

Synthesis and In-Depth Characterization of Fe-Based Catalysts and Zeolites for Efficient CO₂ Hydrogenation to Hydrocarbons

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Summary

Nowadays, global warming caused by CO₂ emissions has a wide range of negative impacts, both environmentally and socially. To address this issue, this doctoral work focuses on the conversion of CO₂ into liquid hydrocarbons through the hydrogenation process.

The main investigation took place at the Polytechnic University of Turin. In this initial stage, the NaFe₃O₄_CP catalyst was tested in physical mixture with both a commercial MFI zeolite (labelled HZSM5) and a homemade hierarchical MFI zeolite (labelled HZ). These configurations showed higher catalytic activity than the corresponding core-shell samples having the same active phase and zeolite. In particular, the catalyst labeled NaFe₃O₄_CP+HZ (physical mixture) demonstrated the best catalytic performance. The superior catalytic performance of the hierarchical zeolite can be attributed to the presence of mesopores, which facilitate the desorption of aromatic and/or long-chain products due to the larger pore size of the zeolite. In an attempt to introduce innovation, the exploration continued with the creation of core-shell structures. However, from this inaugural study emerged the central role of sodium as a promoter and, in particular, the effects of its migration. In fact, it was significant to confirm that sodium migration from bulk iron to the acidic sites of the zeolite compromises the selectivity for desired hydrocarbon products, especially gasoline [1].

These preliminary conclusions prompted an extension of the research at the Instituto de Tecnología Química (ITQ) in Valencia, , where the focus remained on sodium-promoted iron catalysts but was supported by a hydrophobic material to limit the migration of the alkaline metal. Specifically, the decision was made to support sodium-promoted iron catalysts externally and internally on carbon nanotubes (CNTs) with various external diameters in order to evaluate if the confinement of sodium and iron inside materials with an inherently hydrophobic nature could effectively achieve the goal. In addition to diameter variations, impregnated CNTs were synthesized with different percentages of iron while keeping the iron-sodium ratio constant. These CNTs underwent individual tests and were also examined together with an MFI-type zeolite in two different contact modes: a granular mixture and a powder mixture, specifically using a commercial HZSM-5 zeolite. In particular, for the CNT-S-O10FeNa catalyst, it was found that confining iron inside the nanotube greatly limits sodium migration. Consequently, no substantial difference in terms of CO₂ conversion and selectivity to CO and CH₄ was noted when testing this catalyst in the two above-mentioned contacts with acid sites of the zeolite. All fresh, used, and reduced catalysts were extensively characterized to ascertain the position of iron rather than the CNT, especially through

TEM analysis, examining the nanoparticles of iron in each sample in different grid regions in order to establish their position (in or out of the CNT) and to calculate the particle diameter distribution as accurately as possible. To support the catalytic results obtained, other advanced characterizations like Raman investigation and XPS analysis were carried out.

Based on the results of this comprehensive experimental campaign, attention shifted to a particular iron- and sodium-impregnated CNT named CNT-M-O15FeNa, which showed sodium migration from iron sites to the acidic sites of the zeolite. This subsequent experimental phase explored the surface properties, Si/Al ratio, grain sizes, and pore sizes of MFI-type structure zeolites. Most of these zeolites were synthesized and/or modified at the ITQ laboratories, which highlighted how reducing the number of surface acid sites can be a valid alternative to counteract sodium migration. In particular, among all tested zeolites, μ MFI35, characterized by a very low external surface area, proved to be the best zeolite at achieving this goal.

Finally, the last work carried out had a slightly diversified goal. Recognizing the migratory capacity of sodium and identifying alternatives, the choice was made to focus on examining zeolites with different frameworks (FAU, MFI, BEA, MWW, TON and ITQ-2), Si/Al ratios, and the impact of mesoporosity on their ability to modulate selectivity across different ranges of liquid hydrocarbon products. To eliminate potential distortions of selectivity results due to sodium migration, this study was conducted in a double-bed mode. However, despite the intention to use different zeolite structures to modulate hydrocarbon selectivity, the obtained cutting was predominantly gasoline-like, and the MFI zeolite was reaffirmed as the most effective material for this purpose.

However, it is important to emphasize that numerous challenges have been faced, and much effort is still needed to address issues related to energy input, catalytic challenges, raw material availability, operating costs, and environmental impact to maximize their potential and effectiveness.