Exploiting Supercritical Reaction Media in Catalytic Fuels Processing

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Density and transport properties can be pressure-tuned with near critical reaction media to obtain unique fluid properties (e.g., gas-like transport properties and liquid-like solvent power), which offer the following advantages in solid-catalyzed reactions: (i) the in situ extraction of heavy hydrocarbons (i.e., coke precursors) from the catalyst surface and their transport out of the pores before they are transformed to consolidated coke, thereby extending catalyst lifetime; (ii) enhanced pore-transport of reactants such as hydrogen to the catalyst surface thereby promoting desired reaction pathways; and (iii) enhanced desorption of primary products preventing secondary reactions that adversely affect product selectivity. Pressure-tuning effects on catalyst activity and product selectivity are discussed for 1-butene/isobutane alkylation on solid acid catalysts and Fischer-Tropsch synthesis on a supported Fe catalyst.

INTRODUCTION

In heterogeneous solid-catalyzed reactions, the fluid phase containing the reactants and products is either a gas phase, liquid phase, or a combination of liquid and gas phases (multiphase slurry reactor operation). For many reactions, none of these phases is optimal. Rather, a single phase that possesses liquid-like densities and gas-like transport properties is desirable for optimizing catalyst activity and product selectivity. Such unique combinations of fluid properties are accessible in the near-critical (nc) region.

Figure 1 shows the typical variations of density and transport properties of a supercritical fluid.

The Science Behind Kyoto: the Role of Universities

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FINAL PART OF A TWO PART SERIES

In the last issue of Energeia, I concentrated on the need of scientists to refocus the debate over global warming back to reality and away from media hype. I am not exempting industry from becoming more involved. I represent the petroleum industry, a special interest which has a large economic stake in the outcome of this debate. I don’t expect anyone to accept my views automatically. Whatever the topic, you should bring scientific skepticism to bear and ask: “Tell me why you think that — show me the evidence, and show me your logic.” However, since I am from industry I am used to such skeptical challenging. While I may not always enjoy it, it is good for me and for others who engage in advocacy. But in fairness, vigilance should be extended to others, since it would be equally foolish to accept without question the views of other participants. Advocates of the Kyoto Protocol wrap themselves in robes of concern for the environment. Some of this is real, but much of it is pure gamesmanship. There are also special interests of various sorts, including economic ones. Some businesses see the possibility of subsidies, market share, and competitive advantage.
fluid (CO2 shown as an example) with pressure along a near-critical isotherm (1.01 Tc). It is clear that the physical and transport properties of the fluid can be altered drastically, from gas-like to liquid-like behavior, simply by isothermally varying the pressure around Pc, the critical pressure.

For example, at slightly above the critical pressure, while the fluid possesses roughly 70% of the liquid density, the diffusivity and viscosity values are more gas-like. By pressure-tuning fluid properties around the critical pressure, optimal combinations of product desorption and pore transport can be obtained. This note highlights recent research in our laboratory exploiting nc operation in fuels-related heterogeneous fluid/solid catalytic reactions to (i) mitigate the coking of solid acid catalysts (e.g., 1-butene/isobutane alkylation on solid acids), and (ii) alleviate mass transfer resistances and pressure-tune product selectivity in multiphase reactions (e.g., Fischer Tropsch synthesis on a Fe catalyst). Rational strategies for exploiting nc media in heterogeneous catalytic reactions are discussed.

MITIGATING COKING OF SOLID ACID CATALYSTS

Reactions of olefins in porous solid acid catalysts typically involve the formation of undesired olefinic oligomers as byproducts in the catalyst pores. In low temperature (<100°C) olefin conversion processes (such as in isobutane/butene alkylation on solid acid catalysts), the oligomers have low volatilities. In a gas phase reaction environment, very little of these oligomers is solubilized in the reaction medium, causing the oligomers to accumulate in the catalyst pores. The adsorbed oligomers could also undergo further chemical transformation to ′consolidated coke.′ When the reaction occurs in a liquid phase, the oligomers may be solubilized easily by the reaction medium. However, pore diffusion limitations hinder the transport of the extracted oligomers out of the catalyst pores. As shown schematically in Figure 2, the optimal reaction medium would be one that has liquid-like densities to solubilize (i.e., desorb) the oligomeric coke precursors and gas-like transport properties to effectively transport the oligomeric species out of the catalyst pores.

Supercritical reaction media have been exploited by our group for the in situ extraction of coke precursors from porous catalysts resulting in extended catalyst activity. Recently, we have extended the in situ supercritical decoking concept to obtain virtually steady alkylation production on solid acid catalysts. In our work, carbon dioxide (Pc = 71.8 bars; Tc = 31.1°C) was employed as a diluent to obtain compressible reaction mixtures with pressure-tunable density and transport properties. In addition to its inertness, CO2 is environmentally safe, non-flammable (actually a fire retardant), inexpensive and recyclable.

Employing a molar excess of CO2 as a diluent, virtually steady alkylation (trimethylpentanes and dimethylhexanes) production was observed on solid acid catalysts (microporous H-ultrastable zeolite (USY) and mesoporous sulfated zirconia (SZ)) for experimental durations of up to nearly three days. At a space velocity of 0.25 kg 1-butene/kcat/h, feed CO2/isobutane: olefin ratio of 86:8:1 (on a molar basis), 50°C and 155 bars, roughly 5-10% alkylation yield (alkylates/C8) and 20% butenes conversion are observed at a quasi-steady state. The ability of the CO2-based nc reaction mixtures to mitigate coking and thereby to maintain better pore accessibilities is also evident in the lighter color of the spent catalyst samples, and relatively low surface-area and pore-volume losses (< 25%) in the spent catalysts. Details of these results are provided elsewhere.

Analysis of the GC/FID product spectrum reveals that the majority of C8 compounds is the butene dimer. Oligomer formation could be inhibited by carrying out the reaction in a well-mixed reactor wherein the olefin concentration is minimized. Another reason for the loss in alkylation selectivity could be due to progressive reaction of the C8 alkylates in the catalyst pores to form higher order alkylates. In other words, pore diffusion limitations may still persist in the high surface area USY zeolite and SZ catalysts despite the enhanced transport properties afforded by the sc reaction mixture. For enhancing C8 alkylation selectivity, a catalyst with reduced pore diffusion limitations and a reduced tendency toward detrimental side reactions such as oligomer formation is preferred. We are currently investigating other solid acid catalysts such as Nafion, a macroporous catalyst with a lower acidity (nearly identical to that of H2SO4). Nafion is an acidic fluoropolymer (essentially Teflon with added SO3H groups) supplied by Aldrich Chemicals, and has been investigated as an acid catalyst in numerous applications including aromatic nitration, aromatic alkylations, and isobutane/2-butene alkylation. Nafion is stable only up to 200°C, beyond which thermal decomposition products (such as SOx, CO2, HF, CO, COF2, etc.) are released as fumes which present health and safety hazards. Hence, unlike zeolites or zirconia catalysts, deactivated Nafion cannot be thermally regenerated at high temperatures. Consequently, gas phase or liquid phase alkylation con-ditions (under which acid catalysts coke) are unsuitable with Nafion. How-ever, a novel process such as nc operation that eliminates catalyst deactivation might be feasible with Nafion. Our initial results show that Nafion provides stable and roughly twofold greater alkylation (trimethyl-pentanes and dimethyl-hexanes) activity than either

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<th>COKE REMOVAL IN CONVENTIONAL REACTION MEDIA</th>
<th>NEAR-CRITICAL MEDIA</th>
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<td>Volatility-driven in gas-phase reaction mixtures (removes only lower order oligomers)</td>
<td>desorption</td>
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<tr>
<td>Solubility-driven in liquid-phase reaction media (heavier coke compounds can be dissolved)</td>
<td>diffusion</td>
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**Figure 2. In situ mitigation of coke buildup with sc reaction media**

For enhanc-
USY zeolite or sulfated zirconia.

**ENHANCED REACTION RATES AND TUNABLE PRODUCT SELECTIVITY**

Near critical reaction media have been investigated for alleviating transport limitations in solid-catalyzed multiphase reactions such as Fischer-Tropsch synthesis and in catalytic hydrogenations. Typically, solid-catalyzed hydrogenations involve sparging hydrogen through a slurry in which the porous catalyst particles are suspended. As shown schematically in Figure 3, such three-phase catalytic reaction systems are characterized by hindered pore-transport of hydrogen to the catalyst sites, adversely affecting product selectivity. By solubilizing the reactants (organic substrate and hydrogen) in a single, environmentally-benign sc solvent such as CO₂ it has been recently shown that a wide variety of organic functional groups (alkene, cyclic alkenes and alkanes, aldehydes, ketones, etc.) can be hydrogenated with good throughput and controllable product selectivity on polysiloxane-supported noble metal catalysts such as Pd and Pt. Selective hydrogenation of vegetable oils and fats (to Pd and Pt) can be hydrogenated with good throughput and controllable product selectivity on polysiloxane-supported noble metal catalysts such as Pd and Pt. Selective hydrogenation of vegetable oils and fats (to cis-fatty acid in favor of trans-fatty acid) on supported Ni catalysts with sc CO₂ as the reaction medium is another example. The enhanced reaction rates reduce holdup of hazardous reactants making the process inherently safer, and selective product formation reduces waste resulting in an environmentally safer process.

Recently, we reported how pressure-tuning with sc reaction media can be exploited to obtain enhanced 1-olefin selectivity during Fischer-Tropsch (FT) synthesis on supported Fe catalysts. Conventional FT synthesis has been performed in both gas and liquid phase reaction media. Gas phase reactions exhibit higher reaction rates and diffusivities when compared to liquid phase reactions, but are hampered by inadequate heat removal resulting in excessive methane formation. Liquid-phase reactions have superior heat removal capabilities when compared to gas phase reactions and are therefore able to maintain a constant reaction temperature without deactivation. However, liquid-phase FT synthesis suffers from mass transfer limitations, requiring relatively large reactor volumes. The ideal FT synthesis medium would therefore be one with gas-like transport properties and liquid-like heat capacity and solubility characteristics.

For FT synthesis on a Co catalyst, Yokota and Fujimoto report superior activity and selectivity in sc n-hexane ($P_c = 29.7$ bar; $T_c = 233.7^\circ$C) compared to either gas (nitrogen) or liquid-phase (n-hexadecane) reaction media. In our work, we exploited the pressure-tunable density (i.e., solubilizing power) and transport properties (i.e., diffusivity and viscosity) of the sc reaction medium (n-hexane) to examine how isothermal pressure-tuning affects catalyst activity and product selectivity during FT synthesis on a Ruhrchemie iron catalyst. At fixed feed rates of syngas (50 sccm/gcat) and n-hexane (1 mL/min), syngas composition ($H_2/CO = 0.5$), catalyst loading (1 g) and catalyst bed-temperature (240°C), syngas conversion attains a steady-state with excellent temperature control. We observed that isothermal pressure tuning from 1.2-2.4 P$_c$ in the supercritical region enhanced the catalyst effectiveness factor implying the alleviation of pore-diffusion limitations at the higher pressures. We attribute the increased pore-accessibilities to the enhanced extraction of the heavier hydrocarbons from the catalyst pores by the liquid-like densities, yet better-than-liquid transport properties, of n-hexane at 55 and 70 bars. Consistent with this explanation, we observe at these pressures an Anderson-Schulz-Flory product distribution characterized by a single chain propagation probability ($\alpha$), higher 1-olefin selectivities and a constant chain termination probability. Our results demonstrate the promising possibility of carrying out FT reactions with near-critical reaction media in fixed-bed reactors with excellent temperature control and tunable product selectivity. It would be interesting to investigate other well-known FT catalysts such as Co-based catalysts with a near-critical reaction medium in order to assess pressure-tuning effects on reaction rates and product selectivity on such catalysts.

**CONCLUSION**

The applications clearly demonstrate the potential for systematic exploitation of sc reaction media for developing environmentally safer processes for fuels production as follows: (i) Replacement of liquid acids such as HF, H$_2$SO$_4$, HNO$_3$ with environmentally-safer solid acids catalyzed processes. Such research efforts should exploit reactor operating conditions (such as sc reaction media) that promote desorption of the coke precursors from the catalyst and extend catalyst activity; (ii) Selective product formation, minimizing waste formation, as a result of enhanced pore-transport of reactants and products in single phase sc medium when compared to multiphase reactions hindered by transport limitations. In such applications, operating regimes within the sc region, wherein the density and transport properties of the reaction media can be pressure-tuned, must be systematically explored to optimize catalyst activity and product selectivity.

**ACKNOWLEDGMENT**

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**Figure 3. Exploiting sc reaction media in multiphase slurry reaction systems**

![Diagram showing a three-phase slurry reactor with gas, liquid, and catalyst particles.]
Others see chances for government grants, foreign travel, and lucrative future consulting. Government officials see opportunities for power, office, and bureaucratic aggrandizement. Environmental organizations see a lever to promote a broader agenda. One that often crosses the line from concern about the environment into opposition to industrial activity and to the personal freedom and mobility that are among our core values as Americans.

This role of imposing scientific order and honesty on the public debate is only part of the job. It is surprising how little we know for certain about Climate Change. One of my many criticisms of politicians is their rush to judgment and hyping of a supposed solution before we even know if a serious problem exists. This has diverted energy from thoughtful efforts to explore the existence and scope of the threat and to develop actions that are consistent with our state of knowledge. For example, we need to know more about past CO₂ levels. The history of the pre-satellite temperature record needs close scrutiny and serious concerns about possible distortions need to be resolved. While I have dismissed concerns about extreme weather events, infectious diseases and similar issues, there is no doubt that these are matters of concern to the public. They need continuing scientific attention. Research is needed on solar activity and its affect on temperature.

This only begins the list of scientific tasks on Climate Change. We need better climate models to replace the ones we have now, which are seriously flawed. This means we need more scientific knowledge about the impact of clouds, water vapor feedback cycles, snow and ice accumulation and reflectivity, the phenomenon of desertification, and other scientific dimensions of surrounding climate issues.

Often, when I raise these issues I am accused of using scientific uncertainty as an excuse for inactivity and delay. Our choices are not between action or inaction but between responsible and irresponsible actions. Thus my final point concerns the Climate Change issue as a problem in public policy and as a problem in choosing among possible actions.

My background is not in science but in economics, business, and policy analysis. To those of my ilk, the details of the Climate Change issue are complicated, but the basic structure of the problem is simple — Climate Change is a problem in decision-making under conditions of uncertainty. Those of us in business confront such problems every day, and we know the rules for dealing with them.

The first rule is to be slow to commit. Until you must, do not bet your company (or your country) on something that might turn out to be an error. To the extent possible, postpone major decisions while you reduce uncertainties. Given this rule, the first question to ask is, “Do we have time?” With respect to Climate Change, the answer is clearly, “Yes.” We do not need to drastically reduce emissions in the short term because nothing we do in the next 15 or 20 years will have an appreciable impact on the world’s average temperature in 2050 or 2100. In fact, nothing we in the US do during the next decade will have much impact on the atmospheric concentration level of greenhouse gases in the year 2020. According to the former Chairman of the Intergovernmental Panel on Climate Change (IPCC), the effect of the Kyoto Protocol on CO₂ concentration levels in 2010 is four tenths of one percent. And it wouldn’t be much greater in the following decade.

Since our concern should be with the accumulation of CO₂ and not with emissions per se, decisions on accelerated reductions in emissions can be safely postponed. This fact is crucial, because the costs of these reductions are exceedingly sensitive to timing. Many capital investments, including those in energy, are longterm. If change can be deferred until current equipment reaches the end of its useful life, and is replaced by more efficient technology, costs will decline drastically. Recently, some confusion over the potential costs of Kyoto was triggered by the Administration’s release of an optimistic study by the Council of Economic Advisors (CEA). The Council of Economic Advisors reached its rosy conclusion by three assumptions - all of which are unrealistic. It assumed the US could meet about 80% of our emission reduction obligations by buying credits from abroad. Put another way, only 20% of our obligations would be met by domestic action. The Kyoto Protocol does not provide for this and no mechanism is in place. CEA made two other critical assumptions. First, that there is a truly global emission trading system in place even though 138 developing countries are exempted from the Protocol. Second, that electric utilities would switch from coal to natural gas in 10 years. That is economically impractical. A more realistic recent appraisal came from the Department of Energy, which estimated that Kyoto could, by 2010, raise gasoline prices 53%, raise electricity rates 86%, and reduce the gross national product by 4.1 percent. Make no mistake. The value of deferring decisions on Climate Change while we collect more knowledge is not trivial.

This leads logically to the second rule: Invest in information. Spend money to narrow the range of possibilities. Use sensitivity analysis — what information forms the hinge of the decision, and how can we get it? We need to invest in gaps in climate science. We need better climate models. We need to invest in analyzing basic issues. And we need to invest in creating contingency plans.

The third rule is called “no regrets.” Look for actions that will produce benefits under any set of circumstances. Business has developed a list of actions that would be worthwhile even if the threat of Climate Change turns out to be a hobgoblin, and we are happy to share it with anyone who wants to see it. In contrast, policies of committing to near term emissions rollbacks, regardless of the state of knowledge or the timing of investment decisions, is guaranteed to cause a lot of regret.

The final rule is to consider alternatives. It is a truism that, the further ahead you try to predict, the greater the number of uncertain factors, and the larger probability that any single guess will be wrong. This wisdom that a broad net should be cast to be sure that all alternatives are considered certainly
applies to Climate Change. Even if the problem turns out to be real, it may well be that a crash program of prevention is the wrong option. In much of the world the impact of warming could be neutral or even benign. In other cases, it might make more sense to commit resources to adaptation. These options need serious consideration and analysis, and serious scientific work. They are not getting it.

These four principles rule — use time as a friend rather than an enemy; invest in information; look for “no regrets” actions; consider all the alternatives — provide the basis for sound Climate Change policy. Their wisdom is thoroughly supported by the facts.

So, to return to my initial theme — the role of scientists — the scientific community must hold firm to scientific habits of mind in addressing the climate issue, whether that work takes the form of research, education, or participation in the policy debate.

William F. O’Keefe, Executive Vice President, American Petroleum Institute, the Washington DC based national trade association representing the petroleum industry. Mr. O’Keefe may be reached at API 202-682-8000.

Three graduate students from the University of Burgundy at Dijon in France are currently working at the CAER in order to complete their advanced materials engineering degrees. The students are (from left): Stephane Villain, Bouchra Safadi, and Francois Vilain. Their efforts are part of a new student exchange program with the University of Kentucky. All are working within the carbon materials group. Stephane is concentrating on the synthesis of multi-walled carbon nanotubes; Bouchra is investigating nanotube polymer composites and; Francois’ research concentrates on nanotube pitch composites. The three will be here until August.

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THE SOUTH AFRICAN COAL ASH ASSOCIATION (SACAA)

An Overview
Guides on the use of South African fly ash as a cement extender

The SACAA is producing a series of guides on the use of South African fly ash as a cement extender and the influence it has on the properties of cement-based products, mainly concrete, but also on mortars and plasters.

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American Chemical Society, Spring Meeting 2000 San Francisco Activated Carbon Separations Symposium

Sessions on activated carbon separations will include discussions of the use of novel feedstock materials, unique manufacture techniques, physical properties of resulting materials, and separation isotherms of activated carbons generated by these techniques. Session Chairs are David A. Rockstraw, New Mexico State University and Frank Derbyshire, University of Kentucky.

One-page abstracts with descriptive titles are being accepted for this session, and should be sent to Dr. Rockstraw at the address to the left by September 1, 1999.
October 18-20
Lexington, Kentucky
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