

# Aqueous-Phase Hydrogenation of Acetic Acid over Transition Metal Catalysts: The Role of the Acetyl Species

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## Introduction

The decrease in fossil fuel reserves along with the problems caused by our dependence on fossil fuels has accelerated research on biofuels. Aqueous-phase hydrogenation (APH) reactions are a crucial component of a number of strategies for the conversion of biomass into fuels and chemicals. This includes the hydrogenation of targeted functionalities of biomass including acids, sugars, aldehydes, furans and alkenes. Aqueous phase hydrogenation reactions are used for ethanol production from organic acids [1], gasoline production from bio-oils [2], and alkane production from carbohydrates [3]. The objective of this study is to gain a better understanding of the fundamentals of aqueous-phase hydrogenation by combining experimental results with insight learned from theoretical calculations. Acetic acid was chosen as a model compound because the acid functionality is one of the more difficult ones to hydrogenate.

## Materials and Methods

Experimental studies were done in a continuous-flow packed-bed reactor. Several well-characterized monometallic catalysts (Ni, Cu, Ru, Rh, Pd, Ir and Pt) were tested for their activity and selectivity in APH of acetic acid into ethanol at 750 psi and over a temperature range of 100-260°C. Theoretical studies were carried out through spin-polarized periodic density functional theory (DFT) calculations performed in the generalized gradient approximation using the Vienna Ab initio Simulation Package [4-6].

## Results and Discussion

Our experiments showed that ruthenium is the most active and selective catalyst for the aqueous-phase hydrogenation of acetic acid to ethanol. The catalytic activity decreased as Ru > Pt ~ Rh > Ir > Pd > Ni > Cu.

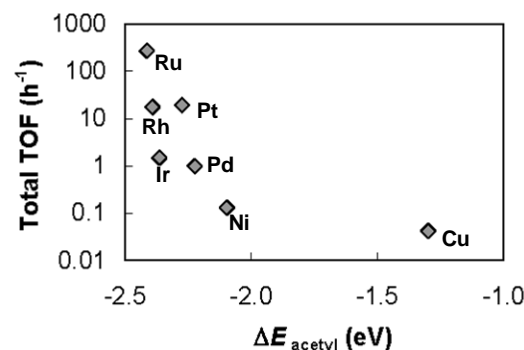
DFT calculations suggest that the formation of acetyl species, either via the dehydroxylation of acetic acid or deoxygenation of acetate formed from acetic acid, is a key step. In the reaction mechanism on Ru, acetyl undergoes a series of hydrogenation reactions forming acetaldehyde, ethoxy and ethanol as the final product.

The combination of experimental and DFT results suggested an empirical correlation between the total turn-over-frequency (TOF) for acetic acid of the catalysts and the adsorption energy of acetyl on the metal surfaces as shown in Figure 1. As the adsorption of acetyl becomes stronger, the catalysts tend to exhibit higher activities.

While previous gas-phase studies in the literature [7] report significant amounts of light alkanes, our aqueous phase experiments have shown that the presence of water in the reaction medium inhibits C-C bond cleavage of oxygenates. The mechanistic origin of this effect is explored both experimentally and theoretically.

## Significance

In this contribution we discuss the mechanism of aqueous-phase hydrogenation reactions. The catalytic activity is correlated to the acetyl binding energy. This indicates that the acetyl binding energy can be used to predict catalytic activity for hydrogenation reactions. We also discuss the role that water plays in the reaction chemistry.



**Figure 1.** Total carbon TOF at 200°C plotted against adsorption energy of acetyl ( $BE_{\text{acetyl}}$ ) on different metals.

## References

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