Electronic Supplementary Information

Catalytic Deoxygenation of Guaiacol Using Methane

Yang Xiao and Arvind Varma

School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive,

West Lafayette, Indiana 47907, United States

* To whom correspondence should be addressed.

Telephone: +1-(765) 494-4075. Fax: +1-(765) 494-0805. E-mail: avarma@purdue.edu.

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Figure S1. TEM images for (a) Pt/C and (b) Pt-Bi/C.

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Table S1. Catalyst Characterization Results.

EXPERIMENTAL

Materials and catalyst preparation

The 5%Pt/C catalyst used in this study was purchased from Alfa Aesar. The 5%Pt-1%Bi/C catalysts were prepared following the procedure described in our prior work[1]. The metallic precursors were chloroplatinic acid hydrate (99.9% metal basis) and bismuth chloride (99.999%), both from Sigma Aldrich. The 100-120 mesh activated carbon (AC) support was from Norit Americas Inc. Briefly, Pt and Bi were loaded sequentially using the wet impregnation method. First, the Pt and Bi precursors were dissolved in 1.2 mol/L HCl and then added dropwise to the well-stirred AC slurry, with stirring continued for at least 8 hrs at room temperature. The mixture was rinsed and dried in air at 100 °C before use.

Guaiacol (>98.0%) and all other calibration compounds (cyclopentanone, phenol, and catechol) were purchased from Sigma-Aldrich. Ultra high purity grade gases (99.98% oxygen, 99.999% argon, 99.98% helium and 99.999% hydrogen) were purchased from Indiana Oxygen. The 0.5%Pt/Al_2O_3 (metal dispersion=31±0.5%) standard (for chemisorption calibration) was from Micromeritics.

Catalyst characterization

The BET surface area and pore diameter were measured for the samples using surface area and porosimetry analyzer (ASAP 2000, Micromeritics). Chemisorption measurement was conducted using the H_2-O_2 titration approach[2], and the metal dispersion was obtained by comparison with the 0.5%Pt/Al_2O_3 standard. Transmission

electron microscopy (TEM, FEI Titan 80-300) was used to investigate the morphology and metal particle sizes of catalysts.

Catalyst performance tests

The catalyst performance tests were conducted in a fixed-bed reactor setup, described in our prior work [3]. Prior to reaction, the packed catalyst was activated at 400 °C, 1 atm for 4 h under a gas mixture flow (H_2:N_2 = 1:2). The reactor was then purged using N_2 for 30 min. The standard reactor operating conditions were: 300 °C, 1 atm, 0.50 g catalyst, total gas (reductant gas, H_2 or CH_4:N_2 = 1:1) flow rate 100 mL/min, and guaiacol feed rate 0.025 mL/min (liquid, at room temperature). The feed flow rates correspond to a molar ratio of 10 between reductant gas and guaiacol. Blank tests, using both H_2 and CH_4 as reductants, for carbon support with no metal loading were conducted under the standard reaction conditions, and guaiacol conversion was less than 1%. Without guaiacol, methane exhibited about 5% conversion, to generate H_2 and trace C_2H_6 on both Pt and Pt-Bi catalysts under the standard conditions. All experiments have carbon mass balances of 90 ± 3%, similar to the literature[3-5]. Possible factors affecting mass balance include liquid hold-up in various locations in the system, particularly the condenser, and coke deposit on the catalyst.

Product analysis

As in our prior work, GC (Agilent GC6890) with flame ionization detector (FID), equipped with a DB-1701 column (30 m × 0.25 mm) was used for quantitative

analysis of the liquid products[3]. The gaseous effluent was analyzed using a Micro GC (Agilent 3000A Micro GC) equipped with two columns (Column A, MolSieve 5 A, 10 m × 0.32 mm; Column B: Plot U, 8 m × 0.32 mm) and two thermal conductivity detectors (TCD). For the reaction experiments, good repeatability was achieved for all quantitative analyses.

■ CATALYST CHARACTERIZATION RESULTS

For the two catalysts (5%Pt/C and 5%Pt-1%Bi/C) used in this work, physisorption and chemisorption results are shown in Table S1, while TEM scans are shown in Figure S1. The BET surface areas of both samples are high (>500 m^2/g), which imply good capacity to adsorb reactants. The moderate mean pore diameter (~3 nm) makes the catalyst accessible to larger molecules such as guaiacol (reactant) and catechol (a product). The mean diameters of metal clusters given by TEM and chemisorption techniques are similar for both Pt/C and Pt-Bi/C catalysts.

Table S1. Catalyst Characterization Results.

	Pt/C	Pt-Bi/C
BET surface area, m^2/g	716	587
Mean pore diameter, nm	3.4	3.1
Metal dispersion, %	22	29
Metal particle size from chemisorption, nm	4.9	3.9
Metal particle size from TEM, nm	5.4	3.3

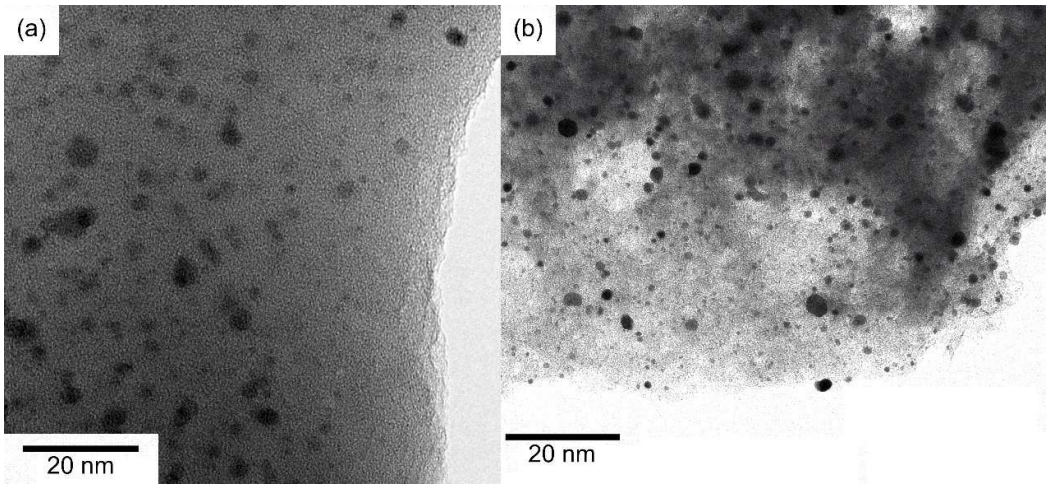

Figure S1. TEM images for (a) Pt/C and (b) Pt-Bi/C.

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