

Supplementary Materials

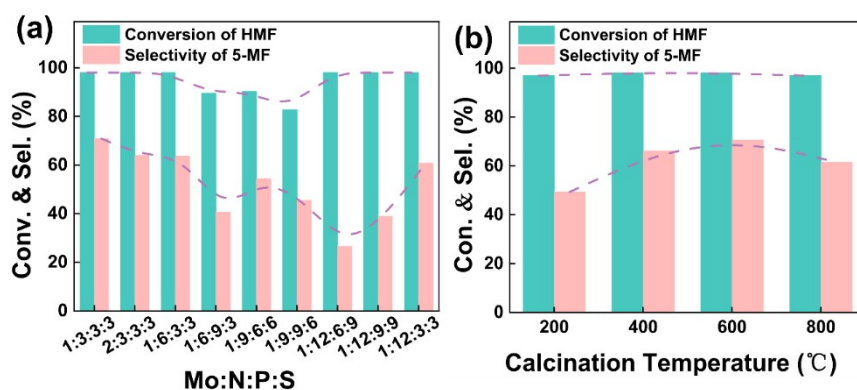


Figure S1. Catalytic performance of (a) influence of N, P, S ratio; (b) influence of calcination temperature.

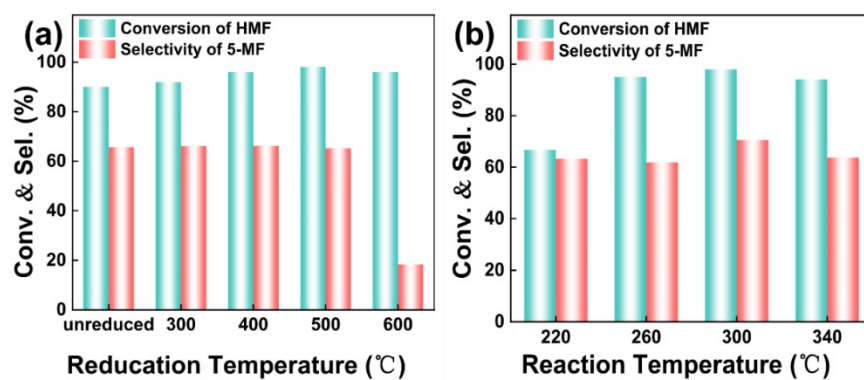


Figure S2. Catalytic performance of (a) influence of reduction temperature; (b) influence of reaction temperature.

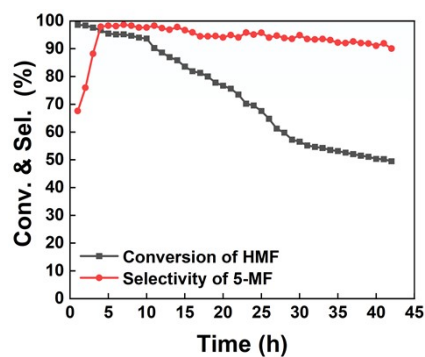


Figure S3. Real-time data of Mo-NPS catalyst in HMF hydrogenolysis.

Table S1 ICP-MS qualitative results of the reaction solution after Mo-NPS catalytic reaction

Analytes	Detection Status	Concentration (ppm)
Mo	Detected	0.0386
P	Detected	0.1575
N	Not Detected	—
S	Not Detected	—

Table S2 Catalytic performance for different reactants

Catalyst	Reactant	C (%)	S _{2,5-DMF} (%)	S _{5-MF} (%)	S _{DFP} (%)	S _{others} (%)
Mo-NPS	HMF	90.7	0	97.6	0	2.4
Mo-NPS	5-MF	3.6	32.7	—	15.1	52.2
Mo-NPS	DFP	87.6	0	47.4	—	52.6

Table S3. XPS element content of fresh catalyst NPS-Mo

catalyst	Elemental composition(%)						Mo-composition(%)			
	Mo	N	P	S	O	C	Mo ²⁺	Mo ³⁺	Mo ⁴⁺	Mo ⁶⁺
Mo-DCD-dppb	2.51	8.52	6.97	1.31	26.07	54.62	0	22.47	60.28	17.25
AMT-DCD-dppb	2.74	9.39	6.36	3.56	20.87	57.08	13.43	32.58	0	53.99
Mo-urea-dppb	1.96	6.07	5.55	2.67	19.17	64.58	5.84	35.49	0	58.67
Mo-phen-dppb	2.43	9.91	9.02	1.39	38.12	39.13	0	18.4	0	81.6
Mo-urea-dppe	2.56	8.59	9.38	3.13	37.17	39.17	0	34.82	0	65.18
Mo-ADP	3.4	11.89	14.76	1.31	57.66	10.98	0	19.66	0	80.34

Table S4. XPS element content of NPS-Mo catalyst after reaction

Catalyst	Elemental composition(%)						Mo-composition(%)		
	Mo	N	P	S	O	C	Mo ³⁺	Mo ⁴⁺	Mo ⁶⁺
Mo-DCD-dppb	3.11	11.67	8.57	0.98	34.34	41.33	25.46	0	74.54
AMT-DCD-dppb	2.62	10.03	6.02	2.35	28.79	50.19	25.34	0	74.66
Mo-urea-dppb	3.58	12.47	7.29	2.76	32.03	41.87	24.2	0	75.8
Mo-phen-dppb	3.13	11.4	10.84	1.82	45.22	27.56	28.29	0	71.71
Mo-urea-dppe	2.72	9.07	12.63	1.84	52.01	21.73	26.61	0	73.39
Mo-ADP	3.87	13	10.81	3.23	42.65	26.44	30.75	31.87	37.38

Table S5. The adsorption energy of H₂ and HMF on catalysts with different coordinates

Entry	Catalyst	H ₂ (eV)	HMF(eV)
1	Mo-N ₄ P ₀ S ₀ C ₀	-1.02185	-0.57632
2	Mo-N ₀ P ₄ S ₀ C ₀	-0.64324	-0.302
3	Mo-N ₀ P ₀ S ₄ C ₀	-1.01369	-0.43467
4	Mo-N ₀ P ₀ S ₀ C ₄	-0.34978	-0.78841
5	Mo-N ₁ P ₃ S ₀ C ₀	-1.07192	-0.88183
6	Mo-N ₂ P ₂ S ₀ C ₀	-0.88439	-0.46156
7	Mo-N ₃ P ₁ S ₀ C ₀	-0.69601	-0.27962
8	Mo-N ₁ P ₀ S ₃ C ₀	-1.5644	-1.5644
9	Mo-N ₂ P ₀ S ₂ C ₀	-0.89143	-1.34542
10	Mo-N ₃ P ₀ S ₁ C ₀	-1.12922	-1.88287
11	Mo-N ₁ P ₀ S ₀ C ₃	-0.41496	-0.73467

Table S5(Continued)

12	Mo-N ₂ P ₀ S ₀ C ₂	-0.6773	-0.94059
13	Mo-N ₃ P ₀ S ₀ C ₁	-0.68863	-0.75841
14	Mo-N ₀ P ₁ S ₃ C ₀	-0.66193	-0.46228
15	Mo-N ₀ P ₂ S ₂ C ₀	-0.78787	-0.77877
16	Mo-N ₀ P ₃ S ₁ C ₀	-0.72607	-0.66981
17	Mo-N ₀ P ₁ S ₀ C ₃	-0.52423	-0.63719
18	Mo-N ₀ P ₂ S ₀ C ₂	-0.83865	-0.67092
19	Mo-N ₀ P ₃ S ₀ C ₁	-0.62876	-0.72559
20	Mo-N ₀ P ₀ S ₁ C ₃	-0.56666	-0.68442
21	Mo-N ₀ P ₀ S ₂ C ₂	-0.70299	-0.57497
22	Mo-N ₀ P ₀ S ₃ C ₁	-0.59305	-0.32371
23	Mo-N ₁ P ₁ S ₂ C ₀	-1.66589	-0.7722
24	Mo-N ₁ P ₂ S ₁ C ₀	-0.98297	-0.86705
25	Mo-N ₂ P ₁ S ₁ C ₀	-1.03528	-1.443
26	Mo-N ₁ P ₁ S ₀ C ₂	-1.11751	-0.77709
27	Mo-N ₁ P ₂ S ₀ C ₁	-0.6243	-0.56816
28	Mo-N ₂ P ₁ S ₀ C ₁	-0.71567	-0.62613
29	Mo-N ₁ P ₀ S ₁ C ₂	-0.62955	-0.53331
30	Mo-N ₁ P ₀ S ₂ C ₁	-0.41294	-1.27799
31	Mo-N ₂ P ₀ S ₁ C ₁	-0.83494	-0.54133
32	Mo-N ₀ P ₁ S ₁ C ₂	-0.58995	-0.50518
33	Mo-N ₀ P ₁ S ₂ C ₁	-0.44977	-0.36353

Table S5(Continued)

34	Mo-N ₀ P ₂ S ₁ C ₁	-0.8154	-0.45696
35	Mo-N ₁ P ₁ S ₁ C ₁	-0.87586	-1.41169

Table S6. Summary of noble metal catalysts reported for 5-HMF to 5-MF

Entry	Catalyst	Catalyst (mg)	HMF (mmol)	T(°C)	t (h)	H ₂ Pressure (MPa)	Solvent	Conv. (%)	S _{5-MF} (%)	STY (mg·g ⁻¹ _{cat} ·h ⁻¹)	Ref
1	Pt@PVP/Nb ₂ O ₅	40	0.3	140	24	4	THF	100	92	31.7	1
2	Au@NPC	400	1	180	1.5	0.1	1,4-dioxane	100	95	174.3	2
3	Ru/TiO ₂	500	23.8	220	3	7	THF	99	10.3	178.2	3
4	FPhS-Pd/C	50	2	100	6	4	H ₂ O	99	90.1	654.8	4
5	Pd/Al ₂ O ₃	50	0.5	25	1	0.1(Air)	H ₂ O+THF	91	45.0	450.9	5
6	Pt -CoO _x -TiO ₂	50	2	300	6	2.5	THF	99	99	719.5	6
7	Pd/C	20	1	120	1	6.2	Acetonitrile	19	51	533.5	7
8	NPS-Mo	10	0.1	300	1	0.13(20 mL/min)	H ₂ O+1,3-dioxolan	90.7	97.6	974.7	This work

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