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## Mechanistic Insight in Hydrodeoxygenation on Nickel Based Catalysts

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### Introduction

Pyrolysis of biomass followed by hydrodeoxygenation (HDO) of the produced bio-oil has been identified as a prospective route to engine fuels. Through pyrolysis practically any source of biomass can be converted into bio-oil [1]. Despite of the higher energy density than the original biomass, bio-oil has a lower heating value compared to crude oil, a low shelf storage time, is viscous and polar, making it unsuitable as an engine fuel. These characteristics are all associated with high contents of water and organic bound oxygen in the bio-oil [1]. It will be advantageous if bio-oil can be upgraded to an oil similar to conventional crude oil through HDO, where hydrogen is used to remove the oxygen functionality in the bio-oil. To accomplish this, a suitable catalyst is required and recent research has indicated that nickel based catalysts could be interesting candidates for this task [2]. We have investigated the mechanistic details of a set of Ni catalysts for HDO of phenol as a model compound of bio-oil.

### Materials and Methods

All catalysts were prepared by the incipient wetness technique with a Ni loading of 5 wt%. Hereafter they were dried at 100 °C over night and calcined at 400 °C for 4 h. Catalyst testing was performed in a 300ml batch reactor (Parr 4566) with 1 g of catalyst, 50 g of phenol, a temperature of 275 °C, a pressure of 100 bar and a reaction time of 5 h. Analysis of the product was made on a Shimadzu GCMS/FID-QP2010UltraEi.

### Results and Discussion

Nickel was tested as catalyst for HDO of phenol on a series of supports in the batch reactor. Generally, it was observed that the reaction proceeds through the reaction scheme in Figure 1 (solid arrows). However, as the conversion of cyclohexanone into cyclohexanol and cyclohexene into cyclohexane are very fast reactions, the effective reaction scheme could be described as: phenol → cyclohexanol → cyclohexane. On this basis a kinetic model was developed which described the system on the basis of two parameters: the rate constant of hydrogenation ( $k_1$ ) and the rate constant of deoxygenation ( $k_2$ ). These can be correlated to the TOF of respectively hydrogenation ( $\text{TOF}_{\text{Hyd}}$ ) and deoxygenation ( $\text{TOF}_{\text{Deox}}$ ).

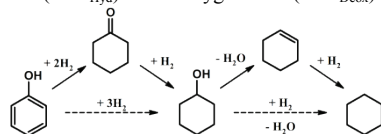


Figure 1. Reaction scheme for phenol hydrodeoxygenation.

Table 1 summarizes the results from HDO of phenol with Ni/CeO<sub>2</sub>, Ni/ZrO<sub>2</sub>, Ni/SiO<sub>2</sub>, and Ni/C (as examples of the obtained results). Ni/CeO<sub>2</sub> was found as the best performing

hydrogenation catalyst (largest  $\text{TOF}_{\text{Hyd}}$ ), but Ni/ZrO<sub>2</sub> was the overall best HDO catalyst with the highest yield of cyclohexane. Ni/C was found to be practically inactive. On this basis it is proposed that nickel only functions in combination with an oxide support.

Table 1. Activity of nickel catalysts for HDO of phenol. T = 275 °C, P = 100 bar, t = 5 h.

Catalyst	X <sub>Phenol</sub> [%]	Y <sub>C-Hexanol</sub> [%]	Y <sub>C-Hexane</sub> [%]	TOF <sub>Hyd</sub> [min <sup>-1</sup> ]	TOF <sub>Deox</sub> [min <sup>-1</sup> ]
Ni/CeO <sub>2</sub>	100	88	4	1497.9	0.4
Ni/ZrO <sub>2</sub>	100	10	83	64.9	23.7
Ni/SiO <sub>2</sub>	80	30	38	22.5	15.6
Ni/C	2	0	0	0.3	0.7

Ni/SiO<sub>2</sub> was investigated with varying nickel dispersion as seen in Figure 2. The results show that the  $\text{TOF}_{\text{Hyd}}$  decreased with dispersion, while the  $\text{TOF}_{\text{Deox}}$  increased with dispersion. Figure 2 also shows the relative fractions of different sites on nickel crystals as function of dispersion. Comparing the trend of  $\text{TOF}_{\text{Deox}}$  to the fraction of available low coordinated sites (step & corner) shows that they behave similarly with the dispersion. This indicates that the deoxygenation probably takes place on the low coordinated nickel atoms, preferably.

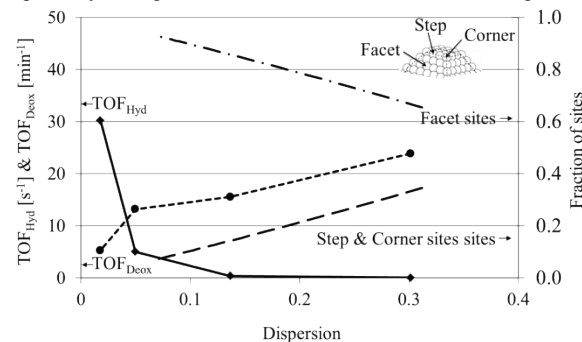


Figure 2. TOF of Ni/SiO<sub>2</sub> catalyst with varying dispersion (determined by TEM) compared to the fraction of step, corner, and facet sites on a crystal. T = 275 °C, P = 100 bar, t = 5 h.

### Significance

Among the tested nickel catalysts, Ni/ZrO<sub>2</sub> was the best performing HDO catalyst, with balanced rates of hydrogenation and deoxygenation. The presence of an oxide support is of key importance for the catalyst performance, as the oxycompound activation takes place on this through heterolytic dissociation. Furthermore, the actual deoxygenation site on nickel can possibly be linked to the low coordinated sites (step/corners) on the crystallite. This insight can be used for better design of HDO catalysts.

### References

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