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CO dissociation on clean and hydrogen precovered Fe(111) surfaces

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Abstract

Spin-polarized density functional theory calculations were performed to investigate CO dissociation on clean and hydrogen precovered Fe(111) at 1/3 monolayer coverage. On clean Fe(111), the adsorbed CO first diffuses from the shallow-hollow site to the bridge-like site by elevating 0.20 eV in energy, and then dissociates into C and O atoms by overcoming a barrier of 1.53 eV. Interestingly, the CO dissociation process is accelerated in the presence of H_2 via intermediate CHO_{ads} ($CO_{ads} + 2H_{ads} \rightarrow CHO_{ads} + H_{ads} \rightarrow CH_{ads} + O_{ads} + H_{ads}$). This stepwise path is kinetically more favored with the lowest barrier of 1.17 eV. In contrast, the previously suggested paths, $CO_{ads} + 2H_{ads} \rightarrow C_{ads} + O_{ads} + 2H_{ads}$ and $CO_{ads} + 2H_{ads} \rightarrow C_{ads} + OH_{ads} + H_{ads}$, are not competitive due to higher barriers (1.76 and 1.79 eV, respectively). The activity of different low-index Fe surfaces toward CO is also compared.

Keywords: DFT; CO dissociation; Iron surfaces

1. Introduction

The interaction of CO with transition metal surfaces is of great fundamental and practical importance in many catalytic processes, including Fischer–Tropsch (FT) synthesis and methanation [1–3]. For iron-based catalysts, the FT reactivity is associated with the reducibility of iron oxides, the reoxidation of iron metal, and the reduction of iron carbides in connection with the coexistence of metal, oxide, and carbide phases [4,5]. Therefore, the reaction mechanism is extremely complicated [6]. It is believed that the adsorbed CO first dissociates into surface C and O ($CO_{ads} \rightarrow C_{ads} + O_{ads}$), which react with the dissociatively adsorbed H to form surface CH_x and OH_y ($C_{ads} + xH_{ads} \rightarrow CH_{x,ads}$, $O_{ads} + yH_{ads} \rightarrow OH_{y,ads}$) [7,8]. Consequently, considerable attention has been paid to the CO/Fe and (CO + H_2)/Fe systems [4–11]. However, most experimental and theoretical studies focused on the densely packed Fe(110) [12–18] and Fe(100) [15,19–31] surfaces. Only a few investigations have explored the very open Fe(111) surface, and the process for CO dissociation on Fe(111) remains unclear.

A thermal desorption spectroscopy (TDS) and high resolution electron energy loss spectroscopy (HREELS) study by Seip et al. [32] showed three molecular CO adsorption states on Fe(111), distinguished by their characteristic C–O stretch frequencies (ν_{C-O}): *state a* ($\nu_{C-O} = 1500\ cm^{-1}$), *state b* ($\nu_{C-O} = 1815\ cm^{-1}$), and *state c* ($\nu_{C-O} = 2000\ cm^{-1}$). Based on these, Seip et al. [32] further identified *state a* as the deep-hollow (dh) site (bonded to the exposed third-layer Fe atom), *state b* as the shallow-hollow (sh) site (bonded to the exposed second-layer Fe atom), and *state c* as the on-top site (bonded to the first-layer Fe atom). The subsequent HREELS study by Bartosch et al. [33] resolved the broad *state a* in two distinct peaks: *state* a_1 ($\nu_{C-O} = 1325$–$1485\ cm^{-1}$) and *state* a_2 ($\nu_{C-O} = 1520$–$1575\ cm^{-1}$). They found that *state* a_1 is formed primarily at low coverage but can be converted to *state* a_2 at high coverage when the on-top site becomes occupied.

In addition, Seip et al. [32] concluded that CO dissociation occurs only through the sh site (*state b*) regardless of coverage, whereas Bartosch et al. [33] suggested that *state* a_1 (dh site) dissociates directly, but it can convert to *state b* (sh site) before dissociation. Using temperature-programmed des-

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orption (TPD) and time-resolved electron energy loss spectroscopy (TREELS), Whitman et al. [34] studied the kinetics of CO adsorption and reaction on Fe(111) and found that the site occupancy is highly temperature- and coverage-dependent. CO dissociation proceeds from the sh site at about 300 K. At low monolayer (ML) coverage (0.195 ML), the dissociation reaction occurs with $E = 0.9 \pm 0.2$ eV and $\nu_1 = 10^{11\pm2}/\mathrm{s}$. The resulting surface C and O atoms desorb recombinatively at about 760 K with $E \approx 2.1$ eV and $\nu_1 \approx 0.1\ \mathrm{cm}^2/\mathrm{s}$. At higher coverage (0.312 ML), in addition to dissociation, some of the adsorbed CO in the sh site desorbs with $E \approx 1.4$ eV and $\nu_1 \approx 10^{17}/\mathrm{s}$.

Based on atom superposition and molecular orbital theory, Mehandru and Anderson [16] studied the binding and orientation of CO on Fe(111) using a three-layer, 27-atom cluster model. They calculated that CO adsorbs in the order di-σ bridge > on-top > shallow-hollow > deep-hollow, in disagreement with the experimental order of shallow-hollow > deep-hollow > on-top reported by Seip et al. [32] and Bartosch et al. [33]. It is likely that the level of the theory and the model used by Mehandru and Anderson were insufficient to give a quantitative (or even qualitative) description of the process.

More recently, a detailed study of CO adsorption on Fe(111) performed at the level of density functional theory (DFT) [35] found that CO site occupancies depend on the coverage. At low coverage (1/3 and 1/2 ML), the sh adsorption site is the most stable site, whereas the sh and the bridge (br) sites are equally favored at 1 ML. In contrast, bent on-top and triply capping adsorptions are the most favored forms at very high coverage (2 ML).

It is well known that the surface carbon from CO dissociation may stay on the surface or lead to carburization of the catalyst. The rate of carburization reaction is faster in the presence of H_2 than in the absence of H_2 [36]. A study of CO/H_2 reaction on a Ni catalyst by Ho and Harriott [37] proposed the following hydrogen-assisted CO dissociation reactions:

$$\mathrm{CO_{ads}} + \mathrm{H_{ads}} \rightarrow \mathrm{COH_{ads}} \tag{1}$$

and

$$\mathrm{COH_{ads}} + \mathrm{H_{ads}} \rightarrow \mathrm{C_{ads}} + \mathrm{H_2O_{(g)}}. \tag{2}$$

But this mechanism was ruled out by Bianchi and Bennett [38] on the Fe–Al_2O_3 catalytic system, because $H_2O_{(g)}$ was not detected in the effluent during the reaction. By determining the amount of CO_2 formed during contact of the feed gas (10% CO + 1% H_2 + 89% He and 10% CO + 90% He) with the surface or the quantity of CH_4 produced by etching the spent catalyst with pure H_2, Bianchi and Bennett proposed an alternative mechanism,

$$\mathrm{H_2} \rightarrow 2\mathrm{H_{ads}} \tag{3}$$

and

$$\mathrm{CO_{ads}} + \mathrm{H_{ads}} \rightarrow \mathrm{C_{ads}} + \mathrm{OH_{ads}}. \tag{4}$$

Here we present a systematic DFT study of CO dissociation on clean and hydrogen-precovered Fe(111) surfaces. The aim is to describe the changes of the surface structure and energy during CO dissociation, and also to elucidate the role of hydrogen in the mechanism of FT synthesis.

2. Computational details

2.1. Methods

All calculations were performed at the DFT level with the CASTEP program [39,40] in the Materials studio of Accelry Inc. For geometry optimizations, the exchange and correlation energies were calculated using the Perdew, Burke, and Ernzerhof (PBE) functional [41] within the generalized gradient approximation (GGA) [42]. The electron–ion interactions were described by ultrasoft pseudopotentials (USPPs) [43] with the plane-wave basis set cutoff at 340 eV. A Fermi smearing of 0.1 eV was used to evaluate occupancy numbers. Because of its significant effect on the adsorption energies for magnetic systems [44–46], spin polarization was included in the calculations for the system with Fe. The convergence criteria for structure optimization and energy calculation were set to MEDIUM quality with the tolerance for SCF, energy, maximum force, and maximum displacement of 2.0×10^{-6} eV/atom, 2.0×10^{-5} eV/atom, 0.05 eV/Å and 2.0×10^{-3} Å, respectively. The linear synchronous transit (LST)/optimization method [47] was used to locate the transition states for CO dissociation. The transition state structure was estimated by a linear synchronous search from reactant and product, followed by a conjugate gradient energy minimization in the directions conjugating to the reaction pathway.

It should be noted that the PBE functional can give reliable optimized geometry but tends to overestimate the adsorption energies by 0.2–0.6 eV. Based on this finding, a revised PBE (RPBE) method was developed [48]. The RPBE systematically improves the atomization energies for a large database of small molecules and the chemisorption energies of atoms and molecules on a transition-metal surface. Therefore, we further carried out RPBE single-point calculations on the PBE-optimized geometries. In the following sections, we use the RPBE energies for discussion and provide the PBE values for comparison.

2.2. Models

Fe(111) has a step-like or defect-like surface with atoms of both the second and the third layers exposed. The top and side views are shown in Fig. 1; the first, second, and third iron layers are labeled Fe1, Fe2, and Fe3, respectively. Both experimental [49] and our previous DFT [35,50] studies verified that the very open structure of the clean Fe(111) surface exhibits significant multilayer relaxation. For modeling Fe(111), a slab with seven iron layers was used, in which the top three layers were allowed to relax, while the bottom four layers were fixed in their bulk position (3Fe/4Fe) to represent the semi-infinite bulk crystal beneath the surface. All adsorbates were put on only one side of the slab. The free CO or H_2 molecule was placed in a 10 Å cubic box to minimize the interaction of neighboring molecules, and the equilibrium bond length of CO or H_2 is predicted to be 1.144 or 0.753 Å (comparable to the experimental values of 1.128 or 0.741 Å [51]). The energy of an isolated C or O atom was computed in its ^{3}P ground state (as indicated by the population analysis, i.e., C: $2s^2 2p^2$ or O: $2s^2 2p^4$) by putting a C or