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Microwave-driven hydrothermal synthesis of α-Fe_2O_3 nanorings as CeO_2 catalyst support for CO_2 conversion

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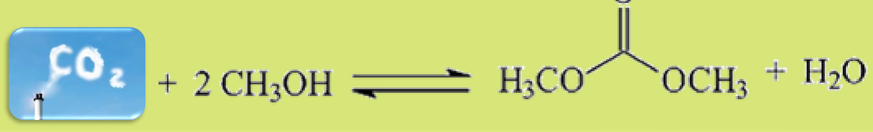
Introduction

- ✓ Hematite (α-Fe_2O_3) is abundant in nature and can present several morphologies, depending on the preparation method;
- ✓ The conventional hydrothermal procedure is the most used to prepared nanoring-shaped hematite. However, with prolonged reaction time (48 h);
- ✓ Microwave-driven (MW) methods have been used to reduce time and energy in different processes;
- ✓ α-Fe_2O_3 presents interesting properties for catalysis applications and can be doped or impregnated with CeO_2;
- ✓ The conversion of CO_2, a greenhouse gas, to valuable products is an important and sustainable process;
- ✓ In this work, we show the potential synergistic effect between CeO_2 and α-Fe_2O_3 nanorings (NR) as a green and sustainable catalysts in the CO_2 conversion into DMC.



Methodologies

α- Fe_2O_3 Hematite

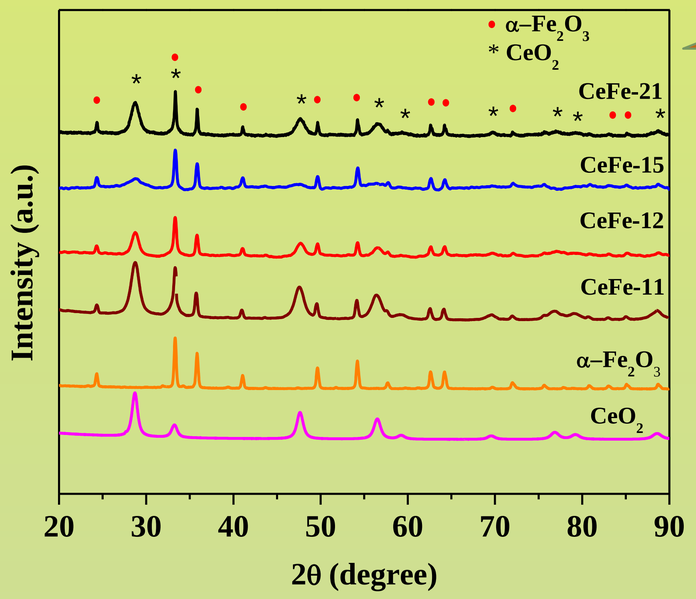
$FeCl_3$, NaH_2PO_4 and Na_2SO_4 → Microwave, 250 °C, 2h → Ethos X (Milestone) → Centrifugation, Washing until pH 7, Dry 60 °C

CeO_2-decorated α-Fe_2O_3

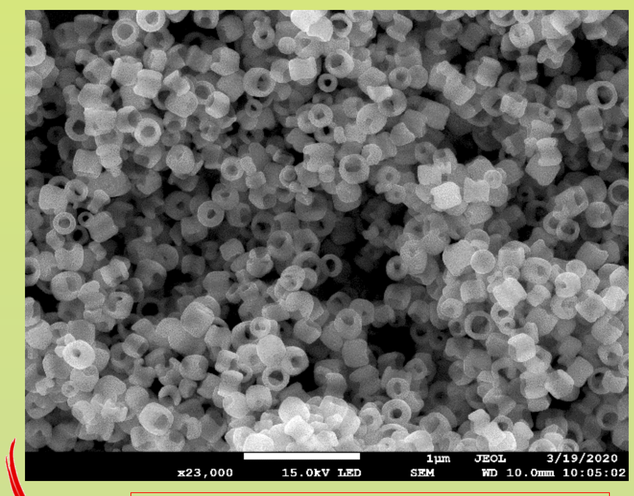
α-Fe_2O_3 → 1) X Ce^{3+}, 60°C; 2) NaOH → Centrifugation, Washing until pH 7, Dry 60 °C → Calcination 4 h / 400 °C

X= 0,5,1, 2 and 5.

Results and discussion

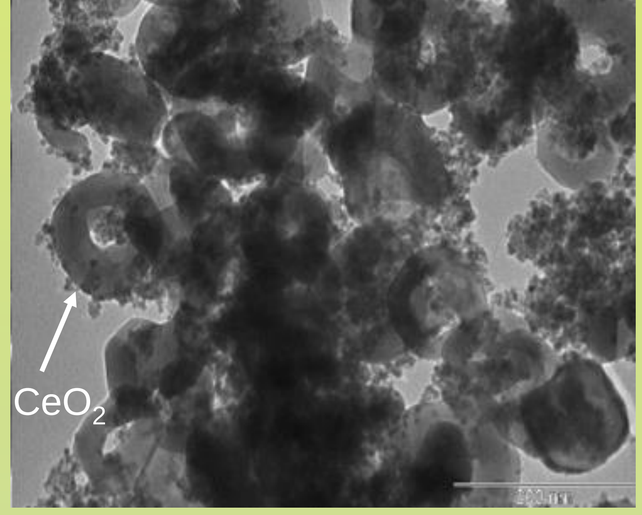


Powder XRD patterns: two crystalline phases, *hematite* (PDF 33-0664) and *CeO_2* (JCPDS 34-0394).



SEM: α-Fe_2O_3 presented highly ordered nanorings, mostly with edge lengths between 100 and 110 nm.

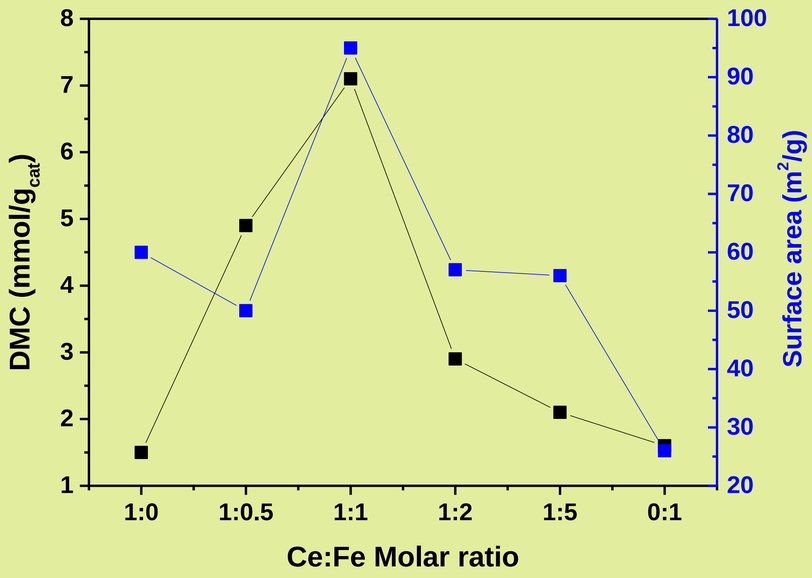
+ CeO_2



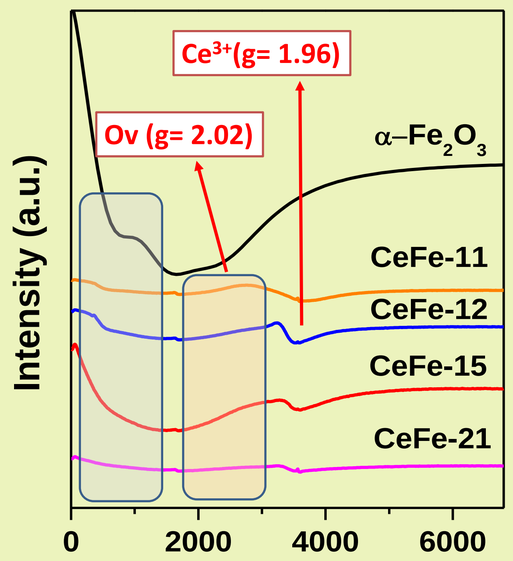
TEM image of CeFe-11 shows the presence of α-Fe_2O_3 nanorings well decorated with CeO_2 nanoparticles.

Catalytic performance

50 bar CO_2 → (a) → 100 mg Cat. + MeOH 15 mL → 140°C/3 h → Catalyst was separated by centrifugation → The product was analyzed by GC-MS



- ➢ All α-Fe_2O_3 nanoring catalysts impregnated with CeO_2 showed higher DMC yield compared to pure CeO_2 (1.5 $mmol_{DMC}/g_{cat}$) and α-Fe_2O_3 (1.6 $mmol_{DMC}/g_{cat}$);
- ➢ The results may be associated with the higher surface area, which seems to be essential in the synthesis of DMC;
- ➢ The CeFe-11 presented the best catalytic activity for CO_2 conversion to DMC.



EPR was used to evaluate the presence of oxygen vacancies (Ov) in the lattice; the α-Fe_2O_3 did not present Ov signals; the Ov signal decreases according to the Ce:Fe molar ratio.

Conclusion

- α-Fe_2O_3 nanorings were prepared using a microwave-driven method, which is more sustainable than the conventional method, reducing time and energy;
- The CeFe-11 catalyst presented the best performance (7.2 $mmol_{DMC}/g_{cat}$) in converting CO_2 to organic carbonate (DMC). This result may be associated with its high surface area (95 m^2/g) and the presence of oxygen vacancies.

Acknowledgements

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