

# Atomic Level Studies of Advanced Catalysts for Hydrodeoxygenation

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## Objectives

The utilization of biomass for the production of fuels and chemicals is currently an area of great activity because of the recognition that fossil fuels are a finite resource and because of the imminent threat of global warming from the release of carbon dioxide. Biomass pyrolysis has great potential for the production of drop-in replacements for petroleum products, but the pyrolysis oil product has low heating value and stability and high corrosivity, and improvements are needed. This project involves the development of advanced hydrodeoxygenation (HDO) catalysts to reduce the oxygen content of the oil.

## Technical Barriers

A fundamental challenge is the design of catalysts that have high activity and selectivity in HDO. The biggest barriers in catalyst development is the formulation of compositions that do not deactivate with the bio-oil feedstock, which has high acidity and is highly functionalized.

## Abstract

The catalysts that will be developed are a class of highly active and stable materials, the transition metal phosphides. Initial tests in our laboratory and elsewhere have demonstrated that the catalysts are highly effective in oxygen removal from model bio-oil compounds. We propose to build on these findings to develop advanced compositions using new preparation methods. The specific compounds will be bimetallic phosphide catalysts composed of the elements Ti, V, Cr, W, Fe, Co, Ni encompassing Groups 4-9 in the Periodic Table. The support will be fluid catalytic cracking materials with high Si-Al ratio, of interest because they have a bimodal mesoporous/microporous structure and are highly attrition resistant. The study of bimetallic compositions is motivated by our recent finding that NiFeP has outstanding catalytic properties. The catalysts will be highly dispersed and will

be studied by x-ray absorption spectroscopy (XAS) and  $^{31}\text{P}$  solid-state nuclear magnetic resonance spectroscopy.

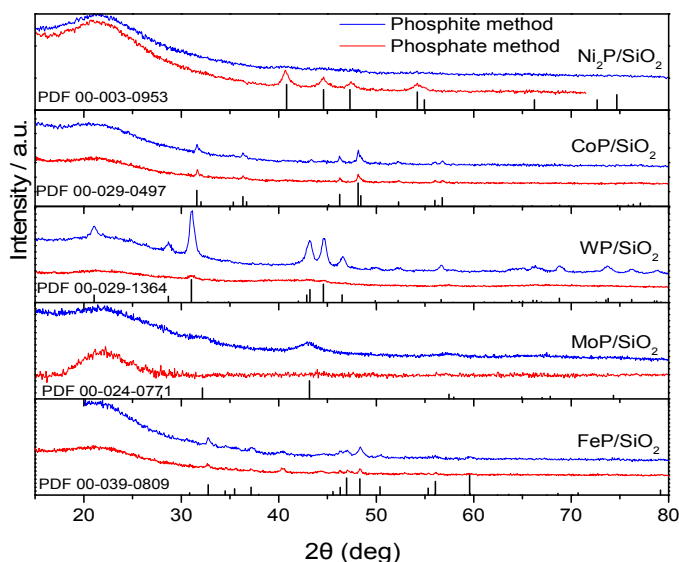
The novel catalysts will be tested with model compounds and the best compositions will be tried in a pilot scale unit with real feeds at realistic pyrolysis conditions. The substrates to be used will be 2-methyltetrahydropyran (2-MTHP) and guaiacol (GCOL), which are, respectively, models for cellulose and lignin. The compounds are chosen because they can react by several pathways to give information about the reaction mechanism. The work will include detailed studies of kinetics and spectroscopy to understand the mechanism of the HDO reaction and to relate it to the structure of the catalysts in their working state. Knowledge of the partial pressure dependency of the rates of reaction on the reactants and various co-reactants ( $\text{H}_2$ ,  $\text{CO}$ ) and products ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , organics) will set the kinetic constraints to the mechanism. Then in situ studies by Fourier transform infrared and XAS will be used to identify key intermediates during reaction and will be used to distinguish between mechanisms. Importantly, these measurements will be carried out simultaneously at a synchrotron facility with specially designed equipment. Dynamic studies with methods we have developed will be used to establish the role of observed intermediates in the catalytic reactions. The overall objective is to obtain information that can be used to improve the catalyst action by understanding the key factors that govern reactivity.

## Progress Report

### Synthesis of Catalysts

A series of silica-supported metal phosphides was prepared by two methods involving the reduction of phosphite ("I") or phosphate ("A") precursors and was studied for the hydrodeoxygenation (HDO) of 2-methyltetrahydrofuran (2-MTHF). The "I" method required lower temperature than the "A" method and resulted in catalysts with higher surface area.

The activity was evaluated in a packed-bed reactor on the basis of equal CO chemisorption sites (30  $\mu\text{mol}$ ) loaded in the reactor with comparison made to a commercial Pd/ $\text{Al}_2\text{O}_3$  catalyst. At 300 °C and 1 atm the order of activity was  $\text{Ni}_2\text{P} > \text{WP} > \text{MoP} > \text{CoP} > \text{FeP} > \text{Pd}/\text{Al}_2\text{O}_3$ . The principal HDO products for the iron group phosphides ( $\text{Ni}_2\text{P}$  and  $\text{CoP}$ ) were pentane and butane, whereas for the group 6 metal phosphides ( $\text{MoP}$  and  $\text{WP}$ ) the products were mostly pentenes and pentadienes. For the  $\text{Pd}/\text{Al}_2\text{O}_3$  and the low-activity  $\text{FeP}/\text{SiO}_2$  catalyst the products were mostly pentenes and C4 mixtures. There were no significant differences in the turnover frequency between materials



**FIGURE 1.** X-ray diffraction patterns of catalysts prepared by the phosphite and phosphate methods.

prepared by the two methods, except possibly for the case of WP. There were likewise no great changes in selectivity towards HDO products at 5% total conversion, except for WP. The differences in the case of WP were attributed to the surface P/W ratio which x-ray photoelectron spectroscopy (XPS) showed to be twice as large for the I method than the A method. Contact time studies were used to develop reaction networks for the most active catalysts,  $\text{Ni}_2\text{P}/\text{SiO}_2$  and  $\text{WP}/\text{SiO}_2$ . For  $\text{Ni}_2\text{P}/\text{SiO}_2$  by both methods the selectivity profiles were similar, and could be explained by a rake mechanism with pentenes as primary products, 2-pentanone as a secondary product, and pentane as a final product. In contrast, for  $\text{WP}/\text{SiO}_2$  the selectivity depended greatly on the preparation method, but produced a preponderance of unsaturated compounds. The results could be explained from the surface composition.

#### Reactions of 2-Methyltetrahydrofuran (cellulose model compound)

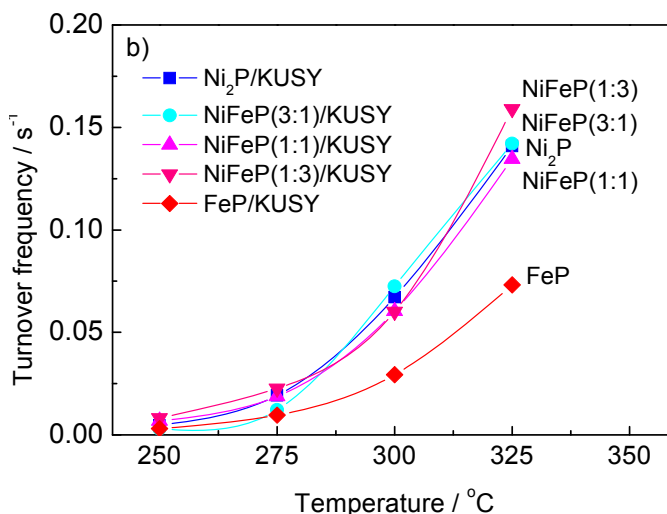
A series of supported nickel-iron phosphide catalysts were used to study the hydrodeoxygenation of 2-methyltetrahydrofuran (2-MTHF), a model compound for biomass-derived pyrolysis oil. The catalysts were prepared by incipient wetness impregnation of the active components onto potassium ion-exchanged USY zeolites followed by temperature-programmed reduction. The samples were denoted as  $\text{Ni}_2\text{P}/\text{KUSY}$ ,  $\text{NiFeP}(3:1)/\text{KUSY}$ ,  $\text{NiFeP}(1:1)/\text{KUSY}$ ,  $\text{NiFeP}(1:3)/\text{KUSY}$ , and  $\text{FeP}/\text{KUSY}$ , where the numbers in parenthesis are the Ni:Fe molar ratios. The results of the studies can be understood from ensemble and ligand effects. X-ray diffraction analysis indicated the presence of alloys in the mixed composition samples, and this was supported by CO chemisorption and infrared measurements. Uptakes

of CO decreased as the iron content increased, suggesting that iron present on the surface of the catalysts blocked chemisorption sites. Fourier transform infrared (FTIR) measurements showed a single peak for linearly adsorbed CO whose intensity decreased with Fe content, in agreement with the uptake results. Moreover, the FTIR peak shifted monotonically consistent with a ligand effect in an alloy formed in the  $\text{Ni}_2\text{P}$  and FeP particles. The reactivity in 2-MTHF HDO was studied at 250-325 °C and 0.5 MPa and it was found that the conversion was highest for the  $\text{Ni}_2\text{P}/\text{KUSY}$  sample and decreased steadily with Fe content. However, the turnover frequency did not change significantly, indicating that the rate-determining step was activation of 2-MTHF on single Ni sites.

The selectivity at low conversion (3%) changed from mostly n-pentane and n-butane for  $\text{Ni}_2\text{P}/\text{KUSY}$  to mostly 1-pentanol for the iron-containing samples, suggesting that in subsequent steps an ensemble effect was operational with the iron influencing the reaction chemistry. At high conversion (70%) all the samples produced mostly n-pentane and n-butane.

#### Reactions of Guaiacol (lignin model compound)

Several types of Ni phosphides with different phosphorus contents ( $\text{Ni}_2\text{P}$ ,  $\text{Ni}_{12}\text{P}_5$ , and  $\text{Ni}_3\text{P}$ ) were prepared by temperature-programmed reduction (TPR) and were tested for hydrodeoxygenation (HDO) of guaiacol at various temperatures,  $\text{H}_2$  pressures, and contact times. Low phosphorus content in the precursors leads to the formation of Ni-rich phosphides such as  $\text{Ni}_3\text{P}$  and  $\text{Ni}_{12}\text{P}_5$  with high concentration of metallic sites, while high phosphorus levels results in the formation of  $\text{Ni}_2\text{P}$  with low numbers of metallic sites. The reactivity of the catalysts for the HDO of guaiacol displays a strong dependence on the phosphorus content.



**FIGURE 2.** Activity of different Ni-Fe catalysts showing similar TOFs

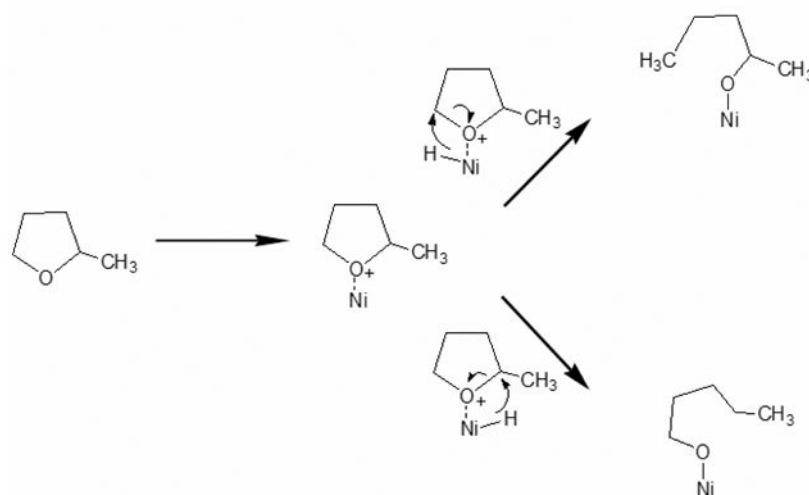


FIGURE 3. Reaction of 2-methyltetrahydrofuran involving a single Ni atom

At temperatures higher than 260 °C, high-phosphorus catalysts have higher turnover frequencies (TOFs) than low-phosphorus samples and carry out complete HDO to the product benzene. In comparison, metallic Ni catalyst has little ability to produce benzene or hexane but produces only phenol, cyclohexanone, or cyclohexanol at different  $H_2$  pressures. The reaction pathways for guaiacol HDO is proposed to involve catechol as primary product and phenol as secondary product, based on the effect of contact time on the product distribution (Fig. 4).

### Future Directions

Understanding of the relationship between the physical properties of catalysts and their activity is important to develop new improved compositions. The objectives are given below.

1. Advanced preparation of bimetallic phosphide catalysts and atomic-level characterization. Materials will be prepared by combining the most active single-elements, Ni and W, with Ti, V, Cr, Mn, Fe, and Co. The catalysts will be highly dispersed, and x-ray absorption fine structure (XAFS) and  $^{31}P$  NMR spectroscopy will be used to determine the structure of the active phase
2. Reactivity studies with model compounds and real feeds. Hydrodeoxygenation will use two compounds, guaiacol (GCOL and 2-methyltetrahydro-pyran (2-MTHP), which are models of lignin and cellulose-hemicellulose. Contact time measurements will provide the reaction network, and isotopic labeling the mode of ring-opening. The best catalysts will be evaluated in catalytic pyrolysis with actual biomass.

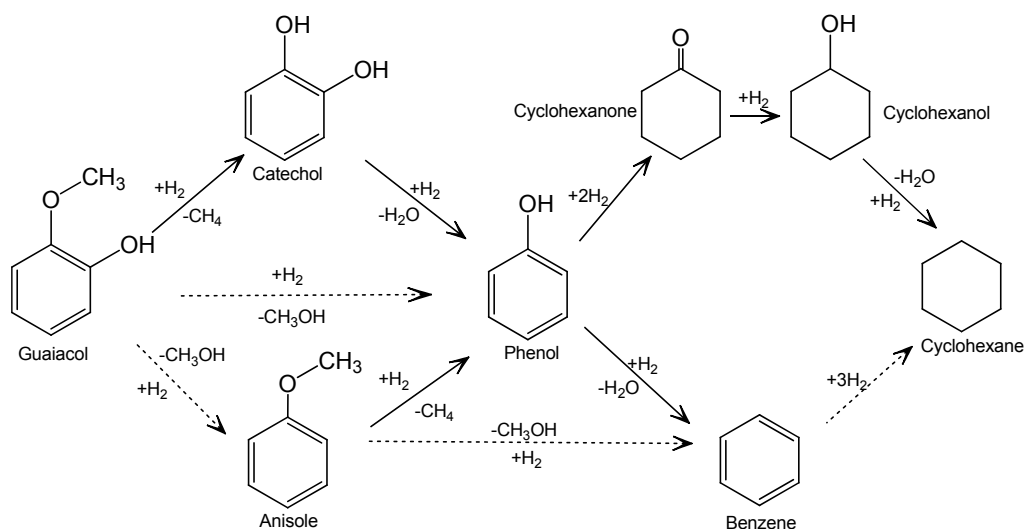


Figure 4. Reaction network for guaiacol hydrodeoxygenation

3. Studies of kinetics and mechanisms.  
For the best catalysts partial pressure dependency and contact time measurements will be used to derive a plausible reaction sequence which will be checked spectroscopically.  
Kinetic rate expressions will be tested statistically.
4. Studies with in situ Fourier transform infrared (FTIR) spectroscopy and XAFS.  
Adsorbed species will be probed by FTIR and XAFS spectroscopy using a dynamic method where changes in coverage ( $d\theta/dt$ ) will be compared to the turnover frequency. In situ measurements will relate changes in catalyst structure with adsorption to identify active sites.

### **Publication list (including patents) acknowledging the DOE grant or contract**

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2. Jieun Shin, Ara Cho, Atsushi Takagaki, Ryuji Kikuchi, S. Ted Oyama, Ligand and ensemble effects in bimetallic NiFe phosphide catalysts for the hydrodeoxygenation of 2-methyltetrahydrofuran *Topics Catal.* **2012**, 55, 969–980.
3. Oxygen-removal from dibenzofuran as a model compound in biomass derived bio-oil on nickel phosphide catalysts: Role of phosphorus  
Juan Antonio Cecilia, Antonia Infantes-Molina, Enrique Rodríguez-Castellón, Antonio Jiménez-López, S. Ted Oyama, *Appl. Catal. B: Env.* **2013**, 136-137, 140-149.