



# High methane selective Pt cluster catalyst supported on Ga<sub>2</sub>O<sub>3</sub> for CO<sub>2</sub> hydrogenation

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## ABSTRACT

In heterogeneous catalysis, the CO<sub>2</sub> hydrogenation reaction is an important class of reactions that has been widely studied for decades. Particularly, the particle size of the metal plays a crucial role in controlling the selectivity of the CO<sub>2</sub> hydrogenation reaction. However, there have only been a few studies investigating the selectivity for sub-nanometer sized particles. Here, we report the effect of Pt particle size on the catalytic activity and selectivity of CO<sub>2</sub> hydrogenation. The size of the Pt particles was tuned by changing the amount of loading. With low Pt loading on gallium oxide, Pt clusters were formed; however, Pt nanoparticles were synthesized with high Pt loading. The Pt clusters were mainly edge and step sites where CO<sub>2</sub> adsorbs more strongly, while the Pt nanoparticles were mainly composed of terrace sites. The catalytic performance of the Pt catalysts was examined using CO<sub>2</sub> hydrogenation. The Pt clusters showed a higher methane selectivity than that of the Pt nanoparticles. The reaction mechanism was analyzed by diffuse reflectance infrared fourier transform (DRIFT) spectroscopy at reaction conditions. The Pt clusters mainly showed the formate peak, while showing fewer carbonate peaks than the support. These results suggest that the formation of CH<sub>4</sub> follows the formate route.

## 1. Introduction

Utilization of CO<sub>2</sub> to produce high energy density chemicals, including methanol, methane, and dimethyl ether, has used heterogeneous catalysts with transition metals (Cu, Ni, Ru, Pd, etc.) as active sites [1–7]. One of the major reactions to convert CO<sub>2</sub> is the Sabatier reaction (CO<sub>2</sub> + 4 H<sub>2</sub> → CH<sub>4</sub> + 2 H<sub>2</sub>O, Δ = −165.0 kJ mol<sup>−1</sup>), which is also known as CO<sub>2</sub> methanation to produce methane. This reaction is thermodynamically favorable but still a challenging topic because of the high kinetic barrier. Therefore, a high CO<sub>2</sub> conversion rate and high CH<sub>4</sub> selectivity is required for CO<sub>2</sub> methanation catalysts. Various metals have been studied for CH<sub>4</sub> production from CO<sub>2</sub>, and group VIII metals, including Ni, Pd, Rh, Ru, Pt, etc., are known as active catalysts [8–16]. Ni-based catalysts have been widely studied because of their comparable activity and low cost. Pt-based catalysts showed a different behavior, and it is desirable to control the selectivity for CO and CH<sub>4</sub>. Yu et al. reported that the CO<sub>2</sub> adsorption on Pt nanoparticles was enhanced by depositing the Pt on a TiO<sub>2</sub> nanotube support. During the CO<sub>2</sub> hydrogenation reaction, Pt/TiO<sub>2</sub> nanotube catalysts showed high activity producing methane at low temperature (100 °C) [17]. Kattel et al. investigated the support effect on Pt. There was less activity for

CH<sub>4</sub> when Pt was loaded on SiO<sub>2</sub> or TiO<sub>2</sub> supports; most of the product was CO [18]. They proposed that Pt alone (without a support) was not able to dissociate CO<sub>2</sub> because of weak binding on the Pt. The CO<sub>2</sub> could be stabilized in the presence of Pt on a support and the catalyst accelerates the reverse water-gas shift (RWGS) reaction to produce CO. However, corresponding selectivity studies of Pt on other oxide supports are limited.

Another important parameter to tune the reaction selectivity is the particle size of the metal [19–21]. Most of the reported studies were based on nanometer-sized particles and showed varied catalytic performance as the size changed. Karelovic and Ruiz synthesized 2–19 nm Rh particles by controlling the amount of metal loading. For CO<sub>2</sub> hydrogenation to methane, the small Rh catalyst (2 nm) showed the lowest activity, whereas the larger particles (> 7 nm) showed the lowest activation energy, which did not change as the particles became larger [22]. Wang et al. investigated the particle size effect of Pt catalysts for CO<sub>2</sub> reduction. They synthesized ~3 nm Pt nanoparticles on CeO<sub>2</sub>. The catalysts began to produce methane at 350 °C and showed high methane selectivity at temperatures over 400 °C [23]. In recent years, however, synthesis and analysis of sub-nanometer particles, even single atoms, is now possible, and these smaller catalysts show unique

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