Supporting Information

Sintering Resistant CuO/CeO_2 Catalysts Prepared by Reversed Impregnation Method for Ethyl Acetate Oxidation

Yuchuan Ye[1,2], Zhouhao Zhu[2], Wanjin Yu[3], Shaohong Zang[4], Yingtang Zhou[5], Liuye Mo*[2], Lei Jiao*[1]

1. Ocean College, Zhejiang University, Zhoushan 316021, PR China
2. School of Petrochemical & Environment, Zhejiang Ocean University, Zhoushan 316022, PR China
3. State Key Lab Fluorinated Greenhouse Gases Replacement control and treatment, Zhejiang Research Institute of Chemical Industry, Hangzhou 310023, PR China
4. National Engineering Research Center for Marine Aquaculture, Zhejiang Ocean University, Zhoushan 316022, PR China
5. Marine Science and Technology College, Zhejiang Ocean University, Zhoushan 316022, PR China

*Correspondence: liuyemo@zjou.edu.cn, jiaolei@zju.edu.cn

* Corresponding author. E-mail address: liuyemo@zjou.edu.cn, jiaolei@zju.edu.cn
[#] These authors contributed equally to this work.

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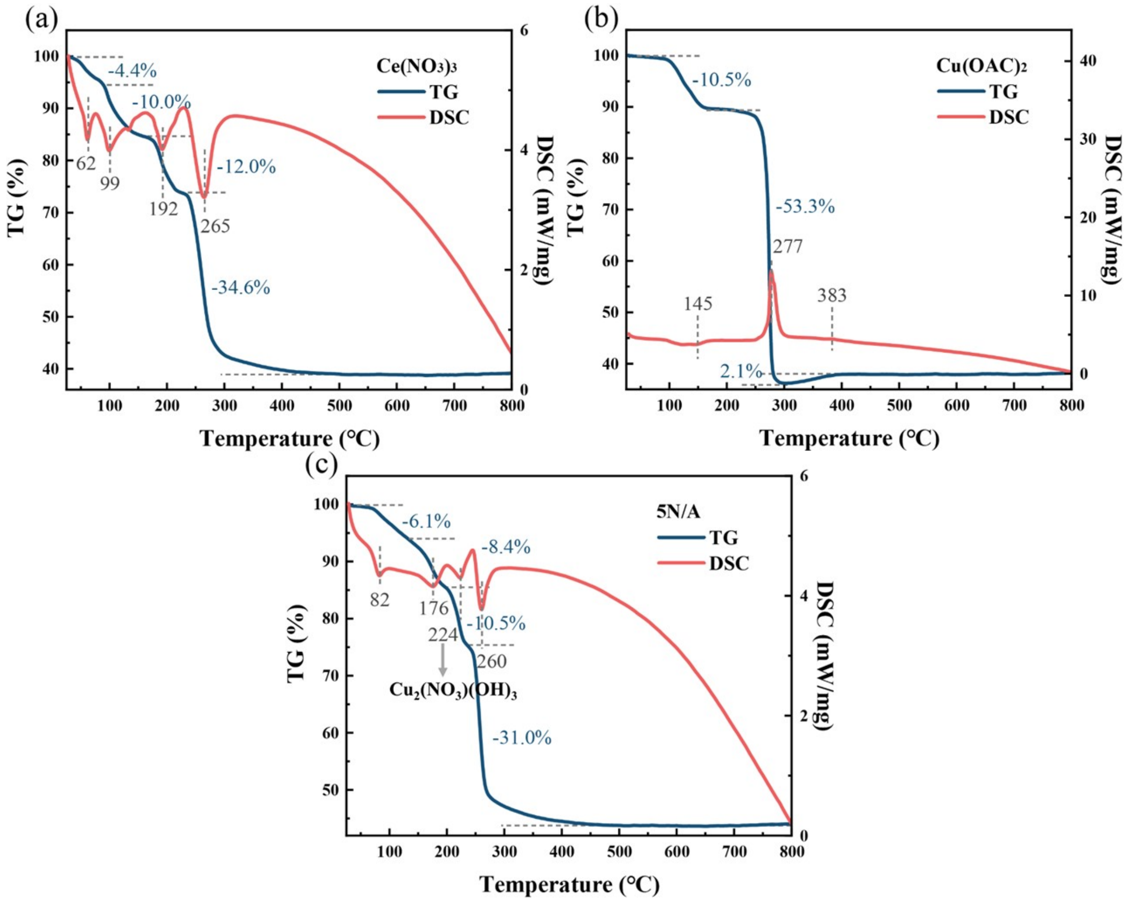


Figure S1. TG-DSC curves of (a) $Ce(NO_3)_3 \cdot 6H_2O$; (b) $Cu(OAc)_2 \cdot H_2O$ and (c) uncalcined 5N/A catalyst.

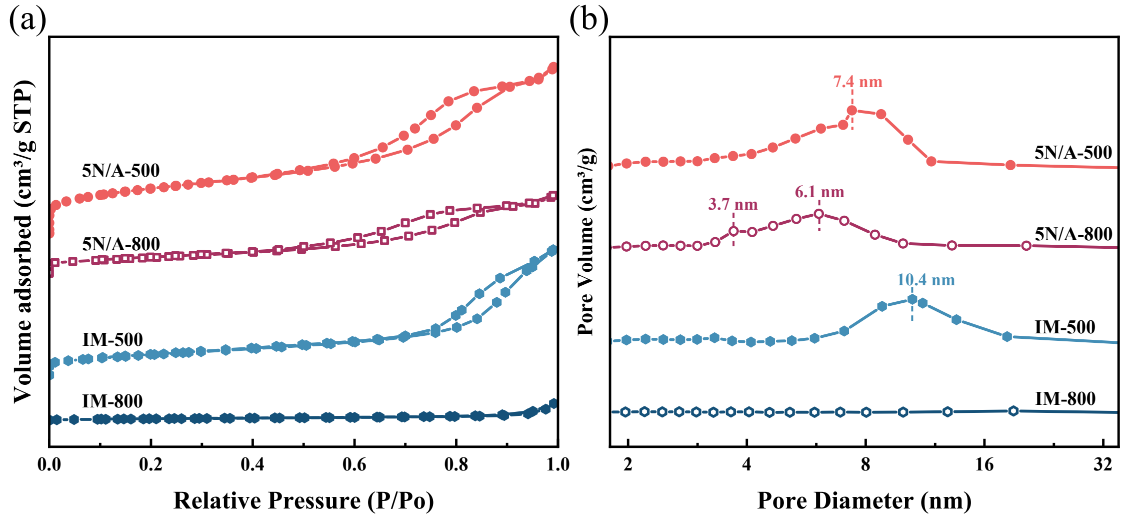


Figure S2. (a) Nitrogen adsorption-desorption isotherms and (b) Pore distributions of the 5N/A-Y and IM-Y catalysts.

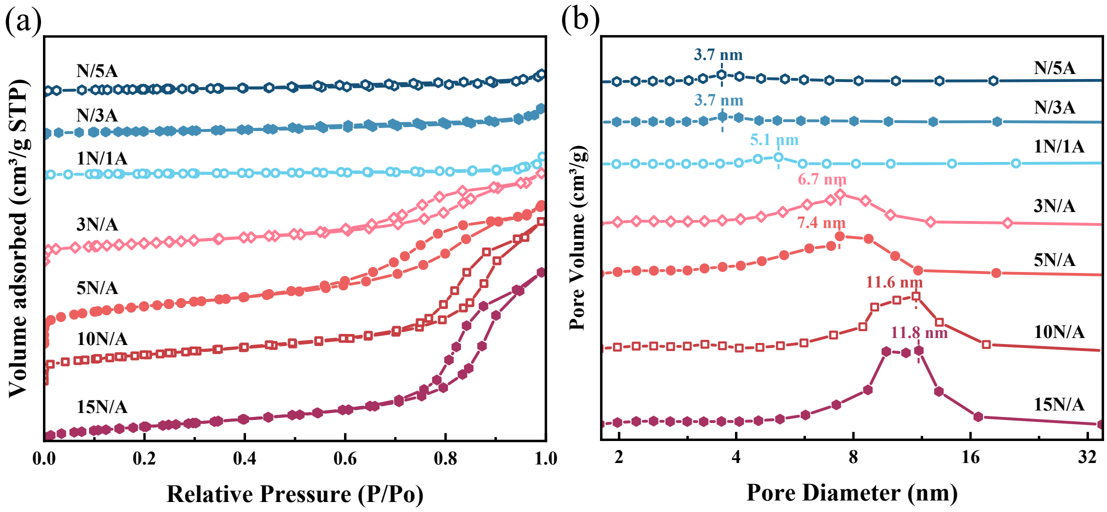
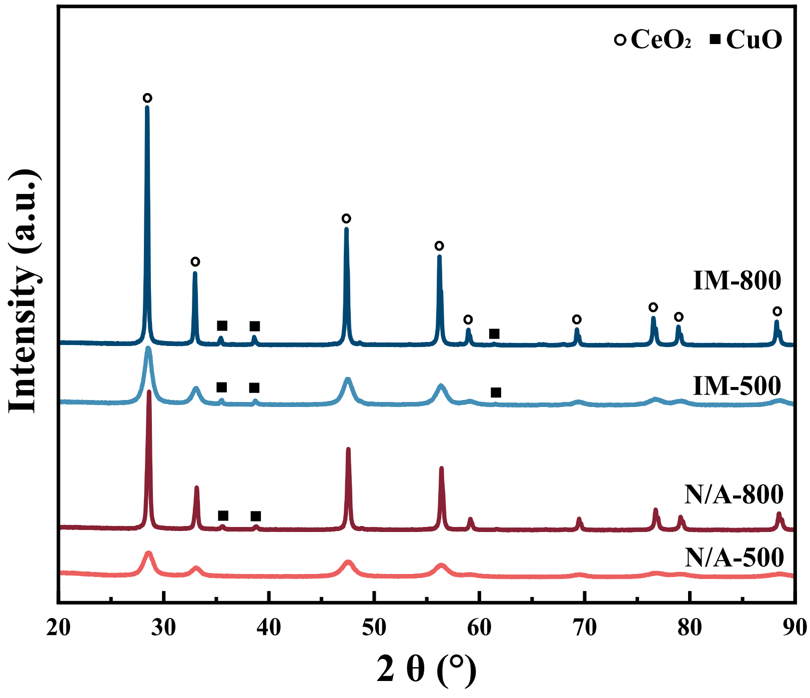


Figure S3. (a) Nitrogen adsorption-desorption isotherms and (b) Pore distributions of the XN/A-500 catalysts.



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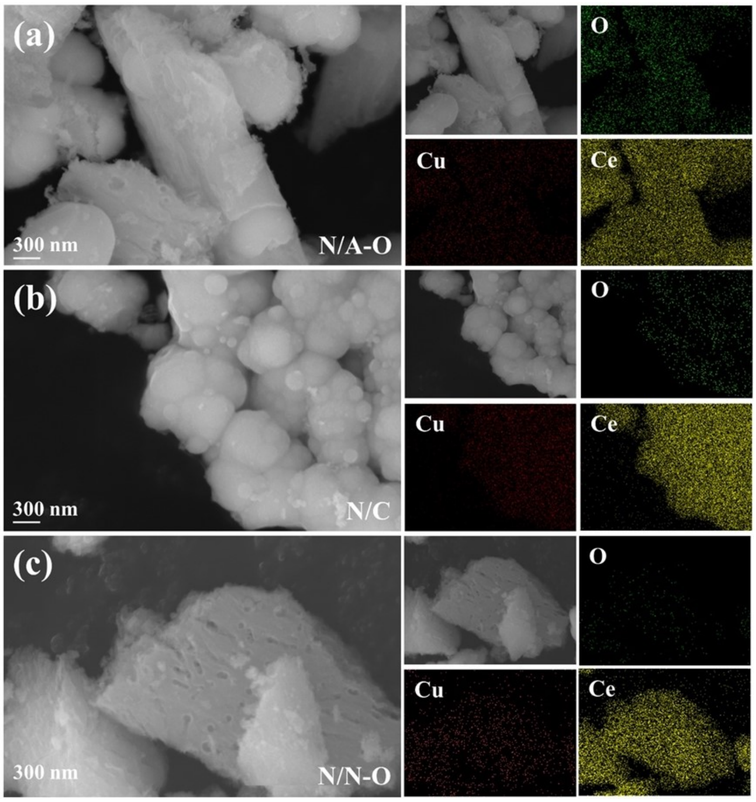

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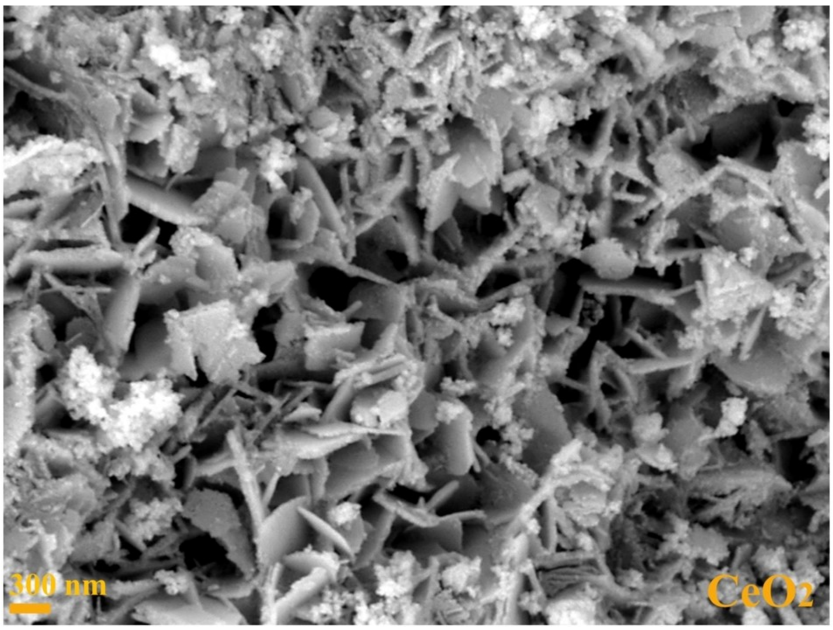


Figure S6. SEM image of CeO_2 sample obtained by calcination of $Ce(OAc)_3$ at 300 °C for 4h.

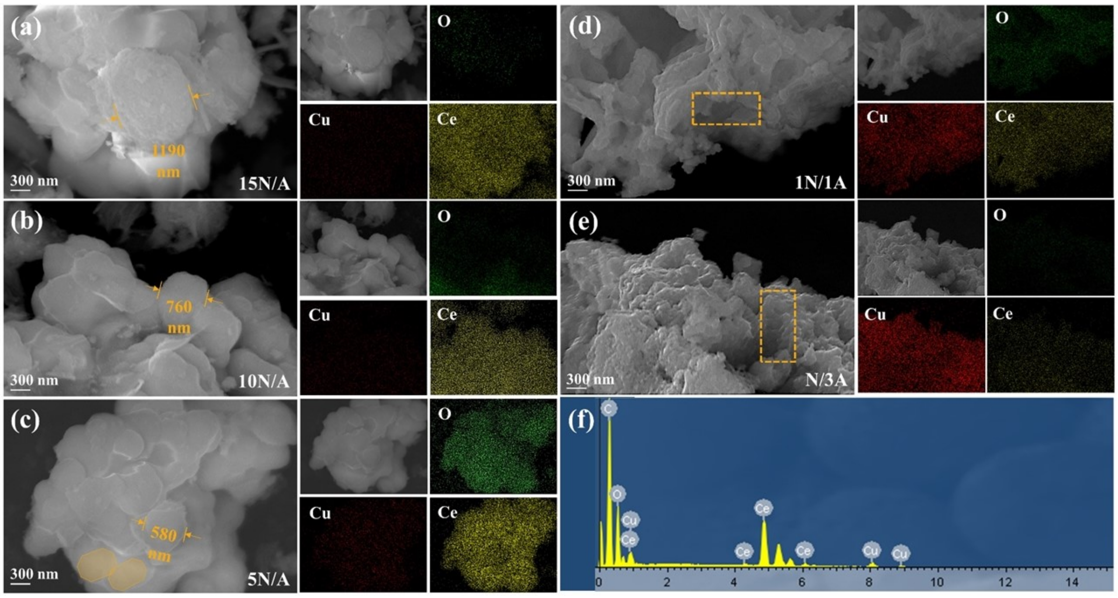
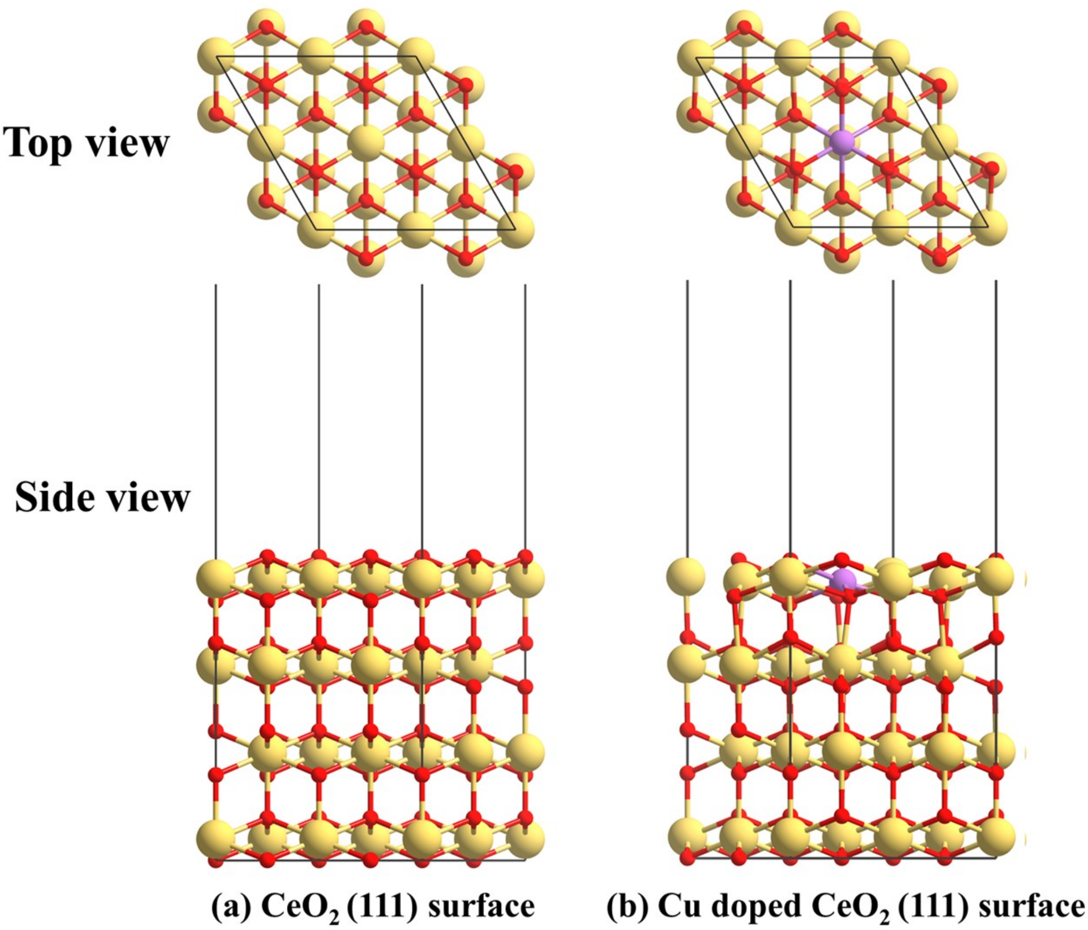


Figure S7. SEM mapping images of XN/A-500 catalysts.



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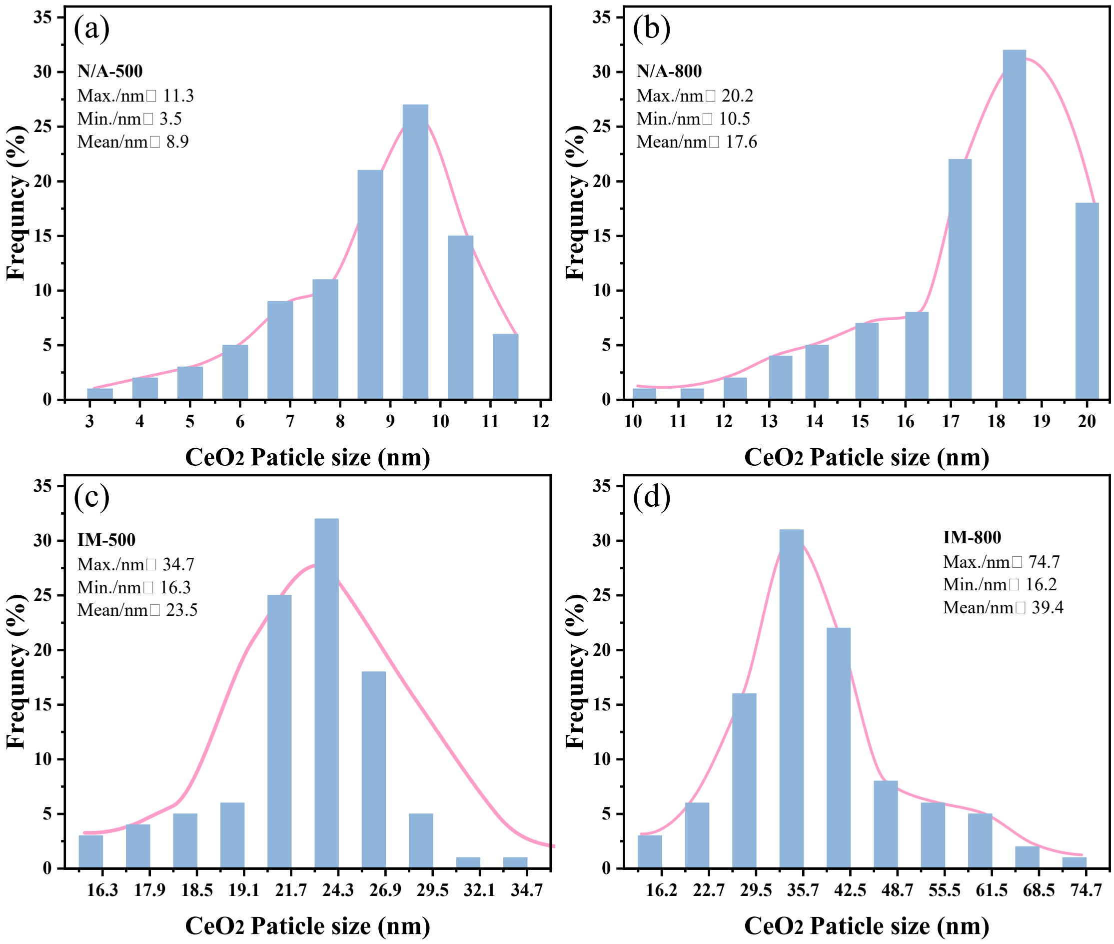

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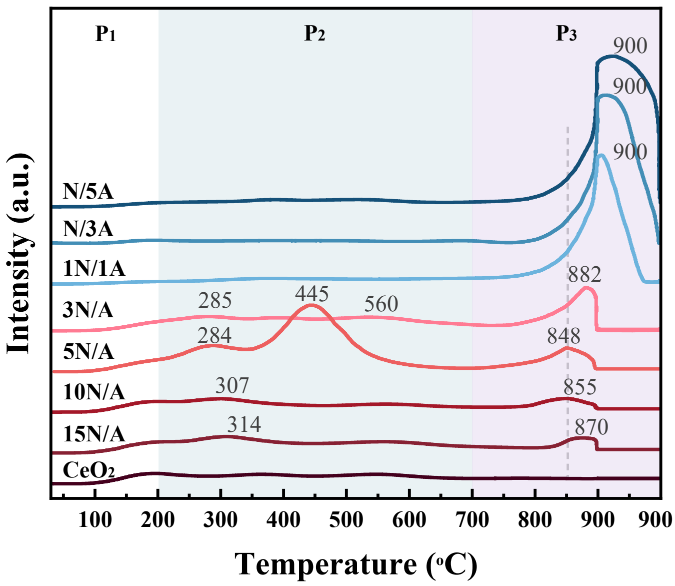

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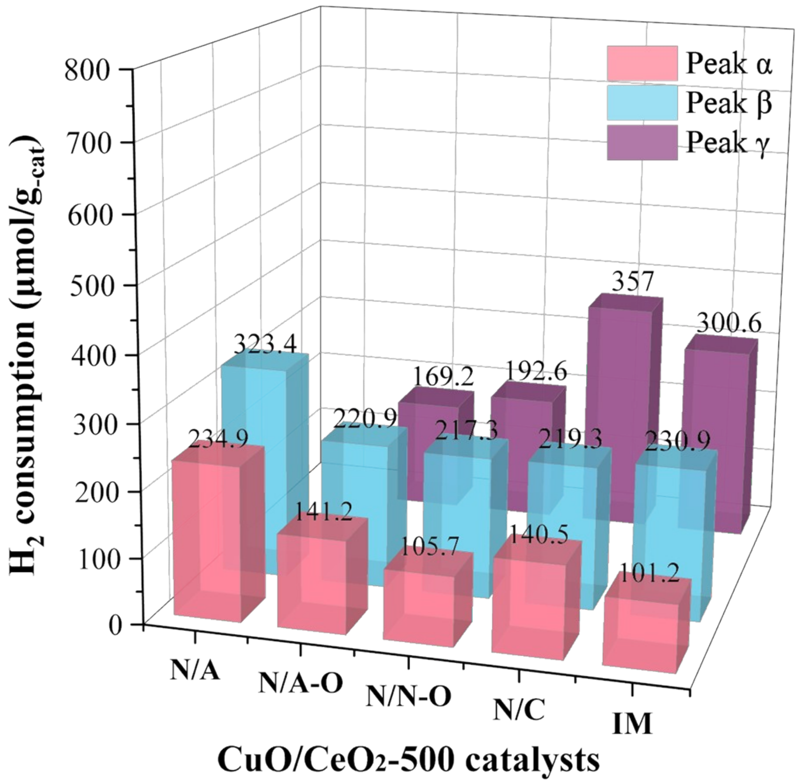

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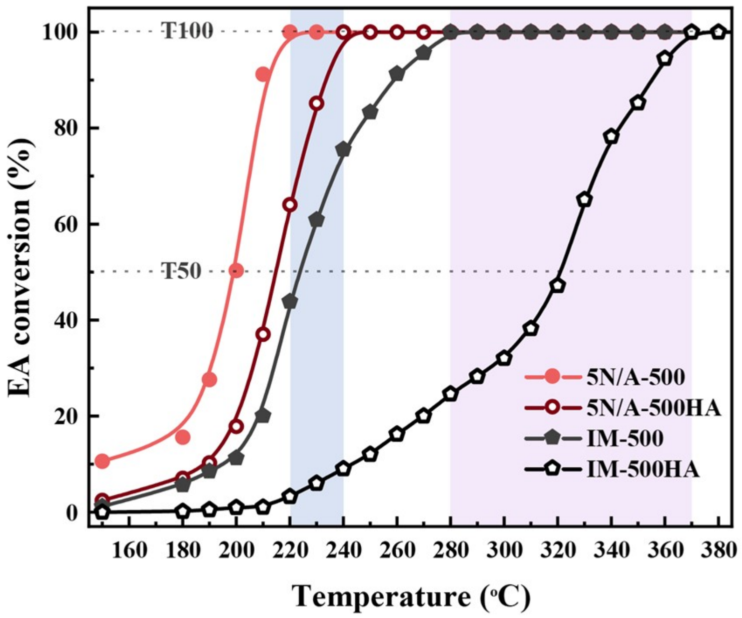

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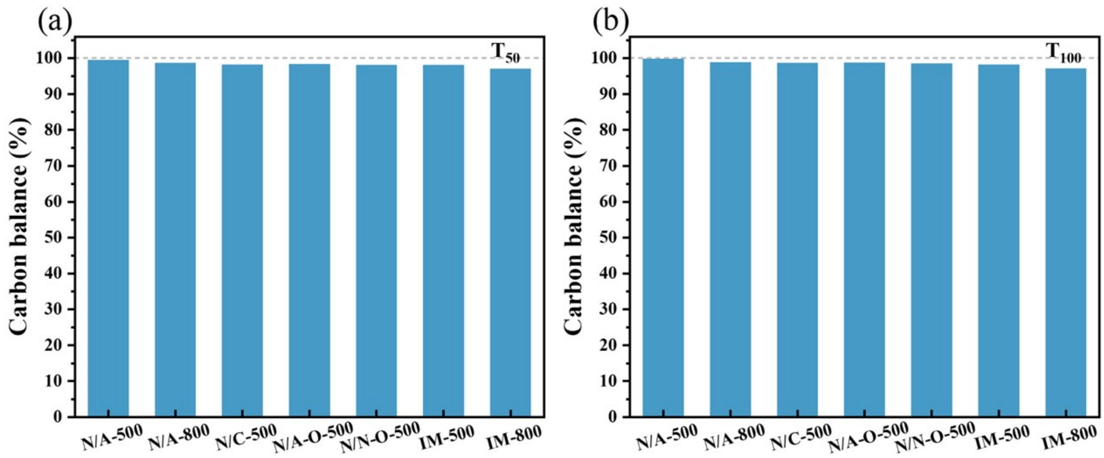

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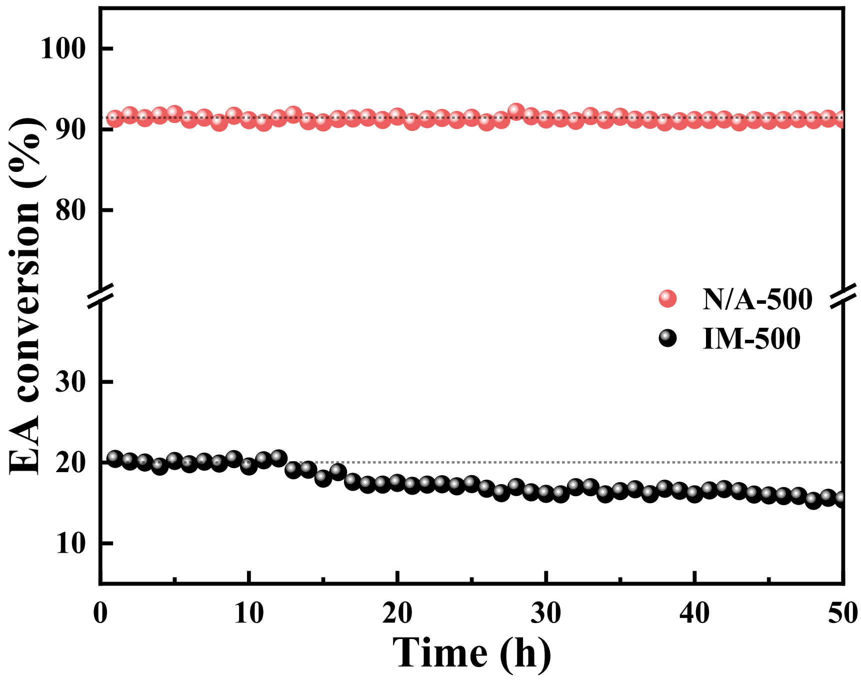

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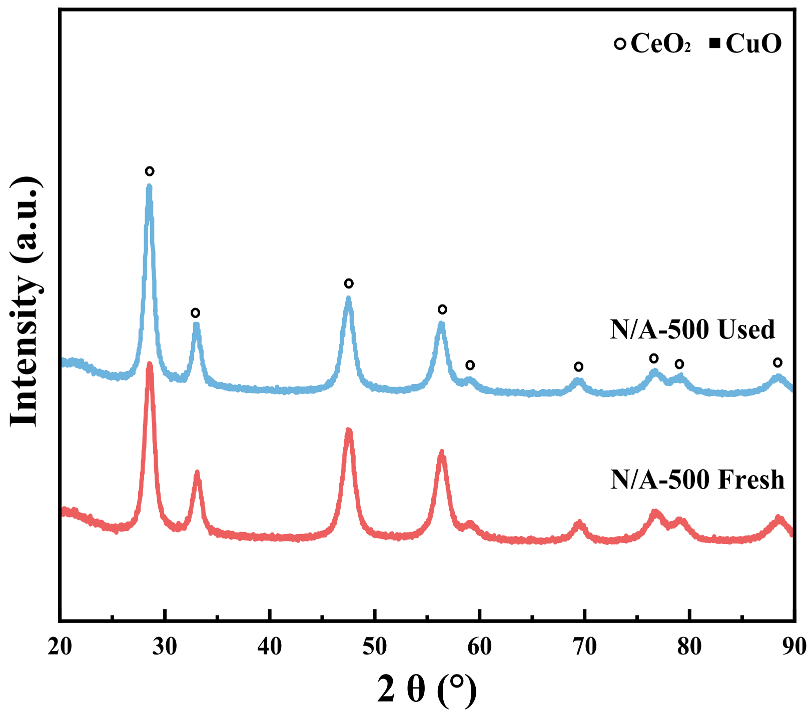

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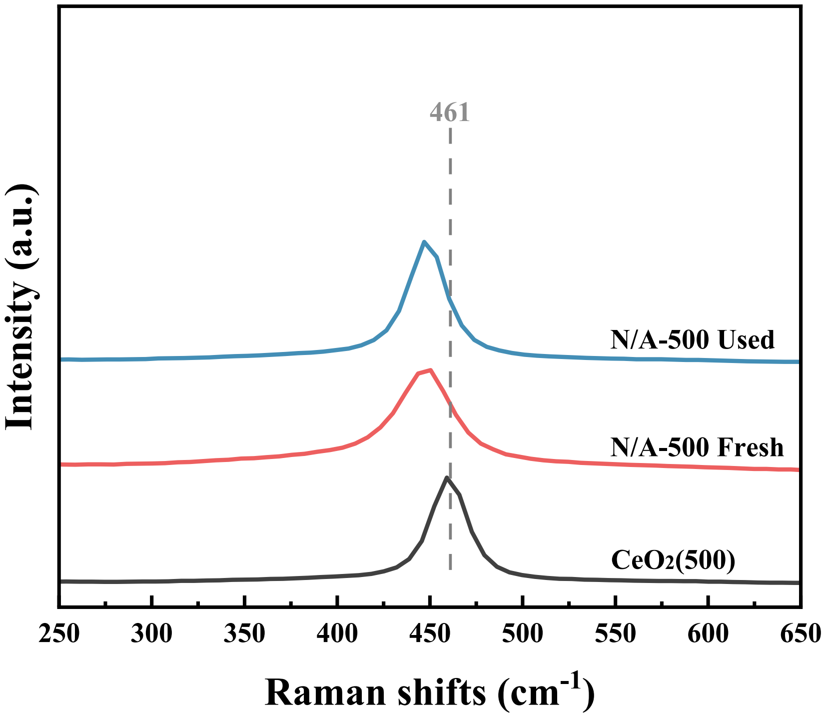

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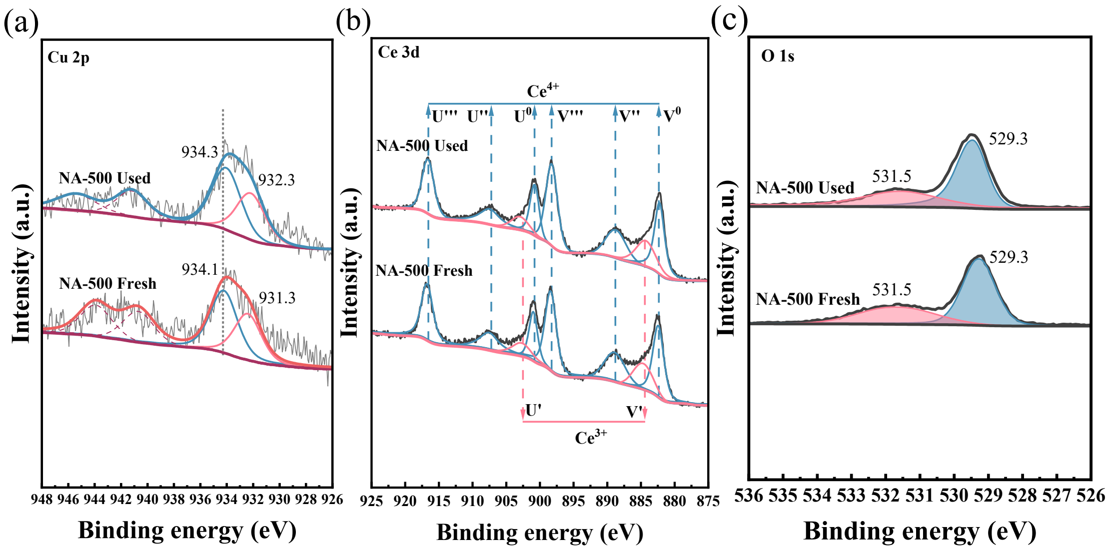

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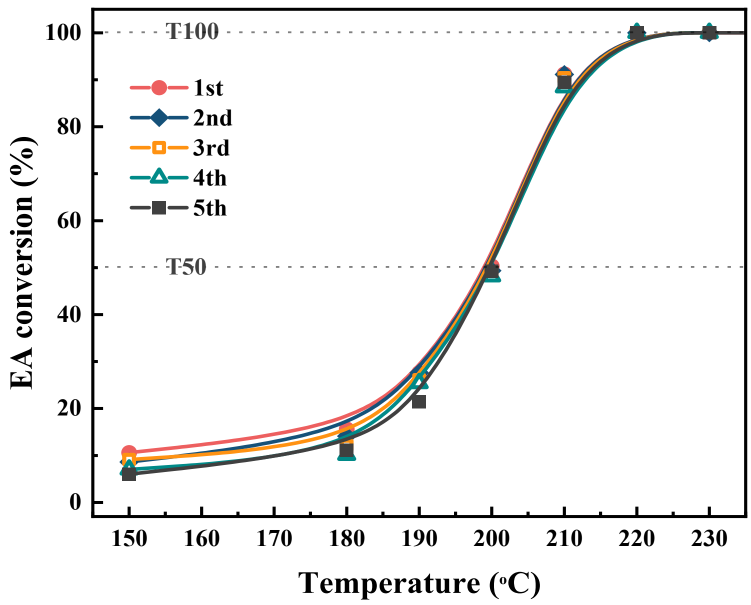

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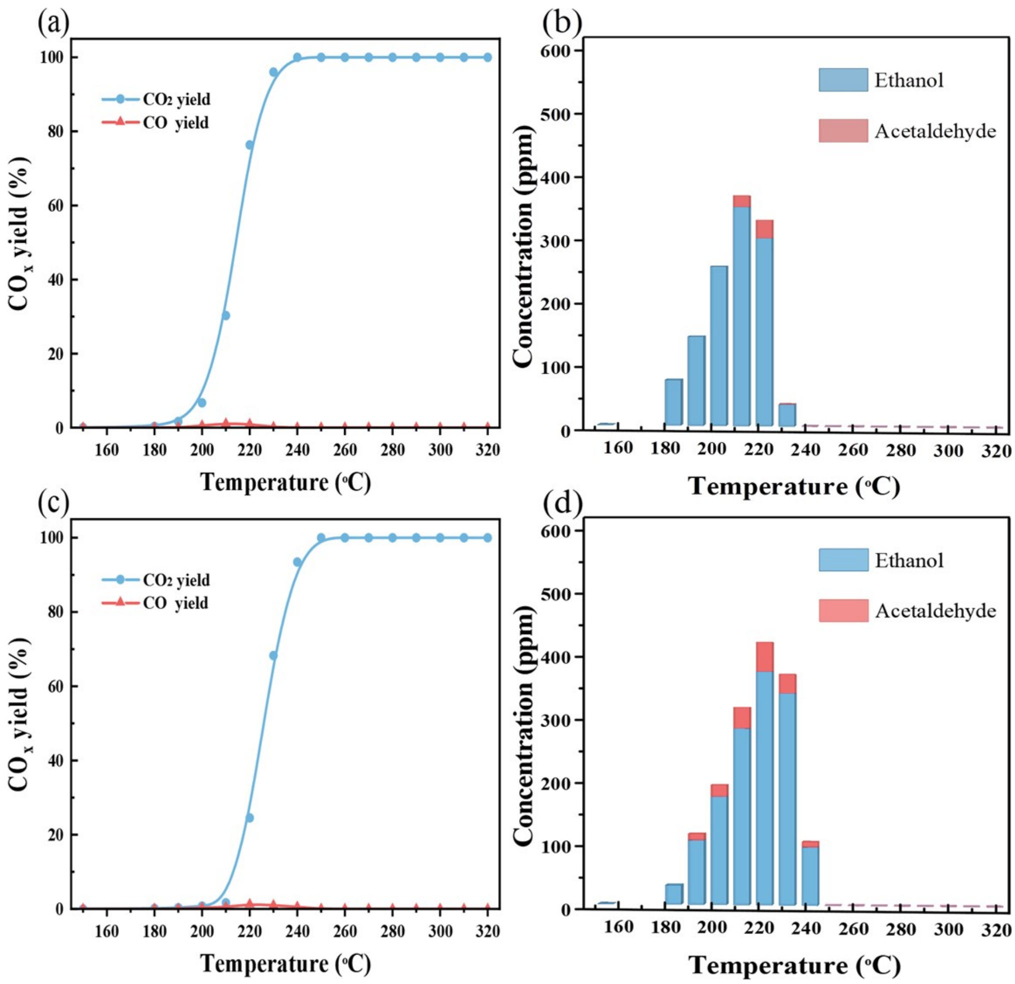

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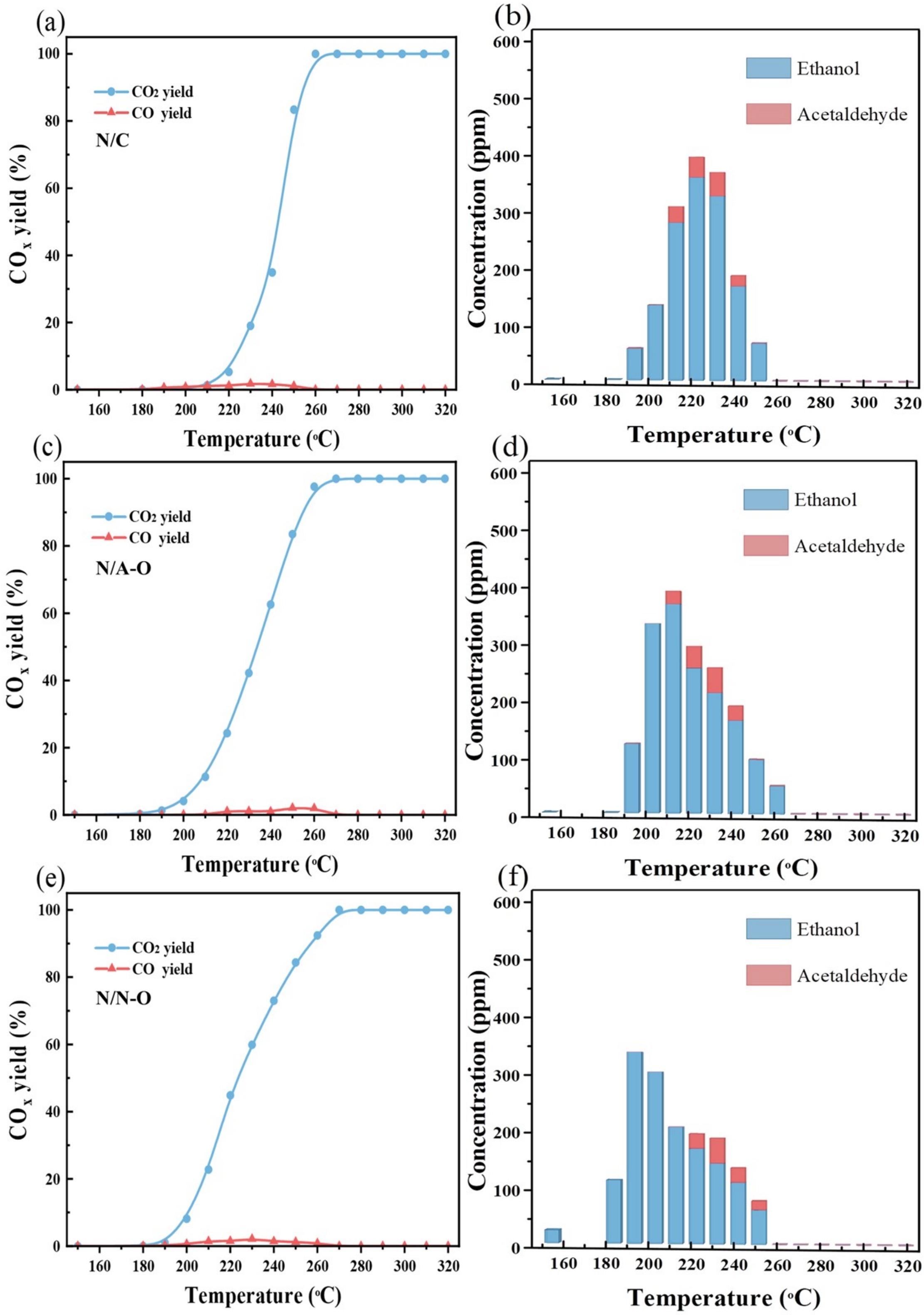

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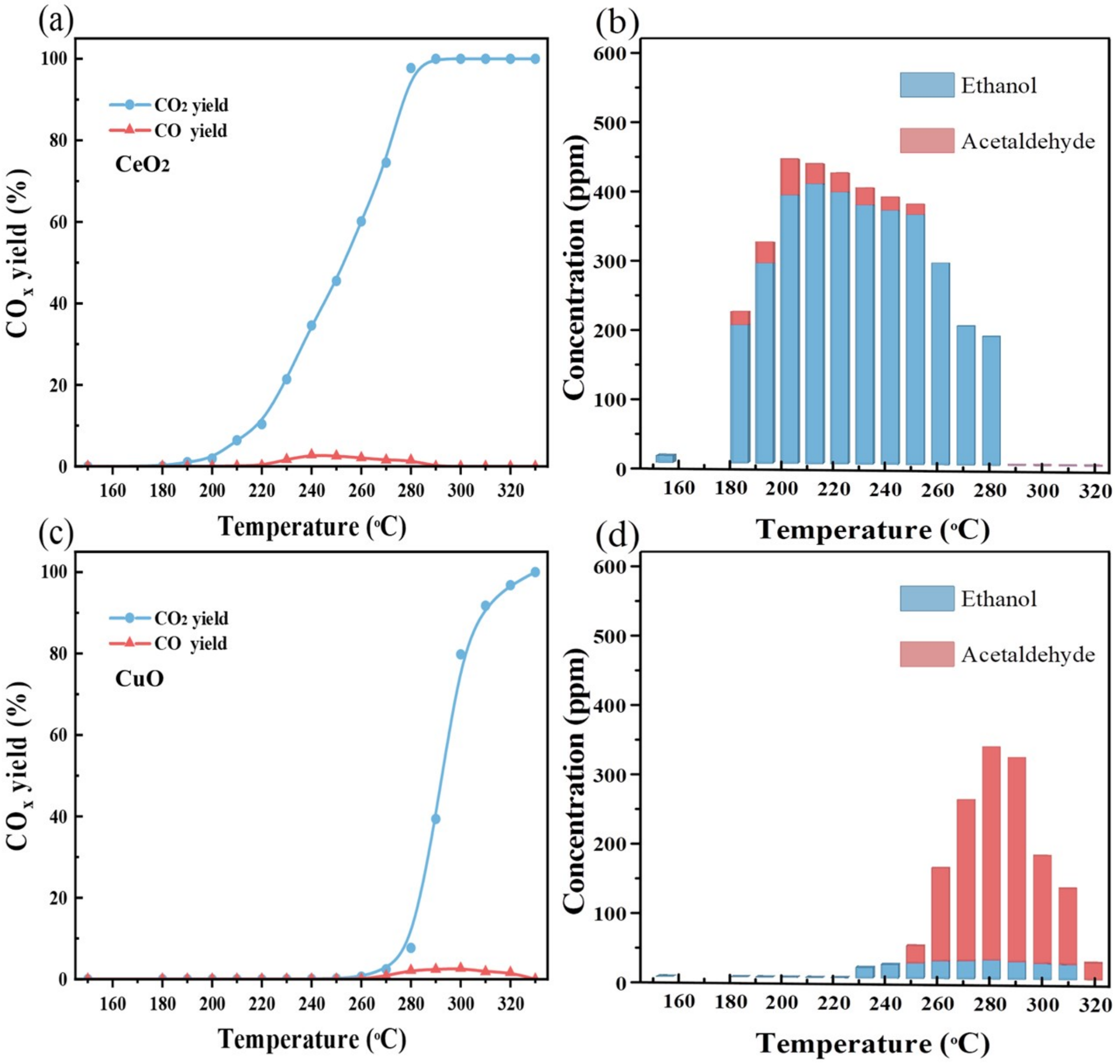

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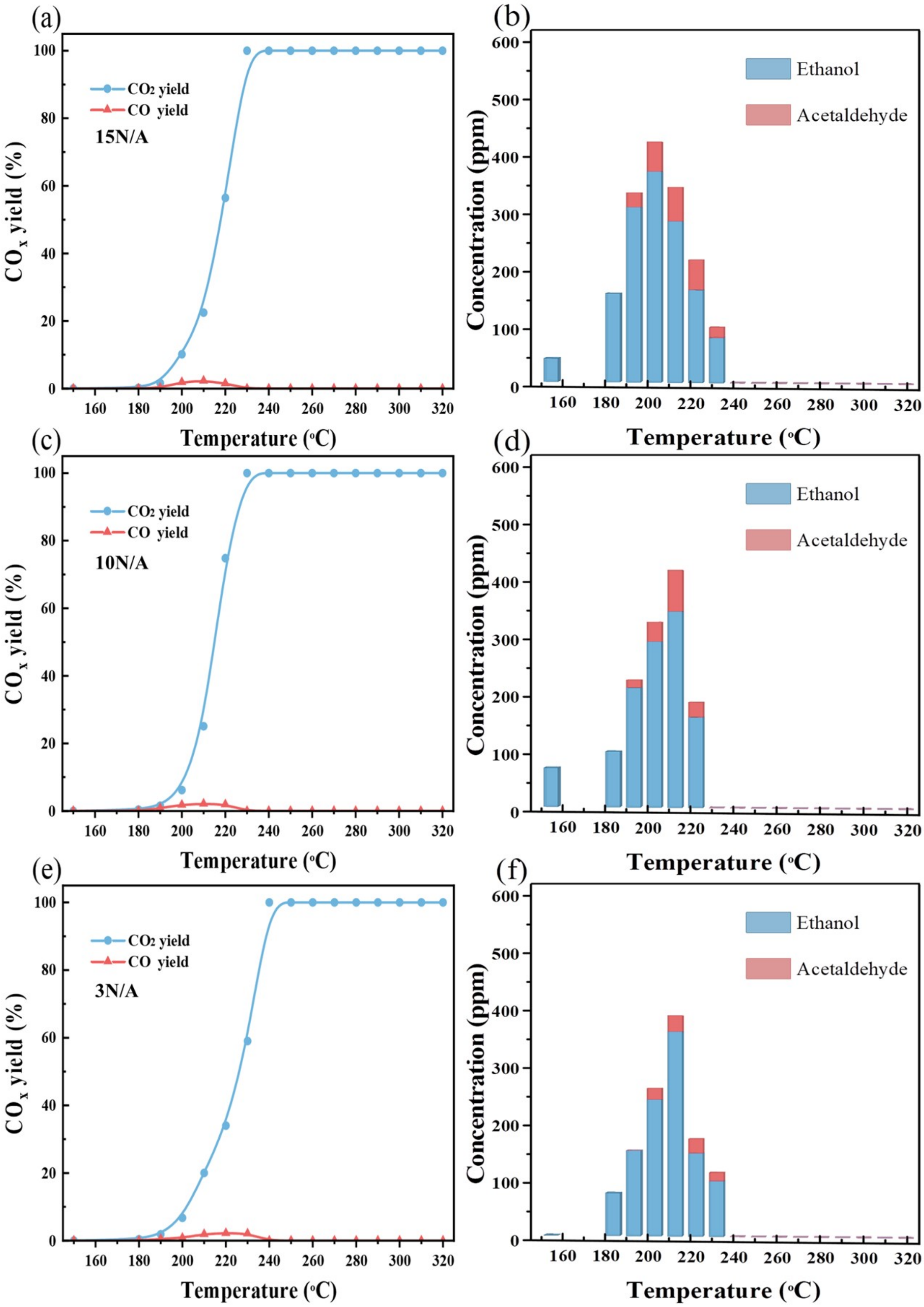

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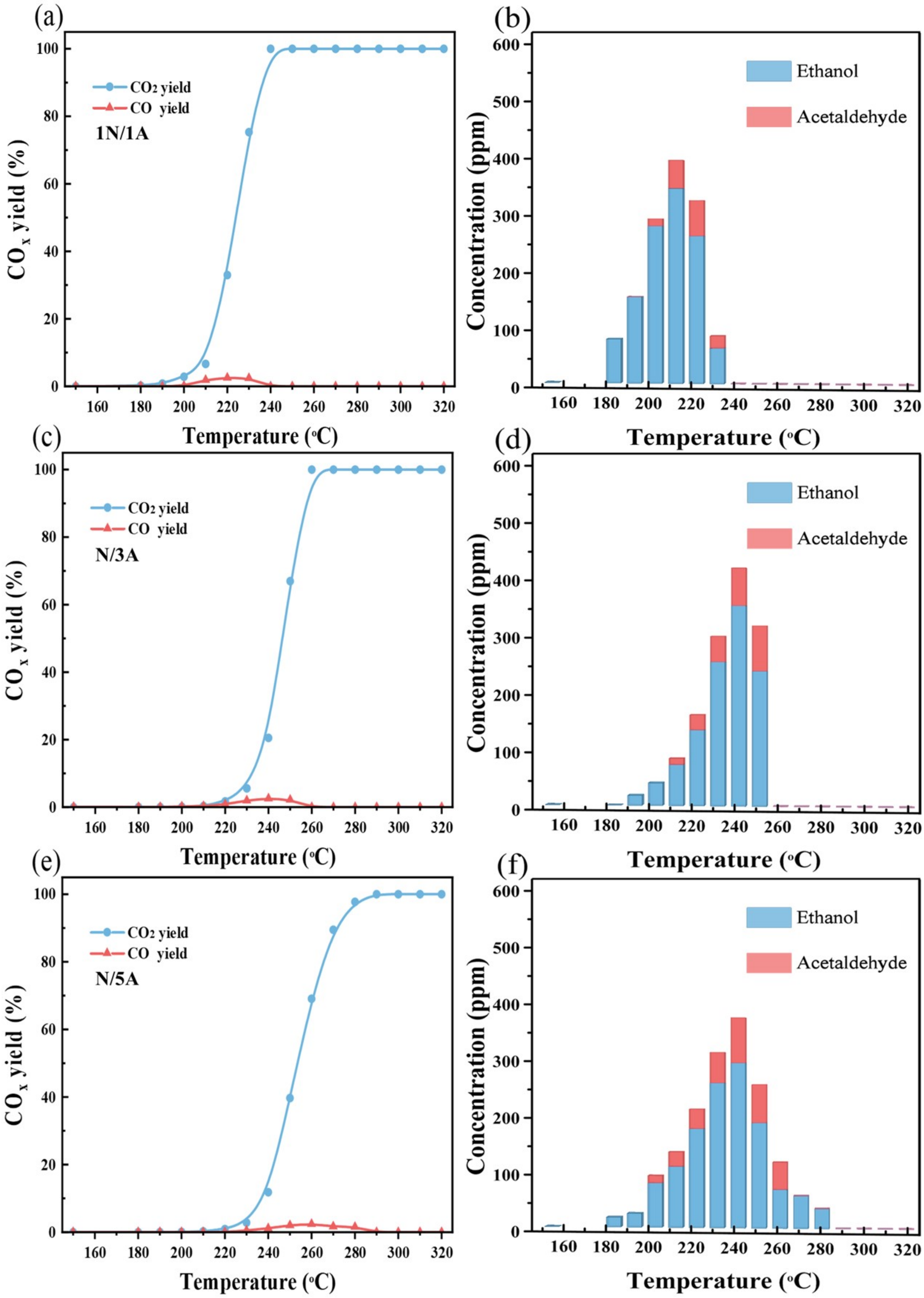

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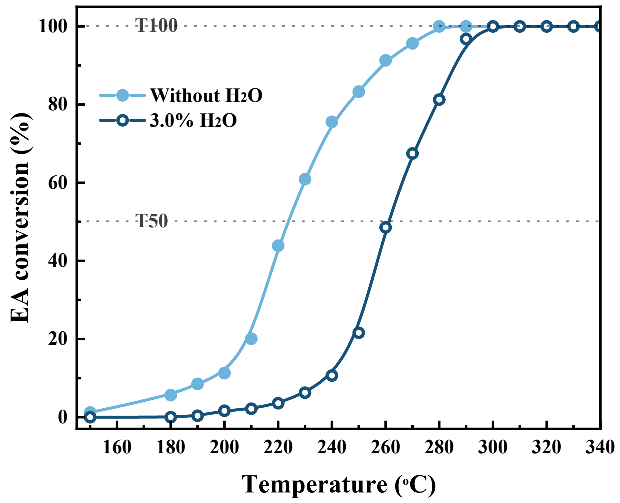

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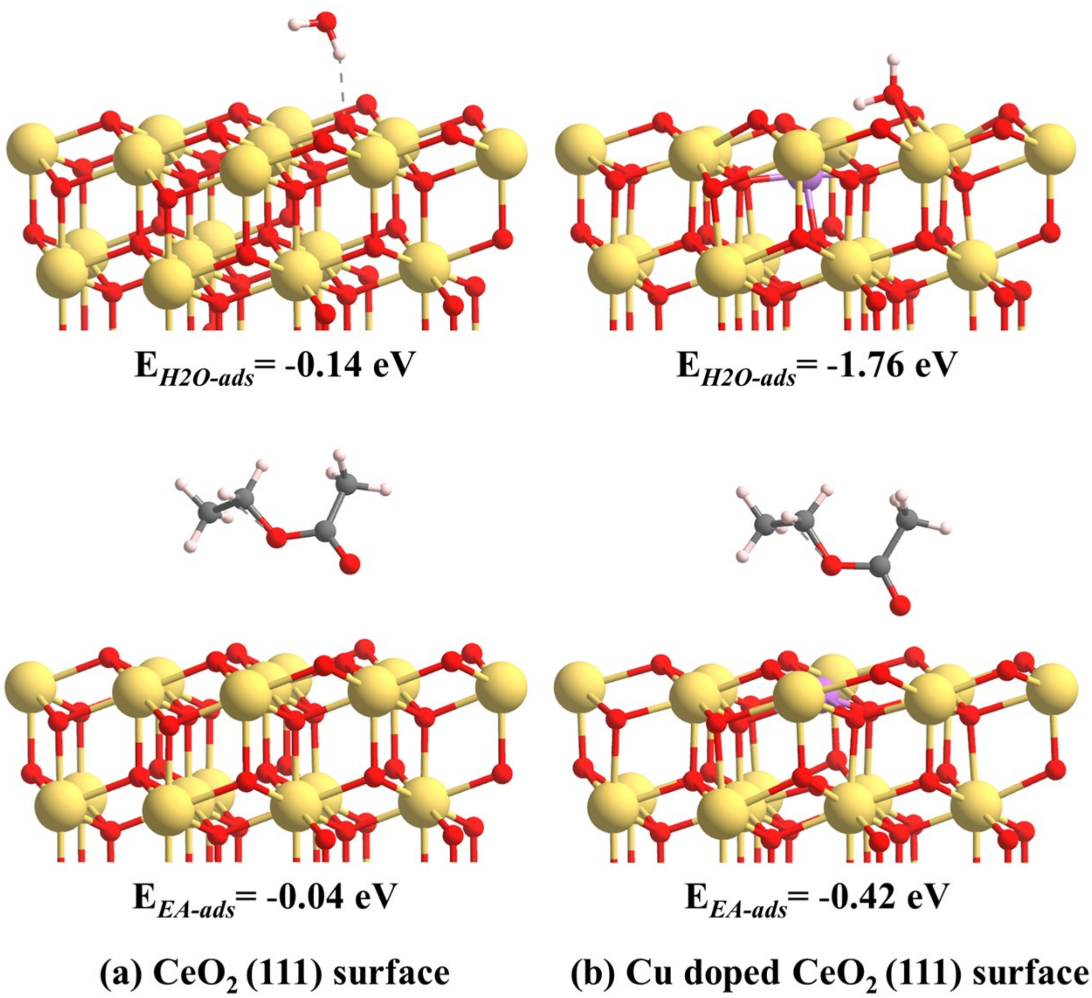

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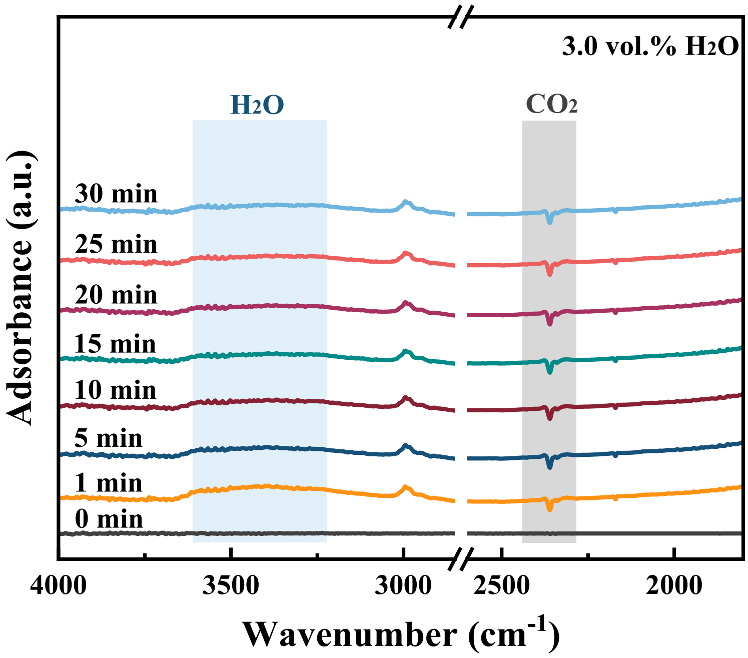

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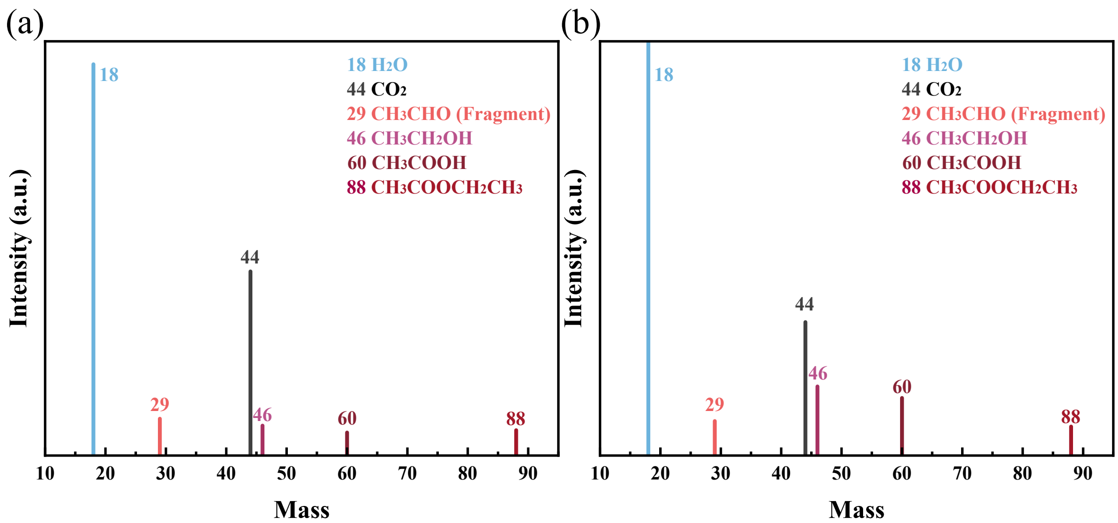

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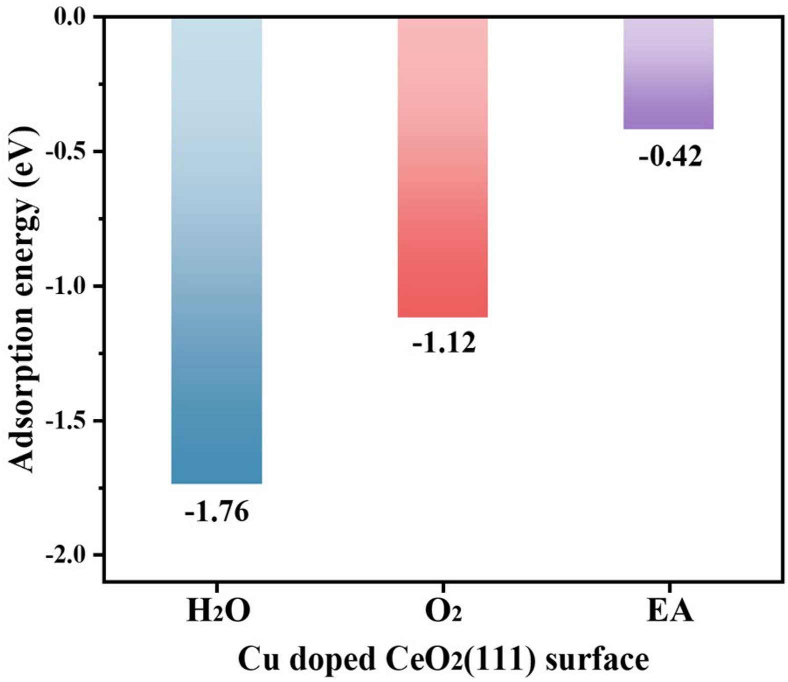

Figure S28. Comparison of adsorption energies of H_2O, O_2 and EA on the Cu doped CeO_2(111) surface.

Table S1 Specific surface areas, crystallite sizes and cell parameters of the CuO/CeO_2 catalysts.

Catalysts	SA (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)	CeO_2 crystallite size [a] (nm)	CuO crystallite size [a] (nm)	Cell parameter (nm)
CeO_2(500)	74	10.8	0.16	18.2	-	0.5401
CuO(A-O)	1	17.3	0.01	-	34.1	-
IM-500	49	10.4	0.13	23.4	7.9	0.5392
5N/C-500	20	5.9	0.03	13.1	2.1	0.5389
5N/N-O-500	62	10.7	0.17	14.9	-	0.5385
5N/A-O-500	64	9.6	0.19	13.7	-	0.5382
5N/A-500	106	7.9	0.20	9.4	-	0.5370
15N/A-500	74	11.9	0.22	12.6	-	0.5381
10N/A-500	74	10.5	0.19	10.9	-	0.5379
3N/A-500	53	8.2	0.11	11.8	-	0.5375
1N/1A-500	12	10.7	0.03	15.3	3.2	0.5383
N/3A-500	10	9.1	0.02	15.3	4.7	0.5387
N/5A-500	5	6.8	0.02	12.9	8.1	0.5391
5N/A-300	58	10.2	0.16	10.3	-	0.5401
5N/A-400	65	9.4	0.15	9.8	-	0.5387
5N/A-600	105	6.8	0.20	9.6	-	0.5373
5N/A-700	75	6.2	0.16	14.7	1.4	0.5378
5N/A-800	38	6.1	0.08	18.7	2.6	0.5380
IM-800	5	14.7	0.02	42.5	18.7	0.5408

[a] The crystallite sizes were calculated by the Scherrer equation.

Table S2 The Cu, Ce and O contents of energy dispersion spectrum (EDS) over the CuO/CeO_2 catalysts

	Catalysts	Cu (wt.%)	Ce (wt.%)	O (wt.%)
Different preparation methods	IM-500	7.84	52.11	40.05
	5N/C-500	6.95	51.17	41.88
	5N/A-O-500	6.87	51.84	41.29
	5N/N-O-500	7.12	52.65	40.23
	5N/A-500	6.34	49.19	44.47
Different calcination temperatures	5N/A-300	7.56	51.61	40.83
	5N/A-400	7.32	50.33	42.35
	5N/A-500	6.34	49.19	44.47
	5N/A-600	6.47	49.65	43.88
	5N/A-700	6.52	50.17	43.31
	5N/A-800	6.78	50.35	42.87
	IM-800	8.36	54.5	37.14

Table S3 H_2-TPR analysis of the 5N/A-Y catalysts

Catalysts	Peak temperature (°C)			H_2 consumption ($\mu mol/g_{cat}$)			H_2 consumption ratio of $\alpha/(\alpha+\beta+\gamma)$
	α	β	γ	α	β	γ	
5N/A-300	-	202	225	-	306.8	380.9	-
5N/A-400	173	198	216	243.3	197.9	180.1	0.39
5N/A-500	164	195	-	234.9	323.4	-	0.42
5N/A-600	163	195	-	201.4	302.2	-	0.40
5N/A-700	160	192	225	56.3	297.3	28.6	0.14
5N/A-800	160	190	225	21.3	233.1	42.5	0.07

Table S4 XPS analysis of the 5N/A-500 catalysts fresh and after durability test

Catalysts	Surface composition (at.%)			Surface element molar ratio		
	Cu	Ce	O	Cu^+/Cu^{2+}	Ce^{3+}/Ce^{4+}	O_{ads}/O_{latt}
Fresh	7.79	12.00	50.94	0.65	0.29	0.65
Used	7.81	12.16	50.72	0.65	0.28	0.64

Table S5 Comparison of the conversion temperature for EA with other catalysts

Catalysts	T_{100}	GHSV (h^{-1})	Loading (wt.%)	Treatment (°C, h)	Preparation method	Rf.
5N/A-500	220	60,000	8.5%Cu	500, 4	Reversed Impregnation	This work
5N/A-800	230	60,000		800, 4		
Cu/Al_2O_3/COR	255	32,000	1.9%Cu	550, 4	Impregnation	1
Cu–Mn–La($(NH_4)_2CO_3$)	240	12,500	35.6%Cu	550, 4	Co-precipitation	2
Cu-Ce	240	120,000	29.3%Cu	400, 3	Impregnation	3
15Cu/OMS-2	240	120,000	15%Cu	400, 4	Pre-incorporation	4
$CeCuY_2O_3$-S5	250	15,000	-	500, 4	Sol-Gel	5
$CeCuY_2O_3$-S8	260			800, 4		
Cu/CeO_2	275	60,000	20%Cu	550, 2	Impregnation	6
Cu/CeO_2	260	60,000	20%Cu	550, 2	Impregnation	7
$Cu_{0.15}Ce_{0.85}$	240	50,000	15%Cu	550, 2	Urea–nitrate Combustion	8
CuO/CeO_2-800	260	60,000	5%Cu	800, 4	Modified Impregnation	9
$Cu10/Al_2O_3$-SiO_2	300	5,000	10%Cu	600, 4	Impregnation	10
$Ce_{0.8}Sn_{0.2}O_2$-500	235	60,000	-	500, 6	Combustion	11
$Ce_{0.8}Sn_{0.2}O_2$-800	250			800, 4		
$0.37AuPd_{2.72}/TiO_2$	260	40,000	0.37%AuPd	450, 4	Impregnation	12
$Pt/CeMnO_X$	240	20,000	0.5%Pt	500, 4	Impregnation	13
Pd/CeCuO-Y_2O_3-500	260	40,000	0.28%Pd	500, 4	Impregnation	14
Pd/CeCuO-Y_2O_3-800	270			800, 4		
Pt/ZrO_2	230	30,000	1%Pt	600, 4	Impregnation	15
Pt/Al_2O_3	250	30,000	1%Pt	600, 4	Impregnation	15
Pt/Co_3O_4-CeO_2	220	30,000	2%Pt	400, 1	Hydrothermal	16
Pt/Al_2O_3	240	30,000	2%Pt	400, 1	Hydrothermal	16
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