

Catalytic Deoxygenation of Guaiacol Using Methane

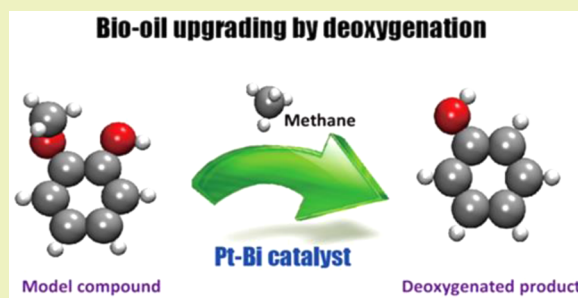
Yang Xiao and Arvind Varma*

School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, Indiana 47907, United States

S Supporting Information

ABSTRACT: Guaiacol, produced by thermal degradation of lignin, represents a model compound for upgrading of fast pyrolysis bio-oils by deoxygenation. In our prior work, with Pt/C catalyst, such a process using H₂ was studied. To overcome the high cost of H₂, methane is used in this work to deoxygenate guaiacol. On Pt/C catalyst, in terms of guaiacol conversion and product distribution, methane is found to exhibit as good deoxygenation performance as H₂. The lifetime of this catalyst, however, is short (<3 h). The lifetime of Pt–Bi/C catalyst is extended (no significant deactivation in 5 h), by addition of bismuth as a promoter. This work provides a new approach for bio-oil upgrading using methane as a reductant instead of hydrogen.

KEYWORDS: Biomass, Fast pyrolysis, Bio-oil upgrading, Pt–Bi bimetallic catalyst, Deactivation



■ INTRODUCTION

Owing to the scarcity of known reserves as well as environmental concerns, increased attention is being paid to developing new fossil or renewable resources, such as shale oil/gas, tar sands, and biomass.^{1,2} In particular, biomass has been shown to be an important renewable source, which can be converted into both sustainable fuels and chemicals.^{3–6} Among various techniques for biomass conversion, fast pyrolysis is attractive for bio-oil production, which can subsequently be upgraded to alternative liquid fuels or converted into chemicals.^{3,7–10} The high oxygen content of bio-oils, however, remains a major challenge because it decreases stability, combustion performance, and heating value of fuels.^{11,12} Hydrodeoxygenation (HDO) is a promising strategy to overcome this problem. Because bio-oil is a complex mixture of generally more than 400 chemical species, and its composition depends on the type of biomass and the operating conditions used to produce it, a model compound is typically used to obtain insight into the HDO process.^{13,14} Guaiacol is one such representative compound owing to its two common oxygenated groups: hydroxyl and methoxyl. Extensive research has been conducted using this model compound.^{15–20} In general, group VIII metals (Pt, Pd, Ni, Rh, Ru, etc.) are used to activate guaiacol and to facilitate hydrogen donation, whereas Al₂O₃, ZrO₂, SiO₂, and activated carbon are considered to be effective supports.^{17,21,22}

Although the use of hydrogen for deoxygenation of guaiacol is advantageous because it generates clean products (mainly water), it has economic penalty arising from its production and transportation.²³ In this context, methane, as the main component in natural gas (CH₄ > 95%) and major component of shale gas (typically CH₄ > 70%), is attractive as an alternative to H₂ because it can serve as a hydrogen donor by releasing

hydrogen at high temperature on noble metal surfaces,²⁴ which makes it a potential promising reductant.

In our prior work, with Pt/C as catalyst, a guaiacol deoxygenation process using H₂ was studied. On the basis of kinetics and catalyst characterization, deactivation mechanism and reaction pathways were also proposed.²⁵ To overcome the high cost of H₂, methane is used in the present work to deoxygenate guaiacol.

■ RESULTS AND DISCUSSION

In preliminary work with Pt/C catalyst, the use of CH₄ was shown to be successful for guaiacol deoxygenation, but significant catalyst deactivation was observed. This observation is similar to other works for CH₄ reactions and is related to coking/carbon deposition.^{24,26} The deactivation issue has been addressed for other reactions by use of bimetallic catalysts, containing a primary metal and a promoter.^{27–32} Thus, in the present work, based on our prior studies of guaiacol deoxygenation²⁵ and Pt–Bi catalyst,³³ a guaiacol deoxygenation process using methane is developed via Pt–Bi catalyst.

Four cases (PtH₂, PtCH₄, PtBiH₂, and PtBiCH₄), derived from two catalysts (Pt/C, Pt–Bi/C) using either H₂ or CH₄ as the reductant, were tested for deoxygenation of guaiacol under standard operating conditions: 300 °C, 1 atm, 0.50 g of catalyst, total gas (reductant gas, H₂ or CH₄:N₂ = 1:1) flow rate of 100 mL/min, and guaiacol feed rate of 0.025 mL/min (liquid, at room temperature), corresponding to contact time of 0.3 g catalyst·h/g guaiacol. A Van Krevelen diagram (Figure 1a) is used to evaluate the deoxygenation levels by analyzing O/C

Received: July 10, 2015

Revised: August 31, 2015

Published: September 28, 2015

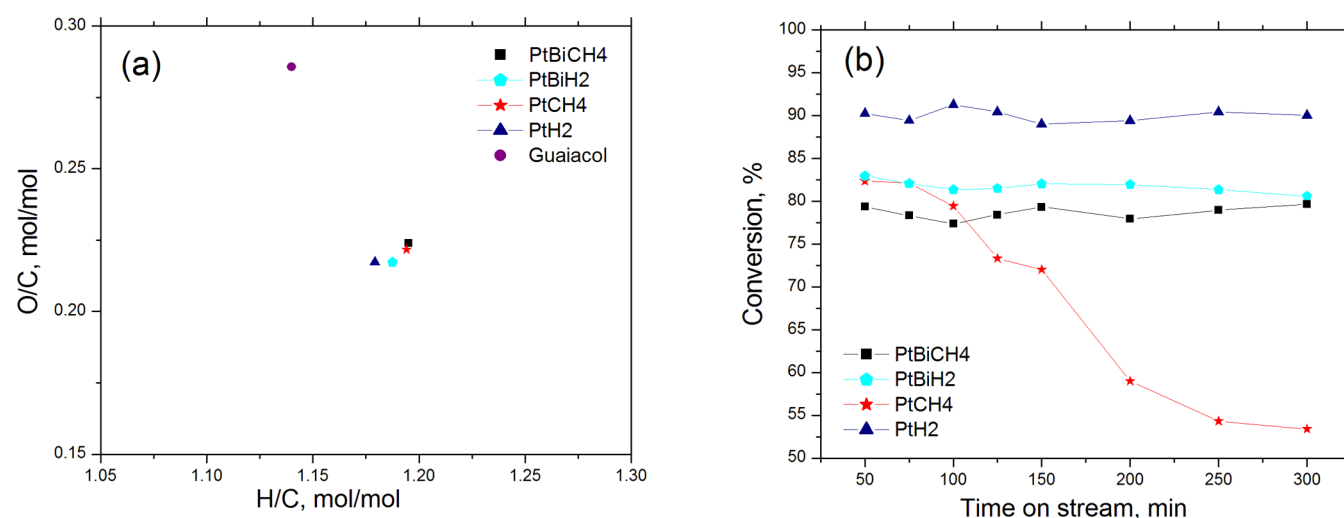


Figure 1. Catalyst performance: (a) Van Krevelen diagram at 60 min time on stream (TOS), and (b) conversion vs TOS.

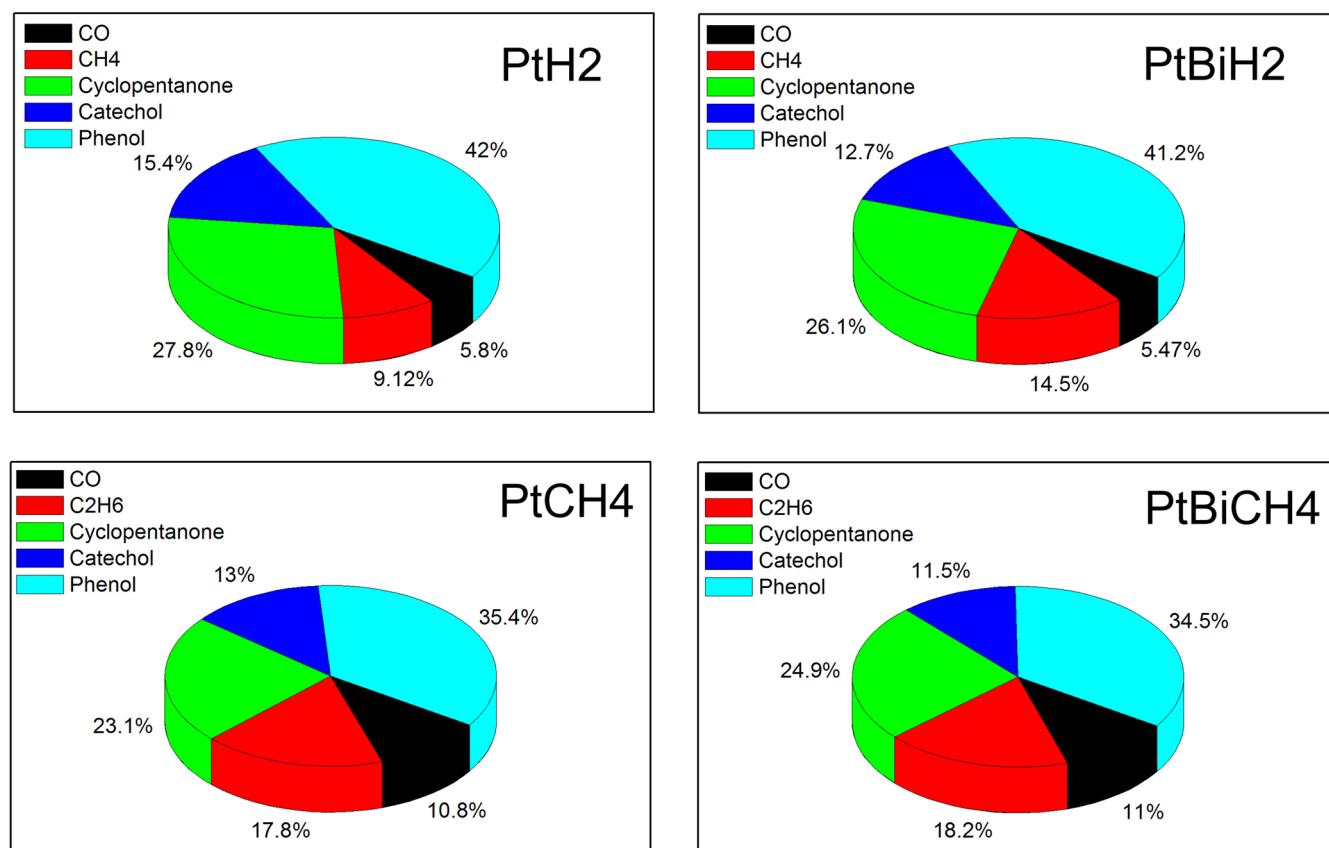


Figure 2. Distribution of major products at 60 min TOS.

and H/C molar ratios in the liquid products,³⁴ which compares hydrogenation vs deoxygenation performance. Owing to catalyst deactivation, data taken at 60 min time on stream (TOS) is reported in Figure 1a. It shows that guaiacol has H/C 1.14 and O/C 0.28, implying a high O content. The H/C ratios increase to 1.18–1.20 and O/C ratios decrease to 0.21–0.22 for all the four cases after deoxygenation, indicating that both hydrogenation and deoxygenation occur. It clearly shows that all four cases behave similarly in the early stages of TOS, although the initial conversions of guaiacol vary from 79% to 90% (Figure 1b). The high yield and good stability of the PtH₂

case have been reported previously in other literature and our prior work.^{15,25} Because CH₄ decomposes on the Pt surface donating hydrogen,²⁴ the PtCH₄ case has a high initial guaiacol conversion. In fact, H₂ is detected in the gaseous products. As shown in Figure 1b, with increasing TOS, however, the PtCH₄ case exhibits sharp deactivation, whereas the other three cases maintain good stability. As noted above, a possible reason for rapid deactivation in the PtCH₄ case is carbon deposit²⁶ and/or coking,^{35,36} resulting from CH₄ decomposition.

In the PtBiH₂ case of Figure 1b, good stability is obtained although the conversion is decreased by ~10%, as compared to

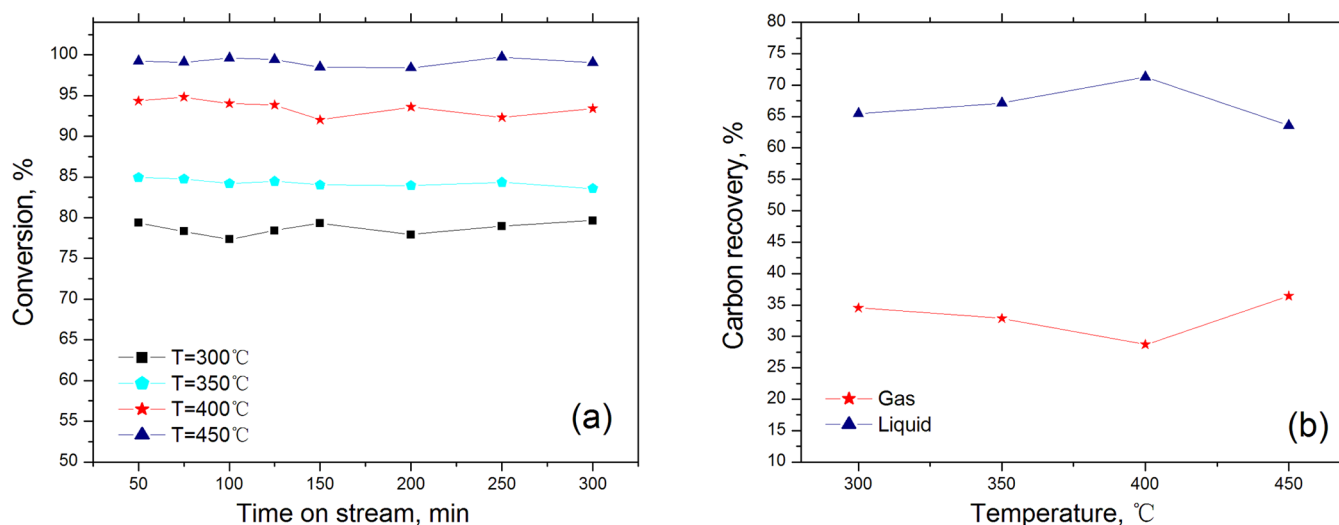
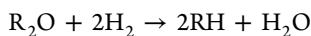


Figure 3. Effect of temperature for Pt–Bi/C catalyst: (a) guaiacol conversion, and (b) carbon recovery in liquid and gaseous products.

the PtH₂ case. Remarkably, PtBiCH₄ also shows good catalyst stability, although the conversion is decreased further. For a C₈ hydrocarbon reforming process using catalyst containing a group VIII metal and low amounts of bismuth, a patent disclosed that addition of bismuth extended catalyst lifetime.²⁹ In fact, this is the only prior work demonstrating catalyst stability using Bi as a promotor for gas-phase reactions at high temperature (>300 °C). Although the mechanism is unclear, our experiments also show that Bi promotor extends catalyst lifetime. It should also be noted that in a patent application, Fernando et al.³⁷ describe the use of methane with an oxygenate to dehydrate and produce deoxygenated hydrocarbons, but no bimetallic catalysts or data for catalyst stability were reported.

Figure 2 shows distribution of major components in both gaseous and liquid products at 60 min TOS under standard conditions. Note that components less than 2 wt % are neglected and all compositions are normalized with respect to the remaining components. As in our prior work,²⁵ only three main products (phenol, catechol, and cyclopentanone, total content >95 wt % for all four cases) in the liquid are shown. For liquid products, all four cases have similar distributions and compositions. For gaseous products, the PtH₂ and PtBiH₂ cases generated CO and CH₄, whereas PtCH₄ and PtBiCH₄ produced CO and C₂H₆ instead. Because our prior work using Pt and H₂ suggested that CO and CH₄ are generated along with cyclopentanone,²⁵ we can conclude that C₂H₆ is generated by the use of CH₄. Thus, on the basis of the product distribution in Figure 2 and our prior work, a conceptual scheme is proposed for comparison of H₂ and CH₄ deoxygenation processes.

For hydrogen deoxygenation:



For methane deoxygenation:



It is proposed that CH₄ decomposes on Pt surface and contributes one H atom for guaiacol deoxygenation and water formation, similar to the H₂ process, whereas the residual methyl combines with another methyl to form ethane. This assumption is supported by the low reaction barrier of CH₄

decomposition at elevated temperature,²⁴ along with detected H₂ and C₂H₆ molecules in our experiments.

To understand further Pt–Bi performance for guaiacol deoxygenation using CH₄ as a reductant, different temperatures (300–450 °C) were investigated for guaiacol conversion and carbon recovery in liquid and gaseous products, as shown in Figure 3. Figure 3a shows increase of guaiacol conversion with temperature, where conversions >90% are reached for 400–450 °C. Remarkably, as shown in Figure 1, such conversion is obtained at 300 °C when Pt and H₂ are used. Therefore, it may be deduced that reaction rate is decreased by either using CH₄ as a reductant or Pt–Bi as a catalyst. Besides guaiacol conversion, carbon recovery in the liquid phase is another important factor to assess the catalyst performance, as shown in Figure 3b. Two major factors are considered to affect carbon recovery in the liquid phase: guaiacol conversion (to the three main liquid products) and other reactions that decompose guaiacol to produce gaseous products, which occur on carbon-supported noble metal catalysts.³⁰ Along with temperature increase, carbon recovery in liquid product first increased and then decreased after 400 °C, whereas carbon recovery in gaseous products shows the opposite trend. From the present work, 400 °C may be considered as the optimal temperature accounting for trade-off between guaiacol conversion and carbon recovery in liquid products.

The kinetic behavior of Pt–Bi catalyst at 400 °C was studied by varying feed rates of guaiacol and CH₄ under otherwise standard conditions. The data for each contact time, taken at 60 min TOS, is shown in Figure 4. It illustrates that phenol, as the main product, rises as contact time increases, while the other two products remain essentially unchanged. As compared to the PtH₂ case (Figure 1; 300 °C, 0.3 g catalyst·h/g guaiacol), results of Figures 3 and 4 demonstrate that equivalent guaiacol conversion can be achieved for the case of Pt–Bi catalyst with methane by compensating with either higher temperature or longer contact time (>0.5 g catalyst·h/g guaiacol).

Future work will be conducted to optimize operating conditions, develop kinetic models, and reveal the role of bismuth in the Pt–Bi bimetallic catalyst for improving its stability.

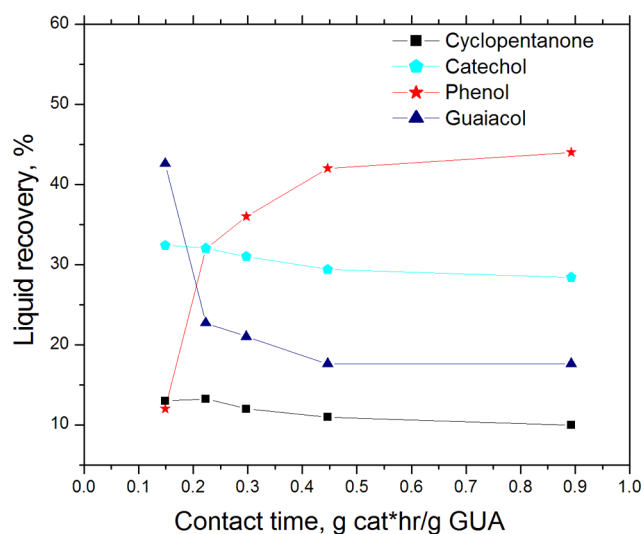


Figure 4. Kinetic behavior of Pt-Bi catalyst at 400 °C.

CONCLUSIONS

In the present work, CH₄ is used as novel reductant to deoxygenate guaiacol, a model compound of pyrolysis bio-oils. With the Pt/C catalyst, CH₄ exhibits as good deoxygenation performance as H₂ with respect to guaiacol conversion and product distribution. The lifetime of Pt/C catalyst, however, was short (<3 h). With addition of bismuth as a promoter, the lifetime of Pt-Bi/C is extended (no significant deactivation in 5 h), although catalyst performance decreases somewhat, which could be compensated by either higher reaction temperature or longer contact time. The current work provides a new approach for bio-oil upgrading using methane as a reductant instead of hydrogen.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00669.

Experimental and characterization results (BET, TEM, and metal dispersion) for Pt and Pt-Bi catalysts (PDF).

AUTHOR INFORMATION

Corresponding Author

*A. Varma. Tel.: +1-(765) 494-4075. Fax: +1-(765) 494-0805. E-mail: avarma@purdue.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the R. Games Slayter Fund. The authors thank Dr. Danni Gao for valuable discussions and Mr. Yucheng Wang for preliminary experiments.

REFERENCES

- (1) Savaliya, M. L.; Dhorajiya, B. D.; Dholakiya, B. Z. Recent advancement in production of liquid biofuels from renewable resources: a review. *Res. Chem. Intermed.* **2015**, *41*, 475–509.
- (2) Nigam, P. S.; Singh, A. Production of liquid biofuels from renewable resources. *Prog. Energy Combust. Sci.* **2011**, *37*, 52–68.

- (3) Bridgwater, A. V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94.
- (4) Tuck, C. O.; Perez, E.; Horvath, I. T.; Sheldon, R. A.; Poliakov, M. Valorization of Biomass: Deriving More Value from Waste. *Science* **2012**, *337*, 695–699.
- (5) Shrotri, A.; Tanksale, A.; Beltramini, J. N.; Gurav, H.; Chilukuri, S. V. Conversion of cellulose to polyols over promoted nickel catalysts. *Catal. Sci. Technol.* **2012**, *2*, 1852–1858.
- (6) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106*, 4044–4098.
- (7) Meier, D.; van de Beld, B.; Bridgwater, A. V.; Elliott, D. C.; Oasmaa, A.; Preto, F. State-of-the-art of fast pyrolysis in IEA bioenergy member countries. *Renewable Sustainable Energy Rev.* **2013**, *20*, 619–641.
- (8) Dickerson, T.; Soria, J. Catalytic Fast Pyrolysis: A Review. *Energies* **2013**, *6*, 514–538.
- (9) Hu, X.; Mourant, D.; Gunawan, R.; Wu, L. P.; Wang, Y.; Lievens, C.; Li, C. Z. Production of value-added chemicals from bio-oil via acid catalysis coupled with liquid-liquid extraction. *RSC Adv.* **2012**, *2*, 9366–9370.
- (10) Ramsurn, H.; Gupta, R. B. Nanotechnology in Solar and Biofuels. *ACS Sustainable Chem. Eng.* **2013**, *1*, 779–797.
- (11) Xiu, S. N.; Shahbazi, A. Bio-oil production and upgrading research: A review. *Renewable Sustainable Energy Rev.* **2012**, *16*, 4406–4414.
- (12) Mortensen, P. M.; Grunwaldt, J. D.; Jensen, P. A.; Knudsen, K. G.; Jensen, A. D. A review of catalytic upgrading of bio-oil to engine fuels. *Appl. Catal., A* **2011**, *407*, 1–19.
- (13) Furimsky, E. Catalytic hydrodeoxygenation. *Appl. Catal., A* **2000**, *199*, 147–190.
- (14) Elliott, D. C.; Wang, H. M. Hydrocarbon Liquid Production via Catalytic Hydroprocessing of Phenolic Oils Fractionated from Fast Pyrolysis of Red Oak and Corn Stover. *ACS Sustainable Chem. Eng.* **2015**, *3*, 892–902.
- (15) Zhao, H. Y.; Li, D.; Bui, P.; Oyama, S. T. Hydrodeoxygenation of guaiacol as model compound for pyrolysis oil on transition metal phosphide hydroprocessing catalysts. *Appl. Catal., A* **2011**, *391*, 305–310.
- (16) Bui, V. N.; Laurenti, D.; Afanasiev, P.; Geantet, C. Hydrodeoxygenation of guaiacol with CoMo catalysts. Part I: Promoting effect of cobalt on HDO selectivity and activity. *Appl. Catal., B* **2011**, *101*, 239–245.
- (17) Gutierrez, A.; Kaila, R. K.; Honkela, M. L.; Slioor, R.; Krause, A. O. I. Hydrodeoxygenation of guaiacol on noble metal catalysts. *Catal. Today* **2009**, *147*, 239–246.
- (18) Lee, C. R.; Yoon, J. S.; Suh, Y. W.; Choi, J. W.; Ha, J. M.; Suh, D. J.; Park, Y. K. Catalytic roles of metals and supports on hydrodeoxygenation of lignin monomer guaiacol. *Catal. Commun.* **2012**, *17*, 54–58.
- (19) Nimmanwudipong, T.; Runnebaum, R. C.; Block, D. E.; Gates, B. C. Catalytic Conversion of Guaiacol Catalyzed by Platinum Supported on Alumina: Reaction Network Including Hydrodeoxygenation Reactions. *Energy Fuels* **2011**, *25*, 3417–3427.
- (20) Zhang, W.; Chen, J. Z.; Liu, R. L.; Wang, S. P.; Chen, L. M.; Li, K. G. Hydrodeoxygenation of Lignin-Derived Phenolic Monomers and Dimers to Alkane Fuels over Bifunctional Zeolite-Supported Metal Catalysts. *ACS Sustainable Chem. Eng.* **2014**, *2*, 683–691.
- (21) Bu, Q.; Lei, H. W.; Zacher, A. H.; Wang, L.; Ren, S. J.; Liang, J.; Wei, Y.; Liu, Y. P.; Tang, J.; Zhang, Q.; Ruan, R. A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis. *Bioresour. Technol.* **2012**, *124*, 470–477.
- (22) Wu, S. K.; Lai, P. C.; Lin, Y. C.; Wan, H. P.; Lee, H. T.; Chang, Y. H. Atmospheric Hydrodeoxygenation of Guaiacol over Alumina-, Zirconia-, and Silica-Supported Nickel Phosphide Catalysts. *ACS Sustainable Chem. Eng.* **2013**, *1*, 349–358.
- (23) Stocker, M. Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials. *Angew. Chem., Int. Ed.* **2008**, *47*, 9200–9211.

- (24) Li, Y. D.; Li, D. X.; Wang, G. W. Methane decomposition to CO_x-free hydrogen and nano-carbon material on group 8–10 base metal catalysts: A review. *Catal. Today* **2011**, *162*, 1–48.
- (25) Gao, D.; Schweitzer, C.; Hwang, H. T.; Varma, A. Conversion of guaiacol on noble metal catalysts: reaction performance and deactivation studies. *Ind. Eng. Chem. Res.* **2014**, *53*, 18658–18667.
- (26) Zhang, Y.; Smith, K. J. Carbon formation thresholds and catalyst deactivation during CH₄ decomposition on supported Co and Ni catalysts. *Catal. Lett.* **2004**, *95*, 7–12.
- (27) Gonzalez-Borja, M. A.; Resasco, D. E.; Anisole, and Guaiacol Hydrodeoxygenation over Monolithic Pt-Sn Catalysts. *Energy Fuels* **2011**, *25*, 4155–4162.
- (28) Bui, V. N.; Laurenti, D.; Delichere, P.; Geantet, C. Hydrodeoxygenation of guaiacol Part II: Support effect for CoMoS catalysts on HDO activity and selectivity. *Appl. Catal., B* **2011**, *101*, 246–255.
- (29) Innes, R. A.; Sugimoto, M.; Fukunaga, T. Reforming process using monofunctional catalyst containing bismuth. U.S. Patent No. 5,851,379, December 22, 1998.
- (30) Sun, J. M.; Karim, A. M.; Zhang, H.; Kovarik, L.; Li, X. H. S.; Hensley, A. J.; McEwen, J. S.; Wang, Y. Carbon-supported bimetallic Pd-Fe catalysts for vapor-phase hydrodeoxygenation of guaiacol. *J. Catal.* **2013**, *306*, 47–57.
- (31) Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem. Soc. Rev.* **2012**, *41*, 8075–8098.
- (32) Maris, E. P.; Ketchie, W. C.; Murayama, M.; Davis, R. J. Glycerol hydrogenolysis on carbon-supported PtRu and AuRu bimetallic catalysts. *J. Catal.* **2007**, *251*, 281–294.
- (33) Hu, W. B.; Knight, D.; Lowry, B.; Varma, A. Selective Oxidation of Glycerol to Dihydroxyacetone over Pt-Bi/C Catalyst: Optimization of Catalyst and Reaction Conditions. *Ind. Eng. Chem. Res.* **2010**, *49*, 10876–10882.
- (34) Krevelen, D. V. Graphical-statistical method for the study of structure and reaction processes of coal. *Fuel* **1950**, *29*, 269.
- (35) Wang, S. B.; Lu, G. Q. Catalytic activities and coking characteristics of oxides-supported Ni catalysts for CH₄ reforming with carbon dioxide. *Energy Fuels* **1998**, *12*, 248–256.
- (36) Ermakova, M. A.; Ermakov, D. Y.; Kuvshinov, G. G.; Plyasova, L. M. New nickel catalysts for the formation of filamentous carbon in the reaction of methane decomposition. *J. Catal.* **1999**, *187*, 77–84.
- (37) Fernando, S.; Gunawardena, D. A. Deoxygenation of biomass derived oxygenates to hydrocarbons via direct methane intervention. U.S. Patent Application No. US 2011/0313219 A1, December 22, 2011.

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.

The number of pages: 5

The number of figures: 1

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

The number of tables: 1

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 work¹. 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/Al₂O₃ (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 H₂-O₂ titration approach², and the metal dispersion was obtained by comparison with the 0.5%Pt/Al₂O₃ 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 work³. Prior to reaction, the packed catalyst was activated at 400 °C, 1 atm for 4 h under a gas mixture flow ($\text{H}_2:\text{N}_2 = 1:2$). 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 $\text{CH}_4:\text{N}_2 = 1:1$) 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 $90 \pm 3\%$, similar to the literature³⁻⁵. 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 $\times$ 0.25 mm) was used for quantitative

analysis of the liquid products³. 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 m²/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

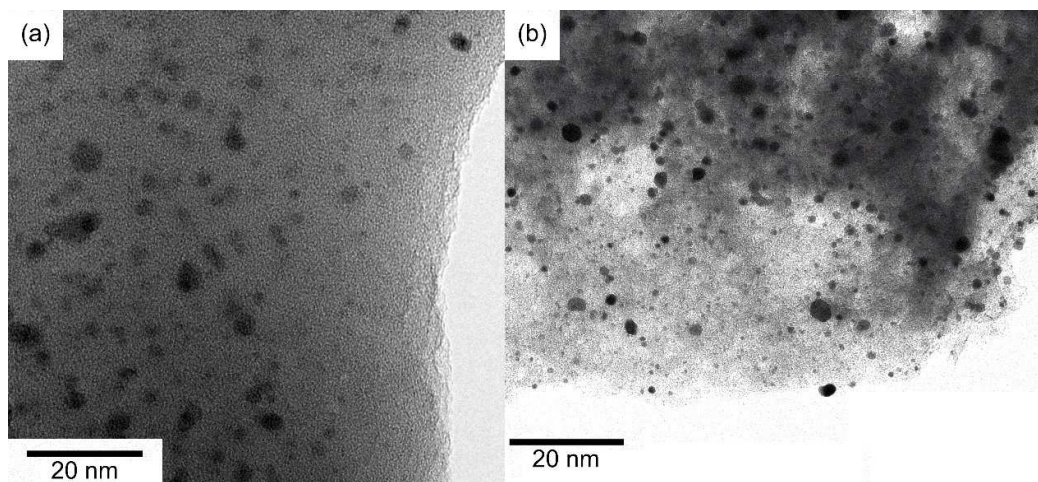


Figure S1. TEM images for (a) Pt/C and (b) Pt-Bi/C.

■ REFERENCES

1. Hu, W. B.; Knight, D.; Lowry, B.; Varma, A. Selective Oxidation of Glycerol to Dihydroxyacetone over Pt-Bi/C Catalyst: Optimization of Catalyst and Reaction Conditions. *Ind Eng Chem Res* 2010, 49, 10876-10882.
2. Benson, J. E.; Boudart, M. Hydrogen-Oxygen Titration Method for the Measurement of Supported Platinum Surface Areas. *J Catal* 1965, 4, 704-710.
3. Gao, D.; Schweitzer, C.; Hwang, H. T.; Varma, A. Conversion of guaiacol on noble metal catalysts: reaction performance and deactivation studies. *Ind Eng Chem Res* 2014, 53, 18658-18667.
4. Chang, J.; Danuthai, T.; Dewiyanti, S.; Wang, C.; Borgna, A. Hydrodeoxygenation of Guaiacol over Carbon-Supported Metal Catalysts. *Chemcatchem* 2013, 5, 3041-3049.
5. Jongerius, A. L.; Gosselink, R. W.; Dijkstra, J.; Bitter, J. H.; Bruijninx, P. C. A.; Weckhuysen, B. M. Carbon Nanofiber Supported Transition-Metal Carbide Catalysts for the Hydrodeoxygenation of Guaiacol. *Chemcatchem* 2013, 5, 2964-2972.