Supplementary material

Efficient and sustainable production of *p*-xylene from biomass-derived 2,5-dimethylfuran and ethylene using alkali metal doped phosphotungstic acid catalysts

Chengming Wu, Zhao Yang, Jifan Li, Chun-Ling Liu, Wen-Sheng Dong*

Key Laboratory of Applied Surface and Colloid Chemistry (SNNU), MOE, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China

*Corresponding author.

E-mail address: wsdong@snnu.edu.cn.

Fig. S1. N_2 adsorption-desorption isotherms of the pure HPW and $M_xH_{3-x}PW$ catalysts.

Fig. S2. Effect of initial ethylene pressure on the conversion of DMF and ethylene to PX. (Reaction conditions: DMF, 1.15 g; 1,4-dioxane, 14.3 g; catalyst, 12.5wt% DMF; 250 °C for 6 h; stirring speed, 800 rpm.)

Notation: CH: 1,4-dimethyl-7-oxabicyclo[2.2.1]hept-2-ene; AP: 1-methyl-4-propylbenzene; CP: 3-methyl-2-cyclopentenone; HDO: 2,5-hexanedione; DM: dimers; Others: undetectable byproducts by the GC.

Fig. S3. Effect of catalyst dosage on the conversion of DMF and ethylene to PX. (Reaction conditions: DMF, 1.15 g; 1,4-dioxane, 14.3 g; 4 MPa C_2H_4; 250 °C for 6 h; stirring speed, 800 rpm.) Notation: CH: 1,4-dimethyl-7-oxabicyclo[2.2.1]hept-2-ene; AP: 1-methyl-4-propylbenzene; CP: 3-methyl-2-cyclopentenone; HDO: 2,5-hexanedione; DM: dimers; Others: undetectable byproducts by the GC.

Fig. S4. Effect of reaction temperature and time on the HDO and AP selectivity (a), DM and CP selectivity (b), carbon balance (c). (Reaction conditions: DMF, 1.15 g; 1,4-dioxane, 14.3 g; catalyst, 12.5wt% DMF; 4 MPa C_2H_4, stirring speed, 800 rpm.)

Notation: HDO: 2,5-hexanedione; AP: 1-methyl-4-propylbenzene; CP: 3-methyl-2-cyclopentenone; DM: dimers; Others: undetectable byproducts by the GC.

Fig. S5. Effect of water content on the conversion of DMF and ethylene to PX. (Reaction conditions: DMF, 1.15 g; 1,4-dioxane, 14.3 g; catalyst, 12.5wt% DMF; 4 MPa C_2H_4; 250 °C for 6 h; stirring speed, 800 rpm.)

Table S1 A summary of various catalysts for the conversion of DMF and ethylene to PX.

Catalyst	DMF concentration (M)	Solvent	T (°C)	Time (h)	X_{DMF} (%)[a]	Y_{PX} (%)[b]	Catalyst stability	Ref.
Cs_1H_2PW	0.80	1,4-dioxane	250	6	86.8	60.4	stable	This work
			250	8	91.8	64.0	stable	This work
SiO_2-SO_3H	1.04	n-heptane	250	6	67.0	56.6	~26% activity loss in the next run	1
H_3PO_4/TiO_2	0.88	n-dodecane	250	6	80.0	56.8	~20% activity loss in the next run	2
HPA/SiO_2	1.08	1,4-dioxane	250	6	91.2	80.0	~45% activity loss in the next run	3
WO_X/ZrO_2	0.80	hexadecane	250	6	60.0	46.0	stable	4
SAA-57	0.73	1,4-dioxane	250	6	90.0	60.0	stable	5
HY	2.35	n-heptane	250	6	95.0	57.0	stable	6
SAPO-34	1.00	n-hexane	250	24	61.4	33.1	stable	7
WO_3/SBA-15	1.35	n-heptane	250	24	64.4	51.1	stable	8
H-ZSM-5	3.00	n-octane	250	24	90.0	63.7	stable	9
SA-60	2.35	n-heptane	250	24	96.8	75.0	stable	10
MFI zeolite	2.35	n-heptane	250	9	55.7	39.6	stable	11
			250	24	89.1	75.8	stable	11
NSP-BEA	2.35	n-heptane	250	9	88.4	62.4	stable	12
			250	24	99.3	79.4	stable	12
H-BEA	1.00	n-heptane	250	6	81.5	69.2	stable	13
			250	24	99.0	90.0	stable	13
SnOP	1.04	n-heptane	250	18	99.7	93.0	stable	14

[a] X_{DMF} = DMF conversion; [b]Y_{PX} = PX yield.

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