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An *in Situ* CIR-FTIR Study of *n*-Heptane Cracking over a Commercial Y-Type Zeolite under Subcritical and Supercritical Conditions

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An *in situ* cylindrical internal reflection infrared technique (CIR-FTIR) was used in order to understand the behavior of subcritical and supercritical hydrocarbons processing over a commercial Y-type zeolite (P-Octacat) at 475°C and pressures up to 41.6 bar. The changes in the concentrations of the active catalytic sites were monitored *in situ* by CIR-FTIR during the catalytic cracking of *n*-heptane at subcritical and supercritical conditions. High-quality *in situ* spectra were acquired for the first time at such high temperatures and pressures. The results showed that the catalyst maintained higher activity when catalytic cracking was performed under the supercritical conditions of the hydrocarbon, whereas the subcritical conditions led to a rapid deactivation of the catalyst. The subcritical IR spectra showed dramatic reductions in the concentration of the acid sites and in the interactions of the acid sites with the olefinic and paraffinic products of the reaction. Supercritical fuel showed an extraordinary dense behavior within the pores of the zeolite, which was significantly higher than the values estimated by equations of state under the same conditions. Higher amounts of carbonaceous deposits under subcritical conditions were also observed. Finally, reactivation studies on a deactivated catalyst resulted in a partial regeneration of the catalyst under supercritical conditions, provided with a complete experimental proof by CIR-FTIR.

INTRODUCTION

The deactivation of zeolite catalysts during endothermic fuel conversion processes (i.e., catalytic cracking) is essentially due to the formation of undesirable heavy hydrocarbons or "coke deposits", which poison the acid sites and/or block the catalyst pores (1, 2). Detailed studies on the nature of coking and deactivation of zeolites may be found elsewhere (3–9).

The behavior of supercritical fluids (SCFs) has attracted a great deal of interest in recent years and research in this area has led to a number of practical applications which are reviewed elsewhere (10, 11). Especially in heterogeneous catalysis, supercritical reaction media have been employed to regenerate porous catalysts by the *in situ* extraction of coke compounds (12–23). The cited advantages of supercritical processing over conventional gas-phase processing included enhanced activity maintenance, higher reaction rates, and desirable product selectivity. The main reason for such improvements was a result of the enhancements of the physicochemical properties of the fluid in the critical state (14, 24) (i.e., liquid-like density, hence high solvation power), which could result in the *in situ* extraction of low volatile components deactivating the catalyst, together with the faster diffusion of the reaction products in the porous network (gas-like diffusivities).

Most of the supercritical hydrocarbon reactions in the literature were performed in a narrow range around the critical temperature ($1 < T/T_c < 1.1$) since in this region significant changes in the fluid density occur with relatively small changes around the critical pressure ($0.8 < P/P_c < 1.7$). Therefore, SCFs were effective in isomerization of olefins, on γ-Al_2O_3/Al–metal (12–14), on Pt/γ-Al_2O_3 (16–21), and in Fischer–Tropsch (FT) synthesis on silica-supported metal-based FT catalysts (22, 23) since these reactions could be effectively performed around the critical temperature. However, the use of SCFs in high-temperature hydrocarbon reactions (i.e., catalytic cracking) might seem thermodynamically unfeasible since very high pressures are required to reach high reduced densities due to the high-compressibility factor of the fluid. However, studies that were carried out at United Technologies on the processing of jet fuels over SAPOs (silicoaluminophosphates having zeolitic structures), and other metal-supported catalysts under high pressures and temperatures, resulted in high catalyst stabilities (25). The fact that the catalysts did not deactivate under severe conditions was promising for the operation of similar catalysts in commercial petroleum processing, such as catalytic cracking, reforming, isomerization, and hydrodesulfurization.

Supercritical catalytic cracking studies performed in our laboratories over a commercial Y-type zeolite catalyst (P-Octacat) at 475°C also clearly showed that the catalyst maintained high activities under these reaction conditions. The reason for such a behavior, as discussed later, was attributed to the fact that feed hydrocarbon within the zeolite micropores showed an extraordinary dense

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behavior (hence high solvation power), significantly higher than the estimated values by equations of state. Therefore, supercritical catalytic cracking resulted in enhanced activity maintenance through extraction of coke from the microporous lattice by the dense SCF. While there is ample evidence for enhanced catalytic activities in the critical state (12, 16–21), no spectroscopic studies that attempted to monitor the *in situ* interactions of the active catalytic sites with a supercritical hydrocarbon during an endothermic fuel conversion process have been reported. Recently Jolly *et al.* (26) studied the conversion of *n*-hexane on dealuminated HY zeolites, by *in situ* monitoring the reaction by IR Spectroscopy up to temperatures of 400°C but at ambient pressures. Their results showed that the 3600 cm^{-1} OH groups were consumed during cracking due to coke deposition with a concomitant increase in the 1586 cm^{-1} band which was assigned to carbonaceous deposits.

The latest development in our laboratories permits the *in situ* analysis of heterogeneous catalyzed processes by cylindrical internal reflection infrared spectroscopy (CIR-FTIR) under autogeneous reaction conditions (27). The technique was first applied by Moser *et al.* for the *in situ* analysis of homogeneous metal-catalyzed reactions (28, 29) and zeolite synthesis (30) under ambient and moderate temperatures and/or high pressures. The advantage of the CIR-IR technique is that it can be used on powders for the *in situ* analysis of a wide variety of chemical reactions when mounted in the appropriate reactor cells. We recently reported that the CIR-FTIR technique demonstrated a definite superiority for *in situ* heterogeneous catalyst analysis, permitting direct infrared observation of molecular thermal transition that a hydrocarbon undergoes in the supercritical regime, the properties of a hydrocarbon within the pores of zeolite (i.e., higher densities than the bulk phase), and the interactions of a hydrocarbon with the active sites of the catalyst during catalytic cracking at subcritical and supercritical conditions (475°C, 6.7–68 bar) (27).

The objective of this study was to understand why supercritical catalytic cracking avoids severe catalyst deactivation. The elucidation of the mechanism for enhanced catalytic activities will be demonstrated by: (1) *in situ* monitoring of the acid site concentrations during supercritical and subcritical cracking; (2) *in situ* monitoring of the interactions of the active sites with the reactants and products; and (3) *in situ* infrared observation of the thermodynamic behavior of the supercritical hydrocarbons within the zeolite micropores, by the CIR-FTIR technique.

METHODS

Catalyst and Chemicals

The catalyst employed to study catalytic cracking of *n*-heptane under subcritical and supercritical conditions was a commercial H–Y zeolite catalyst (Promoted Octacat) supplied by Grace-Davison Chemicals. The catalyst consisted of 27 wt% H–Y zeolite (Si/Al = 9), containing 0.4 wt% Na_2O and no rare earths, 3 wt% H-ZSM5 (Si/Al = 25), and the balance was kaolin clay. The SEM analysis of the catalyst sample showed a particle size distribution of 30–60 μm. CIR crystals were purchased from Spectral Systems, while heptane of 99+% purity was obtained from Aldrich.

Experimental

The experimental procedure and instrumentation required for the *in situ* analysis of a heterogeneous catalyzed system by CIR-FTIR spectroscopy has already been described in detail (27). The cracking reaction was carried out in a specially designed cylindrical internal reflection (CIR) microreactor (Fig. 1) mounted directly on the optical bench of a mid-range FT-IR Spectrometer (Nicolet 510P). A Perkin–Elmer gas chromatograph was connected to the exit of the reactor in the FT-IR cell for on-line product analysis. A precision metering, high-pressure, low-volume liquid pump was used for introducing the feed hydrocarbon. The facilities used 1/16-in.-stainless-steel high pressure lines and included a downstream back-pressure regulator, mass flowmeters, and pressure gauges. The flow system was designed to operate at temperatures up to 500°C and pressures up to 68 bar.

A ZnSe crystal of 0.25 in. diameter and 3.25 in. long with conical ends polished at 45° to the axis was embedded in the reactor, and the catalyst was packed tightly in the annular space (Fig. 1). The details of the reactor, crystal element, and basic principles involved in the CIR-IR technique were previously reported (27).

The IR spectra were collected at a spectral resolution of 4 cm^{-1} by coadding 1024 scans to obtain the desired signal to noise ratio unless otherwise specified. This gave an acquisition time of 10 min for each spectrum. Spectral manipulations such as baseline correction, peak integration, and smoothing were performed using the Galactic Grams 386 software. The products were analyzed by a flame ionization

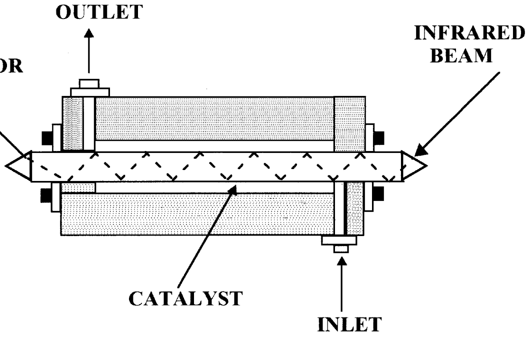

FIG. 1. Schematic of heterogeneous microreactor, illustrating also the principles of CIR-FTIR technique.

detector (FID), separated by a Chrompack 10 ft × 0.125 in.-column of *n*-octane over 80/100 mesh Porasil C. Each GC run was acquired in 20 min.

The catalyst samples were calcined at 450°C for 8 h in air prior to each cracking experiment. Fresh catalyst (1.6 g) was used in each experiment. The temperature was set to 475°C and the runs were carried out at different pressures ranging from 6.7 to 41.6 bar. Residence times for the cracking reactions were kept constant at 0.9 s for each pressure by adjusting the liquid hourly space velocity of the hydrocarbon. The density of the hydrocarbon under subcritical and supercritical conditions was evaluated using the Pitzer correlation (31) and checked by the Peng Robinson equation of state (32). The critical conditions of heptane are 267°C and 27.4 bar.

RESULTS AND DISCUSSION

Catalytic Activities at Subcritical and Supercritical Conditions

Figure 2 shows the activity of the catalyst at 475°C at different times on stream under subcritical (6.7 and 16.5 bar) and supercritical (41.6 bar) processing conditions. The activity of the catalyst was calculated by taking the ratio of the macroscopic rate of reaction at time equal to zero to that of time at *t*. The initial rates ($t = 0$) were evaluated by extrapolating the rate versus time on stream curve. As can be clearly seen from Fig. 2, the slope of the deactivation curve increased significantly as the operating pressure decreased, especially under subcritical conditions. This suggested a faster build-up of coke in the zeolite pores under subcritical conditions, which eventually led to a rapid pore mouth plugging and suppression of the active sites in the zeolite pores. The most important aspect, however, was that the activity of the catalyst for supercritical *n*-heptane cracking (41.6 bar) was significantly higher at all reaction times. The catalyst lost 48% of its original activity under supercritical conditions of 475°C and 41.6 bar, whereas it lost 80 and 85% of its original activity under subcritical conditions of 475°C and 16.5 and 6.7 bar, respectively. The 6.7-bar experiment led to very rapid coke formation and the reactor plugged after a short time on stream (1 h). The detailed kinetic analysis (activities, product distributions, selectivities, and yields) will be presented in a subsequent publication.

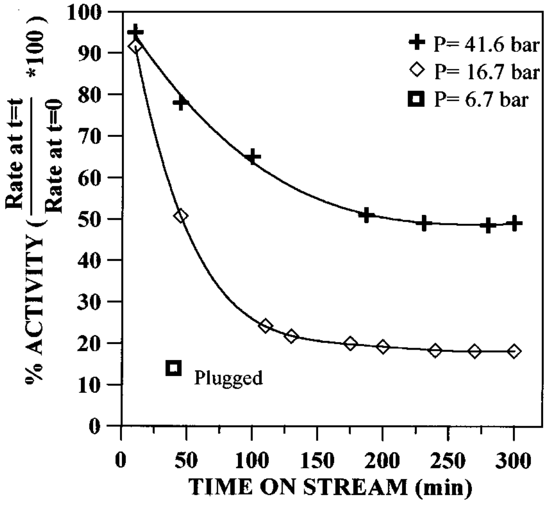

FIG. 2. The catalytic cracking of heptane over P-Octacat at 475°C and pressures of 6.7, 16.5, and 41.6 bar. All experiments were performed at a constant residence time of 0.9 s.

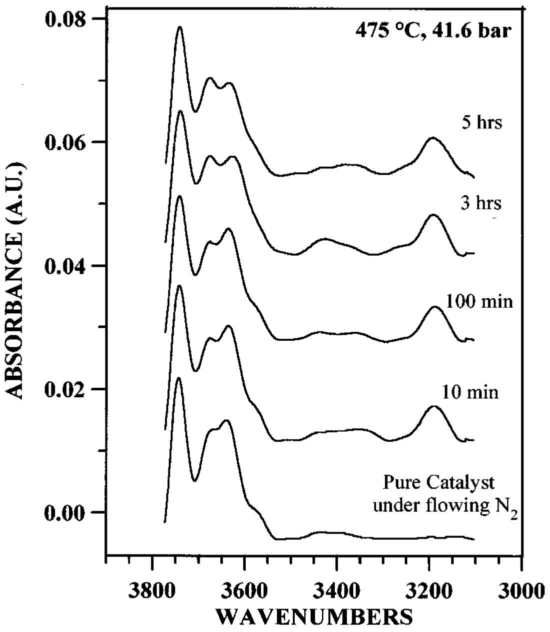

FIG. 3. *In situ* monitoring of the acid sites of P-Octacat performing heptane cracking under supercritical conditions of 475°C, 41.6 bar. The pure spectra were corrected for the changes in the refractive index due to N_2. The critical conditions of heptane are 267°C and 27.4 bar.

Physical Significance of in Situ Monitoring of Acid Sites by CIR-FTIR

It is known that coke formation accounts for the consumption of the active sites of the catalyst. Therefore, the corresponding intensities of hydroxyl groups in the IR spectra should reflect the performance of the catalyst. For example the reduction in the intensity of Brønsted acid sites has been interpreted as catalyst deactivation since they are strongly acidic and mostly responsible for catalytic cracking (33, 34). A reduction in the intensity of terminal silanols was interpreted as surface coverage by carbon as a result of the overflow of coke from the supercages to the external surface of the catalyst (4, 33, 34).

In Situ CIR-FTIR Analysis of Subcritical and Supercritical n-Heptane Cracking

Figure 3 presented the spectral region between 3800 and 3100 cm^{-1} during heptane cracking under supercritical con-

TABLE 1

Band Assignments for the Hydroxyl Region (3800–3100 cm^{-1})

Wavenumber (cm^{-1})	Assignments
3740	Terminal silanols (Si–OH)
3680, 3650	Physically adsorbed water bound to Na^+ through oxygen in kaolin clay
3626	Brønsted acid sites (Si–Al–OH)
3585	OH groups in the sodalite cage
3450–3300	H-bonding interactions of hydroxyl groups with paraffins
3300–3100	H-bonding interactions of hydroxyl groups with olefins

ditions of 475°C and 41.6 bar. This spectral region corresponded to the stretching frequencies of the zeolite hydroxyl groups and their interactions with reactants and products. The band assignments have already been reported (27). The results are summarized in Table 1.

No dramatic changes were observed in the absolute intensities of the strongly acidic Brønsted acid sites appearing at 3626 cm^{-1} and weakly acidic terminal silanols appearing at 3740 cm^{-1} in CIR-FTIR spectra during supercritical cracking at 475°C and 41.6 bar (Fig. 3). Curve-fitting results of these spectral bands showed that 27% of the Brønsted acid sites and 8% of the terminal silanols disappeared from the spectra after 5 h of catalytic cracking at supercritical conditions (Fig. 4). These results are in good agreement with the activity results presented in Fig. 2. The rate of deactivation of the catalyst at 475°C and 41.6 bar was slow and the catalyst maintained 52% of its original activity even after 5 h of catalytic cracking.

When the same experiment was performed under subcritical conditions of 475°C and 16.5 bar, dramatic changes occurred in the zeolite hydroxyl region (Fig. 5). Curve-fitting results showed that the catalyst lost 57% of the Brønsted acid sites and 68% of the terminal silanols (Fig. 4). The GC results showed an 80% loss in catalytic activity under those conditions after 5 h of catalytic cracking.

The next phase of this study was to perform the same experiment at a much lower subcritical pressure (6.7 bar). The reactor plugged after 1 h of operation due to rapid coke formation. During this period one GC (5% conversion at 40 min) and four successive CIR-FTIR runs were acquired and no further data could be taken. As can be clearly seen from Fig. 2, the rate of deactivation was much faster when compared with the supercritical conditions and the catalyst was essentially inactive after 1 h.

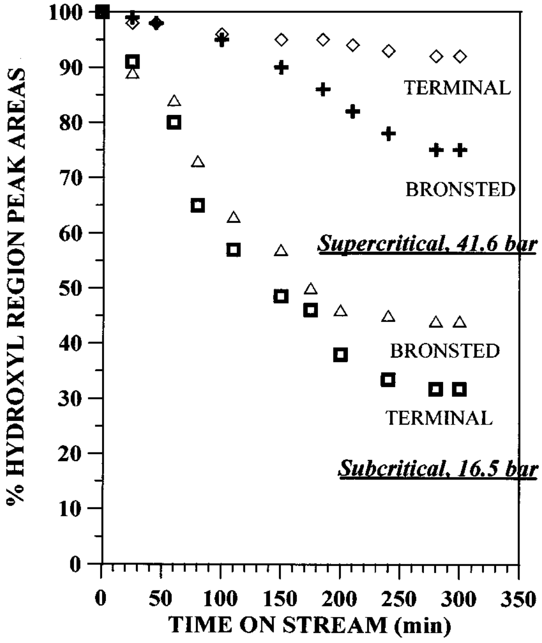

FIG. 4. The changes in the concentrations of terminal silanols and Brønsted acid sites during cracking of heptane at supercritical conditions of 475°C, 41.6 bar (top curve) and subcritical conditions of 475°C, 16.5 bar (bottom curve).

Comparison of Subcritical and Supercritical n-Heptane Cracking by CIR-FTIR

Figure 6 compares the steady-state CIR-IR spectra of the zeolite hydroxyl region of the catalyst after 5 h of cracking at two subcritical pressures (6.7, 16.5 bar) and one supercritical pressure (41.6 bar). For comparison, the spectrum of pure zeolite collected at 475°C under flowing nitrogen is also presented. Figure 6 clearly shows that the concentration of active sites of the catalyst was significantly higher under supercritical conditions (475°C and 41.6 bar) relative

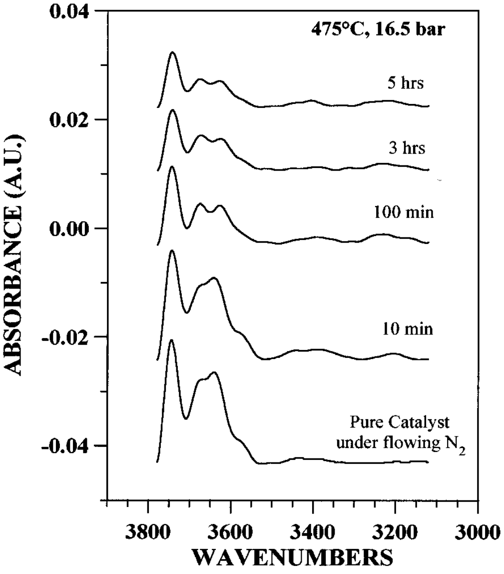

FIG. 5. *In situ* monitoring of the acid sites of P-Octacat performing heptane cracking under subcritical conditions of 475°C, 16.5 bar. The pure spectra were corrected for the changes in the refractive index due to N_2.

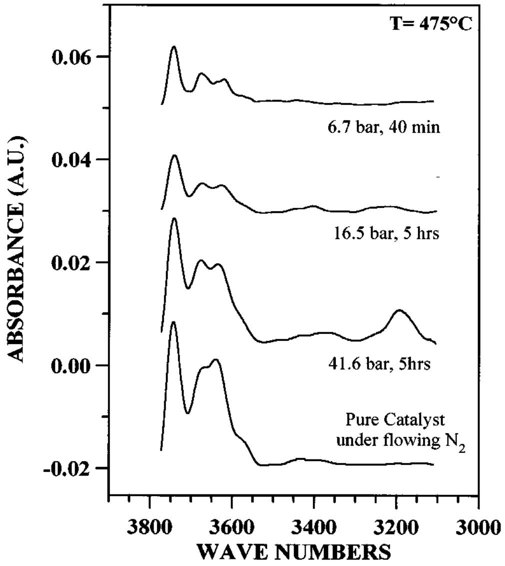

FIG. 6. Steady-state CIR-IR spectra of P-Octacat performing catalytic cracking at 475°C under subcritical (6.7 and 16.5 bar) and supercritical (41.6 bar) conditions.

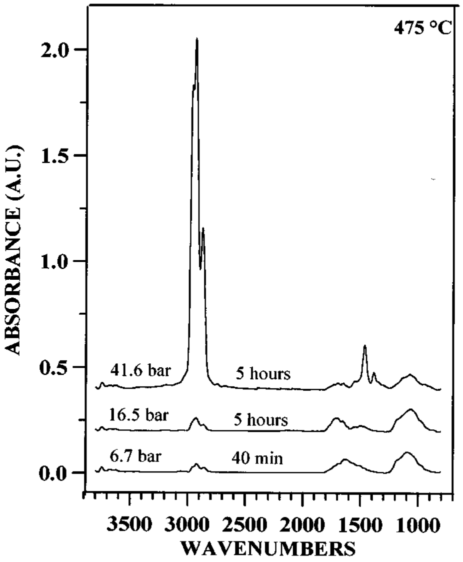

FIG. 7. Steady-state broad range (4000–700 cm^{-1}) CIR-IR spectra of P-Octacat performing catalytic cracking at 475°C under subcritical (6.7 and 16.5 bar) and supercritical conditions (41.6 bar).

to the subcritical conditions (6.7 and 16.5 bar). The hydroxyl peaks were intense even after 5 h of cracking in the supercritical regime, which indicated a high catalytic activity. However, the intensities of Brønsted acid sites and terminal silanols were significantly reduced in the subcritical experiments. This was a strong indication of the fact that coke laydown was accelerated in the subcritical regime, resulting in a higher degree of acid site occupation and therefore a significant reduction in catalytic activity. The H-bonding interactions with paraffins (3450–3300 cm^{-1}) and olefins (3300–3100 cm^{-1}) were much stronger in the supercritical spectra, showing a higher degree of product formation and a lower degree of occupation of the supercages by the solid coke molecules. These observations were in excellent agreement with the kinetic measurements which showed almost a twofold increase in both total olefin and paraffin yields for supercritical (41.6 bar) cracking over subcritical (16.5 bar) cracking at steady state.

The above results suggested that the supercritical reaction medium, well known for its enhanced solubilization power, continuously extracted coke from the microporous lattice and thereby reduced coke laydown.

Superdense Phases in Zeolite Micropores

Figure 7 illustrates the steady-state *in situ* absorbance CIR-IR spectrum of P-Octacat performing catalytic cracking of heptane at 475°C and at variable pressures of 6.7, 16.5, 41.6 bar respectively. The quality of the spectra at such high temperatures and pressures should be emphasized. This broad range spectrum was of special importance since it probed the catalyst, the reactant hydrocarbon, and products. As stated earlier (27), the spectral region between 3800 and 3100 cm^{-1} corresponds to the stretching frequencies of the zeolite's hydroxyl groups. The region between 3100 and 2700 cm^{-1} corresponds to the stretching C–H modes of the hydrocarbons while the spectral region between 1750–1650 cm^{-1} and 1625–1500 cm^{-1} corresponds to the stretching vibration modes of the C=C bonds of the olefinic and aromatic coke products, respectively. The band assignments and the corresponding integrated intensities for the spectral region between 1750 and 1500 cm^{-1} at different operating pressures are presented in Table 2. Finally, the region between 1480–1360 cm^{-1} and 1350–700 cm^{-1} correspond to the C–H bending modes of the hydrocarbons and the vibrational modes of the structural units of the zeolite framework (external linkages and internal tetrahedra), respectively. Two important conclusions could be drawn from this figure. First, the integration of the spectral region between

TABLE 2

Analysis of the C=C Stretching Vibration Modes for Coke Compounds

	Integrated intensities		
	($P = 41.6$ bar)	($P = 16.5$ bar)	($P = 6.7$ bar)
	Olefinic bands		
1730, 1695, 1650 cm^{-1}	2.70	4.00	4.47
	Aromatic bands		
1620, 1550, 1500 cm^{-1}	2.00	3.42	10.30
Total area	4.70	7.42	14.77
Aromatic/olefinic	0.74	0.86	2.30

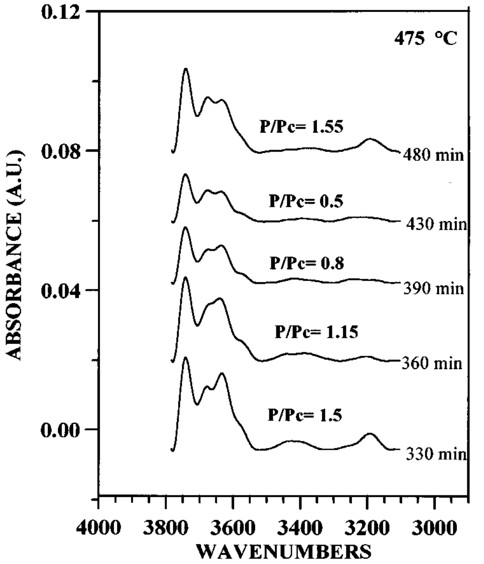

FIG. 8. *In situ* monitoring the spectral region that corresponded to the C–H stretching frequencies of *n*-heptane at variable reduced pressures during reaction over P-Octacat. The spectral region was compared to *n*-heptane flowing in an empty bed at 475°C and 41.6 bar.

1750 and 1500 cm^{-1} (Table 2) showed that both olefinic (1750–1650 cm^{-1}) and aromatic coke (1625–1500 cm^{-1}) were much higher for the subcritical experiments (6.7 and 16.5 bar). The aromatics showed almost a two and a five-fold increase for the subcritical experiments of 16.5 and 6.7 bar, respectively, whereas the olefinic products showed almost a twofold increase for the same subcritical experiments. These results clearly demonstrate a higher degree of aromaticity for the coke compounds produced under subcritical conditions (Table 2). Second, the spectral intensity of *n*-heptane C–H stretching vibrations (3100 to 2700 cm^{-1}) under supercritical conditions (41.6 bar) was much higher than the subcritical experiments (6.7 and 16.5 bar). Furthermore, the intensity at 41.6 bar was much stronger than that in a reactor containing pure heptane with no catalyst under the same conditions (Fig. 8). This behavior is a strong indication of a denser phase of *n*-heptane in the zeolite micropores under supercritical conditions since the absolute intensity is directly proportional to the concentration of the compound by Beer's law. Therefore, increases in the density of *n*-heptane would be reflected as an increase in the absolute intensity of the spectral region that corresponded to the C–H stretching frequencies of *n*-heptane. However, this result suggested the possibility that the density of *n*-heptane within the zeolite micropores might be higher than the values calculated by the equations of state. All these facts are clearly demonstrated in Fig. 8. As this figure shows, the absolute intensity of supercritical *n*-heptane over the catalyst at 475°C and a reduced pressure of 1.55 was almost 17 times higher than supercritical *n*-heptane flowing in an empty bed (no catalyst) under the same operating conditions. Decreasing the reduced pressure further during heptane flowing through the catalyst bed resulted in the reduction of the absolute intensity of the *n*-heptane spectral region (i.e., almost nine times for $P/P_c = 1.15$ and three times for $P/P_c = 0.5$). The above results clearly explained the increase in the catalytic activities and the decrease in the deactivation rates as a function of reduced pressures (Fig. 2) due to the formation of a denser phase in zeolite micropores, which would eventually result in a more facile coke removal rate.

We are currently working on the quantification of supercritical fluid densities in the catalyst micropores by CIR-FTIR analysis. The studies will be further extended to the determination of the effect of pore volume on the supercritical fluid densities.

Reactivation of a Moderately Deactivated Catalyst

To investigate the possibility of regenerating a moderately deactivated catalyst, the following experiment was performed: After 5.5 h of reaction at 475°C and 41.6 bar (48% of the original activity was lost after 5.5 h of catalytic cracking under these conditions), the system pressure was reduced gradually to subcritical values at constant residence time, for further deactivation of the catalyst. The results are illustrated in Fig. 9. In this figure, the bottom curve presents the final status of the catalyst after 5.5 h of cracking under supercritical conditions. Reducing the pressure gradually from 41.6 bar ($P/P_c = 1.55$) to 13.7 bar ($P/P_c = 0.5$) through 29.4 bar ($P/P_c = 1.15$) and 21.6 bar ($P/P_c = 0.8$) in 100 min at a constant residence time of 0.9 s caused a significant reduction in the active site concentrations (3800–3500 cm^{-1}) and in the olefin and paraffin interactions, (3450–3100

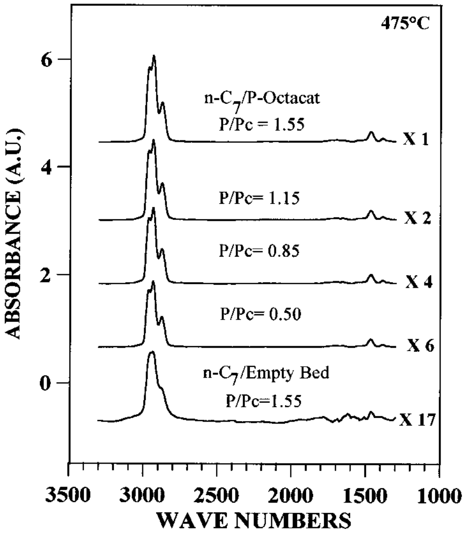

FIG. 9. *In situ* monitoring of the active sites of P-Octacat partially deactivated at 475°C and 41.6 bar . The catalyst was further tested under subcritical conditions by reducing the pressure from 41.6 bar to 29.4, 21.6, and 13.7 bar, respectively. The pressure was later increased back to 41.6 bar.

cm^{-1}). The kinetic measurements showed that the activity decreased from 52 to 22% with the corresponding reduction in pressure from 41.6 to 13.7 bar. However, when the pressure was increased back to 41.6 bar, as can be clearly seen from the top spectrum in Fig. 9, the acid sites that were lost during subcritical cracking reappeared in the spectrum with a considerable increase in the olefin and paraffin interactions. However, both the curve-fitting and the activity results revealed that the recovery was not complete. The final activity level achieved was 38.4%.

These results clearly showed that the supercritical fluid not only dissolved the freshly formed precursors and maintained catalytic activity (15) but it also partially dissolved the extra coke that was formed under subcritical conditions and resulted in a comparably more active catalyst.

CONCLUSIONS

The *in situ* CIR-IR technique showed a definite superiority for the quantitative analysis of a high-temperature heterogeneous catalytic process (catalytic cracking) under subcritical and supercritical conditions. High-quality spectra were acquired at temperatures of 475°C, and up to 41.6 bar.

The concentration of acid sites decreased dramatically during catalytic cracking under subcritical conditions. Almost 80% of the catalytic activity was lost under those conditions (475°C, 16.5 bar). Approaching industrial operating pressures caused a rapid carbon build-up and plugged the reactor (6.7 bar). However, when the system was operated under supercritical conditions of the hydrocarbon, comparably smaller changes were observed in the acid site concentrations. The catalyst lost only 48% of its original activity after 5 h of operation under these conditions (41.6 bar).

The CIR-FTIR technique clearly showed that the supercritical fluid exhibited a superdense behavior (i.e., high coke solubilization power) within the micropores of the catalyst more than the estimated density by the equations of state. The effect became stronger at higher pressures. This important finding will allow us to gain better insights into the determination of optimum operating conditions (i.e., reaction densities) for different catalysts to be used in supercritical hydrocarbon processing.

The catalyst that partially deactivated at 475°C and 41.6 bar was further processed under subcritical conditions. The acid site concentrations and the olefin and paraffin interactions dramatically reduced during subcritical processing. However, the transition from subcritical to supercritical conditions provided a partial recovery of the acid sites with a corresponding increase in catalytic activity.

The *in situ* CIR-FTIR technique coupled with on-line gas chromatography analysis provided strong experimental proof of the fact that supercritical reaction media can be successfully employed to extract coke and coke precursors from porous catalysts. This eventually resulted in higher catalytic activities and a longer lifetime of the catalyst.

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