# Experimental Determination, Modeling and Utilization of the Phase Behavior in the Selective Oxidation of Alcohols in Dense $CO_2$

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### Introduction

The use of pressurized or "supercritical" $CO_2$ as a solvent in catalysis has in many cases resulted in higher reaction rates than in conventional organic solvents. One example is the aerobic oxidation of alcohols [1] which was shown to critically depend on the oxygen concentration and the phase behavior of the ternary system alcohol – $O_2$ – $CO_2$, forming either a single phase or two phases depending on pressure and temperature [2]. Knowledge on phase behavior is crucial to optimize the catalytic reaction but is often only obtained by trial-and-error. Here, we report on the use of an advanced model to predict the phase behavior of systems relevant in the aerobic oxidation of benzyl alcohol (Scheme 1) and demonstrate its usefulness in optimizing a catalytic reaction.
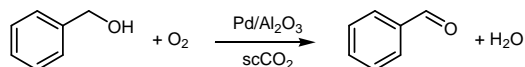
Scheme 1. Palladium-catalyzed oxidation of benzyl alcohol by molecular oxygen.

### Experimental

The phase behavior of the ternary systems benzyl alcohol – $O_2$ – $CO_2$ and benzaldehyde – $H_2O$ – $CO_2$ was modeled with the Cubic plus Association Equation of State [3]. Model results were validated experimentally in a high-pressure view cell. Catalytic studies were performed in a high-pressure fixed-bed reactor over a commercial 0.5%Pd/$Al_2O_3$ (Engelhard 4586) catalyst usually at 80 °C varying the system pressure.

### Results and Discussion

The phase behavior of ternary systems relevant in the oxidation of benzyl alcohol (*cf.* Scheme 1) was modeled with the Cubic plus Association (CPA) Equation of State. The predicted pressures at which a phase transition occurred were found to be in good agreement with experimental results [4]. In general, the predicted dew point pressures were slightly higher

than those experimentally observed. The catalytic reaction was studied in a tubular reactor containing a fixed bed of the supported Pd catalyst. The conversion was monitored as a function of pressure. Both the experimental and model dew point pressures described the pressure region in between which a significant change in catalytic activity was observed (Figure 1). The model thus proved to be a useful tool in predicting the optimal reaction conditions which was further validated under different flows and substrate concentrations. In general, biphasic conditions close to the dew point resulted in the best catalytic performance. The selectivity was furthermore found to critically depend on the flow (not shown), possibly due to the complex mass transport under biphasic conditions. The presented approach might be of general interest for other continuous catalytic reactor studies in dense $CO_2$.
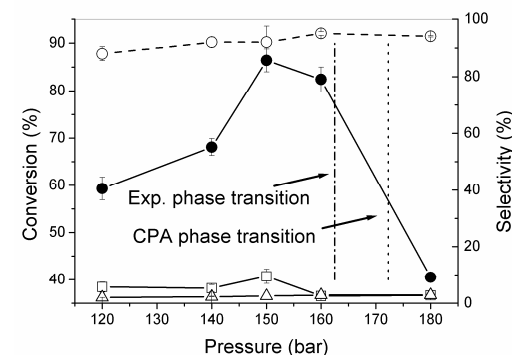
Figure 1. Oxidation of benzyl alcohol over 0.5%Pd/$Al_2O_3$ as a function of pressure. Conditions: 80 °C, 1.25 g catalyst in a fixed bed reactor; feed composition: 0.9 mol-% benzyl alcohol, 0.45 mol-% $O_2$, rest $CO_2$, total flow 0.118 mol/min; (●) conversion, (○) benzaldehyde selectivity, (□) toluene selectivity, (Δ) selectivity to overoxidation products.

### Conclusions

The catalytic performance of the selective oxidation of benzyl alcohol was correlated with the phase behavior of the reaction mixture in dense carbon dioxide. The Cubic plus Association Equation of State was shown to be a useful tool for predicting the optimal reaction conditions.

### References

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