

THE ROLE OF THE SUPPORT AND REACTION CONDITIONS ON THE VAPOR PHASE HYDRODEOXYGENATION OF *m*-CRESOL OVER Pt/TiO₂ AND Pt/C CATALYSTS

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Abstract

Ex-situ catalytic fast pyrolysis offers a promising route for the sustainable production of liquid transportation fuels. However, a clear understanding of the mechanistic details involved in this process has yet to be achieved, and questions remain regarding the role of the catalyst support and the influence of reaction conditions. In order to gain insight into these questions, the hydrodeoxygenation of *m*-cresol was investigated over Pt/C and Pt/TiO₂ catalysts using experimental and computational techniques. Ring-hydrogenation, direct deoxygenation, and tautomerization mechanisms were calculated over hydrogen-covered Pt(111) and oxygen vacancies on the surface of TiO₂(101). Over Pt(111), ring-hydrogenation to 3-methylcyclohexanone and 3-methylcyclohexanol was found to be the most energetically favorable pathway. Over TiO₂(101), tautomerization and direct deoxygenation to toluene were identified as possible additional routes, although with slightly higher barriers. These calculations are consistent with the experimental results in which Pt/TiO₂ was shown to be more active on a metal site basis and exhibited higher selectivity to toluene than Pt/C. These results suggest that under *ex-situ* catalytic fast pyrolysis conditions a synergistic effect between noble metals and reducible metal oxide supports provides access to deoxygenation pathways that are not accessible to the active phase alone.

Keywords

Hydrodeoxygenation, catalytic fast pyrolysis, TiO₂

Introduction

Biomass deconstruction using fast pyrolysis offers a promising route for the production of renewable bio-oil. However, the high oxygen content of bio-oil contributes to a number of undesirable characteristics, and bio-oil must be upgraded before it is suitable for use as a drop-in transportation fuel or blendstock (Ruddy et al., 2014). *Ex-situ* catalytic fast pyrolysis (CFP) provides a route for bio-oil upgrading in which pyrolysis vapors are catalytically deoxygenated in the presence of hydrogen prior to condensation (Griffin et al., 2015). However, a clear understanding of the mechanistic details involved in this process has yet to be achieved, and questions remain about the role of the support and effect of reaction conditions. To

better understand the fundamental chemical transformations that contribute to *ex-situ* catalytic fast pyrolysis, the hydrodeoxygenation of *m*-cresol, a model compound representative of the lignin-derived components contained within bio-oil, was investigated over Pt/C and Pt/TiO₂ catalysts using a combination of experimental and computational techniques.

Materials and Methods

Carbon- and TiO₂-supported Pt were prepared from Pt(NH₃)₄(NO₃)₂ via standard incipient-wetness impregnation methods. Each catalyst was characterized using powder X-ray diffraction, NH₃ temperature

programmed desorption, inductively coupled plasma optical emission spectroscopy, transmission electron microscopy, N₂ physisorption, and CO pulse chemisorption. The performance of each catalyst was evaluated in a packed bed reactor under two conditions (523 K, 2.0 MPa and 623 K, 0.5 MPa). In both cases, a 8:1 molar ratio of molecular hydrogen to *m*-cresol was maintained for the duration of the reaction period. Quantitative analysis was carried out using gas chromatographs equipped with flame ionization and thermal conductivity detectors, which had been calibrated with standards of known concentrations. In all cases the mass balance closure was > 90%. Calculations were performed using the Vienna Ab initio Simulation Package (VASP) 5.3. The periodic density functional calculations used the projector augmented wave (PAW) potentials and an energy cutoff of 400 eV for the plane wave basis set for all calculations. The Perdew-Burke-Ernzerhof (PBE) generalized gradient corrected functional was used for all periodic calculations with Monkhorst-Pack 5×5×1 *k*-point sampling for metals and 3×3×1 *k*-point sampling for metal oxides.

Results and Discussion

The carbon selectivity and turnover frequency (TOF) for each catalyst is compared at 35% (± 3%) conversion in **Figure 1**. Toluene was the dominant product for both catalysts under *ex-situ* CFP conditions. 3-Methylcyclohexanone, 3-methylcyclohexanol, and 3-methylcyclohexane were also observed over each catalyst. In terms of turnover frequency on a metal site basis, Pt/TiO₂ exhibited more than double the activity of Pt/C. Under HT conditions, the production of 3-methylcyclohexanone and 3-methylcyclohexanol was highly favorable over both catalysts.

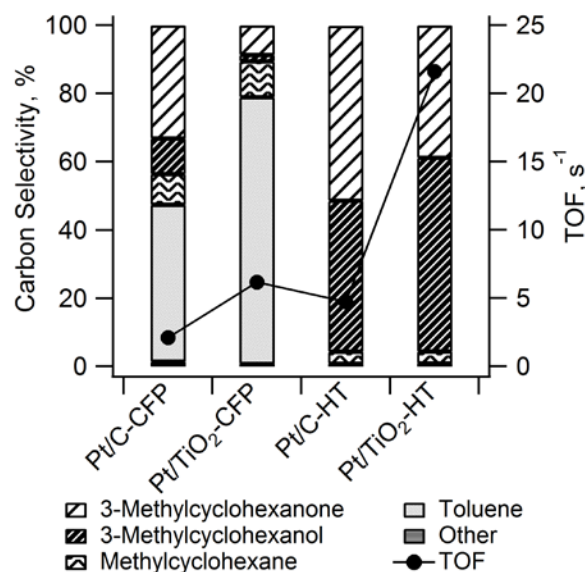


Figure 1. The carbon selectivity and turnover frequency (TOF) for each catalyst compared at 35% conversion (± 3%) under *ex-situ* CFP (623 K, 0.5 MPa) and HT (523 K, 2.0 MPa) conditions.

Ring-hydrogenation, direct deoxygenation, and tautomerization mechanisms were calculated over hydrogen covered Pt(111) and oxygen vacancies on the surface of TiO₂(101). The results show that ring-hydrogenation to 3-methylcyclohexanone and 3-methylcyclohexanol is the most energetically favorable pathway over Pt(111). Over TiO₂(101), tautomerization and direct deoxygenation to toluene were identified as possible additional routes, although with slightly higher barriers. These calculations are consistent with the experimental results in which Pt/TiO₂ was shown to be more active on a metal site basis and exhibited comparatively high selectivity to toluene at 623 K relative to Pt/C. Based on these findings, it is likely that the reactivity of Pt/TiO₂ and Pt/C is driven by the active phase at 523 K while contributions from the TiO₂ support enhance deoxygenation at 623 K.

Conclusions

The activity and selectivity observed during the deoxygenation of *m*-cresol was shown to be dependent on the choice of support and reaction conditions. Pt/TiO₂ was more active on a Pt site basis and exhibited higher selectivity to toluene than Pt/C. Computational modeling of *m*-cresol over Pt(111) and TiO₂(101) surfaces was used to develop a reaction mechanism that describes deoxygenation pathways over the active phase and identifies additional pathways that deoxygenate *m*-cresol to toluene over oxygen vacancies on TiO₂. These results suggest that synergistic effects between hydrogenation catalysts and reducible metal oxide supports provide access to additional deoxygenation pathways that are not accessible to the active phase alone.

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References

- Griffin, M. B., et al. (2015). Evaluation of silica supported metal and metal phosphide nanoparticle catalysts for the hydrodeoxygenation of guaiacol under *ex situ* catalytic fast pyrolysis conditions. *Top. Catal.*, in press, doi 10.1007/s11244-015-0512-8.
- Ruddy, D. A., et al. (2014). Recent advances in heterogeneous catalysis for bio-oil upgrading via "ex situ catalytic fast pyrolysis": catalyst development through the study of model compounds. *Green Chem.*, 16, 454.