Adsorption of carbon monoxide on a SmO_x film

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A weak adsorption state of CO, characterized by extremely high binding energy photoemission features, was formed on samarium oxide film prepared in UHV.

Molecule/surface interactions on metal oxides are of interest owing to the importance of metal oxides in catalysis. A number of investigations of the chemisorption properties of metal oxides have been carried out under ultrahigh vacuum (UHV) conditions.[1] Little work, however, has dealt with molecular adsorbates on rare earth oxide surfaces,[2,3] since it is difficult to obtain well defined surfaces of such materials. In order to investigate the chemisorption property of a rare earth oxide in detail with surface science techniques, we prepared a samarium oxide (SmO_x) film in UHV. Here, we report the interaction of CO with the surface of the SmO_x film, using ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD).

All experiments were performed in a commercial UHV apparatus (ESCALAB Mark II) with a base pressure of $< 1 \times 10^{-8}$ Pa. The SmO_x film was prepared in the UHV system by oxidizing a Sm overlayer, which was vapor-deposited on a Ru(001) single crystal sample (*ca.* 10 mm diameter and 1 mm thickness). Since the SmO_x films obtained here completely covered the Ru(001) surface, we did not have to take into account any effect of the Ru surface or the Ru/SmO_x interface on CO adsorption. UP and XP spectra were recorded at *ca.* 105 K using He II and Al-Kα radiation, respectively.

Fig. 1(*a*) shows the UP spectrum for the SmO_x film on Ru(001), which was prepared by repeating cycles of Sm deposition at 300 K and heating to 800 K in O_2 (*ca.* 10^{-5} Pa). The thickness of the SmO_x film was determined to be *ca.* 4.5 nm from the attenuation of Ru 3d signal intensity. Fig. 1(*b*) was recorded after the surface was saturated with CO at *ca.* 105 K. The difference spectrum, (*b*) − (*a*), shows the appearance of a pair of peaks at *ca.* 11.8 and 14.3 eV below E_F. These two peaks disappeared after heating to 150 K and desorption of CO was observed at *ca.* 125 K in TPD measurements at a heating rate of 5 K s^{-1}. These results suggest that the two observed peaks are attributed to CO species, which adsorbs weakly on the SmO_x surface. Supposing a first-order desorption, the activation energy of desorption of *ca.* 31 kJ mol^{-1} was obtained for this CO species from the desorption temperature of 125 K and a frequency factor of 10^{13} s^{-1}.

As shown in Fig. 1(*e*), two peaks at *ca.* 8.0 and 11.0 eV were observed for CO on the Ru(001) surface, which have been assigned to $5\sigma/1\pi$ and 4σ emissions, respectively.[4] The binding energies of the two peaks from CO on SmO_x are remarkably larger than those of CO on Ru(001) as well as on other metal surfaces. Similar very high binding energy features have been reported for CO on a partially reduced Cr_2O_3(111) surface.[5] This CO species interacts weakly with chromium atoms, and was not observed on a completely oxidized Cr_2O_3(111) surface. The higher binding energies of photoemissions compared with those of CO on metal surfaces were explained by σ bonding between CO and chromium atoms without π^* back-donation, which plays an important role in CO adsorption on most metal surfaces. The bonding character of this distinct CO species is essentially different from that of CO on a metal surface.

Fig. 1(*c*) and (*d*) were recorded for an Ar^+-ion-bombarded SmO_x surface before and after CO adsorption, respectively. In the difference spectrum, (*d*) − (*c*), two peaks also appear, at *ca.* 11.8 and 14.3 eV. The intensities of these two peaks are apparently larger than those observed in (*b*) − (*a*) for the non-bombarded surface, suggesting that the Ar^+-ion-bombardment of the surface caused an increase in the number of CO adsorption sites. An explanation for this result is that the adsorbed CO molecules interact with defect sites, which are likely to increase for the rough ion-bombarded surface.

According to a previous report for a TiO_2 surface,[1] the lower part of the valence band (*ca.* 4 eV below E_F) is mostly composed of non-bonding 2p orbitals of oxygen in the oxide. Comparing Fig. 1(*c*) with (*a*), the non-bonding O 2p peak decreases in intensity significantly as a result of the ion bombardment. This fact suggests that the population of the oxygen atoms located at the SmO_x surface, which are less coordinated compared with bulk oxygen atoms, are reduced by the ion bombardment. Therefore, the ion-bombarded surface has a number of oxygen vacancy defect sites, where samarium

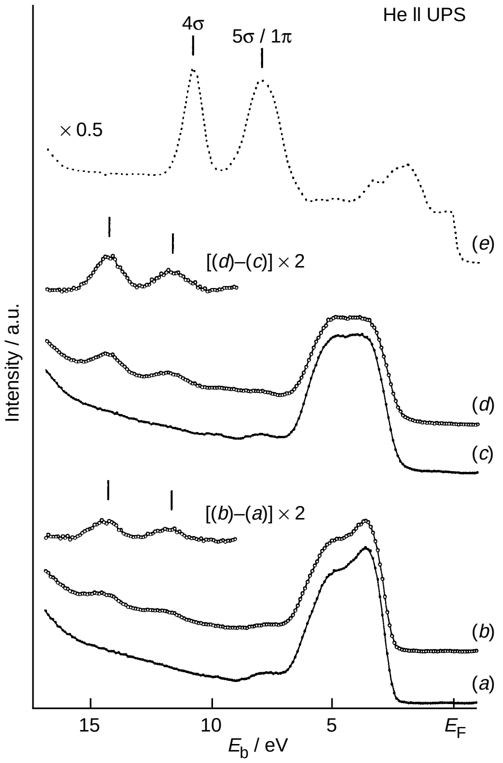

Fig. 1 He II UP spectra recorded on a SmO_x film surface (*a*) before and (*b*) after saturating with CO at *ca.* 105 K and on the Ar^+ ion bombarded SmO_x surface (*c*) before and (*d*) after saturating with CO. Spectrum (*e*) was recorded for CO on Ru(001).

atoms are exposed and probably exhibit an ability to bond to CO.

Fig. 2(*a*) and (*b*) show XP spectra in the O 1s region, which were recorded on a SmO_x film before and after CO adsorption at *ca*. 105 K, respectively. The main O 1s peak at *ca*. 529.6 eV is due to oxygen atoms in the SmO_x film. Comparing the peak area of this O 1s feature with that of Sm 3d, we obtained the stoichiometry of SmO_x : *ca*. 1.44 for *x*. This result is consistent with a previous report for the oxidation of a Sm metal surface by O_2 exposure in UHV system, where Sm_2O_3 was obtained.[6] The difference spectrum (*b*) − (*a*) has a small peak at *ca*. 537.8 eV. Since this O 1s feature disappeared after heating the sample to 150 K, it can be attributed to the weakly adsorbed CO species described above. The binding energy of this O 1s feature is much larger than that of CO on most metal surfaces, as well as those of the valence level emissions. Additionally, a high binding energy feature of C 1s was also observed at *ca*. 291.8 eV for this CO species. These higher binding energies must result mainly from poor screening of the holes induced by photoemission processes, and suggest a lack of π^* back-donation and a very weak interaction of CO with the SmO_x surface.

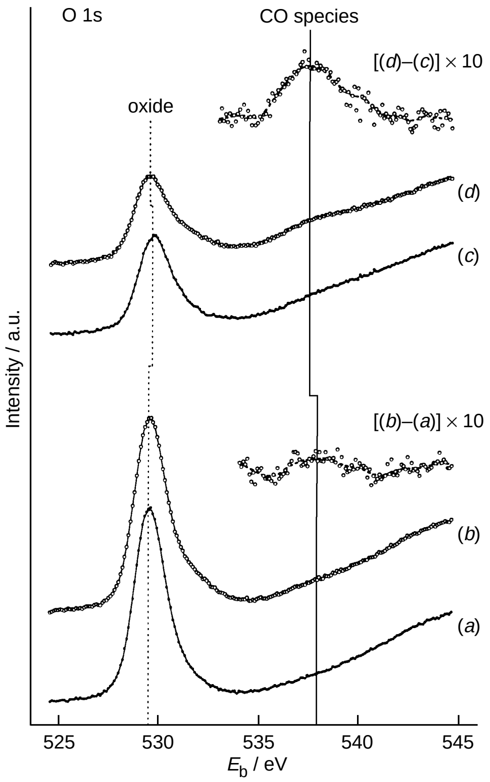

Fig. 2 O 1s XP spectra recorded on a SmO_x film prepared by oxidation of Sm with O_2, (*a*) before and (*b*) after saturating with CO at *ca*. 105 K and on the SmO_x film, which was prepared by oxidation of Sm with CO, (*c*) before and (*d*) after saturating with CO

Fig. 2(*e*) was recorded on a SmO_x film which was prepared by the reaction of deposited Sm with CO in UHV. In this spectrum, the O 1s feature at *ca*. 529.6 eV is obviously smaller than that in Fig. 2(*a*) for the SmO_x produced by O_2 exposure, although the amounts of deposited Sm were almost the same (*ca*. five monolayers). For this CO-produced SmO_x film, which probably consists of the corresponding amount of carbon as a component, the stoichiometry was determined to be *ca*. 0.73 for *x*. It is expected that the CO-produced SmO_x film has a larger number of exposed Sm atoms on the surface than the O_2-produced SmO_x film.

Fig. 2(*d*) was recorded on the surface of this SmO_x film after exposure to CO at *ca*. 105 K. In this spectrum, a more intense O 1s feature at *ca*. 537.6 eV was observed than in Fig. 2(*b*). Comparing the O 1s peak area with that of a saturated CO layer on Ru(001), the coverage of CO observed here was estimated to be *ca*. 0.2 with respect to the Ru(001) substrate. The SmO_x film produced by CO exposure has a larger number of weak CO bonding sites than that produced by O_2 exposure. This result also supports the fact that the weakly bound CO species interact with samarium atoms at oxygen vacancy defect sites.

With respect to the catalytic abilities of rare earth oxides for CO hydrogenation, Sakata *et al.* have studied CO adsorption on a practical Sm_2O_3 catalyst, using *in situ* IR spectroscopy.[7] They have reported that CO chemisorbed reactively on a Sm_2O_3 surface to form several types of species, which were also detected on other rare earth oxides.[8] On the other hand, under UHV conditions, no CO chemisorption was observed on rare earth oxide films[2] or single crystal surfaces of a rare earth oxide[3] at room temperature. The characteristic weak adsorption state of CO observed here on the SmO_x surface was not stable at room temperature under UHV condition. Under atmospheric pressure, however, it may be possible that this CO species becomes a precursor of the species such as those reported by Sakata *et al.*, or plays other important roles in catalytic reactions.

Notes and References

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