

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI) FOR

Surface species in direct liquid phase synthesis of dimethyl carbonate from methanol and CO₂: an MCR-ALS augmented ATR-IR study

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|--|----|
| S1. Literature trend on DMC synthesis over ZrO ₂ and CeO ₂ | S2 |
| S2. Rietveld refinement of PXRD data | S3 |
| S3. Volumetric adsorption of N ₂ at 77K | S4 |
| S4. Reagents feeding setup schematic | S5 |
| S5. Transmission IR | S6 |
| S6. MCR-ALS including DMC as sixth component | S8 |
| References | S9 |

S1. Literature trend on DMC synthesis over ZrO_2 and CeO_2

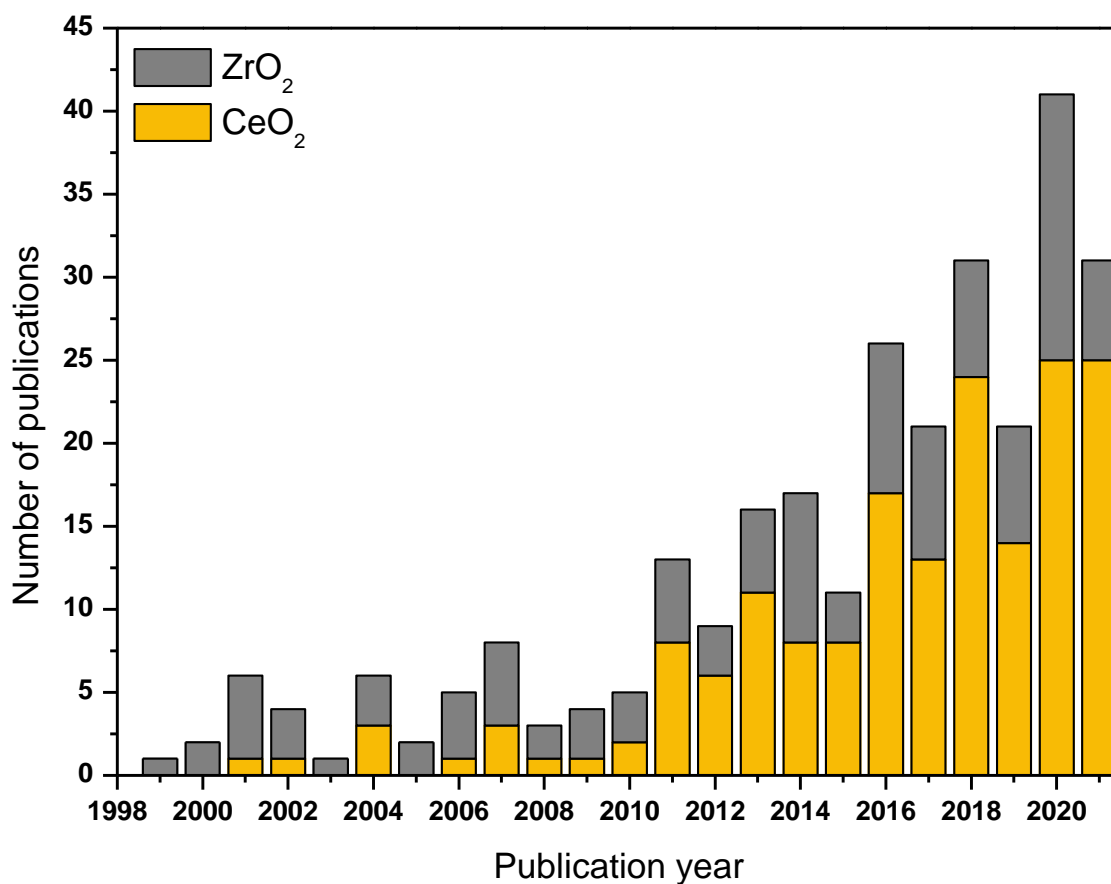


Figure S1. Publications/year distribution related to DMC production from CO_2 and CH_3OH over CeO_2 and ZrO_2 catalysts.¹

S2. Rietveld refinement of PXRD data

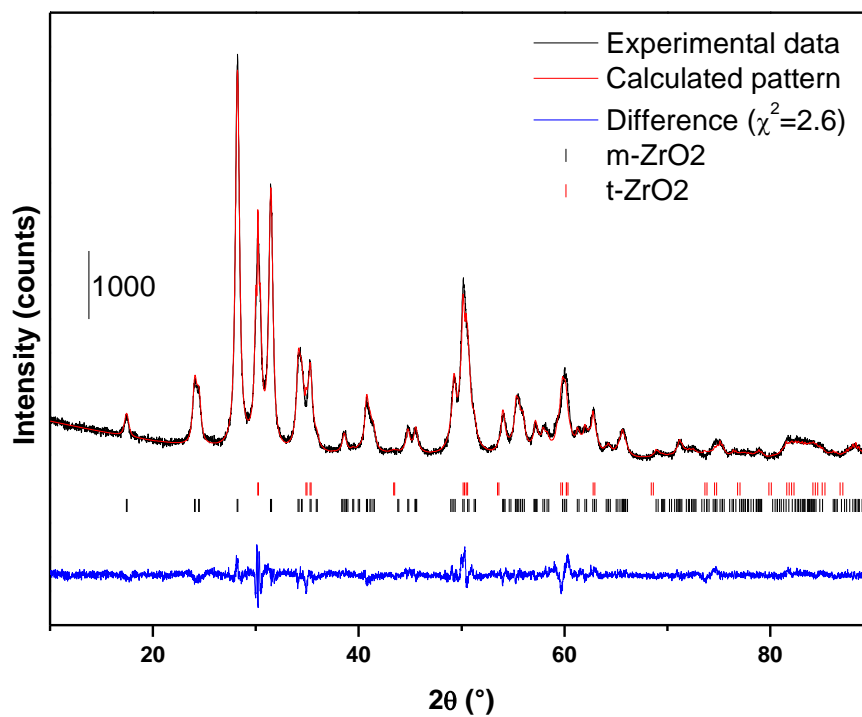


Figure S2. Experimental and refined PXRD patterns of the ZrO₂ catalyst. Bragg reflections of monoclinic (m-ZrO₂) and tetragonal (t-ZrO₂) phases are indicated.

S3. Volumetric adsorption of N₂ at 77K

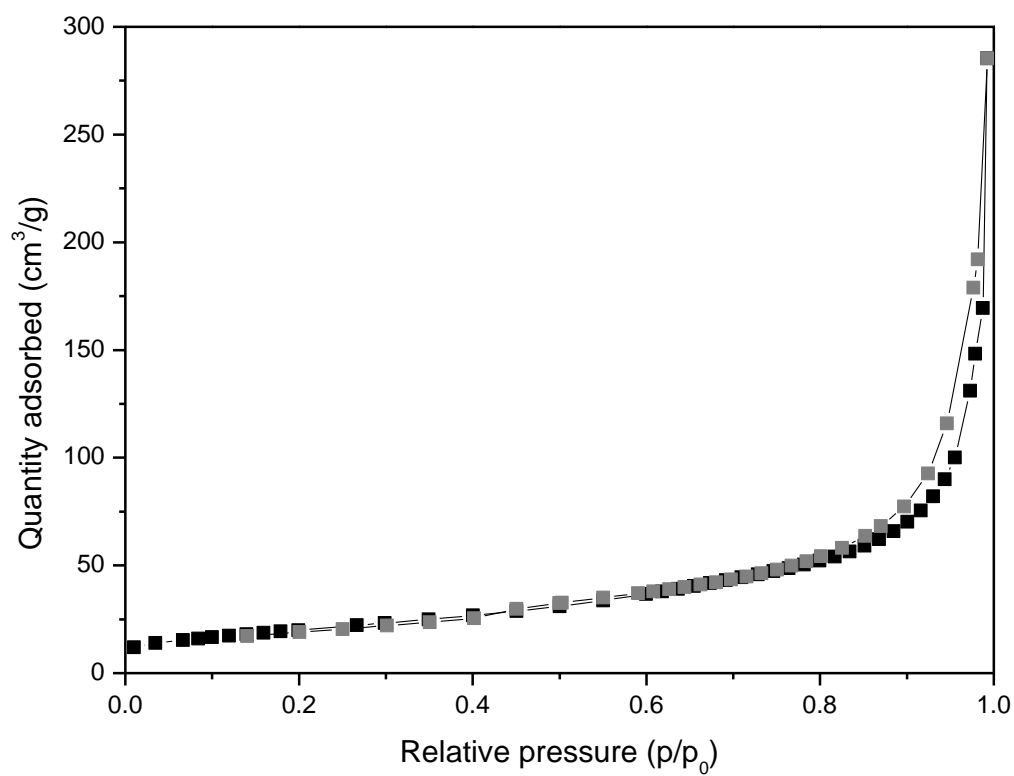


Figure S3. Adsorption (black) and desorption (gray) isotherms of N₂ at 77 K.

S4. Reagents feeding setup schematic

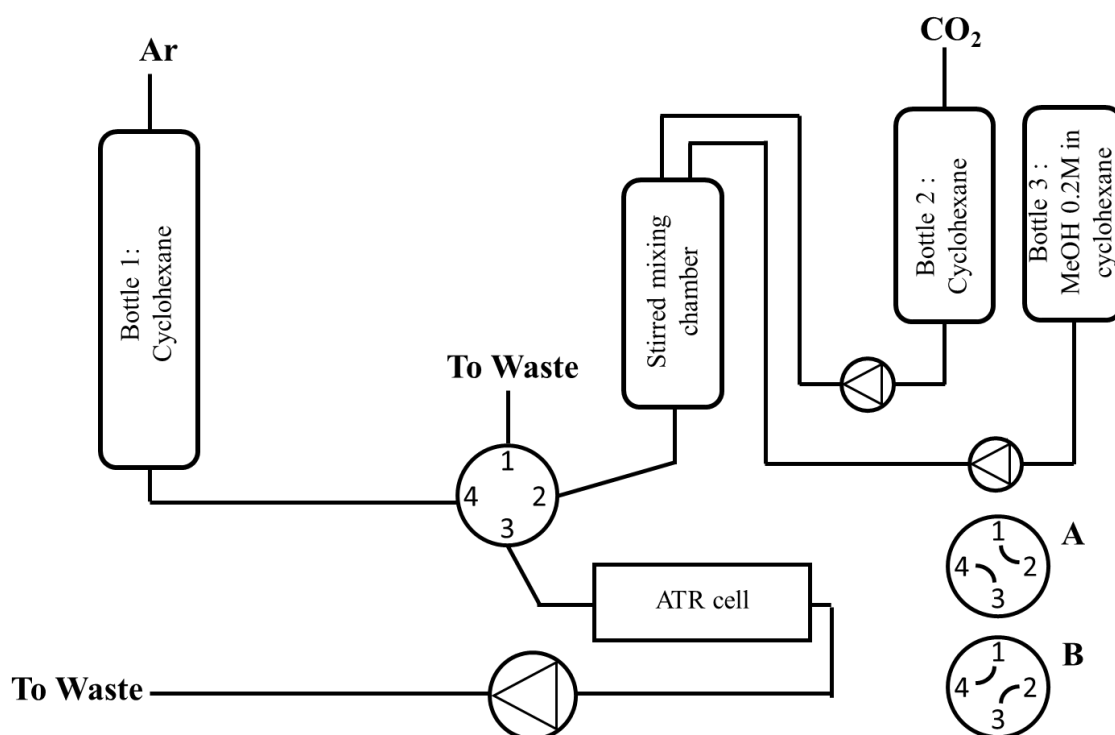


Figure S4. Schematic of the ATR-IR experimental set-up. The two possible positions for the 4-way valve (A and B) are indicated.

S5. Transmission IR

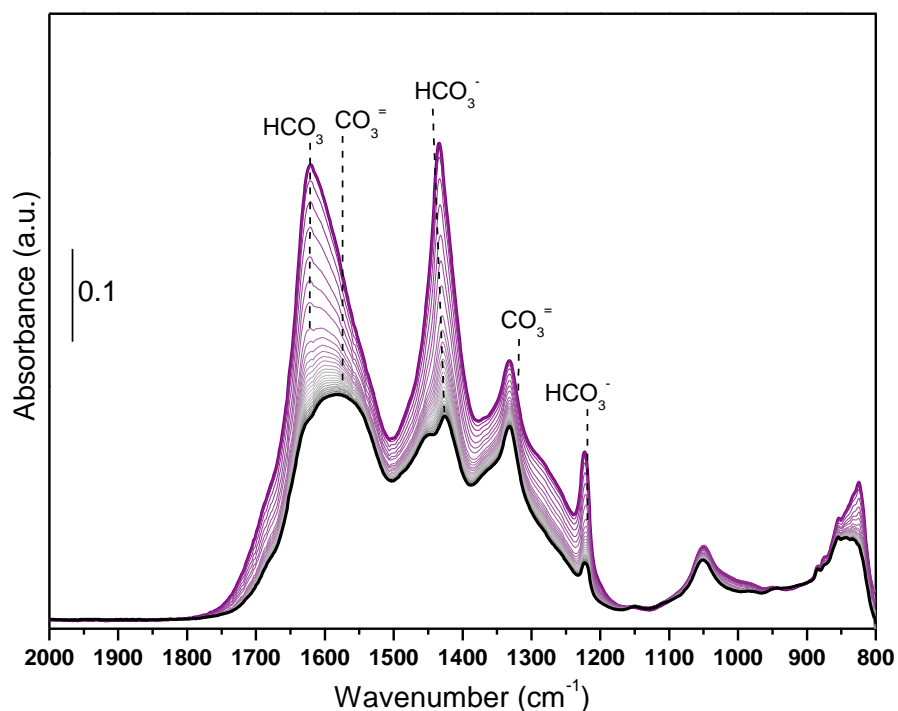


Figure S5. Transmission IR spectra of CO₂ adsorbed over ZrO₂. CO₂ partial pressure decreases from the purple (80 mbar) to the black (<5 × 10⁻⁴ mbar) curve. Bands were assigned according to the literature.^{2,3}

Adsorption of 80 mbar of CO₂ over clean ZrO₂ surface (Figure S5) showed formation of carbonates and bicarbonates species. The formed species and their relative intensities ratio are well reported in the literature and associated to carbonates/bicarbonates formed over ZrO₂ monoclinic polymorph. During desorption, we observed a different kinetic between carbonates and bicarbonates bands. In fact, the latter presented a faster desorption kinetic, typical of weakly bonded species, whilst the former were more stable during desorption.^{2,3}

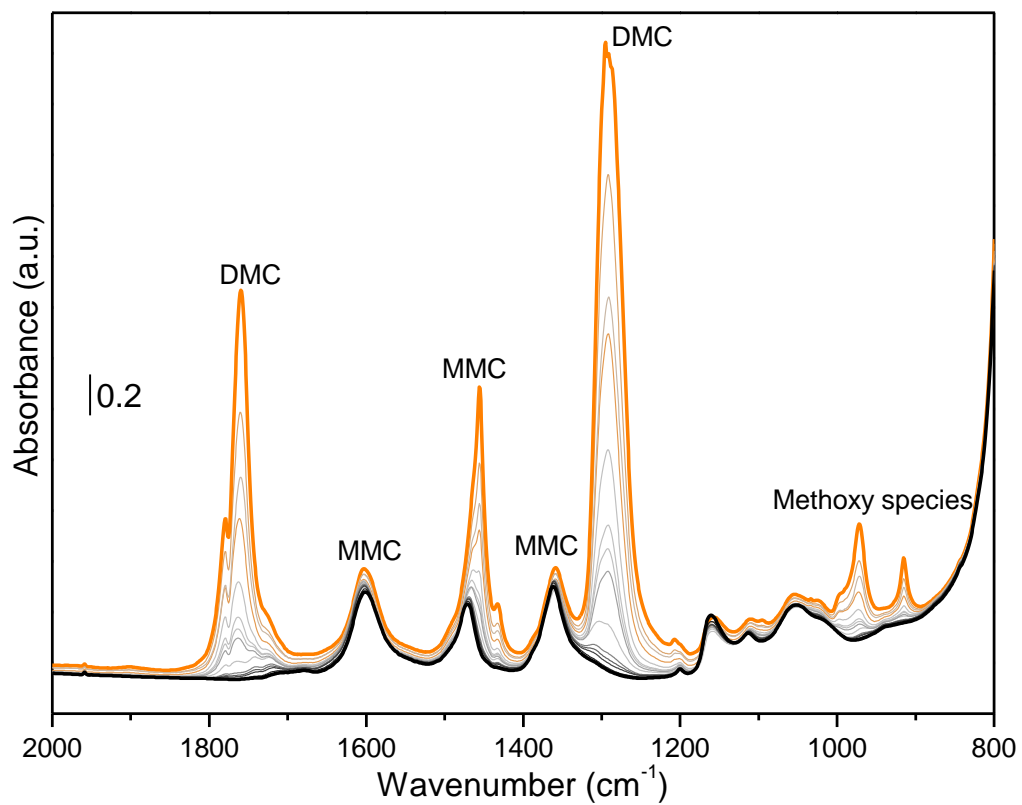


Figure S6. Transmission IR spectra of DMC adsorbed over ZrO₂. DMC partial pressure increases from the black (44 mbar) to the orange curve. Formation of monomethyl carbonate (MMC) is observed.⁴

S6. MCR-ALS including DMC as sixth component

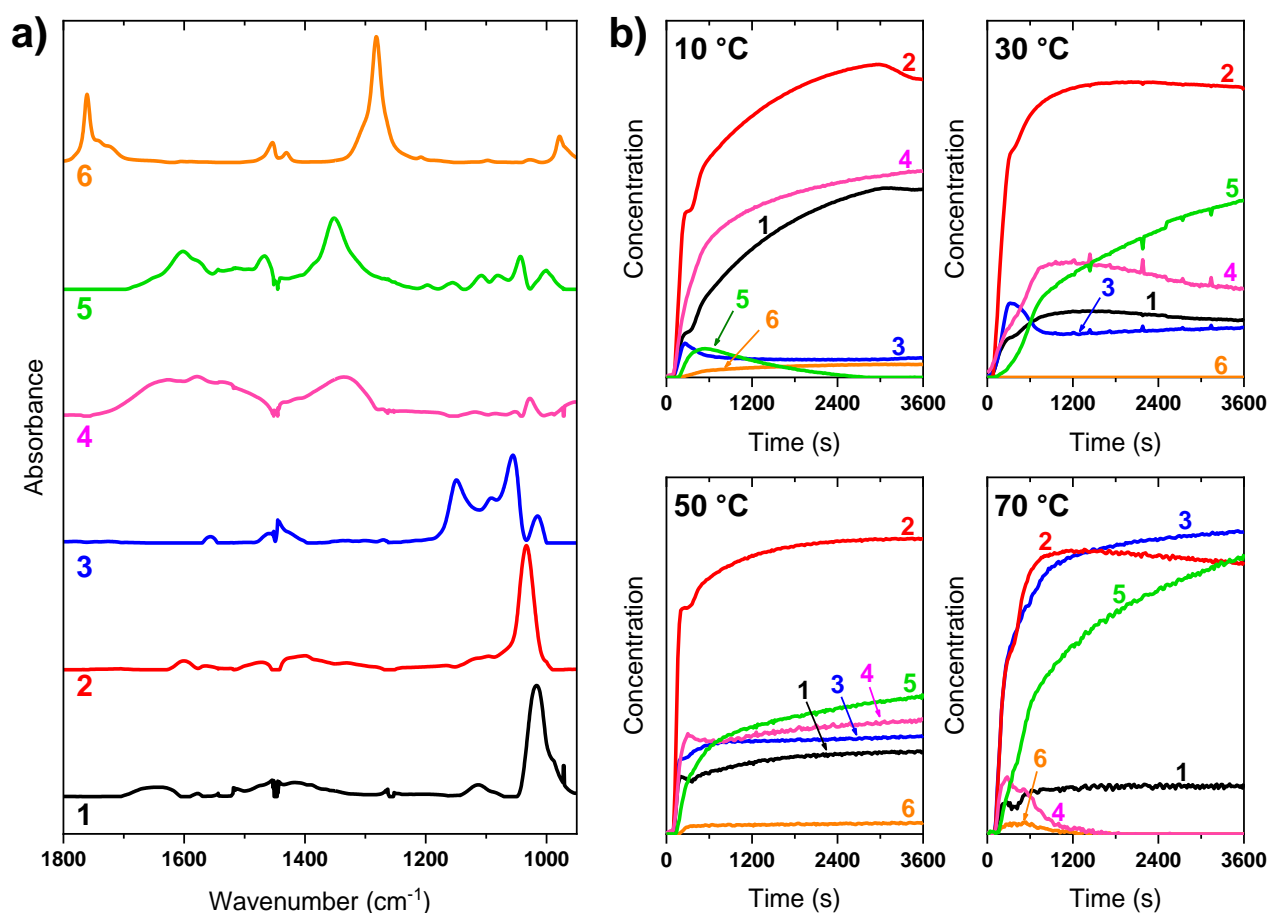


Figure S7. a) Spectra of pure components and b) their concentration profiles obtained from MCR-ALS for reactivity experiments carried out at different temperatures. MCR-ALS has been performed on all the datasets collected at different temperatures simultaneously. The spectrum of DMC adsorbed on ZrO₂ was included in the dataset, and six components were optimized by the algorithm.

The introduction of a sixth component in the MCR-ALS analysis aimed at attempting to include the spectral contribution due to DMC, weakly interacting with the ZrO₂ surface, is shown in Figure S7.

The component **6**, representative for adsorbed DMC, has a very low concentration compared to most of other components, regardless of the reaction temperature. This is not surprising since i) the DMC yield is expected to be very low, also keeping in mind that the experimental conditions adopted here are not optimal for reaching the maximal DMC productivity (however not exceeding 1% at 160 °C under 50 bar of CO₂);⁵ and ii) the interaction of DMC with the surface is expected to be weak and

most of the surface sites are already strongly bound by carbonates/methoxides/MMC. Nonetheless, some inconsistencies are observed, in particular the remarkable concentration of DMC at 10 °C compared to higher temperatures, where the catalytic activity should be superior. The complete absence of DMC at 30 °C is also difficult to explain. Possibly, the concentration of component **6** derived by MCR-ALS is not reliable as a consequence of the very low amount of DMC produced in the experiment.

References

- 1 Citation Report graphic, source: <https://www.webofscience.com/>, (accessed 28 April 2022).
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- 3 K. Pokrovski, K. T. Jung and A. T. Bell, Investigation of CO and CO₂ adsorption on tetragonal and monoclinic zirconia, *Langmuir*, 2001, **17**, 4297–4303.
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