Fe-Co bimetallic catalysts with tailored nano-morphology for CO_2 hydrogenation to light olefins

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Scope & Objectives

- The direct production of light olefins (C_2-$C_4^=$), such as ethylene, propylene and butenes, is of significant interest, since such products are widely used as basic building blocks in the chemical industry [1].
- Modified Fischer-Tropsch synthesis (mFTS) over Fe-based catalysts represents one of the most promising pathways for direct CO_2 conversion to short-chain olefins. Iron catalysts are particularly attractive due to their abundance, cost-effectiveness, and ability to form multiple active phases such as Fe_2O_3, Fe_3O_4 and iron carbides [2].
- Among the transition metals, cobalt has received particular attention due to its established activity in FTS and its ability to affect the reduction and carburization behaviour of Fe species.

In the present study, Fe-Co bimetallic catalysts of nanopolyhedral morphology (NP) with different Fe/Co ratios, namely 3, 5, and 7, were synthesized via a one-step hydrothermal method. The effect of Co loading on the physicochemical properties (of fresh, CO activated and aged samples) and the CO_2 hydrogenation performance is thoroughly investigated.

Experimental part

Materials synthesis and characterization

➢Iron oxide (Fe-NP) and iron-cobalt (Co-Fe-X-NP) nanopolyhedra of different Fe/Co ratios equal to 3, 5 and 7, were synthesized through the hydrothermal method at 180 °C for 24 h. The samples are denoted as Co-Fe-X-NP, where X stands for the Fe/Co ratio of 3, 5 and 7.

➢The materials were physicochemically characterized using BET, XRD, TEM/EDS, TPR and CO_2-TPD, and XPS techniques, while their activation was performed under 20% CO/He flow in order to induce the formation of iron carbide phases.

Catalytic evaluation

➢The catalytic tests were carried out at H_2:CO_2 = 3:1, WHSV =6 $L \cdot g_{cat}^{-1} \cdot h^{-1}$, P = 20 bar, and TOS = 6 h. Furthermore, the samples were characterized in their fresh, CO-pretreated, and spent states to further elucidate the relationships between Co addition, phase evolution, surface basicity, and catalytic activity.

Physicochemical characterization

Table 1. Crystalline phases and average crystallite sizes of the Fe-NP and Co-Fe-X-NP catalysts in the as-prepared, CO-activated and spent states.

Sample	XRD patterns			Average crystallite size (nm)		
	Fresh	Activated	Spent	Fresh	Activated	Spent
Co-Fe-3-NP	α-Fe_2O_3, Fe_3O_4, Co_3O_4	Fe_3C, Fe_5C_2, FeCo	Fe_3O_4, CoO, Fe_3C, Fe_5C_2	67	12	36
Co-Fe-5-NP	α-Fe_2O_3, Fe_3O_4, Co_3O_4, $CoFe_2O_4$			58	11	32
Co-Fe-7-NP				61	21	22
Fe-NP	α-Fe_2O_3, Fe_3O_4	Fe_3C, Fe_5C_2	Fe_3O_4, Fe_3C, Fe_5C_2	47	24	32

- The Fe-NP sample is composed of highly crystalline, well-ordered hematite (α-Fe_2O_3), as well as magnetite (Fe_3O_4).
- The coexistence of α-Fe_2O_3, Fe_3O_4, $CoFe_2O_4$ and Co_3O_4 phases in Co-Fe-5-NP and Co-Fe-7-NP suggests that part of the cobalt is incorporated into the Fe-Co spinel structure, while an additional fraction remains in the form of a separate cobalt oxide phase.
- The Co-Fe-3-NP sample, which contains the highest amount of cobalt, shows that increasing the Co content favours the formation of highly disordered spinel-type oxide phases over the well-defined hematite structure.

Physicochemical characterization

As shown in **Figure 1**, the samples are composed of aggregated nanoparticles with predominantly irregular morphologies. The catalysts exhibit a Gaussian distribution of particle size, calculated by using the ImageJ software, with an average particle size following the order: Co-Fe-5-NP (23.6 ± 5.7 nm) > Co-Fe-3-NP (21.7 ± 6.7 nm) > Co-Fe-7-NP (13.5 ± 4.8 nm).

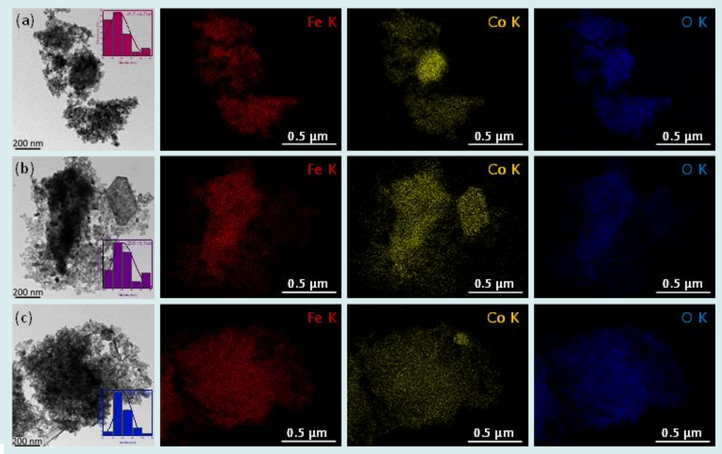


Figure 1. TEM images, particle-size distributions and EDS elemental maps of the as-prepared (a) Co-Fe-3-NP, (b) Co-Fe-5-NP and (c) Co-Fe-7-NP catalysts.

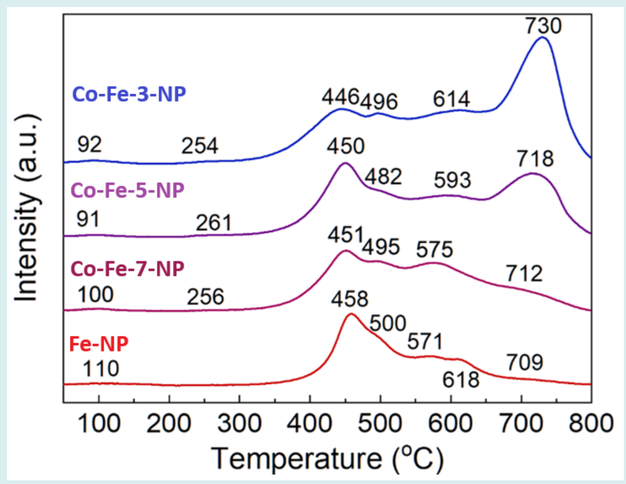


Figure 2. CO_2-TPD profiles of the pretreated with 20% CO/He mono- and bimetallic oxide nanopolyhedra.

Figure 2 demonstrates the CO_2-TPD profiles of the CO-pretreated mono- and bimetallic oxide nanopolyhedra. The addition of cobalt modifies the CO_2 adsorption behaviour of the activated catalysts. In particular, the total CO_2 desorption amounts follow this order: Co-Fe-3-NP (1484 µmol/g) > Co-Fe-5-NP (1436 µmol/g) > Co-Fe-7-NP (924 µmol/g) > Fe-NP (721 µmol/g).

Catalytic evaluation studies

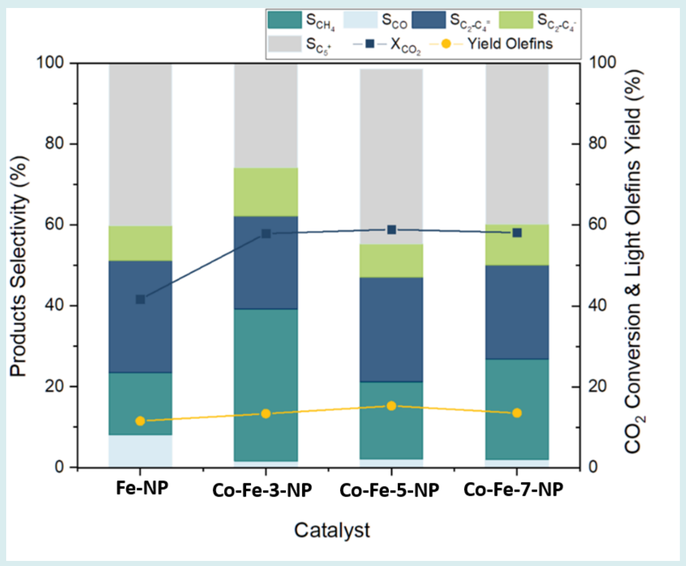


Figure 3. Catalytic performance of Fe-NP and Co-Fe-X-NP catalysts under standard reaction conditions: 340 °C, 20 bar, H_2/CO_2 = 3/1 and WHSV = 6 $L \cdot g_{cat}^{-1} \cdot h^{-1}$.

The highest olefin yield was obtained over Co-Fe-5-NP, reaching 15.2%, compared with 11.5% for Fe-NP, 13.3% for Co-Fe-3-NP and 13.5% for Co-Fe-7-NP, indicating that Co-Fe-5-NP provides the most favourable balance between CO_2 conversion and olefin formation under the standard reaction conditions.

Co addition enhanced CO_2 conversion from 41.6% for Fe-NP to 57.8% for Co-Fe-3-NP and up to 62.4% for Co-Fe-5-NP, confirming the promotional role of Co.

Fe-NP exhibited a olefin-to-paraffin (O/P) ratio of 3.2, while the corresponding values for Co-Fe-3-NP, Co-Fe-5-NP and Co-Fe-7-NP were 1.9, 2.6 and 2.3, respectively, indicating that Co promotes secondary hydrogenation.

Conclusions

- **Fe-Co nanopolyhedral catalysts were successfully synthesized and evaluated for CO_2 hydrogenation. Co addition enhanced CO_2 conversion through Fe-Co synergy, but excessive Co loading promoted methane formation due to over-hydrogenation.**
- **The Co-Fe-5-NP catalyst exhibited the best balance between activity and selectivity, combining high CO_2 conversion (62.4%) with the highest olefin yield (15.2%).**
- **Controlled Co incorporation optimizes CO_2 activation while preserving sufficient Fe carbide-related sites associated with C-C coupling, highlighting the importance of precise Fe/Co ratio tuning.**

References

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