

Supplementary data

Table 1S. Final pressure reached after 1 h of reaction, versus different introduction times of liquid CO₂

CO ₂ introduction time in 12 g of MeOH / mn	Liquid CO ₂ flow rate / ml.min ⁻¹	Final pressure in reactor heated at 413K /bar
3.6	5	120
6	3	140

Table 2S. Water mass balance during a catalytic test with 0.5 g of catalyst, 12 g of MeOH and 0.375 mol CO₂

Water source	Initial H ₂ O in CH ₃ OH	Initial H ₂ O in CO ₂	Initial H ₂ O in catalyst	H ₂ O produced by reaction
Hypothesis	0.375 mol MeOH with 300 ppm H ₂ O	0.375 mol CO ₂ with 5 ppm H ₂ O	500 mg wet catalyst 15 wt.% H ₂ O	Final conversion is assumed to be 0.7% based on MeOH
H ₂ O mass (g)	0.002	<10 ⁻³ g	0.075	0.0236
H ₂ O balance (g)	H₂O Initial mass : 0.077			H₂O produced : 0.0236

Table 3S. Activities of pure oxides from literature in direct synthesis of DMC

Results from literature: Activity / μmol.g ⁻¹ .s ⁻¹		
Oxide	Activity/ μmol.g ⁻¹ .s ⁻¹	Reference / Comment
La ₂ O ₃	0	[32]
Ce ₂ O ₃	0	[32]
SiO ₂	0	[25]
Al ₂ O ₃	0	[25] Selectivity to DME
TiO ₂	0	[25] Selectivity to DME
ZnO	0	[25]
MoO ₃	0	[25]
Bi ₂ O ₃	0	[25]

Fig. 15. Activities of various cerias versus specific surface area in direct synthesis of DMC

Entry	Ceria sample
A	Ceria 1 supplied by Johnson Matthey
B	Ceria 2 supplied by Johnson Matthey
C	Ceria 3 flame sprayed supplied by Johnson Matthey
D	Ceria precipitated
E	Ceria HSA Solvay
F	CeO ₂ Aldrich nanopowder (25 nm < particle size)
G	CeO ₂ Aldrich micro
H	CeO ₂ fused (3-6 mm)

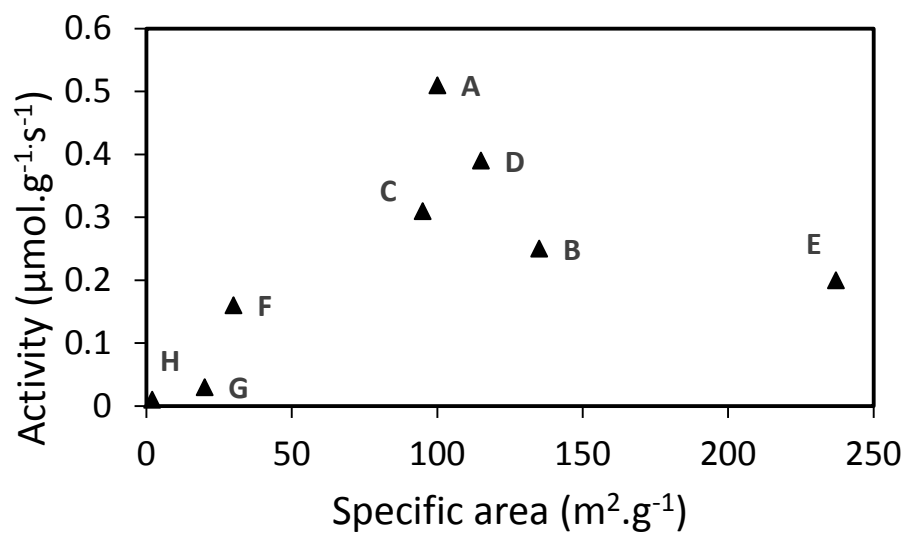


Table 4S. Impregnated cerias

Reference (% weight)	Thermal treatment temperature K	Specific surface area $\text{m}^2.\text{g}^{-1}$	Activity $\mu\text{mol}.\text{g}^{-1}.\text{s}^{-1}$
P-CeO ₂	773	115	0.39
1% Al/CeO ₂	773	82	0.03
1% Al/CeO ₂ -750	1023	57	0.10
1% Zn/CeO ₂	773	92	0.50
1% Fe/CeO ₂	773	89	0.39
1% La/CeO ₂	773	85	0.68
5% La/CeO ₂	773	90	0.39
5% La/CeO ₂ -750	1023	63	0.68
1% Y/CeO ₂	773	78	0.43
1% Gd/CeO ₂	773	77	0.40
1% Sm/CeO ₂	773	98	0.43
1% Zr/CeO ₂	773	99	0.41
1% Nd/CeO ₂	773	97	0.55

Table 5S. Ceria and zirconia mixed oxides prepared by co-precipitation with a second metal oxide

Reference (molar composition)	Crystallite size nm	Specific surface area $\text{m}^2.\text{g}^{-1}$	Activity $\mu\text{mol}.\text{g}^{-1}.\text{s}^{-1}$
P-CeO ₂	6.2	115	0.38
Ce _{0.88} La _{0.12} O _x	5.1	134	0.56
Ce _{0.83} Fe _{0.17} O _x	4.2	136	0.53
Ce _{0.98} Al _{0.02} O _x	5.0	109	0.54
Ce _{0.95} Al _{0.05} O _x	4.5	103	0.50
Ce _{0.99} Gd _{0.01} O _x	6.1	95	0.42
Ce _{0.68} Nb _{0.32} O _x	4.7	132	0.02
Ce _{0.98} Ti _{0.02} O _x	5.6	115	0.39
Ce _{0.90} Ti _{0.10} O _x	5.7	132	0.10
P-ZrO ₂	6.8	99	0.01
Zr _{0.98} Ti _{0.02} O _x	5.7 / 6.3	98	0.03
Zr _{0.91} Ti _{0.09} O _x	5.1 / 5.7	119	0.03
Zr _{0.99} Al _{0.01} O _x	7.2	90	0.02
Zr _{0.97} Al _{0.03} O _x	6.0	129	0.01
TiO ₂	40	128	0.00
Ce _{0.77} Zr _{0.23} O ₂	6.1	118	0.50

Fig. 2S. DRX patterns of CP $Ce_xZr_{1-x}O_2$

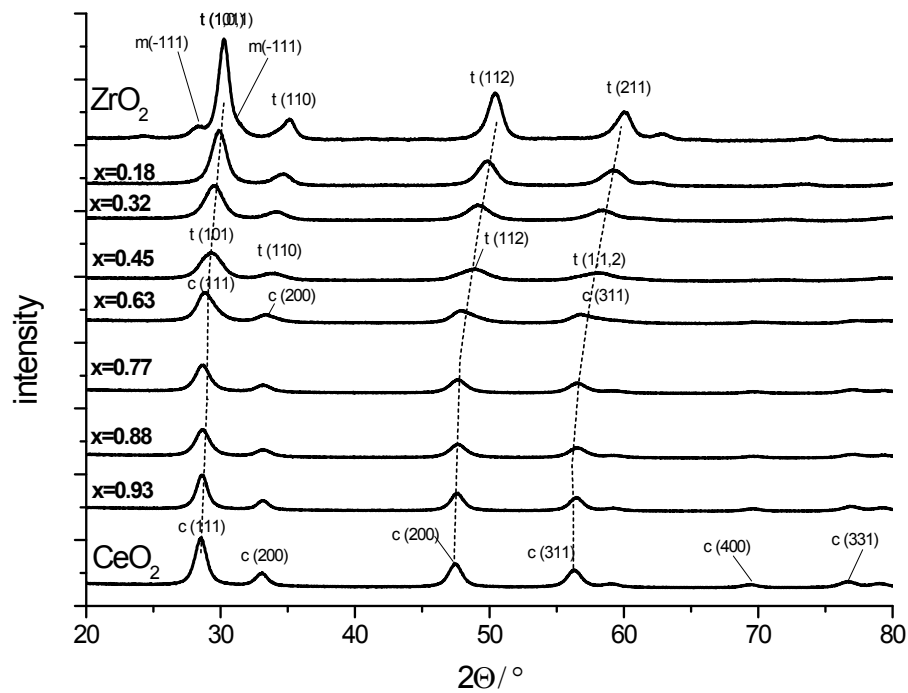


Fig. 3S DRX patterns of FSP $Ce_xZr_{1-x}O_2$

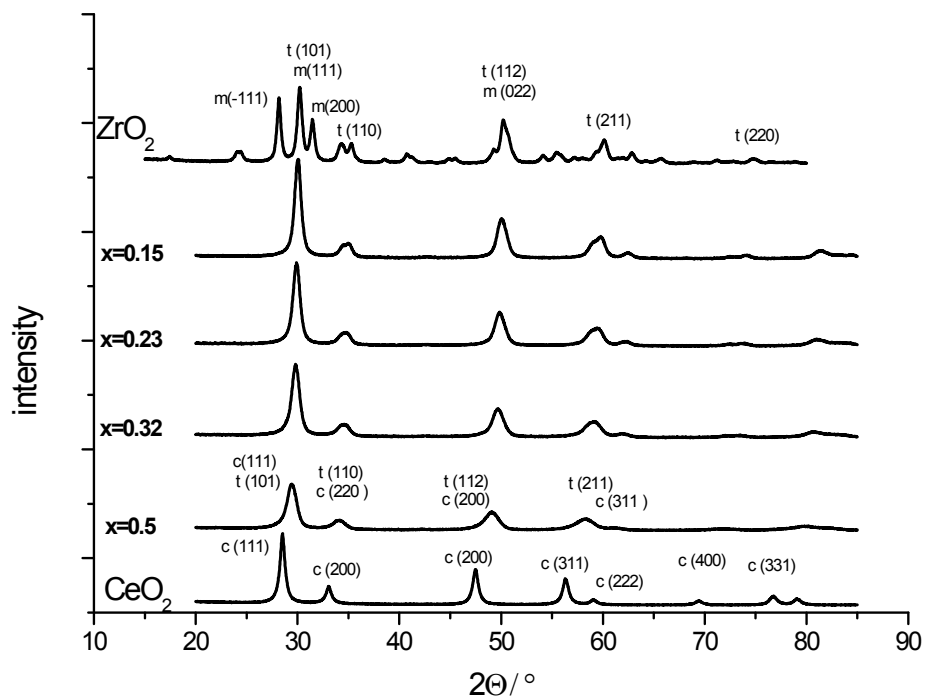


Table 6S. Ceria-zirconia mixed oxides, co-precipitated

Reference (molar composition)	Crystallite size nm	Specific surface area $\text{m}^2.\text{g}^{-1}$	Activity $\mu\text{mol}.\text{g}^{-1}.\text{s}^{-1}$
CeO_2	8	115	0.382
$\text{Ce}_{0.93}\text{Zr}_{0.07}\text{O}_2$	6.8	95	0.399
$\text{Ce}_{0.88}\text{Zr}_{0.12}\text{O}_2$	6.6	105	0.417
$\text{Ce}_{0.77}\text{Zr}_{0.23}\text{O}_2$	5.8	118	0.495
$\text{Ce}_{0.63}\text{Zr}_{0.27}\text{O}_2$	3.9	113	0.269
$\text{Ce}_{0.45}\text{Zr}_{0.55}\text{O}_2$	3.6	119	0.244
$\text{Ce}_{0.32}\text{Zr}_{0.68}\text{O}_2$	3.9	126	0.141
$\text{Ce}_{0.18}\text{Zr}_{0.82}\text{O}_2$	5.7	92	0.095
ZrO_2	7.2	87	0.01

Table 7S. Ceria-zirconia mixed oxides, flame-sprayed

Reference (molar composition)	Crystallite size nm	Specific surface area $\text{m}^2.\text{g}^{-1}$	Activity $\mu\text{mol}.\text{g}^{-1}.\text{s}^{-1}$
CeO_2	11.8	95	0.31
$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	6.3	99	6
$\text{Ce}_{0.32}\text{Zr}_{0.68}\text{O}_2$	7	95	3.4
$\text{Ce}_{0.23}\text{Zr}_{0.77}\text{O}_2$	7.13	88	1.75
$\text{Ce}_{0.15}\text{Zr}_{0.85}\text{O}_2$	9.4	93	0.73
ZrO_2	17	48	0.06

Table 8S. Other flame-sprayed ceria-based oxides

Reference (% weight)	Specific surface area $\text{m}^2.\text{g}^{-1}$	Activity $\mu\text{mol}.\text{g}^{-1}.\text{s}^{-1}$
1% La/ CeO_2	99	0.63
1% Nd/ CeO_2	105	0.58
1% Zn/ CeO_2	96	0.49

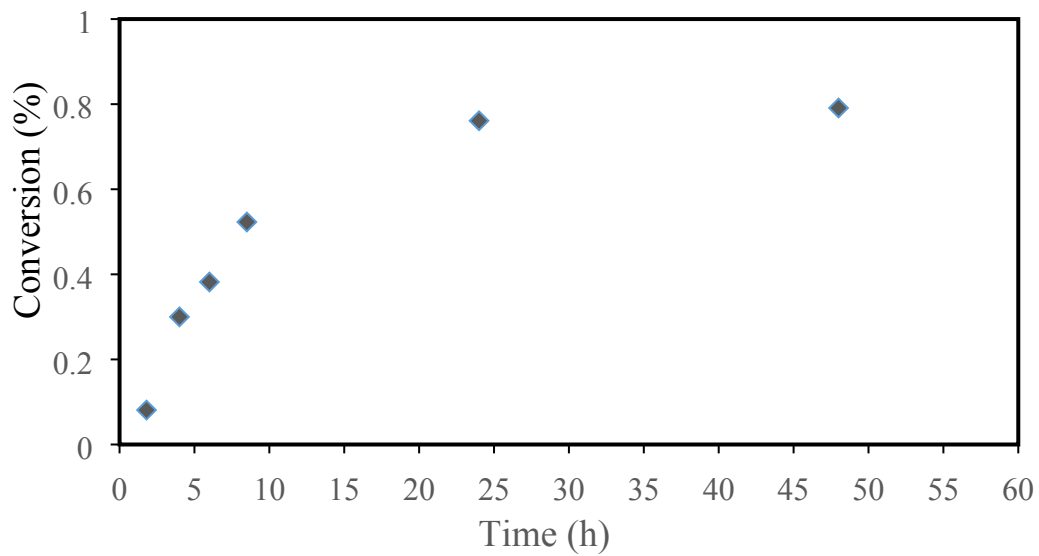


Fig 4S: Conversion over CP-Ce_{0.63}Zr_{0.37}O₂ at 413K versus time, molar ratio MeOH/catalyst =577 mol/mol. P=120 bar, T = 413K, MeOH:CO₂=1:1,Wcat= 0.1 g