

Gas-phase oxidative dehydrogenation of long chain alkenols for the production of key fragrances ingredients: from Rosalva isomers to Costenal analogues

Jacopo De Maron,^a Tommaso Tabanelli,^{*a} Francesca Ospitali,^a Carlos Lopez Cruz,^b Paolo Righi^a and Fabrizio Cavani^{*a}

^a *Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum - Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy.*

^b *IFF Benicarló S.L., Avenida Felipe Klein 2, 12580 Benicarló, Spain.*

Chapter S1: detailed description of CO₂-TPD, NH₃-TPD and TPR

All experiments were carried out on 0.2 g of sample using a Micromeritics Autochem II 2920 instrument equipped with a TCD detector.

S1.1: CO₂-TPD

The sample was heated up from room temperature to calcination temperature at a rate of 10 °C/min in a flow of pure He (30 mL/min) to clean surface of the material from physisorbed and chemisorbed molecules. The final temperature was kept for 60 min. After cooling down to 40 °C in a pure He flow (30 mL/min), the chemisorption of CO₂ was carried out by flowing a 10% CO₂/He mixture (30 mL/min) for 60 minutes. After the chemisorption, the sample was flown with pure He (30 mL/min) for 60 min to remove the weakly physisorbed probe molecules. Finally, the temperature programmed desorption was carried out by heating the sample from 40 °C up to calcination temperature at a rate of 10 °C/min in a flow of pure He (30 mL/min); the final temperature was kept for 60 minutes. In order to remove any traces of water before the TCD detector, the effluents from the samples were flown through an empty trap immersed in ethylene glycol cooled down to around -60 °C with liquid N₂.

S1.2: NH₃-TPD

The sample was heated up from room temperature to calcination temperature at a rate of 10 °C/min in a flow of pure He (30 mL/min) to clean surface of the material from physisorbed and chemisorbed molecules. The final temperature was kept for 60 min. After cooling down to 100 °C in a pure He flow (30 mL/min), the chemisorption of NH₃ was carried out by flowing a 10% NH₃/He mixture (30 mL/min) for 20 minutes. After the chemisorption, the sample was flown with pure He (30 mL/min) for 60 min to remove the weakly physisorbed probe molecules. Finally, the temperature programmed desorption was carried out by heating the sample from 100 °C up to calcination temperature at a rate of 10 °C/min in a flow of pure He (30 mL/min); the final temperature was kept for 60 minutes. In order to remove any traces of water before the TCD detector, the effluents from the samples were flown through trap filled with soda lime and kept at room temperature.

S1.3: TPR

The sample was heated up from room temperature to calcination temperature at a rate of 10 °C/min to clean surface of the material from physisorbed and chemisorbed molecules by flowing a 5 % O₂/He mixture (30 mL/min). The final temperature was kept for 60 min. After cooling down to 50 °C in a pure He flow (30 mL/min), the sample was flown with a 5% H₂/Ar mixture (50 mL/min) for 30 minutes to allow stabilization of the TCD detector signal. Then, the sample was heated up from 50 °C to calcination temperature at a rate of 10 °C/min and the final temperature was kept for 60 min. In order to remove any traces of water before the TCD detector, the effluents from the samples were flown through trap filled with a 3Å molecular sieve and kept at room temperature.

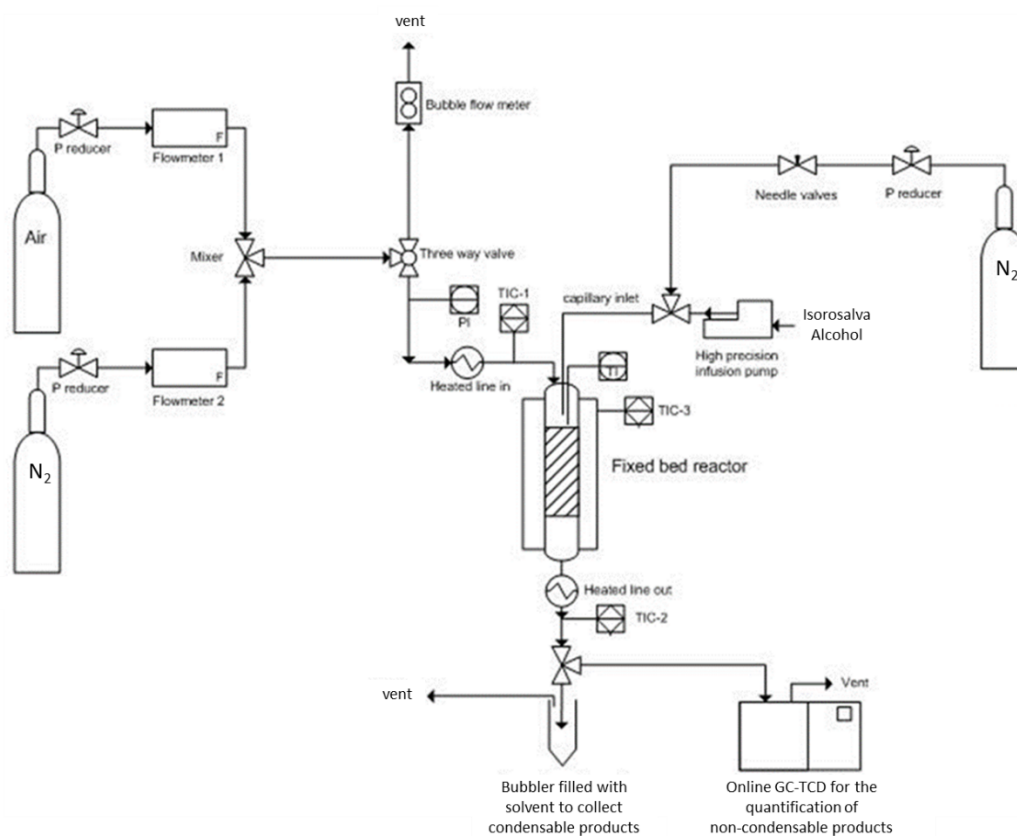


Figure S1: Schematic illustration of the gas-phase plant and the analytical system used to carry out the catalytic tests. Symbols: PI = pressure indicator, F = flowmeter, TIC-1 = temperature controller 1 (N_2 and air inlet), TI = temperature indicator (catalytic bed), TIC2 = temperature controller 2 (reactor outlet), TIC-3 = temperature controller 3 (furnace heating up the reactor).

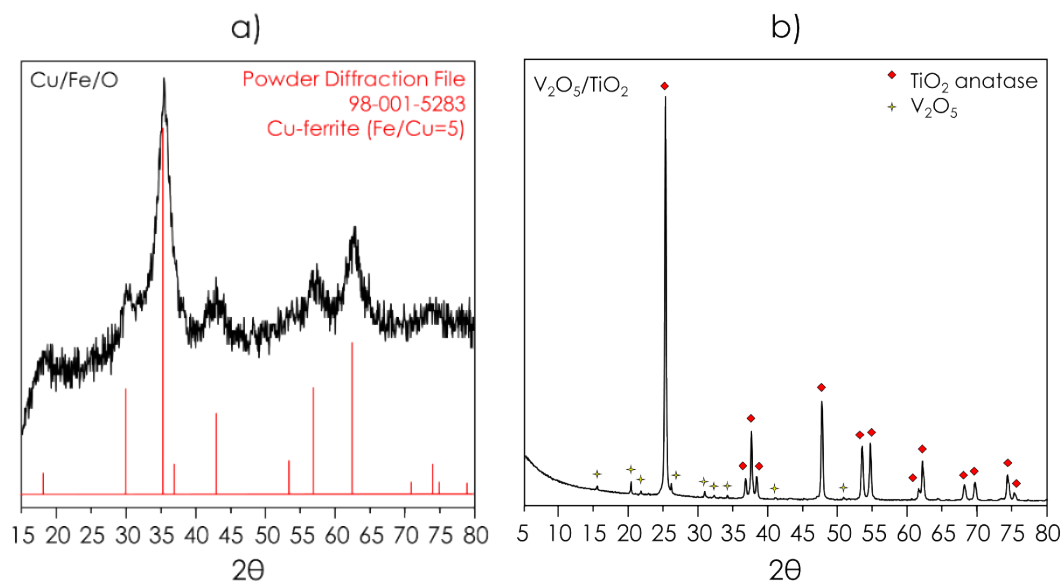


Figure S2: X-ray powder diffraction pattern of a) $Cu/Fe/O$ and b) V_2O_5/TiO_2 .

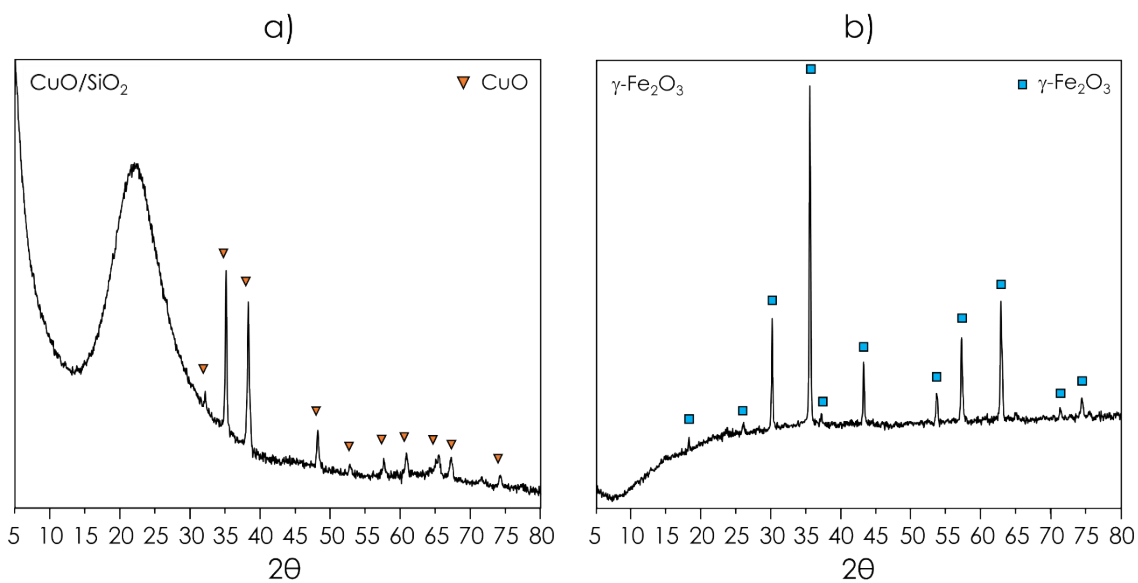


Figure S3: X-ray powder diffraction pattern of a) CuO/SiO₂ and b) γ-Fe₂O₃.

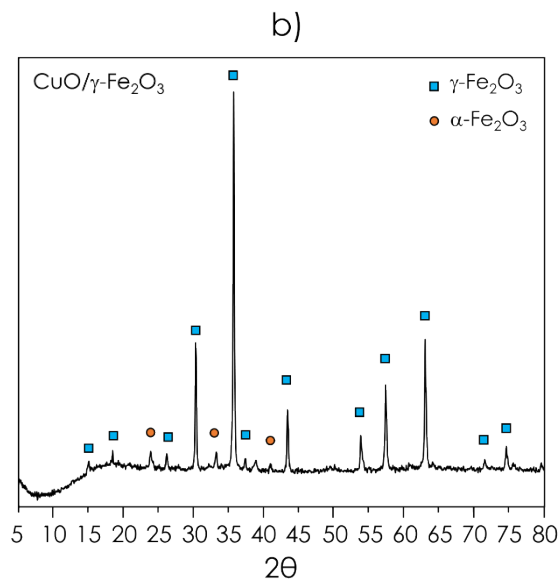


Figure S4: X-ray powder diffraction pattern of CuO/γ-Fe₂O₃.

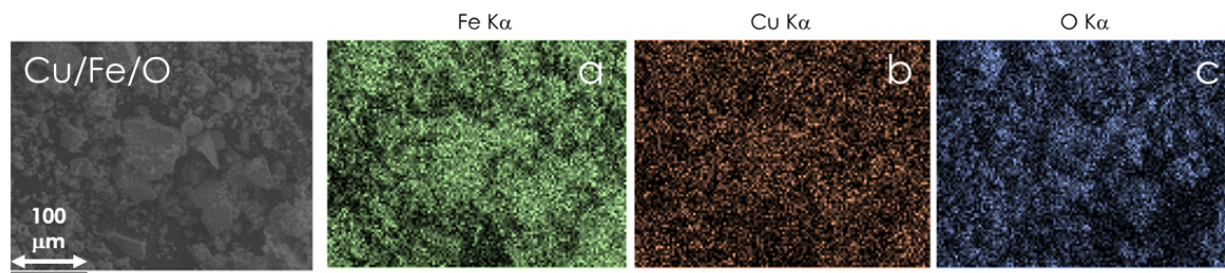


Figure S5: SEM electron image and EDS elemental maps of a) iron, b) copper and c) oxygen for Cu/Fe/O.

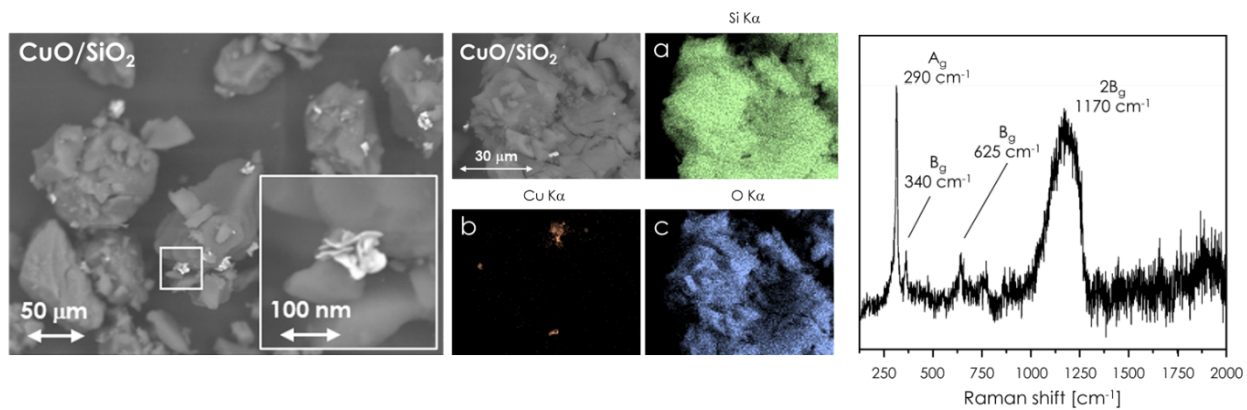


Figure S6: SEM electron image and EDS elemental maps of a) silicon, b) copper and c) oxygen for Cu/SiO₂; Raman spectrum (excitation source diode laser, 785.0 nm) of CuO/SiO₂.

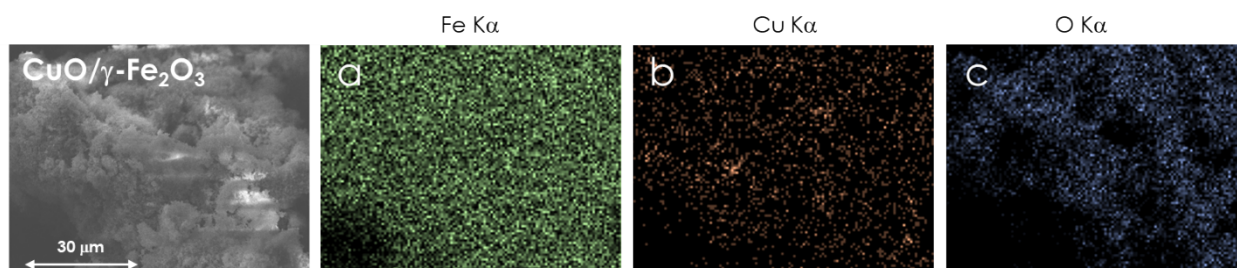


Figure S7: SEM electron image and EDS elemental maps of a) iron, b) copper and c) oxygen for Cu/Fe/O.

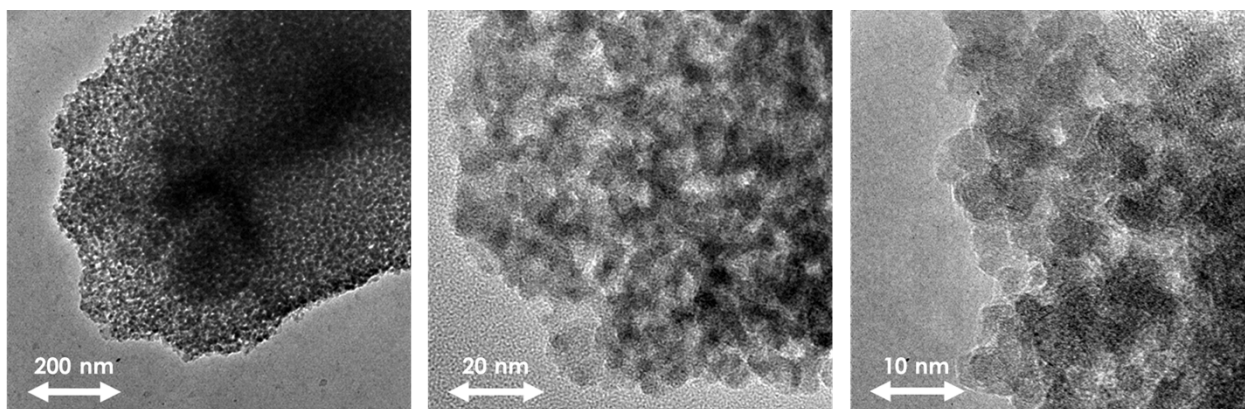


Figure S8: High resolution TEM electron images of Cu/Fe/O.

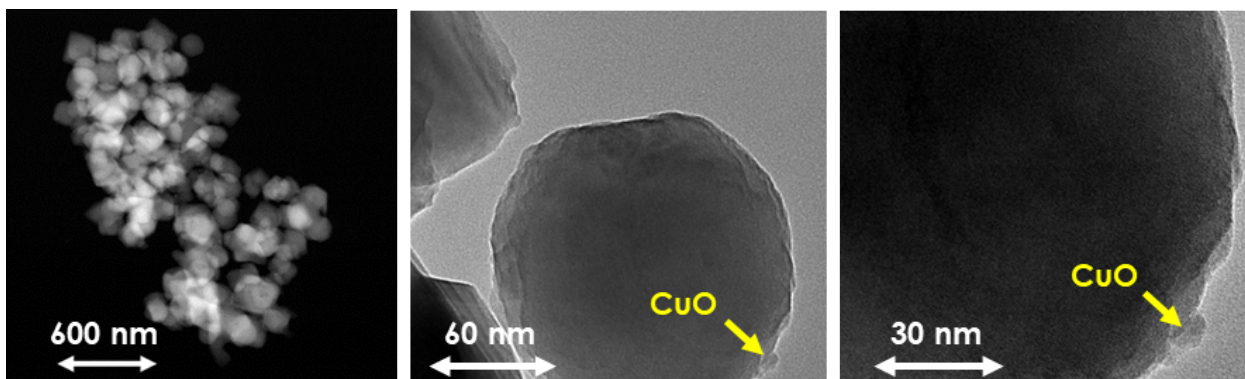


Figure S9: High resolution TEM electron images of CuO/γ-Fe₂O₃.

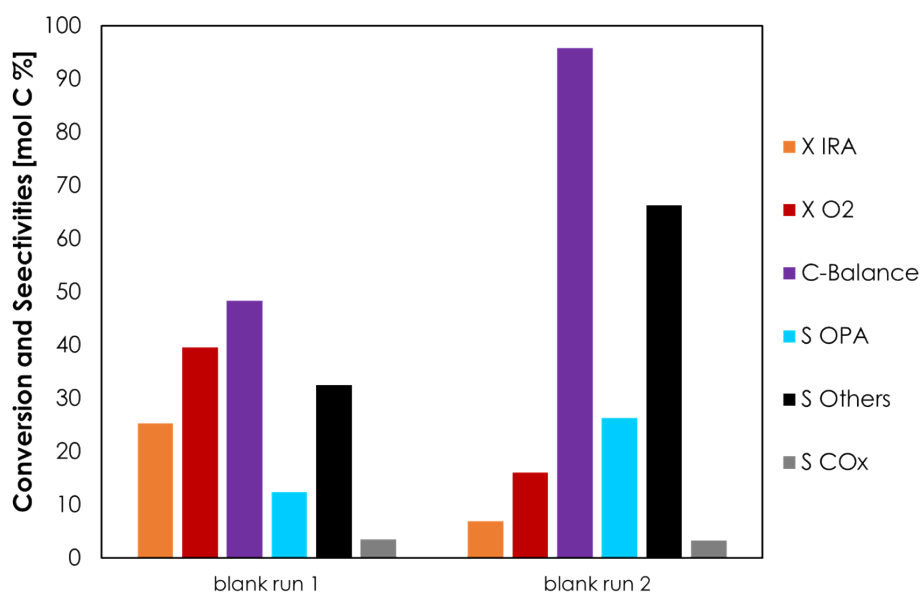


Figure S10: results of the ODH of IRA without catalyst depending on the feeding system. Blank run 1 was carried out by vaporizing IRA in a stainless steel line heated at 250 °C before the reactor; blank run 2 was carried out by feeding IRA directly into the reactor (≈ 5 cm above the catalytic bed) with a thin stainless steel line. Reaction conditions: temperature = 350 °C, IRA/O₂/N₂ = 5/5/90 mol %, contact time = 1 second (assuming a volume of catalyst of 1 cm³). Symbols: Isorosalva Alcohol conversion (X IRA, orange), Oxygen conversion (X O₂, dark red) carbon balance (C-balance, purple), Opalene selectivity (S OPA, light blue), other by-products selectivity (S Others, black) and CO_x selectivity (S CO_x, grey).

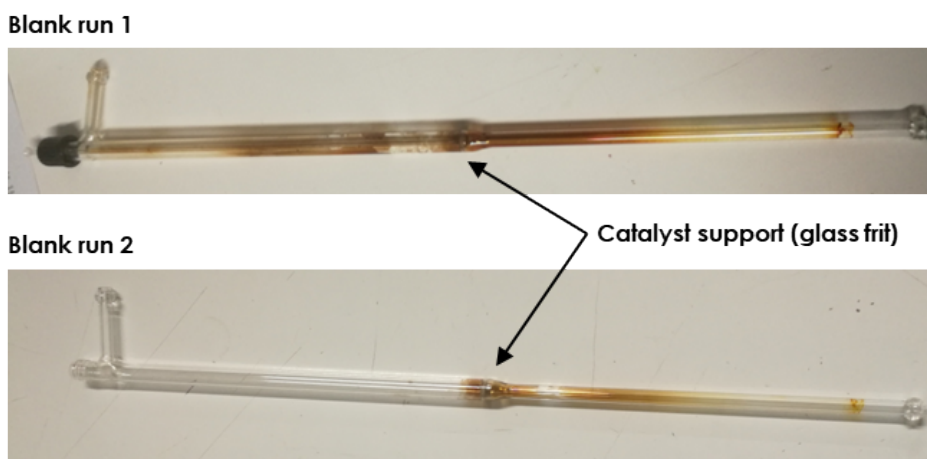


Figure S11: Top: catalytic reactor after blank run 1; Bottom: catalytic reactor after blank run 2.

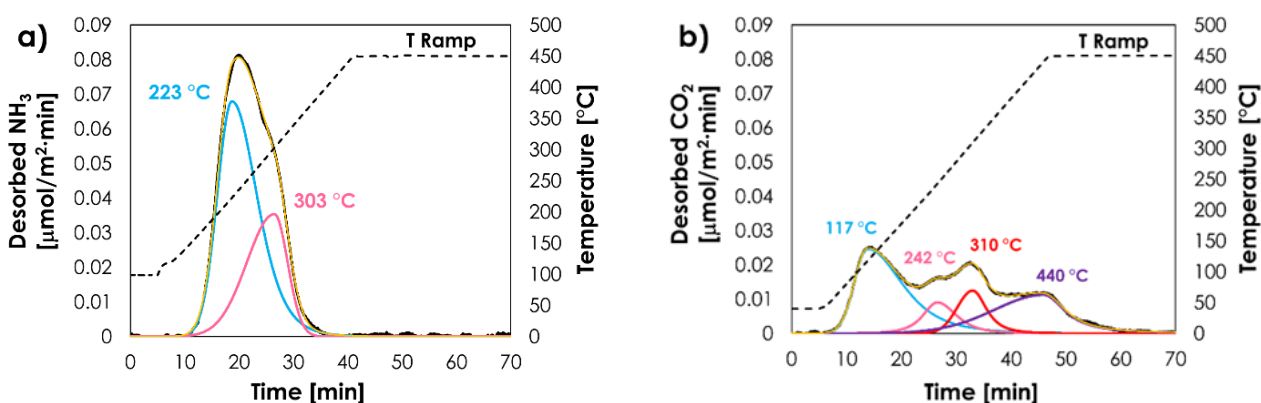


Figure S12: a) Temperature programmed desorption profiles of NH_3 and b) temperature programmed desorption profiles of CO_2 for Cu/Fe/O .

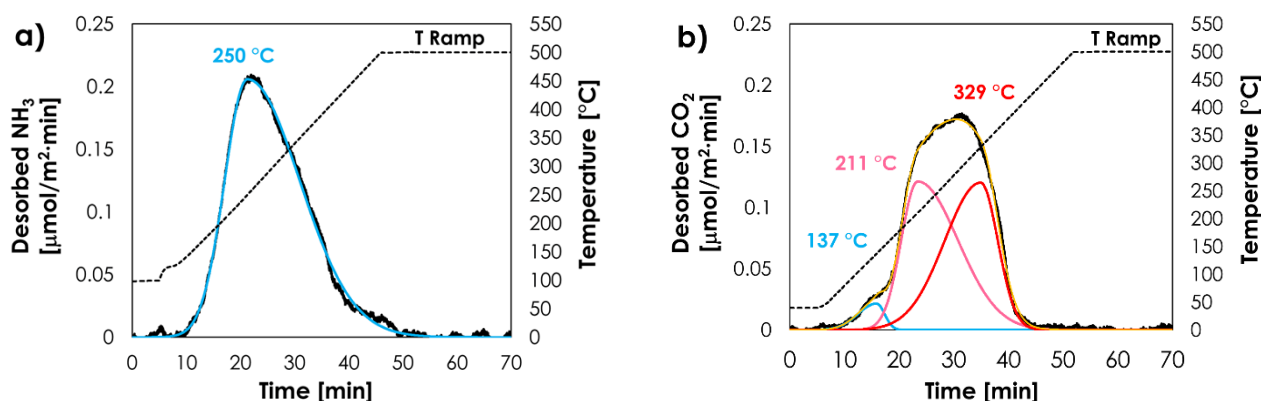


Figure S13: a) Temperature programmed desorption profiles of NH_3 and b) temperature programmed desorption profiles of CO_2 for $\text{V}_2\text{O}_5\text{-TiO}_2$.

Chapter S2: detailed discussion of the TPR characterization of fresh Cu/Fe/O and $\text{V}_2\text{O}_5/\text{TiO}_2$

The TPR profiles for Cu/Fe/O and $\text{V}_2\text{O}_5/\text{TiO}_2$ are shown in Figure S14. The reduction of $\text{V}_2\text{O}_5/\text{TiO}_2$ started around 390°C and continued up to 500°C , when the temperature ramp reached the final isotherm. The temperature range in which the reduction occurred was in good agreement with previous literature [1], reporting that the reduction with H_2 of V^{5+} cations to V^{4+} for $\text{V}_2\text{O}_5/\text{TiO}_2$ materials started around 400°C and continued above 500°C . The H_2 uptake was 0.58 mL (2.8 mL/g), which corresponded to the reduction of one third of the V^{5+} cations to V^{4+} (degree of reduction = 33.6 %). Therefore, the reduction of V_2O_5 to VO_2 was not complete in these conditions.

On the other hand, Cu/Fe/O was more reducible than $\text{V}_2\text{O}_5/\text{TiO}_2$ and its TPR profile displayed three maxima of H_2 consumption at 185 , 218 and 295°C plus a very broad band during the final isotherm. According to literature [2], the CuFe_2O_4 stoichiometric spinel is firstly reduced to Cu(0) and Fe_3O_4 between 190 and 400°C and then the reduction of Fe_3O_4 to Fe(0) occurs in a broad temperature range ($400\text{-}700^\circ\text{C}$). In our case the H_2 uptake until 450°C was 19.9 mL (96 mL/g), that is enough to reduce all Cu^{2+} to Cu(0) and 28.1 % of Fe^{3+} to Fe^{2+} , in good agreement with the theoretical value of 33.3 % required to obtain Fe_3O_4 from Fe_2O_3 .

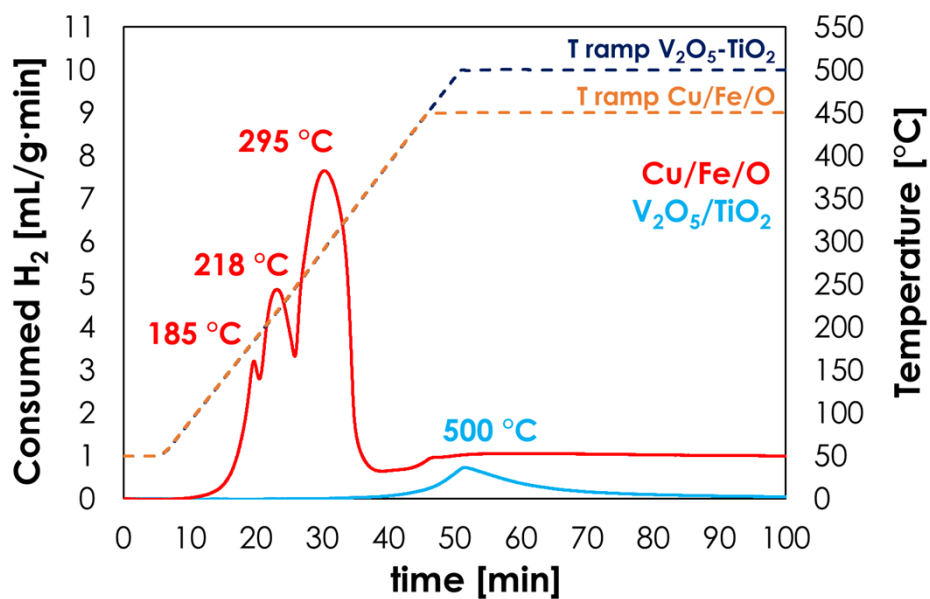
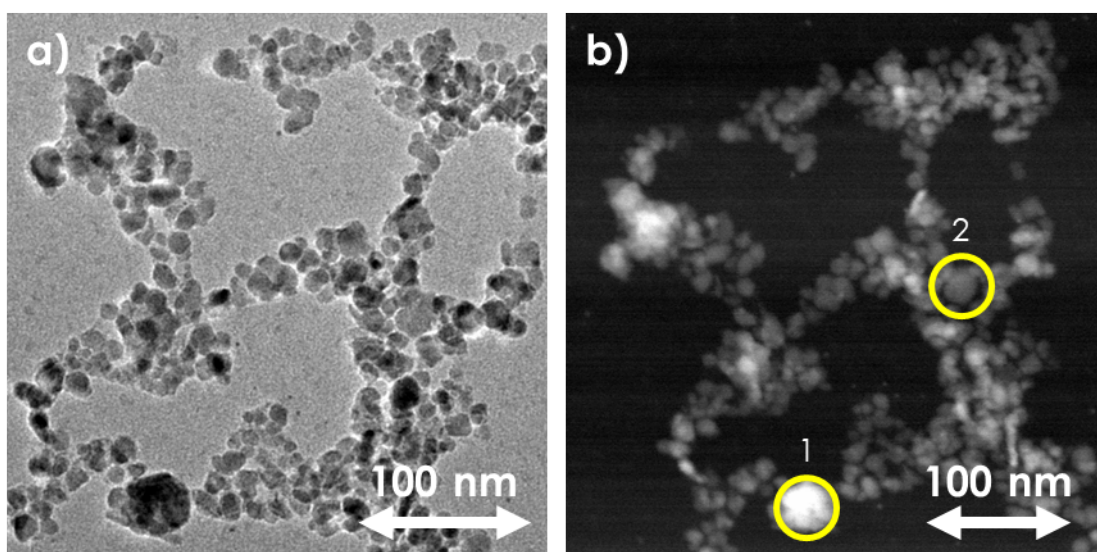


Figure S14: Temperature programmed reduction profiles for Cu/Fe/O (red) and V₂O₅-TiO₂ (light blue).



	O Ka [atom. %]	Fe Ka [atom. %]	Cu Ka [atom. %]	Fe/Cu atom. ratio
1	20.53	1.3	78.1	0.02
2	66.53	31.0	2.4	12.9

Figure S15: TEM images and TEM-EDS microanalysis of Cu/Fe/O-AR: a) High resolution TEM image, b) HAADF-STEM image.

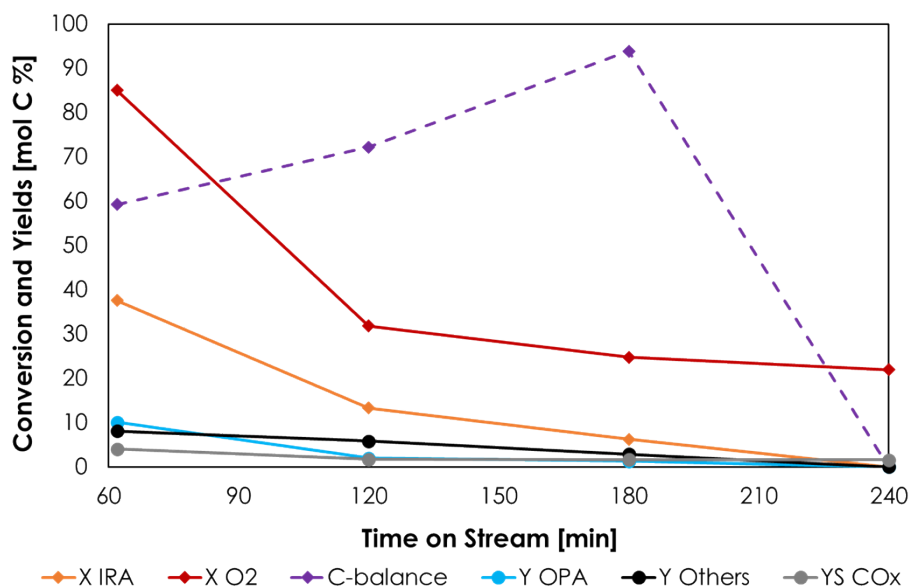
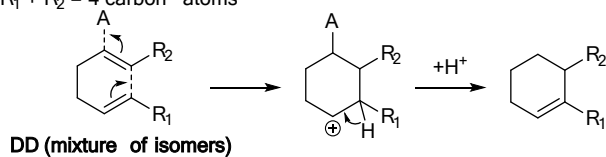
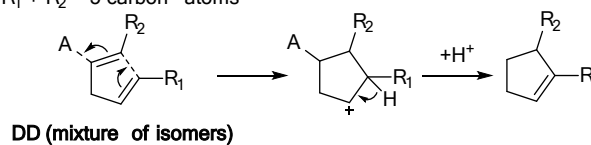


Figure S16: results of the ODH of IRA over $\gamma\text{-Fe}_2\text{O}_3$. Reaction conditions: : volume of catalyst = 1 cm^3 , temperature = $300\text{ }^\circ\text{C}$, IRA/O₂/N₂ = 5/5/90 mol %, contact time = 1 second. Symbols: Isorosalva Alcohol conversion (X IRA, orange), Oxygen conversion (X O₂, dark red) carbon balance (C-balance, purple), Opalene selectivity (S OPA, light blue), other by-products selectivity (S Others, black) and CO_x selectivity (S CO_x, grey).

A = H⁺ or Lewis acidic site
 R₁, R₂ = alkyl groups
 R₁ + R₂ = 4 carbon atoms



A = H⁺ or Lewis acidic site
 R₁, R₂ = alkyl groups
 R₁ + R₂ = 5 carbon atoms



Scheme S1: Proposed mechanism of DD cyclization towards CD over CuO/SiO₂.

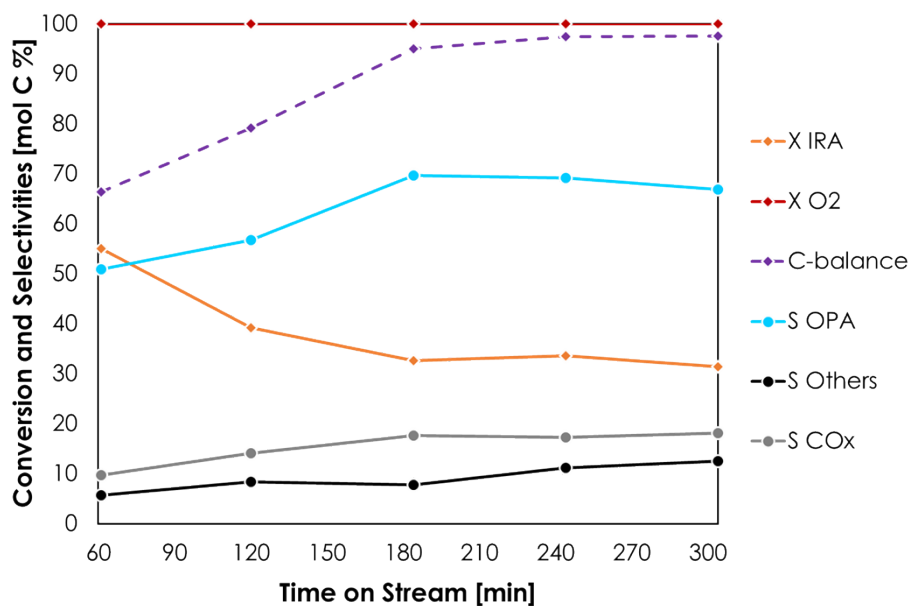


Figure S17: results of the ODH of IRA over CuO/ $\gamma\text{-Fe}_2\text{O}_3$ as a function of the time on stream. Reaction conditions: volume of catalyst = 1 cm^3 , temperature = $300\text{ }^\circ\text{C}$, contact time (τ) = 1 second. Symbols: Isorosalva Alcohol conversion (X IRA, orange), Oxygen conversion (X O₂, dark red) carbon balance (C-balance, purple), Opalene selectivity (S OPA, light blue), other by-products selectivity (S Others, black) and CO_x selectivity (S CO_x, grey).

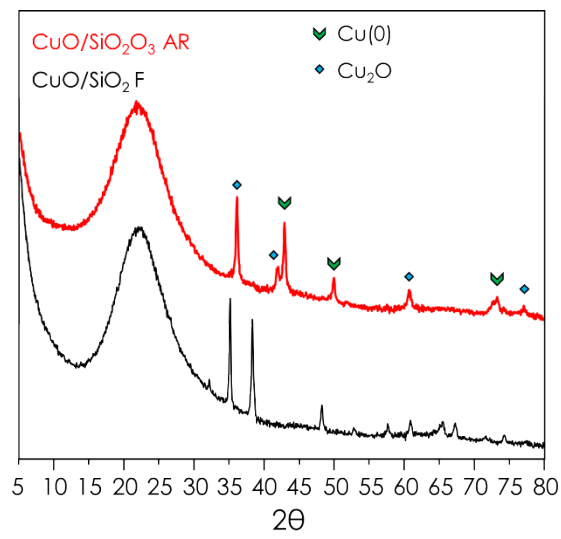


Figure S18: X-ray powder diffraction pattern of a) CuO/SiO_2 fresh (F, black) and after reaction (AR, red).

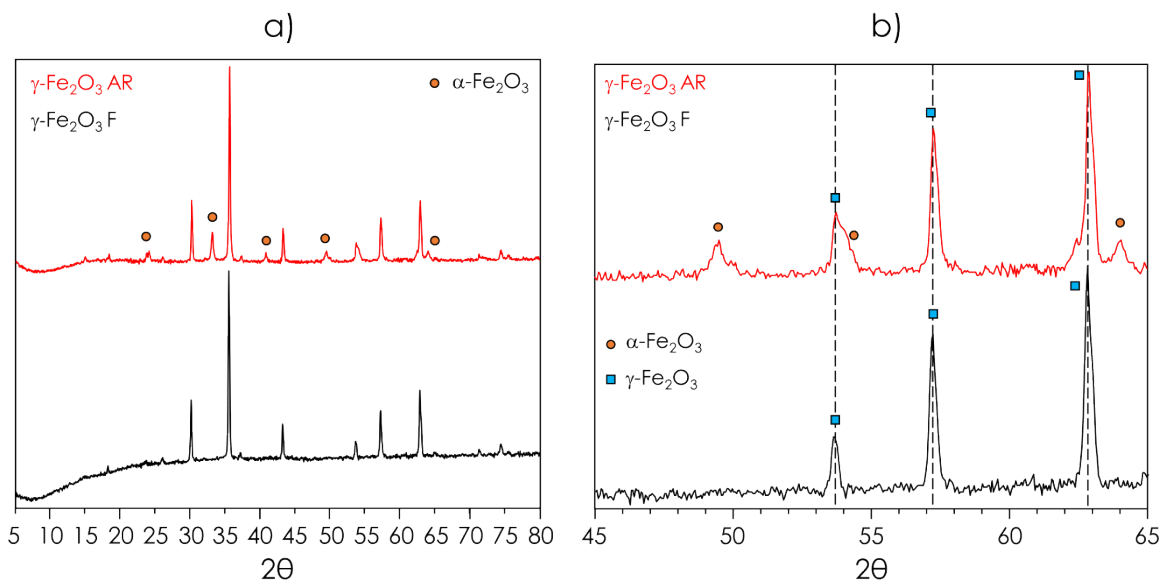


Figure S19: X-ray powder diffraction pattern of $\gamma\text{-Fe}_2\text{O}_3$ fresh (F) and after reaction (AR).

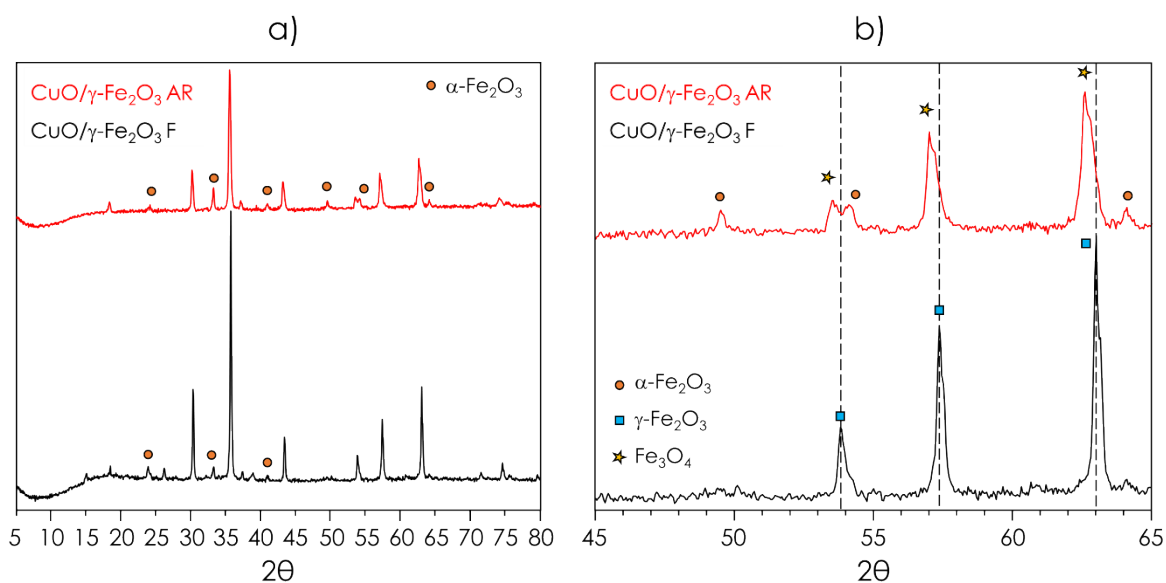


Figure S20: X-ray powder diffraction pattern of CuO/ γ -Fe₂O₃ fresh (F) and after reaction (AR).

Chapter S3: Detailed discussion of the TPR characterization of CuO/ γ -Fe₂O₃, γ -Fe₂O₃ and CuO/SiO₂

The TPR reduction profiles of CuO/SiO₂, CuO/ γ -Fe₂O₃ and γ -Fe₂O₃ are shown in Figure S21. The reduction of CuO/SiO₂ (orange line) started at 200 °C already, with a maximum of H₂ consumption centred at 316 °C, which was in good agreement with the previous results (e.g., the presence of reduced species of copper in the catalyst after the ODH of IRA at 300 °C). On the other hand, γ -Fe₂O₃ (light blue line) was less reducible, and the hydrogen consumption started at a much higher temperature (> 350 °C), with a maximum at 450 °C when the temperature ramp reached the final isotherm.

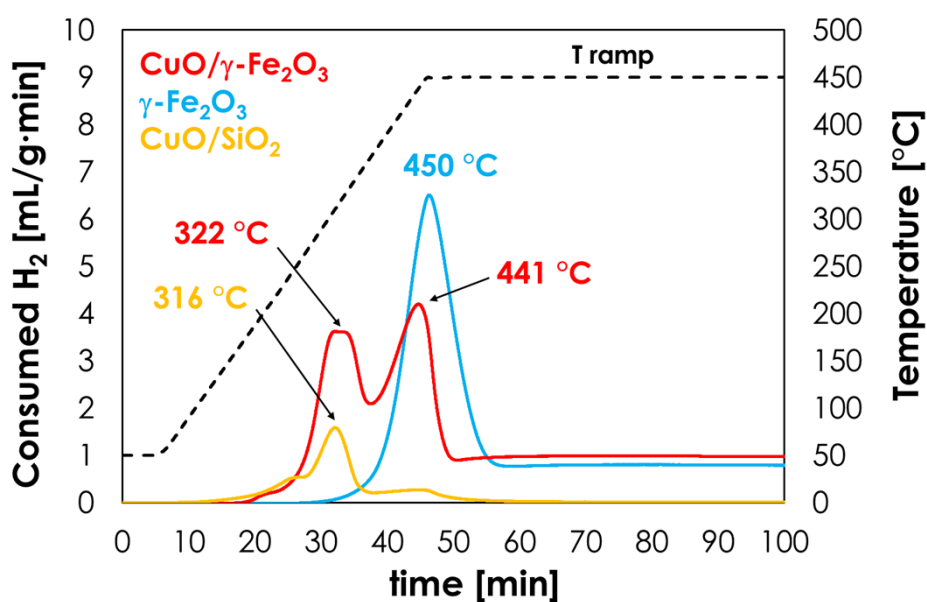


Figure S21: Temperature programmed reduction profiles for CuO/ γ -Fe₂O₃ (red), γ -Fe₂O₃ (light blue) and CuO/SiO₂.

Finally, the TPR profile of CuO/ γ -Fe₂O₃ (red line) was characterized by two maxima of H₂ consumption plus a very broad band during the final isotherm. The first maximum, similarly to CuO/SiO₂, was centred at 323 °C

while the second maximum was centred at 441 °C, similarly to γ -Fe₂O₃ (450 °C). The first consumption corresponded to the reduction of supported CuO to Cu and the second corresponded to the reduction of the support. However, it was found the H₂ uptake calculated integrating the area of the first maximum (322 °C) was 6.4 mL (30.5 mL/g), corresponding to twice the moles of H₂ required to reduce all the supported CuO to Cu(0). Therefore, also a fraction of Fe(III) of the maghemite support, possibly the oxide supporting Cu-species, is reduced at this low temperature. Finally, the total H₂ uptake (peak centred at 322 plus peak centred at 441 °C) was 13.5 mL (64.9 mL/g) and matched very well the theoretical value required to reduce all CuO/ γ -Fe₂O₃ to Cu(0) + Fe₃O₄ (13.2 mL).

Notes and references

- [1] W. Zhang, G. Innocenti, M. Ferbinteanu, E. Ramos-Fernandez, A. Sepulveda-Escribano, H. Wu, F. Cavani, G. Rothemberg e R. Shiju, «Understanding the oxidative dehydrogenation of ethyl lactate to ethyl pyruvate over vanadia/titania,» *Catal. Sci. Technol.*, vol. 8, pp. 3707-3978, 2018.
- [2] Y.-H. Huang, S.-F. Wang, A.-P. Tsai e S. Kameoka, «Reduction behaviors and catalytic properties for methanol steam reforming of Cu-based spinel compounds CuX₂O₄ (X = Fe, Mn, Al, La),» *Ceram. Int.*, vol. 40, pp. 4541-4551, 2014.