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Isomerization of 1-Hexene over Pt/γ-Al_2O_3 Catalyst: Reaction Mixture Density and Temperature Effects on Catalyst Effectiveness Factor, Coke Laydown, and Catalyst Micromeritics

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The coking of a highly porous commercial Pt/γ-Al_2O_3 catalyst via an olefinic precursor, viz., 1-hexene, was investigated in a CSTR over a range of temperatures and pressures that encompass low density subcritical as well as dense supercritical regions of operation. Temporal changes in catalyst effectiveness factor, a measure of catalyst activity, are presented for coking in subcritical and supercritical reaction mixtures at three different reactor temperatures between 1.01 and 1.10 T_c. The coke laydown during each run along with coked catalyst characteristics such as BET surface area, pore volume, and pore volume distribution are also reported. The maintenance or decay of catalyst activity is dependent upon the relative rates of coke formation and of coke extraction through the catalyst pores. Each of these rates is dictated by density and temperature. At each temperature studied, there is insignificant coke extraction in subcritical reaction mixtures and hence catalyst effectiveness factor decreases with time. Also, when 1-hexene isomerization is kinetically controlled, there is volume loss in both high activity (20–80 Å) and low activity (100–600 Å) pores indicating coke laydown throughout the catalyst pore structure. In low to moderate supercritical density reaction mixtures, the effectiveness factor decreases rapidly accompanied by reduced coke laydown and virtually no volume loss in the high activity pores. This is attributed to extensive pore mouth plugging of the high activity pores caused by increased coke formation rates relative to coke extraction rates. In dense supercritical reaction mixtures ($>1.7\ \rho_c$), the enhanced solubilities of the coke compounds in the reaction mixture alleviate pore mouth plugging of the high activity pores, as evidenced by an increase in the effectiveness factor and by extensive volume and surface area losses in the high activity pores. At the highest density studied ($2.53\ \rho_c$), while effectiveness factors are smaller than subcritical values at 1.01 T_c, up to two-fold enhancements in temporal effectiveness factors are seen at 1.10 T_c. A theoretical model is needed to better understand the density and temperature effects on the physicochemical processes underlying coke deposition with simultaneous extraction in porous catalysts.

INTRODUCTION

The chemistry of coke formation and the physical mechanism of coke deposition on metal catalysts have been the focus of numerous investigations over the last three decades. These topics are reviewed in detail in several papers and books (*1–8*). The primary reasons for coke buildup are the relatively low volatilities of the coke compounds that are formed and the low densities (and hence low coke solubilizing power) of the subcritical gas phase reaction mixtures. The coke buildup eventually leads to total deactivation of the catalyst. By employing supercritical reaction mixtures as solvent media to extract the coke compounds, it has been demonstrated that the activity of *low surface area, low activity* catalysts can be maintained constant with time (*9*). The cited advantages include *in situ* maintenance of catalyst activity at mild thermal conditions under which thermal degradation of the catalyst is avoided.

More recently, the feasibility of using supercritical reaction mixtures for maintain-

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ing the activity of *porous, highly active* industrial catalysts was assessed through experimental investigations of the Pt/γ-Al_2O_3 catalyzed isomerization of an olefinic coke precursor, viz., 1-hexene, in a continuous stirred tank reactor (CSTR) (*10*). The temporal variation of 1-hexene conversion with time is employed as the primary measure to assess catalyst activity variation with time. At subcritical densities, there is virtually no coke extraction and hence 1-hexene conversion decays with time. At low to moderate supercritical densities, coke formation rates increase without any appreciable increase in coke extraction. This leads to a faster decay of 1-hexene conversion as compared to subcritical operation. At relatively high densities ($>1.7\ \rho_c$), the enhanced solubilities of the coke compounds in the reaction mixture leads to increased 1-hexene conversions and a slower decay of conversion with time.

While the 1-hexene conversion versus time profiles provide an indication of the maintenance or decay of catalyst activity, they do not provide direct information about the fraction of the catalytically active sites that are available for reaction. This paper focuses on the effects of subcritical and supercritical operation on catalyst effectiveness factor and catalyst coking at the *pellet level.* The "effectiveness factor" is defined as the ratio of the observed 1-hexene isomerization rate to that attainable in the absence of catalyst deactivation *and* transport resistances. The effectiveness factor provides a better measure (as compared to mere 1-hexene conversion values) of the ability of the reaction mixture to uncover coked surfaces of the catalyst or to maintain catalyst activity at a given level. Temporal changes in catalyst effectiveness factor, a measure of catalyst activity, are presented for the Pt/γ-Al_2O_3 catalyzed isomerization of 1-hexene in a CSTR at subcritical and supercritical reactor operating conditions. In addition, the amount of coke laydown during a run along with the surface area, pore volume, and pore volume distribution for the coked catalyst are reported. Based on these results, the relative effectiveness of subcritical and supercritical reaction mixtures to maintain activity of a porous catalyst and the physical mechanism of coke buildup at the various reactor operating conditions are discussed.

METHODS

Catalyst

The catalyst employed for 1-hexene isomerization is a commercial Engelhard E-302 Pt/γ-Al_2O_3 reforming catalyst. The fresh catalyst was aged for 14 h in a flowing stream of bone dry CO_2 at 330°C and 20 bar prior to each run. The properties of the fresh and aged catalysts are summarized in Table 1. Note that while the aging process results in a decrease in pore volume and surface area, virtually all of the surface area and nearly all of the pore volume reside in pores in the 20–200 Å diameter range. The catalyst can therefore be characterized as microporous to mesoporous, and the *in situ* extraction of certain high molecular weight coke compounds may be hindered by pore diffusion limitations.

Experimental

The experimental unit consists of an Autoclave Engineers' Supercritical Extraction Screening System equipped with a 300-cc CSTR. The unit is composed of the feed preparation, the autoclave reactor, and the sampling sections. The reaction takes place on the catalyst housed in three symmetrically positioned stationary beds in the reactor. More details of construction, safety features, and sample analysis are provided elsewhere (*11, 12*).

The experiments consist of measuring 1-hexene conversion and product isomer composition with process time. The experimental pressures and temperatures were chosen to cover a wide range of reduced densities ranging from low density gaseous reaction mixtures to dense supercritical reaction mixtures. The lower temperature limit is constrained by the critical tempera-

TABLE 1

Properties of the Fresh and Aged Catalysts

Cat. properties			% Pore volume				% Surface area			
			Pore diameter range (Å)				Pore diameter range (Å)			
State	SA[a] (m^2/g)	PV[b] (cc/g)	20–50	50–100	100–200	200+	20–50	50–100	100–200	200+
Fresh	225	0.62	17	45	30	8	39	44	15	2
Aged	140	0.38	13	37	39	12	32	40	24	3

Note. Englehard E-302 1/16 in. Pt/γ-Al_2O_3 catalyst extrudates, chlorided and sulfided, Pt loading: 0.6 wt%.

[a] Total BET surface area.

[b] Total pore volume.

ture of 1-hexene (T_c = 231°C), while the upper temperature limit is dictated by the safest allowable reactor pressures for dense supercritical operation. Critical phase behavior of 1-hexene/product isomer reaction mixtures was predicted theoretically as described elsewhere (*11, 12*).

The experimental procedure consists of pumping 1-hexene into the reactor starting from a nil pressure head. When the desired operating pressure is reached, reactor effluent flow is established. Reactor effluent is expanded through a micrometering valve, condensed in a separator vessel, and then subjected to GC/FID analysis. The 1-hexene conversions and reaction rates are then easily calculated. At the end of each run, the reactor content is rapidly emptied (in less than 5 min.), and then flushed with CO_2 for about 1 h. The reactor furnace is then turned off and, after sufficient cooling, the coked catalyst particles are removed from the reactor. After weighing for determination of coke laydown, the coked catalyst particles are characterized with respect to surface area, pore volume, and pore volume distribution using a Digisorb 2500 surface area and pore volume analyzer.

Intrinsic kinetic parameters of the 1-hexene isomerization reaction, needed to transform conversion versus time profiles into temporal effectiveness factor profiles, were obtained from conversion data acquired under conditions of negligible transport resistances, and under essentially no catalyst deactivation. Details of the experimental procedure and data analysis for obtaining kinetic parameters may be found elsewhere (*12*). The isomerization of 1-hexene over Pt/γ-Al_2O_3 catalyst was found to be first order with respect to 1-hexene concentration, with an activation energy of approximately 69.5 kJ/mol. This value agrees well with those previously reported for similar reactions (*13, 14*). The kinetic parameters are then used in a CSTR model to predict 1-hexene isomerization rates that may be expected in the absence of deactivation and transport limitations. The ratio of the observed to the predicted rates yields the effectiveness factor. The results are presented in the form of the catalyst effectiveness factor versus time profiles at the various reactor operating conditions.

RESULTS AND DISCUSSION

Temporal Variation of Catalyst Effectiveness Factor in Subcritical and Supercritical Reaction Mixtures

Results at 238°C. Figure 1 provides results of effectiveness factor versus time obtained at 238°C (1.01 T_c) and various pressures (0.87–5.6 P_c). The 1-hexene feed

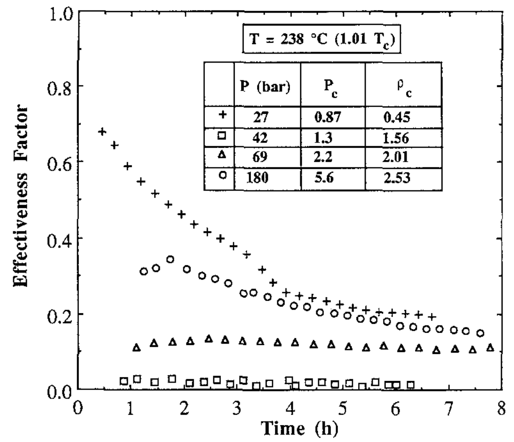


FIG. 1. Temporal variations of catalyst effectiveness factor at 238°C (1.01 T_c) and different reaction mixture densities (0.45–2.53 ρ_c).

flow rates varied between 222 and 209 cc/h, and catalyst loading was 1 g. The results of all runs were reproducible within 5–15%. The initial time corresponds to the time at which 1-hexene injection was commenced, and the effectiveness factor values are based on the average composition of the cumulative sample between two consecutive sampling times following reactor fill-up.

In the absence of catalyst deactivation, the effectiveness factor should be constant over time (unity in the absence of mass transfer limitations). For the subcritical run at 27 bar (0.87 P_c, 0.45 ρ_c), the density or solvent power of the reaction mixture is too low to extract the heavy coke compounds from the catalyst in appreciable amounts. Therefore, as seen in Fig. 1, the effectiveness factor decreases with time due to the buildup of coke compounds. Note that initial values of the effectiveness factors (i.e., values based on analysis of the first samples collected following reactor fill-up) are relatively high as compared to the supercritical runs. This is to be expected because at this pressure and temperature, diffusivities are gas-like and reaction rates are relatively low. Two modes of catalyst deactivation that are typical of reactions in porous catalysts at subcritical operating conditions are observed in this run. The high deactivation rate between 0.5 and 4.3 h corresponds to direct suppression of active catalytic sites, while the relatively lower deactivation rate between 4.3 and 6.8 h is attributed to catalyst deactivation by transformation of the coke precursors to heavier coke compounds.

Initial effectiveness factors for the supercritical runs are relatively low for all runs, implying that a large fraction of catalyst activity was lost during the reactor fill-up period. The value during the run at 42 bar is generally low (2%) during most of the run, indicating that a significant loss of catalyst activity has taken place in going from 27 to 42 bar (1.3 P_c, 1.56 ρ_c) during the fill-up period. Effectiveness factors at 69 bar (2.2 P_c, 2.01 ρ_c) are at least an order of magnitude higher than those at 42 bar. An increase in pressure from 69 to 180 bar (5.6 P_c, 2.53 ρ_c) induced an at least three-fold increase in the catalyst effectiveness.

The increased catalyst effectiveness is attributed to the enhanced solubilities of the coke compounds in the dense supercritical reaction mixture. In contrast to the clear effluents during the subcritical run at 27 bar, the product effluent bore a yellow color throughout the supercritical runs at 42 bar (1.56 ρ_c) and 69 bar (2.01 ρ_c) and a light brown color throughout the run at 180 bar (2.53 ρ_c) indicating increased amounts of coke compounds in the reactor effluent. GC/FID analysis of the effluent confirmed increased extraction of heavy hydrocarbons (C_{12}–C_{24}) with increasing densities. However, an isothermal increase from moderate to dense supercritical pressures brings about only partial catalyst reactivation. Effectiveness factors continue to be smaller than those at subcritical pressures. Clearly, the increase in solubilization of the coke deposits brought about by an increase in reaction mixture densities is offset by an accompanying increase in coking rates. The decrease in catalyst activity at supercritical pressures and the higher rate of activity

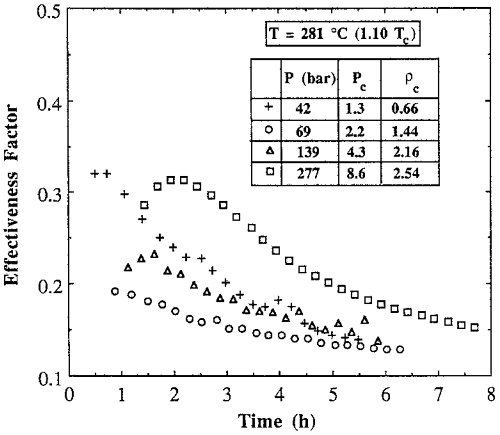


FIG. 2. Temporal variations of catalyst effectiveness factor at 281°C (1.10 T_c) and different reaction mixture densities (0.66–2.54 ρ_c).

loss at subcritical pressures have also been observed for the disproportionation of 1-4-diisopropyl benzene on a highly porous zeolite catalyst (*15*).

Results at 281°C. Figure 2 presents effectiveness factor versus time profiles at 281°C (1.1 T_c) and at several pressures. As observed at 238°C, a majority of the catalyst activity was lost during the fill-up period, which lasted about 17 min for the run at 42 bar (1.3 P_c, 0.66 ρ_c), 35 min for the 69 bar (2.2 P_c, 1.44 ρ_c) run, 69 min for the 139 bar (4.3 P_c, 2.16 ρ_c) run, and 90 min for the 277 bar (8.6 P_c, 2.54 ρ_c) run. As before, initial effectiveness factor during the subcritical run is higher than in other runs at higher pressures. For operation at 42 bar, about 66% of the original catalyst activity was lost by the end of the reactor fill-up period. An increase in pressure to 69 bar resulted in an additional 15% loss of the catalyst activity at the end of the fill-up period, which remained unrecoverable at that pressure. A further increase in pressure to 139 bar resulted in a 5% recovery of the original catalyst activity and a final increase to 277 bar resulted in an additional recovery of up to 8% of the original catalyst activity. Hence, an overall gain in activity of about 13% results when increasing the mixture density from 1.44 ρ_c to 2.54 ρ_c. GC/FID analysis of the reactor effluent indicated that at higher densities greater amounts of heavy hydrocarbons were extracted with a wider molecular weight distribution (C_{12}–C_{30}). While effectiveness factors at the highest density (2.53 ρ_c) are smaller than subcritical values at 238°C, up to two-fold increases in the effectiveness factors are observed at a similar density at this higher temperature.

Reaction Mixture Density Effects on Coke Laydown, Surface Area, Pore Volume, and Pore Volume Distribution

Following the various runs depicted in Figs. 1 and 2, catalyst weight, adsorption isotherms, surface area, and pore volume distributions were determined for the coked catalyst samples. Table 2 summarizes the measured values of coke laydown, BET surface area, total pore volume, and the percentage of initial volume remaining in the pores of the coked catalyst. Coke laydown is reported as the percentage gain in catalyst weight at the end of a run. This weight gain is attributed to coke deposits that are not volatile at the reactor operating temperature and at atmospheric pressure. Figures 3(a)–3(c) display the trends pertaining to the variations of coke laydown, surface area, and pore volume with reaction mixture densities at 238 and 281°C. Figures 4 and 5 provide the relative pore volume distributions in the aged and coked catalysts. The percentage of cumulative pore volume remaining in the catalyst is plotted versus pore diameter. Percent pore volume up to a given average pore diameter d_p is defined as the fraction of the total pore volume occupied by pores of diameter in the range 20-d_p. Note from Figures 3(a)–3(c) that minimum coke laydown, and maximum surface area and pore volume, are seen to occur at a reaction mixture density of roughly 2.0, the value near which the catalyst activity is also a minimum. At both temperatures, an increase in coke laydown has the effect of reducing both the surface area as well as the pore volume.

TABLE 2

Reaction Mixture Density Effects on Coked Catalyst Characteristics

Coking conditions			Catalyst properties			Pore volume of aged catalyst remaining (%)					
						Pore diameter range (Å)					
P (bar)	T (°C)	ρ_c	CL[a] (wt%)	SA[b] (m_2/g)	PV[c] (cc/g)	20–40	40–60	60–80	80–100	100–300	300–600
27	238	0.45	25.8	27.2	0.095	26	16	15	15	30	50
42	238	1.56	17.0	59.9	0.202	103	110	89	23	56	100
69	238	2.01	11.2	126	0.352	193	160	119	64	66	100
207	238	2.53	13.2	65.4	0.222	20	50	86	76	53	85
42	281	0.66	13.4	96.1	0.300	58	52	78	68	72	100
69	281	1.44	12.9	112	0.308	82	64	73	75	73	62
277	281	2.54	23.9	5.6	0.049	0	0	0	9	21	53

[a] Coke laydown.

[b] Surface area.

[c] Pore volume.

Results at 238°C. The coke laydown during the run at 27 bar is relatively high (25.8 wt%) and the surface area and pore volume are the lowest. Furthermore, as shown in Table 2, a majority of the pore volume is lost in both the high and low activity pore diameter ranges, shifting the pore volume distribution curve below that for the aged catalyst (see Fig. 4). This suggests that at this relatively low temperature and subcritical pressure, because of gas-like diffusivities, the reactions occur throughout the catalyst pores and the entire catalyst pore structure is affected by coking. This mode of catalyst coking is characteristic of coking

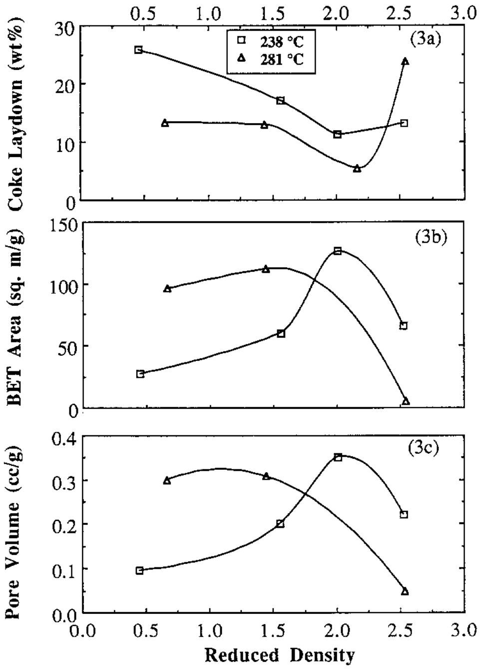


FIG. 3. Effect of reaction mixture density on (a) overall coke laydown, (b) BET surface area, and (c) total pore volume, at 238 and 281°C.

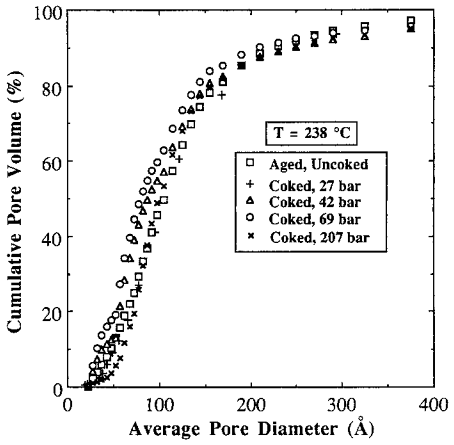


FIG. 4. Pore volume distribution in catalysts coked at 238°C and in subcritical and supercritical reaction mixtures.

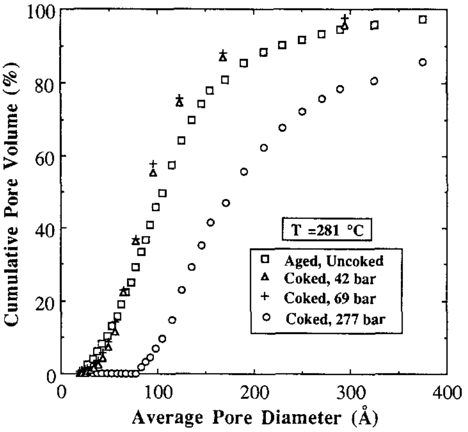


FIG. 5. Pore volume distribution in catalysts coked at 281°C and in subcritical and supercritical reaction mixtures.

mechanisms wherein the reaction rates are kinetically controlled (*16*). The coke deposits eventually cause total pore blockage.

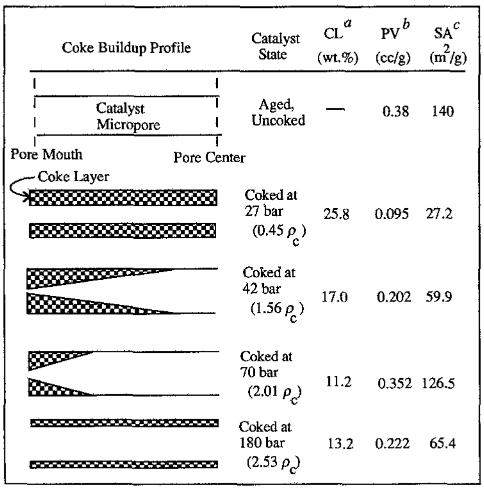
The coke laydown decreases, and the surface area and pore volume increase, as the reaction mixture density is increased to a moderate supercritical value of 1.56 ρ_c. Note that pore volumes in the high activity, 20–80 Å, pores and in the low activity, 300–600 Å, pores are intact and virtually coke-free. However, there is appreciable loss of pore volume in the 80–300 Å pores. This is possible only if the high activity pores (20–80 Å) are blocked and are therefore inaccessible to the reactants. The extremely low (2%) effectiveness factors during this run support this explanation. In the pressure range between 27 and 42 bar, the self-diffusivity of 1-hexene, evaluated using the generalized correlation of Lee and Thodos (*17*), decreases from 7.8 (10^{-8}) to 3.7 (10^{-8}) $m^2\ s^{-1}$. This two-fold decrease in diffusivity and the nearly three-fold increase in reaction mixture density (i.e., in reaction rate) have apparently led to severe pore diffusion limitations resulting in pore mouth blockage of the smaller pores. Note, however, that the reaction mixture is able to maintain coke-free zones in the low activity, 300–600 Å pores.

A further increase in the reaction mixture density to 2.01 ρ_c leads to a reduction in coke laydown and an increase in the remaining surface area and pore volume. Most interesting is the observation of almost one-and-a-half times as much pore volume in the 20–80 Å pores as compared to that in the uncoked, aged catalyst. This is also reflected in Fig. 4 by the shift in the pore volume distribution curve above that for the aged catalyst. Once again, there seems to be pore mouth plugging of the high activity pores due to severe pore diffusion limitations. The significant additional volume in the 20–60 Å pores as compared to the aged catalyst is most likely due to coking of the larger pores, which produces pores of smaller diameter. Although the reaction is confined to a smaller surface area, the catalyst activity during this run is nearly an order of magnitude higher than in the 1.56 ρ_c reaction mixture. The increase in activity, the darker reactor effluent, and the decrease in coke laydown in going from low supercritical (1.56 ρ_c) to moderate supercritical (2.01 ρ_c) reaction mixtures seem to be primarily due to enhanced solubilities of the coke compounds, which result in longer sustainment of catalyst activity. It appears that this density marks the onset of solubilization of coke compounds in appreciable amounts.

An increase in reaction mixture density from 2.01 to 2.53 ρ_c induced a roughly three-fold increase in the effectiveness factor. While coke laydown increased by roughly 18%, the surface area and pore volume decreased by roughly 48 and 37% respectively. The enhanced extraction of the deposited coke compounds renders virtually all pores accessible to the reactants as evidenced by volume losses in pores of all sizes. Hence, despite a reduction in the diffusivity of the reactants, the increase in solvent power at higher densities has apparently caused some alleviation of pore blockage, rendering the high activity pores more accessible to reactants. High activity regions are most susceptible to coking as evidenced by the rather notable decrease in the pore volume in the 20–80 Å diameter range (see Table 2 and Fig. 4). These observations corroborate well with the larger effectiveness factors and higher rates of activity loss observed at this pressure (see Fig. 1).

Based on the foregoing explanations, a conceptual model for coke buildup in a micropore is presented in Fig. 6 for operating conditions ranging from low density subcritical to dense supercritical reaction mixtures. The shading of the coke layer, although not truly representative of the geometric structure of the coke deposits, is reasonably appropriate since coke forms as aggregates around specific sites in the catalyst pores and not as a continuous layer (*4*). At the subcritical density, pores of all sizes are affected by coking, and coke laydown is highest because of the low coke solubilizing power of the reaction mixture. An increase in the reaction mixture density from 0.45 to 1.56 ρ_c results in extensive pore-mouth plugging of the micropores due to a combination of increased reaction rates, decreased diffusivities, and relatively low solvent power of the reaction mixture.

An isothermal increase in the reaction mixture density to 2.01 ρ_c leads to more severe pore diffusion limitations as evidenced by the larger remaining surface area and remaining pore volume in the coked catalyst. The higher catalyst activity in the 2.01 ρ_c reaction mixture (as compared to that in the 1.56 ρ_c reaction mixture) is attributed to the enhanced solvent power, and therefore enhanced coke extraction, of the 2.01 ρ_c reaction mixture which is able to maintain a larger fraction of uncoked catalyst surface during the run. A further increase in the reaction mixture density to 2.53 ρ_c results in an appreciable increase in the extraction of the coke compounds and therefore in an alleviation of pore-mouth plugging. All pores are now accessible to the reactants as evidenced by the loss in surface area and pore volume in pores of all sizes. Hence, the enhancement in solvent power allows the reactants to diffuse farther into the pores. In such a case, catalyst coking occurs progressively from the wall to the center, eventually resulting in pore closure.



[a] Coke laydown
[b] Pore volume
[c] Surface area

FIG. 6. Proposed mechanism of coke buildup in a micropore at subcritical and supercritical operating conditions.

The foregoing explanation based on coked catalyst micromeritics is also corroborated by the predominantly parallel coking mechanism observed at subcritical and supercritical densities at 238°C (*18*). It thus appears that, for similar coking pathways, the physical mechanism of coke buildup with simultaneous coke extraction depends on the density of the reaction mixture and is quite different from the buildup in the absence of any coke extraction. Therefore, new theoretical models are needed to establish the interdependence between coking pathways and coke buildup mechanism in the presence of coke extraction.

Results at 281°C. There is little difference in coke laydown, surface area, and pore volume in the catalysts coked in subcritical to moderate supercritical density (0.66–1.44 ρ_c) reaction mixtures. In the latter case, however, smaller pores were less affected by coking supporting the hypothesis that pore diffusion limitations increase with increasing densities. The coke laydown decreases to 5.4 wt% at 2.16 ρ_c and then increases significantly to 23.9 wt% as the density is increased to 2.54 ρ_c. At this density, there is virtually total loss of volume in pores of diameter less than 100 Å. The increased amount of coke laydown and the extensive loss of surface area and pore volume in the 2.54 ρ_c reaction mixture are therefore attributed to the ability of the reaction mixture to pervade all catalyst pores. Thus, despite the decreased diffusivity of the dense supercritical reaction mixture, the enhanced solubilities of the coke compounds seem to alleviate pore mouth plugging and thereby to allow the reactants to diffuse farther into the pores. Note also from Table 2 that the high activity, 20–100 Å pores are more rapidly plugged than the larger ones. This is more clearly seen in Fig. 5 from the significant shift in the pore volume distribution to larger pores. Thus, the qualitative trends of the variations of catalyst activity and coke laydown with reaction mixture density are similar at the two temperatures studied.

The foregoing observations indicate that initial catalyst activity, pressure, temperature, and catalyst pore size distribution play a major role in determining the extent of catalyst activity maintenance at supercritical conditions. It is clear that an optimum combination of these parameters that yields a low reaction rates, high reaction mixture densities, and large pores (relative to the size of the molecules to be extracted) is needed for continuous, *in situ* maintenance of catalyst activity at supercritical conditions. Indeed, it has been shown that a combination of lower coking rates and dense supercritical reaction mixtures, obtained by introducing an equimolar feed mixture of 1-hexene and carbon dioxide, favors continuous maintenance of catalyst activity (*10*).

Temperature Effects

The variation of activity with density and temperature may be better discerned from Fig. 7. The data points represent catalyst effectiveness factors determined from analysis of the initial samples during the runs represented in Figs. 1 and 2. Since the feed flow rates are roughly the same, Fig. 7 may also be viewed as the change in catalyst activity during reactor fill-up. Note that for eventual operation at a supercritical density, the reaction mixture density has to pass through a subcritical phase. At each temperature, the data were regressed with a second degree polynomial. At 238°C, extrapolation of the left branch of the curve to low densities yields an initial effectiveness factor around unity. Indeed, at the lower densities of this operating temperature, the gas-like diffusivities are high relative to the reaction rates, resulting in appreciable catalyst effectiveness factors and catalyst activities.

In sharp contrast, extrapolation of the left branch of the activity curve at 281°C yields an initial effectiveness factor of roughly 0.53. This deviation from unity may indicate the existence of mass transfer limitations at these operating conditions. As the reaction mixture density is increased to low supercritical values, catalyst activity decreases at both temperatures due to pore

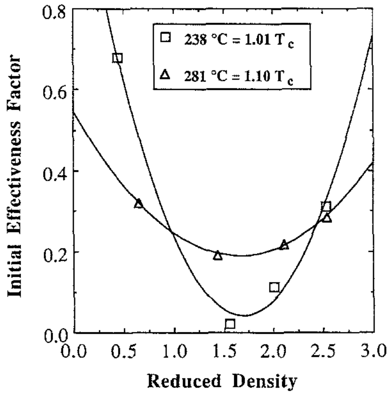


FIG. 7. Effect of reaction mixture density on catalyst effectiveness factor at 238 and 281°C.

diffusion limitations resulting in pore mouth plugging and in lower catalyst activities. As the density is increased further, a minimum activity occurs at a reduced density of 1.7 ρ_c. Beyond this density, the increased solubilities of the coke compounds in the reaction mixture has the effect of opening up blocked catalyst pores and thereby providing renewed access for the reactants to the catalytic sites, resulting in increased activities.

The reasons for the crossover of the activity curves at the two temperatures are not clear at this stage. Temperature appears to be a double-edged parameter. While solubilities of coke compounds are enhanced by the increase in vapor pressure of the coke compounds at higher temperatures, higher temperatures also lead to an increase in coking rates and to the formation of heavier coke compounds whose extraction may require much higher reaction mixture densities. Clearly, the magnitude of the effectiveness factor will be dictated by the types and amounts of the coke compounds formed, and by the ability of the reaction mixture to solubilize them.

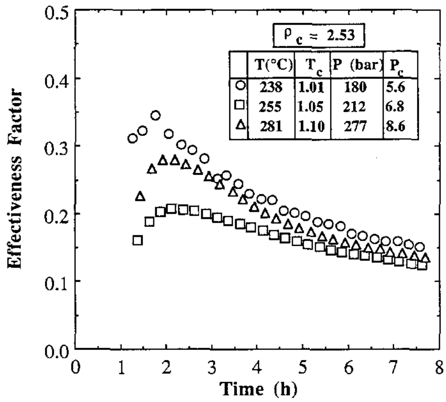


FIG. 8. Temporal variations of catalyst effectiveness factor at different temperatures (1.01–1.10 T_c) in reaction mixtures of similar density (2.53 ρ_c).

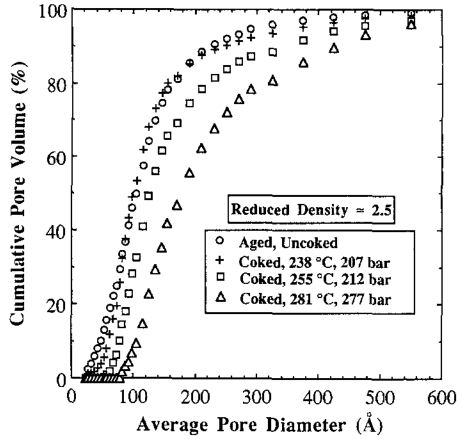


FIG. 9. Pore volume distribution in catalysts coked at different temperatures (1.01–1.10 T_c) in reaction mixtures of similar density (2.53 ρ_c).

The effect of temperature on the effectiveness factor may be better understood by considering Fig. 8, which compares the temporal effectiveness factor profiles obtained at three different temperatures in reaction mixtures of similar densities (2.53 ρ_c, 0.50 g/cc). Table 3 summarizes the measured values of coke laydown, BET surface area, total pore volume, and the percentage of initial volume remaining in the pores of the coked catalysts. Note that in dense supercritical reaction mixtures, catalyst activity decreases, passes through a minimum, and then increases with an increase in temperature from 238 to 281°C. The reasons for this behavior are unclear at this stage. The initial decrease in catalyst activity may be due to the formation of heavier coke compounds (which require much higher densities for their solubilization) while the recovery in catalyst activity at the higher temperature is due likely to vapor pressure enhancements of the coke solubility in the reaction mixture. As seen from Table 3, significant losses in catalyst surface area and in pore volume occur in the entire range of temperatures studied. These losses, along with the amount of coke laydown, increase with temperature. Increased temperatures bring about higher coking rates and thereby plugging of larger fractions of the catalyst pores. At 281°C, virtually all the 20–80 Å pores are totally plugged. This is also seen

TABLE 3

Temperature Effects on Coked Catalyst Characteristics

Coking conditions			Catalyst properties			Pore volume of aged catalyst remaining (%)					
						Pore diameter range (Å)					
P (bar)	T (°C)	ρ_c	CL^a (wt%)	SA^b (m²/g)	PV^c (cc/g)	20–40	40–60	60–80	80–100	100–300	300–600
207	238	2.53	13.2	65.4	0.222	20	50	86	76	53	85
212	255	2.53	20.4	22.3	0.097	0	4	23	29	32	71
277	281	2.54	23.9	5.6	0.049	0	0	0	9	21	53

[a] Same definitions as in Table 2.

in the rightward shift in the pore volume distribution curve with increasing temperatures in Fig. 9, which provides pore volume distribution curves for the uncoked aged catalyst, and for catalysts coked in a dense supercritical reaction mixture at three different supercritical temperatures.

The foregoing results indicate that the maintenance or decay of activity in porous catalysts depends upon the relative rates of coke formation on the catalyst and of subsequent extraction of the coke compounds from the porous matrix. While the intrinsic rate of coke formation is primarily affected by concentration (i.e., density) and temperature, the extraction rate is affected by the solubility of the coke compounds in the reaction mixture and by the effective diffusivity of the extracted compounds through the porous matrix. The solubility and the effective diffusivity are in turn dictated by density and temperature (*19, 20*). However, the individual effects of density and temperature on these rates are difficult to discern from the effectiveness factor versus time profiles and are as yet unclear. A suitable model is needed to better understand the physicochemical processes underlying the phenomenon of coke deposition with simultaneous extraction.

CONCLUSION

The coking of a highly porous commercial Pt/γ-Al_2O_3 catalyst via an olefinic precursor, viz., 1-hexene, was investigated in a CSTR over a range of temperatures and pressures that encompass low density subcritical as well as dense supercritical regions of operation. Employing 1-hexene/product isomer reaction mixtures as solvent media to extract the coke compounds, temporal changes in catalyst effectiveness factor are presented for catalyst coking in subcritical and supercritical reaction mixtures at three different reactor temperatures between 1.01 and 1.10 T_c. The coke laydown during each run along with coked catalyst characteristics such as BET surface area, pore volume, and pore volume distribution are also reported.

At each temperature studied, there is insignificant coke extraction in subcritical reaction mixtures and hence effectiveness factor decreases with time. Also, since 1-hexene isomerization at subcritical conditions is kinetically controlled, there is volume loss in both high activity (20–80 Å) and low activity (100–600 Å) pores indicating coke laydown throughout the pores. In low to moderate supercritical density reaction mixtures, the effectiveness factor decays rapidly, accompanied by a decrease in coke laydown and virtually no volume loss in the high activity pores. This is attributed to extensive pore mouth plugging of the high activity pores caused by increased coke formation rates as compared to coke extraction rates. In relatively dense reaction mixtures (>1.7 ρ_c), the enhanced solubilities of the coke compounds in the reaction mixture alleviate pore mouth plugging of the high activity pores, as evidenced by an increase in effectiveness factor, and by extensive volume and surface area losses in the high activity pores. At the highest density studied, while effectiveness factors are smaller than subcritical values at the lower temperature, up to two-fold enhancements in temporal effectiveness factors are seen at the higher temperature. Our results indicate that the maintenance or decay of catalyst activity with time is dependent upon the relative rates of coke formation and of coke extraction through the catalyst pores. Each of these rates is affected by reaction mixture density and temperature. However, the density and temperature effects are not clear from the effectiveness factor versus time profiles. In order to uncouple and better discern density and temperature effects, a single pore model that accounts for coke deposition and simultaneous extraction is needed.

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