COBALT-MODIFIED IRON NANOPOLYHEDRA FOR TUNING CO_2 HYDROGENATION TO LIGHT OLEFINS

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Abstract:

The catalytic hydrogenation of CO_2 to light olefins has attracted increasing attention as a route for converting captured CO_2 emissions into value-added chemical intermediates [1]. In this context, Fe-based catalysts are among the most investigated systems, owing to their ability to combine CO_2 activation through the reverse water-gas shift reaction with subsequent C-C coupling through Fischer-Tropsch-type pathways. Nevertheless, the performance of monometallic Fe catalysts is often limited by the difficulty of controlling the relative distribution of oxidic and carbidic phases, as well as by the competing formation of CO, methane, paraffins, and heavier hydrocarbons [2]. The incorporation of a second transition metal represents a promising strategy to tune the electronic, redox, and carburization properties of Fe-based catalysts. Among the possible dopants, cobalt is particularly interesting because of its well-known hydrogenation ability, its potential interaction with iron phases, and its capacity to modify the balance between CO_2 activation, CO conversion, and hydrocarbon chain growth [3-4].

In this work, the most promising unsupported Fe-based catalyst from a previous study, namely Fe-NP (NP: Nano-Polyhedra), was selected as the parent material for the development of Co-modified Fe catalysts. A series of Co-Fe-NP catalysts with different Fe/Co ratios (Fe/Co=0, 2, 3, 5, 7, 9) was synthesized in order to investigate how cobalt incorporation affects the structural evolution, redox behavior, surface composition, and catalytic performance of the system. The materials were characterized by XRD, TEM, BET, H_2-TPR, CO-TPR, CO_2-TPD, and XPS, while their catalytic behavior was evaluated for CO_2 hydrogenation to light olefins under fixed reaction conditions. The results showed that cobalt addition significantly modified the physicochemical properties of the parent Fe-NP catalyst. Depending on the Co loading, changes were observed in reducibility and carburization behavior, which directly influenced the balance between RWGS and Fischer-Tropsch-type pathways, leading to variations in CO_2 conversion and product distribution. In particular, moderate Co incorporation appeared to promote a more favorable catalytic environment by improving the interaction between Fe- and Co-containing phases, reaching a CO_2 conversion of 62.8%, a C_2-$C_4^=$ selectivity of 23.7%, and the highest olefin yield of 14.8% under the examined reaction conditions (340 ^oC, H_2/CO_2 = 3/1, WHSV = 6 L $gcat^{-1}h^{-1}$, 20 bar, TOS = 6 h).

Keywords: CO_2 hydrogenation, light olefins, Co-Fe catalysts, cobalt modification, iron carbides, modified Fischer-Tropsch synthesis

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