

Tailoring Particle Behavior for Phase Transfer Catalysis: Recent Developments by the Center for Interfacial Reaction Engineering

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Center for Interfacial Reaction Engineering (CIRE)

ABSTRACT

This presentation highlights recent advances by the Center for Interfacial Reaction Engineering (CIRE) in designing and tailoring catalytic particles for use in phase-transfer catalysis. CIRE consists of researchers across several disciplines including nanotechnology, thermodynamics, interfacial phenomena, and catalysis from three different universities. The results highlight the importance of particle wetting on dynamic interfacial and overall emulsion behavior and has potential importance for a variety of applications in the biofuels, pharmaceuticals, and energy sectors.

Keywords: emulsions, carbon nanotubes, nanoparticles, catalysis, interfacial behavior

1 INTRODUCTION

Phase-transfer catalysis involves carrying out chemical reactions in a biphasic mixture of two immiscible liquids, and it is a potentially useful technique that combines standard heterogeneous catalysis with the equivalent of a solvent extraction separation. Figure 1 illustrates the four central themes of CIRE that address phase-transfer catalysis. The first theme of CIRE focuses on synthesizing and characterizing nanoparticles that optimize the reactivity, emulsion stability, mass transfer, and interfacial

area of phase-transfer catalysis processes. Second, CIRE focuses on understanding how catalytic reaction mechanisms and kinetics change when the reactions take place at a liquid-liquid interface. Third, CIRE uses spectroscopy and molecular modeling to understand the reaction pathways, competitive adsorption, and thermodynamics of model reactions on interfacial catalysts. Finally, CIRE combines experimentation, theory, and modeling to understand the kinetics of mass transfer and phase equilibrium in dynamic, phase-transfer environments and how altering particle properties can be used to optimize phase transfer.

Phase-transfer catalysis does more than just combine the reaction and separation steps common in numerous industrial applications. It allows engineers and scientists to tune the reactivity and selectivity of specific reactions by controlling solvent/catalyst interactions and taking advantage of differences in reactant/product solubilities in the two liquid phases. The technique is also extremely useful when the desired reaction product would be unstable under reaction conditions in one solvent, but can quickly partition into the other solvent where it is more stable. Much early work into phase-transfer catalysis has used molecular surfactants to create emulsions, which increase the interfacial area and increase total interphase mass transfer. However, molecular surfactants can be very difficult to separate from the reaction product mixtures, a problem that can be mediated by using interfacially active nanoparticles as both catalyst supports and emulsion

stabilizers since the nanoparticles can be more easily recovered via centrifugation or filtration.

This presentation highlights recent advances by the Center for Interfacial Reaction Engineering in designing phase-transfer catalytic systems that show improved selectivity and reactivity when compared to standard heterogeneous catalysis. Our most recent work involves studying photocatalytic partial oxidation of cyclohexane on a titania catalyst and hydrogenation of alkenes using a palladium catalyst supported on multi-walled carbon nanotubes.

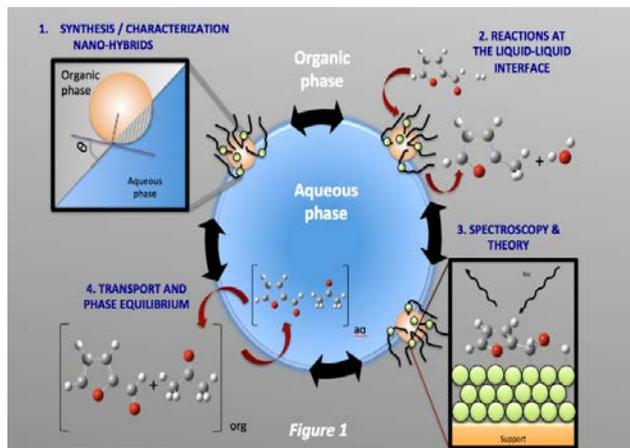


Figure 1. Four central research thrusts of CIRE.

2 EXPERIMENTAL TECHNIQUES

2.1 Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) is a core tool used by CIRE to probe emulsion morphology, speciation, and the impact of water and other species on catalyst performance. CIRE recently employed NMR to provide fundamental insight regarding the impact of water on zeolite catalysis [1]. Diffusion NMR techniques [2] are currently being employed by CIRE to quantify the impact of reactions on emulsion morphology and separation efficiency. NMR has the unique ability to simultaneously quantify droplet size distributions and speciation, thereby providing critical information about the impact of reactions on emulsion morphology. NMR is not dependent on the optical properties of the emulsions, so it is ideally suited for concentrated emulsion characterization where the systems are generally opaque.

2.2 Electron Microscopy

To determine the location of MWNTs at the interface MWNT Pickering emulsion wax droplet stabilized with oxidized MWNTs, pristine MWNTs with alkyl glucoside, or pristine MWNTs with 2-hydroxyethyl cellulose were filtered using a Whatman 1 filter and rinsed with water to remove any unattached particles. After this 3.5 wt% of the

wax droplets covered with MWNTs was mixed with LR White resin, a hydrophilic resin. The solution was then hand shook for several minutes to disperse the wax droplets in the resin. After mixing the solution was put in a gel capsule and then placed in an oven at 40°C to allow the LR White Resin to polymerize. The gel capsule was removed and the polymerized LR White was then thin sectioned using an ultramicrotome, making 100 nm thick sections. These sections were then placed on a TEM grid. TEM of the samples was then performed to see the location of the MWNTs at the interface using a JEOL 2000-FX with an acceleration voltage of 200 kV.

2.3 Immersion Microcalorimetry

A Setaram C80 micro-calorimeter with a specially designed pair of powder cells was used to measure the heat of immersion for all of the modified nanoparticles. The heat of immersion is related to the particle contact angle using the theoretical approach described by Yan.²⁹ The method uses the enthalpy of immersion, a result of the change in Gibbs free energy that results from replacing a solid-gas interface with a solid-liquid interface, and relates it to the solid-liquid contact angle using the Young-Laplace equation. The resulting contact angle equation yields:

$$\cos\theta = \frac{-KT - h_i - \pi_e}{\gamma_{lv}} \quad (1)$$

Where θ is the solid-liquid contact angle, K is the difference between the temperature dependence of solid-liquid interfacial tension and solid surface tension, T is the absolute temperature, h_i is the enthalpy of immersion, γ_{lv} is the liquid-vapor surface tension, and π_e is the difference between the solid surface tension and the solid-vapor surface tension ($\gamma_s - \gamma_{sv}$), which is assumed to be negligible for systems with reasonably large contact angles. In this case, K is assumed to be $7.0 \cdot 10^{-5} \text{ J/m}^2 \cdot \text{K}$, corresponding to a low-energy surface and a γ_{sl} that is temperature independent, following the assumptions made by Yan. The powder cells consist of a stainless steel cylinder and a pair of brass sealing rings that hold a

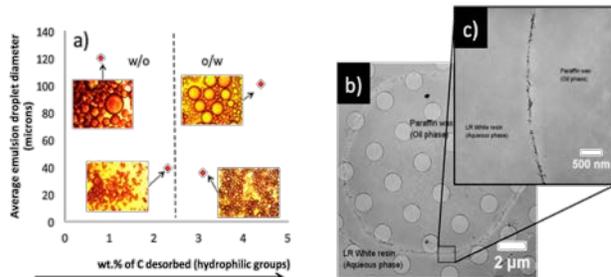


Figure 2. Plot showing how droplet size and emulsion type change with CNT hydrophilicity, and two micrographs that show nanotubes adsorbed at the interface of an emulsion droplet after thin-sectioning the droplet with an ultramicrotome.

membrane in place and seal each end of the cell; one cell is used as the sample cell, while the other is used as a reference cell. The calorimeter cells are designed by Setaram with a breaking rod that has been modified in-house with a sharp, pointed tip which is used to puncture the powder cell's membrane. Prior to each experiment the modified nanoparticles are dried in a vacuum oven at 120°C for at least 12 hours. Then, a known quantity of sample is placed into each powder cell, and the cell is sealed with a nitrile rubber membrane. Both powder cells are then placed in the larger stainless steel, calorimetry cells (manufactured by Setaram) with approximately 8 mL of the wetting liquid. Both calorimeter cells are then installed into the microcalorimeter and allowed to equilibrate at 40°C. After the heat signal and cell temperatures stabilize, both membranes of the sample cell are punctured with the breaking rod, allowing the liquid to enter the cell and immerse the nanoparticles. The thermal energy released or absorbed by the sample immersion is then measured and recorded by the microcalorimeter. A series of eight blank punctures of sealed, empty powder cells were used to estimate the heat released by only puncturing the nitrile rubber membranes and subtracted from the measured immersion enthalpy as a constant background. The heat of immersion is measured at least four times for each sample and the average was used to calculate the particle contact angle.

2.4 Chemical Reactions

Hydrogenation reactions were carried out using 1-dodecene as a oil soluble reactant and cis-2-butene-1,4-diol as a water soluble reactant. Both of these molecules have high solubility in either the water or oil. When operating under mass transfer limitations the reactants will have limited mass transfer through the other phase.

Reactions were carried out in oil, water, and emulsions. Reactants 1-dodecene and cis-2-butene-1,4-diol were used when the solvent which the reactant was soluble in was used.

Emulsions were created by first dispersing Pd/MWNTs in either oil or water by horn sonication. Then adding the opposite phase and horn sonicating to form an emulsion. After emulsification the catalyst was reduced for 3 hours under H₂. Then the reactant injected and allowed to react for 1 hour. Reduction and reaction were both carried out at 45°C or 70°C.

Chemical reactions were carried out using a glass reflux system with a three neck round bottom flask. One neck was connected to the reflux condenser, another to a gas line to inject hydrogen, and the last a septum seal for injecting the reactants once reduction of the catalyst was completed.

3 RESULTS

Sample	Heat of Immersion, mJ/m ²	Contact Angle
Bare Ludox	-110.2 ± 6.7	<0
Low Coverage SAPTMS	-135.5 ± 28.8	<0
High Coverage SAPTMS	-170.1 ± 23.9	<0
Low Coverage MPTMS	-60.2 ± 2.6	58
High Coverage MPTMS	-65.8 ± 16.4	53
Low Coverage PhTCS	-65.8 ± 5.1	52
High Coverage PhTCS	-47.5 ± 3.3	69
Low Coverage TMCS	-5.1 ± 7.3	104
High Coverage TMCS	1.9 ± 3.9	109
Low Coverage OTCS	-0.4 ± 7.9	107
High Coverage OTCS	13.0 ± 2.1	120

Table 1. Heats of immersion and calculated water contact angles of surface-modified silica nanoparticles measured using microcalorimetry

Multi-walled carbon nanotubes have been found to adsorb at the interface of emulsion droplets and prevent droplet coalescence, as shown in the TEM micrographs shown in Figure 2. Oxidizing the multi-walled carbon nanotubes and adding surfactants or polymers to the nanotube dispersion can control the number of nanotubes at the interface and the thickness of the interface. Droplet size and emulsion type (oil-in-water vs. water-in-oil) can also be controlled by tuning the hydrophobicity of the carbon nanotube via oxidation or surfactant addition, as illustrated in Figure 2. Furthermore, droplet size and emulsion type can be further tuned by varying the particle ratio when stabilizing emulsions with mixtures carbon nanotubes with different levels of oxidation.

The wettability and contact angle of spherical silica nanoparticles can be controlled by reacting alkyl silanes with hydroxyl groups on the nanoparticle surface. The final contact angle, as measured with a variety of methods, was found to strongly depend on the type of alkyl group grafted onto the nanoparticle, and a less pronounced dependence on the level of surface coverage. Phenyl, trimethyl, and octadecyl chlorosilanes were grafted onto the silica surface and the particle contact angle was evaluated using a heat of immersion method, the results of which are shown in Table 1 [3]. Heat of immersion tests also confirmed the results of Oh [4] in regards to the creation of superhydrophilic surface moieties when mercaptopropyl trimethoxy silane-modified silica is successively exposed to hydrogen peroxide and sodium hydroxide solutions.

Silanization can also be used to control the properties of Pickering emulsions stabilized with the modified silica nanoparticles. Emulsions stabilized by the various hydrophobically modified silica nanoparticles were shown to follow four general trends: 1) low surface coverage nanoparticles stabilized oil-in-water emulsions while high surface coverage nanoparticles stabilized water-in-oil emulsions in almost all cases; 2) emulsions stabilized by

high surface coverage nanoparticles have slightly smaller average droplet sizes than emulsions stabilized by low surface coverage nanoparticles in every case but the oil-dispersed trimethyl chlorosilane-modified particles; 3) when the particles are initially dispersed in water, the emulsions stabilized by more hydrophobic nanoparticles had smaller average droplet sizes than emulsions stabilized by more hydrophilic nanoparticles, regardless of surface coverage; and 4) when the particles are initially dispersed in decane, the emulsions stabilized by more hydrophilic nanoparticles had smaller average droplet sizes than emulsions stabilized by more hydrophilic nanoparticles, in most cases.

Pickering emulsions offer a variety of methods to control reaction selectivity. One way is by controlling the location of the catalytically active portion of the particles relative to the oil and water phases. Janus particles made with a hydrophobic and hydrophilic side offer this ability. By depositing palladium particles on one side of the Janus particles the reaction in the aqueous or oil phase of the emulsion can be highly favored [5]. Another way to control selectivity in emulsions is by operating under surface reaction, temperature of 45°C, or hydrogen diffusion limitations, temperature of 70°C. Operating under hydrogen diffusion limitations utilizes the speed of hydrogen to diffuse through the two phases. By switching between these two limiting steps, the rate of reaction normalized to a single aqueous phase system can be cut in half or doubled for the aqueous phase of an emulsion system, as shown in Figure 3.

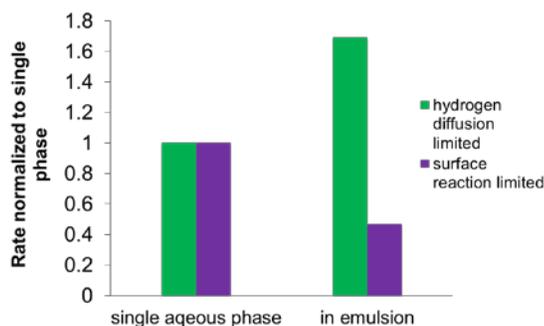


Figure 3. Use of an emulsion to control reaction selectivity when operating under surface reaction limited or hydrogen diffusion limitations. A Pd/MWNT catalyst was used.

4 CONCLUSIONS

The Center for Interfacial Reaction Engineering (CIRE) leverages core experimental capabilities to probe fundamental interfacial properties and phase transfer catalysis. Recent work by the center has shown the importance of emulsion morphology and particle behavior on the overall performance of bi-phasic, catalytic systems. Future work will focus on developing advanced catalysts and catalyst supports to improve the efficiency of the

production of desired products while leveraging the advantageous properties of emulsions.

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