4ce Studies in Reaction Kinetics, Density Functional Theory, and Catalysis

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My research interests are in the area of kinetic modeling and using computational chemistry methods like density functional theory to study the mechanisms of chemical reactions. I am interested in using these methods to study the optimization of catalysts and biomaterials.

A. DFT Design and Optimization of Single-Site Aryloxide Polymerization Catalysts

Single-site transition metal complexes are useful olefin polymerization catalysts because the molecular architecture of the polymer can be optimized by varying the catalyst ligand structure. Density functional theory (DFT) has been used to study the mechanism of olefin polymerization by Ti and Zr organometallic complexes containing one aryloxide and one cyclopentadienyl ligand. The relative rates of chain initiation, propagation, transfer, and termination control the overall molecular weight distribution of the polymer. Detailed reaction mechanisms, transition states, and energies for each reaction step have been computed for several catalysts in order to explore relationships between catalyst structure and reactivity. DFT has also been used to compute basic descriptors of the electronic and steric properties of the catalysts in order to correlate catalyst structure to performance. This project was carried out in collaboration with researchers who synthesized catalysts and carried out polymerization reactions. (PhD work, Advisors: K.T. Thomson (co-chair), J.M. Caruthers (co-chair), W.N. Delgass, M. Abu-Omar)

B. Selective Hydrogenation of Butyronitrile on Promoted Raney(r) Nickel Catalysts

The reaction kinetics of nitrile hydrogenation were studied over Raney(r) nickel catalysts. Catalysts were synthesized and then characterized using optical microscopy, liquid nitrogen adsorption, x-ray diffraction, atomic absorption, and x-ray photoelectron spectroscopy. Room temperature, 1 atmosphere, liquid phase batch reactions (methanol-water solvent) were carried out in order to evaluate catalyst performance. Catalysts promoted with iron and chromium had the highest activity and selectivity to primary amine. Adsorption studies showed that there were two types of catalyst sites: those which could be blocked by bases (acidic sites) and those which could not (nonacidic sites). The acidic sites were postulated to play a role in the formation of secondary amines because addition of sodium hydroxide to the reaction mixture improved the selectivity to primary amine. A kinetic model for the hydrogenation reaction was developed based on these findings. (MS Thesis, Advisor: W.N. Delgass)

References:

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[2] S.N. Thomas-Pryor, T.A. Manz, Z. Liu, T.A. Koch, S.K. Sengupta, and W.N. Delgass, “Hydrogenation of Butyronitrile by Promoted Raney(r) Nickel Catalysts,” Catalysis of Organic Reactions, F. Herkes, ed., Marcel Dekker, New York (1998) 195-206.