Electronic Supplementary Information

New insights on the valorisation of glycerol over MgO catalysts in the gas-phase.

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Glycerol to MeOH: Analysis conditions; *GC1* Varian CP 3800 gas chromatograph equipped with a capillary column (ZB-Wax plus, 30 m x 0.53 mm x 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 x 0.32 mm x 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 Product list from GC analysis.

Product	**Retention time**		
	GC1	GC2	GC3
Acetaldehyde	1.907		
Propionaldehyde	2.387		
Acetone	2.60		
Acrolein	2.840		
Butyraldehyde	3.133		
Methanol	3.48		
2-propanol	3.907		
Ethanol	4.013		
2,3-butanedione	4.547		
2-butanol	5.56		
1-propanol	5.800		
3-hexanone	5.907		
2-hexanone	6.360		
2-methyl-1-propanol	6.680		
Allyl alcohol	7.053		
Cyclopentanone	8.013		
Hydroxyacetone	9.373		
3-ethoxy-1-propanol	9.987		
Acetic acid	10.547		
Glycidol	10.790		
Propionic acid	11.240		
1,2-propanediol	11.747		
Ethylene glycol	12.013		
1,3-propanediol	13.080		
Phenol	14.760		
Glycerol	18.787		
CO		5.02	
CH_4		5.12	
CO_2		5.38	
H_2			2.222
O_2			2.902

Table S2a. Catalyst free product list without SiC.			
	320 °C	**400 °C**	**480 °C**
Product	**Selectivity (%)**		
acetaldehyde	0.00	3.9	6.4
propionaldehyde	0.00	0.5	0.7
acetone	0.00	0.4	0.7
acrolein	0.00	2.7	2.8
methanol	0.00	2.5	4.9
ethanol	0.00	0.0	0.4
2,3-butanedione	0.00	0.0	0.7
1-propanol	0.00	0.0	0.1
3-hexanone	0.00	0.0	0.2
allyl alcohol	0.00	16.2	17.6
cyclopentanone	0.00	0.0	0.2
hydroxyacetone	0.00	30.9	26.6
acetic acid	0.00	1.1	1.7
propionic acid	0.00	1.3	2.7
1,2-propanediol	0.00	3.1	3.4
unknown(s)	0.00	22.0	19.4
ethylene glycol	0.00	4.3	8.3
1,3-propanediol	0.00	1.6	0.9
CO	0.00	0.7	0.8
CO_2	0.00	2.3	1.5
CH_4	0.00	0.4	0.1

Table S2b. Catalyst free product list with SiC.				
	320 °C	**360 °C**	**400 °C**	**480 °C**
Product	**Selectivity (%)**			
acetaldehyde	0.0	4.0	5.2	12.9
propionaldehyde	0.0	0.0	0.3	0.8
acetone	0.0	0.4	0.4	0.7
acrolein	0.0	1.7	2.3	7.0
butyraldehyde	0.0	0.0	0.0	0.1
methanol	0.0	0.6	1.8	2.1
ethanol	0.0	0.0	0.3	0.5
2,3-butanedione	0.0	0.0	0.5	0.5
1-propanol	0.0	0.0	0.0	0.2
3-hexanone	0.0	0.0	0.1	0.1
2-hexanone	0.0	0.0	0.0	0.3
allyl alcohol	43.1	34.7	30.4	22.3
cyclopentanone	0.0	0.0	0.0	0.1
hydroxyacetone	56.9	37.3	33.5	23.3
3-ethoxy-1-propanol	0.0	0.0	0.3	0.2
acetic acid	0.0	2.5	2.0	1.3
propionic acid	0.0	1.5	1.9	1.1
1,2-propanediol	0.0	1.9	2.0	4.2
unknown(s)	0.0	5.7	9.2	10.3
ethylene glycol	0.0	2.3	3.2	5.9
1,3-propanediol	0.0	1.0	1.0	1.3
phenol	0.0	0.0	0.0	0.3
CO	0.0	0.7	0.7	0.6
CH_4	0.0	0.4	0.1	0.1
CO_2	0.0	3.9	3.3	1.3

Table S3. Product lists over MgO at different temperatures.			
	360 °C	**400 °C**	**440 °C**
Product	**Selectivity (%)**		
acetaldehyde	9.1	13.3	17.0
propionaldehyde	0.7	1.6	3.0
acetone	0.2	0.4	0.6
acrolein	1.3	1.7	3.2
butyraldehyde	0.0	0.1	0.1
methanol	23.4	27.9	25.6
2-propanol	0.1	0.1	0.1
ethanol	1.0	1.5	1.6
2,3-butanedione	1.7	1.9	1.9
2-butanol	0.0	0.1	0.1
1-propanol	0.1	0.3	0.3
3-hexanone	0.2	0.2	0.2
2-hexanone	0.1	0.0	0.0
2-methyl-1-propanol	0.0	0.1	0.0
allyl alcohol	1.0	1.6	2.3
cyclopentanone	0.1	0.4	1.0
hydroxyacetone	25.9	17.9	15.5
3-ethoxy-1-propanol	0.5	0.9	1.3
acetic acid	1.7	2.0	2.0
propionic acid	0.4	0.6	0.7
1,2-propanediol	2.4	1.3	0.9
unknown(s)	10.8	9.5	8.0
ethylene glycol	10.9	5.8	2.5
1,3-propanediol	1.2	0.8	0.5
phenol	0.1	0.2	0.3
CO	3.8	3.9	5.8
CH_4	0.0	2.3	0.4
CO_2	3.3	3.8	5.3

Table S4. Influence of GHSV over MgO catalysts on the glycerol conversion and product selectivity. 0.5 g MgO at 400 °C			
	2300 h^{-1}	**4615 h^{-1}**	**6920 h^{-1}**
Glycerol Conversion (%)	**99.9**	**89.9**	**73.8**
Product	**Selectivity (%)**		
acetaldehyde	18.7	13.3	11.0
acetone	5.3	0.4	0.3
methanol	26.8	27.9	13.0
hydroxyacetone	11.5	17.9	32.7
1,2-propanediol	1.3	1.3	6.6

Table S5. Product lists over MgO at 400 °C with different wt. % glycerol feed-stocks.

	10 wt. % (1.8)[a]	10 wt. %[b] (0.3)	20 wt. % (0.8)	40 wt. % (0.4)	50 wt. % (0.3)
Product	**Selectivity (%)**				
acetaldehyde	18.0	**14.6**	18.0	17.2	13.3
propionaldehyde	3.8	0.5	3.5	2.1	1.6
acetone	1.0	0.6	0.9	0.4	0.4
acrolein	2.2	2.3	2.5	2.9	1.7
butyraldehyde	0.2	0.0	0.2	0.1	0.1
methanol	34.9	**31.6**	32.0	29.5	27.9
2-propanol	0.0	0.0	0.1	0.1	0.1
ethanol	3.2	1.2	2.6	1.9	1.5
2,3-butanedione	2.6	0.7	2.3	1.9	1.9
2-butanol	0.1	0.0	0.1	0.1	0.1
1-propanol	0.7	0.0	0.6	0.3	0.3
3-hexanone	0.4	0.1	0.3	0.2	0.2
2-hexanone	0.0	0.0	0.0	0.0	0.0
2-methyl-1-propanol	0.0	0.0	0.0	0.0	0.1
allyl alcohol	2.2	6.2	2.1	2.0	1.6
cyclopentanone	2.2	0.3	1.6	1.0	0.4
hydroxyacetone	3.6	**18.7**	6.4	14.8	17.9
3-ethoxy-1-propanol	1.7	0.9	1.5	1.1	0.9
acetic acid	0.7	0.8	1.4	1.5	2.0
propionic acid	0.5	0.4	0.8	0.6	0.6
1,2-propanediol	0.2	1.5	0.3	0.8	1.3
unknown(s)	10.1	**8.8**	10.6	9.6	9.5
ethylene glycol	0.2	**7.0**	1.0	2.5	5.8
1,3-propanediol	0.3	0.1	0.2	0.5	0.8
phenol	1.3	0.3	0.1	0.3	0.2
CO	3.5	1.5	3.9	4.2	3.9
CH_4	0.2	0.0	0.4	0.9	2.3
CO_2	6.6	1.9	6.8	3.7	3.8

[a] values in parenthesis represent the catalyst to glycerol ration (g/g); [b] 100 mg catalyst used.

Table S6. Product lists over MgO at 400 °C as a function of reaction time.

	2 h	4 h	6h	24 h	48 h
Product	**Selectivity (%)**				
acetaldehyde	18.2	14.7	14.8	12.8	14.6
propionaldehyde	2.9	2.1	2.0	1.8	2.1
acetone	0.7	0.5	0.7	0.6	0.5
acrolein	2.4	2.3	2.3	2.0	2.4
butyraldehyde	0.1	0.1	0.1	0.1	0.1
methanol	32.2	27.8	26.9	29.7	26.9
2-propanol	0.0	0.0	0.0	0.0	0.1
ethanol	2.1	1.5	1.5	1.2	1.2
2,3-butanedione	2.7	2.6	2.6	2.3	2.5
2-butanol	0.1	0.1	0.1	0.1	0.1
1-propanol	0.4	0.3	0.3	0.2	0.2
3-hexanone	0.4	0.3	0.3	0.3	0.3
2-hexanone	0.0	0.0	0.0	0.0	0.0
2-methyl-1-propanol	0.0	0.0	0.0	0.0	0.0
allyl alcohol	1.7	1.4	1.4	1.2	1.3
cyclopentanone	0.8	0.6	0.5	0.4	0.4
hydroxyacetone	10.6	17.6	17.3	18.1	19.7
3-ethoxy-1-propanol	1.6	1.4	1.4	1.3	1.3
acetic acid	1.4	2.1	1.8	1.7	1.7
propionic acid	0.6	0.7	0.6	0.6	0.6
1,2-propanediol	0.7	1.4	1.6	1.5	1.5
unknown(s)	7.7	10.5	10.0	10.3	10.1
ethylene glycol	1.4	3.7	4.6	4.5	4.3
1,3-propanediol	0.3	0.3	0.3	0.3	0.3
phenol	0.5	0.0	0.4	0.4	0.4
CO	4.4	3.7	3.9	4.0	3.5
CH_4	0.3	0.2	0.2	0.2	0.2
CO_2	5.8	4.3	4.5	4.3	3.9

Table S7. Crystallite size of fresh and used pelleted MgO catalyst, estimated by applying the Scherrer equation to the MgO(200) reflection in the corresponding XRD patterns (Fig. 6).

The used MgO corresponds to the MgO catalyst after reaction with 50 wt.% glycerol in H_2O for 3 h at 400 ºC.

Pelleted Catalyst	Crystallite Size (Å)
Fresh MgO	94
Used MgO	89

Table S8. The total carbon content observed in a reaction over MgO for 6 h.

Reaction conditions; 400 °C, glycerol flow (0.016 mL/min), 0.5 g MgO, 50 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*	5.5
CO_X	11.7
CHN Analysis	76.8
Total Carbon Content	94.0

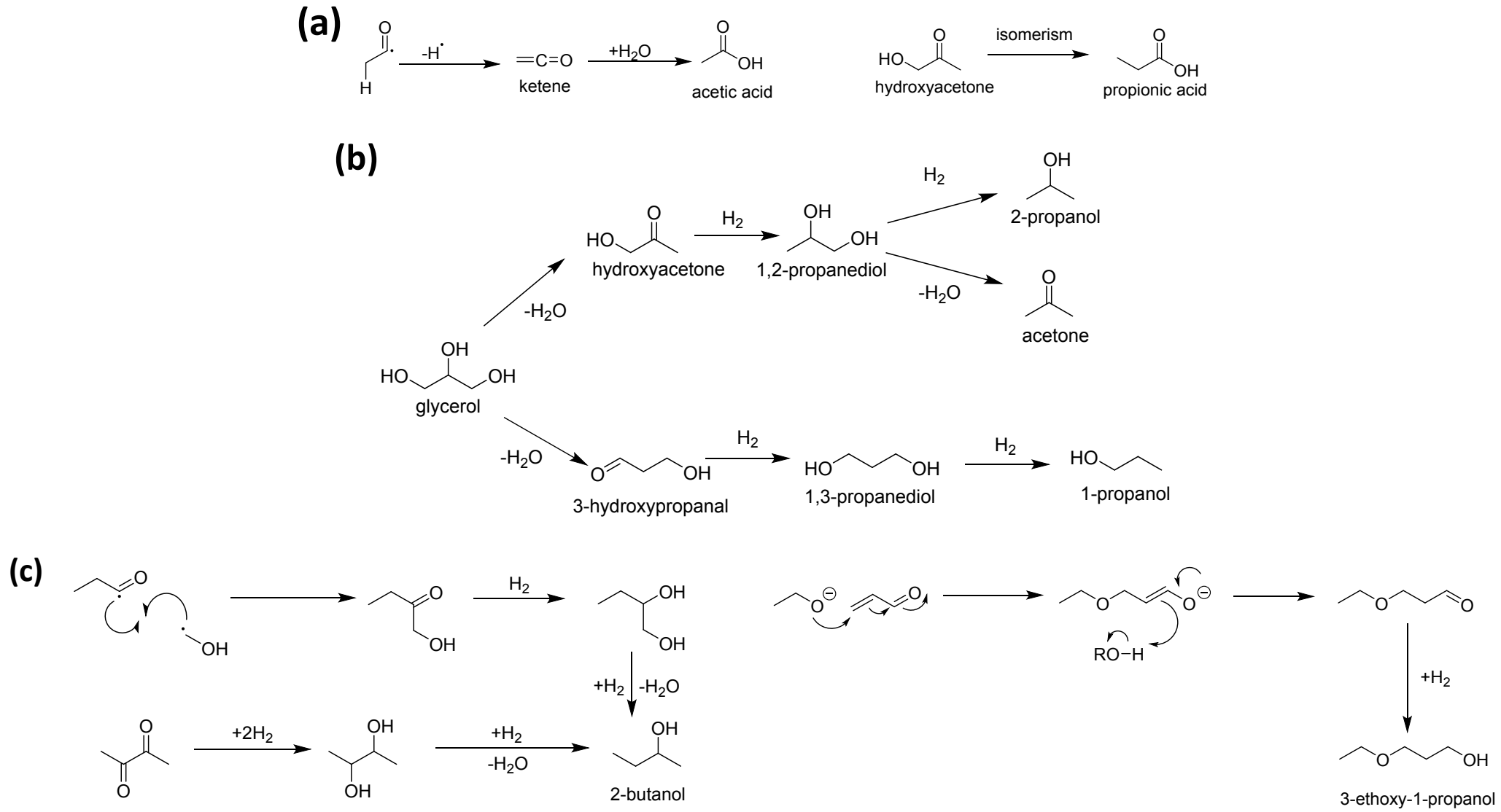

Fig. S1. Potential routes to several products identified with commercial standards according to their retention time in GC1. (a) Formation of acetic and propionic acids from acetaldehyde and hydroxyacetone respectively.[1] (b) Formation of acetone, and 1- and 2-propanol from glycerol. (c) Formation of 2-butanol *via* a radical mechanism or via hydrogenation of 2,3-butanedione and formation of 3-ethoxy-1-propanol *via* ethanol addition to acrolein. 1. A. Corma *et al., J. Catal.*, 2008, 257, 163–171.

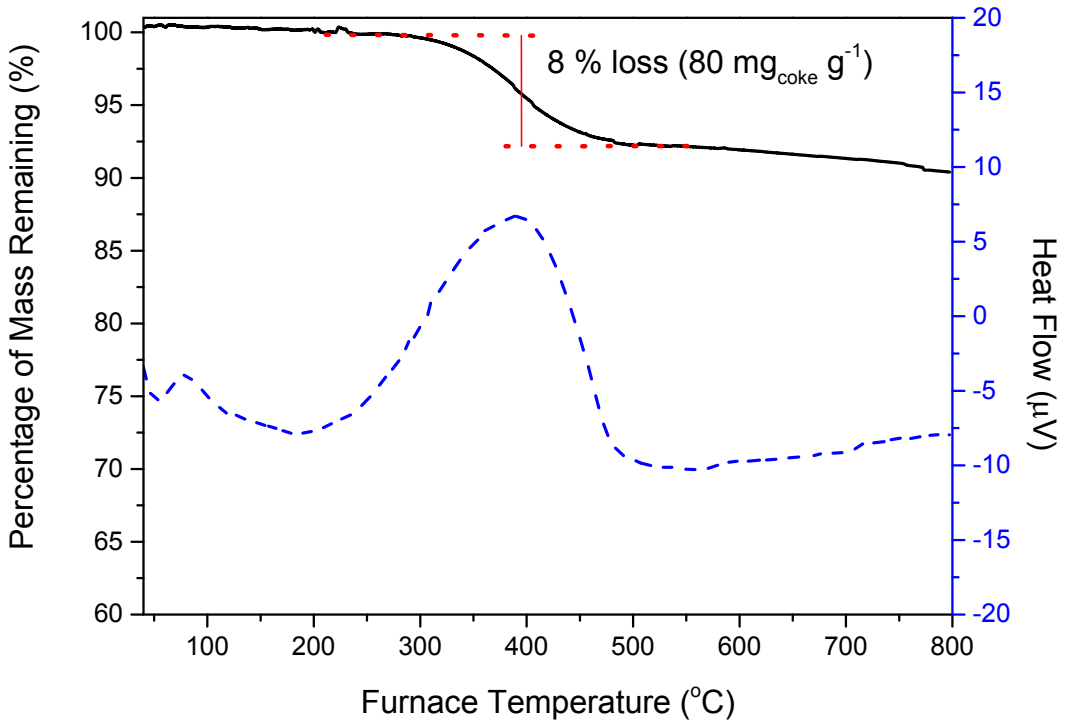

Fig. S2. Thermal gravimetric analysis of an MgO sample following the 135 minutes taken to reach steady glycerol flow over the catalyst bed prior to a reaction (such as Table 4 entry 5). Reaction conditions; 400 °C, glycerol flow (0.016 mL/min), 0.5 g MgO, 50 mL/min Ar.

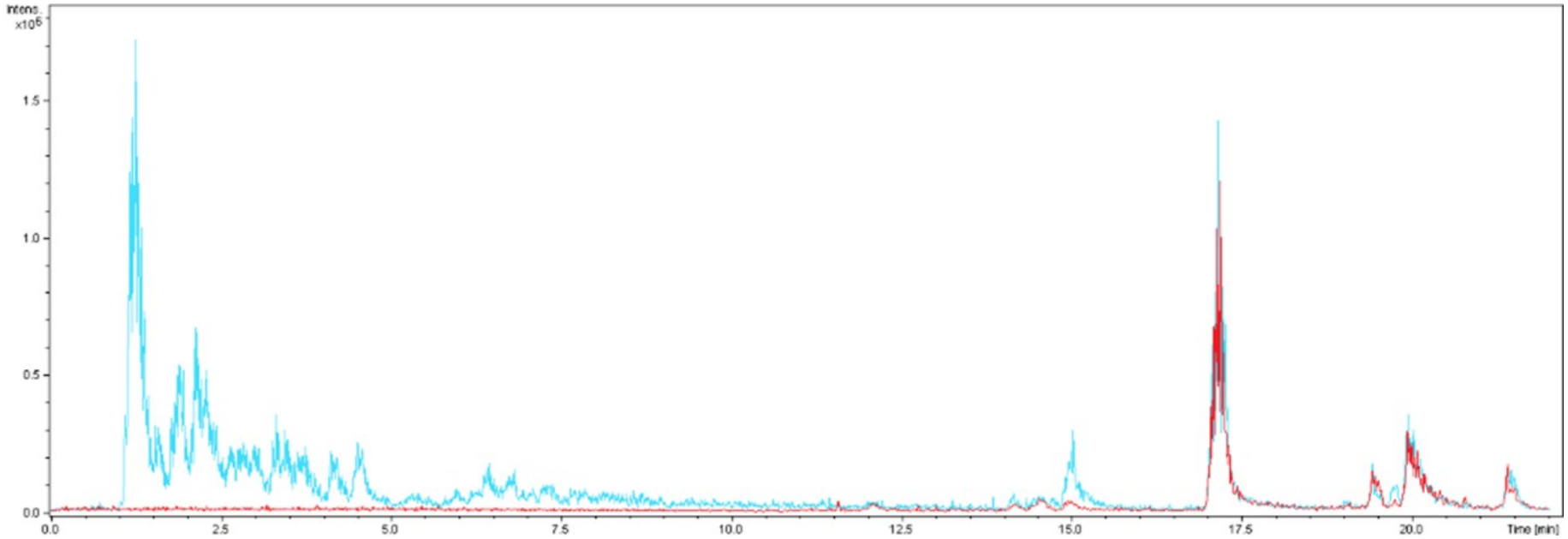

Fig. S3. LC-MS chromatogram corresponding to the post reaction solution of a reaction run over MgO for 6 h. Detection parameters are fixed at 100 - 1000 m/z. Reaction conditions; 400 °C, glycerol flow (0.016 mL/min), 0.5 g MgO, 50 mL/min Ar. Blue line – chromatogram of the post reaction solution. Red line – chromatogram of a H_2O blank solution.