Supplementary Materials for

Designing a multifunctional catalyst for the direct production of gasoline range isoparaffins from CO₂

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**Figure S1**: Time on stream data for catalytic performance of (a) InCo + beta dual bed (b) InCo + beta mixed bed (c) InCo + Zn-beta dual bed and (d) InCo + Zn-beta mixed bed. ‘C’ denotes proportion of olefin with carbon number ‘N’ in hydrocarbons. Both linear and branched olefins have been summed up in the above results. ‘C’ and ‘iso-C’ denote proportion of linear and branched paraffins of carbon number ‘N’ in the hydrocarbon fraction of products respectively. ‘Oxygenates’ denotes cumulative proportion of methanol and dimethylether among hydrocarbons.
Figure S2: XRD patterns of zeolite beta and Zn modified beta (Cu Kα emission)

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Figure S7: FTIR spectra of the unmodified and Zn-impregnated zeolite beta after exposure to pyridine with bands at 1545 cm$^{-1}$ and at 1456 cm$^{-1}$ characterizing Brønsted and Lewis acid sites respectively.

Figure S8: Ethane + propane proportion among hydrocarbons for a) InCo + plain beta and b) InCo + Zn-beta.
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**Figure S10:** Ethylene hydrogenation over the InCo catalyst. Experiment carried out at 300 °C, 30 bar, C$_2$H$_4$:H$_2$ ratio of 1:4 and GHSV of 15000 ml·gcat$^{-1}$·h$^{-1}$
Figure S11: CO$_2$ hydrogenation carried out over (a) InCo catalyst and (b) InCo-Zn catalyst. Experiment carried out at 300 °C, 50 bar, CO$_2$:H$_2$ ratio of 1:4 and GHSV of 15000 ml·g$_{cat}$·h$^{-1}$. X(CO$_2$) denotes conversion of CO$_2$, S(CO), S(MeOH) and S(C$_1$) denote selectivities of CO, methanol and methane respectively.
## Supplementary Tables

**Table S1: Catalytic performance comparison of our catalyst with the state of the art**

| Ref. | Catalyst used | Temperature (°C) | Pressure (bar) | GHSV (ml·g_{cat}^{-1}·h^{-1}) | H₂:CO₂ | CO₂ conversion (%) | HC distribution iso-C₄-C₇ (%)\(^a\) |
|------|---------------|------------------|----------------|-------------------------------|--------|-------------------|----------------------------------|
| [1]  | Na-Fe₃O₄/HZSM-5 | 320              | 30             | 4000                          | 3      | 33.6              | ~18.0                            |
| [2]  | Na-Fe₃O₄/Hbeta | 320              | 30             | 4000                          | 2      | 25.8              | ~56.5                            |
| [2]  | Na-Fe₃O₄/HMCM-22 | 320             | 30             | 4000                          | 2      | 25.9              | ~50.5                            |
| [3]  | Fe-Zn-Zr/HY   | 360              | 50             | 3000                          | 3      | 17.2              | 38.0\(^b\)                        |
| [4]  | Fe-Zn-Zr@HZSM-5-Hbeta | 340         | 50             | 4500                          | 3      | 14.9              | 81.3                             |
| [5]  | NaFe/SAPO-11/ZSM5 | 320            | 30             | ~3700                         | 3      | 31.2              | ~27.4\(^c\)                      |
| [6]  | Fe-Zn-Zr@HZSM-5 | 340              | 50             | 3000                          | 3      | 18.0              | ~53.9\(^d\)                      |
|      | This work     | 300              | 50             | 7500                          | 4      | 16.0              | ~70.0                            |
|      | This work     | 300              | 50             | 7500                          | 4      | 16.9              | ~85.0                            |

\(^a\)Hydrocarbon distribution of branched alkanes ranging from iso-butane to isomers of heptane.

\(^b\)HC distribution for iso-C₄ only. HC distribution for iso-C₅-C₇ not provided

\(^c\)HC distribution for iso-C₅-C₁₁. Detailed product distribution not provided.

\(^d\)HC distribution for iso-C₅⁺. Detailed product distribution not provided.

## Supplementary XAS details

### Co K-edge XANES spectra results and discussion

Co K-edge XANES spectra were recorded under air at RT and 1 bar pressure, under He flow at RT and 1 bar pressure, under He flow at 300 °C and 50 bar pressure, and finally a CO₂:H₂ flow (1:4) at 300 °C and 50 bar pressure. The data presented in Figure S12 for InCo + beta and InCo + Zn-beta catalysts are presented as full line and short dots, respectively. The spectra for each
catalyst are perfectly superimposed for all experimental conditions which imply that there is no effect of the bed configuration regarding the structure of the InCo catalyst. In air, the Co K-edge spectrum displays a weak peak in the pre-edge region due to the 1s → 3d quadrupolar transitions and an intense white line characteristic of an oxidized state of Co in octahedral environments. [7-8] Comparison with cobalt oxide standards regarding the pre-edge energy position and the absorption threshold energy also suggests that Co is mainly in its +II oxidation state (Figure S21a).

Further qualitative assessment of the FT-EXAFS spectra (not corrected for the phase shift) for cobalt oxide standards shows a main peak at about 1.5 Å attributed to Co-O scattering paths and several peaks between 2.5 and 6 Å assigned mainly to Co-Co paths with some minor contributions from Co-O scattering and some multiple scattering processes (Figure S21b). In contrast, the FT-EXAFS spectrum of InCo catalyst show one peak centred around 1.5 Å for Co-O scattering paths and another weak peak at 2.5 Å assigned either to Co-In or Co-Co scattering paths (Figure S21b). The lack of contribution from more distant coordination is associated with a limited long-range order and is consistent with our former study of this catalytic system [9].

After the InCo catalyst is brought into contact with He at room temperature, the pre-edge is significantly modified, and its shape approaches that observed for the metallic state of Co. This last observation is also consistent with the simultaneous decrease in the white line intensity which indicates a partial reduction of the Co atoms. Increasing the He pressure to 50 bar and the temperature to 300 °C had almost no noticeable effect. But switching to CO₂ hydrogenation conditions (T = 300 °C, P = 50 bar, CO₂:H₂ = 1:4) further amplifies the previous spectral trends and advances the reduction of the InCo catalyst. In this instance, prior knowledge of the relevant phases gained during our previous ex-situ study, allowed us to carry out a successful linear combination fitting of the XANES data. [9] Those are the Co₃InC₀.₇₅ phase, a CoOₓ amorphous phase, and the metallic Co phase. For the CoOₓ phase we simply used the spectrum corresponding to the initial state of the InCo catalyst (in the air). For the metallic Co phase we selected a spectrum recorded previously for metallic Co nanoparticles (5-6 nm) distributed on a ZrO₂ support. [10] Indeed, a nanoparticle system is more representative of the metallic component in the InCo catalyst than a bulk metal counterpart. After 24 h of reaction, the InCo catalyst contains mainly Co⁰ NPs (~ 63%), amorphous CoOₓ (~29%) and a small amount of Co₃InC₀.₇₅ carbide (~8%) (Figure S12b). The lasting presence of CoOₓ in spite of the high hydrogen partial pressure is related to surface
oxidation of the metallic Co under reaction conditions, as already elucidated with transmission electron microscopy observations. [9]

**Figure S12:** (a) Evolution of the operando Co K-edge XANES spectra of the InCo + beta (mixed bed shown as solid lines) and InCo + Zn-beta (dual bed, shown as short dots) catalysts after dehydration under He \((T = [25, 300] \, ^{\circ}C, \, P = [1, 50] \, \text{bar}, \, \text{pure He})\), and after 20 hours of CO2 hydrogenation \((T = 300 \, ^{\circ}C, \, P = 50 \, \text{bar}, \, \text{CO2:H2} = 1:4)\). (b) Linear combination fit of the Co K-edge XANES spectrum of the InCo + beta (mixed bed) catalyst. The modeling was done using XANES spectra of Co\(^0\) NPs, amorphous CoO\(_x\) and Co\(_3\)InC\(_{0.75}\). The contributions of the individual phases as well as the fit (blue lines) are plotted together with the original data (blue open circles).

**Geometry optimization for structural models representing Zn sites**

First-principles calculations were performed for periodic structure with CASTEP code (Cambridge Sequential Total Energy Package, CASTEP Developers’ Group, Cambridge, UK) code [11], which employs pseudopotentials [12] to describe electron-ion interactions and represents electronic wave functions using a plane-wave basis set, based on density functional theory (DFT). [13] The exchange-correlation energy of many-electron systems is described by the generalized gradient approximation (GGA) with the parametrization of Perdew-Burke-Ernzerhof (PBE) method. [14] Brillouin zone sampling was restricted to the Γ-point. Using OTFG ultrasoft pseudopotentials, an energy cut-off of 571.4 eV for the plane wave expansion was selected with a convergence criteria for the total energy of \(1 \times 10^{-3} \, \text{meV/atom level}\). The dispersive interactions were taken into account using the D3 method by Grimme et al. [15].
The aim of the DFT calculations is to provide relevant atomic coordinates for the subsequent analysis of the XANES and EXAFS spectroscopies data. Our efforts are focused on the investigation of the dehydrated state of the Zn-beta catalyst. The tetragonal cell of BEA (polymorph A) was selected for the periodic calculations. The bulk cell parameters and initial ionic positions were obtained from the International Zeolite Association database [16]: \( P4_122_1 \) (91), \( a = 12.6320 \text{ Å}, b = 12.6320 \text{ Å}, c = 26.1860 \text{ Å}, \alpha = \beta = \gamma = 90.000^\circ \). In the tetragonal cell, there are 9 non-equivalent metal sites labelled as T-sites for a total of 64 metal atoms. The pore system of the beta zeolite is three-dimensional with straight 12-ring channels parallel to \( a \) and \( b \) (Figure S1 1). Isomorphous substitution of a Si with an Al cation results in formation of a local negative framework charge, which is compensated with an exchanged cation or proton and consequently removes the crystal symmetry (\( P1 \)). The Al occupation of the individual T-sites is described when it’s relevant with a reference to the individual rings of the BEA zeolite framework (4-MR, 5-MR, 6-MR, Figure S13).

![Figure S13: Visualization of the 12-ring pore channel and the general framework structure of the BEA polymorph A viewed along [010] and [001]. The structure is drawn as straight lines connecting adjacent T-sites (oxygen lies near to the midpoints of each of the T-T vectors).](image)

Several families of Zn structures were geometry optimized and were all inspired by former published studies involving various site in zeolite frameworks. [17-30] All cells were fully optimized until all the forces were smaller than 0.1 eV/Å. Considering the elemental analysis (Si/Al \( \approx 22 \)) of zeolite beta used in this work, an average of \( \sim 3 \) aluminium atoms per unit cell is expected which is a relatively low Al density. Since having two Al sites in close proximity seems unlikely at first glance and XANES spectroscopy indicate the presence of Zn\(^{2+}\), the charge
compensation can be envisaged through the binding of a single hydroxyl ligand to the Zn centre and a negative charge created by an Al substitution on a T-site and localized on the coordinating oxygen atoms. Hence, the first family of Zn structure consists of substituting each single T-site (T1-T9) with an aluminium atom and having the corresponding Zn atom and its hydroxyl ligand pointing towards the centre of the 12-ring pore (as initial coordinate prior to geometry optimisation). Those relaxed Zn species are shown and labelled on Figure S14 as 1Al[Tx] with Tx being the position of the aluminium atom with respect to the T-site label of the original BEA framework.
Figure S14: Visualization along [010] direction of the BEA framework for all 1Al[Tx] Zn species. Those Zn species are labelled as 1Al[Tx] with Tx the position of the aluminium atom in respect to the T-site label of the original BEA framework. The main framework is drawn as straight lines connecting adjacent T-sites (oxygen lies near to the midpoints of each of the T-T vectors) while the atoms and bonds involved in the local order around the Zn centre are drawn as ball and stick. Atom colour code as follows: Zn, blue; H, white; O, red; Al, pink; Si, yellow.

A similar type of structure was also proposed by the research group at Torino university with a [Zn(OH)] species stabilized in the 5-membered ring (5-MR) of the ZSM-5 framework structure (Si/Al = 15 and 40 with Zn loading ranging from 0.7 to 1.9 wt.%). [21] They identified with a DFT-assisted EXAFS fitting methodology that the metal centre adopts a highly distorted pseudotetrahedral coordination with the hydroxyl ligand pointing towards the centre of the 10-MR. For the present beta zeolite, we have also optimized the geometry of [ZnOH] species where the Zn centre is initially nesting in middle of the four-, five- and six-membered rings available in the pore channel. The resulting structures are drawn on Figure S15 and labelled as y-MR-1Al[Tx] with y-MR the type of membered-ring and Tx the position of the aluminium atom in respect to the T-site label in the original BEA framework.
**Figure S15**: Visualization along [010] direction of the BEA framework for all y-MR-1Al[Tx] Zn species. Those Zn species are labelled as y-MR-1Al[Tx] with y-MR the type of membered-ring position and Tx the position of the aluminium atom in respect to the T-site label in the original BEA framework. The main framework is drawn as straight lines connecting oxygen atoms and T-sites while the atoms and bonds involved in the local order around the Zn centre are drawn as ball and stick. Atom colour code as follows: Zn, blue; H, white; O, red; Al, pink; Si, yellow.

Even if the number of aluminium atoms per unit cell is on average rather low (~3), it is still possible to have different local concentration of Al/Si substitutions. For the three types of rings in the BEA framework there are several combinations possible for the two aluminium substitutions following the Löwenstein's rule. [31] In those Zn structures, the presence of the hydroxyl ligand is not required anymore since the BEA framework is now bearing two negative charges. We have optimized the geometry of the most relevant combinations of Al substitution with the Zn atoms initially sitting in the middle of the 4-MR, 5-MR and 6-MR ring type. The resulting relaxed structures are drawn on Figure S16-S18 and labelled as y-MR-2Al[Tx-Tx] with y-MR the type of membered-ring position and Tx the position of the aluminium atom with respect to the T-site label in the original BEA framework. Note also that some structures are labelled with an additional “-Zn” which denote a structure where only the position of the Zn atom was relaxed while the atoms included in the BEA framework were kept frozen. This is because two studies dealing with XANES calculations have shown that the long range order of the crystalline host can build sometimes a better average of the local structure around dopants compared to fully relaxed structural models. [32-33]
**Figure S16:** DFT-optimized geometry of 4-MR-2Al[Tx-Tx] structures as potential local environments of the Zn$^{2+}$ sites. Structure labelled with an additional “-Zn” which denote a structure where only the position of the Zn atom was relaxed while the atoms included in the BEA framework were kept frozen. Atom colour code as follows: Zn, blue; H, white; O, red; Al, pink; Si, yellow.

**Figure S17:** DFT-optimized geometry of 5-MR-2Al[Tx-Tx] structures as potential local environments of the Zn$^{2+}$ sites. Structure labelled with an additional “-Zn” which denote a structure where only the position of the Zn atom was relaxed while the atoms included in the BEA framework were kept frozen. Atom colour code as follows: Zn, blue; H, white; O, red; Al, pink; Si, yellow.
Since zeolite beta is particularly known by crystallographers for its stacking faults [34-35], we have also investigated the case where the Zn species condense during calcination via hydroxyl groups available on the crystalline defects. For the geometry optimisation, this is materialised by the substitution of a silicon atom from a T-site by a Zn atom together with the adjunction of two protons on neighbouring oxygen atoms. For each Zn substitution on the nine T-sites, there is a combination of six possible $\mu_2$-OH position, which make a grand total of 54 structures to calculate. To limit the consumption of calculation resources, we have considered arbitrarily only the Zn substitution on the T4 site which is located at the intersection of two 12-ring pore channels. The resulting relaxed structures are drawn on Figure S19 and labelled as Zn[T4]-2OH[Tx-Tx] with Tx corresponding to the T-site connected directly to the bridging hydroxyls.
Figure S19: DFT-optimized geometry of Zn[T8]-2OH[Tx-Tx] structures as potential local environments of the Zn\(^{2+}\) sites. The main framework is drawn as straight lines connecting oxygen atoms and T-sites while the atoms and bonds involved in the local order around the Zn centre are drawn as ball and stick. Atom colour code as follows: Zn, blue; H, white; O, red; Al, pink; Si, yellow.

Finally, we have explored more complex cases where the Zn loading is considered as relatively high compared to the aluminium content (Zn/Al >1) (Figure S20). The first possibility is to build (Zn-O)\(_n\) chains between two cation-exchange sites. In this work, we only relaxed the dimeric and trimeric Zn species labelled Zn-O-Zn and Zn-O-Zn-O-Zn, respectively. Next, we optimized the geometry of a Zn\(_9\)O\(_9\) cluster extracted from the ZnO crystal structure that was intentionally a bit too large to fit in the BEA pore channel. The relaxation resulted in a poorly ordered Zn\(_9\)O\(_9\) cluster, and this structural model was labelled as Zn\(_9\)O\(_9\)-1.

During the last decade, theorists have studied the stability and electronic properties of Zn\(_m\)O\(_m\) cluster. [36-40] The most favourable atomic structures of Zn\(_m\)O\(_m\) clusters are all ring types. But the most stable structures are the one involving a Zn\(_3\)O\(_3\) hexagonal ring since the latter is actually a key building block of the zincite hexagonal structure. Following those theoretical studies, we have relaxed a neutral Zn\(_3\)O\(_3\) cluster inserted in the centre of the 12-ring pore channel of a neutral BEA framework (structure labelled as Zn\(_3\)O\(_3\)). We also tried two different initial conditions where
the Zn$_3$O$_3$ ring is positioned in the vicinity of a six membered ring of the BEA framework. Doing so, we obtained two different configurations of the Zn$_3$O$_3$ ring in interaction with the silicon and the oxygen atoms from the BEA framework (labelled as Zn$_3$O$_3$-6-MR-1 and Zn$_3$O$_3$-6-MR-2). Those two structures are very similar to the one proposed by Stepanov et al. in their most recent studies about the role of Zn$^{2+}$ species and ZnO clusters in olefin aromatization. [41] Finally, we have increased the nuclearity of the Zn$_m$O$_m$ cluster up to $m = 6$ and 9. Two orientations of Zn$_6$O$_6$ cluster were relaxed in the 12-ring pore channel labelled as Zn$_6$O$_6$-1 and Zn$_6$O$_6$-2. Note that starting with a position close to the 6-membered ring of the BEA framework resulted in a cluster shifted towards the middle of the pore. It seems that increasing the coordination of the Zn atoms in the ZnO cluster is reducing the interaction with the framework atoms. For the Zn$_9$O$_9$ cluster, a stable position was found when the latter is built from a stack of three Zn$_3$O$_3$ rings with their vertical axis aligned with a 12-ring pore channel (labelled as Zn$_9$O$_9$-2).

**Figure S20:** DFT-optimized geometry of dimeric, trimeric zinc oxide structures and Zn$_m$O$_m$ clusters ($m = 3, 6, 9$) as potential local environments of the Zn$^{2+}$ sites. The main framework is drawn as straight lines connecting oxygen atoms and T-sites while the atoms and bonds involved in the local order around the Zn centre are drawn as ball and stick. Atom colour code as follows: Zn, blue; H, white; O, red; Al, pink; Si, yellow.
**Figure S21**: Co K-edge XANES spectra (a), EXAFS $k^2 \chi(k)$ functions (b) and their related Fourier transforms (c) for CoO, Co$_3$O$_4$, Co(OH)$_2$ references and the InCo + beta catalyst as-synthesized. The spectrum of the Co(OH)$_2$ standard was downloaded from the Farrel Lytle database (http://ixs.iit.edu/database/index.html).

**Figure S22**: Zn K-edge XANES for a [Zn(H$_2$O)$_6$]$^{2+}$ solution, Zn(NO$_3$)$_2$·6 H$_2$O, ZnO, Zn$^0$ references and the InCo + beta catalyst as-synthesized and dehydrated at 300 °C, under He flow using a pressure of 50 bar. The spectrum of the [Zn(H$_2$O)$_6$]$^{2+}$ solution is provided as a kind courtesy of E. Borfecchia et al. [21]
Table S2: Parameters extracted for a first shell analysis of the EXAFS data for the ZnO standard and the Zn-beta catalyst in air, after dehydration under He (T = [25, 300] °C, P = [1, 50] bar, pure He), and after 20 hours of CO₂ hydrogenation (T = 300 °C, P = 50 bar, CO₂:H₂ = 1:4). Underlined number denotes a fixed parameter.

| Sample                   | Scattering Paths | N  | R [Å]    | σ² [Å²] | ΔE [eV] | R-factor [%] |
|--------------------------|------------------|----|----------|---------|---------|--------------|
| ZnO (S_o² = 0.87 ± 0.09)| Zn-O             | 4  | 1.97 ± 0.04 | 0.004 ± 0.001 | 4 ± 1 | 0.1          |
| Air-RT-1 bar             | Zn-O             | 5.2 ± 0.3 | 2.005 ± 0.006 | 0.010 ± 0.001 | 1.7 ± 0.6 | 0.08         |
| He-RT-1 bar              | Zn-O             | 3.6 ± 0.2 | 2.001 ± 0.006 | 0.0078 ± 0.0005 | 1.8 ± 0.4 | 0.03         |
| He-300°C -50 bar         | Zn-O             | 2.66 ± 0.09 | 1.959 ± 0.004 | 0.0079 ± 0.0006 | 1.7 ± 0.4 | 0.04         |
| CO₂:H₂-300°C-50 bar      | Zn-O             | 2.8 ± 0.1 | 1.962 ± 0.004 | 0.0079 ± 0.0006 | 1.7 ± 0.4 | 0.04         |

Figure S23: (a) Magnitude of the Fourier transform for the EXAFS k²χ(k) functions acquired at Zn K-edge for ZnO and the Zn-beta catalyst in air, after dehydration under He (T = [25, 300] °C, P = [1, 50] bar, pure He), and after 20 hours of CO₂ hydrogenation (T = 300 °C, P = 50 bar, CO₂:H₂ = 1:4), and (b) their related back Fourier transforms (imaginary part) applied within their respective R-range for EXAFS fitting. Open circles represents experimental data whereas solid line corresponds to fit results conducted with [1.1–2.2] Å as R-range and with [3–11] Å⁻¹ as k-range.
Figure S24: Experimental (open circles) and calculated by RMC/EA (solid line) Zn K-edge FT-EXAFS spectra for various structural models optimized by DFT: Zn$^{2+}$ cations exchanged on 4-, 5-, and 6-membered rings of the BEA framework, Zn$^{2+}$-OH species, framework Zn$^{2+}$ species located on T-site, dimeric and trimeric Zn oxide and zinc oxide clusters, (cf. Figure S12-S18 for the visualisation of the structural models).
Figure S25: Radial distribution functions (RDFs) calculated from the coordinates of atoms for the best structural models fitting the experimental EXAFS spectra of the Zn-beta (mixed bed) catalyst after dehydration under He ($T = 300 \, ^\circ C$, $P = 50$ bar).
Figure S26: Comparison of the experimental and theoretical spectra calculated with the FDMNES code at Zn K-edge for Zn⁰, ZnO, ZnS, ZnSO₄·7 H₂O, ZnCO₃ and Zn(NO₃)₂·6 H₂O. Apart from the Zn and ZnO standards that were measured at SAMBA beamline, all others spectra were downloaded from the X-ray absorption data library from IXAS. [https://xaslib.xrayabsorption.org/]
Figure S27: Theoretical XANES spectra calculated at Zn K-edge for various structural models optimized by DFT: Zn$^{2+}$ cations exchanged on 4-, 5-, and 6- membered rings of the BEA framework, Zn$^{2+}$-OH species, framework Zn$^{2+}$ species located on T-site, dimeric and trimeric Zn oxide and zinc oxide clusters, (cf. Figures S12-S18 for the visualisation of the structural models).
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