Interaction of carbon dioxide with Ni(110): a combined experimental and theoretical study

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Abstract. We performed a combined experimental and theoretical study of CO_2 adsorption on the Ni(110) surface with the aim of understanding the details of the molecule-surface interaction, thus identifying the adsorption sites and evaluating the relevant energy barriers in the adsorption and in the diffusion processes. In this contribution we mainly focus on the results of numerical simulations, performed within the framework of density functional theory using ab-initio pseudopotentials. We discuss the results obtained together with experimental data.

Keywords: Surface Science; Carbon dioxide; Ni surfaces; Chemisorption; Density Functional Theory; First-principles Pseudopotentials; TPD; XPS; HREELS
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INTRODUCTION

CO_2 is a key compound e.g. for methanol synthesis, according to the reaction $CO_2+3H_2 \longleftrightarrow CH_3OH + H_2O$ [1]. Cu-based catalysts are normally used, but it has been pointed out [2] that Cu/Ni catalysts are 60 times more active for CO_2 hydrogenation than traditional pure Cu catalysts. It is of crucial interest to understand the complete reaction path, but also the basic question concerning the CO_2 interaction with pure Ni is still open.

Interestingly, CO_2 chemisorption in Ultra-High Vacuum is observed only on Ni(110) and not on other low Miller index surfaces, where on the contrary it is typically promoted only by pre-adsorbed alkali atoms. The available experimental and theoretical data agree in relating CO_2 chemisorption on Ni(110) with the formation of

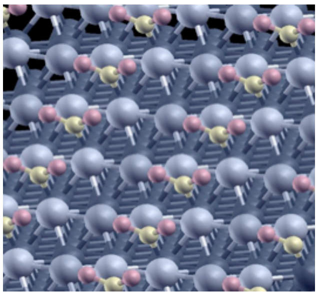

FIGURE 1. Ball-and-stick model of chemisorbed CO_2 on Ni(110) obtained by periodically repeating the supercell used for the simulation in the directions parallel to the surface.

CO_2^-, a charged and bent species [1]. However, it is not yet clear which is the most favorable adsorption geometry or whether there are different possible configurations and how their occupation depends on coverage and temperature. In absence of direct information about the chemisorption configuration of CO_2 on Ni(110), a symmetric C_{2v} configuration with the molecule in a reversed "V" shape (bound to surface with the two O atoms) has been proposed, in analogy with formate (HCOO), which is known to bind to metallic surfaces mainly in a reversed "Y" configuration. Our aim is to clarify this issue by combining experimental and theoretical investigations, the former including Temperature-Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS) and High Resolution Electron Energy Loss (HREELS) measurements, the latter based on accurate first-principles numerical simulations.

EXPERIMENTAL RESULTS

TPD and XPS indicate the presence of two CO_2 species, physisorbed and chemisorbed. The TPD peaks are at ~100 K and ~220 K, corresponding to desorption energies of ~0.26 eV for physisorption and ~0.60 eV for chemisorption, on the basis of a simple application of the Readhead approximation. No direct information about adsorption sites and geometries can be derived by these experiments only.

THEORETICAL RESULTS

We performed calculations within the framework of Density Functional Theory (DFT) in the local density approximation using first-principles pseudopotentials to describe the valence electrons and plane wave as a basis set to expand the electronic wavefunctions. The Quantum-Espresso package has been used [2]. For a convenient reciprocal space formulation of the problem, periodically repeated supercells with slab geometry are used, therefore describing a fictitious order on surface (Fig. 1) that is not observed experimentally. However, the supercell used (3x2 on surface) is large enough to guarantee that the molecule-molecule interactions are very small.

The results of total energy and force minimization suggest the existence of different inequivalent chemisorption sites, short-bridge (SB) and hollow (H) sites, all characterized by the bent, negatively charged molecule, and a predominant surface-carbon coordination. In the SB site, the molecular plane is perpendicular to the surface and parallel to the [1-10] direction; both a fully symmetric configuration (C_{2v} symmetry) and a slightly asymmetric one (C_s symmetry) are found to be stable. They are however very similar. The most stable configuration turns out to be very similar to the one reported by Wang et al. [4], i.e. with C almost in the hollow site, with a dominant carbon coordination and with Ni and oxygen atoms pointing upwards and the molecular plane inclined with respect to the Ni surface normal (hereafter indicated as *hollow-up* (HU) configuration) (Fig. 2).

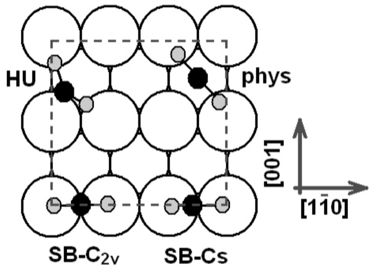

FIGURE 2. Schematic top view of Ni(110) with CO_2 in different possible adsorption sites.

DISCUSSION

SB and HU configurations differ in energy by only 0.07 eV/molecule and are separated by a diffusion barrier SB—>HU of 0.15 eV/molecule, calculated using the Nudged Elastic Band approach [5]. The adsorption energy in the SB site is of 0.26 eV. A further indication coming from numerical simulations is that the chemisorption process is activated, with an activation barrier slightly smaller than 0.1 eV/molecule. These values are compatible with the measured desorption energies and with a simultaneous population of both HU and SB sites at low temperature.

Vibrational frequencies have been calculated for the different chemisorption configurations and for a linear, neutral metastable configuration with the CO_2 molecule parallel to the surface, which is representative of a 'physisorbed' state. A clear correspondence can be established between the calculated values and the main peaks detected by HREELS (Table 1). With the exception of the hindered rotation modes, that are not observable due to dipole scattering rules, all the other modes characterizing the adsorption geometries can be identified; in particular, one peak detected at about 168 meV can be interpreted as a clear fingerprint of the presence of the HU configuration and attributed to its asymmetric stretching mode, which is clearly different from the SB case.

TABLE 1. Vibrational frequencies (in meV) obtained from DFT calculations for different adsorption configurations, and the corresponding (in parenthesis) peaks observed in the HREELS spectra.

Vibrational mode	HU	SB	'phys'
Asymmetric stretching	174 (168)	218 (-)	287 (290)
Symmetric stretching	138 (141)	142 (141)	160 (168)
Bending	90 (90)	81 (81)	79 (81)
Hindered rotation (out of plane)	52 (-)	63 (-)	78 (-)
External stretching	47 (46)	44 (46)	25 (-)
Hindered rotation (in plane)	41 (-)	35 (-)	25 (-)

The transition states reached during the adsorption process both in the SB sites and in the HU sites are characterized by sudden changes of the O-C-O bond angle and atomic charges with respect to the gas phase, indicating that *bending* and *electron transfer* are two important features in the chemisorption process. A charge density plot is shown in Fig. 3 for the molecule in the SB site.

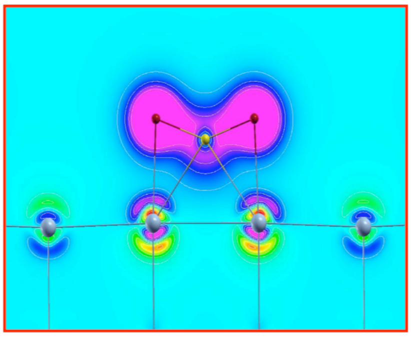

FIGURE 3. Contour plot of the differential charge density distribution of CO_2 adsorbed on SB site on Ni(110). The difference is with respect to the neutral molecule and the neutral Ni slab considered separately but in the same positions of the chemisorbed configuration.

CONCLUSIONS

Experimental and theoretical investigations concerning energetics and vibrational frequencies yield consistent indications about two inequivalent adsorption sites for CO_2 on Ni(110) that can be simultaneously populated at low temperature: short-bridge site with the molecular plane perpendicular to the surface and hollow site with the molecular plane inclined with respect to the surface. In both cases CO_2 is negatively charged and bent. At variance with widely accepted previous literature data, in both sites the molecule has pure carbon or mixed oxygen-carbon coordination with the metal.

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