



Size-controlled model Ni catalysts on Ga₂O₃ for CO₂ hydrogenation to methanol

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ABSTRACT

The effect of particle size for Ni nanoparticles supported on β-Ga₂O₃ was investigated for CO₂ hydrogenation to methanol at 0.5 MPa. Model Ni nanoparticles ranging from 3.3 to 10.2 nm were synthesized using the hot injection method by controlling the reaction temperature and time. The smallest Ni nanoparticles (3.3 nm) showed the highest catalytic activity across the entire temperature range and the largest Ni nanoparticles (10.2 nm) showed the highest methanol selectivity. The apparent activation energies for methanol with Ni nanoparticles increased from 6.0 to 18.4 kcal mol^{−1} as the nanoparticle size increased. Furthermore, it was found that the smallest Ni nanoparticles favor the reverse water gas shift reaction. In situ DRIFT analysis revealed that the gallium oxide itself could produce an intermediate species and the addition of Ni on the oxide support increases the hydrogenation rate. The Ni supported catalysts showed a CO peak, but the smallest Ni nanoparticles showed a larger CO peak than that for the largest Ni nanoparticles, which clearly supports that the smaller nanoparticles favor the reverse water gas shift reaction.

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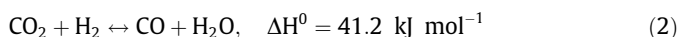
1. Introduction

Much effort has gone into reducing CO₂ levels in the atmosphere caused by the combustion of fossil fuels. A powerful way to reduce the CO₂ in the atmosphere is by recycling CO₂ into other valuable chemical products. If renewable hydrogen is used when converting CO₂ into methanol, this reaction would have a beneficial effect on reducing greenhouse gas emission. Methanol is one of the most common commodity chemicals and it can be produced from the hydrogenation of CO and CO₂. This methanol could be used as a fuel or as a raw material to produce other chemicals, such as olefins, gasoline, formaldehyde, dimethyl ether, and so on [1–3]. The methanol production reaction from CO₂ requires high pressure (at least 5 MPa) and high temperature (between 200 and 300 °C). To date, copper-based catalysts have been widely used [4–11]. In the reaction, CO becomes another important issue because methanol synthesis (reaction (1)) and the reverse water gas shift (RWGS) reaction (reaction (2)), which produces CO, are competing reactions.



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As shown above, the methanol synthesis reaction is exothermic, meaning it favors low temperature, whereas the RWGS reaction is endothermic and favors higher temperature. However, the use of copper-based catalysts for methanol production also produces significant CO as a by-product during the RWGS reaction. Although the CO by-product is fed back into the reactor, there is still a need to develop new catalysts with low CO selectivity and high methanol activity and selectivity [12,13].

The first use of Ga₂O₃ for CO₂ hydrogenation to methanol was reported in 1995 [14]. Fujitani et al. reported a 20-fold higher catalytic activity with Pd supported on Ga₂O₃ than Cu/ZnO, and it showed a 120-fold higher activity than Pd supported on SiO₂. Since these results were first reported, Ga has been utilized for the CO₂ hydrogenation to methanol reaction in the form of gallium oxide and with a promoter [5,8–10]. Ga doped into Pd supported on SiO₂ catalysts showed higher catalytic activity from 160 to 250 °C at ambient pressure than that of Cu/ZnO/Al₂O₃ catalysts [15]. New Ni-Ga intermetallic catalysts supported on SiO₂ were reported and the Ni₅Ga₃ catalyst showed higher activity and stability at ambient pressure than that of conventional Cu/ZnO/Al₂O₃ [13]. S. E. Collins et al. showed 20- and 4-fold higher methanol TOF and selectivity, respectively, with Ga₂O₃ than SiO₂ as the support [16]. Furthermore, they increased the catalytic activity by adding