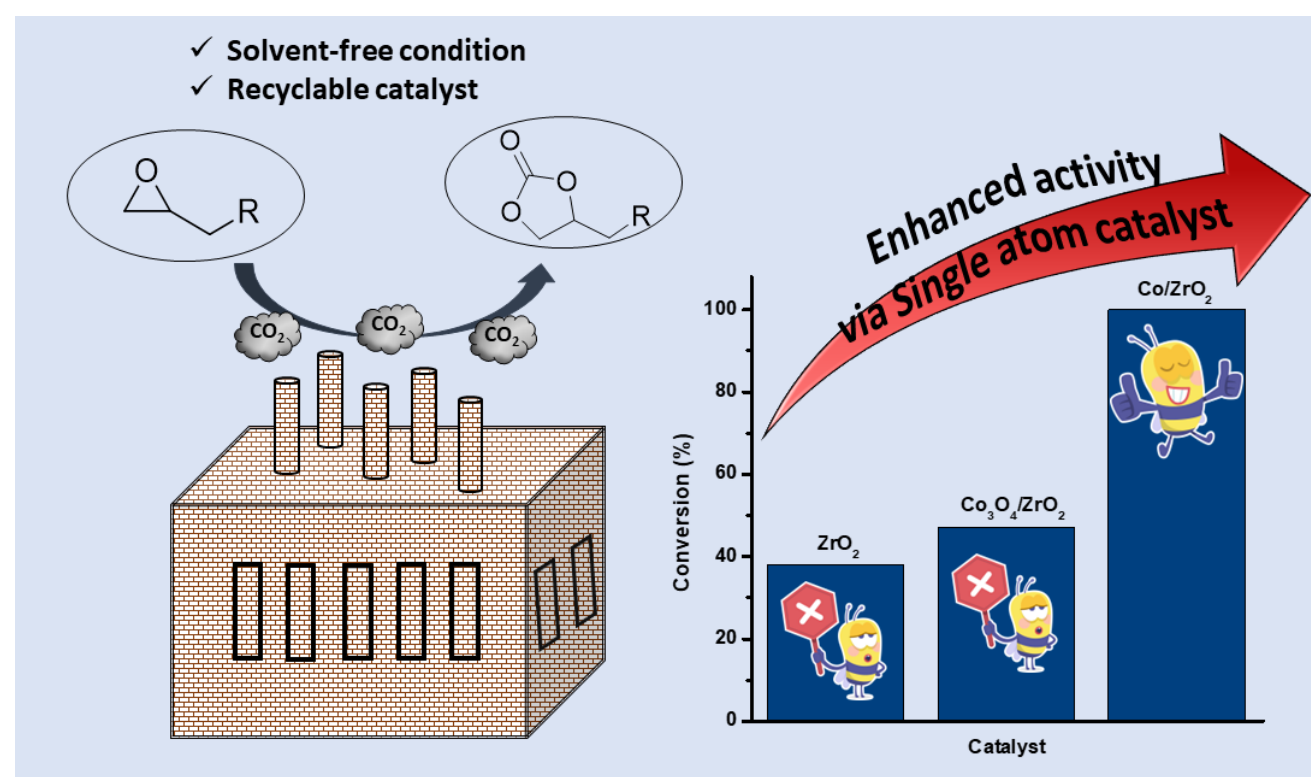
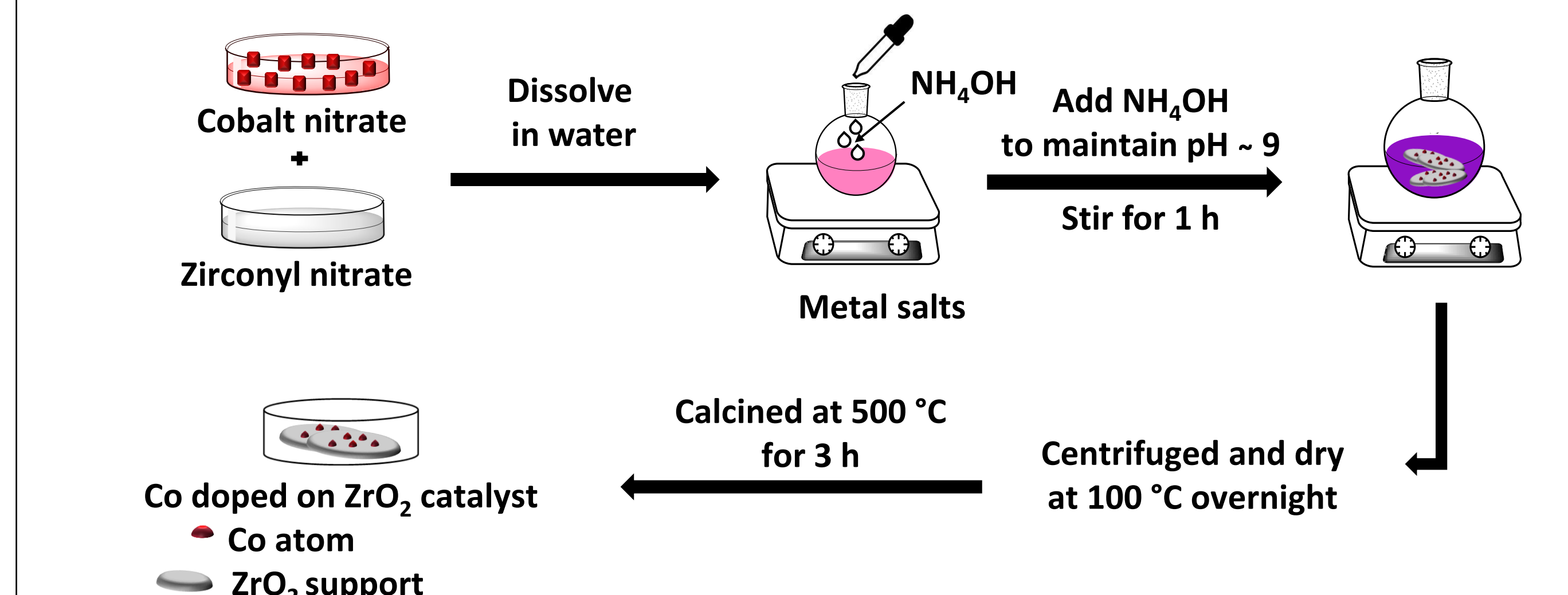


Abstract

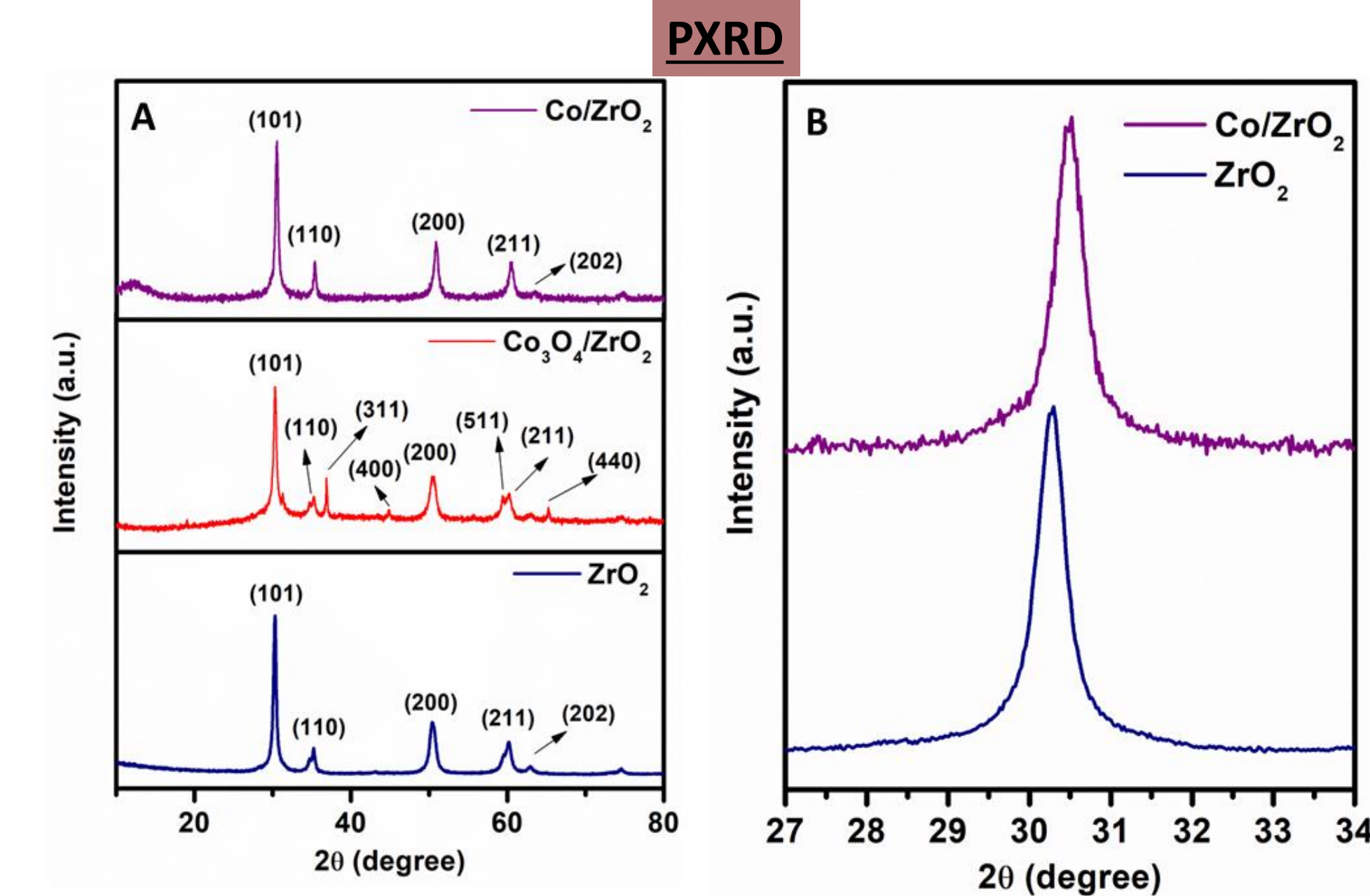
The presence of single atoms as active sites on a metal oxide support can dramatically enhance catalytic activity. Here, we demonstrate that Cobalt doped ZrO₂ constitutes a single atom catalyst where each Co²⁺ ion is active for CO₂ fixation. The synthesized Co/ZrO₂ catalyst was characterized by EXAFS and STEM to confirm the presence of isolated Co²⁺ on the ZrO₂ support. The STEM-EDS data showed uniform distribution of Co over the surface of the ZrO₂ support. The catalytic results reveal that Co active sites on ZrO₂ enhance catalytic performance and provide 100% conversion into carbonate products in the presence of trace amounts of tetrabutylammonium bromide (TBAB). When undoped ZrO₂ and Co₃O₄ impregnated ZrO₂ catalyst was utilized for comparison, less than 50% conversion of epoxides was obtained. The single atom catalyst (SAC) showed a broad substrate scope, solvent-free reaction and higher catalytic activity and selectivity.



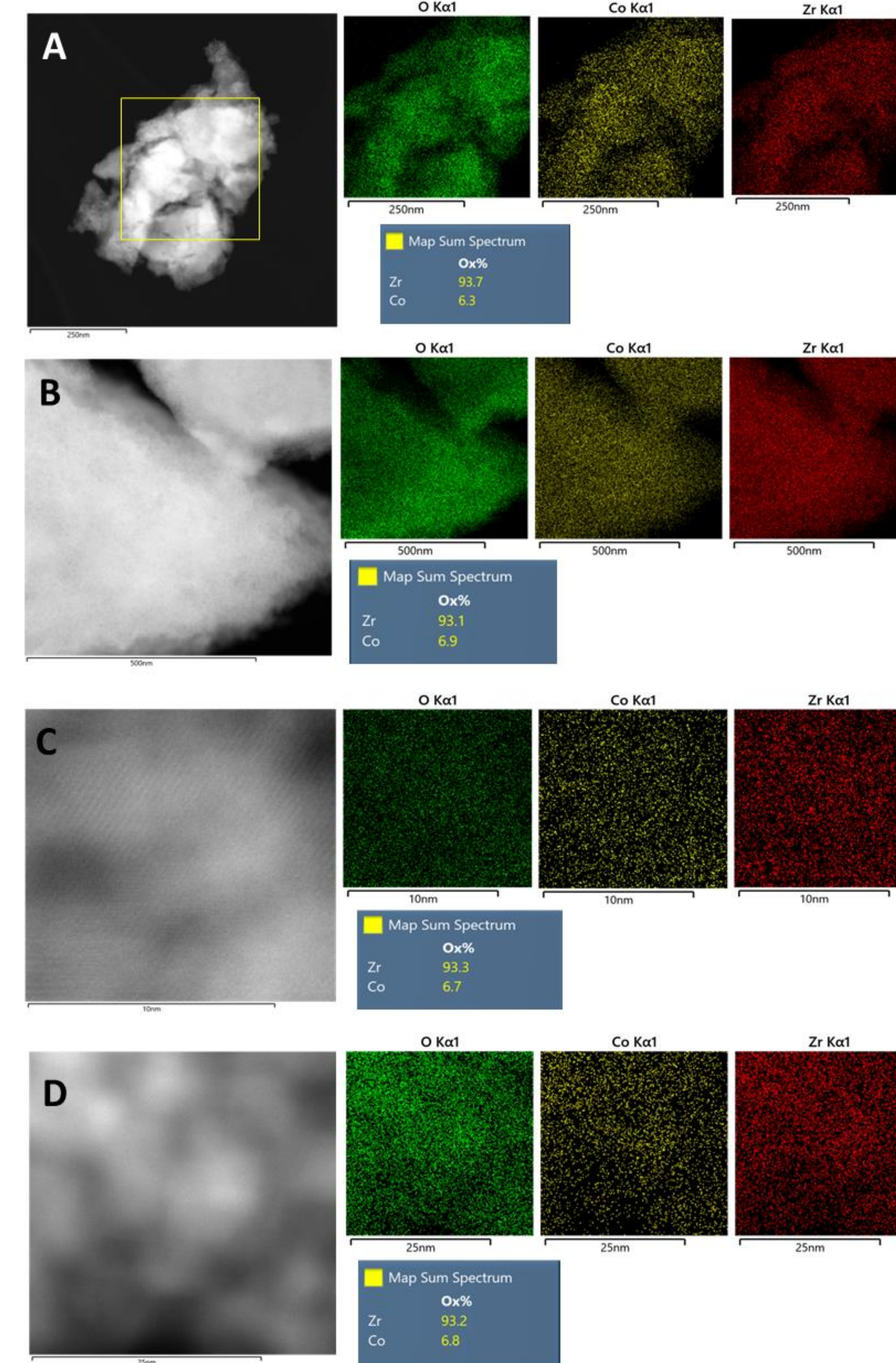
Co/ZrO₂ catalyst synthesis



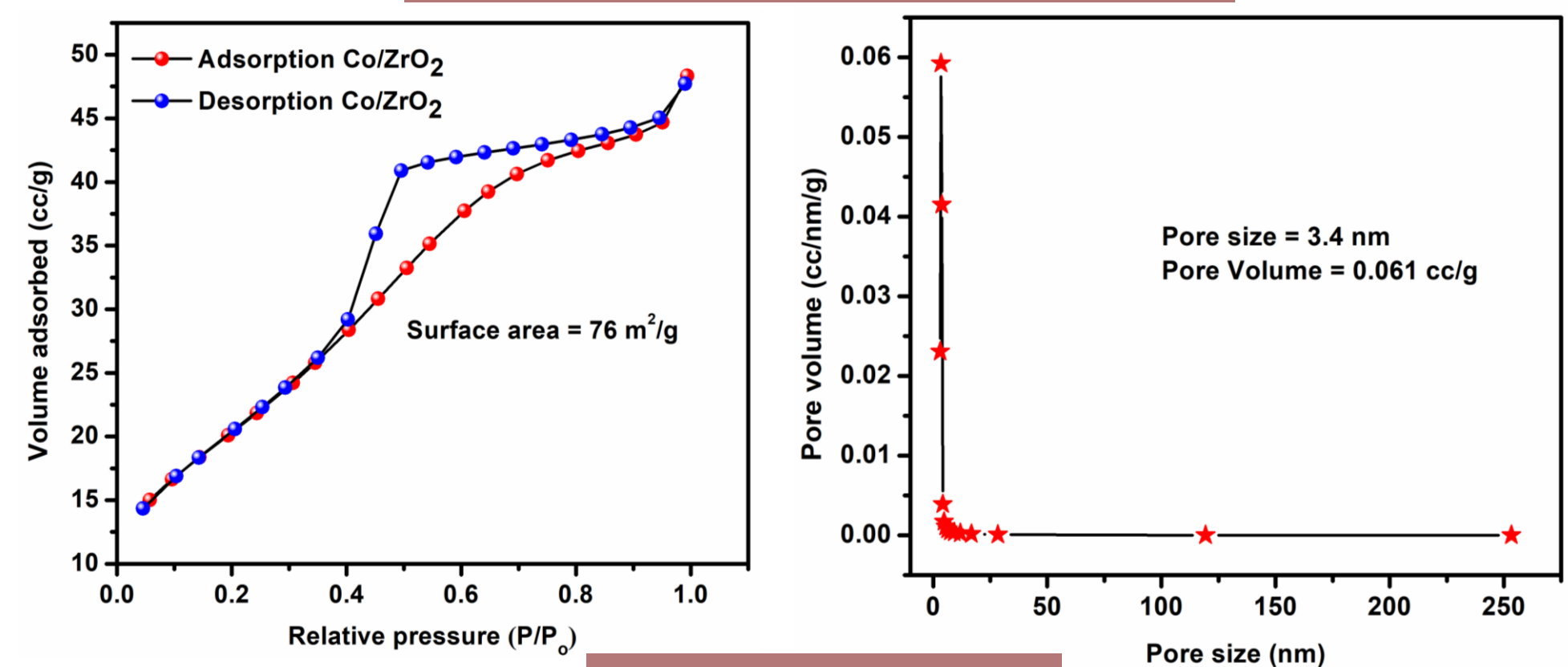
Catalyst characterizations



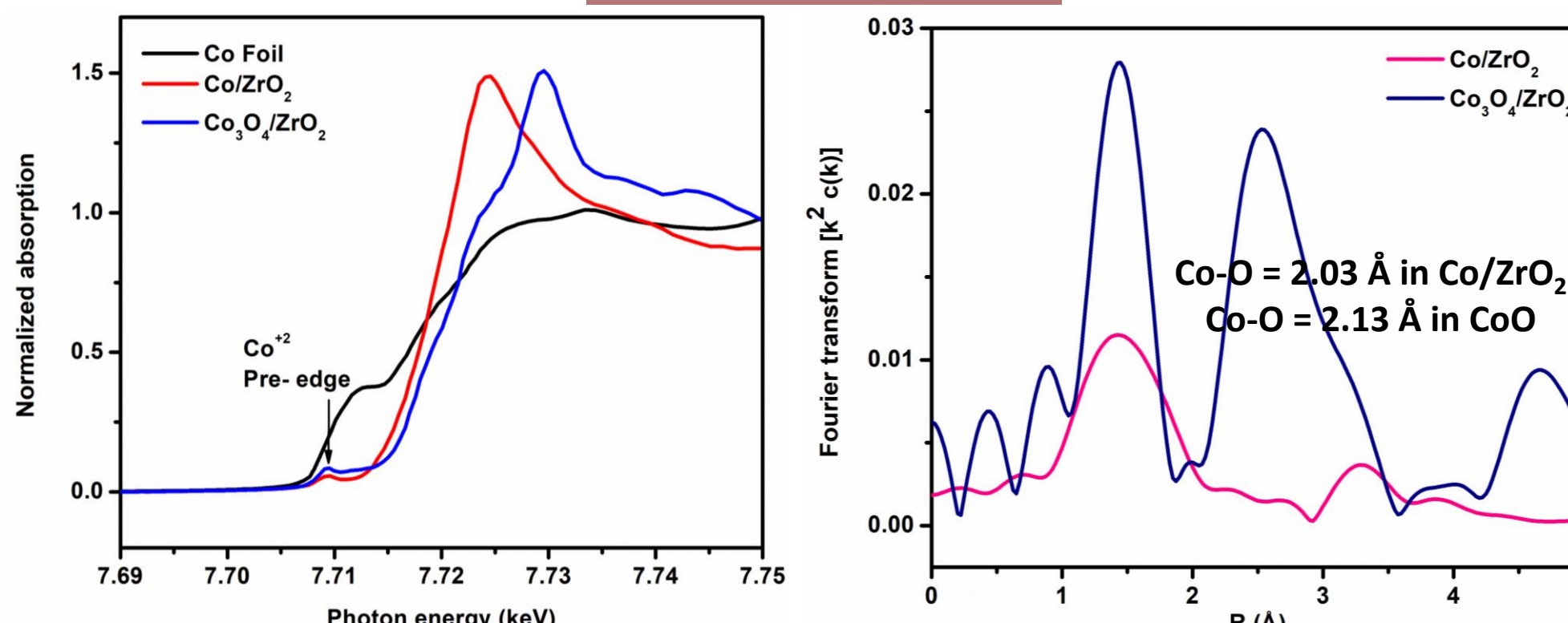
STEM EDS spectra



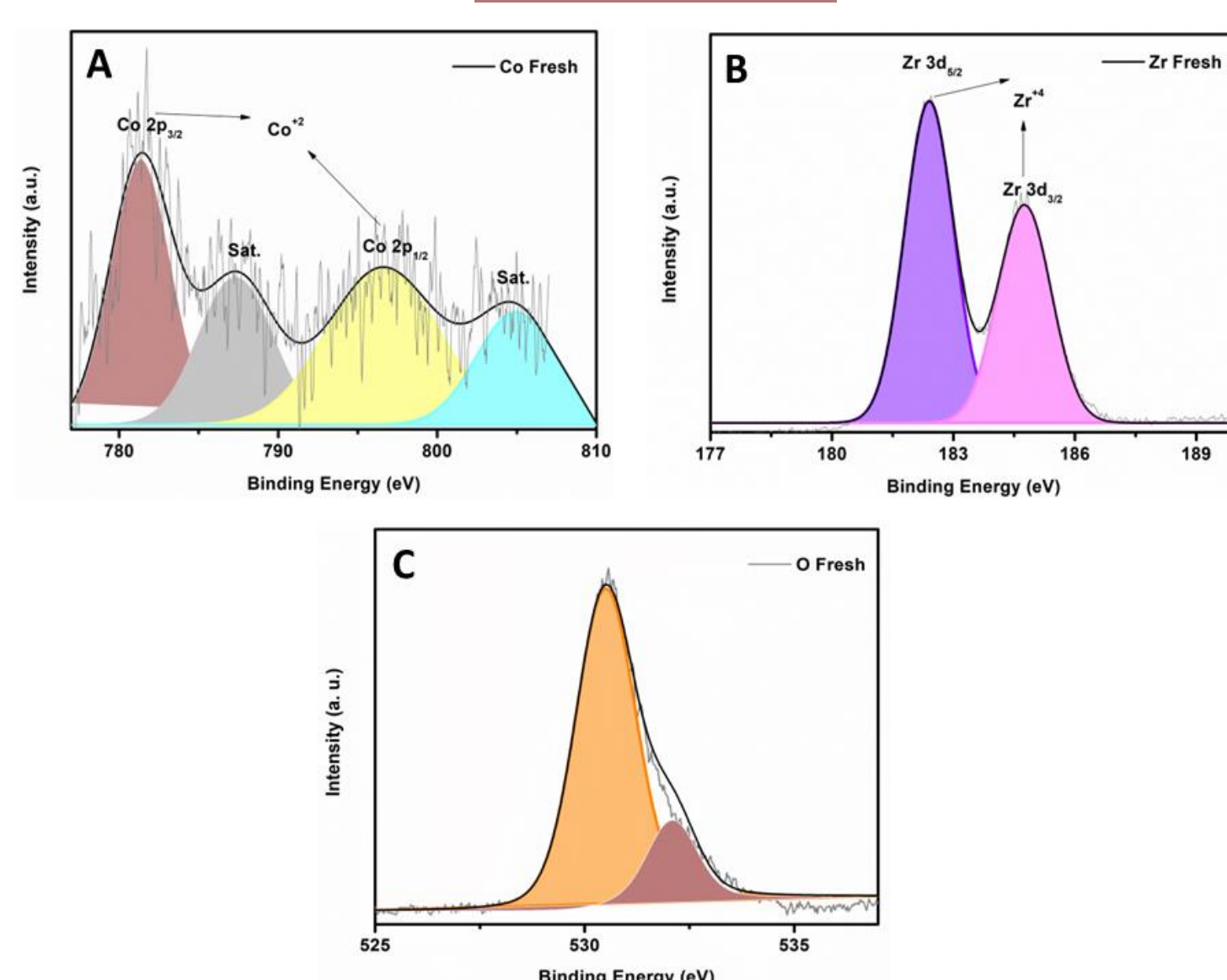
N₂ Adsorption-desorption study



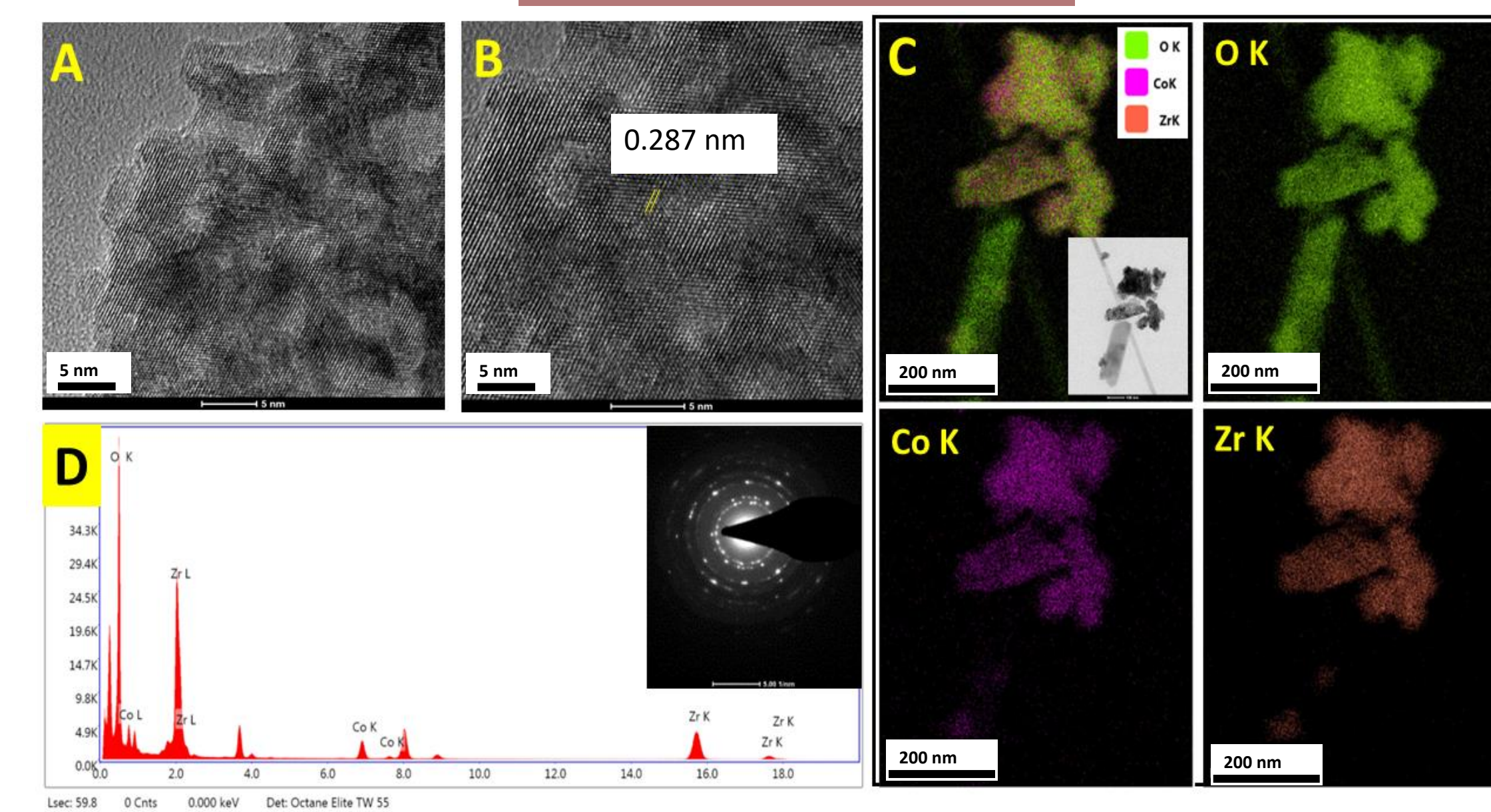
XANES and EXAFS



XPS analysis



HR-TEM and EDS analysis



Catalytic optimization of CO₂ fixation

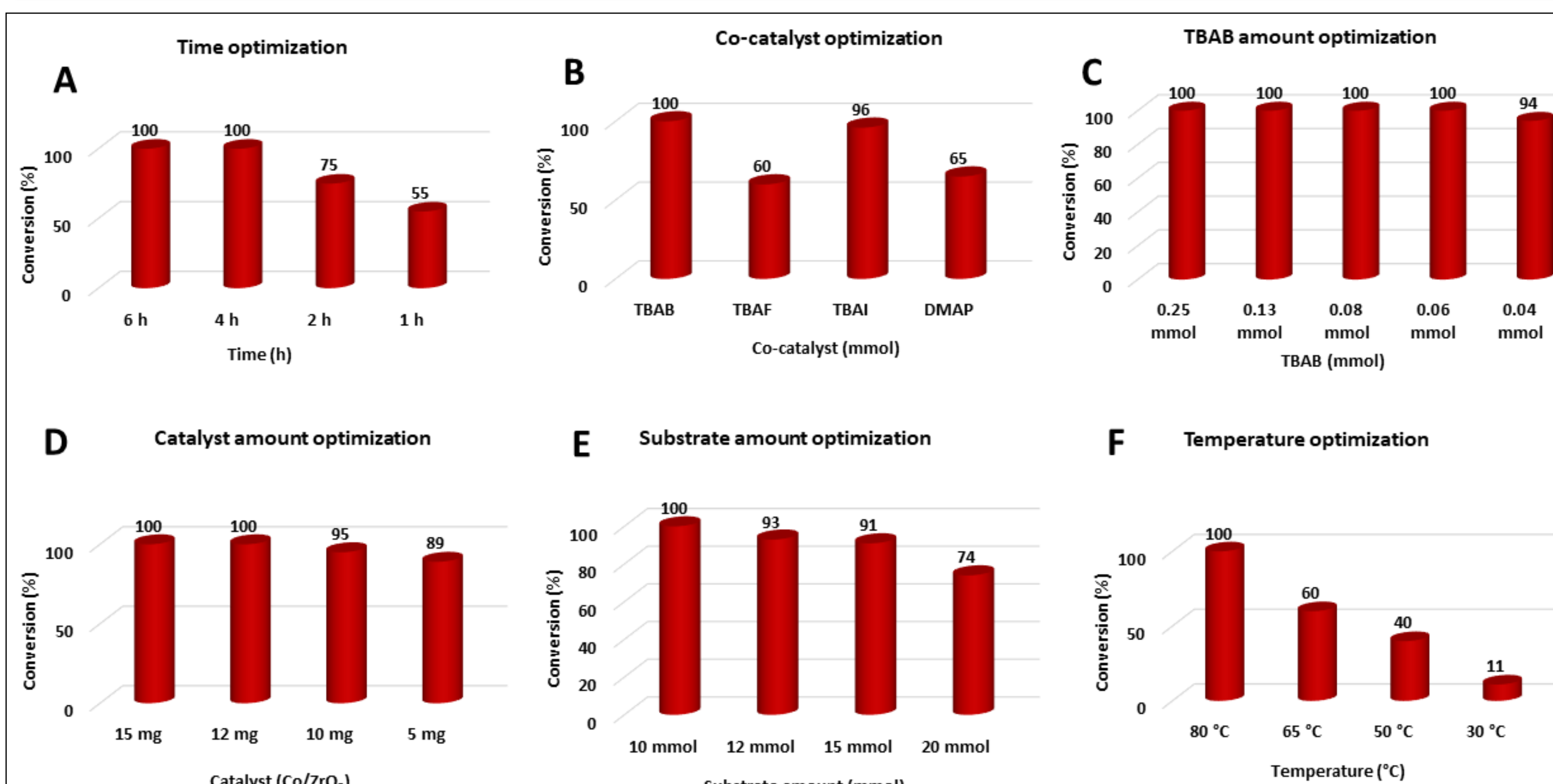
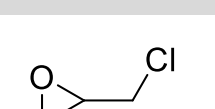
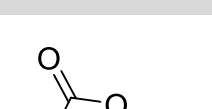
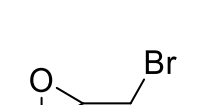
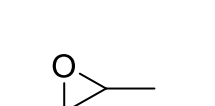
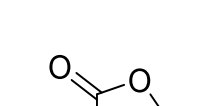
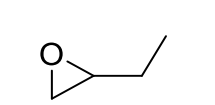
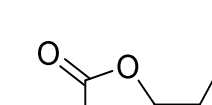
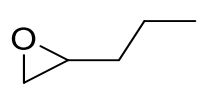
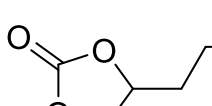
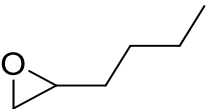
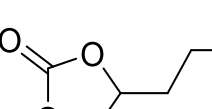
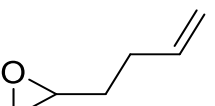
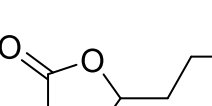
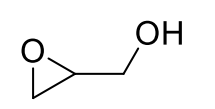
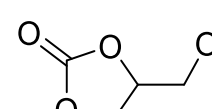
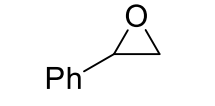
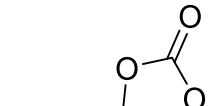
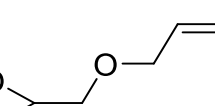
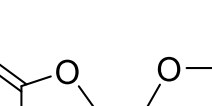


Figure. Catalytic optimization of CO₂ fixation reaction at various reaction conditions. **Reaction conditions:** (A) substrate = 10 mmol, catalyst (Co/ZrO₂) = 15 mg, TBAB = 0.25 mmol, temperature = 80 °C, time = 1-6 h, CO₂ = 2 bar. (B) substrate = 10 mmol, catalyst (Co/ZrO₂) = 15 mg, TBAB = 0.25 mmol, temperature = 80 °C, time = 4 h, CO₂ = 2 bar. (C) substrate = 10 mmol, catalyst (Co/ZrO₂) = 15 mg, TBAB = 0.25-0.04 mmol, temperature = 80 °C, time = 4 h, CO₂ = 2 bar. (D) substrate = 10 mmol, catalyst (Co/ZrO₂) = 5-15 mg, TBAB = 0.06 mmol, temperature = 80 °C, time = 4 h, CO₂ = 2 bar. (E) substrate = 10-20 mmol, catalyst (Co/ZrO₂) = 12 mg, TBAB = 0.06 mmol, temperature = 80 °C, time = 4 h, CO₂ = 2 bar. (F) substrate = 10 mmol, catalyst (Co/ZrO₂) = 12 mg, TBAB = 0.06 mmol, temperature = 30-80 °C, time = 4 h, CO₂ = 2 bar.

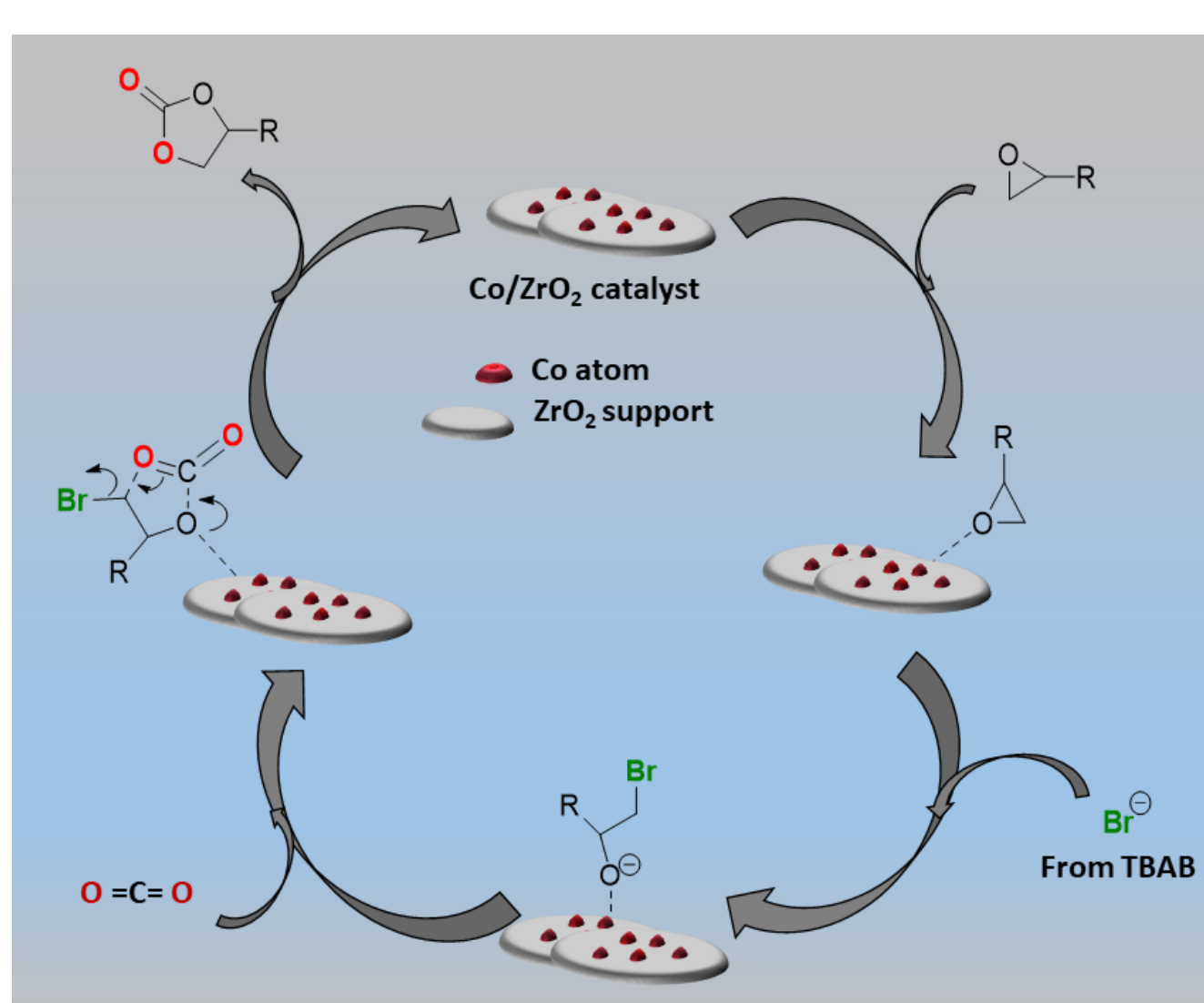
Conclusions

- ✓ Cobalt Single atom catalyst supported on ZrO₂ synthesized with facile method at room temperature with high surface area.
- ✓ CO₂ fixation into epoxides explored with solvent-free condition which make it greener and sustainable for industrial application with six recyclable cycles.
- ✓ For comparison, undoped ZrO₂ and Co₃O₄/ZrO₂ catalyst were utilized which were much less active for CO₂ fixation.
- ✓ A cost-effective, recyclable and reusable catalyst was utilized for large epoxide substrate conversion into cyclic carbonates.
- ✓ So far to the best of our knowledge, no reports using Co doped ZrO₂ for CO₂ fixation into epoxides to cyclic carbonate

Substrate scope, plausible reaction mechanism and recyclability

Entry	Substrate	Product	Time (h)	Conv. (%)
1			4	100
2			4	100
3			4	100
4			4	100
5			5	100
6			6	100
7			7	100
8			9	100
9			5	100
10			8	100

Reaction mechanism



Reaction condition: Substrate = 10 mmol, catalyst = 15 mg, TBAB = 0.06 mmol, temp. = 80 °C, time = 4-15 h, CO₂ = 2 bar.

References and acknowledgements

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- [2] Q. Yang, C.-C. Yang, C.-H. Lin, H.-L. Jiang,, *Angew. Chem. Int. Ed.* **2019**, *58*, 3511–3515.
- [3] G. Li, X. Sui, X. Cai, W. Hu, X. Liu, M. Chen, Y. Zhu, **2021**, *133*, 10667–10670.