Supporting information

Spinel copper-iron-oxide magnetic nanoparticles with cooperative Cu(I) and Cu(II) sites for enhancing catalytic transformation of 1,2-propanediol to lactic acid under anaerobic conditions

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Methods for DFT calculations

Vienna *ab initio* simulation package (VASP) [1] was employed to study the pathway, as well as the mechanism. Primary calculation methods have been described in our previous work. [2] For the models, we substituted the Fe of surface with Cu, which could represent the increase of Cu. And the reaction steps for this works are designed by experimental data and the reported work.[3]

For each step, the reaction Gibbs free energy ΔG is defined by Eq. (S1).

$$\Delta G = \Delta E + \Delta ZPE \qquad \text{(S1)}$$

where ΔE is the electronic energy difference, ΔZPE is the change of zero-point energies.

And the electronic energy difference is defined by Eq. (S2).

$$\Delta E=\sum E(\text{products})-\sum E(\text{reactions}) \qquad \text{(S2)}$$

It should be noted that the aqueous solution effect is not considered in this work since the Gibbs free energy cannot be heavily influenced by solution.

Elimination of the diffusion limitations

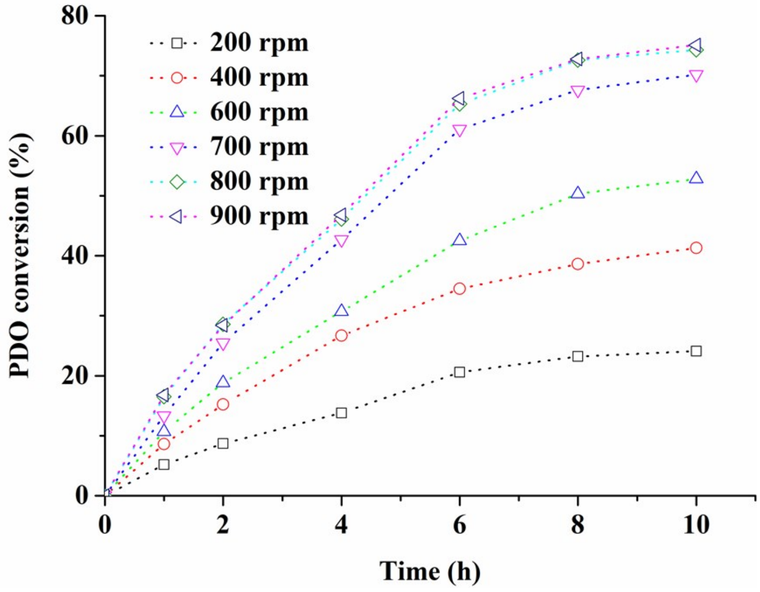

Figure S1. PDO conversion vs stirring speed. Reaction conditions: PDO concentration = 0.2 M (40 mL), NaOH/PDO (mol/mol) = 2, reaction temperature = 160℃, N_2 = 1.0 MPa, catalyst loading = 0.06 g.

In order to eliminate the external diffusion, the catalytic oxidation of PDO was tested at different stirring speeds (see Figure S1). As shown in Figure S1, when the stirring rates are increased to 800 and 900 rpm, the PDO conversions were over-lapped at different reaction times. The results show that the external diffusion can be completely eliminated at the stirring speed of 800 rpm.

The Weisz–Prater criterion [4] was used to estimate the intraparticle diffusion limitations:

$$\emptyset_i = \frac{(-r_{obs,i})\rho_p R_p^2}{D_{eff,i}\, C_i} \qquad \text{(S3)}$$

where the C_i was the concentration of PDO [mol/m^3], D_{eff} was the effective diffusion [m^2/s × m$^3_{liq}$/m$^3_{cat}$], R_p indicated the main particle radius [m], r_{obs} was the initial observed rate of PDO consumption [mol/s kg$_{cat}$], and ρ_p was the apparent density of the catalyst [kg/m^3]. The W–P criterion indicated that when $\Phi_i < 1$, there were no diffusional problems for i.[5] Herein, the PDO conversion at initial 1 h (16.5%) was used to calculate the r_{obs}, which was calculated as ca. 6.1×10^{-3} mol/s kg$_{cat}$. The apparent bulk density of catalyst particles (ρ_p) is 1200 kg/m^3. The catalyst particle diameter (R_p) is 4.5×10^{-5} m (300 mesh) and the C_{PDO} is 200 mol/m^3. The effective diffusivity (D_{eff}) was estimated using a porosity (ε_p) of 0.5 and a tortuosity (τ) of 4 as recommended in Davis and Davis.[6] The estimated Φ_{PDO} (0.6) was smaller than 1, and thus the internal diffusion can also be neglected.

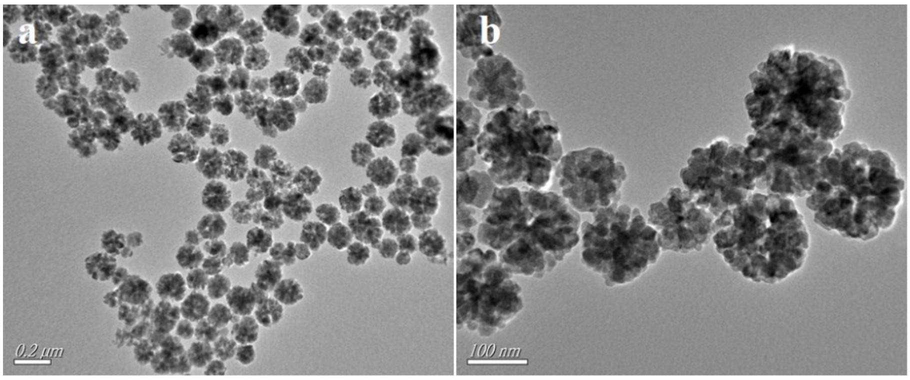

Figure S2. TEM images of $CuFe_2O_4$ porous nanoparticles prepared by hydrothermal method.[5]

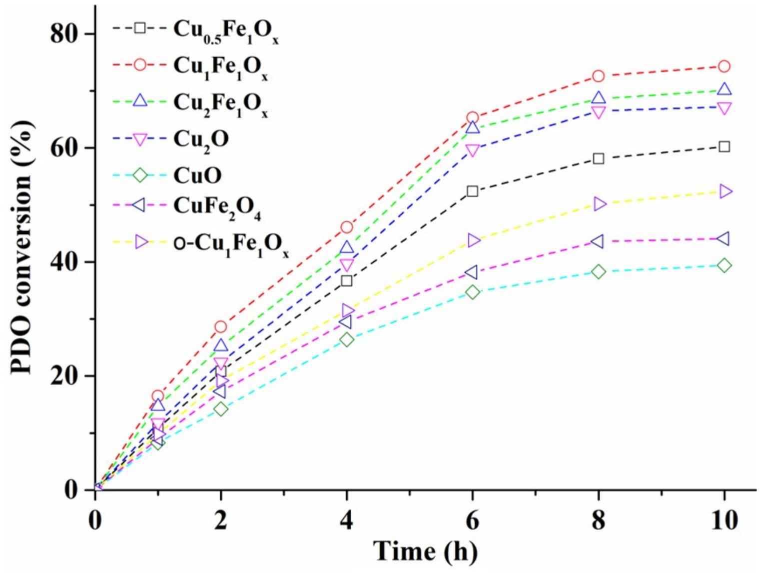

Figure S3. PDO conversion vs reaction time for different copper based catalysts. Reaction conditions: PDO concentration = 0.2 M (40 mL), NaOH/PDO (mol/mol) = 2, reaction temperature = 160℃, N_2 = 1.0 MPa, catalyst loading = 0.06 g.

H_2 production from catalytic PDO and glycerol transformation under anaerobic and basic aqueous conditions

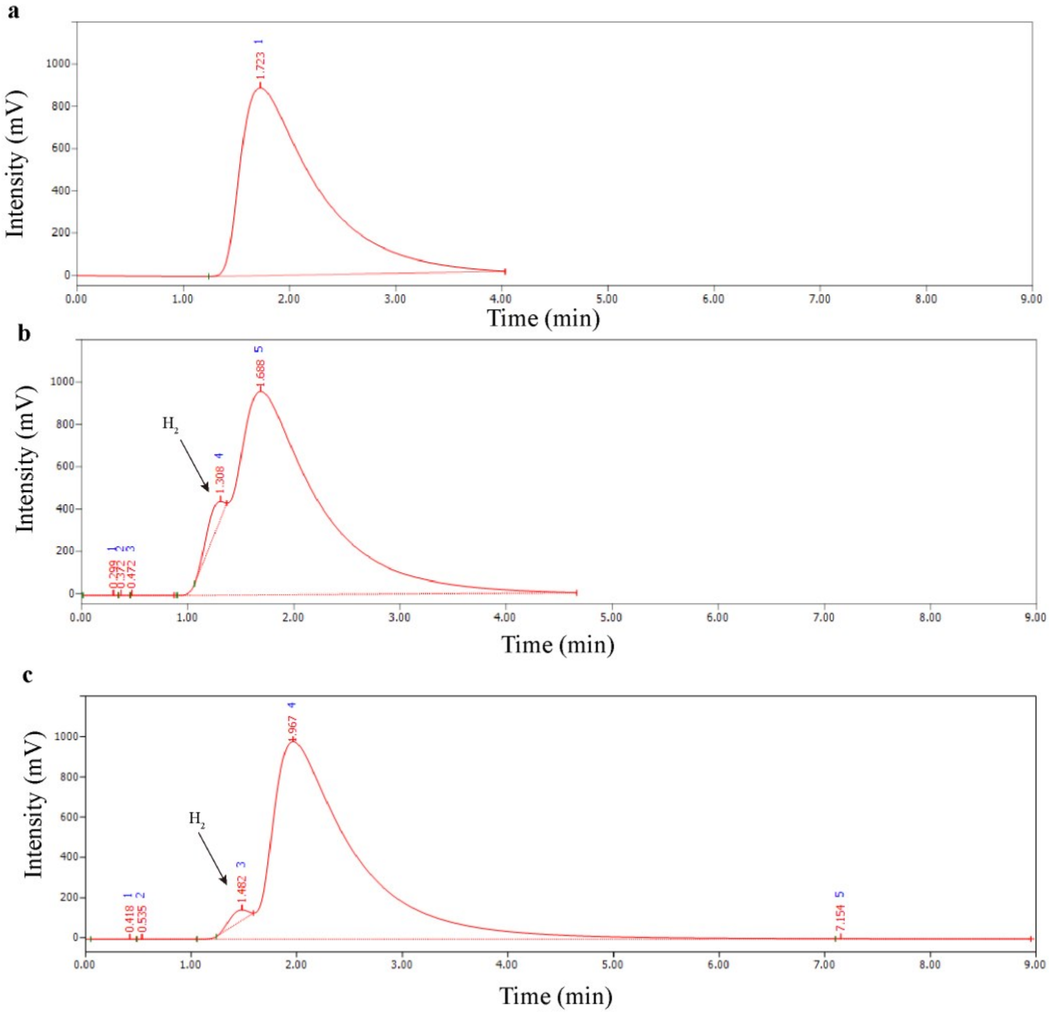

Figure S4. Profile of H_2 in gas products from catalytic conversion of PDO before (a) and after (b) reaction, and the catalytic conversion of glycerol after reaction (c).

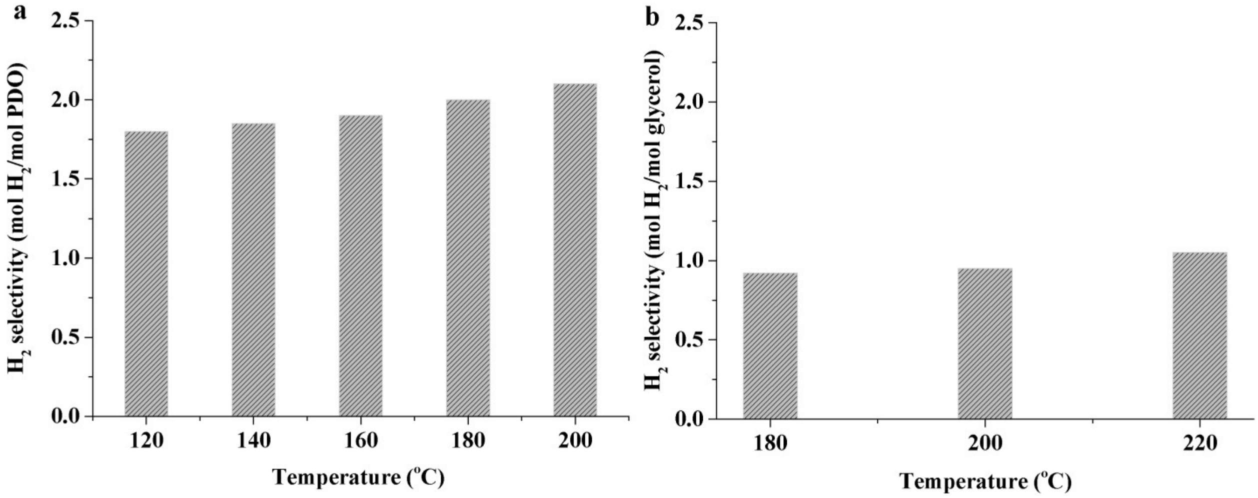

Figure S5. H_2 selectivity vs temperature for catalytic PDO (a) and glycerol (b) transformations. Reaction conditions for PDO transformation: reaction temperature = 120–200℃, PDO concentration = 1.0 M (30 mL), NaOH/PDO (mol/mol) = 2.0, N_2 pressure = 1.0 MPa, catalyst loading = 0.2 g, reaction time = 8 h. Reaction conditions for glycerol conversion: reaction temperature = 180–220℃, glycerol concentration = 1.1 M (30 mL), NaOH concentration = 1.2 M, N_2 pressure = 1.4 MPa, catalyst loading = 0.2 g, reaction time = 6 h.

Figure S4 shows that H_2 was produced from the catalytic PDO and glycerol transformation under anaerobic and basic aqueous conditions. On basis of the mole ratios of H_2/PDO (ca. 2.0) and H_2/glycerol (ca. 1.0) (Figure S5), the reaction can be written as (S4) for the formation of lactic acid from PDO and (S5) for the formation of lactic acid from glycerol.

$C_3H_8O_2$ (1,2-propanediol) + H_2O → $C_3H_6O_3$ (lactic acid) + $2H_2$ (S4)

$C_3H_8O_3$ (glycerol) → $C_3H_6O_3$ (lactic acid) + H_2 (S5)

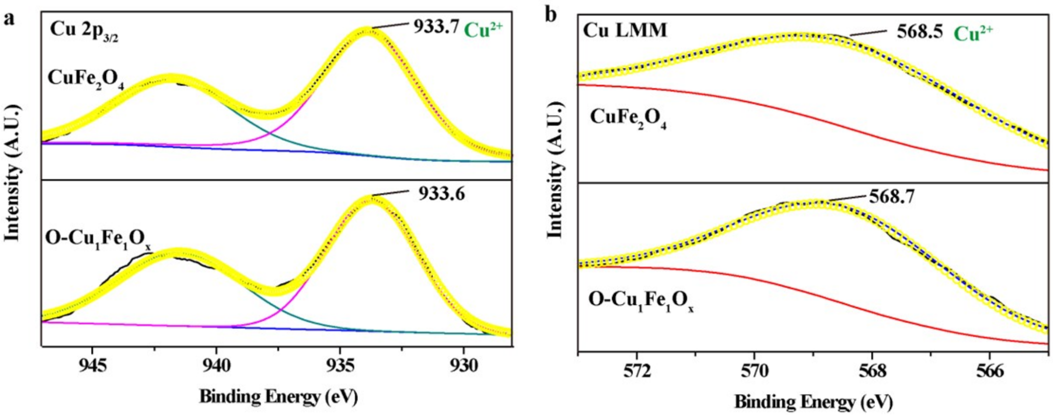

Figure S6 XPS and XAS spectra for $CuFe_2O_4$ and O-$Cu_1Fe_1O_x$ MNs with dominant copper species of Cu^{2+}.

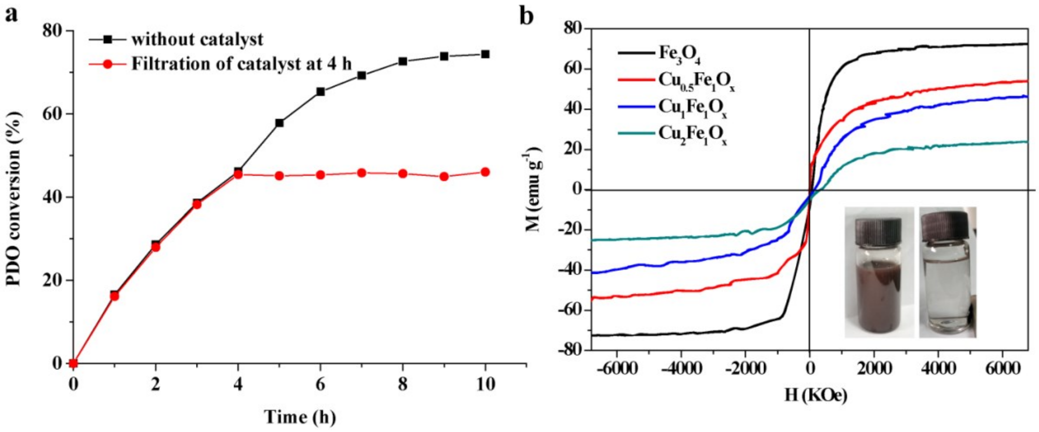

Figure S7. (a) Hot catalyst filtration test for $Cu_1Fe_1O_x$ MNs; (b) Field-dependent magnetization curves of $CuFeO_x$ MNs at room temperature. The insets photographs of magnetic recovery of $Cu_1Fe_1O_x$ after applying the external magnetic field.

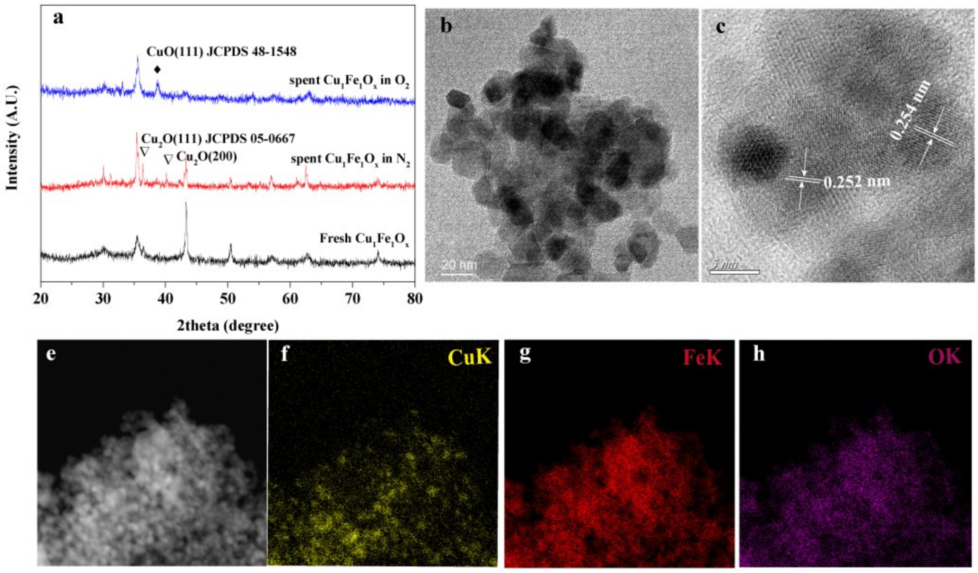

Figure S8. XRD patterns (a), TEM (b) and HRTEM (c) images of spent $Cu_1Fe_1O_x$ MNs, and HAADF-STEM image (e) and element-mapping of Cu (f), Fe (g), and O (h).

Table S1. Consumption of H_2 over different catalysts

Catalysts	$Cu_{0.5}Fe_1O_x$	$Cu_1Fe_1O_x$	$Cu_2Fe_1O_x$	$CuFe_2O_4$	Fe_3O_4	Cu_2O	CuO
Consumption of H_2 (mmol g^{-1})	9.78	7.80	4.16	13.69	10.13	24.12	12.5

Table S2. Concentration of acid and base site according to CO_2-TPD and NH_3-TPD profiles

Samples	Acid sites (mmol g^{-1})				Base sites (mmol g^{-1})		
	A_{NH3}[a]	A_W[b]	A_M[c]	A_S[d]	B_{CO2}[e]	B_W[f]	B_S[g]
Fe_3O_4	0.80	0.06	0.03	0.71	0.18	0.02	0.16
$Cu_{0.5}Fe_1O_x$	0.76	0.03	0.33	0.40	0.16	0.03	0.13
$Cu_1Fe_1O_x$	0.23	0	0.11	0.12	0.13	0.03	0.10
$Cu_2Fe_1O_x$	0.11	0	0	0.11	0.12	0.04	0.08

[a] A_{NH3} represents the total concentration of acid sites, which is calculated based on the result of NH_3-TPD.

[b-d] A_W, A_M, and A_S are the concentration of weak, medium, and strong acid site, respectively.

[e] B_{CO2} represents the total concentration of base sites, which is calculated on the basis of the results of CO_2-TPD.

[f-g] B_W and B_S are the concentration of weak and strong base site, respectively.

Table S3 Cu/Fe weight ratios of fresh $Cu_1Fe_1O_x$ and spent $Cu_1Fe_1O_x$ MNs[a]

Sample	Metal content (wt%)		Cu/Fe ratio
	Cu	Fe	
fresh $Cu_1Fe_1O_x$	18.5	16.9	1.10
spent $Cu_1Fe_1O_x$	17.5	16.4	1.07
Mother liquid (after filtration)	1.92 ppm	1.83 ppm	-

[a] As detected by ICP.

Table S4 Catalytic performance of $Cu_1Fe_1O_x$ MNs for PDO, glycerol (GLY), and ethylene glycol (EG) transformation in anaerobic and basic aqueous solution.

Substrate	Conditions						Conversion (%)	Selectivity (%)		Mole ratio of H_2/substrate	TOF[a] (h^{-1})
	concentration (M)	NaOH (M)	T (℃)	P_{N2} (MPa)	t (h)	catalyst loading (g)		LA	glyceric acid		
PDO	0.2	0.4	160	1.0	8	0.06	72.6	94.5	0	1.9	1410
GLY	1.08	1.2	200	1.4	6	0.2	72.3	98.5	0	0.95	2280
EG	0.2	0.4	160	1.0	8	0.06	87.4	0	97.8	1.95	1690

[a] Activity expressed as turn-over-frequency (TOF) calculated by the around 20% conversion (at initial reaction time of 1 h).

Table S5. Summary of the bond distance of C-H and O-H near Cu or Fe atoms, as well as their atomic charge based on DFT calculation

$Cu_{20}Fe_{40}O_x$	Origin-Structure-1						Origin-Structure-2						Origin-Structure-3	
Terms	O82-H8	-	C2-H4	-	H7-O81	O82-H8	O82-H6	-	C3-H4	-	C2=O81	-	C3_H4	-
Bond lengths	0.9732	-	1.09593	-	0.97565	0.9732	0.97101	-	1.10638	-	1.24686	-	1.11134	-
Terms	O82	H8	C2	H4	O81	O82	O82 (142）	H6 (151)	H4 (149)	C3 (145)	C2 (144)	O81 (141)	C3	H4
Valene state	-1.66759	1	0.5361	0.11	-1.6121	-1.66759	-1.75623	1	0.100246	0.723539	1.454105	-1.66467	0.840295	0.094468
$Cu_{21}Fe_{39}O_x$	Cu-Fe-Structure-1						Cu-Fe-Structure-2						Cu-Fe-Structure-3	
Terms	O82-H8		C2-H4		H7-O81		O82-H6		C3-H4		C2=O81		C3-H5	
Bond lengths	0.97191		1.10357		0.97312		0.97279		1.09828		1.24027		1.11255	
Terms	O82	H8	C2	H4	O81	H7	O82 (142）	H6 (151)	H4 (149)	C3 (145)	C2 (144)	O81 (141)	C3	H5
Valene state	-1.59829	1	0.588013	0.1411	-1.66519	1	-1.6186116	1	0.1105666	0.5634567	1.5807554	-1.7563967	1.498611	0.047535

Table S6. Catalytic transformation of proposed intermediates in PDO conversion over $Cu_1Fe_1O_x$, CuO, and Cu_2O catalysts[a]

Substrates	Catalysts	Conversion（%）	Selectivity（%）				
			PA	LA	FA	AA	HA
PDO	$Cu_1Fe_1O_x$	16.5	7.1	87.9	1.1	2.8	1.1
	CuO	8.3	4.2	82.6	4.5	8.0	0.7
	Cu_2O	11.8	1.0	72.3	10.5	15.4	0.8
HA	$Cu_1Fe_1O_x$	100	0.8	82.1	1.3	15.8	-
	CuO	100	5.4	78.8	7.4	8.4	-
	Cu_2O	100	2.8	76.3	6.4	14.5	-
PAD	$Cu_1Fe_1O_x$	100	10.0	78.6	3.8	7.6	-
	CuO	100	8.6	73.6	6.7	10.1	-
	Cu_2O	100	7.5	71.1	7.3	14.1	-
PA	$Cu_1Fe_1O_x$	38.7	-	-	-	100	-
	CuO	40.3	-	-	-	100	-
	Cu_2O	79.5	-	-	-	100	-
LA	$Cu_1Fe_1O_x$	63.8	100	-	-	-	-
	CuO	18.1	100	-	-	-	-
	Cu_2O	31.9	100	-	-	-	-
AA	$Cu_1Fe_1O_x$	0	-	-	-	-	-
FA	$Cu_1Fe_1O_x$	0	-	-	-	-	-

[a] Reaction conditions: substrate concentration, 0.2 M (40 mL); NaOH/substrate (mol/mol) = 2; reaction temperature, 160℃; N_2, 1.0 MPa; catalyst loading, 0.06 g; reaction time, 1 h. PDO = 1,2-propanediol, LA = lactic acid, AA = acetic acid, FA = formic acid, PA = pyruvic acid, HA = hydroxyacetone, PAD = pyruvaldehyde.

References

1. G. Kresse and J. Furthmuller, Phys Rev B 1996; 54: 11169-11186.
2. D. Rao, H. Yang, X. Shen, X. Yan and G. Qiao, Phys. Chem. Chem. Phys., 2019, 21, 10895-10901.
3. D. J. Chadderdon, L. Xin, J. Qi, B. Brady, J. A. Miller, K. Sun, M. J. Janik and W. Li, ACS Catal., 2015, 5, 6926-6936.
4. P. Weisz, D. Prater, Adv. Catal. ,1954, 6, 143-196.

5. C.M. Piqueras, G. Tonetto, S. Bottini, D.E. Damiani, Catal. Today, 2008,133-135, 836-841.

6. M. E. Davis and R. J. Davis, Fundamentals of Chemical Reaction Engineering, Dover Publications, Mineola, New York, 1st edn, 2012.

7. M. Zhu, D. Meng, C. Wang, G. Diao, ACS Appl. Mater. Interfaces, 2013, 5, 6030-6037.