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Adsorption of CO and C_2H_4 on Rh-loaded thin-film dysprosium oxide

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Abstract

A dysprosium oxide thin film was deposited on Ru(0001) by vapor depositing Dy in 2×10^{-7} torr O_2 while the Ru was at 700 K. The film was ca. 5 nm thick and produced a p(1.4 × 1.4) LEED pattern relative to the Ru(0001) substrate. The adsorption and reaction of CO and C_2H_4 adsorbed on Rh supported on the Dy_2O_3 film were studied by TPD and SXPS. The CO initially reacted with loosely bound oxygen in the substrate to produce CO_2. After the loosely bound oxygen was removed, the CO adsorbed non-dissociatively in a manner similar to what is seen on Rh(111). C_2H_4 adsorbed on the Rh particles and underwent progressive dehydrogenation to produce H_2 during TPD. The C from the C_2H_4 reacted with the O in Dy_2O_3 to produce CO. CO dissociation on the Rh particles could be promoted by treating the Dy_2O_3 with C_2H_4 before CO exposure.

Keywords: Dysprosium; Rhodium; Carbon monoxide; Ethylene; Soft X-ray photoelectron spectroscopy; Catalysis

1. Introduction

Dysprosium oxide, Dy_2O_3, forms the bcc type-c or bixbyite crystal structure. The structure is closely related to the fluorite structure formed by quadrivalent rare-earth and actinide oxides such as CeO_2 and UO_2. The metallic ions occupy the same positions in the bixbyite and the fluorite structures. In the bixbyite structure the oxygen atoms occupy three quarters of the positions occupied in the fluorite structure. The oxygen atoms relax slightly from their ideal fluorite positions in response to the oxygen vacancies.

The ideal (111) surface terminations of fluorite and bixbyite are shown in Fig. 1. Previous work using ion scattering [1] and STM [2] have indicated that CeO_2 terminates on a single oxygen layer. On the bixbyite surface, the oxygen vacancies cluster in groups of four. Ion scattering and STM have also shown that the reduction of CeO_2 to CeO_{2-X} progresses from a fluorite to a bixbyite-like structure through the removal of O anions. Therefore, the (111) surface of Dy_2O_3 may be similar to CeO_{2-X}.

We have observed that the activity of Rh supported on CeO_X changes as a function of the Ce oxidation state. In particular, the Rh particles are more effective in dissociating CO [3,4] or NO [5] if the Ce is reduced. One proposal is that the change in activity is the result of the Rh particle's morphology. The morphology may be influenced by the presence of O vacancies on the surface which may act as nucleation sites and may also stabilize the particles. Alternatively, the Rh activity may be influenced by an electronic interaction between the Ce and the Rh.

The structural, i.e. O vacancy hypothesis can be tested by using a surface where the O vacancies are present yet the cations cannot be oxidized further, thus mitigating any electronic interaction. Dy_2O_3 provides such a surface.

Our results indicate that Rh supported on as-grown Dy_2O_3 does not dissociate CO. This demonstrates that O vacancies by themselves are not sufficient for activating the Rh particles. Surprisingly, however, the Rh can be activated by treating the Rh/Dy_2O_3 surface with C_2H_4.

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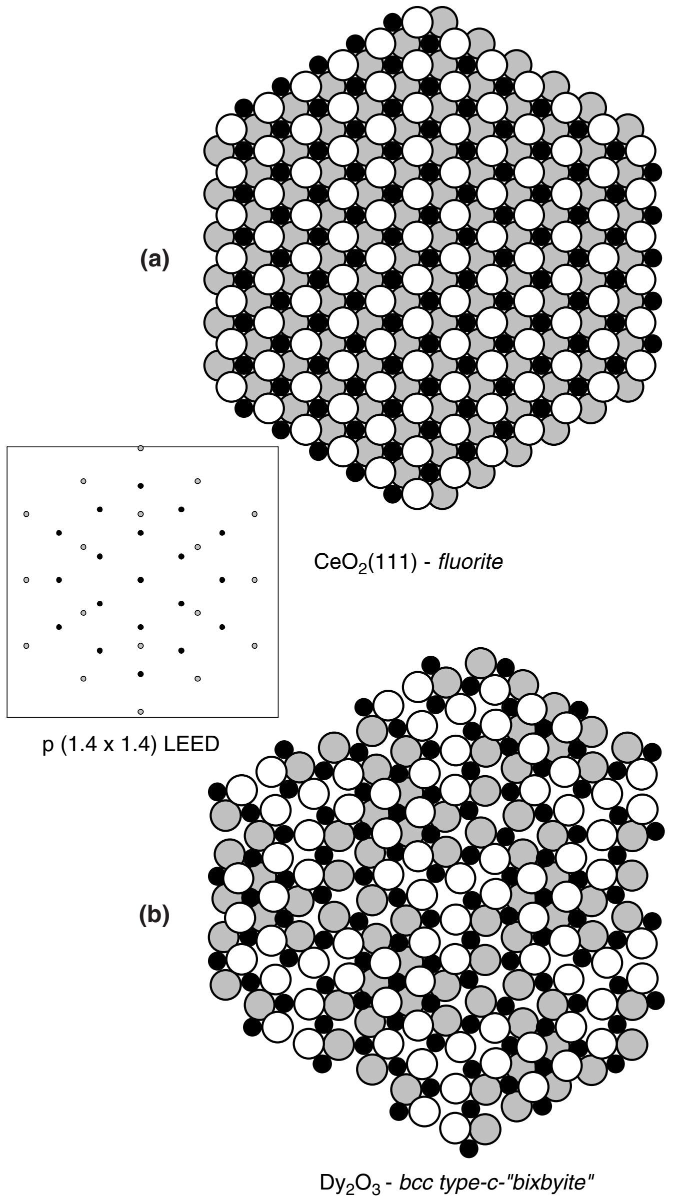

Fig. 1. (1 1 1) surface planes of (a) the fluorite lattice formed by CeO_2 and (b) the bcc type-c or "Bixbyite" lattice formed by Dy_2O_3. The white circles are first layer oxygen atoms, the black circles are Dy cations and the gray circles are subsurface O atoms. The inset shows the p(1.4 × 1.4) LEED pattern from the CeO_2 film (black circles) relative to the p(1 × 1) LEED pattern from the Ru(0 0 0 1) substrate (gray circles).

Ethylene adsorbed on Rh/Dy_2O_3 thermally decomposes and produces H_2 and CO. Therefore chemical reduction of the dysprosia will activate the Rh particles. This is surprising since, unlike ceria, it should not be possible to easily remove O from the dysprosia.

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) was performed in a chamber at the National Synchrotron Light Source. Experiments were conducted on beamline U12A. C 1s and Dy 4d spectra were recorded using 480 eV excitation. The binding energies were referenced relative to the Ru(0 0 0 1) Fermi edge.

Dy_2O_3 films were grown in situ on Ru(0 0 0 1) in a manner similar to that used for growing CeO_2(1 1 1) films [1]. The dysprosia films were estimated to be ca. 5 nm thick based on the attenuation of the Ru 3d SXPS intensity. Dy_2O_3 was produced by depositing Dy metal in an O_2 ambient of 2×10^{-7} torr while the Ru was at 700 K. The Dy flux was monitored by a mass spectrometer during deposition to ensure reproducible results. The flux and film thickness were nominally the same as those used when growing CeO_2. After deposition the sample was annealed to 900 K.

Rh was deposited from a resistively heated evaporative source while the sample was maintained at 300 K. The Rh coverage was 8 ± 1 nm^{-2}. After deposition the sample was annealed to 800 K. The Rh flux was monitored by a mass spectrometer during deposition. The Rh flux was calibrated by evaporating Rh onto clean Ru(0 0 0 1) and recording the Rh and Ru AES intensities (ORNL) or the Rh 3d intensity (NSLS) as a function of Rh exposure. Rh on Ru has been shown to grow in a layer-by-layer manner [6]. The data indicated very distinct inflection points in plots of the AES or SXPS intensities vs. Rh exposure (not shown). These inflection points correspond to the completion of a Rh monolayer on the Ru(0 0 0 1) surface.

The samples were exposed to $^{13}C^{16}O$ (Cambridge Isotope Labs) through a directional doser. The CO contained ca. 10% $^{13}C^{18}O$ and the precise ratio of $^{13}C^{16}O$ to $^{13}C^{18}O$ was determined to be 9:1 by recording a TPD of the mixture from Ru(0 0 0 1) before dysprosia was deposited. Since the dysprosia films were grown with $^{16}O_2$, loss of the ^{18}O label in the CO TPD indicated exchange of oxygen between the CO and the dysprosia support [3,7]. $^{12}C^{16}O$ (Matheson) was used in the SXPS experiments. $^{12}C_2H_4$ (Matheson) was used for TPD and SXPS. All gases were dosed to ensure saturation, i.e. further exposure resulted in no changes in the SXPS or TPD spectra. The typical exposure was approximately equal to 20 L. The CO coverages were calibrated relative to the integrated CO desorption intensity from CO adsorbed on Ru(0 0 0 1) at 200 K which has been shown to have a coverage of 9.2 nm^{-2} [8].

3. Results

3.1. Growth and characterization of Dy_2O_3

Dy_2O_3 was grown on Ru(0 0 0 1) by evaporating Dy onto the Ru in an O_2 ambient of 2×10^{-7} torr while the Ru was at 700 K. The Ru was subsequently annealed to 900 K. When a similar procedure was followed for CeO_2, the