Catalysis Today 352 (2020) 212–219

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

High methane selective Pt cluster catalyst supported on Ga_2O_3 for CO_2 hydrogenation

Hanseul Choi[a,b], Sunyoung Oh[a,b], Jeong Young Park[a,b,*]

[a] Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 34141, Republic of Korea
[b] Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon, 34141, Republic of Korea

ARTICLE INFO

Keywords:
Pt cluster
CO_2 hydrogenation
Selectivity
Reaction mechanism
Heterogeneous catalyst

ABSTRACT

In heterogeneous catalysis, the CO_2 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_2 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_2 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_2 adsorbs more strongly, while the Pt nanoparticles were mainly composed of terrace sites. The catalytic performance of the Pt catalysts was examined using CO_2 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_4 follows the formate route.

1. Introduction

Utilization of CO_2 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_2 is the Sabatier reaction ($CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$, $\Delta = -165.0\,kJ\,mol^{-1}$), which is also known as CO_2 methanation to produce methane. This reaction is thermodynamically favorable but still a challenging topic because of the high kinetic barrier. Therefore, a high CO_2 conversion rate and high CH_4 selectivity is required for CO_2 methanation catalysts. Various metals have been studied for CH_4 production from CO_2, 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_4. Yu et al. reported that the CO_2 adsorption on Pt nanoparticles was enhanced by depositing the Pt on a TiO_2 nanotube support. During the CO_2 hydrogenation reaction, Pt/TiO_2 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_4 when Pt was loaded on SiO_2 or TiO_2 supports; most of the product was CO [18]. They proposed that Pt alone (without a support) was not able to dissociate CO_2 because of weak binding on the Pt. The CO_2 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_2 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_2 reduction. They synthesized ~3 nm Pt nanoparticles on CeO_2. 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

* Corresponding author at: Department of Chemistry and Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 34141, Republic of Korea.
E-mail address: jeongypark@kaist.ac.kr (J.Y. Park).

https://doi.org/10.1016/j.cattod.2019.11.005
Received 20 June 2019; Received in revised form 16 October 2019; Accepted 7 November 2019
Available online 11 November 2019
0920-5861/