



In-operando elucidation of bimetallic CoNi nanoparticles during high-temperature CH₄/CO₂ reaction

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ABSTRACT

Dry reforming of methane (DRM) proceeds via CH₄ decomposition to leave surface carbon species, followed by their removal with CO₂-derived species. Reactivity tuning for stoichiometric CH₄/CO₂ reactants was attempted by alloying the non-noble metals Co and Ni, which have high affinity with CO₂ and high activity for CH₄ decomposition, respectively. This study was focused on providing evidence of the capturing surface coverage of the reactive intermediates and the associated structural changes of the metals during DRM at high temperature using *in-operando* X-ray absorption spectroscopy (XAS). On the Co catalysts, the first-order effects with respect to CH₄ pressure and negative-order effects with respect to CO₂ pressure on the DRM rate are consistent with the competitive adsorption of the surface oxygen species on the same sites as the CH₄ decomposition reaction. The Ni surface provides comparatively higher rates of CH₄ decomposition and the resultant DRM than the Co catalyst but leaves some deposited carbon on the catalyst surface. In contrast, the bimetallic CoNi catalyst exhibits reactivity towards the DRM but with kinetic orders resembling Co catalyst, producing negligible carbon deposition by balancing CH₄ and CO₂ activation. The *in-operando* X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements confirmed that the Co catalyst was progressively oxidized from the surface to the bulk with reaction time, whereas CoNi and Ni remained relatively reduced during DRM. Density functional theory (DFT) calculation considering the high reaction temperature for DRM confirmed the unselective site arrangement between Co and Ni atoms in both the surface and bulk of the alloy nanoparticle (NP). The calculated heat of oxygen chemisorption became more exothermic in the order of Ni, CoNi, Co, consistent with the catalytic behavior. The comprehensive experimental and theoretical evidence provided herein clearly suggests improvement to the catalyst design protocol by selecting the appropriate composition of Co-Ni alloy.

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1. Introduction

The conversion of methane to syngas is a process of continuously gaining interest in the market for the natural gas and hydrogen industries [1–4]. The dry reforming of methane (DRM) is attractive because it utilizes a large amount of CO₂ (which may coexist in natural gas fields) into a mixture of higher-value compounds, with a tunable H₂/CO ratio ~1 (CH₄ + CO₂ = 2CO + 2H₂) and a concu-

rent reverse water gas shift (RWGS) reaction (H₂ + CO₂ = CO + H₂O) [5–11]. To achieve high conversion, DRM must be performed at high temperature (700–900 °C) because of its high endothermicity (ΔH° = 246 kJ mol⁻¹). The high reaction temperature leads to metal sintering and carbon formation (coking), which cause catalyst deactivation [5–11]. A similar reaction, steam reforming of methane (SRM), can be performed industrially for a long period using relatively inexpensive Ni-based catalysts [1]. However, these catalysts produce a large amount of carbon on the catalyst surface (in whisker and encapsulating morphologies) under DRM, causing catalyst deactivation and reactor plugging (increase in back pres-

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sure) [5]. The commercialization of DRM therefore faces the serious challenge of completely suppressing carbon formation [4].

A number of studies have been reported on Ni catalysts for DRM [12–22]. Wei and Iglesia conducted a careful kinetic assessment of the forward conversion rate by taking approach-to-equilibrium without facing heat and mass transfer artifacts [15]. They reported that C–H bond activation of CH₄ is the sole kinetically relevant step for the overall DRM on a Ni/MgO catalyst at 600–700 °C (first-order with respect to CH₄ pressure) [15]. The reaction proceeds on a clean Ni surface, which is confirmed by the kinetic being independent of the co-reactant (CO₂) and product (CO, H₂, H₂O) pressures. The concurrent RWGS is quasi-equilibrated under the investigated conditions. However, the kinetics do not provide information about undesired carbon formation, which occurs at a different time scale [15]. The mechanism proposed by Bengaard and Nørskov et al. based on DFT simulations together with experiments by Rostrup-Nielsen et al. suggested that the nucleation of unwanted carbon deposits is initiated by step sites of the Ni surface, which can be occupied by other elements, such as potassium, sulfur, and gold and other elements which explains their role of enhancement of selectivity [17,18]. In particular, the continuous addition of sulfur is performed industrially to suppress carbon formation during SRM (namely, SPARG process) [6]. Their study noted the critical role for the growth of carbon fiber/nanotube catalyzed by metal step sites [17,18]. It was suggested that the small size of nanoparticles (NPs) gives tolerance to carbon formation, which is consistent with DFT calculations, where surface graphite cannot form on small particles [18]. It is critical to consider the metal particle size and coordination number of surface metal sites to suppress carbon formation.

Co has gained attention as an active metal for DRM [23–26], despite its lower DRM rate than Ni [27]. The catalytic behavior of the Co catalyst is relatively distinct among the other group 8 metals. Depending on the metal loading, there is a clear trend where metallic Co is deactivated by carbon deposition (high loading) or metal oxidation (low loading) [23–25]. This trend was observed by varying the metal loading on both Co/Al₂O₃ and Co/TiO₂ under various reaction conditions [23,24]. Metal oxidation was evidenced by the consumption of oxygen from CO₂ and inactive mixed oxide formation, such as CoAl₂O₄ or CoTiO₃ [24,25], depending on the support. However, these findings suggest that there is kinetic competition between reduction (CH₄ activation) and oxidation (CO₂ activation) at the same surface. Although the Co-based catalyst has the potential to show high stability without causing carbon deposition for DRM, it still lacks accurate control of the kinetics through the design of the Co metal particle size because the reaction conditions, such as the reaction pressure [23,25], alter the appropriate catalyst to be used.

To further tune the reactivity of the metal, attempts have been made to produce stable catalysts by combining Co and Ni [27–48]. Because Ni is more reactive towards CH₄ decomposition, providing a reductive surface relative to monometallic Co, the resultant bimetallic CoNi alloy catalyst was proposed to tune the reactivity towards CH₄ and CO₂ activation, according to its metal composition [27–29]. Generally, a high Co content causes deactivation due to metal oxidation, while a high Ni content causes deactivation by carbon deposition, as reported for a TiO₂ supported catalyst at 750 °C [27–29]. For example, Nagaoka et al. found 0.5 wt.% Co₉Ni₁/TiO₂ provided relatively stable DRM performance, even at 2 MPa [29]. Similarly, the synergetic effect of the combination of Co and Ni was explained by the formation of a reducible alloy phase [28,33,34,39]. Recent literature has investigated the effects of the support, such as CeO₂–ZrO₂, known to provide active oxygen, which is generally claimed to suppress carbon deposition [36,39,40,47]. This approach, however, contradicts the kinetic findings of Wei and Iglesia for various metal catalysts, where the forward CH₄ turnover rate is independent of the type of support, including ZrO₂ and CeO₂–

ZrO₂ [49]. None of the studies on bimetallic CoNi catalyst carefully analyzed the state and composition of the CoNi alloy on the surface and bulk in each NP and the resultant reactivity towards DRM. Despite the potential of the bimetallic CoNi catalysts for DRM, there is limited understanding of the composition and the degree of oxidation of the surface and the bulk of catalyst particles during DRM conditions. The mechanistic understanding of such system and associated kinetic analysis, to pin down the reaction intermediate is crucial to design stable catalysts. There is little information available in the literature regarding the catalyst structure monitored during the DRM catalysis at high temperatures.

This analysis of literature motivated us to investigate the precise control of the reactivity of bimetallic CoNi and to conduct *in-operando* characterization to capture its structural changes during the high-temperature DRM catalysis. The support selected in this study was ZrO₂, which does not form mixed oxides with Co or Ni, ensuring a lack of thermodynamic driving force of the metal to be oxidized by the presence of the support, phenomena which occur on alumina or titania. Monometallic Co and Ni and bimetallic CoNi catalysts were prepared by an aqueous route known as homogeneous deposition precipitation (HDP) to reproducibly produce the fine-metal NPs with consistent size [50]. The high metal dispersion obtained was a key to improve surface/bulk ratio, to enhance the signals originating from surface structure. These metal NP catalysts were investigated using *in-operando* XAS supported by DFT calculations at high temperatures to fully understand the reactivity and susceptibility towards carbon formation and metal oxidation. By comparing the monometallic Co and Ni and bimetallic CoNi catalysts, direct experimental evidence is provided for the oxidation of Co under DRM condition, while CoNi and Ni maintain their reductive form. In turn, DFT calculations show that alloying Ni and Co allows one to control the oxophilicity of the catalyst in order to balance the kinetics of DRM. By including kinetic analysis, this study clearly demonstrates a technique to control the metal reactivity of CH₄ and CO₂ activation (redox capability) by metal identity (Co, Ni), as well as resultant inhibition of both carbon deposition and metal oxidation, thus explaining the stable DRM performance of the bimetallic CoNi catalyst.

2. Experimental and theoretical methods

2.1. Catalyst preparation

The ZrO₂ support (RC100, DAIICHI KIGENSO KAGAKU KOGYO CO., LTD) was first pretreated in static air at 900 °C to prevent sintering during DRM. Monometallic Co and Ni and bimetallic CoNi/ZrO₂ catalysts with intended total metal loadings of 0.5 wt.% (or 5 wt.% for characterization purpose) were prepared by HDP. The required amount of an aqueous solution of nickel (II) chloride hexahydrate (NiCl₂·6H₂O, Sigma-Aldrich, 99.999%) and cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, Sigma-Aldrich) was added after dissolving 2.5 g of urea (Sigma-Aldrich, ≥99.5%) in 100 mL of pure water. For the CoNi samples, 1:9, 5:5, 9:1 molar amounts of Co and Ni were used to achieve total metal loading of 0.5 wt.%. The sample with metal loading of ~4–5 wt.% was synthesized for XRD measurements only. Typically, 1 g of heat-treated ZrO₂ support was added to the solution. Then, the mixture was heated to 90 °C for 1 h, causing the hydrolysis of urea, shifting the pH to ~10 and leading to the precipitation of metal hydroxide species. After cooling to room temperature, 100 mL of ethylene glycol (Sigma-Aldrich, 99%) was added, and the solution was heated to 150 °C for 3 h for stabilization. The resulting materials were filtered, washed with 300 mL of pure water and 100 mL of ethanol, and dried overnight at 100 °C.

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