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Structure sensitivity of CO methanation on Co (0 0 0 1), $(1 0 \bar{1} 2)$ and $(1 1 \bar{2} 0)$ surfaces: Density functional theory calculations

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ABSTRACT

Density functional theory (DFT) calculations have been carried out to investigate the structural sensitivity of the elementary processes in CO methanation at low coverage of 0.25 ML, including CO dissociation via either direct or H-assisted path and CH_x ($x = 0$–3) hydrogenation, on Co (0 0 0 1), $(1 0 \bar{1} 2)$ and $(1 1 \bar{2} 0)$ surfaces. CO direct dissociation was found to be structurally most sensitive, whereas CH_x hydrogenation is structurally least sensitive. Specifically, the barrier of CO direct dissociation, H-assisted dissociation and CH_x hydrogenation on different surfaces varies in range of 1.12, 0.54 and 0.34 eV, respectively. Regardless of Co surfaces considered, the CO activation is the rate-limiting step of methanation reactions, which would proceed through the H-assisted pathway on Co (0 0 0 1), whereas through both direct and H-assisted pathways on more active Co $(1 0 \bar{1} 2)$ and $(1 1 \bar{2} 0)$ surfaces. The structure sensitivity of CO activation leads to methanation reaction structural sensitive.

1. Introduction

The nature of the active sites and structure sensitivity of heterogeneous catalysis has been a longstanding subject of catalysis. The understanding of the structure sensitivity of reactions has progressed enormously with the development of theoretical calculations and ultra-high vacuum technology. For instance, using scan tunneling microscope (STM) and density functional theory (DFT) calculations, Dahl et al. [1] found that the N_2 dissociation on Ru (0 0 0 1) is at least nine orders of magnitude slower than that on steps. The reaction barrier on steps was calculated to be 1.5 eV lower than that on flat surfaces. DFT calculation and experimental studies showed CO dissociation is extremely structure sensitive and flat Rh surface cannot dissociate CO under most conditions [2]. The same was also found for NO dissociation on flat and stepped Ru (0 0 0 1) [3,4]. DFT calculations showed that the transition state (TS) of various diatomic molecules on monatomic steps involving for instance so-called B5 sites is kinetically more favorable than the TS on close packed surfaces. It was only after the origin of the structure sensitivity of reaction is well understood that the catalysts can be discovered based on rational design.

The methanation reaction has attracted much interest as an alternative to the preferential oxidation of CO (PROX) [5] for removing similar remote amount of CO from the hydrogen feed to proton exchange membrane fuel cells. Industrially, it is a technologically important reaction to remove CO and CO_2 from the hydrogen supply for ammonia production [6,7]. Methanation is also used in connection with gasification of coal and Fischer–Tropsch synthesis [8,9]. In addition, methanation is one of the simplest catalytic reactions and can serve as a test bed for the fundamental understanding of heterogeneous catalysis.

A number of experimental [10–25] and theoretical studies [26–30] have been conducted to elucidate the reaction mechanism and to investigate the structure dependence of the methanation reaction. Two possible mechanisms for CO methanation have been proposed, i.e., CO dissociation followed by hydrogenation (direct CO dissociation mechanism), or vice versa (hydrogen-assisted CO dissociation mechanism) to produce CH_x ($x = 0$–3) species, which then undergo sequential hydrogenation, leading to the formation of methane eventually. By the kinetics analysis and H_2/D_2 isotope experiment, Bell et al. [16,17] suggest that the CO activation is fast through direct dissociation route over Ru catalysts, and that CH_3 hydrogenation is rate determining for the synthesis of methane. Ho and Harriott [18] proposed that hydrogen-assisted CO dissociation is the rate limiting step in methanation reaction on nickel catalysts, and this assumption was confirmed by Coenen et al. [21] using isotope labeling method. The H-assisted CO dissociation on Ni is also supported by the DFT calculations that proceed via COH intermediate [22]. Surface science experiments on Co single crystals showed that direct CO dissociation on Co $(1 1 \bar{2} 0)$ and Co $(1 0 \bar{1} 2)$ are much faster compared to the close packed Co (0 0 0 1), and that the apparent activation energy for methane formation on Co $(1 1 \bar{2} 0)$ is equal to the value observed on Co (0 0 0 1) surface,

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which reflects the nature of the similar rate limiting step on the surfaces. These authors proposed that α-hydrogenation of a C_nH_{2n+1} surface species is the rate limiting in FT reactions [23,24]. Iglesia et al. [26] proposed a Fischer–Tropsch synthesis pathway limited by H-assisted CO dissociation on both Fe and Co by combining experiment and theoretical calculation. Jiao et al. [27] observed that step surface has higher activity than flat surface for CO activation and CH_x are formed mainly via the HCO intermediate dissociation on double stepped Co (0 0 0 1) surface. Recently, Shetty and van Santen [28] reported that CO direct dissociation is easier than H-assisted pathway on open Co $(10\bar{1}0)$B and Ru $(10\bar{1}0)$B surfaces. The hydrogenation of CH_x (x = 0–3) on flat and stepped Co (0 0 0 1) is studied by Hu and co-workers [29] using DFT calculations. They found that CH_3 hydrogenation ($CH_3 + H \rightarrow CH_4$) is the most difficult among all the hydrogenation steps and CH_x hydrogenation process is not structure sensitive.

Nickel is the commonly used catalyst for methanation [30] due to its high selectivity towards methane and lower price. However, cobalt has attracted much attention due to higher reactivity [31] and resistance towards carbon deposition [32]. To shed light on the structure sensitivity of CO methanation on Co in particular surface orientations, we systematically investigated two possible pathways proceeding via either direct or H-assisted CO dissociation using DFT, on the close packed Co (0 0 0 1), and more open Co $(10\bar{1}2)$ and $(11\bar{2}0)$ surfaces. The results are compared with previous UHV and real catalytic experiments, and the dependence of the structure sensitivity on reaction conditions is discussed.

2. Calculation methods

All the spin-polarized DFT calculations were carried out using the Vienna ab initio simulation package (VASP) [33,34]. Projector augmented wave (PAW) [35,36] potentials and the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional were used [37]. The kinetic energy cutoff for the plane wave basis set was specified by 400 eV. During the electronic optimization, the change of the total energy and the band structure energy are converged to10^{-4} eV/atom. When the forces on the ions are below 10^{-2} eV/Å, the optimizations have been considered to be converged.

Calculated lattice constant of hcp Co are a = 2.49 Å and c = 4.03 Å, which agrees well with previous calculation (a = 2.56 Å and c = 4.14 Å) [38] and experimental measurement (a = 2.51 Å and c = 4.06 Å) [39]. Co (0 0 0 1), $(10\bar{1}2)$ and $(11\bar{2}0)$ surfaces are represented as four closed packed layers, twelve layers and seven layers with $p(2 \times 2)$ periodicity consisting of 16, 48 and 56 cobalt atoms, respectively. In order to avoiding the periodic interactions, the two neighboring slabs are separated by a vacuum of 15 Å. Monkhorst–Pack mesh k-points sampling of (7 × 7 × 1), (3 × 7 × 1) and (4 × 4 × 1) was separately used for (0 0 0 1), $(10\bar{1}2)$ and $(11\bar{2}0)$ surface calculations. The bottom two, six and three layers were kept fixed for (0 0 0 1), $(10\bar{1}2)$ and $(11\bar{2}0)$ surfaces, while the other cobalt layers and the adsorbates were relaxed completely, respectively.

An efficient force reversed method [40] was used to determine the transition states and a force tolerance of 0.03 eV/Å was used. A couple of the transition states identified were selected and calculated again using the climbing-image nudged elastic band (CI-NEB) method [41] implemented in VASP to guarantee the same transition states found.

The chemisorption energy E_{ads} of the intermediate A involved in CO methanation process can be expressed as $E_{ads} = E_{A/slab} - E_{slab} - E_A$, where $E_{A/slab}$ and E_{slab} are the total energies for the slab with chemisorbed species A and the clean surface, respectively, and E_A is the radical or molecule A in the gas phase. The reaction energies can be calculated as the difference between the total energies of the products and the reactants.

3. Results and discussions

3.1. Intermediates adsorption

The geometric structures of Co (0 0 0 1), $(10\bar{1}2)$ and $(11\bar{2}0)$ surfaces are shown in Fig. 1. It can be seen that flat (0 0 0 1) surface is hexagonal close packed and consists of hcp and fcc hollow adsorption sites. The $(10\bar{1}2)$ surface is a stepped surface with unique 4-fold hollow sites and bridge site at the step edge. The $(11\bar{2}0)$ surface is characterized by zigzag grooves, and has long and short ridge sites and hollow sites, respectively. The coordination number is nine on Co (0 0 0 1) surface, higher than that of seven for Co atom at the step of $(10\bar{1}2)$ surface and the ridge of $(11\bar{2}0)$ surface.

We first calculated the adsorption of the intermediates (CO, HCO, CH_x (x = 0–4), C, H, O) involved in CO methanation reactions on Co (0 0 0 1), $(10\bar{1}2)$ and $(11\bar{2}0)$ surfaces. The energetic and geometric information of the most stable state of various intermediates on all the three surfaces is listed in Table 1, and the selected corresponding structures are given in Fig. 2. Atomic adsorbates, carbon, oxygen and hydrogen, and CH_x species (x = 1, 2) prefer hcp/fcc, 4-fold hollow and hollow sites on Co (0 0 0 1), $(10\bar{1}2)$ and $(11\bar{2}0)$ surfaces, respectively. Except that atomic H binds at the short bridge site on Co $(11\bar{2}0)$. Compared to CH and CH_2, CH_3 and CH_4 tend to bind with less surface Co atoms as shown in Fig. 2(c and d) and (e and f): CH_3 binds in hcp, short bridge and bridge sites on Co (0 0 0 1), $(10\bar{1}2)$ and $(11\bar{2}0)$ surfaces respectively, and CH_4

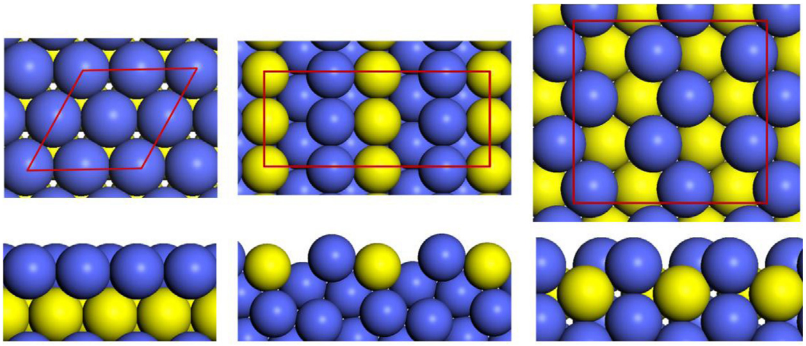
(a) (0001) (b) $(10\bar{1}2)$ (c) $(11\bar{2}0)$

Fig. 1. Top (up panel) and side view (bottom panel) of (a) Co (0 0 0 1), (b) Co $(10\bar{1}2)$ and (c) Co $(11\bar{2}0)$ clean surfaces. The spheres stand for Co atoms and the subsurface Co atoms are represented as yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)