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Effects of structure and size of Ni nanocatalysts on hydrogen selectivity via water-gas-shift reaction—A first-principles-based kinetic study

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ABSTRACT

The effects of structure and size of nickel nanocatalysts on hydrogen production via water-gas shift reaction (WGSR) were investigated using a first-principles-based kinetic model. Using periodic density functional theory and statistical calculations, thermochemistry and kinetics of the WGSR and competing methanation was calculated on Ni(111), Ni(100), and Ni(211) facets. The kinetics of the elementary reactions involving C—H, O—H, and C—O bond was found to fit to a general Brønsted–Evans–Polanyi (BEP) type linear relationship on all Ni facets considered. A mechanism describing the competition between the hydrogen and methane formation routes is constructed for further microkinetic modeling. The hydrogen production turnover frequency (TOF) via the WGSR route suggests the preference to the low-coordinated surface sites with the reaction activities following the order of Ni(211) > Ni(100) > Ni(111) using a simulated feed gas with a molar ratio of $CO:H_2O = 1:2$. Due to the methanation, the TOF of methane production follows the same trend of hydrogen production. Consequently, the TOF of hydrogen production decreases with increasing particle diameters, due to the decreasing fractions of low-coordinated surface nickel atoms. It is also found that the presence of H_2 in feed gas can largely enhance the methanation reaction.

1. Introduction

Hydrogen is an important clean fuel for efficient and clean power generation [1–3]. In addition, hydrogen is also widely used for fuel upgrading [4], ammonia synthesis [5], and fine chemicals production [6]. Steam reforming of hydrocarbons (e.g., CH_4 as shown by Eq. (1)) is a major industrial route to obtain hydrogen source in the form of syngas [7–9]. Alternative routes that utilize biomass-derived polyols (e.g., glycerol as shown in Eq. (2)) have been successfully employed to demonstrate the feasibility of obtaining biorenewable hydrogen [10–12]. Water-gas shift reaction (WGSR) (Eq. (3)) is ubiquitous in reforming reactions, and consumes CO to form CO_2 and boosts hydrogen [10,13]. To a great extent, WGSR provides the benefits of boosting hydrogen productivity and mitigating catalyst poisoning effects by removing the strong-binding CO molecules from active sites [14–16].

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g),\ \Delta H^\circ_{298\,K} = 206.2\ \text{kJ/mol} \tag{1}$$

$$C_3H_8O_3(l) \rightleftharpoons 3CO(g) + 4H_2(g),\ \Delta H^\circ_{298\,K} = 350\ \text{kJ/mol} \tag{2}$$

$$H_2O(l) + CO(g) \rightleftharpoons CO_2(g) + H_2(g),\ \Delta H^\circ_{298\,K} = -41.1\ \text{kJ/mol} \tag{3}$$

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(l),\ \Delta H^\circ_{298\,K} = -206.2\ \text{kJ/mol} \tag{4}$$

Abbreviations: WGSR, water-gas shift reaction; DFT, density functional theory; BEP, Brønsted-Evans-Polanyi; TOF, turnover frequency; VASP, Vienna ab initio simulation package; GGA-PBE, generalized gradient approximation Perdew-Burke-Ernzerhof; NEB, Nudged Elastic Band; CatMAP, Catalysis Microkinetic Analysis Package; BE, binding energy.

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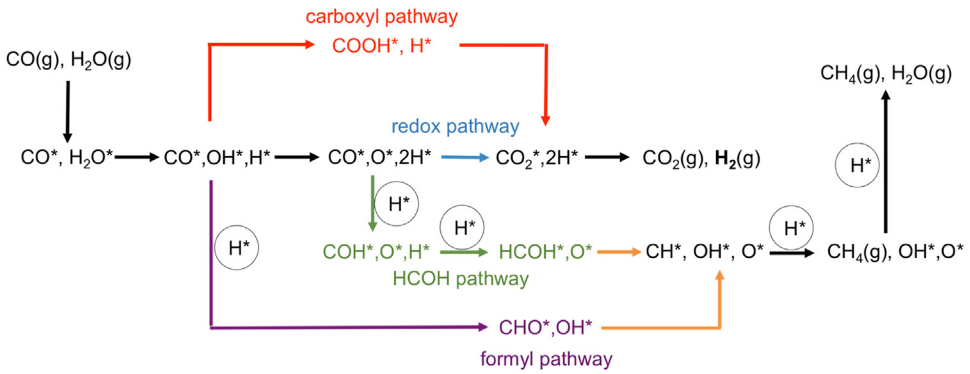

Fig. 1. The reaction scheme illustrating the carboxyl (red) and redox (blue) pathways for hydrogen production; and the formyl (purple), and HCOH (green) pathways. The orange arrows represent C—O bond scission steps. H* in the circle represents hydrogen consumed due to methanation. The asterisks (*) represent surface intermediates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Like reforming, WGSR is also catalyzed on transition metals. Therefore, an important guiding principle in the search for optimal reforming catalysts is to enable effective C—H, O—H, and C—C bond scissions [10]. Studies [17–20] performed on a number of monometallic catalysts suggest that Ni would exhibit promising reforming and WGSR activities, compared to Co, Cu, Fe, Ir, Rh, Ru, Pt, and Pd. The natural abundance enables Ni-based catalysts to be an appealing material for practical, large-scale hydrogen production [21–23]. For Ni, one of the challenges in heterogeneous catalysis is the tendency to cleave the C—O bond via methanation (as in Eq. (4)) [24,25] or hydrogenolysis [20], adversely affecting hydrogen selectivity. The hydrogen production selectivity can be further manipulated by alloying [11] or chemical doping [26].

The WGSR pathways leading to hydrogen formation via different intermediates have been extensively elucidated using first-principles methods, as illustrated in Fig. 1 [26–33]. Among different transition metals, the path via the carboxyl (i.e., COOH, red path in Fig. 1) intermediate is preferred on Cu(111) [27,29], Pt(111) [28], and Rh(111) [30]. On Ni(111), both carboxyl and redox pathway are competitive [26,33]. In comparison, the formate (HCOO) pathway is less competitive than the redox and carboxyl pathways [26–28,31], and HCOO has been considered as a spectator species. Based on the analysis of such elementary mechanisms, the general kinetic trends of WGSR over various transition metal catalysts are understood [34,35]. Particularly, microkinetic modelings based on the rate-determining steps (redox or carboxyl) has facilitated the assessment of the performance of monometallic WGSR catalysts.

A systematic kinetic study on methanation via CO hydrogenation has been conducted by Vannice over group VIII metals [18], where Ni, Co, Ru, and Fe are among the most active methanation catalysts. Methanation has also been extensively examined in the context of Fischer-Tropsch synthesis [36]. The detailed Fischer-Tropsch mechanism is still under debate, various reaction pathways have been investigated using density functional theory (DFT) calculations [26,37,38] to reveal that the C—O bond scission elementary steps are the rate-determining step. Regarding C—O bond scission, both direct and hydrogen-assisted methanation mechanisms have been proposed [26,37,39], where the energy barrier can be significantly reduced once CO is partially hydrogenated. The two main hydrogen-assisted C—O bond scission pathways are illustrated in Fig. 1, where the purple path involves the formation of a formyl group (CHO) and the green path involves the formation of COH. It has been shown that on Ni(111), the energy barriers can be significantly reduced [26].

This paper aims to elucidate the hydrogen selectivity on Ni, where the adverse effect of methanation cannot be neglected. WGSR and methanation are both sensitive to catalyst surface structures [31,37,40]. Stamatakis et al. [40] performed kinetic Monte Carlo modeling of WGSR on Pt(111), Pt(211), and Pt(322) at 180–345 °C and 1 atm, and proposed that at low CO:H_2O ratios (e.g., 10^{-3}), the step sites are much more active than the terraces sites; but at the CO:H_2O ratios of 0.5, the coverages of CO and H and TOFs show less sensitivity to the surface structures. Catapan et al. [31] compared the WGSR and coke formation on Ni(111) and Ni(211) and concluded that the Ni(211) facet is more active for C—O bond scissions than Ni(111). Low-coordination surface atoms, i.e., at the step sites, are able to enhance the binding of H_2O [41] and CO and dissociate the adsorbates. The facilitated H_2O dissociation is beneficial toward WGSR, however, the enhanced C—O bond scission will also increase the selectivity to methanation. Therefore, a mechanistic understanding of the competition between WGSR and methanation and its structure-dependence will help address a fundamental heterogeneous catalysis issue.

Modern nanotechnologies have tremendously advanced the preparation of tailored nanocatalysts [42,43]. Control of nanoparticle shape and size will ultimately determine the dominant surface active terrace, edge, and corner sites. One prominent example of CO oxidation on gold demonstrated by Haruta et al. [44] suggests that catalytic activity and selectivity can be dramatically enhanced on highly dispersed nanoparticles (< 5 nm). In WGSR, it has been found by Shekhar et al. that the low-coordinated corner Au sites can be seven times more active than the perimeter Au sites [45], both of which also depend on Au nanoparticle sizes. CO methanation is also found to be strongly dependent on the Ni nanoparticle sizes (0.5–13 nm) by van Meerten et al. [46]. A systematic investigation on the effect of Ni nanoparticle sizes (5–10, 10–20, and 20–35 nm) in Ni/α-Al_2O_3 on CO methanation by Gao et al. showed that nanoparticle size of 1–20 nm results in the highest CO turnover frequency (TOF) and CH_4 yield [47].

In this work, using a uniform computational framework that consolidates periodic, spin-polarized DFT calculated thermochemistry and kinetics and the mean field kinetic modeling, we investigated the competition between WGSR and methanation to elucidate the key factors, i.e., temperature, surface coverage on hydrogen selectivity on nanoscale Ni catalysts. A mechanism consisting of only the dominant WGSR (i.e., redox and carboxyl pathways), and methanation pathways (i.e., CHO and HCOH pathways) was constructed [26]. The universal kinetic Brønsted-Evans-Polanyi (BEP) relationships describing elementary steps involving C—H, O—H, and C—O bonds have also been established on Ni(111), Ni(100), and Ni(211) facets.

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