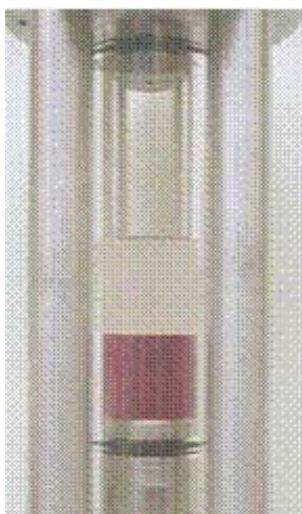


Carbon Dioxide Homogeneous Switch for Fluorous Biphasic Systems

Fluorocarbons, or fluorous solvents, have interesting properties that set them apart from their hydrocarbon analogues and other organic solvents. In the past decade, this phenomenon has given birth to the field of fluorous biphasic catalysis as a novel methodology for the sequestration and subsequent recovery of fluorous-phase immobilized homogeneous catalysts.

The present work extends binary fluorous/organic phase behavior to ternary systems, the third component being gaseous carbon dioxide. In such systems, CO₂ acts as a co-solvent in both phases and induces miscibility of the two phases. Depressurization of the system releases the CO₂ and the phase splits. With this scheme, CO₂ can be used as a "switch" to turn homogeneous phase behavior "on" and "off," creating a medium for homogeneous reactions coupled with heterogeneous separations. An example of this novel phase behavior is shown below.



0.1 MPa CO₂



3.2 MPaCO₂



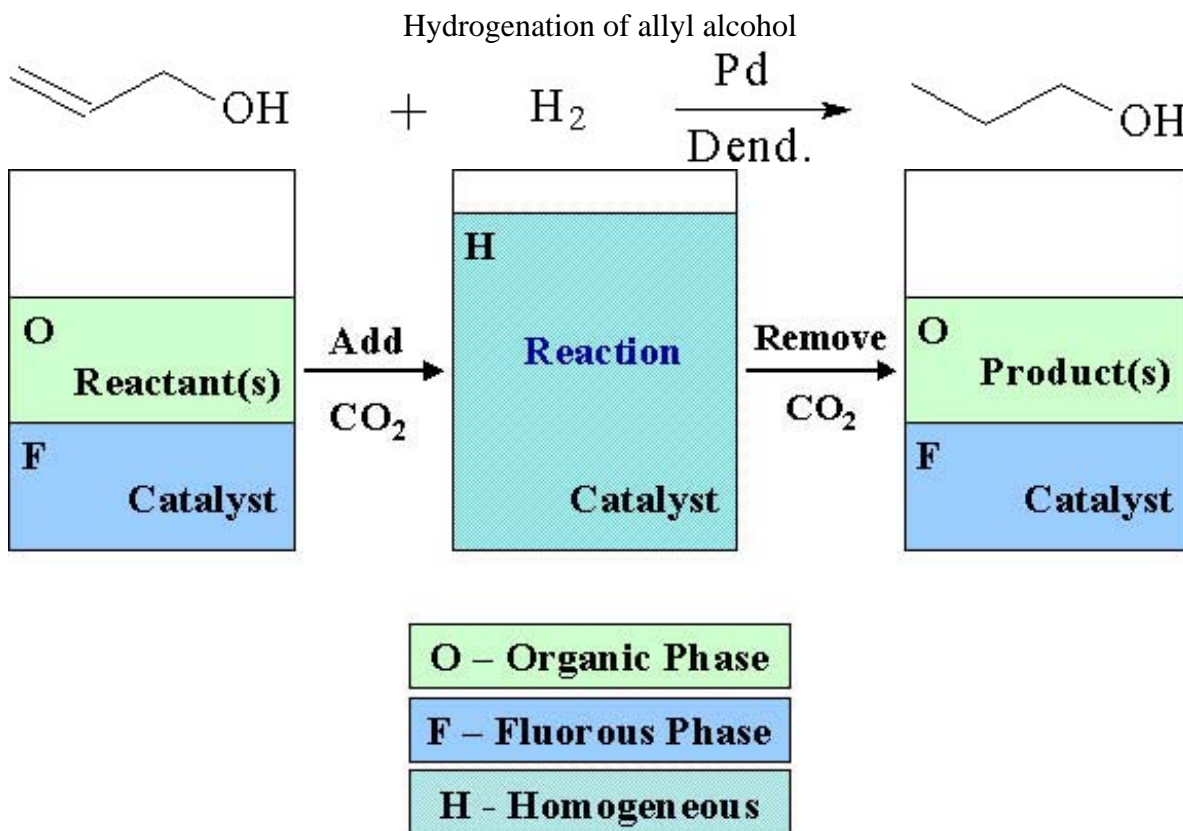
3.3 MPaCO₂

CO₂ used to homogenize an organic (toluene, clear liquid) and a fluorous (FC-75, pink liquid) phase. The fluorous phase is pink because of a dissolved catalyst. Note that extensive phase mixing occurs just prior to miscibility. The pictures were taken of the sapphire tube apparatus designed for this work.

Fluorous solvents have higher molecular weights and larger densities (around 1.8 gm/cm³) than most organic solvents. Fluorinated compounds are usually clear, colorless and odorless liquids at room temperature, with relatively high gases dissolving power. They are chemically inert even at high temperatures, totally nonflammable, have zero ozone depletion potential and are nontoxic. They do possess high greenhouse gas potentials and are fairly expensive. They are also completely immiscible with most common organic solvents. While the biphasic nature of these systems is conducive to separation processes, mass transfer limitations arising from slow inter-phase diffusion can retard reaction rates. To ameliorate this, the temperature of the system is often increased to induce miscibility. This technique imposes an important limitation though, as

only thermally stable, higher boiling, nonpolar organics can be used. Polar reactants must be diluted in a nonpolar solvent in order to induce a homogeneous mixture upon heating, introducing a volatile organic compound (VOC) into the process. As an alternative, in this work CO₂ is used to induce miscibility of fluorocarbon-hydrocarbon mixtures, even those involving polar compounds. The required pressure to induce miscibility is typically mild (1-5 MPa).

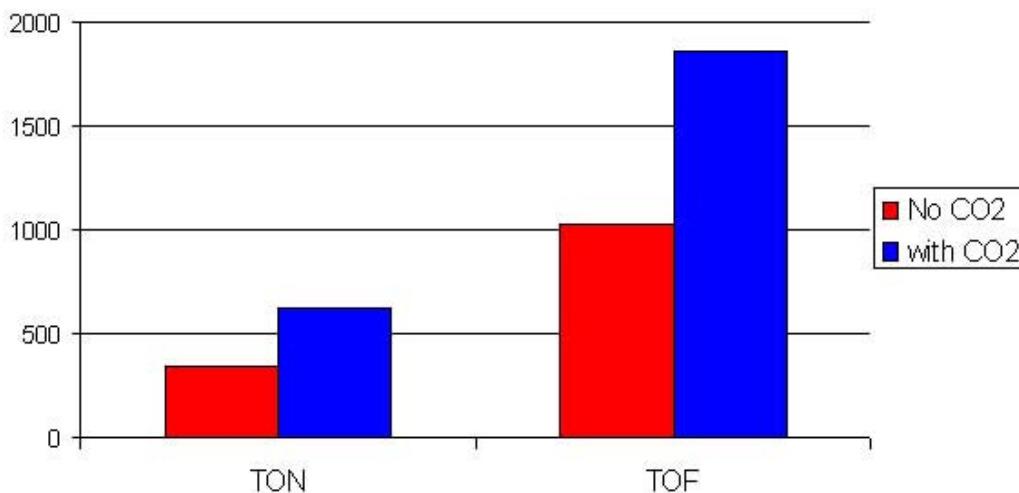
A fluorine-modified dendrimer-encapsulated Pd⁰ nanoparticles was chosen as an easily synthesized model system for testing the phase switching technique. The original biphasic system consisted of a fluorine solvent (FC-75) and an immiscible organic reactant (allyl alcohol). The solubility of the fluorine catalyst in the organic phase is negligible. This concept is here extended via CO₂ expansion. The hypothesis is that addition of CO₂ to the reaction mixture will enhance the reaction rate at ambient temperature by creating a single-phase solution, eliminating the mass transfer limitations inherent in any biphasic process. Catalyst recovery is still a simple matter, as depressurization effects a phase split. This process is illustrated below. The reaction studied is hydrogenation of allyl alcohol to form n-propanol. The CO₂-expanded monophasic and unaltered biphasic processes are compared under identical conditions.



CO₂ as a miscibility switch. The first picture is a biphasic system under ambient conditions, with the reactants and catalyst in separate phases. CO₂ is then added, homogenizing the liquids for reaction. Depressurization splits the liquids apart once more, segregating the catalyst from the products for easy separation and recycle.

Results

The hydrogenation of allyl alcohol to form n-propanol was used to establish that CO₂ addition would enhance reaction rates in fluoruous biphasic systems. Rates were determined from one hour batch experiments. For the traditional biphasic system, an average of multiple runs at 250 rpm and 25 °C yielded an average turnover frequency (TOF) of 100 hr⁻¹. The TOF is defined as the number of moles of substrate converted per mole of catalyst per hour. For the gas-expanded system, catalytic runs under the same conditions as for the biphasic system (i.e. reactant and catalyst amounts, stirring speed, temperature and H₂ partial pressure) were carried out with addition of enough gaseous CO₂ to create a single liquid phase. Under 7.58 MPa CO₂, multiple catalytic runs yielded an average TOF of 180 hr⁻¹. Depressurization of the reactor split the homogeneous phase, with the brown color characteristic of palladium observed in the fluoruous phase only. No palladium or dendrimer was detected in the organic phase. The fluoruous solution could be recycled without loss of catalytic activity. The observed reaction rate enhancement of the monophasic reaction relative to the biphasic system was 80%. In the absence of the dendrimer catalyst, no product was detected after 24 hrs.



Rate enhancement for CO₂-expanded fluoruous solvent system. The reaction was the hydrogenation of allyl alcohol.

Conclusions

The novel technique of using CO₂ to homogenize a biphasic fluoruous/organic system, and the application to catalytic systems has been demonstrated. Rate enhancements of CO₂-expanded monophasic systems have been established relative to traditional fluoruous biphasic systems. Using this methodology, the fluoruous techniques for homogeneous reactions with heterogeneous separations can be extended to systems at ambient temperatures, with polar organic solvents, or thermally labile substrates.