

Evidence for the Formation of Strongly Bound Molecular CO₂ Species on a Polycrystalline Silver Catalyst

Graeme J. Millar, John Seakins, James B. Metson, Graham A. Bowmaker and Ralph P. Cooney*

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

In situ FT-IR spectroscopy has been used to identify for the first time an unusually stable molecular CO₂ species at *ca.* 2337 cm⁻¹ on a polycrystalline silver catalyst; it is proposed that adsorption occurred at silver sites modified by the presence of subsurface oxygen species, which were located in the vicinity of grain boundary defects.

Silver catalysts are used extensively for the selective oxidation of ethylene to ethylene oxide, and methanol to formaldehyde. A considerable number of studies have been dedicated to the elucidation of the reaction mechanisms involved.¹⁻³ Carbon dioxide can be a component of both systems as it is known to be formed from the combustion of ethylene and also the non-selective oxidation of methanol.¹ In addition it has been claimed that the presence of carbon dioxide in the feedstock can inhibit the undesired combustion of ethylene, thus it is pertinent to examine the interaction of CO₂ with a polycrystalline silver catalyst.

Silica (Cab-O-Sil M5, 200 m² g⁻¹) was impregnated with an aqueous solution of silver acetate (Aldrich, 99.99%) and then dried at 383 K for 5 h. A self-supporting disc was placed in an *in situ* FT-IR cell⁴ attached to a conventional vacuum line. The catalyst sample was then calcined in oxygen at 573 K for 1.5 h and subsequently reduced in hydrogen at 623 K for 18 h. Typically the sample was cooled under evacuation to 220 K and then dosed with CO₂ (1.01 × 10⁵ Pa). Following evacuation at this temperature the catalyst was heated linearly at 6 K min⁻¹ and the IR spectra recorded as a function of catalyst temperature. A more detailed account of the method for catalyst preparation and the apparatus used to acquire the IR spectra is presented elsewhere.⁵ Curve-fitting analysis was performed by use of Spectracalc software (Galactic Ind.) It was assumed that all peaks were 100% Gaussian in nature.

Fig. 1(a) displays the spectrum obtained by exposing a reduced silver catalyst (Ag/SiO₂) to CO₂ at 254 K and subsequently evacuating the cell to remove gaseous species. An intense peak developed at *ca.* 2345 cm⁻¹ which appeared to be slightly asymmetric in shape. Curve-fitting analysis suggested that the observed profile was composed of two distinct subbands at 2346 and 2336 cm⁻¹. Ueno and Bennett⁶ reported that weakly physisorbed CO₂ molecules on SiO₂ were characterised by a single band at 2346 cm⁻¹, which they noted was almost coincident with the value of 2344 cm⁻¹ typical for the ν_{as} mode of solid CO₂. This data was in excellent agreement with the subband at 2346 cm⁻¹ determined in this study. Further heating of the catalyst caused the rapid decrease of the maximum at *ca.* 2345 cm⁻¹ leaving a peak centred at 2337 cm⁻¹ [Fig. 2(a)]. The similarity between this maximum and the subband at 2336 cm⁻¹, indicated that the attenuation of the band at 2345 cm⁻¹ [Fig. 1(a)] was primarily due to the desorption of CO₂ molecules from the silica support. Elevation of the catalyst temperature caused a gradual reduction in intensity of the peak at 2337 cm⁻¹ [Fig. 2(b)-(g)]. The species responsible for the subband at 2336 cm⁻¹ presumably corresponded to CO₂ molecules adsorbed on the silver surface. The relationship between the absorbance of the subband at 2336 cm⁻¹ ascribed to CO₂ species on silver, as a function of catalyst temperature is shown in Fig. 3. From the data of Redhead⁷ it could be calculated from this profile that the maximum rate of desorption occurred at a temperature (*T*_{max}) of *ca.* 261 K. Stuve *et al.*⁸ indicated that no CO₂ adsorption happened on a clean Ag(110) single crystal. However, preadsorbed atomic oxygen species were found to induce both the adsorption of molecular CO₂ and the reaction of CO₂ with surface oxygen to produce adsorbed carbonate species. Significantly Stuve *et al.*⁸ reported that the desorption of molecular CO₂ from the Ag(110) face took place at a

temperature of 130 K, a value which was *ca.* 130 K lower than that discerned in the present study. This discrepancy in behaviour may indicate the presence of adsorption sites on a polycrystalline silver catalyst of a type not normally found on individual single crystal planes. Recently Wu *et al.*⁹ have suggested that grain boundary defects present in polycrystalline silver were capable of stabilizing the adsorption of molecular oxygen species. Grant and Lambert¹⁰ also observed an anomalously strongly bound molecular oxygen species on Ag(111), which was related to the presence of subsurface oxygen species. Data obtained from formic acid adsorption on the silver catalyst used in this investigation implied that in addition to Ag(111) and Ag(110) crystal planes, the catalyst contained a substantial number of grain boundary defect sites.⁵ Moreover, subsurface oxygen species located below the uppermost silver layer were determined to be present only in the immediate vicinity of the aforementioned grain boundary defects. It is therefore proposed that 'strongly bound' molecular CO₂ species on polycrystalline silver existed at silver sites modified by the presence of subsurface oxygen, which were located in the proximity of grain boundary defects. The shift in position of the $\nu_{as}(\text{OCO})$ mode from 2346 (CO₂ on SiO₂) to 2336 cm⁻¹ (CO₂ on silver) indicated that silver was

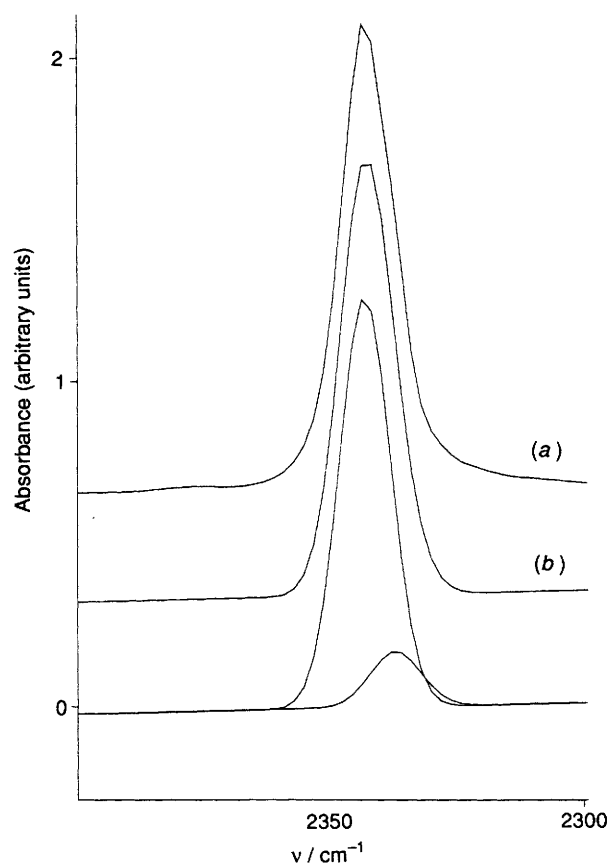


Fig. 1 (a) IR spectrum of CO₂ (1.01 × 10⁵ Pa) on a reduced silver catalyst at 254 K. (b) Overall curvefit of profile obtained in (a); remaining bands are the calculated subbands.

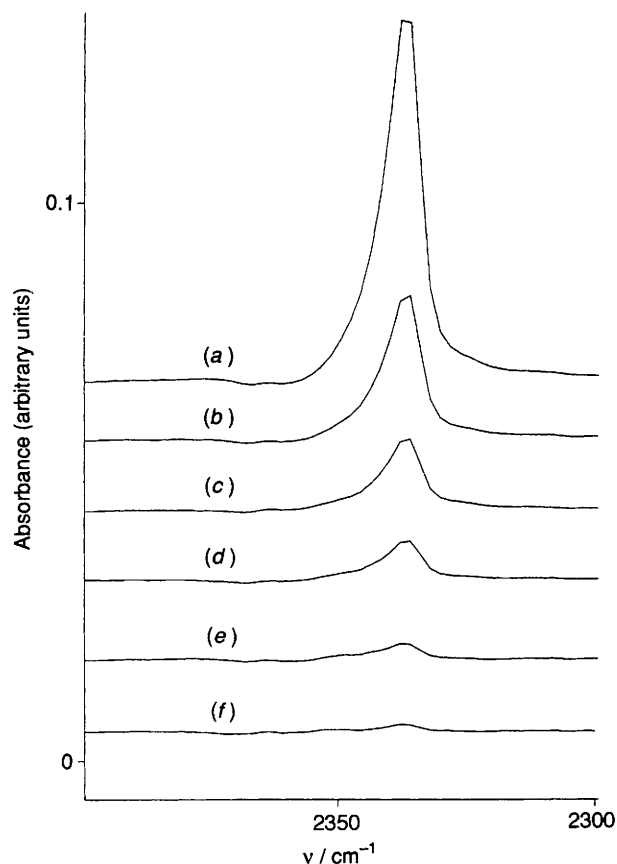


Fig. 2 Continuation of the experiment outlined in Fig. 1. IR spectra were recorded as a function of catalyst temperature (a) 263, (b) 275, (c) 287, (d) 299, (e) 335 and (f) 347 K.

able to donate substantially more electron density to the antibonding orbitals of CO_2 , causing the observed decrease in bond strength. This was in harmony with previous observations that subsurface oxygen species, which are nucleophilic in nature, were able to transfer electron density to incoming adsorbates on silver.⁵

As a test of this hypothesis CO_2 was exposed to a silver catalyst which had undergone the calcination but not reduction. This treatment has been shown to give a catalyst of comparable morphology to a reduced catalyst, the major difference being that the surface was now saturated with adsorbed atomic oxygen.⁵ In addition the number of sites involving subsurface oxygen species was found to be similar in both cases. If 'stepped sites' on a high-index silver plane (which are known to increase the sticking probability of species such as oxygen¹¹) were responsible for the observed stabilization of CO_2 , then blocking these sites with adsorbed atomic oxygen should cause the disappearance of the subband at 2336 cm^{-1} . However, the IR spectra recorded after exposure of a calcined silver catalyst to carbon dioxide were almost identical to those obtained for the reduced catalyst (Figs. 1 and 2). Consequently the idea that 'strongly bound'

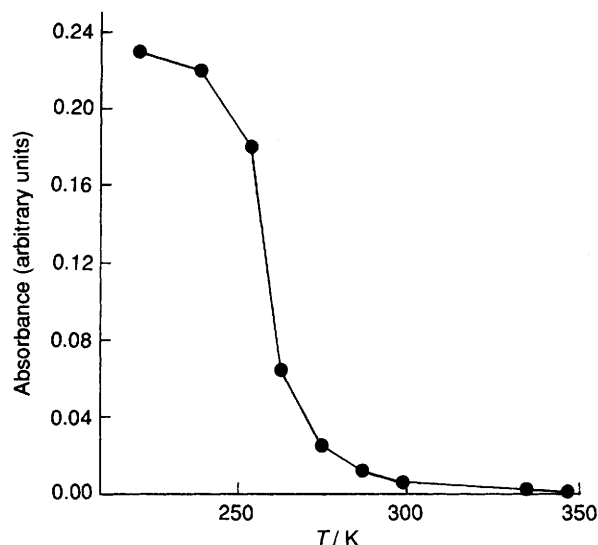


Fig. 3 Correlation between the absorbance of the subband at 2336 cm^{-1} ascribed to CO_2 molecules adsorbed on silver defect sites, and the catalyst temperature.

molecular CO_2 species were associated with silver sites modified by subsurface oxygen species present in the vicinity of grain boundary defects, was reinforced. Finally we note that in accordance with Backx *et al.*¹² carbonate species were not detected on either the reduced catalyst or the calcined sample which had an almost complete coverage of surface atomic oxygen.

G. J. M. acknowledges the New Zealand Vice Chancellors Committee for provision of a postdoctoral award. The authors thank the Vice Chancellors Committee, the Auckland University Research Committee and the Lottery Boards (Science and Health) for support for equipment used in this project.

Received, 5th October 1993; Com. 3/05968E

References

- 1 R. A. Van Santen and P. C. E. Kuipers, *Adv. Catal.*, 1987, **35**, 265.
- 2 P. A. Kilty and W. M. H. Sachtler, *Catal. Rev. Sci. Eng.*, 1974, **10**, 1.
- 3 S. Tan, R. B. Grant and R. M. Lambert, *Appl. Catal.*, 1987, **31**, 159.
- 4 G. J. Millar, D. Newton, G. A. Bowmaker and R. P. Cooney, *Appl. Spectrosc.*, submitted for publication.
- 5 G. J. Millar, J. B. Metson, G. A. Bowmaker and R. P. Cooney, *J. Catal.*, in the press.
- 6 A. Ueno and C. O. Bennett, *J. Catal.*, 1978, **54**, 31.
- 7 P. A. Redhead, *Vacuum*, 1962, **12**, 203.
- 8 E. M. Stuve, R. J. Madix and B. A. Sexton, *Chem. Phys. Lett.*, 1982, **89**, 48.
- 9 K. Wu, D. Wang, X. Wei, Y. Cao and X. Guo, *J. Catal.*, 1993, **140**, 370.
- 10 R. B. Grant and R. M. Lambert, *Surf. Sci.*, 1984, **146**, 256.
- 11 J. Eickmans, A. Otto and A. Goldman, *Surf. Sci.*, 1985, **149**, 293.
- 12 C. Backx, C. P. M. De Groot, P. Biloen and W. M. H. Sachtler, *Surf. Sci.*, 1983, **128**, 81.