

## Selective Catalytic Conversion of Guaiacol to Phenols over Molybdenum Carbide Catalyst

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### 1. Experimental

#### 1.1 Materials and synthesis

The chemicals were purchased from commercial suppliers and used as received. The activated carbon (AC) with a surface area (B. E. T.) of 851 m<sup>2</sup>/g, and bulk density of 370 kg/m<sup>3</sup> was obtained from Norit (product model: GSX). AR reagent grade chemicals and solvents including ammonium paramolybdate, ammonium hydroxide, guaiacol, ethanol, methanol, isopropanol, tetralin, catechol, anisole, phenol and tridecane were purchased from Guangfu Inc.

The activated carbon supported molybdenum carbide catalysts ( $\alpha$ -Mo<sub>1-x</sub>C/AC) were prepared by a temperature programmed reaction procedure according to our previous report [1]. Typically, AC was incipient-wetness impregnated with an aqueous solution containing of ammonium paramolybdate. The material was dried at 100 °C for 12 h. The sample was first reduced at 350 °C under pure hydrogen flow for 12 h. The gas was then switched to 15% CH<sub>4</sub>/H<sub>2</sub>, and the temperature was increased with 2.67 °C/min to 590 °C and then held at this temperature for 2 h. The freshly synthesized material was transferred under H<sub>2</sub> to the reaction solvent.

#### 1.2. Catalyst activity measurements

All the reactions were carried out in a 300 mL batch reactor (Parr 4566, made of Hastelloy) equipped with a temperature controller (Parr 4848) and a pressure sensor. In a typical test, 2.0 g of guaiacol was dissolved in 60 mL of ethanol as feedstock. The feedstock and 0.5 g of catalyst were added into the autoclave. After the leakage test, the reactor was purged 5 times with nitrogen to remove the remaining air. The reactor was heated to the reaction temperature (280–340 °C) with a heat-up rate of 5.0 °C/min,

and kept for the desired reaction time with stirring at 400 rpm. Then the reactor was rapidly cooled down by immersing the reactor into a cold water bath and the liquid products and the spent catalyst were recovered and separated.

The reaction products were analyzed and quantified using tridecane as internal standard with a Gas chromatography equipped with a flame ionization detector (GC-FID, Agilent Technologies, model 6890) and a HP-5 MS capillary column (Agilent, 30 m × 0.25 mm × 0.25 μm). The GC parameters used for the analysis were as follows: injector temperature 280 °C; detector temperature 300 °C; split ratio 1:50. The temperature program started by holding at 100 °C for 2 min; then the temperature was increased at 10 °C min<sup>-1</sup> to 250 °C, followed by a 5 min holding. Products were identified using a mass selective detector (MSD, Agilent Technologies, model 5973). Compounds were identified by means of the National Institute of Standards and Technology (NIST) library.

Guaiacol conversion (C (%)) and a product specific selectivity (S(%)) were calculated according to Eqs (1), (2). In these equations, *n* presents the amount of the species in moles. The conversion and yield were determined by averaging the data measured in three times.

$$C (\%) = \frac{n(GUA)_{initial} - n(GUA)_{final}}{n(GUA)_{initial}} \times 100 \quad (1)$$

$$S (\%) = \frac{Y_{prod.}}{X_{GUA}} \times 100 \quad (2)$$

### 1.3. Characterization

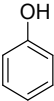
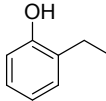
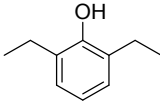
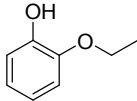
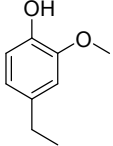
N<sub>2</sub> adsorption-desorption analyses of the catalyst were carried out with Quantachrome Autosorb-1. The catalyst was degassed in He at 200 °C for 4 h prior to BET analysis. After degassing, 30% N<sub>2</sub>/He was flown over the samples, and the temperature was reduced to -196 °C. Specific surface areas of the sample were calculated according to the Brunauer–Emmett–Teller (BET) method. Pore size distributions were estimated by the Barrett–Joyner–Halenda (BJH) and micropore (HK) methods. The structure of the prepared catalyst samples was identified with an X-ray diffraction (XRD) technique (Bruker AXS, D8-S4), operated at 40 kV and 40

mA, using a Cu-K $\alpha$  monochromatized radiation source. Scans were done between  $2\theta$  of  $20^\circ$  and  $80^\circ$  at a rate of  $1^\circ \text{ min}^{-1}$ . Particle size of the catalyst was determined by laser light scattering with particle size analyzer (Mastersizer 2000, Malvern). In brief, the samples were suspended in ethanol and sonicated to prevent particle aggregation and to form uniform dispersion of nanoparticles. The measuring time is 10 s. The data reported here represent the average of ten measurements. Thermogravimetric analysis was performed with a Netzsch TG 209. Typically, 10 mg of the sample was heated with a ramp of  $5^\circ\text{C}/\text{min}$  to  $1000^\circ\text{C}$  in a  $10 \text{ mL}/\text{min}$  flow of air. Raman spectra were obtained by using a Renishaw inVia reflex spectrometer. Approximately, 50 mg of samples was used with an argon laser of 325 nm and a power of 2 mW.

**Table S1** Particle size distribution of fresh catalyst and reused catalysts.

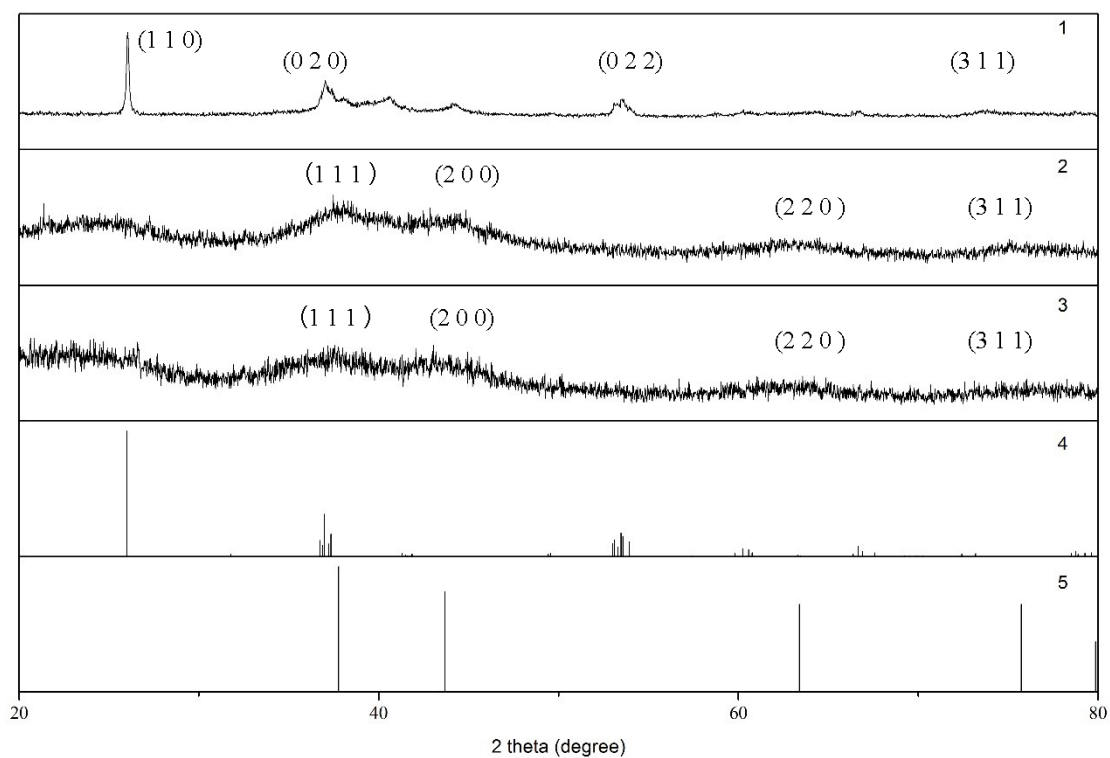
	D (0.5) / $\mu\text{m}$	D (0.1) / $\mu\text{m}$	D (0.9) / $\mu\text{m}$
Fresh catalyst	32	5	147
First reuse	29	5	138
Second reuse	26	4	132
Third reuse	24	4	129

**Table S2** Effect of stirring rate on the conversion of guaiacol and selectivities of products.

Stirring rate / rpm	C <sup>a</sup> (%)	S <sup>b</sup> (%)				
						
200	85	15	31	38	3	4
400	87	15	32	38	3	4
600	87	14	32	38	3	4
800	88	15	32	38	3	4

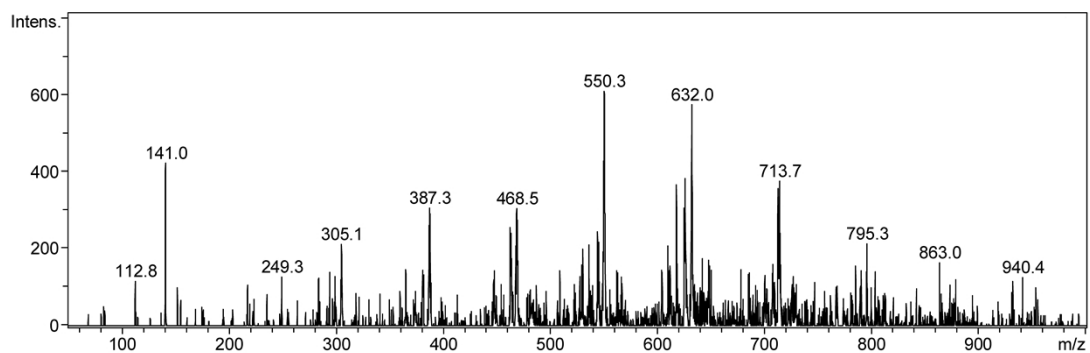
*Reaction conditions:* guaiacol (2.0 g), catalyst (0.5 g), Ethanol (60 ml), initial N<sub>2</sub> pressure at room temperature 0 MPa (gauge), 340 °C, 4 h,

<sup>a</sup> C: Conversion of guaiacol. <sup>b</sup> S: Selectivity.



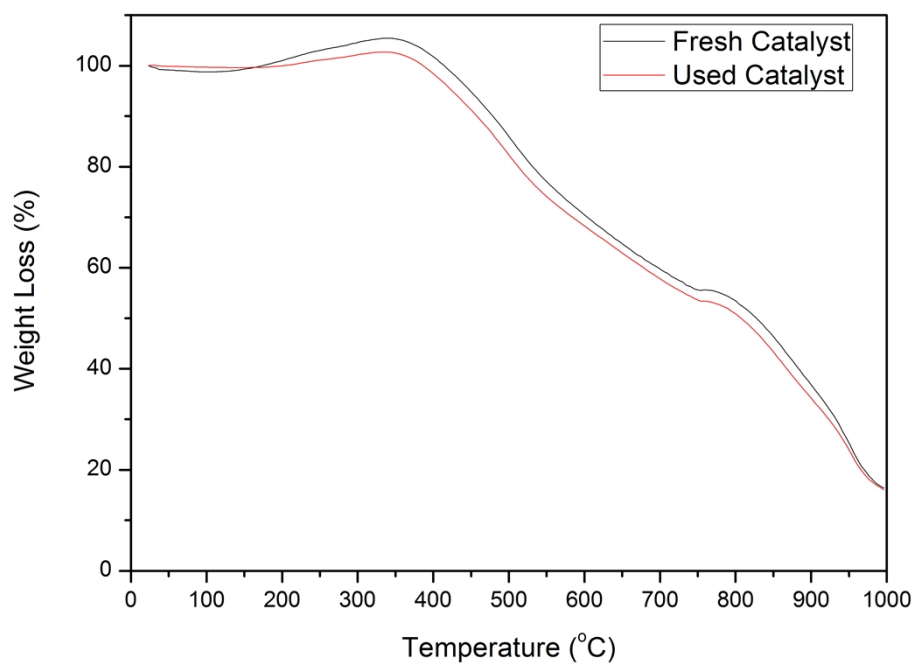
**Figure S1.** X-ray diffraction patterns of the catalyst samples.

1: spent  $\text{Mo}_{1-x}\text{C}/\text{AC}$  in water solvent at 340 °C for 4 h, 2: spent  $\text{Mo}_{1-x}\text{C}/\text{AC}$  in ethanol solvent after the third recycle at 340 °C for 4 h, 3: fresh  $\text{Mo}_{1-x}\text{C}/\text{AC}$ ,  
 4: PDF 65-5787,  $\text{MoO}_2$ , 5: PDF 15-0457,  $\text{Mo}_{1-x}\text{C}$



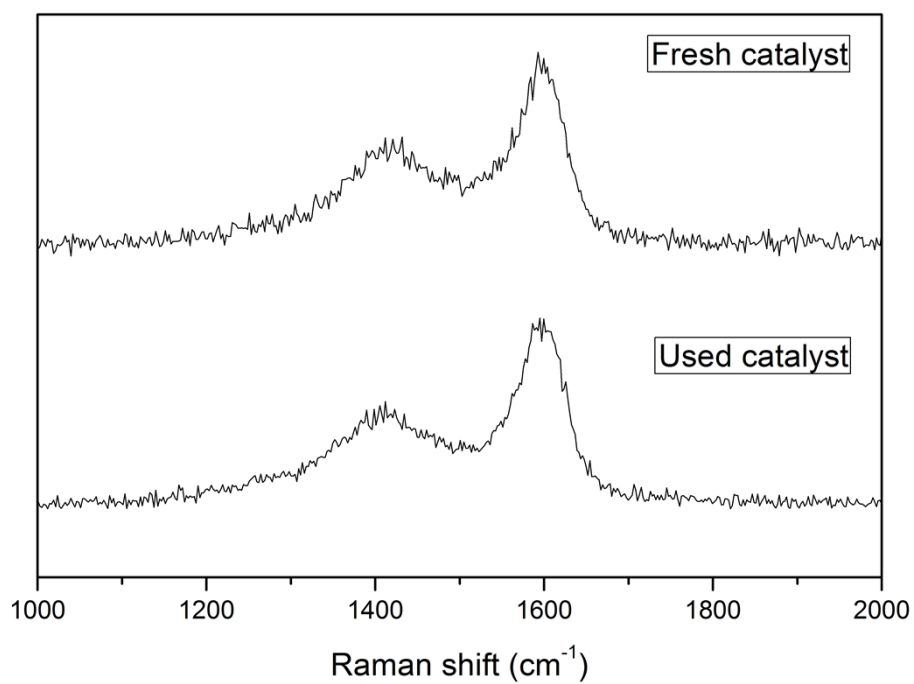
**Figure S2.** ESI-MS analysis of the reaction mixture.

*Reaction conditions:* guaiacol (2.0 g), catalyst (0.5 g), Ethanol (60 ml), initial N<sub>2</sub> pressure at room temperature 0 MPa (gauge), 340 °C, 4 h, 400 rpm



**Figure S3.** TG curves of fresh and used MoC<sub>1-x</sub>/AC





**Figure S4** Raman spectra of fresh and used MoC<sub>1-x</sub>/AC

#### References

1. R. Ma, W. Y. Hao, X. L. Ma, Y. Tian, Y. D. Li, *Angew. Chem.*, 2014, 126, 7438–7443