Supplementary Information (SI) for New Journal of Chemistry.

Supplementary Materials

Table S1. Catalytic Performance of Cu/WO_3 Under Different Active Metals (typical reaction conditions: 200 mg of catalyst, HMF concentration of 12.6 mg·mL^{-1}, water as solvent, atmospheric pressure, reaction temperature: 300 ℃. All products were collected between hours 7 and 8 of the reaction for GC analysis.)

Catalyst	*C* (%)	$S_{5\text{-MF}}$ (%)	S_{DFF} (%)	S_{other} (%)
Zn/WO_3	9.4	40.9	24.9	34.2
Fe/WO_3	22.8	31.8	18.4	49.8
Co/WO_3	5.9	44.9	23.6	31.5
Ni/WO_3	15.3	37.2	16.3	46.5
Mn/WO_3	11.5	31.2	20.5	48.3
Cu/WO_3	100	72.7	0	27.3
Ag/WO_3	89.7	73.9	0	26.1
Au/WO_3	68.4	67.3	0	32.7

(a) The loading of Ag is 3 wt%, the loading of Au is 1 wt%, and the loading of other metals is 9 wt%. (b) S_{other} includes products that are undetectable by chromatography.

Table S2. Catalytic Performance of Cu/WO_3 Under Different Organic Solvents (typical reaction conditions: 200 mg of catalyst, HMF concentration of 12.6 mg·mL^{-1}, water as solvent, atmospheric pressure, reaction temperature: 300 ℃. All products were collected between hours 7 and 8 of the reaction for GC analysis.)

Catalyst	Solvent	*C* (%)	$S_{2,5\text{-DMF}}$ (%)	$S_{5\text{-MF}}$ (%)	S_{DFF} (%)	S_{others} (%)[b]
Cu/WO_3	1,4-dioxane[a]	100	0	94.3	0	5.7
Cu/WO_3	1,3-dioxolan	100	0	90.5	0	9.5
Cu/WO_3	Tetrahydrofuran	100	0	89.1	0	10.9
Cu/WO_3	Acetonitrile	47.6	0	85.9	0	14.1
Cu/WO_3	n,n-dimethylformamide	100	0	84.7	0	15.3
Cu/WO_3	propionic acid	100	0	79.3	0	20.7
Cu/WO_3	acetic acid	100	0	77.8	0	22.2
Cu/WO_3	Acetone	100	5.1	76.2	0	18.7
Cu/WO_3	formic acid	100	0	73.0	0	27.0
Cu/WO_3	Water	100	0	72.7	0.	27.3
Cu/WO_3	n,n-dimethylacetamide	100	0	71.3	0	28.7
Cu/WO_3	dimethyl sulfoxide	16.3	0	18.4	29.1	52.5
Cu/WO_3	1-methyl-2-pyrrolidinone	100	0	14.1	0	85.9
Cu/WO_3	n-butylamine	100	0	11.8	0	88.2
Cu/WO_3	Ethylenediamine	100	0	8.2	13.2	78.6

(a) All solvents used are mixtures of organic solvent and water in a 4:1 volume ratio. (b) S_{other} includes products that are undetectable by chromatography.

Table S3. Catalytic Performance of Cu/WO_3 Under Different pH Conditions (typical reaction conditions: 200 mg of catalyst, HMF concentration of 12.6 mg·mL^{-1}, water as solvent, atmospheric pressure, reaction temperature: 300 ℃. All products were collected between hours 7 and 8 of the reaction for GC analysis.)

Catalyst	Solvent	pH	*C* (%)	$S_{2,5\text{-DMF}}$ (%)	$S_{5\text{-MF}}$ (%)	S_{DFF} (%)	S_{others} (%)[b]
Cu/WO_3	Trifluoroacetic acid (1ml)[a]	0.21	100	0	73.3	0	26.7
Cu/WO_3	formic acid (16ml)	1.21	100	0	73.0	0	27.0
Cu/WO_3	acetic acid (16ml)	1.81	100	0	77.8	0	22.2
Cu/WO_3	propionic acid (16ml)	1.92	100	0	79.3	0	20.7
Cu/WO_3	propionic acid (1.1ml)	2.50	100	0	78.2	0	21.8
Cu/WO_3	propionic acid (0.11μl)	4.50	100	0	74.8	0	25.2
Cu/WO_3	Water (20ml)	7.0	100	0	72.7	0.	27.3
Cu/WO_3	Ethylenediamine (0.02ml)	11.05	100	0	54.4	0	45.6
Cu/WO_3	Ethylenediamine (0.04ml)	11.20	100	0	38.3	0	61.7
Cu/WO_3	Ethylenediamine (0.06ml)	11.29	100	0	23.7	0	76.3
Cu/WO_3	Ethylenediamine (1.3ml)	11.96	100	0	5.2	0	94.8
Cu/WO_3	Ethylenediamine (16ml)	12.50	100	0	8.2	13.2	78.6
Cu/WO_3	n-butylamine (16ml)	12.77	100	0	11.8	0	88.2

(a) The values in parentheses represent the amount of organic acid or base solution added. All solvents are mixed solvents prepared with 20 mL total volume by combining the aqueous solutions. (b) S_{other} includes products that are undetectable by chromatography.

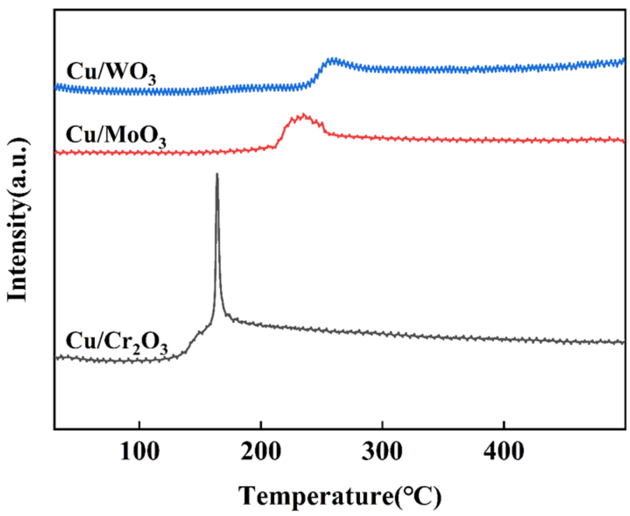

Figure S1. N_2O-TPD Profiles of Cu/MO_x (M = Cr, Mo, W)

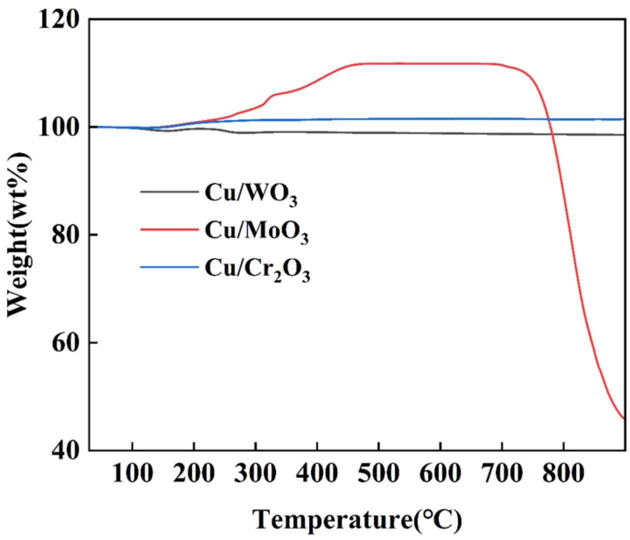

Figure S2. TGA Analysis of Cu/MO_x (M = Cr, Mo, W) Under an Air Atmosphere

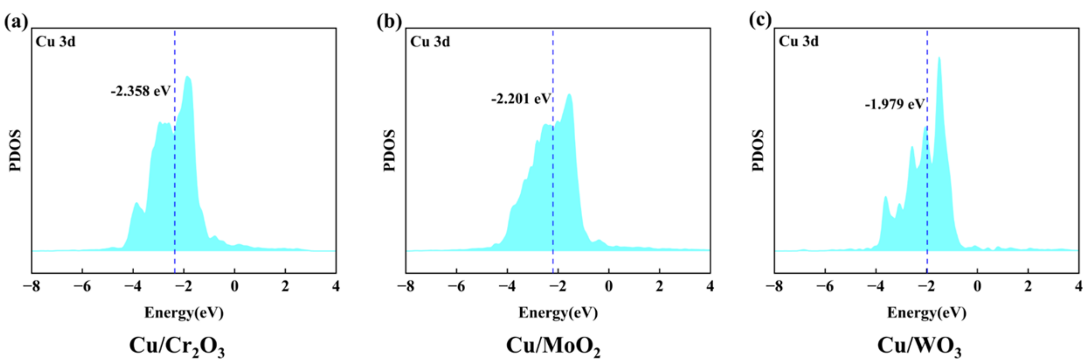

Figure S3. Partial density of states for d orbitals of Cu in Cu/MO_x (M=Cr, Mo, W)

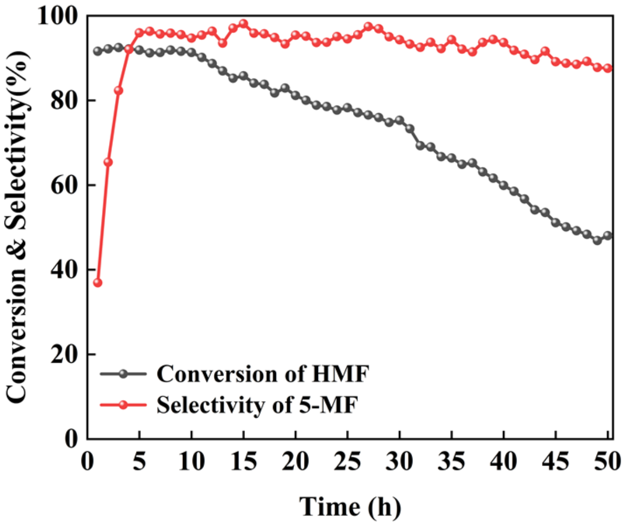

Figure S4. The lifespan experiment of Cu/WO_3 (typical reaction conditions: 50 mg of catalyst, HMF concentration of 12.6 mg·mL^{-1}, 1,4-dioxane:water = 4:1 as a mixed solvent, atmospheric pressure, reaction temperature: 300 °C.)

Table S4. Summary of catalysts reported for 5-HMF to 5-MF

Entry	Catalyst	Catalyst (mg)	HMF (mmol)	*T* (℃)	*t* (h)	H_2 Pressure (MPa)	Solvent	*Conv.* (%)	$S_{5\text{-MF}}$ (%)	Ref
1	Au/TiO_2@NPC	400	1	180	1.5	0.1 (N_2)	1，4-Dioxane	100.0	95.0	1
2	Pt1/Nb_2O_5-Ov	20	0.3	160	4	4.0	THF	100.0	100.0	2
3	Pd-PVP/C(1:2)	50	2	200	7.5	0.5 (N_2)	THF	87.0	90.0	3
4	Pt/Nb/SiO_2	236	1.2	180	6	0.4	BDO	47.0	31.0	4
5	CoAl-MMO	100	2	180	6	1	THF	15.9	41.5	5
6	30W_2C/AC	152	1	200	3	5	THF	99.0	88.0	6
7	Fe-N-C-900	100	0.5	240	1	4	n-butanol	95.0	22.0	7
8	Pt@PVP/Nb_2O_5	40	0.3	140	24	4	THF	100.0	92.0	8
9	10%MoO_x/C	100	4	180	1	1.5	n-butanol	39.9	37.5	9
10	Au/a-TiO_2	100	1.6	230	8	5	THF	100	83.1	10
11	Fe_2O_3	200	0.2	300	1	0.13 （20 mL·min^{-1}）	H_2O+1，4-Dioxane	85.8	84.9	11
12	Ni@NbO_x	10	0.1	160	4	4	THF+dodecane	94.3	91.8	12
13	Ni/$TiO_{2(PC500)}$	150	7.93	220	1	5	1，4-Dioxane	97.0	90.0	13
14	Mn_N_Graphene	10	0.3	160	12	1	THF	99.0	92.0	14
15	Pd/Nb2O5–500H	10	0.1	160	4	3.7(H_2)+0.3(CO)	THF+dodecane	100.0	81	15
16	FPhS–Pd/C	50	2	100	6	4	H_2O	99.0	90.1	16
17	Cu/WO_3	200	0.1	300	1	0.13 （20 mL·min^{-1}）	H_2O	100	72.7	This work
18	CuZn/WO_3	200	0.1	300	1	0.13 （20 mL·min^{-1}）	H_2O	100	76.2	This work
19	Cu/WO_3	200	0.1	300	1	0.13 （20 mL·min^{-1}）	H_2O+1，4-Dioxane	100	94.3	This work
20	CuZn/WO_3	200	0.1	300	1	0.13 （20 mL·min^{-1}）	H_2O+1，4-Dioxane	100	95.3	This work

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