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Density functional theory study of the mechanism of CO methanation on Ni₄/t-ZrO₂ catalysts: Roles of surface oxygen vacancies and hydroxyl groups

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ABSTRACT

The mechanism of methane synthesis from syngas on a Ni₄/t-ZrO₂(101) surface, as well as the effect of oxygen vacancies and hydroxyl groups, was systematically investigated using density functional theory. Our results showed that CO hydrogenation to a CHO intermediate was more favorable than direct CO dissociation on both perfect and defect surfaces; the main pathway for CH₄ formation on Ni₄/t-ZrO₂(101), Ni₄/V_O-t-ZrO₂(101) and Ni₄/H-t-ZrO₂(101) surfaces were as follows: CO + 4H → CHO + 3H → CH₂O + 2H → CH₃O → CH₃ + H → CH₄. The highest barrier energies during CH₄ formation on Ni₄/t-ZrO₂(101), Ni₄/V_O-t-ZrO₂(101) and Ni₄/H-t-ZrO₂(101) surfaces were 258.0, 147.6 and 233.6 kJ mol⁻¹, and the corresponding reaction energies were -77.4, 85.1 and -84.5 kJ mol⁻¹, respectively. Hydroxyl groups and oxygen vacancies on Ni₄/t-ZrO₂ surfaces were beneficial to the formation of CH₄, and the selectivity of methane was significantly improved because of the oxygen vacancies.

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Introduction

Fossil fuels, primarily coal, petroleum and natural gas are the major sources of energy worldwide. As important raw materials in modern industry, synthesis nature gas (SNG) has attracted increasing interest in recent years owing to the continuous increase in natural gas prices and increasing concern for the depletion of natural gas [1]. Coal-based SNG production is attractive in some regions of the world where coal is highly abundant and where natural gas from coal is

considered the most promising low greenhouse gas emission option [2]. Interest in the CO methanation reaction has grown significantly owing to the production of a syngas, which can be then converted to methane, containing mainly H₂ and CO, during the gasification of coal, pet coke, biomass or municipal solid waste. This key reaction (reaction 1: CO + 3H₂ = CH₄ + H₂O) is highly exothermic (-206.1 kJ mol⁻¹) and thermodynamically feasible while kinetically unfavorable at low temperatures [3,4].

To develop catalysts that are highly efficient and extremely stable against sintering and carbon deposition, many catalytic

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systems have been proposed for the methanation of CO [5]. Numerous studies have been conducted on selective CO methanation over Ru, Ni and Ru–Ni catalysts [6]. However, Ru-based catalysts are expensive and Ru can react with CO easily by forming $\text{Ru}(\text{CO})_x$ compounds during methanation. Furthermore, $\text{Ru}(\text{CO})_x$ is easily sublimated at high temperature, which can decrease the activity of Ru catalysts [7]. Recently, some publications have shown that Ni/ZrO₂ catalysts are very active for CO methanation as compared to Ni/MgO, Ni/Al₂O₃, Ni/SiO₂ and Ni/TiO₂ catalysts [5]. Takenaka et al. [8] showed that the support plays an important role in the CO methanation. Kramer et al. [9] suggested that the interfacial region between Ni and ZrO₂ is very relevant for the generation of active sites for the methanation reaction.

Much information is available in the literature regarding the methanation of CO employing ZrO₂. Notably, the phase of ZrO₂ strongly affects the activity of catalysts in many reactions. Habazaki et al. [10] concluded that the phases of ZrO₂ are an important parameter for this reaction. Yamasaki et al. [11] concluded that nickel supported on tetragonal ZrO₂ (t-ZrO₂) was more active than that supported on monoclinic ZrO₂. Furthermore, in our previous work [12] we also found that ZrO₂ polymorphs significantly affect the activity of Ni/ZrO₂ catalysts in CO₂ methanation. And the conclusion was obtained that with increasing t-ZrO₂ content, the activity of CO/CO₂ methanation also increased. The improved catalytic activity of the Ni/t-ZrO₂ catalyst can be ascribed to several reasons: the supply of reactants through surface diffusion, the change of electronic properties, and the modified morphology of the metal clusters as compared to extended surfaces [13]. Combined with previous research, the effects of lattice oxygen vacancies or hydroxyl groups which occur in many processes [14–18], were a reflection of the key reasons for this reaction. How lattice oxygen vacancies and hydroxyl groups affect the reactions taking place on the catalysts are still not known. Hence, investigation of the impact of these factors on CO methanation is important.

Although the interaction and growth of Ni_n clusters with cubic, monoclinic and tetragonal ZrO₂ surfaces was investigated in our previous work [19], few theoretical studies have been carried out to explore the CO methanation mechanism over Ni/t-ZrO₂ catalysts. Up to now, to the best of our knowledge, although a large number of studies have been performed to explore methane formation from syngas on Ni catalysts [20–23], few studies have been carried out to fully understand the mechanism of methane formation on Ni/t-ZrO₂ catalysts and the behavior of the support, oxygen vacancies and hydroxyl groups on a fundamental level owing to the complexity of the reactions. Also, Remediakis et al. [24] reported that hydrogenation of CO was favored to form CHO on flat Ni(111) surfaces, leading to CH₃OH formation. Kang et al. [25] reported that the formation of CH₃OH is more favored than that of CH₄ with CO hydrogenation on Ni₄/γ-Al₂O₃ catalysts. How can CH₃OH formation influence CO methanation on the Ni/t-ZrO₂ surface? Whether the selectivity and yield of CH₄ and the mechanism can be improved or decreased by the existence of lattice oxygen vacancies or hydroxyl groups are also unknown.

In this study, the mechanism of methane formation from syngas on Ni₄/t-ZrO₂(101), Ni₄/t-ZrO₂(101) with oxygen

vacancies and Ni₄/t-ZrO₂(101) with hydroxyl groups were systematically investigated by density functional theory (DFT) and the periodic slab model. First, the stable adsorption configurations of all possible species deposited on Ni/ZrO₂ catalysts were obtained; then, both the reaction energies and activation barriers of all possible elementary reactions involved in CH₄ formation from syngas are discussed. The results of this effort are expected to identify preferable reaction mechanisms, determine the kinetics, and understand the role of the support, oxygen vacancies and hydroxyl groups in this process.

Computational methodology

Surface model

A standard supercell approach was employed with the t-ZrO₂ substrate (P₄₂/nmc space group symmetry), as in our previous work [19]. Test calculations showed that further increase of the slab thickness and/or the number of relaxed layers did not significantly affect the obtained results. Furthermore, supercells of the same vertical size were used in all computations, with a sufficiently thick vacuum spacer to prevent artificial interactions between consecutive slabs. The t-ZrO₂(101) surface [see Fig. 1(a)] was modeled with a 2 × 3 supercell built from an optimized t-ZrO₂ bulk unit cell with lattice parameters $a = b = 3.64 \text{ \AA}$ and $c = 5.27 \text{ \AA}$ [26,27]. The supercell had dimensions of 12.69 Å × 7.26 Å × 22.68 Å. The surface slab consisted of 72 O atoms and 36 Zr atoms distributed in three layers and separated by a vacuum spacer of 15 Å. The optimized Ni₄ cluster with a tetrahedral structure was supported on the t-ZrO₂(101) surface to generate the Ni₄/t-ZrO₂ model catalyst [see Fig. 1(b)].

The reduced t-ZrO₂ surface (V_O-t-ZrO₂) was modeled by creating an oxygen vacancy (V_O) in various positions such as the surface, subsurface and bulk sites of the t-ZrO₂(101) surface described above. The reducibility of the oxide surface was determined by the formation energy of an O vacancy with respect to the stoichiometric oxide and a gas-phase oxygen molecule. According to Ref. [28], the most stable vacancy is V_O4, which is obtained by removing an oxygen atom from the subsurface. However, when the Ni₄ cluster was deposited on reduced t-ZrO₂(101), the O₂ site at the surface transferred easily to O₄ site. Hence, we modeled the V_O-t-ZrO₂(101) surface by removing the O₂ directly from the stoichiometric t-ZrO₂(101) surface. The optimized models of the V_O-t-ZrO₂(101) surface and the Ni₄/V_O-t-ZrO₂ model catalyst are shown in Fig. 2.

We also considered the hydroxylated t-ZrO₂(101) surface (H-t-ZrO₂(101)) by depositing an H₂O molecule at the top site of Zr₁ of the t-ZrO₂(101) surface described above. According to Ref. [29–31], one H₂O molecule will dissociate into a hydroxyl (O_wH_a) and a proton (H_b) binding to a neighboring surface O. Thus, there are two hydroxyls produced in each surface unit cell. Furthermore, the Ni₄ cluster will be deposited on the surface of this kind of catalyst. The optimized models of the H-t-ZrO₂(101) surface and Ni₄/H-t-ZrO₂(101) model catalyst are shown in Fig. 3.

In all calculations, atoms in the bottom two layers of the t-ZrO₂(101) slab are frozen at their equilibrium bulk positions whereas the top layer together with the Ni₄ cluster and other species involved in CO methanation are allowed to relax.

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