A density functional theory study of CO methanation mechanism on Ni$_4$/SiC catalyst

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ABSTRACT

The reaction mechanism of CO methanation on the Ni$_4$/3C-SiC(1 1 1) catalyst surface was explored by the density functional theory in this paper. The configuration of Ni$_4$/3C-SiC(1 1 1) is built and the binding energy of Ni$_4$ cluster on Ni$_4$/3C-SiC(1 1 1) is higher than that on Ni$_4$/t-ZrO$_2$ and Ni$_4$/Al$_2$O$_3$ surface, which may be contributed to improve the dispersion and stability of Ni-based catalyst. And the main pathway of CH$_4$ formation on Ni$_4$/3C-SiC(1 1 1) surface is CO + H → CHO + H → CH$_2$O + H → CH$_3$O → CH$_3$ + H → CH$_4$. The results show that the rate-determining step for CO methanation on Ni$_4$/3C-SiC(1 1 1) is the formation of CH$_3$ from CH$_3$O dissociation with an energy barrier of 241.3 kJ/mol, which is lower than that on Ni$_4$/t-ZrO$_2$. In addition, the activation energy of CH$_3$OH formation is higher than that of CH$_4$ synthesis on Ni$_4$/3C-SiC(1 1 1) surface (254.5 vs. 241.3 kJ/mol). Different from Ni(1 1 1), Ni$_4$/γ-Al$_2$O$_3$, and Ni$_4$/t-ZrO$_2$ catalysts, the Ni$_4$/3C-SiC(1 1 1) catalyst has a much higher selectivity for CH$_4$ in the reaction of CO methanation, which may be attributed to the lower activation energy of CH$_3$O dissociation to CH$_3$ than that hydrogenation to CH$_3$OH. Therefore, Ni$_4$/3C-SiC(1 1 1) can be recommended preferentially for CH$_4$ synthesis via CO hydrogenation, rather than CH$_3$OH formation.

1. Introduction

Natural gas has been considered as the most efficient and cleanest energy form in fossil fuel. Recently, the technology of synthetic natural gas (SNG) from syngas (H$_2$/CO) has drawn more attention because of due to the low reserves, higher depletion, and rising price of natural gas [1–4]. CO methanation is a key reaction in the synthesis of natural gas and also has gained importance and been used to remove CO from the ammonia-synthesis reaction, upstream proton-exchange membrane fuel cells [5–8]. The key of CO methanation technology is the design and development of highly efficient and stable catalyst used for CO methanation reaction. Compared with containing Ru catalyst, Ni-based catalysts have been used in the reaction of CO methanation because of their low cost, high reactivity, and desired selectivity [1,9–11]. Efforts have been made to improve the activity of Ni-based catalysts through various support materials, promoters, and preparation methods [9,12–14]. And the nature of the support is an important factor to modify the performance and CH$_4$ selectivity of Ni-based catalyst [5,15]. Various oxide materials, such as Al$_2$O$_3$ [1,10], ZrO$_2$ [5,16], TiO$_2$ [17], CeO$_2$ [18], SiO$_2$ [15], MgO [15,19], supported Ni nanoparticles show the outstanding catalytic performance for CO methanation. Compared

with Ni/MgO, Ni/Al$_2$O$_3$, Ni/SiO$_2$, and Ni/TiO$_2$ catalysts, Takenaka et al. found that Ni/ZrO$_2$ is most active for the CO methanation [5,16]. However, the reaction of CO methanation (CO + 3H$_2$ = CH$_4$ + H$_2$O, $\triangle$H = −206 kJ/mol) is strongly exothermic, and catalytically active nanoparticles suffer from sintering or coalescence to minimize their surface energies due to the rapid accumulation of reaction heat [20,21].

Literature reports that Ni nanoparticles that are supported on silicon-carbide (Ni/SiC) catalysts display outstanding anti-sintering performance for CO methanation [22–24]. Compared with Ni/Al$_2$O$_3$ and Ni/TiO$_2$ catalysts, Ni/SiC displays the high activity and stability in the reaction of CO methanation [22–24]. Silicon carbide has been considered a promising support material in place of the traditional insulated supports for the highly endothermic or exothermic reactions of CO methanation [22–24], methane reforming [25,26], automotive exhaust treatment [26], methane combustion [27], Fischer–Tropsch synthesis [28,29], and the oxidative coupling of methane [30], which is attributed to its high thermal conductivity and chemical inertness, excellent thermal stability, superior mechanical strength, and outstanding anti-oxidation properties [31,32].

Many experiential and theoretical studies focus on the mechanism exploration of CO methanation and the possible mechanisms are

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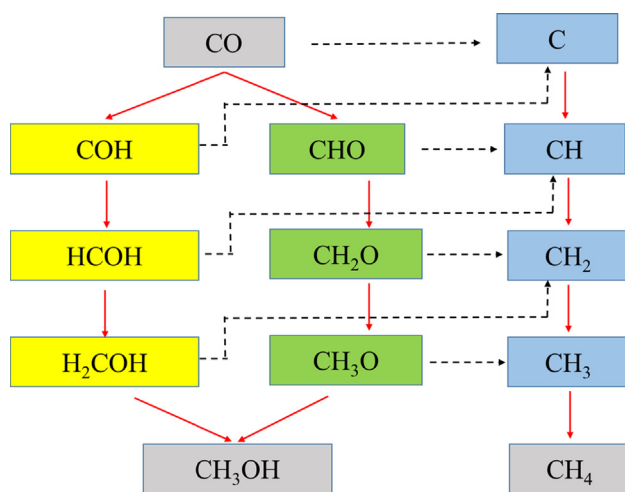 E-mail addresses: hanxiaoxia@tyut.edu.cn (X. Han), renjun@tyut.edu.cn (J. Ren).

Fig. 1. The network of CO hydrogenation. Red line represents hydrogenation reaction and black line represents the breakage of CsbndO bond. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

summarized in Fig. 1: (1) carbide mechanism (CO direct dissociation); (2) H-assisted CO dissociation mechanism (including CH_xO or CH_xOH intermediates) [33–40]. Previous study displays that CO dissociation as the source of surface carbon is unlikely even on defect-rich Ni surface due to the higher activation energy of CO dissociation, which indicates that the mechanism of CO must include H-assisted CO dissociation, besides CO direct dissociation [41]. However, the by-product of CH_3OH may be formed by continuously hydrogenation of CH_xO or CH_xOH intermediates in the reaction of CO methanation [42,43]. Remediakis and Zhi et al. illustrated that CH_4 was formed on Ni(1 1 1) surfaces via the intermediates of H_xCO (x = 1–3), leading to CH_3OH by-product formation during CO hydrogenation [11,43]. Ashwell et al. [42] also reported that the most energetically favorable outcome is CH_3OH on Ni (1 1 0) surface going through a pathway involving the sequential hydrogenation of CO to a CH_3O intermediate, followed by the final hydrogenation to CH_3OH. Kang et al. [44] reported that CH_3OH synthesis on Ni_4/γ-Al_2O_3 catalysts surface is more favorable than CH_4 in the reaction of CO hydrogenation. The facilitating the C-O bond breakage of the hydrogenated $CH_xO(H)$ intermediates and reducing $CH_xO(H)$ hydrogenation to CH_3OH byproduct benefit to the improvement of CH_4 productivity. Cui et al. [45] found that Zr modified Ni-based catalyst has been shown high activity and selectivity for CH_4 in CO methanation due to the lower activation energy of CH_2OH dissociation into CH_2 than that final dehydrogenation to CH_3OH. It has been found that the introducing Fe into Ni_4/γ-Al_2O_3 displays the lower the energy barrier of CHO dissociation, resulting in the higher productivity and selectivity for methane [44]. In our previous study, the synthesis of CH_3OH on perfect tetragonal ZrO_2 support Ni nanoparticles (Ni/t-ZrO_2) catalyst surface is more favorable than CH_4 in the reaction of CO hydrogenation, while the presence of hydroxyl groups and oxygen vacancies on Ni_4/t-ZrO_2 surfaces can enhance the breakage of C—O bond of CH_3O, leading to the improvement of CH_4 productivity in the process of CO methanation [46]. Additionally, Zhang and Liu et al. [23,47] has found that the selectivity of CH_4 on Ni/SiC catalyst is much higher than that on Ni_4/γ-Al_2O_3 in the reaction of CO methanation.

Up to now, although lots of works have been carried out to investigated methane formation from CO on Ni-based catalysts, intensive work to explore the mechanism of CO methanation on Ni/SiC catalyst is highly desirable. DFT method plays the significant role in studying the properties of catalyst, catalyst design and screening, understanding catalytic reaction mechanism [48,49]. Therefore, it is significant to investigate the structure and mechanism of CO methanation of Ni/SiC catalyst at atomic and molecular level. In this paper, a systematic study

using DFT method was carried out to explore the mechanism of CO methanation on Ni/SiC catalyst surface. Interestingly, our calculated results display that the activation energy of C−O bond breakage of CH_3O is lower than that of CH_3O hydrogenation to CH_3OH. Hence, the formation of CH_4 is much favorable than CH_3OH on Ni_4/3C-SiC(1 1 1) catalyst surface.

2. Computational models and methodology

2.1. Computational models

3C–SiC was modeled by the cubic SiC with a zinc blend structure. The space group is F-43 m and the corresponding lattice parameters are a = b = c = 4.348 Å, α = β = γ = 90°. The (1 1 1) surface of 3C-SiC has the lowest surface energy, compared with other planes [50,51]. Meanwhile, the XRD spectrogram of 3C-SiC and Ni/3C-SiC indicated that the intensity of (1 1 1) diffraction peak at is highest [22,47,52,53]. And the highly oriented 3C-SiC(1 1 1) also can be successfully prepared in experiments [54,55]. Hence, the (1 1 1) surface of 3C-SiC with a supercell of 4 × 3 has been selected as a support because of its lowest energy. The 3C-SiC(1 1 1) mode included eight atomic layers (four Si–C bilayer molecular layers), where two lower layers were fixed, whereas the top layers and the adsorbate were relaxed in calculation. The vacuum region of 15 Å in the z direction was set to separate the slabs that were perpendicular to the surface [56,57]. In addition, the smallest three-dimensional structure, namely the Ni_4 cluster, was selected to investigate the interactions between Ni nanoparticles, and between Ni particles and the support [58,59].

2.2. Computational methodology

DFT calculations were performed by using Dmol³ code on Materials studio 5.5 Package [60,61]. The generalized gradient approximation (GGA) and Perdew–Burke–Ernzerh (PBE) functional were used to investigate the exchange and correction effects [62]. Double numerical plus polarization (DNP) [63] basis sets were used, and the inner electrons of the Ni atoms were kept frozen and were replaced by an effective core potential (ECP) [63,64]. Other atoms were treated with an all-electron basis set. The spin unrestricted condition was used and the convergence criterion for the energy, maximum force, and maximum displacement changes were set at 2.0×10^{-5} Hartree, 4.0×10^{-3} Hartree/Å, and 5.0×10^{-3} Å, respectively. The self-consistent field (SCF) convergence and the k-point were set as 1×10^{-5} Hartree and $4 \times 4 \times 1$, respectively. A thermal smearing value of 0.005 Ha was used. The linear synchronous transit (LST/QST) in the Dmol³ code was applied to identify the reaction transition state [65].

The reaction energy (ΔH) and activation energy (Ea) were calculated on the basis of the following formulae [66]:

$$\Delta H = E_{reactant/catalyst} - E_{product/catalyst} \tag{1}$$

$$Ea = E_{TS/catalyst} - E_{reactant/catalyst} \tag{2}$$

where $E_{reactant/catalyst}$, $E_{product/catalyst}$, and $E_{TS/catalyst}$ stand for the total energies of the reactant, product, and transition state adsorbed on the catalyst surface, respectively.

The binding energy (E_b) of the Ni_4 cluster with the 3C-SiC(1 1 1) surface was calculated as follows [67,68]:

$$E_b = (E_{support} + E_{metalcluster} - E_{metalcluster/support})/N \tag{3}$$

In this formula, $E_{support}$, $E_{metal\ cluster}$, and $E_{metal\ cluster/support}$ are the total energies of the bare 3C-SiC(1 1 1) slab, the Ni_4 cluster, and the 3C-SiC(1 1 1) slab with Ni_4 cluster, respectively. And N is the atom number of the metal cluster.

The adsorption energy (E_{ads}) was defined as: