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# BESH2013 Dual Site Requirements for Hydrodeoxygenation of Model Biomass Compounds

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## Program Scope

This program supports the Office of Basic Energy Sciences mission through the development of unifying principles in hydrotreating catalysis. This goal will be achieved through detailed theoretical investigations using density functional theory (DFT) and kinetic modeling performed on high performance computing clusters, which will be interpreted along with available experimental data. This major goal is pursued by accomplishing two specific aims, (a) identification of the active site and mechanism of known hydrodeoxygenation catalysts using model bio-oil compounds, and (b) juxtaposition of the active site and reaction pathways of oxides and their corresponding sulfides, to develop universal design principles for hydrotreating catalysts.

## FY 2016 Highlights

### 1. Introduction

Fast pyrolysis of biomass is a promising low-cost technology that produces bio-oil suitable for the production of chemicals and use as transportation fuel after an appropriate upgrade step. The upgrade is necessary to increase the heating value, lower the viscosity and improve the long-term stability, and can be achieved by reducing the oxygen content through hydrotreatment over heterogeneous catalysts. [1] However, the complexity of bio-oils and the fact that this technology has only recently gained interest are both responsible for the lack of fundamental knowledge in this field. In the recent literature there is a growing number of bifunctional catalyst combinations that show good activity and selectivity for hydrodeoxygenation (HDO). [2-4] These catalysts have in common that they have two types of sites: one with metallic character and one with acidic character. In this study we use DFT to generate fundamental insight into the role of each type of site and propose a dual site structure-performance relationship for efficient HDO catalysts.

Our study combining theory and experiments provides evidence for the direct deoxygenation of phenol and *m*-cresol on Ru/TiO<sub>2</sub> catalysts to occur at perimeter sites at the interface between the Ru metal and the TiO<sub>2</sub> support. A key step in producing this active perimeter site is heterolytic H<sub>2</sub> cleavage across the interface. Electron density difference and Bader charge analysis suggests that this step forms a support site with Brønsted acid character and a metal-hydride on the metallic Ru cluster. The following direct C-O scission in phenol or *m*-cresol is then assisted by the support proton, which results in a substantial reduction of the activation barrier. We propose that the key property of the support is its amphoteric character, i.e., its ability to accept protons during H<sub>2</sub> activation and to donate protons during C-O scission. Another example of an amphoteric support suitable for HDO is ZrO<sub>2</sub> [9], especially when combined with Pd as metal.

We find that this dual site requirement extends to other catalysts systems as well. Of particular interest are Mo-oxycarbides, which have acidic sites similar to those of Mo-oxide, whereas Mo-carbide sites have metallic character. We have compared the potential energy diagram for HDO of furan on Mo-oxide and Mo-carbide with the equivalent reaction of thiophene hydrodesulfurization (HDS) on MoS<sub>2</sub>. Our results show that H<sub>2</sub> activation for both HDO and HDS requires metallic sites, which are present on the brim sites of MoS<sub>2</sub> or are provided by Mo-carbide-like phases in Mo-oxycarbide. Once H<sub>2</sub> dissociates, the acid site for C-O scission can readily form.

In conclusion, we have obtained DFT results for HDO of phenolics and furan on Ru/TiO<sub>2</sub>, Pd/ZrO<sub>2</sub>, and MoO<sub>3</sub>/Mo<sub>2</sub>C, which support the hypothesis that a good HDO catalyst requires both metal and acid sites. However, the acid sites should not be too strong such that reprotonation is hindered. Amphoteric materials that are readily protonated/deprotonated appear most suitable. Ultimately, our work suggests that the right balance between metal and acid character is necessary for the design of an optimal HDO catalyst.

## References

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