Supplementary Information

Enhanced catalytic phenol hydroxylation by CuZnFeAl layer double hydroxides: synergistic effects of Cu+ and oxygen vacancies

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Table S1 The properties of probes used for IGC Measurements

Probe	Character	$a\times10^{20}/m^2$	$\gamma_l^d/mJ\cdot m^2$	AN*/KJ.mol^{-1}	DN/KJ·mol^{-1}	$2aN(\gamma_l^d)^{0.5}$
n-hexane	apolar	0.515	18.4	--	--	2.6598
n-heptane	apolar	0.570	20.3	--	--	3.0921
n-octane	apolar	0.630	21.3	--	--	3.4896
n-nonane	apolar	0.690	22.7	--	--	3.9581
DCM	acidic	0.315	27.6	16.32	0.00	1.9925
TCM	acidic	0.440	25.9	22.60	0.00	2.6960
DEE	amphoteric	0.470	47.0	5.86	80.37	2.1916
THF	basic	0.450	22.5	2.09	83.72	2.5700
Acet	amphoteric	0.480	19.6	6.28	71.58	2.5586

*DCM-Dichloromethane; TCM-Chloroform; THF-Tetrahydrofuran; DEE-Diethylether; Acet-Ethylacetate.

The corresponding donor and corrected acceptor numbers were taken from reference [1].

[1] F. L. Riddle and F. M. Fowkes, J. Am. Chem. Soc., 1990, 112, 3259-3264.

5/CuZnFeAl-LDH catalyst

Table S2 Retention time, Vn, and RTlnVn of LDH catalyst in different temperatures

Temperature	Probe	Retention time / min	Vn	RTlnVn
	n-hexane	0.247	0.341	-3.066
	n-heptane	0.528	0.728	-0.905
	n-octane	3.006	4.145	4.052
	n-nonane	4.819	6.645	5.398
343.15 K	DCM	0.652	0.899	-0.306
	TCM	2.609	3.597	3.648
	DEE	0.454	0.626	-1.334
	THF	0.851	1.174	0.456
	Acet	0.635	0.875	-0.382
	n-hexane	0.125	0.177	-5.091
	n-heptane	0.450	0.639	-1.317
	n-octane	2.532	3.593	3.760
	n-nonane	4.296	6.097	5.315
353.15 K	DCM	0.231	0.328	-3.277
	TCM	1.733	1.733	1.616
	DEE	0.271	0.271	-3.841
	THF	0.611	0.611	-1.450
	Acet	0.420	0.420	-2.552
	n-hexane	0.106	0.155	-5.630
	n-heptane	0.389	0.567	-1.714
	n-octane	1.802	2.629	2.919
	n-nonane	3.375	4.923	4.814
363.15 K	DCM	0.250	-1.385	-4.183
	TCM	1.168	0.155	0.467
	DEE	0.197	-1.627	-4.914
	THF	0.482	-0.729	-2.203
	Acet	0.309	-1.176	-3.551
	n-hexane	0.078	0.117	-6.651
	n-heptane	0.364	0.546	-1.876
	n-octane	1.469	2.202	2.447
	n-nonane	3.135	4.699	4.797
373.15 K	DCM	0.1001	0.150	-5.882
	TCM	0.496	0.744	-0.917
	DEE	0.090	0.135	-6.206
	THF	0.217	0.326	-3.474
	Acet	0.141	0.212	-4.805

343.15 K y=7.0189x-21.7917 R^2=0.9701

353.15 K y=8.3981x-27.0460 R^2=0.9761

363.15 K y=8.3310x-27.3944 R^2=0.9826

373.15 K y=8.9671x-29.9111 R^2=0.9855

Table S3 γ_s^d values of LDH catalyst versus temperature

	γ_s^d / mJ·mol^{-1}			
Temperature	343.15	353.15	363.15	373.15
5/CuZnFeAl-LDH	49.26	70.53	69.41	80.41

Table S4 Adsorption free energy and adsorption enthalpy of polar probes on the surface of LDH catalyst

	$-\Delta G^{SP}$ / KJ·mol^{-1}				
Temperature/ K	343.15K	353.15K	363.15K	373.15K	$-\Delta H_a^s$ / KJ·mol^{-1}
DCM	7.501	7.036	6.612	6.162	22.2978(R^2=0.9999)
TCM	6.517	6.021	5.401	4.819	26.1069(R^2=0.9994)
DEE	5.075	4.800	4.222	4.053	17.7296(R^2=0.9887)
THF	4.209	4.013	3.781	3.392	13.7420(R^2=0.9930)
Acet	3.451	3.007	2.528	2.163	18.2427(R^2=0.9990)

$y=0.1324x+1.2793$ (R^2=0.9978)

K_a=0.1324

K_b=1.2973

K_a+K_b=1.4297

K_a / K_b =0.1021

10/CuZnFeAl-LDH catalyst

Table S5 Retention time, Vn, and RTlnVn of LDH catalyst in different temperatures

Temperature	Probe	Retention time / min	Vn	RTlnVn
343.15 K	n-hexane	0.307	0.423	-2.452
	n-heptane	1.025	1.413	0.985
	n-octane	2.519	3.473	3.548
	n-nonane	4.181	5.765	4.993
	DCM	2.959	4.080	4.008
	TCM	4.042	5.573	4.897
	DEE	2.560	2.560	2.680
	THF	1.908	1.908	1.842
	Acet	1.358	1.358	0.873
353.15 K	n-hexane	0.253	0.359	-3.012
	n-heptane	0.654	0.928	-0.220
	n-octane	1.500	2.129	2.222
	n-nonane	3.268	4.638	4.511
	DCM	1.938	2.751	2.975
	TCM	2.234	3.171	3.393
	DEE	1.084	1.539	1.267
	THF	1.328	1.885	0.634
	Acet	0.574	0.814	-0.606
363.15 K	n-hexane	0.147	0.214	-4.656
	n-heptane	0.298	0.435	-2.514
	n-octane	0.892	1.301	0.795
	n-nonane	2.111	3.080	3.397
	DCM	0.725	1.058	0.170
	TCM	0.958	1.398	1.013
	DEE	0.451	0.658	-1.262
	THF	0.337	0.492	-2.141
	Acet	0.225	0.328	-3.364
373.15 K	n-hexane	0.130	0.195	-5.068
	n-heptane	0.180	0.270	-4.059
	n-octane	0.620	0.929	-0.228
	n-nonane	1.580	2.368	2.672
	DCM	0.454	0.681	-1.191
	TCM	0.713	1.069	-0.208
	DEE	0.292	0.437	-2.564
	THF	0.230	0.345	-3.299
	Acet	0.129	0.194	-5.080

343.15 K y=5.7740x-17.2850 R^2=0.9803

353.15 K y=5.8174x-18.3216 R^2=0.9978

363.15 K y=6.3868x-21.8204 R^2=0.9955

373.15 K y=6.2930x-22.4371 R^2=0.9779

Table S6 γ_s^d values of LDH catalyst versus temperature

	γ_s^d / mJ·mol^{-1}			
Temperature	343.15	353.15	363.15	373.15
10/CuZnFeAl-LDH	33.34	33.84	40.79	39.60

Table S7 Adsorption free energy and adsorption enthalpy of polar probes on the surface of LDH catalyst

	-ΔG^{SP} / KJ·mol^{-1}				
Temperature/ K	343.15K	353.15K	363.15K	373.15K	-ΔH_a^s / KJ·mol^{-1}
DCM	9.788	9.705	9.265	8.707	23.0111(R^2=0.9849)
TCM	6.615	6.031	5.615	5.263	22.1883(R^2=0.9963)
DEE	7.311	6.839	6.561	6.081	20.7991(R^2=0.9977)
THF	4.288	4.005	3.265	2.965	20.5662(R^2=0.9879)
Acet	3.385	2.831	2.115	1.256	27.0355(R^2=0.9961)

y=0.2144x+1.2224 (R^2=0.9912)

K_a=0.2144

K_b=1.2224

K_a+K_b=1.4368

K_a / K_b =0.1754

15/CuZnFeAl-LDH catalyst

Table S8 Retention time, Vn, and RTlnVn of LDH catalyst in different temperatures

Temperature	Probe	Retention time / min	Vn	RTlnVn
	n-hexane	0.264	0.364	-2.880
	n-heptane	0.695	0.695	-1.037
	n-octane	1.351	1.351	0.857
	n-nonane	2.112	2.112	2.131
343.15 K	DCM	2.018	2.782	2.916
	TCM	3.773	5.202	4.699
	DEE	1.243	1.714	1.535
	THF	1.241	1.711	1.530
	Acet	2.575	3.550	3.610
	n-hexane	0.195	0.277	-3.774
	n-heptane	0.425	0.603	-1.487
	n-octane	1.265	1.795	1.720
	n-nonane	1.892	2.685	2.904
353.15 K	DCM	0.939	1.332	0.844
	TCM	2.396	3.401	3.600
	DEE	0.628	0.891	-0.337
	THF	0.630	0.894	-0.330
	Acet	1.603	2.275	2.415
	n-hexane	0.156	0.228	-4.465
	n-heptane	0.356	0.519	-1.981
	n-octane	1.035	1.510	1.245
	n-nonane	1.359	1.983	2.068
363.15 K	DCM	0.663	0.967	-0.102
	TCM	1.751	2.555	2.831
	DEE	0.424	0.619	-1.451
	THF	0.382	0.557	-1.767
	Acet	0.834	1.217	0.593
	n-hexane	0.103	0.154	-5.799
	n-heptane	0.269	0.403	-2.817
	n-octane	0.865	1.297	0.806
	n-nonane	1.163	1.743	1.722
373.15 K	DCM	0.346	0.518	-2.039
	TCM	0.989	1.483	1.221
	DEE	0.197	0.296	-3.772
	THF	0.193	0.290	-3.840
	Acet	0.422	0.632	-1.422

343.15 K $y=3.9303x-13.2017$ $R^2=0.9935$

353.15 K $y=5.3815x-17.9178$ $R^2=0.9811$

363.15 K $y=5.2781x-18.2004$ $R^2=0.9712$

373.15 K $y=6.0552x-21.5035$ $R^2=0.9703$

Table S9 γ_s^d values of LDH catalyst versus temperature

	γ_s^d / mJ·mol^{-1}			
Temperature	343.15	353.15	363.15	373.15
15/CuZnFeAl-LDH	15.48	28.96	27.86	36.67

Table S10 Adsorption free energy and adsorption enthalpy of polar probes on the surface of LDH catalyst

	-ΔG^{SP} / KJ·mol^{-1}				
Temperature/ K	343.15K	353.15K	363.15K	373.15K	-ΔH_a^s / KJ·mol^{-1}
DCM	8.287	8.039	7.582	7.400	18.4667(R^2=0.9953)
TCM	7.305	7.009	6.802	6.409	17.9583(R^2=0.9975)
DEE	6.123	5.787	5.182	4.461	25.7829(R^2=0.9923)
THF	4.631	3.757	2.869	2.102	24.5657(R^2=0.9988)
Acet	6.756	6.564	5.289	4.589	33.3109(R^2=0.9769)

y=0.2673x+1.1930 (R^2=0.9831)

K_a=0.2673

K_b=1.1930

K_a+K_b=1.4603

K_a / K_b =0.2241

20/CuZnFeAl-LDH catalyst

Table S11 Retention time, Vn, and RTlnVn of LDH catalyst in different temperatures

Temperature	Probe	Retention time / min	Vn	RTlnVn
	n-hexane	0.555	0.765	-0.763
	n-heptane	1.514	2.088	2.098
	n-octane	2.806	3.869	3.856
	n-nonane	4.528	6.244	5.220
343.15 K	DCM	2.590	3.572	3.629
	TCM	3.475	4.792	4.465
	DEE	1.892	2.609	2.733
	THF	2.959	4.080	4.008
	Acet	2.292	3.161	3.280
	n-hexane	0.340	0.483	-2.140
	n-heptane	0.774	1.098	0.275
	n-octane	2.036	2.889	3.119
	n-nonane	3.447	4.892	4.668
353.15 K	DCM	1.146	1.627	1.433
	TCM	1.855	2.633	2.847
	DEE	0.894	1.269	0.701
	THF	1.534	2.177	2.286
	Acet	1.194	1.694	1.549
	n-hexane	0.264	0.385	-2.883
	n-heptane	0.679	0.991	-0.027
	n-octane	1.272	1.856	1.868
	n-nonane	1.875	2.735	3.039
363.15 K	DCM	0.810	1.181	0.500
	TCM	1.209	1.763	1.712
	DEE	0.495	0.722	-0.986
	THF	0.896	1.307	0.808
	Acet	0.625	0.912	-0.277
	n-hexane	0.123	0.184	-5.248
	n-heptane	0.254	0.381	-2.991
	n-octane	0.706	1.058	0.175
	n-nonane	1.175	1.761	1.754
373.15 K	DCM	0.232	0.348	-3.269
	TCM	0.431	0.646	-1.353
	DEE	0.145	0.217	-4.739
	THF	0.277	0.415	-2.725
	Acet	0.204	0.306	-3.669

343.15 K $y=4.5761x-12.4979$ $R^2=0.9825$

353.15 K $y=5.3971x-16.3295$ $R^2=0.9900$

363.15 K $y=4.5608x-14.5511$ $R^2=0.9783$

373.15 K $y=5.6050x-20.0733$ $R^2=0.9886$

Table S12 γ_s^d values of LDH catalyst versus temperature

	γ_s^d /mJ·mol^{-1}			
Temperature	343.15	353.15	363.15	373.15
20/CuZnFeAl-LDH	20.94	29.13	20.80	31.42

Table S13 Adsorption free energy and adsorption enthalpy of polar probes on the surface of LDH catalyst

	-ΔG^{SP} / KJ·mol^{-1}				
Temperature/ K	343.15K	353.15K	363.15K	373.15K	-ΔH_a^s / KJ·mol^{-1}
DCM	7.009	6.391	5.964	5.636	22.9934(R^2=0.9946)
TCM	4.626	4.412	3.967	3.609	16.8564(R^2=0.9951)
DEE	5.202	4.513	3.570	3.050	30.0486(R^2=0.9961)
THF	4.745	4.098	3.638	2.943	24.6341(R^2=0.9981)
Acet	4.069	3.619	2.605	2.063	28.2833(R^2=0.9910)

y=0.2670x+1.2343 (R^2=0.9974)

K_a=0.2670

K_b=1.2343

K_a+K_b=1.5013

K_a / K_b =0.2163

25/CuZnFeAl-LDH catalyst

Table S14 Retention time, Vn, and RTlnVn of LDH catalyst in different temperatures

Temperature	Probe	Retention time / min	Vn	RTlnVn
343.15 K	n-hexane	0.418	0.576	-1.572
	n-heptane	1.183	1.631	1.394
	n-octane	1.933	2.665	2.794
	n-nonane	3.819	5.266	4.735
	DCM	2.150	2.965	3.097
	TCM	2.382	3.284	3.387
	DEE	1.078	1.486	1.129
	THF	1.403	1.935	1.881
	Acet	1.588	2.190	2.233
353.15 K	n-hexane	0.258	0.366	-2.955
	n-heptane	0.849	1.205	0.548
	n-octane	1.524	2.163	2.268
	n-nonane	2.850	4.045	4.109
	DCM	1.058	1.502	1.197
	TCM	1.290	1.831	1.779
	DEE	0.471	0.668	-1.184
	THF	0.728	1.033	0.096
	Acet	0.684	0.971	-0.085
363.15 K	n-hexane	0.197	0.287	-3.770
	n-heptane	0.549	0.801	-0.670
	n-octane	1.233	1.799	1.773
	n-nonane	1.765	2.575	2.856
	DCM	0.666	0.972	-0.086
	TCM	0.918	1.340	0.886
	DEE	0.249	0.363	-3.056
	THF	0.455	0.664	-1.236
	Acet	0.386	0.563	-1.734
373.15 K	n-hexane	0.184	0.276	-3.991
	n-heptane	0.458	0.687	-1.164
	n-octane	1.018	1.526	1.310
	n-nonane	1.443	2.163	2.392
	DCM	0.571	0.856	-0.483
	TCM	0.722	1.083	0.247
	DEE	0.180	0.270	-4.062
	THF	0.311	0.466	-2.367
	Acet	0.288	0.431	-2.609

343.15 K y=4.7317x-13.7762 R^2=0.9884

353.15 K y=5.3273x-16.5870 R^2=0.9823

363.15 K y=5.1713x-17.0175 R^2=0.9748

373.15 K y=5.0096x-16.8943 R^2=0.9780

Table S15 γ_s^d values of LDH catalyst versus temperature

	γ_s^d / mJ·mol^{-1}			
Temperature	343.15	353.15	363.15	373.15
25/CuZnFeAl-LDH	22.39	28.38	26.74	25.10

Table S16 Adsorption free energy and adsorption enthalpy of polar probes on the surface of LDH catalyst

	-ΔG^{SP} / KJ·mol^{-1}				
Temperature/ K	343.15K	353.15K	363.15K	373.15K	-ΔH_a^s / KJ·mol^{-1}
DCM	7.445	7.065	6.628	6.430	19.0520(R^2=0.9959)
TCM	4.407	4.016	3.962	3.635	12.0494(R^2=0.9841)
DEE	4.535	3.656	2.628	1.853	35.0073(R^2=0.9990)
THF	3.497	2.983	2.491	1.653	24.0072(R^2=0.9930)
Acet	3.903	2.861	2.052	1.468	31.0367(R^2=0.9934)

y=0.2649x+1.3686 (R^2=0.9855)

K_a=0.2649

K_b=1.3686

K_a+K_b=1.6335

K_a / K_b =0.1936

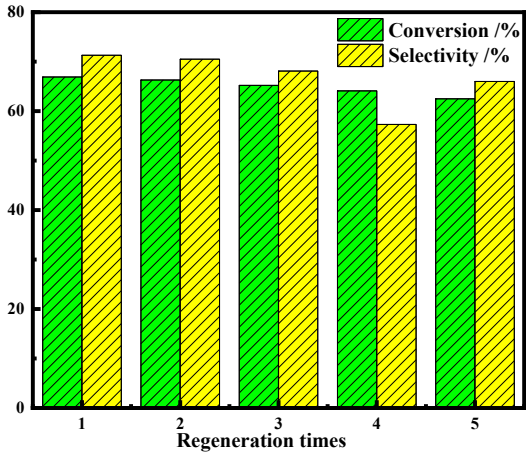

Figure. S1. The regeneration performance of the 15/CuZnFeAl-LDH.

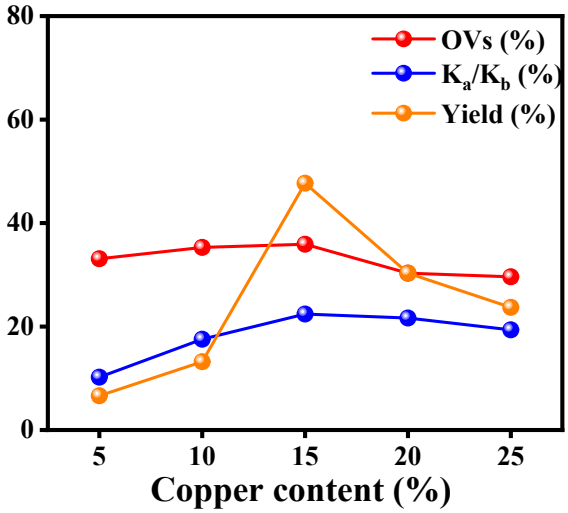

Figure S2. The relationship between the values of K_a/K_b, oxygen vacancies percentage and benzenediol yield.