**Área: CAT**

# Na-Promoted CoCu/$MgAl_2O_4$ Catalyst for Superior $CO_2$ Hydrogenation and Ethanol Steam Reforming Performance

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## Highlights

Na promotion significantly enhanced $CO_2$ hydrogenation, boosting higher alcohol formation up to $C_4$. In parallel with ethanol steam reforming, the Na-promoted catalyst also exhibited higher selectivity toward $CO_2$ and $H_2$.

## Abstract

Exploring alternatives to reduce the $CO_2$ concentration in the atmosphere, the $CO_2$ hydrogenation forming ethanol has emerged as a promising strategy for mitigating this critical greenhouse gas. From the chemistry perspective, the inherent stability of $CO_2$ combined with the challenges of C-C bond formation and selectivity control required to produce high alcohols remains challenging. However, insights gained at ambient pressure in the reverse reaction, i.e., the steam reforming of ethanol-producing $CO_2$ and $H_2$, represent a valuable opportunity to deepen our understanding of the requirements to produce high alcohols from $CO_2$. A crucial step is identifying distinct catalytic sites capable of adsorbing $CO_2$ with different strengths, directly influencing the selectivity. Co and Cu-based catalyst systems show considerable promise, mainly when promoted with Na. These materials allow for the fine-tuning of the metallic phase's electronic structure and the optimization of interfacial sites through interactions between the metallic species and the catalyst support, for this reason, catalysts based on $Cu_xCo_{x-1}/MgAl_2O_4$ (x = 1, 5, and 9) and promoted with Na were explored here. **Figures 1 a** and **b** show the catalytic result in terms of $CO_2$ conversion and selectivity toward $CH_4$, CO, methanol, ethanol, and hydrocarbons (HCs) as a function of CuCo atomic ratio. Higher Cu loadings favor the CO and MeOH formation, hindering the formation of C-C coupling, but with low activity. On the other hand, higher loadings of Co favor the $CH_4$ and the C-C coupling and formation of HCs, with higher $CO_2$ conversion. Among the different compositions, the 5Co5Cu catalyst showed the best performance in the hydrogenation of $CO_2$, with the formation of 27 $mg_{MeOH}.g_{CoCu}^{-1}.h^{-1}$ and 1 $mg_{EtOH}.g_{CoCu}^{-1}.h^{-1}$. The impact of Na as a promoter was evaluated in this catalyst. **Figure 1c** shows that the presence of Na favored chain growth, expanding the products' distribution to high alcohols up to $C_4$ (7 $mg_{MeOH}.g_{CoCu}^{-1}.h^{-1}$, 2 $mg_{EtOH}.g_{CoCu}^{-1}.h^{-1}$, 0,2 $mg_{PrOH}.g_{CoCu}^{-1}.h^{-1}$and 0.2 $mg_{BuOH}.g_{CoCu}^{-1}.h^{-1}$). Complementary data was obtained by the steam reforming of ethanol, **Figure 1d**. While Co directs the selectivity toward $CO_2$, favoring C-C bond cleavage, Cu directs the desorption of acetaldehyde. When the catalyst was promoted with Na, it increased the production of $CO_2$, while acetaldehyde production decreased.

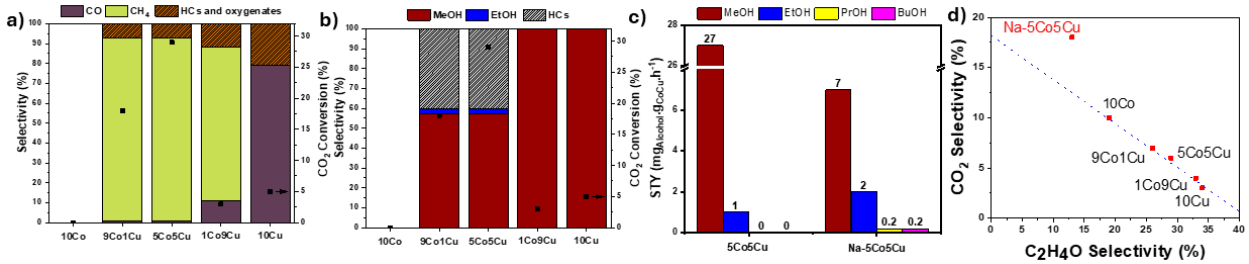


**Figure 1: a)** Selectivity of CO, $CH_4$, HCs and oxygenates during $CO_2$ hydrogenation on $Cu_xCo_{x-1}$ catalysts (x = 1, 5, and 9) under $H_2/CO_2$ = 4, 200°C, and 100 bar. **b)** Zoom of HCs and oxygenate selectivity, highlighting methanol, ethanol, and HCs. **c)** Space-time yield (STY, $mg_{Alcohol}\cdot g_{CoCu}^{-1}\cdot h^{-1}$) of alcohols for the 5Co5Cu catalyst compared to Na-doped 5Co5Cu. **d)** $CO_2$ and $C_2H_4O$ selectivity during ethanol steam reforming after pre-reduction at 500°C, with reaction conditions of 400°C, atmospheric pressure, and $H_2O$:EtOH = 3.

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