

CO₂ HYDROGENATION BY UTILIZING NICKEL-POOR AND ALUMINUM-RICH LAYERED DOUBLE HYDROXIDES, WITH DIFFERENT INTERLAYER ANIONS VIA REVERSE WATER GAS SHIFT ROUTE

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Abstract

The concentration of the predominant greenhouse gas, CO₂, is remarkably increasing in the atmosphere due to combustion emissions of fossil fuels. A state-of-the-art and relatively simple synthetic path of preparing NiAl₄-layered double hydroxides (LDHs) were developed through high-energy mixer milling pretreatment of Al(OH)₃ followed by impregnation with Ni(II) nitrate salt under mild circumstances (atmospheric pressure and 90°C). This method proved to be improved by the ion exchange technique, and thus various counters (H₂PO₂⁻, HPO₃²⁻, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻, B₄O₇²⁻, CO₃²⁻ and HCO₃⁻) anions could be intercalated. The modified LDHs proved to be active in CO₂ hydrogenation reactions at atmospheric pressure. The catalysts were characterized using XRD, TG-DTA, FT-IR and H₂-TPR. The quality of interlayer anions was found to exert a considerable influence on the topotactic transformation of LDHs, the in situ reduction of nickel, and the formation of spinel-type oxides. Furthermore, their performance in CO₂ reverse water gas shift (RWGS) reaction was investigated. The data analysis demonstrated that the highest catalytic performance was occurred at 550 °C pre-activation. The catalysts obtained from LDHs with tetraborate and hypophosphite interlayer anions clearly exhibits the highest CO selectivity among the studied catalysts in the range of 350–600 °C and the lowest CH₄ formation. Meanwhile, those generated from nitrate and carbonate counters comprising LDHs facilitated mostly and vigorously the methane formation and the intercalation of phosphate ions resulted in balanced production for both CO and CH₄. Catalysts from B₄O₇ counter containing they possessed significantly high (>70%) CO selectivity slightly dependent on the reaction temperatures, it is promising to exploit efficient RWGS reaction catalytic system.

Keywords: Nickel-poor layered double hydroxides, mechanochemistry, intercalation, CO₂ hydrogenation, reverse water gas shift (RWGS)