

Supplementary information

Highly selective conversion of guaiacol to tert-butylphenols in supercritical ethanol over a H₂WO₄ catalyst

Fuhang Mai^{a,b}, Kai Cui^{a,b}, Zhe Wen^{a,b}, Kai Wu^{a,b}, Fei Yan^{a,b}, Mengmeng Chen^{a,b}, Hong Chen^{d,*}, Yongdan Li^{a,b,c}

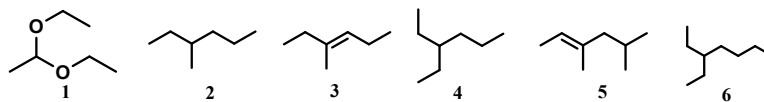
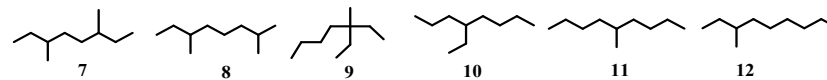
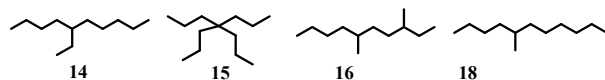
- a. State Key Laboratory of Chemical Engineering (Tianjin University), Tianjin Key Laboratory of Applied Catalysis Science and Technology, School of Chemical Engineering, Tianjin University, Tianjin 300072, China.
- b. Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China.
- c. Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, Espoo, P.O. Box 16100, FI-00076 Aalto, Finland.
- d. School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China.

Table S1 The textural properties of the WO₃ catalyst, fresh H₂WO₄ catalyst and spent catalyst.

Catalyst	S _{BET} ^a (m ² ·g ⁻¹)	V _t ^b (cm ³ ·g ⁻¹)	d _a ^c (nm)
H ₂ WO ₄	12.475	0.044	14.09
Third run	17.964	0.043	9.87
WO ₃	18.765	0.045	9.67

^a S_{BET}: specific surface area; ^b V_t: total pore volume; ^c d_a: average pore size.

Table S2 Product distribution of the liquid products obtained from ethanol conversion^a.

Type	Molecule	Overall yield
Aliphatic hydrocarbons and oxygenated derivatives		
		
		
		
		1535.2mg

^a The numbers in the table correspond to those product peaks marked in the TIC (Figure 4).

Table S3 Recyclability of H₂WO₄ catalyst in ethanol guaiacol conversion. ^a

Catalyst	C ^b /%	M ^c /%	S ₁ ^d	S ₂	S ₃	S ₄	S ₅	S ₆
First run	>99	96.7	16.7	80.0	71.6	2.10	28.5	35.2
Second run	96.6	89.7	43.9	45.4	39.3	14.4	12.6	22.9
Third run	86.0	94.7	82.1	11.8	9.7	56.9	3.1	6.4

^a Reaction conditions: guaiacol (1.0 g), catalyst (0.5 g), 300 °C, 6 h, 600 rpm, 0 MPa (gauge) initial N₂ pressure at room temperature. ^b C: conversion. ^c M: mass balance. ^d S₁: aromatic ethers, S₂: alkylphenols, S₃: tert-butylphenols, S₄: 2-ethoxyphenol, S₅: 2, 6-di-tert-butylphenol, S₆: 2, 6-di-tert-butyl-4-ethylphenol.

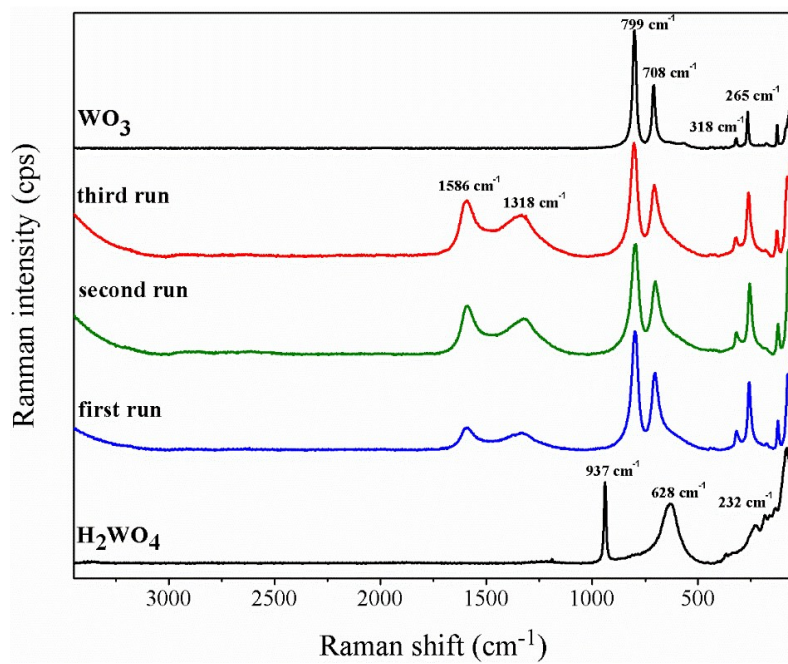


Figure S1 Raman spectra of the WO_3 catalyst, fresh H_2WO_4 catalysts and spent catalysts.

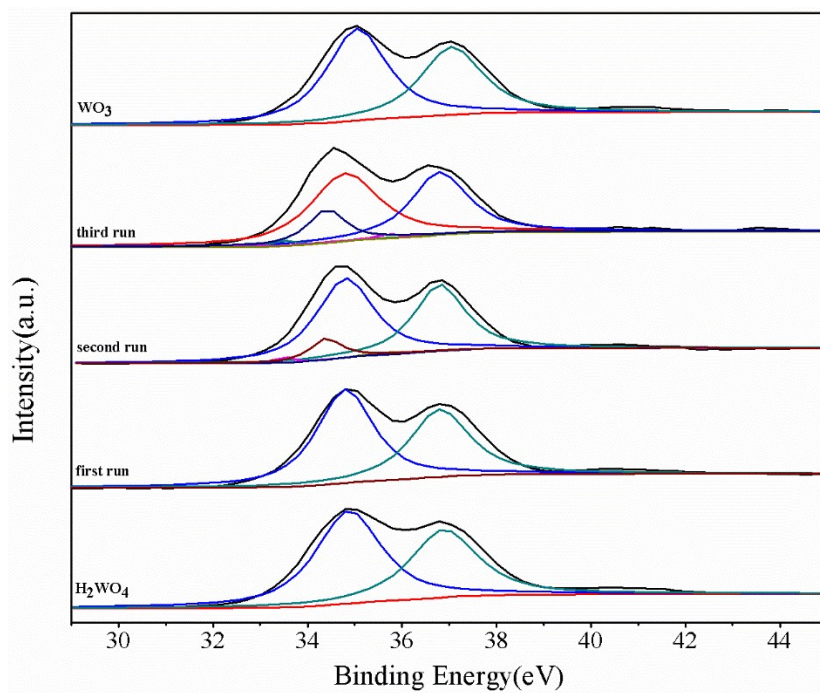


Figure S2 XPS profiles of the W (4f) energy region of the WO_3 catalyst, fresh H_2WO_4 catalyst and spent catalysts.

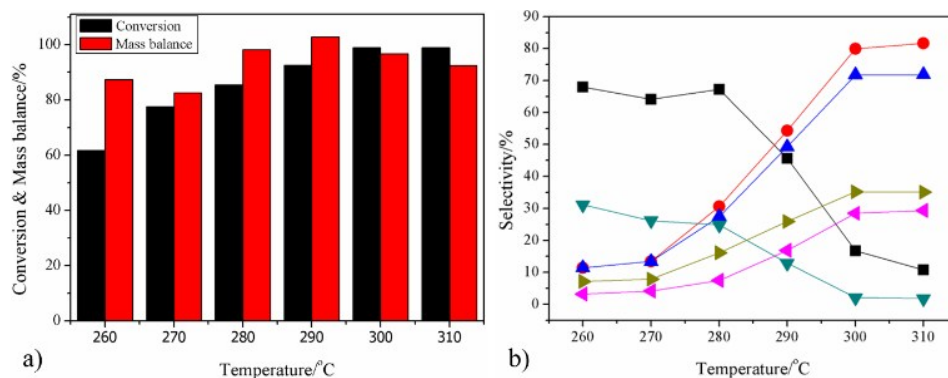


Figure S3 Guaiacol conversion at different temperatures (260 °C - 310 °C). a) Conversion and carbon balance. b) The selectivity of aromatic ethers (■), alkylphenols (●), 2-ethoxyphenol (▼), tert-butylphenols (▲), 2, 6-di-tert-butylphenol (◄), 2, 6-di-tert-butyl-4-ethylphenol (►). Reaction conditions: guaiacol (1.0 g), catalyst (0.5 g H₂WO₄), 600 rpm, 6 h, 0 MPa (gauge) initial N₂ pressure at room temperature, 80 ml ethanol.

The conversion of guaiacol increased sharply as the temperature increased, and complete conversion was achieved at 300 °C. In addition, the mass balance kept at a high level except for the point obtained at 270 °C. As described in Figure S2b the overall selectivity of alkylphenols increased from 11.5% to 80.0% when the temperature raised from 260 °C to 300 °C. However, the sum selectivity of aromatic ethers markedly decreased from 68.0% to 16.7% in the same temperature interval.

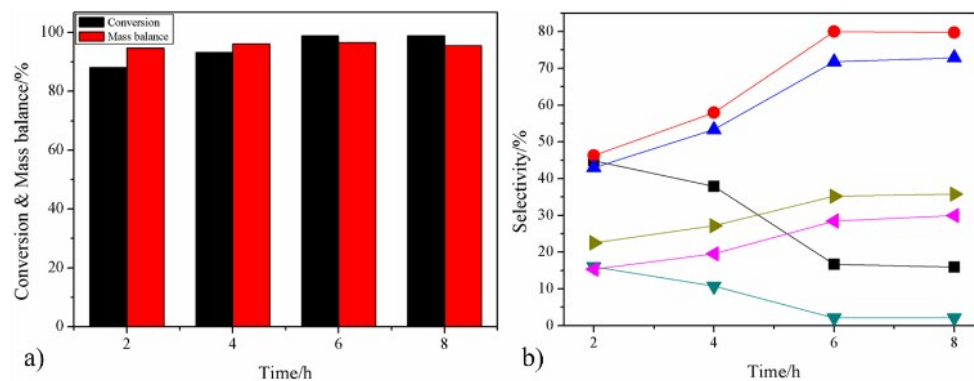


Figure S4 Guaiacol conversion at different reaction time (2 h - 8 h). a) Conversion and carbon balance. b) The selectivity of aromatic ethers (■), alkylphenols (●), 2-ethoxyphenol (▼), tert-butylphenols (▲), 2,6-di-tert-butylphenol (◄), 2,6-di-tert-butyl-4-ethylphenol (▶). Reaction conditions: guaiacol (1.0 g), catalyst (0.5 g H_2WO_4), 600 rpm, 300 °C, 0 MPa (gauge) initial N_2 pressure at room temperature, 80 ml ethanol.

As expected, approximately 12% guaiacol was unconverted after 2 h, and the complete consumption was achieved after 6 h. Besides, the overall selectivity of alkylphenols was 46.3% at 2 h, and peaked at 6 h. On the contrary, the total selectivity of aromatic ethers underwent a gradual decline from 44.9% to 16.7%. Overall, alkylphenols and aromatic ethers are two category products from guaiacol conversion, and the higher temperature and longer time enhance the yield of alkylphenols.

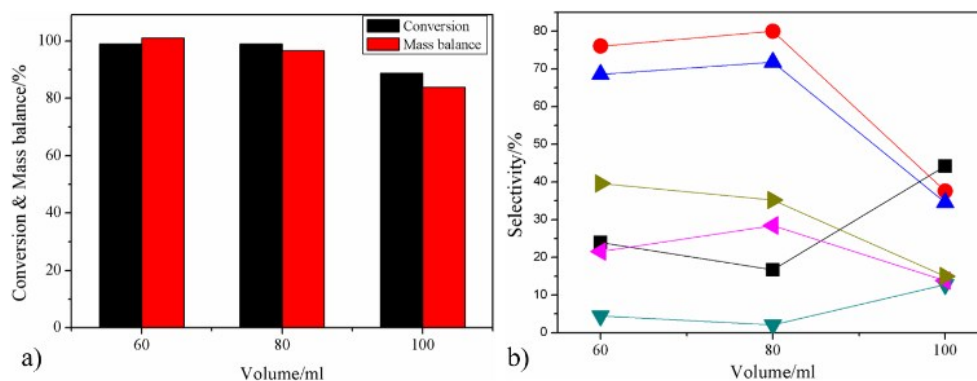
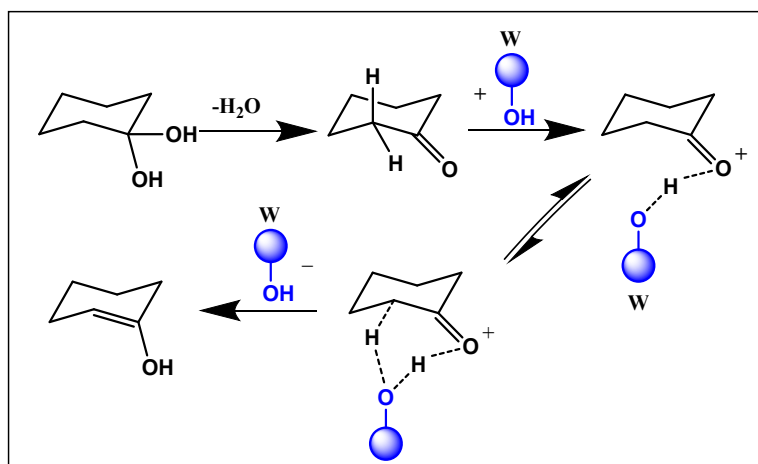


Figure S5 Guaiacol conversion with various original ethanol volumes. a) Conversion and carbon balance. b) The selectivity of aromatic ethers (■), alkylphenols (●), 2-ethoxyphenol (▼), tert-butylphenols (▲), 2, 6-di-tert-butylphenol (◀), 2, 6-di-tert-butyl-4-ethylphenol (▶). Reaction conditions: guaiacol (1.0 g), catalyst (0.5 g H₂WO₄), 600 rpm, 300 °C, 6 h, 0 MPa (gauge) initial N₂ pressure at room temperature.

The original volume of ethanol had minor effects on the product distribution when it was smaller than 80 ml. However, when the volume increased to 100 ml only 88.8% guaiacol was converted and the product distribution appeared obvious difference, in which 44.2% aromatic ethers, and 37.6% alkylphenols were obtained. However, 2, 6-di-tert-butylphenol and 2, 6-di-tert-butyl-4-ethylphenol were still the two major aromatic products, with selectivities of 13.8% and 15.0%, respectively. When the solvent volume increased from 80 to 100 ml, the transesterification reaction between guaiacol and ethanol accelerated due to the increase in the volume, resulting in an obvious increase in the production of the aromatic ethers. Hence, the yield of alkylphenols became lower than that obtained when 80 ml ethanol was used.



Scheme S1 Partial deoxygenation of 1, 2-cyclohexanediol over $\text{H}_2\text{WO}_4/\text{TS-1}$ catalyst [1].

Notes and references

- [1] J. Dai, W. Zhong, W. Yi, M. Liu, L. Mao, Q. Xu and D. Yin, *Applied Catalysis B: Environmental*, 2016, **192**, 325-341.