Electronic supplementary information

for

Methanol synthesis over Cu/CeO_2-ZrO_2 catalyst: The key role of multiple active components

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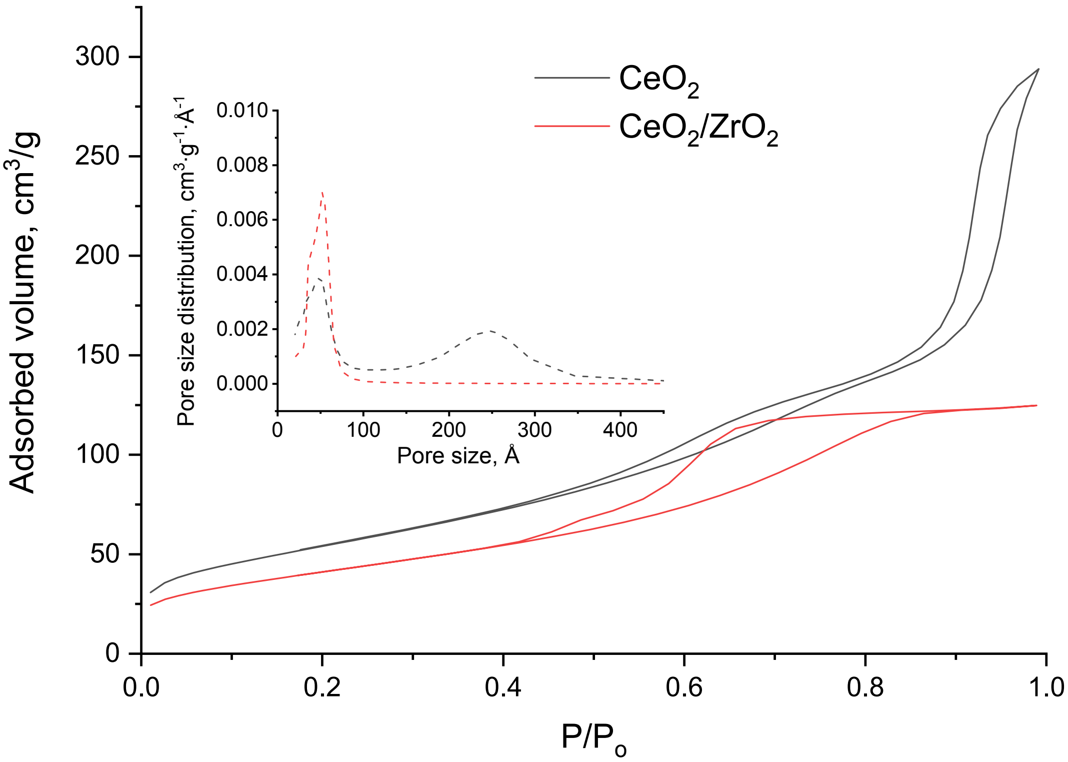

Figure S1. Nitrogen adsorption-desorption isotherms of pure ceria and ceria-zirconia materials prepared by glycothermal approach. The inset shows pore size distribution for these two samples.

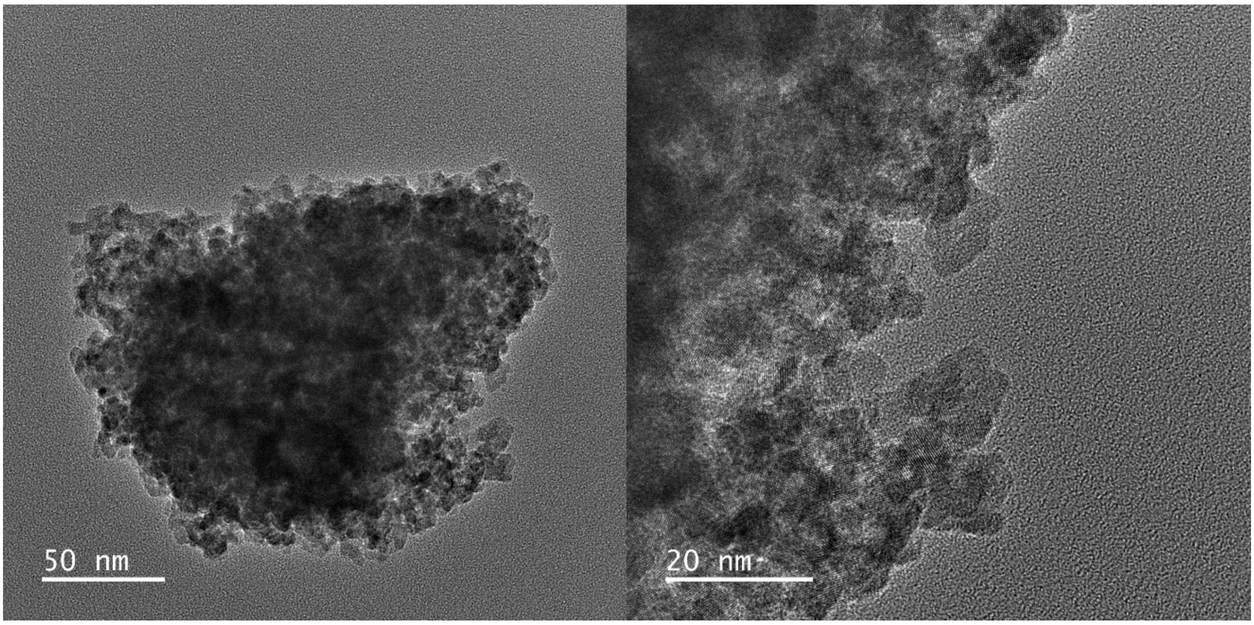

Figure S2. TEM micrographs of synthesized ceria-zirconia sample.

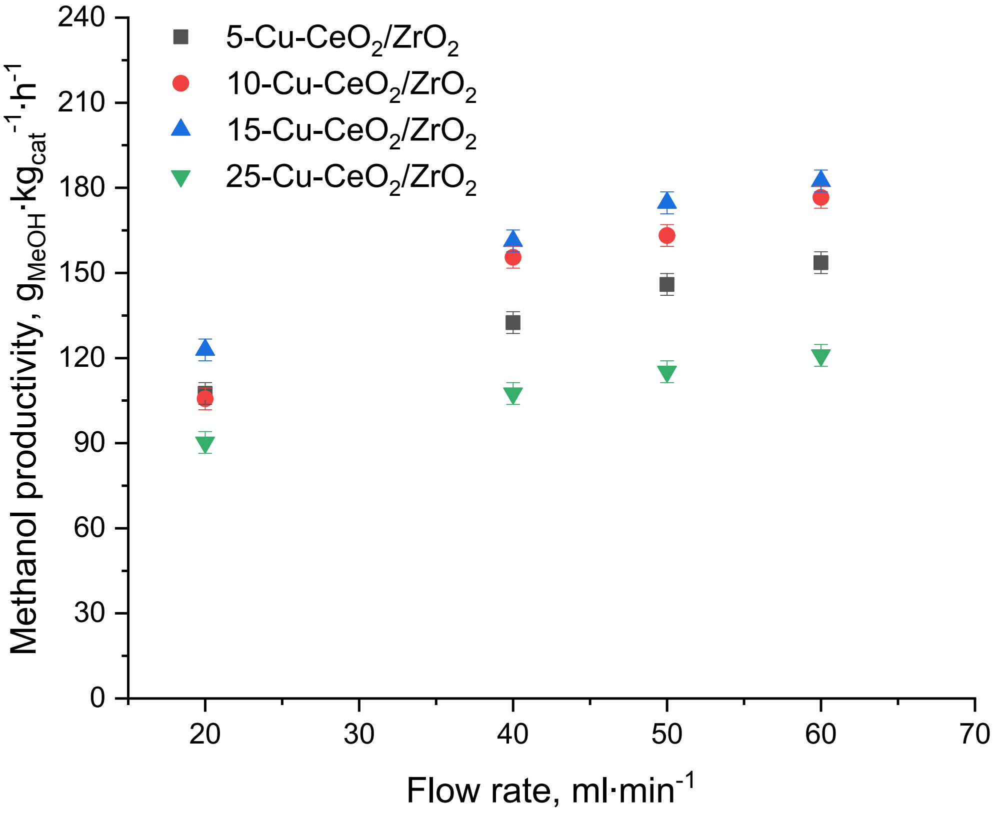

Figure S3. Methanol productivity per catalyst mass as a function of feedstock flowrate during catalytic carbon dioxide hydrogenation over Cu-CeO_2/ZrO_2 materials at 260 °C and 50 bar.

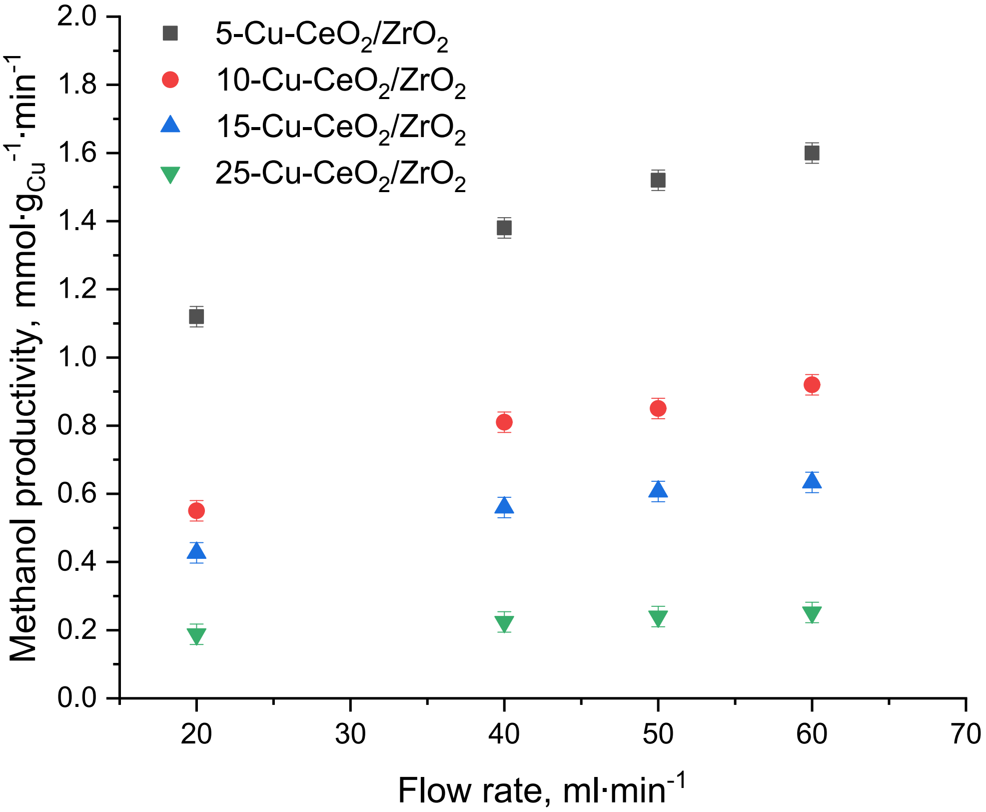

Figure S4. Methanol productivity per mass of copper as a function of feedstock flowrate during catalytic carbon dioxide hydrogenation over Cu-CeO_2/ZrO_2 materials at 260 °C and 50 bar.

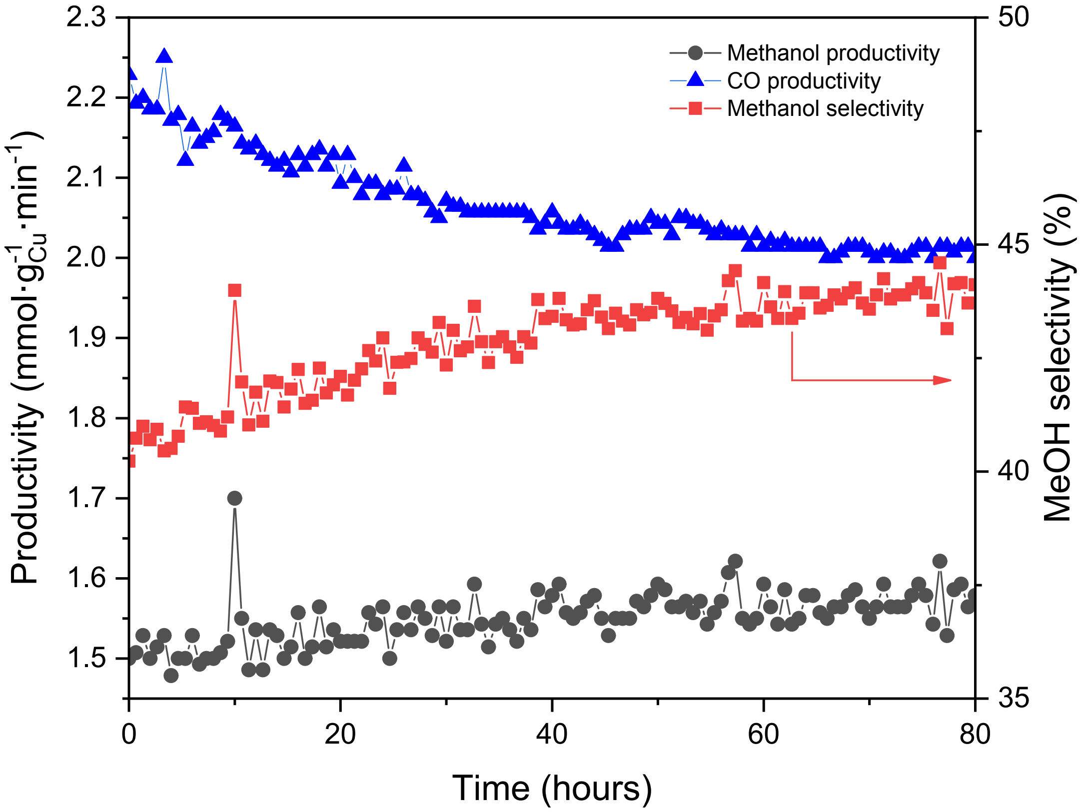

Figure S5. Long term stability test performed over 5-Cu-CeO_2/ZrO_2 material at 260 °C and 50 bar.

Table S 1. Results of physico-chemical characterization of Cu-CeO_2/ZrO_2 catalysts.

Sample	[a]Dispersion of Cu, %	[a]Crystallite size of Cu, nm	[b]H_2 consumption, STP cm^3/g_{cat}	[c]H_2 consumption, STP cm^3/g_{cat}	[d]Support co-reduction, STP cm^3/g_{cat}
5-Cu-CeO_2/ZrO_2	44.1	2.5	32.6	17.3	15.3
10-Cu-CeO_2/ZrO_2	19.9	5.5	46.4	35.6	10.8
15-Cu-CeO_2/ZrO_2	7.4	14.9	63.1	52.2	10.9
25-Cu-CeO_2/ZrO_2	4.3	25.8	99.3	88.5	10.8
5-Cu-CeO_2	49.3	2.2	29.4	17.3	12.1
5-Cu-ZrO_2	35.6	3.1	19.5	17.3	2.2

[a] Calculation based on oxygen chemisorption at – 120 °C and taking into account partial reduction of ceria-zirconia support; [b] Amount of consumed hydrogen during H_2-TPR experiment; [c] Theoretical amount of hydrogen required for stoichiometric reduction of copper oxide presented in the investigated sample; [d] Amount of hydrogen consumed for co-reduction of ceria-zirconia, ceria or zirconia supports. Similar amounts of hydrogen consumed for co-reduction of ceria-zirconia support can be attributed to well-known redox properties of this material and hydrogen spillover. Ceria and ceria-zirconia supports are well-reducible materials allowing hydrogen spillover. As was shown in previous work of our group,[1] hydrogen spillover results in uniform support reduction and even allows reduction of supported iron oxide that is not in direct contact with the platinum catalyst (both phases are supported on titania support at distance - 45 nm). As such taking into account small size of ceria-zirconia nanoparticles (~5 nm accordingly to Scherrer equation) and well-known reducibility of CeO_2-ZrO_2 materials, we can assume complete surface co-reduction of CeO_2-ZrO_2 support independently of the length of copper-ceria-zirconia interfacial perimeter.

Notes and references

1 W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. Vandevondele, Y. Ekinci and J. A. Van Bokhoven, *Nature*, 2017, **541**, 68–71.