Effect of Solvents on the Liquid Phase Epoxidation of 1-Hexene with Titanium Silicalite-1

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Introduction
In the development of more environmentally friendly chemical processes, titanium silicalite-1 (TS-1) has attracted considerable attention for its high selectivity and activity in heterogeneous liquid phase epoxidation reactions. In such reactions, the reactivity and selectivity can be significantly affected by solvent properties, but the mechanisms are poorly understood and only recently beginning to come to light [1]. The solvent can influence the observed catalysis by affecting the intrinsic kinetics, the partitioning of species between the fluid phase and the adsorbed phase, and the rates of diffusion for reactants and products. Typical kinetic measurements are not able to deconvolute the contributions of each of these effects. True initial rate data are essential in understanding reaction kinetics but are only available for limited conditions due to deactivation problems. In addition, the effect of water, which is introduced into the system by the use of aqueous hydrogen peroxide as well as generated at the active sites, has not been properly accounted for in the literature.

The goal of this study is to evaluate how the properties of the solvent affect the intrinsic kinetics, adsorption, and diffusion in a representative system, namely, the epoxidation reaction of 1-hexene with aqueous hydrogen peroxide oxidant and TS-1 catalyst in the presence of various solvents. Our approach is to quantify the role of the solvent through batch reaction studies, adsorption studies, diffusion studies using pulsed field gradient NMR, and quantitative modeling using kinetic Monte Carlo techniques.

Experimental
TS-1 catalyst was synthesized hydrothermally [2] and characterized by several spectroscopic and microscopic methods, including XRD, XPS, ICP, and UV-Vis. Batch reaction experiments were carried out in 40 mL reactors, with 45 mg TS-1, under constant 900 rpm stirring at constant temperature, ranging from 0°C to 35°C. The reactions were started by injection of H₂O₂ (aq). During the course of the reaction, samples were drawn periodically, diluted, filtered, and analyzed via GC-FID and GC-MS.

Results and Discussion
Characterization results showed that the catalyst was a high quality TS-1 with 1.3 Ti per unit cell and no extraframework Ti or anatase. Kinetic data obtained through batch reaction experiments with various solvents have yielded reliable and accurate initial rates. An example of the well-known effect of methanol versus acetonitrile on reaction kinetics is shown in Figure 1. Accurate initial rates have led to an extensive
set of information on the reaction order in 1-hexene, \( \text{H}_2\text{O}_2 \), and water concentrations. An example of the reaction order in \( \text{H}_2\text{O}_2 \) concentration is shown in Figure 2, where the reaction order in methanol decreases from one as the \( \text{H}_2\text{O}_2 \) concentration is increased. The same is true in acetonitrile solvent, although the it has a lower reaction order at the same \( \text{H}_2\text{O}_2 \) concentration. Interestingly, it was also found that the reaction order in bulk water concentration is negative one for the methanol system.

These results, coupled with recent findings on the active site species [3,4], have led us to postulate a mechanism based on Eley-Rideal kinetics and an initial rate equation that embodies the observed trends in this reaction. To relate the intraporous concentration terms to the macroscopic bulk concentrations, we obtained adsorption isotherms for both physisorbed and chemisorbed species in the catalyst by comparing isotherms from TS-1 and silicalite. This allows us to relate the reaction rates directly to the observable bulk concentrations. Finally, modeling is used to bring together all the experimental information in order to develop a complete picture of solvent effects.

References