

## In situ CIR-FTIR Characterization of Catalytic Cracking of Supercritical Endothermic Fuels Over Different Zeolites

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### INTRODUCTION

Endothermic hydrocarbon fuels offer the potential to be utilized as heat sinks for increased cooling for high aircraft flight speeds by undergoing cracking reactions on a zeolite catalytic substrate prior to injection into the combustion system (1, 2). For maintaining high catalytic activities over the required fuel processing times, it is necessary to minimize the amount of coke that is rapidly formed on the catalyst as a by-product in these reactions. Early studies on different hydrocarbon catalytic processes under supercritical conditions including paraffin and olefin isomerization (3-7), xylene isomerization on Ga-containing molecular sieves (8), benzene and ethyl benzene disproportionation over USHY (9), isoparaffin-olefin alkylation over MCM materials (10) and Fisher-Tropsch synthesis on silica supported metal based catalysts (11) demonstrated the beneficial effect of supercritical reaction conditions on the catalyst activity. Product selectivity differences were also observed by comparing gas phase with supercritical processes. However, all these processes were performed at temperatures only slightly above the critical temperature of the system ( $1 < T/T_c < 1.1$ ) where significant changes in the fluid density occur with changes of the pressure near the critical pressure (12). Therefore, the observed differences were attributed to gas-like diffusivities and liquid-like densities of the supercritical fluid. The liquid-like density of the supercritical fluid should result to the in situ extraction of the coke precursors from the catalyst pores.

Sobel et al. (2) demonstrated that high temperature cracking of endothermic jet fuels at supercritical pressures ( $1 < P/P_c < 4$ ) over zeolites resulted in an increase of the catalyst life time relative to gas phase process conditions. This was surprising since at the high temperatures required for catalytic cracking of hydrocarbon fuels (well above 450 °C), very high pressures (above 2500 psi, i.e.  $P/P_c > 8$ ) are demanded for the supercritical fuel to reach liquid-like densities. However, the development of high temperature, high pressure packed bed autogeneous infrared monitoring microreactors for heterogeneous catalysis based on Cylindrical Internal Reflectance (CIR) revealed for the first time that hydrocarbons exposed to micropores under supercritical catalytic cracking conditions led to super dense liquid like phase within the fine pore structure (13, 14). The super dense phase observed had the effect of maintaining the activity of zeolites under high conversion cracking conditions by solubilizing in situ coke precursor molecules, resulting in lower amounts of coke deposited within the zeolitic micropores.

### EXPERIMENTAL

In situ infrared spectra were acquired using a Cylindrical Internal Reflectance (CIR) annular packed-bed micro-reactor described elsewhere (13, 14). The principle of this technique is the following: When an IR beam is directed through a polished cylindrical crystal at an incident angle exceeding the critical angle, it undergoes a number of internal reflections at the interface with the catalyst sample and penetrates into it. The penetration depth at each point of internal reflection (usually around 1-1.5  $\mu\text{m}$ ) depends on the incidence angle, the radiation wavelength and the ratio of the refractive indices of the sample and the crystal while the number of total internal reflections for a specified incident angle is a function of the length and diameter of the crystal. The high-pressure CIR-micro-reactor was mounted in the sample compartment of the FTIR spectrometer. The cell was encapsulated within a heated copper-alloy block. A high-pressure metering pump and a downstream back-pressure regulator were used to control fuel circulation. Approximately 20 seconds were required for the reactor to reach steady-state conditions. The nominal residence times (contact times) were kept con-

steady-state conditions. The nominal residence times (contact times) were kept constant and equal to 1.3 sec for tests performed at different pressures by adjusting the fuel flow rates. A Sigma 2000 gas chromatograph was used for reaction-product identification and analysis. The products were analyzed by a flame ionization detector and separated by a Chrompack 10-ft x 0.125-in. column of n-octane on 80/100 mesh Poracil C.

## RESULTS AND DISCUSSION

Two different aluminosilicate zeolites were evaluated in this study:

(1) Promoted Octacat, a commercial mixture of 27 wt. percent ultra-stable H-Y zeolite (Si/Al = 9), 3 wt. percent HZSM-5 (Si/Al = 25) and 70 wt. percent dilution matrix (mainly kaolinite clays).

(2) Two commercial HZSM-5's with different Si/Al ratios (Si/Al = 30 and 126).

The Y-type zeolite has large-pores (7.4 Å) and three-dimensional structure formed by rings of 12 linked tetrahedra with circular-pore openings, while the ZSM-5 is a medium-pore, three-dimensional, 10-membered-ring system of circular (5.5 Å) and elliptical (5.1 x 5.7 Å) interconnecting channels. Norpar 12 (a mixture of C<sub>10</sub> to C<sub>13</sub> normal paraffins) was selected as a surrogate jet fuel. Tests were conducted at pressures up to 1000 psia and temperatures up to 1300 F.

### Promoted Octacat

The FTIR spectra of the C-H bonds during catalytic cracking of Norpar 12 at 950 F are shown in Figure 1 for subcritical (180 psia), critical (300 psia) and supercritical (600 and 950 psia) pressures. The substantial increase in the spectrum intensity with pressure suggests an increased concentration of the hydrocarbon molecules within the zeolitic micro-pores. This is illustrated more clearly in Figure 2, which compares the density measured within the zeolite pores (proportional to the IR signal) with the density determined from thermophysical properties data for hydrocarbon mixtures provided in the NIST computer program SUPERTRAPP<sup>3</sup>. (Both fuel densities are normalized to the density at the critical point.) The results suggest a super-dense or liquid-like reaction mixture within the pores of the zeolite at supercritical pressures. This behavior should be beneficial for the in situ solubilization/extraction of the coke precursors from the zeolitic micro-pores, resulting in a stabilization of the catalyst. However, very dense fuel could limit the diffusion within the zeolitic micro-pores and, therefore, lower the reaction rate. Thus, there may be an optimum supercritical pressure (i.e., reaction mixture density) at which the catalyst performance is maximized, for a specified operating temperature and flow rate. Outside the micro-pores and on the external surface of the catalyst, the fuel behaves as a gas, with no coke-precursor extraction potential. Buildup of coke on the external surface could eventually block the pore openings, restricting access into the active sites, and result in a partial deactivation of the catalyst.

The catalytic cracking of Norpar 12 on P-Octacat at 950 F for subcritical and supercritical pressures is presented in Figure 3. For each operating pressure, the catalyst activity decreased with time-on-stream for the first 100 minutes, and then reached a steady state with no further deactivation over the 4-hour test. As shown in the figure, conversion to gaseous products is low at this moderate operating temperature, which was specified as the maximum allowable for preserving the optical properties of the ZnSe crystal. The results demonstrate that, for a constant residence time, the catalyst activity increases with increasing pressure.

The CIR-FTIR technique is capable of monitoring in situ the amount of coke formed during the course of the reaction because the area under the coke infrared spectral bands is roughly proportional to the amount of coke deposited on the catalyst. In Figure 4, the area of the infrared coke bands is plotted as a function of the time-on-stream. This figure illustrates that coke builds up rapidly, until a steady state is reached at which time the rate of coke formation apparently equals the rate of solubility of the coke precursors by the supercritical fluid. After 4 hours of reaction at 950 psia, the pressure was gradually decreased and a significant increase in the intensity of the coke spectral bands was observed that was accompanied by a corresponding decrease in the concentration of active zeolitic acid sites.

### HZSM-5

In general, HZSM-5 would be expected to have a lower tendency for coke formation than P-Octacat due to the structural geometry and position of the acid sites, which make it difficult to form large polynuclear hydrocarbons. As previously mentioned,

the channels are narrower than the Y-type zeolite, and there are no large internal cavities. Therefore, there is little space available within the zeolitic micro-pores for coke precursor molecules to grow. Thus, coke formation occurs predominately on the external surface. The catalytic activity of HZSM-5 depends strongly on the Si/Al ratio, which determines the concentration of acid sites within the zeolite lattice. The lower the Si/Al ratio, the higher the conversion, but also the higher the tendency for coke formation within the micro-pores. Therefore, there is an optimum Si/Al ratio.

The effect of pressure on coke formation during the catalytic cracking of Norpar 12 over P-Octacat and HZSM-5 (Si/Al = 126) at 950 F is illustrated in Figure 5. These experiments were conducted by initiating the reaction at the highest pressure and maintaining it for 4 hours, whereupon the pressures were reduced sequentially. Infrared spectra were collected after 1 hour of steady operation at each of the lower pressures. As this figure indicates, the integrated area under the coke infrared bands is always significantly lower for HZSM-5 than for P-Octacat, most likely due to the smaller pore openings which restrict the size (molecular weight) of the coke precursors that can form and engender a higher fluid density (solubility) within.

The conversion to gaseous products by HZSM-5 is compared to that by P-Octacat in Figure 6. In these tests, HZSM-5 was tested at 700 psia while P-Octacat was tested at 950 psia. Since the HZSM-5 contains the smaller pores, its performance is expected to optimize at a lower supercritical pressure than P-Octacat, because of the trade-off between coke precursor solubility and species diffusion. As shown in the figure, HZSM-5 with Si/Al = 126 can operate at 60-percent conversion to gaseous products for long reaction times, while a lower Si/Al ratio of 30 resulted in high initial conversion but rapid deactivation. In comparison, P-Octacat (which contains 3 percent HZSM-5 with Si/Al=25) can maintain only 10-percent conversion to gaseous products at this temperature.

#### Reaction Endotherms

The chemical heat sink (endotherm) is a function of not only conversion but also product distribution. Furthermore, many applications of interest involve operation at fuel temperatures that are considerably higher than the 950 F limit of the CIR apparatus. To determine the heat sink attainable with the two catalysts at higher temperatures, tests were conducted in a Bench-Scale Reactor Rig. The results of these tests are presented in Figure 7, and show that P-Octacat has approximately twice the cooling capacity as HZSM-5. These results imply that P-Octacat has the higher selectivity for unsaturated olefinic species, and suggest that a choice between catalysts should be made based on the requirements of the application, i.e., lifetime vs. heat sink capacity. Furthermore, the data suggest that the P-Octacat could be improved by replacing HZSM-5, Si/Al=25 with Si/Al=126, and increasing its concentration.

#### CONCLUSIONS

Supercritical catalytic cracking of Norpar 12 over different zeolites resulted in higher catalyst activity and lower coke deposition within the zeolitic micropores relative to the low pressure gas phase reaction conditions. In situ CIR-FTIR analysis demonstrated that this beneficial effect was due to the condensation effect of the supercritical hydrocarbon fuel within the zeolitic micropores. The liquid-like density of the fuel resulted in an in situ extraction of coke precursors, suppressing the coke deposition in the catalyst. Supercritical catalytic cracking of Norpar 12 over various HZSM-5's resulted in higher fuel conversion and lower coke deposition relative to P-Octacat (a commercial faujasite-type zeolite) but also in lower fuel endotherm (i.e. lower fuel cooling capacity). However, a ZSM-5 with a Si/Al ratio of 126 was found to be the optimum catalyst, since it maintained its activity for long operating times.

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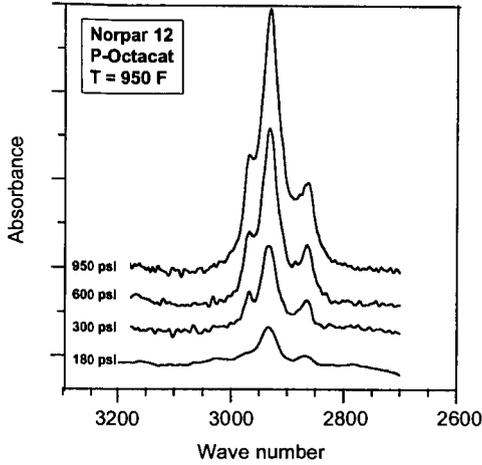


Figure 1. Infrared spectra of Norpar 12 hydrocarbon fuel C-H bonds within zeolite pores.

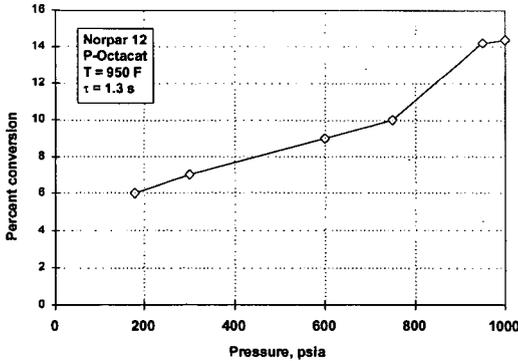


Figure 2. Reduced fuel density within zeolite pores.

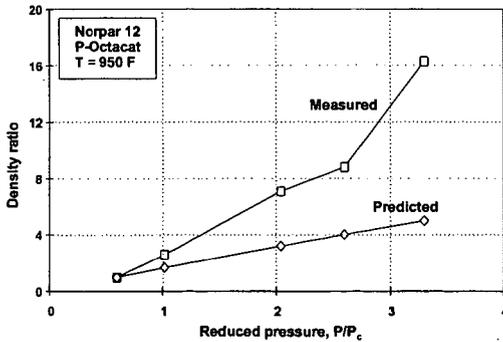


Figure 3. Conversion of Norpar 12 during catalytic cracking over P-Octacat.

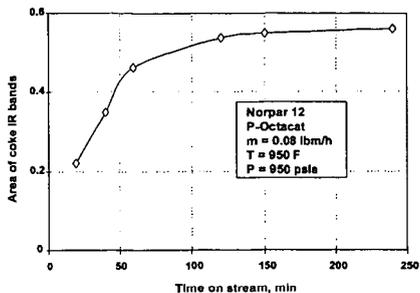


Figure 4. Area of coke infrared spectral bands.

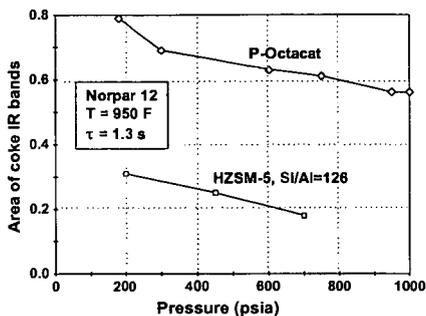


Figure 5. Effect of catalyst on coke deposition.

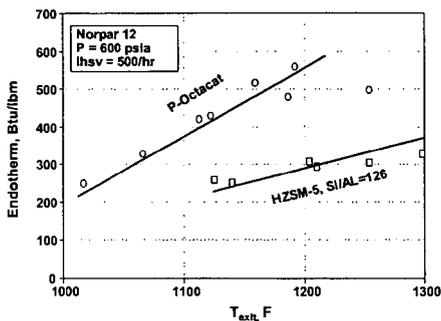


Figure 6. Degradation of catalytic activity

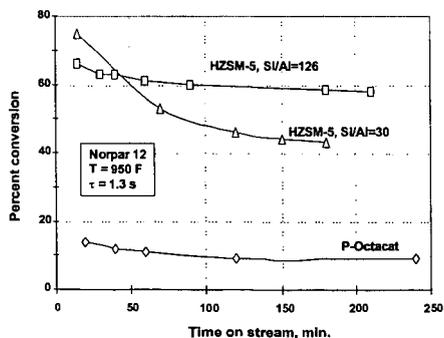


Figure 7. Endotherms for P-Octocat and ZSM-5, Si/Al=126.