

Role of Hydroxyl Group in CO Adsorption on SnO₂ (110) Surface Investigated by a First-principle Study

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ABSTRACT

Tin dioxide SnO₂ is a wide band gap (3.6 eV) n-type semiconductor with rutile bulk structure¹. It has a wide application in solar cells, catalysis and gas sensors^{2,3}. SnO₂ (110) surface is the most stable one thermodynamically among the low-index surfaces, which is usually covered with hydroxyl groups (OH) formed by dissociative chemisorption of H₂O. Their presence on the surface influences the adsorption of molecules such as CO,⁴ NO₂,⁵...etc. The aim of this work is to investigate the adsorption of CO on SnO₂ (110) surface in the presence of hydroxyl group.

Density functional theory (DFT) calculations were performed using the program CRYSTAL09 package⁶, which employ the LDA and the hybrid B3LYP exchange- correlation functionals. Pseudo-potential (ECP) of Durand-Barthelat's⁷ were used to describe the Sn, O, and C centers, and those proposed by Otero-de-la Roza et al.⁸ for H center. The stoichiometric SnO₂ (110) surface has a rectangular structure, corresponding to the Pmm2 (C_{2v}) space group with lattice parameters a=3.186Å and b=6.69Å. The SnO₂ (110) surface is represented by *p*(4x1) supercell with a periodic slab of three layers (3L), as shown in Fig. 1(a). CO molecule was adsorbed on two different sites (O_{2c}, Sn_{5c}) to determine the favorable site, while the H atom was adsorbed on bridging oxygen O_{2c} atom thus modeling quarter monolayer coverage (1/4 ML), as shown in Fig. 1(b-d). The cut-off energy is fixed at 10⁻⁸ Hartree. The Brillouin zone integrations were performed with a 6x6x1 Monkhorst-Pack grid, corresponding to 16 k-points in the irreducible part of the first Brillouin zone (IBZ).

Calculation of CO adsorption on SnO₂ (110) surface was studied firstly to determine favorable site of adsorption. Two possible adsorption sites are considered: bridging oxygen (O_{2c}) and 5-fold tin (Sn_{5c}) as shown in Fig. 1(b) and Fig. 1(c), respectively. When CO is adsorbed on top of O_{2c} atom site, the adsorption energy is positive at about 1.44 eV, which indicate energetically disfavored adsorption site. Our results indicate that the CO molecule preferentially adsorbs with the C end on a Sn_{5c} atom site, and the adsorption energy is -0.79 eV. The following calculations only focus on this stable configuration (Fig. 1(c)).

In the presence of the hydroxyl group on the SnO₂ (110) surface, where the H atom is adsorbed on O_{2c} site resulting bridging hydroxyl group (OH_b), the adsorption energy is calculated to be -3.42 eV. The absolute value of adsorption energy increases by 2.63 eV in the presence of OH_b. This indicate that the hydroxyl group is present to facilitate CO adsorption on Sn_{5c}. Band structures, total and projected density of states and Mulliken charge were investigated to discuss our results.

Finally, we concluded that the hydroxyl group plays a significant role in the adsorbed CO molecule and its reactivity on SnO₂ (110) surface.



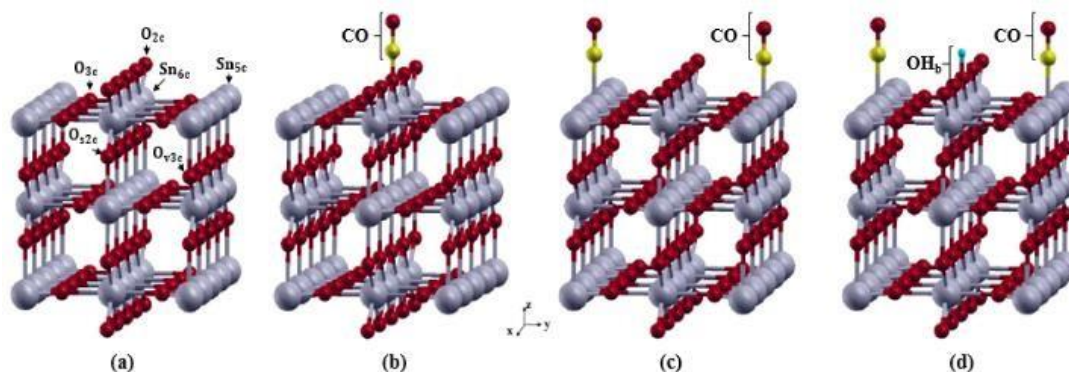


Fig. 1: stoichiometric SnO₂ (110) surface (a) before and after adsorption of CO on (b) O_{2c} site and (c) Sn_{5c} site, adsorption of both CO and H on Sn_{5c} and O_{2c}, respectively.

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