II.B.8 Atomic-Scale Design of Cobalt Fischer-Tropsch Catalysts: A Combined Computational Chemistry, Experimental, and Microkinetics Modeling Approach

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Objectives

Demonstrate the success of a technology to effectively and economically produce a pure hydrogen stream by coal gasification with integrated capture of CO_2 emissions, for its subsequent sequestration. A high reactivity, mesoporous calcium oxide will be demonstrated for *in situ* carbon dioxide separation. The regenerability of the sorbent over multiple calcination-carbonation cycles will be tested.

Introduction

This microkinetics model will enable prediction of catalyst activity and hydrocarbon selectivities over a range of temperatures, pressures, H_2/CO ratio, and as a function of promoter type and concentration, and of surface/subsurface carbon coverage. It will address the molecular principles governing the relative rates of chain growth versus termination on iron Fischer-Tropsch (F-T) catalysts, thereby providing a basis for maximizing desirable products (e.g. diesel liquids and waxes) while minimizing formation of undesirable products such as methane, LPG, and alcohols.

Approach

Use state-of-the-art computational chemistry methods and experiments for developing and validating a detailed microkinetics model to describe the rates of the important elementary steps that occur during F-T synthesis on the surface of an iron catalyst. Special emphasis will be placed on the effects of noble metal promoters (specifically Ru, Re, and Pt) on the steps outline above.

Accomplishments

- Developed calculations of binding energies, reaction barriers, and pre-exponential estimates for key elementary steps in the F-T synthesis mechanism based on first-principles.
- Developed kinetic parameters for key elementary steps including CO and H_2 adsorption/dissociation, the hydrogenation of various carbon-containing species, and olefin adsorption on unpromoted and promoted Fe/K_2O/Cu, under high pressure conditions using temperature-programmed reaction spectroscopies combined with isotopic tracer studies.

Future Directions

- Develop a statistical set of rate and selectivity data on Fe/K_2O/Cu catalysts over a relevant range of reaction temperatures, reactant compositions, and H_2/CO ratios that can be used to validate mechanistic models.
- Finalize the microkinetics model that will predict catalyst activity and hydrocarbon selectivities over a range of temperatures, pressures, H_2/CO ratio, as a function of promoter type and the surface/subsurface carbon coverage. The model is expected to address the molecular principles governing the relative rates of chain growth versus termination on iron F-T catalysts, thereby providing a basis for maximizing desirable products.