X-ray photoelectron spectroscopy study of the interaction of carbon monoxide and propylene with dysprosium and yttrium surfaces

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Abstract

X-ray photoelectron spectroscopy has been used to study adsorption of oxygen, carbon monoxide and propylene on dysprosium and yttrium polycrystalline surfaces at ambient temperature. O 1s peaks produced by the adsorption of CO and O_2 in the low uptake region have the same binding energy (about 530.8 eV), suggesting the same type of oxygen species formed from CO and low amounts of O_2. C 1s spectra of adsorbed CO and C_3H_6 are composed of three peaks whose binding energies do not depend on the parent molecule. They correspond to different carbon species produced by dissociation of the given compound.

1. Introduction

Most rare earth metals are highly reactive towards gases. Their surfaces when clean or only slightly covered usually completely disintegrate molecules of adsorbed simple gases into atoms. With an increase in the amount adsorbed the degree of disintegration gradually decreases. The nature of the species formed and their behaviour have been considered in a number of studies [1, 2].

The measured heats of adsorption [3–5] seemed to indicate that molecules of oxygen and carbon monoxide dissociate on dysprosium and yttrium surfaces. The aim of this paper is to obtain additional, more direct experimental evidence on the nature of the species formed at room temperature on polycrystalline surfaces of dysprosium and yttrium by measuring the C 1s and O 1s photoelectron spectra.

2. Experimental details

The spectra were taken in a VG ESCA 2 MkII electron spectrometer. The base pressure in the spectrometer was in the low 10^{-10} mbar range.

The samples were prepared by vapour deposition of a pure metal onto a molybdenum polycrystalline substrate cleaned by argon ion sputtering and maintained at room temperature. The background pressure during the metal deposition did not exceed 5×10^{-10} mbar. No impurity peaks were visible in the wide scan X-ray photoelectron spectroscopy (XPS) spectra of the deposited metal. The thicknesses of the deposited metal layers were about 50 nm. Gas exposures were carried out at room temperature by leaking the gas into the spectrometer chamber through a precision leak valve. The XPS spectra were excited using an Al $K\alpha$ source at 220 W. The electrostatic hemispherical analyser was operated in the fixed analyzer transmission (FAT) mode with a fixed pass energy of 20 eV. Detailed scans were taken over the C 1s and O 1s regions. The spectrum collection time was typically 20 min. The XPS peak positions and areas were determined by fitting the unsmoothed experimental data after subtracting the clean metal background spectrum. The binding energies were referred to the Au $4f_{7/2}$ line (84.0 eV).
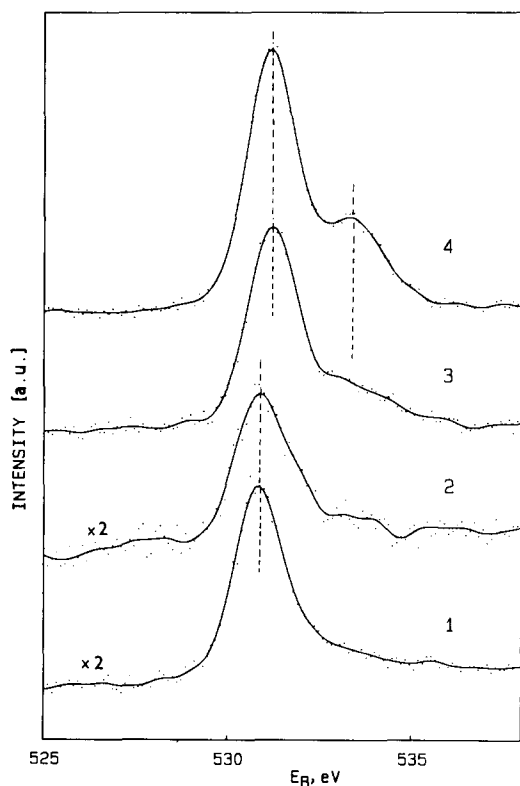
Fig. 1. O 1s core level spectra of CO and O_2 adsorbed on dysprosium for exposure of 100 L CO (spectrum 1), 0.2 L O_2 (spectrum 2), 1.0 L O_2 (spectrum 3) and a large dose (above 1000 L) of O_2 (spectrum 4).

3. Results and discussion

When dysprosium was exposed to oxygen, an O 1s peak at 530.8 eV appeared at low exposure (about 0.2 L). Increasing exposure resulted in the gradual shift of this peak to 531.2 ± 0.1 eV, and in the region of rather high exposures to simultaneous development of a second, less intensive O 1s peak centred at 533.3 ± 0.1 eV (Fig. 1). Contamination by water vapour was suggested to account for this peak [6–8]. More recently this peak was assigned [9] to surface hydroxyl species produced by the reaction of hydrogen present in the residual atmosphere of the vacuum system with the oxidized metal surface.

With yttrium we obtained under the same conditions a single O 1s peak at 530.8 ± 0.2 eV on exposure to oxygen. This binding energy increased slightly (up to 531.1 ± 0.2 eV) at higher exposures, but no second O 1s peak was observed, in contrast to the O_2–Dy system. If the explanation given in ref. 9 is correct then this finding points to a lower reactivity of yttrium oxide towards hydrogen compared with dysprosium oxide.
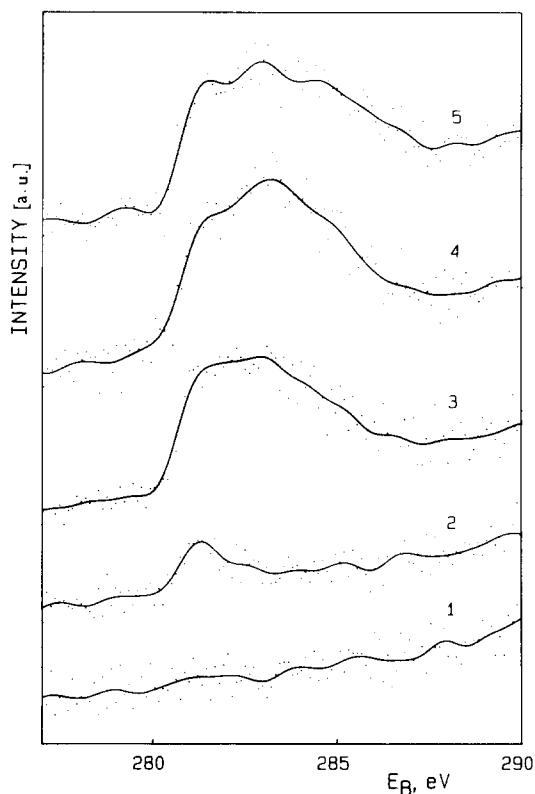

Fig. 2. C 1s core level spectra of CO adsorbed on yttrium: clean metal surface (spectrum 1) and after exposure to 0.15 L (spectrum 2), 2.2 L (spectrum 3), 52 L (spectrum 4) and more than 100 L (spectrum 5).
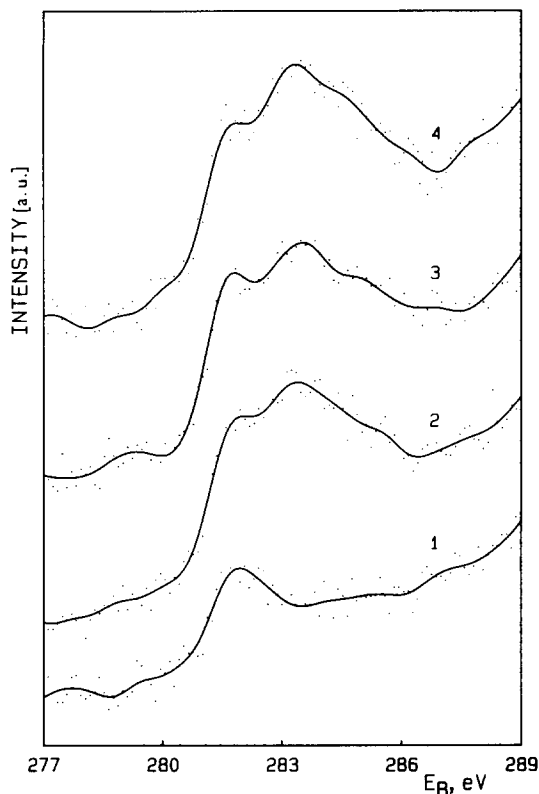
Fig. 3. C 1s core level spectra of CO adsorbed on dysprosium for exposures of 0.05 L (spectrum 1), 0.125 L (spectrum 2), 0.23 L (spectrum 3) and 3.23 L (spectrum 4).

The observed binding energies of the main O 1s peak fall into the range 530.5–531.5 eV reported for the surface layers formed by the reaction of oxygen with most rare earth metals [6–9]. The metal core level shifts on oxidation were also measured and are discussed elsewhere [10, 11].

The O 1s binding energy of the oxygen species formed at low oxygen exposures is the same as in the adsorption of CO (Fig. 1) which amounts to 530.7 ± 0.1 eV and 530.8 ± 0.1 eV for the CO–Y and CO–Dy systems respectively. This suggests that the same type of oxygen species, *i.e.* chemisorbed oxygen atoms, is formed from the two molecules at the given conditions.

The C 1s spectra resulting from the adsorption of CO on dysprosium and yttrium display similar features for both metals (Figs. 2 and 3). At low CO exposures only one C 1s peak is observed, located at 281.5 ± 0.2 eV. At higher exposures, two additional overlapping C 1s peaks appear. Their binding energies amount to 283.1 ± 0.2 eV and 284.9 ± 0.2 eV.

Figure 4 shows C 1s spectra obtained after saturation of the yttrium surface by the adsorption of CO and of propylene. The C 1s spectrum observed with the CO–Dy system under the same conditions is also given for the sake of comparison. In all these systems, three C 1s peaks result,
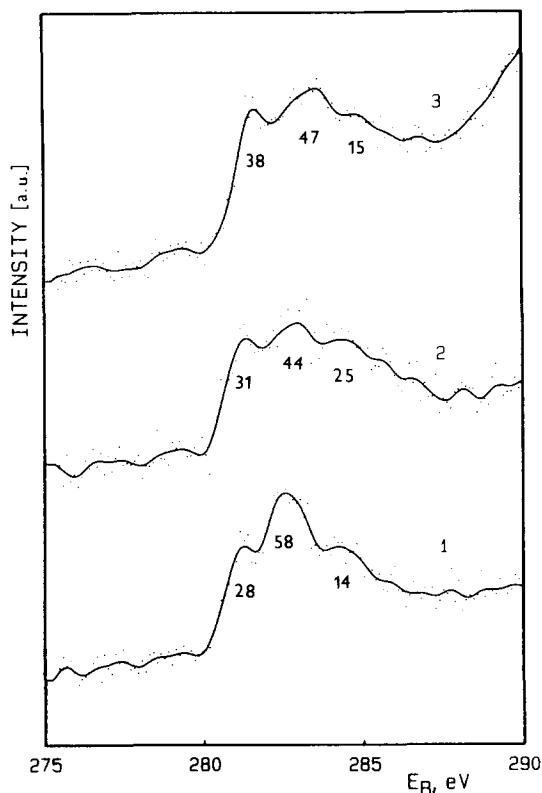
Fig. 4. C 1s core level spectra for saturation coverage of propylene–Y (spectrum 1), CO–Y (spectrum 2) and CO–Dy (spectrum 3). The values under the peaks give the relative contributions (in per cent) to the total C 1s intensity. They were obtained by curve fitting of the spectra.

suggesting that similar or identical types of carbon species are formed from CO and C_3H_6. The first peak around 281 eV can be assigned to carbidic carbon formed by the dissociation of CO or C_3H_6 on the most active sites. This assignment is based on comparison of the C 1s binding energies with the published binding energies for metallic carbides [12, 13].

The second peak around 283 eV can be ascribed [10, 11] to carbon formed on the less active sites which are populated at higher surface coverage.

The third C 1s peak is assigned to graphitic carbon formed at high surface concentrations of the dissociated carbon atoms. This assignment, accounting for the peaks found for both CO and C_3H_6 adsorption, appears to be more realistic than the originally suggested assignment [11] to non-dissociated CO which was based on the assumed analogy with the results reported for the CO–Sc system [14].

It is well known that adsorption of CO on numerous metals occurs without dissociation [15] and multiple peaks are observed in the XPS spectra of the C 1s region. However, the C 1s binding energies found [15, 16]

(typically 285.8 eV) are higher than those obtained for dysprosium and yttrium surfaces.

Results similar to ours were reported for the CO–Sc [14], CO–Co [17], CO–Ru [18] and C_2H_2, C_2H_4–Gd(0001) [19] systems. In contrast to dysprosium and yttrium, only one asymmetric C 1s peak was observed for scandium saturated by CO. The asymmetry was ascribed to the presence of non-dissociated molecules of CO. Dissociation of a fraction of the CO adsorbed on cobalt and ruthenium above 300 K gave rise to two C 1s peaks assigned to carbidic and graphitic carbon.

The results obtained lend support to a simple idea [20, 21] based on the energy level diagram, namely that a low work function of the metal promotes dissociative adsorption of CO.

Some additional information can be gained from the intensities of the C 1s and O 1s peaks of adsorbed CO. The atomic ratio O:C calculated from the integral intensities of the above lines normalized to the photoionization cross-sections [22] is approximately unity for the surfaces saturated with CO. This indicates that the both atomic species produced by dissociative adsorption remain at or close to the surface.

In conclusion, our results give experimental evidence indicating that carbon monoxide and propylene adsorbed at room temperature on poly-crystalline dysprosium and yttrium surfaces are completely dissociated. In the C 1s spectra three chemically different forms of carbon species, the relative concentrations of which are a function of the surface coverage, were identified.

References

1 F. P. Netzer and E. Bertel, in K. A. Gschneidner, Jr., and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 5, North-Holland, Amsterdam, 1982.
2 F. P. Netzer and J. A. D. Matthews, *Rep. Prog. Phys.*, *49* (1986) 621.
3 S. Černý and M. Kovář, *Coll. Czech. Chem. Commun.*, *53* (1988) 2412.
4 S. Černý and M. Smutek, *J. Catal.*, *123* (1990) 275.
5 S. Černý and Z. Pientka, *Surf. Sci.*, *191* (1987) 449.
6 B. D. Padalia, J. K. Gimzewski, S. Affrossman, W. C. Lang, L. M. Watson and D. J. Fabian, *Surf. Sci.*, *61* (1976) 468.
7 G. Praline, B. E. Koel, R. L. Hance, H.-I. Lee and J. M. White, *J. Electron Spectrosc. Relat. Phenom.*, *21* (1980) 17.
8 K. Wandelt and C. R. Brundle, *Surf. Sci.*, *157* (1985) 162.
9 P. D. Schulze and E. L. Hardegree, *J. Phys. Chem.*, *93* (1989) 5254.
10 Z. Bastl, S. Černý and J. Dubský, *Commun. Dep. Chem. Bulg. Acad. Sci.*, *22* (1989) 402.
11 Z. Bastl, S. Černý and J. Dubský, in J. Koukal (ed.), *Physics of Solid Surfaces 1987*, Studies in Surface Science and Catalysis, Vol. 40, Elsevier, Amsterdam, 1988, p. 188.
12 L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman and C. Nordling, *J. Phys. Chem. Solids*, *30* (1969) 1835.
13 L. Ramqvist, K. Hamrin, G. Johansson, U. Gelius and C. Nordling, *J. Phys. Chem. Solids*, *31* (1970) 2669.
14 S. Affrossman, *Surf. Sci.*, *111* (1981) 1.
15 S. Ishi and Y. Ohno, *Surf. Sci.*, *143* (1984) L405.
16 G. Wedler and J. Ertel, *Ber. Bunsenges. Phys. Chem.*, *87* (1983) 469.

17 L. Papagno, L. S. Caputi, F. Ciccacci and C. Mariani, *Surf. Sci.*, *128* (1983) L209.

18 J. Nakamura, I. Toyoshima and K. Tanaka, *Surf. Sci.*, *201* (1988) 185.

19 R. J. Simonson, J. R. Wang and S. T. Ceyer, *J. Phys. Chem.*, *91* (1987) 5681.

20 Z. Bastl, *Colloq. Czech. Chem. Commun.*, *48* (1983) 3196.

21 B. E. Nieuwenhuys, *Surf. Sci.*, *105* (1981) 505.

22 J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, *8* (1976) 129.