

Selective Catalytic Ethanol Synthesis[†]

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selective homogeneous catalytic ethanol synthesis chemistry discovered in the Fluid Catalysis Program under BES/Chemical Sciences funding.

The catalytic cycle for an early version of this chemistry is shown in Fig. 1. Unlike the conventional $\text{HCo}(\text{CO})_4$ catalyzed homologation process first reported by Wender, et al, that carbonylates methanol to a mixture of water and higher alcohols in a proposed carbonium ion mechanism, the new catalytic chemistry depicted in Fig.1 produces ethanol in a selective $\text{S}_{\text{N}}2$ process without the coproduction of significant amounts of either water or higher alcohols. The $\text{HFe}(\text{CO})_4^-$ catalyzed reaction occurs in the temperature range of 180-220 °C at pressures ($3\text{CO} + \text{H}_2$) near 300 atm in accord with stoichiometry of Eqn. 1.



The rate determining step in the catalytic reaction (nucleophilic attack of $\text{HFe}(\text{CO})_4^-$ on $(\text{CH}_3)_4\text{N}^+$) was selected for separate study and in 1-methyl-2-pyrrolidinone solvent was determined to have an enthalpy and entropy of activation of 44 kcal/mol and +17 eu, respectively. The catalytic approach used for the original iron based catalyst works well with a variety of metal carbonyls, some of which function especially well in combination with each other. Our future activities are focused on the mechanism of synergistic effects in the improved heterobimetallic catalysts.

DOE Interest

a. In catalytic ethanol synthesis

Our research on homogeneous carbonylation chemistry produced a selective catalytic ethanol synthesis route that is timely in today's energy circumstances. Our recent work and planned future activities on this system are aimed at uncovering the mechanism of an interesting and unusual heterobimetallic synergistic catalytic effect in this system wherein a mixture of iron and manganese carbonyl ions was demonstrated to be more active than either of the complexes when used separately. We believe that understanding of such synergistic effects is important because this knowledge might lead to new possibilities for catalyst design.

b. In related activities

In earlier high-pressure kinetic studies, the Fluid Catalysis Program demonstrated the first mononuclear catalyst for homogeneous carbon monoxide hydrogenation and determined the rate law and the currently accepted mechanism for the $\text{HCo}(\text{CO})_4$ catalyzed reaction (see F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Sixth Edition, 1999, p. 1253). More recently, in research aimed at experimental and theoretical parameterization of the reaction coordinates of this mechanistically important reaction, it conducted kinetic measurements on homogeneous catalytic carbon monoxide hydrogenation, in situ, in an NMR probe for the first time. Also, supercritical carbon monoxide was used as a gas-like reaction medium (to aid in the theoretical calculations) for the first time in homogeneous CO hydrogenation.

This program pioneered the use of homogeneous catalysts in supercritical fluids and invented supercritical hydroformylation catalysis. To conduct in situ spectroscopic studies of supercritical and other high-pressure industrial process chemistry, it developed the toroid-pressure probe, the R&D 100 Award winning toroid-cavity imager, and most recently, a magic-angle-spinning toroid-cavity probe that imparts the high sensitivity and imaging capability of toroids to high-resolution solid-state NMR spectroscopy. This program recently reported the first high-pressure NMR characterization of reverse micelles in supercritical carbon dioxide.

Future Research

In earlier work we had shown that $\text{Co}_2(\text{CO})_8$ catalyzes the hydrogenation of $\text{Mn}_2(\text{CO})_{10}$ by forming a rapidly hydrogenated heterobimetallic species, $(\text{CO})_5\text{MnCo}(\text{CO})_4$, which quickly reached equilibrium concentrations under the reaction conditions and could be observed in the solutions at high pressures using both ^{55}Mn and ^{59}Co NMR spectroscopy. In solutions containing both carbonyls, the catalytic effect is due to the fact that the two step process of forming the mixed heterobimetallic dimer and its hydrogenation to form $\text{HMn}(\text{CO})_5$ is faster than the direct reaction of hydrogen with $\text{Mn}_2(\text{CO})_{10}$. Hydrogenation of the mixed dimer also produces $\text{HCo}(\text{CO})_4$, which reversibly loses hydrogen to produce $\text{Co}_2(\text{CO})_8$, thereby regenerating the catalyst. We suspect that chemistry of this sort is responsible for the heterobimetallic synergistic catalyst effect observed in the mixed $\text{HFe}(\text{CO})_4/\text{Mn}(\text{CO})_5$ ethanol synthesis system. We will test this hypothesis by searching for mixed metallic intermediates and examining their fate kinetically using operando spectroscopic methods at high pressures and temperatures.

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