Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Title: Production of *p*-xylene from bio-based 2,5-dimethylfuran over high performance catalyst WO_3/SBA-15

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Supporting information

1. *Material synthesis*

Preparation of WO_3. WO_3 was synthesized according to the literature.[1] Solution A was prepared by dissolving 3.33 g of $CaCl_2$ (Aladdin) and 0.20 g of PVP (Sigma) in 25 mL of water and solution B was prepared by dissolving 1.65 g of $Na_2WO_4 \cdot 2H_2O$ (Sinopharm) and 0.20 g of PVP in 25 mL of water. Then solution B was added dropwise into solution A and the mixture was stirred for another 30 min. And then 16 mL of 6 N HCl was added. Finally the mixture was transferred into 150 mL round-bottom flask and reacted at 80 ℃ for 3 h to get the yellow precipitate. The precipitate was collected by filtration, dried, and calcined at 550 ℃ for 2 h to get WO_3.

Preparation of WO_3/ZrO_2 WO_3/ZrO_2 was synthesized according to the literature.[2, 3] 1.0 g of P123 ($EO_{20}PO_{70}EO_{20}$, average Mn=5800, Aldrich) and 3.222 g of $ZrOCl_2 \cdot 8H_2O$ (Sinopharm) were added in 25 mL of water under stirring at 60 ℃. After P123 was absolutely dissolved, $NH_3 \cdot H_2O$ was added dropwise until the pH of the resulting synthesis gel reached 9.0. After further stirring for another 20 h, the synthesis gel was transferred into a Teflon-lined stainless steel autoclave and kept at 100 ℃ for 24 h. The solid product was washed with a large amount of water and ethanol to wipe off P123 and dried at 80 ℃ to obtain $Zr(OH)_4$. The as-synthesized $Zr(OH)_4$ was added to the $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ aqueous solution by the impregnation method. The mixture was treated with an ultrasonic cleaner for 0.5 h to sufficiently disperse WO_3. It was afterwards stirred for another 4 h and dried at 120 ℃ overnight. Finally, it was calcined in air at 700 ℃ for 3 h with a rate of 2 ℃/min and 0.20-WO_3/ZrO_2-700 was obtained.

Preparation of Sn-Beta Sn-Beta was prepared by a post-synthetic insertion of Sn atoms into framework vacancy defects of dealuminated Beta zeolites via isopropanol flux.[4] Dealumination treatment of Al-Beta (SiO_2/Al_2O_3=25, Nankai University Catalyst Co., Ltd) was performed using HNO_3 (Beijing Chemical Plant). 5.0 g of Al-Beta was treated by 100 mL of concentrated HNO_3 (65 wt%) at 80 ℃ for 20 h. Then the dealuminated zeolite Beta was collected by centrifugation, washed by water until the supernatant approached a neutral pH and dried at 80 ℃ overnight. Then 2.0 g of the dealuminated zeolite Beta was added to 54 mmol of $SnCl_4·5H_2O$ (Sigma) in 200 mL of dried isopropanol (anhydrous grade, Aladdin) and placed in a reflux setup under inert atmosphere. After 7 h, the product was filtered, washed with dry isopropanol, dried, and calcined at air (3 ℃/min to 200 ℃, dwell 6 h, 3 ℃/min to 550 ℃, dwell 6 h).

2. *Figures and Tables*

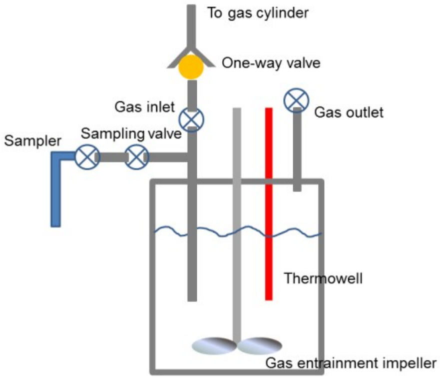

Figure S1 The reactor and sampling system

The reactor and sampling system were designed as described in Figure S1. The inlet gas valve was connected with the gas cylinder by a one-way valve to ensure safety and realize the constant supply of ethylene. There was also a sampling system which can be operated under the reaction conditions by turning off the inlet valve and opening the sampling valve. The sample (2~3 mL) was temporarily stored in a sampling tube and cooled to ambient temperature. When the sample was taken, about 50~80 psi pressure was lost. The inlet valve was opened to restore the initial pressure.

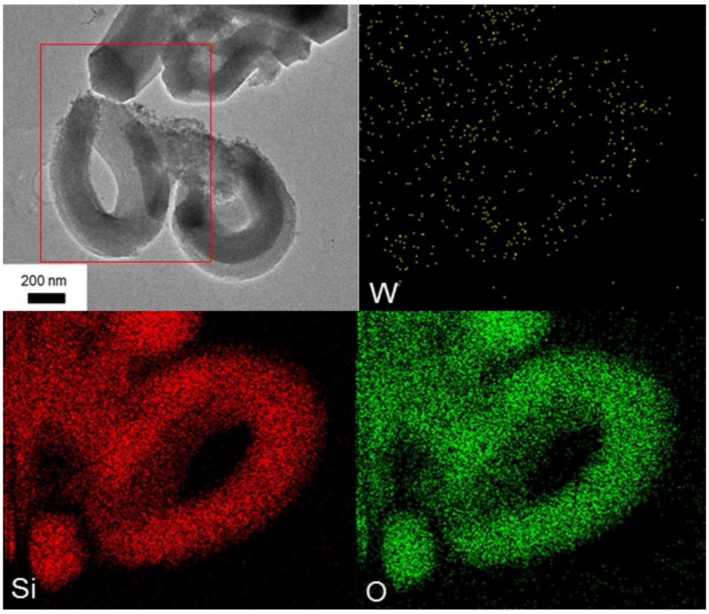

Figure S2 EDS images of 0.05-WO_3/SBA-15-700

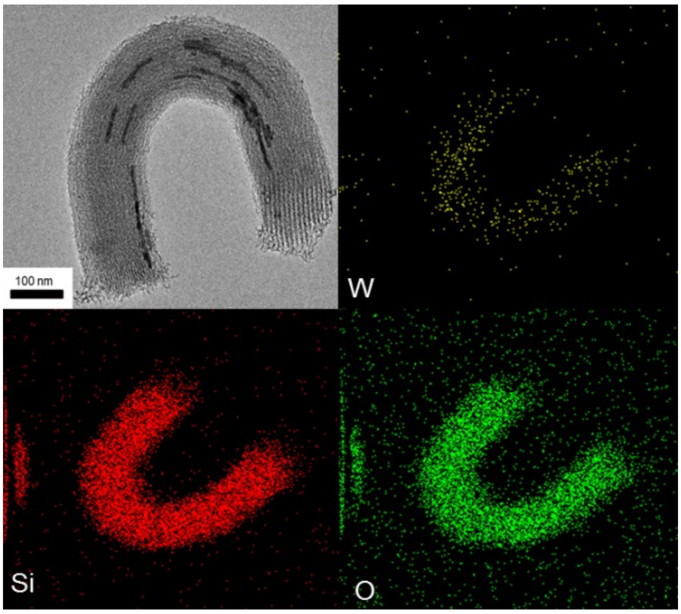

Figure S3 EDS images of 0.20-WO_3/SBA-15-700

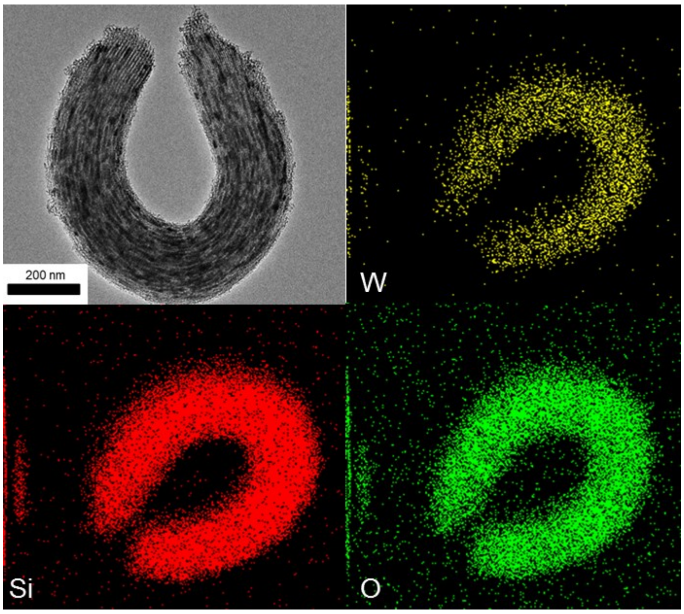

Figure S4 EDS images of 0.35-WO_3/SBA-15-700

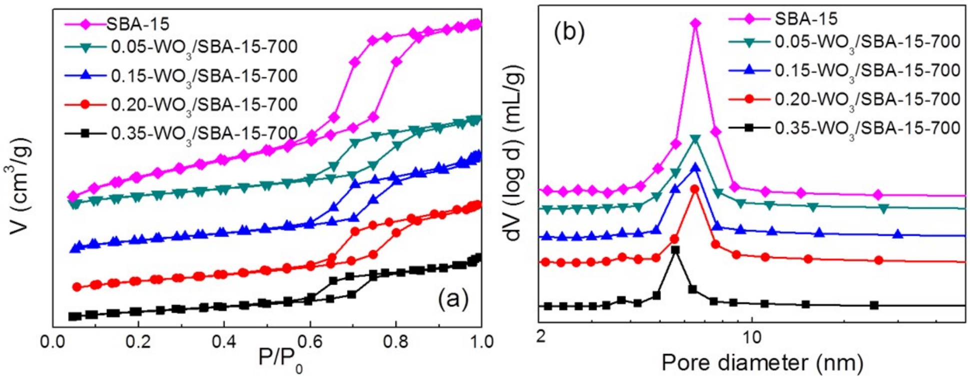

Figure S5 (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of SBA-15 and WO_3/SBA-15 with different loading

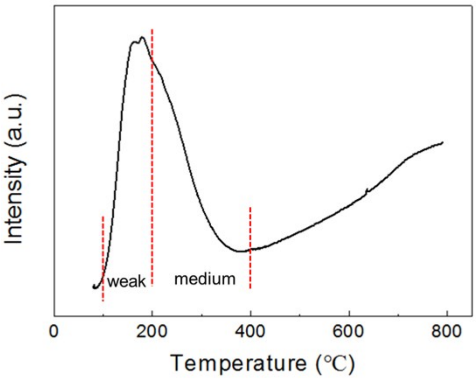

Figure S6 NH_3-TPD profiles of 0.20-WO_3/SBA-15-700.

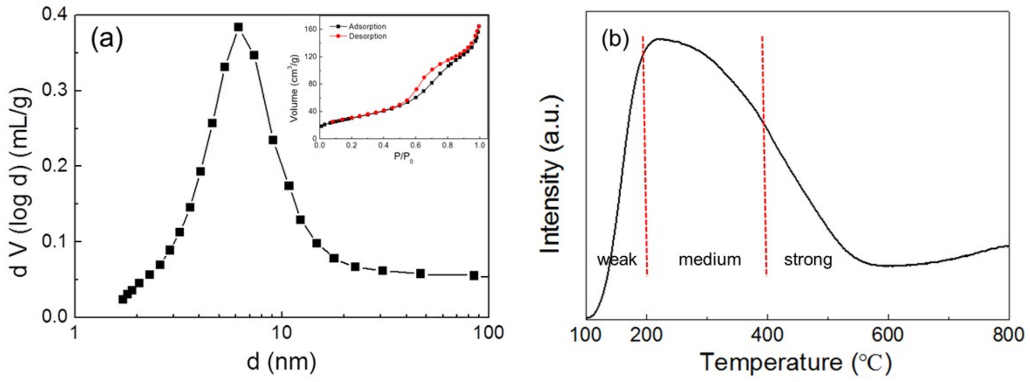

Figure S7 (a) Pore size distribution (corresponds to the desorption branch) of WO_3/ZrO_2 and (b) NH_3-TPD profiles of WO_3/ZrO_2.

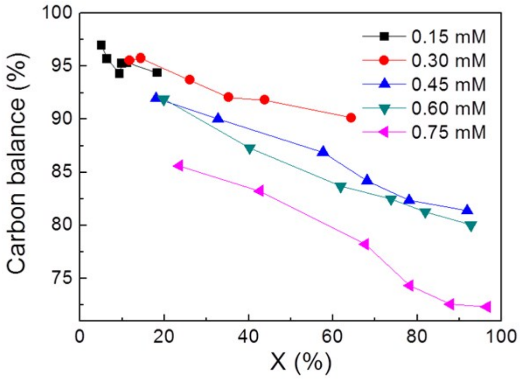

Figure S8 Carbon balance versus X with different concentrations of acid sites (catalyst: 0.20-WO_3/SBA-15-700)

Table S1 Catalytic results of 0.20-WO_3/SBA-15-y with varying calcined temperature

(Reaction conditions: catalyst amount, 1.0 g; reaction time, 24 h)

Calcined temperature (℃)	X of DMF (%)	Carbon balance (%)	Product distribution (%)				
			PX	HDO	MPB	Cycloadduct	MCP
400	93.5	71.6	88.8	5.0	4.7	0.8	0.7
500	71.9	75.7	80.2	7.9	9.5	0.9	1.5
600	73.7	79.4	82.9	6.7	8.5	0.8	1.1
700	88.7	80.0	88.0	3.0	7.8	1.0	0.2
800	73.2	83.8	85.2	5.0	8.0	0.9	0.9

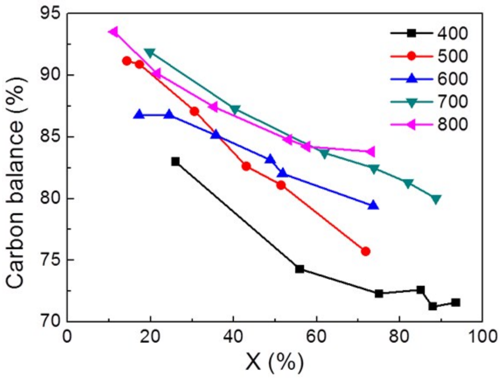

Figure S9 Carbon balance versus X with catalysts calcined at different temperatures

(catalyst amount: 1.0 g)

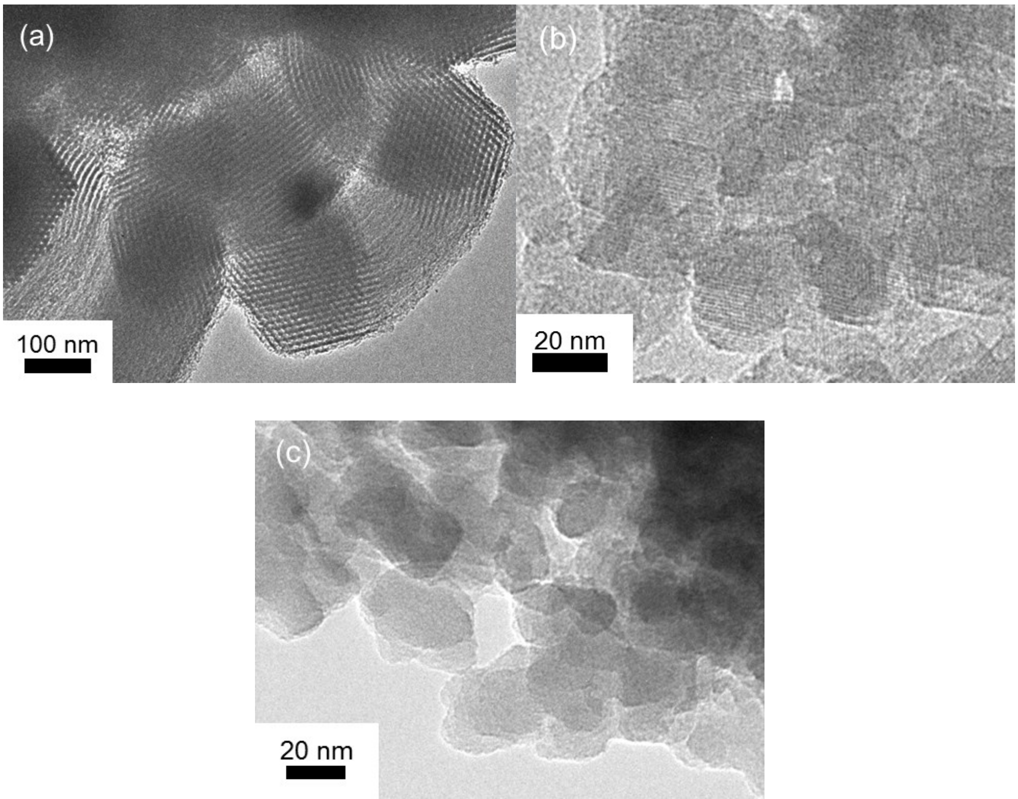

Figure S10 (a) TEM image of 0.20-WO_3/SBA-15-700 after reaction; (b) TEM image of fresh Sn-Beta; (c) TEM image of Sn-Beta after reaction

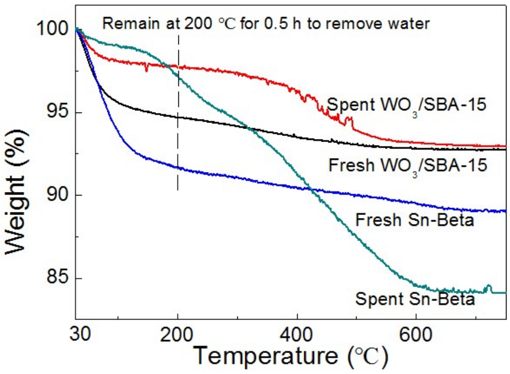

Figure S11 TG curves of the fresh and spent catalysts

Table S2 Selectivity for other products after 24 h of reaction

Catalyst	X (%)	Carbon balance (%)	Product distribution (%)				
			PX	HDO	MPB	Cycloadduct	MCP
0.20-WO_3/SBA-15-700	92.7	81.0	88.1	3.3	7.7	0.9	0
Sn-Beta	58.8	78.1	83.8	5.4	4.5	1.7	4.6

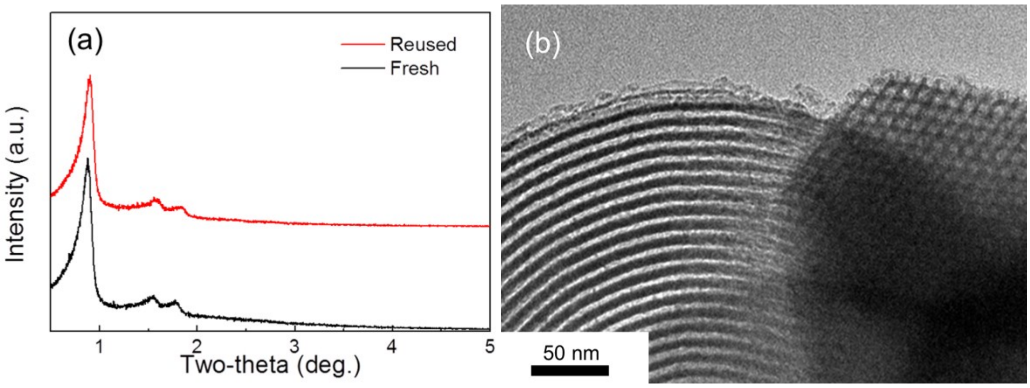

Figure S12 (a) XRD patterns of fresh and reused (after five runs) 0.20-WO_3/SBA-15-700; (b) TEM image of regenerated 0.20-WO_3/SBA-15-700 after five runs

References

(1) X. Xiao, H. Zhong, C. Zheng, M. Lu, X. Zuo and J. Nan, *Chem. Eng. J.*, 2016, **304**, 908–916.

(2) Y. Sun, L. Yuan, W. Wang, C. Chen and F.-S. Xiao, *Catal Lett*, 2003, **87**, 57–61.

(3) Y.-Q. Zhang, S.-J. Wang, J.-W. Wang, L.-L. Lou, C. Zhang and S. Liu, *Solid State Sci.* 2009, **11**, 1412–1418.

(4) J. Dijkmans, M. Dusselier, D. Gabriëls, K. Houthoofd, P. C. M. M. Magusin, S. Huang, Y. Pontikes, M. Trekels, A. Vantomme, L. Giebeler, S. Oswald and B. F. Sels, *ACS Catal.*, 2015, **5**, 928−940.