Supplementary Materials to the article

In Situ-Generated, Dispersed Cu Catalysts for the Catalytic Hydrogenolysis of Glycerol

By Iuliana Porukova, Vadim Samoilov, Dzhamulutdin Ramazanov, Mariia Kniazeva, Anton Maximov

Table S1. The average values of conversion of glycerol ($\mathbf{X}_{Gly}$), yields of products (**Y**) under different reaction conditions during glycerol hydrogenolysis (*S* – standard derivation of the value on the left, N – the number of experiments). Conditions: T = 200°C, Gly/H_2O = 4.1 vol, precursor salt = $Cu(OAc)_2 \cdot H_2O$

Entry	Gly/Cu, mol	KOH/Cu, mol	τ, h	p(H_2), MPa	X_{Gly},%	S_x,%	Y_{EG},%	S_y,%	Y_{PG},%	S_y,%	Y_{LA},%	S_y,%	Y_{GA},%	S_y,%	N
1	50	0	5	3	3.1	0.4	-	-	0.1	0.1	1.4	0.4	1.6	0.1	2
2		5.8	2.5	1	9.9	0.5	0.2	0.1	3.7	0.3	4.5	0.4	1.5	0.1	2
3				2	11.5	0.6	0.3	0.1	5.4	0.6	4.2	0.1	1.6	0.1	2
4				3	13.0	2.3	0.2	0.1	7.7	1.5	3.2	0.3	1.9	0.4	2
5				4	13.0	1.2	0.4	0.2	7.2	0.9	3.7	0.5	1.7	0.1	2
6			5	3	14.8	0.2	0.3	0.1	8.9	0.4	3.7	0.2	1.9	0.1	2
7			10		15.5	0.6	0.6	0.1	8.0	0.2	5.7	0.3	1.2	0.1	2
8	100		5		7.0	0.5	0.1	0.1	3.6	0.5	2.6	1.3	0.7	0.4	3
9			10		7.1	0.6	0.2	0.1	3.7	0.3	2.5	0.3	0.7	0.1	2

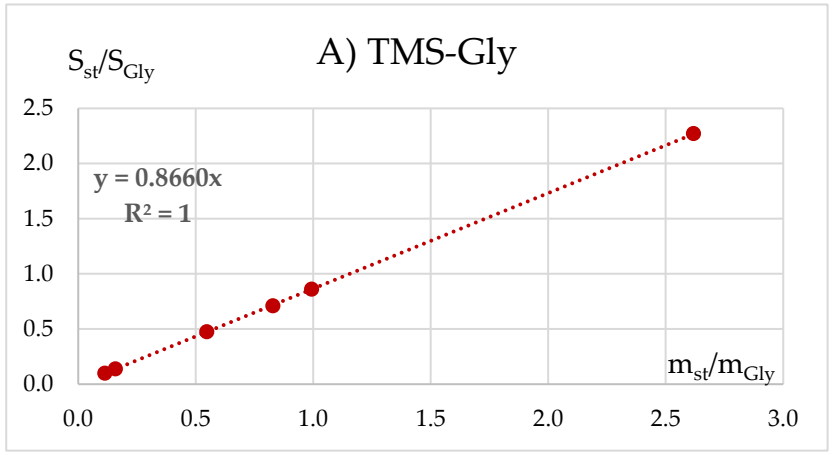
Table S2. The average values of conversion of glycerol ($\mathbf{X}_{Gly}$), yields of products (**Y**) under different reaction conditions during glycerol hydrogenolysis (*S* – standard derivation of the value on the left, N – the number of experiments). Conditions: T = 220°C, $p(H_2)$ = 3 MPa, precursor salt = $Cu(OAc)_2 \cdot H_2O$

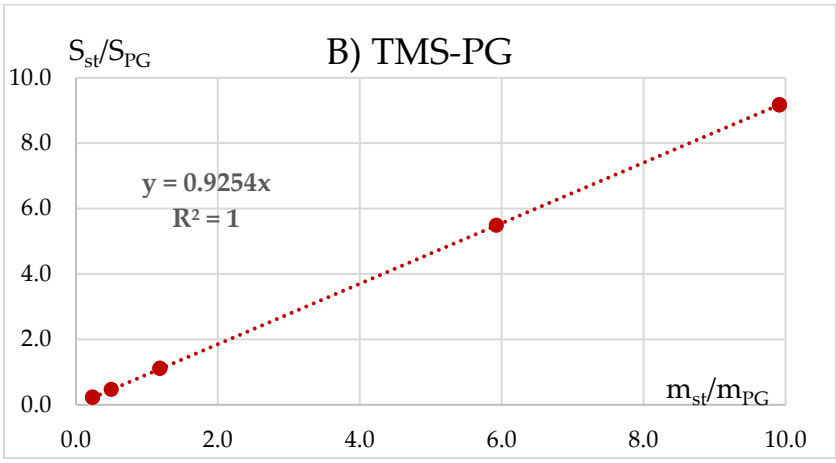
Entry	Gly/Cu, mol	KOH/Cu, mol	Gly/H_2O, vol	τ, h	X_{Gly},%	S_x,%	Y_{EG},%	S_y,%	Y_{PG},%	S_y,%	Y_{LA},%	S_y,%	Y_{GA},%	S_y,%	N
1	50	0	4.1	5	3.4	1.1	0.2	0.1	0.8	0.6	0.9	0.5	1.5	0.1	16
2		0.3			2.8	0.2	-	-	0.8	0.2	0.6	0.1	1.4	0.1	2
3		0.8			3.5	-	-	-	1.1	-	1.1	-	1.3	-	1
4		2.3		1	2.9	0.6	0.1	0.1	1.9	0.5	0.7	0.1	0.2	0.1	2
5				2.5	8.0	1.4	0.3	0.1	6.1	1.2	1.0	0.1	0.6	0.1	2
6				5	13.4	1.5	0.7	0.1	10.0	1.1	1.7	0.5	1.0	0.2	2
7				10	15.3	2.4	0.8	0.3	11.2	2.0	2.5	0.1	0.8	0.1	2
8				15	23.8	2.1	1.1	0.4	17.9	2.6	3.9	0.9	0.9	0.2	3
9				30	30.6	1.1	1.1	0.2	22.9	1.2	5.7	1.4	0.9	0.1	3
10				60	32.7	0.9	1.5	0.1	26.0	0.1	4.0	0.7	1.2	0.4	2
11		3.6		5	12.6	-	0.4	-	6.3	-	4.7	-	1.2	0.1	1
12		4.6			12.8	-	0.4	-	6.4	-	4.4	-	1.6	0.1	1
13		5.8	0.4	5	13.3	1.4	0.4	0.1	4.0	0.4	7.3	1.2	1.6	0.6	2
14			0.8		14.5	1.8	0.6	0.1	6.8	1.8	5.9	0.3	1.2	0.1	3
15			1.4		13.7	0.1	0.3	0.1	6.5	1.4	5.3	2.0	1.6	0.5	2
16			2.1	30	13.4	0.6	0.4	0.1	5.9	0.5	5.8	0.1	1.3	0.1	2
17			4.1	1	12.6	1.7	0.4	0.1	6.9	1.0	4.0	0.8	1.3	0.2	13
18				2.5	14.4	1.0	0.4	0.1	7.5	0.8	5.1	0.9	1.4	0.3	3
19				5	16.8	2.4	0.7	0.2	8.5	1.6	6.8	1.2	0.8	0.4	21
20				10	18.5	1.3	0.8	0.2	9.4	0.8	7.4	0.6	0.9	0.3	2
21				15	20.3	2.4	0.8	0.2	10.4	1.6	8.4	1.1	0.7	0.3	13
22				30	24.4	2.8	1.1	0.4	13.5	2.4	9.1	0.1	0.7	0.1	2
23				60	23.2	2.5	0.8	0.2	12.9	2.8	8.9	0.3	0.6	0.3	2
24	100	0	4.1	5	2.9	0.3	0.1	0.1	1.4	0.3	0.7	0.1	0.7	0.1	2
25		0.3			2.5	0.2	0.1	0.1	1.1	0.3	0.6	0.1	0.7	0.1	2
26		5.8			7.8	0.6	0.2	0.1	4.0	0.4	3.2	0.1	0.4	0.1	2
27				10	11.5	0.7	0.3	0.2	5.1	0.1	5.6	0.4	0.5	0.1	2
28				15	8.6	0.7	0.3	0.1	4.4	0.4	3.4	0.3	0.5	0.1	2
29				10	10.6	-	0.5	-	5.3	-	4.2	-	0.6	-	1

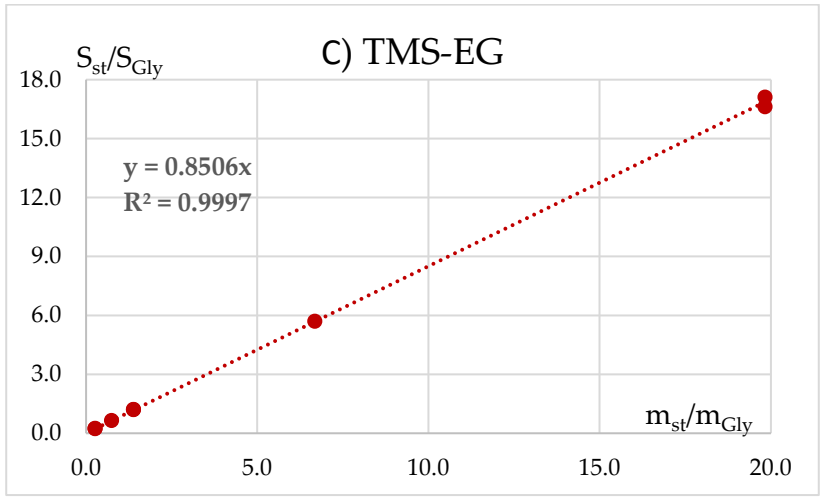
30	200	5.0			3.9	0.4	0.1	0.1	2.0	0.1	1.5	0.3	0.3	0.1	2
31	219	11.0			5.9	2.1	0.2	0.1	2.6	1.2	2.9	0.6	0.2	0.2	2

Table S3. The average values of conversion of glycerol ($\mathbf{X}_{Gly}$), yields of products (**Y**) under different reaction conditions during glycerol hydrogenolysis (*S* – standard derivation of the value on the left, N – the number of experiments). Conditions: p(H_2) = 3 MPa, Gly/H_2O = 4.1 vol

Entry	Precursor salt or catalyst	T, °C	Gly/Cu, mol	KOH/Cu, mol	τ, h	X_{Gly},%	S_x,%	Y_{EG},%	S_y,%	Y_{PG},%	S_y,%	Y_{LA},%	S_y,%	Y_{GA},%	S_y,%	N
1	$CuSO_4 \cdot 5H_2O$	200	50	5.8	5	15.0	0.1	0.4	0.1	7.0	0.2	7.0	0.2	0.6	0.1	2
2					10	15.2	1.6	0.5	0.1	8.9	1.2	5.0	0.4	0.8	0.1	3
3			100		5	7.0	-	0.2	-	4.0	-	2.5	-	0.3	-	1
4					10	8.1	-	0.4	-	4.7	-	2.9	-	0.1	-	1
5		220	50		5	16.6	1.2	0.8	0.2	10.4	1.5	5.1	1.9	0.3	0.2	2
6					10	18.4	1.8	0.9	0.2	10.7	1.2	6.8	0.7	-	-	2
7			100		5	8.5	-	0.4	-	4.7	-	3.3	-	0.1	-	1
8					10	8.5	-	0.3	-	4.8	-	3.4	-	-	-	1
9	$Cu\text{-}Cr_2O_3$	200	50	0	5	7.4	1.9	0.1	0.1	6.0	2.0	1.3	0.1	-	-	2
10					10	10.6	2.7	0.1	0.1	10.1	2.0	0.4	0.3	-	-	2
11			100		5	3.6	0.5	-	-	3.6	0.4	-	-	-	-	2
12					10	9.3	1.2	0.3	0.2	8.3	1.6	0.7	0.2	-	-	3
13		220	50		5	19.0	1.6	0.2	0.1	17.3	1.7	1.5	0.1	-	-	2
14					10	26.1	0.9	0.2	0.1	25.4	1.3	0.5	0.4	-	-	2
15				5.8	5	34.5	-	1.5	-	23.6	-	9.4	-	-	-	1
16			100	0	5	11.8	0.9	0.1	0.1	8.6	0.8	3.1	0.1	-	-	2
17					10	19.5	3.7	0.1	0.1	19.0	4.1	0.4	0.4	-	-	3
18		230	50		5	31.8	-	1.3	-	20.7	-	9.8	-	-	-	1
19	$CuCl_2 \cdot 2H_2O$	200	50	5.8	5	11.0	3.6	0.3	0.1	5.8	3.0	4.3	0.3	0.6	0.3	2
20		220				16.2	1.0	0.5	0	6.7	0.1	8.3	1.0	0.7	0.1	2







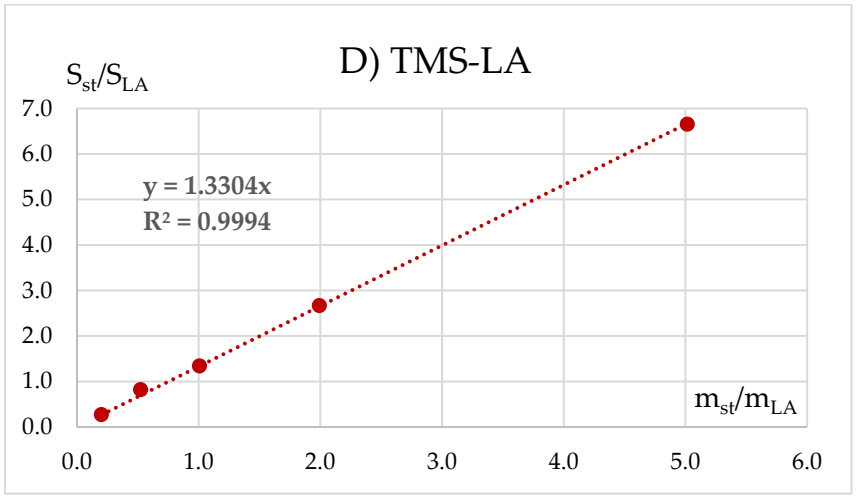
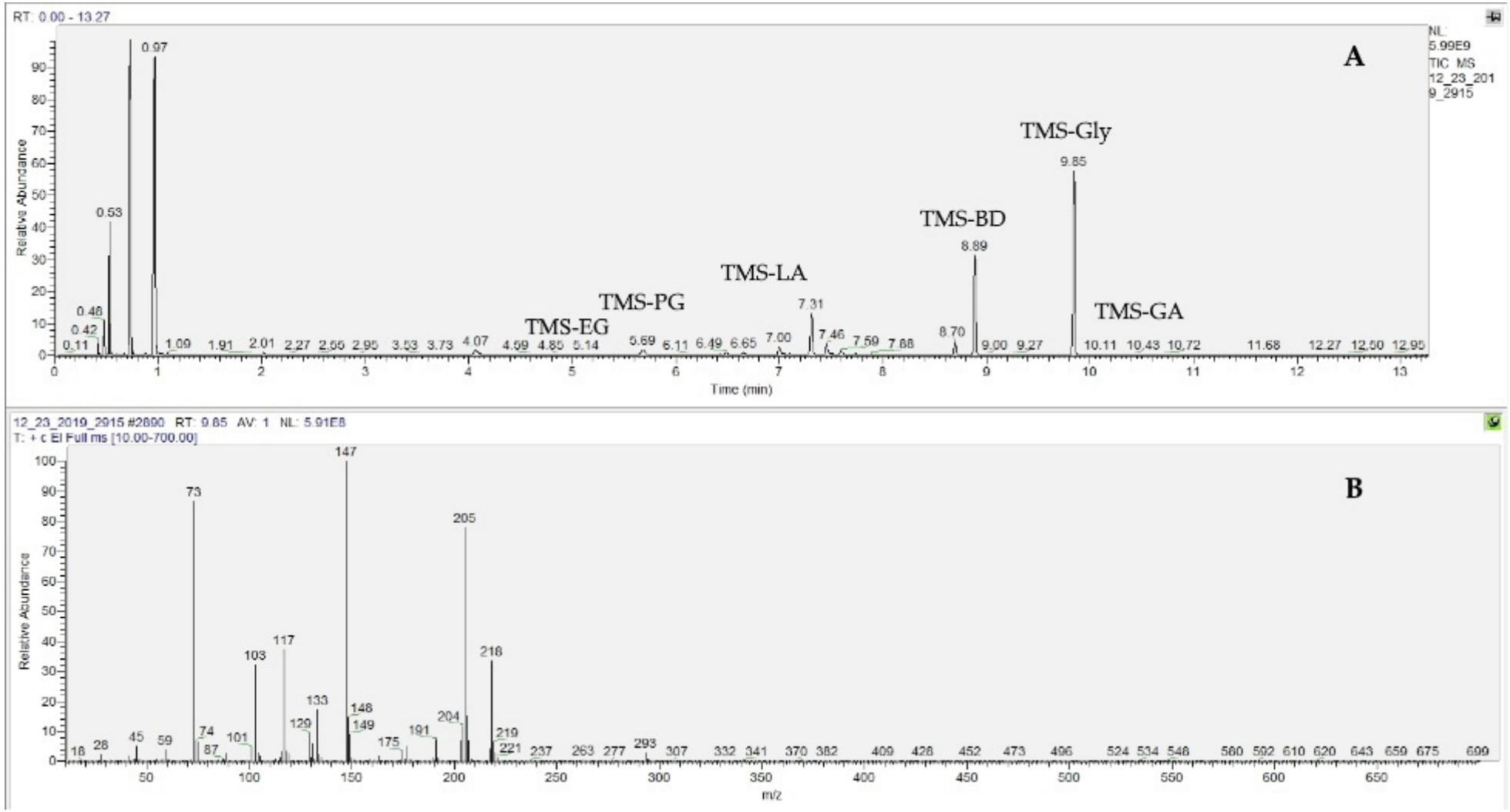
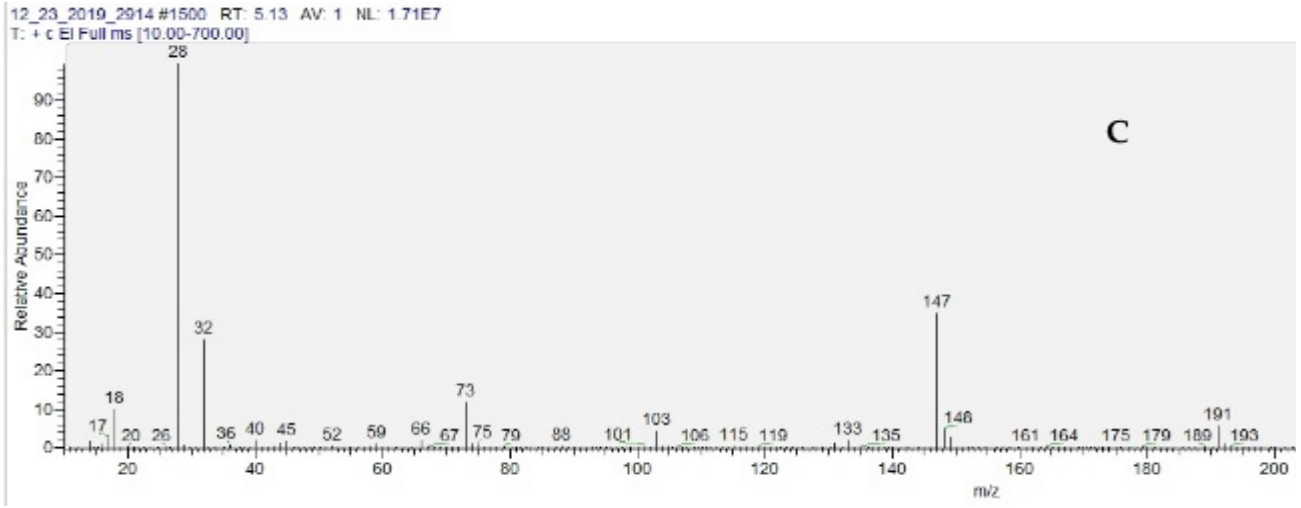
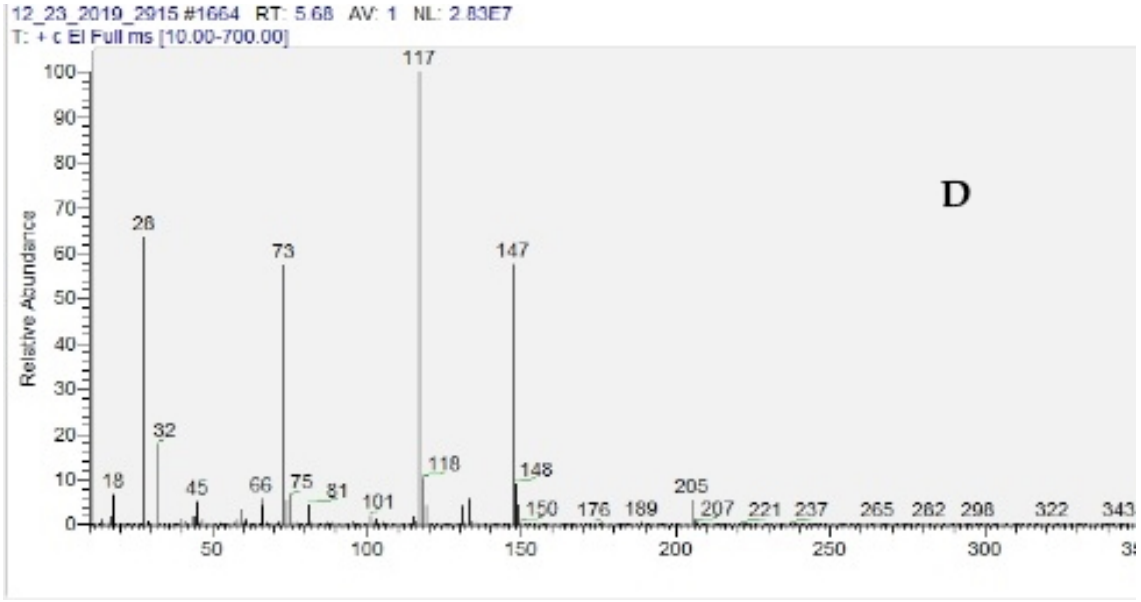
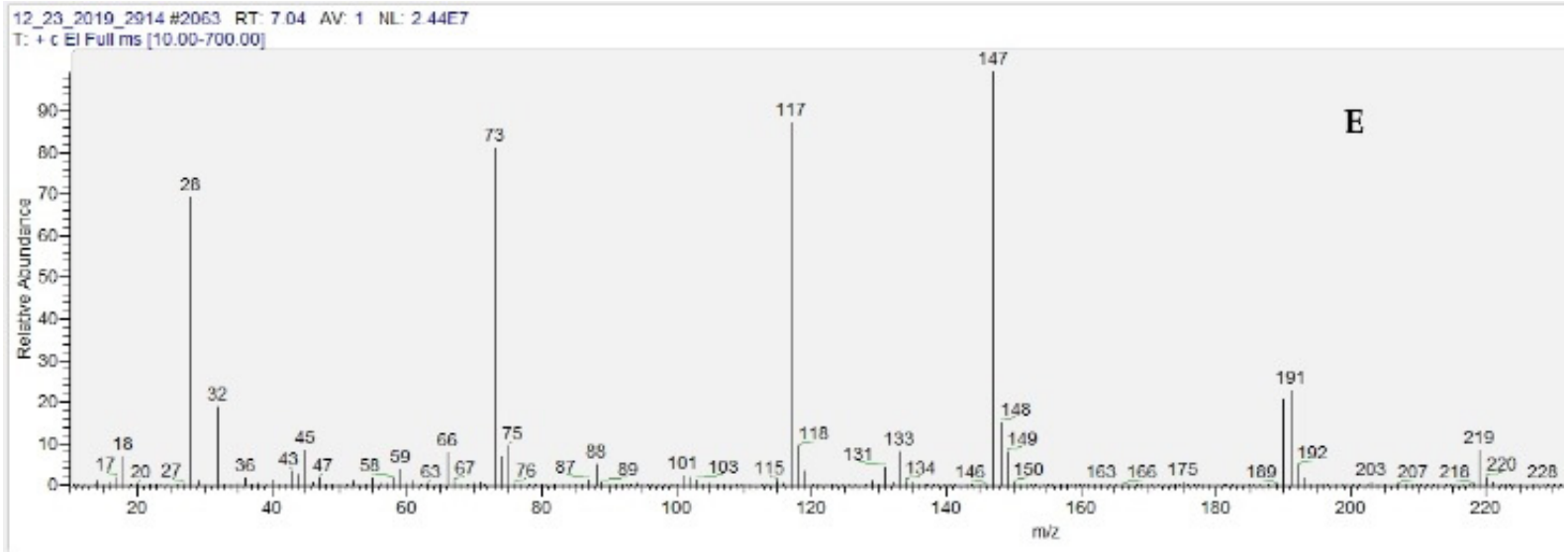


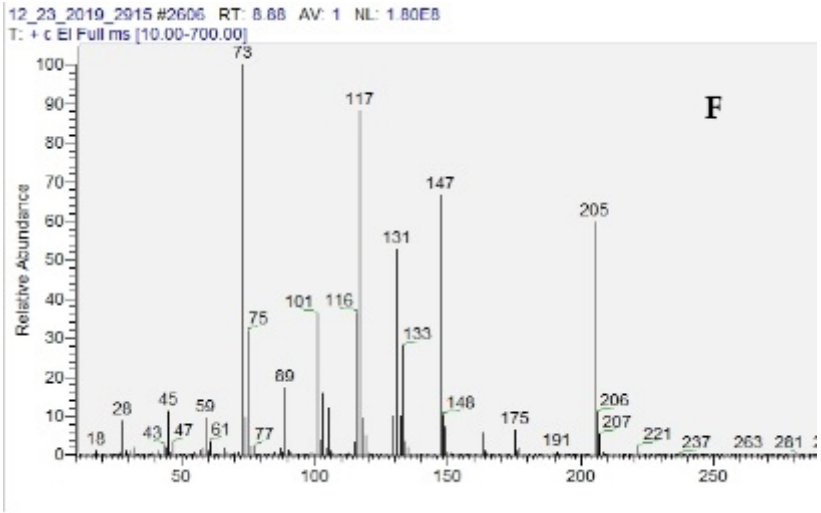
Figure S1. Calibration plots of response ratio (S_{st}/S) versus mass ratio (m_{st}/m) for internal standardization by GC-FID for A: TMS-Gly derivative; **B:** TMS-PG derivative; **C:** TMS-EG derivative; **D:** TMS-LA derivative. For GA, the same coefficient was used as for Gly.


RT: 0.00 - 13.27
A
NL:
5.99E9
TIC MS
12_23_201
9_2915
Relative Abundance
Time (min)
TMS-Gly
TMS-BD
TMS-LA
TMS-PG
TMS-EG
TMS-GA
0.97
0.53
0.46
0.42
0.11
9.85
8.89
7.31
12_23_2019_2915 #2890 RT: 9.85 AV: 1 NL: 5.91E8
T: + c EI Full ms [10.00-700.00]
B
Relative Acundance
m/z
147
73
205
218
103
117
133
148
149
129
204
219
191
175
74
87
101
45
59
28
18


12_23_2019_2914 #1500 RT: 5.13 AV: 1 NL: 1.71E7
T: + c EI Full ms [10.00-700.00]
C
Relative Abundance
m/z


12_23_2019_2915 #1664 RT: 5.68 AV: 1 NL: 2.83E7
T: + c EI Full ms [10.00-700.00]
D
Relative Abundance


12_23_2019_2914 #2063 RT: 7.04 AV: 1 NL: 2.44E7
T: + c EI Full ms [10.00-700.00]
E
Relative Abundance
m/z


12_23_2019_2915 #2606 RT: 8.88 AV: 1 NL: 1.80E8
T: + c EI Full ms [10.00-700.00]
F
Relative Abundance

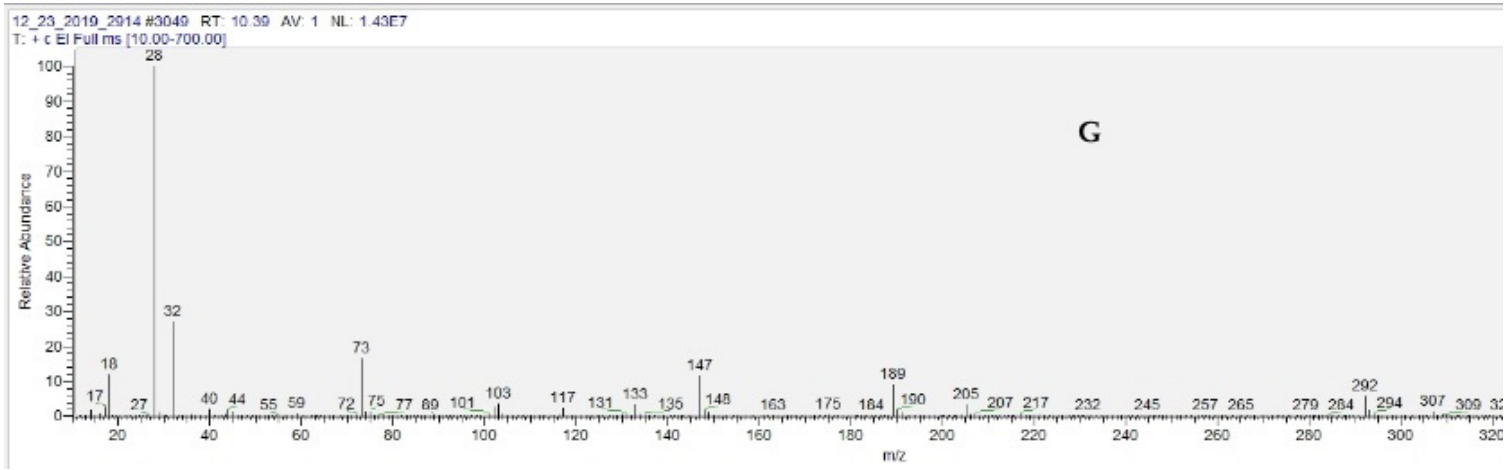
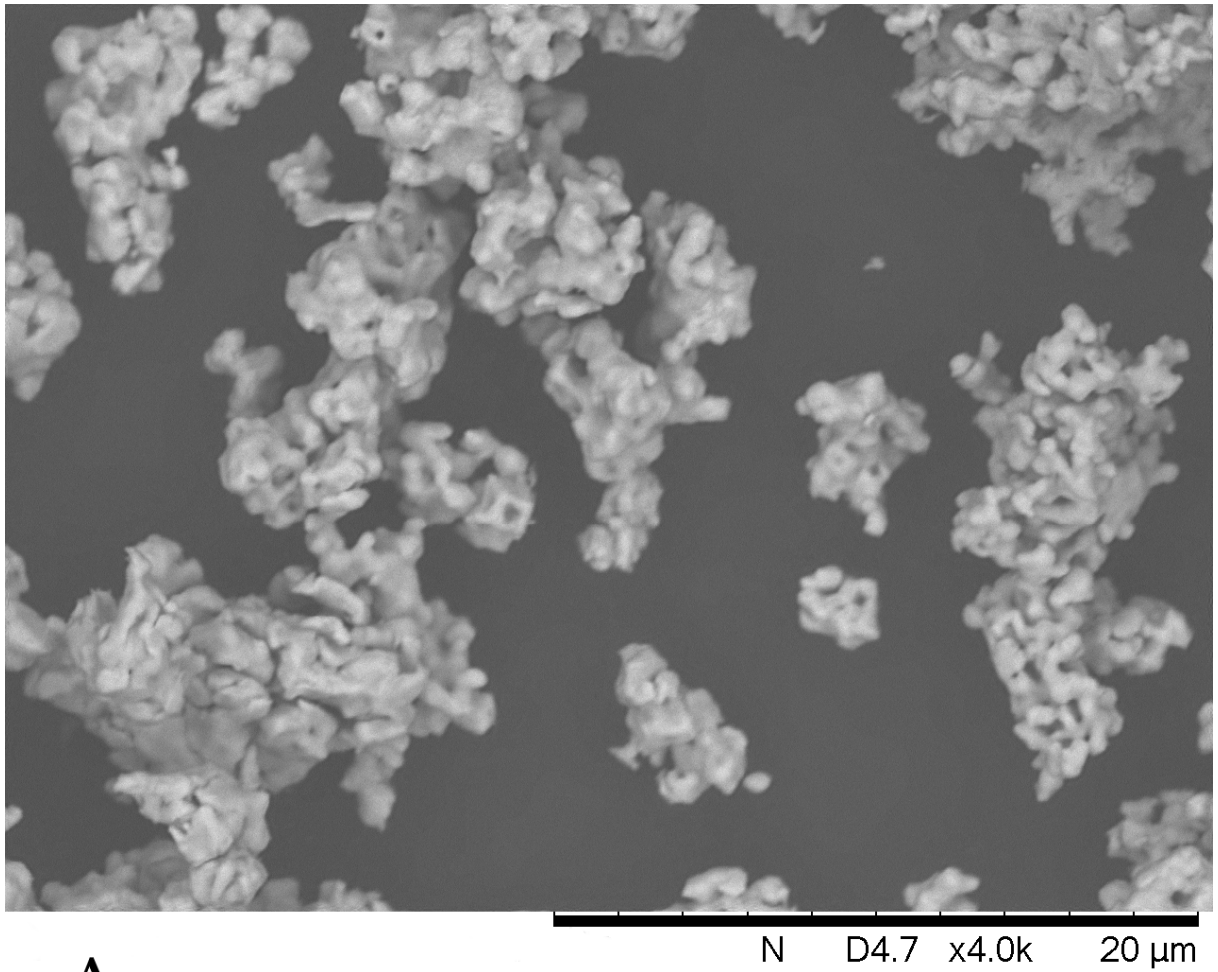


Figure S2. **A**: The mass spectrum of silylated liquid sample after glycerol hydrogenolysis reaction; **B**: The mass spectrum of TMS-Gly; **C**: The mass spectrum of TMS-EG; **D**: The mass spectrum of TMS-PG; **E**: The mass spectrum of TMS-LA; **F**: The mass spectrum of TMS-BD; **G**: The mass spectrum of TMS-GA.



A

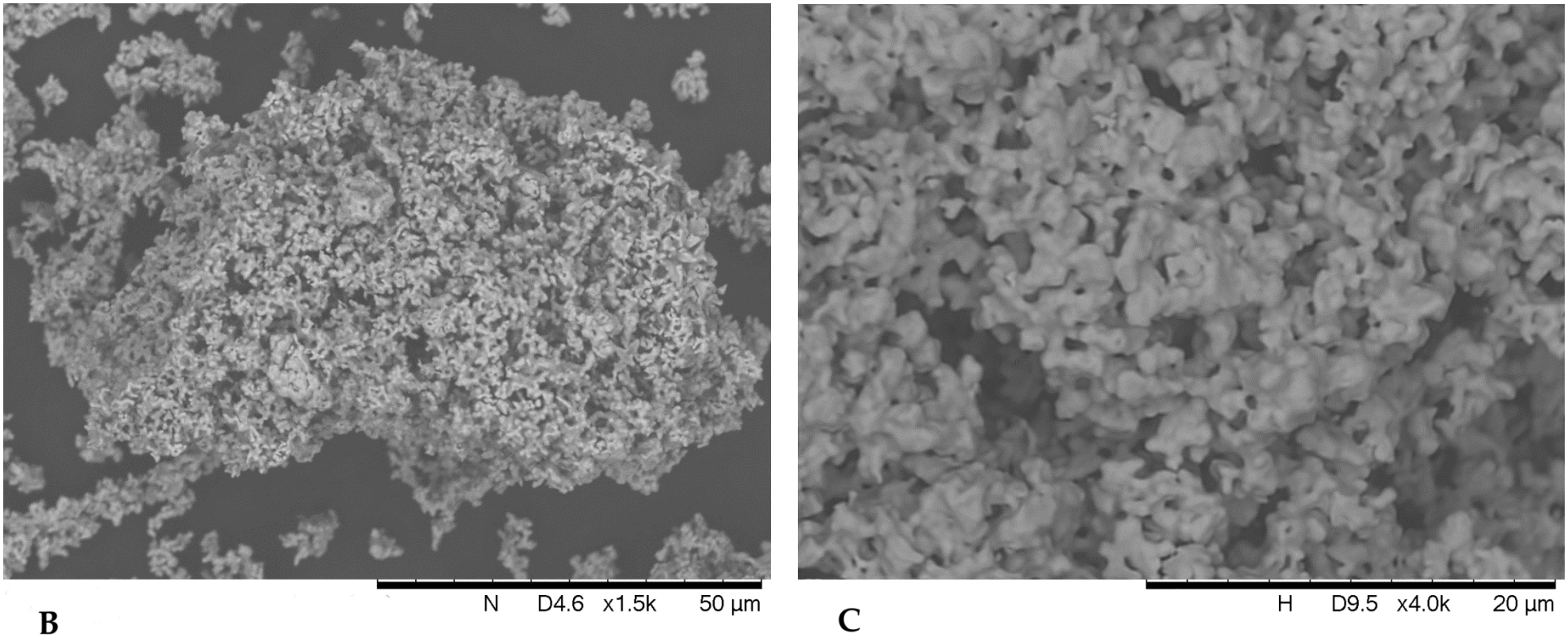


Figure S3. The SEM microphotographs of the copper catalysts generated *in situ* in the reaction medium during hydrogenolysis of glycerol. **A, B:** Cu-5; **C**: Cu-15.

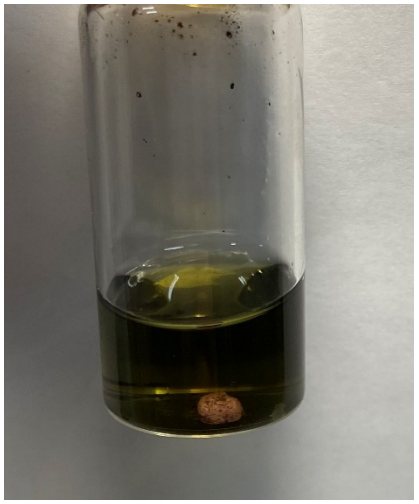


Figure S4. The appearance of the catalyst after 60 h of glycerol hydrogenolysis.

Figure S5. $Cu(OAc)_2$ in a water–glycerol solution prior to adding potassium hydroxide.