CO ADSORPTION OF DIOXYGEN AND CARBON MONOXIDE ON A Mg(100) SURFACE

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ABSTRACT: The activation of carbon monoxide by oxygen on Mg(100) surface has been investigated by X-ray photoelectron spectroscopy (XPS). Carbon monoxide is only weakly adsorbed (dispersion-type forces) on a magnesium surface. The XPS result has shown that the dissociation of carbon monoxide leading to the formation of a metastable surface carbonate species occurs through the participation of an oxygen surface O⁻(s). A stepwise mechanism involving a weakly adsorbed CO molecule present at very low surface coverage (<0.1) undergoing surface diffusion and interaction with the transient oxygen adatoms is suggested. The Frenkel equation has been used to estimate the mean residence time of CO molecule on the surface, and the residence time of a molecule on a specific surface site has also been estimated.

KEY WORDS: Coadsorption of CO + O₂, Carbonate formation, Residence time of CO molecule, Transient species, Hopping mechanism.

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INTRODUCTION

The chemisorption and reactivity of carbon monoxide on metal surfaces has been extensively studied both by the IR [1] and photoelectron spectroscopies (XPS) [2] and explained in terms of the Dewar-Chatt models. In general, bonding is weak for s-electrons (ΔH ≲ 40 kJ mol⁻¹), whereas transition metals chemisorb carbon monoxide, in some cases dissociatively, with a high heat of adsorption (ΔH ≳ 120 kJ mol⁻¹).

A photoelectron spectroscopic study of carbon monoxide adsorption on an aluminium surface has shown that dissociation of carbon monoxide is induced at low temperatures by an oxygen transient present at an Al surface exposed to CO-O₂ mixtures (100:1); a metastable surface carbonate was first formed which deoxygenated in the temperature range 120-295K [3].

Photoelectron spectroscopic studies of carbon dioxide on an aluminium surface have shown the adsorption to be dissociative, again leading to the formation of a surface carbonate with subsequent deoxygenation in the temperature range 120-295K [4]. Dissociative chemisorption of carbon dioxide has also been observed at low temperatures on magnesium surfaces [5].

Studies on the activation of ammonia by dioxygen on Mg[0001], when both the "clean" metal and the oxide overlayer were unreactive, has been interpreted as activation by a surface transient, O⁺(s) [6]. The essential feature of the mechanism involves the hopping of the ammonia molecule intercepting the surface transient prior to it becoming part of the oxide overlayer. If a similar mechanism operates for CO-O₂ mixtures then it should be possible to oxidize CO in a step-wise manner to give first CO₂ and then the surface carbonate CO₃²⁻(s). Clearly this process would be feasible only in mixtures rich in CO₂, otherwise a potentially inactive oxide layer would form preferentially. The heat of adsorption of carbon monoxide on Mg is small (< 20 kJ mol⁻¹) so that if a surface hopping mechanism applies there are obvious advantages in working at low temperatures.

In this work experiments have been carried out to study the reactivity of a Mg(100) surface. The main objective of these experiments was to highlight the role of oxygen transients in the formation of surface carbonate species from CO, an otherwise unreactive molecule, on Mg(100).

EXPERIMENTAL

The electron spectrometer used in this study is a purpose-built instrument designed to enable both photoelectron spectra (XPS) and (UPS), (VG Scientific, East Grinstead, England) and high resolution electron energy loss spectra (HREELS, VSW Manchester, England) of surface species to be obtained. This instrument is capable of base pressures of 10⁻¹⁰ mbar.

The two most important photon sources used in X-ray photoelectron spectroscopies are the aluminium and magnesium Kα emission lines due to their high energy and narrow line widths. The X-ray source used in our spectrometer has a dual, tapered anode with two inclined faces on which magnesium and aluminium films are deposited. Each face has a filament of its own, so either aluminium or magnesium Kα radiation can be conveniently used. Characteristic emission lines Al Kα and Mg Kα at 1486.6 eV and 1253.6 eV respectively are produced when the Al and Mg films are bombarded with high energy electrons. In the present study only Al Kα radiation was used. The emission line Ka₁/₂ having an energy 1486.6 eV arises from the 2P_{3/2} → 1S and 2P_{1/2} → 1S transitions. In addition to these lines satellites arising from valence band → 1S transition are also observed. These X-ray satellites can be easily removed by using a monochromator. However this has the disadvantage of a loss of the source intensity and it is not used in our work.

The Mg(100) single crystal was mechanically polished on successively finer grades of diamond past down to 1 μm diameter. A number of techniques may be used to produce clean surfaces. A very popular technique involves
removing surface contamination by ion bombardment or sputtering. Argon ions are most commonly used with energies in the range 1-10 keV [7]. In the present study cleaning was carried out by repeated cycles of Argon ion bombardment (5kV; 20 μA cm⁻²) at room temperature, and annealing to 220°C, until no evidence for any surface impurities including carbon and oxygen was present.

The single crystal sample can be maintained at temperatures in the range 80-699K. Liquid nitrogen cooling enabled the sample temperature to be reduced to 80K. Surface structure can be monitored by low energy electron diffraction. The high purity gases were supplied in 1 L Pyrex bulbs (99.9%, P.J. Mason Ltd., England) and attached to a separately pumped gas handling system. The dioxygen and carbon monoxide was admitted via a liquid nitrogen trapped cold finger in order to remove condensable impurities. Gases were admitted to the chamber via all metal leak valves and their purity checked using a quadrupole mass spectrometer (Multiquad, Ledamass Ltd.). Spectra were acquired using commercial software (SPECTRA) and analysed on a data system developed in this laboratory [8].

XPS RESULTS AND DISCUSSION

Fig.1(b) shows the O(1s) spectrum obtained after an atomically clean Mg(100) surface has been exposed to carbon monoxide at 80K and at a pressure of 1x10⁻⁵ torr for 300sec (a 3000L exposure). The XP spectrum shows there to be very little resultant adsorption. However when the clean surface was exposed to 3000L of a carbon monoxide : dioxygen mixture (CO:O₂=200:1) at 80K, two peaks are observed in the O(1s) region (Fig.1c). One is assigned to surface oxide and has a binding energy of 430.8eV, and the other at 533.7eV is assigned to surface carbonate. Warming to room temperature (Fig. 1d) and then to 493K (Fig. 1e) causes the carbonate to decompose, thereby its intensity and that of the oxide increases.

The C(1s) data compliment the O(1s) data. Fig. (2b) shows the C(1s) spectrum observed after clean Mg(100) surface was exposed to 3000L of carbon monoxide. The XP spectrum shows there is no evidence for adsorbed carbon monoxide at 80K. However, when a mixture of carbon monoxide and dioxgen was exposed to the clean surface at 80K, the oxygen content being about 1%, four peaks were observed in the C(1s) region of the spectrum (Fig. 2c). Their binding energies are 291.2eV, 288.5eV, 286.3eV and 283.8eV, and these have been assigned to CO₂⁺⁺ (a), CO₂⁺⁺⁺ (a), C(a) and C⁻⁻ (a) respectively [9]. On heating the adlayer, both the C(1s) and O(1s) spectra (see Figs.1 and 2) become less complex with essentially a single peak in each case at 493K. We propose that the carbon
monoxide is oxidized to give a carbon dioxide species which is then oxidized to give a surface carbonate. This is then deoxygenated to generate surface carbon atoms. This is illustrated in the following reaction scheme:

(i) \[ \text{CO(g)} \xrightarrow{k_1} \text{CO(a)} \]
(ii) \[ \text{O}_2(g) \xrightarrow{k_2} 2\text{O}^3^-(s) \]
(iii) \[ \text{O}^3^-(s) \xrightarrow{k_3} \text{O}^{2-}(a) \]
(iv) \[ \text{O}^{2-}(s) + \text{CO(s)} \xrightarrow{k_4} \text{CO}_2(s) \]
(v) \[ \text{CO}_2(s) + \text{O}^{2-}(s) \xrightarrow{k_5} \text{CO}_3^{2-}(a) \]
(vi) \[ \text{CO}_3^{2-}(a) \xrightarrow{k_6} \text{C}(a) + 3\text{O}^{2-}(a) \]

The symbol \((s)\) represents the transient or short-lived nature of a species. Steps (i) to (v) occur at 80K, with step (vi) becoming more significant as the temperature is increased to 298K. \(\text{O}^{2-}(s)\) is known as an oxygen transient and is a reactive intermediate whereas \(\text{O}^{2-}(a)\) forms a comparatively stable oxide layer. It was suggested earlier that it is important to keep the \(\text{CO}_2 : \text{O}_2\) ratio high. This would prevent \(k_3\) being greater than \(k_4\) or \(k_5\), so allowing the reaction to proceed. If step (iii) is the dominant reaction, a stable oxide layer forms; as the oxide coverage increases so the coverage of \(\text{O}^{2-}(s)\) will decrease. We have therefore a mechanism by which, the strong carbon-oxygen bond in the CO molecule can be cleaved through the participation of an oxygen surface transient \(\text{O}^{2-}(s)\).

It has already been shown that, at 80K, CO adsorption is not detectable by XPS, i.e. the coverage can be assumed to be less than 0.02 of a monolayer. This implies a low heat of adsorption which, by comparison with another sp-metal (Aluminium [4]) can be taken as approximately 20 kj mol\(^{-1}\).

This allows us to use the Frenkel equation [10] to estimate the mean residence time of a CO molecule at the surface at a temperature \(T\):

\[ t_{\text{surface}} = t_0 \exp \frac{\Delta H_{\text{CO}}}{RT} \]

Where \(t_0\) is the period of oscillation of the molecule in the adsorbed state (approximately \(10^{-13}\) sec). This gives a surface lifetime of \(\approx 1\) sec at 80K. Similarly the residence time of a molecule at a specific surface site is given by:

\[ t_{\text{site}} = t_0 \exp \frac{E_d}{RT} \]

where \(E_d\) is the activation energy for surface diffusion. If we assume that this activation energy for diffusion by a hopping mechanism is \(0.25\Delta H\) then \(t_{\text{site}} = 1.9 \times 10^{-10}\) sec. From these two calculations we can work out the hopping rate \((R = \text{number of hops per sec})\) and the number of hops during the surface lifetime of the CO molecule \((N_{\text{sur}})\). Similar calculations have been performed for 295K and results are summarized in Table 1.

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**Fig.2:** C(1s) spectra for coadsorption of carbon monoxide and dioxygen (200:1) at an Mg(100) surface; spectra show (a) the clean surface, (b) the effect of exposure to 3000L of CO at 80K [Mg(100) surface does not adsorb CO(g) at 80K], (c) the effect of exposure to 3000L of mixture at 80K followed by warming to 298K and 493K (d) and (e). Note the formation of \(\text{CO}_3^{2-}(a), \text{CO}_2^{2-}(a)\) and \(\text{C}(a)\) with binding energies of 291.7eV, 286.8eV and 284.6eV respectively.
Table 1: Values of surface lifetime, hopping rate, specific site lifetime and number of sites visited for a CO molecule with a 20 kJ mol\(^{-1}\) heat of adsorption and 5 kJ mol\(^{-1}\) heat of diffusion.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>(t_{\text{surface}}) (sec)</th>
<th>(R) (sec(^{-1}))</th>
<th>(t_{\text{site}})</th>
<th>(N_{t\text{surface}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1</td>
<td>(5.4\times10^{9})</td>
<td>(1.9\times10^{-10})</td>
<td>(6.3\times10^{5})</td>
</tr>
<tr>
<td>295</td>
<td>(3.5\times10^{-10})</td>
<td>(1.1\times10^{12})</td>
<td>(7.7\times10^{-13})</td>
<td>(\approx400)</td>
</tr>
</tbody>
</table>

As can be seen, the number of sites visited by a CO molecule at 80K is many times greater than at 295K, demonstrating why the reactions proceed so rapidly at 80K.

The mechanism for the reaction can be thought of as an Eley-Rideal type mechanism. The adsorbed species is a surface transient, \(O^5^-\) (s), and the non-adsorbed species is a hopping CO molecule.

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REFERENCES