

## Supplementary information

### **Regioselective hydrogenolysis of aryl ether C–O bonds by tungsten carbides with controlled phase compositions**

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## 1. Catalyst preparation

Tungsten carbides ( $W_xC@CS-t$ ) were prepared by polycondensation of resorcinol with formaldehyde according to the literature with modified method. Typically, 1.2 g resorcinol and 5.0 g meta-tungstate were dissolved in distilled water with vigorous stirring for 30 min. Then 2.3 mL formaldehyde was added in the solution and the mixed solution was heated to reflux at 85 °C for 24 h for polymerization to occur. The obtained yellow powder was filtered, washed several times with distilled water and dried overnight at 100 °C. The as-prepared solid mixture was carburized at 850 °C under  $H_2$  for 1-6 h. Prior to exposure to air, the as-prepared carbides were passivated by 1%  $O_2$ –99%  $N_2$  for 30 min. The obtained catalysts were denoted as  $W_xC@CS-t$  ( $x=1, 2$ ; CS and  $t$  represent carbon spheres and carburizing time, respectively). For comparison, a catalyst treated at 700 °C for 2 h under  $H_2$  using the same precursor was labeled as  $W@CS$ . These catalysts were used directly in conversion of guaiacol or stored under  $N_2$  to prevent additional oxidation of carbide surface.

## 2. Catalytic testing

The catalytic performance for guaiacol conversion was evaluated on a conventional fixed flow reactor with a computer-controlled auto-sampling system. Typically, 200 mg of the newly prepared catalyst was loaded in the center of quartz tubular reactor and sandwiched by quartz powers. Prior to the evaluation of catalytic performance, the catalyst was pretreat under 5%  $H_2$ –95%  $N_2$  at 450 °C for 4 h at a ramping rate of 3 °C/min. Then the catalyst bed was cooled to the target reaction temperature, pure  $H_2$  was fed into the reactor and held at required pressure. Pure guaiacol was pumped into the reactor by using a Series III digital HPLC pump (Scientific Systems, Inc.) with required weight liquid hourly space velocity (WLHSV). The products were analyzed by an Agilent 7890A gas chromatograph (GC) equipped with an auto-sampling valve, DB-Wax capillary column and flame ionization detector (FID). A GC 2060 with a TDX column and thermal conductivity detector was used for analysis of gas products ( $CO$ ,  $CH_4$ ,  $CO_2$ , and  $H_2O$ ).

The conversion of guaiacol and selectivity of products were calculated as follows:

$$Conversion = \frac{(moles\ of\ GUA)_{in} - (moles\ of\ GUA)_{out}}{(moles\ of\ GUA)_{in}} \times 100\% \quad (1)$$

$$S_{C6i} = \frac{moles\ of\ ring\ product\ i}{the\ sum\ moles\ of\ guaiacol\ consumed} \times 100\% \quad (2)$$

$$S_{C1i} = \frac{\text{moles of produced methane or methanol}}{\text{the sum moles of methane and methanol}} \times 100\% \quad (3)$$

The details of reactor and product analysis, and the calculation of conversion and selectivity are described in our previous work.<sup>1</sup>

### 3. Catalyst characterizations

#### 3.1 X-ray diffraction (XRD) analysis

XRD analysis was carried out by a Phillips PANalytical X'pert Pro diffractometer equipped with a Cu-K $\alpha$  radiation (40 kV and 30 mA) at scanning 2 $\theta$  from 10° to 90°. The JCPDS database was used to analyze the obtained diffraction data and identified the phase of the samples.

The W/W<sub>2</sub>C/WC ratio was calculated by the XRD Rietveld refinement using Topas software. For the Rietveld refinement, the XRD pattern was collected at a scan rate of 5 degree/min in order to get high quality data. Due to the fact that there are 3 kinds of diffraction peaks ascribed to W, W<sub>2</sub>C, WC, we applied multi-phase simulation. The structures of models corresponding to W, W<sub>2</sub>C, and WC were identified using X'pert HighScore software, and the standard data were downloaded from the The Inorganic Crystal Structure Database (<https://icsd.fiz-karlsruhe.de>).

#### 3.2 Scanning electron microscopy (SEM) measurements

The morphology of samples were observed on a scanning electron microscopy SEM, Hitachi S4800) equipped with energy dispersive X-ray spectroscopy.

#### 3.3 Transmission electron microscopy (TEM) measurements

TEM images were obtained by a Philips Analytical FEI Tecnai 30 electron microscope equipped with a high resolution pole piece and operated at an acceleration voltage of 300 kV. The samples with pretreatment were ultrasonically dispersed and then dropped and dried on copper grids coated with C films.

#### 3.4 X-ray photoelectron spectroscopy (XPS)

XPS spectra were performed on an Omicron Sphera II photoelectron spectrometer equipped with an Al-K $\alpha$  X-ray radiation source (h $\nu$ = 1486.6 eV). The samples were treated in an in situ chamber with 5%H<sub>2</sub>/N<sub>2</sub> at 450 °C for 4 h before measurements. The binding energy was calibrated using the C<sub>1s</sub> peak at 284.5 eV.

#### 3.5 N<sub>2</sub> adsorption-desorption analysis

N<sub>2</sub> adsorption-desorption isotherm was determined at 77 K by using a Micromeritics TriStar II 3020 porosimetry analyzer. The fresh sample was degassed at 573 K for 3 h prior to

the measurements. Specific surface area was measured through Brunauer–Emmett–Teller (BET) method. Pore size and average pore diameter distributions were calculated from the desorption isotherm branch according to the Barret–Joyner–Halenda method.

**Table S1** BET surface area and average pore size of  $W_xC@CS-t$  samples with different carburizing time.

Sample	$S_{BET}$ ( $m^2 g^{-1}$ )	Average $D_{pore}$ (nm)
W@CS	261	2.5
$W_xC@CS-1h$	113	3.1
$W_xC@CS-2h$	81	3.5
$W_xC@CS-3h$	56	3.8
$W_xC@CS-4h$	52	4.2
$W_xC@CS-5h$	50	5.4
$W_xC@CS-6h$	52	6.5

**Table S2** Refined structure parameters for the W-based sample.

Sample	Crystal phase	Weight percent /%	Crystal structure	Lattice parameters /Å	Statistical parameters
W@CS	W	100	Im-3m	a=b=c=3.1648	$R_{wp}=1.37$
$W_xC@CS-1h$	W	6	Im-3m	a=b=c=3.1648	$R_{wp}=10.50$
	$W_2C$	70	P-31m	a=b=2.9900, c=4.7273	
$W_xC@CS-2h$	WC	24	P-6m2	a=b=2.9017, c=2.8486	$R_{wp}=5.38$
	$W_2C$	59	P-31m	a=b=2.9900, c=4.7273	
$W_xC@CS-3h$	WC	41	P-6m2	a=b=2.9017, c=2.8486	$R_{wp}=4.19$
	$W_2C$	43	P-31m	a=b=2.9900, c=4.7273	
$W_xC@CS-4h$	WC	57	P-6m2	a=b=2.9017, c=2.8486	$R_{wp}=6.27$
	$W_2C$	18	P-31m	a=b=2.9900, c=4.7273	
$W_xC@CS-5h$	WC	82	P-6m2	a=b=2.9017, c=2.8486	$R_{wp}=14.37$
	$W_2C$	4	P-31m	a=b=2.9900, c=4.7273	

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W <sub>x</sub> C@CS-6h	WC	100	P-6m2	a=b=2.9017, c=2.8486	R <sub>wp</sub> =2.05
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**Table S3** Catalytic performance of W@CS and W<sub>x</sub>C@CS-3h catalysts for hydrogenolysis of anisole

Catalyst	<i>T</i> /°C	Conv. /%	C6 product selec. /%					C1 product selec. /%	
			PhOH	Benzene	Cresols	Cyclo- hexanol	Others	CH <sub>4</sub>	CH <sub>3</sub> OH
W@CS	275	32.1	82.8	0.7	3.2	4.9	8.4	84.9	15.1
	300	46.7	83.7	1.6	4.6	2.4	7.7	83.0	17.0
W <sub>x</sub> C@CS-3h	275	53.9	2.1	94.1	0.0	2.9 <sup>a</sup>	0.0	56.3	43.7
	300	100	0.0	96.0	0.0	4.0 <sup>a</sup>	0.0	58.9	41.1

Reaction conditions: WLHSV= 3.0 h<sup>-1</sup>, *P*(H<sub>2</sub>)=3.0 MPa, H<sub>2</sub>/Anisole molar ratio = 50;

<sup>a</sup> cyclohexane.

**Table S4** PhOH selectivity and C1 product selectivity over W-based catalysts for hydrogenolysis of GUA

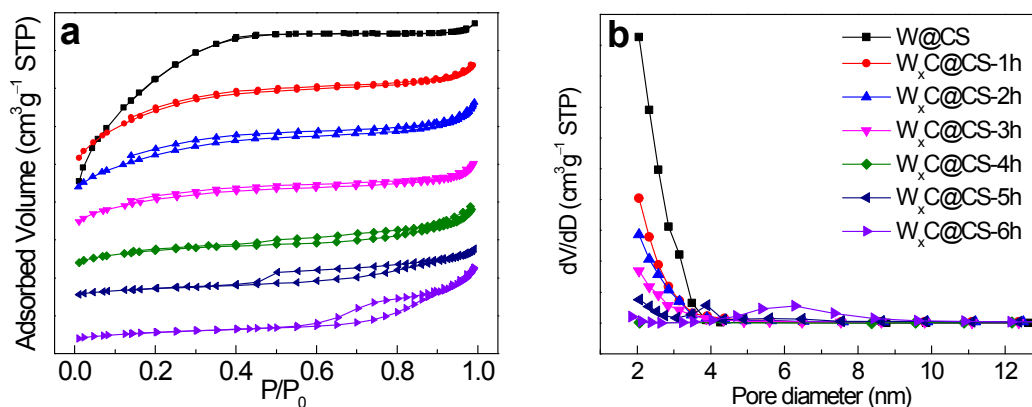
Catalyst	W/W <sub>2</sub> C/WC ratio /%	Conv. /%	PhOH selec. /%	C1 product Selec. /%	
				CH <sub>4</sub>	CH <sub>3</sub> OH
W@CS	100/0/0	28.2	30.3	61.2	38.8
W <sub>x</sub> C@CS-1h	6/70/24	79.9	78.6	16.3	83.7
W <sub>x</sub> C@CS-2h	0/59/41	90.3	80.7	17.5	82.5
W <sub>x</sub> C@CS-3h	0/43/57	99.8	92.7	18.8	81.2
W <sub>x</sub> C@CS-4h	0/18/82	64.7	83.5	20.3	79.5
W <sub>x</sub> C@CS-5h	0/4/96	33.1	73.6	24.3	75.7
W <sub>x</sub> C@CS-6h	0/0/100	30.1	70.7	20.2	79.8
WC	0/0/100	7.1	51.0	23.3	76.7

Reaction conditions: WLHSV = 3.0 h<sup>-1</sup>, *P* (H<sub>2</sub>) = 3.0 MPa, H<sub>2</sub>/GUA molar ratio = 50, *T* = 300 °C. *Note*: The catalytic performance of Table S2 is associated to Table 1.

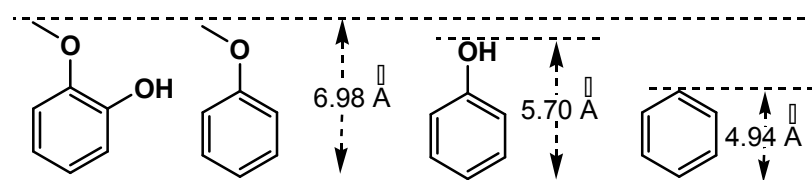
**Table S5** Catalytic performance of selective hydrogenolysis of various ethers over the  $W_xC@CS-3h$

Ether	$T$ /°C	Conv. /%	C6 product selec. /%					Yield <sup>e</sup> / %
			PhOH	Benzene	Anisole	Cresols	Others	
Diphenyl ether	250	100	100	100	0.0	0.0	0.0	200
Anisole	300	100	0.0	96.0	–	0.0	4.0 <sup>b</sup>	96.0
Phenetole	325	97.1	17.3	71.6	–	3.5	7.6	86.3
Veratrole <sup>a</sup>	325	98.6	10.9	60.1	5.1	0.0	27.0 <sup>c</sup>	70.0
Dimethoxyphenol	350	93.1	86.3	0.6	0.0	1.3	11.8 <sup>d</sup>	80.9

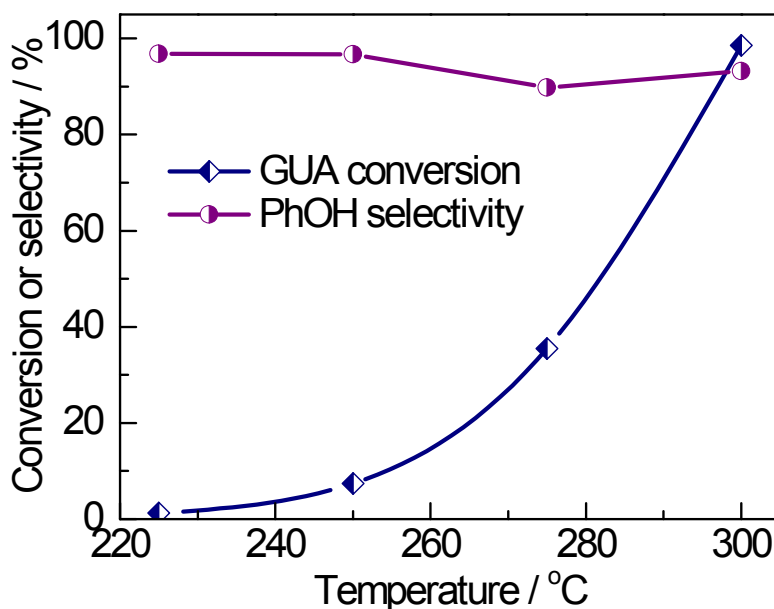
Reaction conditions: WLHSV= 3.0 h<sup>-1</sup>, P (H<sub>2</sub>) = 3.0 MPa, H<sub>2</sub>/Ether molar ratio = 50; <sup>a</sup> H<sub>2</sub>/Ether molar ratio = 90; <sup>b</sup> Cyclohexane; <sup>c</sup> Trace aromatic ring-saturated products and some other unknown products; <sup>d</sup> Trace GUA and some other unknown products; <sup>e</sup> Total yield of PhOH and benzene.



**Fig. S1**  $N_2$  adsorption-desorption isotherm for (a) and BJH pore size distribution for (b) of  $W_xC@CS-t$  samples with different carburizing time.



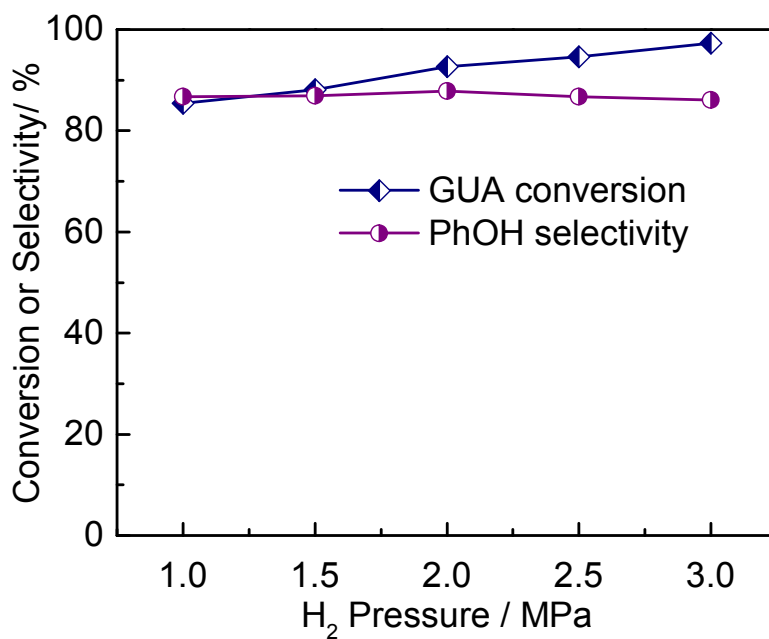
**Fig. S2** The diameter of molecules (GUA, anisole, PhOH, and benzene) calculated by Gauss View software.



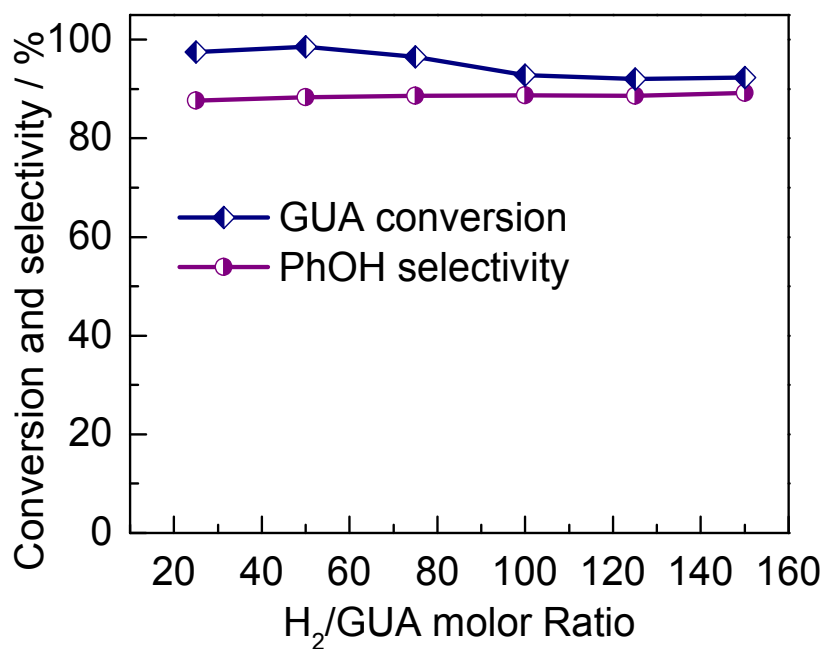
**Fig. S3** Effect of temperature on GUA conversion and PhOH selectivity.

Reaction conditions:  $WLHSV = 3.0 h^{-1}$ ,  $P(H_2) = 3.0 MPa$ ,  $H_2/GUA$  molar ratio = 50.

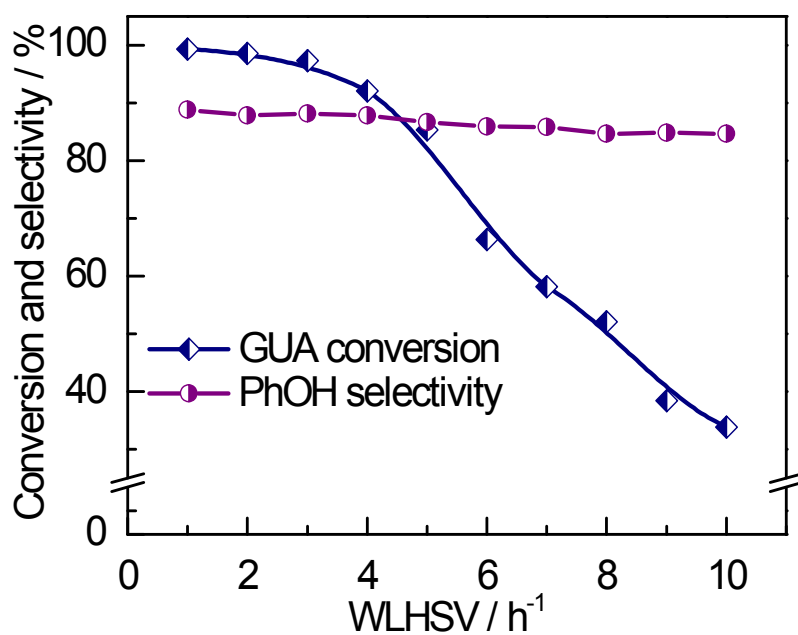




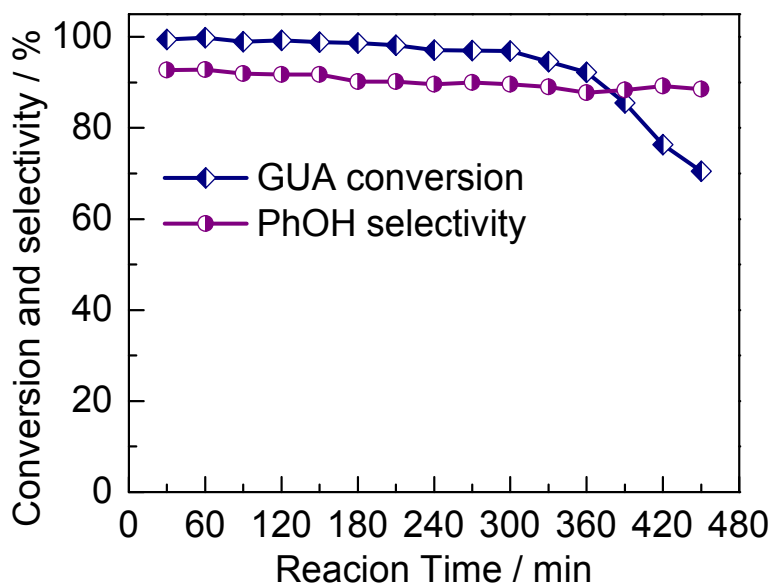
**Fig. S4** Effect of H<sub>2</sub> pressure on GUA conversion and PhOH selectivity.  
 Reaction conditions: WLHSV = 3.0 h<sup>-1</sup>, H<sub>2</sub>/GUA molar ratio = 50, T = 300 °C.



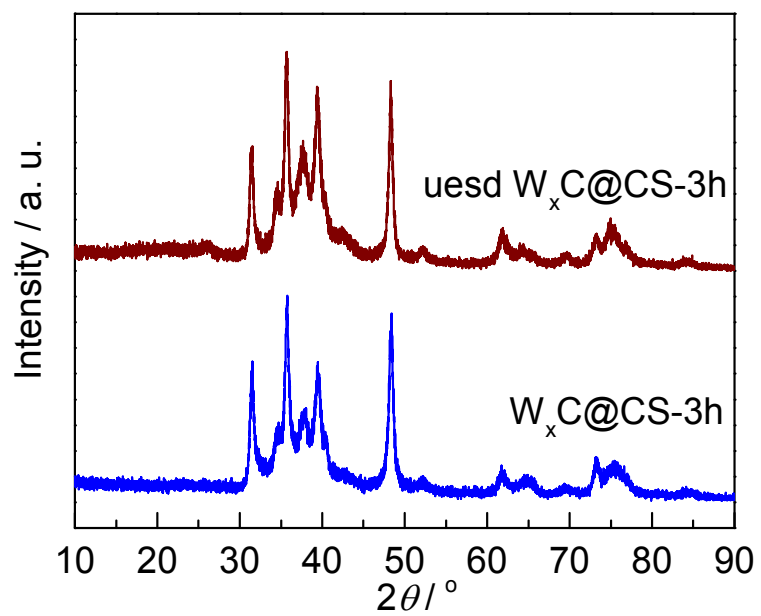
**Fig. S5** Effect of H<sub>2</sub>/GUA molar ratio on GUA conversion and PhOH selectivity.  
 Reaction conditions: WLHSV = 3.0 h<sup>-1</sup>, P(H<sub>2</sub>) = 3.0 MPa, T = 300 °C.



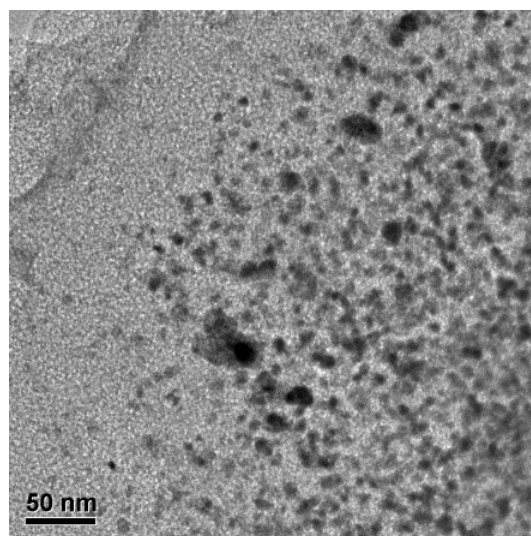
**Fig. S6** Effect of WLHSV on GUA conversion and PhOH selectivity. Reaction conditions:  $P(\text{H}_2)=3.0$  MPa,  $\text{H}_2/\text{GUA}$  molar ratio = 50,  $T=300$  °C.



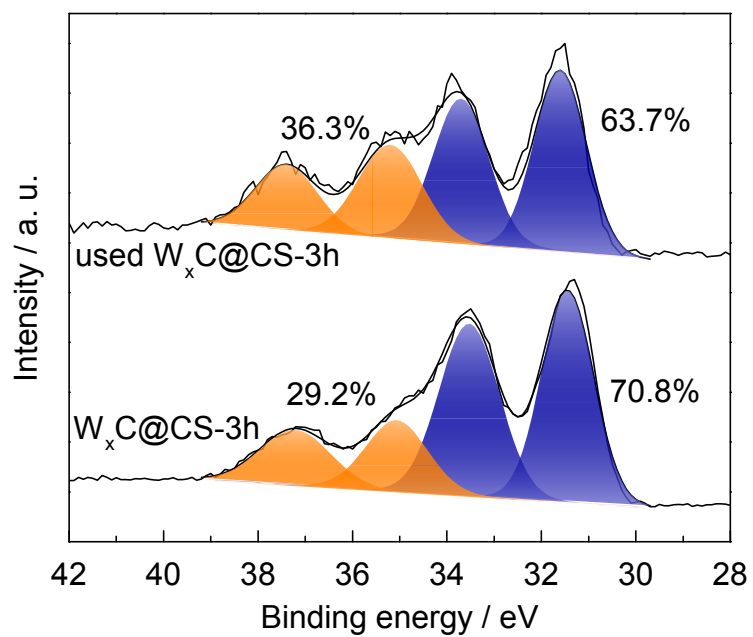
**Fig. S7** GUA conversion and PhOH selectivity over the  $\text{W}_x\text{C}@\text{CS-3h}$  catalyst as a function of time.



**Fig. S8** XRD patterns of fresh and used  $W_xC@CS-3h$  catalysts.



**Fig. S9** TEM image of the used  $W_xC@CS-3h$  catalyst.



**Fig. S10** XPS profiles of fresh and used  $W_xC@CS-3h$  catalysts.

### Reference

1. H. H. Fang, J. W. Zheng, X. L. Luo, J. M. Du, A. Roldan, S. Leoni and Y. Z. Yuan, Appl. Catal. A: Gen., 2017, 529, 20.