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Catalytic Deoxygenation of Guaiacol Using Methane

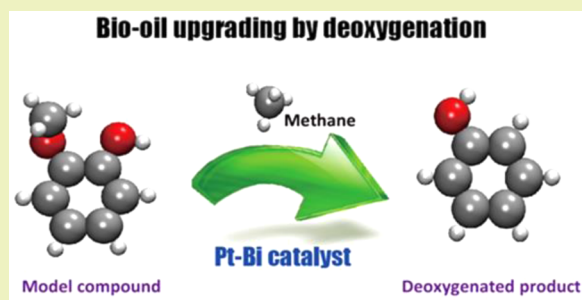
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S Supporting Information

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

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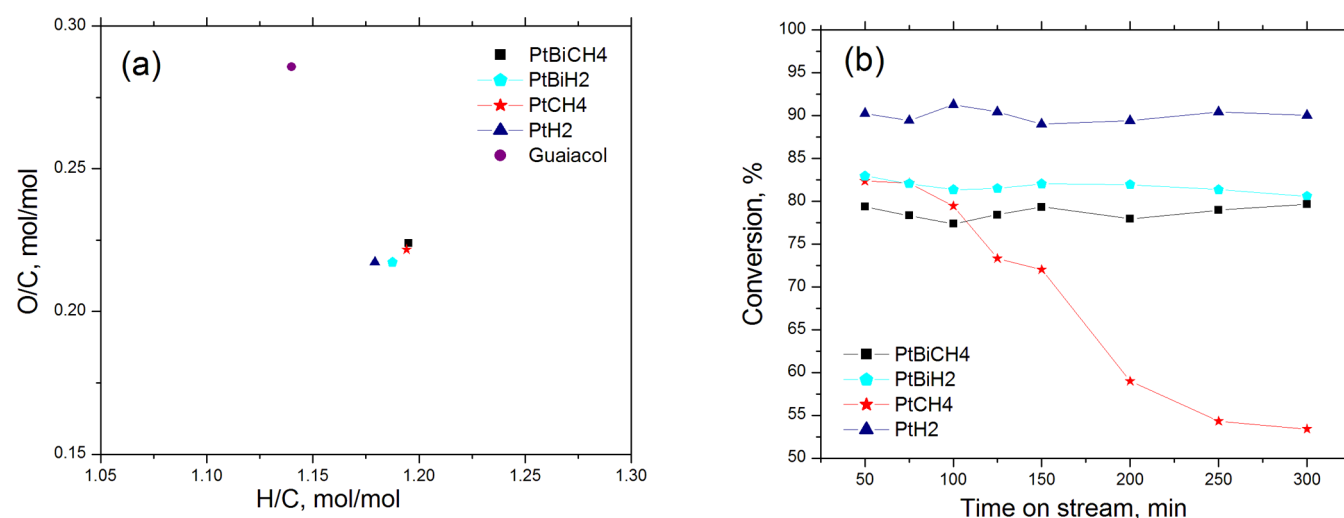


Figure 1. Catalyst performance: (a) Van Krevelen diagram at 60 min time on stream (TOS), and (b) conversion vs TOS.

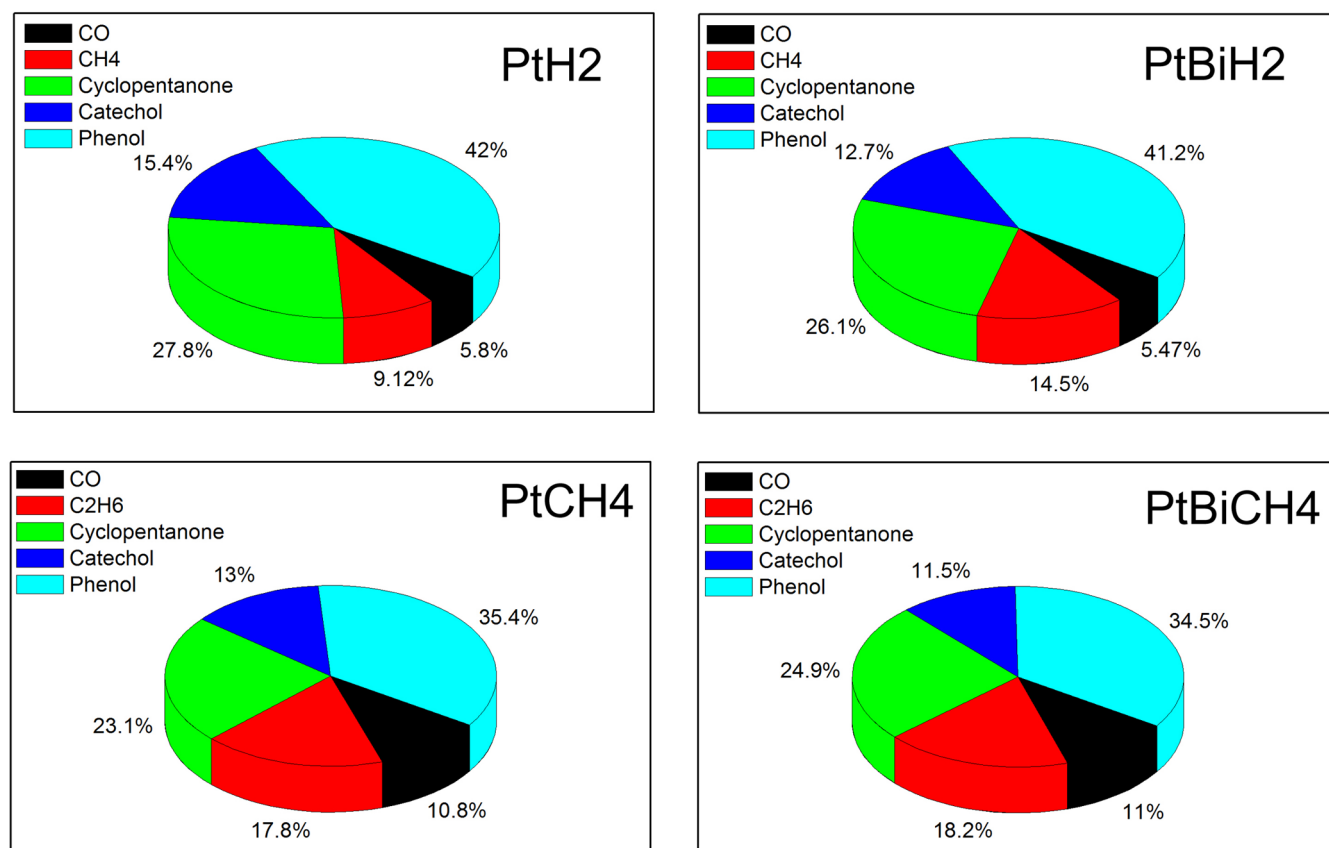


Figure 2. Distribution of major products at 60 min TOS.

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

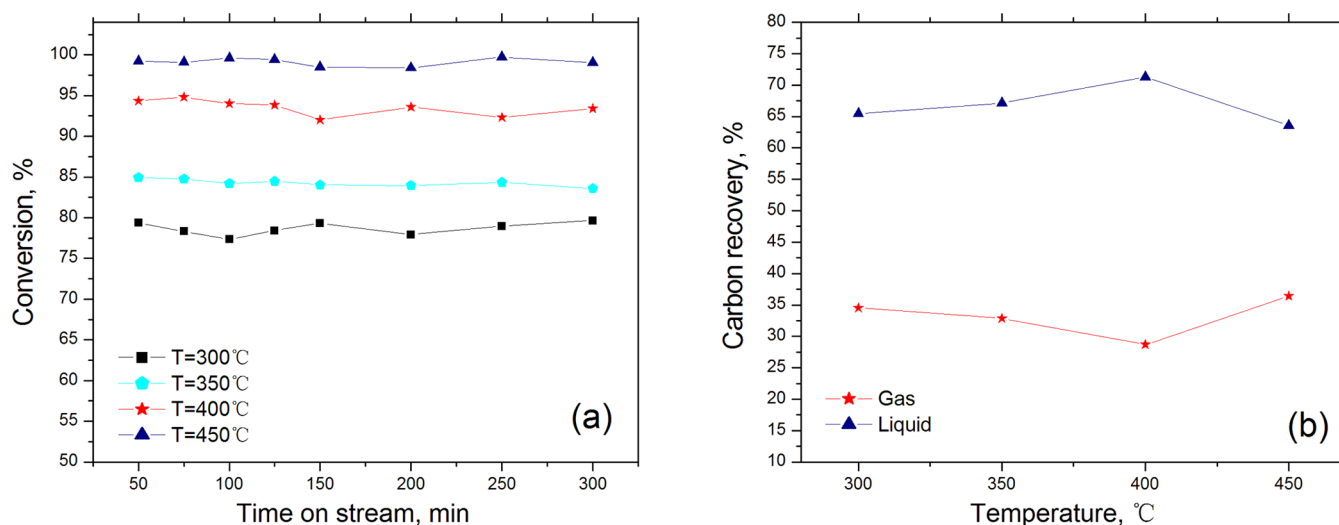
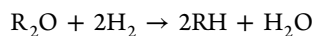


Figure 3. Effect of temperature for Pt–Bi/C catalyst: (a) guaiacol conversion, and (b) carbon recovery in liquid and gaseous products.

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.

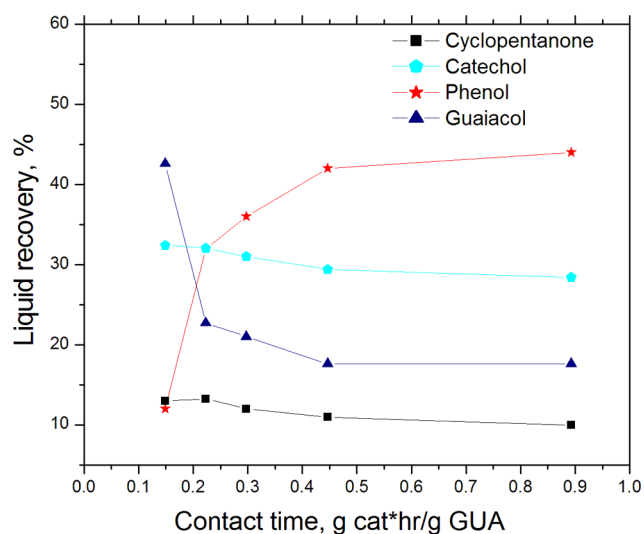


Figure 4. Kinetic behavior of Pt-Bi catalyst at 400 °C.

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).

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Notes

The authors declare no competing financial interest.

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