Supplemental Information

Investigating the Influence of Reaction Conditions and the Properties of Ceria for the Valorisation of Glycerol.

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Glycerol to MeOH: Full product list (Analysis conditions: GC1 Varian CP 3800 gas chromatograph equipped with a capillary column (ZB-Wax plus, 30 m × 0.53 mm × 1 μm)). The injector port was maintained at 250 °C and a split-less injection was used. The initial column temperature (40 °C) was held for 2 mins, then ramped (20 °C min^{-1}) to 60 °C where it was held for 2 minutes before ramping to 220 °C (20 °C min^{-1}) and holding for 15 minutes. Products were analysed by an FID maintained at 300 °C. GC2 Varian 450 gas chromatograph equipped with a capillary column (CP-Sil5CB, 50 m × 0.32 mm × 5 μm). The injector port was maintained at 200 °C and a 20:1 split ratio used. The initial column temperature (35 °C) was held for 15 mins and ramped (50 °C min^{-1}) to 100 °C where it was held for 3 minutes. Products were analysed by an FID with a methanizer, held at 200 °C and 350 °C respectively. GC3 Varian CP3380 gas chromatograph equipped with a Porapak Q column. The injector was held at 50 °C; the column was maintained at 30 °C for 15 minutes. Products were analysed by a TCD, with the filament maintained at 200 °C.

Table S1. Liquid and gas product list.

Product	**Retention Time**		
	GC1	GC2	GC3
Acetaldehyde	1.91		
Propionaldehyde	2.39		
Acetone	2.60		
Acrolein	2.84		
Butyraldehyde	3.13		
Methanol	3.48		
2-propanol	3.91		
Ethanol	4.01		
2,3-butanedione	4.55		
2-butanol	5.56		
1-propanol	5.80		
3-hexanone	5.91		
2-hexanone	6.36		
2-methyl-1-propanol	6.68		
Allyl alcohol	7.05		
Cyclopentanone	8.01		
Hydroxyacetone	9.37		
3-ethoxy-1-propanol	9.99		
2-oxopropyl acetate	10.41		
Acetic acid	10.55		
Glycidol	10.79		
Propionic acid	11.24		
1,2-propanediol	11.75		
Ethylene glycol	12.01		
1,3-propanediol	13.08		
Phenol	14.76		
Glycerol	18.79		
CO		5.02	
CH_4		5.12	
CO_2		5.38	
H_2			2.22
O_2			2.90

Table S2. Influence of contact time on dilute glycerol reaction.

Temperature °C (catalyst mass g)	320 (0.5g)	320 (1.5g)	320 (4g)
Glycerol conversion (%)	5	21	56
MeOH S.T.Y. ($mmol_{MeOH}$ kg^{-1}_{cat} h^{-1})	474	454	346
Intrinsic S.T.Y. ($mmol_{MeOH}$ m^2 h^{-1})	0.06	0.06	0.04
Aldehyde S.T.Y. ($mmol_{ald.}$ kg^{-1}_{cat} h^{-1})	203	199	160
MeOH STY by mass (g_{MeOH} kg^{-1}_{cat} h^{-1})	**15.8**	**15.2**	**11.6**
Carbon mole balance (%)	105	100	92
Oxygen mole balance (%)	107	95	82
Hydrogen mole balance (%)	111	97	85
	Carbon mole selectivity (%)		
Acetaldehyde	4.58	4.41	4.25
Propionaldehyde	0.37	0.45	0.48
Acrolein	1.33	0.85	0.77
Butyraldehyde	0.10	0.05	0.06
Acetone	0.24	0.37	0.44
2,3-Butanedione	0.78	1.55	1.49
3-Hexanone	0.00	0.02	0.24
2-Hexanone	0.00	0.02	0.02
Cyclopentanone	0.10	0.08	0.10
Hydroxyacetone	49.13	45.41	40.88
Methanol	6.72	6.04	5.53
2-butanol	0.04	0.01	0.00
2-propanol	0.07	0.05	0.08
Ethanol	0.33	0.24	0.34
1-propanol	0.08	0.17	0.06
2-methyl-1-propanol	0.00	0.01	0.02
Allyl alcohol	1.39	1.08	0.89
3-ethoxy-1-propanol	1.03	1.93	2.34
Phenol	0.00	0.07	0.00
1,2-propanediol	5.68	5.96	6.01
Ethylene glycol	9.21	8.32	7.99
1,3-propanediol	0.00	0.13	0.00
Acetic acid	7.12	1.30	0.20
Propionic acid	1.47	1.65	2.50
2-oxopropyl acetate	0.03	5.88	5.70
CO	1.20	1.73	1.92
CH_4	0.10	0.02	0.06
CO_2	0.96	1.31	1.59
Unknown(s)	7.63	10.90	16.08

Table S3. Influence of reaction temperature on dilute glycerol reaction.

Temperature (°C)	320	360	400	440
Glycerol conversion (%)	21	84	98	100
MeOH S.T.Y. ($mmol_{MeOH}$ kg^{-1}_{cat} h^{-1})	454	1785	3013	4390
Intrinsic S.T.Y. ($mmol_{MeOH}$ m^2 h^{-1})	0.06	0.22	0.37	0.55
Aldehyde S.T.Y. ($mmol_{ald.}$ kg^{-1}_{cat} h^{-1})	199	935	2441	3635
MeOH STY by mass (g_{MeOH} kg^{-1}_{cat} h^{-1})	15.8	59.8	100.2	145.7
Carbon mole balance (%)	100	87	80	77
Oxygen mole balance (%)	95	72	62	57
Hydrogen mole balance (%)	97	78	68	62
		Carbon mole selectivity (%)		
Acetaldehyde	4.58	5.80	12.21	16.95
Propionaldehyde	0.37	0.81	2.68	6.46
Acrolein	1.33	1.31	4.10	6.91
Butyraldehyde	0.10	0.08	0.24	0.38
Acetone	0.24	0.83	3.18	7.23
2,3-Butanedione	0.78	2.32	3.63	3.69
3-Hexanone	0.00	0.03	0.04	0.05
2-Hexanone	0.00	0.02	0.01	0.01
Cyclopentanone	0.10	0.18	0.57	0.92
Hydroxyacetone	49.13	31.59	11.23	0.62
Methanol	6.72	6.93	10.40	15.72
2-butanol	0.04	0.02	0.02	0.02
2-propanol	0.07	0.08	0.15	0.30
Ethanol	0.33	0.38	0.81	1.18
1-propanol	0.08	0.32	0.53	0.51
2-methyl-1-propanol	0.00	0.01	0.01	0.04
Allyl alcohol	1.39	2.04	3.84	2.89
3-ethoxy-1-propanol	1.03	2.21	1.01	0.54
Phenol	0.00	0.03	0.21	0.40
1,2-propanediol	5.98	6.63	3.94	0.97
Ethylene glycol	9.21	8.81	3.05	0.22
1,3-propanediol	0.00	0.11	0.27	0.18
Acetic acid	7.05	3.54	4.41	2.15
Propionic acid	1.45	4.27	6.22	4.19
2-oxopropyl acetate	0.03	1.98	2.08	1.35
CO	1.20	2.52	3.97	7.10
CH_4	0.10	0.05	0.04	0.12
CO_2	0.96	1.85	2.88	4.53
Unknown(s)	7.63	15.47	18.44	14.32

Table S4. Methanol stability over commercial CeO_2 at 400 °C; dilute methanol (10 wt.%) solution flow rate 0.016 ml min^{-1} GHSV 3600 h^{-1}.

Reaction temperature (°C)	400
MeOH conversion (%)	13
Carbon mole balance (%)	96
Oxygen mole balance (%)	100
Hydrogen mole balance (%)	96
	Products formed (mmol)
CO	0.5
CO2	0.4
H_2	1.8

Table S5. Influence of CeO_2 calcination temperature on dilute glycerol reaction with GHSV *ca.* 3450 h^{-1}.

CeO_2 calcination temperature (°C)	400	500	600	700
Glycerol conversion (%)	83	83	80	84
MeOH S.T.Y. ($mmol_{MeOH}$ kg^{-1}_{cat} h^{-1})	2507	2318	1766	1531
Intrinsic S.T.Y. ($mmol_{MeOH}$ m^2 h^{-1})	0.07	0.07	0.07	0.07
Aldehyde S.T.Y. ($mmol_{ald.}$ kg^{-1}_{cat} h^{-1})	1296	1177	916	609
MeOH STY by mass (g_{MeOH} kg^{-1}_{cat} h^{-1})	84	78	59	51
Carbon mole balance (%)	82	80	84	81
Oxygen mole balance (%)	67	66	70	67
Hydrogen mole balance (%)	75	72	76	74
	Carbon mole selectivity (%)			
Acetaldehyde	9.33	8.62	9.24	7.48
Propionaldehyde	1.11	1.19	1.38	1.15
Acrolein	1.88	1.94	1.72	1.16
Butyraldehyde	0.05	0.06	0.07	0.06
Acetone	0.99	1.05	1.29	1.09
2,3-Butanedione	2.52	2.80	2.10	2.09
3-Hexanone	0.11	0.11	0.16	0.13
2-Hexanone	0.00	0.00	0.00	0.00
Cyclopentanone	0.11	0.14	0.19	0.17
Hydroxyacetone	32.11	32.99	28.81	29.14
Methanol	10.98	10.58	10.93	11.37
2-butanol	0.02	0.02	0.03	0.02
2-propanol	0.06	0.06	0.07	0.06
Ethanol	0.63	0.61	0.78	0.57
1-propanol	0.01	0.01	0.02	0.01
2-methyl-1-propanol	0.01	0.01	0.01	0.01
Allyl alcohol	1.71	1.56	2.16	2.64
3-ethoxy-1-propanol	0.25	0.28	0.29	0.26
Phenol	0.04	0.04	0.05	0.05
1,2-propanediol	4.03	4.08	4.14	4.84
Ethylene glycol	4.54	4.57	3.68	5.11
1,3-propanediol	0.07	0.07	0.05	0.06
Acetic acid	3.34	3.43	4.00	3.99
Propionic acid	4.20	4.26	5.43	5.24
2-oxopropyl acetate	1.19	1.23	1.16	0.99
CO	2.69	2.71	3.18	3.59
CH_4	0.01	0.00	0.02	0.01
CO_2	1.55	1.63	1.88	1.91
Unknown (s)	15.25	14.69	15.99	15.79

Table S6. The total carbon content (%) observed in a reaction over CeO_2 for 6 hour at GHSV *ca.* 3600 h^{-1}.

Reaction conditions; 340 °C, glycerol flow (0.016 mL/min), 0.7 g CeO_2, 20 mL/min Ar. Total carbon content was normalised against the total carbon content observed by CHN analysis in the starting glycerol solution. *Coking calculated from the mass loss observed by TGA of the post reaction catalyst.	
Catalytic Coking *	1.4
CO_X	6.1
CHN Analysis/liquid GC analysis	87.1/79
Total Carbon Content	94.6

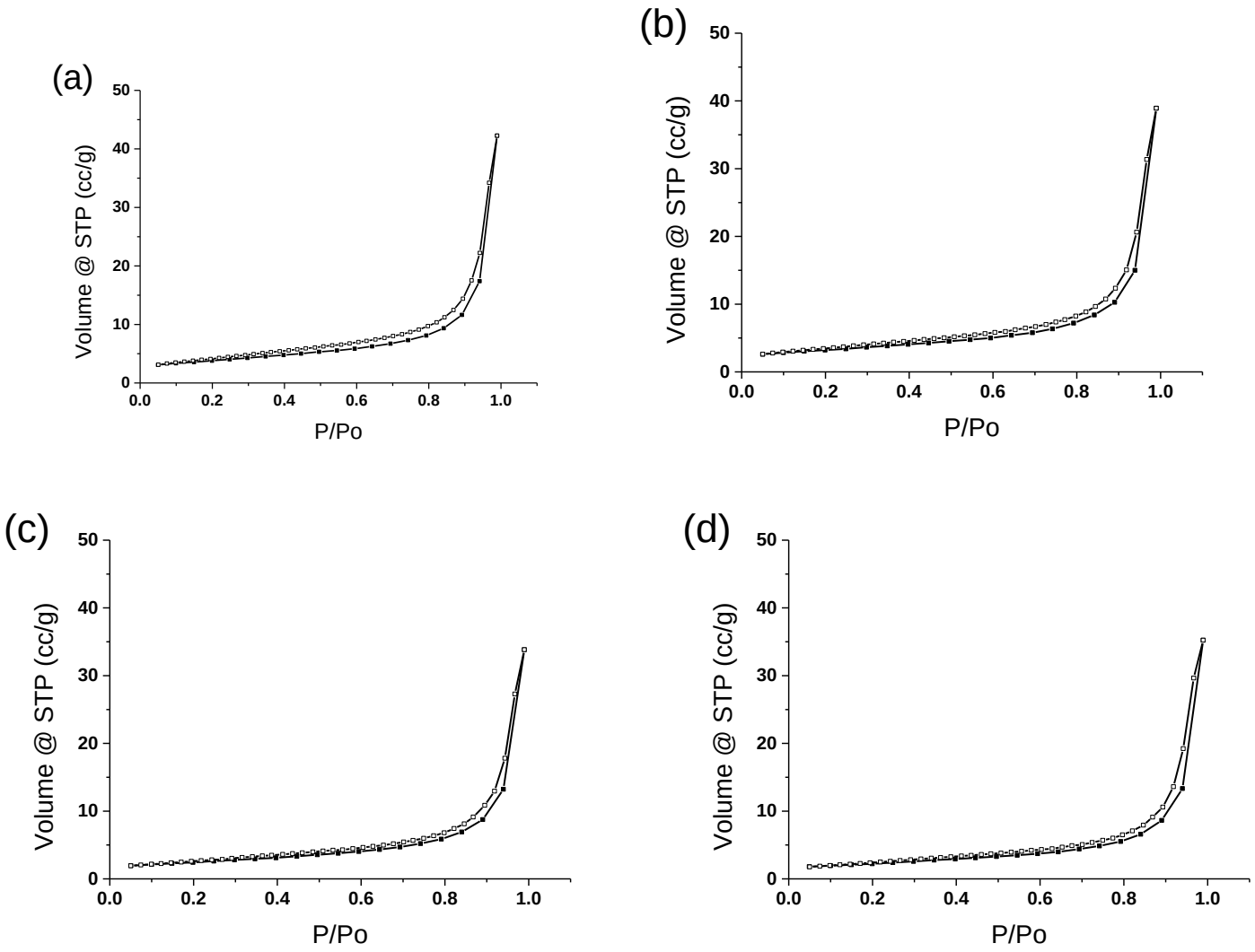

Figure S1. Nitrogen adsorption and desorption isotherms for ceria calcined at 400 (a), 500 (b), 600 (c) and 700 °C (d); adsorption closed symbol, desorption open symbols

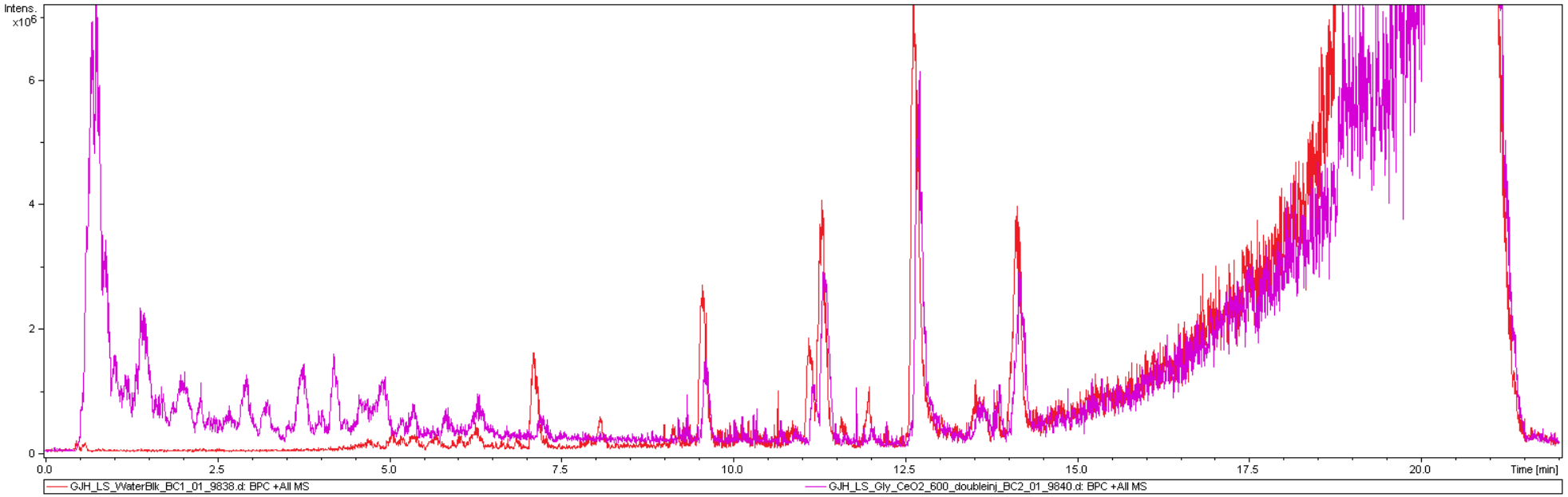

Figure S2. LC-MS chromatogram corresponding to the post reaction solution of a reaction run over CeO_2 for 6 h. Detection parameters are fixed at 100–1000 m/z. Reaction conditions; 340 °C, glycerol flow (0.016 mL/min), 0.7 g CeO_2, GHSV *ca.* 3600 h^{-1}. Pink line—chromatogram of the post reaction solution. Red line—chromatogram of a H_2O blank solution.