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Reaction pathway of CH_4/CO_2 reforming over Ni8/MgO(100)

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ABSTRACT

First-principles calculations depended on density functional theory have been employed to explore the reaction mechanism of CH_4/CO_2 reforming on Ni/MgO catalyst. The Ni8 cluster supported on the MgO(100) slab has been used to model the Ni/MgO catalyst. CO_2 can decompose on a Ni8 cluster and produce O species through either direct dissociation or hydrogenated dissociation. As a key intermediate produced by CH_4 dissociation, CH_2 could be oxygenated by O species (atomic O or OH), generating CH_2O or CH_2OH; or dehydrogenate into CH, which is then oxygenated by atomic O, resulting in the CHO dissociating. These three pathways can occur in parallel because of the similar energy barrier of their rate-determining steps (less than 0.1 eV). Furthermore, the formation and removal of surface carbon have been analyzed at length. Atomic H from CH_x decomposition has the best reactivity to surface C elimination, followed by O and OH species.

1. Introduction

CH_4/CO_2 reforming has aroused wide concern from researchers due to the low H_2/CO ratio of its generated syngas (1/1) [1–5]. The cheap supported Ni catalysts would have most probable industrialization prospects for this reaction, due to their high catalytic activity and selectivity. However, the supported Ni catalyst is easily deactivated because of coke deposition, which is the main obstacle for the commercialization of CH_4/CO_2 reforming [6–9].

The Ni/MgO catalysts which use MgO as the support have shown the great catalytic activity and stability for CO_2 reforming of methane [10–12]. Hu and Ruckenstein [13,14] attributed the excellent anti-coking performance of Ni/MgO catalysts to the basicity of the support surface and the high dispersion of reduced Ni species, due to the solid solution structure of the NiO/MgO precursor. Feng et al. [15] found that the NiO/MgO precursor calcined at 800 °C showed a higher catalytic activity, which derived from the strong interactions between Ni and MgO support. However, most of the investigations into Ni/MgO catalysts remained in the experimental stage. Discussion of the results was mostly qualitative, including size effect, metal-support interaction, support surface acidity and alkalinity, etc. The improvements of Ni/MgO catalysts are more based on the experiences but not the theories. A certain reaction mechanism would help to realize the whole process and make pertinent improvement to the catalysts, but the mechanisms of CH_4/CO_2 reforming investigated by different groups with experiments are still controversial even contradictory [16–21].

Density functional theory (DFT) technique has become a powerful tool for investigating the reaction mechanism and designing catalysts at an atomic level with its rapid development [22–26]. Wang et al. [27] used DFT method to investigate the reaction pathways of CH_4/CO_2 reforming on Ni(111) surface. In their mechanism, the rate-determining step (RDS) of this reaction was CH_4 dissociated adsorption, and the CH was oxygenated by atomic O which was generated from CO_2 direct decomposition. DFT research by Zhu et al. [28] showed that the oxidation step determined the overall reaction rate under 973.15 K, while the CH_4 dissociation was found to be the RDS at 0 K. Fan et al. [29] explored the application of this conclusion to Ni(100) and Ni(211) in their recent work. Liu et al. [30] investigated the CH_4 sequential dissociation on the perfect or defective Ni4/MgO(100), and found that the O vacancy of MgO(100) changed the d-band structure of Ni4 clusters, which would have an effect on CH_4 dissociation. However, their research was limited to the process of CH_4 dissociation; the integrated reaction pathway of CH_4/CO_2 reforming on Ni/MgO catalysts was still uncertain.

In this work, the adsorption configurations of reactants, intermediates and products in CH_4/CO_2 reforming over the Ni/MgO catalyst

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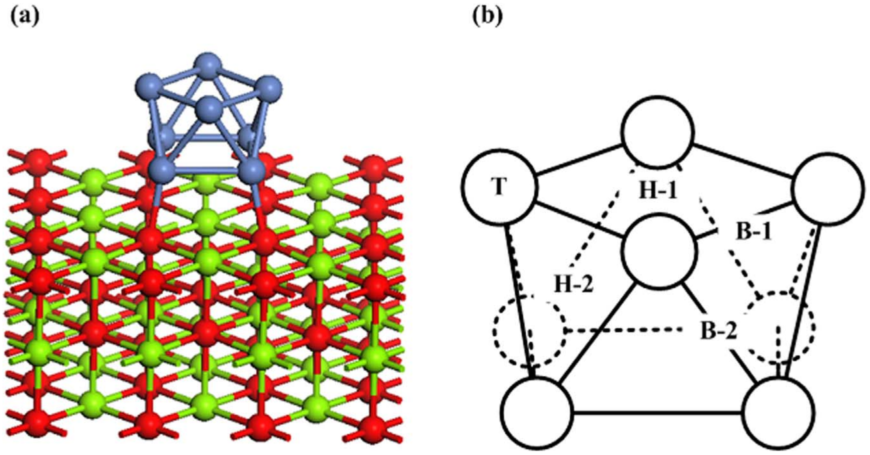

Fig. 1. Structure of Ni8 supported on MgO(1 0 0) surface. Color coding: Red-O atom; Green-Mg atom; Blue-Ni atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

have been studied using the DFT method. MgO(100) face is dominant for most MgO powders. The regular tetrahedron cluster containing four metal atoms was widely used in the supported catalyst models because it is the simplest three-dimension structure [31–33], but the experimental result of HRTEM pictures showed the Ni(100) surface was dominant on Ni/MgO catalyst [34]. So, a Ni8 cluster with a D_{4d} structure is chosen to represent Ni particles because it is three-dimension and similar to Ni(100) surface from a top view. Ni8/MgO(100) is similar to the models Giordano et al. [35,36] used in their investigation. As a result, Ni8/MgO(100) has been used to model the Ni/MgO catalyst. The reaction mechanism of CH_4/CO_2 reforming on Ni8/MgO(100) has been inferred from the systematic investigation of the configurations and energy barriers, and the formation and removal of surface carbon have also been discussed.

2. Computational details

2.1. Computational method

CH_4/CO_2 reforming on Ni8/MgO(100) is calculated with CASTEP (Cambridge Sequential Total Energy Package) program based on DFT method [37,38]. The exchange correlation energy is treated with the Perdew–Burke–Ernzerhof (PBE) function depended on the generalized gradient approximation (GGA) [39,40]. Ultra-soft pseudopotential [41] is used to describe the ionic cores and a plane wave basis with a cutoff energy of 400 eV is expanding the Kohn–Sham one-electron states [42–45]. Brillouin zone integration is performed using the Monhorst–Pack scheme, and the k-point grid is set as (2×2×1) [46]. Configurations are optimized until the force, energy, and maximum displacement converge on 0.05 eV/Å, 2×10^{-5} eV/atom, and 2×10^{-3} Å, respectively.

All calculations of the energies and geometric optimizations consider the impact of spin polarization. Complete LST/QST method is used to locate the transition states [47]. In the first step, the linear synchronous transit (LST) is applied to search a maximum as the transition state (named as TS_1) along an idealized linear path connecting the reactant and the product. Then, quadratic synchronous transit (QST) calculation is devoted to search a minimum from TS_1 in the direction perpendicular to the previous linear path. From that way, another quadratic path through the reactant, the minimum point and the product can be obtained, and the maximum of this quadratic path is named TS_2. The cycle is repeated until the root-mean-square distance of transition states is below 0.25 eV/Å per atom.

For adsorption configurations, adsorption energy was defined as E_{ads}=E[S-Ni8/MgO(100)]−E(S)−E[Ni8/MgO(100)], where E[S-Ni8/MgO(100)] is the energy of the Ni8/MgO(100) with the adsorbed species, E(S) is the energy of the free species, and E[Ni8/MgO(100)] is the energy of the clean Ni8/MgO(100). As a result, a negative E_{ads} means the process of the adsorption is favorable thermodynamically.

For a co-adsorbed configuration X+Y, we define

$$E_{ads}(c) = E[(X+Y)\text{–Ni8/MgO(100)}] - E(\mathrm{X}) - E(\mathrm{Y}) - E[\text{Ni8/MgO(100)}]$$

$$E_{ads}(s) = E[X\text{–Ni8/MgO(100)}] + E[Y\text{–Ni8/MgO(100)}] - E(\mathrm{X}) - E(\mathrm{Y}) \\ -2\times E[\text{Ni8/MgO(100)}]$$

where E[(X+Y)-Ni8/MgO(100)], E[X-Ni8/MgO(100)], and E[Y-Ni8/MgO(100)] are the total energies for the separately adsorbed (X+Y)/[Ni8/MgO(100)] complex, X/[Ni8/MgO(100)], and Y/[Ni8/MgO(100)], respectively. The difference between E_{ads}(c) and E_{ads}(s) is the interaction between X and Y in the co-adsorbed configuration.

2.2. Structure model

The lattice constant of optimized MgO unit cell is 4.31 Å, which is close to the experimental result (4.24 Å) [48]. The MgO surface is represented by a three-layer MgO(100) slab with a p(3×3) super-cell. The bottom layer is fixed in their crystal lattice positions. The vacuum region between two neighboring slabs is set to 20 Å to avoid the significant interaction. The Ni8 cluster has D_{4d} structure adsorbed on the center of MgO(100) surface, as shown in Fig. 1a. Liu et al. [30] had calculated the deformation energies of Ni4/MgO in CH_x dissociation, and the numbers were obviously smaller than adsorption energies. The deformation energies of N8/MgO(100) in O adsorption is tested and it is also one magnitude lower than adsorption energies. So the atomic coordinates of Ni8/MgO(100) are fixed during the calculation in order to reduce time cost.

On Ni8/MgO(100) model, there are five types of adsorption sites: the top site (T), the bridge site on the surface Ni (B-1) or between different layers Ni (B-2), the hollow site on the surface (H-1) or between two layers (H-2), as shown in Fig. 1b. The species cannot adsorb on the sites at the bottom Ni layer stably because of the stereo hindrance effect, so these sites are neglected in this paper.

3. Results and discussion

3.1. CH_4 dehydrogenation

Wei and Iglesia [21] found the activation of C–H bond was the sole kinetically limitation in CH_4/CO_2 reforming on Ni/MgO catalysts. The DFT calculations performed by Wang et al. [27] showed CH_4 dissociative adsorption was the RDS in the CH_4/CO_2 reforming on the Ni(111) surface. The adsorption configurations in CH_4 sequential