Supporting information

Hydrogenolysis of 5-Hydroxymethylfurfural by *in-situ* produced hydrogen from water on Fe catalyst

Xin Li[1#], Peng Rui[1#], Tongqi Ye[1]*, Xin Yao[1], Rulong Zhou[2], Dongdong Li[2], Sheng Wang[3], James H. Carter[4]*, Graham J. Hutchings[4]

1. School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei, Anhui, 230009, P.R. China;

2. School of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui, 230009, P.R. China;

3. Research Institute of Petroleum Processing, Sinopec, Beijing, 100083, P.R. China;

4. Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom.

* *Correspondence: E-mail: yetq@hfut.edu.cn*

* *Correspondence: E-mail: carterj5@cf.ac.uk*

Table S1 Catalytic performance of some first transition period elements in HMF hydrogenolysis [a]

Catalyst precursors	260 ℃			300 ℃		
	C (%)	S_{MF} (%)	S_{DFF} (%)	*C* (%)	S_{MF} (%)	S_{DFF} (%)
Cr_2O_3	46.4	15.6	14.3	39.0	31.4	19.7
MnO_2	39.4	16.3	34.9	49.0	31.0	47.2
Fe_2O_3[b]	40.5	75.8	6.3	84.2	75.8	0.0
Co_3O_4	61.4	13.3	0.0	32.4	14.1	6.2
NiO	11.5	0.0	0.0	4.3	0	53.7
CuO	27.2	21.2	11.5	33.6	24.3	37.5
ZnO	10.4	16.6	53.8	21.7	11.4	24.8
Fe_2O_3[c]	90.2	77.3	0	100.0	69.0	0

a: reaction conditions: 0.2 g catalyst, 12.6 mg/ml HMF solution, 1 ml/h fed into the reactor, 20 ml/min H_2.

b: commercial Fe_2O_3 nano powder

c: home-made Fe_2O_3 nano catalyst

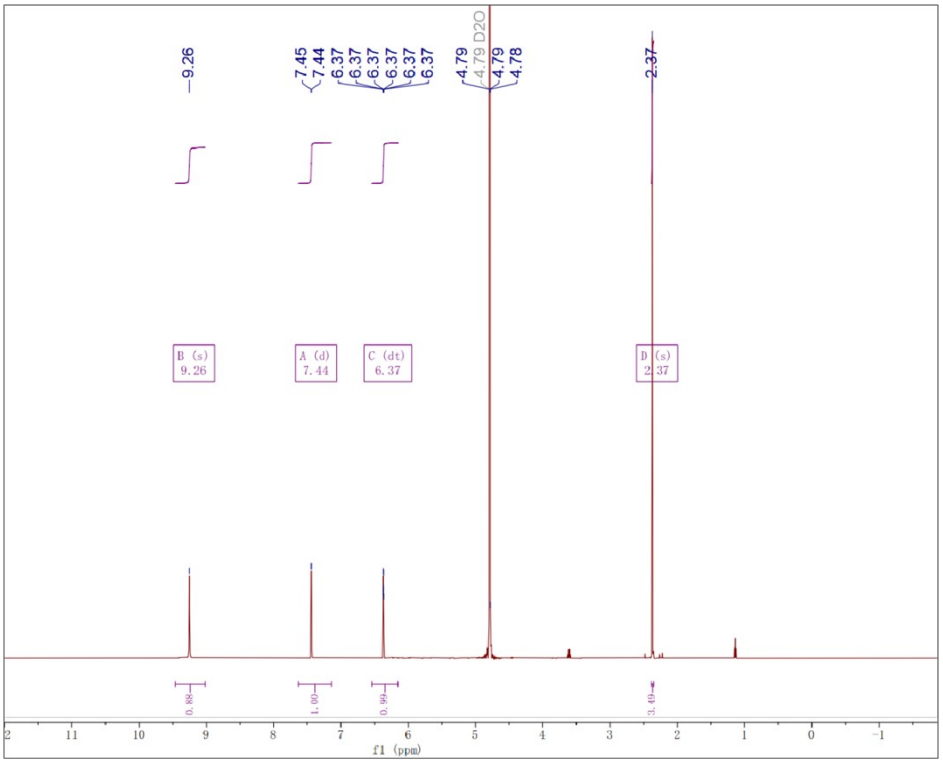

Fig. S1 ^{1}H NMR spectrum of purchased 5-mythylfuraldehyde in D_2O (^{1}H NMR (600 MHz, d_2o) δ 9.26 (s, 1H), 7.44 (d, J = 3.6 Hz, 1H), 6.37 (dt, J = 3.6, 1.0 Hz, 1H), 2.37 (s, 3H))

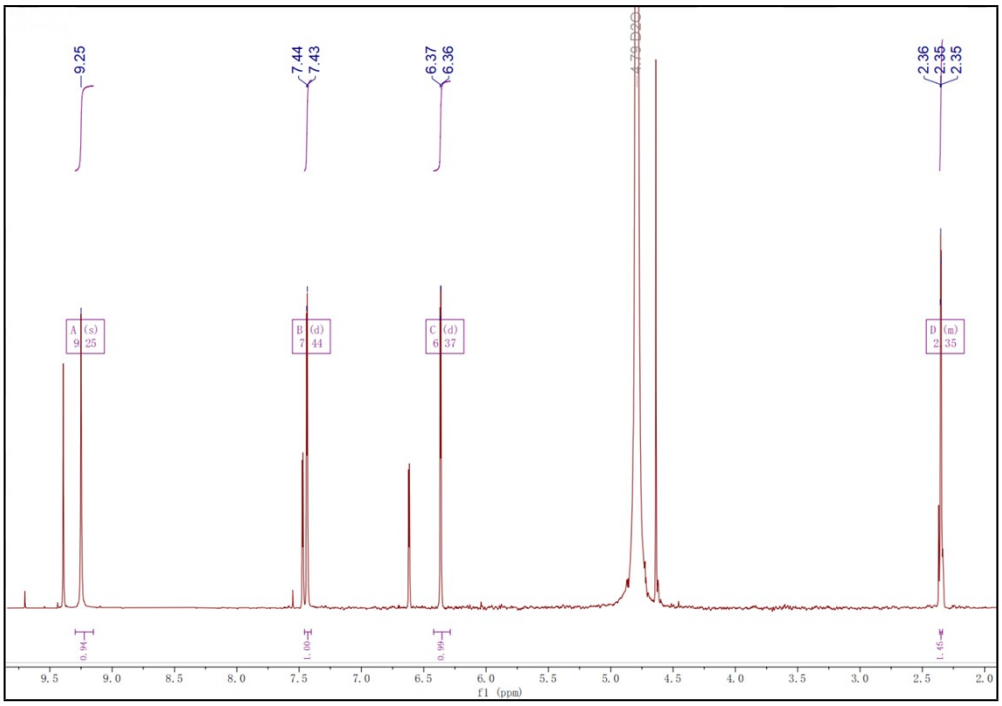

Fig. S2 ^{1}H NMR spectrum of deuterated 5-mythylfuraldehyde product in D_2O (1H NMR (600 MHz, d2o) δ 9.25 (s, 1H), 7.44 (d, J = 3.6 Hz, 1H), 6.37 (d, J = 3.5 Hz, 1H), 2.36 – 2.34 (m, 1H))

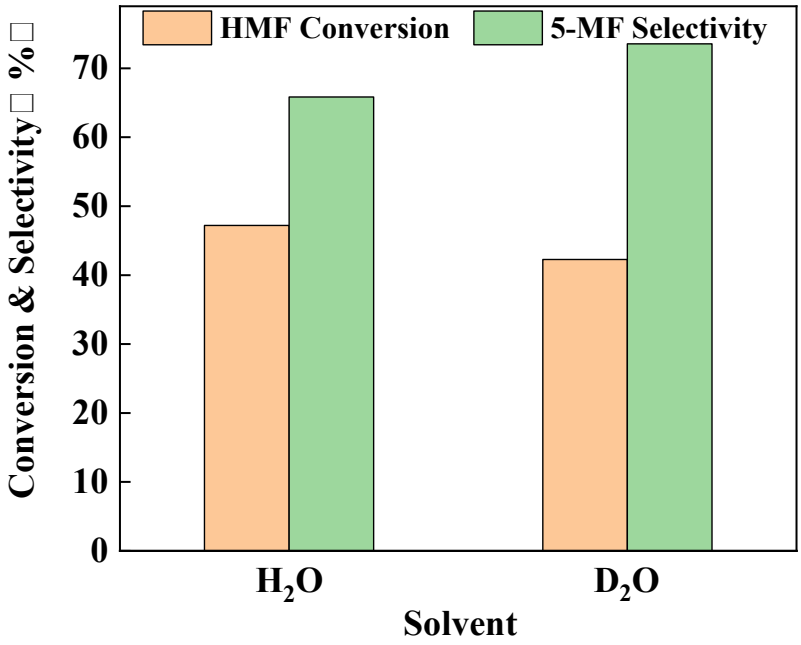

Fig. S3 The influence of solvent on the catalytic performance (reaction condition: 252 mg/ml of HMF, 1 ml/h feed speed, 300 ℃)

Table S2 Summary of catalysts reported for 5-HMF to 5-MF

Catalyst	Catalyst (mg)	HMF (mmol)	*T* (℃)	*t* (h)	H_2 Pressure (MPa)	Solvent	*Conv.* (%)	$S_{5\text{-MF}}$ (%)	STY ($mmol \cdot g^{-1} \cdot h^{-1}$)	Ref
Au/TiO_2@NPC	400	1	180	1.5	0.1 (N_2)	1,4-Dioxane	100.0	95.0	1.58	1
$Pt1/Nb_2O_5$-Ov	20	0.3	160	4	4.0	THF	100.0	100.0	3.75	2
Pd-PVP/C(1:2)	50	2	200	7.5	0.5 (N_2)	THF	87.0	90.0	4.27	3
$Pt/Nb/SiO_2$	236	1.2	180	6	0.4	BDO	47.0	31.0	0.12	4
CoAl-MMO	100	2	180	6	1	THF	15.9	41.5	0.22	6
$30W_2C/AC$	152	1	200	3	5	THF	99.0	88.0	1.91	7
Fe-N-C-900	100	0.5	240	1	4	*n*-butanol	95.0	22.0	1.05	8
$Pt@PVP/Nb_2O_5$	40	0.3	140	24	4	THF	100.0	92.0	0.29	9
10% MoO_x/C	100	4	180	1	1.5	*n*-butanol	39.9	37.5	5.98	10
Fe_2O_3	200	0.6	300	1	0.3 (20 mL/min)	H_2O	33.6	61.8	0.62	This work
Fe_2O_3	200	0.2	300	1	0.3 (20 mL/min)	H_2O + 1,4-Dioxane	85.8	84.9	0.73	This work

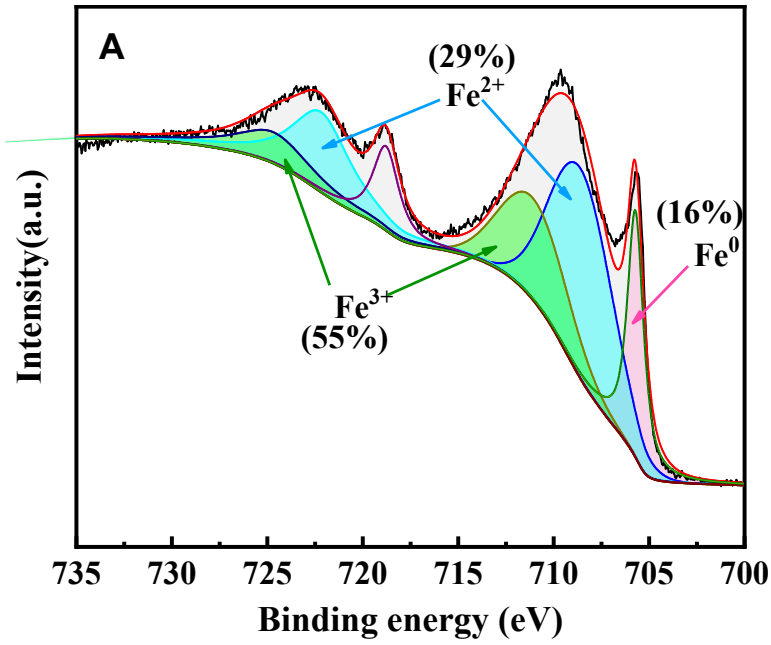

Fig. S4 XPS analysis of Fe catalyst after reduction at 500 ℃ for 2 h

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