Supporting Information for

Hydrogen-mediated acid-base transformation of Ni supported Mo₅N₆ for hydrogenative rearrangement of furfural derivatives

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Materials

Furfural, 5-methyl furfural, 5-hydroxymethyl furfural, 5-ethyl furfural, 2-acetyl furan, 2propionyl furan and activated carbon were supplied by Shanghai Maclin Biochemical Technology Company. 5-Methylfurfuryl alcohol, 2,5-hexanedione, isopropyl alcohol, n-hexane, sodium molybdate (Na₂MoO₄·2H₂O), nickel nitrate (Ni(NO₃)₂·6H₂O), benzoic acid, 2,6-dimethylpyridine, pyridine, hydrochloric acid (37wt% HCl) and N,N-dimethyl formamide were supplied by Sinopharm Chemical Reagent Company. All the chemicals were utilized without further purification.

Preparation of NiMoO₄

NiMoO₄ was synthesized through a simple hydrothermal method. Briefly, 25 mL of 0.1 mol/L Ni(NO₃)₂·6H₂O aqueous solution were added in 25 mL of 0.1 mol/L Na₂MoO₄·2H₂O aqueous solution under vigorous stirring for 10 min. Then, the mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave, and heated at 150 °C for 6 h. The NiMoO₄ was obtained by filtration, washed by water, and dried at 60 °C for 12 h, the calcinated at 400 °C for 2 h under an air atmosphere.

Catalyst characterizations

The crystal structure of the catalyst was detailed on a Panalytical Empyrean diffractometer with a Cu target and Cu-Kα radiation through powder X-ray diffraction (XRD). The scanning electron microscope (SEM) images and Energy dispersive spectroscopy (EDS) were determined by Hitachi SU8100 scanning electron microscope at 200 K. The morphology and Ni nanoparticle size of the catalysts were revealed exploiting a JEM-2100 transmission electron microscope (TEM). The X-ray photoemission spectroscopy (XPS) data were implemented exploiting an ESCALAB 250Xi instrument furnished with a monochromatic Al anode X-ray gun. The Pore Volume and the specific surface areas (BET) were achieved on an ASAP 2046 surface analyzer via accomplishing N₂ adsorption-desorption at -196 °C. The content of Ni, Mo was carried out on a PerkinElmer Optima 8000 spectrometer exploiting Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The contents of N elements were determined by an elemental analyzer (Vario MICRO). Raman spectra were collected using a HR Evolution Raman microscope with 473 nm (1.96 eV) laser excitation. Acid properties were analyzed by the infrared spectroscopy of adsorbed pyridine using a Thermo Fisher Nicolet iS50 FTIR spectrometer. The sample was tabled to a wafer (10 mg/cm²) and degassed under vacuum at 100 °C for 20 min, and pyridine adsorption was performed at 60 °C for 30 min. Then, the temperature was gradually increased to 150 and 250 °C, and the spectra were recorded. The signals detected at 150 and 250 °C were attributed to total acid sites and strong acid sites, respectively. The acid and base strength was characterized by determining the temperature-programmed desorption of ammonia and carbon dioxide on a Micromeritics AutoChem II 2920 instrument. The *in situ* near ambient pressure X-ray photoelectron spectroscopy (*In situ* NAP-XPS) measurements were carried out on a SPECS NAP-XPS system. All spectra were obtained using monochromatized Al K α irradiation generated by an Al anode (SPECS XR-50) and an excitation source power fixed at 50 W. XPS measurements at pressures up to -25 mbar are allowed owing to a differential pumping system, which separates the electron analyser (SPECS Phoibos NAP-150) from the reaction area. Through a pressure reducing valve the reaction pressure was kept at 1 mbar.

In situ attenuated total reflection infrared (ATR-IR) measurements

The in situ attenuated total reflection infrared (ATR-IR) measurement was acquired with a Nicolet iS 50 spectrometer equipped with a highly sensitive MCT detector and a heating chamber equipped with CaF windows. An ethanol suspension of catalyst was added dropwise onto the surface of the diamond probe equipped on the instrument, dried at 120 °C, and the background spectrum was recorded. ATR-IR spectra were recorded by averaging 32 scans at a resolution of 2 cm⁻¹. For the acid transformation mechanism, a D₂/Ar gas stream was inlet with a flow rate of 20 mL/min at 130 °C, and the in situ spectrum of D₂-activated catalyst was recorded. For the catalytic reaction mechanism, the catalyst was activated in an Ar atmosphere at 130 °C for 1 h, documented the background spectrum. Then, liquid MF was purged to the surface of the catalyst by 40 mL/min Ar gas flow. At 130 °C, the catalyst was adsorbed by MF for 30 min, and later the physically adsorbed MF will be eliminated by continuous Ar gas flow. Ultimately, the original solid-liquid surface ATR-IR spectroscopy was documented. For treated catalyst, to be as consistent with the experimental conditions as possible, the catalyst was reduced at 130 °C for 1 h in a 5% H₂/Ar atmosphere, and the substrate was added after recording the background spectrum. Similar to the experiment above, ATR-IR spectroscopy was recorded.



Figure S1. (A) EDS of Ni/Mo₅N₆; (B) SEM of Ni/Mo₅N₆; TEM images of (C) Ni/Mo₅N₆, (D) Ni/C, (E-F) Mo₅N₆, (G) N₂ adsorption-desorption isotherms of various catalysts; (H) Raman of different catalyst.



Figure S2. Mass spectra of (A) MF, (B) MFA, (C) HED, (D) HD, (E) MCPEO (F) MCPO and THMFA; Time-dependent product evolution curves (H) Ni/Mo₅N₆; (I) XRD pattern, (J) TEM image of recycled Ni/Mo₅N₆ after 6 cycles of reaction. Reaction conditions: reactant 5-MF (0.5 mmol), catalyst (0.05 g), H₂O (10 mL), H₂ pressure (2.0 MPa), temperature (130 °C). The products were quantified by GC.



Figure S3. (A) Reaction route of furfural to cyclopentanone; time-dependent product distribution over (B) Ni/Mo₅N₆, (C) Ni/C, (D) Mo₅N₆. Reaction conditions: reactant furfural (0.5 mmol), catalyst (0.05 g), H₂O (10 mL), H₂ pressure (2.0 MPa), temperature (130 °C). The products were quantified by GC.



Figure S4. Reaction pathway and time-dependent product distribution over Ni/Mo₅N₆ of (A-B) Reaction route of 5-ethyl furfural to 3-ethyl cyclopentanone; (C-D) 2-acetylfuran to 2-methyl cyclopentanone, (E-F) 2-propionyl furan to 3-ethyl cyclopentanone. Reaction conditions: reactant (0.5 mmol), catalyst (0.05 g), H₂O (10 mL), H₂ pressure (2.0 MPa), temperature (130 °C). The products were quantified by GC.



Figure S5. Time-dependent of (A) HMF and (B) BHF transform product distribution. Reaction conditions: reactant (0.5 mmol), catalyst (A) Mo_5N_6 and (B) Ni/Mo₅N₆ (0.05 g), H₂O (10 mL), H₂ pressure (2.0 MPa), temperature (130 °C). The products were quantified by GC.



Figure S6. (A) C=O of MF hydrogenation kinetic over various catalyst; Catalytic performance over (B) Ni/C, (C) Ni/Mo₅N₆, (D) Mo₅N₆ with different MF concentration; Catalytic performance over (E) Ni/C, (F) Ni/Mo₅N₆, (G) Mo₅N₆ with different H₂ Pressure. Reaction conditions: temperature (130 °C), catalysts (0.05 g) , reaction time (1 h); (A) MF (0.5 mmol), H₂O (10 mL); (B, C, D) H₂O (10 mL), H₂ pressure (2.0 MPa), MF (0.025-0.1 mol/L); (E, F, G) MF (0.5 mmol), H₂O (10 mL), H₂ pressure (1.5-3.0 MPa). The products were quantified by GC.



Figure S7. (A) MS signals of HD generation over metal phosphides during H_2 - D_2 exchange reaction; (B) Effect of Ni loading on reaction performance; (C) Effect of solvent on reaction performance over Ni/Mo₅N₆; (D) kinetic isotope effect; Photographs of WO₃ + Ni/Mo₅N₆ (D) before and (E) after H_2 reduction, WO₃ + Ni/C+Mo₅N₆ (F) before and (G) after H_2 reduction. Reduction conditions: WO₃ (1 g), catalyst (0.05 g), temperature (30 °C), time (0.5 h); (H) Time-dependent product distribution over physical mixture of Ni/C and Mo₅N₆. Reaction conditions: temperature (130 °C), H_2 or D_2 pressure (2.0 MPa), MF (0.5 mmol), organic solvent or H_2O (10 ml), Ni/C (0.05 g) and Mo₅N₆ (0.05 g). The products were quantified by GC.



dependent product distribution over Ni/Mo₅N₆-800; Reaction conditions: reactant MF (0.5 mmol), catalyst (0.05 g), H₂O (10 mL), H₂ pressure (2.0 MPa), temperature (130 °C). The products were quantified by GC.



Figure S9. (A) Ni 2P XPS spectra of Ni/Mo₅N₆ in in situ NAP-XPS; Reaction performance for the hydrolysis of MFA using different catalyst under (B) nitrogen and (C) hydrogen atmosphere; (D) in situ pyridine-adsorbed FTIR spectra detected at 250 °C; (E) Reaction performance for the hydrolysis of MFA with addition of pyridine and 2,6-dimethylpyridine under hydrogen atmosphere over Ni/Mo₅N₆. Reaction conditions: temperature (130 °C), H₂O (10 mL), catalyst (0.05 g), reaction time (1 h). (B-C) N₂ or H₂ pressure (2.0 MPa), MFA (0.5 mmol); (E) 2,6-dimethylpyridine (0.02 mmol), pyridine (0.02 mmol).



Figure S10. Reaction performance for the reclose of HD using different catalyst under (A) nitrogen and (B) hydrogen atmosphere; (C) HD aldol condensation reaction performance with addition of varied amount of PY or benzoic acid under H₂-atmosphere over Ni/Mo₅N₆; (D) CO₂-TPD. Reaction conditions: catalyst (0.05 g), H₂O (10 mL). temperature (130 °C), reaction time (1 h). (A-B) N₂ or H₂ pressure (2.0 MPa), HD (0.5 mmol); (C) pyridine (0.02 mmol), benzoic acid (0.02 mmol); (D) H₂ pressure (2.0 MPa), HD (0.5 mmol). The products were quantified by GC.

	Т	Time	H_2	Conversion	Selectivity	
Catalyst	(°C)	(h)	(MPa)	(%)	(%)	Ref.
Ni/Mo ₅ N ₆	130	10	2	99.9	90.3	This work
Au/TiO ₂	160	8	4	99	97	Green Chem. 18 , 2155 (2016)
Co@N-CNT	160	12	0.5	99.9	93	Nano Res. 14, 2846 (2021)
$Sr_2P_2O_7/Ni_2P$	150	20	0.1	99.9	72.1	J. Catal. 421 , 117 (2023)
Ni@C	150	4	2	99.9	98.2	Appl. Catal. B 306 , 121140 (2022)

Table S1. Conversion of MF to MCPO under various catalytic systems.

Soundas	Ni	Мо	N
Samples	(wt%)	(wt.%)	(wt.%)
Ni/Mo ₅ N ₆	18.7	30.2	5.2
Ni/Mo_5N_6 after 6 cycles of reaction	18.0	29.5	4.8

 Table S2 Physicochemical properties of various catalysts.

Catalant	Т	Time	H ₂	Conversion	Selectivity	D - f
Catalyst	(°C)	(h)	(MPa)	(%)	(%)	Kei.
Ni/Mo ₅ N ₆	130	10	2	99.9	93.5	This work
Au/TiO ₂	160	3	4	99.0	99.0	Green Chem. 18 , 2155 (2016)
Ru/CNTs	160	5	1	99.9	93.0	ACS Sus. Chem. Eng. 5 , 744 (2017)
$Sr_2P_2O_7/Ni_2P$	150	4	0.1	99.9	91.0	<i>J. Catal.</i> 421 , 117 (2023)
Pd/NiMoO ₄	150	6	4	99.9	85.3	J. Catal. 405 , 363 (2022)
$Pd/K_2Zn_3[Fe(CN)_6]_2$	150	6	4	99.9	96.6	J. Catal. 378 , 201 (2019)
$Pd/Y_2(Sn_{0.7}Ce_{0.3})_2O_{7-\delta}$	150	6	4	99.9	95.0	ACS Catal. 10, 7355 (2020)
Ru/MIL-101	160	2.5	4	99.9	96.0	Green Chem. 17 , 4183 (2015)
Pd/ZSM-5	150	2	3	99.9	91.8	<i>Fuel</i> 314 , 123074 (2022)
NiCu/SBA-15	160	4	4	99	62.6	Green Chem. 15 , 1932 (2013)
CuNi/Al-MCM-41	160	2	5	99.9	96.7	<i>Chin. J. Catal.</i> 42 , 2216 (2021)
CuCo@C	150	3	0.5	99.9	90.2	ACS Sus. Chem. Eng. 6 , 14919 (2018)
Ni ₃ Sn ₂ -ReO _x /TiO ₂	140	3	6	99.9	92.5	Appl. Catal. B 340 , 123191 (2024)

Table S3. Conversion of furfural to cyclopentanone under various catalytic systems.

Catalyst	T (°C)	Time (h)	H ₂ (MPa)	Conversi on (%)	HCPN Selectivity (%)	MCPO Selectivity (%)	Ref.
Ni/Mo ₅ N ₆	130	10	2	99.9	31.6	52.6	This work
Au/Nb ₂ O ₅	140	12	8	99.9	86.7	-	Green Chem. 18 , 676 (2016)
Cu-Al ₂ O ₃	180	6	2	99.9	86.2	-	<i>Green Chem.</i> 19 , 1701 (2017)
Pd/K ₂ Zn ₃ [Fe(CN) ₆] ₂	150	12	4	99.9	96.6		J. Catal. 378 , 201 (2019)
Pd/NiMoO ₄ -Cl	150	12	4	99.9	56.3	-	J. Catal. 405 , 363 (2022)
5%Pd/Y ₂ (Sn _{0.7} Ce _{0.3}) ₂ O ₇₋₈)	150	12	4	99.9	92.5	-	ACS Catal. 10, 7355 (2020)
Pd/MIL-100	150	12	4	99.9	85.4	-	Appl. Catal. A Gen 575 , 152 (2019)
Ni-Cu/MOF-74	140	5	2	99.9	70.3	-	Green Chem 21 , 1702 (2019)

Table S4. Conversion of HMF to HCPO and MCPO under various catalytic systems.

Table S5. Actually of M/Mo ₅ N ₆ .							
Sample	acid amount (μmol/g)	Lewis acid (µmol/g) at 150 °C	Brønsted acid (µmol/g) at 150 °C	Ratio of Brønsted/Lewis acid at 150 °C	Ratio of Brønsted/Lewi s acid at 250°C		
Parent Ni/Mo ₅ N ₆	150	149.0	1.0	0.01	0.01		
Treated Ni/Mo ₅ N ₆	176.8	85.0	91.8	1.08	1.26		

Table S5. Acidity of Ni/Mo₅N₆.