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Effect of the redox properties of support oxide over cobalt-based catalysts in high temperature water-gas shift reaction



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ABSTRACT

The present study focused on the effect of reducibility of support oxide (CeO₂, ZrO₂, TiO₂, and Al₂O₃) over the activity of cobalt-based catalysts in high temperature water-gas shift (HT-WGS) reaction. The H₂ temperature programmed reduction (TPR) and CO chemisorption characterization results showed that dispersion of cobalt over the support was increased with the increase of the reducibility of the support oxide. The supported catalysts were characterized by X-ray diffraction (XRD) and N₂ adsorption-desorption. The results indicated that the Co/CeO₂ catalyst possesses the highest surface area and metal dispersion in the series; Co/CeO₂ > Co/ZrO₂ > Co/Al₂O₃ > Co/TiO₂. The activity results showed that Co/CeO₂ was the highly active among the tested catalysts in the temperature range of 350–550 °C. Moreover, the time-on-stream study revealed that the Co/CeO₂ catalyst was relatively more stable than cobalt supported on ZrO₂ and Al₂O₃ oxides. The excellent activity and stability of the Co/CeO₂ catalyst were attributed to its high metal dispersion, which is found strongly dependent on the reducible nature of the support.

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1. Introduction

The removal of CO from syngas to produce high-purity hydrogen through the water-gas shift (WGS) reaction has garnered increased attention in the fuel cell industry to generate electrical energy with high efficiency and low environmental impact [1]. The WGS reaction is a catalytic process that involves oxidation of CO to CO₂ (using labile oxygen of the catalyst) followed by oxidation of the reduced catalyst by H₂O to produce H₂. The reaction is moderately exothermic ($\Delta H = -41$ kJ/mol), reversible, and thermodynamically limited at high temperatures, and kinetically controlled at low temperatures [2]. The WGS reaction is industrially performed over Fe-Cr catalyst for high temperature shift (HTS) at 350–500 °C and Cu-Zn-Al catalyst for low temperature shift (LTS) at 190–250 °C [3]. However, due to the potential environmental

concerns related to Cr, recent investigations have focused on the development of Cr-free catalysts for the HTS reaction [4]. Currently, cobalt-based catalysts have drawn large amount of attention in various chemical transformations such as Fischer-Tropsch synthesis, the oxygen evolution reaction, hydrodesulfurization, photocatalytic water oxidation, and a large set of C1 chemistry reactions (CO oxidation and dry reforming of CH₄) [5–9]. The outstanding performance of cobalt oxide in these reactions is attributed to the weaker bond strength of Co–O (bond length = 1.934 Å and 1.963 Å for Co₃O₄) and the low hopping barrier for oxygen at the surface compared to other 3d transition metals (bond length = 1.81 Å for CuO; and bond length = 1.89 and 2.06 Å for Fe₃O₄) [10–13]. This observation has led to the investigation of cobalt-based catalysts as a substitute for Fe-Cr catalysts, which are employed in HTS reactors. The literature survey shows that cobalt has been used in the WGS reaction as a sulfur-resistant catalyst [14,15]. Recently, Majima et al. investigated K/Co₃O₄ catalyst for the WGS reaction. They found that addition of K in Co₃O₄ increased the activity and stability of the resulting catalyst [16].

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We previously found that doping of cobalt into ceria was effective for improving the activity and stability of Co_3O_4 catalysts in the HTS reaction [17]. The time-on-stream study revealed that the Co/CeO_2 catalyst was highly stable compared to bulk Co_3O_4 . The stable performance of the Co/CeO_2 catalyst was attributed to the water dissociation ability of ceria, which makes cobalt stable under HTS reaction conditions. To further verify the role of ceria in WGS reaction, we prepared a series of cobalt-based catalysts using the same composition over different support oxides. The reducibility of cobalt, crystallite size, dispersion, and number of active cobalt metal sites are crucial factors to influence a chemical reaction. These variables are directly related to the nature of the support oxide as well as to the interaction between cobalt and the support. The effect of the support on the catalytic performance can occur via direct participation of the support or by an indirect role (e.g., by influencing the morphology and size of the supported metal particles, by charge transfer between the metal and support oxide, or by stabilizing the supported ionic metal species) [18]. Zhao et al. performed studies on cobalt supported on various metal oxides (ZrO_2 , CeO_2 , SiO_2 , Al_2O_3 , and TiO_2) for the preferential oxidation (PROX) of CO [19]. Their results showed that Co/ZrO_2 possessed the highest CO oxidation activity; this was related to the highest dispersion of cobalt in the Co/ZrO_2 catalyst. Ozkan et al. investigated cobalt-based catalysts supported on $\gamma\text{-Al}_2\text{O}_3$, TiO_2 and ZrO_2 in a bio-ethanol steam reforming reaction. They found that the ZrO_2 -supported catalyst exhibited the best dispersion and the best catalytic performance in the reaction [20].

Thus, to investigate how the nature of the support can influence cobalt-based catalysts in the HT-WGS reaction, we have prepared a series of supported cobalt catalysts by varying the reducible and non-reducible support oxides. CeO_2 , ZrO_2 , and TiO_2 oxides were selected as reducible supports and Al_2O_3 was selected as a non-reducible support. The activity and time-on-stream study revealed that the ceria-supported cobalt catalyst is preferable for the HTS reaction among the tested catalysts. Based on the characterization and activity results, the effects of the support on cobalt-based catalysts was discussed and elucidated.

2. Experimental

2.1. Materials

Cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) average $M_n \sim 5800$, 1-butanol ($\text{C}_4\text{H}_9\text{OH}$) titanium (IV) *tert*-butoxide ($[\text{Ti}(\text{OC}(\text{CH}_3)_3]_4$ cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and nitric acid (HNO_3) were purchased from the Sigma-Aldrich, South Korea. Zirconyl nitrate trihydrate $\text{ZrO}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was supplied by South Korea.

2.2. Catalyst synthesis

A series of cobalt-based catalysts with 15 wt.% cobalt loadings on various supports were synthesized by the incipient-wetness impregnation method. All of the support oxides, including CeO_2 , ZrO_2 , TiO_2 , and Al_2O_3 , were prepared by the inverse micelle sol-gel method [21]. Synthesis of the support oxides involved dissolution of 0.02 mol of the corresponding metal precursors into a solution of 2.0 g P123 surfactant, 1.6 mL HNO_3 acid, and 14.0 g *n*-butanol. The resulting mixtures were stirred for 24 h to obtain clear gels, which were placed in an oven at 120 °C for 6 h to dry. Next, the powder material was calcined at 500 °C for 6 h. The as obtained solid materials were used as supports for cobalt catalysts. The nitrate precursor of cobalt (0.755 g equivalent to the 15 wt.%) was dissolved in 0.5 mL

of distilled water and the prepared solution was impregnated over the 0.85 g of calcined support oxide. The impregnation process was performed in 5–6 times repeatedly to load all of the precursor solution. Between two successive steps, the sample was dried at 100 °C for 1 h in the oven. Finally, the catalyst was dried at 100 °C for 12 h and then calcined at 500 °C for 6 h.

2.3. Catalyst characterization

The BET surface area was measured by nitrogen adsorption at -196°C using ASAP 2010 (Micromeritics). XRD patterns were recorded using a Rigaku D/MAX-IIIc diffractometer (Ni filtered $\text{Cu-K}\alpha$ radiation, 40 kV, 100 mA). The XRD measurement conditions were as follows: slit size = 2.5° , step size & time per step: 0.02° step/0.5 s. Prior to XRD measurement, all of the catalysts were reduced at 400 °C under a 5% H_2 flow (30 mL/min) for 1 h to investigate which phase of the metallic cobalt (i.e. *hcp* or *fcc* phase) is available for the WGS reaction. The crystallite size of metallic cobalt was estimated using the Debye-Scherrer equation. The reducibility and strength of the metal-support interaction in the catalysts were evaluated through H_2 -TPR. The H_2 -TPR experiments were conducted on an Autochem 2920 (Micromeritics). Typically, 0.1 g of sample was loaded into a quartz reactor and reduced with 10% H_2 in Ar from room temperature to 800 °C at a heating rate of 10 °C/min. The sensitivity of the detector was calibrated by reducing a known weight of NiO. The dispersion of cobalt on various support oxides was measured by CO chemisorption at 50 °C using an Autochem 2920 instrument (Micromeritics). The calcined catalyst was reduced at 400 °C for 1 h in 10% H_2/Ar flow. After that, catalyst was cooled down to 50 °C. Then, CO pulses [$\text{CO}/\text{He} = 10/90$ (vol.%)] were passed to the catalyst surface till they were saturated with CO. The amounts of CO adsorbed on the metallic cobalt were calculated from the decrease in the peak area of CO due to its adsorption on the catalysts. From the chemisorbed amount, the cobalt dispersion was calculated by assuming the adsorption stoichiometry of 2 CO per cobalt surface atom ($\text{CO}/\text{Co} = 2$). The thermogravimetric (TG) analysis of samples were performed from 50 to 900 °C with a (TGA/DSC 1 STAR^e system SF 1100) instrument under the flow of O_2 at a heating rate of 10 °C⁻¹.

2.4. Catalytic reaction

The activity of the prepared catalysts was measured from 350 °C to 550 °C at atmospheric pressure in a continuous-flow, fixed-bed micro-tubular quartz reactor. Typically, 30 mg of catalyst was loaded into a reactor (length = 600 mm and i.d. = 4 mm). The length and volume of a packed catalyst bed were 3.5 mm and 175.9 mm³, respectively. The length/diameter ratio of the reactor was 150 (600 mm/4 mm). A T-union was employed at the exit of the quartz reactor to install a thermocouple. The thermocouple was inserted into the catalyst bed to measure the reaction temperature. Prior to each catalytic measurement, all of the catalysts were reduced by 5% H_2/N_2 from room temperature to 400 °C at a heating rate of 4.6 °C min⁻¹. The temperature was then maintained for 1 h. After the temperature was lowered to 350 °C, the simulated reformed gas (consisting of 38.0% CO, 21.33% CO_2 , 2.30% CH_4 , 29.30% H_2 , and 9.07% N_2 , which is representative of typical syngas from a waste gasifier) was fed into the WGS reactor. The flow rate of the feed gas and water were 31.95 sccm and 1.9 mL/h, respectively. In the presence of water, concentration of the gases will change. The actual concentration of the gases enters into the WGS reactor was: $\text{CO} = 17.02\%$, $\text{CO}_2 = 9.55\%$, $\text{CH}_4 = 1.03\%$, $\text{H}_2 = 13.12\%$, and $\text{N}_2 = 4.06\%$. The feed $\text{H}_2\text{O}/[\text{CH}_4 + \text{CO} + \text{CO}_2]$ ratio was fixed at 2.0. A GHSV of 143,000 mL/g_{cat} h. was used to screen all of the catalysts. Water was fed into the reactor using a syringe pump, vaporized at 180 °C upstream of the reactor. The product gas was chilled, passed

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