

THE REACTIVE CHEMISORPTION OF CARBON DIOXIDE AT Mg(100) SURFACE

*Zeini-Isfahani, Asghar**

*Department of Chemistry University of Isfahan, P.O.Box: 81744
Isfahan, Iran.*

Roberts, M.W., Carley, A.F., Read, S.

*School of Chemistry and Applied Chemistry University of Wales,
CF1 3TB, Cardiff., England*

(Received: Jan. 23rd 1994 , Accepted: Jul. 4th, 1994)

ABSTRACT : *X-ray Photoelectron and electron energy loss spectroscopic (XPS-EELS) studies reveal that the following species are present when a mixture of CO₂ and water vapour is exposed to the clean Mg(100) surface at 110K: CO_{3(a)}, C_(a), CH_(a), OH_(a). The reactive chemisorption of CO₂ and H₂O vapour coadsorbed on a Mg surface leads to the formation of CH bond. Increasing the temperature to 400 K shows the peaks in the C(1s) region of the spectrum disappears suggesting the CH containing species are not stable at 400K.*

KEY WORDS : *Coadsorption of CO₂ + H₂O, Dissociative chemisorption, X-ray photoelectron spectroscopy, C-H formation , Carbonate species.*

INTRODUCTION :

The discovery that the production of methanol from synthesis gas (a mixture of CO, CO₂ and H₂O) proceeds through CO₂ and not CO [1] has led to a resurgence of interest in the study of the activation of CO₂ at metal surfaces.

Some of the earliest spectroscopic investigations of chemisorption were of CO₂ on various supported metals [2]. More recently there have been X-ray photoelectron spectroscopy (XPS) and electron energy-loss spectroscopy (EELS)

*Corresponding author

studies of CO₂ on Al [3] and Mg(0001) [4]. In this work we report the reactive chemisorption of CO₂ and water vapour coadsorbed on an Mg(100) surface, leading to the formation of a C-H bond.

EXPERIMENTAL :

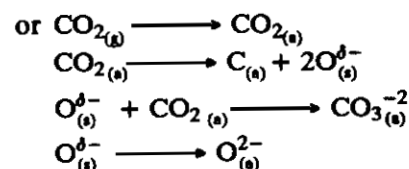
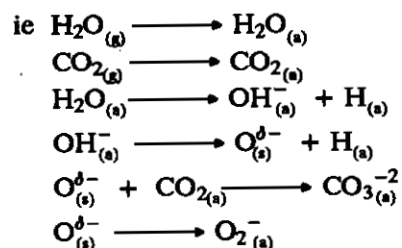
The spectrometer used in this investigation combines both photoelectron (V.G. Scientific) and vibrational (Vacuum Science Workshop) spectroscopies, with facilities also for low-energy electron diffraction. The data from the spectrometers were collected using a commercial acquisition package (SPECTRA), and analysed using software developed in this laboratory [5]. Surface coverages were calculated [6] using photoionisation cross-section data from *Scofield* [7] and *Reilman* [8], and electron mean free path data from *Penn*[9].

A 99.9% pure Mg(100) crystal (Metal and Oxides Ltd., Cambridge) was mechanically polished on successively finer grades of diamond paste down to 1 μ diameter. Cleaning was carried out by repeated cycles of argon ion bombardment (5kV; 20 μ A cm⁻²) at room temperature, and annealing to 220°C. The high purity CO₂ was supplied in 1L pyrex bulbs (99.9%, P.J. Mason Ltd.). This was further purified with several freeze-pump-thaw cycles. The frozen gas was then allowed to warm slowly and the first evaporate captured in the separately pumped, stainless-steel gas handling line, thus leaving any less volatile impurities (such as water) behind in the bulb. Triply distilled water, further purified by several freeze-pump-thaw cycles was used. Gases were admitted to the chamber via all metal leak valves, and their purity and mixture composition checked using a Multiquad quadrupole mass spectrometer (Ledamass Ltd.).

RESULTS AND DISCUSSION :

Fig. (1) shows the O(1s) and C(1s) spectra observed when an atomically clean Mg(100) surface is exposed to a mixture of CO₂(g) and

H₂O(g) (approximately 1.5% H₂O(g) at 110K, and then warmed to 298K and finally to 400K. After an exposure of 50L (1L = 10⁻⁶ torr for 1 second) an intense O(1s) peak is observed at 533.1eV binding energy, together with a shoulder at 530.5eV and a component at 535.3eV. It is interesting to note that the EELS spectrum (Fig. 2) contains a loss peak at approximately 3600cm⁻¹, assigned to the O-H stretch. This corresponds to the component at 535.3eV in the O(1s) region and is assigned to molecularly adsorbed water [10]. The C(1s) spectrum shows three peaks, one at a binding energy of 290.4eV, one at 287.4eV and the other at 285.1eV. The EELS spectrum shows loss peaks at 3600cm⁻¹, 2900cm⁻¹, 1400cm⁻¹ and 600cm⁻¹. The peaks at 2900cm⁻¹ and 1400cm⁻¹ can be assigned to the C-H stretch and CH₂ scissors modes, as seen on Ni(100) [11]. This suggests that some hydrogenation of a carbon species has taken place although it is not clear what the final hydrogenated species is. The O(1s) peak at 533.1eV can be assigned to CO_{3(a)}²⁻ [4]. For carbonate to be produced there must have been some dissociative chemisorption of either H₂O, CO₂ or both:



There is evidence for the existence of O_(a)^{δ-}, an oxygen transient, on Mg(0001) [2] and Al [3,13], which is much more reactive than the O_(a)²⁻ species in the stable oxide layer. This oxide layer gives rise to a peak at 530.5eV [3], accounting for the shoulder on the low binding

energy side of the main O(1s) peak. The C(1s) spectrum is also consistent with the work of Campbell et al [4] on oxidised Mg(0001) surfaces, the peak at 290.4eV being assigned to a

carbonate species. We assign the peak at 287.4eV to a CH containing species and the peak at 285.1eV to a graphitic carbon ($C_{(a)}^{0-}$) species.

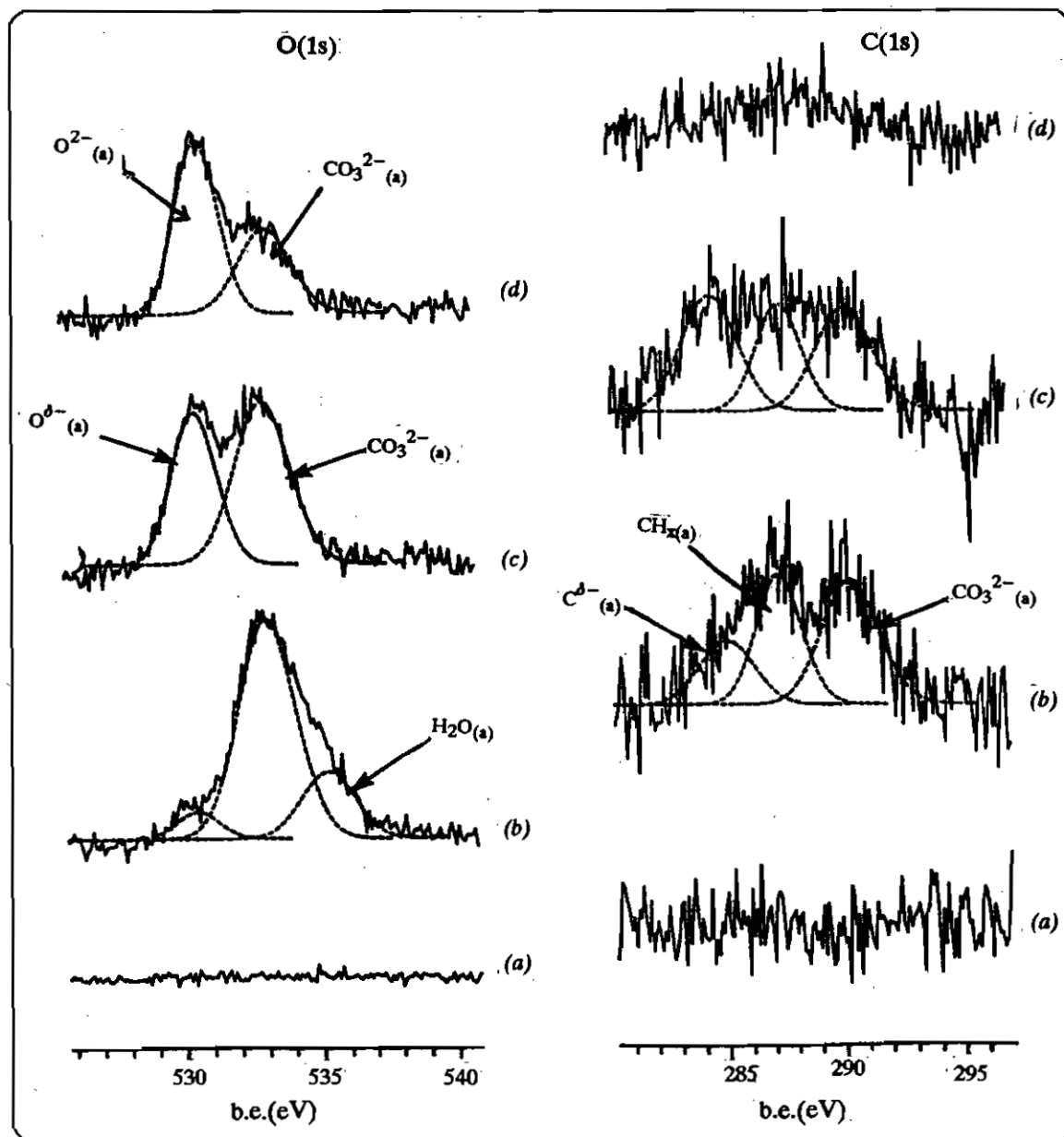


Fig. 1 : O(1s) and C(1s) Spectra observed after exposing an atomically clean Mg(100) surface to a CO_2/H_2O Mixture. The complete line shows the raw data and the dotted line shows curvefitted data. Spectra show (a) the clean surface, (b) the effect of exposure to 50L of the mixture at 110K ($1L = 10^{-6}$ torr for 1 second), (c) and (d) the effect of heating the adlayer to 298K and 400K. The O(1s) and C(1s) spectra were recorded at pass energies of 50 and 200 eV respectively.

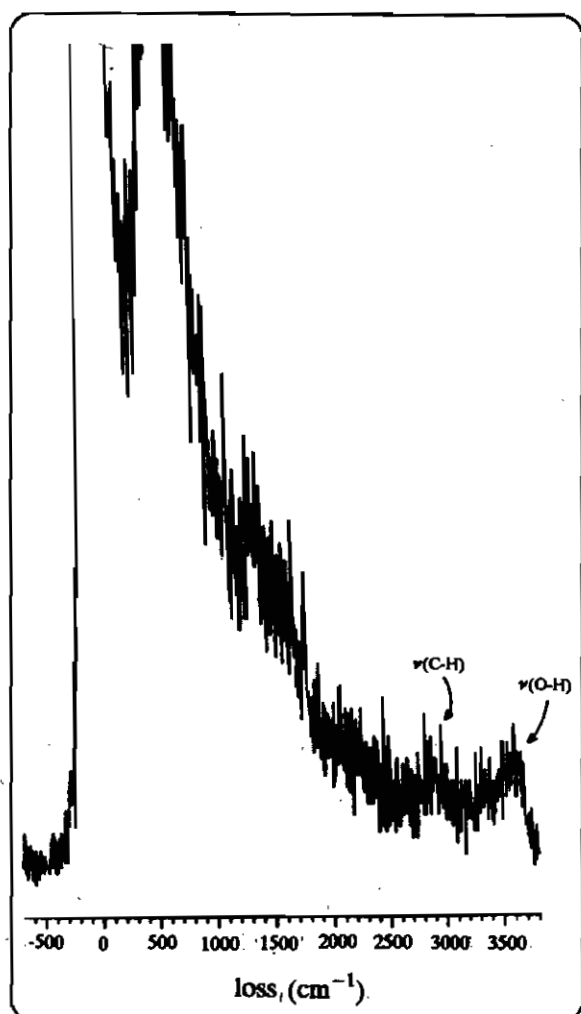
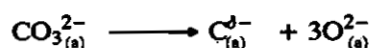


Fig. 2 : EELS of an atomically clean Mg(100) surface exposed to 50L of CO₂/H₂O mixture at 100K.

On warming the surface to 298K the O(1s) spectrum shows two clear peaks. The feature identified with surface oxide has increased in intensity, the oxide coverage increasing significantly due to decomposition of the carbonate species, accordingly the peak due to graphitic carbon (C_(a)^{d-}) at 285.1eV has also increased in intensity,



From the surface coverage data we can suggest the CH containing species is not a surface bicarbonate. The ratio of the O(1s) peak

at 533.1eV to the C(1s) peak at 290.4eV, both of which have been assigned to carbonate, is 3.5:1. This means there is no C(1s) peak at 287.4eV.

Increasing the temperature to 400K causes further decomposition of CO_{3(a)}²⁻ and a decrease in the intensity of the O(1s) component arising from surface oxide. This latter observation can be explained by diffusion of the oxide into the adlayer and the formation of MgO. The peaks in the C(1s) region of the spectrum have all decreased in intensity suggesting the CH containing species is not stable at 400K. Hong He et al [11] observed a similar result on Ni(100).

ACKNOWLEDGEMENT :

The author would like to acknowledge the Iranain Ministry of Culture and Higher Education for its financial support.

REFERENCES :

- [1] Chinchin, G.C., Spencer, M.S., Waugh, K.C., and Whan, D.A., *J.Chem. Soc. Faraday Trans.(I)*, **83**, p. 2193 (1987).
- [2] Eischens, R.P., *Elektrochem, Z.*, **60**, p. 782 (1956).
- [3] Carley, A.F., Gallagher, D.E., and Roberts, M.W., *Spectrochimica Acta*, **43a**, p. 1447 (1987).
- [4] Campbell, S., Hollins, P., McCash, E., and Roberts, M.W., *J. Electron Spec. Rel. Phen*, **39**, p. 145 (1986).
- [5] Carley, A.F., *Ph.D. Thesis*, Bradford University (1980).
- [6] Roberts, M.W, *Advances in Catalysis*, **29**, p. 55 (1980).
- [7] Scofield, J.H., *J. Electron Spec. Rel. Phen.* **8**, p. 129 (1976).
- [8] Reilman, R.F., Msezane, A., and Mason, S.T., *J. Electron Spec. Rel. Phen.*, **8**, p. 389 (1976).
- [9] Penn, D.R., *J. Electron Spec. Rel. Phen.*, **9**, p. 29 (1976).
- [10] Fuggle, J., Watson, L.M., Fabian, D.J., and Affrossman, S., *Surf. Sci.*, **49**, p. 61 (1975).

- [11] Hong He, Junji Nakamura and Ken-ichi Tanaka, *Catal. Letts.*, **16**, p. 407 (1992):
- [12] (a) Au, C.T., and Roberts, M.W., *Nature*, **319**, p. 209 (1989).
(b) Au, C.T., Li Xing- Chang, Tang Ji-An and Roberts, M.W., *J. Catal.*, **106**, p. 538 (1987).
(c) Au, C.T., and Roberts, M.W., *J. Chem. Soc. Faraday Trans.*, **83**, p. 2047 (1987).
- [13] Carley, A.F., and Roberts, M.W., *J. Chem. Soc. Chem. Commun.*, p. 355 (1987).