Supplementary Information

Ag-promoted Co/Al_2O_3 Catalyst without Reduction Pretreatment for the Selective Hydrogenolysis of High-concentration Glycerol to 1,2-Propanediol

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Table S1 the performances of the typical Co-based catalysts

Entry	Catalyst	Reduction conditions	Reaction conditions	X_{gly} (%)	$S_{1,2\text{-PDO}}$ (%)	Ref.[a]
1	Co-Ca-Al	600 °C/H_2	15mL 20wt% glycerol aqueous solution; 0.5 g catalyst; 210 °C; 4 MPa H_2; 10 h	100	91	[16]
2	Co/MgO	350 °C/H_2	40g 10wt% glycerol aqueous solution; 0.2 g catalyst; 200 °C; 2 MPa H_2; 9 h	45	42	[17]
3	Co-Zn-Al	600 °C/H_2	40g 10wt% glycerol aqueous solution; 0.3g catalyst; 200 °C; 2 MPa H_2; 12 h	71	58	[18]
4	CoCu/TiO_2	350 °C/H_2	20mL 50v/v% glycerol aqueous solution; catalyst-to-glycerol ratio of 0.028 (on a weight basis); 250 °C; 4 MPa H_2; 4 h	95	73	[19]
5	Co/Dol	600 °C/H_2	20mL 20wt% glycerol aqueous solution; 1.0 g catalyst; 200 °C; 4 MPa H_2; 10 h	61	58	[20]
6	HSiW/Co-Al	400 °C/H_2	10 wt% glycerol aqueous solution; the feed rate of solution, 9.7mL/h; the flow of hydrogen, 100 mL/min; 4.0g catalyst; 230 °C; 3.5 MPa H_2;	76	60	[21]
7	Co-Al_2O_3	400 °C/H_2	10wt% glycerol aqueous solution; the feed flow rate, 9.7mL/h; the flow of hydrogen, 100 mL/min; 4.0g catalyst; 230 °C; 3.5 MPa H_2	54	76	[22]
8	Co/MSAPO-11	600 °C/H_2	65g 7.7wt% glycerol aqueous solution; 1.0 g catalyst; 220 °C; 5 MPa H_2; 8 h	94	91	[23]
9	Co-ZnO	450 °C/H_2	20g 20wt% glycerol aqueous solution; 0.6g catalyst; 180 °C; 4 MPa H_2; 8 h	70	80	[24]
10	CoAg/Al_2O_3	without pre-reduction	12.5g 80wt% glycerol aqueous solution; 1.0 g catalyst; 220 °C; 3 MPa H_2; 6 h	79	90	This work
11	CoAg/Al_2O_3	without pre-reduction	12.5g 80wt% glycerol aqueous solution; 1.0 g catalyst; 220 °C; 3 MPa H_2; 8 h	92	90	This work

a The reference numbers are corresponding to the ones in the main paper.

Table S2 Effects of glycerol concentration on the hydrogenolysis of glycerol over $Co_{2.0}Ag_{0.5}/Al_2O_3$

Entry	Catalyst	Glycerol concentration (wt.%)	X_{gly} (mol%)	$Y_{1,2\text{-PDO}}$ (mol%)	Selectivity (mol%)		
					1,2-PDO	EG	Others
1	$Co_{2.0}Ag_{0.5}/Al_2O_3$	20	91.1	82.5	90.6	7.3	2.1
2	$Co_{2.0}Ag_{0.5}/Al_2O_3$	50	84.4	77.1	91.3	6.1	2.6
3	$Co_{2.0}Ag_{0.5}/Al_2O_3$	80	79.3	70.7	90.2	8.1	1.7

Reaction conditions: 12.5 g of glycerol aqueous solution and 1 g of catalyst, 220 °C, 3.0 MPa H_2, 6 h; 1,2-propanediol-1,2-PDO, ethylene glycol-EG, unidentified and unlisted product mixtures were labeled as "Others".

Table S3 Effects of promoters on the hydrogenolysis of glycerol over $Co_{2.0}X_{0.5}/Al_2O_3$ (X=Ag, Cu, Fe, and Ni)

Entry	Catalyst	X_{gly} (mol%)	$Y_{1,2\text{-PDO}}$ (mol%)	Selectivity (mol%)		
				1,2-PDO	EG	Others
1	$Co_{2.0}Ag_{0.5}/Al_2O_3$	79.3	70.7	90.2	8.1	1.7
2	$Co_{2.0}Cu_{0.5}/Al_2O_3$	17.8	12.3	69.4	0	30.6
3	$Co_{2.0}Fe_{0.5}/Al_2O_3$	1.7	0.8	60.0	0	40.0
4	$Co_{2.0}Ni_{0.5}/Al_2O_3$	6.2	1.2	20.3	0	79.7

Reaction conditions: 10 g of glycerol and 1 g of catalyst in 2.5 g of deionized water, 220 °C, 3.0 MPa H_2, 6 h; 1,2-propanediol-1,2-PDO, ethylene glycol-EG, unidentified and unlisted product mixtures were labeled as "Others".

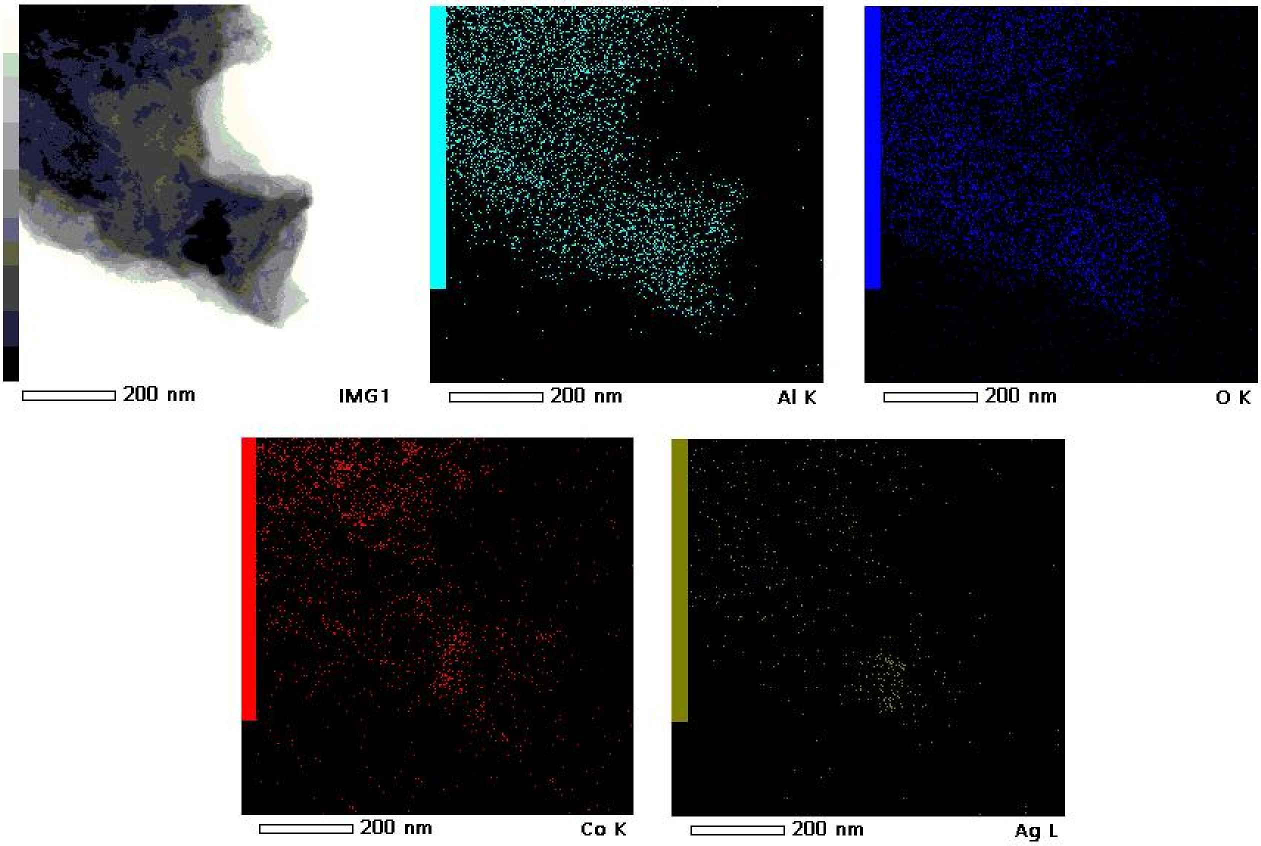

Fig. S1 TEM image of $Co_{2.0}Ag_{0.5}/Al_2O_3$ and its EDS element diagram

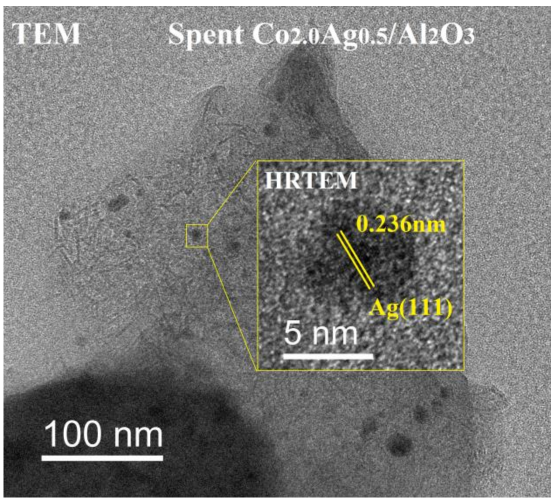

Fig. S2 TEM, HRTEM images of spent $Co_{2.0}Ag_{0.5}/Al_2O_3$

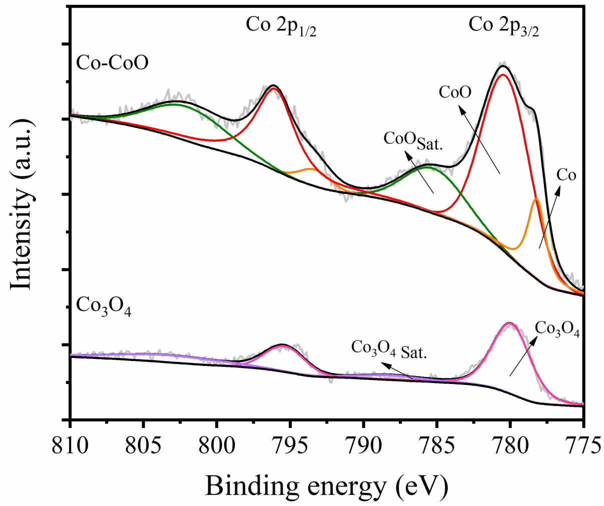

Fig. S3 XPS of Co_3O_4 and Co-CoO (Co-CoO is prepared by reduction of CoO at 400 ℃ for 1 h in a 5 v% H_2/Ar stream)

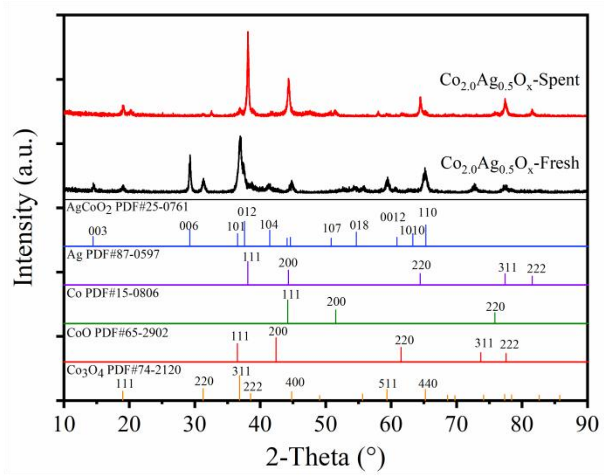

Fig. S4 XRD patterns of the fresh and spent $Co_{2.0}Ag_{0.5}O_x$ catalysts

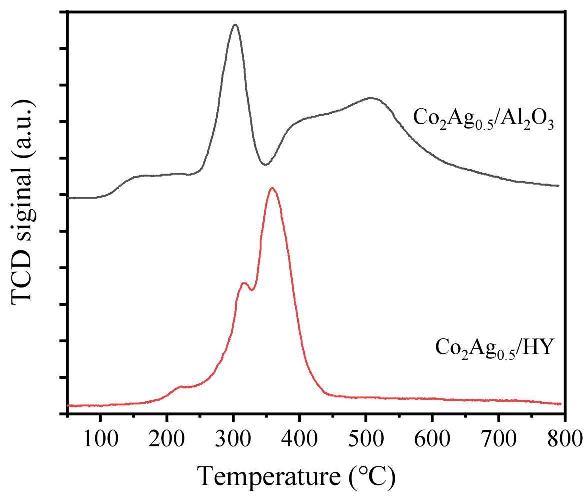

Fig. S5 H_2-TPR analysis results of $Co_{2.0}Ag_{0.5}/Al_2O_3$, $Co_{2.0}Ag_{0.5}$/HY

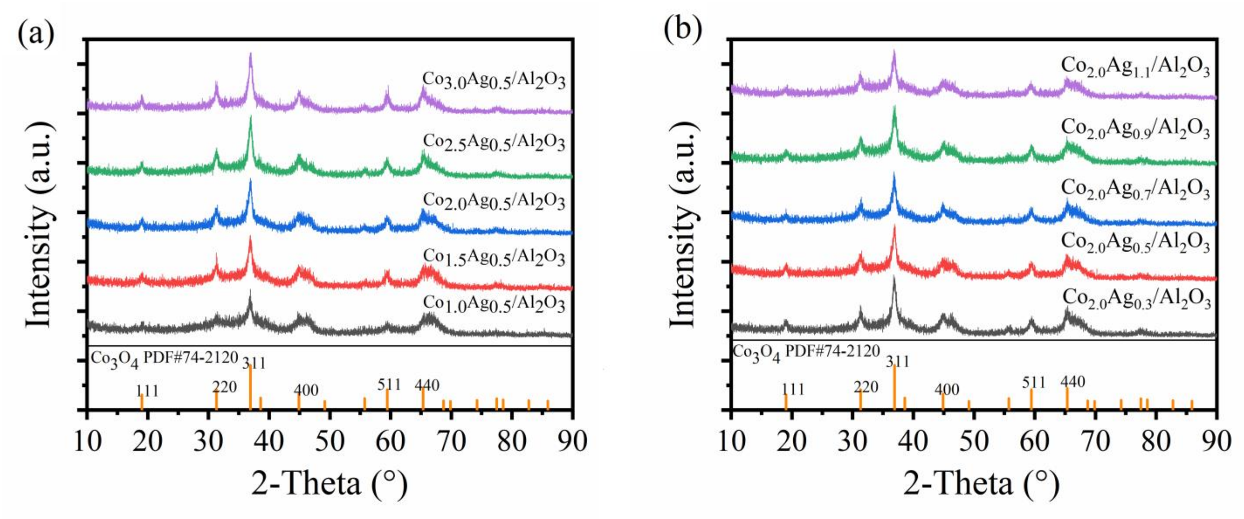

Fig. S6 (a) XRD patterns of $Co_xAg_{0.5}/Al_2O_3$ with different Co loading amounts; (b) XRD patterns of $Co_{2.0}Ag_x/Al_2O_3$ with different Ag loading amounts

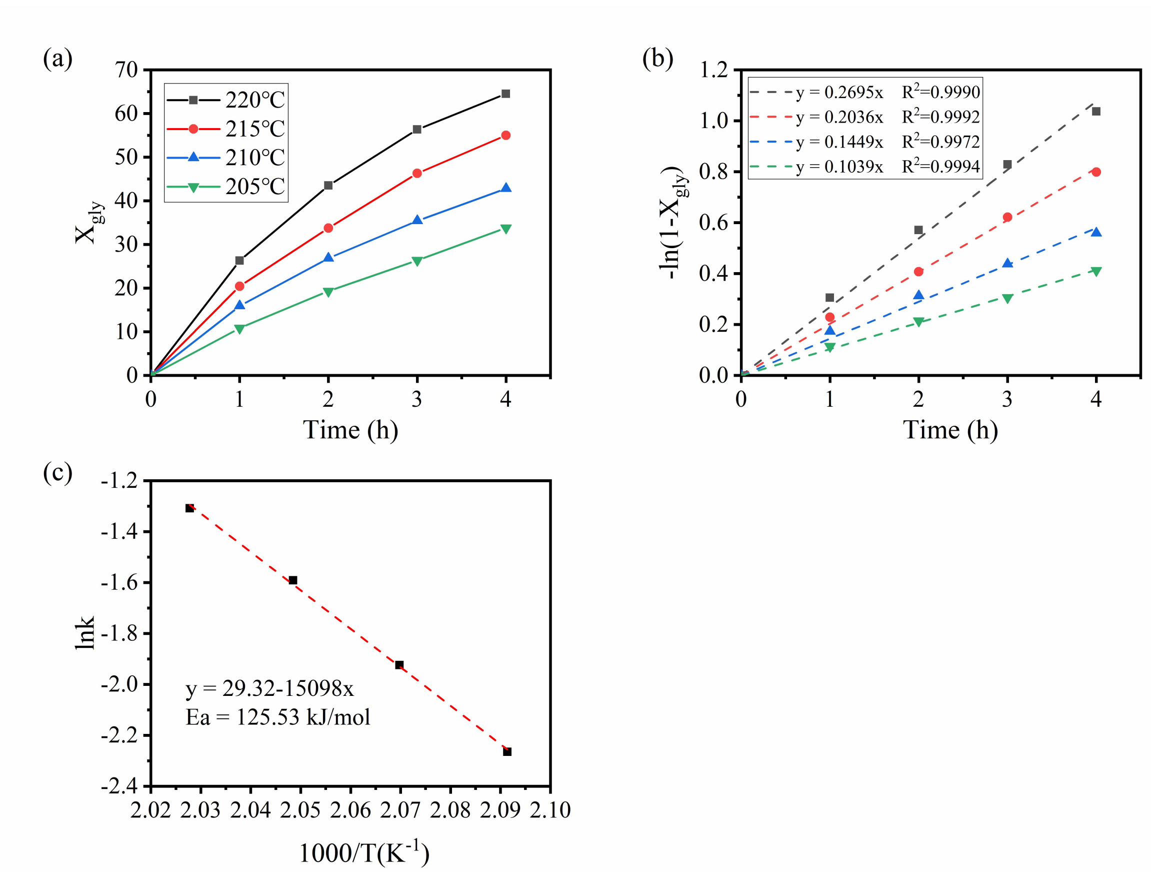

Fig. S7 (a) Graph of glycerol conversion over time at different temperatures; (b) $-\ln(1-X_{gly})$ versus time diagram to calculate the rate constant k; (c) Arrhenius diagram to calculate the activation energy of 1,2-PDO from glycerol hydrogenolysis.