CO₂ hydrogenation to methanol by Ni-Ga alloy catalysts via hydrotalcite-like precursors

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Abstract

Mitigating efforts to reduce the CO₂ concentration in the atmosphere include CO₂ capture and storage, as well as CO₂ utilization, with the latter gradually gaining increasing scientific attention in the past few decades. CO₂ derivatives are good candidates for the synthesis of useful chemicals and energy carriers and CO₂ acts as a carbon source to produce chemicals, from C₁ chemicals such as methanol, DME, formic acid, to long chain hydrocarbons. Among these products, methanol is not only an outstanding fuel for the internal combustion engines, but also a promising starting material for light olefins, and further processing to produce hydrocarbons.

Commercial catalysts for CO₂ hydrogenation to methanol are copper-zinc-alumina, however, CO₂ conversion is restricted by thermodynamic equilibrium at high-pressure (50-100 bar) and methanol selectivity is limited due to the Reverse Water Gas Shift reaction. Recently, Nickel-Gallium alloy, particularly the Ni₅Ga₃ phase, was found to reveal good catalytic performance under milder reaction conditions compared to commercial catalysts.

Conventional methods for preparing Ni-Ga catalysts are co-precipitation and incipient wetness impregnation. Hydrotalcite-like compounds (HTLc) as precursor has the advantages of a better dispersion for active metals and strong resistance to coke deposition. In this work, we applied this novel method to produce bimetallic Ni-Ga catalysts for CO₂ hydrogenation to methanol.

By characterization techniques, such as powder X-ray diffraction, scanning electron microscope and energy dispersive spectroscopy (SEM-EDS), the purity of Ni₅Ga₃ was investigated and the morphology was also demonstrated. The surface area and pore distribution were tested by BELSORP under N₂ atmosphere at 77K, and CO₂ chemisorption under reaction temperature was also investigated and analyzed by BELSORP in CO₂ atmosphere. In addition, the reducibility was investigated by temperature programmed reduction in H₂ (H₂-TPR), and the acid as well as basic sites were detected by temperature programmed desorption in NH₃ (NH₃-TPD) and CO₂ (CO₂-TPD) respectively.

CO₂ hydrogenation reaction was carried out in a fixed bed reactor using Ni₅Ga₃ from HTLc precursors and commercial Cu/Zn/Al catalysts respectively. Mixture gas (H₂/CO₂=3:1) was fed into the reactor and the exhaust gas was tested by gas chromatograph (GC).

The CO₂ conversion increased with temperature increasing from 200 °C (under 10%) to 250 °C (above 25%), however, 300 °C witnessed a sharp decrease in CO₂ conversion to about 12%. The
methanol selectivity was much higher than traditional copper-based catalysts at 250 °C, reaching a selectivity of 95%. The by-product CO was sharply decreased compared with the commercial Cu/Zn/Al catalysts. The result indicated that Ni₅Ga₃ prepared by HTLc precursors revealed better catalytic reactivity especially for methanol synthesis reaction, and also prevented the reverse water gas shift reaction at the same time, achieving an overwhelmingly higher selectivity than commercial Cu/Zn/Al catalysts.