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DFT study of the structure sensitivity for the adsorption of methyl, methoxy, and formate on Ni(1 1 1), Ni(1 0 0), and Ni(1 1 0) surfaces

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ABSTRACT

The chemisorption of radical species (CH_3, CH_3O, and HCOO) on Ni(1 1 1), Ni(1 0 0), and Ni(1 1 0) surfaces has been systematically studied by means of self-consistent, periodic, density functional theory (DFT–GGA) calculations. The calculated results showed that the adsorption energies are structure sensitive to the surface structure, that is, Ni(1 1 1) < Ni(1 0 0) < Ni(1 1 0) for CH_3O and HCOO species, and Ni(1 0 0) < N(1 1 1) < Ni(1 1 0) for CH_3 species. In addition, it is found that the adsorption energy of CH_3O is larger than that of CH_3 on a given metal surface.

1. Introduction

A fundamental understanding of heterogeneous catalytic reactions at the microscopic level is the major subject of surface chemistry and relies on the studies of the elementary surface processes. And a complete mechanistic study of surface reactions can be best accomplished with the knowledge of the identification of the stable surface intermediates under investigations, and it is vital to the characterization of dynamical pathways of the reactions. Intensive investigations of the adsorption of small molecules and radicals on metal surfaces have been carried out in the past few decades using conventional surface vibration spectroscopic techniques as well as theoretical studies. Methyl, methoxy, and formate intermediates are of great importance in many heterogeneous reactions. They are formed as stable intermediates via the abstraction of the hydrogen atom from the adsorbed molecular species, i.e., methane, methanol, and formic acid, respectively.

The dissociative chemisorption of methanol has received a great deal of attentions due to the possible usage as a hydrogen source in fuel cell application, as well as for methane and formic acid as the basis of syngas synthesis, and the Fisher–Tropsch synthesis, among other industrially important processes. In an effort to gain a fundamental understanding of such processes, a number of studies of methane, methanol and formic acid adsorption and decomposition on transition metal surfaces have been undertaken.

Examples include the Fischer–Tropsch process [1,2] methane partial oxidation or oxidative coupling, and water–gas shift reactions [3–5]. Since early work of Prettre et al. [6] it has been accepted that the reaction process involves the oxidation of CH_4 primarily to H_2O and CO_2 followed in the first stage. However, the other mechanism is direct oxidation via methane pyrolysis as proposed by Schmidt et al. [7,8] based on a series of recent pulse studies [9–11]. On the basis of the methane pyrolysis mechanism, methane decomposition on 'reduced transition metals' results in the formation of adspecies CH_3 and H in the first step, and the breaking of a C–H bond in methane is the key to transforming the resources of natural gas into useful products like hydrogen and petrochemicals.

There has been a growing interest in the experimental studies relating to the methanol reactions on a variety of transition metal surfaces, including STM [12] on Cu(1 1 0), UPS [13] on Ni foil, TPE-ELS [14] on Ni(1 1 0), XPS, SIMS [15] on Pd(1 1 1), IRAS [16] on Pt(1 1 1), RAIRS [17] on Ru(0 0 0 1), HREELS and TPRS [18] on Fe(1 0 0), and so on. The previous investigations have demonstrated that methanol adsorbs in multilayer without dissociation at lower temperature. When the surface is heated, it decomposes to the adsorbed methoxy intermediate.

Decomposition of formic acid on transition and post-transition metal surfaces has also been investigated for their great interest, and it is found that formation of formate is much more favorable than formyl both thermodynamically and kinetically on Mo [19], Ru [20], Rh [21], Ni [22], Pd [23], Pt [24], and Cu [25,26] suggesting that the formate species appears to be formed barrierlessly and is a

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stable intermediate by the deprotonation process of HCOOH on metal surface. Formate is also observed during the methanol oxidation reaction, and it is thought to be an intermediate in the methanol synthesis reaction.

Methyl adsorbed on Ni(1 1 1) has been investigated through static secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) [27]. In the dynamical studies of the activated dissociative chemisorption of methane on Ni(1 1 1) by a combination of molecular beam techniques and high-resolution electron energy loss spectrometry (HREELS), CH_3 species has been identified as the primary product of the reaction [28] and with an estimated adsorption energy of 313 kJ/mol in Ref. [29], based on the exothermicity of methane dissociation and the known adsorption energy of hydrogen. An unusually low C–H vibration frequency has also been obtained from HREELS, which could be indicative of a formation of a C–H$\cdots$metal bond and seems to be directly related to the dehydrogenation process. They conclude that the reason methyl radicals have not been observed before is that they are not stable and dissociated or recombined above 150 K, which is below the temperature where the methanation reaction is normally carried out. The adsorption of methyl radicals has also been studied by X-ray photoelectron spectroscopy and temperature programmed desorption (TPD) [30] on clean Ni(1 0 0) surface, the Ni(1 0 0) with a chemisorbed oxygen overlayer, and Ni(1 0 0) with a NiO(1 1 1) oxide overlayer. They found that methyl radical disappears at surface temperatures of 120–170 K, and also suggested that the dominate mechanism of methane formation on Ni(1 0 0) seems to be the combination reaction of methyl groups with surface hydrogen while the mechanism on Ni(1 1 1) seems to be a hydrogen transfer between a short-lived hydrocarbon complex, although this cannot be confirmed from the data alone.

The surface chemistry of methoxy is also of considerable practical interest, especially, for the metal-catalyzed synthesis of hydrogenated products of CO or for its reverse reaction. Experiments explored the kinetic isotope effect in combination with HREELS [31], MBRS [32], (molecular beam relaxation spectrometry), and LID (laser induced desorption) [33], and X-ray photoelectron spectroscopy (XPS) [34] have clearly illustrated the formation of methoxy on Ni surface. As regards on Ni(1 1 1), the early high-resolution electron energy loss spectroscopy (HREELS) studies indicated that the methoxy methyl group was inclined away from the surface normal by an unspecified angle [35], while the ultraviolet photoemission studies were interpreted in terms of a perpendicular orientation of the methyl group [36]. A very recent FTIR overtone spectroscopic study of adsorbed methoxy on Ni(1 1 1) also indicates the tilted methyl group [37]. Two adsorption configurations for adsorbed methoxy species on Ni(1 1 0) are identified using reflection adsorption infrared spectroscopy (RAIRS) and both of them are 2-fold coordinated and tilted with respect to the surface normal but in different adsorbed angles [38]. XPS [34] measurements also indicated a tilted methoxy species, which bonded via the oxygen atom to the Ni(1 1 0) surface, and was in contrast to the perpendicular methoxy on Ni(1 1 1) [39]. Fourier transform infrared studies have been made on several isotopomers of CH_3O on Ni(1 0 0) by Huberty and Madix [40] and concluded that the C–O bond of the methoxy species lies normal or nearly normal to the surface at low coverages but may tilt slightly at high coverage. The XPD [39] studies showed that the O–Ni and C–O distances are 1.93 ± 0.04 and 1.44 ± 0.05 Å, respectively, and that the oxygen atom adsorbs at the fcc 3-fold hollow site. CH_3O/Ni(1 1 1) is stable near 180 K [35,36,41] and is known to decompose near 300 K or above [35,41]. Gates et al. [31] specify that the CH_3O/Ni(111) decomposition temperature as 290 K, in excellent agreement with the experiment reported above, indicating that CH_3O/Ni(1 1 1) is a stable intermediate in reaction of methanol decomposition.

The interaction of formate with nickel surfaces has been studied by different experimental techniques on Ni(110) [22,42–44,34,45] Ni(111) [46,47], and Ni(1 0 0) [48,49]. HCOO has been identified by Auger electron spectrometric (AES), low energy electron diffraction (LEED) [42], thermal desorption spectroscopy (TDS), electron energy loss spectroscopy (EELS), reflection–absorption infrared spectroscopy (RAIRS) [43,46] HREELS [22,44], X-ray photoelectron spectroscopy (XPS) [34] and time-resolved infrared–visible sum-frequency generation (SFG) spectroscopy [47,50,51]. As investigated previously using low energy electron diffraction (LEED) and high-resolution electron energy loss spectroscopy (HREELS) [44] the adsorption of formate on Ni(1 1 0) yielded a $c(2 \times 2)$ LEED pattern, EELS data and symmetry arguments were also used to suggest that HCOO binds to the surface via its two oxygen atoms (bidentate) across short-bridge sites, with the plane of the molecule aligned along the[$1\bar{1}0$]-direction. From the results obtained with these techniques, we could conclude that the presence of surface formate species is either after the adsorption of formic acid at room temperature or after the adsorption of formic acid at low temperature followed by heating surface to an appropriate reaction temperature. The orientation and the bonding site of HCOO have been identified: through two carbonyl oxygen atoms, that is, either to two Ni atoms (bridged configuration) or to one atom (bidentate configuration), and tilted with the surface.

On the theoretical study side, the extended Hückel method with cluster model was first employed on the studies of CH_3 on Ni(1 1 1) by Gavin et al. [52]. Later, the generalized valence bond ab initio studies have been reported for methyl adsorption on Ni(1 0 0) by Upton [53]. Siegbahn et al. also reported that the CH_x adsorption on Ni(1 1 1) and Ni(1 0 0) using bond prepared cluster calculations with varying the cluster sizes [54,55]. Burghgraef et al. [56] have carried out quasi-relativistic calculations based on density functional theory (DFT) by using the Amsterdam density functional program package (ADF). Yang and Whitten [57] have studied CH_3 chemisorption on Ni(1 1 1) using ab initio valence orbital CI calculations with an embedded cluster. Recently, Liao et al. [58] have carried out the methane dissociation on Ni(1 1 1) surfaces using a quasi-relativistic density functional method. Watwe et al. [59] have studied CH_x species on Ni(1 1 1) in the $p(2 \times 2)$ unit cell (corresponding to the coverage of 0.25 ML) using the periodic infinite plane wave slab calculations in conjunction with density functional theory and ultrasoft pesudopotentials. Hu et al. [60–63] also studied the CH_x species on Ni(1 1 1) with spin polarized density functional theory calculations with gradient corrections in a $p(2 \times 2)$ unit cell, too.

As the case of methoxy adsorption on nickel surface, Yang et al. have carried out ab initio embedding calculations for CH_3O on Ni(1 1 1) [64] with the adsorption energy of 376 kJ/mol. In their newer study [65] they also investigated the adsorption energies of methoxy in the presence or absence of CO on Ni(1 0 0) surface by a many-electron theory, the results indicate the coadsorption of CO causes the methoxy C–O axis to tilt more, and increases the adsorption energy of CH_3O from 385 to 418 kJ/mol. As the case of CH_3O on Ni(1 1 0), Zeroka have focused on the identification of the electronic structure and the charge redistribution after adsorption [66].

Only a few theoretical investigations of HCOO on Ni(1 1 1), Ni(1 0 0) and Ni(1 1 0) were found although many experimental studies have been reported. Upton has investigated the formate chemisorption in a symmetric bidentate configuration at the bridge on Ni(1 0 0) through generalized valence bond and configuration interaction calculations, and reported an adsorption enthalpy of 492 kJ/mol with the oxygen atoms above surface of 1.45 Å [67]. The studies of chemisorption on Ni(1 1 0) in which the Ni4 and Ni7 cluster were employed as the surface model, Ushio et al. [68] have obtained the two possible adsorption sites of formate