STRUCTURE-PROPERTY RELATIONSHIPS IN IRON OXIDE CATALYSTS FOR CO_2 HYDROGENATION TO LIGHT OLEFINS

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Abstract:

The need to reduce greenhouse gas emissions has accelerated research into catalytic pathways that can transform CO_2 from a waste stream into value-added chemicals and fuels [1]. Among these routes, CO_2 hydrogenation to light olefins through modified Fischer-Tropsch synthesis represents a promising strategy, since C_2-C_4 olefins are essential building blocks for the chemical and polymer industries [2]. To this end, iron-based catalysts are particularly attractive for this process due to their abundance, cost-effectiveness, and ability to form multiple active phases, including iron oxides and iron carbides [3]. However, the catalytic state of Fe-based systems is highly dynamic, while the relationship between initial structure, phase evolution, surface chemistry, and catalytic performance remains difficult to isolate, especially in supported or promoted catalysts [4-5]. The primary objective of this study is to elucidate the intrinsic structure-property-performance relationships governing CO_2 hydrogenation over unsupported Fe-based systems. For this purpose, a series of unsupported iron oxide catalysts were synthesized through different preparation routes, leading to materials with different morphological, structural, redox, and surface properties. The catalysts were comprehensively characterized by XRD, TEM, BET, H_2-TPR, CO-TPR, CO_2-TPD, and XPS, while their catalytic performance was evaluated at 340 ^oC, H_2/CO_2 = 3/1, WHSV = 6 L $gcat^{-1}.h^{-1}$, 20 bar, TOS = 6 h.

The results showed that, despite pronounced differences in crystallite size, morphology, and reducibility, CO pretreatment resulted in a homogenization of the bulk phase composition toward iron carbides, mainly Fe_5C_2 and Fe_3C, for all samples. Notably, however, significant differences in catalytic behavior were still observed, indicating that bulk phase similarity does not necessarily translate into identical catalytic performance. Among the investigated systems, the Fe-NP nano-polyhedra catalyst exhibited the highest selectivity toward light olefins, reaching a CO_2 conversion of 41.6%, a C_2-$C_4^=$ selectivity of 27.7%, and the highest olefin yield of 11.5% under the examined reaction conditions. This superior behavior was mainly attributed to a more favorable balance between surface iron carbidic and oxidic species. In this respect, the coexistence of Fe_3O_4 and Fe_xC_y species appears to facilitate the coupling between CO_2 activation via RWGS and subsequent C-C coupling through Fischer-Tropsch-type pathways.

Keywords: CO_2 hydrogenation, light olefins, unsupported iron catalysts, iron carbides, modified Fischer-Tropsch synthesis

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