



Rapid evaluation of coke resistance in catalysts for methane reforming using low steam-to-carbon ratio

Jiyeon Jeon, Seongju Nam, Chang Hyun Ko*

School of Chemical Engineering, Chonnam National University, 77, Yongbong-ro, Buk-gu, Gwangju, 61186, Republic of Korea

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ABSTRACT

The formation and subsequent accumulation of coke is one of the major reasons for the catalyst deactivation in methane reforming reaction. Although the investigation of coke-resistant catalysts is closely related to their long-term stability of given catalysts, it takes a long time to quantitatively measure the amount of carbon deposition on catalysts under normal reaction operational conditions. To overcome this problem, we used the steam deficient reaction condition, i.e. a low steam-to-carbon ratio (S/C) of 0.5 to accelerate the carbon deposition on catalysts. In this condition, the base catalyst of 10 wt.% Ni/alumina rapidly lost its catalytic activity, indicating fast coke deposition. However, adding proper additives, such as Ru among various precious metals (Ru, Rh, Pt, and Pd) and alkaline earth metals (Mg, Ca, Sr, and Ba) with the appropriate loading (5 wt.%) effectively suppressed coke formation. The optimized catalyst composition is 0.5 wt.% Ru/5 wt.% Mg/10 wt.% Ni/alumina, which displayed coke resistance in the long-term stability test of steam methane reforming and 40 h test of dry reforming of methane. These experimental results indicate that the method developed in this study is useful for the rapid evaluation of given catalysts for their coke resistance.

1. Introduction

Steam methane reforming (SMR) is important because it is the only practical solution for producing hydrogen on a large scale [1–4]. A series of nickel-based commercial catalysts have been implemented for the large-scale production of hydrogen using SMR. These systems use a high steam-to-carbon ratio (S/C = 3.0) to suppress coke formation, which is closely related with the deactivation of catalysts. Recently, various kinds of oxygenates (ethanol, glycerol, and ethylene glycol) [5–9] and hydrocarbons (propane, benzene, and toluene) [10–14] have been considered in place of methane. In the dry reforming of methane (DRM), CO₂ instead of H₂O was used to produce syngas (CO + H₂) [4,15–17]. In these reactions, commercial Ni-based catalysts quickly lose their catalytic activity mainly due to severe coke formation. To overcome this problem, precious metals (Ru, Rh, Pt, Pd, etc.) [2–4,18], alkaline earth metals (Mg, Ca, Ba, Sr, etc.) [19–25], and rare earth metals (La, Ce, Pr, etc.) [2,26–30] have been tested as additives to enhance coke resistance. Different catalyst preparation methods [31–33] and catalyst supports [1–4,34,35] have also been studied so far. As the formation and subsequent accumulation of coke is among the major reasons for the catalyst deactivation in methane reforming reaction, the investigation of coke-resistant catalysts is closely related to their long-term stability. However, it takes a long time to quantitatively

measure the amount of carbon deposition on catalysts under normal operational conditions [36–38]. In this study, we developed a new method to rapidly evaluate the coke resistance of given catalysts, by using a low S/C of 0.5 and high space velocity of 30,000 h⁻¹ within 5 h in SMR. Using this method, the effects of various kinds of additives were investigated. An optimized catalyst with the composition of 0.5 wt.% Ru/5 wt.% Mg/10 wt.% Ni/alumina was applied to long-term (250 h) stability test of SMR and 40 h test of DRM. These results confirmed that the method developed here is valid for the rapid evaluation of coke resistance for given catalysts.

2. Experimental section

2.1. Catalyst preparation

The nickel-based base catalysts were prepared by incipient wetness impregnation method. Nickel nitrate hexahydrate (1.701 g, 97%, Aldrich) was dissolved in deionized water. Then, this solution was added into alumina (3 g, γ -Al₂O₃, SASOL) by incipient wetness impregnation method. After impregnation, this sample was dried in an oven at 100 °C for 12 h, and further calcined in a furnace at 700 °C for 4.5 h in air. The product is denoted as “calcined 10 wt.% Ni/alumina”.

For the precursors of precious metals (Pd, Pt, Rh, and Ru, added in

* Corresponding author.

E-mail address: chko@jnu.ac.kr (C.H. Ko).

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Table 1
Physical properties of various catalysts, obtained by N₂ adsorption isotherms and CO chemisorption.

	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Dispersion (%)	Average particle diameter (nm)
10 wt.% Ni/alumina	88	0.044	0.88	115
10 wt.% Ni/0.5 wt.% Ru/alumina	89	0.044	11.7	8.6
10 wt.% Ni/0.5 wt.% Rh/alumina	85	0.042	3.96	26
10 wt.% Ni/0.5 wt.% Ru/5 wt.% Mg/alumina	83	0.042	9.61	11
10 wt.% Ni/0.5 wt.% Ru/5 wt.% Ca/alumina	76	0.039	4.38	23
10 wt.% Ni/0.5 wt.% Ru/5 wt.% Sr/alumina	80	0.042	5.03	20

the small amount of 0.5 wt.%), palladium(II) Chloride (99.9%), tetraammineplatinum(III) nitrate (99.995%), rhodium(III) nitrate solution, and ruthenium(III) nitrosyl nitrate solution (all from Aldrich) were dissolved in deionized water, and then impregnated into calcined 10 wt.% Ni/alumina. After drying at 100 °C for 12 h in the oven, this sample was reduced at 700 °C for 4.5 h in 10% H₂/90% N₂ environment with a space velocity (SV) of 30,000 mL h⁻¹g⁻¹. Space velocity was defined as total gas flow volume per weight of catalyst per one hour.

For alkaline earth metal additives (added at 1–15 wt.%), Mg(NO₃)₂, Ca(NO₃)₂, Sr(NO₃)₂, and Ba(NO₃)₂, (all 99.0%, Aldrich) were dissolved in deionized water, and then impregnated into calcined 10 wt.% Ni/alumina. After drying at 100 °C for 12 h in the oven, this sample also calcined at 700 °C for 4.5 h in air.

The catalysts loaded with both the alkaline earth metal (5 wt.%) and Ru (0.5 wt.%) were prepared by sequentially impregnating alkaline earth metals and Ru on the calcined 10 wt.% Ni/alumina, and designated as 10 wt.% Ni/0.5 wt.% Ru/5 wt.% M/alumina (M = Mg, Ca, Sr, Ba). After drying at 100 °C for 12 h in the oven, these samples were reduced at 700 °C for 4.5 h in a 10% H₂/90% N₂ environment.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) analysis was performed using an TECANAI F20 operating at 200 kV (installed at Korea Basic Science Institute in Gwangju). The X-ray diffraction (XRD) patterns of reduced catalysts were obtained in the 2θ range between 20° and 80° by an X'Pert PRO Multi-Purpose X-Ray Diffractometer (at Cu 2 kW, 40 kV and 40 mA). Before analysis, samples were reduced at 700 °C in 10% H₂/90% N₂ gas for 4.5 h. The surface area and pore size of the reduced catalysts were determined by nitrogen adsorption isotherms using an ASAP 2020 system (Micromeritics Inc.). The size of metallic Ni particles supported on alumina was analyzed by CO chemisorption using a BEL-CAT (MicrotracBEL) catalyst analyzer. Carbon deposition on the catalysts was measured by thermogravimetric analysis (TGA) using a TGA-

50 (Dongil-Shimadzu) deviec. During the TGA, the temperature of the sample chamber was increased from room temperature to 900 °C at the ramping rate of 10 °C/min.

2.3. Reactivity test

The SMR and DRM reactions were conducted in a quartz reactor. The calcined catalyst was loaded in the middle of the quartz tube. Under atmospheric pressure, the catalyst was reduced by heating from room temperature to the reaction temperature of 700 °C with a ramping rate of 5.0 °C/min in 10% H₂/90% N₂ environment. The reactions were performed at SV = 30,000 mL h⁻¹g⁻¹, and the amount of catalyst used was 0.15 g. The composition of the effluent gas stream was analyzed by a MicroGC3000 system (inficon).

3. Results and discussion

3.1. Physical properties and nickel dispersion of catalysts

Table 1 shows the physical properties of various catalysts. All samples had the similar surface area and pore volumes. Using various additives (ruthenium and/or magnesium) on 10 wt.% Ni/alumina slightly decreased the surface areas and pore volume. Nevertheless, these additives at relatively low loading (< 5 wt.%) did not change the surface area and pore volume significantly. The CO chemisorption results indicate that the addition of precious metals (Ru or Rh) and/or alkaline earth metal reduced the size of Ni particles. The smallest Ni particles (8.6 nm) were obtained when using 0.5 wt.% Ru on 10 wt.% Ni/alumina. When 0.5 wt.% Ru and 5 wt.% of alkaline earth metal (Mg, Ca, or Sr) were combined, the Ni particle size remained below that of 10 wt.% Ni/alumina, which is an important factor in determining the activity of catalysts.

TEM images appeared in Fig. 1 supports these results. The Ni particle size of 10 wt.% Ni/alumina (~ 20 nm) was larger than that of

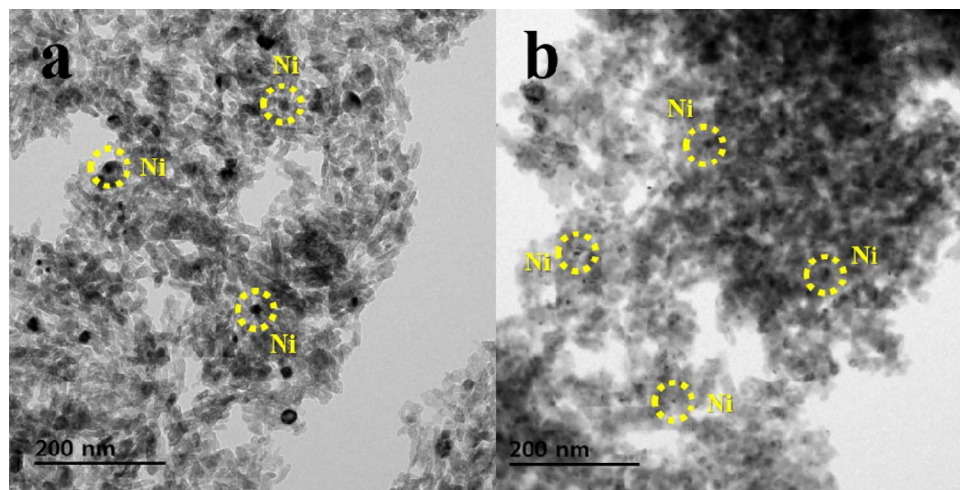


Fig. 1. TEM images of catalysts before reaction: (a) 10 wt.% Ni/alumina and (b) 10 wt.% Ni/5 wt.% Mg/0.5 wt.% Ru/alumina.

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