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Tuning e-fuel product distribution by combining a Na-promoted Fe-based catalyst with BETA zeolites in CO₂-modified Fischer-Tropsch synthesis

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ABSTRACT

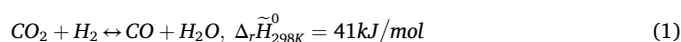
The integration of acidic zeolites with Fe-based catalysts provides a promising strategy to overcome the broad hydrocarbon distribution of CO₂-modified Fischer-Tropsch synthesis (FTS) through in situ product upgrading. In this work, a 5 wt% Na-Fe₃O₄ catalyst is combined with commercial BETA zeolites having nominal SiO₂/Al₂O₃ ratios of 25, 38, and 360 to investigate the effects of zeolite acidity and catalyst configuration at 360 °C and 2.3 MPa. CO₂ conversion remains within 37–44%, whereas BETA markedly alters hydrocarbon selectivity by promoting cracking, isomerization, and H-transfer reactions. Mössbauer spectroscopy and STEM-EDS show that close contact between the catalytic functions modifies the iron-phase distribution and promotes Na migration toward the zeolite. Physical separation in the dual-bed configuration reduces the Na content detected on BETA-38 from 1.02 to 0.20 mmol_{Na} g_{zeolite}⁻¹. NH₃-TPD reveals a substantial loss of acidity after reaction, although the residual acid sites remained sufficient to sustain secondary upgrading. Detailed Hydrocarbon Analysis (DHA) and GC-MS show a strong depletion of linear olefins and enrichment in branched and cyclic hydrocarbons. For the layered BETA-38 system, the reconstructed liquid product contains 71.3 vol% naphtha-range and 21.7 vol% kerosene-range hydrocarbons, with only 7.0 vol% gasoil and heavier residue. The dual-bed configuration promotes more extensive cracking and an almost entirely naphtha-range liquid. Despite the wide initial acidity range, product distributions are similar, identifying catalyst architecture as the dominant parameter for tuning CO₂-derived fuel composition.

1. Introduction

Global energy-related CO₂ emissions increased by 0.4% in 2025, reaching a record high of 38.4 Gt, while the global mean atmospheric CO₂ concentration reached 427 ppm, around 2.4 ppm above the 2024 value and 50% higher than pre-industrial levels [1]. CO₂ is the main anthropogenic driver of climate change and a key cause of ocean acidification [2,3]. In response, international and European policy frameworks have been introduced to accelerate decarbonization, including the Paris Agreement, the revised Renewable Energy Directive (RED III), and the ReFuelEU Aviation Regulation [4–7]. Within this framework, RFNBOs offer a viable alternative to fossil-derived liquid and gaseous

fuels in hard-to-abate sectors that are expected to rely on high-energy-density fuels, particularly aviation and maritime transport. RFNBOs can be synthesized from renewable H₂ produced via water electrolysis and captured CO₂, thereby enabling renewable energy to be stored in transportable liquid fuels [6,8,9].

In this context, Fischer-Tropsch Synthesis (FTS) is a well-established catalytic process for converting syngas into liquid hydrocarbons (HCs) [3,10]. When applied to CO₂ hydrogenation, the process involves a coupled reaction sequence in which CO₂ is first reduced to CO via RWGS reaction (equation (1)), followed by CO hydrogenation to HCs (equation (2) and (3)) [10–13].



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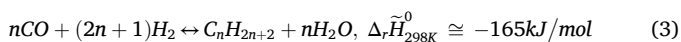
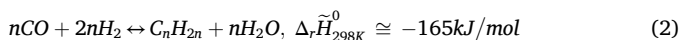
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Nomenclature

ASF	Anderson-Schulz-Flory
ASTM	American Society for Standards and Materials
BAS	Brønsted acid sites
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
DFT	Density Functional Theory
DHA	Detailed hydrocarbon analysis
EDS	Energy-dispersive X-ray spectroscopy
FE-SEM	Field-emission scanning electron microscopy
FID	Flame ionization detector
FT-IR	Fourier-transform infrared
FTS	Fischer-Tropsch synthesis
GC	Gas-chromatograph
GHG	Greenhouse Gases
HAADF	High-angle annular dark-field
HC	Hydrocarbons
HPLC	High-performance liquid chromatography
LAS	Lewis acid sites
MS	Mass spectrometer
NDIR	Non-dispersive infrared detector
PDA	Photodiode array
RFNBO	Renewable fuel from non-biological origin
RID	Refractive index detector
RWGS	Reverse water gas shift
SSA	Specific surface area (m ² /g)
STEM	Scanning transmission electron microscopy
TCD	Thermal conductivity detector
TOS	Time-on-stream
TPD	Temperature-programmed desorption
XRD	X-Ray Diffraction
A	Relative area, hyperfine parameter for Mössbauer

	spectroscopy, (%)
B	Internal magnetic field, hyperfine parameter for Mössbauer spectroscopy, (T)
C _x	The average carbon number for the liquid product (-)
$\dot{n}_{in}$	Total inlet molar flow rate (mol/s)
$\dot{n}_{out}$	Total outlet molar flow rate (mol/s)
$N_{c,i}$	Number of carbon atoms in the i-th hydrocarbon (-)
$\dot{n}_{i,in}$	Inlet molar flow rate of i-th species (mol/s)
$\dot{n}_{i,out}$	Outlet molar flow rate of i-th species (mol/s)
$W_a(N_{c,i})$	Mass fraction of HC with “i” carbon atoms evaluated with the ASF distribution (%)
X_i	Volume concentration of each carbon number in the light liquid phase (-)
$y_{N_2,in}$	Inlet gas phase concentration of N ₂ (-)
$y_{N_2,out}$	Outlet gas phase concentration of N ₂ (-)
α	Chain growth probability factor of the ASF distribution (-)
Γ_+	Half linewidth at half maximum, hyperfine parameter for Mössbauer spectroscopy, (mm/s)
δ	Isomer shift, hyperfine parameter for Mössbauer spectroscopy, (mm/s)
Δ	Quadrupole splitting, hyperfine parameter for Mössbauer spectroscopy, (mm/s)
$\Delta_r \tilde{H}_{298K}^0$	Molar enthalpy of reaction at standard conditions (kJ/mol)
ϵ	Quadrupole shift, hyperfine parameter for Mössbauer spectroscopy, (mm/s)
ζ_{CO_2}	CO ₂ conversion (%)
η_i	Yield of generic i-th hydrocarbon (%)
σ_{CO}	CO selectivity (%)
σ_i	Selectivity of generic hydrocarbon or group of hydrocarbons (CO-free) (%)



The nature of the active metal plays a critical role in determining catalytic performance. Fe-based catalysts are generally preferred for CO₂-modified FTS because they can promote both the RWGS reaction and the subsequent FTS. Conversely, Co-based catalysts, despite their excellent performance in conventional syngas-based FTS, exhibit limited RWGS activity and predominantly favor CH₄ formation under CO₂ hydrogenation conditions [3,14–16]. Magnetite is commonly associated with RWGS reaction, while iron carbides, particularly Hägg carbide (χ -Fe₅C₂), are considered among the principal active phases responsible for CO dissociation, C-C coupling and HC chain growth [15,17]. Since CO₂ hydrogenation generates large amounts of water, the local carbon and oxygen chemical potentials continuously affect the oxidation and carburization balance of the catalyst, making its phase composition highly dynamic under reaction conditions [17].

Although the overall FTS mechanism has been extensively investigated, the nature of the chain-growth intermediates remains under debate. FTS is generally described as a surface-polymerization process involving C₁ intermediates, with chain propagation proceeding through CH_x coupling, according to the carbide mechanism, or through CO insertion into the growing HC chain [15,18,19]. DFT calculations and microkinetic simulations have shown that catalyst surface structure strongly influences the elementary reaction pathways. Pilot et al. [18] showed that stepped Ru surfaces containing low-coordination atoms facilitate CO dissociation and the formation of longer HC through the insertion of CH intermediates, whereas planar Ru surfaces are limited by high energy barrier for CO activation and predominantly form CH₄ via

formyl route [18]. Analogous facet-dependent effects have also been reported for iron carbides. Pham et al. [20] showed that the χ -Fe₅C₂ (510) surface suppresses CH₄ formation and favors C-C coupling, while Wu et al. [21] experimentally demonstrated that the activity and stability of χ -Fe₅C₂ depend strongly on the exposed crystal facet. Therefore, the competition among CO activation, C-C coupling, chain propagation, and chain termination controls the selectivity toward long-chain HCs relative to CH₄. Nevertheless, the carbon-number distribution generally follows the ASF model, making it difficult to selectively produce HCs within a narrow carbon-number range [15,18,19].

To overcome this limitation, bifunctional catalytic systems combining FTS catalysts with acidic zeolites have been extensively investigated. Primary FT products, mainly olefins and longer-chain linear HCs, can undergo secondary reactions such as cracking, isomerization, oligomerization, and aromatization over the acid sites of zeolites, thereby reshaping the primary ASF-derived product distribution [3]. Among the available zeolite structures, BETA zeolite (BEA-type structure) is a promising candidate for FT product upgrading because its three-dimensional large-pore system provides access to long-chain HCs, while its acidity promotes secondary cracking and isomerization reactions [22,23]. Different catalyst architectures have therefore been developed to control the proximity between the FTS and acid functions, including: (i) direct deposition of metal on zeolite supports (ii) physical mixtures and encapsulated composite catalysts, and (iii) sequential dual-bed reactor system [8,23–28].

Wei et al. [29] systematically investigated the influence of both zeolite topology and component proximity by combining a Na-Fe₃O₄ catalyst with several zeolites, including HBEA and HZSM-5 (MFI-type structure). For the Na-Fe₃O₄/HZSM-5 system, granule mixing provided the most favorable balance between the two catalytic functions, whereas

powder mixing was detrimental and the dual-bed configuration gave a slightly lower C₅–C₁₁ selectivity [29]. In the topology comparison, the granule-mixed catalyst containing HBEA with SiO₂/Al₂O₃ = 25 achieved a CO₂ conversion of ~35%, with selectivity values of 13% to CO, 11% to CH₄, 45% to C₅–C₁₁ hydrocarbons and only 2% to C₁₂+ HCs [29].

Dual-bed reactor system has been widely investigated on K-promoted Fe-based catalyst. Dokania et al. [30] found that the addition of Pt-BETA shifted the product distribution toward an almost entirely paraffinic and isoparaffinic mixture up to C₁₀, presumably through a combination of cracking and hydrogenation. Under optimal conditions, the CO₂ conversion was ~31% and C₅–C₁₀ paraffins selectivity was ~28%. Garcia-Hurtado et al. [31] observed that the addition of ZSM-5 zeolite maximized the formation of aromatics, while BETA zeolite increased the C₁–C₄ gas fraction, with a high olefin selectivity, while both aromatic and aliphatic HCs were detected in the condensed liquid fraction [31]. These differences were attributed to shape-selective secondary reactions: ZSM-5 predominantly favored aromatization of alkenes, whereas BETA promoted a combination of oligomerization and cracking, whose net effect was a decrease of the C₅+ fraction and an increase of the light olefin yield [31].

Consistent shape-selective trends were subsequently observed by Ramirez et al. [32]. Their spectroscopic and computational analyses showed that product selectivity cannot be explained by pore size alone but depends on the combined effects of framework confinement and HCs intermediates trapped in the zeolite [32]. In particular, 10-membered-ring frameworks, such as MFI-type zeolites, produced the strongest shape selectivity toward gasoline-range HCs, whereas 12-membered-ring frameworks, such as BEA-type zeolites, allow the formation and diffusion of heavier HCs, including kerosene-range products [32,33].

Accordingly, the three-dimensional 12-membered-ring channel system of zeolite BETA provides less sterically restricted access for relatively longer-chain HCs than medium-pore MFI framework. However, the large pores of BETA do not inherently guarantee the formation of heavier or kerosene-range HCs, since framework confinement, acid-site properties, and crystalline properties that act jointly in determining the extent of secondary reactions.

Previous studies have primarily compared different zeolite structures, while the specific influence of acid-site density and nature within BEA framework under CO₂-modified FTS conditions remains insufficiently studied [31–35]. Moreover, the interaction between Na-Fe₃O₄ catalysts and BETA zeolites under different reactor configurations, as well as its effect on iron-phase evolution and HC selectivity have not been yet comprehensively elucidated, limiting the design of bifunctional systems for specific HC range.

In this context, the present study aims to investigate the effect of BETA zeolite acidity and catalyst configuration on HCs formation during CO₂-modified FTS, with particular attention to the distribution of gasoline- and kerosene-range products. For this purpose, a 5 wt% Na-Fe₃O₄ catalyst was combined with three commercial BETA zeolites with nominal SiO₂/Al₂O₃ ratios of 25, 38 and 360 in a layered configuration, while BETA-38 was also evaluated in a dual-bed arrangement to assess proximity effects. By correlating iron-phase evolution and sodium migration, investigated by means of Mössbauer spectroscopy and XRD, and STEM-EDS, with changes in zeolite acidity and liquid product composition determined by DHA and GC-MS, this work provides insight into how zeolite acidity and catalyst architecture govern secondary upgrading reactions and fuel composition. These findings contribute to the design of more effective bifunctional catalytic systems for the production of synthetic liquid fuels from CO₂.

2. Methodology

2.1. Synthesis of the catalyst

The Fe₃O₄ catalyst was synthesized via co-precipitation method [2, 8]. FeCl₂ and FeCl₃ precursors were dissolved in a mixture containing

150 mL of Milli-Q water and 20 mL of 12.1 M of HCl and the resulting solution was heated at 90 °C and continuously stirred for 10 min. Subsequently, aqueous ammonia (28 wt% NH₃·H₂O) was added dropwise until a pH value of 10 was reached. The suspension was then aged at 90 °C for 3 h under constant stirring to complete the precipitation process. The solid product was then recovered, centrifugated and washed with Milli-Q water repeatedly, until neutral pH was achieved, and dried overnight at 60 °C. The dried Fe₃O₄ was impregnated using a 0.3 M NaNO₃ aqueous solution to obtain 5 wt% Na-Fe₃O₄. Commercial ammonium-form BETA zeolites with nominal SiO₂/Al₂O₃ molar ratios of 25, 38 and 360 were converted into the protonic form by calcination at 500 °C for 5 h using a heating rate of 2 °C·min⁻¹. Lastly, prior to the testing, all powders were pelletized and sieved in the range 250–500 µm [2,8].

2.2. Characterizations

2.2.1. Catalyst characterization

The textural properties of the catalysts were determined by N₂ adsorption–desorption measurements at 77 K using a Micromeritics TriStar II 3020 analyzer. Prior to analysis, the samples were degassed at 200 °C for 2 h under a nitrogen flow in a Micromeritics FlowPrep 060 system to remove adsorbed species from the surface. The SSA was calculated according to the BET method, whereas pore size distribution and pore volume were derived from the desorption branch of the isotherm using the BJH model [36–38].

The morphology of the catalysts was investigated by FE-SEM using a Zeiss Merlin microscope equipped with a Gemini-II column. The elemental composition and spatial distribution of the elements were evaluated by EDS coupled to the same instrument. Additional structural and local compositional information at the nanoscale was obtained by TEM and STEM-EDS, employing a FEI Tecnai F20ST microscope operated at an accelerating voltage of 200 kV.

Powder XRD patterns were recorded at room temperature using a Malvern Panalytical Empyrean diffractometer equipped with a high-resolution Bragg–Brentano HD optical system. Measurements were performed by employing Ni β-filtered Cu-Kα radiation with a wavelength (λ) of 1.5406 · 10⁻¹⁰ m, with the X-ray source operated at 40 kV and 40 mA. Diffraction data were collected by scanning over the 2θ angle range of 5°–80° with a step size of 0.026 ° 2θ and a dwell time of 0.3 s per step.

Room-temperature Mössbauer spectroscopy measurements were performed in transmission geometry using a constant acceleration spectrometer equipped with a ⁵⁷Co source in a Rh matrix (nominal activity: 1850 MBq). For each analysis, approximately 80 mg of sample were dispersed in petroleum jelly and spread over an area of 1.13 cm². The spectra were fitted assuming Lorentzian line profiles using Recoil software, with the quality of the fit assessed through the reduced χ² parameter. The estimated hyperfine parameters are the isomer shift (δ, mm·s⁻¹), the quadrupole splitting (Δ, mm·s⁻¹) or quadrupole shift (ε, mm·s⁻¹), when magnetic coupling is present, the half linewidth at half maximum (Γ₊, mm·s⁻¹), the internal magnetic field (B, T), and the relative area (A, %). The velocity was calibrated against a α-Fe foil and δ is quoted relative to metallic iron at room temperature.

The acidic properties of the zeolites were investigated by NH₃-TPD using an AMI-300Lite system equipped with a TCD. Approximately 100 mg of sample was loaded in a 4 mm I.D. quartz tube reactor between two quartz wool layers. Samples were first pretreated under He flow (25 mL·min⁻¹) by heating to 350 °C at a rate of 5 °C·min⁻¹ and holding for 60 min, then cooled to 100 °C at a rate of 10 °C·min⁻¹. Under these conditions, NH₃ adsorption was performed at 100 °C using 10 vol% NH₃/He (40 mL·min⁻¹) for 30 min. Excess ammonia was subsequently removed by helium purging (40 mL·min⁻¹) for an additional 30 min. Desorption profiles were then collected between 100 and 600 °C at a heating rate of 10 °C·min⁻¹ under He flow, maintaining the final temperature for 30 min. Lastly, TCD calibration was performed by injecting

10 gas pulses (0.524 mL·pulse⁻¹) of 10 vol% NH₃/He into a He flow (25 mL·min⁻¹). NH₃-TPD was applied to the as-calcined zeolite and the spent sample after regeneration. Regeneration of spent samples was performed in the same equipment prior to the NH₃ saturation by flowing pure O₂ (20 mL·min⁻¹) while heating from 350 °C to 650 °C at 5 °C·min⁻¹, holding at 650 °C for 1 h, and cooling to 100 °C under He (25 mL·min⁻¹) [39].

The quantification of zeolite acidity and the distinction between BAS and LAS were further examined by in situ FT-IR spectroscopy using deuterated acetonitrile (CD₃CN) as a probe molecule [40–42]. Spectra were recorded on a Bruker Invenio S spectrometer equipped with a liquid-N₂ cooled mercury-cadmium-telluride detector, in transmittance mode over 400–4000 cm⁻¹ (2 cm⁻¹ resolution, 64 scans). The catalyst powder was pressed into a self-supported disk (2 t load, 10–40 mg·cm⁻²) and mounted in a custom-designed quartz cell with KBr windows. After collecting a reference spectrum under ambient conditions, the sample was pretreated at 300 °C for 2 h under vacuum (5 °C·min⁻¹), cooled to room temperature, and then CD₃CN was dosed stepwise at room temperature up to spectral stabilization (1.3 kPa, 30 min). Desorption was monitored by progressively decreasing CD₃CN pressure, followed by evacuation under vacuum for 50 min to remove physisorbed species. Band assignments were taken from Miletto et al. [43] and Giglio et al. [44,45]: 2275 cm⁻¹ (CD₃CN on isolated silanols, molar extinction coefficient (ϵ) of 0.74 cm²·μmol⁻¹), 2285–2300 cm⁻¹ (H-bonded CD₃CN on BAS, ϵ = 2.05 cm²·μmol⁻¹), and 2310–2325 cm⁻¹ (coordinated CD₃CN on LAS, ϵ = 3.60 cm²·μmol⁻¹). BAS and LAS concentrations were obtained by integrating the corresponding bands and applying the respective molar extinction coefficients.

2.2.2. Characterization of liquid products

With regard to the analysis of liquid products, using two condensation stages at different temperatures, two types of oil with different HCs fractions were collected. The lighter HC fraction (hereafter referred as “light oil”) was thoroughly characterized by means of DHA employing an Agilent GC System 8890 with a standard ASTM D6730 method. A total of 1 μL of oil was injected on a HP-1 column (dimensions 100 m x 0.25 mm x 0.25 μm) composed entirely of dimethylpolysiloxane, a completely non-polar phase, in split mode with a split ratio of 150:1. The composition of the heavy HC fraction (“heavy oil”), on the other hand, was characterized using GC (Agilent 7890 A GC) coupled with a mass spectrometer (MS Agilent 5975 C). Samples were diluted 1:100 vol/vol in dichloromethane and a total of 1 μL of diluted oil was injected on a DB-5 ms column (dimensions 30 m x 0.25 mm x 0.25 μm) in split mode with a split ratio 20:1 [46]. The helium flow was set at 1 mL/min, using the following temperature monitoring protocol: 40 °C (3 min hold), then increase at a rate of 5 °C/min up to 300 °C (30 min hold) to allow the elution of the heavier compounds. Compounds were identified using Agilent MassHunter Unknown Analysis software with the NIST 17 library [47].

The aqueous phase collected during the catalytic tests from both the condensers was characterized by HPLC to derive information on its composition. The analysis was performed using a Rezex ROA-Organic acid H + (8%) column (length: 300 mm, diameter: 7.8 mm) at 50 °C flowing 0.7 mL·min⁻¹ of 5 mM H₂SO₄ aqueous solution [48]. The instrument is equipped with an RID and a PDA detector that were used to quantify the compounds after being properly calibrated with the corresponding standards.

2.3. Catalytic tests

2.3.1. Description of the catalytic bench

Both the pretreatments and the catalytic tests were carried out using a fixed-bed reactor configuration. The reactor is made of stainless steel and has an I.D. of 10 mm and is equipped with an inner thermowell (O. D. 3 mm), into which a thermocouple can be inserted to measure the temperature along the entire length of the catalytic bed in the axial

direction. Gases were supplied from high-purity cylinders (H₂ 4.5, CO₂ 4.0, CO 3.7, N₂ 6.0, He 6.0, and air 5.5) and the flow rates were regulated by mass flow controllers, while the operating pressure was maintained through a back-pressure controller. A schematic representation of the experimental setup is provided in Figure S1.

The products leaving the reactor were directed to a hot trap (140–150 °C), where heavy HCs (C₁₃₊) and most of the water are condensed, then to a cold trap (4–5 °C), where the light HCs and the remaining water are collected. The remaining gas mixture exiting the cold trap is sent to the on-line analytical section and periodically analyzed by a gas chromatographer (7890B GC System, Agilent Technologies) equipped with a heated transfer line (120 °C), a dual-column separation system (HP-5 and HP-PLOT/Q), a TCD and an FID. In parallel, after dehydration on a silica-gel trap, the gas composition was continuously monitored with an in-line Emerson X-STREAM analyzer, equipped with two NDIR sensors and a TCD for measuring CO, CO₂, and H₂ concentrations, respectively. Liquid phases were periodically sampled from the hot and cold condensate traps. Heavy oil was analyzed by simulated GC-MS, whereas light oil was analyzed by DHA (ASTM D6730). The composition of the aqueous phase was determined by HPLC analysis.

2.3.2. Catalytic tests procedure

For the catalytic tests, 2 g of 5% Na-Fe₃O₄ catalyst and 2 g of zeolite (both in the range 250–500 μm) were loaded into the reactor. The catalytic bed consisting of 10 alternating layers of zeolite and iron catalyst was placed between two layers of glass beads. As for the dual-bed (DB) configuration, the two beds were separated by two layers of glass beads (10 mm each) and a layer of quartz wool.

Prior to the tests, samples were first calcinated under pure N₂ (5 NL·gFe₃O₄⁻¹·h⁻¹) at 400 °C (5 °C·min⁻¹) for 3 h, and then cooled to 150 °C. After that, they were activated in 90 vol% H₂/N₂ (6 NL·gFe₃O₄⁻¹·h⁻¹) at 0.2 MPa and 450 °C (1 °C·min⁻¹) for 16 h. Samples were finally carburized at 0.2 MPa and 400 °C for 5 h flowing 6 NL·gFe₃O₄⁻¹·h⁻¹ with H₂/CO/N₂ molar ratios of 1/1/2. Catalytic tests were performed at 2.3 MPa using an inlet H₂/CO₂/N₂ molar ratio equal to 15/5/3 and a specific flow rate of 7 NL·gFe₃O₄⁻¹·h⁻¹. The temperature was maintained at 360 °C, as this was considered the best compromise between catalytic activity and thermal degradation. At the end of the test, each sample was passivated at room temperature for 1 h in 1 vol% O₂/N₂ (12 NL·gFe₃O₄⁻¹·h⁻¹) [49] and stored under inert conditions prior to characterizations. In the result section of the paper, the abbreviation “AC” refers to the test using only the iron-based catalyst following the activation and carburization pre-treatment. Tests involving the addition of BETA zeolite designated as “ACB” and are followed by a number that refers to the nominal SiO₂/Al₂O₃ molar ratio and the abbreviation “DB” refers to the dual bed configuration.

The CO₂ conversion (ζ_{CO_2}) and the selectivity toward the generic *i*-th product (σ_i) were determined according to equations (4) and (5), respectively. Product selectivity is reported on a CO-free basis, considering only hydrocarbon species in the product distribution.

$$\zeta_{\text{CO}_2} = \frac{\dot{n}_{\text{CO}_2, \text{in}} - \dot{n}_{\text{CO}_2, \text{out}}}{\dot{n}_{\text{CO}_2, \text{in}}} \quad (4)$$

$$\sigma_i = \frac{\dot{n}_{\text{C}, i, \text{out}}}{\dot{n}_{\text{CO}_2, \text{in}} - \dot{n}_{\text{CO}_2, \text{out}}} \cdot \frac{1}{(1 - \sigma_{\text{CO}})} = \frac{N_{\text{C}, i} \cdot \dot{n}_{i, \text{out}}}{\dot{n}_{\text{CO}_2, \text{in}} - \dot{n}_{\text{CO}_2, \text{out}}} \cdot \frac{1}{(1 - \sigma_{\text{CO}})} \quad (5)$$

CO selectivity is reported in equation (6), while product yields (η_i) were evaluated according to equation (7).

$$\sigma_{\text{CO}} = \frac{\dot{n}_{\text{CO}, \text{out}}}{\dot{n}_{\text{CO}_2, \text{in}} - \dot{n}_{\text{CO}_2, \text{out}}} \quad (6)$$

$$\eta_i = \frac{N_{\text{C}, i} \cdot \dot{n}_{i, \text{out}}}{\dot{n}_{\text{CO}_2, \text{in}} - \dot{n}_{\text{CO}_2, \text{out}}} \cdot \zeta_{\text{CO}_2} \quad (7)$$

The total molar outlet flow rate ($\dot{n}_{\text{out}}$) is reported in equation (8) and

it was determined accounting for N₂ constant flow rate.

$$\dot{n}_{out} = \dot{n}_{in} \frac{y_{N_2, in}}{y_{N_2, out}} \quad (8)$$

FID response factors for light hydrocarbons, including methane, ethylene, ethane, propylene, propane, 1-butene, n-butane, 1-pentene, and n-pentane, were experimentally determined using certified calibration gas mixtures. For all remaining hydrocarbon species, response factors were estimated according to the procedure reported in the literature [50].

ASF distribution was evaluated by minimizing the sum of squared errors between the experimental and calculated hydrocarbon mass fractions, excluding CH₄ from the analysis [51]. The fitting procedure was carried out using equation (9).

$$W_{\alpha}(N_{C,i}) = N_{C,i} \cdot (1 - \alpha)^2 \cdot \alpha^{N_{C,i}-1} \quad (9)$$

The average carbon number (C_X) for the light oil phase was evaluated as the weighted average volume concentration of each carbon number (X_i) determined by DHA according to equation (10).

$$C_X = \sum_{i=1}^{20} (N_{C,i} \cdot X_i) \quad (10)$$

3. Results and discussion

3.1. Fresh as-prepared catalyst characterization

Before starting with the laboratory tests, the physicochemical properties of fresh Na-Fe₃O₄ catalyst and fresh BETA zeolites were investigated. The properties of the iron-based catalyst were consistent with those reported in our previous works [2,8]; therefore, the following discussion focuses on the zeolite characteristics.

The N₂ adsorption and desorption isotherms, shown in Figure S2, indicate the presence of additional mesoporosity and interparticle voids within the intrinsically microporous BETA framework. BETA-25 zeolite exhibits a relatively narrow hysteresis loop consistent with more uniform, predominantly cylindrical, pores, whilst the hysteresis observed for BETA-38 and BETA-360 are attributable mainly to interparticle porosity between the aggregates of flat particles. The textural properties are summarized in Table S1. Zeolite BETA-38 has the largest BET surface area (624 m²·g⁻¹), while zeolite BETA-25 exhibits the largest pore volume (0.55 cm³·g⁻¹) and average pore size (110 Å). By comparison, BETA-38 and BETA-360 exhibit smaller pore volumes of 0.2 and 0.1 cm³·g⁻¹ and average pore diameters of 49 and 46 Å, respectively.

The FE-SEM images in Figure S3 are consistent with these differences in particle morphology. BETA-25 exhibits a uniform surface morphology, consisting of particles of approximately 250 nm in size, while the other two samples contain aggregates of well-defined crystals ranging from 100 to 500 nm. As shown in Table S2, SEM-EDS measurements gave atomic Si/Al ratios of 12.4, 17.9, and 184.5 for fresh BETA-25, BETA-38, and BETA-360, respectively. These values are in good agreement with the nominal commercial specifications.

The XRD profiles of fresh zeolites are illustrated in Figure S4. All samples display diffraction peaks at the same positions as the dehydrated Al-rich BETA reference zeolite, confirming preservation of the BEA crystalline framework. No additional crystalline phases were detected within the sensitivity of the measurement.

The acidic properties of the H-form BETA zeolites are summarized in Table 1, while the corresponding NH₃-TPD and CD₃CN-FTIR profiles are presented in Figure S5. BETA-38 zeolite exhibits the highest total acidity (0.95 mmol·g⁻¹), exceeding that of BETA-25 (0.71 mmol·g⁻¹). Its NH₃-TPD profile shows larger low- and high-temperature desorption peaks, associated with weak and strong acid sites, indicating a greater overall concentration of accessible acid sites. A higher total acidity may also be due to a larger surface area. However, when the total acidity is

Table 1

Evaluation and classification of acidic sites for the three samples of fresh zeolites.

Parameter	Unit	BETA-25	BETA-38	BETA-360	Peak position
Silanols ^a	mmol·g ⁻¹	0	0	0.09	~2275 cm ⁻¹
Brønsted ^a	mmol·g ⁻¹	0.08	0.44	0.02	~2271 cm ⁻¹
Brønsted ^b	mmol·g ⁻¹	0.09	0.09	0.01	~2288 cm ⁻¹
Lewis ^a	mmol·g ⁻¹	0.13	0.18	0	~2315 cm ⁻¹
BAS/LAS ^a	-	1.31	2.94	-	-
Total acid sites ^b	mmol·g ⁻¹	0.71	0.95	0.13	-
W/S ^b	-	2.01	2.16	2.58	-

^a Values obtained by CD₃CN FT-IR measurements.

^b Total acidity and weak-to-strong (W/S) ratios were obtained by NH₃-TPD

normalized by the BET surface area, BETA-25 and BETA-38 show very similar acid-site densities, approximately 1.48 and 1.37 μmol·m⁻², respectively. As expected from its higher SiO₂/Al₂O₃ ratio, BETA-360 is considerably less acidic, with a total acidity of only 0.13 mmol·g⁻¹.

CD₃CN FT-IR measurements indicate that in all zeolites BAS predominate over LAS in BETA-25 and BETA-38, with BAS/LAS ratios of 1.31 and 2.94, respectively. This result is consistent with a substantial contribution from bridging hydroxyl groups associated with framework Al. BETA-38 contains the highest concentrations of both BAS and LAS, whereas no LAS contribution was detected for BETA-360. In that latter sample, silanol groups represent the predominant surface hydroxyl species, consistently with its low framework-Al content. BAS are able to promote olefin activation and isomerization through carbenium-ion intermediates and can also contribute to cracking, cyclization, and aromatization reactions depending on their density and strength [52–54]. LAS also participate in olefin transformations, although through different intermediates, such as allylic species and alkoxyl groups [53]. Therefore, BAS and LAS should not necessarily be regarded as sites selectively responsible for completely different secondary reactions, but rather as acid functionalities capable of promoting related transformations through different reaction mechanisms. The similar product distributions obtained with BETA-25 and BETA-38 despite their different BAS/LAS ratios indicate that the BAS/LAS ratio alone is not sufficient to describe the secondary upgrading behavior, for which pore topology and acid-site accessibility also play an important role.

3.2. Catalytic tests results

This section presents the results of the catalytic tests, which were conducted at 360 °C and 2.3 MPa using a specific flowrate of 7 NL·gFe₃O₄⁻¹·h⁻¹ and an H₂/CO₂/N₂ molar ratio of 15/5/3. CO₂ conversion, CO selectivity and HC distribution are shown in Fig. 1, whilst the average values calculated over the entire duration of the test are reported in Table S3. During the time-on-stream, the bifunctional system exhibited relatively stable catalytic performance, as shown in Figure S6 for sample ACB-38, with the conversion remaining close to the average value. Compared with AC sample, the ACB samples show only moderate variations in CO₂ conversion and CO selectivity, with values ranging from 37% to 44% and from 9% to 11%, respectively. A similar behavior has also been reported in the literature [31,32]. By contrast, the HC distribution is markedly affected, indicating that the main role of BETA is associated with secondary upgrading of the primary FT products.

The most evident changes concern the C₂-C₅ fraction. Experimental evidence shows that, compared with AC, the layered BETA configurations exhibit a lower light olefin selectivity and a simultaneous increase in the corresponding paraffinic fraction. This behavior is consistent with secondary conversion of olefins over the acid sites the zeolite, involving H-transfer reaction together with cracking and isomerization. The effect is particularly pronounced for ACB-38.DB, which exhibits the highest C₂-C₅ paraffin selectivity, approximately 19%. CH₄ selectivity, on the other hand, depends strongly on catalyst configuration: it increases from

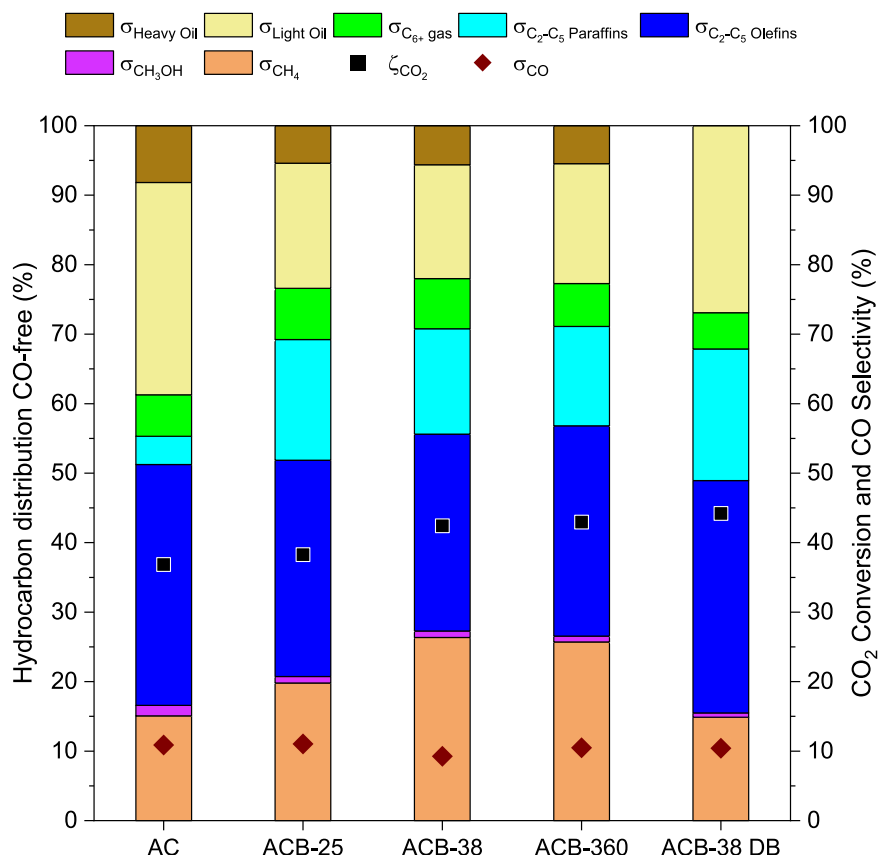


Fig. 1. CO₂ conversion, CO selectivity and HCs selectivity (CO-free) of the tests with the addition of BETA zeolite compared to the test using only iron oxide. Reaction conditions: 7 NL·gFe₃O₄⁻¹·h⁻¹ (H₂/CO₂/N₂ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe₃O₄, 2 g zeolite. For the sake of clarity, the values are reported as an average over the entire duration of the test, taking into account the intermittent oil samples as well.

13.9% for AC to 19.8–26.4% in the layered ACB systems, while ACB-38_DB gives a value of 14.8%, close to that of the reference AC test. This behavior can be rationalized considering the different local environments established in the two configurations. In the layered configuration, the water formed during the reaction and retained by the zeolite can influence the local oxidation-carburization balance of the iron phases and facilitate Na migration from the iron component to the zeolite, as subsequently evidenced by STEM-EDS analysis [8]. This alteration in electronic structure changes the local concentration of CO₂, affects iron carbide phase transitions and can shift the balance between chain propagation and termination reactions [55]. By contrast, the physical separation of the two components in the dual-bed configuration limits both direct contact between water retained by the zeolite and iron carbides and Na migration, likely resulting in a lower surface H₂/CO₂ ratio and thus reducing chain termination reactions and CH₄ production [28]. The interpretation proposed above is further examined in the following section through the characterization of the spent catalysis, which provides experimental evidence for the different extent of Na migration and the evolution of the iron phases in the two reactor configurations.

The addition of BETA zeolite also decreases the selectivity toward liquid HCs, consistent with the occurrence of cracking reactions. Nevertheless, unlike previously investigated MFI-based systems [8], a significant heavy oil fraction, approximately 25% of the total oil volume, was collected from all layered ACB samples. This behavior is consistent with the larger 12-membered-ring pores of BETA zeolite, which provides greater accessibility through the structure. In contrast, no heavy oil was collected from ACB-38_DB. This difference can be rationalized by the spatial arrangement of the two catalytic functions. In the layered configuration, FTS and secondary upgrading occur sequentially at

multiple positions along the reactor, so HCs generated in progressively downstream iron layers experience a shorter contact time with the zeolite. In the dual-bed configuration, instead, the entire FT product stream formed in the upstream Fe-based catalytic bed subsequently passes through a contiguous bed of zeolite, increasing its overall exposure to acid sites promoting cracking and isomerization. This more extensive secondary upgrading is consistent with the absence of a recovered heavy oil fraction. Despite this stronger redistribution toward lighter products, ACB-38_DB achieved the highest C₆₊ HC yield among ACB systems, equal to 12.8%, owing also to its comparatively high CO₂ conversion.

Within the layered ACB samples, no systematic relationship is observed between the initial zeolite acidity and the average catalytic product distribution, despite the whole range of nominal SiO₂/Al₂O₃ ratios investigated. These results suggest that the different initial acidities of BETA zeolites do not result in substantial differences in the extent of the secondary reactions responsible for HC upgrading. The stability of the zeolite was investigated in detail by examining the selectivity towards gaseous paraffins in the C₂-C₅ range during the TOS. As can be seen in Figure S7, the selectivity toward C₂-C₅ paraffins decreases during the test, with the largest variation occurring between approximately 6 h and 15 h of TOS. Although this trend does not directly measure zeolite acidity, it is consistent with an initial evolution of secondary upgrading activity. After this period, the selectivity becomes considerably more stable. Together with the post-reaction NH₃-TPD results, this behavior suggests that the residual acidity remains sufficient to sustain secondary isomerization, cracking and H-transfer reactions, as further supported by the persistent differences in liquid-product composition relative to AC.

3.3. Characterization of spent catalysts

The characterization of spent catalysts is essential for observing changes during the reaction and for correlating them directly with catalytic activity. HAADF-STEM combined with STEM-EDS measurements were used to examine the spatial distribution of Fe, Si and Na and to assess the extent of Na migration, initially introduced on the Fe-based catalyst, toward the zeolite component. Fig. 2 compares ACB-38 and ACB-38_DB, allowing the effect of catalyst configuration to be evaluated while maintaining the same zeolite composition. In the layered ACB-38 sample, the Na signal overlaps extensively with the Si-rich zeolite domains, consistently with substantial Na migration from the Fe-based catalyst to the zeolite. In contrast, physical separation of the two catalytic functions in ACB-38_DB markedly limits Na transfer. The STEM-EDS maps of ACB-25 and ACB-360, reported in Figure S8 and Figure S9, show that Na migration toward the Si-rich zeolite domains

also occur in the other layered configurations.

The quantitative STEM-EDS results summarized in Table S4 confirm this general trend and highlight the effect of catalyst configuration. Similar Na amounts were detected on the zeolite in the layered ACB-25 and ACB-38 samples, equal to 1.03 and 1.02 $\text{mmol}_{\text{Na}} \cdot \text{g}_{\text{zeolite}}^{-1}$, respectively, whereas a lower value of 0.54 $\text{mmol}_{\text{Na}} \cdot \text{g}_{\text{zeolite}}^{-1}$ was obtained for ACB-360. In contrast, physical separation in ACB-38_DB reduced the Na amount on the zeolite to 0.20 $\text{mmol}_{\text{Na}} \cdot \text{g}_{\text{zeolite}}^{-1}$, corresponding to an approximately 80% decrease relative to ACB-38. The Na/Al atomic ratio similarly decreased from 1.14 to 0.22. However, Na/Al atomic ratios should be compared cautiously across zeolite with markedly different Al contents. In particular, the high Na/Al ratio measured for ACB-360, equal to 3.11, mainly reflects its low Al concentration and does not indicate a greater absolute extent of Na migration. Overall, these results provide clear experimental evidence that the dual-bed architecture effectively mitigates Na transfer between the two phases. Based on these experimental observations, a plausible explanation is that in the layered configuration, the closer contact between the two phases, together with the contribution of the water produced by the reaction and partially retained by microporosities, could promote Na migration toward the zeolite [27,56].

At the micrometric scale, SEM-EDS mapping of the spent ACB-25 sample, reported in Figure S11, exemplifies the preferential association of the C signal with Fe-rich domains, while the corresponding elemental composition is summarized in Table S5. This spatial correlation is consistent with C accumulation in the Fe-containing component but does not allow iron carbides to be distinguished from other carbonaceous species. The identity and relative abundance of the iron phases were therefore investigated by XRD and Mössbauer spectroscopy.

The XRD profiles of the spent layered samples are reported in Figure S12. The full-range diffractograms are dominated by the intense reflections of the highly crystalline BETA zeolites, which overlap with the weaker reflections of the iron-containing phases and hinder their unambiguous identification. Hence, Figure S13 shows a magnification of the 35° – 60° 2θ region, where the main reflections associated with iron carbides occur. In this range, reflections compatible with Hägg carbide (χ -Fe₅C₂), cementite (θ -Fe₃C), and magnetite (Fe₃O₄) can be identified in the three layered ACB samples. However, because of peak overlap and the dominant zeolite contribution, the XRD results were used primarily for qualitative phase identification, while the relative phase fraction were determined by Mössbauer spectroscopy.

The distribution of iron phases derived from the fitted Mössbauer spectra, illustrated in Figure S14, are summarized in Fig. 3, while the corresponding hyperfine parameters are reported in Table S6. Hägg carbide (χ -Fe₅C₂), commonly associated with FTS chain-growth activity, is the most abundant phase in all samples, with relative fractions ranging from 57% to 68%. In particular, ACB-38 contains 65% χ -Fe₅C₂, the highest fraction among the layered ACB samples, although the difference is modest. ϵ' -Fe_{2.2}C, often associated with enhanced HC chain growth, is also detected in all samples, both with and without the addition of zeolites, in fractions ranging from 4% to 17%. However, the relative abundance of the iron carbide phases can not fully govern the final HC distribution, as the primary FT products can undergo subsequent secondary reactions over BETA zeolite. In fact, Heavy oil was recovered from all layered ACB configurations, while it was not collected from ACB-38_DB despite this sample containing the highest ϵ' -Fe_{2.2}C fraction, equal to 17%. This result indicates that the final product distribution is also strongly governed by catalyst configuration and by the cracking reactions occurring in the downstream zeolite bed.

Compared with the AC reference test, the addition of zeolite led to the appearance of cementite (θ -Fe₃C). The layered ACB samples contain cementite fractions between 14% and 22%, together with lower χ -Fe₅C₂ and Fe₃O₄ fractions than AC. By contrast, ACB-38_DB contains only 8% cementite, while retaining a χ -Fe₅C₂ fraction of 68% and a ϵ' -Fe_{2.2}C fraction of 17%, consistently with the lower extent of Na migration observed when the two catalytic functions are physically separated

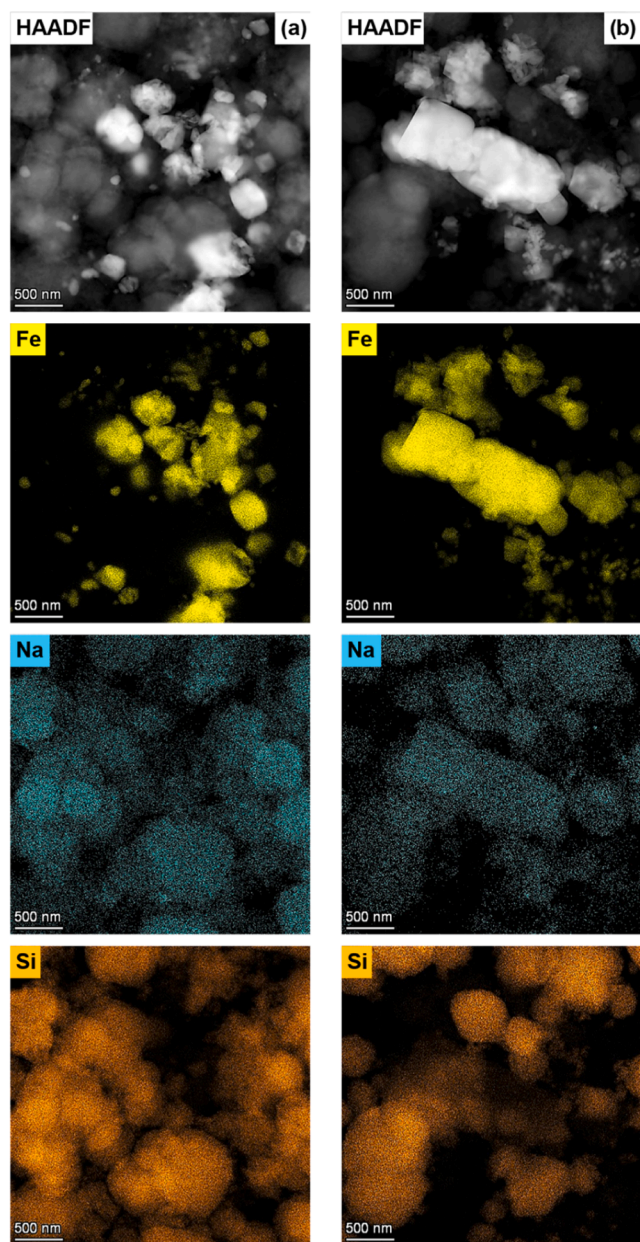


Fig. 2. HAADF-STEM images and corresponding STEM-EDS elemental maps of the spent samples: (a) ACB-38 and (b) ACB-38_DB. The maps show the spatial distribution of Fe, Na and Si for both samples.

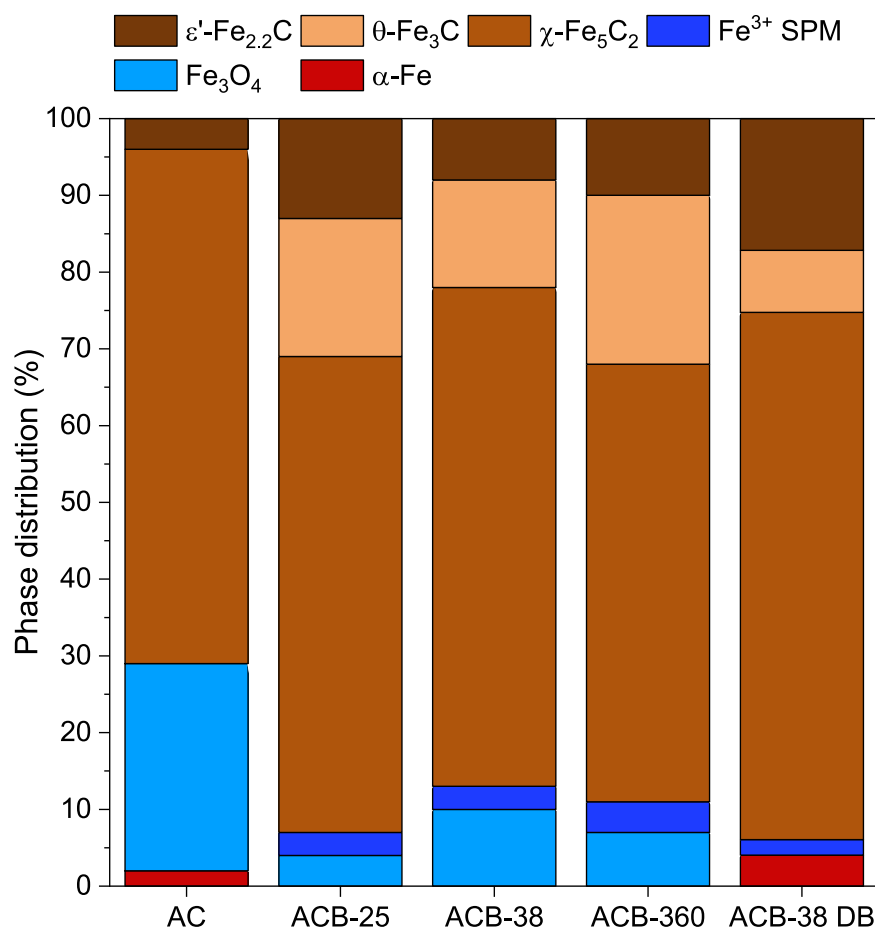


Fig. 3. Distribution of the iron phases in spent samples as determined by Mössbauer spectroscopy. Reaction conditions: 7 NL·gFe₃O₄⁻¹·h⁻¹ (H₂/CO₂/N₂ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe₃O₄, 2 g zeolite.

(Fig. 2 and Table S4). These observed differences may reflect changes in the local carburizing and oxidizing environment. A possible explanation is that these changes arise from the combined effects of Na migration and water retention. In particular, Na migration could alter the electronic properties and reduce the CO₂ coverage, leading to a change in the carbon chemical potential and favoring the formation of iron carbides with a higher Fe/C ratio, such as cementite, at the expense of C-rich iron carbides, such as Hägg carbide.

The fraction of Fe₃O₄, responsible for converting CO₂ to CO, decreases significantly from 28% in AC to 4–10% with the addition of zeolite. This observation indicates more clearly that the phase evolution cannot be explained by an enhanced oxidizing effect of the water retained by the zeolite, but it is also related to a combined effect with alkali migration. The depletion of Na from the iron surface may also reduce CO₂ adsorption and the stabilization of oxidized iron species [56]. Despite these differences in phase composition, CO₂ conversion remains broadly comparable among the samples, as presented in the catalytic results section, indicating that the amount of iron oxide detected under reaction conditions is sufficient to convert CO₂ through RWGS reaction. This suggests that, in our reaction conditions, the rate-limiting step is more likely associated with the HC chain growth process, rather than with the initial adsorption and conversion of CO₂. Accordingly, Na migration appears to primarily influence product selectivity by modifying the balance between chain propagation and chain-termination reactions, with only limited influence on overall CO₂ conversion. In the ACB-38_DB spectrum (Figure S14-d), weak spectral features are observed in the velocity region compatible with the magnetic subspectra of Fe₃O₄. However, the characteristic A-site and B-site sextets are too poorly defined and of insufficient intensity to allow a

reliable fit and quantification. The Fe₃O₄ phase was therefore not included in the quantitative phase distribution, although its presence was clearly confirmed by STEM-EDS analysis (Figure S10).

The NH₃-TPD profiles of the regenerated spent samples are reported in Figure S15, while the corresponding total residual acidity and weak-to-strong (W/S) acid site ratios are summarized in Table S7. Compared with fresh zeolites, the total acidity decreased by approximately one order of magnitude, corresponding to losses of about 89–97%. Among the ACB samples, ACB-38 retained the highest residual acidity (0.062 mmol·g⁻¹), consistently with the higher acidity of the corresponding fresh sample. ACB-25 and ACB-360 retained 0.033 and 0.015 mmol·g⁻¹, respectively. In the dual-bed configuration, ACB-38_DB exhibited a lower residual acidity of 0.029 mmol·g⁻¹, despite the reduced extent of Na migration observed by STEM-EDS. Although a quantitative critical acidity threshold cannot be established from the present data, the behavior of ACB-360 indicates that a residual acidity of 0.015 mmol·g⁻¹ is still compatible with sustained secondary upgrading under the investigated conditions. Moreover, the W/S ratio increased from 2.16 for fresh BETA-38 to 3.3 for ACB-38 and 6.6 for ACB-38_DB, indicating a preferential depletion or weakening of the high-temperature desorption peak, particularly in the dual-bed sample. Since the spent catalysts were regenerated before NH₃-TPD analysis, this decrease cannot be attributed solely to reversible pore blockage by carbonaceous compounds, but it may also reflect partially irreversible neutralization of acid sites by migrated Na and hydrothermal steaming of the BEA framework caused by the prolonged exposure to a water-rich reaction environment [57–59]. Steaming of BEA-type zeolites has previously been shown to induce framework dealumination, formation and migration of extra-framework Al species, and redistribution of Brønsted acidity [59].

Despite the substantial acidity loss, the remaining acid sites were sufficient to promote secondary upgrading reactions throughout the catalytic tests, as indicated by the persistent differences between the gaseous and liquid products obtained with and without zeolite. The similar product distributions obtained with BETA-25, BETA-38 and BETA-360 therefore suggest that, under the investigated conditions, secondary upgrading is strongly influenced by the zeolite topology, pore accessibility, and catalyst architecture than by the initial total acidity. Lastly, the relatively stable product distribution after the initial reaction period

suggests that most of the zeolite deactivation may have occurred during the early stages of the test.

3.4. Liquid product analysis

The composition of the collected oils was investigated by DHA for the light oil and by GC-MS analysis for the heavy oil fraction. For the layered ACB systems, light oil samples were analyzed every 24 h to evaluate the evolution of the product distribution with time on stream. Fig. 4

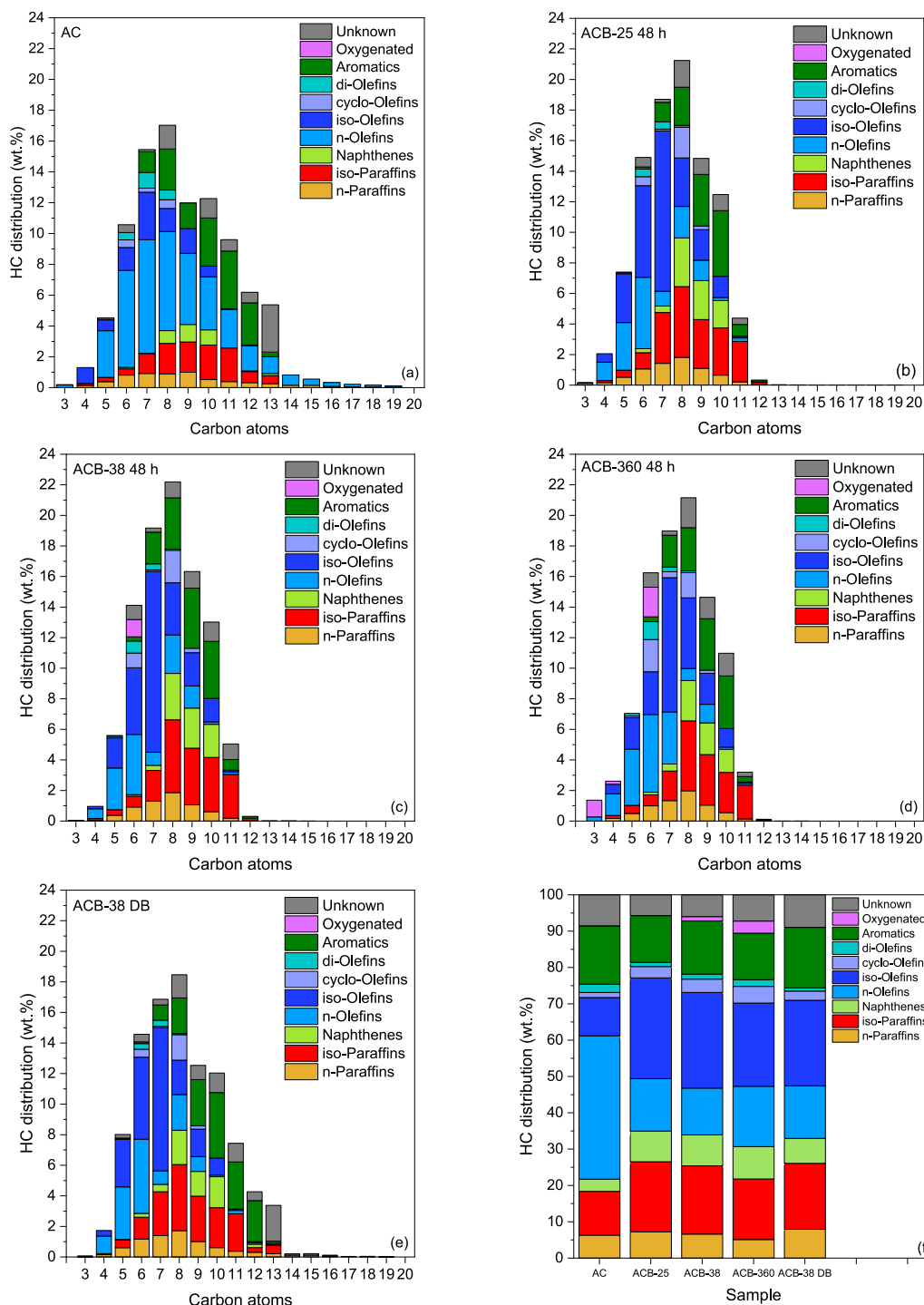


Fig. 4. HC distributions subdivided by class after DHA analysis of the light oil: (a) AC, (b) ACB-25, (c) ACB-38, (d) ACB-360, (e) ACB-38 DB and (f) total HC distribution. Reaction conditions: $7 \text{ NL} \cdot \text{gFe}_3\text{O}_4^{-1} \cdot \text{h}^{-1}$ ($\text{H}_2/\text{CO}_2/\text{N}_2 = 15/5/3$), 360°C , 2.3 MPa , $2 \text{ g Na/Fe}_3\text{O}_4$, 2 g zeolite . For the sake of clarity, AC, ACB-25, ACB-38, and ACB-360 refer to the samples collected after 48 h, while the ACB-38_DB test had a shorter duration.

compares the HC distributions obtained over the bifunctional systems with that produced by the 5 wt% Na-Fe₃O₄. Compared with the AC test, the addition of BETA markedly modifies both the carbon-number distribution and the HC classes, indicating extensive secondary upgrading of the primary FT products over the zeolite acid sites. The distribution becomes narrower and shifts toward the C₅-C₁₂ range, consistently with cracking of longer HCs. More importantly, the predominantly linear olefinic fraction of reference AC oil is strongly modified. As summarized in Table S8, the n-olefin fraction decreases from 39.5 wt% for AC to 12.9–16.6 wt% for the layered ACB systems, while iso-olefins increase from 10.5 wt% to 22.9–27.7 wt%. Iso-paraffins and naphthenes also increased significantly. Considering ACB-38 as a representative example, the iso-paraffin, iso-olefin, and naphthene fractions reach 18.8, 26.3 and 8.52 wt%, respectively, compared with 12.1, 10.5, and 3.36 wt% for AC. These changes are consistent with extensive isomerization and cyclization of the primary FT products.

The DHA data reported in Table S9 provides further evidence of this transformation. The light oil produced by AC is characterized by a pronounced series of terminal α -olefins, including 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene at 6.09, 7.00, 6.25, 4.61 and 3.44 wt%, respectively. These compounds are strongly depleted in the ACB samples, generally falling below 0.7 wt%. Conversely, internal and branched olefins such as 2-methyl-2-butene, trans-2-pentene, trans-2-hexene, and 2-methyl-1-hexene become prominent in all ACB oil. This redistribution of the molecules confirms that BETA primarily isomerizes the olefinic products.

The effect of zeolite acidity on the oil composition appears to be relatively limited. Despite the wide variation in nominal SiO₂/Al₂O₃ ratio, the ACB samples exhibit similar overall HC class distribution (Table S8) and most of the major molecular species identified in Table S9 occur at comparable concentrations. Hence, the dominant effect is related to the shape-selectivity of BETA zeolites, rather than its acidity. The DHA profiles collected at 24, 48 and 72 h of test for ACB-25, ACB-38, and ACB-360 further show that the HC class distribution remain broadly comparable after the initial reaction period (Figures S16–S18). These observations, together with the post-reaction NH₃-TPD results, suggest that although significant zeolite deactivation occurs, the remaining acid function is sufficient to sustain cracking, isomerization, and related secondary upgrading throughout the test.

No substantial increase in the total aromatic fraction is observed upon addition of BETA. Aromatics account for 12.8–14.7 wt% in the layered ACB samples, compared with 16.1 wt% for AC, while ACB-38_DB reaches 16.7 wt% (Table S8). Thus, under the investigated conditions, BETA does not promote overall aromatization to the same extent previously observed with medium-pore MFI zeolites [8]. Instead, its main effect on the light oil is the conversion of linear olefins toward branched and internal olefins, and cyclic hydrocarbons.

The heavy oil fraction was further characterized by GC-MS to evaluate the effect of BETA on the heavier FT products. The resulting boiling curves are reported in Fig. 5, while representative chromatograms of AC and ACB-38 are compared in Figure S19. The latter clearly shows the shift induced by the zeolite: the AC heavy oil contains a broad homologous series extending to approximately C₂₅, whereas the ACB-38 chromatogram is concentrated at shorter retention times, with the main identified HCs falling within the C₁₀–C₁₉ range, a trend also observed for the other layered ACB samples. Fig. 5 highlights this shift toward lighter heavy oil components. The three layered ACB samples exhibit almost overlapping boiling curves, with most of the distribution approximately within the 200–400 °C range and a 50% cumulative area reached at around 250 °C. In contrast, the AC heavy oil shows a broader and heavier boiling distribution, reaching 50% cumulative area at approximately 315 °C and retaining a significant fraction above 350 °C, with the heaviest compounds extending to about 450 °C.

As already observed for the light oil fraction, BETA markedly modifies the chemical composition of the heavy oil. The predominantly linear olefins obtained with AC are replaced by oil with a highly varied

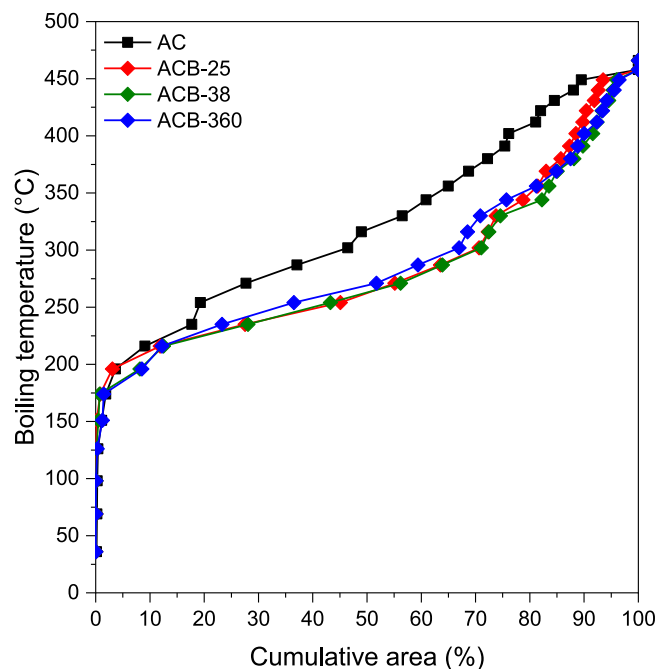


Fig. 5. Reconstructed boiling curves of the heavy oil collected for AC, ACB-25, ACB-38 and ACB-360 samples. Reaction conditions: 7 NL·gFe₃O₄⁻¹·h⁻¹ (H₂/CO₂/N₂ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe₃O₄, 2 g zeolite. For the sake of clarity, the ACB-38_DB sample did not produce an heavy oil fraction.

composition, including branched and cyclic HCs together with poly-substituted aromatics. In contrast, no preferential formation of light BTX aromatics in the C₆–C₈ range is observed. This behavior is consistent with the large-pore BEA framework, which imposes weaker shape-selectivity than MFI framework and allows aromatic intermediates and larger molecules to form and diffuse through the zeolite channels.

To evaluate the practical impact of BETA upgrading on fuel quality, the light and heavy oil fractions were recombined according to their experimentally collected amounts, and the resulting boiling-range distributions were reconstructed by fractionating the total liquid into naphtha, kerosene, gasoil and heavier residue fractions. The layered ACB-25, ACB-38 and ACB-360 exhibit very similar distributions, consistently with their comparable light and heavy oil compositions and relative amounts. Fig. 6 compares the reconstructed distributions of AC, ACB-38 and ACB-38_DB, thereby highlighting the effects of both BETA addition and catalyst configuration.

For ACB-38, approximately 71.3 vol% of the produced oil consists of naphtha and 21.7 vol% of kerosene, while gasoil and heavier residue together account for only 7.0 vol%. In contrast, the AC reference exhibits a considerably broader product distribution, consisting of 36.2 vol% naphtha, 33.0 vol% kerosene, 11.2 vol% gasoil and 19.6 vol% residue. Thus, although AC produces a higher relative fraction of kerosene, this is accompanied by significant formation of gasoil and heavier waxes, which would require additional downstream upgrading, such as hydrocracking. Conversely, BETA shifts the FT liquid toward lighter boiling fractions already within the catalytic reactor, strongly enriching naphtha and kerosene-ranges while suppressing the heaviest fractions.

This effect is further enhanced in the dual-bed configuration. Since no heavy-oil fraction was recovered from ACB-38_DB, its reconstructed liquid product is concentrated almost entirely in the gasoline boiling range, consistently with the more extensive secondary cracking observed when the complete FT product stream passes through the downstream zeolite bed.

From a regulatory perspective, such synthetic hydrocarbons may qualify as RFNBOs under RED III when produced in compliance with the applicable renewable-energy and greenhouse-gas criteria. In addition,

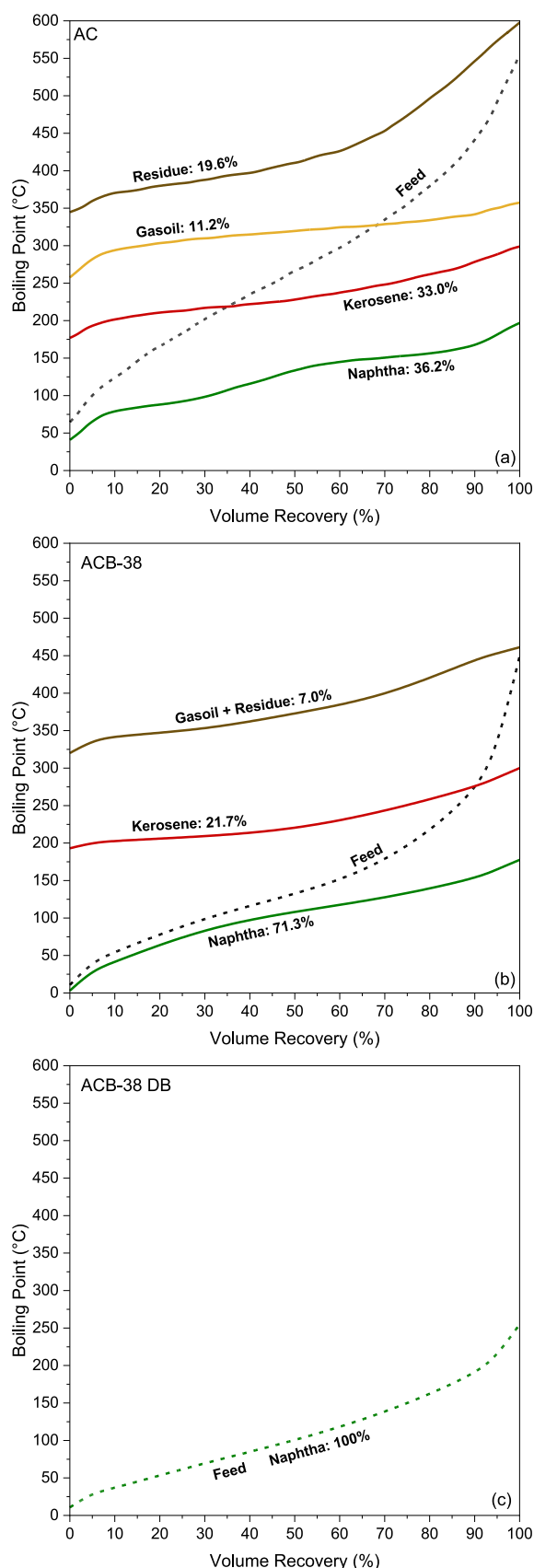


Fig. 6. Distillation curves for light + heavy oil (denoted as feed), fractionated into the main fractions, for the samples: (a) AC, (b) ACB-38 and (c) ACB-38_DB. Reaction conditions: 7 NL·gFe₃O₄⁻¹·h⁻¹ (H₂/CO₂/N₂ = 15/5/3), 360 °C, 2.3 MPa, 2 g Na/Fe₃O₄, 2 g zeolite.

the greater naphtha-range fraction produced by the bifunctional catalysts may broaden the potential application of the process beyond e-kerosene production, while the Regulation (EU) 2023/851 also envisages a future framework for vehicles operating exclusively on CO₂-neutral fuels after 2035.

Finally, the aqueous-phase samples collected from the hot (150 °C, 23 bar) and cold (5 °C, 23 bar) traps were characterized using HPLC analysis, and their compositions are shown in Table S10 and Table S11, respectively. The two condensates show different compositions. The hot-trap aqueous phase is dominated by formic and acetic acids, with formic acid concentrations ranging from approximately 26–38 g·L⁻¹, whereas alcohols are present only in minor amounts. Conversely, the cold-trap aqueous phase is strongly enriched in ethanol, particularly for the layered ACB samples, where concentrations range from approximately 120–177 g·L⁻¹, with acetic acid representing the second most abundant oxygenate. No systematic dependence on BETA acidity is apparent from the aqueous-phase composition. However, ACB-38_DB exhibits a substantially lower ethanol concentration in the cold condensate than the layered samples, together with the highest formic acid concentration in the hot condensate.

4. Conclusions

The influence of BETA zeolite with nominal SiO₂/Al₂O₃ ratio of 25, 38 and 360 on CO₂-modified FTS was systematically investigated over a 5 wt% Na-Fe₃O₄ catalyst using layered and dual-bed reactor configurations. Mössbauer spectroscopy and STEM-EDS analysis revealed that the presence and spatial arrangement of BETA significantly affect Na migration and iron catalyst evolution. In the layered configuration, the closer interaction between the two catalytic components, together with water retention by the zeolite, was associated with enhanced Na migration from the iron component toward the zeolite, and a change of local carbon and oxygen chemical potentials that promote a redistribution of the iron phases toward iron carbides with a higher Fe/C ratio, such as cementite. Conversely, the physical separation in the dual-bed configuration strongly limited Na migration and, as expected, resulted in a different iron phase distribution. These structural modifications were reflected in the catalytic performance, with the layered configuration showing higher CH₄ selectivity and lower liquid HC selectivity than the dual-bed configuration, where the highest C₆₊ hydrocarbon yield was achieved, amounting to 12.8%.

DHA and GC-MS analyses confirmed that the bifunctional catalysts produced a substantially different liquid composition from that obtained with the iron catalyst alone, with a narrower carbon-number distribution centered in the naphtha- and kerosene-range. The large three-dimensional 12-membered-ring pore system of BETA also allowed long HCs to diffuse through the zeolite channels, explaining the formation of a significant kerosene fraction equal to 21.7 vol%. In contrast, the more extensive cracking occurring in the dual-bed configuration resulted in the formation of lighter products, preventing heavy oil collection and reducing the kerosene fraction.

Despite the wide range of investigated nominal SiO₂/Al₂O₃ ratios (25–360), the initial zeolite acidity exerted only a limited influence on the final product distribution. The substantial acidity loss observed after reaction, together with the similar product distributions obtained over the three BETA zeolites, suggests that even the reduced residual acidity (0.015 mmol·g⁻¹ for ACB-360) was sufficient to sustain secondary cracking and isomerization reactions. Reactor configuration and evolution of the iron catalyst therefore played a more decisive role in determining the final HC distribution.

Overall, this work demonstrates that the combination of the large-pore BETA zeolite with a Na-promoted Fe₃O₄ catalyst represents an effective strategy for in situ upgrading of primary FT products. While the dual-bed configuration favors the production of naphtha-range HCs, the layered configuration preserves a significant kerosene fraction while strongly suppressing gasoil and heavy residue production compared

with the AC reference. Further improvement of kerosene yield may therefore be pursued by optimizing the proximity between the two catalytic functions to limit excessive cracking and chain-termination reactions.

CRedit authorship contribution statement

Fabrizio Celoria: Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Alessio Tauro:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Fabio Salomone:** Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Conceptualization. **Giulia Torretti:** Methodology, Investigation. **Luca Nodari:** Writing – review & editing, Software, Resources, Methodology, Investigation. **Emanuele Felli:** Project administration, Funding acquisition. **Raffaele Pirone:** Supervision, Resources, Funding acquisition. **Samir Bensaid:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.cattod.2026.116026](https://doi.org/10.1016/j.cattod.2026.116026)

Data availability

Data will be made available on request.

References

- [1] 2026, IEAGlobal energy review2025.
- [2] A. Tauro, F. Salomone, F. Celoria, M. Armandi, L. Nodari, L. Romagnoletti, E. Felli, R. Pirone, S. Bensaid, Effect of pre-treatment conditions on Fe-based catalyst for e-fuel production via modified Fischer-Tropsch synthesis, *Chem. Eng. J.* 515 (2025) 163154, <https://doi.org/10.1016/j.cej.2025.163154>.
- [3] Y. Jiang, K. Wang, Y. Wang, Z. Liu, X. Gao, J. Zhang, Q. Ma, S. Fan, T.-S. Zhao, M. Yao, Recent advances in thermocatalytic hydrogenation of carbon dioxide to light olefins and liquid fuels via modified Fischer-Tropsch pathway, *J. CO₂ Util.* 67 (2023) 102321, <https://doi.org/10.1016/j.jcou.2022.102321>.
- [4] The Paris Agreement | UNFCCC, (n.d.). <https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement> (accessed May 16, 2018).
- [5] European Commission, Directive (EU) 2023/2413 of the European Parliament and of the Council of 18 October 2023 amending Directive (EU) 2018/2001, Regulation (EU) 2018/1999 and Directive 98/70/EC as regards the promotion of energy from renewable sources, and repealing Council Directive (EU) 2015/652, 2023. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32023L2413&qid=1785851025105> (accessed August 4, 2026).
- [6] European Commission, Commission Delegated Regulation (EU) 2023/1184 of 10 February 2023 supplementing Directive (EU) 2018/2001 of the European Parliament and of the Council by establishing a Union methodology setting out detailed rules for the production of renewable liquid and gaseous transport fuels of non-biological origin, 2023. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv%3AOJ.L_.2023.157.01.0011.01.ENG&toc=OJ%3A1%3A2023%3A157%3ATOC (accessed August 4, 2026).
- [7] 2023, European Commission, RegulationEU2405 of the European Parliament and of the Council of 18 October 2023 on ensuring a level playing field for sustainable air transport (ReFuelEU Aviation), 2023<https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32023R2405>(accessed August 3, 2026)..
- [8] A. Tauro, F. Celoria, M. Pietro Mezzapesa, F. Salomone, L. Nodari, L. Romagnoletti, E. Felli, R. Pirone, S. Bensaid, Effective E-Gasoline Production via CO₂-Modified Fischer-Tropsch Synthesis, *ChemCatChem* 18 (12) (2026), <https://doi.org/10.1002/cctc.70882>.
- [9] J. Wei, R. Yao, Y. Han, Q. Ge, J. Sun, Towards the development of the emerging process of CO₂ heterogeneous hydrogenation into high-value unsaturated heavy hydrocarbons, *Chem. Soc. Rev.* 50 (19) (2021) 10764–10805, <https://doi.org/10.1039/D1CS00260K>.
- [10] L. Krausser, Q. Yang, E.V. Kondratenko, CO₂ Hydrogenation to Hydrocarbons over Fe-Based Catalysts: Status and Recent Developments, *ChemCatChem* 16 (13) (2024), <https://doi.org/10.1002/cctc.202301716>.
- [11] Y. Wang, S. Kazumi, W. Gao, X. Gao, H. Li, X. Guo, Y. Yoneyama, G. Yang, N. Tsubaki, Direct conversion of CO₂ to aromatics with high yield via a modified Fischer-Tropsch synthesis pathway, *Appl. Catal. B* 269 (2020) 118792, <https://doi.org/10.1016/j.apcatb.2020.118792>.
- [12] M. Xu, C. Cao, J. Xu, Understanding kinetically interplaying reverse water-gas shift and Fischer-Tropsch synthesis during CO₂ hydrogenation over Fe-based catalysts, *Appl. Catal. A Gen.* 641 (2022) 118682, <https://doi.org/10.1016/j.apcata.2022.118682>.
- [13] K. Opeyemi Otun, Y. Yao, X. Liu, D. Hildebrandt, Synthesis, structure, and performance of carbide phases in Fischer-Tropsch synthesis: A critical review, *Fuel* 296 (2021) 120689, <https://doi.org/10.1016/j.fuel.2021.120689>.
- [14] F.G. Botes, W. Böhringer, The addition of HZSM-5 to the Fischer-Tropsch process for improved gasoline production, *Appl. Catal. A Gen.* 267 (1–2) (2004) 217–225, <https://doi.org/10.1016/j.apcata.2004.03.006>.
- [15] M.V. Landau, N. Meiri, N. Utsis, R. Vidruk Nehemya, M. Herskowitz, Conversion of CO₂, CO, and H₂ in CO₂ Hydrogenation to Fungible Liquid Fuels on Fe-Based Catalysts, *Ind. Eng. Chem. Res.* 56 (45) (2017) 13334–13355, <https://doi.org/10.1021/acs.iecr.7b01817>.
- [16] J. Liu, Y. Song, X. Guo, C. Song, X. Guo, Recent advances in application of iron-based catalysts for CO hydrogenation to value-added hydrocarbons, *Chin. J. Catal.* 43 (2022) 731–754, [https://doi.org/10.1016/S1872-2067\(21\)63802-0](https://doi.org/10.1016/S1872-2067(21)63802-0).
- [17] E. de Smit, F. Cinquini, A.M. Beale, O.V. Safonova, W. van Beek, P. Sautet, B. M. Weckhuysen, Stability and Reactivity of ϵ - χ -0 Iron Carbide Catalyst Phases in Fischer-Tropsch Synthesis: Controlling μ_c , *J. Am. Chem. Soc.* 132 (42) (2010) 14928–14941, <https://doi.org/10.1021/ja105853q>.
- [18] I.A.W. Pilot, R.A. van Santen, E.J.M. Hensen, The Optimally Performing Fischer-Tropsch Catalyst, *Angew. Chem. Int. Ed.* 53 (47) (2014) 12746–12750, <https://doi.org/10.1002/anie.201406521>.
- [19] A. Keuncke, M. Dossow, V. Dieterich, H. Spliethoff, S. Fendt, Insights into Fischer-Tropsch catalysis: current perspectives, mechanisms, and emerging trends in energy research, *Front. Energy Res.* 12 (2024), <https://doi.org/10.3389/fenrg.2024.1344179>.
- [20] T.H. Pham, Y. Qi, J. Yang, X. Duan, G. Qian, X. Zhou, D. Chen, W. Yuan, Insights into Hägg Iron-Carbide-Catalyzed Fischer-Tropsch Synthesis: Suppression of CH₄ Formation and Enhancement of C-C Coupling on χ -Fe₃C₂ (510), *ACS Catal.* 5 (2015) 2203–2208, <https://doi.org/10.1021/cs501668g>.
- [21] W. Wu, J. Luo, J. Zhao, M. Wang, L. Luo, S. Hu, B. He, C. Ma, H. Li, J. Zeng, Facet sensitivity of iron carbides in Fischer-Tropsch synthesis, *Nat. Commun.* 15 (2024) 6108, <https://doi.org/10.1038/s41467-024-50544-1>.
- [22] A. Corma, V. Fornés, J.B. Montón, A. V. Orchillés, Catalytic activity of large-pore high Si/Al zeolites: Cracking of heptane on H-Beta and dealuminated HY zeolites, *J. Catal.* 107 (1987) 288–295, [https://doi.org/10.1016/0021-9517\(87\)90295-8](https://doi.org/10.1016/0021-9517(87)90295-8).
- [23] X. Li, J. He, M. Meng, Y. Yoneyama, N. Tsubaki, One-step synthesis of H- β zeolite-enraptured Co/Al₂O₃ Fischer-Tropsch catalyst with high spatial selectivity, *J. Catal.* 265 (1) (2009) 26–34, <https://doi.org/10.1016/j.jcat.2009.04.009>.
- [24] Z.-W. Liu, X. Li, K. Asami, K. Fujimoto, Syngas to iso-paraffins over Co/SiO₂ combined with metal/zeolite catalysts, *Fuel Process. Technol.* 88 (2) (2007) 165–170, <https://doi.org/10.1016/j.fuproc.2006.02.009>.
- [25] Z.-W. Liu, X. Li, K. Asami, K. Fujimoto, Iso-paraffins synthesis from modified Fischer-Tropsch reaction—Insights into Pd/beta and Pt/beta catalysts, *Catal. Today* 104 (2005) 41–47, <https://doi.org/10.1016/j.cattod.2005.03.030>.
- [26] R.B. Borade, A. Clearfield, Iron-substituted Beta molecular sieve: Synthesis and characterization, *Microporous Mater.* 2 (3) (1994) 167–177, [https://doi.org/10.1016/0927-6513\(93\)E0050-Q](https://doi.org/10.1016/0927-6513(93)E0050-Q).
- [27] E. Corrao, F. Salomone, E. Giglio, M. Castellino, S.M. Ronchetti, M. Armandi, R. Pirone, S. Bensaid, CO₂ conversion into hydrocarbons via modified Fischer-Tropsch synthesis by using bulk iron catalysts combined with zeolites, *Chem. Eng. Res. Des.* 197 (2023) 449–465, <https://doi.org/10.1016/j.cherd.2023.07.052>.
- [28] A.V. Karre, A. Kababji, E.L. Kugler, D.B. Dadyburjor, Effect of addition of zeolite to iron-based activated-carbon-supported catalyst for Fischer-Tropsch synthesis in separate beds and mixed beds, *Catal. Today* 198 (1) (2012) 280–288, <https://doi.org/10.1016/j.cattod.2012.04.068>.

- [29] J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun, Directly converting CO₂ into a gasoline fuel, *Nat. Commun.* 8 (2017) 15174, <https://doi.org/10.1038/ncomms15174>.
- [30] A. Dokania, A. Ramirez, G. Shterk, J.L. Cerrillo, J. Gascon, Modifying the Hydrogenation Activity of Zeolite Beta for Enhancing the Yield and Selectivity for Fuel-Range Alkanes from Carbon Dioxide, *Chempluschem* 87 (6) (2022), <https://doi.org/10.1002/cplu.202200177>.
- [31] E. García-Hurtado, A. Rodríguez-Fernández, M. Moliner, C. Martínez, CO₂ hydrogenation using bifunctional catalysts based on K-promoted iron oxide and zeolite: influence of the zeolite structure and crystal size, *Catal. Sci. Technol.* 10 (16) (2020) 5648–5658, <https://doi.org/10.1039/D0CY00712A>.
- [32] A. Ramirez, X. Gong, M. Caglayan, S.-A.F. Nastase, E. Abou-Hamad, L. Gevers, L. Cavallo, A. Dutta Chowdhury, J. Gascon, Selectivity descriptors for the direct hydrogenation of CO₂ to hydrocarbons during zeolite-mediated bifunctional catalysis, *Nat. Commun.* 12 (2021) 5914, <https://doi.org/10.1038/s41467-021-26090-5>.
- [33] T. Lu, W. Yan, R. Xu, Chiral zeolite beta: structure, synthesis, and application, *Inorg. Chem. Front.* 6 (2019) 1938–1951, <https://doi.org/10.1039/C9QI00574A>.
- [34] M.U. Azam, A. Fernandes, M.J. Ferreira, W. Afzal, I. Graça, Pore-Structure Engineering of Hierarchical β Zeolites for the Enhanced Hydrocracking of Waste Plastics to Liquid Fuels, *ACS Catal.* 14 (21) (2024) 16148–16165, <https://doi.org/10.1021/acscatal.4c05354>.
- [35] S. Bessell, Investigation of bifunctional zeolite supported cobalt Fischer-Tropsch catalysts, *Appl. Catal. A Gen.* 126 (1995) 235–244, [https://doi.org/10.1016/0926-860X\(95\)00040-2](https://doi.org/10.1016/0926-860X(95)00040-2).
- [36] I. Langmuir, THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM, *J. Am. Chem. Soc.* 40 (9) (1918) 1361–1403, <https://doi.org/10.1021/ja02242a004>.
- [37] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of Gases in Multimolecular Layers, *J. Am. Chem. Soc.* 60 (2) (1938) 309–319, <https://doi.org/10.1021/ja01269a023>.
- [38] E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, *J. Am. Chem. Soc.* 73 (1) (1951) 373–380, <https://doi.org/10.1021/ja01145a126>.
- [39] R. Liu, Y. Bian, W. Dai, Qualitative and quantitative analysis of Brønsted and Lewis acid sites in zeolites: A combined probe-assisted ¹H MAS NMR and NH₃-TPD investigation, *Chin. J. Struct. Chem.* 43 (4) (2024) 100250, <https://doi.org/10.1016/j.cjsc.2024.100250>.
- [40] M. Boronat, A. Corma, What Is Measured When Measuring Acidity in Zeolites with Probe Molecules? *ACS Catal.* 9 (2) (2019) 1539–1548, <https://doi.org/10.1021/acscatal.8b04317>.
- [41] G. Bonura, M. Migliori, L. Frusteri, C. Cannilla, E. Catizzzone, G. Giordano, F. Frusteri, Acidity control of zeolite functionality on activity and stability of hybrid catalysts during DME production via CO₂ hydrogenation, *J. CO₂ Util.* 24 (2018) 398–406, <https://doi.org/10.1016/j.jcou.2018.01.028>.
- [42] A.G. Pelmenschikov, R.A. van Santen, J. Janchen, E. Meijer, Acetonitrile-d₃ as a probe of Lewis and Brønsted acidity of zeolites, *J. Phys. Chem.* 97 (42) (1993) 11071–11074, <https://doi.org/10.1021/j100144a028>.
- [43] I. Miletto, E. Catizzzone, G. Bonura, C. Ivaldi, M. Migliori, E. Gianotti, L. Marchese, F. Frusteri, G. Giordano, In Situ FT-IR Characterization of CuZnZr/Ferrierite Hybrid Catalysts for One-Pot CO₂-to-DME Conversion, *Materials* 11 (11) (2018) 2275, <https://doi.org/10.3390/ma11112275>.
- [44] E. Giglio, G. Ferrarelli, F. Salomone, E. Corrao, M. Migliori, S. Bensaid, R. Pirone, G. Giordano, Tailoring the acidity of ZSM-5 via surface passivation: Catalytic assessment on dimethyl ether to olefins (DTO) process, *Fuel* 362 (2024) 130559, <https://doi.org/10.1016/j.fuel.2023.130559>.
- [45] F. Salomone, G. Ferrarelli, E. Giglio, E. Corrao, M. Migliori, S. Bensaid, R. Pirone, G. Giordano, Hierarchical zeolites for dimethyl ether dehydration into light olefins, *Catal. Today* 463 (2026) 115618, <https://doi.org/10.1016/j.cattod.2025.115618>.
- [46] E. Tito, D. Landi, F. Demichelis, G. Pipitone, S. Bensaid, R. Pirone, Hydrothermal liquefaction of digestate from the organic fraction of municipal solid waste: Optimization of operating parameters, *Energy Convers. Manag.* 336 (2025) 119881, <https://doi.org/10.1016/j.enconman.2025.119881>.
- [47] M. Andriolo, E. Tito, G. Pipitone, R. Pirone, S. Bensaid, Aqueous phase reforming of wastewaters from the hydrothermal carbonization of microalgae: tackling the catalyst deactivation challenge via upstream pretreatment, *Int. J. Hydrog. Energy* 248 (2026) 155972, <https://doi.org/10.1016/j.ijhydene.2026.155972>.
- [48] G. Zoppi, G. Pipitone, H. Gruber, G. Weber, A. Reichhold, R. Pirone, S. Bensaid, Aqueous phase reforming of pilot-scale Fischer-Tropsch water effluent for sustainable hydrogen production, *Catal. Today* 367 (2021) 239–247, <https://doi.org/10.1016/J.CATTOD.2020.04.024>.
- [49] M.D. Shroff, A.K. Datye, The importance of passivation in the study of iron Fischer-Tropsch catalysts, *Catal. Lett.* 37 (1-2) (1996) 101–106, <https://doi.org/10.1007/BF00813526>.
- [50] J.T. Scanlon, D.E. Willis, Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept, *J. Chromatogr. Sci.* 23 (8) (1985) 333–340, <https://doi.org/10.1093/chromsci/23.8.333>.
- [51] R.A. Friedel, R.B. Anderson, Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C₅ – C₈ Paraffin Isomers from Cobalt Catalyst, *J. Am. Chem. Soc.* 72 (3) (1950) 1212–1215, <https://doi.org/10.1021/ja01159a039>.
- [52] J. Wei, R. Yao, Q. Ge, D. Xu, C. Fang, J. Zhang, H. Xu, J. Sun, Precisely regulating Brønsted acid sites to promote the synthesis of light aromatics via CO₂ hydrogenation, *Appl. Catal. B* 283 (2021) 119648, <https://doi.org/10.1016/j.apcatb.2020.119648>.
- [53] F. Yi, H. Chen, L. Huang, C. Hu, J. Wang, T. Li, H. Wang, Z. Tao, Y. Yang, Y. Li, Effects of the acidity and shape selectivity of dealuminated zeolite beta on butene transformations, *Fuel* 300 (2021) 120694, <https://doi.org/10.1016/j.fuel.2021.120694>.
- [54] E. Giglio, M. Migliori, G. Giordano, E. Catizzzone, CO₂ Capture and Valorization, in: *Zeolites: From Fundamentals to Emerging Applications*, Royal Society of Chemistry, 2025, pp. 482–522, <https://doi.org/10.1039/9781837676859-00482>.
- [55] Y. Bai, J. Liu, P. Ren, W. Guo, T. Wang, W. Chen, X. Liu, Q. Peng, Y.-F. Song, Y. Yang, Y.-W. Li, X. Wen, Oxygen Adsorption-Induced Morphological Evolution of Hägg Iron Carbide at High Oxygen Chemical Potentials, *J. Phys. Chem. C* 125 (2021) 3055–3065, <https://doi.org/10.1021/acs.jpcc.0c10822>.
- [56] C. Wen, C. Wang, L. Lu, X. Zhang, L. Chen, Q. Zhang, L. Ma, Effect of Na⁺ migration and the component proximity on direct conversion of aromatics into aromatics over Fe-based zeolite bifunctional catalysts, *Chem. Eng. J.* 490 (2024) 151675, <https://doi.org/10.1016/j.cej.2024.151675>.
- [57] A.M. Camiloti, S.L. Jahn, N.D. Velasco, L.F. Moura, D. Cardoso, Acidity of Beta zeolite determined by TPD of ammonia and ethylbenzene disproportionation, *Appl. Catal. A Gen.* 182 (1999) 107–113, [https://doi.org/10.1016/S0926-860X\(98\)00418-9](https://doi.org/10.1016/S0926-860X(98)00418-9).
- [58] V. Daligaux, R. Richard, M.-H. Manero, Deactivation and regeneration of zeolite catalysts used in pyrolysis of plastic wastes—a process and analytical review, *Catalysts* 11 (2021) 770, <https://doi.org/10.3390/catal11070770>.
- [59] S.M. Maier, A. Jentys, J.A. Lercher, Steaming of Zeolite BEA and Its Effect on acidity: a comparative NMR and IR spectroscopic study, *J. Phys. Chem. C* 115 (16) (2011) 8005–8013, <https://doi.org/10.1021/jp108338g>.