

The structure and bonding of carbonate on Ag(110): a density-functional theory study

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Abstract

The local bonding site of the carbonate species, CO_3 , on the Ag(110) surface has been determined through the use of density functional theory (DFT) slab calculations based on the CASTEP code. A number of experimental investigations have established that on this surface the molecular plane is approximately parallel to the surface [1, 2], but the adsorption site is less clear. The surface carbonate is formed by reaction of CO_2 with surface oxygen in the (2x1)-O phase, comprising Ag-O-Ag $\langle 100 \rangle$ added rows, but the surface reaction leads to a new (1x2) reconstruction, thought to be due to $\langle 110 \rangle$ Ag close-packed rows. Initial STM studies identified features atop Ag atoms in added rows as being due to the carbonate [3, 4], but Guo and Madix [5, 6] have argued that these are due to chemisorbed CO_2 and that the carbonate species occupy sites to the side of the added Ag rows and approximately atop Ag atoms in the underlying Ag(110). Most recently a scanned-energy mode photoelectron diffraction (PhD) study [7] has concluded that the structure is essentially that proposed by Guo and Madix, but has also provided detailed information on the spacing of the molecule above the surface and the azimuthal orientation such that one O atom is essentially bridging two adjacent added row Ag atoms and one C-O bond approximately parallel to the $\langle 110 \rangle$ added row direction. Our DFT calculations, performed on a 5-layer Ag slab with one carbonate per (2x2) surface mesh, show an optimum structure remarkably similar to that found in the PhD study. The calculations also show that the site atop an added-row Ag atom is particularly energetically unfavourable, and indeed a lower energy configuration above these rows is with the molecular plane essentially perpendicular to the surface. The main difference between the optimal DFT and PhD structures is that the DFT calculations show some tilt of the molecular plane such that all three O atoms can bond to Ag atoms in the '(111) nanofacet' formed by the (1x2) added row structure. The DFT calculations also show that the added row Ag atoms relax outwards from the surface, but the Ag atom below the C atom is contracted in towards the bulk. Charge-density difference contours provide further insight into the nature of the associated bonding and reveal a significant charge transfer from the metal to the carbonate.

References

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