



Effect of supports on the performance of Co-based catalysts in methane dry reforming



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ABSTRACT

The effect of different supports (Al₂O₃, CeO₂, MgAl₂O₄, SiO₂, and ZrO₂) on the catalytic performance of an aluminum-incorporated cobalt catalyst in the dry reforming of methane (DRM) was investigated. DRM observations revealed the highest CH₄ and CO₂ conversion levels with CoAl/MgAl₂O₄. These levels decreased in the order: CoAl/MgAl₂O₄ > CoAl/Al₂O₃ > CoAl/ZrO₂ > CoAl/CeO₂ > CoAl/SiO₂. Due to the proximity of the Co and Mg ionic radii, the cobalt species strongly interacted with MgAl₂O₄ resulting in the formation of a solid solution. The CH₄/CO₂ thermogravimetric results indicated that the performance of the CoAl/MgAl₂O₄ catalyst was superior to that of the other catalysts. This was attributed to the balance between the rates of carbon deposition from CH₄ decomposition and surface oxidation from CO₂ dissociation. In addition, the apparent activation energy on this catalyst (54.6 kJ/mol) was much lower than that of CoAl/Al₂O₃ (77.5 kJ/mol), indicating a marked improvement in CH₄ reforming activity for CoAl/MgAl₂O₄. Overall, the characterization results revealed that the catalytic performance was influenced by the synergistic effect between CoAl and its support.

1. Introduction

Although the dry reforming of methane (DRM, CH₄ + CO₂ → 2H₂ + 2CO, ΔH_{298K} = + 247 kJ/mol) is not an industrially mature process, it has gained increasing attention as a promising process for the removal of greenhouse gases (CO₂ and CH₄) and the production of synthesis gases (CO and H₂) [1–3]. A syngas with a H₂/CO ratio of ~1 is suitable to produce hydrocarbons via the Fischer–Tropsch process, including methanol synthesis [1–6]. However, the endothermic nature of the DRM implies that a high reaction temperature is required to achieve high conversion levels [4]. This harsh operating condition risks catalyst deactivation from metal sintering and carbon deposition via methane decomposition (CH₄ → C + 2H₂, ΔH_{298K} = + 74.9 kJ/mol), CO disproportionation (2CO → C + CO₂, ΔH_{298K} = – 172.0 kJ/mol), CO₂ hydrogenation (CO₂ + 2H₂ → C + 2H₂O, ΔH_{298K} = – 90.0 kJ/mol), and CO hydrogenation (H₂ + CO → C + H₂O, ΔH_{298K} = – 131.3 kJ/mol) during the DRM [2]. Therefore, the DRM requires stable and affordable catalysts.

Noble metals such as Pt, Rh, and Ru have been used as catalysts for the DRM because of their excellent catalytic reactivity and anti-coking property [1,2]. However, these metals are expensive and less abundant and are therefore not suitable for commercial applications. More

affordable transition metals such as Ni and Co have been studied as alternative catalysts for the DRM. Because of their low cost and good catalytic performance, lots of studies on Ni-based catalyst systems for the DRM have been conducted [7–14]. However, under severe reaction conditions, these systems are prone to deactivation from carbon deposition. On the other hand, while susceptible to deactivation from oxidation of the active metals, Co-based reforming catalysts have exhibited better resistance against carbon deposition than Ni-based catalysts [15,16].

To achieve both a stable catalytic performance and resistance against carbon deposition during the DRM, the reaction between the coexisting reductive (CH₄, H₂, and CO) and oxidative (CO₂, and H₂O) species should be controlled with a reforming catalyst. In contrast, an imbalanced reaction would result in catalyst deactivation induced by carbon deposition and metal oxidation [16]. Therefore, the choice of an appropriate support is crucial in developing a reforming catalyst with good catalytic activity and stability. Numerous supports (Al₂O₃, SiO₂, MgO, MgAl₂O₄, ZrO₂, and TiO₂) for transition metal-based catalysts for the DRM have been studied [19–25]. These influence the metal–support interactions, acid–base properties, and metal dispersion of the supported catalysts. For example, Co catalysts supported on MgO exhibited high and stable catalytic activity in the DRM due to the strong

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interactions between the Mg and Co species [20,24]. Co-based catalysts supported on TiO₂(P25) provided better catalytic performance and stability in the DRM due to improved metal–support interactions over those of other oxide supports such as Al₂O₃, SiO₂, and CeO₂ [25]. In addition, Co-based catalysts supported on Al₂O₃, which initially exhibited considerable activity, deactivated rapidly as the metallic cobalt was oxidized. The oxidized cobalt species react with the Al₂O₃ surface to form an irreducible CoAl₂O₄ phase that leads to the loss of active sites [26]. Furthermore, the catalytic performance can be tuned by adding support modifiers. Thus, the addition of a small amount of K₂O to Ni/ZrO₂ enhanced the basicity and CO₂ adsorption capacity of the catalyst, thereby increasing the catalytic activity and stability [27]. A Co-Ni catalyst supported on Mg- and Sc-modified SBA-15 displayed improved catalytic activity and stability over the bare SBA-15 supported catalyst [28]. Therefore, the nature of the supports and modifiers significantly affect the catalytic activity and stability of the catalysts.

A 1 wt.% Al-incorporated Co/ZrO₂ catalyst exhibited better catalytic performance and stability in the DRM than the Co/ZrO₂ catalyst. In this study, the effect of various oxide supports (MgAl₂O₄, Al₂O₃, SiO₂, CeO₂, and ZrO₂) on the catalytic properties of a 1 wt.% Al-incorporated Co catalyst was investigated. Various characterization tools were employed, to elucidate the effect of the supports on the catalytic performance during the DRM.

2. Experimental

2.1. Preparation of the catalysts

Mg(NO₃)₂·6H₂O (Junsei, 99%), Al(NO₃)₃·9H₂O (Junsei, 98%), ZrOCl₂·8H₂O (Junsei, 90%), Ce(NO₃)₃·6H₂O (Alfa, 99.5%), Co(NO₃)₂·6H₂O (Samchun, 98%), commercial γ -Al₂O₃ (Strem, $S_{\text{BET}} = 157 \text{ m}^2/\text{g}$), and SiO₂ (Sigma, 35–60 mesh, Davisil grade, $S_{\text{BET}} = 264 \text{ m}^2/\text{g}$) were used as precursors without further purification. MgAl₂O₄, ZrO₂, and CeO₂ were prepared using a precipitation method. For MgAl₂O₄, 12.82 g Mg and 37.51 g Al (molar ratio of 1/2) precursors were dissolved in 200 mL of deionized water. The solution pH was adjusted to 10 by adding ammonia solution (NH₄OH, Samchun, 28 vol.%). The solution was then aged for 20 h at 50 °C with vigorous stirring and subsequently filtered, washed, and dried at 100 °C overnight. For ZrO₂ and CeO₂, the respective metal precursors (28.64 g Zr precursor and 19.30 g Ce precursor) were dissolved in 200 mL of deionized water. The pH was maintained at 9.5 by an NH₄OH solution. The solutions were aged for 1 h at 80 °C and washed, filtered and dried at followed at 100 °C overnight. The supports were then calcined at 800 °C for 6 h in a muffle furnace under static air. All samples were prepared on the basis of 3 g oxide supports. The 5 wt.% Co and 1 wt.% Al catalysts on the different supports were all prepared via an impregnation method in an aqueous solution of 0.74 g Co(NO₃)₂·6H₂O and 0.42 g Al(NO₃)₃·9H₂O. The resulting suspensions were aged for 2 h at 25 °C. Subsequently, the excess water was removed using a rotary evaporator (BUCHI R – 210) at 60 °C. The samples were dried at 100 °C for 12 h, and then calcined at 400 °C for 6 h in a muffle furnace under static air. The catalysts produced were designated as CoAl/M, where M represents the abbreviation of the prepared supports (M = A for Al₂O₃, C for CeO₂, MA for MgAl₂O₄, S for SiO₂, and Z for ZrO₂).

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV diffractometer with Ni-filtered CuK α radiation (1.5418 Å) operating at 40 kV and 40 mA at a scan rate of 1.2°/min to identify the phases of the CoAl/M catalysts. The transmission electron microscopy (TEM) images and elemental compositions of catalysts before and after the DRM were measured using a Jeol JEM-2000FXII electron microscope operating at 200 kV. The samples were prepared by drop-casting

using samples dispersed in ethanol on a holey copper grid.

The surface area and total pore volumes of the catalysts were measured using Micromeritics ASAP 2020 apparatus at liquid nitrogen temperature –196 °C from the N₂ adsorption and desorption isotherms. To remove the water and ant other impurities from the catalyst surface, the samples (0.2–0.3 g) were first degassed under a flow of N₂ at 250 °C for 4 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method in the relative pressure range 0.05–0.20. Additionally, the total pore volume was calculated from the amount of N₂ adsorbed at $P/P_0 = 0.995$.

The reducibility of the catalysts was examined by the temperature-programmed reduction of hydrogen (H₂-TPR) using Micromeritics ASAP 2920 apparatus. The experiments were performed under two different conditions: normal TPR for calcined samples and TPR after reduction and oxidation. For normal TPR, 0.05 g of each sample was first pretreated in Ar (30 cm³/min, 15.3 Ncm³/min) at 300 °C for 1 h and cooled down to 30 °C. Subsequently, the temperature was raised to 1000 °C at a ramp rate of 10 °C/min under a stream of 5% H₂/Ar. For TPR, after reduction and oxidation, the sample was reduced at 850 °C for 1 h under 5%H₂/Ar flow (30 cm³/min, 7.8 Ncm³/min), and then treated with 5%O₂/Ar for 1 h (30 cm³/min, 7.8 Ncm³/min). The analysis was conducted in the same manner as the normal TPR procedures.

The metal dispersion of the catalysts was measured by H₂-chemisorption using Micromeritics ASAP 2920 apparatus; a H/Co stoichiometry factor of 1 was assumed. Prior to analysis, the sample was first reduced under a 5% H₂/Ar flow (30 cm³/min, 7.8 Ncm³/min) at 850 °C for 1 h and then cooled down to 30 °C under the same atmosphere. After cooling, the 10%H₂/Ar was introduced into the catalyst bed for 1 h at a flow rate of 30 cm³/min (23.6 Ncm³/min) and then purged with Ar at 100 °C to remove the physically adsorbed H₂ species. The samples were heated to 900 °C at a ramp rate of 10 °C/min. The metal dispersion was calculated according to a previously reported method [29].

To examine the degree of CH₄ and CO₂ activation on the catalysts, thermogravimetric analysis (TGA) was performed using a Mettler Toledo DSC 1. Prior to the analysis, the weighted samples were reduced under a flow of 4%H₂/Ar (30 cm³/min, 7.8 Ncm³/min) at 850 °C for 1 h. TGA was then conducted under 5%CO₂/Ar, 4%CH₄/Ar, and 4%CH₄/4%CO₂/Ar flows. The degree of CH₄ and CO₂ activation was calculated assuming carbon deposition (CH₄ → C + 2H₂) and metal oxidation (Co + O = CoO_x), respectively. The amount of carbon deposited on the catalysts after the DRM was measured by TGA (TA Instruments SDT 2960 analyzer). The samples were heated from 30 to 900 °C at a heating rate of 10 °C/min under air.

2.3. Dry reforming of methane

The DRM was performed in a continuous-flow, fixed bed reaction system with a quartz reactor (1/4 in. h diameter and 50 cm length) at atmospheric pressure. Prior to the reaction, the catalyst sample (0.05 g, 50–70 mesh) was loaded in the reactor and pretreated at 850 °C for 1 h under 5% H₂/Ar flow. After the reduction, CH₄, CO₂, and N₂ (40:40:20 vol.%) were introduced into the reactor at a constant flow rate of 50 cm³/min (13.1 Ncm³/min). To compare the catalytic reactivity of the different CoAl/M catalysts, the light-off experiments were performed in the temperatures range 650 – 850 °C at 50 °C intervals, while the isothermal reaction was carried out at 850 °C for 20 h. Gas products were analyzed using on-line gas chromatography (GC, Donam DC 6200 series) on a Carboxen 1000 column (2 m length and 1/8 in. h diameter) with a thermal conductivity detector. A schematic of the catalytic evaluation system is presented in Fig. 1. The CH₄ turnover frequency (TOF) was calculated by dividing the number of moles of reacted CH₄ per unit time by the exposed cobalt metal on the catalyst for the same mass of catalyst. The CH₄ and CO₂ conversion rates and H₂/CO ratio were calculated using the following equations:

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