

Supplementary Materials: Improving Product Yield in the Direct Carboxylation of Glycerol with CO₂ through the Tailored Selection of Dehydrating Agents

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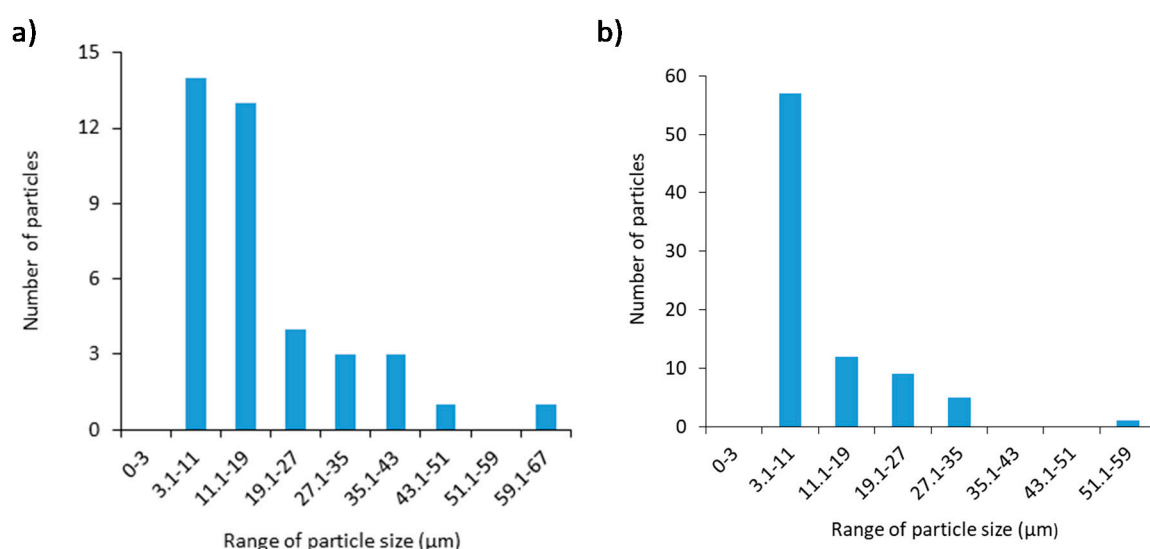


Figure S1. Particle size distributions for (a) CP-La₂O₂CO₃ and (b) HT-La₂O₂CO₃ determined from analysis of multiple SEM micrographs.

Table S1. Mass spectrometry fragmentation pattern of unidentified by-product (chromatogram retention time = 35.5 min) from the carboxylation of glycerol in the presence of benzonitrile as a dehydrating agent. Reaction conditions: reaction pressure = 45 bar, 6 wt.% La₂O₃ to glycerol ratio, 22.5 mmol glycerol, 45 mmol benzonitrile, 18 h and reaction temperature = 160 °C.

m/z	Relative Intensity
105	100
45	57.3
77	42.91
123	19.5
89	15.95
43	15.44
44	14.92
51	13.94
73	9.47
87	9.35
165	9.18
59	8.9
74	7.82
106	7.24
136	5.62
92	5.15

58

5.06

Table S2. Influence of the dehydrating agents on by-product formation. Reaction conditions: reaction pressure = 45 bar, 6 wt.% La_2O_3 to glycerol ratio, 22.5 mmol glycerol, 45 mmol dehydrating agents, 18 h and reaction temperature = 160 °C. The by-products detected from the reaction were measured qualitatively, value shown in the table correspond to chromatogram peak area ($\times 10^5$).

Products	Adiponitrile	Acetonitrile	Benzonitrile	Acetic anhydride
4HMO	2	6	3	0
Unknown 1 (minute 30.8)	2	10	0	0
Unknown 2 (minute 31.3)	4	3	0	0
Unknown 3 (minute 33.9)	2	0	0	0
Unknown 4 (minutes 35.5)	0	0	21	0

Table S3. Influence of catalyst synthesis method on by-product formation. Reaction conditions: reaction pressure = 45 bar, 6 wt.% catalyst to glycerol ratio, 22.5 mmol glycerol, 45 mmol adiponitrile, 18 h and reaction temperature = 160 °C. The by-products detected from the reaction were measured qualitatively, value shown in the table correspond to chromatogram peak area ($\times 10^5$).

Products	$\text{La}_2\text{O}_3\text{-C}$	$\text{La}_2\text{O}_3\text{CO}_3\text{-CP}$	$\text{La}_2\text{O}_3\text{CO}_3\text{-HT}$	$\text{La}_2\text{O}_3\text{CO}_3\text{-SG}$
4HMO	2	5	13	2
Unknown 1 (minute 30.8)	2	10	14	N/A
Unknown 2 (minute 31.3)	4	21	9	N/A
Unknown 3 (minute 33.9)	2	8	17	N/A