



## Full Length Article

Enhanced stability of Co catalysts supported on phosphorus-modified  $\text{Al}_2\text{O}_3$  for dry reforming of  $\text{CH}_4$ 

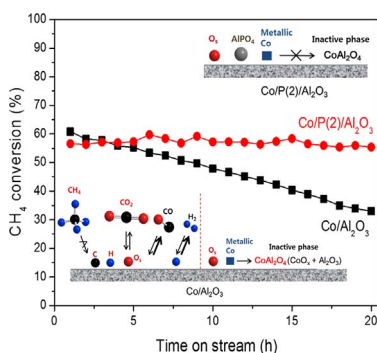
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## GRAPHICAL ABSTRACT

Partially formed  $\text{AlPO}_4$  phase can suppress the phase transformation of metallic cobalt to oxidized cobalt and inactive  $\text{CoAl}_2\text{O}_4$ .



## ARTICLE INFO

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## ABSTRACT

Phosphorous-modified  $\gamma\text{-Al}_2\text{O}_3$  support is used to prepare cobalt-based catalysts ( $\text{CoP}(x)\text{Al}$ ,  $x = 0\text{--}4$  wt%) for dry reforming of methane (DRM). From the studied catalysts,  $\text{CoAl}$  displays the highest conversions of  $\text{CH}_4$  and  $\text{CO}_2$  at the initial stage due to good cobalt dispersion. However, both conversions decrease significantly after 20 h on stream due to the formation of inactive  $\text{CoAl}_2\text{O}_4$  phase through the reaction of oxidized  $\text{CoO}_x$  with the alumina surface. For the  $\text{CoP}(x)\text{Al}$  catalysts, although the initial  $\text{CH}_4$  and  $\text{CO}_2$  conversions decrease gradually as the phosphorus loadings increased, all catalysts show more stable catalytic activity than the  $\text{CoAl}$  catalyst. Formation of aluminum phosphate ( $\text{AlPO}_4$ ) on the alumina surface can be achieved by the addition of phosphorus. The  $\text{AlPO}_4$  phase has the capacity to suppress the formation of  $\text{CoAl}_2\text{O}_4$  phase. Phosphorous loadings on alumina surface of up to 1–2 wt% exerted positive effect on catalyst stability, whereas loadings above this threshold exerted opposite effect.

**Abbreviations:** BET, Brunauer–Emmett–Teller; DRM, dry reforming of methane; GC, gas chromatogram; FEG, field-emission gun; RWGS, reverse watergas shift; TEM, transmission electron microscopy; TGA, thermogravimetric analysis; TOF, turnover frequency; TPD, temperature-programmed desorption; TPR, temperature-programmed reduction; XRD, X-ray diffraction

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## 1. Introduction

Dry reforming of CH<sub>4</sub> with CO<sub>2</sub> (DRM) is receiving considerable attention as a promising technology for the utilization of two greenhouse gases, namely CO<sub>2</sub> and CH<sub>4</sub>, for the production of synthesis gas [1–3]. The produced syngas with a low H<sub>2</sub>/CO ratio of unity is suitable for methanol synthesis and production of hydrocarbons as base platform of chemical intermediates [1–8]. However, activation of CH<sub>4</sub> and CO<sub>2</sub> is very difficult owing to the high bond energies of the C–H (436 kJ/mol) bonds in methane and C–O (803 kJ/mol) in CO<sub>2</sub> [4]. Therefore, DRM reaction requires high reaction temperature in order to achieve high conversions of CH<sub>4</sub> and CO<sub>2</sub> as a results of the highly endothermic nature of the DRM process. The harsh operating conditions can cause catalyst deactivation, which arises as a result of metal sintering and carbon deposition on the catalyst surface. It is generally accepted that carbon deposition occurs through methane decomposition (CH<sub>4</sub> → C + 2H<sub>2</sub>) and CO disproportionation (2CO → C + CO<sub>2</sub>) during the DRM reaction [2].

Supported noble metal catalysts such as Pt, Rh, Ru, and Ir have been used as catalysts for DRM because of their excellent C–H bond breaking ability and resistance to carbon deposition [1,2,5–8]. However, their high cost and limited availability are disadvantages that hamper their widespread use in practical applications for DRM. Supported Ni-based catalysts have been investigated as a possible alternative owing to their low cost and good catalytic performance for DRM reaction [9–13]. However, Ni-based catalysts are prone to deactivation due to carbon deposition and/or reactor plugging. It has been reported that large Ni assemblies lead to facile deposition of carbon on metallic sites. The carbon deposited on the surface of Ni particles diffuses into the bulk phase and forms different types of graphite carbon such as onion- and bamboo-like carbon nanotubes [14–16]. Although Co-based catalysts are considerably underexplored when it comes to the DRM, they do show considerable activity for this reaction [17,18], which suggests that cobalt might be a suitable active metal. The Co-based catalysts reported exhibit high resistance to carbon deposition during DRM and can control the rate of carbon formation by oxidizing the carbon surface [19–21].

During the DRM, CH<sub>4</sub> is decomposed to various CH<sub>x</sub> species on the active metal sites and the final form of C<sub>ads</sub> (carbon adsorbed on metal surface) remains on the metallic sites, while CO<sub>2</sub> is adsorbed on the support [22,23]. The C<sub>ads</sub> is oxidized by its reaction with oxygen species derived from CO<sub>2</sub> adsorbed on the support. To minimize carbon deposition, the catalyst should be designed to (i) suppress the formation of large metal ensembles that facilitates carbon formation and (ii) to improve the sorption ability of CO<sub>2</sub> on the support in order to reduce carbon deposited on the metal surface. Therefore, the choice of an appropriate support is important factor in the preparation of the catalyst with good catalytic activity and resistance to deactivation. Numerous supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, ZrO<sub>2</sub>, and TiO<sub>2</sub> for transition metal based catalysts have been investigated for DRM and these supports are known to influence the metal-support interactions, acid-base properties, and metal dispersion of the supported catalysts [18,24]. Zhang and Verykios [25] studied the effect of support in the activation of CH<sub>4</sub>, showing that a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst displays higher initial reaction rate compared to a Ni/La<sub>2</sub>O<sub>3</sub> catalyst, which suggests that acidic sites on Al<sub>2</sub>O<sub>3</sub> assist in the activation of CH<sub>4</sub>. Ruckenstein and Wang [24] reported that the Co catalysts supported on MgO exhibit high and stable catalytic activity for DRM due to the strong interactions between Mg and Co species. However, Co-based catalysts are susceptible to oxidation of metallic cobalt, which results in their deactivation. In addition, Co catalysts supported on Al<sub>2</sub>O<sub>3</sub> showed initially a considerable activity, but, deactivated rapidly due to the oxidation of the metallic Co species [18]. The oxidized cobalt species can react with the Al<sub>2</sub>O<sub>3</sub> surface to form an irreducible CoAl<sub>2</sub>O<sub>4</sub> phase that leads to the loss of active sites [26]. The DRM catalyst is always exposed to reductive and oxidative atmosphere due to the coexistence of reductive

(CH<sub>4</sub>, H<sub>2</sub>, and CO) and oxidative (CO<sub>2</sub>, and H<sub>2</sub>O) species and these reaction conditions can affect the catalytic activity significantly. For example, the activity of a DRM catalyst can be stable when the reaction between reductive and oxidative species is kinetically controlled. By contrast, imbalanced reaction conditions can result in the deactivation of the catalysts over time due to carbon deposition and metal oxidation. Nagaoka et al. [27] studied the role of Pt, Ru, and Ni in a Co/TiO<sub>2</sub> catalyst, showing that the stability of the modified Co/TiO<sub>2</sub> catalyst was drastically enhanced by the suppression of carbon deposition and metal oxidation.

With this regard, to utilize the Co catalyst for DRM reaction, we try to design the Co catalyst which has a resistance for oxidation of metallic cobalt. In this study, we report on the catalytic behavior of Co catalysts supported on phosphorus-modified Al<sub>2</sub>O<sub>3</sub> for DRM reaction. The phosphorus-modified Al<sub>2</sub>O<sub>3</sub> support with phosphorus loadings of 1–4 wt% based on Al<sub>2</sub>O<sub>3</sub> was prepared using the impregnation method. The effect of the phosphorus modifier on the structural properties and catalytic activities of the catalysts for DRM was investigated. To elucidate the effect of the phosphorus modifier, various characterization tools were employed.

## 2. Experimental

### 2.1. Preparation of the catalysts

All chemicals used in this study were of analytical grade and used without any further purification. Phosphorus-modified Al<sub>2</sub>O<sub>3</sub> supports with different phosphorus loadings (ranging from 1 to 4 wt%) were prepared using the impregnation method with H<sub>3</sub>PO<sub>4</sub> (Samchun, 85%) solution on a commercial γ-Al<sub>2</sub>O<sub>3</sub> (Strem, S<sub>BET</sub> = 157 m<sup>2</sup>/g). The resulting suspensions were aged for 1 h at 25 °C, and the excess water was removed using a rotary evaporator (BUCHI R–210) at 60 °C. The phosphorus-modified Al<sub>2</sub>O<sub>3</sub> supports were dried at 100 °C for 12 h and subsequently calcined at 500 °C for 4 h in a muffle furnace in static air. The Co catalysts supported on Al<sub>2</sub>O<sub>3</sub> and phosphorus-modified Al<sub>2</sub>O<sub>3</sub> were prepared using the impregnation method with an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Samchun, 98%). In this study, the Co loading was fixed at 5 wt% for all samples. The remaining steps were identical to those described for impregnation of Al<sub>2</sub>O<sub>3</sub> with phosphorus. The resulting catalysts are designated as CoP(x)Al, where x (x = 0, 1, 2, 3, and 4) represents the weight percentage of phosphorus.

### 2.2. Catalyst characterization

The bulk and crystalline structures of the catalysts were recorded by powder X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with Ni-filtered CuKα radiation (1.5418 Å) operating at 40 kV and 40 mA at a scan rate of 1.2°/min. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT 2960 analyzer. The samples were heated from 30 to 900 °C at a heating rate of 10 °C/min under a flow of air. To examine the chemical state of the phosphorus species on the catalyst surface, IR spectra were recorded on a FT-IR spectrophotometer (Bruker Optic IFS 66/S).

The surface areas and total pore volumes of the samples were determined from the adsorption and desorption isotherms at liquid nitrogen temperature of –196 °C with a volumetric method using Micromeritics ASAP 2020 instrument. Prior to these measurements, 0.2 g of each catalyst were degassed under a flow of N<sub>2</sub> at 150 °C for 4 h. The Brunauer–Emmett–Teller (BET) method was used to determine the surface areas that were measured at P/P<sub>0</sub> values in the range of 0.05–0.20. The total pore volumes were measured at P/P<sub>0</sub> = 0.995. The method of Barrett, Joyner, and Halenda (BJH) was used to determine the pore size distribution of the catalysts by using desorption isotherms.

The reduction properties of the catalysts were studied by temperature-programmed reduction of H<sub>2</sub> (H<sub>2</sub>-TPR) through Micromeritics

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