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# Synergy of carbon defect and transition metal on tungsten carbides for boosting the selective cleavage of aryl ether C—O bond



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depth characterizations.

ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Transition metal carbide Carbon defect Transition metal Synergy effect CO bond hydrogenolysis	Transition-metal carbides are attractive heterogeneous catalysts for the transformation of lignin-derived com- pounds. However, the effects of the surface carbon defect (C-defect) remain unclear due to coke deposition and exposed C terminations. Herein, we transform inert tungsten carbides (WC) into active catalysts via surficial C- etching using transition metals in the presence of H <sub>2</sub> . An optimized 1% Pt–WC catalyst with synergy of Pt and C- defects can perform a 78.6% conversion in the selective hydrogenolysis of guaiacol to phenol with 89.0% selectivity at 300 °C, while the intact WC only gives a 7.1% guaiacol conversion with 51.0% phenol selectivity under the same conditions. As a result, the 1% Pt–WC catalyst exhibits 19-fold higher reaction rate and 12.6-fold higher turnover frequency than those of WC. Moreover, no substantial loss of catalytic performance has been

#### 1. Introduction

Phenol is an important platform chemical and commonly used as an intermediate in chemical industry such as pesticide production [1]. The production of phenol is essentially based on the petroleum-based feedstocks by cumene process [2]. Lignocellulose is the abundant renewable feedstock which is mainly composed of aromatics. Transformation of lignocellulose into aromatic chemicals like phenol is an attractive and alternative process for fossil energy substitution [3–7]. It is well known that the fast pyrolysis is the most cost-effective process to produce lignin-derived bio-oil, but these bio-oils are far from commercial use due to the formation of complex oxygenated mixtures such as (alkyl-) guaiacols, resulting in high viscosity, overfunctionlization and chemical instability [8,9]. Hydrodeoxygenation (HDO) is a viable and effective bio-oil upgrading process to remove extensive oxygen contents.

HDO of lignin-derived oxygenates into phenolics with high selectivity via direct cleavage of aryl C—O bonds remains challenging due to strong bonding linkages in lignin compounds and the competing side reactions such as hydrogenation of aromatic rings and dehydroxylation [10-12]. Guaiacol (GUA) is the most typical compound in lignin-derived oils and regarded as the ideal model molecule in HDO reactions. It contains three types of C—O bonds with different bond energies,

namely, Carvl-OCH<sub>3</sub> (356 kJ mol<sup>-1</sup>), CarvlO-CH<sub>3</sub> (247 kJ mol<sup>-1</sup>) and  $C_{arvl}$ —OH (414 kJ mol<sup>-1</sup>), which are characteristic components of lignocellulose [13]. The HDO of GUA involves the cleavage of aryl C-O bond, aliphatic C—O bond, and the hydrogenation of arene (Scheme 1), posting the importance and challenging of catalyst design towards different value-added products. Apparently, the phenol production requires the direct hydrogenolysis of  $\mathrm{C}_{\mathrm{aryl}}\mathrm{-OCH}_3$  without the cleavage of CarvlO-CH3, Carvl-OH and saturation of arene. Two common types of HDO systems including batch liquid-phase HDO using autoclave and continuous HDO using fixed-bed reactor are employed. Usually, the liquid-phase HDO requires high H2 pressures (1-20 MPa) to ensure better H<sub>2</sub> solubility into the reaction media, the high cost of high-pressure equipment and additional solvent requirement [14]; whereas the continuous HDO with a fixed-bed reactor can proceed at a wide range of H<sub>2</sub> pressures although sometimes requires high reaction temperatures and it suppresses the recondensation of reactants and further hydrogenation of aromatic ring [15]. Table S1 summarizes the previous reports on the GUA HDO by various catalysts with fixed-bed reactors. From the point of view of HDO products, a total HDO of GUA and lignin-derived oxygenates into hydrocarbons that can be used as bio-fuels and has been intensively studied. However, a partial HDO into O-containing chemicals is more valuable in lignin utilization; the

observed with 1% Pt-WC for 50 h on stream. A rational reaction pathway is accordingly proposed through in-

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process needs lower  $H_2$  consumption and has higher industry value. Therefore, it is important and attractive to develop novel catalysts to achieve high product selectivity in GUA HDO and understand the relationship between the structure and performance.

To date, supported metal catalysts are applied as common hydrogenation catalysts in conversion of lignin biomass [16–22]. Previous studies have shown that metal catalysts such as Pt [16,17], Pd [18], Ru [19], Ni [20,21], and Cu [22] exhibit promising activity in transformation of lignin-derived chemicals. Yet, the excellent ability for H<sub>2</sub> disassociation over these metals allows both of the cleavage of C—O bonds and the saturation of aromatic rings, resulting in wide product distribution, less value of products and excessive hydrogen consumption [23,24]. Therefore, constructing an active catalyst towards value-added products like phenol in lignin utilization is important and highly desirable.

Transition-metal carbides (TMCs) are considered as attractive materials in heterogeneous catalysis due to their outstanding catalytic behavior [25–27]. TMCs are used in wide-ranging important reactions, such as HDO, hydrogenation, isomerization, and hydrogen evolution reactions (HER) [28–32]. TMCs also serve as excellent carriers for the dispersion of metals due to the strong metal–support interaction and modification of the electronic structure [33–35].

The TMC-based materials are typically synthesized by temperatureprogrammed reduction with gaseous carbon precursors, such as CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, and CO [36,37]. The insertion of carbon atoms into parent metals induces the structural rearrangement and redistribution of the density of state and then provides superior catalytic performance [38,39]. However, the rapid diffusion of carbons at the gas-solid interface normally causes the deposition of carbon layer on the surface. Matus et al. [40] found a graphite layer of approximately 2 nm thick with the formation of Mo<sub>2</sub>C in the presence of CH<sub>4</sub>; Ma et al. [41] demonstrated the similar graphite layers on the carbide particles during the synthesis of Co<sub>6</sub>Mo<sub>6</sub>C<sub>2</sub>/<sup>g</sup>C. These graphitic carbons block the pores and prevent the exposure of active sites and the chemisorption of reactants, negatively influencing the catalytic activity [39,42]. For example, Kimmel et al. [42] synthesized WC with different monolayers of surface carbon and investigated the effect of these coated carbon layers. They found that the catalytic performance decrease when the particles were coated by several carbon layers. Carbothermal reduction was further proposed by using solid carbon sources such as activated carbon, carbon nanotubes (CNTs), and carbon fibers in the synthesis of metal carbides [43-45]. Gong et al. [44] prepared phase-pure W<sub>2</sub>C nanoparticles without coating of surface carbon layer on CNTs and HER performance through carbon diffusion from carbon nanotubes to metal tungsten. In addition, Xu and Wu et al. [46,47] used metal-organic frameworks as precursors to synthesize metal carbide nanoparticles by pyrolysis and carbon

diffusion. This method effectively slows down carbon diffusion through the solid-solid interface and then avoids the excessive formation of surface carbon. On the other hand, Yang et al. [48] used oxygen plasma treatment to remove surface carbon and activate WC and thus improve HER activity and methanol oxidation. Recently, W2C nanorods with abundant C-defects for HDO reactions have been reported [49]. Our previous investigation has also demonstrated the significance of surface reconstruction on inert WC to promote C-O bond cleavage [50]. Importantly, Hunt et al. [51] synthesized metal-terminated tungsten carbide nanoparticles on carbon supports by using SiO<sub>2</sub> as the template and during the carburization in the presence of CH<sub>4</sub> and following etching treatment. This strategy allows the exposure of metal sites and displayed 100-fold higher HER activities than commercial WC. Therefore, the design of high-quality TMC-based materials (e.g., free from surface carbon, controllable phase, and surface defects) is of great importance. Another strategy for boosting TMC-based materials is by incorporating second metals. Previous reports have shown that Au and Cu supported on molybdenum carbides are highly active in (reverse) water-gas shift reactions due to their excellent capability for H<sub>2</sub> activation and C-O bond scission [52,53]. Ni-W<sub>2</sub>C/AC was adopted for the conversion of cellulose and lignin compounds and show remarkable activities for selective C—O bond cleavage [45,54]. Results indicate the strong synergistic interaction and surface modification between metals and carbide supports. Thus, to construct active TMC-based materials by introducing second metals is attractive and highly desired.

Herein, we report a simple but powerful strategy to synthesize metalpromoted tungsten carbide for the efficient hydrogenolysis of the aryl ether C—O bond. The key procedure is C-etching on inert WC surface by metal-activated hydrogen species under thermal pretreatment. An asbuilt Pt–WC catalyst exhibits unique catalytic activity through direct aryl ether C—O bond scission, whereas normal Pt/AC and Pt–WC without C-etching facilitate ring saturation and show 19-fold higher activity than intact WC. Other metals such as Pd, Ru, Ni, and Cu display similar catalytic behaviors. Further designed experiments illustrate that the incorporated metals serve as sites for  $H_2$  activation, whereas C-defects are responsible for reactant adsorption. Finally, a rational reaction pathway is proposed.

#### 2. Experimental

#### 2.1. Catalyst preparation

The initial bulk WC was commercially available from Aladdin Co. Ltd. Pt-promoted WC catalysts with different synthesis methods were prepared as follows. In a typical procedure, 1.0 g of WC was dispersed in 50 mL of distilled water with sonication and continuous stirring for 30



Scheme 1. Reaction pathway for GUA HDO.

min. The required amount of H<sub>2</sub>PtCl<sub>6</sub> solution was added, and the different Pt loadings were accordingly adjusted within the range of 0.1%-5%. After stirring for 3 h, the mixed solution removed the excess solvent under vacuum with an oil bath at 100 °C, forming a gel-like slurry. The slurry was left at room temperature for 12 h for further diffusion of Pt precursors. Then the Pt supported precursors were obtained after solvent removal under vacuum and dried at 100 °C overnight. For C-etching thermal treatment, the catalysts were in situ treated at 450 °C with a heating ramp of 2 °C/min for 2 h in the presence of pure H<sub>2</sub>. The obtained catalysts were denoted as (0.1%-5%) Pt-WC. In the designed experiments, the catalyst without C-etching was reduced at 400 °C for 2 h under 5%  $H_2/N_2$ , which was denoted as 1% Pt–WC<sup>#</sup>. The catalysts with different C-defects were treated at 450  $^\circ$ C for 0–6 h in the presence of pure H<sub>2</sub>. The catalyst with almost W terminations was treated at 850 °C for 2 h, denoted as 1% Pt-WC-850. All catalysts were used directly in the conversion of GUA or stored under N<sub>2</sub> to prevent additional oxidation of the carbide surface.

#### 2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained from a Rigaku Ultima IV X-ray diffractometer equipped with Cu-K<sub>a</sub> radiation (40 kV and 30 mA) at a scanning 20 range of  $10^{\circ}$ –90°. The JCPDS database was used to identify the obtained diffraction data. Transmission electron microscopy (TEM) and high-angle annular dark field-scanning TEM (HAADF-STEM) with energy-dispersive spectroscopy (EDS) were performed with a Philips Analytical FEI Tecnai 20 electron microscope at an acceleration voltage of 200 kV. Fresh samples were dispersed ultrasonically and then dropped and dried on copper grid with lacey support films. In situ X-ray photoelectron spectroscopy (XPS) data were obtained on an Omicron Sphera II photoelectron spectrometer equipped with an in situ chamber and an Al-K<sub> $\alpha$ </sub> X-ray radiation source (h $\nu$ = 1486.6 eV). The binding energy was calibrated using the C 1s peak at 284.5 eV. High-sensitivity low-energy ion scattering (HS-LEIS) profiles were obtained on an Ion-TOF Qtac100 instrument. He was selected as the ion source at a kinetic energy of 3 keV with an ion flux of 6000 pA  $m^{-2}$  and a spot size of 2000  $\mu m \times 2000 \ \mu m$  to obtain surface information and minimize surface damage. The C/W atomic ratio on the surface was calculated by integrating the relative intensity of W and C from HS-LEIS and XPS measurements. Before XPS experiments, the samples were pretreated with 5%  $H_2/N_2$  at 400 °C for 4 h to ensure these samples are in similar states with fresh ones before the activity test. The C/W atomic ratio on the surface was calculated by integrating the relative intensity of W and C from HS-LEIS measurement. To eliminate the interference of surface oxidation as much as possible, the data were collected based on the deconvoluted spectra by excluding the influence of oxide species. To eliminate the interference of surface oxidation as much as possible, data were collected based on the deconvoluted spectra by excluding the influence of oxide species. CO and H<sub>2</sub> temperature-programmed desorption (TPD) measurements were carried out with a Micromeritics AutoChem II 2920 chemisorption analyzer. Before tests, the sample was in situ pretreated under the condition similar to that of the activity evaluation of the catalysts. Temperature-programmed reduction-mass spectrometry (TPR-MS) was conducted on a Micromeritics AutoChem II 2920 chemisorption analyzer equipped with a mass spectrometry. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of GUA adsorption was conducted on a Nicolet 6700 spectrometer equipped with a mercury cadmium telluride detector cooled by liquid nitrogen. Prior to adsorption, the catalyst samples were in situ reduced under the same conditions as that of fresh catalyst. Spectra recorded under N2 flow were used as reference. Then, GUA was introduced by dropping trace liquid onto the powder sample. Next, the cell was evacuated to remove excess GUA at 80  $^\circ\text{C}$  until the spectra became constant. Thermogravimetric analysis (TGA) was carried out on a NETZSCH-TG209 F1 analyzer to evaluate the weight loss of the precursor upon calcination. During the measurements, the samples were heated from 50 °C to 800 °C

#### at a heating rate of 10 $^\circ C$ /min in H\_2.

#### 2.3. Catalytic testing

The selective hydrogenolysis of GUA was carried out on a fix-bed flow reactor with an auto-sampling system. In a typical procedure, 200 mg of fresh catalyst was sieved with a size of about 200 µm and loaded in the center of a quartz tubular reactor and sandwiched by quartz sand. The catalysts were pretreated under 5% H<sub>2</sub>/N<sub>2</sub> at required temperatures to minimize the effect of surface oxide species, and then the catalyst bed was cooled to the target reaction temperature. Then, pure H<sub>2</sub> was fed into the reactor at 3.0 MPa followed by the introduction of GUA to the reactor by using a Series III digital HPLC pump (Scientific Systems, Inc., USA) with the required weight liquid hourly space velocity (WLHSV). An on-line Agilent 7890A gas chromatograph (GC) equipped with an auto-sampling value, DB-Wax capillary column, and flame ionization detector was used for product analysis. A GC 2060 with a TDX column and thermal-conductivity detector was used to analyze gas products, such as CO, CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>O. The absence of heat and mass transfer limitations were confirmed by the estimated Thiele modulus and Mears criterion [55-57]. GUA conversion, product selectivity and carbon balance were calculated by the following Eqs. (1) and (2).

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

Product Selectivity = 
$$\frac{\text{moles of ring product i}}{\text{the sum moles of GUA consumed}} \times 100\%$$
 (2)

The reaction rate for GUA HDO was calculated by Eq. (3).

$$k = \frac{F}{m} ln \frac{1}{1 - X}$$
(3)

where k represents the rate constant expressed as moles of GUA consumed per second and per gram of catalyst, F is the molar flow rate of GUA, m represents catalyst mass, and X is the GUA conversion. All the catalysts were evaluated twice to ensure the accuracy of measurements (the errors are below 5%). The activation energies calculated by the Arrhenius plots were based on the performance at different temperatures on the condition of conversions below 40%. The turnover frequency (TOF) values were based on the H<sub>2</sub> and CO chemisorption uptake, indicating the moles of GUA converted by per site at the catalyst surface per second (mol-GUA mol-site<sup>-1</sup> h<sup>-1</sup>, for short, s<sup>-1</sup>). The GUA conversion for the TOF calculation was lower than 10%. The carbon balance was calculated by Eq. (4). Unless otherwise noted, the carbon balance was about 95%  $\pm$  2%.

Carbon balance = 
$$\frac{\text{sum of moles of C in all compounds in the effluent}}{\text{moles of C in the GUA feed}}$$
 (4)

#### 3. Results and discussion

#### 3.1. Construction of Pt-WC with C-defects

Pt–WC was synthesized by combining methods including impregnation for Pt loading and careful H<sub>2</sub> thermo-treatment for C-etching (Scheme 2). The inert bulk WC, commercially available from Aladdin Co. Ltd., was selected as support, and Pt species was incorporated by wet impregnation. This step was followed by C-etching through the reaction of H<sub>2</sub> and carbons under thermo-treatment (detailed in Experimental section). XRD patterns (Fig. S1) showed that the initial WC displays typical diffractions located at  $2\theta = 31.70^{\circ}$ ,  $35.89^{\circ}$ ,  $48.65^{\circ}$ , and  $66.23^{\circ}$ (PDF#65-4539). No obvious diffractions ascribed to Pt species was found in representative 1% Pt–WC catalysts, indicating the good dispersion of Pt species on WC support. For confirming the role of Pt species in the C-etching treatment, TPR–MS measurement was carried



Scheme 2. Illustration of the synthesis of active Pt-WC catalyst.

out as shown in Fig. S2. 1% Pt–WC shows a significant CH<sub>4</sub> signal which is located at about 400 °C, which is due to reaction of H<sub>2</sub> and carbon atoms of WC (Fig. S2a). In this case, only CH<sub>4</sub> was found and no obvious signal of C<sub>2</sub>H<sub>6</sub> was observed. In contrast, the formation of CH<sub>4</sub> could be also observed in WC catalyst, while the CH<sub>4</sub> peak is located at about 520 °C, which is much higher than that of 1% Pt–WC (Fig. S2b). That is to say, the Pt species is beneficial for activation of H<sub>2</sub> and then hydrogenation of C atoms of WC, achieving C-defects on their surface of WC surface. To further investigate the structures, TEM and HAADF–STEM images were collected, as shown in Fig. 1. WC showed a smooth surface, clear atom formulation, and typical lattice fringes with interplanar

distances of 0.252 nm, corresponding to the WC(100) facet (Fig. 1a). By contrast, the surface of 1% Pt–WC roughened and acquired rich stacking faults and black spots (Fig. 1b). The lattice fringe was 0.236 nm, which was primarily ascribed to the W<sub>2</sub>C(002) facet. This finding was due to the gasification of carbon atoms with H<sub>2</sub> to form C-defects, which benefited the adsorption and activation of reactants. STEM–EDS elemental-mapping analysis demonstrated that almost all Pt species were distributed in the W domain with high dispersion (Fig. 1c and d). For WC and Pt-WC catalysts, N<sub>2</sub> sorption was further studied as shown in Fig. S3 and Table S2. The BET surface area ( $S_{\text{BET}}$ ) of commercial WC demonstrates a small surface area of 2.9 m<sup>2</sup> g<sup>-1</sup> with an average pore



Fig. 1. TEM images of (a) WC and (b) 1% Pt-WC; HAADF-STEM image (c) and EDS elemental mappings of (d) 1% Pt-WC.

diameter of 12.7 nm. With further C-etching treatment over the Pt–WC catalysts, the surface area has a slight increase from 2.9 to 4.0 m<sup>2</sup> g<sup>-1</sup> with average pore diameter in the range of 13.1–15.0 nm (Table S2). TGA Results in Fig. S4 revealed easier weight loss in 1% Pt–WC than in WC, indicating the promotion of C-etching through the incorporation of Pt into 1% Pt–WC.

To gain insight into surficial properties, XPS and HS-LEIS analyses were carried out. As shown in Fig. 2a, the W 4f profile in WC had two typical peaks centered at 31.8 and 33.7 eV, corresponding to carbide species (Fig. 2a). The carbide peaks shifted to lower binding energy with 31.6 eV in the 1% Pt-WC catalyst. This finding implied that W had higher electron density due to the removal of surrounding C atoms and decrease in coordination number. As evident in Fig. 2b, the deconvoluted C 1s profile demonstrated a significant decrease in carbide species with unchanged graphitic carbon species. This result indicated the successful C-etching and the formation of low-C interstitial structure on the outer surface of WC, confirming that photoelectrons escaping depth can be penetrated up to a few nanometers. Accordingly, HS-LEIS was conducted to confirm the information on the topmost layer. An obvious decline in C intensity was found (Fig. S5). As summarized in Table S3 for quantitative analysis, the C/W atomic ratios in WC determined by XPS and HS-LEIS were approximately 1.12:1 and 16.3:1, respectively. The C/W atomic ratio by XPS was similar to the phase composition of bulk WC; however, the ratio found by HS-LEIS was relatively high, indicating abundant C-terminations on the outer surface. By contrast, 1% Pt-WC showed decreased C/W ratios of 0.66 : 1 and 5.3 : 1, as determined by XPS and HS-LEIS, respectively. These results revealed that 1% Pt-WC



Fig. 2. XPS profiles of WC and 1% Pt-WC: (a) W 4f and (b) C 1s.

subjected to integrated  $H_2$  treatment activated the WC surface with rich C-defects and W-terminations. These C-defects benefited the exposure of active hollow sites and adsorption of reactants. Therefore, supported Pt–WC with well-dispersed Pt species and rich C-defects was successfully synthesized.

#### 3.2. Synergy of Pt and C-defects for guaiacol transformation

The hydrogenolysis of GUA was selected as the typical reaction for aryl ether C—O bond scission because it is a structure sensitive reaction for carbide-based catalysis. As shown in Fig. 3 and Table S4, WC displayed relatively low GUA conversion (7.1%) with poor phenol selectivity (51.0%), whereas GUA conversion and phenol selectivity significantly increased over 1% Pt-WC [Unless otherwise noted, 1% Pt-WC represents the catalyst with C-etching under 450 °C under H<sub>2</sub> for 4 h (Table S5, Entry 5)], reaching 78.6% and 89.0%, respectively. WC\* with C-defects was constructed at 600 °C under H<sub>2</sub> for 4 h (Table S5). The catalytic activity for GUA hydrogenolysis of WC\* shows an enhancement than that of intact WC, reaching 15.2% of GUA conversion and 72.2% of phenol selectivity, respectively. However, the activity is still much lower than that of 1% Pt-WC. That is to say, the incorporation of Pt species enhances the hydrogenolysis of GUA compared with the WC\* with C-defects along. This is presumably due to the improved activation of H<sub>2</sub> on Pt sites and adsorption of GUA on C-defects, which shows a synergistic effect over the 1% Pt-WC catalyst. In contrast, 1% Pt–WC<sup>#</sup> without C-etching treatment was prepared and found to have low GUA conversion (39.3%) with diverse products. The selectivity of phenol through C-O bond cleavage was 56.7%, and ring-saturated products including cyclohexanol, cyclohexenol, and cyclohexane were also formed. On the other hand, 1% Pt/AC with the same Pt loading demonstrated satisfactory GUA conversion but relatively different product distribution compared with 1% Pt-WC, primarily producing ring-saturated products. Fig. S6 shows the effect of WLHSV on the performance of 1% Pt–WC and 1% Pt/AC. The GUA conversion over the 1% Pt-WC decreases from 98.7% to 30.9% with a slight fluctuation of phenol selectivity in the range of 87% and 93% when the WLHSV was increased from 0.5–10.0  $h^{-1}$  (Fig. S6a). Notably, no ring-saturated products nor obvious change on product distribution was were found



**Fig. 3.** Performance for GUA conversion over different catalysts. WC\* was synthesized by construction of C-defects on intact WC at 600 °C under H<sub>2</sub> for 4 h. 1% Pt–WC<sup>#</sup> was synthesized by wet impregnation without C-etching treatment. 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, and *T* =300 °C.

with change of WLHSV. On the other hand, the 1% Pt/AC displays a decreasing GUA conversion and the product distribution varied with the increase of WLHSV (Fig. S6b). The cyclohexenol selectivity show a volcano-type curve with decreasing cyclohexanol and increasing phenol selectivity when the WLHSV was increase from 1.0 to  $10.0 \text{ h}^{-1}$ , which is presumably due to the shorter residence time of reactants on the surface of 1% Pt/AC. To further investigate the roles of these catalysts on the product selectivity, we evaluated the catalytic performance with similar GUA conversion by varying the WLHSV, as shown in Fig. S7. The 1% Pt-WC demonstrates a high selectivity of phenol while other catalysts display wide product distributions although they have similar GUA conversion. Accordingly, the as-built active 1% Pt-WC facilitated the selective cleavage of aryl ether C—O bonds toward phenol production. Fig. 4 shows the phenol space-time yield (STY) over the 0-5.0% Pt-WC catalysts with similar C-etching treatment. WC alone displayed relatively low phenol STY (0.25 umol  $g_{cat}^{-1} s^{-1}$ ). With increased amount of Pt added to WC, the phenol STY, as well as GUA conversion and phenol selectivity, drastically increased and reached the maximum of 4.77 µmol  $g_{cat}^{-1}$  s<sup>-1</sup> when the Pt loading was 1 wt.% (Fig. 4 and Table S4). The increase in activity was approximately 19.1-fold compared with that of intact WC. The TOF values were further calculated to quantify the efficiency of these active sites based on the H<sub>2</sub> and CO chemisorption uptakes, as summarized in Table S6. The intact WC shows low TOF(H<sub>2</sub>) and TOF(CO) values of 0.9 and 0.7  $s^{-1}$ , respectively. In contrast, the WC\* with C-defects displays a slight increasing TOF values since the construction of C-defects improve the activation of reactants including GUA and hydrogen. Significantly, there is a great increase on TOF(H<sub>2</sub>) and TOF(CO) values over the 1% Pt–WC, giving values of 11.4 and 9.0  $s^{-1}$ , respectively, which are nearly 12.6-fold higher than those of intact WC. The results indicate that the active sites contributed by construction of C-defects and synergy of Pt incorporation achieve superior catalytic behaviors for GUA conversion. Considering the great enhancement in phenol production, Arrhenius plots were used to derive the apparent activation energy (Ea). The intact commercial WC displays an Ea of 171.6 kJ mol<sup>-1</sup> (Fig. 5), which is higher than those of tungsten carbide catalysts in HDO reactions in a range of 120–152 kJ mol<sup>-1</sup> [50,58,59]. This is due to the lack of active sites on the surface of commercial WC. However, the Ea over 1% Pt–WC was 91.8 kJ mol<sup>-1</sup>, which was almost half of that on initial WC, indicating the successful construction of active sites and thus resulting in a high efficiency of C-O bond cleavage over the C-etched 1% Pt–WC catalyst.

Supported Pt catalysts are commonly used for hydrogenation and also for HDO reactions. Both saturation of aromatic ring through hydrogenation and the C—O bond cleavage occur during the transformation of lignin-derived compounds, resulting in wide product distributions [60–62]. In our case, Pt supported on activation carbon (Pt/AC) with different Pt loadings was also prepared and evaluated for GUA conversion for comparison, as shown in Table S7. As predicted, ring-saturated products such as cyclohexanol, cyclohexenol, and





Fig. 5. Arrhenius plots of reaction rate (Lnk) versus 1/T for GUA hydrogenolysis over WC and 1.0 % Pt–WC.

cyclohexane formed in all Pt/AC catalysts, even in the case of 0.1% Pt/AC. Thus, C-O bond scission and arene reduction occurred, and no specific selectivity of products was observed among Pt/AC catalysts. Previous studies have shown that the Ea over Pt/C is about 93-126 kJ  $mol^{-1}$  [17,63,64]. We performed the Arrhenius plot of as-prepared Pt/AC and the Ea is about 93.2 kJ mol<sup>-1</sup> (Fig. S8). Even though the Pt/AC displays similar Ea compared with that of Pt-WC, the phenol selectivity is quite poor, which indicates the uncontrollable product selectivity in GUA HDO over the Pt/AC. These results are corresponding with previous reports [58,59]. It is worth noting that Pt–WC catalysts with the same Pt loading attained only the products with C-O bond cleavage, especially for phenol production. Moreover, Pt-WC catalysts showed higher conversion than Pt/AC catalysts. This finding was presumably due to the good dispersion of Pt on the WC surface and the C-defects for reactant adsorption, thereby altering the reaction mechanism via synergistic effect. Further increasing the amount of Pt in 5% Pt-WC resulted in obviously declined phenol selectivity, and ring-saturated products formed (Table S7). As evidenced in Fig. S9, the typical TEM image of 5% Pt-WC showed that extensive Pt species overlapped with the WC surface, which can cover available C-defect sites and greatly enhance the activation of dihydrogen, resulting in similar catalytic property to that of 5% Pt/AC. Thus, the rational incorporation of Pt species onto the WC surface with C-defects benefited the activation of dihydrogen and reactants, thereby inducing the production of phenol via C—O bond cleavage.

To further investigate the effect of C-defects, 1% Pt-WC catalysts with different C-etching treatments were fabricated and evaluated for GUA conversion. The details of C-etching are summarized in Table S5. Fig. 6 demonstrates the phenol STY as a function of surface C/W atomic ratio. The changes in phenol STY showed a volcano-type trend with increased C/W atomic ratio. At high C/W atomic ratio, the surface had exposed abundant C terminations and was covered by numerous carbon atoms during the carbide preparation; these carbons prevented the chemisorption of reactants. The 1% Pt–WC<sup>#</sup> catalyst without C-etching had an atomic ratio of 14.3 C/W with 1.51  $\mu$ mol g<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>. C-etching to decrease the C/W atomic ratio, thereby facilitating the formation of Cdefects and thus the activation and chemisorption of reactants. Consequently, the phenol STY significantly increased and reached the maximum value at the C/W atomic ratio of 7.5. Further decreasing the C atoms resulted in a decline in the phenol STY, which was due to the exposure of abundant W atoms. The 1% Pt-WC-850 catalyst (Table S5, Entry 7) with extensive C-etching at 850 °C obtained a low phenol STY with catechol as by-product (Table S8). This finding was due to the formation of a metallic W phase, as confirmed by the XRD profile (Fig. S10), in agreement with a previous report.<sup>2</sup> These results revealed



**Fig. 6.** Phenol STY for GUA conversion as a function of surface C/W atomic ratio in 1.0% Pt–WC catalysts with different C-etching treatments. 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, and T = 300 °C.

the significance of rational surface-carbon removal to construct C-defects. Therefore, the rational surface configuration between W and C atoms is highly important to afford numerous hollow C-defects and strong Pt incorporation for the promotion of phenol production.

#### 3.3. Understanding the origin of catalytic performance

Chemisorption behavior on catalysts is worthy of study to gain insights into the proper reaction mechanism. The HDO of GUA involves the activation and adsorption of H<sub>2</sub> and GUA on the active sites of catalyst surface. In our case, H2 and CO were used as typical probe molecules, and the TPD profiles are shown in Fig. 7. The intact WC showed nearly no H<sub>2</sub> adsorption on the surface due to surface C termination and the lack of hollow C-defects. However, 1% Pt-WC displayed a significant desorption peak located at 78 °C with a shoulder peak at 130  $^{\circ}$ C, indicating better activation of H<sub>2</sub> and hydrogen bonding on the surface. In addition to similar peaks at low temperatures, 5% Pt-WC and 5% Pt/AC catalysts showed an extra-large H<sub>2</sub> desorption peak at about 320 °C; this peak was ascribed to the stronger adsorption of hydrogen species on the two catalysts, thereby promoting the activation and reduction of aromatic rings. These results were consistent with the catalytic performance of Pt/AC and 5% Pt-WC. It is well accepted that CO can be used as the typical probe molecule to investigate the adsorption behavior of oxygenates on catalysts, especially on the surface of metal carbides [27,38,65,66]. Previous studies show that CO binding with C end down was favored on the metallic sites [27]. Lee et al. [65, 66] studied the CO chemisorption behavior and used CO chemical titration to investigate the active sites of Mo<sub>2</sub>C in HDO of anisole (containing the Carvl-OCH3 functional group), which is quite similar with GUA HDO. They found that the hydrogenolysis rate of Carvl-OCH3 bond significantly decreases with introduction of CO and they can be restored after removing CO, indicating the CO reversible poisoning of the active sites. As indicated by the CO-TPD measurements (Fig. 7b), CO desorbed as an obvious peak at 85 °C on the WC catalyst, whereas 1% Pt-WC displayed a broader and larger peak. A previous report has shown that CO binding with a C end down is favored on metallic sites [67]. Thus, 1% Pt-WC exposed numerous metallic sites such as tungsten on the surface. Conversely, 5% Pt-WC and 5% Pt/AC showed large CO desorption peaks at similar temperatures, as well as a tiny peak at high temperatures. These results indicated the strong interaction between the substrates and catalysts, favoring the further conversion of intermediates.



Fig. 7. H<sub>2</sub>-TPD (a) and CO-TPD (b) of WC-based catalysts.

adsorption behavior on these catalysts. Fig. 8 shows the typical spectra of GUA between 1050 and 1650 cm<sup>-1</sup>. The initial WC displayed several typical peaks that contributed to the aromatic C=C bond, -OH group, and Carvl-OCH<sub>3</sub> vibrations at 1500, 1362, 1259, and 1225 cm<sup>-1</sup>, respectively [68]. No shift on wavenumbers was observed in this case, indicating the weak interaction and only physical adsorption of GUA on the WC surface. Over 1% Pt–WC<sup>#</sup>, a new band at 1494  $\text{cm}^{-1}$  was detected with the disappearance of 1500 cm<sup>-1</sup>; on the other hand, the -OH group vibration was unchanged. This finding indicated the presence of a direct electrodonation from the catalyst surface to the aromatic ring. The Carvl-OCH<sub>3</sub> position slightly shifted to higher wavenumbers (1271 cm<sup>-1</sup>) due to the interaction between methoxyl groups and the catalyst surface. Results suggested the strong adsorption of aromatic ring and the interaction of C—O bond on 1% Pt-WC<sup>#</sup>. Interestingly, 1% Pt-WC with rational C-etching demonstrated different GUA adsorption behaviors. For the  $C_{aryl}$ —OCH<sub>3</sub> vibration, the peak at 1225 cm<sup>-1</sup> disappeared and a new band at 1253  $\rm cm^{-1}$  was found, which was assigned to the vibration of asymmetric C–O bond. Moreover, the 1259 cm<sup>-1</sup> signal shifted to higher wavenumbers with unchanged --OH group vibration. These results illustrated the strong adsorption of C-O bond over 1% Pt-WC. The position at 1500 cm<sup>-1</sup> also remained. The slight shift to higher wavenumber (1500 cm<sup>-1</sup>) can be recognized as the electron-withdrawing effect on the aromatic by the C-O bond adsorption. Thus, 1% Pt-WC showed strong adsorption of Caryl-OCH3 but weak interaction with aromatic ring, resulting in boosted C-O bond scission.

In situ DRIFTS analysis was carried out to further investigate the



Fig. 8. (a) DRIFTS measurement of GUA absorbed on WC, 1% Pt–WC<sup>#</sup>, and 1% Pt–WC. (b) Adsorption behavior schematics.

#### 3.4. Appropriate reaction mechanism over 1% Pt-WC

The GUA contains three types of C-O bonds with different bind energies, including Carvl-OCH3, CarvlO-CH3 and Carvl-OH. Rational design of catalysts achieves regioselective cleavage of C-O bonds towards different products. Previous reports demonstrate that molybdenum carbides and tungsten carbides are efficient for direct cleavage of Carvl-OCH3 bond in GUA conversion to produce phenol, which is due to the distinct catalytic behaviour [59,69-75]. Moreira and co-workers [73] showed that a high selectivity of phenol can be obtained in GUA HDO without benzene production over the Mo<sub>2</sub>C/CNF, which is in agreement with the previous studies in tungsten and molybdenum carbide catalysts [71]. Ochoa et al. [74,75] investigated the influence of carburizing time of carbides for GUA HDO and posted the importance of carburization process. Our previous results also showed that different carbide compositions can catalyse the HDO of GUA with different product selectivity [29,50]. Metal W displays high catechol by cleavage of  $C_{aryl}O$ —CH<sub>3</sub>, where the  $W_xC$  (1 < x < 2) achieves high yield of phenol by cleavage of Carvl-OCH3. In contrary, W2C produces phenol, anisole and benzene which indicating the non-selectivity on the cleavage of aryl C-O bonds. Similarly, Tran et al. [59] investigated the bimetallic MoWC carbide for GUA HDO and demonstrated that the introduction of W into Mo<sub>2</sub>C increased the oxophilicity to oxygenated reactants and H<sub>2</sub>-activating sites, thus inducing the further transformation of phenol to benzene. These results reveal the phase control and surface construction of metal carbides are of great importance in product selectivity in GUA HDO. Suitable C/W ratio on the outer surface of catalyst is beneficial for the production of phenol.

Based on our results and above discussion, appropriate reaction pathways were proposed, as shown in Scheme 3. In the case of 1% Pt-WC, the incorporation of Pt species followed by the thermal treatment allows the successful carbon etching on the outer surface of intact WC which can be confirmed by the XPS and HS-LEIS analysis. These Cdefects benefited the adsorption and activation of C-O bond, which can be observed clearly from DRIFTS profiles. Besides, the incorporated Pt shows a better adsorption and activation of H<sub>2</sub>, as shown in Fig. 7a. As depicted in Scheme 3a, over 1% Pt-WC, the methoxyl groups in GUA were trapped in hollow C-defects and bound to the exposed W sites due to the superficial C-defect sites and then the aryl ether C-O bond weakened. The Pt species were responsible for the greatly enhanced activation and dissociation of H<sub>2</sub>. Thus, hydrogen facilitated the attack of the O atom to efficiently form methanol and phenol. The high selectivity of the C-O bond cleavage was due to the weak interaction between the Pt surface and aromatic ring. It is worth noting that 5% Pt-WC displays low phenol selectivity with ring-saturated products as by-products, which is due to the extensive activation of H<sub>2</sub>, resulting in further hydrogenation of aromatic ring. On the other hand, extensive Cetching over the 1% Pt-WC-850 leads to the formation of metal W phase with almost W atoms on the outer surface of catalyst and demonstrates a low phenol selectivity. That is to say, the balance between the C-defects and the incorporated Pt species with rational compositions achieve highly-efficient cleavage of Carvl-OCH3 bond and thus high yield of phenol. Meanwhile, Pt NPs/WC and Pt/AC were preferred for the adsorption of the aromatic ring with  $\pi$ - $\pi$  interaction, as well as the weak adsorption of the C-O bond, inconsistent with previous reports. As shown in Scheme 3b, two reaction pathways involving ring saturation and C-O bond cleavage occurred in parallel. The 2-methoxyl-cyclohexanol that originated from the ring saturation can be further hydrogenated by C-O bond cleavage. Phenol produced from another pathway can be strongly absorbed on the Pt surface and hydrogenated further, resulting in low efficiency for catalytic transformation and diverse product distribution. Therefore, 1% Pt-WC with suitable C-etching demonstrated a catalytic activity different from that of normal Pt catalysts. Pt activated the WC surface to construct C-defects for strong C-O bond adsorption, replacing the activated aromatic rings on the Pt surface. The exposed Pt surface enhanced the H<sub>2</sub> activation, achieving high production of phenol through C—O bond cleavage.

#### 3.5. Catalytic stability

It is well known that the stability of a catalyst is one of the important issues. The susceptibility of TMC-based catalysts to undergo surface oxidation, phase change, particle sintering, and coke deposition normally results in limitation for further industrial applications. We have investigated the stability of 1% Pt–WC during the conversion of GUA. Fig. 9 displays the GUA conversion and phenol selectivity over the 1% Pt–WC as a function of reaction time on stream at 300 °C under a high WLHSV of 9 h<sup>-1</sup>. It can be seen that the initial GUA conversion is 38.7 % and there is only a slight decrease after the reaction on stream for 50 h.



Scheme 3. Suggested pathway of GUA HDO over (a) 1% Pt–WC and (b) 1% Pt–WC<sup>#</sup> or 1% Pt/AC.



**Fig. 9.** GUA conversion and phenol selectivity as a function of reaction time on stream over the 1% Pt–WC. Reaction conditions: WLHSV=9.0 h<sup>-1</sup>, *P* (H<sub>2</sub>) = 3.0 MPa, H<sub>2</sub>/GUA molar ratio = 50, and *T* = 300 °C.

The catalytic performance remains at a GUA conversion of 35.3 %, which is comparable with the initial activity. The selectivity towards phenol slightly fluctuates in the range of 86.3% and 89.6% during the reaction. Thus, our as-built 1% Pt-WC exhibits a satisfied stability in the hydrogenolysis of GUA. XRD patterns of fresh and spent catalysts are shown in Fig. S11. There is no obvious changes in diffractions of tungsten carbides and Pt species, indicating no obvious phase deconstruction or particle sintering in our case. TEM analysis was conduct to further study the spent catalyst and the image is shown in Fig. S12. No obvious particle sintering was found in the used 1% Pt-WC, which is presumably due to the strong metal-support interaction between Pt and WC. Fig. S13 shows the XPS profiles of fresh and spent catalysts. The carbidic species are clearly observed without change in both catalysts, although a slight increase in intensity ascribable to oxide species is detected for the spent catalyst, most probably due to surface oxidation. These results reveal that the 1% Pt-WC possess a satisfying tolerance on structure changes during the HDO of O-containing GUA. Briefly, the results demonstrate the 1% Pt-WC catalyst shows a good performance and stability for the selective HDO of GUA towards phenol production.

#### 3.6. Catalytic performance over the supported metal-WC with C-etching

Having identified the applicability of our proposed strategy, we adopted other metals, and the catalytic performance is shown in Table S9. Interestingly, all catalysts displayed promoted catalytic behavior with the production of C—O bond scission. In general, these metals were used to induce ring saturation in GUA conversion under similar reaction conditions, whereas phenol was the main product in our case. Pt showed the highest activity, and the phenol synthesis rate followed the order 1.0% Pt–WC > 1.0% Ru–WC > 1.0% Pd–WC > 1.0% Ni–WC > 1.0% Cu–WC. The distinctive catalytic activity was attributed to the C-etching process for the activation and adsorption of reactants and the metal incorporation for enhanced H<sub>2</sub> activation, thereby synergistically boosting the aryl ether C—O bond cleavage.

#### 4. Conclusions

We have demonstrated the significance of constructed surficial Cdefects for the activation of inert WC. Our simple strategy involved the incorporation of transition metal and C-etching treatment. Pt and other transition metals served as efficient sites for H<sub>2</sub> activation, whereas Cdefects were responsible for the adsorption and activation of aryl—OCH<sub>3</sub> bond. Due to the existence of C-defects, the GUA adsorption behavior on Pt–WC catalyst was distinct from WC and Pt/AC, benefiting for the selective cleavage of aryl—OCH<sub>3</sub> bond to produce phenol. The intact WC displayed 7.1% GUA HDO conversion with 51.0 % phenol selectivity, whereas the optimized 1% Pt–WC catalyst with C-defects and Pt on WC afforded 78.6% GUA conversion and 89.0% phenol selectivity under the reaction conditions of 3.0 M P H<sub>2</sub>, 300 °C and 3.0 h<sup>-1</sup> GUA WLHSV. The phenol formation rate through the C—O bond cleavage of GUA over 1% Pt–WC was 19 times higher than that over intact WC. The GUA conversion and phenol selectivity over 1% Pt–WC were maintained for at least 50 h without considerable changes. Other transition metals like Ru, Pd, Ni, and Cu could also be employed to activate the inert WC by creating the C-defects and thus generating the synergy effects for hydrogenolysis catalysis. We envision that our findings may provide a deeper understanding on surface catalysis and new approaches to the activation and application of TMCs.

#### Contribution

H.H. developed the sample synthesis approach and performed most of the experiments. L.J. helped to carry out the experiments in early stage. W.C provided help in the TEM measurements. Y.Y. designed and guided the work. H.H. and Y.Y. wrote and revised the manuscript. All the authors read and commented on the manuscript.

#### **Declaration of Competing Interest**

There are no conflicts to declare.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118023.

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