

The Role of Defect Sites and Oxophilicity of the Support on the Phenol Hydrodeoxygenation Reaction

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ABSTRACT

This work studies the effect of support defect sites on the performance of Pd/Ce_xZr_{1-x}O₂ (x=0.00; 0.25; 0.50; 0.75; 0.90) catalysts for the hydrodeoxygenation of phenol in the gas phase at 573 K. The activity and selectivity for hydrodeoxygenation of phenol depends significantly on the support used. Increasing the Zr content from x=0.0 to 0.5, the reaction rate for hydrodeoxygenation and the selectivity to benzene remains very low. However, upon increasing the Zr content above x=0.5 a sudden jump in reaction rate and selectivity to benzene is observed. The selectivity to deoxygenated products is found to depend on the oxophilicity of the support. Increasing the Zr content enhances the strength of the interaction between the O of the carbonyl group and the oxophilic site. It is proposed that the oxophilicity of these catalysts is related to the structure of the Ce_xZr_{1-x}O₂ solid solution formed. In addition, it is observed that the degree of deactivation during the reaction also depends on the Ce/Zr molar ratio of the support. Pd/ZrO₂, Pd/Ce_{0.10}Zr_{0.90}O₂ and Pd/Ce_{0.25}Zr_{0.75}O₂ catalysts readily deactivate during reaction, whereas the phenol conversion only slightly decreases for Pd/CeO₂, Pd/Ce_{0.75}Zr_{0.25}O₂ and Pd/Ce_{0.50}Zr_{0.50}O₂ catalysts. The results reveal that the density of Zr species on the surface is responsible for catalyst deactivation. The stronger adsorption between the oxygen from the phenol with Zr cations resulted in an accumulation of O-containing byproducts and catalyst deactivation.

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.

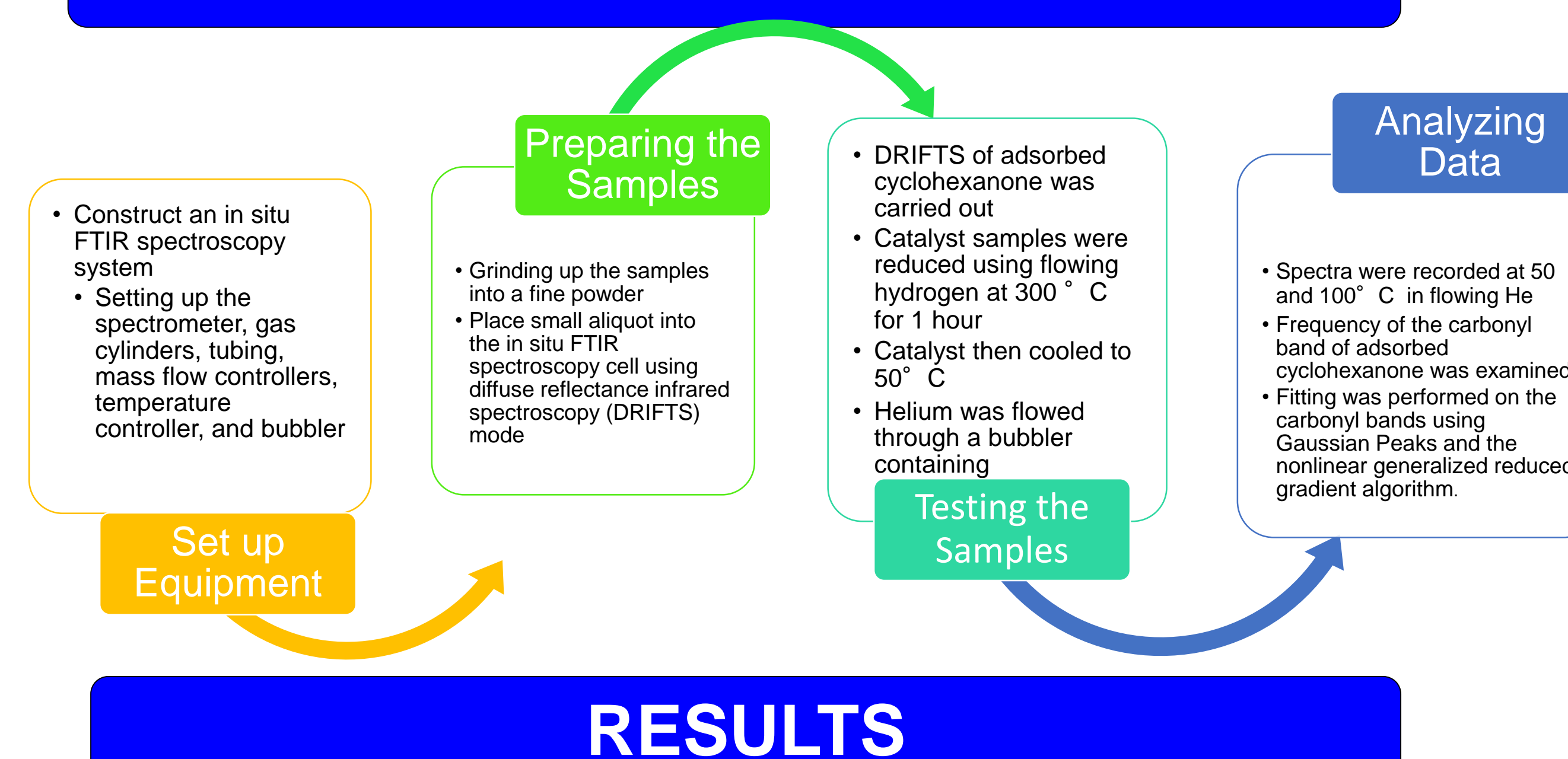
PURPOSE

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_xZr_{1-x}O₂ catalysts for the HDO of phenol reaction, and its link to benzene (desired product) selectivity.

METHODOLOGY



RESULTS

The HDO of phenol over all supports not exhibit any significant activity even at high W/F (0.46 h). The main products formed were benzene, cyclohexanone (ONE), cyclohexanol (OL) as well as small amounts of cyclohexane for Pd/Ce_xZr_{1-x}O₂ catalysts. Product distribution significantly depended on the Ce/Zr molar ratio of the support and W/F. At low W/F (< 0.5 h), cyclohexanone was the main product formed for Pd/CeO₂. The addition of Zr increased the formation of benzene in this region. Higher formation of benzene only occurred at high conversions and small yields of cyclohexanol were also observed over these catalysts. For Pd/ZrO₂ catalyst, benzene was the main product over the whole range of W/F. The reaction rate of HDO of phenol was calculated and the selectivity of all catalysts was compared at low phenol conversion. The deoxygenation rate was approximately the same for Pd/CeO₂, Pd/Ce_{0.75}Zr_{0.25}O₂ and Pd/Ce_{0.50}Zr_{0.50}O₂ catalysts. However, the reaction rate significantly increased for catalysts with Zr content higher than 0.5. Pd/ZrO₂ catalyst exhibited the highest reaction rate that was about 30-fold higher than the one obtained for Pd/Ce_{0.75}Zr_{0.25}O₂. The reaction rates displayed the following trend: Pd/ZrO₂ >> Pd/Ce_{0.10}Zr_{0.90}O₂ > Pd/Ce_{0.25}Zr_{0.75}O₂ > Pd/Ce_{0.50}Zr_{0.50}O₂ ≈ Pd/Ce_{0.75}Zr_{0.25}O₂ ≈ Pd/CeO₂. The product distribution varied significantly with the Ce/Zr molar ratio. Pd/CeO₂, Pd/Ce_{0.75}Zr_{0.25}O₂ and Pd/Ce_{0.50}Zr_{0.50}O₂ catalysts exhibited a high selectivity to cyclohexanone and cyclohexanol. Increasing the Zr content favored the formation of benzene and decreased the selectivity to cyclohexanone and cyclohexanol. Pd/ZrO₂ showed the highest selectivity to benzene without the formation of cyclohexanol. For instance, Pd/ZrO₂ catalyst showed selectivity to benzene that was 10-fold higher than that of either Pd/CeO₂ or Pd/Ce_{0.75}Zr_{0.25}O₂ catalysts. These results suggest that the Zr content on the mixed oxide significantly affects the deoxygenation activity and product distribution of the catalysts for HDO of phenol. In figure 4 (the mechanism), it shows that for the catalysts that are more oxophilic, the adsorbed keto tautomer intermediate get hydrogenated more at the O atom, leading to a cyclohexenone intermediate that more readily dehydrates to benzene (the desired product, which is a feedstock for the chemical industry). Those that are less oxophilic get hydrogenated more at the ring, leading to undesired byproducts (lower selectivity to benzene).

Figure 1:

Distribution of the different regions of the band associated with $\nu(\text{C}=\text{O})$ of cyclohexanone.

Catalyst	% Wavenumber bands		
	High $\geq 1695 \text{ cm}^{-1}$	Medium $1660 - 1695 \text{ cm}^{-1}$	Low $1620 - 1660 \text{ cm}^{-1}$
Pd/CeO ₂	75.0	25.0	0.0
Pd/Ce _{0.75} Zr _{0.25} O ₂	70.0	30.0	0.0
Pd/Ce _{0.50} Zr _{0.50} O ₂	68.7	31.3	0.0
Pd/Ce _{0.25} Zr _{0.75} O ₂	64.4	31.4	4.2
Pd/Ce _{0.10} Zr _{0.90} O ₂	63.0	28.3	8.7
Pd/ZrO ₂	55.1	32.9	12.0

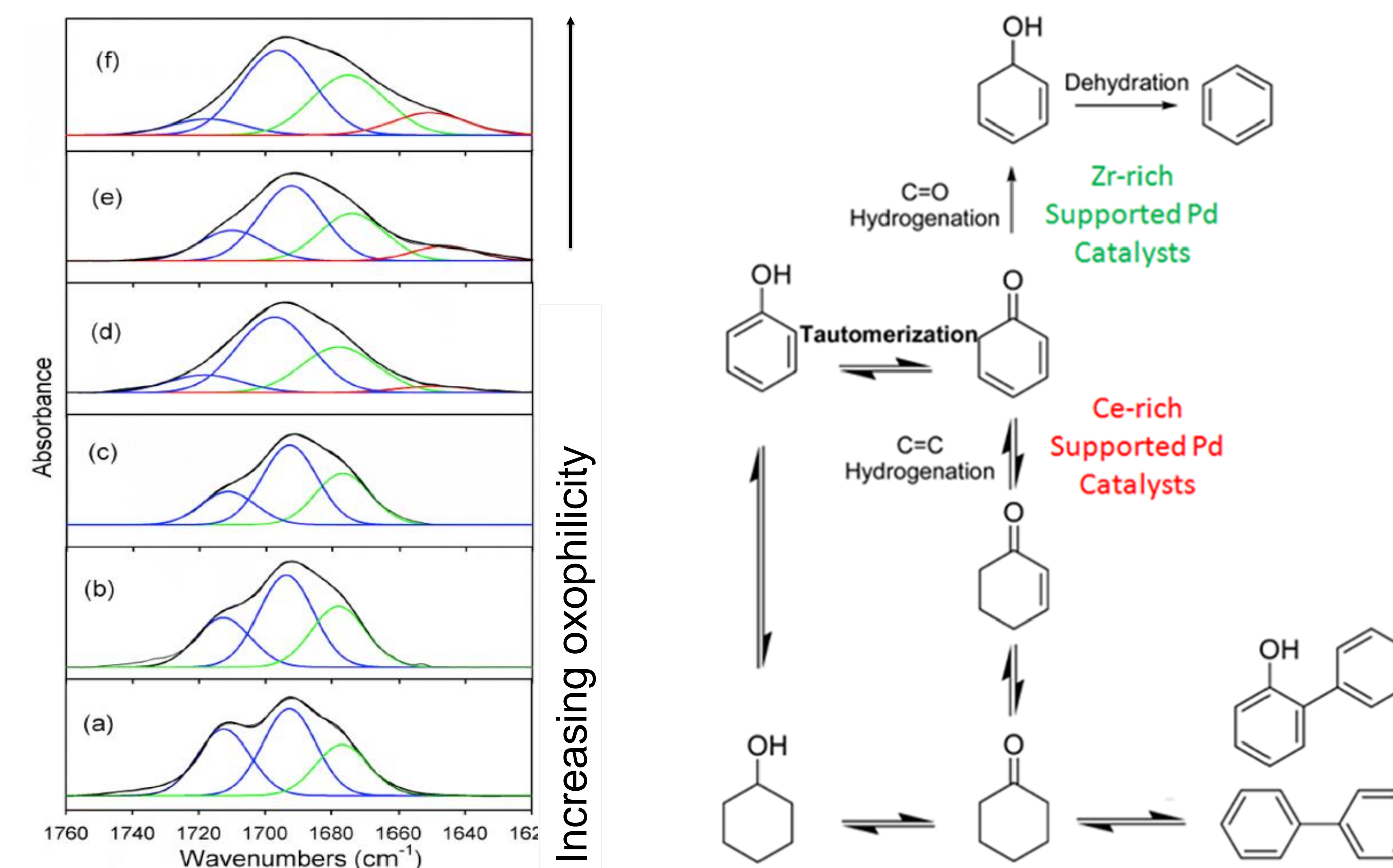


Figure 2. Gaussian Peak fitting for the DRIFTS of adsorbed cyclohexanone probe molecule. Cyclohexanone spectra after desorption at 323 K over: (a) Pd/CeO₂; (b) Pd/Ce_{0.75}Zr_{0.25}O₂; (c) Pd/Ce_{0.50}Zr_{0.50}O₂; (d) Pd/Ce_{0.25}Zr_{0.75}O₂; (e) Pd/Ce_{0.10}Zr_{0.90}O₂; (f) Pd/ZrO₂. Blue curves: High wavenumber bands; green curves: medium wavenumber bands; red curves: low wavenumber bands

Figure 4: Mechanism for the reaction.

Figure 3: Catalysts having greater oxophilicity (the ones with greater ZrO₂ content) have a higher selectivity to benzene.

Reaction rate of HDO of phenol and product distribution at low conversion.

Catalyst	Conversion (%)	Rate of HDO (mmol. min ⁻¹ .g _{cat} ⁻¹)	Selectivity (%)		
			BZ	ONE	OL
Pd/CeO ₂	12.2	0.09	4.4	86.3	9.3
Pd/Ce _{0.75} Zr _{0.25} O ₂	15.1	0.04	4.7	80.7	14.6
Pd/Ce _{0.50} Zr _{0.50} O ₂	13.9	0.09	4.6	84.6	10.9
Pd/Ce _{0.25} Zr _{0.75} O ₂	15.5	0.19	14.5	78.5	4.9
Pd/Ce _{0.10} Zr _{0.90} O ₂	11.9	0.43	18.0	80.1	1.9
Pd/ZrO ₂	9.1	1.20	44.2	55.8	0.0

BZ: benzene; ONE: cyclohexanone; OL: cyclohexanol.

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

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