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journal homepage: [www.elsevier.com/locate/apcata](http://www.elsevier.com/locate/apcata)Effects of Ru addition to Pd/Al<sub>2</sub>O<sub>3</sub> catalysts on methanol steam reforming reaction: A mechanistic studyGeo Jong Kim<sup>a</sup>, Min Su Kim<sup>a</sup>, Ji-Young Byun<sup>b</sup>, Sung Chang Hong<sup>a,\*</sup><sup>a</sup> Department of Environmental Energy Engineering, Graduate School of Kyonggi University, 94-6 San, Iui-dong, Youngtong-ku, Suwon-si, Gyeonggi-do 443-760, Republic of Korea<sup>b</sup> Center for Materials Architecturing, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

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## ABSTRACT

In this study, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Ru/Al<sub>2</sub>O<sub>3</sub> catalysts were used to investigate the mechanism of the methanol steam reforming (MSR) reaction and the factors affecting the reaction activity. First, the MSR reaction activity was evaluated using Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. The MSR reaction activities increased with the addition of Ru. In addition, FT-IR analysis was performed to investigate the MSR reaction mechanism. The reactions with the Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Ru/Al<sub>2</sub>O<sub>3</sub> catalysts proceeded through the same mechanism. After methanol was adsorbed on the catalyst surface as methoxy and formate species, it was converted into CO through decomposition and reaction with water, and then desorbed from the catalyst surface. TEM analysis revealed that the addition of Ru to the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst resulted in small particle sizes with highly dispersed Pd on the catalyst surface, which increased the conversion to CO. Lastly, analysis of adsorption characteristics showed that the addition of Ru enhanced the desorption rate of adsorbed CO species to promote the MSR reaction activity by weakening the adsorption intensity of CO. The desorption of CO adsorption species was the rate-determining step of the MSR reaction.

## 1. Introduction

Currently, there is an urgent need to find eco-friendly energy resources to address the environmental pollution problems caused by the use of fossil fuels. As an ideal fuel, there is increasing interest in obtaining energy from hydrogen because water is the only waste product. However, owing to the intrinsic properties of hydrogen, it is not an ideal energy medium. According to adsorption and decomposition studies on catalyst surfaces, methanol can be considered a hydrogen carrier, as it has a high content of hydrogen and can be easily decomposed without breaking C–C bonds [1–3]. Methanol has also attracted attention as one of the most promising energy carriers owing to its high power density and eco-friendly properties [4,5]. Hydrogen can be produced directly from methanol via the following reactions: methanolysis (CH<sub>3</sub>OH → CO + 2H<sub>2</sub>) and methanol steam reforming (MSR) (CH<sub>3</sub>OH + H<sub>2</sub>O → CO<sub>2</sub> + 3H<sub>2</sub>). As methanol is one of the most common synthetic chemicals and can provide chemical information about more complex carbon compounds, understanding the reaction mechanisms and properties of methanol on the surface of catalysts has attracted considerable attention.

The methanolysis and MSR reactions are effective methods for

hydrogen production. In general, Cu-based catalysts are used to produce hydrogen from methanol because of their excellent activity and selectivity [6–9]. However, there are several problems associated with Cu-based catalysts, such as requiring a pretreatment process in the hydrogen atmosphere for several hours and coagulation at temperatures above 300 °C owing to low thermal stability [10–12]. For this reason, Pd-based catalysts have recently been investigated to replace Cu-based catalysts for the production of hydrogen from methanol [10,13–15]. Previous studies have examined the mechanisms of methanol degradation on metal surfaces and transition metal catalysts [16,17]. The MSR reaction mechanism of Pd-based catalysts was first proposed by Iwasa et al. [16], who reported that the intermediate species formed on the catalyst surface varies depending on the metallic Pd and Pd alloys present, with the reactions proceeding via different reaction pathways. In addition, Easwar et al. [17] reported that the methanol conversion rate was proportional to the H<sub>2</sub> chemisorption amount and that the rate-determining step (RDS) was dependent on Pd when Pd/CeO<sub>2</sub> and Pd/ZnO catalysts were compared. In addition, the selectivity for CO<sub>2</sub> depended on the reaction pathway, and the reaction pathway was determined by the intermediate species adsorbed on the catalyst surface. However, there are few studies on step experiments to

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