Formation of weakly bound, ordered adlayers of CO on rutile TiO$_2$(110): A combined experimental and theoretical study

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The adsorption of CO on the rutile TiO$_2$(110) surface was investigated using He atom scattering (HAS), high resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS), and different types of ab initio electronic structure calculations. The experimental and theoretical results allow to put forward a consistent picture for this rather complicated adsorbate system. At 70 K a (2 × 1) adlayer with a glide symmetry plane is formed, containing two molecules per unit cell which are tilted in alternate directions by about 20° relative to the surface normal. For this high density phase, the theoretical calculations reveal a substantial repulsion between CO molecules on neighboring lattice sites, in accord with the results of a detailed analysis of the experimental TDS data. The CO binding energy depends strongly on coverage and varies between 0.20 eV for the saturated monolayer and 0.36 eV for isolated molecules. The CO–CO repulsion leads to the desorption of about half of the CO molecules above 70 K and the formation of low density phases. HAS gave no indication of ordered adlayers at these lower coverages. For the internal stretching vibration of the CO molecules a value of 273 meV was determined by HREELS, in very good agreement with the theoretical calculations. © 2009 American Institute of Physics. [DOI: 10.1063/1.3098318]

I. INTRODUCTION

With regard to chemisorption on metal surfaces, carbon monoxide is the molecular adsorbate for which the most experimental investigations have been published. For CO adsorbed on metal surfaces, a rather large variety of different structures has been observed experimentally and analyzed on the basis of wave-function-based methods and density functional theory (DFT). As a result of repulsive interactions between adsorbed CO molecules, frequently rather open structures with large unit cells are observed at low coverages which convert to more densely packed phases at higher coverages. A different situation is encountered for metal oxide single crystals. Here, the information available for adsorbed CO is rather scarce. Whereas IR spectroscopy carried out for metal oxide powders has been able to demonstrate that CO adsorbs on oxide surfaces with small- to medium-range binding energies, only very few detailed studies on oxide single crystal surfaces have been reported. The most detailed IR spectroscopy investigations were published for the cleaved MgO(001) surface. In the case of the other most important vibrational spectroscopy, high resolution electron energy loss spectroscopy (HREELS), a few more studies are available, including ZnO (for a review, see Ref. 7). To our knowledge there is only one fairly recent report on the stretch frequency for CO adsorbed on rutile TiO$_2$(110). Most of the previous studies reported for CO adsorbed on oxide single crystal surfaces have focused on the determination of binding energies using thermal desorption spectroscopy (TDS) and spectroscopic studies using XPS or UPS. In particular, the lateral structures of CO adlayers on well-defined oxide surface are largely unknown. There is neither information about ordered phases at high coverages nor about high-order commensurate structures at lower coverage. This is an unfortunate situation, since more precise information on the adsorption of CO at oxide surfaces is required for a better understanding of catalytic processes involving CO, either as reactant or as a possible catalyst poison, e.g., in the case of methanol synthesis on ZnO (Ref. 9) or CO oxidation on the Au/TiO$_2$ system. Previous work for CO adsorption on ZnO has shown that CO can also be used as a probe molecule to distinguish between different possible geometries of an oxide surface, see Refs. 12–14 for the case of the polar O-terminated ZnO surface.

In the case of titania, the oxide surfaces which have so far received the most attention (for a recent review, see Ref. 15), we are not aware of any experimental work on the structure of CO overlayers formed on any surface of the three different TiO$_2$ modifications (rutile, anatase, and brookite). Most experimental studies on the interaction of CO with titania have been carried out for anatase and rutile powders using IR spectroscopy. The first IR study on CO adsorbrates on the rutile TiO$_2$(110) single crystal surface has became available only very recently. In all studies...