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Olefinic Oligomer and Cosolvent Effects on the Coking and Activity of a Reforming Catalyst in Supercritical Reaction Mixtures

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During investigations of 1-hexene isomerization on a Pt/γ-Al_2O_3 catalyst, hexene oligomers are found to form in the fluid phase. The total amount of oligomers increased by roughly an order of magnitude with isothermal increases in pressure from subcritical to supercritical values. These oligomers are significant coke precursors, increasing the coke formation and catalyst deactivation rates. Dilution of the hexene feed with an inert cosolvent like *n*-pentane, such that the reaction mixture is at supercritical conditions, reduces oligomer concentrations while maintaining the *in situ* extraction of the coke-forming compounds. Consequently, coke laydown is significantly reduced resulting in increased isomerization rates and decreased deactivation rates. Although oligomer formation and coke laydown decrease continuously with cosolvent addition, there exists an optimum cosolvent fraction beyond which the isomerization rate becomes limited by 1-hexene concentration and hence decreases. It was determined that ppm levels of organic peroxides in the hexene feed, formed as a result of exposure to air during either storage or the experiments, aid the formation of hexene oligomers in the fluid phase. Pretreatment of the hexene feed with activated alumina results in the virtual elimination of the peroxides and a severalfold decrease in total oligomer concentration. Our results indicate that peroxide removal from the hexene feed *and* cosolvent addition can significantly improve isomerization rates, catalyst activity maintenance, and pore accessibility in supercritical reaction mixtures.

INTRODUCTION

The unique solvent and transport properties of supercritical fluids have been exploited in recent years for the *in situ* extraction of coke-forming compounds from porous catalysts (1–9). These and other applications of supercritical fluids in heterogeneous catalytic reactions are reviewed elsewhere (10). The cited advantages include faster reaction rates, enhanced activity maintenance, and desirable product selectivity. For 1-hexene (P_c = 31.7 bar; T_c = 231°C) isomerization on a Pt/γ-Al_2O_3 reforming catalyst, we recently showed that *near-critical* reaction mixtures are better than either subcritical (gas-like) or dense supercritical (liquid-like) mixtures for maximizing isomerization rates and minimizing deactivation rates (9). The 2-hexene/3-hexene selectivity ratio follows the 1-hexene isomerization rate trend. Coke laydown is more than twofold lower at near-critical relative to subcritical conditions. The *in situ* extraction of the coke compounds by near-critical and supercritical reaction mixtures prevents pore plugging that otherwise occurs at subcritical conditions during the 8-h runs. Although coke laydown continues to decrease in denser supercritical reaction mixtures, the isomerization rates are lower and the deactivation rates are higher due to pore diffusion limitations in liquid-like reaction mixtures. *Near-critical* reaction mixtures thus provide an optimum combination of solvent and transport properties for the better *in situ* extraction of the coke-forming compounds (when compared to gas-phase reaction mixtures) *and* for the faster transport of reactants and products (when compared to liquid-like reaction mixtures).

For 1-hexene reaction over α-Al_2O_3 and Pt/γ-Al_2O_3 catalysts, both Tiltscher *et al.* (1) and Saim *et al.* (11) report the presence of hexene oligomers (up to C_{30}) in the reactor effluent. Tiltscher *et al.* also noted that oligomers were present in the effluent *only* when the reaction is carried out at supercritical conditions. Since the increased appearance of the oligomers in the reactor effluent was accompanied by enhanced activity maintenance, Tiltscher *et al.* concluded that these oligomers were coke compounds extracted *in situ* from the catalyst. While Tiltscher *et al.* do not report the actual amounts of oligomers, Saim *et al.* reported over 4 wt% oligomers in the reactor effluent. Since coke laydown on the catalyst is typically up to 0.05 wt% of the reactor throughput, it seems unlikely that the oligomers, at two orders of magnitude higher production, could form entirely on the catalyst.

This paper addresses the following questions aimed at a better understanding of oligomer formation and its effect on catalyst activity and coking: (a) How does hexene oligomer formation vary in subcritical, near-critical, and dense supercritical conditions with and without the cata-

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TABLE 1

Operating Conditions for Oligomer Formation Studies at 281°C (1.1 T_c)

Pressure (bar)	Density (g/cc)[a]	Reduced density
21.7	0.050	0.21
35.5	0.101	0.42
52.7	0.204	0.85
70.0	0.287	1.20
139	0.412	1.72
222	0.475	1.98
277	0.502	2.09
346	0.528	2.20

[a] Evaluated using Peng–Robinson equation of state (13).

lyst? (b) How do the oligomers affect the isomer formation rate, catalyst deactivation rate, coke laydown, coked catalyst micromeritics, and coke density? (c) What is the major causative factor for oligomer formation? To what extent is oligomer formation mitigated by the addition of an inert cosolvent? How does this reduction in hexene oligomers affect the quantities mentioned in (c)? Answers to these questions have provided a better understanding of the effects of hexene oligomers and cosolvent addition on catalyst coking and activity in supercritical reaction mixtures, and thereby, rational strategies for catalyst activity maintenance in supercritical reaction mixtures.

EXPERIMENTAL

The reaction of 1-hexene on 1/16-in. Pt/γ-Al_2O_3 (Engelhard E-302) reforming catalyst extrudates was studied in a low-volume (10 ml) stainless-steel tubular reactor that permits rapid startup. With the reactor held at the operating temperature, the critical density was reached or passed in 2 min and the operating pressure was reached in less than 3 min in all supercritical density experiments. The reactor operating pressure was controlled with a computer-actuated, stepping-motor-driven micrometering valve. Details of construction and operation of the reactor unit are provided elsewhere (9, 12).

The Pt loading on the catalyst is 0.6 wt%. The catalyst was first pretreated in flowing nitrogen at 100 sccm in a pretreatment reactor at 330°C for 18 h, followed by hydrogen at 100 sccm at 330°C for 4 h. The pretreated catalyst was found to have a BET surface area of 175 m^2/g, total pore volume of 0.44 cm^3/g, and an average pore radius of roughly 50 Å. Oligomer formation with and without the catalyst was investigated at 281°C (1.1 T_c) and at several pressures that yielded reaction mixture densities ranging from gas-like to liquid-like values as shown in Table 1. Because the reaction mixture contains mostly hexene and its isomers, the critical properties remain virtually constant with 1-hexene conversion. For the catalytic runs, typical catalyst loading was 1 g and the space velocity was roughly 135 g hexene/g catalyst/h. By performing experiments at various hexene feed rates, it was found that the isomerization rates are free of external mass transfer limitations at the chosen space velocity (12).

In order to decrease the coke-precursor concentrations while maintaining the solubility of coke-forming compounds in the supercritical reaction mixture, a set of constant density experiments was performed by adding various proportions of an inert cosolvent to the hexene feed. The experiments were performed at 281°C with 1 g of catalyst at a feed flow rate of approximately 135 g/h. The operating pressures and densities for various cosolvent fractions are summarized in Table 2. The inert cosolvents chosen were *n*-pentane (P_c = 29.7 bar; T_c = 197.2°C) and *n*-hexane (P_c = 33.4 bar; T_c = 233.7°C). These solvents did not show either measurable reaction or coke laydown at a space velocity 135 g/h/g catalyst after 3 h of operation at 281°C and a pressure that yielded a reaction mixture density of 0.47 g/cc (318 bar in the case of *n*-pentane and 229 bar for *n*-hexane). Most of the runs were made with *n*-pentane as the cosolvent. The *n*-pentane fraction in the binary feed was varied from none to roughly 80 mole%. For each run, the operating pressure was varied to yield a supercritical density of 0.47 g/cc, equivalent to that with neat 1-hexene feed at 222 bar, and a density of 1.98 ρ_c. To obtain insights into cosolvent type and density effects, two additional runs were made at 50% cosolvent addition: one retaining *n*-pentane as a cosolvent but at a reduced pressure yielding a lower density of 0.29 g/cc (equivalent to the run without cosolvent addition at 70.0 bar with a density of 1.20 ρ_c) and the other with *n*-hexane instead of *n*-pentane added as a cosolvent at a density of 0.47 g/cc. Due to insufficient availability of 1-hexene from Lot

TABLE 2

Operating Conditions for Cosolvent Effect Studies

Cosolvent	Cosolvent fraction in feed (mole%)	Pressure (bar)	Density[a] (g/cc)	Run time (h)
None	—	222	0.475	10
n-Pentane	23.5	242	0.475	8
n-Pentane	49.2	265	0.475	8
n-Pentane	82.0	296	0.474	10, 14
n-Pentane	48.8	86.5	0.289	8
n-Hexane[b]	52.2	226	0.474	8

[a] Estimated using the Peng–Robinson equation of state (13).
[b] 1-Hexene feed contained 35% 1-hexene from Lot PT 060592.

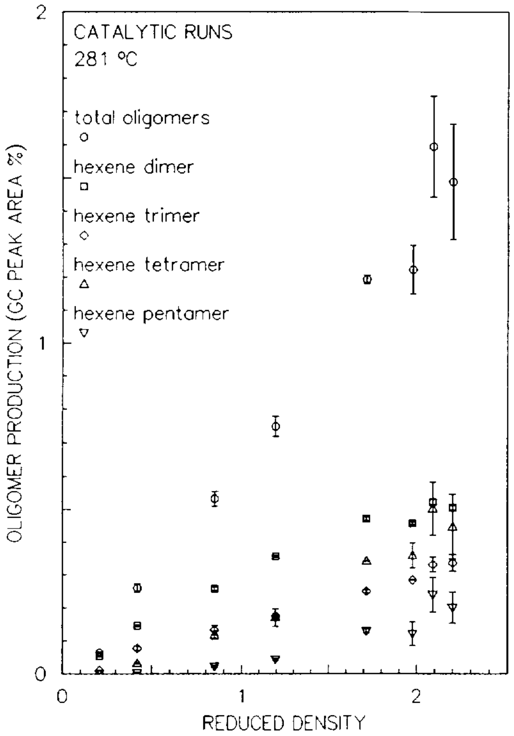

FIG. 1. Hexene oligomer production for catalytic runs.

851201, approximately 35% of the hexene feed used in the n-hexane cosolvent experiment was from Lot PT 060592.

An HP5890 GC/FID system was employed to measure the hexene isomers and oligomers in the reactor effluent. A Nermag R10-10 GC/MS system was used for structural identification of the hexene oligomers. Isomer formation rates, oligomer content, and product selectivity were calculated from these measurements. At the end of each run (typically 8 h), the catalyst was removed and characterized with respect to: (a) the quantity of coke laydown by gravimetric analysis, and (b) the pore volume and surface area distributions by nitrogen physisorption. Details of analytical instrumentation and procedures may be found elsewhere (9, 12).

RESULTS AND DISCUSSION

Oligomer Formation and Its Effects on Catalyst Activity and Coking

The amounts of hexene oligomers in the effluent of the catalytic and blank runs were measured as a function of reaction mixture density. Figure 1 shows the production of the hexene oligomers for the catalytic runs based on samples collected from 6 to 8 h of operation. The oligomer production plotted in Fig. 1 (and also in Figs. 2 and 4) is a measure of the oligomer concentration in the reactor effluent. The GC area% represents the fraction of the total area under the various oligomer peaks, the hexene isomer peaks, the unreacted hexene peak, and any inert cosolvent peak.

The amounts of the various hexene oligomers (dimer, trimer, tetramer, and pentamer) are seen to increase with isothermal increases in density. The *total* oligomer production was relatively minor at subcritical densities (0.064% at 0.208 ρ_c), but increased almost linearly by about 25-fold at a supercritical density of 2.09 ρ_c. As seen in Fig. 2, a similar behavior of oligomer production was seen in the blank runs performed in the absence of catalyst. Total oligomer production at 0.208 ρ_c was 0.24% and increased linearly with density to a maximum of 1.75% at 2.20 ρ_c. In both the catalytic and the blank runs, the average molecular weight of the oligomers increased with reaction mixture density. For the catalytic runs, the average oligomer molecular weight increased roughly 50% from 183 AMU at 0.208 ρ_c to 272 AMU at 2.20 ρ_c. In the absence of catalyst, the average oligomer molecular weight increased 36% from 210 AMU at 0.208 ρ_c to 284 AMU at 2.20 ρ_c. Tests for possible catalytic activity due to the reactor material of construction revealed that the oligomer formation rate was proportional to the residence time based on the homogeneous reactor volume and *not* on the reactor surface area. Virtually all the oligomer formation therefore occurred in the fluid phase.

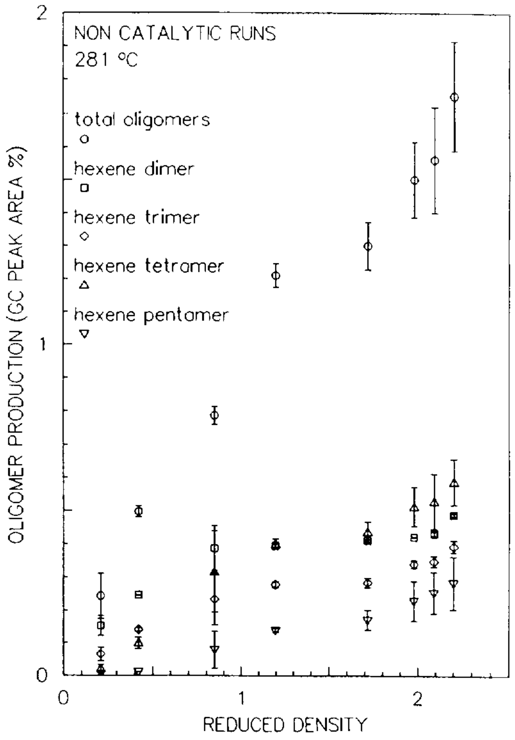

FIG. 2. Hexene oligomer production in the absence of catalyst.

The end-of-run (8 h) isomerization rates, the end-of-run deactivation rates (expressed as the percentage decrease in the isomerization rate between 6 and 8 h of operation), and coked catalyst properties corresponding to the catalytic runs were reported previously (9). The variation of these quantities in subcritical, near-critical, and supercritical reaction mixtures is as explained under Introduction. Despite the higher concentration of coke-forming oligomers in supercritical reaction mixtures, the isomerization rates were higher and deactivation rates were lower when compared to subcritical reaction mixtures. This is attributed to the enhanced desorption of coke-forming oligomers in higher-density reaction mixtures. Comparing Figs. 1 and 2, it can be seen that at the lowest subcritical density, the total oligomers in the reactor effluent were almost fourfold lower in the presence of the catalyst when compared to the blank run. In contrast, the corresponding decrease at the highest supercritical density was only 10%. These results indicate that while the oligomers formed in the fluid phase adsorb strongly on the catalyst surface at subcritical conditions leading to increased coke formation, near-critical and supercritical reaction mixtures favor desorption of the oligomers.

Coke formation on acid catalysts is believed to involve the polymerization and cyclization of olefins on the catalyst surface to yield higher-molecular-weight polynuclear compounds. These undergo extensive dehydrogenation, aromatization, and further polymerization to form "coke" (14). The formation of oligomers in the bulk fluid phase would therefore be an added detriment to catalyst activity. To investigate the effect of oligomers on catalyst coking, an experimental run was performed in which a known amount of oligomers was added to the hexene feed. For this purpose, the effluent stream collected from the blank run at 281°C and 277 bar, containing mostly 1-hexene and roughly 1.6 wt% oligomers, was used as the feedstock. This feed was introduced at 123 g/h to the reactor containing 1 g of pretreated catalyst. The reactor was operated at 281°C and 21.7 bar, yielding a reduced reaction mixture density of 0.208.

A comparison of the isomerization rate histories for runs performed with and without added oligomers is shown in Fig. 3. The isomerization rate is computed as the measured conversion of 1-hexene to its isomers (2- and 3-hexene) times the space velocity. For the experiment with 1.6 wt% oligomers in the feed: (i) the initial reaction rate was roughly a third relative to experiments with no oligomers; (ii) the 3-h isomerization rate was roughly one-half of the rate obtained with no added oligomers in the feed; and (iii) the isomerization rate declined in less than 15 min to a value observed at 3 h for the experiment where no oligomers were added. In other words, the catalyst deactivation rate was 12 times faster when 1.6 wt% oligomers were present in the feed. From Table 3, it is seen that the addition of oligomers to the feed increased coke laydown by 35%, decreased catalyst surface area by 55%, and catalyst pore volume by 41%. Clearly, the hexene oligomers formed in the *fluid phase* are significant coke precursors and accelerate catalyst deactivation.

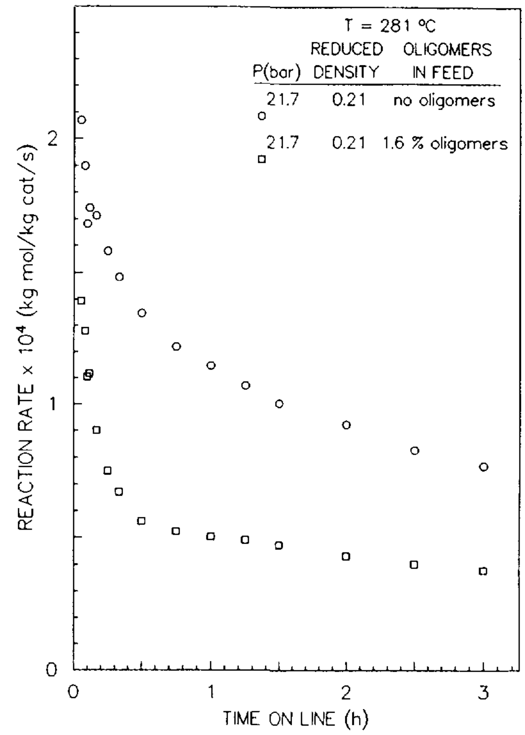

FIG. 3. Comparison of isomerization rate histories with no added oligomers and 1.6 wt% oligomers added to the feed.

Effects of Cosolvent Addition

While the increase in 1-hexene concentration over the experimental pressure range was roughly one order of magnitude (see Table 1), the corresponding increase in oligomer production was over two orders of magnitude

TABLE 3

Effect of Feed Oligomers on Properties of Catalyst Coked at 281°C and 21.7 bar

Catalyst property	Pretreated catalyst	No added oligomers	1.6 wt% oligomers
Coke laydown (wt%)	—	16.8	22.7
BET Surface area (m^2/g)	174.9	93.1	42.1
Pore volume (cc/g)	0.440	0.230	0.136

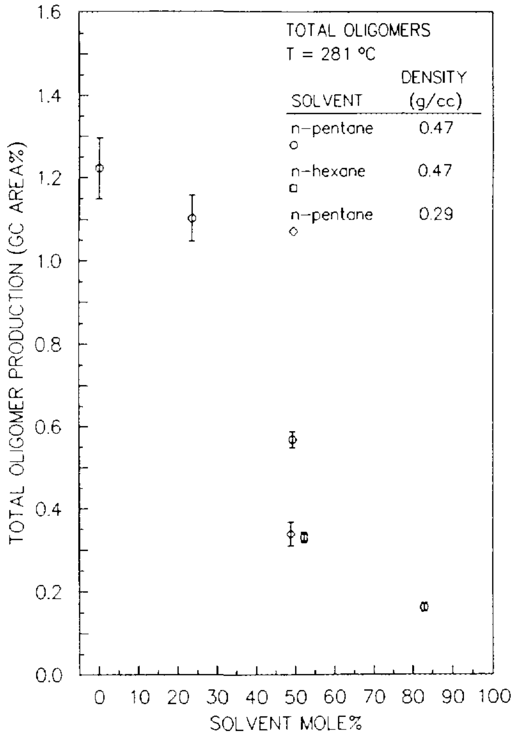

FIG. 4. Cosolvent effect on hexene oligomer production.

(see Figs. 1 and 2). Yet, in the near-critical and supercritical density range, reaction mixture density (which controls coke-compound solubility) increased by only twofold (see Table 1). In order to decrease the coke-precursor (i.e., hexene oligomer) concentrations while maintaining the *in situ* extraction of the coke-forming compounds, a set of constant density experiments was performed in which an inert cosolvent was added as explained under Experimental.

The oligomer formation in the cosolvent runs, measured from 6 to 8 h of operation, is shown in Fig. 4. Total oligomer production decreased sixfold from 1.2% in the absence of cosolvent to 0.2% with 80 mole% *n*-pentane in the feed. At approximately 50 mole% *n*-pentane addition, hexene oligomer production decreased as expected at the lower density of 0.29 g/cc. We also observed lower oligomer production when *n*-hexane instead of *n*-pentane was employed as the cosolvent. This result was puzzling at first since, in both cases, the cosolvent fraction (50 mole%) and reaction mixture density (0.47 g/cc) were identical. As discussed in the next section, we later determined that the 1-hexene from Lot PT 0605921 (that makes up 35% of the 1-hexene in the *n*-hexane cosolvent run) produced lower amounts of oligomers than the 1-hexene from Lot 851201 that was used in the runs with *n*-pentane as the cosolvent.

Figure 5 shows the effect of an inert cosolvent addition on hexene isomerization rate histories. The initial (10 min) isomerization rates decreased as expected when the *n*-pentane fraction in the feed is increased. In contrast, the rates at later run times (>6 h) showed a crossover. Figure 6 shows the initial and end-of-run (8 h) isomerization rates as a function of *n*-pentane addition at a constant density of 0.47 g/cc. While the initial reaction rate decreased nearly fourfold with *n*-pentane addition up to 80 mole%, the end-of-run reaction rates increased with *n*-pentane addition up to 50 mole% and then decreased. This trend is seen more clearly in Fig. 7. The increase in reaction rate despite the decrease in 1-hexene concentration is attributed to the reduction in oligomer formation (and hence in the deactivation rate) with cosolvent addition while maintaining the *in situ* extraction of the coke-forming compounds. Even though the oligomer production continues to decrease at higher cosolvent fractions (>0.5), the isomerization rate eventually becomes limited by 1-hexene concentration and hence decreases. At roughly 50 mole% cosolvent addition, neither the decrease in reaction mixture density nor the substitution of *n*-hexane as the cosolvent significantly affects the isomerization rates.

Figure 8 shows the effect of cosolvent addition on the catalyst deactivation rate. The overall deactivation (defined as the percentage decrease between the 10 min and 8 h isomerization rates) decreased almost twofold, from 9.6 to 5.5%/h, when the cosolvent fraction was increased

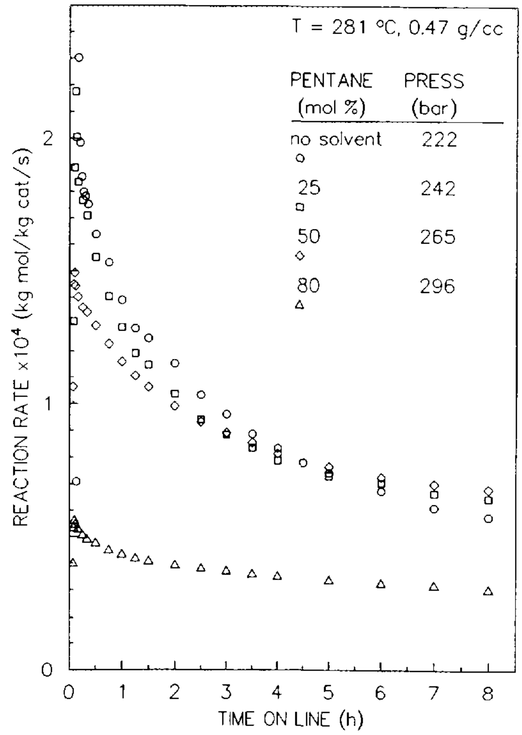

FIG. 5. Cosolvent effect on isomerization rate histories.

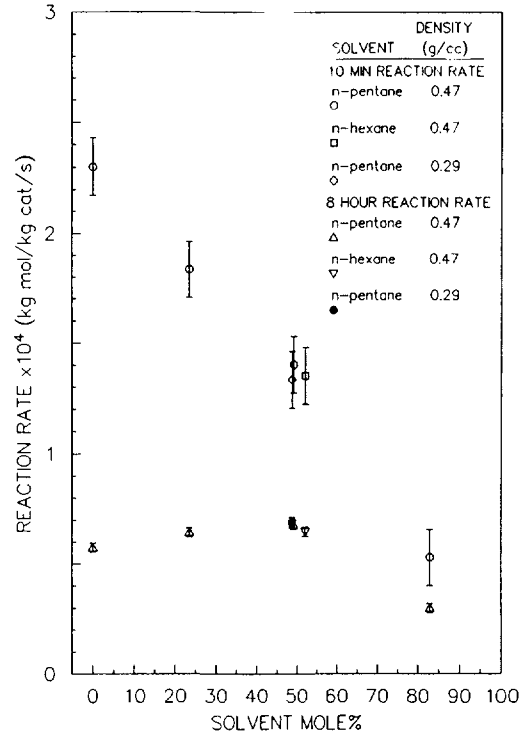

FIG. 6. Cosolvent effect on initial and end-of-run isomerization rates.

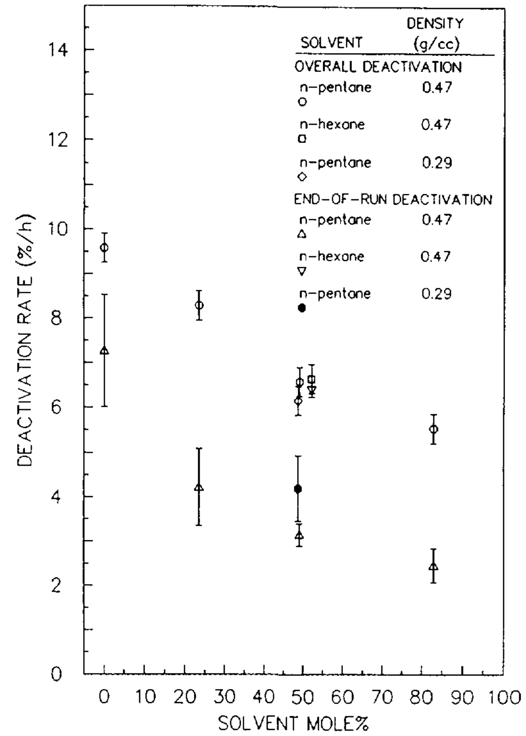

FIG. 8. Cosolvent effect on catalyst deactivation rates.

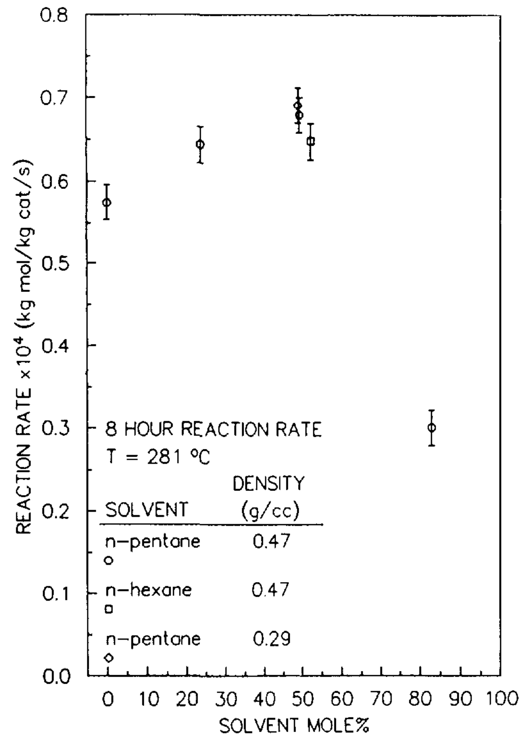

FIG. 7. Cosolvent effect on end-of-run isomerization rates.

from 0 to 80 mole%. The corresponding decrease in the end-of-run deactivation rate (defined as the percentage decrease in the isomerization rates between 6 and 8 h) was threefold. While the overall deactivation rate at 50% cosolvent addition was virtually unaffected either at the lower density or by using *n*-hexane as the cosolvent, the end-of-run deactivation rates were 3.1, 4.2, and 6.4%/h for *n*-pentane at 0.47 g/cc (T = 281°C, P = 265 bar), *n*-pentane at 0.29 g/cc (T = 281°C, P = 86.5 bar), and *n*-hexane at 0.47 g/cc (T = 281°C, P = 226 bar), respectively. Thus, the use of higher density *n*-pentane as an inert cosolvent produces a significantly lower deactivation rate. This result is somewhat surprising considering the lower oligomer formation in the latter two cases (see Fig. 4) and may be explained based on reported evidence that transition metals catalyze hydrogen transfer from supercritical solvents such as *n*-pentane (15, 16). It seems plausible that *n*-pentane undergoes dehydrogenation on the Pt metal (14). The transfer of the resulting hydrogen to the surrounding coke is facilitated by the dense supercritical reaction mixture. Hydrogen donation would soften the coke and facilitate the *in situ* extraction of the coke-forming compounds from the catalyst resulting in a lower deactivation rate.

In an attempt to determine if a steady catalyst activity can be attained with cosolvent addition, one experiment was run for an extended period of 14 h. For a feed contain-

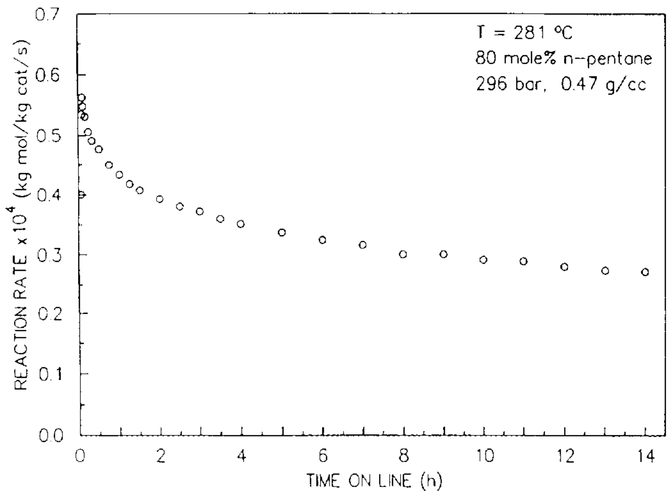

FIG. 9. Temporal isomerization rates during an extended run with cosolvent.

ing 80 mole% *n*-pentane, Fig. 9 shows the 1-hexene isomerization rate history at 281°C and 296 bar (reaction mixture density of 0.47 g/cc) at a space velocity of 135 g feed/h/g catalyst. The reaction rate was observed to decrease throughout the entire run, dropping nearly 10% from 8 to 14 h. Although a steady state was not achieved in this time period, the 2-h deactivation rate decreased 60% from 2.5%/h between 6 and 8 h to 1.5%/h between 12 and 14 h. Thus, for the run time examined, the catalyst continued to deactivate although at progressively lower rates.

Figure 10 shows the effect of cosolvent addition on product selectivity. The 2- to 3-hexene ratio followed the variation of the isomerization rate as observed with the pure hexene runs (9); however, substantially higher selectivities were obtained in the presence of a cosolvent. The 2- to 3-hexene selectivity ratio increased over twofold from 4.1 to 8.8 as the *n*-pentane fraction was varied from 0 to 50 mole%, and decreased to 4.8 as the cosolvent fraction was further increased to 80 mole%. At 50 mole% cosolvent fraction, while a decrease in the density had little effect on the selectivity ratio, the use of *n*-hexane produced a 50% increase in the ratio yielding a value of 13.2. Similarly, higher *cis*- to *trans*-2-hexene ratios were obtained in the presence of a cosolvent, as shown in Fig. 11.

As seen in Fig. 12, coke laydown decreased over threefold as *n*-pentane addition increased from 0 to 80 mole% at a constant density of 0.47 g/cc. At 50 mole% cosolvent addition, coke laydown was lower when *n*-hexane was used as the cosolvent. As inferred from Fig. 13, the remaining surface area increased from 84 to 94% and the remaining pore volume increased from 78 to 85% as *n*-pentane fraction in the feed was increased from 0 to 80 mole%. Although the values at 50 mole% *n*-pentane addi-

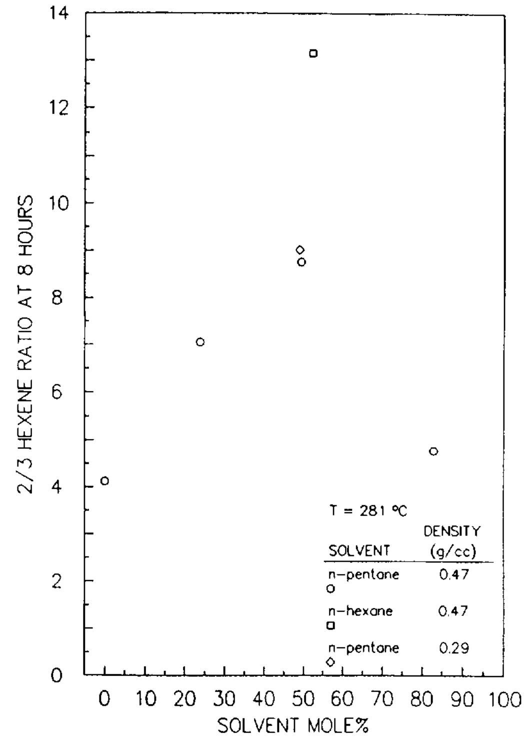

FIG. 10. Cosolvent effect on 2-hexene/3-hexene selectivity.

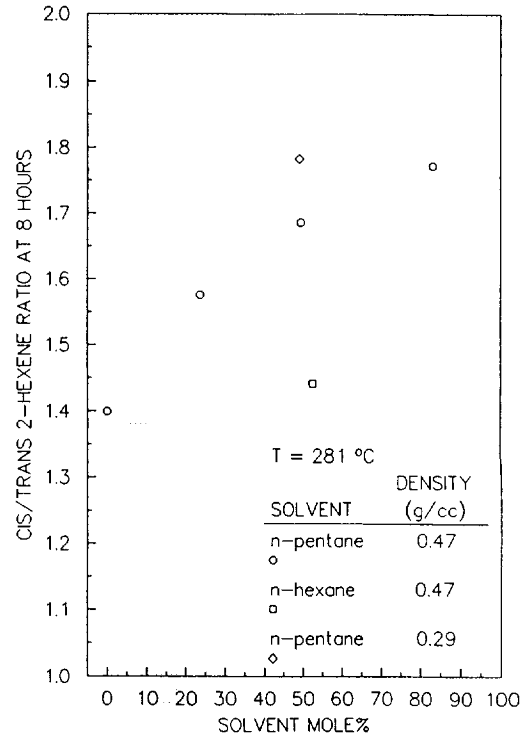

FIG. 11. Cosolvent effect on *cis*-2-/*trans*-2-hexene selectivity.

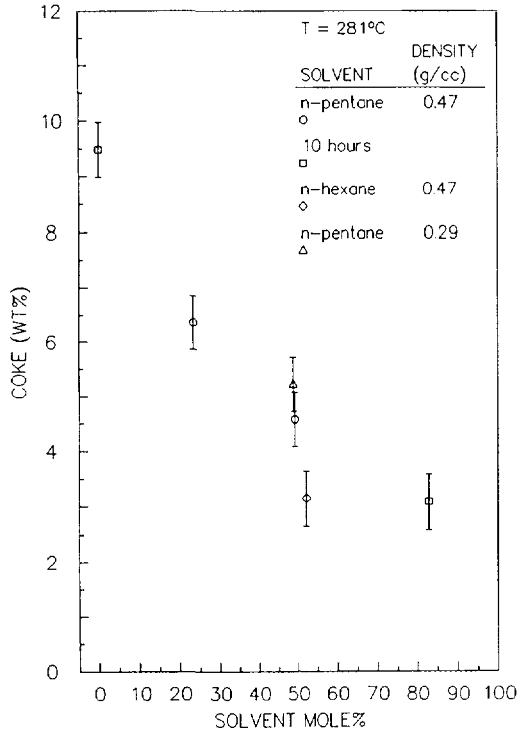

FIG. 12. Cosolvent effect on end-of-run coke laydown.

tion were only mildly affected by a decrease in reaction mixture density, the pore volume and surface area improved noticeably when *n*-hexane was employed as the cosolvent. This improvement is consistent with the reduced coke laydown during the run. As shown in Fig. 14, coke density decreased from 1.5 to 0.6 g/cc when the cosolvent fraction was increased from 0 to 80 mole%. This decrease is attributed to lower oligomer concentrations (with lower average molecular weight) at higher cosolvent fractions (see Fig. 4), suggesting that both the amount as well as the average molecular weight of the oligomers influence the density (i.e., the chemical composition) of the coke.

Effect of Feed Peroxide Content on Oligomer Production and Catalyst Performance

The unexpected decrease in coke laydown when *n*-hexane instead of *n*-pentane was used as the cosolvent led us to analyze the two different 1-hexene sources used in these runs for possible impurities. Analysis by Ethyl Corp. (the suppliers) revealed a significant difference in peroxide concentrations between the two hexene feedstocks. The peroxide content was determined by sodium thiosulfate titration following a contacting step with sodium iodide, as described by O'Quinn (17). The hexene from Lot 851201, used for the majority

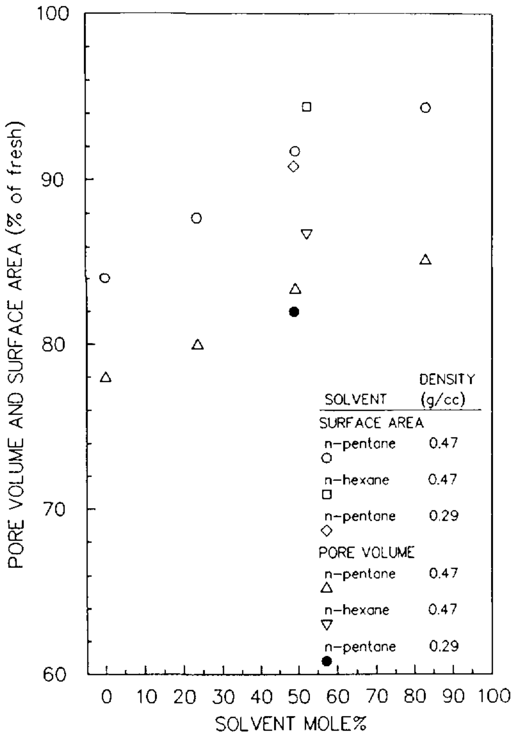

FIG. 13. Cosolvent effect on end-of-run catalyst surface area and pore volume.

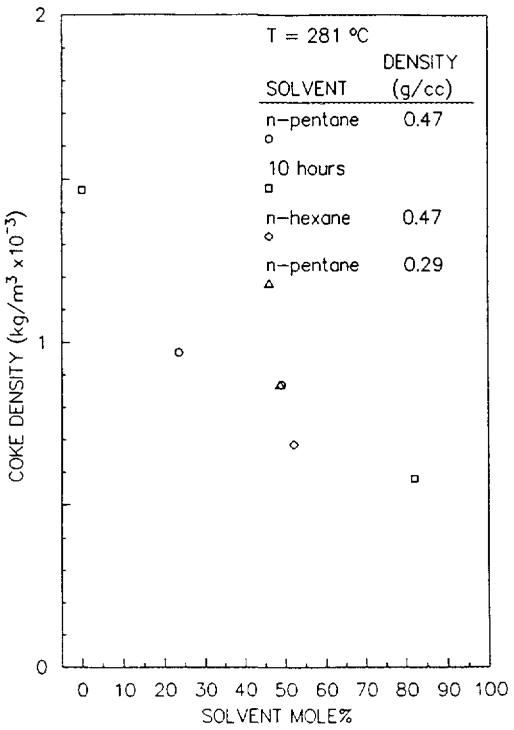

FIG. 14. Cosolvent effect on coke density.

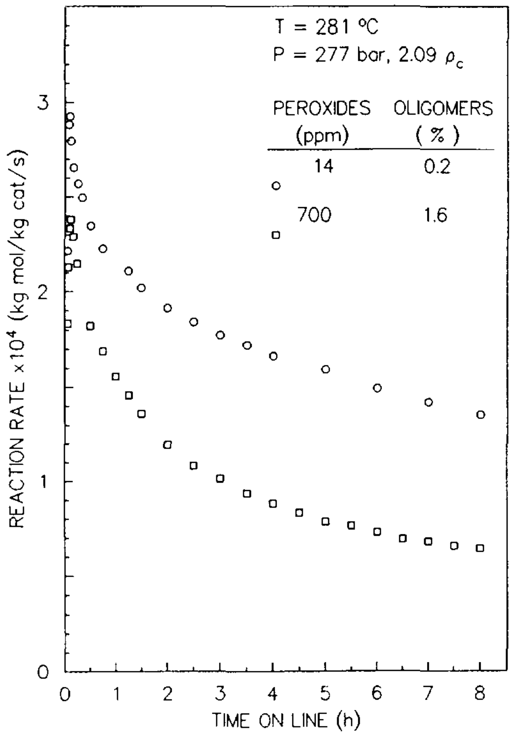

FIG. 15. Effect of feed peroxide content on isomerization rate histories.

of experiments, contained 700 ppm peroxide, while hexene from Lot PT 060592 contained 14 ppm peroxide, as ppm oxygen.

Given that organic peroxide radicals aid polymerization (18), the two feeds were examined separately by flowing each at approximately 136 g/h over 1 g of catalyst at 281°C and 277 bar, yielding a supercritical density of 2.09 ρ_c. Under similar operating conditions, the 14 ppm peroxide feed (Lot PT 060592) produced 0.2 wt% total oligomers, while the 700 ppm peroxide feed (Lot 851201) produced 1.6 wt% total oligomers. The reaction rate histories are compared in Fig. 15 for the two feeds. The isomerization rate was higher throughout the run when the feed peroxide content was 14 ppm. A summary of reaction and deactivation rates is presented in Table 4. The initial (10 min) isomerization rate increased 16% in the case of 1-hexene feed with reduced peroxide content, while the end-of-run (8 h) reaction rate increased over twofold. The overall deactivation rate decreased 65% and the end-of-run deactivation rate decreased 19% in the case of the low peroxide feed when compared to the high peroxide feed. As summarized in Table 5, the corresponding coke laydown decreased roughly ninefold with over 90% maintenance of the pore volume and surface area. The coke density decreased by roughly fourfold with a decrease in feed peroxide content (i.e., in oligomer production) reinforcing the dependence of coke density on the amounts and average molecular weight of the oligomers. The improvements in isomerization rates, deactivation rates, and catalyst properties accompanying lower oligomer production are consistent with the observed deterioration in these values when oligomers are added to the reactor feed (see Table 3).

TABLE 4

Effect of Feed Peroxide Content on 1-Hexene Isomerization Rates and Catalyst Deactivation Rates at 281°C and 277 bar

Measured quantity	700 ppm Peroxides	14 ppm Peroxides
Total oligomer production (%)	1.6	0.2
Initial reaction rate (kg mol/kg cat/s × 10^4)	2.29	2.66
End-of-run rate (kg mol/kg cat/s × 10^4)	0.64	1.35
Overall deactivation rate (%/h)	9.2	6.3
End-of-run deactivation rate (%/h)	5.8	4.7

In industrial practice, the 1-hexene feedstock is typically passed over a bed of activated alumina to reduce peroxide content and stored in containers blanketed with nitrogen to prevent exposure to oxygen (18). To determine the effect of peroxide content on hexene oligomer formation, hexene feeds at four different peroxide levels were subjected to blank runs with the reactor operated at 281°C, 277 bar (yielding a supercritical density of 2.09 ρ_c), and a feed flow rate of 135 g/h.

Hexene feeds with 14 and 700 ppm peroxides were provided from hexene lots PT 060592 and 851201, respectively. Peroxides were reduced to 2 ppm by passing hexene from Lot PT 060592 over 50 g of dry activated neutral alumina at a flow rate of approximately 200 g/h. Peroxides

TABLE 5

Effect of Feed Peroxide Content on Properties of Catalyst Coked at 281°C and 277 bar

Catalyst property	Pretreated catalyst	700 ppm Peroxides	14 ppm Peroxides
Coke laydown (wt%)	—	8.7	1.0
BET Surface area (m^2/g)	174.9	141.5	170.0
Pore volume (cc/g)	0.440	0.335	0.398
Coke density (g/cc)	—	1.1	0.3

TABLE 6

Effect of Feed Peroxide Content on Blank Oligomer Production at 281°C and 277 bar

Feed peroxide (ppm)	Oligomer production (GC area%)				
	Dimer	Trimer	Tetramer	Pentamer	Total
2	0.037	0.024	0.015	0.002	0.077
14	0.047	0.031	0.021	0.003	0.102
21	0.054	0.037	0.027	0.005	0.123
700	0.43	0.36	0.58	0.30	1.67

were increased to 21 ppm by stirring the hexene from Lot PT 060592 in the presence of air for 68 h. All samples were degassed in a mild vacuum following treatment to improve pump efficiency, and the feed vessels were allowed to be in contact with air during the noncatalytic experiments.

Bulk-phase oligomer production for the various feed peroxide levels is shown in Table 6. Oligomer amounts are based on three samples taken at 30-min intervals after the reactor reached steady state. Oligomer production increased with peroxide content, with total oligomers increasing almost 22 times from the alumina-treated hexene (2 ppm peroxide content) to the untreated hexene in Lot 851201 (700 ppm peroxide content). The corresponding increases in the dimer, trimer, tetramer, and pentamer formation rates are 12, 15, 39, and 150 times, respectively. As noted earlier, the higher-molecular-weight oligomers are more prolific coke producers and lead to rapid deactivation.

Except with the feed containing 2 ppm peroxides, the total oligomer production reached a steady state in the other cases. In the former case, total oligomers increased 36% from 0.066 to 0.089% over the 1-h sampling time. The alumina-treated hexene was in contact with air in the reactor feed vessel during the blank runs. Following the alumina treatment and just prior to the runs, the hexene was degassed in a mild vacuum. Hence, it seems plausible that the oxygen was absorbed into the feed material during the course of the experiment, and that the peroxide level in the reaction mixture increased with time. It seems unlikely that the peroxide level increased in the feed vessel itself, since the increase in peroxide level during storage of hexene Lot 851201 corresponds to a total oligomer increase of only 5×10^{-5} %/h. This rate is two to three orders of magnitude slower compared to the increase in oligomer formation during the experiment with alumina pretreated feed. More likely, as oxygen was absorbed by the feed mixture, peroxides were formed rapidly in the high-pressure, high-temperature reactor leading to increasing oligomer formation with time. These results clearly bring out the importance of removing peroxides from olefinic feeds, especially in high-pressure processing over acid catalysts.

CONCLUSIONS

During investigations of 1-hexene isomerization on a Pt/γ-Al_2O_3 catalyst, hexene oligomers are found to form in the fluid phase. These oligomers are significant coke precursors, increasing the coke formation and catalyst deactivation rates. The total amount and average molecular weight of the oligomers increased with isothermal increases in pressure from subcritical to supercritical values increasing the density of the coke.

The dilution of the feed with an inert cosolvent such as *n*-pentane at a constant supercritical density and space velocity reduces oligomer concentrations while maintaining the *in situ* extraction of the coke compounds. Hence, coke laydown is significantly reduced. Consequently, the isomerization rate increases and deactivation rate decreases. Although oligomer formation continues to decrease with cosolvent addition, the isomerization rate eventually becomes limited by the low feed concentrations of 1-hexene and hence passes over a maximum.

It was determined that ppm levels of organic peroxides in the hexene feed, formed as a result of exposure to air during either storage or the experiments, aid the formation of hexene oligomers in the fluid phase. The feed peroxide content can be reduced by pretreating the feed with activated alumina. For reactor operation at 281°C and 277 bar (2.09 ρ_c), this pretreatment resulted in the virtual elimination of the peroxides and an eightfold decrease in total oligomer concentration at a space velocity of 135 g/h/g cat. Consequently, increased isomerization rates and significantly lower deactivation rates are attainable.

Our results indicate that peroxide removal from the feed *and* cosolvent addition can significantly improve catalyst activity maintenance and pore accessibility in supercritical reaction mixtures. We are currently investigating this possibility and the effect of cosolvents such as *n*-pentane on the chemical nature (i.e., H/C ratio) of the coke formed at supercritical conditions. This will allow us to gain better mechanistic insights into the mitigation of coke buildup in supercritical reaction mixtures.

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