

Supporting Information

Tandem Catalyzing the Hydrodeoxygenation of 5-Hydroxymethylfurfural over Ni₃Fe Intermetallic Supported Pt Single-Atom Site Catalyst

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1. Experimental Section

1.1 Materials

Chloroplatinic acid hexahydrate (99.9%), iron (III) nitrate nonahydrate (99%) and nickel (II) nitrate hexahydrate (99%) from Alfa Aesar; Sodium hydroxide from Beijing Chemical Reagents, P.R. China; 5-hydroxymethylfurfural (5-HMF, 97%) from TCI; Toluene (99%) and tetrahydrofuran (THF, 99%) from Theromofisher. All the reagents were used without further purification.

1.2 Synthesis of Pt₁/Ni₃Fe, Ni₃Fe IMCs and Pt₁/NiFe-LDHs

The Pt₁/Ni₃Fe IMC was prepared through an LDH-precursor method, including the co-precipitation process¹ and thermal reduction treatment. Firstly, solution A was prepared with Ni(NO₃)₂·6H₂O (16 mmol) and Fe(NO₃)₃·9H₂O (5.33 mmol) dissolved in deionized water (20 ml). Then, solution B with 34.15 mmol NaOH and 0.1 mmol H₂PtCl₆ in 20 ml deionized water was prepared. Afterwards, 40 ml of deionized water and a magnetic rotor in a beaker (solution C) was placed on a magnetic stirrer under a rotation speed of 600 rpm. Solution A and B were dropwise and simultaneously added to C, during which the pH indicator was used to adjust the solution maintain in pH 8.5. It is worth noting that the deionized water should be boiled before using to partially remove the dissolved CO₂. After another 12 h of stirring, the brown precipitate was collected and washed by high-speed centrifugation for six times (ethanol and water, alternately). After 60 °C drying for at least 4 h and grind, PtCl₆²⁻ adsorbed NiFe-LDHs (PtCl₆²⁻/NiFe-LDHs) were obtained. Then, the as-prepared PtCl₆²⁻/NiFe-LDHs were thermal reduced at 300 °C under the 5% H₂/N₂ atmosphere with a 2 °C min⁻¹ of heating rate for 3 h. Finally, Pt₁/Ni₃Fe IMC was obtained and collected for further use.

Ni₃Fe IMC was prepared with a similar synthetic procedure without H₂PtCl₆ addition. Pt₁/NiFe-LDHs were also synthesized with a similar method with Pt₁/Ni₃Fe IMC, except that the as-prepared PtCl₆²⁻/NiFe-LDHs were thermal reduced at 100 °C for 2 h under 5% H₂/N₂.

1.3 Synthesis of Pt NPs/Ni₃Fe IMC

Pt nanoparticles (Pt NPs) were firstly prepared according to the previously reported method.² 133 mg PVP (M_w=30,000) and 49.2 mg dihydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O) were dissolved in 180 ml methanol in a 500 mL flask, forming a homogenous solution. Then, the solution was heated and refluxing at 80°C for 3h under stirring. After reaction, the methanol solvent was removed by rotary evaporator and the Pt NPs were collected and washed by acetone using centrifugation. Subsequently, 5 mg of the resulting Pt NPs and 195 mg Ni₃Fe IMC were dispersed in 20 ml ethanol solvent under stirring for 6 h. Then, the precipitate was collected and dried (60 °C, 4 h). To remove the surfactants (PVP) adsorbed on Pt NPs surface, the compounds were calcined at 200°C for 4 h under air atmosphere, and further thermal reduced at 300 °C under 5% H₂/N₂ atmosphere for 3 h. The final product (Pt NPs/Ni₃Fe IMC) was collected without any treatment for further characterizations and tests.

1.4 Catalysis testing

The reaction of producing DMF from 5-HMF was performed in a 100 ml stainless-steel autoclave with mechanical stirring (Parr, 5500). In a typical run, the loading of 5-HMF was 0.5 wt.% in 60 ml THF solvent. The catalyst dosage was introduced according to the 5-HMF/Pt molar ratio of 100/1 for Pt₁/Ni₃Fe IMC (196.0 mg), Pt NPs/Ni₃Fe IMC (184.6 mg) and Pt₁/NiFe-LDHs (316.7 mg). For Ni₃Fe IMC, the mass dosage was the same as Pt₁/Ni₃Fe IMC for comparison. After the solution and catalyst were transferred into the autoclave, it was sealed and purged with N₂ three times before being pressurized with H₂ to 1.0 MPa and initiating the temperature programmer. The stirring speed was set to 600 rpm. After the reaction, the catalyst was separated by simple filtration. The concentrations of products were analyzed by gas-chromatography (Trace-1300) from Thermo Fisher equipped with flame-ionization detector (FID) and high-temperature capillary column (DB-1, 60 m × 0.32 mm × 0.5 μm), in which toluene was used as the internal standard. Further

confirmation of the products was performed by GC-MS (Agilent 7890B-5977A) with a nonpolar HP-5MS column (30 m × 0.32 mm × 0.25 μm). For the cyclic stability evaluation, the catalyst was collected and washed by centrifugation and dried for the recycled tests.

The yield of products (**Y**), conversion of 5-HMF (**X**) and Selectivity of DMF (**S**) are defined as follows:

$$Yield (mol\%) = \left(\frac{n_{product,t_i}}{n_{HMF,t_0}} \right) \times 100\%$$

$$5-HMF \text{ conversion } (mol\%) = \frac{n_{HMF,t_0} - n_{HMF,t_i}}{n_{HMF,t_0}} \times 100\%$$

$$Selectivity (mol\%) = \left(\frac{n_{product,t_i}}{n_{HMF,t_0} - n_{HMF,t_i}} \right) \times 100\%$$

1.5 Characterizations

The morphologies were tested on Hitachi H-800 TEM (100 kV) and FEI Tecnai G2 F20 S-Twin HRTEM (200 kV). The crystal phases were measured by a Rigaku RU-200b X-ray powder diffractometer (XRD, Cu K α radiation with λ of 1.5406 Å). The AC-HAADF-STEM results were measured by an ARM-200CF (JEOL, Tokyo, Japan) transmission electron microscope (300 keV). The Pt concentrations were collected on ICP-OES measurement. XPS results were obtained by the Thermo Fisher Scientific ESCALAB 250Xi XPS System. XAFS tests were performed at BL14W1 beamline in Shanghai Synchrotron Radiation Facility (SSRF).

1.6 XAFS measurements and analysis details

All XAFS data were measured at BL14W1 beamline in Shanghai Synchrotron Radiation Facility. Pt L_3 -edge data of Pt₁/Ni₃Fe IMC were measured in fluorescence mode with a Lytle detector full of argon gas. Fe and Ni K -edge data of Pt₁/Ni₃Fe IMC were measured in transmission mode. Metal foils were carried out in transmission mode for energy calibration.

EXAFS data were processed according to the standard procedures using the

ATHENA module. The k^2 -weighted $\chi(k)$ data of Pt L_3 -edge and k^3 -weighted $\chi(k)$ data of Fe and Ni K -edge were obtained by subtracting the post-edge background. Subsequently, the data were Fourier transformed to real (R) space using a hanning windows ($d_k = 1.0 \text{ \AA}^{-1}$) to separate the EXAFS contributions from different coordination shells. Least-squares curve fitting was performed with the ARTEMIS module to obtain the local structural parameters around absorption atoms.³

This equation was used in EXAFS data fitting:

$$\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k)}{k R_j^2} \exp[-2k^2 \sigma_j^2] \exp\left[\frac{-2R_j}{\lambda(k)}\right] \sin[2kR_j + \phi_j(k)]$$

N_j : coordination number in the j^{th} atomic shell.

S_0^2 : amplitude reduction factor.

$F_j(k)$: effective curved-wave backscattering amplitude.

R_j : the distance between the absorbing atom and the atoms in the j^{th} atomic shell (backscatterer).

λ : the mean free path (\AA).

$\phi_j(k)$: the phase shift.

σ_j : the Debye-Waller parameter of the j^{th} atomic shell.

The functions $F_j(k)$, λ and $\phi_j(k)$ were calculated with the *ab initio* code FEFF8.4.⁴

1.7 Computational details

Based on the periodic spin-polarized density functional theory, all the simulations are performed using the Vienna *ab initio* simulation package (VASP),⁵ and the exchange-correlation interactions are calculated with Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA),⁶ and atomic cores and valence electrons were treated with the projector augmented wave (PAW) pseudopotentials.⁷ A cutoff energy of 400 eV is used in plane-wave basic sets, and the Monkhorst-Pack K-point sampling is generated with a $2 \times 2 \times 1$ grid. Van der Waals interactions are considered by dispersion corrections based on the DFT + D3 method of Grimme,⁸ and the dipole corrections were applied in the simulations. For electronic self-consistency calculation, the convergence parameter is 10^{-4} eV in total energy with a Methfessel-

Paxton smearing of 0.1 eV, and the geometric optimization was performed until the force on each atom was lower than 0.02 eV/Å. The transition state (TS) between the known initial and final states are predicted by the climbing image nudged elastic band (CI-NEB)⁹ as well as the dimer method,¹⁰ and the force in TS is converged to 0.05 eV/Å. Ni₃Fe alloy was constructed by replacing Ni atoms in Ni unit cells with Fe in the ratio of 3:1. We cleaved (111) surface of Ni₃Fe alloy with three atomic layers and then expanded a 3 × 3 × 1 supercell containing 27 Fe and 81 Ni atoms. Pt/Ni₃Fe was modeled by replacing a single Ni atom with Pt on the surface of Ni₃Fe (111). Pt (111) surface was cleaved from pristine Pt metal, containing four-atomic layers. The bottom layer of Ni₃Fe (111) and Pt₁/Ni₃Fe (111) and the bottom two layers of Pt (111) were fixed during the simulations. In model construction, a gap spacing of 20 Å is added to the adjacent slabs to ignore the repeating-layers interactions.

2. Supplementary Figures, Scheme and Tables

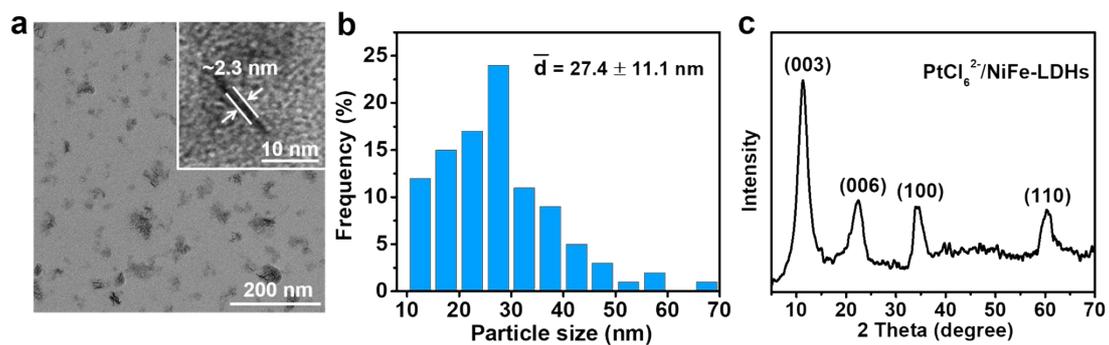


Figure S1. (a) TEM image, (b) particle size histogram obtained from TEM analysis and (c) XRD pattern of PtCl₆²⁻/NiFe-LDHs.

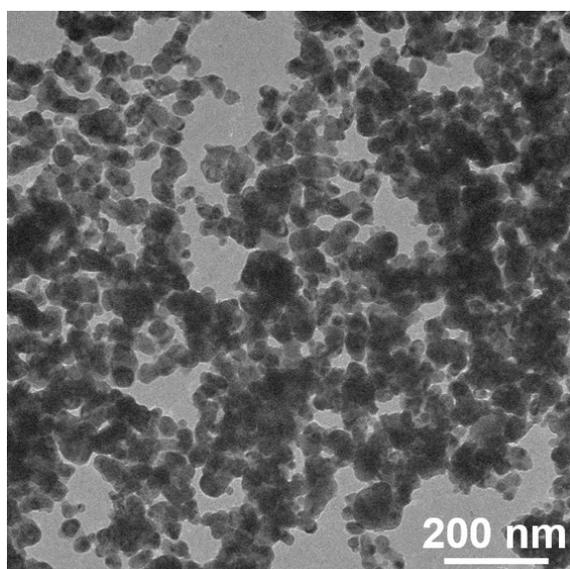


Figure S2. TEM image of Pt₁/Ni₃Fe IMC.

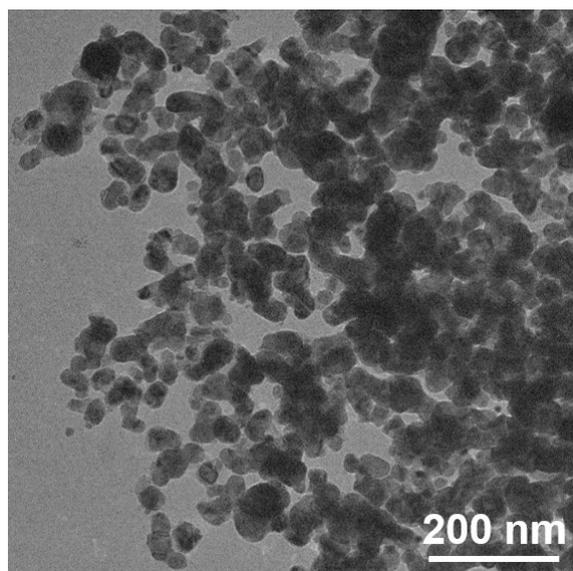


Figure S3. TEM image of the Ni₃Fe IMC catalyst.

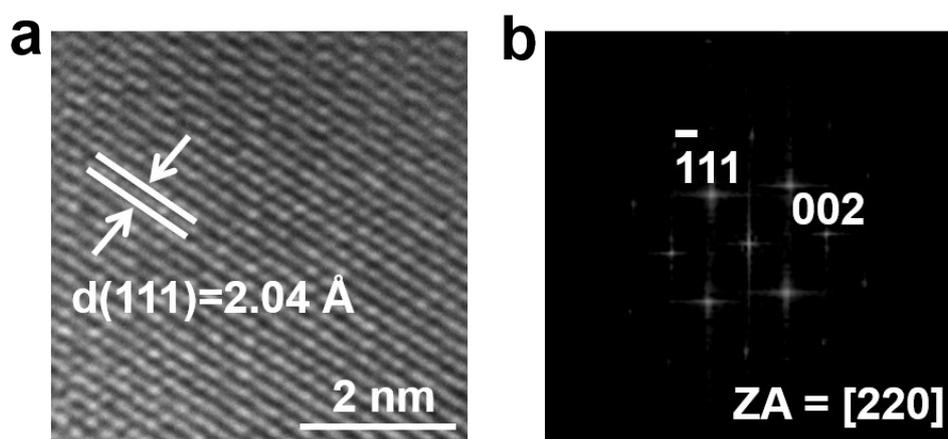


Figure S4. HRTEM image (a) and FFT pattern (b) of Pt₁/Ni₃Fe IMC nanocrystal oriented along the [220] zone axes.

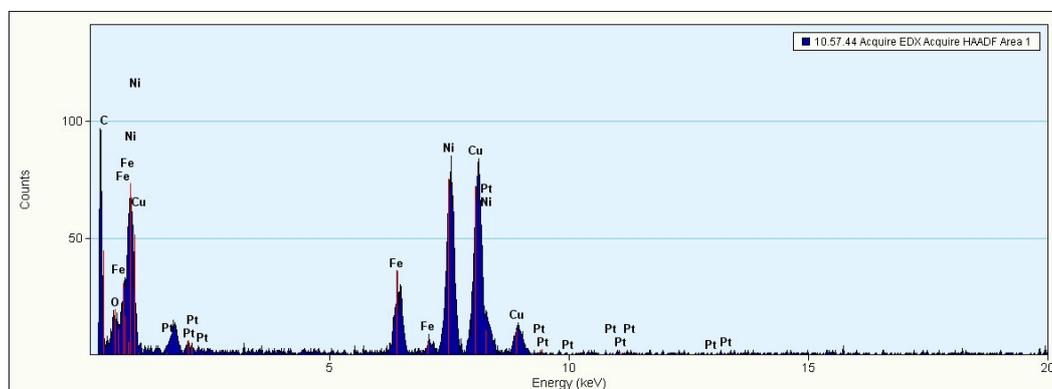


Figure S5. EDXA pattern of Pt₁/Ni₃Fe IMC.

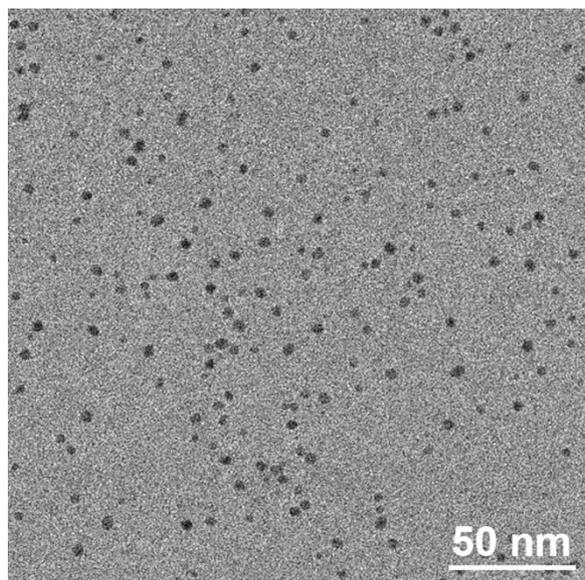


Figure S6. TEM image of the as-prepared Pt nanoparticles with an average diameter of ~ 5 nm.

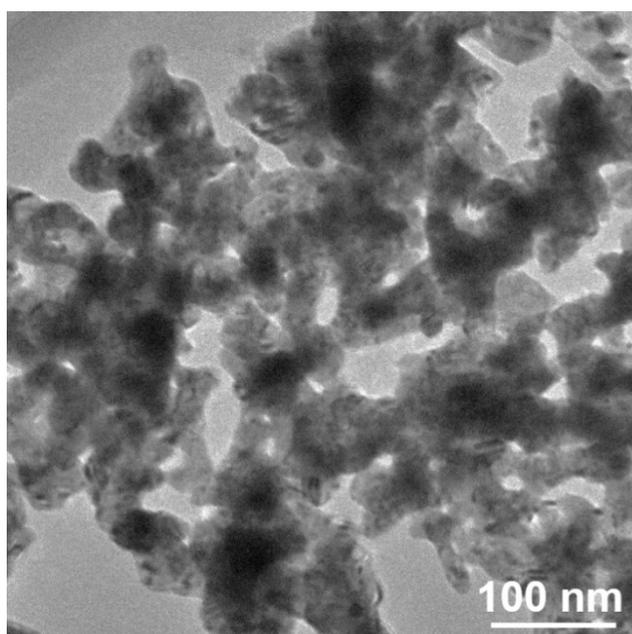


Figure S7. TEM image of the Pt NPs/ Ni_3Fe IMC catalyst. It can be observed that the high-contrast Pt nanoparticles are uniformly dispersed on Ni_3Fe IMC support.

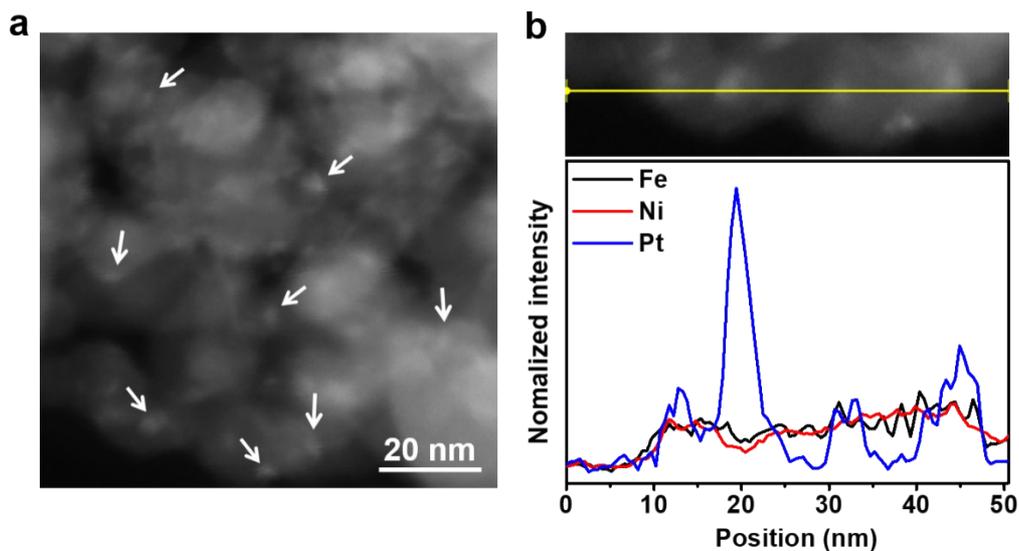


Figure S8. (a) HAADF-STEM image of the Pt NPs/ Ni_3Fe IMC catalyst; (b) EDS line scan profile of Fe (black), Ni (red) and Pt (blue) along the yellow line. The brighter Pt nanoparticles can be observed in the HAADF-STEM image. The corresponding Pt peaks in EDS line scan profile along the yellow line further confirms the Pt nanoparticles loading on the Ni_3Fe IMC support.

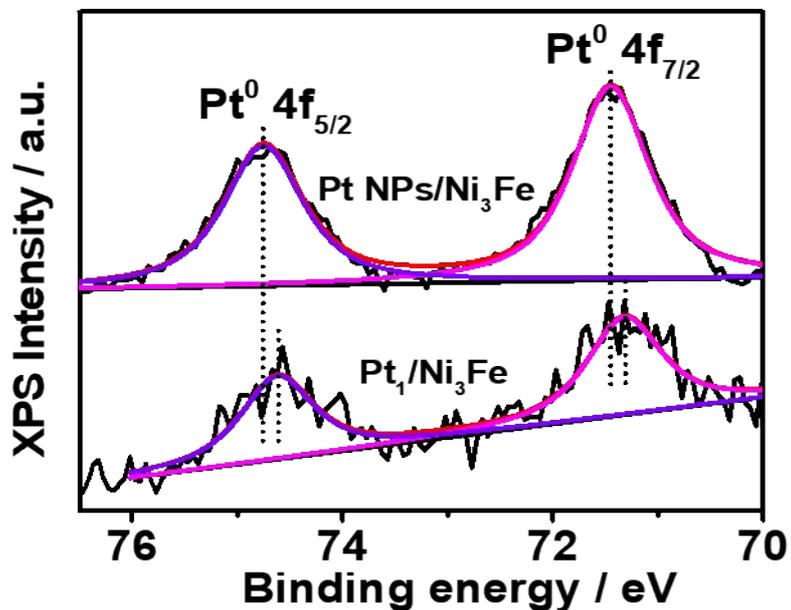


Figure S9. Pt 4f XPS spectra of the $\text{Pt}_1/\text{Ni}_3\text{Fe}$ IMC and Pt NPs/ Ni_3Fe IMC.

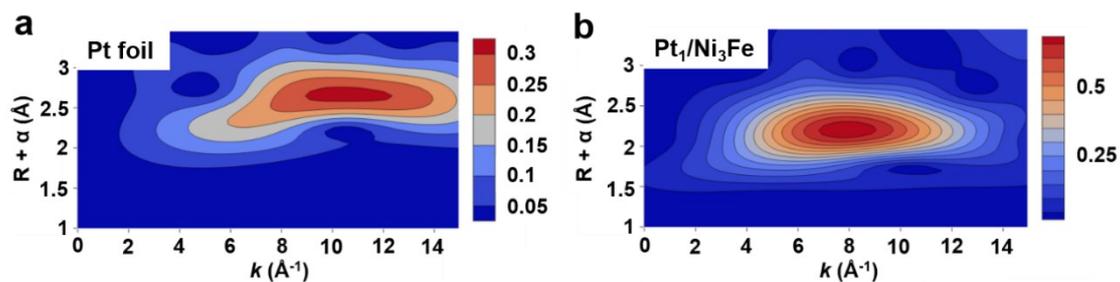


Figure S10. WT-EXAFS of Pt foil (a) and Pt₁/Ni₃Fe IMCs (b).

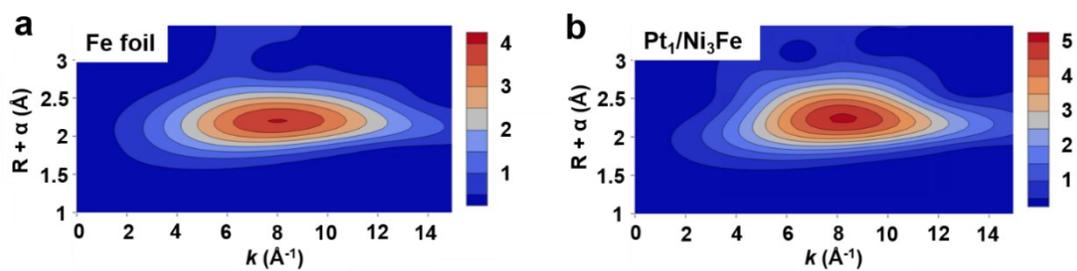


Figure S11. WT-EXAFS of Fe foil (a) and Pt₁/Ni₃Fe IMCs (b).

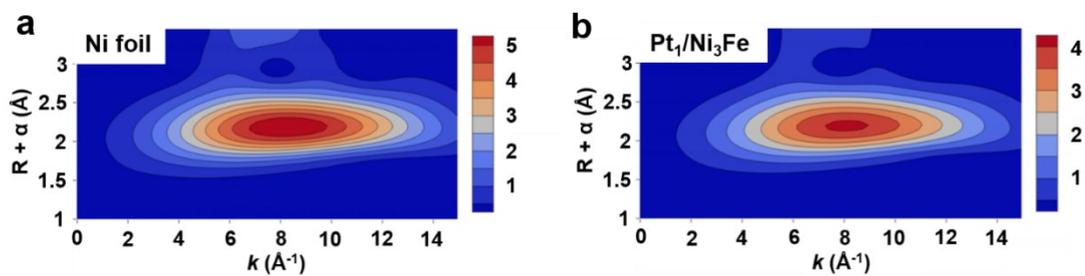


Figure S12. WT-EXAFS of Ni foil (a) and Pt₁/Ni₃Fe IMC (b).

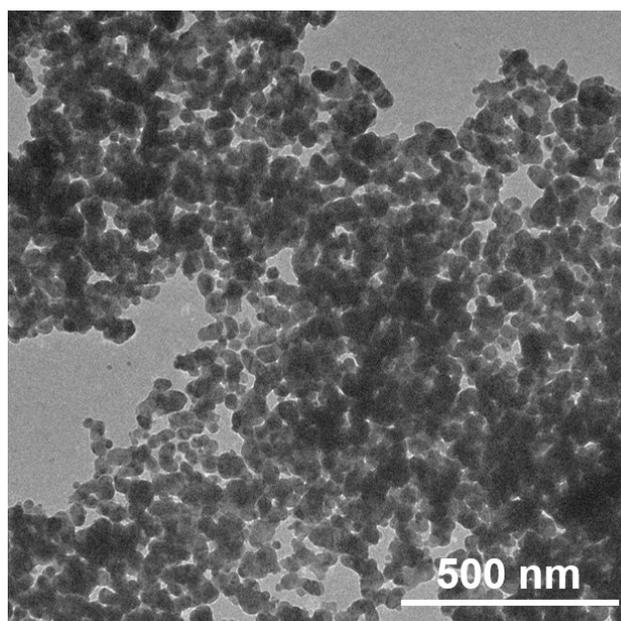


Figure S13. TEM image of Pt₁/Ni₃Fe IMC after cycling tests.

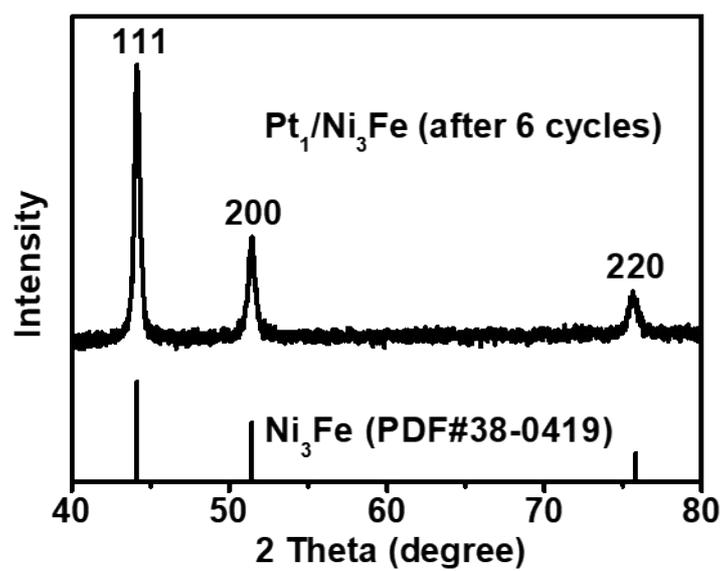


Figure S14. XRD pattern of Pt₁/Ni₃Fe IMC after cycling tests.

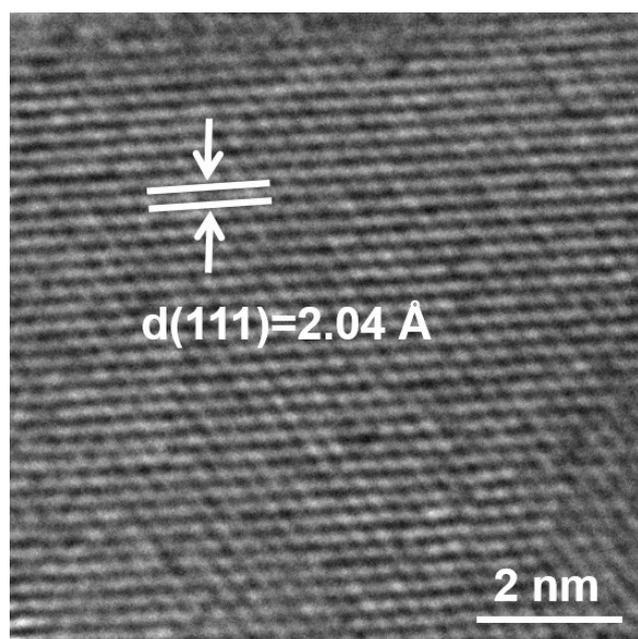


Figure S15. HRTEM image of Pt₁/Ni₃Fe IMC after cycling tests.

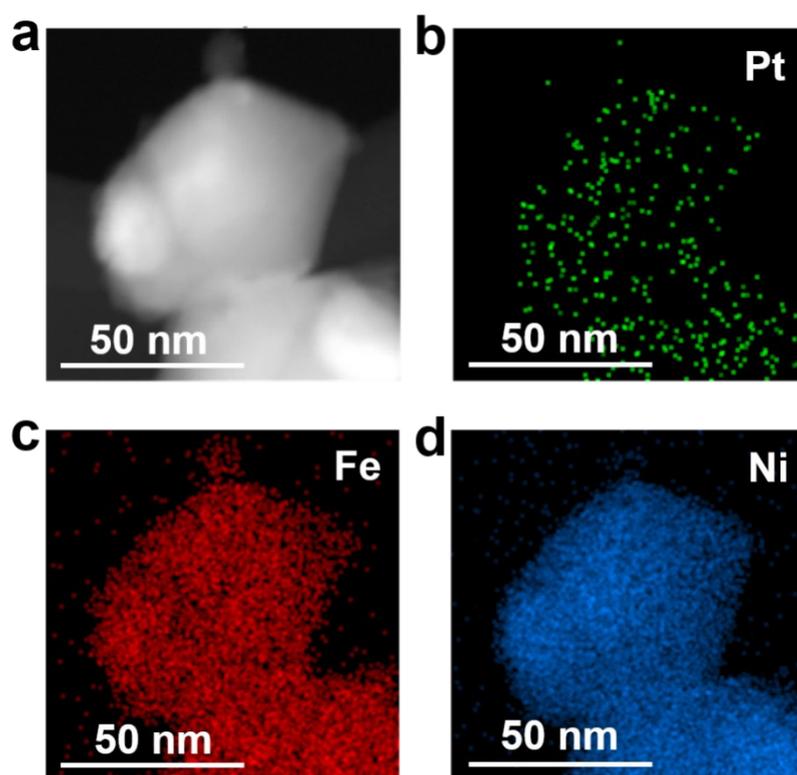


Figure S16. HAADF-STEM and corresponding element mapping images showing the distribution of Pt (green), Fe (red) and Ni (blue) of the Pt₁/Ni₃Fe IMC catalyst after cycling tests.

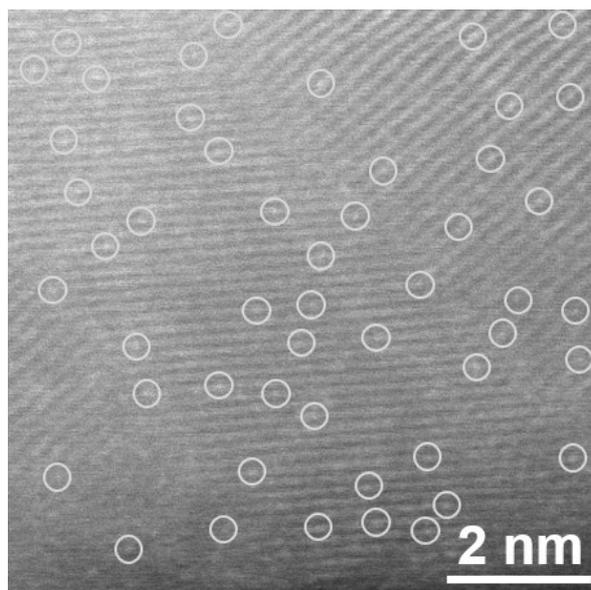


Figure S17. AC-HAADF-STEM image of the Pt₁/Ni₃Fe IMC catalyst after cycling tests.

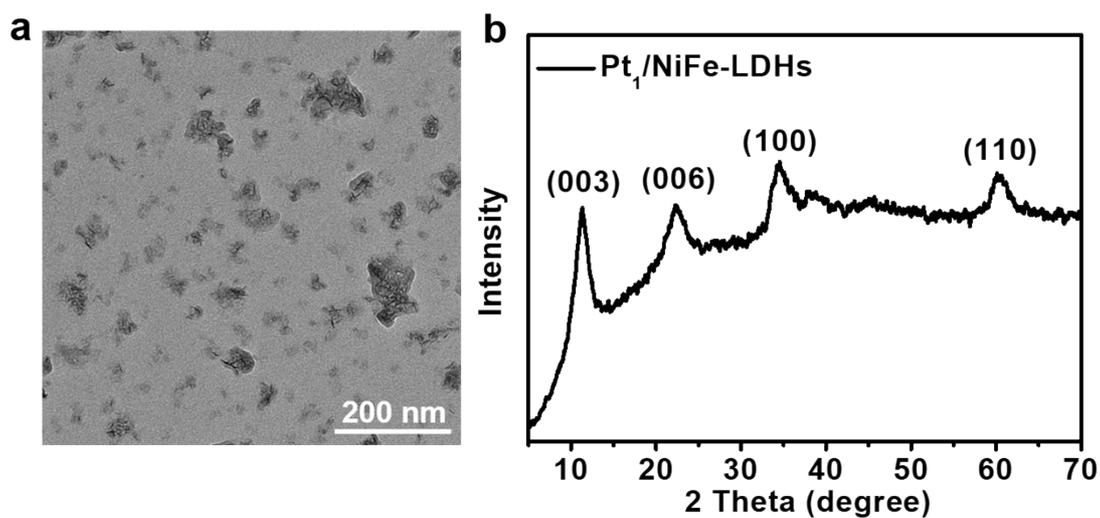


Figure S18. TEM image (a) and XRD pattern (b) of Pt₁/NiFe-LDHs. As revealed by the TEM image, the obtained Pt₁/NiFe-LDHs retain a nanosheet morphology. The XRD pattern of Pt₁/NiFe-LDHs present the characteristic diffraction peaks of LDHs around 11.5, 22.5, 34.5° and 60°, which are originate from the in-plane (003), (006), (100) and (110) reflections, confirming that the two-dimensional LDH nanosheet structure was well preserved.

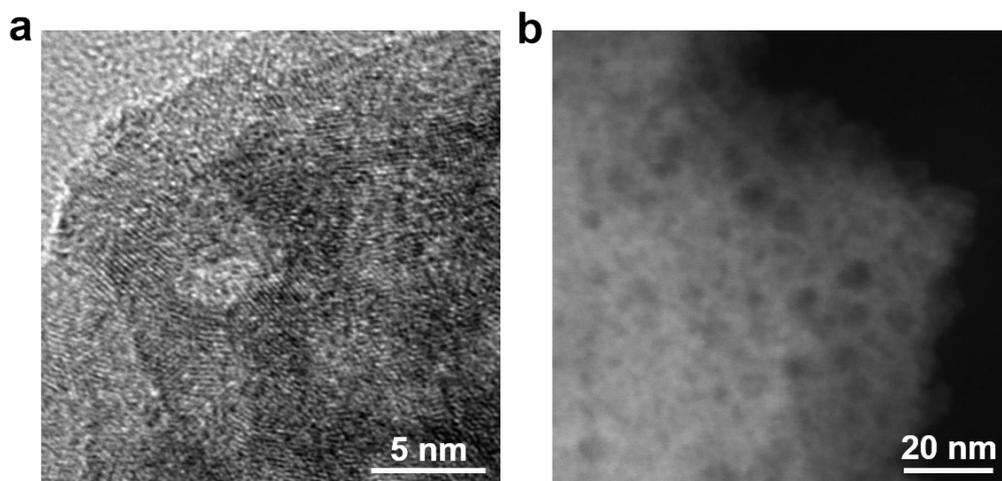


Figure S19. HRTEM (a) and HAADF-STEM (b) images of the Pt₁/NiFe-LDHs catalyst. It shows that the surface of Pt₁/NiFe-LDHs is rough and mesoporous. Moreover, no obvious brighter Pt nanoparticles can be observed in the HAADF-STEM image.

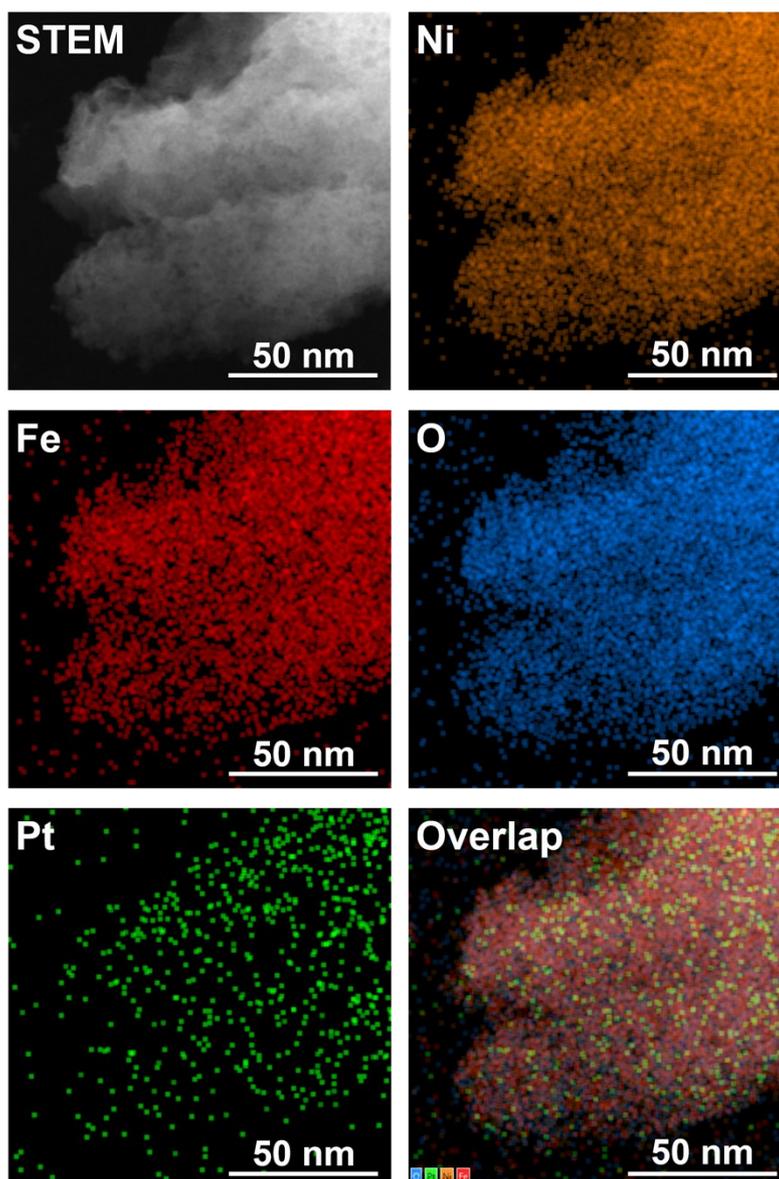


Figure S20. HAADF-STEM and corresponding element mapping images showing the distribution of Ni (orange), Fe (red), O (blue) and Pt (green) of the Pt₁/NiFe-LDHs catalyst. It reveals that Ni, Fe, O and Pt elements are homogeneously distributed without observable Pt nanoparticles.

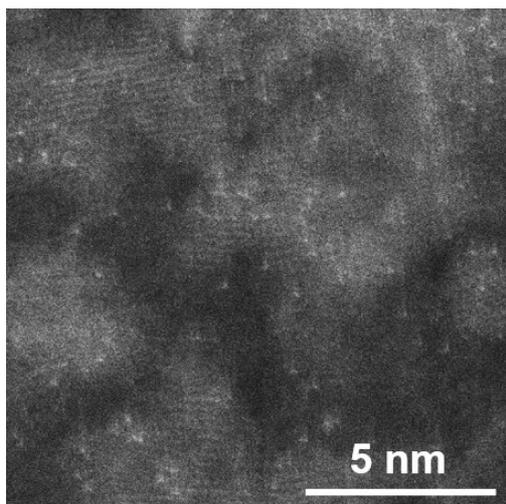


Figure S21. AC-HAADF-STEM image of the Pt₁/NiFe-LDHs catalyst. Many isolated bright dots can be observed. Combining the TEM, HRTEM, HAADF-STEM, EDXA and AC-HAADF-STEM tests, it demonstrates that the isolated Pt atoms are uniformly anchored on the surface of NiFe-LDHs nanosheets.

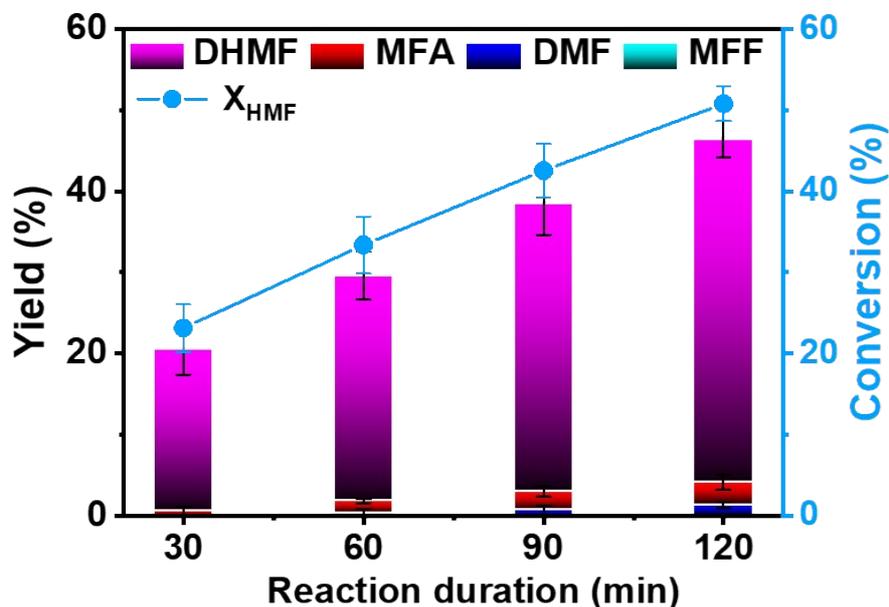


Figure S22. 5-HMF conversion and product yields as a function of reaction time over Pt₁/NiFe-LDHs. Reaction conditions: The reaction was run at 160 °C and 1.0 MPa H₂. The loading of 5-HMF was 0.5 wt.% in 60 ml THF solvent. The catalyst dosage was introduced according to the 5-HMF/Pt molar ratio of 100/1 for Pt₁/NiFe-LDHs (316.7 mg). All the error bars were evaluated from >3 times of independent measurements.

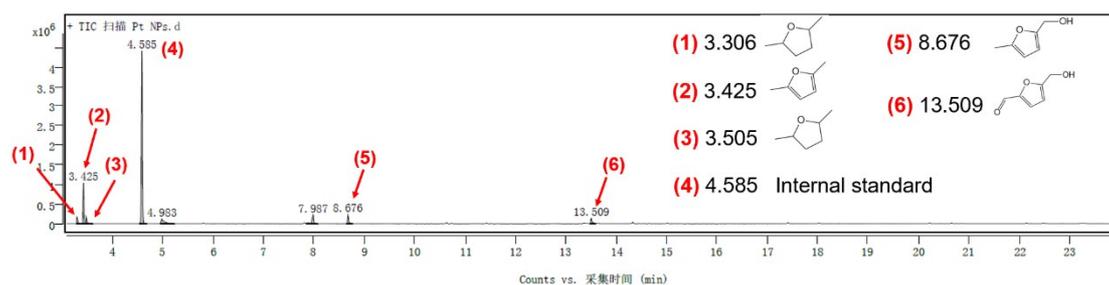


Figure S23. GC-MS analysis of the Pt NPs/Ni₃Fe IMC catalyzed hydrodeoxygenation reaction. Reaction conditions: The reaction was run at 160 °C and 1.0 MPa H₂ for 120 min with toluene as internal standard. The loading of 5-HMF was 0.5 wt.% in 60 ml THF solvent. The catalyst dosage was introduced according to the 5-HMF/Pt molar ratio of 100/1 for Pt NPs/Ni₃Fe IMC (184.6 mg).

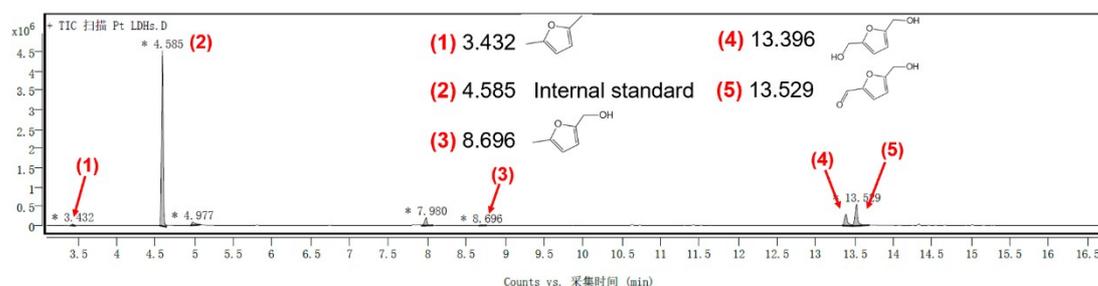


Figure S24. GC-MS analysis of the Pt₁/NiFe-LDHs catalyzed hydrodeoxygenation reaction. Reaction conditions: The reaction was run at 160 °C and 1.0 MPa H₂ for 120 min with toluene as internal standard. The loading of 5-HMF was 0.5 wt.% in 60 ml THF solvent. The catalyst dosage was introduced according to the 5-HMF/Pt molar ratio of 100/1 for Pt₁/NiFe-LDHs (316.7 mg).

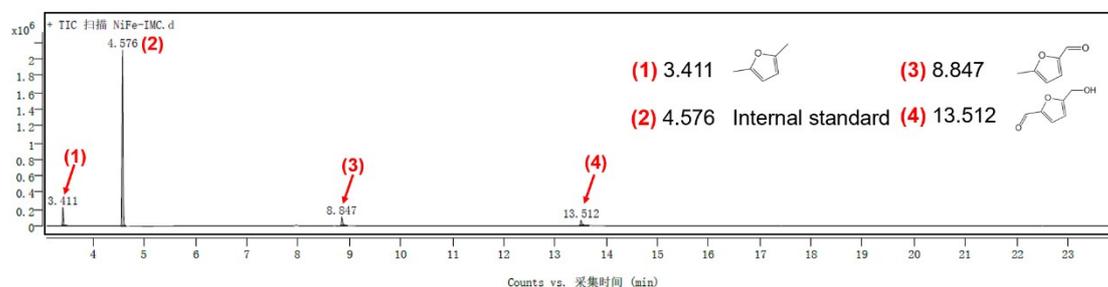


Figure S25. GC-MS analysis of the Ni₃Fe IMC catalyzed hydrodeoxygenation reaction. Reaction conditions: The reaction was run at 160 °C and 1.0 MPa H₂ for 120 min with toluene as internal standard. The loading of 5-HMF was 0.5 wt.% in 60 ml THF solvent. The Ni₃Fe IMC catalyst dosage was 196.0 mg.

Table S1. Pt contents in Pt₁/Ni₃Fe IMC analyzed by ICP-OES, EDX and XPS techniques.

Analytical techniques		ICP-OES	EDX	XPS
Pt content	wt. %	2.10	2.19	5.12
	at. %	0.64	0.66	1.58

Table S2. Structural parameters of the Pt₁/Ni₃Fe IMCs and reference samples extracted from the Pt *L*₃-edge EXAFS fitting. ($S_0^2=0.92$)^a.

Samples	Atomic scatter	No. of atoms (CN) ^b	Interatomic distance (Å) ^c	Debye-Waller factor ($10^{-3} \times \text{Å}^2$) ^d	ΔE_0 (eV) ^e	<i>R</i> factor
Pt foil	Pt-Pt	12	2.76±0.03	5.0±0.3	7.1	0.003
Pt ₁ /Ni ₃ Fe IMCs	Pt-Ni/Fe	10.6±2.1	2.54±0.03	4.7±0.3	6.0	0.001

^a) S_0^2 was fixed as 0.92 during EXAFS fitting, based on the known structure of Pt foil.

^b) CN is the coordination number.

^c) Interatomic distance is the bond length between Ir central atoms and surrounding coordination atoms.

^d) Debye-Waller factor is a measure of thermal and static disorder in absorber-scattering distances.

^e) ΔE_0 is the difference between the zero kinetic energy value of the sample and that of the theoretical model.

Table S3. Structural parameters of Pt₁/Ni₃Fe IMCs and reference sample extracted from the Fe *K*-edge EXAFS fitting. ($S_0^2=0.73$)^a.

Samples	Atomic scatter	No. of atoms (CN) ^b	Interatomic distance (Å) ^c	Debye-Waller factor ($10^{-3} \times \text{Å}^2$) ^d	ΔE_0 (eV) ^e	<i>R</i> factor
Fe foil	Fe-Fe	8	2.47±0.03	4.8±0.4	6.2	0.001
	Fe-Fe	6	2.84±0.03	6.2±0.7	3.2	
Pt ₁ /Ni ₃ Fe IMCs	Fe-Ni/Fe	10.7±2.1	2.50±0.03	7.1±0.3	6.8	0.001

^a) S_0^2 was fixed as 0.73 during EXAFS fitting, based on the known structure of Fe foil.

^b) CN is the coordination number.

^c) Interatomic distance is the bond length between Ir central atoms and surrounding coordination atoms.

^d) Debye-Waller factor is a measure of thermal and static disorder in absorber-scattering distances.

^e) ΔE_0 is the difference between the zero kinetic energy value of the sample and that of the theoretical model.

Table S4. Structural parameters of the Pt₁/Ni₃Fe IMCs and reference samples extracted from the Ni *K*-edge EXAFS fitting. ($S_0^2=0.76$)^a.

Samples	Atomic scatter	No. of atoms (CN) ^b	Interatomic distance (Å) ^c	Debye-Waller factor ($10^{-3} \times \text{Å}^2$) ^d	ΔE_0 (eV) ^e	<i>R</i> factor
Ni foil	Ni-Ni	12	2.48±0.03	6.1±0.3	5.7	0.001
Pt ₁ /Ni ₃ Fe IMCs	Ni-Ni/Fe	10.1	2.50±0.03	6.8±0.2	5.1	0.001

^a) S_0^2 was fixed as 0.76 during EXAFS fitting, based on the known structure of Ni foil.

^b) CN is the coordination number.

^c) Interatomic distance is the bond length between Ir central atoms and surrounding coordination atoms.

^d) Debye-Waller factor is a measure of thermal and static disorder in absorber-scattering distances.

^e) ΔE_0 is the difference between the zero kinetic energy value of the sample and that of the theoretical model.

Table S5. Hydrodeoxygenation of 5-HMF to DMF*.

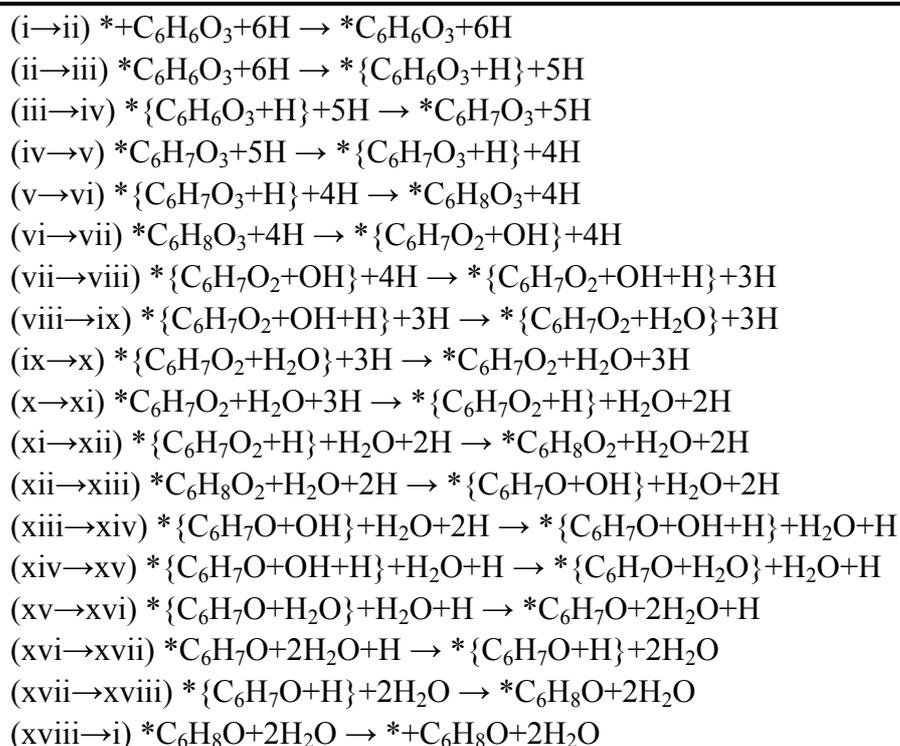
Entry	Catalysts	Time (min)	Con (%)	Yield (%)				
				DMF	MFA	MF	DHMF	Others
1	Pt ₁ /Ni ₃ Fe	90	99.0	98.1	0.5	-	-	-
2	Pt NPs/Ni ₃ Fe	120	90.9	51.1	19.9	-	7.1	~12.0
3	Pt ₁ /NiFe-LDHs	120	50.8	1.3	2.7	-	42.4	~4.0
4	Ni ₃ Fe	120	42.8	15.7	3.3	19.8	1.9	-

*Reaction conditions: All reactions were run at 160 °C and 1.0 MPa H₂. The loading of 5-HMF was 0.5 wt.% in 60 ml THF solvent. The catalyst dosage was introduced according to the 5-HMF/Pt molar ratio of 100/1 for Pt₁/Ni₃Fe IMC (196.0 mg), Pt NPs/Ni₃Fe IMC (184.6 mg) and Pt₁/NiFe-LDHs (316.7 mg). The mass dosage of Ni₃Fe IMC (196.0 mg) was the same as Pt₁/Ni₃Fe IMC for comparison.

Table S6. Hydrodeoxygenation of 5-HMF to DMF by noble-metal based catalysts reported in literatures.

Catalyst	Temp/time (°C/min)	Solvent	Conversion (%)	Yield of DMF (%)	Ref
Pt ₁ /Ni ₃ Fe	160/90	THF	99	98.1	Our work
PtCo@HCS	160/120	butanol	100	96	Nat. Mater. 2014, 13, 293-300.
CuRu/C	220/600	1-butanol	100	71	Nature 2007, 447, 982-985.
CuRu/C	220/600	1-butanol	-	49	J. Am. Chem. Soc. 2009, 131, 1979-1985.
Pd/C and H ₂ SO ₄	THF refluxing/900	THF	-	~70	Angew. Chem. Int. Ed. 2010, 49, 6616-6618.
Pd/C	120/900	THF	100	95	Angew. Chem. Int. Ed. 2010, 122, 6766.

Scheme S1. Elementary steps for the hydrogenolysis of 5-HMF.



3. References

- 1 D. Zhou, Z. Cai, Y. Bi, W. Tian, M. Luo, Q. Zhang, Q. Xie, J. Wang, Y. Li, Y. Kuang, X. Duan, M. Bajdich, S. Siahrostami, X. Sun, *Nano Res.*, 2018, **11**, 1358-1368.
- 2 J. Shen, X. Yin, D. S. Karpuzov, N. Semagina, *Catal. Sci. Technol.*, 2013, **3**, 208-221.
- 3 B. Ravel, M. Newville, *J. Synchrotron. Radiat.*, 2005, **12**, 537-541.
- 4 A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, *Phys. Rev. B*, 1998, **58**, 7565-7576.
- 5 G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
- 6 J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- 7 P.E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
- 8 S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 9 G. Henkelman, B.P. Uberuaga, H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901-9904.
- 10 A. Heyden, A. T. Bell, F. J. Keil, *J. Chem. Phys.*, 2005, **123**, 224101.