Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Promoting Effect of Solvent on Cu/CoO Catalyst for Selective Glycerol Oxidation under Alkaline Condition

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Table S 1. Observed selectivities for glycerol oxidation experiments over reduced Cu/CoO catalysts with different solvent mixtures. The shown values correspond to the conversion profiles shown in Figure 2 in the manuscript.

Detected Product	Solvent mixture (X/water)	Solvent content X / vol%			
		0	5	20	50
Glyceric acid	Methanol	19	20.5	19.5	12
	Ethanol		19.5	15.5	9.5
	n-Propanol		16.5	12.5	7.5
	tert-Butanol		17	15	12
Oxalic acid	Methanol	2.5	0	3	0
	Ethanol		3.5	5.5	2.5
	n-Propanol		3	5	11
	tert-Butanol		3	4.5	9.5
Glycolic acid	Methanol	47	46	41	39.5
	Ethanol		48.5	47	37
	n-Propanol		45	42.5	37
	tert-Butanol		47	45.5	39.5
Tartronic acid	Methanol	1.5	0	0	0
	Ethanol		1.5	1.5	1
	n-Propanol		1.5	1	0.5
	tert-Butanol		0.5	1.5	0.5
Lactic acid	Methanol	0	0	0	0
	Ethanol		0	0	3
	n-Propanol		4	9	7
	tert-Butanol		0	0	0
Formic acid	Methanol	30	33.5	36.5	48.5
	Ethanol		27.5	30.5	45
	n-Propanol		30.5	30	34.5
	tert-Butanol		32.5	33.5	38.5

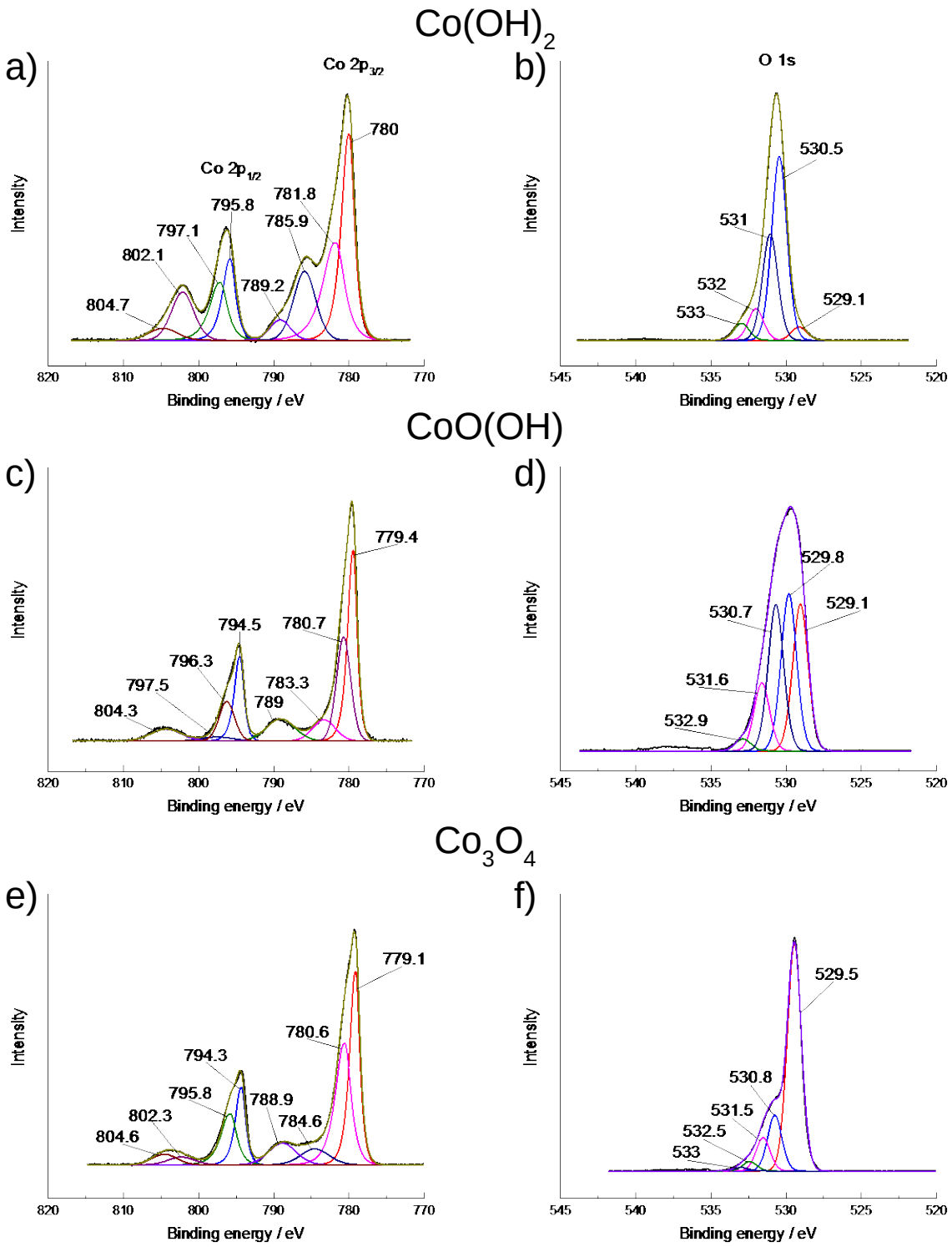

Figure S1. XPS spectra of $Co(OH)_2$, CoO(OH), and Co_3O_4. The presented spectra are in good accordance to the spectra reported in the literature.[1-2]

Table S2. List of fitted XPS signals for the profiles shown in Figure 4 in the manuscript.

a)	Cu $2p_{3/2}$ I	Cu $2p_{3/2}$ II	Cu Sat I	Cu Sat II	Cu $2p_{1/2}$ I	Cu $2p_{1/2}$ II	Cu Sat III
water	932.7	934.5	940.1	943.2	952.7	954.6	962.0
ethanol	932.4	934.4	940.4	943.4	952.3	954.3	962.0
n-propanol	932.9	934.8	940.3	943.3	952.7	954.6	962.0

b)	Co $2p_{3/2}$ I	Co $2p_{3/2}$ II	Co Sat I	Co Sat II	Co $2p_{1/2}$ I	Co $2p_{1/2}$ II	Co Sat III	Co Sat IV
water	779.7	781.3	785.4	789.4	794.8	796.5	802.0	805.2
ethanol	779.7	781.3	785.1	789.4	794.9	796.5	802.1	805.4
n-propanol	779.6	780.8	784.4	789.2	794.7	796.2	802.4	805.2

c)	O 1s I	O 1s II	O 1s III	O 1s IV	O 1s V
water	529.7	-	531.1	531.8	532.9
ethanol	529.6	530.7	531.4	532.3	533.5
n-propanol	529.7	-	531.1	532.2	533.3

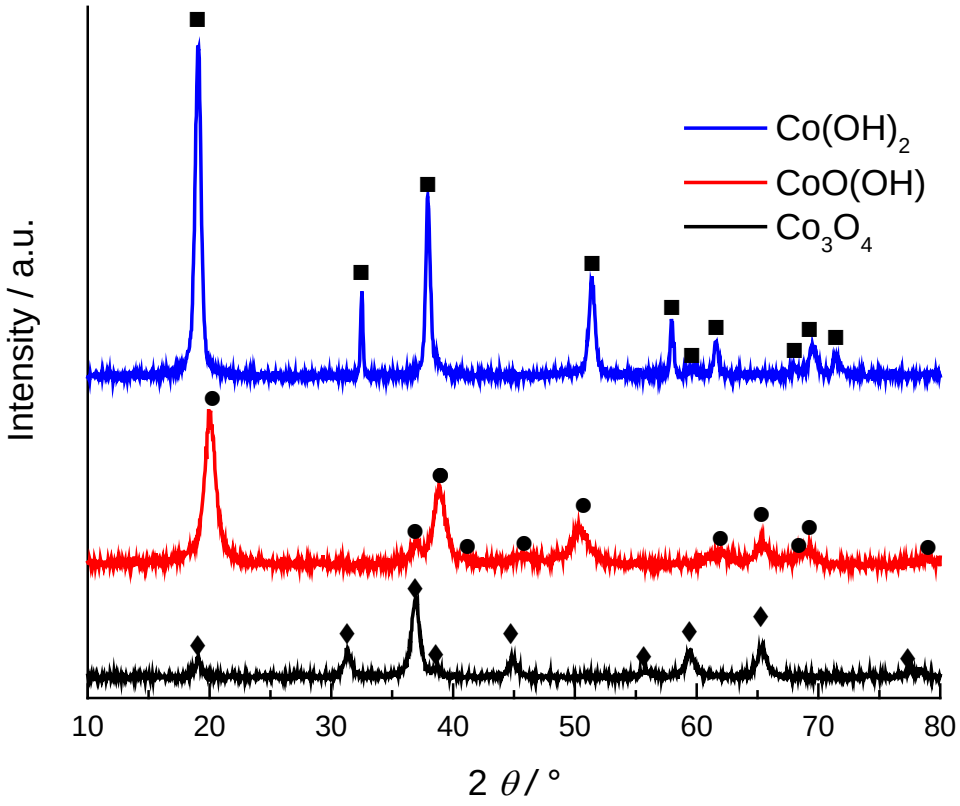

Figure S2. XRD patterns of $Co(OH)_2$, CoO(OH), and Co_3O_4. Black squares: $Co(OH)_2$ PDF 74-1057; black circles: CoO(OH) PDF 7-169; black diamonds: Co_3O_4 PDF 42-1467.

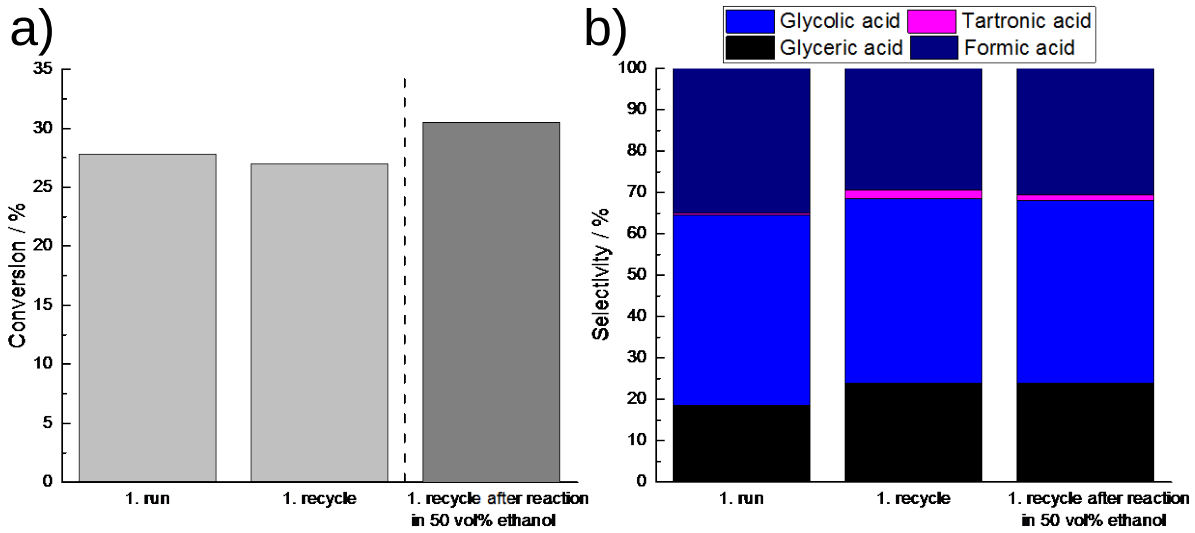

Figure S3. Conversions a) and selectivities b) for glycerol oxidation over Cu/CoO catalysts. The first recycling was conducted under the same reaction conditions performed for the first run. In a separate reaction, the first run was conducted in 50vol% ethanol (see Figure 2 for reaction conditions) and the recycling experiment was conducted in pure water as reaction solvent. It is clearly shown that the catalysts spent in water or ethanol/water reaction mixtures show decent stability for glycerol oxidation and that ethanol as co-solvent does not have a detrimental impact on the stability of the catalyst. Reaction conditions: 1 g L^{-1} catalyst, 15 mL of 0.05 M aqueous glycerol solution, 4:1 NaOH to glycerol ratio, 90 °C, 10 bar pure O_2, 1 h reaction time, 750 rpm stirring speed.

[1] J. Yang, H. Liu, W. N. Martens, R. L. Frost, *J. Phys. Chem. C* **2010**, *114*, 111-119.

[2] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. S. Smart, *Appl. Surf. Sci.* **2011**, *257*, 2717-2730.