ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium
on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Upgrading Bio-Oil Model Compound over Pt-Based Catalysts: A Comparative Study Using Hydrogen and Methane

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Highlights

- Methane Used as Hydrogen Donor
- The Addition of Bismuth Enhances Stability of Platinum Catalyst
- Economic Bio-oil Upgrading Approach

1. Introduction

The abundant and diverse agricultural and forest resources, unused cropland and favorable climates in the world, result in large amount of surplus biomass. Bio-oils, obtained from fast pyrolysis, represent second generation bio-fuels, which address the problem (e.g. causing high food prices) associated with first generation bio-fuels. Bio-oil upgrading, by removing/decreasing high oxygen content, needs to be conducted for better stability, combustion performance, and ease of transportation. Hydrogen, typically used in bio-oil upgrading as reductant, may make bio-oil uneconomic owing to its high cost. Methane can also be used as hydrogen donor, decreasing operating cost for bio-oil upgrading. In the present work, using guaiacol as a model compound of bio-oil derived from lignin, we conducted a comparative study of guaiacol deoxygenation employing hydrogen and methane as reductants.

2. Methods

The catalysts used in this study were prepared by impregnation method. The catalysts were characterized by BET, XRD, H_2-O_2 titration, TEM, etc. The catalyst performance tests and kinetic data measurements were conducted in a fixed-bed reactor setup. The product compositions were analyzed by gas chromatography. The kinetic model developments were based on the power-law form.

3. Results and discussion

Figure 1 (a) shows the proposed reaction network, including guaiacol (GUA), catechol (CAT), cyclopentanone (CYC) and phenol (PHE), where two pathways exist for PHE production: direct demethoxylation of GUA and dehydrolysis of CAT. A comparison of H_2 and CH_4 performance over Pt and Pt-Bi catalysts is shown in Figure 1 (b). It describes that all four cases behave similarly in the early stages of time-on-stream (TOS), although the initial conversions of guaiacol vary somewhat. The high yield and good stability of the PtH2 case have been reported previously in the literature and our prior work [1, 2]. With increasing TOS, however, the PtCH4 case exhibits sharp deactivation. A likely reason is carbon deposit and/or coking, resulting from CH_4 decomposition. The addition of Bi to Pt suppressed catalyst deactivation, leading to better stability [3, 4]. The parity plots of all investigated data for H_2 and CH_4 cases are shown in Figure 1 (c) and (d), respectively. Both plots demonstrated good fits, indicating successful developments of kinetic models. The reaction activation energies for both H_2 and CH_4 cases are listed in Table 1 [4], which shows that the corresponding values for the CH_4 case are always higher than those for the H_2 case, implying relatively inactive nature of CH_4.

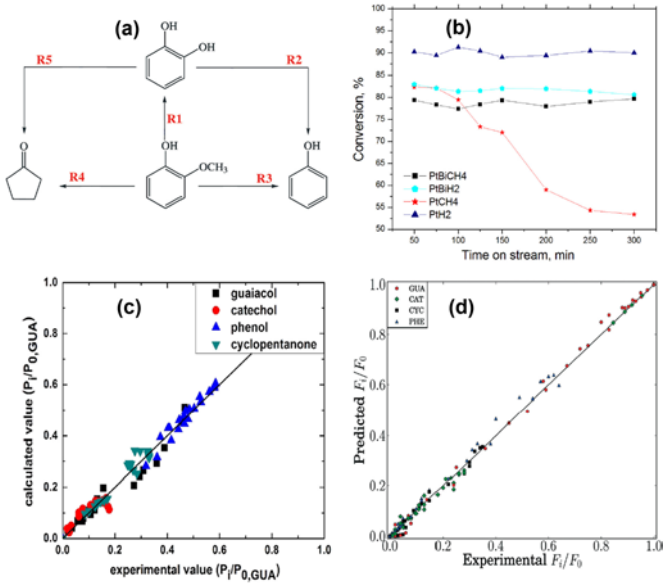

Figure 1. The Guaiacol Deoxygenation over Pt -Based Catalyst for a) Proposed Network, b) Catalyst Performance and Stability, c) Parity Plot for H_2 Case and d) Parity Plot for CH_4 Case.

Table 1. Reaction Activation Energy Values for CH_4 and H_2 Cases

E_a, kJ mol^{-1}	R_1	R_2	R_3	R_4	R_5
CH_4 case	146 ± 11	110 ± 8	166 ± 13	184 ± 14	141 ± 9
H_2 case	126 ± 6	100 ± 4	93 ± 3	149 ± 5	125 ± 2

4. Conclusions

Both experimental and modeling studies were carried out to compare the performance of H_2 and CH_4, used as reductants for guaiacol deoxygenation. It was found that over Pt-based catalysts, CH_4 exhibits essentially as good performance as H_2, while the addition of Bi to Pt suppressed catalyst deactivation caused by coking from CH_4. Kinetic modeling results for both H_2 and CH_4 cases match experimental data well.

References

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Keywords
Guaiacol; Deoxygenation; Pt-Based Catalysts; Kinetic Study