Supporting Information

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Scheme S1

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1. Figures. S1 to S12

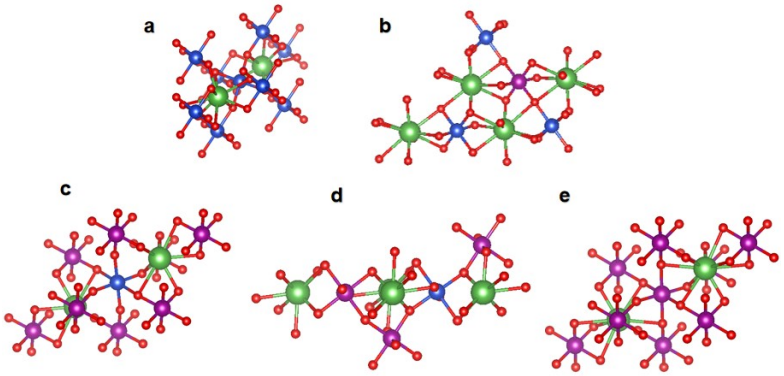


Figure S1. schematic illustrations of (a) La_2CuO_4, (b) $LaMn_{0.25}Cu_{0.75}O_3$, (c) $LaMn_{0.5}Cu_{0.5}O_3$, (d) $LaMn_{0.75}Cu_{0.25}O_3$, (e) $LaMnO_3$

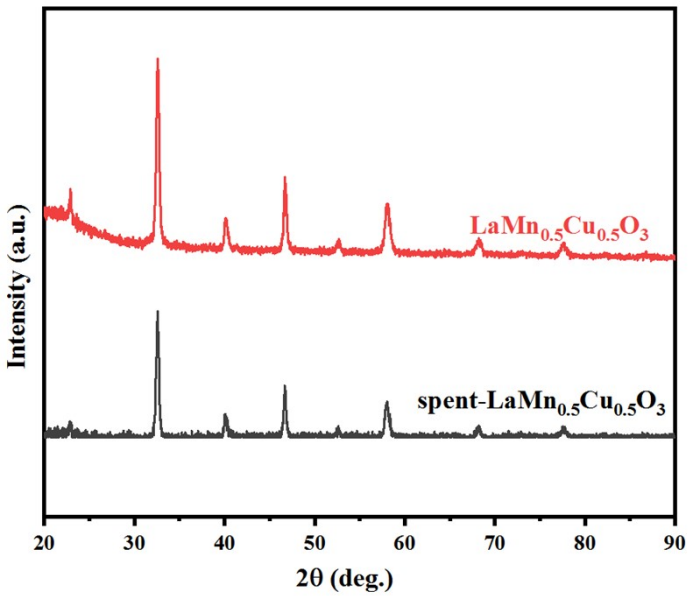


Figure S2. XRD patterns of as-prepared $LaMn_{0.5}Cu_{0.5}O_3$ sample and spent-$LaMn_{0.5}Cu_{0.5}O_3$ sample

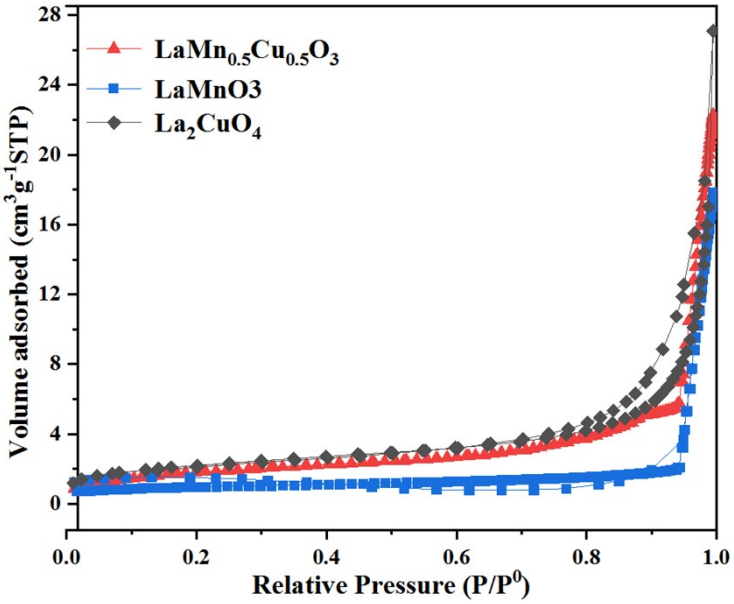


Figure S3. N_2 adsorption/desorption isotherms of La_2CuO_4, $LaMn_{0.5}Cu_{0.5}O_3$ and $LaMnO_3$.

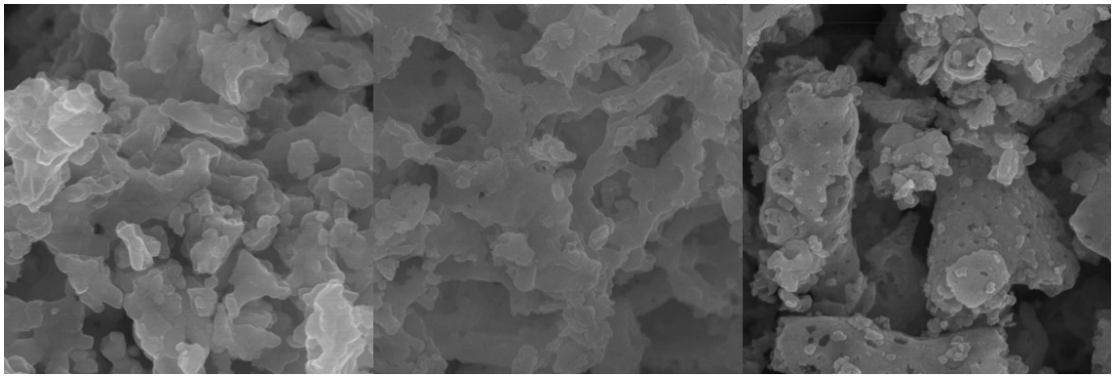


Figure S4. SEM images of spent $LaMn_xCu_{1-x}O_3$ samples (from left to right x = 1, 0.5, 0)

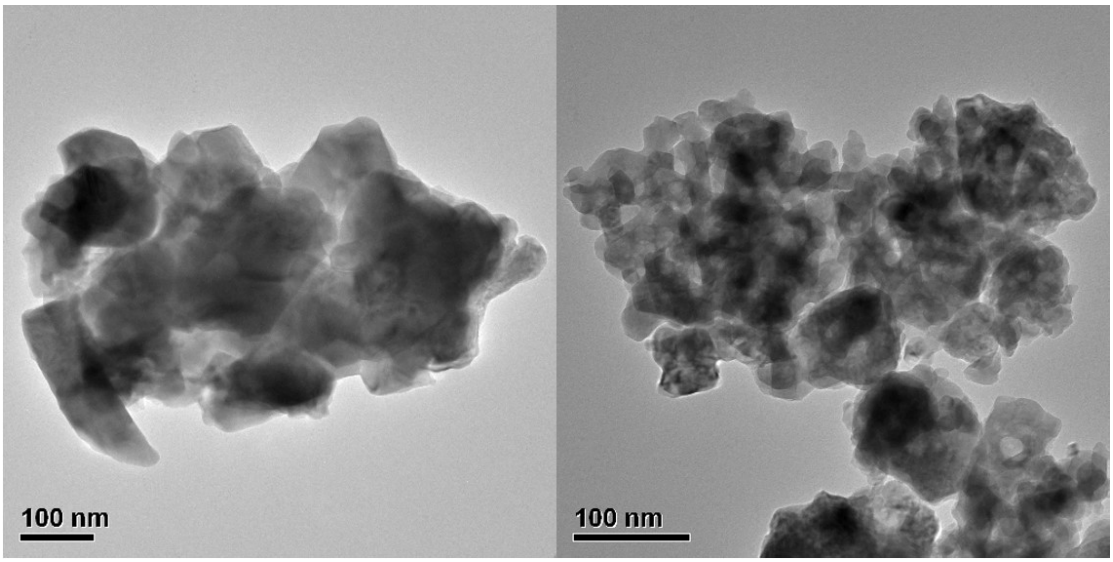


Figure S5. TEM images of spent $LaMn_xCu_{1-x}O_3$ samples (from left to right x = 0, 0.5)

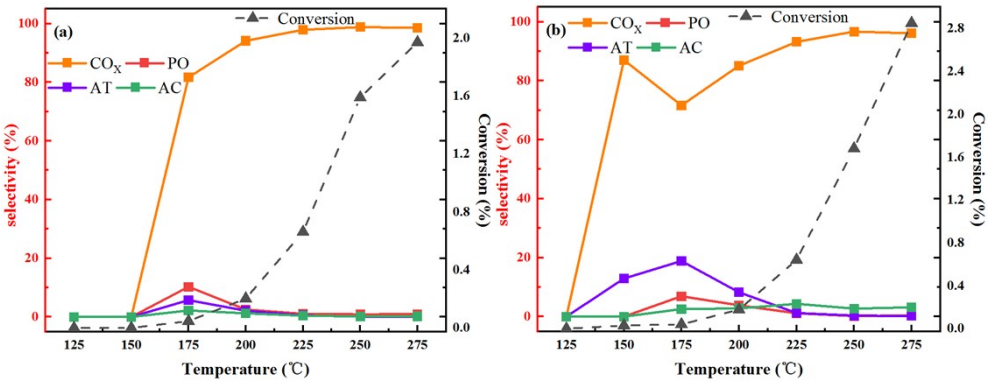


Figure S6. Products (PO: propylene oxide, AC: acrolein, AT: acetone) selectivity and propylene conversion over $LaMn_{0.75}Cu_{0.25}O_3$ and $LaMn_{0.25}Cu_{0.75}O_3$ in DEP reaction from 125 to 275 °C

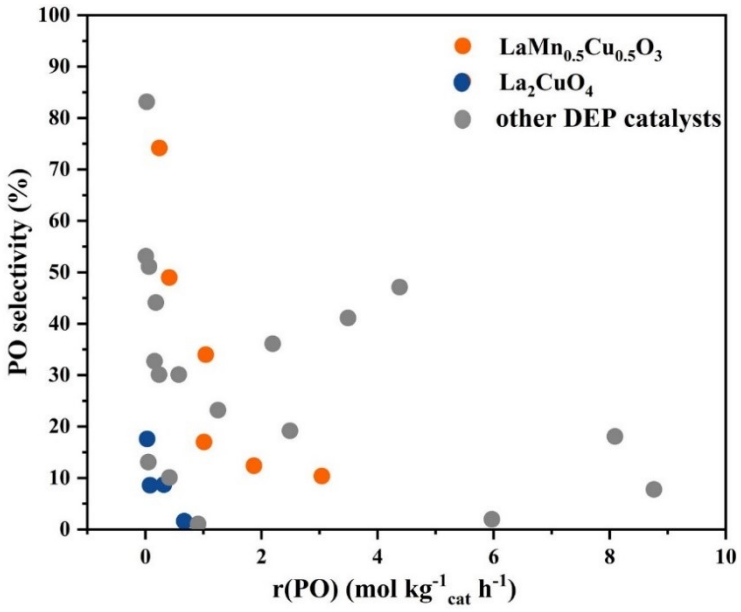


Figure S7. PO selectivity for $LaCu_{0.5}Mn_{0.5}O_3$, La_2CuO_4 and other DEP reaction catalysts as a function of PO formation rate.

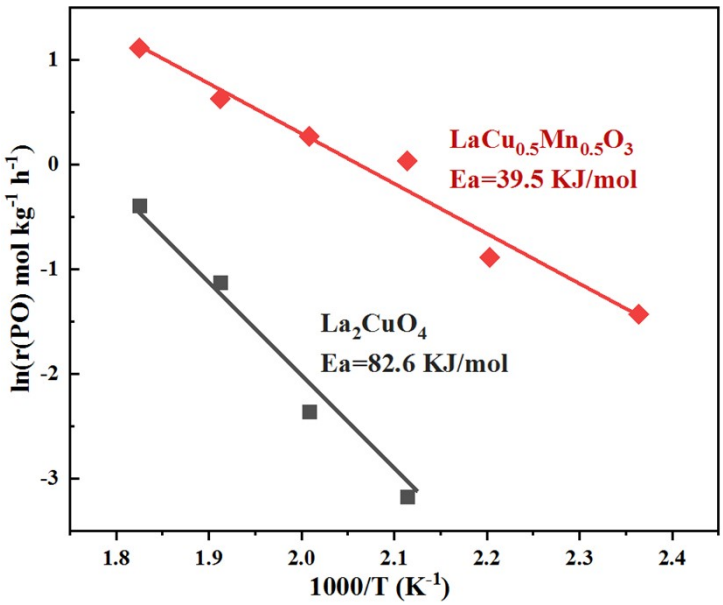


Figure S8. Apparent activation energy of La_2CuO_4 and $LaMn_{0.5}Cu_{0.5}O_3$ calculated by Arrhenius equation.

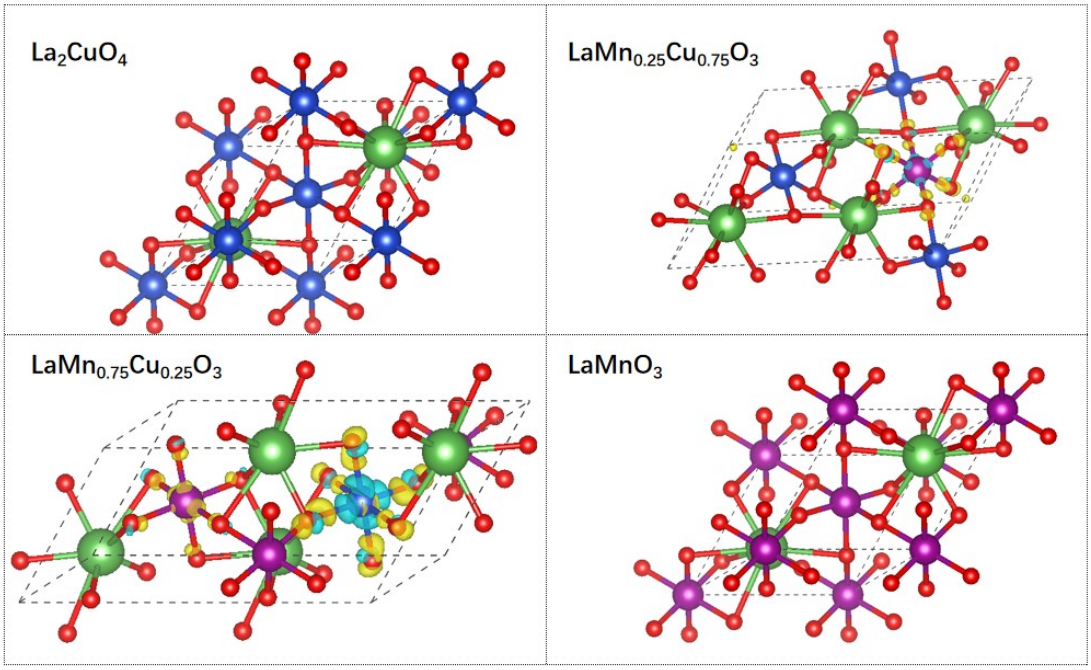


Figure S9. Electron density difference plots for $LaMn_xCu_{1-x}O_3$ (x = 0, 0.25, 0.75, 1) samples

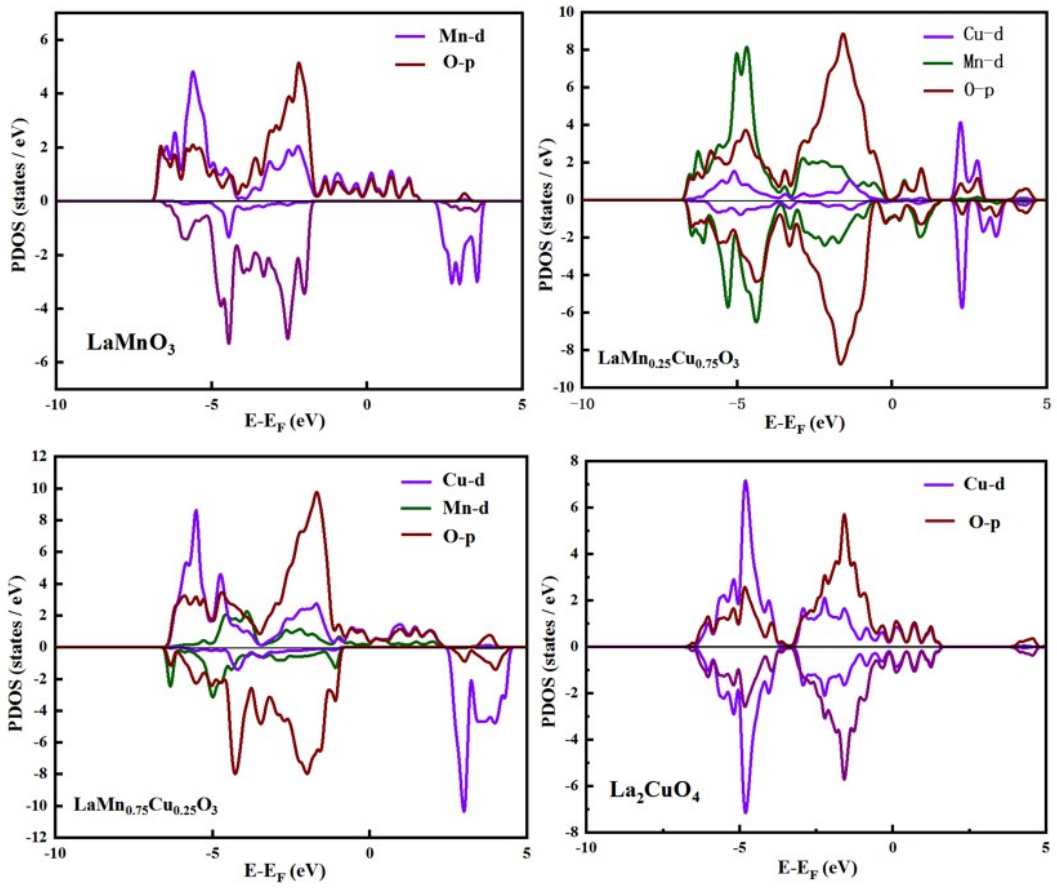


Figure S10. Density of states (DOS) plots for $LaMn_xCu_{1-x}O_3$ (x = 0, 0.25, 0.75, 1)

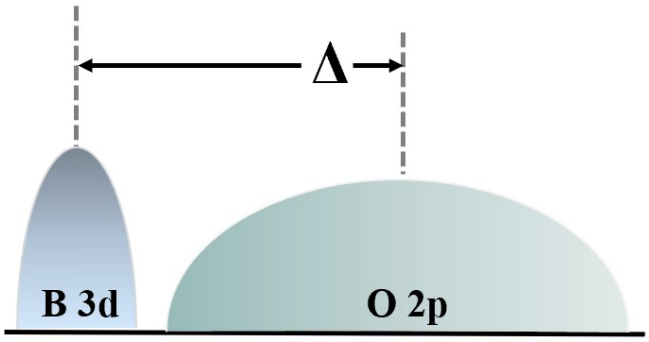


Figure S11. Charge-transfer energy schematic diagram of perovskite type oxides.

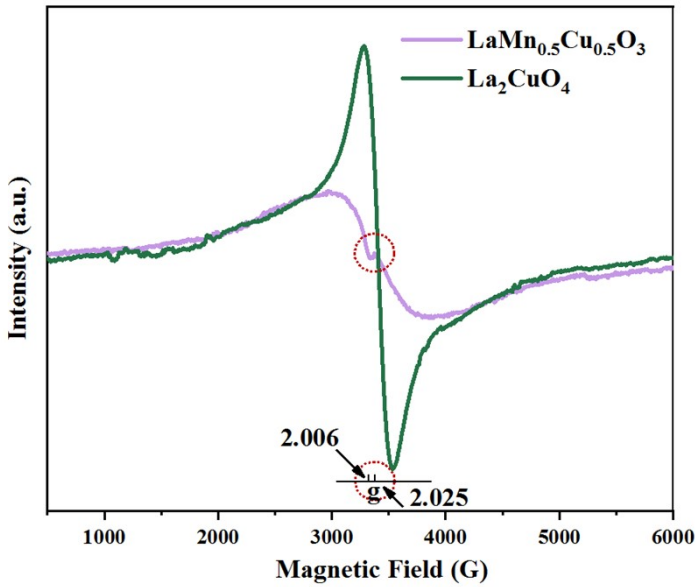
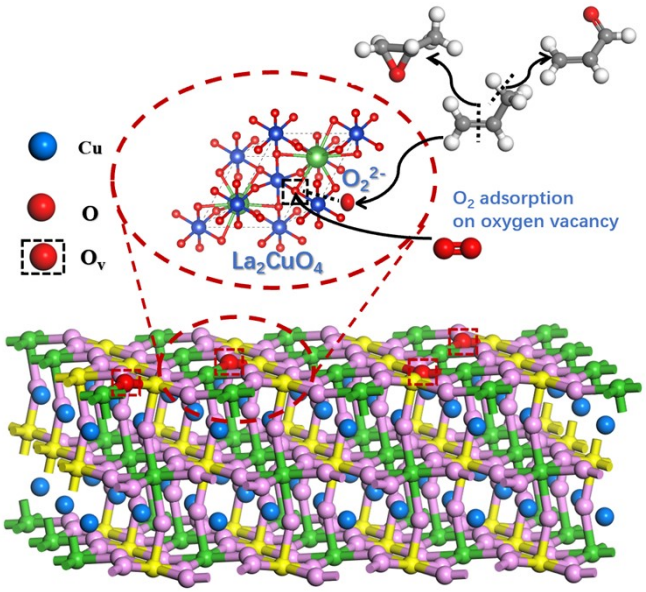


Figure S12. The EPR spectra of $LaMn_{0.5}Cu_{0.5}O_3$ sample tested at room temperature

2. Scheme S1



Scheme S1. Possible reaction model of the direct epoxidation of propylene with molecular oxygen over La_2CuO_4 sample

As represented in Scheme S1, O_2 was adsorbed and activated in the electronegative oxygen vacancies over La_2CuO_4 sample forming O_2^{2-}/O^-, then reacted with propylene adsorbed on the surface of the metal cation at the B position. After desorption of the formed products, the oxygen vacancies sites on the perovskite oxides' surface were recovered. Based on previous studies,[1] the activation of dioxygen on oxygen vacancies not only required higher reaction temperature, but also the nucleophilicity of activated oxygen species was enhanced. Therefore, the La_2CuO_4 catalyst showed poor low-temperature reducibility and poor selectivity for DEP reaction.

3. Table. S1 to S3

Table S1. Catalytic performance of $LaCu_XMn_{1-X}O_3$ with different Cu/Mn molar ratios[a]

X	r(PO) ($mol \cdot kg^{-1}_{cat.} h^{-1}$)	Selectivity (%)				Conversion (%)
		PO	AT	AC	CO_x	
0	0	0	0	0	1	1.71
0.25	0.08	2.6	2.1	1.2	94.1	0.21
0.5	1.04	33.9	5.6	4.2	56.3	0.20
0.75	0.11	3.8	8.3	2.8	85.1	0.18
1	0.04	17.4	0	33.7	48.9	0.02

[a]The data in the table above are tested at 200 °C.

Table S2. Catalytic performance of La_2CuO_4 and $LaCu_{0.5}Mn_{0.5}O_3$ at different reaction temperatures

Catalyst	temp. (°C)	r(PO) ($mol \cdot kg^{-1}_{cat.} h^{-1}$)	Selectivity (%)				Conversion (%)
			PO	**AT**	**AC**	**CO_x**	
La_2CuO_4	200	0.04	17.4	0	33.7	48.9	0.02
	225	0.09	8.4	0	17.8	73.8	0.06
	250	0.33	8.5	1.4	9.2	80.9	0.24
$LaCu_{0.5}Mn_{0.5}O_3$	275	0.68	1.4	2.2	4.8	91.6	0.29
	150	0.24	74.2	25.8	0	0	0.02
	175	0.41	49	12.3	10.1	28.6	0.05
	200	1.04	33.9	5.6	4.2	56.3	0.20
	225	1.01	17.0	0	9.7	73.3	0.37
	250	1.87	12.4	0.4	0.2	87.0	0.97
	275	3.04	10.4	0.6	0.8	88.2	1.82

Table S3. Catalytic performance of previous representative Cu-based samples on DEP reaction.

No	Catalyst	PO sel. (%)	Conv. (%)	r(PO) ($mol \cdot kg^{-1} \cdot h^{-1}$)	Temp. (^oC)	Ref.
1	Cu/SiO_2	53.0	0.25	0.014	225	2
2	$VCe_{0.5}Cu_{0.5}$-NaCl	32.6	0.26	0.165	250	3
3	K^+-CuO_x/SBA-15	36.0	0.53	2.200	200	4
4	Cu/SiO_2-NaCl	44.0	0.16	0.187	215	5
5	RuO_2-CuO-NaCl-TeO_2-MnO_x/SiO_2	23.1	14.55	1.258	250	6
6	CuO-TiO_2/SiO_2	30.0	0.10	0.241	250	7
7	RuO_2–CuO–TiO_2/SiO_2	7.70	15.40	8.776	250	7
8	RuO_2–CuO/SiO_2	1.90	42.50	5.982	250	7
9	(KAc)–Cu/SiO_2	19.1	0.27	2.500	325	8
10	CuO_x-SiO_2	10.0	1.00	0.420	550	9
11	K^+-CuO_x-SiO_2	30.0	0.48	0.580	550	9
12	Cubic-Cu_2O-27	83.0	0.06	0.028	110	1
13	NH_4Cl-RD-Cu_2O	51.0	0.15	0.068	200	10
14	Cu_2O rhombic dodecahedra	13.0	0.82	0.057	250	11
15	RuO_2–CuO–TeO_2/SiO_2	41.0	0.37	3.500	250	12
16	RuO_2–CuO/SiO_2	18.0	20.00	8.103	250	12
17	RuO_2–CuO–TeO_2/SiO_2	47.0	0.35	4.390	250	12
18	RuO2–CuO–NaCl/SiO_2	1.0	—	0.913	250	12

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