Kinetics on a Supported Catalyst at Supercritical, Nondeactivating Conditions

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Intrinsic kinetic parameters are reported for the $Pt/\gamma\text{-}Al_2O_3$ *catalyzed geometric isomerization of 1-hexene* ($P_c = 29.7$ *bar;* $T_c = 231°C$) *under conditions of steady catalyst activity. Deaerating the hexene feed, pretreating it in a bed of activated alumina to reduce the peroxide impurities to 2 ppm or less, and passivating the reactor surface (by silicosteel coating) reduce the formation of hexene oligomers (coke precursors) by about an order of magnitude. This, in conjunction with operation at supercritical conditions (235−304°C, 35−70 bar), results in steady isomerization activity with no measurable coke laydown. Arrhenius plots of rate constants, estimated from the steady isomerization rates, yield an intrinsic activation energy of roughly 109 kJ/mol. This value is up to twofold greater than those reported for similar reaction systems, but on a deactivating catalysts. Our results confirm that optimum conditions that maximize catalyst activity and effectiveness factor exist in the near-critical region with catalyst activity and effectiveness factor.*

Introduction

For investigating the intrinsic activity and coking behavior of acid catalysts, alternate pathways for coke formation that do *not* involve the acidic component of the catalyst must be minimized, if not eliminated. The mechanism of coke formation has been reviewed in detail in several books and articles (Butt and Petersen, 1988; Chen et al., 1994; Gates, 1991; Guisnet et al., 1997). In general, the coking of acid catalysts is caused by side reactions that mainly involve acid-catalyzed polymerization and cyclization of olefins, producing compounds that undergo extensive dehydrogenation, polymerization, and cyclization. The side reactions have been shown to produce polynuclear aromatics at high temperatures (> 450°C), and straight chain and cyclic nonaromatic compounds at lower temperatures (~100°C). At higher temperatures, coke formation may also occur in the gas phase (Trimm, 1985), promoted by free-radical reactions which lead to polycyclic aromatics (tars) or carbon. This coking pathway may be suppressed by minimizing the heated free space in the preheater and reactor.

Oxygen-based feed impurities also contribute to catalyst coking. Yet, this pathway has received relatively little attention in the literature. Cavani (1993) investigated the role of added oxygen during 1-butene reaction on a ZSM-5 catalyst. While the butene conversion is shown to be constant in the absence of oxygen, an 80% decrease in conversion in 2 h was observed when the reaction is performed aerobically in the same temperature range. A similar deactivation trend was observed by Anderson and Tsai (1985), who proposed that the increased coking rate could be a result of oxidative dehydrocondensation processes or oxygen incorporation into the coke. Other authors (Centi and Golinelli, 1989; Hunter et al., 1987; Shih, 1983; Che and Tench, 1982) have implicated that zeolites can activate molecular oxygen, giving rise to electrophilic, free radical species. Pilot-plant studies from a solid-acid xylene isomerization reactor (Koetsier and van Leenen, 1987) indicate that removal of trace amounts of feed contaminants, such as dissolved oxygen, aromatics such as isopropylbenzene and diaryl aromatics, and several unidentified oxygenates with a total oxygen content between 0.5 and 1%, significantly reduces catalyst fouling.

In previous work, we showed that organic peroxides present in the 1-hexene feed catalyzed the *homogeneous* formation of hexene oligomers in the fluid phase (Ginosar and Subramaniam, 1995). These fluid-phase oligomers strongly adsorb on the catalyst and accelerate coking via the acid-catalyzed polymerization mechanism. We later reported that deaeration and alumina pretreatment of the 1-hexene feed

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dramatically increased catalyst activity (Clark and Subramaniam, 1996).

Mechanistic investigations into the role of oxygen compounds in causing deposit formation have been extensively reported in the jet fuels literature. Dissolved oxygen in jet fuels is believed to be a major causative factor in forming ‘‘gums’’ (mobile coke precursors that can be extracted with organic solvents) and deposits (coke that must be removed by high-temperature oxidation in air). The application of light scattering photometry showed that high molecular weight substances formed even after the dissolved oxygen had been removed (Morris and Wechter, 1994). Two possible pathways have been proposed to explain the formation of radicals and/or deposits. The first pathway is promoted by the presence of peroxides, formed when the highly unsaturated jet fuel is exposed to air during either storage or transport. These peroxides initiate the formation of olefinic oligomers. The concentration of free radicals initiating the chain reaction could be as small as 4 parts per billion (Heneghan, 1994). Several additives such as benzyl alcohol, tetrahydroquinoline and tetralin, ranging in concentration from 100 ppm to 5%, have been found to reduce pyrolytic deposition (Sobkowiak et al., 1992; Song et al., 1994). These additives are believed to act as hydrogen-donors, capping radicals which might catalyze the formation of the heavy deposits.

The second plausible pathway to deposit formation is a surface-catalyzed oligomerization reaction. Striebich et al. (1994) compared the adsorption properties of stainless steel with glass and a coke-like soot material. It was found that while the stainless steel was relatively inert to nonpolar solutes like toluene, more polar solutes like phenols and anilines showed an increased adsorption to stainless steel. The coke-like material also showed a dramatic increase in adsorption tendencies when compared to glass. It has been reported that silicosteel surfaces reduce the rate of deposit formation (Jones et al., 1995). Based on the observation that deposit formation decreases as metal surfaces are treated with increasingly stronger bases, Beal and Hardy (1994) suggested that the nickel and chromium surface sites may present a more ‘‘acidic’’ surface to the fuels. This observation is consistent with the well-known coke formation mechanism in catalytic hydrocarbon processing wherein acidic sites on the catalyst promote the polymerization and cyclization of olefinic coke precursors (see, for example, Gates, 1991).

It follows, therefore, that during investigations of the *intrinsic coking behavior* of acid catalysts, alternate pathways for coke formation that do not involve the acidic component of the catalyst must indeed be minimized. In this article, we present *intrinsic* 1-hexene isomerization studies on a Pt/γ-Al_2O_3 catalyst taking steps to reduce dissolved oxygen in the feed and to reduce feed impurities such as organic peroxides by adsorption in an alumina packing prior to entering the reactor. Following a run, the alumina packing is subjected to solid-phase extraction with a solvent to extract and gain insights into the chemical nature of the adsorbed impurities. To minimize oligomer formation, the stainless steel reactor surface is constructed with silicosteel. In addition to these various oligomer reduction steps, supercritical reaction conditions are employed to mitigate coke buildup on the catalyst and to obtain steady isomerization activity as shown previously (Clark and Subramaniam, 1996). Based on steady isomer formation rates at several temperatures and pressures in the near-critical region, we estimate effective rate constants and apparent activation energies with a catalyst operated under nondeactivating conditions with no measurable coke laydown, and compare them to estimates reported previously in the presence of catalyst deactivation. The relevance of these findings to research on developing solid acid catalysts as environmentally safer alternatives to liquid catalysts is also discussed.

Experimental Studies

The experimental unit is identical to the one employed in earlier studies (Clark and Subramaniam, 1996). The 1-hexene feed (Ethyl Corporation, Lot No. PT060592) is contained in an opaque bottle to minimize possible free radical reactions due to exposure to light. The feed is continuously kept deaerated by bubbling high purity helium through it such that the headspace is always blanketed with helium. The hexene feed is passed through a stainless steel tube packed with 53 g of dry activated neutral alumina (Scientific Adsorbents Inc., Lot No. A25M1). Organic peroxides in the untreated and alumina-treated 1-hexene feed were measured using the ASTM method (D 3703-92), which involves titration with sodium thiosulfate following contact with sodium iodide. The untreated and alumina-treated 1-hexene feeds were also analyzed using GC/FID (Hewlett-Packard 5890A) and GC/MS (Varian Star 3600 GC equipped with a Saturn 2000 mass spectrometer).

A nonchlorided, nonsulfided Engelhard E-302 Pt/γ-Al_2O_3 reforming catalyst was investigated. The Pt loading on the catalyst is 0.6 wt. %. For the intrinsic kinetic studies, the catalyst was size-reduced to obtain 100–140 mesh (62–105 μm) particles. The catalyst was pretreated off-line in flowing helium at 100 sccm at 330°C for 18 h, followed by flowing hydrogen at 100 sccm at 330°C for 4 h. The pretreated catalyst has a BET surface area of 188 m^2/g, total pore volume of 0.42 cm^3/g, and an average pore radius of roughly 50 Å. Approximately 1 g of the pretreated catalyst was employed in each run. The catalyst particles were further treated on-line at 330°C by flowing helium for 2 h followed by hydrogen at 100 sccm for 2 h at 330°C.

The reaction experiments were performed at three different supercritical pressures: 35 (1.1 P_c), 50 (1.6 P_c), and 70 (2.2 P_c) bars. At each pressure, steady isomer formation rates are measured at several near-critical temperatures ranging from 235°C (1.01 T_c) to 305°C (1.14 T_c). After a steady state was achieved at the highest temperature, the hexene conversion at the lowest temperature was repeated to verify that the catalyst was not deactivating during the various runs. The temperature ramp experiments at a given pressure were completed in 10 h or less. Following a run, no measurable coke laydown was detected on the catalyst. The shutdown procedure consists of replacing the hexene feed with helium and flushing the reactor at the operating pressure to remove the reactants and products from the lines. The reactor is then depressurized and cooled. The spent catalyst is then analyzed for coke laydown, and pore volume/surface area using a Micromeretics Gemini 2000 Surface Area and Pore Volume Analyzer. Further details of the experimental setup and procedures may be found elsewhere (Clark, 1998).

Results

Curtailing oligomer formation aided by feed peroxides, reactor surface and dissolved oxygen

Figure 1 shows the GC/MS total ion chromatogram (TIC) of the fresh 1-hexene feed and of alumina treated 1-hexene feed. Several impurity peaks, most of them less than 0.02 wt. %, are detected in the untreated 1-hexene. The peaks are labeled by number in order of increasing elution time and include the hexene dimer identified with the GC/MS spectral library. When the fresh 1-hexene feed is treated with alumina, all impurity peaks are reduced to undetectable levels except for the dimer, which remains virtually unchanged.

Figure 2 shows the fragmentation patterns of some of the detected impurities in the feed. The GC/MS NIST spectral database identified six compounds in the 1-hexene feed, 6-dodecene (a hexene dimer), and the five hexene isomers using the automated searching routine (probability $> 90\%$). The fragmentation patterns of unsaturated peroxides, reported by Polzer and Bachmann (1993), were used to identify the peroxide impurities. Impurity peaks 1, 3, 4, 6, and 7 (see Figure 1) correspond to secondary hydroperoxides based on the presence of a dominant RO· fragment ($m/z = 99$). The fragmentation pattern of Peak No. 1 is shown in Figure 2 as an example. The absence of this fragment suggests that peaks 2 and 5 are terminal hydroperoxides. The fragmentation pattern of peak 5 ($m/z = 83$) is shown as an example in Figure 2. Peak 8 coelutes with Peak 7 (see Figure 1), but does not correspond to a hydroperoxide moiety. The fragmentation pattern of peak No. 8 suggests a hydrocarbon species (see Figure 2). The prominent dimer peak in the hexene feed could have formed during storage, aided by the peroxide impurities which form free radicals when the feed is exposed to light and/or heat. The dimer was not removed by alumina pretreatment and no further attempt was made to purify the 1-hexene feed. The presence of such oligomers could affect the intrinsic kinetics.

Figure 3 shows the extent of reduction in oligomer formation in the *absence* of the Pt/γ-Al_2O_3 catalyst following peroxide reduction. At a feed rate of 135 g 1-hexene/h (the same flow rate used in the kinetic studies), roughly 0.2 wt. % hexene oligomers are formed at 281°C when 130 ppm of peroxides are present in the untreated 1-hexene feed. A roughly fivefold decrease in total oligomer formation results when the peroxide content is reduced to less than 2 ppm by alumina pretreatment. The foregoing results clearly implicate the role of peroxide impurities in aiding hexene oligomer formation in the fluid phase.

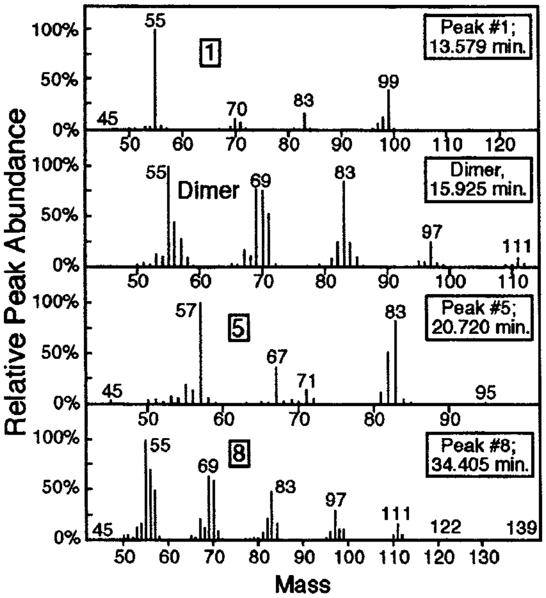

Figure 2. GC/MS fragmentation patterns of impurities in untreated hexene feed.

The peak numbers correspond to those noted in Figure 1b.

As explained in the introduction, acidic sites on stainless steel surfaces were shown to catalyze oligomer formation during jet fuels processing. Silicosteel passivation of stainless

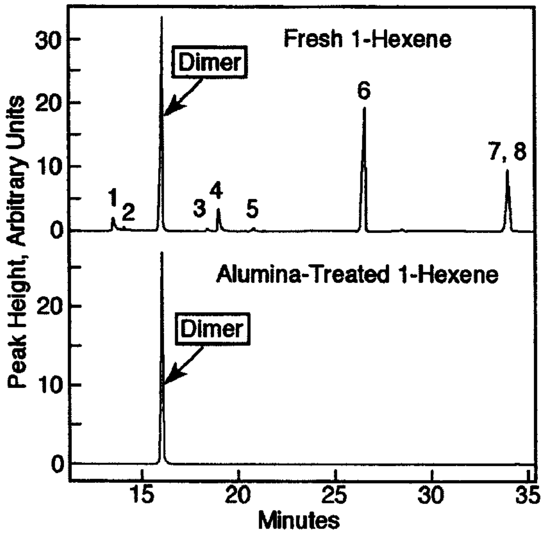

Figure 1. Effect of alumina pretreatment on 1-hexene feed composition.

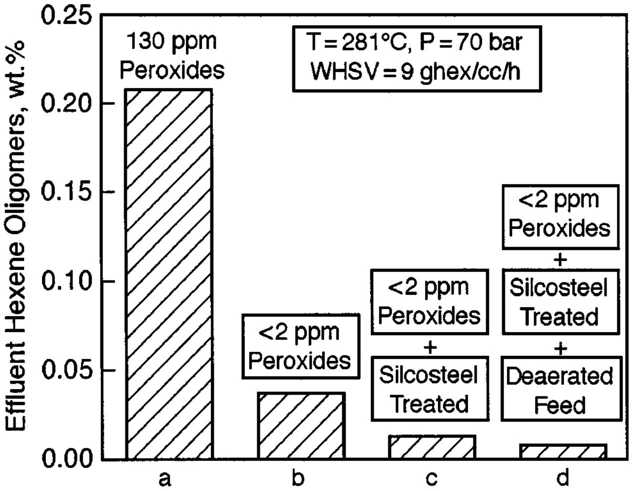

Figure 3. Extent of mitigation of olefinic oligomer formation following alumina pretreatment of feed, surface passivation with silicosteel, and feed deaeration.

steel surfaces reduces surface oligomer formation, as shown by the referenced studies in the jet fuels literature. As shown in Figure 3, surface treatment of the reactor and preheater tubing with silicosteel results in a further twofold reduction in oligomer formation (in addition to that obtained with peroxide reduction).

In addition to the carbon-based impurities, permanent gases such as nitrogen and oxygen were also detected in the 1-hexene feed used in our studies. These gases were stripped by sparging the 1-hexene feed (roughly 4 L) with a steady flow (~ 50 standard cm^3/min) of high purity helium (Linweld, 99.999+%). During sparging, samples were periodically withdrawn and analyzed off-line with a GC/TCD instrument. The dissolved oxygen in the sparged feed is reduced from roughly 40 ppm (roughly 0.004 mole fraction) to undetectable levels (< 10 ppm) in less than an hour. As shown in Figure 3, deaeration of the feed by He sparging further reduces oligomer formation to the order of 0.01 wt. %. Although this reduction is incremental, alumina pretreatment of the feed in conjunction with feed deaeration is essential in maintaining constant isomerization activity at supercritical conditions (Clark and Subramaniam, 1996). This suggests that there might be other coke precursor formation pathway involving molecular oxygen.

Intrinsic kinetics of 1-hexene isomerization

With the oligomer yield suppressed to the order of 0.01 wt. %, the intrinsic kinetics of the primary reaction (hexene isomerization) on the catalyst was investigated with negligible effects from the side reactions. Employing the aforementioned steps to mitigate peroxide and reactor surface-mediated oligomer formation, we obtain steady isomerization activity on the $Pt/\gamma\text{-}Al_2O_3$ catalyst (62–105 μm particles) with supercritical reaction mixtures ($T = 235$–$302°C$; $P = 35$–70 bar). From the steady isomer formation rates, effective first-order rate constants (ηk) are estimated from the following plug-flow reactor equation

$$\eta k = -\left\{\ln\left(\frac{X_e}{X_o}\right)\right\}\left(\frac{\nu}{W}\right)\rho_b \qquad (1)$$

where X_e represents the GC area fraction of the *cis*- and *trans*-hexene isomers in the reactor effluent, X_o represents the GC area fraction of 1-hexene in the feed stream, ν is the volumetric sweep rate in the catalyst bed, W is the weight of the catalyst, and ρ_b is the bulk density ($kg\ m^{-3}$) of the catalyst packing ($0.56\ g/cm^3$). Effective rate constants calculated from the area fraction of the effluent 1-hexene peak were essentially identical. In addition, the mass balance closure in terms of the liquid product collected relative to the 1-hexene fed is over 98%. Furthermore, the response factor of the flame ionization detector, either on a mass or molar basis, is identical for all the hexene isomers. These analytical results provide clear evidence that (a) the 1-hexene is indeed selectively converted to *cis*- and *trans*-isomers, and (b) the area normalization method to obtain the isomer mole fraction from the GC/FID peaks is indeed valid.

Figure 4 shows the Arrhenius plots of the effective rate constants (ηk) for hexene isomerization at three different pressures. The Arrhenius plots virtually overlap in the (235–275)°C temperature range with a statistical mean activation energy of roughly 109 kJ/mol. Doubling the hexene feed rate at a given temperature yields identical rate constants implying the absence of external mass-transfer intrusions (see Figure 5).

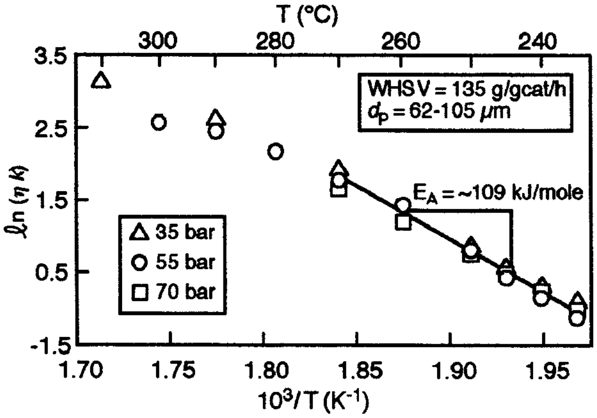

Figure 4. Arrhenius plots for 1-hexene isomerization on $Pt/\gamma\text{-}Al_2O_3$ catalyst particles (mean size = 84 μm).

Discussion

The Engelhard $Pt/\gamma\text{-}Al_2O_3$ reforming catalyst used in this study is only mildly acidic. Consequently, oligomerization reactions that produce coke precursors are less favored on such catalysts when compared to more strongly acidic catalysts such as zeolites and sulfated zirconia, that have been investigated as potential 1-butene/isobutane alkylation catalysts (Corma and Martinez, 1993). As shown in our previous work (Clark and Subramaniam, 1996), when peroxide impurities are present in the feed, the isomerization activity of the catalyst ceases in less than 10 h at subcritical gas-phase conditions. In contrast, when the feed peroxides are reduced to less than 2 ppm, the bulk-phase oligomer formation is significantly curtailed (see Figure 3), and catalyst activity remains constant during the entire run.

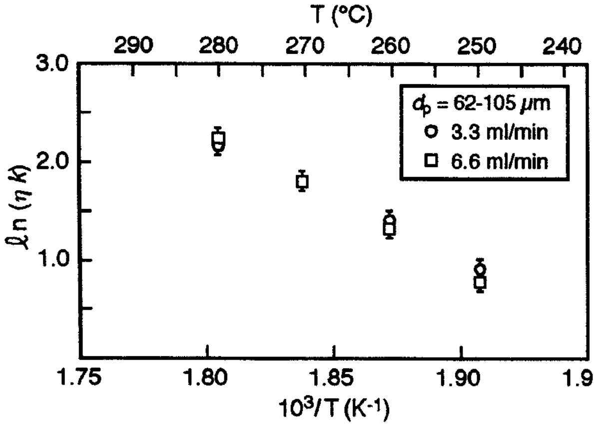

Figure 5. Flow rate effect on 1-hexene isomerization rate constants on $Pt/\gamma\text{-}Al_2O_3$ catalyst particles (mean size = 84 μm).

The foregoing results have significant implications. From a fundamental viewpoint, it is obvious that for performing reliable mechanistic studies of olefin conversion on porous solid catalysts, feed impurities that lead to oligomer formation in the bulk fluid phase must be minimized, if not eliminated. On the practical side, feed impurities that lead to oligomer formation can be a major hindrance to the development of solid acid catalysts as environmentally safer alternatives to liquid acids, as in 1-butene/isobutane alkylation to produce high-octane gasoline. A major technological barrier preventing the practical viability of solid acid catalysts is the rather rapid decline in alkylate production activity due to oligomer formation on the strong acid sites. Clearly, fluid-phase oligomer formation, promoted by feed impurities such as peroxides, exacerbate this problem. Yet, feed pretreatment to remove such impurities has received very little, if any, mention in the catalyst deactivation literature on research efforts aimed at developing solid acid catalysts with enhanced activity.

In the present study, the elimination of deactivation (with no measurable coke laydown) has allowed the determination of the intrinsic activation energy of the geometric isomerization of 1-hexene to *cis*- and *trans*-isomers on the mildly acidic Pt/γ-Al_2O_3 catalyst. The lack of pressure dependence on the rate constants in the 235–270°C range (see Figure 4) *and* the absence of external mass-transfer limitations (see Figure 5) imply that the major reaction pathway for hexene conversion at the operating pressures is indeed the first-order isomerization to the *cis*- and *trans*-isomers. Using the correlation of Lee and Thodos (1983), the bulk diffusivity of 1-hexene at 270°C was estimated to decrease from 1.7 $(10^{-7})\ m^2 \cdot s^{-1}$ at 35 bar to 4.5 $(10^{-8})\ m^2 \cdot s^{-1}$ at 70 bar, an approximately fourfold decrease. If one assumes that bulk diffusion dominates in the pores (a valid assumption for the rather dense reaction mixtures in this pressure range), the effective diffusivity of the hexene molecules in the pores would also decrease by roughly fourfold in the 35–70 bar pressure range (see Eq. 3). In spite of this rather large change in the effective diffusivity, the estimated rate constants in the 235–270°C range change by at most 22% (at 270°C), implying that kinetic control ($\eta = 1$) prevails in the 235–270°C range.

Comparing the activation energy value of 109 kJ/mol with values reported for similar systems, but on deactivating catalysts reveal the expected differences. Schmidt (1988) investigated the kinetics of 1-butene isomerization to 2-butenes on a low activity Al_2O_3 catalyst in a differential recycle reactor, and reported the reaction to be first-order with respect to 1-butene concentration with an activation energy of 54.0 kJ/mol. Saim (1990) studied the isomerization of 1-hexene on a similar Engelhard Pt/γ-Al_2O_3 catalyst and reported an activation energy of 70 kJ/mol based on initial reaction rates observed on a deactivating catalyst. In Saim's study, the 1-hexene feed was neither pretreated to remove any organic peroxides nor deoxygenated with helium, which could have led to the observed deactivation. The greater value of 109 kJ/gmol reported in this work is to be expected. The elimination of catalyst deactivation should also reduce pore diffusion limitations, which when present, yield an apparent activation energy that is up to twofold lower than the intrinsic activation energy.

The decrease in the slope of the Arrhenius plots in the 280–305°C range (Figure 4) indicates the onset of pore-diffusion limitations. Because there is no measurable coke laydown or catalyst deactivation at any of these operating temperatures, the pore-diffusion limitations are not as a result of pore plugging or pore choking. An Arrhenius plot of effective rate constants obtained with larger pellets (105–149 μm) yields a mean activation energy of roughly 56 kJ/mol (see Figure 6). This confirms the existence of pore diffusion limitations in the 280–305°C range. Consistent with intrinsic kinetics control in the 235–270°C range, the kinetic constants *and* the slope of the Arrhenius plot in the 235–270°C range are essentially the same as those obtained with smaller particles (see Figures 4 and 6).

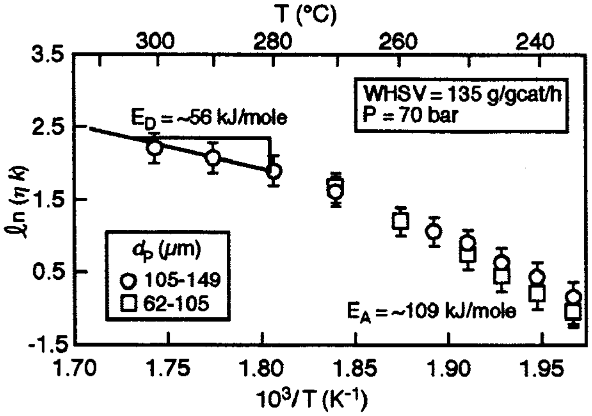

Figure 6. Arrhenius plot for 1-hexene isomerization on Pt/γ-Al_2O_3 catalyst particles (mean size = 127 μm) at 70 bar.

From the pore-diffusion controlled rate constants at 70 bar, the Thiele moduli (ϕ's) were calculated as follows. At a given temperature, the catalyst effectiveness factor (η) was calculated from the experimentally measured effective rate constant (ηk) and the intrinsic kinetic rate constant (k) estimated using the Arrhenius parameters (k_o and E_A) obtained with the low-temperature kinetic data. The Thiele modulus (ϕ) is then estimated from the following well-known η-ϕ equation, valid for isothermal, first-order, irreversible kinetics in spherical particles

$$\eta = \frac{3}{\phi^2}(\phi \coth \phi - 1) \tag{2}$$

where $\phi = (k/D_e)^{0.5}R$, and $R =$ the mean particle radius.

The estimated ϕ values at 290°C (~ 3.2) and 300°C (~ 4.9) suggest that the reaction rates are in the transition regime between kinetic control ($\phi < 0.5$) and severe pore-diffusion control ($\phi > 15$). This would mean that the apparent activation energy estimated from the effective rate constants at the higher temperatures should be more than half the intrinsic activation energy. This relationship is indeed manifest within the uncertainty ranges of the estimated intrinsic and apparent activation energies.

From the ϕ values, the effective diffusivity (D_e) of the hexene molecules in the γ-Al_2O_3 support was estimated and compared with predicted values as follows. Gas-phase effective diffusivity in porous catalyst supports may be predicted with the following equation

$$D_{e,p} = D_b\left(\frac{\epsilon}{\tau}\right) \tag{3}$$

Equation 3 assumes that bulk diffusion dominates in the pores, which is a valid assumption given that the reaction mixture behaves as a dense gas at 70 bar. The bulk diffusivity (D_b) of hexene molecules at supercritical conditions was estimated using the Takahashi (1974) correlation

$$\frac{D_b \cdot P}{(D_b \cdot P)^o} = f(P_r, T_r) \tag{4}$$

where the bulk diffusivity at the low pressure (denoted by the superscript o) is estimated using the Chapman-Enskog equation. The values of porosity ($\epsilon = 0.3$–0.6) and toruosity ($\tau = 4$–10) vary depending on the surface area and nature of the support (Satterfield, 1991). Hence, the $D_{e,p}$ values estimated using Eq. 3 are typically about two orders of magnitude less than D_b values calculated using Eq. 4. As shown in Table 1, the D_e values calculated via Eq. 2 are two to three orders of magnitude lower than the D_b values. This implies that if the experiments were carried out at the limit of pore-diffusion control (by employing sufficiently large pellets), it should be possible to indirectly estimate effective diffusivities of molecules in porous substrates at near-critical conditions from 1-hexene conversion data.

It must be noted that the D_e values reported in Table 1 are typical of those prevalent in liquid-filled pores. Thus, even though coke buildup is effectively thwarted in dense supercritical mixtures, the catalyst effectiveness factor is low because of pore-diffusion limitations. In contrast, at the lower temperatures and pressures in the supercritical region ($T =$ 235–270°C; $P = 35$ and 50 bar), the coke laydown is virtually eliminated *and* catalyst effectiveness is also unity. Thus, there exists an optimum combination of liquid-like densities and gas-like transport properties, which thwarts catalyst coking as well as maximizes catalyst effectiveness. These observations are consistent with predictions of a single-pore model of simultaneous reaction, transport, and decoking in supercritical reaction media (Baptist-Nguyen and Subramaniam, 1992).

Table 1. Effective Diffusion Coefficients Estimated from Experimental Rate Measurements at 70 bar*

T	η	ϕ	D_e ($m^2s^{-1} \times 10^{10}$)	D_b ($m^2s^{-1} \times 10^8$)
(°C)	(from Exp.)	From Eq. 2	From ϕ	From Eq. 4
290	0.65	3.2	0.78	5.9
300	0.49	4.9	0.51	6.3

*Mean particle size = 127 μm. (Effective rate constants are shown in Figure 6.)

Conclusions

For the geometric isomerization of 1-hexene on a Pt/γ-Al_2O_3 catalyst, deaeration of the feed, reduction of peroxide impurities to 2 ppm or less and reactor surface passivation by silicosteel coating significantly reduce the formation of hexene oligomers that are detrimental to the isomerization activity of the catalyst. The reduction in oligomer formation in conjunction with supercritical reactor operation (235–305°C; 35–70 bar) result in constant isomerization activity with neither measurable coke laydown nor surface-area and pore-volume losses. The steady isomerization rates at supercritical conditions allow an intrinsic kinetic study of hexene isomerization on the Pt/γ-Al_2O_3 catalyst under the nondeactivating conditions. Effective rate constants, estimated from the steady isomerization rates assuming plug flow and first-order kinetics, provided an average intrinsic activation energy of 109 kJ/mol in the 235–270°C range, confirming that the hexene isomerization to geometric isomers is indeed the dominant reaction pathway at the pressures studied. At temperatures beyond 280°C, a decrease in the apparent activation energy was observed, suggesting the onset of pore-diffusion limitations. Effective diffusivities of hexene molecules in the pores, estimated from the catalyst effectiveness factor values at 70 bar are on the order of 10^{-10} m^2/s, similar to what one would expect from liquid-like liquid mixtures. Our results confirm that there exist optimum conditions in the near-critical region wherein catalyst activity and effectiveness factor are maximized.

Acknowledgments

This work was supported in part by the American Chemical Society Petroleum Research Fund (ACS-PRF# 31793-AC5) and in part by EPA/NSF, Environmentally Benign Processing Initiative (Grant No. R824729-01-0). We thank Engelhard Corporation for providing the catalysts. The help provided by Brian J. Wright in equipment modification and acquiring some of the experimental data is gratefully acknowledged.

Notation

D_b = bulk diffusivity of hexene molecules ($m^2 \cdot s^{-1}$)
D_e = effective diffusivity of hexene molecules in γ-Al_2O_3 ($m^2 \cdot s^{-1}$)
E_A = intrinsic activation energy ($kJ \cdot mol^{-1}$)
E_D = diffusion influenced activation energy ($kJ \cdot mol^{-1}$)
X_e = 1-hexene effluent mole fraction
X_o = 1-hexene feed mole fraction
η = catalyst effectiveness factor
ν = volumetric flow rate (mL/min at reactor T and P)

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Manuscript received Dec. 15, 1998, and revision received May 4, 1999.