

Electronic Supplementary Material (ESI) for New Journal of Chemistry.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique  
2021

## Supplementary Information

### **One-step conversion of lignin-derived alkylphenols to light arenes by co-breaking of C-O and C-C bonds**

Zegang Qiu<sup>a</sup>, Ying Wang<sup>a</sup>, Yali Di<sup>b</sup>, Xiaoxiong Ren<sup>a</sup>, Weiwei Liu<sup>a</sup>, Zhiqin Li<sup>a\*</sup> and Guangyu Li<sup>c</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an 710065, PR China.

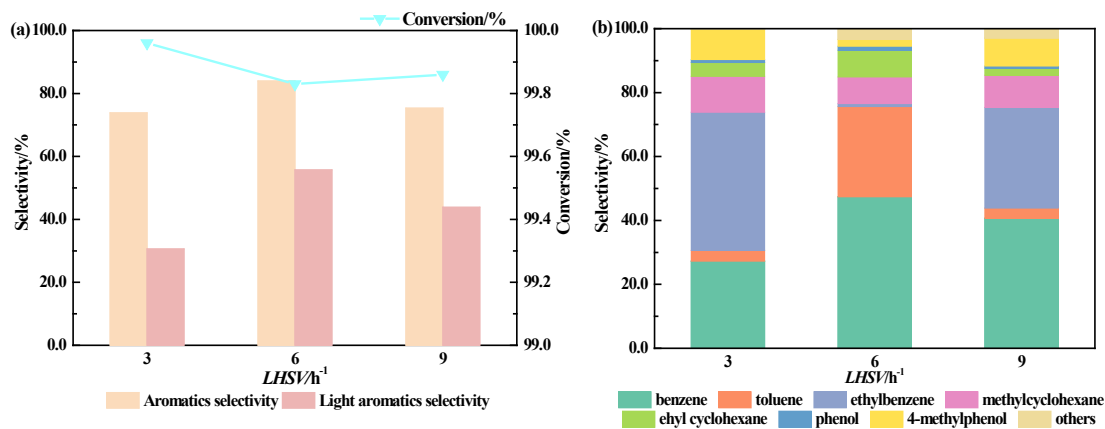
<sup>b</sup> Beijing System Design Institute of Mechanical-Electrical Engineering, Beijing 100854, China.

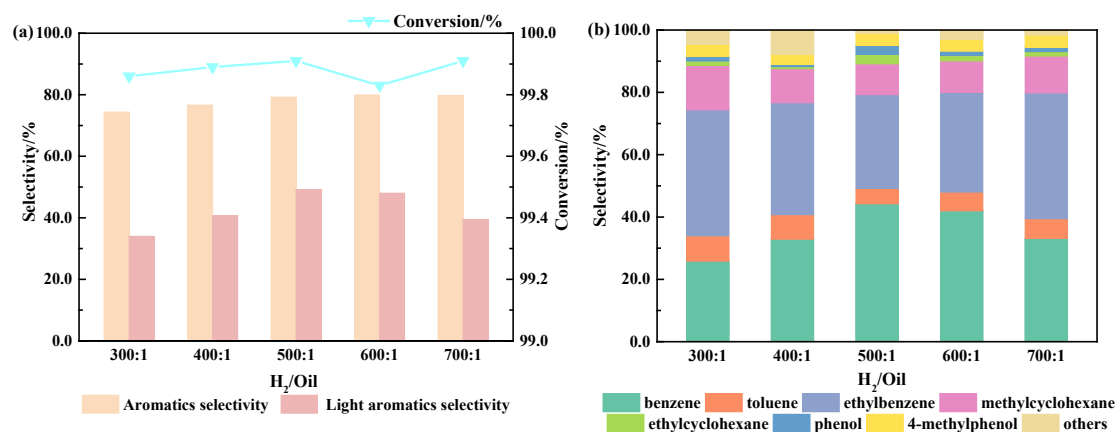
<sup>c</sup> State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, Ningxia University, Yinchuan 750021, China.

\*Corresponding author: lizhiqin@xsyu.edu.cn

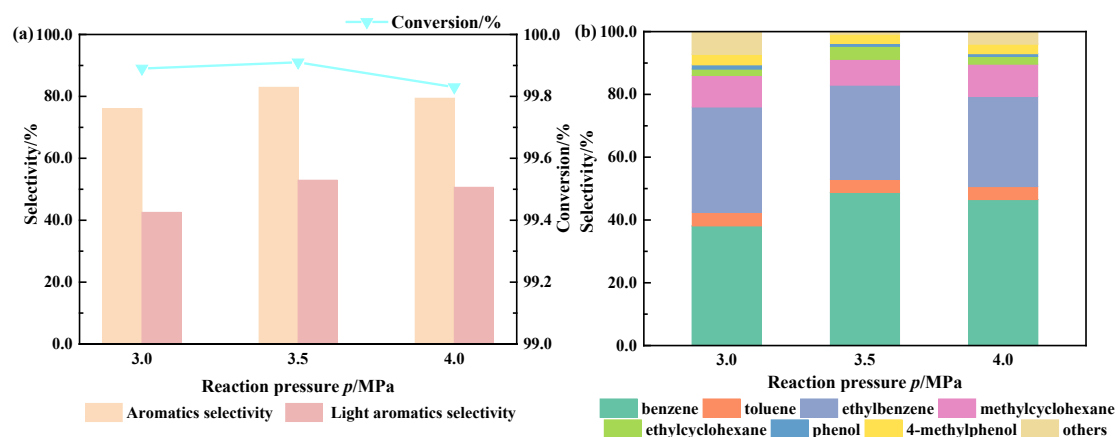
**Table S1** The typical carbon balance for the reaction of 4-ethylphenol over15% Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>

Input/mol		Output/mol	
4-ethylphenol	0.08657	Benzene (C6)	0.029004
		Methylcyclohexane (C7)	0.007574
		Toluene (C6)	0.003788
		Ethylcyclohexane (C8)	0.002634
		Ethylbenzene (C8)	0.026302
		Phenol (C6)	0.001938
		4-methylphenol (C7)	0.00297
		Methane (C1)	0.000504
		Ethane (C2)	0.011387
Total	0.08657		0.08610
Output/Input (%)		99.5%	

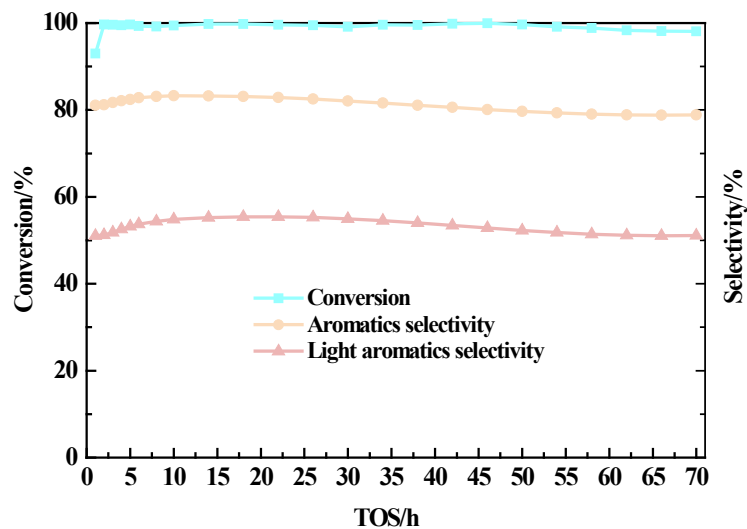
Reaction conditions: LHSV=6 h<sup>-1</sup>, H<sub>2</sub>/Oil=500:1, P=3.5 MPa, T=450 °C**Fig. S1** Effect of LHSV on the performance of 15% Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrogenation of 4-ethylphenol. Reaction conditions: H<sub>2</sub>/Oil=500:1, P=3.5 MPa, T=450 °C. Others: mainly consisted of isomerization or saturation products.



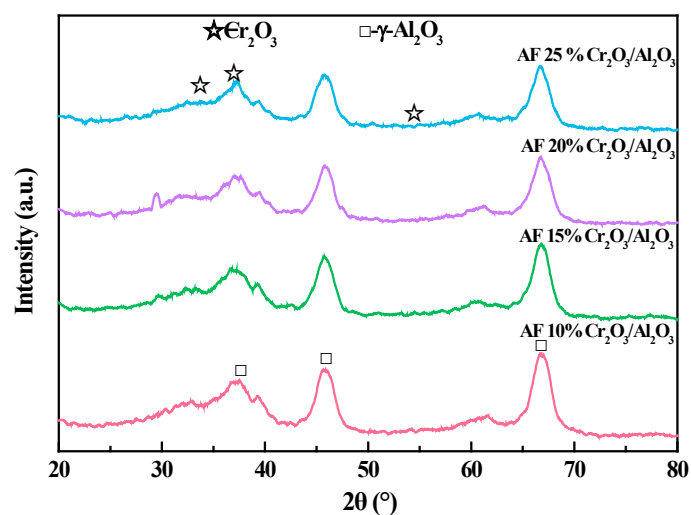
**Fig. S2** Effect of H<sub>2</sub>/oil ratio on the performance of 15% Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrogenation of 4-ethylphenol. Reaction conditions: LHSV=6 h<sup>-1</sup>, P=3.5 MPa, T=450 °C. Others: mainly consisted of isomerization or saturation products.



**Fig. S3** Effect of reaction pressures on the performance of 15% Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrogenation of 4-ethylphenol. Reaction conditions: LHSV=6 h<sup>-1</sup>, H<sub>2</sub>/Oil=500:1, T=450 °C. Others: mainly consisted of isomerization or saturation products.

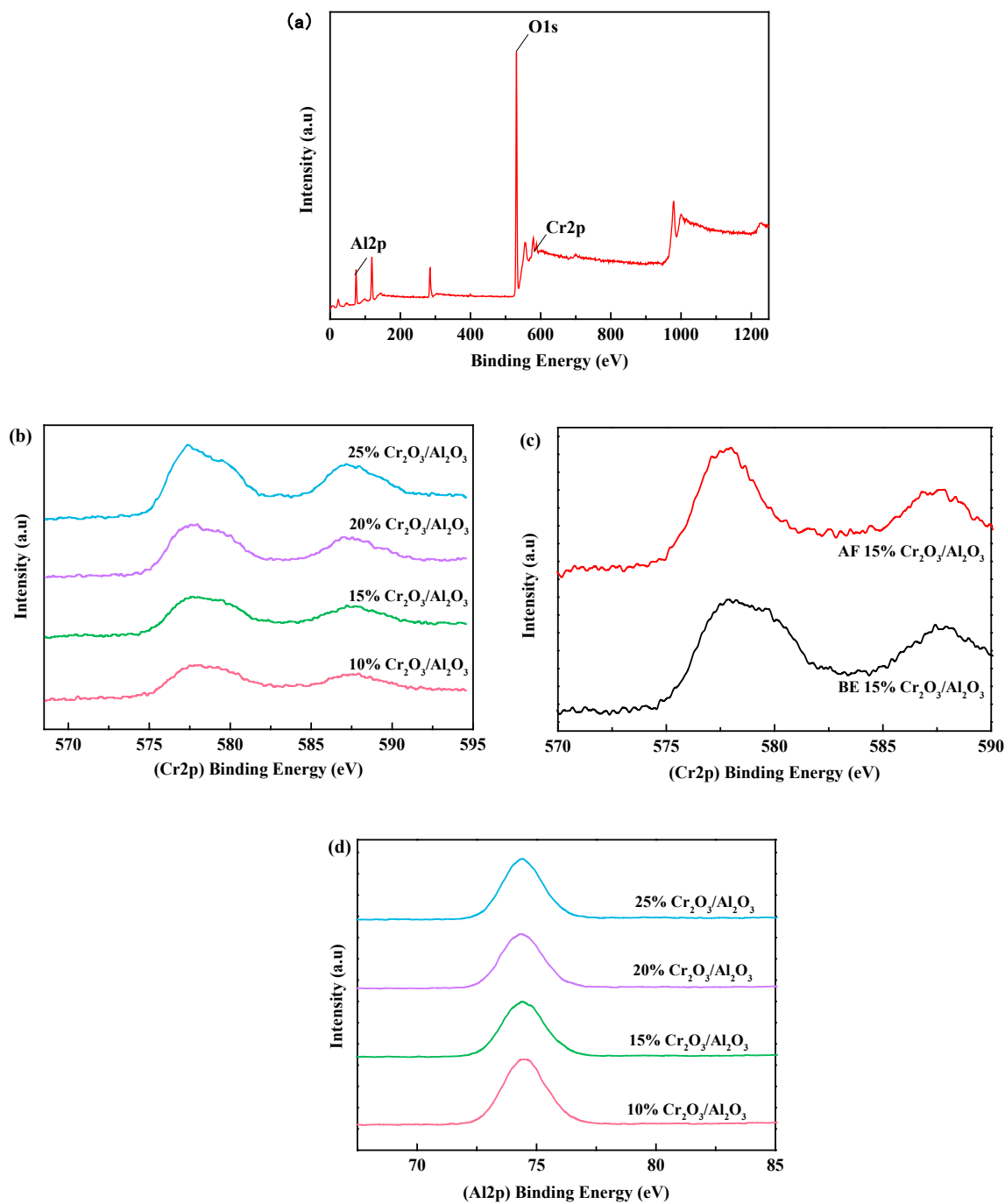


**Fig. S4** Time on stream of the conversion of 4-ethylphenol over 15% Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: LHSV=6 h<sup>-1</sup>, H<sub>2</sub>/Oil=500:1, P=3.5 MPa, T=450 °C.



**Fig. S5** XRD patterns of Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts with different Cr loading after reaction; AF: After

Reaction conditions: LHSV=6 h<sup>-1</sup>, H<sub>2</sub>/Oil=500:1, P=3.5 MPa, T=450 °C.

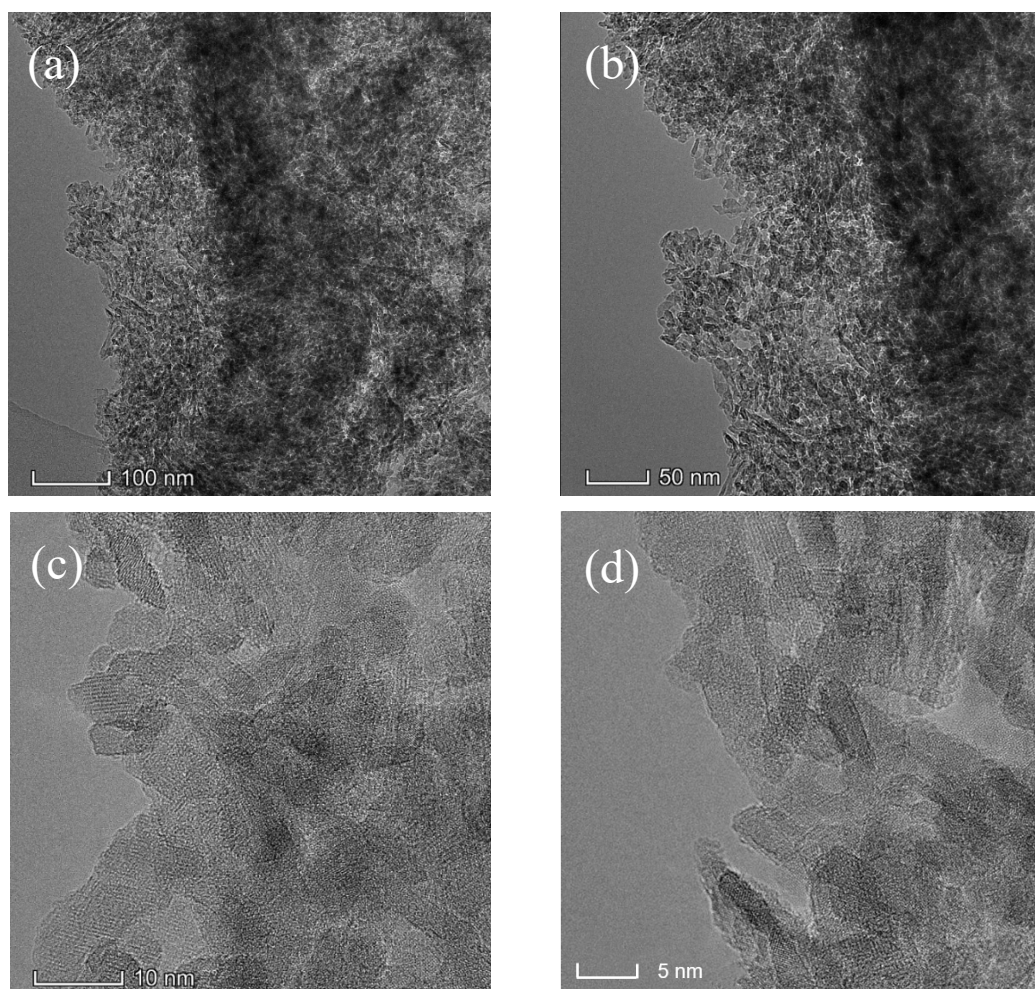


**Fig. S6** XPS spectra of  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst.

(a) Survey scan XPS spectrum of  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ; (b) Cr 2p XPS spectra of  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst with different Cr loading; (c) Cr 2p XPS spectra of 15%  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  before and after the reaction;

(d) Al 2p XPS spectra of  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst with different Cr loading;

Reaction conditions: LHSV=6  $\text{h}^{-1}$ ,  $\text{H}_2/\text{Oil}$ =500:1, P=3.5 MPa, T=450  $^\circ\text{C}$ .



**Fig. S7** HRTEM images of 15% Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst after reaction. Reaction conditions: LHSV=6 h<sup>-1</sup>, H<sub>2</sub>/Oil=500:1, P=3.5 MPa, T=450 °C.

### **Inferring details of the formation paths for products over Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>**

Taking the formation of benzene as an example, benzene can be formed through three possible paths: (1) break C-O bond of 4-ethylphenol to produce 4-ethylbenzene, and then break C<sub>Ar</sub>-C<sub>α</sub> bond of 4-ethylbenzene to form benzene; (2) break C<sub>α</sub>-C<sub>β</sub> bond of 4-ethylphenol to produce 4-methylphenol, then break C-O bond of 4-methylphenol to form 4-methylbenzene, and at last break the C<sub>Ar</sub>-C<sub>α</sub> bond of 4-methylbenzene to form benzene; (3) break C<sub>Ar</sub>-C<sub>α</sub> bond of 4-ethylphenol to produce phenol, and then break C-O bond of phenol to form benzene. For path (1), it could be seen clearly that when the selectivity of benzene increased significantly, the selectivity of 4-ethylbenzene decreased accordingly. (Figure 1-2), suggesting this path of transformation of 4-ethylbenzene to benzene existed. For path (2), when LHSV increased from 3

$\text{h}^{-1}$  to  $6 \text{ h}^{-1}$  (Figure S1), the decrease of selectivity for ethylbenzene (about 13.2% reduction) was smaller than the increase of selectivity for benzene (about 17.4% increase); Meanwhile, the selectivity of 4-methylphenol reduced by about 6.7%. Such results could only be explained reasonably when the partial decrease of the selectivity of 4-methylphenol was attributed to the production of benzene. Therefore, it could be inferred that the path for the formation of benzene via 4-methylphenol existed. For path (3), when the reaction conditions (including LSHV and temperature) changed, the selectivity of phenol was always low and almost remained unchanged, suggesting that the path for the formation of benzene via phenol could be ignored. So far, the path for the formation of benzene could be deduced. By analyzing the formation of each product one by one, the main reaction paths for the hydrogenation of 4-ethylphenol on  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  could be inferred. It should be noted that the product in gas phase was mainly consisted of methane and ethane, which also confirmed the breaking of the  $\text{C}_{\text{Ar}}-\text{C}_{\alpha}$  and  $\text{C}_{\alpha}-\text{C}_{\beta}$  bond, respectively.