Electronic Supplementary Information (ESI)

Mn-doped Ni_2P: nanocrystals-decorated amorphous nanosheets for efficient electrooxidation of 5-hydroxymethylfurfural

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Experimental Section

Materials and Chemicals

Choline chloride (ChCl), oxalic acid ($H_2C_2O_4$), potassium chloride (KCl), and sodium hypophosphite (NaH_2PO_2) were all purchased from Aladdin Chemistry Co., Ltd. Potassium hydroxide (KOH) and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) were obtained from Sinopharm Chemical Regent Co., Ltd. Manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$) was supplied by Shanghai Macklin Biochemical Co., Ltd. 5-hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA), 5-formyl-2-furancarboxylic acid (FFCA) and 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) were purchased from Alfa-Aesar. 2,5-diformylfuran (DFF) was purchased from Tokyo Chemical Industry Co., Ltd. 5 wt% Nafion solution was purchased from the Sigma Co., Ltd. Carbon cloth was obtained from Changsha Lyrun Material Co., Ltd. Nafion 115 membrane was purchased from Wuhan GaossUnion technology Co., Ltd.

Preparation of choline chloride/oxalic acid (ChCl/OA) DES

The deep eutectic solvent (DES) was prepared based on the literature.[1] Specifically, equimolar amounts of choline chloride (ChCl) and oxalic acid (OA) were mixed by magnetic stirring at 80 ^{o}C. The (ChCl/OA) DES was obtained when a colorless and transparent liquid was formed.

Preparation of Mn-doped Ni_2P

The Mn-doped Ni_2P catalysts were labeled as Mn-xNi_2P (Mn-7Ni_2P, Mn-5Ni_2P, and Mn-3Ni_2P), where x represents the original feed atomic ratio of Ni/Mn salts. In a typical procedure for Mn-5Ni_2P, 0.028 mmol $Mn(NO_3)_2·4H_2O$ and 0.14 mmol $NiCl_2·6H_2O$ were dissolved in 1 mL ChCl/OA DES and subjected to ultrasonication at 50 ^oC until a well-dispersed solution was obtained. The solution was then transferred to a microwave oven and microwaved at 100 W for 15 s to obtain the Mn/Ni-based precursors. Then, the precursors were recovered, rinsed with ethanol, and dried under vacuum at room temperature overnight. After that, NaH_2PO_2 and the dried precursors were placed in the upstream and middle of the corundum tube of the tube furnace for heating treatment at 350 °C for 2 h at 10 °C min^{-1} in N_2 atmosphere. The obtained Mn-Ni_2P was washed with water and ethanol. Finally, the samples were dried in the vacuum oven for 12 h. For comparison, the Mn-7Ni_2P and Mn-3Ni_2P were also prepared using the same method as above. Additionally, Ni_xP was synthesized by the same procedure without the addition of $Mn(NO_3)_2·4H_2O$.

Characterizations

X-ray diffraction (XRD) pattern was characterized on the Rigaku SmartLab 9KW X-ray diffractometer. Transmission electron microscopy (TEM) was performed on a JEM-1400 microscope. The high-resolution transmission electron microscopy (HRTEM), high-angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) and energy-dispersive X-ray (EDX) were tested on the FEI Titan G2 60-300. Energy-dispersive X-ray (EDX) spectra was obtained by Zeiss Gemini 300. X-ray photoelectron spectroscopy (XPS) measurements were performed by a Thermo Fisher ESCALAB XI. Nitrogen adsorption-desorption tests were conducted on the micropolitics ASAP 2460. High-performance liquid chromatography (HPLC) analysis was tested using an Agilent G7114A system.

Electrochemical Measurements

Electrochemical testing was conducted on the electrochemical workstation (CHI Model 760E). For preparation of catalyst ink, 4 mg of catalyst was added in the mixture of Nafion solution (20 μL, 5 wt %), ethanol (160 μL), and water (140 μL) under ultrasonication. The catalyst suspension was then coated on the carbon cloth ($1 \times 1\ cm^2$) as a working electrode (loading of 4 mg cm^{-2}). Platinum foil (counter electrode), Ag/AgCl electrode (reference electrode) and catalyst-loaded carbon cloth (working electrode) were used for constructing the three electrode setup. All potentials were normalized to reversible hydrogen electrode (RHE) by the formula:

$$E\ (RHE) = E\ (Ag/AgCl) + 0.197 + 0.059 \times pH\# \qquad (1)$$

The solution of 1.0 M KOH (10 mL) with or without HMF (10 mM) was used as the electrolyte. Electrooxidation performance of the catalysts was studied through chronoamperometry at 1.43 V. Linear sweep voltammetry (LSV) was conducted with a scanning rate of 10 mV s^{-1}. 1 Hz to 100 kHz frequencies was used for electrochemical impedance spectroscopy (EIS) characterization, and cyclic voltammetry (CV) was performed to determine capacitance (Cdl).

Products analysis

Specifically, 10 μL solution during chronoamperometry at 1.43 V was removed from the electrolyte and diluted to 0.5 mL for HPLC analysis.

HMF conversion, FDCA yield, and Faraday efficiency (FE) were calculated using below equations.

$$\text{HMF conversion (\%)} = \left[n\left(\text{HMF}_{\text{consumed}}\right)/n\left(\text{HMF}_{\text{initial}}\right)\right] \times 100 \quad (2)$$

$$\text{FDCA yield (\%)} = \left[n\left(\text{FDCA}_{\text{formed}}\right)/n\left(\text{HMF}_{\text{initial}}\right)\right] \times 100 \quad (3)$$

$$\text{Faradaic efficiency (\%)} = \left[n\left(\text{FDCA}_{\text{formed}}\right)/(Q/(6 \times F))\right] \times 100 \quad (4)$$

Q: total passed charge, F: Faraday constant (96485 C mol^{-1}), n: mol of reactant.

Density functional theory (DFT) Calculation

We carried out all the DFT calculations in the Vienna *ab initio* simulation (VASP5.4.4) code.[2] The exchange-correlation was simulated with PBE functional and the ion-electron interactions were described by the PAW method.[3, 4] The vdWs interaction was included by using the empirical DFT-D3 method.[5] The Monkhorst-Pack-grid-mesh-based Brillouin zone k-points were set as 1×1×1 for all periodic structures with the cutoff energy of 400 eV. The convergence criteria were set as 0.01 eV A^{-1} and 10^{-4} eV in force and energy, respectively. An at least 20 Å vacuum layer along the *z* direction was employed to avoid interlayer interference.

The adsorption free energy ($\Delta G_{adsorption}$) was calculated using the expression

$$\Delta E\text{adsorption} = E\text{total} - E\text{substrate} - E\text{adsorbate} \quad (5)$$

$$\Delta G\text{adsorption} = \Delta E\text{adsorption} + \Delta ZPE - \Delta TS \quad (6)$$

where $E_{substrate}$ is the energy of the surface of the materials, $E_{adsorbate}$ represents the energy of the adsorbates, E_{total} represents the total energy of the single molecule adsorption system. The *ZPE* and *TS* are zero point energy and the product of temperature entropy.

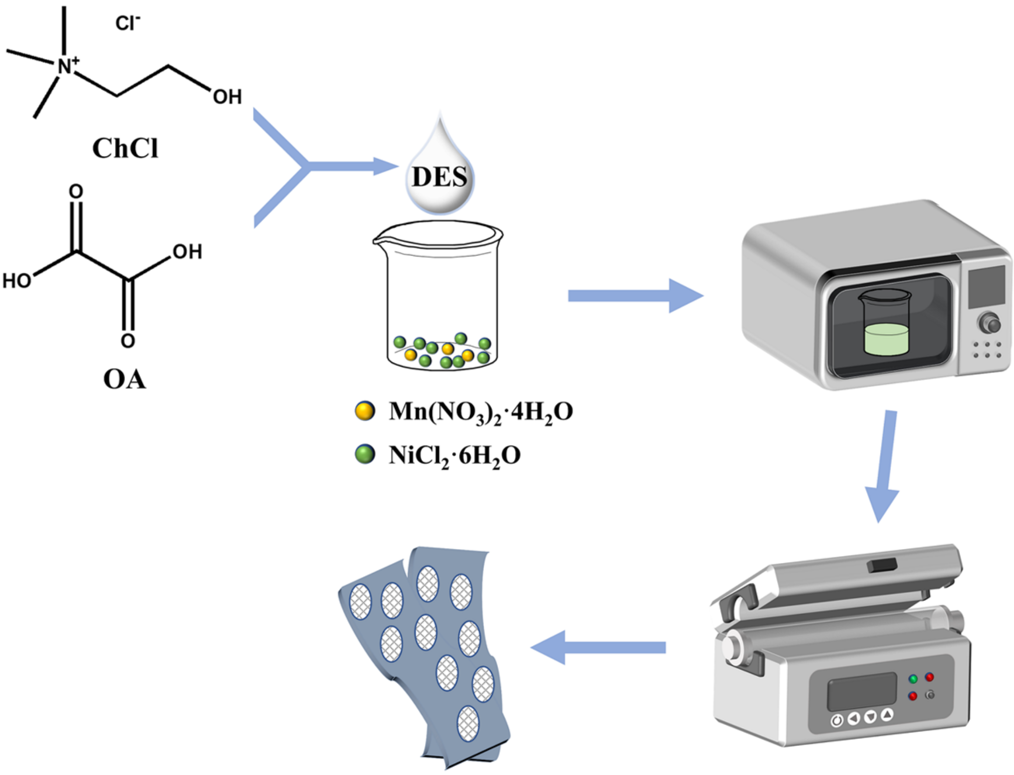

Fig. S1 Schematic diagram of fabricating Mn-doped Ni_2P catalysts.

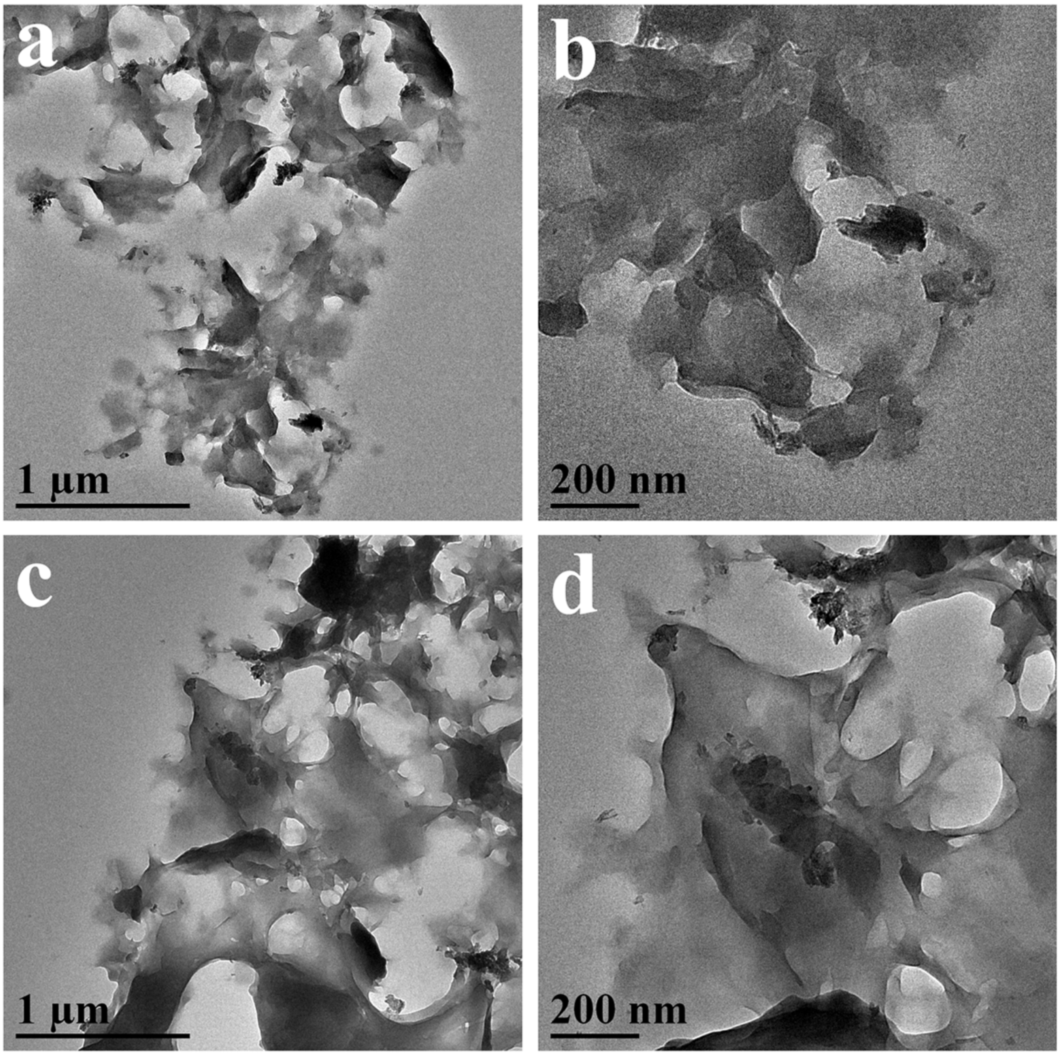

Fig. S2 Low- and high- magnification TEM images of the precursors obtained after microwave heating 1 mL ChCl/OA DES with 7.0 mg $Mn(NO_3)_2 \cdot 4H_2O$ and 33 mg $NiCl_2 \cdot 6H_2O$. This obtained precursor will be used for synthesizing Mn-5Ni_2P.

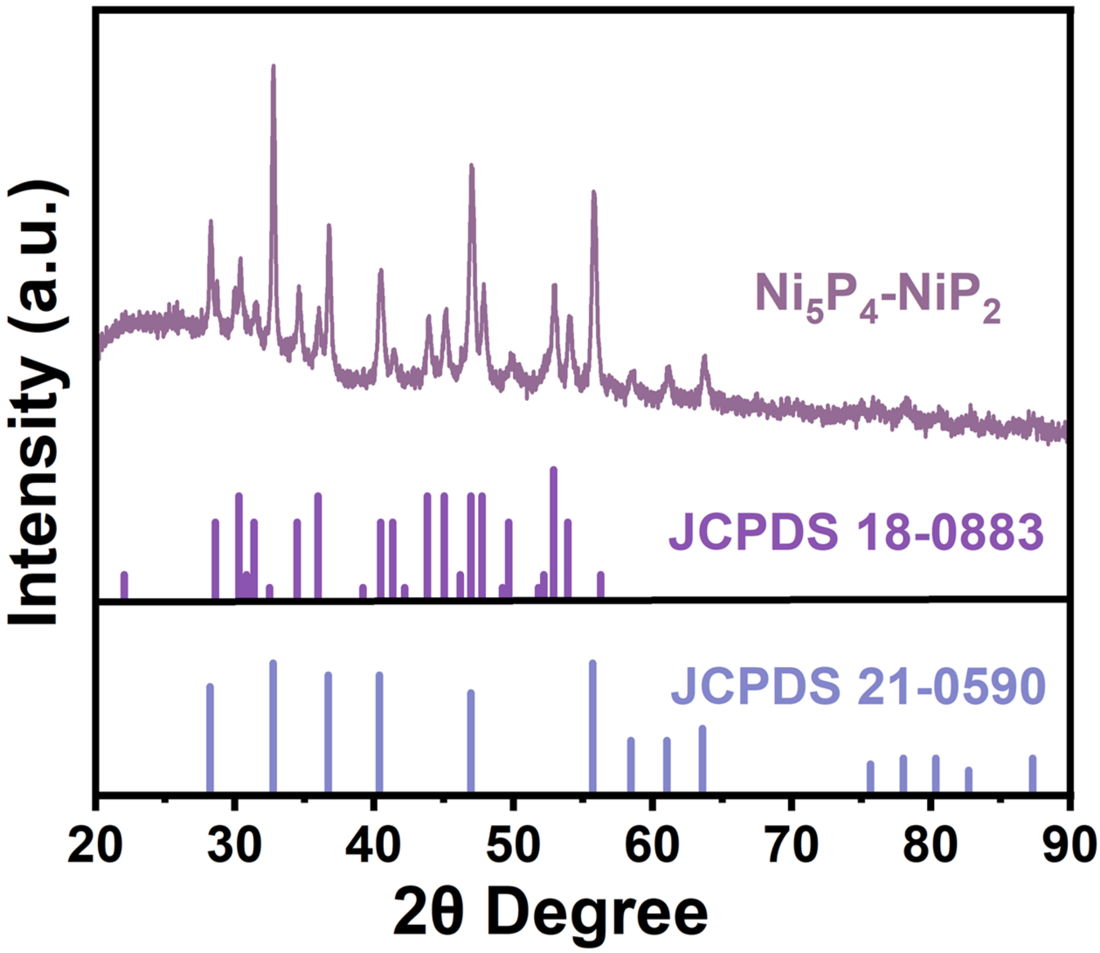

Fig. S3 XRD pattern of the synthesized Ni_xP.

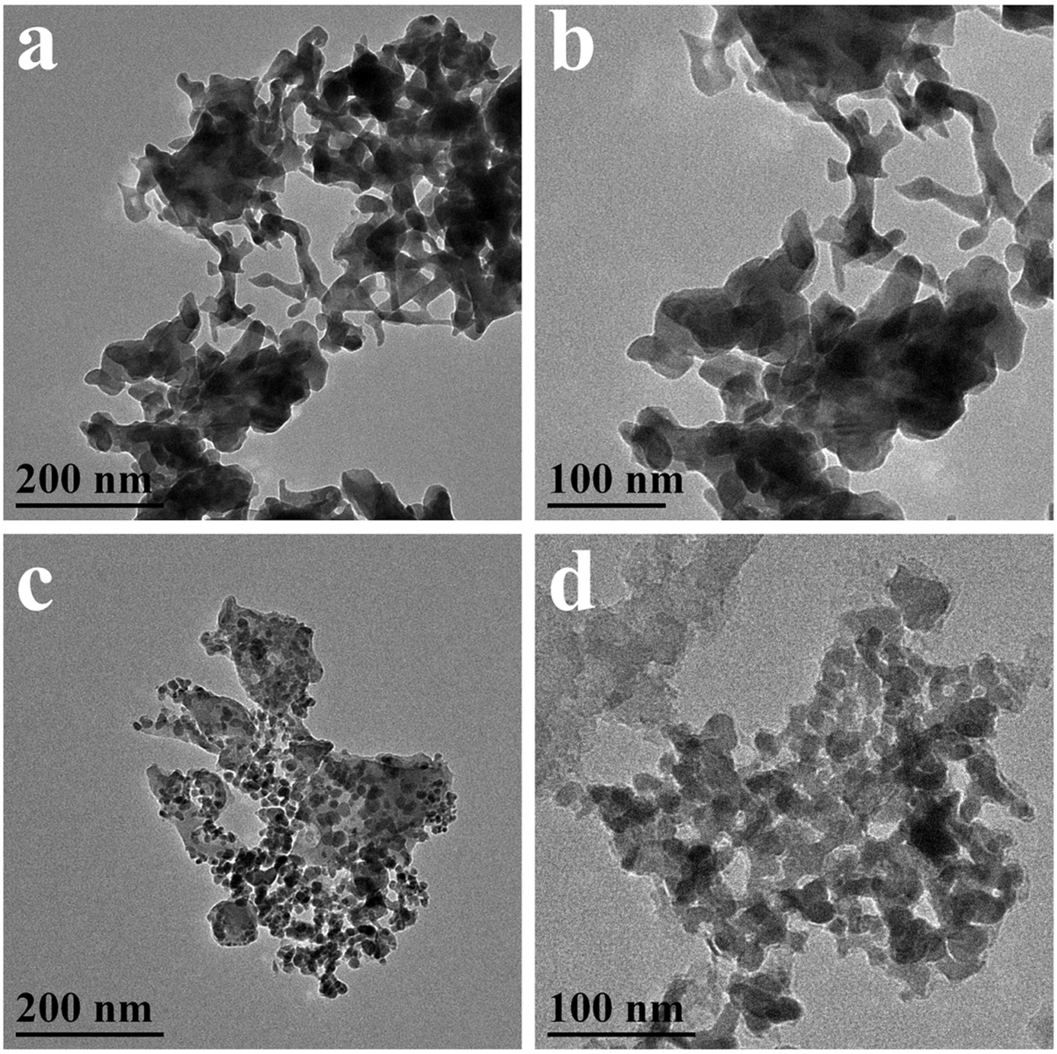

Fig. S4 TEM images of the synthesized (a, b) Ni_xP, (c) Mn-3Ni_2P, (d) Mn-7Ni_2P.

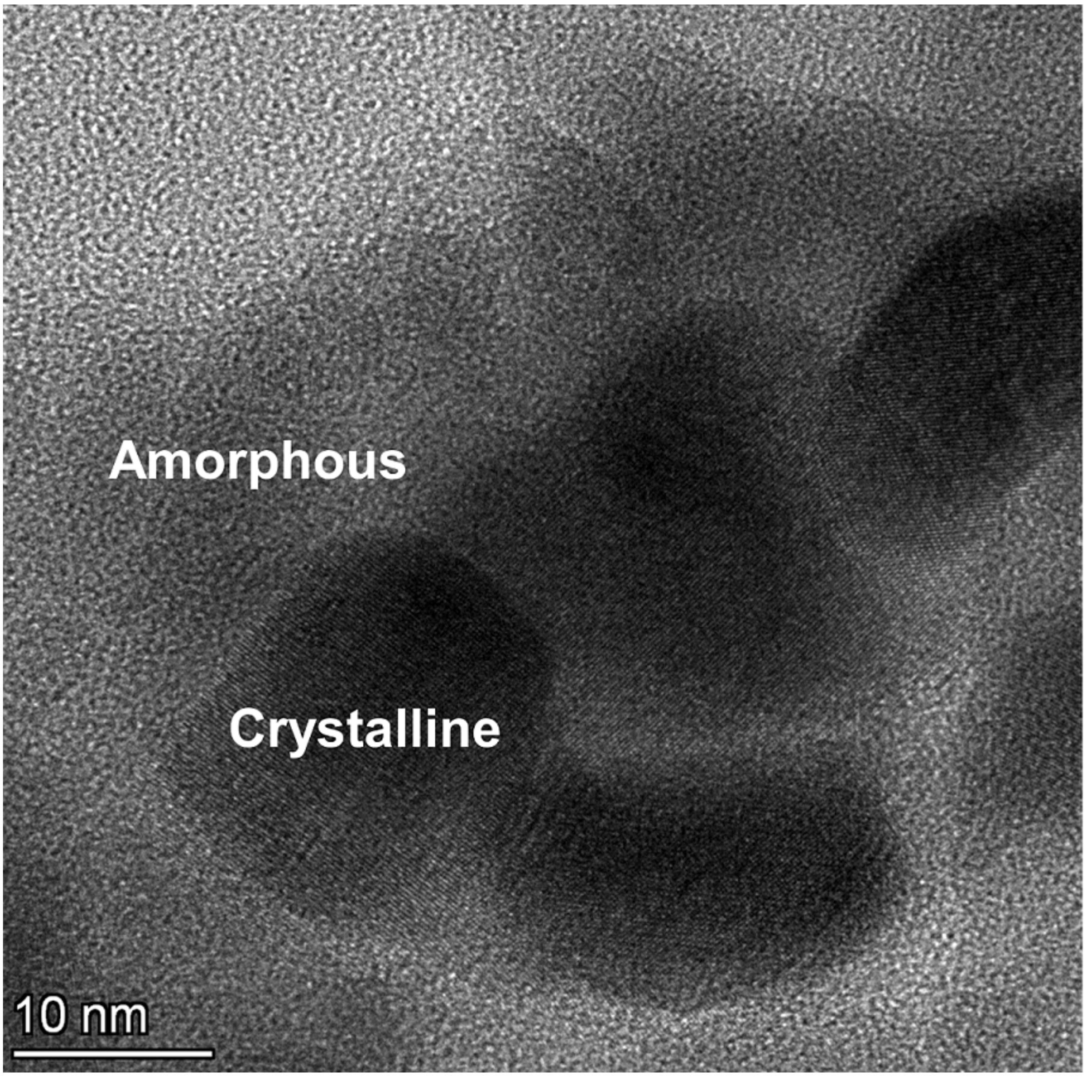

Fig. S5 HRTEM image of Mn-5Ni_2P.

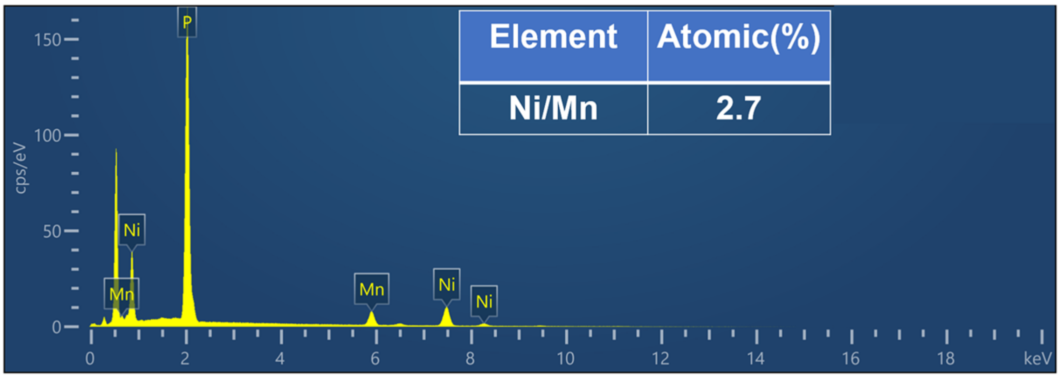

Fig. S6 EDX spectrum of Mn-3Ni_2P which was synthesized from the precursor obtained after microwave heating 1 mL ChCl/OA DES with 10.4 mg $Mn(NO_3)_2{\cdot}4H_2O$ and 29.6 mg $NiCl_2{\cdot}6H_2O$.

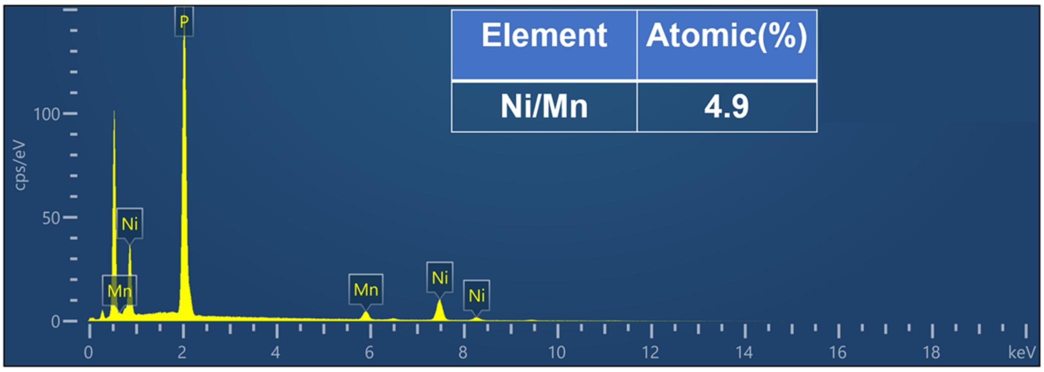

Fig. S7 EDX spectrum of Mn-5Ni_2P which was synthesized from the precursor obtained after microwave heating 1 mL ChCl/OA DES with 7.0 mg $Mn(NO_3)_2{\cdot}4H_2O$ and 33 mg $NiCl_2{\cdot}6H_2O$.

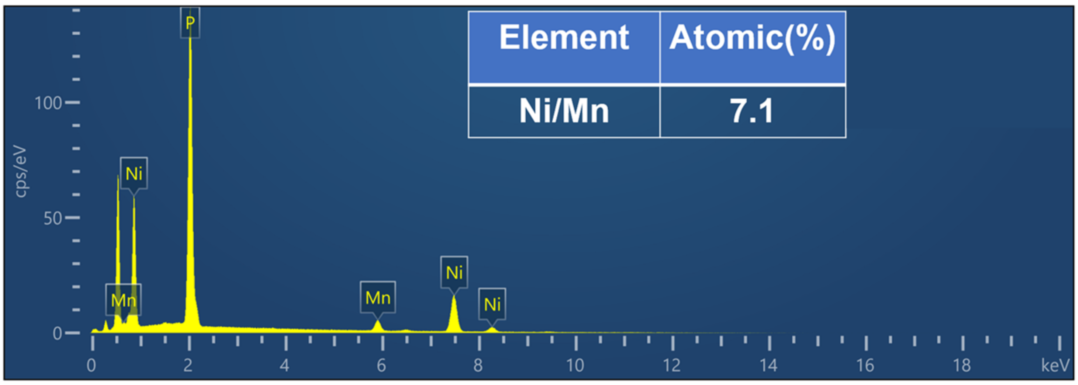

Fig. S8 EDX spectrum of Mn-7Ni_2P which was synthesized from the precursor obtained after microwave heating 1 mL ChCl/OA DES with 5.2 mg $Mn(NO_3)_2{\cdot}4H_2O$

and 34.8 mg $NiCl_2 \cdot 6H_2O$.

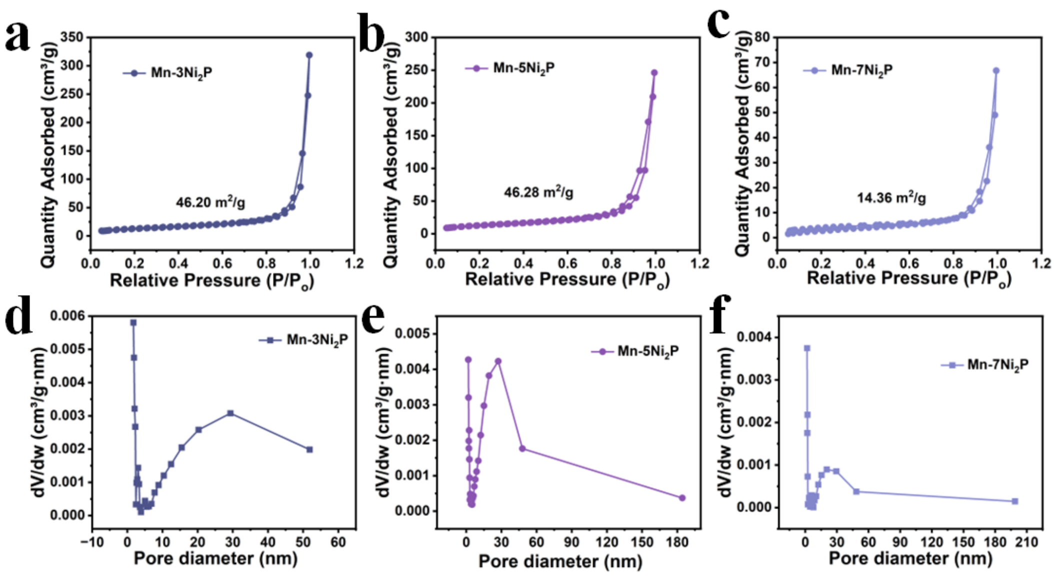

Fig. S9 N_2 adsorption-desorption isotherms of (a) Mn-3Ni_2P, (b) Mn-5Ni_2P, (c) Mn-7Ni_2P. Pore size distributions of the synthesized (d) Mn-3Ni_2P, (e) Mn-5Ni_2P, (f) Mn-7Ni_2P.

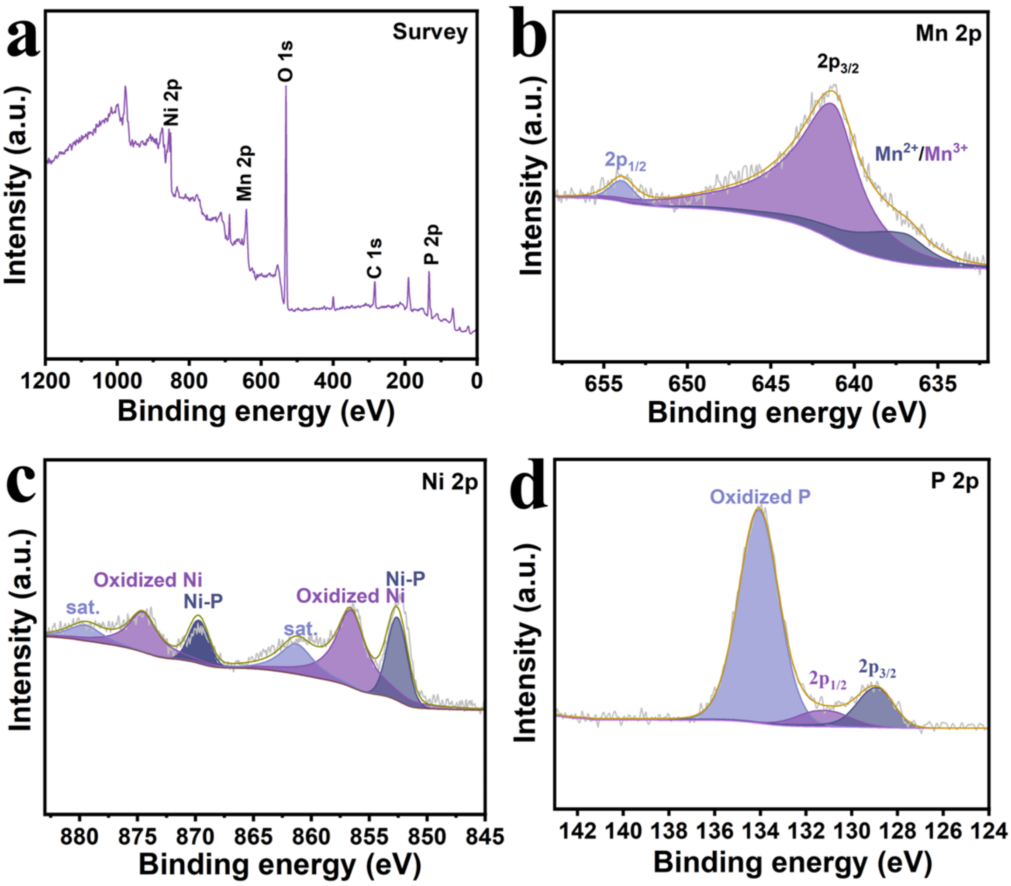

Fig. S10 (a) XPS survey spectrum of Mn-5Ni_2P. High-resolution XPS spectra of (b) Mn 2p, (c) Ni 2p, (d) P 2p for the Mn-5Ni_2P.

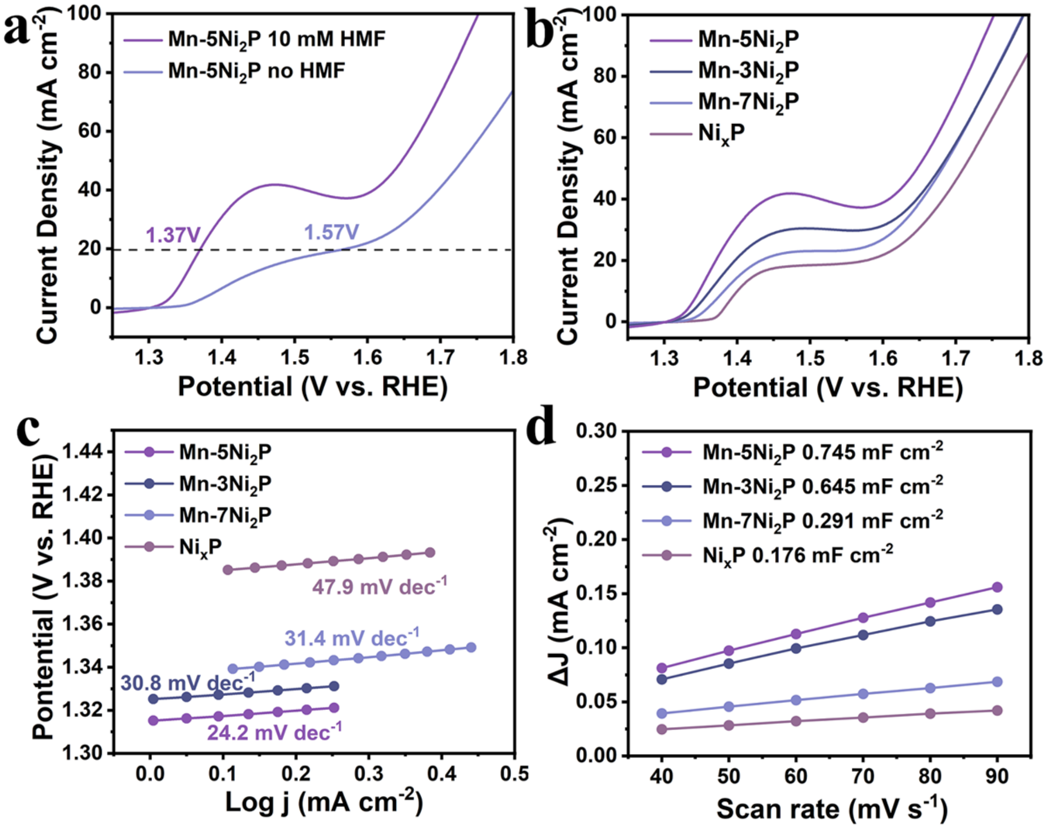

Fig. S11 (a) LSV curves of Mn-5Ni_2P in 1.0 M KOH with and without 10 mM HMF. (b) LSV curves (c) Tafel plots, and (d) electrochemical double layer capacitance (Cdl) of Ni_xP, Mn-3Ni_2P, Mn-5Ni_2P and Mn-7Ni_2P in 1.0 M KOH with 10 mM HMF.

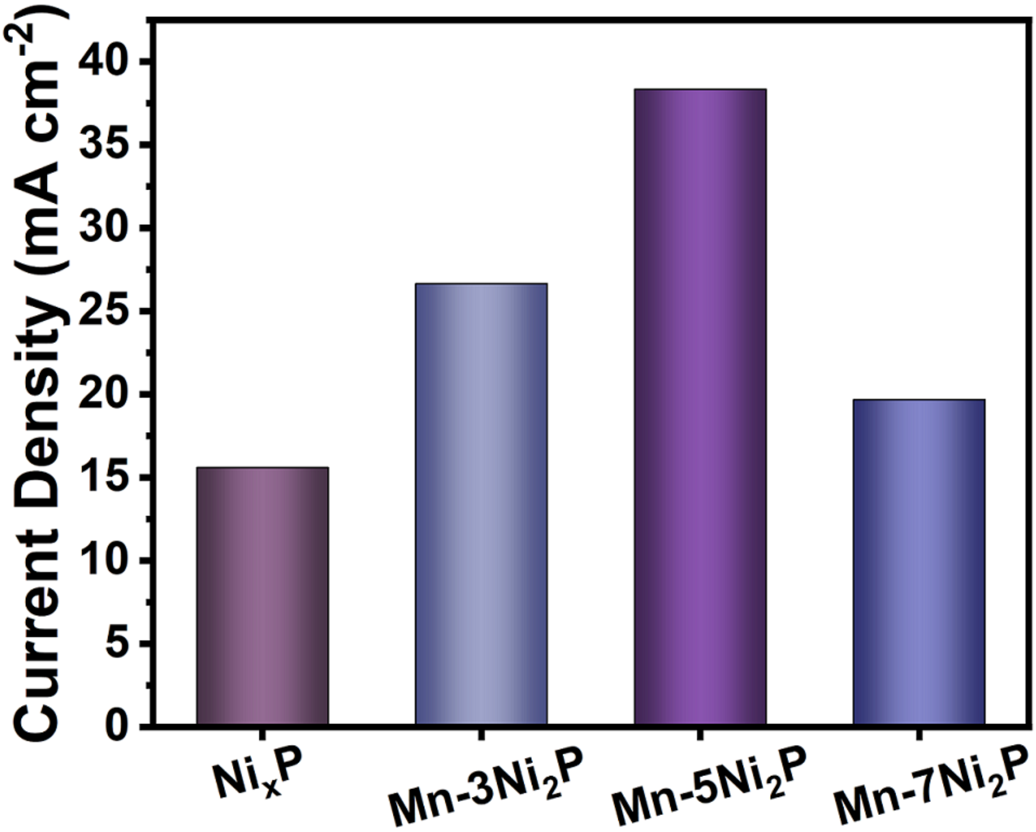

Fig. S12 Corresponding current densities at 1.43 V in 1 M KOH with 10 mM HMF.

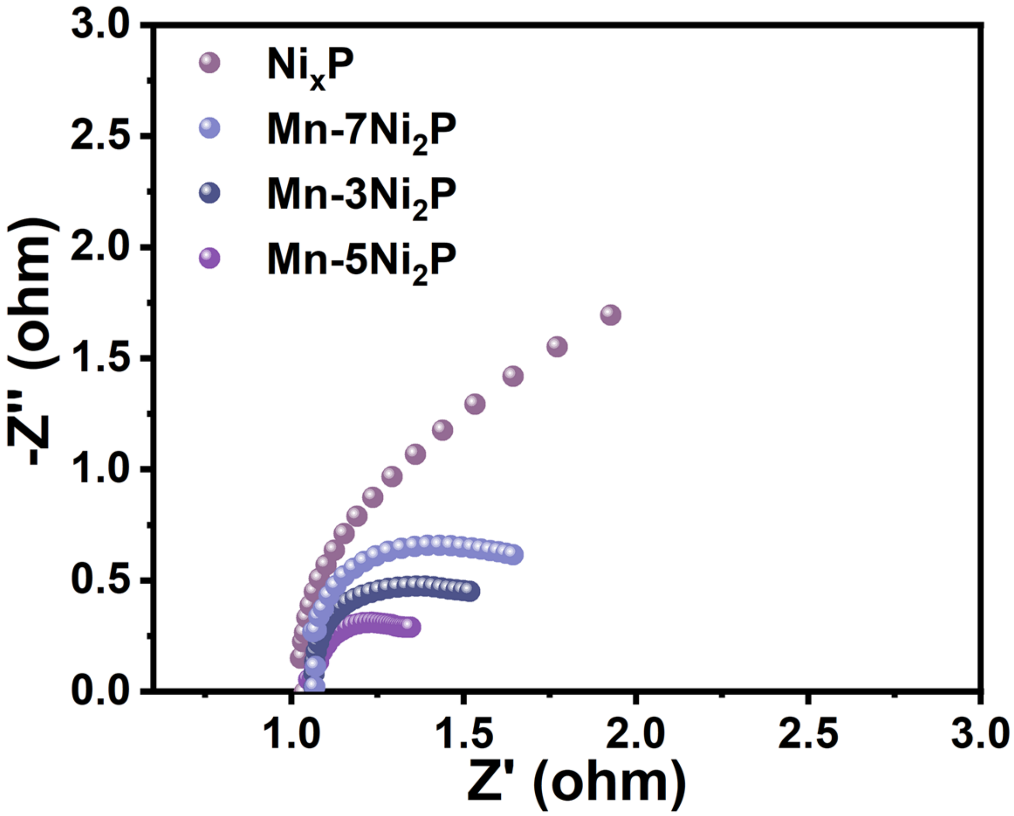

Fig. S13 Electrochemical impedance spectra of different catalysts at 1.43 V.

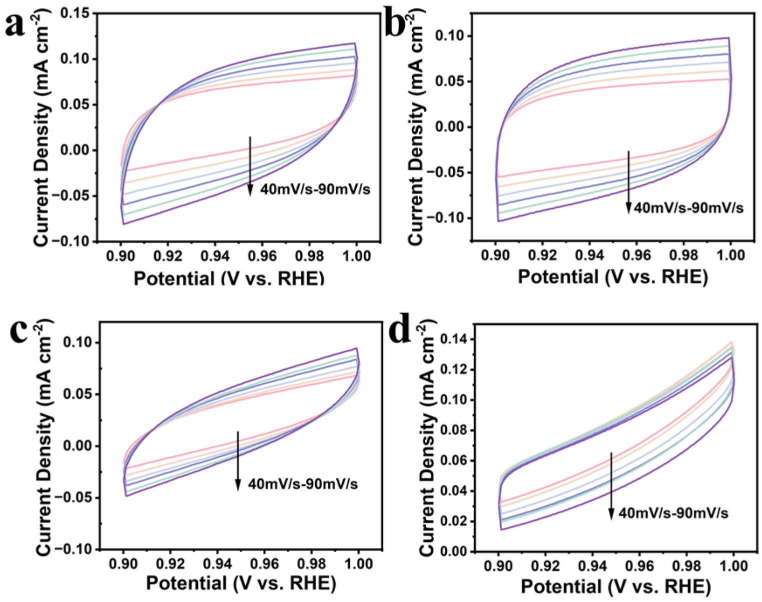

Fig. S14 Cyclic voltammograms of (a) Mn-3Ni_2P, (b) Mn-5Ni_2P, (b) Mn-7Ni_2P, and (d) Ni_xP at different scan rates.

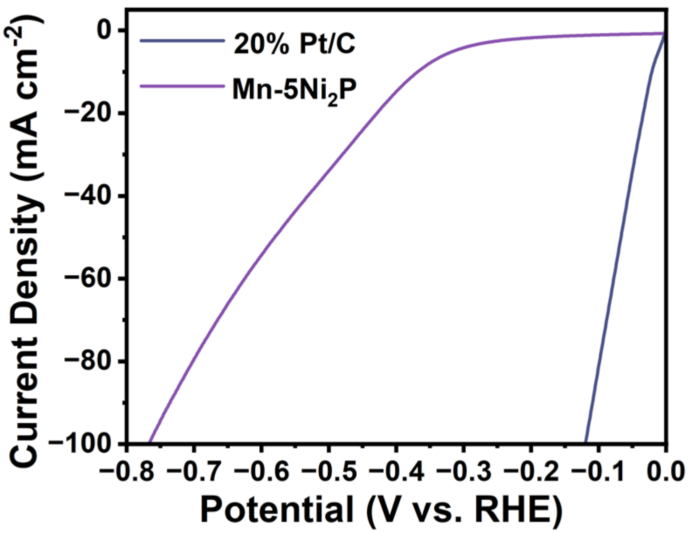

Fig. S15 LSV curves of Mn-5Ni_2P and 20% Pt/C for HER in 1.0 M KOH.

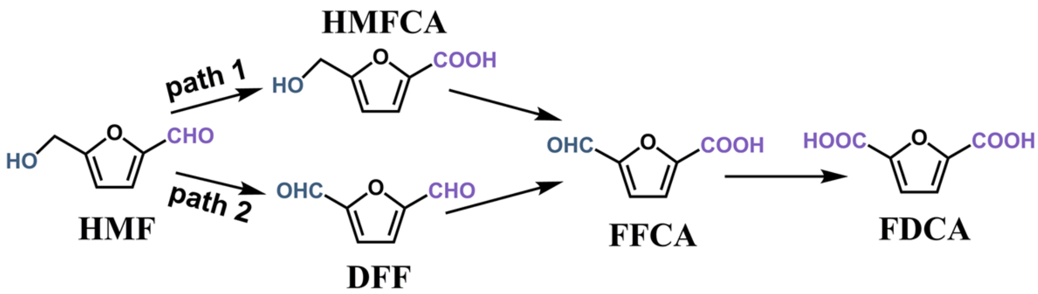

Fig. S16 Possible pathways for the oxidation of HMF to FDCA.

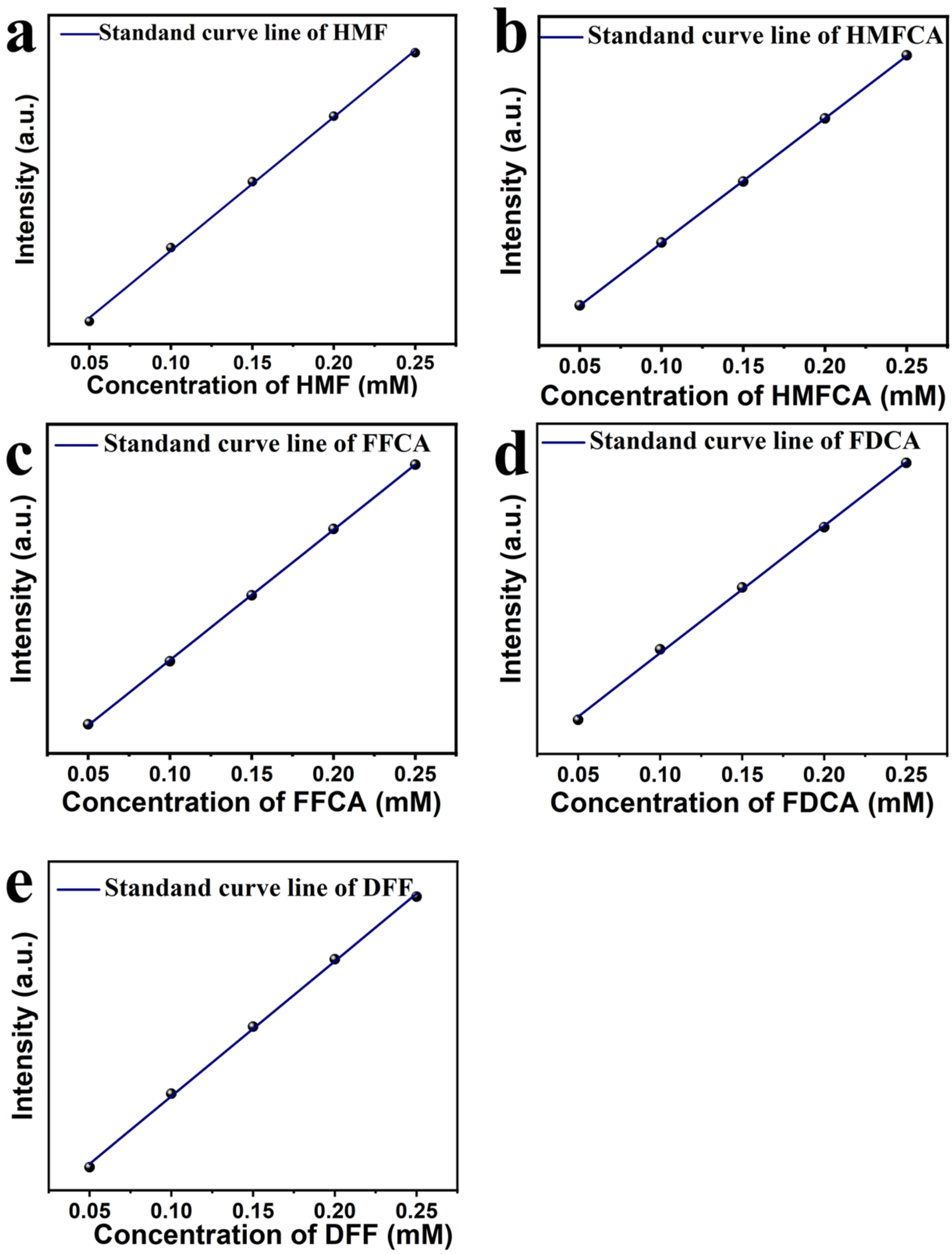

Fig. S17 Standard curves of the HPLC for (a) HMF, (b) HMFCA, (c) FFCA, (d) FDCA, and (e) DFF.

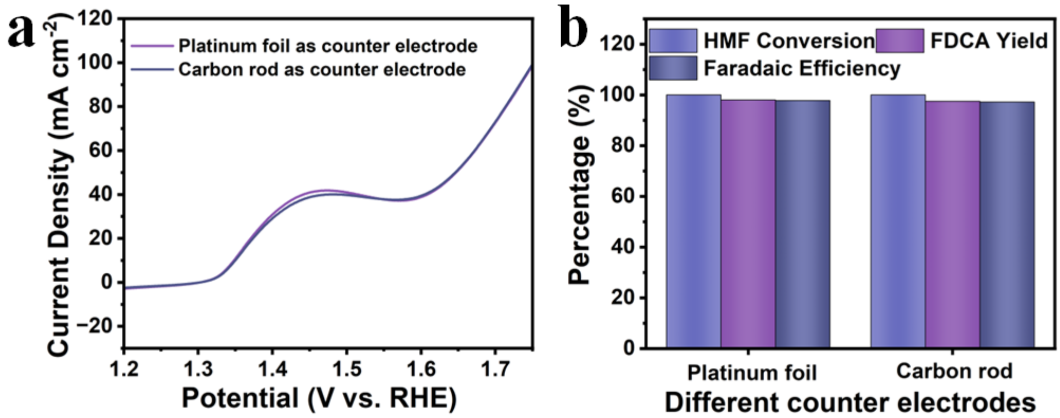

Fig. S18 (a) LSV curves, (b) HMF electrooxidation performance of Mn-5Ni_2P in 1.0 M KOH with 10 mM HMF using platinum foil and carbon rod as counter electrodes, respectively.

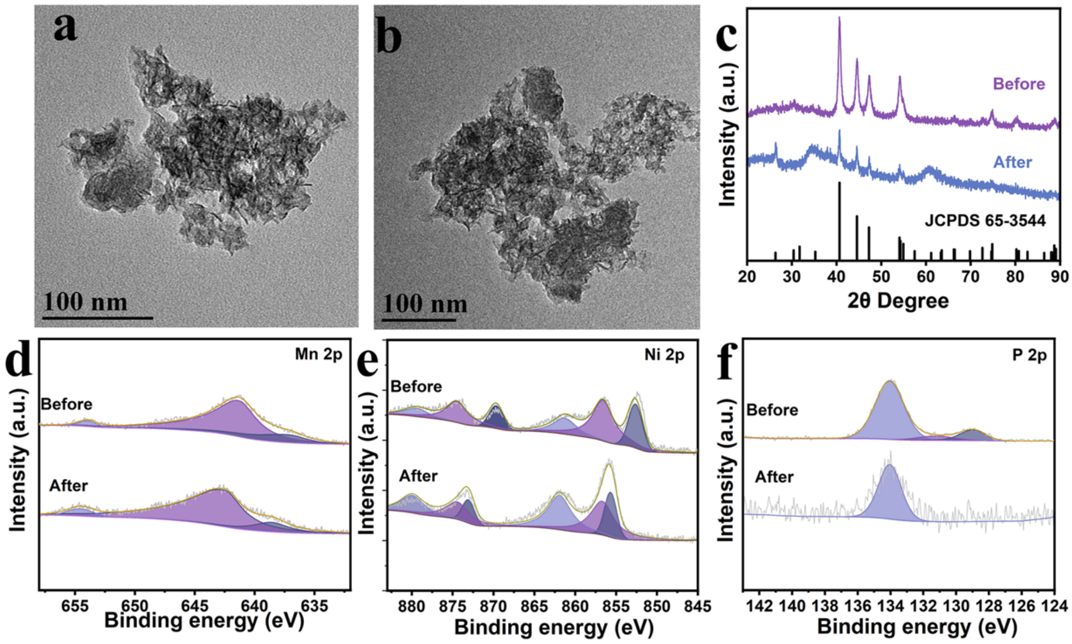

Fig. S19 (a, b) TEM images of Mn-5Ni_2P after four electrolysis cycles. (c) XRD patterns, XPS spectra of (d) Mn 2p, (e) Ni 2p, (f) P 2p of Mn-5Ni_2P before and after four electrolysis cycles.

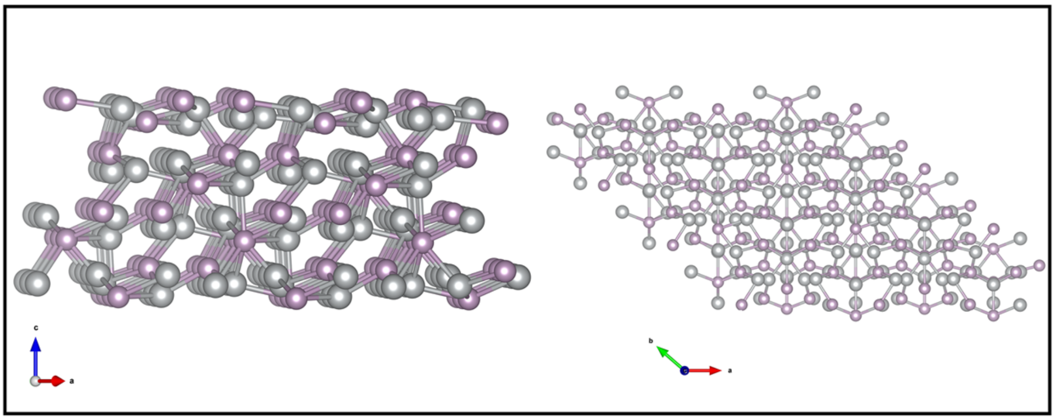

Fig. S20 Side and top views of an optimized structure for the Ni_2P (111) surface.

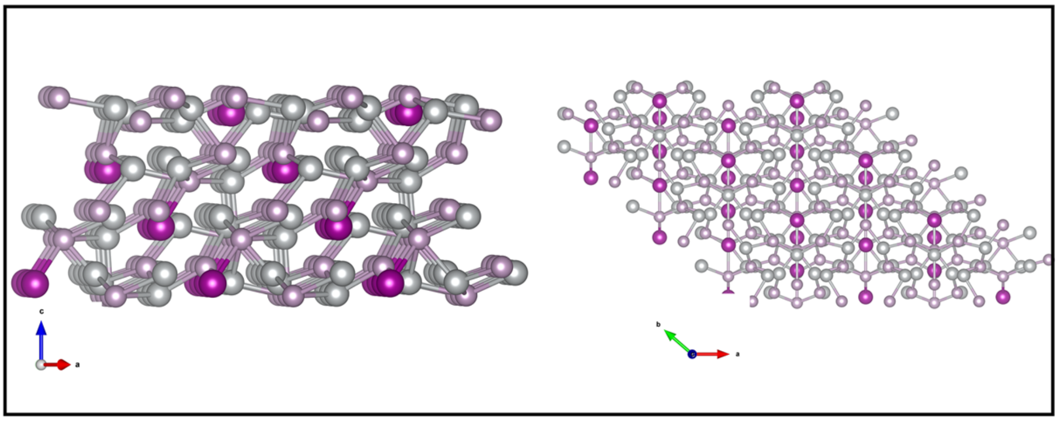

Fig. S21 Side and top views of an optimized structure for the Mn-5Ni_2P (111) surface.

Table S1 Comparison of Mn-5Ni_2P with recently reported catalysts toward HMF electrooxidation.

Catalysts	C_{HMF} (mM)	Potential (V *vs.* RHE)	Conversion (%)	FDCA Yield (%)	FE (%)	Reference
Mn-5Ni_2P	**10**	**1.43**	**100**	**98.0**	**97.8**	**This work**
·$NiMo_3S_4$-R	10	1.45	99.3	98.7	98.5	6
Co_3O_4/CF	10	1.40	100	94.9	94.6	7
CoP/Ni_2P-NiCoP@-600	10	1.45	~100	98.1	97.9	8
F-$NiCo_2O_4$	10	1.47	~	97	96.5	9
5.2%Ce-CoP	10	1.44	100	98	96.4	10
MoO_2-FeP@C	10	1.424	99.4	98.6	97.8	11
Mo-$Ni_{0.85}$Se	10	1.40	~100	91-95	95	12
NiS_x/Ni_2P	10	1.46	~100	98.5	95.1	13
$Co_{0.4}$NiS	10	1.45	~100	~100	99.1	14
NF@Co_3O_4/CeO	10	1.40	98.0	94.5	97.5	15
$NiCo_2O_4$	5	1.5	99.6	90.8	87.5	16

Table S2 Adsorption energy of HMF on different surfaces.

Adsorbed sites	$\mathbf{G_{total}}$	$\mathbf{G_{sub}}$	$\mathbf{G_{mol}}$	$\mathbf{\Delta G}$
Ni_2P*HMF	-1337.139	-1244.948	-91.97799	-0.213066
Mn-Ni_2P (Ni)*HMF	-1423.815	-1331.605	-91.97799	-0.231957
Mn-Ni_2P (Mn)*HMF	-1424.003	-1331.605	-91.97799	-0.420213

*Where G represents the corrected free energy, G_{total} is the total free energy of HMF adsorbed on Ni_2P or Mn-Ni_2P substrates（Mn site or Ni site）, G_{mol} and G_{sub} are the free energies of individual HMF molecules and substrates, respectively.

Table S3 Unit-cell and position parameters of Ni_2P optimization model.

	Ni_2P		
a (Å)		20.56060	
b (Å)		20.39730	
c (Å)		25.00000	
α (deg)		90.00000	
β (deg)		90.00000	
γ (deg)		139.11300	
Atom Coordinates	***x***	***y***	***z***
Ni1	0.16448	0.26031	0.05450
Ni2	0.02565	0.07519	0.14296
Ni3	0.38618	0.22355	0.22991
Ni4	0.25288	0.03498	0.31323
Ni5	0.29794	0.23500	0.03939
Ni6	0.15910	0.04988	0.12786
Ni7	0.02008	0.19595	0.21471
Ni8	0.37577	0.00461	0.30150
Ni9	0.46936	0.26031	0.05450
Ni10	0.33052	0.07519	0.14296
Ni11	0.19343	0.22456	0.22998
Ni12	0.04145	0.03291	0.31332
Ni13	0.49101	0.07053	0.04070
Ni14	0.35217	0.21874	0.12916
Ni15	0.21106	0.03288	0.21755

Ni16	0.07637	0.18536	0.30361
Ni17	0.15203	0.04046	0.02275
Ni18	0.01319	0.18867	0.11122
Ni19	0.37442	0.00335	0.19716
Ni20	0.23250	0.14805	0.29071
Ni21	0.35816	0.07053	0.04070
Ni22	0.21932	0.21874	0.12916
Ni23	0.08104	0.03280	0.21738
Ni24	0.44583	0.18520	0.30239
Ni25	0.66448	0.26031	0.05450
Ni26	0.52565	0.07519	0.14296
Ni27	0.88618	0.22355	0.22991
Ni28	0.75288	0.03498	0.31323
Ni29	0.79794	0.23500	0.03939
Ni30	0.65910	0.04988	0.12786
Ni31	0.52008	0.19595	0.21471
Ni32	0.87577	0.00461	0.30150
Ni33	0.96936	0.26031	0.05450
Ni34	0.83052	0.07519	0.14296
Ni35	0.69343	0.22456	0.22998
Ni36	0.54145	0.03291	0.31332
Ni37	0.99101	0.07053	0.04070
Ni38	0.85217	0.21874	0.12916
Ni39	0.71106	0.03288	0.21755
Ni40	0.57637	0.18536	0.30361

Ni41	0.65203	0.04046	0.02275
Ni42	0.51319	0.18867	0.11122
Ni43	0.87442	0.00335	0.19716
Ni44	0.73250	0.14805	0.29071
Ni45	0.85816	0.07053	0.04070
Ni46	0.71932	0.21874	0.12916
Ni47	0.58104	0.03280	0.21738
Ni48	0.94583	0.18520	0.30239
Ni49	0.16448	0.59364	0.05450
Ni50	0.02565	0.40852	0.14296
Ni51	0.38529	0.55569	0.22968
Ni52	0.25264	0.36811	0.31333
Ni53	0.29794	0.56833	0.03939
Ni54	0.15910	0.38322	0.12786
Ni55	0.02036	0.52948	0.21474
Ni56	0.37662	0.33834	0.30150
Ni57	0.46936	0.59364	0.05450
Ni58	0.33052	0.40852	0.14296
Ni59	0.19278	0.55719	0.23017
Ni60	0.04142	0.36635	0.31338
Ni61	0.49101	0.40386	0.04070
Ni62	0.35217	0.55208	0.12916
Ni63	0.21054	0.36589	0.21762
Ni64	0.07635	0.51899	0.30375
Ni65	0.15203	0.37379	0.02275

Ni66	0.01319	0.52200	0.11122
Ni67	0.37395	0.33612	0.19724
Ni68	0.23184	0.48054	0.29100
Ni69	0.35816	0.40386	0.04070
Ni70	0.21932	0.55208	0.12916
Ni71	0.08053	0.36564	0.21748
Ni72	0.44599	0.51889	0.30242
Ni73	0.66448	0.59364	0.05450
Ni74	0.52565	0.40852	0.14296
Ni75	0.88529	0.55569	0.22968
Ni76	0.75264	0.36811	0.31333
Ni77	0.79794	0.56833	0.03939
Ni78	0.65910	0.38322	0.12786
Ni79	0.52036	0.52948	0.21474
Ni80	0.87662	0.33834	0.30150
Ni81	0.96936	0.59364	0.05450
Ni82	0.83052	0.40852	0.14296
Ni83	0.69278	0.55719	0.23017
Ni84	0.54142	0.36635	0.31338
Ni85	0.99101	0.40386	0.04070
Ni86	0.85217	0.55208	0.12916
Ni87	0.71054	0.36589	0.21762
Ni88	0.57635	0.51899	0.30375
Ni89	0.65203	0.37379	0.02275
Ni90	0.51319	0.52200	0.11122

Ni91	0.87395	0.33612	0.19724
Ni92	0.73184	0.48054	0.29100
Ni93	0.85816	0.40386	0.04070
Ni94	0.71932	0.55208	0.12916
Ni95	0.58053	0.36564	0.21748
Ni96	0.94599	0.51889	0.30242
Ni97	0.16448	0.92698	0.05450
Ni98	0.02565	0.74186	0.14296
Ni99	0.38617	0.89035	0.22998
Ni100	0.25283	0.70122	0.31329
Ni101	0.29794	0.90167	0.03939
Ni102	0.15910	0.71655	0.12786
Ni103	0.02042	0.86322	0.21488
Ni104	0.37568	0.67072	0.30144
Ni105	0.46936	0.92698	0.05450
Ni106	0.33052	0.74186	0.14296
Ni107	0.19319	0.89107	0.23002
Ni108	0.04126	0.69929	0.31346
Ni109	0.49101	0.73719	0.04070
Ni110	0.35217	0.88541	0.12916
Ni111	0.21093	0.69944	0.21776
Ni112	0.07674	0.85233	0.30335
Ni113	0.15203	0.70712	0.02275
Ni114	0.01319	0.85534	0.11122
Ni115	0.37436	0.66991	0.19750

Ni116	0.23248	0.81460	0.29119
Ni117	0.35816	0.73719	0.04070
Ni118	0.21932	0.88541	0.12916
Ni119	0.08097	0.69929	0.21753
Ni120	0.44607	0.85234	0.30254
Ni121	0.66448	0.92698	0.05450
Ni122	0.52565	0.74186	0.14296
Ni123	0.88617	0.89035	0.22998
Ni124	0.75283	0.70122	0.31329
Ni125	0.79794	0.90167	0.03939
Ni126	0.65910	0.71655	0.12786
Ni127	0.52042	0.86322	0.21488
Ni128	0.87568	0.67072	0.30144
Ni129	0.96936	0.92698	0.05450
Ni130	0.83052	0.74186	0.14296
Ni131	0.69319	0.89107	0.23002
Ni132	0.54126	0.69929	0.31346
Ni133	0.99101	0.73719	0.04070
Ni134	0.85217	0.88541	0.12916
Ni135	0.71093	0.69944	0.21776
Ni136	0.57674	0.85233	0.30335
Ni137	0.65203	0.70712	0.02275
Ni138	0.51319	0.85534	0.11122
Ni139	0.87436	0.66991	0.19750
Ni140	0.73248	0.81460	0.29119

Ni141	0.85816	0.73719	0.04070
Ni142	0.71932	0.88541	0.12916
Ni143	0.58097	0.69929	0.21753
Ni144	0.94607	0.85234	0.30254
P1	0.02354	0.20247	0.01998
P2	0.38470	0.01735	0.10844
P3	0.24465	0.16413	0.19731
P4	0.10746	0.31358	0.29356
P5	0.28746	0.10991	0.06421
P6	0.14862	0.25812	0.15267
P7	0.00811	0.07257	0.24240
P8	0.37573	0.22361	0.32657
P9	0.12079	0.10991	0.06421
P10	0.48195	0.25812	0.15267
P11	0.34367	0.07168	0.24189
P12	0.20640	0.22678	0.32606
P13	0.52354	0.20247	0.01998
P14	0.88470	0.01735	0.10844
P15	0.74465	0.16413	0.19731
P16	0.60746	0.31358	0.29356
P17	0.78746	0.10991	0.06421
P18	0.64862	0.25812	0.15267
P19	0.50811	0.07257	0.24240
P20	0.87573	0.22361	0.32657
P21	0.62079	0.10991	0.06421

P22	0.98195	0.25812	0.15267
P23	0.84367	0.07168	0.24189
P24	0.70640	0.22678	0.32606
P25	0.02354	0.53580	0.01998
P26	0.38470	0.35068	0.10844
P27	0.24425	0.49743	0.19777
P28	0.10801	0.64768	0.29353
P29	0.28746	0.44324	0.06421
P30	0.14862	0.59146	0.15267
P31	0.00814	0.40605	0.24235
P32	0.37524	0.55656	0.32666
P33	0.12079	0.44324	0.06421
P34	0.48195	0.59146	0.15267
P35	0.34358	0.40481	0.24201
P36	0.20563	0.55905	0.32630
P37	0.52354	0.53580	0.01998
P38	0.88470	0.35068	0.10844
P39	0.74425	0.49743	0.19777
P40	0.60801	0.64768	0.29353
P41	0.78746	0.44324	0.06421
P42	0.64862	0.59146	0.15267
P43	0.50814	0.40605	0.24235
P44	0.87524	0.55656	0.32666
P45	0.62079	0.44324	0.06421
P46	0.98195	0.59146	0.15267

P47	0.84358	0.40481	0.24201
P48	0.70563	0.55905	0.32630
P49	0.02354	0.86913	0.01998
P50	0.38470	0.68402	0.10844
P51	0.24526	0.83120	0.19785
P52	0.10776	0.98088	0.29352
P53	0.28746	0.77658	0.06421
P54	0.14862	0.92479	0.15267
P55	0.00788	0.73846	0.24232
P56	0.37602	0.89097	0.32659
P57	0.12079	0.77658	0.06421
P58	0.48195	0.92479	0.15267
P59	0.34395	0.73869	0.24199
P60	0.20617	0.89323	0.32663
P61	0.52354	0.86913	0.01998
P62	0.88470	0.68402	0.10844
P63	0.74526	0.83120	0.19785
P64	0.60776	0.98088	0.29352
P65	0.78746	0.77658	0.06421
P66	0.64862	0.92479	0.15267
P67	0.50788	0.73846	0.24232
P68	0.87602	0.89097	0.32659
P69	0.62079	0.77658	0.06421
P70	0.98195	0.92479	0.15267
P71	0.84395	0.73869	0.24199

P72	0.70617	0.89323	0.32663

Table S4 Unit-cell and position parameters of Mn-5Ni_2P optimization model.

	Mn-5Ni_2P
a (Å)	20.56060
b (Å)	20.39730
c (Å)	25.00000
α (deg)	90.00000
β (deg)	90.00000
γ (deg)	139.11300

Atom Coordinates	***x***	***y***	***z***
Ni1	0.16448	0.26031	0.05450
Ni2	0.02565	0.07519	0.14296
Ni3	0.38429	0.22154	0.23247
Ni4	0.24536	0.02232	0.31249
Ni5	0.46936	0.26031	0.05450
Ni6	0.33052	0.07519	0.14296
Ni7	0.19101	0.22165	0.23238
Ni8	0.03143	0.02203	0.31285
Ni9	0.49101	0.07053	0.04070
Ni10	0.35217	0.21874	0.12916
Ni11	0.21140	0.03276	0.21818
Ni12	0.06719	0.17523	0.30720
Ni13	0.15203	0.04046	0.02275

Ni14	0.01319	0.18867	0.11122
Ni15	0.37145	0.99954	0.19786
Ni16	0.22516	0.13796	0.29363
Ni17	0.35816	0.07053	0.04070
Ni18	0.21932	0.21874	0.12916
Ni19	0.08075	0.03219	0.21840
Ni20	0.43932	0.17587	0.30684
Ni21	0.66448	0.26031	0.05450
Ni22	0.52565	0.07519	0.14296
Ni23	0.88429	0.22154	0.23247
Ni24	0.74536	0.02232	0.31249
Ni25	0.96936	0.26031	0.05450
Ni26	0.83052	0.07519	0.14296
Ni27	0.69101	0.22165	0.23238
Ni28	0.53143	0.02203	0.31285
Ni29	0.99101	0.07053	0.04070
Ni30	0.85217	0.21874	0.12916
Ni31	0.71140	0.03276	0.21818
Ni32	0.56719	0.17523	0.30720
Ni33	0.65203	0.04046	0.02275
Ni34	0.51319	0.18867	0.11122
Ni35	0.87145	0.99954	0.19786
Ni36	0.72516	0.13796	0.29363
Ni37	0.85816	0.07053	0.04070
Ni38	0.71932	0.21874	0.12916

Ni39	0.58075	0.03219	0.21840
Ni40	0.93932	0.17587	0.30684
Ni41	0.16448	0.59364	0.05450
Ni42	0.02565	0.40852	0.14296
Ni43	0.38401	0.55408	0.23230
Ni44	0.24549	0.35653	0.31250
Ni45	0.46936	0.59364	0.05450
Ni46	0.33052	0.40852	0.14296
Ni47	0.19056	0.55453	0.23227
Ni48	0.03251	0.35660	0.31258
Ni49	0.49101	0.40386	0.04070
Ni50	0.35217	0.55208	0.12916
Ni51	0.21080	0.36577	0.21809
Ni52	0.06686	0.50825	0.30691
Ni53	0.15203	0.37379	0.02275
Ni54	0.01319	0.52200	0.11122
Ni55	0.37109	0.33279	0.19773
Ni56	0.22478	0.47097	0.29323
Ni57	0.35816	0.40386	0.04070
Ni58	0.21932	0.55208	0.12916
Ni59	0.08039	0.36546	0.21811
Ni60	0.43870	0.50864	0.30651
Ni61	0.66448	0.59364	0.05450
Ni62	0.52565	0.40852	0.14296
Ni63	0.88401	0.55408	0.23230

Ni64	0.74549	0.35653	0.31250
Ni65	0.96936	0.59364	0.05450
Ni66	0.83052	0.40852	0.14296
Ni67	0.69056	0.55453	0.23227
Ni68	0.53251	0.35660	0.31258
Ni69	0.99101	0.40386	0.04070
Ni70	0.85217	0.55208	0.12916
Ni71	0.71080	0.36577	0.21809
Ni72	0.56686	0.50825	0.30691
Ni73	0.65203	0.37379	0.02275
Ni74	0.51319	0.52200	0.11122
Ni75	0.87109	0.33279	0.19773
Ni76	0.72478	0.47097	0.29323
Ni77	0.85816	0.40386	0.04070
Ni78	0.71932	0.55208	0.12916
Ni79	0.58039	0.36546	0.21811
Ni80	0.93870	0.50864	0.30651
Ni81	0.16448	0.92698	0.05450
Ni82	0.02565	0.74186	0.14296
Ni83	0.38415	0.88708	0.23233
Ni84	0.24564	0.68934	0.31257
Ni85	0.46936	0.92698	0.05450
Ni86	0.33052	0.74186	0.14296
Ni87	0.19091	0.88785	0.23240
Ni88	0.03242	0.68939	0.31281

Ni89	0.49101	0.73719	0.04070
Ni90	0.35217	0.88541	0.12916
Ni91	0.21080	0.69893	0.21818
Ni92	0.06692	0.84168	0.30716
Ni93	0.15203	0.70712	0.02275
Ni94	0.01319	0.85534	0.11122
Ni95	0.37096	0.66588	0.19808
Ni96	0.22489	0.80430	0.29337
Ni97	0.35816	0.73719	0.04070
Ni98	0.21932	0.88541	0.12916
Ni99	0.08079	0.69906	0.21816
Ni100	0.43961	0.84210	0.30689
Ni101	0.66448	0.92698	0.05450
Ni102	0.52565	0.74186	0.14296
Ni103	0.88415	0.88708	0.23233
Ni104	0.74564	0.68934	0.31257
Ni105	0.96936	0.92698	0.05450
Ni106	0.83052	0.74186	0.14296
Ni107	0.69091	0.88785	0.23240
Ni108	0.53242	0.68939	0.31281
Ni109	0.99101	0.73719	0.04070
Ni110	0.85217	0.88541	0.12916
Ni111	0.71080	0.69893	0.21818
Ni112	0.56692	0.84168	0.30716
Ni113	0.65203	0.70712	0.02275

Ni114	0.51319	0.85534	0.11122
Ni115	0.87096	0.66588	0.19808
Ni116	0.72489	0.80430	0.29337
Ni117	0.85816	0.73719	0.04070
Ni118	0.71932	0.88541	0.12916
Ni119	0.58079	0.69906	0.21816
Ni120	0.93961	0.84210	0.30689
Mn1	0.29794	0.23500	0.03939
Mn2	0.15910	0.04988	0.12786
Mn3	0.01683	0.19253	0.21611
Mn4	0.36927	0.99687	0.30541
Mn5	0.79794	0.23500	0.03939
Mn6	0.65910	0.04988	0.12786
Mn7	0.51683	0.19253	0.21611
Mn8	0.86927	0.99687	0.30541
Mn9	0.29794	0.56833	0.03939
Mn10	0.15910	0.38322	0.12786
Mn11	0.01670	0.52606	0.21600
Mn12	0.37004	0.33079	0.30528
Mn13	0.79794	0.56833	0.03939
Mn14	0.65910	0.38322	0.12786
Mn15	0.51670	0.52606	0.21600
Mn16	0.87004	0.33079	0.30528
Mn17	0.29794	0.90167	0.03939
Mn18	0.15910	0.71655	0.12786

Mn19	0.01697	0.85926	0.21623
Mn20	0.36945	0.66341	0.30544
Mn21	0.79794	0.90167	0.03939
Mn22	0.65910	0.71655	0.12786
Mn23	0.51697	0.85926	0.21623
Mn24	0.86945	0.66341	0.30544
P1	0.02354	0.20247	0.01998
P2	0.38470	0.01735	0.10844
P3	0.24424	0.16351	0.19893
P4	0.09975	0.30407	0.29195
P5	0.28746	0.10991	0.06421
P6	0.14862	0.25812	0.15267
P7	0.00674	0.07008	0.24172
P8	0.36813	0.21235	0.32922
P9	0.12079	0.10991	0.06421
P10	0.48195	0.25812	0.15267
P11	0.34244	0.07078	0.24152
P12	0.19395	0.21256	0.32869
P13	0.52354	0.20247	0.01998
P14	0.88470	0.01735	0.10844
P15	0.74424	0.16351	0.19893
P16	0.59975	0.30407	0.29195
P17	0.78746	0.10991	0.06421
P18	0.64862	0.25812	0.15267
P19	0.50674	0.07008	0.24172

P20	0.86813	0.21235	0.32922
P21	0.62079	0.10991	0.06421
P22	0.98195	0.25812	0.15267
P23	0.84244	0.07078	0.24152
P24	0.69395	0.21256	0.32869
P25	0.02354	0.53580	0.01998
P26	0.38470	0.35068	0.10844
P27	0.24408	0.49697	0.19877
P28	0.09949	0.63705	0.29199
P29	0.28746	0.44324	0.06421
P30	0.14862	0.59146	0.15267
P31	0.00704	0.40407	0.24095
P32	0.36735	0.54512	0.32932
P33	0.12079	0.44324	0.06421
P34	0.48195	0.59146	0.15267
P35	0.34175	0.40337	0.24113
P36	0.19319	0.54500	0.32886
P37	0.52354	0.53580	0.01998
P38	0.88470	0.35068	0.10844
P39	0.74408	0.49697	0.19877
P40	0.59949	0.63705	0.29199
P41	0.78746	0.44324	0.06421
P42	0.64862	0.59146	0.15267
P43	0.50704	0.40407	0.24095
P44	0.86735	0.54512	0.32932

P45	0.62079	0.44324	0.06421
P46	0.98195	0.59146	0.15267
P47	0.84175	0.40337	0.24113
P48	0.69319	0.54500	0.32886
P49	0.02354	0.86913	0.01998
P50	0.38470	0.68402	0.10844
P51	0.24467	0.83044	0.19877
P52	0.10038	0.97127	0.29240
P53	0.28746	0.77658	0.06421
P54	0.14862	0.92479	0.15267
P55	0.00686	0.73689	0.24149
P56	0.36720	0.87725	0.32924
P57	0.12079	0.77658	0.06421
P58	0.48195	0.92479	0.15267
P59	0.34226	0.73753	0.24146
P60	0.19268	0.87759	0.32909
P61	0.52354	0.86913	0.01998
P62	0.88470	0.68402	0.10844
P63	0.74467	0.83044	0.19877
P64	0.60038	0.97127	0.29240
P65	0.78746	0.77658	0.06421
P66	0.64862	0.92479	0.15267
P67	0.50686	0.73689	0.24149
P68	0.86720	0.87725	0.32924
P69	0.62079	0.77658	0.06421

P70	0.98195	0.92479	0.15267
P71	0.84226	0.73753	0.24146
P72	0.69268	0.87759	0.32909

Table S5 Unit-cell and position parameters of the optimized model for the adsorption of HMF on Ni_2P.

	Ni_2P
a (Å)	20.56060
b (Å)	20.39730
c (Å)	25.00000
α (deg)	90.00000
β (deg)	90.00000
γ (deg)	139.11300

Atom Coordinates	***x***	***y***	***z***
Ni1	0.16448	0.26031	0.05450
Ni2	0.02565	0.07519	0.14296
Ni3	0.38643	0.22283	0.22947
Ni4	0.25310	0.03377	0.31343
Ni5	0.29794	0.23500	0.03939
Ni6	0.15910	0.04988	0.12786
Ni7	0.01911	0.19545	0.21435
Ni8	0.37620	0.00248	0.30122
Ni9	0.46936	0.26031	0.05450
Ni10	0.33052	0.07519	0.14296

Ni11	0.19283	0.22365	0.22988
Ni12	0.04819	0.03833	0.31375
Ni13	0.49101	0.07053	0.04070
Ni14	0.35217	0.21874	0.12916
Ni15	0.21160	0.03307	0.21763
Ni16	0.07517	0.18411	0.30275
Ni17	0.15203	0.04046	0.02275
Ni18	0.01319	0.18867	0.11122
Ni19	0.37377	0.00224	0.19717
Ni20	0.23391	0.14774	0.29026
Ni21	0.35816	0.07053	0.04070
Ni22	0.21932	0.21874	0.12916
Ni23	0.08060	0.03177	0.21750
Ni24	0.44601	0.18439	0.30250
Ni25	0.66448	0.26031	0.05450
Ni26	0.52565	0.07519	0.14296
Ni27	0.88556	0.22196	0.22955
Ni28	0.75192	0.03245	0.31308
Ni29	0.79794	0.23500	0.03939
Ni30	0.65910	0.04988	0.12786
Ni31	0.52064	0.19484	0.21485
Ni32	0.87293	0.00469	0.30110
Ni33	0.96936	0.26031	0.05450
Ni34	0.83052	0.07519	0.14296
Ni35	0.69348	0.22406	0.23012

Ni36	0.53914	0.02992	0.31324
Ni37	0.99101	0.07053	0.04070
Ni38	0.85217	0.21874	0.12916
Ni39	0.71044	0.03221	0.21775
Ni40	0.57605	0.18358	0.30387
Ni41	0.65203	0.04046	0.02275
Ni42	0.51319	0.18867	0.11122
Ni43	0.87338	0.00219	0.19711
Ni44	0.73161	0.14606	0.29081
Ni45	0.85816	0.07053	0.04070
Ni46	0.71932	0.21874	0.12916
Ni47	0.58109	0.03249	0.21743
Ni48	0.94597	0.18477	0.30242
Ni49	0.16448	0.59364	0.05450
Ni50	0.02565	0.40852	0.14296
Ni51	0.38573	0.55606	0.22920
Ni52	0.25207	0.36589	0.31265
Ni53	0.29794	0.56833	0.03939
Ni54	0.15910	0.38322	0.12786
Ni55	0.02003	0.52887	0.21497
Ni56	0.37507	0.33698	0.30047
Ni57	0.46936	0.59364	0.05450
Ni58	0.33052	0.40852	0.14296
Ni59	0.19228	0.55668	0.23001
Ni60	0.04222	0.36604	0.31363

Ni61	0.49101	0.40386	0.04070
Ni62	0.35217	0.55208	0.12916
Ni63	0.21040	0.36569	0.21745
Ni64	0.07537	0.51750	0.30390
Ni65	0.15203	0.37379	0.02275
Ni66	0.01319	0.52200	0.11122
Ni67	0.37338	0.33517	0.19676
Ni68	0.23262	0.48066	0.29062
Ni69	0.35816	0.40386	0.04070
Ni70	0.21932	0.55208	0.12916
Ni71	0.08044	0.36525	0.21757
Ni72	0.44611	0.51850	0.30136
Ni73	0.66448	0.59364	0.05450
Ni74	0.52565	0.40852	0.14296
Ni75	0.88621	0.55530	0.22944
Ni76	0.75191	0.36641	0.31379
Ni77	0.79794	0.56833	0.03939
Ni78	0.65910	0.38322	0.12786
Ni79	0.52014	0.52846	0.21413
Ni80	0.87567	0.33611	0.30152
Ni81	0.96936	0.59364	0.05450
Ni82	0.83052	0.40852	0.14296
Ni83	0.69058	0.55399	0.22925
Ni84	0.54308	0.36606	0.31330
Ni85	0.99101	0.40386	0.04070

Ni86	0.85217	0.55208	0.12916
Ni87	0.71077	0.36516	0.21761
Ni88	0.57456	0.51620	0.30220
Ni89	0.65203	0.37379	0.02275
Ni90	0.51319	0.52200	0.11122
Ni91	0.87398	0.33562	0.19729
Ni92	0.73213	0.47837	0.28907
Ni93	0.85816	0.40386	0.04070
Ni94	0.71932	0.55208	0.12916
Ni95	0.58046	0.36417	0.21735
Ni96	0.94443	0.51616	0.30310
Ni97	0.16448	0.92698	0.05450
Ni98	0.02565	0.74186	0.14296
Ni99	0.38579	0.88846	0.22964
Ni100	0.25165	0.70012	0.31355
Ni101	0.29794	0.90167	0.03939
Ni102	0.15910	0.71655	0.12786
Ni103	0.02108	0.86256	0.21495
Ni104	0.37473	0.67023	0.30155
Ni105	0.46936	0.92698	0.05450
Ni106	0.33052	0.74186	0.14296
Ni107	0.19247	0.89019	0.22991
Ni108	0.03793	0.69630	0.31335
Ni109	0.49101	0.73719	0.04070
Ni110	0.35217	0.88541	0.12916

Ni111	0.21023	0.69875	0.21781
Ni112	0.07592	0.85106	0.30409
Ni113	0.15203	0.70712	0.02275
Ni114	0.01319	0.85534	0.11122
Ni115	0.37386	0.66959	0.19746
Ni116	0.23085	0.81270	0.29087
Ni117	0.35816	0.73719	0.04070
Ni118	0.21932	0.88541	0.12916
Ni119	0.08078	0.69899	0.21760
Ni120	0.44492	0.84988	0.30319
Ni121	0.66448	0.92698	0.05450
Ni122	0.52565	0.74186	0.14296
Ni123	0.88624	0.88938	0.22877
Ni124	0.75319	0.69903	0.31877
Ni125	0.79794	0.90167	0.03939
Ni126	0.65910	0.71655	0.12786
Ni127	0.52002	0.86273	0.21498
Ni128	0.87350	0.66774	0.30118
Ni129	0.96936	0.92698	0.05450
Ni130	0.83052	0.74186	0.14296
Ni131	0.69176	0.88929	0.23001
Ni132	0.54380	0.70030	0.31369
Ni133	0.99101	0.73719	0.04070
Ni134	0.85217	0.88541	0.12916
Ni135	0.71083	0.69765	0.22013

Ni136	0.57532	0.85046	0.30367
Ni137	0.65203	0.70712	0.02275
Ni138	0.51319	0.85534	0.11122
Ni139	0.87325	0.66885	0.19751
Ni140	0.73374	0.81472	0.29036
Ni141	0.85816	0.73719	0.04070
Ni142	0.71932	0.88541	0.12916
Ni143	0.58063	0.69838	0.21768
Ni144	0.94719	0.85481	0.30193
P1	0.02354	0.20247	0.01998
P2	0.38470	0.01735	0.10844
P3	0.24436	0.16359	0.19738
P4	0.10794	0.31351	0.29349
P5	0.28746	0.10991	0.06421
P6	0.14862	0.25812	0.15267
P7	0.00754	0.07145	0.24187
P8	0.37650	0.22332	0.32617
P9	0.12079	0.10991	0.06421
P10	0.48195	0.25812	0.15267
P11	0.34381	0.07135	0.24194
P12	0.20456	0.22369	0.32590
P13	0.52354	0.20247	0.01998
P14	0.88470	0.01735	0.10844
P15	0.74455	0.16370	0.19745
P16	0.60744	0.31187	0.29320

P17	0.78746	0.10991	0.06421
P18	0.64862	0.25812	0.15267
P19	0.50775	0.07131	0.24221
P20	0.87603	0.22313	0.32579
P21	0.62079	0.10991	0.06421
P22	0.98195	0.25812	0.15267
P23	0.84322	0.07152	0.24154
P24	0.70620	0.22544	0.32611
P25	0.02354	0.53580	0.01998
P26	0.38470	0.35068	0.10844
P27	0.24412	0.49719	0.19762
P28	0.10593	0.64576	0.29355
P29	0.28746	0.44324	0.06421
P30	0.14862	0.59146	0.15267
P31	0.00809	0.40530	0.24248
P32	0.37692	0.55796	0.32540
P33	0.12079	0.44324	0.06421
P34	0.48195	0.59146	0.15267
P35	0.34310	0.40415	0.24121
P36	0.20504	0.55809	0.32625
P37	0.52354	0.53580	0.01998
P38	0.88470	0.35068	0.10844
P39	0.74453	0.49647	0.19700
P40	0.60852	0.64671	0.29365
P41	0.78746	0.44324	0.06421

P42	0.64862	0.59146	0.15267
P43	0.50681	0.40330	0.24155
P44	0.87363	0.55395	0.32700
P45	0.62079	0.44324	0.06421
P46	0.98195	0.59146	0.15267
P47	0.84305	0.40386	0.24206
P48	0.70138	0.55200	0.32446
P49	0.02354	0.86913	0.01998
P50	0.38470	0.68402	0.10844
P51	0.24482	0.83061	0.19795
P52	0.10917	0.98092	0.29355
P53	0.28746	0.77658	0.06421
P54	0.14862	0.92479	0.15267
P55	0.00722	0.73790	0.24245
P56	0.37363	0.88733	0.32638
P57	0.12079	0.77658	0.06421
P58	0.48195	0.92479	0.15267
P59	0.34297	0.73803	0.24207
P60	0.20601	0.89226	0.32603
P61	0.52354	0.86913	0.01998
P62	0.88470	0.68402	0.10844
P63	0.74426	0.82957	0.19761
P64	0.60654	0.97906	0.29364
P65	0.78746	0.77658	0.06421
P66	0.64862	0.92479	0.15267

P67	0.50733	0.73782	0.24246
P68	0.88141	0.89848	0.32362
P69	0.62079	0.77658	0.06421
P70	0.98195	0.92479	0.15267
P71	0.84198	0.73568	0.24439
P72	0.70459	0.89060	0.32678
C1	0.46086	0.54238	0.46136
C2	0.62288	0.67618	0.45221
C3	0.58830	0.70793	0.47424
C4	0.48431	0.62223	0.47978
C5	0.36487	0.43357	0.45479
C6	0.71813	0.73163	0.43161
O1	0.54379	0.57361	0.44470
O2	0.28187	0.40866	0.47072
O3	0.73620	0.69445	0.40564
H1	0.63367	0.78502	0.48368
H2	0.43169	0.61853	0.49379
H3	0.36821	0.38825	0.47556
H4	0.35455	0.41457	0.41183
H5	0.77690	0.81380	0.43870
H6	0.27777	0.40563	0.50959

Table S6 Unit-cell and position parameters of the optimized model for the adsorption of HMF on Mn-5Ni_2P (Ni site).

	Mn-5Ni_2P		
a (Å)	20.56060		
b (Å)	20.39730		
c (Å)	25.00000		
α (deg)	90.00000		
β (deg)	90.00000		
γ (deg)	139.11300		
Atom Coordinates	***x***	***y***	***z***
Ni1	0.16448	0.26031	0.05450
Ni2	0.02565	0.07519	0.14296
Ni3	0.38344	0.21938	0.23253
Ni4	0.24426	0.02024	0.31278
Ni5	0.46936	0.26031	0.05450
Ni6	0.33052	0.07519	0.14296
Ni7	0.18942	0.21960	0.23240
Ni8	0.03498	0.02437	0.31302
Ni9	0.49101	0.07053	0.04070
Ni10	0.35217	0.21874	0.12916
Ni11	0.21060	0.03151	0.21837
Ni12	0.06574	0.17358	0.30748
Ni13	0.15203	0.04046	0.02275
Ni14	0.01319	0.18867	0.11122

Ni15	0.37057	0.99806	0.19789
Ni16	0.22463	0.13604	0.29366
Ni17	0.35816	0.07053	0.04070
Ni18	0.21932	0.21874	0.12916
Ni19	0.08046	0.03133	0.21832
Ni20	0.43825	0.17364	0.30713
Ni21	0.66448	0.26031	0.05450
Ni22	0.52565	0.07519	0.14296
Ni23	0.88331	0.21981	0.23267
Ni24	0.74481	0.02122	0.31257
Ni25	0.96936	0.26031	0.05450
Ni26	0.83052	0.07519	0.14296
Ni27	0.69067	0.22047	0.23276
Ni28	0.53005	0.01977	0.31300
Ni29	0.99101	0.07053	0.04070
Ni30	0.85217	0.21874	0.12916
Ni31	0.71051	0.03175	0.21834
Ni32	0.56665	0.17323	0.30766
Ni33	0.65203	0.04046	0.02275
Ni34	0.51319	0.18867	0.11122
Ni35	0.87079	0.99864	0.19777
Ni36	0.72392	0.13567	0.29417
Ni37	0.85816	0.07053	0.04070
Ni38	0.71932	0.21874	0.12916
Ni39	0.58050	0.03136	0.21846

Ni40	0.93865	0.17451	0.30673
Ni41	0.16448	0.59364	0.05450
Ni42	0.02565	0.40852	0.14296
Ni43	0.38356	0.55362	0.23198
Ni44	0.24431	0.35347	0.31182
Ni45	0.46936	0.59364	0.05450
Ni46	0.33052	0.40852	0.14296
Ni47	0.18978	0.55345	0.23243
Ni48	0.03210	0.35511	0.31288
Ni49	0.49101	0.40386	0.04070
Ni50	0.35217	0.55208	0.12916
Ni51	0.21021	0.36510	0.21808
Ni52	0.06575	0.50648	0.30727
Ni53	0.15203	0.37379	0.02275
Ni54	0.01319	0.52200	0.11122
Ni55	0.37015	0.33150	0.19756
Ni56	0.22405	0.46942	0.29319
Ni57	0.35816	0.40386	0.04070
Ni58	0.21932	0.55208	0.12916
Ni59	0.07981	0.36424	0.21840
Ni60	0.43806	0.50748	0.30595
Ni61	0.66448	0.59364	0.05450
Ni62	0.52565	0.40852	0.14296
Ni63	0.88364	0.55301	0.23222
Ni64	0.74501	0.35433	0.31224

Ni65	0.96936	0.59364	0.05450
Ni66	0.83052	0.40852	0.14296
Ni67	0.68873	0.55207	0.23187
Ni68	0.53282	0.35520	0.31250
Ni69	0.99101	0.40386	0.04070
Ni70	0.85217	0.55208	0.12916
Ni71	0.71017	0.36477	0.21820
Ni72	0.56495	0.50577	0.30568
Ni73	0.65203	0.37379	0.02275
Ni74	0.51319	0.52200	0.11122
Ni75	0.87100	0.33218	0.19774
Ni76	0.72429	0.46839	0.29273
Ni77	0.85816	0.40386	0.04070
Ni78	0.71932	0.55208	0.12916
Ni79	0.57994	0.36385	0.21824
Ni80	0.93804	0.50640	0.30689
Ni81	0.16448	0.92698	0.05450
Ni82	0.02565	0.74186	0.14296
Ni83	0.38339	0.88581	0.23248
Ni84	0.24443	0.68751	0.31270
Ni85	0.46936	0.92698	0.05450
Ni86	0.33052	0.74186	0.14296
Ni87	0.18957	0.88627	0.23251
Ni88	0.03091	0.68721	0.31284
Ni89	0.49101	0.73719	0.04070

Ni90	0.35217	0.88541	0.12916
Ni91	0.21046	0.69845	0.21832
Ni92	0.06529	0.83942	0.30765
Ni93	0.15203	0.70712	0.02275
Ni94	0.01319	0.85534	0.11122
Ni95	0.37041	0.66527	0.19802
Ni96	0.22381	0.80240	0.29404
Ni97	0.35816	0.73719	0.04070
Ni98	0.21932	0.88541	0.12916
Ni99	0.08037	0.69817	0.21835
Ni100	0.43823	0.83999	0.30717
Ni101	0.66448	0.92698	0.05450
Ni102	0.52565	0.74186	0.14296
Ni103	0.88456	0.88692	0.23169
Ni104	0.74437	0.68698	0.31596
Ni105	0.96936	0.92698	0.05450
Ni106	0.83052	0.74186	0.14296
Ni107	0.69004	0.88680	0.23243
Ni108	0.53252	0.68854	0.31270
Ni109	0.99101	0.73719	0.04070
Ni110	0.85217	0.88541	0.12916
Ni111	0.71074	0.69774	0.21947
Ni112	0.56617	0.84014	0.30736
Ni113	0.65203	0.70712	0.02275
Ni114	0.51319	0.85534	0.11122

Ni115	0.87021	0.66523	0.19819
Ni116	0.72504	0.80365	0.29281
Ni117	0.85816	0.73719	0.04070
Ni118	0.71932	0.88541	0.12916
Ni119	0.58082	0.69854	0.21819
Ni120	0.93920	0.84255	0.30711
Mn1	0.29794	0.23500	0.03939
Mn2	0.15910	0.04988	0.12786
Mn3	0.01644	0.19169	0.21607
Mn4	0.36815	0.99510	0.30560
Mn5	0.79794	0.23500	0.03939
Mn6	0.65910	0.04988	0.12786
Mn7	0.51624	0.19103	0.21633
Mn8	0.86866	0.99688	0.30492
Mn9	0.29794	0.56833	0.03939
Mn10	0.15910	0.38322	0.12786
Mn11	0.01644	0.52515	0.21610
Mn12	0.36857	0.32851	0.30468
Mn13	0.79794	0.56833	0.03939
Mn14	0.65910	0.38322	0.12786
Mn15	0.51617	0.52516	0.21545
Mn16	0.86895	0.32879	0.30527
Mn17	0.29794	0.90167	0.03939
Mn18	0.15910	0.71655	0.12786
Mn19	0.01638	0.85821	0.21641

Mn20	0.36843	0.66228	0.30549
Mn21	0.79794	0.90167	0.03939
Mn22	0.65910	0.71655	0.12786
Mn23	0.51646	0.85825	0.21629
Mn24	0.86787	0.66087	0.30578
P1	0.02354	0.20247	0.01998
P2	0.38470	0.01735	0.10844
P3	0.24397	0.16284	0.19900
P4	0.09941	0.30285	0.29244
P5	0.28746	0.10991	0.06421
P6	0.14862	0.25812	0.15267
P7	0.00668	0.06968	0.24145
P8	0.36803	0.21135	0.32934
P9	0.12079	0.10991	0.06421
P10	0.48195	0.25812	0.15267
P11	0.34098	0.06825	0.24174
P12	0.19185	0.20918	0.32896
P13	0.52354	0.20247	0.01998
P14	0.88470	0.01735	0.10844
P15	0.74414	0.16315	0.19916
P16	0.59894	0.30162	0.29230
P17	0.78746	0.10991	0.06421
P18	0.64862	0.25812	0.15267
P19	0.50592	0.06837	0.24183
P20	0.86761	0.21106	0.32946

P21	0.62079	0.10991	0.06421
P22	0.98195	0.25812	0.15267
P23	0.84174	0.06995	0.24116
P24	0.69391	0.21115	0.32934
P25	0.02354	0.53580	0.01998
P26	0.38470	0.35068	0.10844
P27	0.24360	0.49633	0.19866
P28	0.09871	0.63555	0.29217
P29	0.28746	0.44324	0.06421
P30	0.14862	0.59146	0.15267
P31	0.00621	0.40246	0.24147
P32	0.36729	0.54489	0.32807
P33	0.12079	0.44324	0.06421
P34	0.48195	0.59146	0.15267
P35	0.34134	0.40278	0.24072
P36	0.19229	0.54312	0.32889
P37	0.52354	0.53580	0.01998
P38	0.88470	0.35068	0.10844
P39	0.74407	0.49652	0.19865
P40	0.59920	0.63593	0.29182
P41	0.78746	0.44324	0.06421
P42	0.64862	0.59146	0.15267
P43	0.50533	0.40118	0.24037
P44	0.86696	0.54293	0.32939
P45	0.62079	0.44324	0.06421

P46	0.98195	0.59146	0.15267
P47	0.84162	0.40297	0.24085
P48	0.68899	0.53867	0.32729
P49	0.02354	0.86913	0.01998
P50	0.38470	0.68402	0.10844
P51	0.24395	0.82951	0.19902
P52	0.10009	0.96953	0.29253
P53	0.28746	0.77658	0.06421
P54	0.14862	0.92479	0.15267
P55	0.00566	0.73537	0.24150
P56	0.36580	0.87517	0.32944
P57	0.12079	0.77658	0.06421
P58	0.48195	0.92479	0.15267
P59	0.34140	0.73628	0.24151
P60	0.19130	0.87564	0.32913
P61	0.52354	0.86913	0.01998
P62	0.88470	0.68402	0.10844
P63	0.74450	0.82967	0.19878
P64	0.59911	0.96918	0.29255
P65	0.78746	0.77658	0.06421
P66	0.64862	0.92479	0.15267
P67	0.50581	0.73548	0.24147
P68	0.87021	0.88240	0.32721
P69	0.62079	0.77658	0.06421
P70	0.98195	0.92479	0.15267

P71	0.84078	0.73497	0.24344
P72	0.69255	0.87682	0.32890
C1	0.45898	0.53961	0.45988
C2	0.62150	0.67087	0.45187
C3	0.58863	0.70502	0.47246
C4	0.48421	0.62082	0.47740
C5	0.36189	0.43128	0.45339
C6	0.71756	0.72368	0.43427
O1	0.54112	0.56844	0.44442
O2	0.28017	0.40829	0.46954
O3	0.73590	0.68499	0.41107
H1	0.63555	0.78265	0.48163
H2	0.43269	0.61911	0.49063
H3	0.36386	0.38469	0.47380
H4	0.35066	0.41231	0.41030
H5	0.77722	0.80603	0.44144
H6	0.27889	0.40941	0.50842

Table S7 Unit-cell and position parameters of the optimized model for the adsorption of HMF on Mn-5Ni_2P (Mn site).

	Mn-5Ni_2P
a (Å)	20.56060
b (Å)	20.39730
c (Å)	25.00000
α (deg)	90.00000
β (deg)	90.00000
γ (deg)	139.11300

Atom Coordinates	***x***	***y***	***z***
Ni1	0.16448	0.26031	0.05450
Ni2	0.02565	0.07519	0.14296
Ni3	0.38208	0.21756	0.23238
Ni4	0.24327	0.02000	0.31292
Ni5	0.46936	0.26031	0.05450
Ni6	0.33052	0.07519	0.14296
Ni7	0.18770	0.21792	0.23234
Ni8	0.02963	0.01932	0.31308
Ni9	0.49101	0.07053	0.04070
Ni10	0.35217	0.21874	0.12916
Ni11	0.20988	0.03075	0.21840
Ni12	0.06504	0.17254	0.30797
Ni13	0.15203	0.04046	0.02275
Ni14	0.01319	0.18867	0.11122

Ni15	0.37012	0.99757	0.19797
Ni16	0.22204	0.13375	0.29367
Ni17	0.35816	0.07053	0.04070
Ni18	0.21932	0.21874	0.12916
Ni19	0.07944	0.03004	0.21851
Ni20	0.43769	0.17248	0.30733
Ni21	0.66448	0.26031	0.05450
Ni22	0.52565	0.07519	0.14296
Ni23	0.88262	0.21779	0.23230
Ni24	0.74352	0.02038	0.31297
Ni25	0.96936	0.26031	0.05450
Ni26	0.83052	0.07519	0.14296
Ni27	0.69071	0.22043	0.23277
Ni28	0.52990	0.01966	0.31301
Ni29	0.99101	0.07053	0.04070
Ni30	0.85217	0.21874	0.12916
Ni31	0.71013	0.03100	0.21842
Ni32	0.56642	0.17324	0.30760
Ni33	0.65203	0.04046	0.02275
Ni34	0.51319	0.18867	0.11122
Ni35	0.87068	0.99815	0.19790
Ni36	0.72295	0.13489	0.29368
Ni37	0.85816	0.07053	0.04070
Ni38	0.71932	0.21874	0.12916
Ni39	0.58040	0.03126	0.21843

Ni40	0.93723	0.17245	0.30768
Ni41	0.16448	0.59364	0.05450
Ni42	0.02565	0.40852	0.14296
Ni43	0.38279	0.55229	0.23236
Ni44	0.24386	0.35291	0.31216
Ni45	0.46936	0.59364	0.05450
Ni46	0.33052	0.40852	0.14296
Ni47	0.19038	0.55356	0.23252
Ni48	0.02936	0.35236	0.31274
Ni49	0.49101	0.40386	0.04070
Ni50	0.35217	0.55208	0.12916
Ni51	0.20929	0.36424	0.21841
Ni52	0.06641	0.50611	0.30750
Ni53	0.15203	0.37379	0.02275
Ni54	0.01319	0.52200	0.11122
Ni55	0.36863	0.33003	0.19754
Ni56	0.22359	0.46828	0.29371
Ni57	0.35816	0.40386	0.04070
Ni58	0.21932	0.55208	0.12916
Ni59	0.07967	0.36409	0.21853
Ni60	0.43703	0.50582	0.30656
Ni61	0.66448	0.59364	0.05450
Ni62	0.52565	0.40852	0.14296
Ni63	0.88365	0.55179	0.23165
Ni64	0.74491	0.35486	0.31241

Ni65	0.96936	0.59364	0.05450
Ni66	0.83052	0.40852	0.14296
Ni67	0.68606	0.55099	0.23010
Ni68	0.52983	0.35243	0.31213
Ni69	0.99101	0.40386	0.04070
Ni70	0.85217	0.55208	0.12916
Ni71	0.70967	0.36415	0.21833
Ni72	0.56171	0.50311	0.30546
Ni73	0.65203	0.37379	0.02275
Ni74	0.51319	0.52200	0.11122
Ni75	0.87087	0.33164	0.19777
Ni76	0.72481	0.47011	0.29157
Ni77	0.85816	0.40386	0.04070
Ni78	0.71932	0.55208	0.12916
Ni79	0.57953	0.36340	0.21825
Ni80	0.93890	0.50561	0.30662
Ni81	0.16448	0.92698	0.05450
Ni82	0.02565	0.74186	0.14296
Ni83	0.38332	0.88566	0.23238
Ni84	0.24505	0.68736	0.31238
Ni85	0.46936	0.92698	0.05450
Ni86	0.33052	0.74186	0.14296
Ni87	0.18882	0.88574	0.23251
Ni88	0.02969	0.68568	0.31213
Ni89	0.49101	0.73719	0.04070

Ni90	0.35217	0.88541	0.12916
Ni91	0.21052	0.69832	0.21832
Ni92	0.06446	0.83811	0.30786
Ni93	0.15203	0.70712	0.02275
Ni94	0.01319	0.85534	0.11122
Ni95	0.37055	0.66479	0.19790
Ni96	0.22372	0.80218	0.29373
Ni97	0.35816	0.73719	0.04070
Ni98	0.21932	0.88541	0.12916
Ni99	0.08048	0.69814	0.21831
Ni100	0.43770	0.83930	0.30702
Ni101	0.66448	0.92698	0.05450
Ni102	0.52565	0.74186	0.14296
Ni103	0.88301	0.88530	0.23225
Ni104	0.74149	0.68371	0.31041
Ni105	0.96936	0.92698	0.05450
Ni106	0.83052	0.74186	0.14296
Ni107	0.69027	0.88668	0.23283
Ni108	0.53024	0.68667	0.31268
Ni109	0.99101	0.73719	0.04070
Ni110	0.85217	0.88541	0.12916
Ni111	0.70929	0.69827	0.21782
Ni112	0.56551	0.83957	0.30723
Ni113	0.65203	0.70712	0.02275
Ni114	0.51319	0.85534	0.11122

Ni115	0.86952	0.66412	0.19918
Ni116	0.72333	0.80183	0.29386
Ni117	0.85816	0.73719	0.04070
Ni118	0.71932	0.88541	0.12916
Ni119	0.58007	0.69822	0.21822
Ni120	0.93595	0.83792	0.30663
Mn1	0.29794	0.23500	0.03939
Mn2	0.15910	0.04988	0.12786
Mn3	0.01557	0.19095	0.21657
Mn4	0.36803	0.99475	0.30578
Mn5	0.79794	0.23500	0.03939
Mn6	0.65910	0.04988	0.12786
Mn7	0.51579	0.19067	0.21630
Mn8	0.86753	0.99446	0.30569
Mn9	0.29794	0.56833	0.03939
Mn10	0.15910	0.38322	0.12786
Mn11	0.01697	0.52476	0.21601
Mn12	0.36627	0.32622	0.30466
Mn13	0.79794	0.56833	0.03939
Mn14	0.65910	0.38322	0.12786
Mn15	0.51454	0.52394	0.21533
Mn16	0.86826	0.32778	0.30548
Mn17	0.29794	0.90167	0.03939
Mn18	0.15910	0.71655	0.12786
Mn19	0.01515	0.85658	0.21637

Mn20	0.36875	0.66141	0.30538
Mn21	0.79794	0.90167	0.03939
Mn22	0.65910	0.71655	0.12786
Mn23	0.51614	0.85802	0.21617
Mn24	0.86974	0.66235	0.32691
P1	0.02354	0.20247	0.01998
P2	0.38470	0.01735	0.10844
P3	0.24299	0.16187	0.19903
P4	0.09824	0.30175	0.29299
P5	0.28746	0.10991	0.06421
P6	0.14862	0.25812	0.15267
P7	0.00594	0.06841	0.24187
P8	0.36415	0.20681	0.32910
P9	0.12079	0.10991	0.06421
P10	0.48195	0.25812	0.15267
P11	0.34059	0.06779	0.24168
P12	0.19101	0.20824	0.32889
P13	0.52354	0.20247	0.01998
P14	0.88470	0.01735	0.10844
P15	0.74388	0.16275	0.19902
P16	0.59866	0.30179	0.29237
P17	0.78746	0.10991	0.06421
P18	0.64862	0.25812	0.15267
P19	0.50581	0.06830	0.24175
P20	0.86454	0.20763	0.32942

P21	0.62079	0.10991	0.06421
P22	0.98195	0.25812	0.15267
P23	0.84048	0.06780	0.24186
P24	0.69308	0.21044	0.32927
P25	0.02354	0.53580	0.01998
P26	0.38470	0.35068	0.10844
P27	0.24357	0.49605	0.19868
P28	0.09942	0.63530	0.29210
P29	0.28746	0.44324	0.06421
P30	0.14862	0.59146	0.15267
P31	0.00568	0.40176	0.24166
P32	0.36642	0.54257	0.32946
P33	0.12079	0.44324	0.06421
P34	0.48195	0.59146	0.15267
P35	0.34077	0.40228	0.24078
P36	0.19291	0.54313	0.32879
P37	0.52354	0.53580	0.01998
P38	0.88470	0.35068	0.10844
P39	0.74364	0.49623	0.19847
P40	0.59771	0.63478	0.29130
P41	0.78746	0.44324	0.06421
P42	0.64862	0.59146	0.15267
P43	0.50306	0.39896	0.24011
P44	0.86496	0.53895	0.32768
P45	0.62079	0.44324	0.06421

P46	0.98195	0.59146	0.15267
P47	0.84133	0.40239	0.24074
P48	0.68766	0.53841	0.32488
P49	0.02354	0.86913	0.01998
P50	0.38470	0.68402	0.10844
P51	0.24381	0.82924	0.19896
P52	0.09708	0.96676	0.29219
P53	0.28746	0.77658	0.06421
P54	0.14862	0.92479	0.15267
P55	0.00459	0.73458	0.24215
P56	0.36572	0.87513	0.32936
P57	0.12079	0.77658	0.06421
P58	0.48195	0.92479	0.15267
P59	0.34178	0.73592	0.24095
P60	0.19126	0.87544	0.32889
P61	0.52354	0.86913	0.01998
P62	0.88470	0.68402	0.10844
P63	0.74402	0.82982	0.19891
P64	0.59823	0.96838	0.29233
P65	0.78746	0.77658	0.06421
P66	0.64862	0.92479	0.15267
P67	0.50568	0.73522	0.24139
P68	0.86505	0.87458	0.32908
P69	0.62079	0.77658	0.06421
P70	0.98195	0.92479	0.15267

P71	0.83957	0.73477	0.24080
P72	0.69130	0.87556	0.32920
C1	0.58663	0.51613	0.45887
C2	0.74914	0.65082	0.45297
C3	0.71059	0.68264	0.46624
C4	0.60664	0.59663	0.46932
C5	0.49146	0.40704	0.45213
C6	0.84519	0.70777	0.43387
O1	0.67170	0.54720	0.44941
O2	0.40689	0.38174	0.46478
O3	0.86853	0.67314	0.41013
H1	0.75398	0.76046	0.47039
H2	0.55147	0.59235	0.47627
H3	0.49298	0.36129	0.47435
H4	0.48452	0.38855	0.40938
H5	0.90108	0.78983	0.43895
H6	0.39689	0.37396	0.50325

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