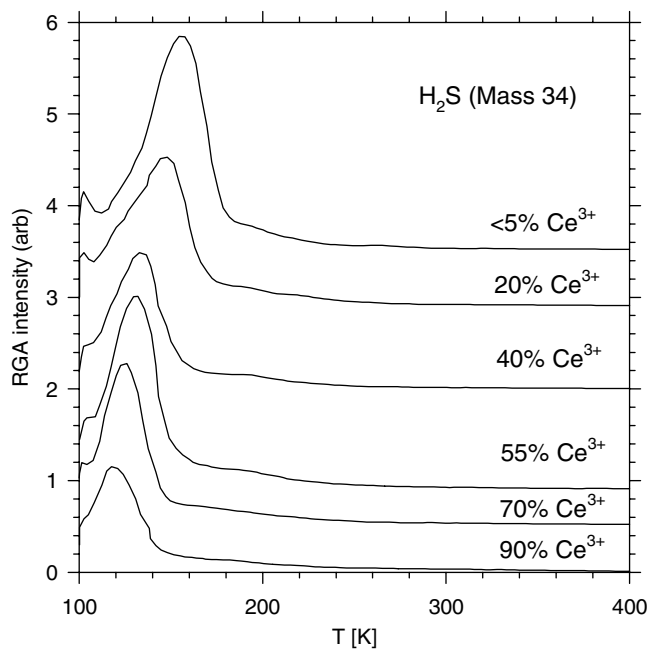


Fig. 1. Desorption of H₂S following H₂S exposure to CeO_x(111) at 100 K as a function of the Ce oxidation state.

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