

# The Role of Oxophilicity on the Mechanism of Hydrodeoxygenation of Phenol

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## ABSTRACT

Phenolic compounds are important products from the flash pyrolysis of biomass. Because they contain oxygen, they have low heating value, are corrosive, and are unstable. However, they can be upgraded by O-removal reactions to selectively make products that are important feedstocks to the petrochemicals industry. Thus, this process is representative of green chemistry. Hydrodeoxygenation (HDO) of phenol was investigated as a means of producing benzene, which is used by the petrochemicals industry to make numerous important chemical products (e.g., detergents, solvents, pharmaceuticals, polymers, etc.). DRIFTS of adsorbed cyclohexanone was carried out to investigate the oxophilicity of catalytic sites on the active supports of supported Pd catalysts. To understand differences in oxophilicity of different catalyst supports, we examined the frequency (i.e., wavenumbers) of the carbonyl band of adsorbed cyclohexanone. When strong adsorption occurs, the carbonyl bond is weakened resulting in a shift to lower wavenumbers. Thus, by comparing the location of the carbonyl band among different catalysts - containing different supports - we can rank them by oxophilicity. Catalysts having supports with higher oxophilicity showed a greater selectivity to benzene due to preferential hydrogenation at the carbonyl rather than the ring.

## BACKGROUND

There has been an increased demand for cleaner and renewable energy as global concerns for the reduction of carbon dioxide emissions have become more apparent and pressing. Biomass from plants is an attractive new source of energy that scientists have recently started looking into, as the bio-oil obtained from fast pyrolysis of the biomass is a greener way to produce transportation liquid fuels. However, bio-oil has high amounts of oxygen containing compounds, which leads to an oil that is high in chemical and thermal instability and has a lower energy density than traditional fossil fuels. The bio-oil then must be upgraded by HDO.

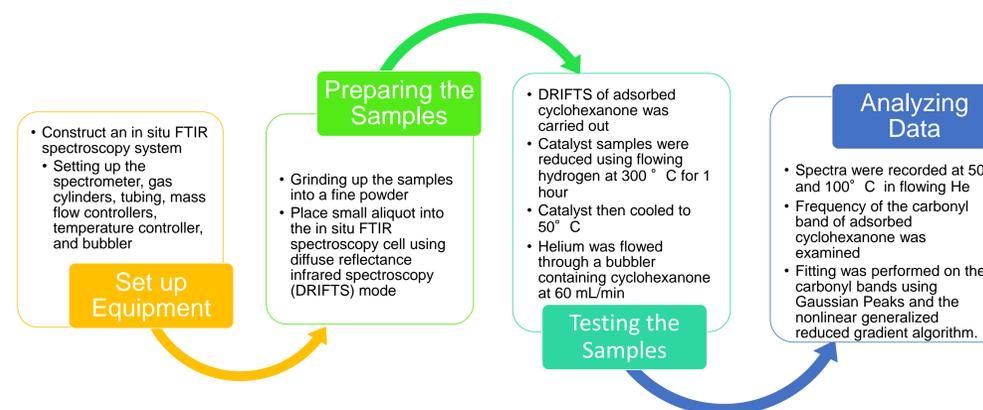
## PURPOSE

The purpose of this research project was to use a probe molecule, cyclohexanone, to explore the oxophilicity characteristic of the catalyst, and relate this parameter to product selectivity. With increasing support oxophilicity, we expect an increase in benzene selectivity due to preferential hydrogenation at the carbonyl rather than the ring.

## HYPOTHESIS

This work investigates the role of support oxophilicity on the performance of Pd/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts for the HDO of phenol reaction, and its link to benzene (desired product) selectivity.

## METHODOLOGY



## RESULTS

It was discovered that the benzene selectivity for HDO of phenol in reaction tests conducted by our partner INT-Brazil directly correlated with the oxophilicity of the catalysts as measured at UTSA using DRIFTS of adsorbed cyclohexanone. The selectivity to benzene was low and approximately the same for Pd/CeO<sub>2</sub>, Pd/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>, and Pd/Ce<sub>0.50</sub>Zr<sub>0.50</sub>O<sub>2</sub> (4.0 – 4.6%). However, further increases in Zr content significantly increased the rate of phenol conversion to benzene. Pd/ZrO<sub>2</sub> and showed a significantly higher benzene selectivity (up to 44.2%) than Pd/CeO<sub>2</sub>. This suggests that the number of oxophilic (oxygen loving) sites increased for x ≤ 0.25. Figure 2 (right) and Table 1 (below) summarize the results of the experiments with the benzene selectivity (INT-Brazil) compared with oxophilicity as measured by the % of low and medium wavenumber bands (UTSA).

Table 1. Reaction Rate of HDO of phenol and product distribution at low conversion.

| Catalyst  | % of Low and Medium Wavenumber Bands (see Fig 2) | Selectivity (%) |      |      |
|---|--|-----------------|------|------|
|   |  | BZ              | ONE  | OL   |
| (a) Pd/CeO <sub>2</sub>                                     | 25.0   | 4.4             | 86.3 | 9.3  |
| (b) Pd/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub> | 30.0   | 4.0             | 81.3 | 14.7 |
| (c) Pd/Ce <sub>0.50</sub> Zr <sub>0.50</sub> O <sub>2</sub> | 31.3   | 4.6             | 88.4 | 11.0 |
| (d) Pd/Ce <sub>0.25</sub> Zr <sub>0.75</sub> O <sub>2</sub> | 35.6   | 12.5            | 82.3 | 5.2  |
| (e) Pd/Ce <sub>0.10</sub> Zr <sub>0.90</sub> O <sub>2</sub> | 37.0   | 15.3            | 82.7 | 2.0  |
| (f) Pd/ZrO <sub>2</sub>                                     | 44.9   | 44.2            | 55.8 | 0.0  |

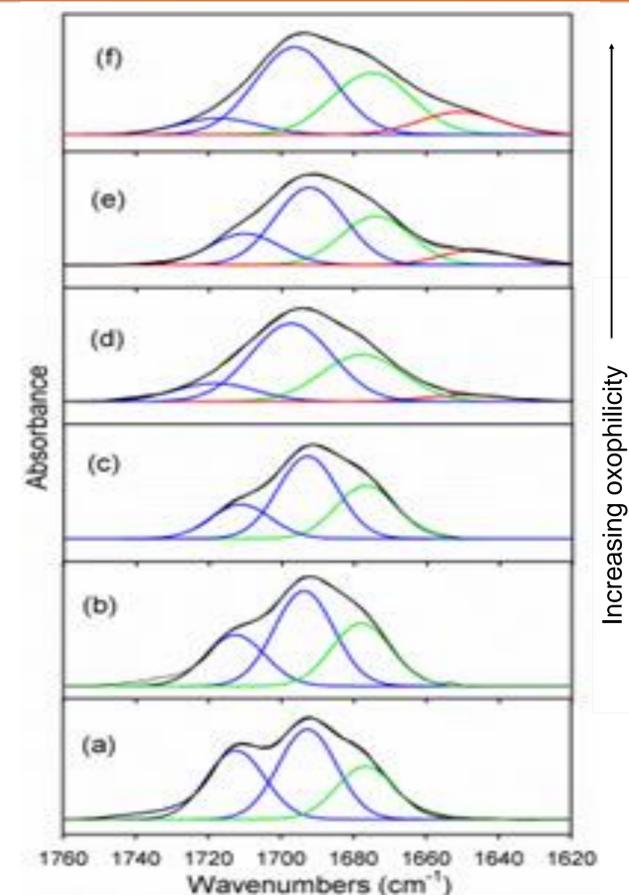


Figure 2. Gaussian Peak fitting for the DRIFTS of adsorbed cyclohexanone probe molecule.

## SUMMARY

- ❖ Flash pyrolysis of biomass produces a bio-oil that contains significant O-content.
- ❖ O-content in fuel lowers its heating value, and makes it corrosive, reactive, and unstable.
- ❖ Hydrodeoxygenation of phenol was investigated over ceria-zirconia supported Pd nanoparticles to remove O and target benzene as a valuable product.
- ❖ DRIFTS of adsorbed cyclohexanone was used to measure the oxophilicity of the catalysts, with the goal of increasing oxophilicity to hydrogenate the carbonyl over the ring.
- ❖ With increasing Zr-content, oxophilicity increased, and this was correlated with significantly higher benzene selectivity.

## REFERENCES

de Souza, P.M.; Rabelo-Neto, R.C.; Borges, L.E.P.; Jacobs, G.; Davis, B.H.; Resasco, D.E.; Noronha, F.B., "Hydrodeoxygenation of phenol over Pd catalysts. Effect of support on reaction mechanism and catalyst deactivation," *ACS Catalysis* 7 (2017) 2058-2073.