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ANALYSIS OF KINETIC DATA ACCOMPANIED BY CATALYST FOULING WITH APPLICATION TO OLEFIN HYDROGENATION

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Abstract—Measurements of kinetic data in experimental catalytic reactors are often plagued by non-constant catalytic activities, for example, due to unexpected fouling of catalysts, even during a relatively short time interval. The purpose of the present work is to illustrate how the data analysis in the composition space can be conveniently employed to derive appropriate kinetic information from such ill-defined rate data. The catalytic reaction considered is the hydrogenation of propene, butene, and their mixtures at 3.5 MPa over a presulfided Co-Mo catalyst supported on gamma-alumina, in which volatile polymer formation of butene at low reaction temperatures and depolymerization at higher temperatures are observed to occur. The present work reports the data analysis methods employed, which eventually have led to consistent reaction pathways and to the determination of relative rate constants associated with them. The results reported herein may be useful for designing and operating commercial hydrotreaters where various C_3/C_4 olefin mixtures are hydrogenated. The methodology adopted here may be extended to any complex reaction system such as catalytic reforming of naphtha.

INTRODUCTION

Measurements of kinetic data in experimental catalytic reactors are often plagued by non-constant catalytic activities, for example, due to unexpected fouling of catalysts, even during a relatively short time interval. Then, the interpretation of the resultant data becomes very difficult, if not impossible. The purpose of the present work is to illustrate how the data analysis in the composition space can be conveniently utilized to derive appropriate kinetic information from such ill-defined rate data. The rationable behind this approach is that, although the composition-reaction time data obtained from catalysts undergoing fouling are inconsistent, they may turn out to be consistent when analyzed in the composition space that is independent of the reaction time.

In the classical work of Wei and Prater [1], the isomerization of butene isomers had been analyzed in the composition space, whereby the relative first-order rate constants were unambiguously determined. This method was also applied to simultaneous isomerization and hydrocracking of five hexane isomers over a Pt/Al_2O_3 catalyst by Christoffel [2]. The Wei-Prater method is essentially based on a transformation of the pure component coordinates in the composition space into the characteristic directions of the rate constant matrix, which culminates in the so-called "straight line reaction path". These paths are experimentally observable only when the starting feeds have specific compositions. However, few experiments are normally carried out this way: Feeds of arbitrary compositions should be tested whenever circumstances arise. Thus an alternative method that does not require specific feed compositions for kinetic studies needs to be developed.

The main objective of this work is to develop such a method for C_3/C_4 olefin hydrogenation. Hydrogenation of light olefins, especially of butenes, is accompanied by polymerization at low temperatures and low hydrogen pressures [3]. In the present work it is found that, even under a high hydrogen pressure, the catalytic activities decrease appreciably due to polymer formation giving rise to poor reproducibility of the kinetic data. The interpretation of the rate data obtained from such a system is very difficult to analyze, if not impossible. The present work reports the methods employed to resolve the problems, which eventually have led to consistent reaction pathways and to the determination of the relative rate constants associated with them.

The catalytic reaction considered here is the hydrogenation of propene and butene under a high pressure over a sulfided Co-Mo catalyst supported on gamma-alumina. This reaction is of practical importance in hydrotreating a light petroleum fraction such as LPG. Hydrotreating of petroleum is normally carried out over a bed of presulfided Co-Mo, Ni-Mo, or Ni-W catalyst supported on gamma-alumina [4, 5]. If substantial olefins are present in LPG, it is often required to hydrogenate them in an existing refinery hydrotreater. In this case, depending on the quantity of olefins present, the associated heat of reaction can be so large that, to avoid excessive local temperature rise, the reaction rate and its temperature dependence should be known for the proper control of reactor inter-cooling duties. Also the feed temperature should be kept as low as possible to prevent excessive temperature rise near the reactor inlet.

Studies on olefin hydrogenation over Co-Mo/γ-Al_2O_3 were reported by several investigators. Using a pulse micro-reactor, Balois and Beaufiles [6] found that the hydrogenation rate of 1-butene was first-order with respect to 1-butene on a sulfided Co-Mo/γ-Al_2O_3. The differential kinetic data of Lee and Butt [7] could be correlated by, in the temperature range between 250 and 320°C on a reduced Co-Mo/γ-Al_2O_3,

$$R_4 = \frac{a\,P_4\,P_H}{1 + b\,P_4} \tag{1}$$

or possibly by

$$R_4 = \frac{c\,P_4\,P_H}{(1 + d\,P_4)^2} \tag{2}$$

where R_4 is the hydrogenation rate of 1-butene, P_4 and P_H are the partial pressures of 1-butene and hydrogen, respectively. Discrimination between these two models was difficult from their data alone. The calculated apparent activation energy was approximately 34 kJ/gmole. The effect of H_2S was to inhibit the reaction. They reported that the hydrogenation activities over sulfided and reduced catalysts were identical when measured after standard pretreatments.

Uchytil et al. [8] investigated hydrogenation of twelve C_2 to C_{10} olefins on a reduced Co-Mo/γ-Al_2O_3 at 300°C. Eq. (2) was proposed as a suitable rate expression, which, based on their earlier works, was equally valid for any type of catalysts. Most interestingly, they found that the initial hydrogenation rate for any olefin attained a maximum at about 0.15 mole fraction of the olefin. Part of their results are summarized in Table 1 for future reference. It is seen from these data that the hydrogenation rates of 1-butene and its isomers exhibit approximately equal rates except for isobutylene which is substantially higher. They also claimed that hydrogenation and olefin isomerization reaction are parallel processes. This observation will be utilized in this work to construct the butene hydrogenation reaction pathways.

Table 1. Initial hydrogenation rates of light olefins [8]

Olefin structure	Initial rate
$CH_2=CH_2$	46
$CH_2=CH\text{-}CH_3$	40
$CH_2=CH\text{-}C_2H_5$	19
t-$CH_3\text{-}CH=CH\text{-}CH_3$	21
c-$CH_3\text{-}CH=CH\text{-}CH_3$	20
$CH_2=C(CH_3)_3$	32

Run conditions: Catalyst = Co-Mo/γ-Al_2O_3 (prereduced), 1 atm, 300°C, differential reactor (<7% conversion)

On reviewing these and other literature data on C_3 and C_4 olefin hydrogenation [9], the followings were noted: (1) When the starting reactant is 1-butene, double bond migration (olefin isomerization) is much more extensive than hydrogenation; (2) Most of the literature data indicates that, irrespective of catalyst compositions, the hydrogenation rate is approximately first-order with respect to H_2 with an apparent activation energy of about 42 kJ/gmole. The reaction order with respect to butene is not conclusive; (3) Propene hydrogenation rate appears to be about twice larger than that of butene as shown in Table 1.

Pozzi and Rase [3] investigated catalyst fouling during isobutylene hydrogenation under atmospheric pressure over a reduced Ni/Kieselgur catalyst. Their experimental observations were: (1) Without H_2, polymer was readily formed by passing isobutylene at 93°C. The polymer consisted of C_6, C_8, and C_{12}, mainly C_8; (2) When both H_2 and isobutylene were contacted with the catalyst, polymer formation was suppressed markedly; (3) After a period of initial rapid fouling, the catalyst activity reached a relatively stable value different from zero; (4) H_2 reduction of the fouled catalyst at 316°C resulted in almost complete recovery of the initial activity. According to Ellis [10], polymerization increases in the order 1-butene, 2-butene, and isobutylene. Notably he also reports that the following isobutylene dimerization reaction

$$2C_4H_8\ (\text{gas}) = C_8H_{16}\ (\text{liquid})$$

is not thermodynamically feasible above 270°C. Since these observations of olefin polymerization are relevent at one atmospheric pressure, polymerization may or may not be significant at the currently employed operating pressure of 3.5 MPa. However, it is observed that, even at this pressure, polymerization is indeed significant at low reaction temperatures.

EXPERIMENTAL PROCEDURE

Experiments were conducted in a standard high pressure continuous flow fixed bed reactor. The catalyst was a commercial Co-Mo/γ-Al_2O_3, 0.16 cm in diameter extrudate. The catalyst was sulfided with 10% H_2S in H_2 before use. The feed olefin in admixture with saturate stored in a pressurized cylinder equipped with dip tubes was delivered by a Ruska pump into the reactor section. The hydrogen flow rate was controlled and monitored by a mass flowmeter. The preheater and reactor both enclosed in a fluidized sand bath were controlled to maintain isothermal conditions. However, at high reaction temperatures, heat transfer through the reactor wall was not sufficient enough to dissipate the heat of reaction that axial temperature gradients along the reactor could not be completely eliminated. The reactor pressure was kept at 3.5 MPa in all experiments by means of a back-pressure regulator. Feed liquid was analyzed by GC and products were analyzed by GC and MS to determine its olefin and hydrogen contents.

The experiments were conducted in the following sequence:

(1) Preliminary runs with propene to search for the reaction initiation temperature followed by hydrogenation at different temperatures and space velocities with the feed composition of hydrogen/propene/propane = 70/9/21 mole%.

(2) Preliminary runs with 1-butene to search for the reaction initiation temperature followed by hydrogenation at different temperatures and space velocities with the feed composition of hydrogen/1-butene/n-butane = 80/10/10 mole%.

(3) Runs with the feed composition of hydrogen/1-butene/n-butane = 80/10/10 mole% to identify polymer formation at 120℃.

(4) Runs with propene and 1-butene mixtures to confirm polymer formation at 120℃.

(5) Runs with propene and 1-butene mixtures at different temperatures and space velocities to determine the blend hydrogenation rates.

For the propene hydrogenation experiments a reactor containing 3.8g of catalyst, diluted sufficiently with inerts to maintain isothermal conditions, was employed while 3.8, 7.6 or 22.8g of catalyst was used for 1-butene experiments to obtain proper space time. The catalysts in the reactor were kept in hydrogen atmosphere when not in service and thus they were not replaced with fresh catalysts until all temperature and space velocity scoping runs in a given series were finished.

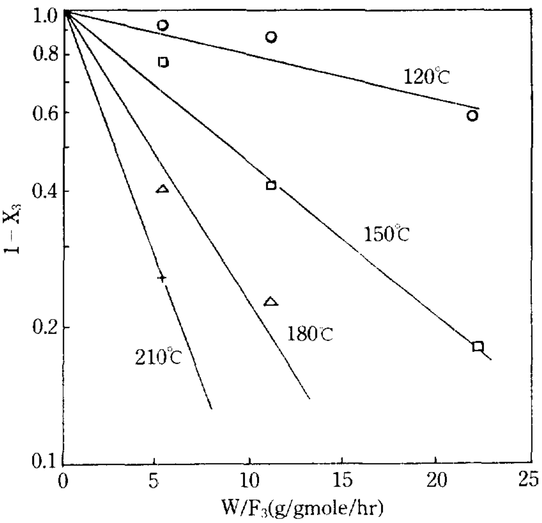

Fig. 1. Propene conversion vs. inverse weight hourly space velocity of propene feed. 3.5 MPa total pressure, feed hydrogen/propene/propane = 70/9/21 mole%.

EXPERIMENTAL RESULTS

1. Propene Hydrogenation

Fig. 1 shows the propene conversion vs. the inverse of the space velocity F_3/W, where F_3 is the molar flow rate of propene at the inlet of reactor and W the weight of catalyst, in the temperature range between 120 and 210℃. The straight lines indicate that the propene hydrogenation rate is roughly first-order with respect to propene. Assuming that the rate is also first-order with respect to hydrogen, it can be written as

$$R_3 = K_3 P_3 P_H \qquad (3)$$

where R_3 is the hydrogenation rate of propene and P_3 the partial pressure of propene. When the calculated rate constants, K_3, are plotted against 1/T the results shown in Fig. 2 are obtained. The calculated activation energy from this figure is 46 kJ/gmole, which is close to the literature data. Since propene and 1-butene are of a homologous olefin series, the hydrogenation of 1-butene at a similar hydrogen pressure is expected to be first-order over the same catalyst.

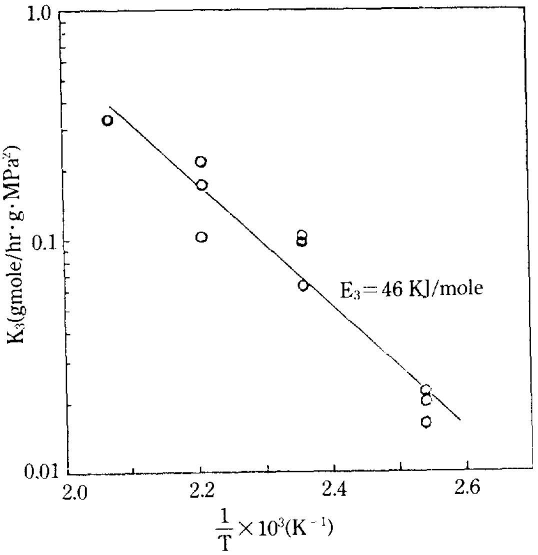

Fig. 2. Arrhenius temperature dependence of first-order rate constant of propene hydrogenation.

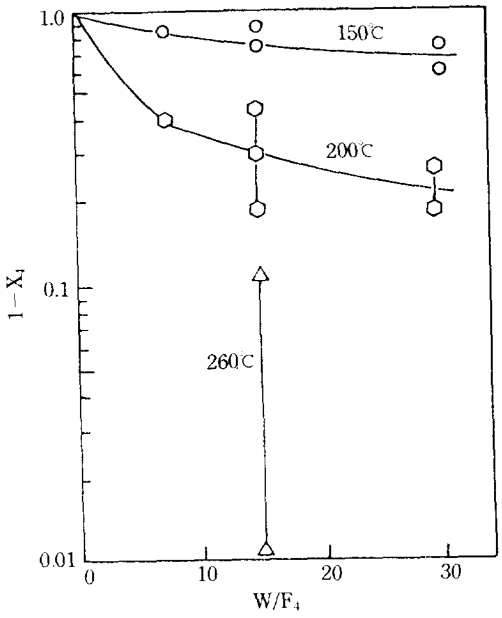

Fig. 3. Butene conversion vs. inverse weight hourly space velocity of 1-butene feed. 3.5 MPa total pressure, feed hydrogen/1-butene/propane=80/10/10 mole %.

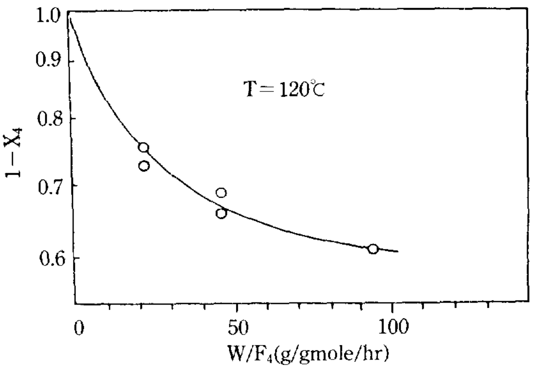

Fig. 4. Butene conversion vs. inverse weight hourly space velocity of 1-butene feed at prolonged space time. 3.5 MPa total pressure, feed hydrogen/1-butene/propane=80/10/10 mole%.

2. Butene Hydrogenation

Fig. 3 shows the butene conversion vs. the inverse of the space velocity F_4/W, where F_4 is the molar flow rate of 1-butene at the inlet of reactor, in the temperature range between 150 and 260℃. During these runs 1-butene was converted rapidly to cis- and trans-2-butene substantiating rapid double bond migration. Thus, the conversion X_4 in this figure actually refers to that of butene mixtures to n-butane, since isomerization of 1-butene to 2-butene is not considered as conversion. Hence the term butene conversion will be used below.

From these results alone the data does not appear to fit into a first-order model. In fact the scatter is so large that even rough estimation of butene hydrogenation rate is difficult. For example, the data at 260℃ shows that butene conversion was 90% in one case and the repeat of this run, shortly afterward, yielded 99% conversion, which is a two-fold increase in the first-order rate constant. Such a discrepancy is considered too significant to be simply attributed to experimental errors, such as reactor non-isothermality.

To resolve this problem, with fresh catalysts, a series of runs at much shorter space velocities to prolong the space time were conducted at 120℃ using the identical feed composition and pressure as before. The results are shown in Fig. 4. As can be seen in this figure, at this low reaction temperature the butene conversion remained less than 35% and throughout these runs the axial temperature profiles could be maintained nearly uniform. However, the results did not show a straight line first-order kinetics. Rather the butene conversion followed the 150 and 200℃ data pattern in Fig. 3, concave downward.

3. Catalyst Fouling due to Polymer Formation

As mentioned previously, according to the observations of Pozzi and Rase [3], reduction of the fouled catalyst at 316℃ could restore the hydrogenation acti-

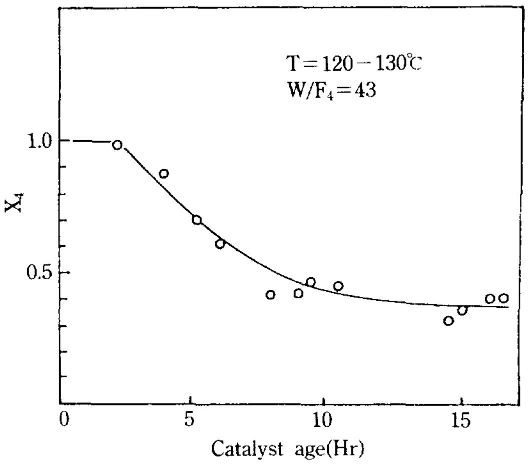

Fig. 5. Deactivation of butene hydrogenation at 120°C. W/F_4=43, 3.5 MPa total pressure, feed hydrogen/1-butene/propane=80/10/10 mole%.

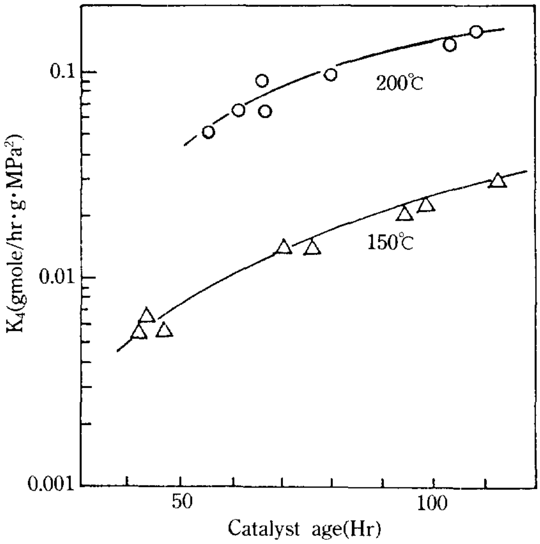

Fig. 6. Increase of butene hydrogenation rate constant with catalyst age. 3.5 MPa total pressure, feed hydrogen/1-butene/propane=80/10/10 mole%.

vity. Thus, catalyst regenerability via H_2 reduction at high temperatures appears to be a convenient way to test the polymerization hypothesis. To confirm this, a batch of catalysts having been tested at 120℃ described in the last paragraph was reduced in hydrogen at 260℃ and was subjected to the identical hydrogenation experiments of Fig. 4 at 120℃ with W/F_4=43. As shown in Fig. 5, immediately after the introduction of 1-butene feed, the butene conversion reached nearly 100% with a high exotherm observed in the reactor inlet. During the subsequent 8 hour span, the exotherm was seen moving down the reactor with rapid decline in butene conversion. For the next 8 hours the butene conversion appeared to be leveled off at 35% which was about the activity of the catalyst that had been obtained prior to reactivation in hydrogen, i.e., the conversion at W/F_4=43 in Fig. 4. Thus, the fouling of catalysts by polymer formation and reactivation in hot hydrogen was substantiated.

A more direct evidence of polymer formation was obtained, while taking samples from the reactor system, by isolating an oily, sticky and volatile material yellowish in color. This material was evidently causing rapid decline in butene conversion.

The scatter of data in Fig. 3 can now be interpreted in terms of catalyst fouling. Prior to the runs shown in Fig. 3, the catalyst was subjected to hydrogenation at low temperatures in order to identify the reaction initiation temperature at which catalyst fouling appeared to have been extensive. Subsequent clean-up of the catalyst surface induced by hydrogenation at higher temperatures might have yielded non-constant catalytic activities resulting in the scatter of data during the ensuing temperature and space velocity scoping runs.

If this hypothesis is real, rearrangement of the kinetic data in Fig. 3 with respect to catalyst age would exhibit a definite trend of activities. In fact, Fig. 6 is the plot of the first-order rate constant of butene hydrogenation rate, K_4, which is define by

$$R_4 = K_4 P_4 P_H \qquad (4)$$

As seen, the catalytic activity increases with the catalyst age.

4. Propene/Butene Mixture Hydrogenation

When a mixture of propene and butene is hydrogenated, the presence of propene may alter the fouling characteristics of butene. To determine this hypothesis two sets of experiments were conducted at 120℃, 3.5 MPa with 80 mole% hydrogen in feed. The results are shown in Fig. 7, which indicates that fouling at this low temperature is unavoidable. The mixture B in Fig. 7 contains more butene than A and the more pronounced deactivation of the former is apparently due to higher content of butene in the blend.

In order to determine the relative rates of hydrogenation of propene and butene, various olefin mixtures were hydrogenated at 3.5 MPa, 150℃ and 180℃. The feed compositions employed were

hydrogen = 60 mole%

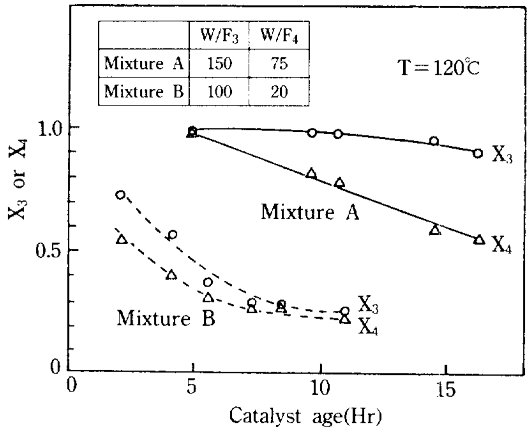

Fig. 7. Deactivation of propene/butene mixture hydrogenation at 120°C. 3.5 MPa total pressure, 80 mole% hydrogen.

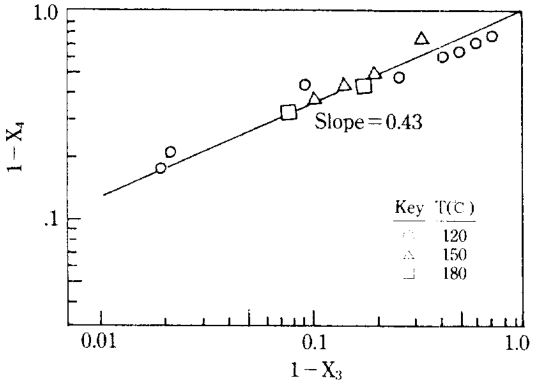

Fig. 8. Selectivities of propene and butene conversions in the temperature range between 120 and 180°C. 3.5 MPa total pressure, 60 or 80 mole% hydrogen.

propene = 6-10 mole%
1-butene = 4-10 mole%

the rest being propane and n-butane.

The results are shown in Fig. 8, which also includes the 120℃ data of Fig. 7. The straight line correlation between log $(1-X_3)$ and log $(1-X_4)$ suggests that the hydrogenation rate of butene is first-order with respect to butene partial pressure due to the reason outlined below.

Assuming that both propene and butene hydrogenation rates are first-order with respect to olefin and to hydrogen as written in Eqs. (3) and (4), respectively, and also assuming that the hydrogen partial pressure is nearly constant along the reactor, the conversions for a blend feed are given by

$$1-X_3=\exp\left[-K_3\frac{W}{F_3}P_{30}P_{H0}\right] \tag{5a}$$

$$1-X_4=\exp\left[-K_4\frac{W}{F_4}P_{40}P_{H0}\right] \tag{5b}$$

where P_{i0} refers to the corresponding component's partial pressure at the reactor inlet. Thus, it follows that

$$\frac{ln(1-X_3)}{ln(1-X_4)}=\frac{K_3}{K_4}\frac{F_4}{F_3}\frac{P_{30}}{P_{40}} \tag{6}$$

Now we have

$$P_{30}=P_t\frac{F_3}{F_t} \tag{7a}$$

$$P_{40}=P_t\frac{F_4}{F_t} \tag{7b}$$

where F_t is the total molar flow rate of feed mixture including hydrogen.

Therefore, from Eqs. (6) and (7), we obtain

$$\frac{ln(1-X_3)}{ln(1-X_4)}=\frac{K_3}{K_4} \tag{8}$$

This relation holds independent of the total pressure and feed compositions. The right-hand side of Eq. (8), the relative magnitude of rate constants, depends only on the temperature through the activation energy. Therefore, the straight line correlation obtained from the selectivity plot of Fig. 8 indicates that the hydrogenation rate of butene is first-order with respect to butene as propene is and that the hydrogenation rate of propene is 2.3 times higher than that of butene. Also it indicates that the activation energies of both propene and butene hydrogenation are nearly equal in the temperature range being investigated, since the observed selectivity is rather insensitive to the temperature. Furthermore, since the selectivity plot of Fig. 8 includes the data over catalysts undergoing fouling, these conclusions are valid for fouled catalysts. The observed rate ratio of 2.3 is roughly consistent with the differential data given in Table 1. The equal activation energies of both propene and butene appear to be consistent with other literature data as mentioned previously.

The preceding blend data indicates clearly that the hydrogenation rate of butene is first-order with respect to butene. However, the previous conversion vs. space time data did not support this unequivocally due to the non-constant nature of catalytic activities during

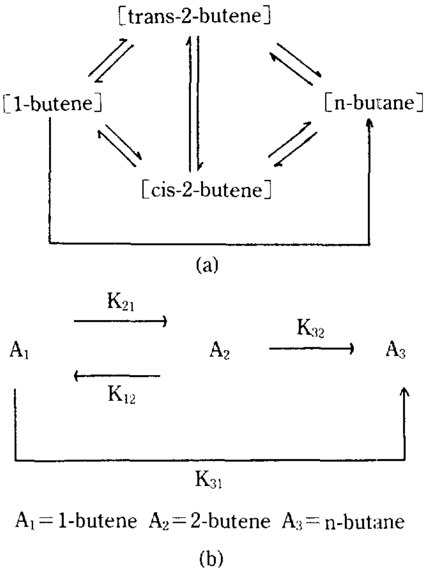

Fig. 9. Proposed reaction pathways of butene hydrogenation.

the test period. Thus, on alternative method of data analysis needs to be developed in order to prove the validity. In the sequel, a method of data analysis in the composition space will be attempted instead of the reaction time, which is the prime purpose of this paper.

ANALYSIS OF BUTENE HYDROGENATION DATA IN THE COMPOSITION SPACE

An inspection of all the butene data revealed that isomerization of 1-butene to 2-butene was much faster than hydrogenation to n-butane. Uchytil et al. [8] suggested that olefin hydrogenation and isomerization are parallel reactions. Thus, the reaction pathways may be constructed as illustrated in Fig. 9a. Assuming that the isomerization rate between trans- and cis-2-butene is much faster than the double bond migration, the reaction paths can be further simplified by lumping these two isomers as 2-butene, as shown in Fig. 9b. We shall reanalyze the previous butene data at 150℃ according to this scheme.

Let us first assume that the rates follow a pseudo-first-order model in hydrocarbon species. Referring to Fig. 9b the rate of change of each species is given by

$$\frac{dA_1}{dt} = -(K_{21}+K_{31})A_1 + K_{12}A_2 \qquad (9a)$$

$$\frac{dA_2}{dt} = K_{21}A_1 - (K_{12}+K_{32})A_2 \qquad (9b)$$

where A_1 and A_2 are mole fractions of 1-butene and 2-butene respectively, and t is a suitably defined reaction time. Here the sum of A_1, A_2 and A_3 is equal to 1, A_3 being the mole fraction of n-butane. The initial conditions are, for the reaction system presently considered,

$$A_1(0)=0.5,\ A_2(0)=0,\ A_3(0)=0.5 \qquad (10)$$

The solutions of Eq. (9) subject to Eq. (10) are

$$A_1(t) = \frac{0.5}{U_2-U_1}[-U_1\exp(-\lambda_1 t)+U_2\exp(-\lambda_2 t)] \qquad (11a)$$

$$A_2(t) = \frac{0.5}{U_2-U_1}[-\exp(-\lambda_1 t)+\exp(-\lambda_2 t)] \qquad (11b)$$

and it follows that

$$A_3(t) = 1 - A_1(t) - A_2(t)$$

In these expressions

$$\lambda_1 = 1/2(K_{12}+K_{21}+K_{31}+K_{32}+\sqrt{D})$$
$$\lambda_2 = 1/2(K_{12}+K_{21}+K_{31}+K_{32}-\sqrt{D})$$
$$D = [(K_{12}-K_{21})+(K_{32}-K_{31})]^2 + 4K_{12}K_{21}$$
$$U_1 = \frac{1}{2K_{21}}[(K_{12}-K_{21})+(K_{32}-K_{31})-\sqrt{D}]$$
$$U_2 = \frac{1}{2K_{21}}[(K_{12}-K_{21})+(K_{32}-K_{31})+\sqrt{D}]$$

Let us first prove that as the reaction goes to completion the ratio A_1/A_2 approaches a constant value. From Eqs. (11a) and (11b) we obtain

$$\frac{A_1(t)}{A_2(t)} = \frac{-U_1\exp[-(\lambda_1-\lambda_2)t]+U_2}{-\exp[-(\lambda_1-\lambda_2)t]+1} \qquad (12)$$

Since $\lambda_1 > \lambda_2$, it follows from Eq. (12) that

$$\lim_{t\to\infty}\frac{A_1(t)}{A_2(t)} = U_2 \qquad (13)$$

Referring to Fig. 9b again, by resorting to the principle of microscopic reversibility (or the principle of detailed balancing), if we isolate the isomerization reaction between 1-butene and 2-butene

$$A_1 \underset{K_{12}}{\overset{K_{21}}{\rightleftarrows}} A_2$$

the ratio of the reverse and forward rate constants K_{12}/K_{21} is equal to the ratio A_1/A_2 at equilibrium that

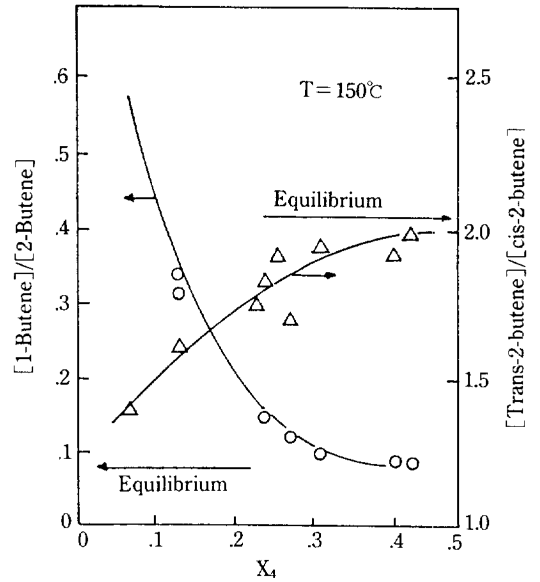

Fig. 10. Approach to equilibrium of butene isomers at 150 °C.

is determined from the free energy change. The estimated equilibrium mole fraction ratios at 150℃ are [11]

$$\text{1-butene/2-butene} = (A_1/A_2)_{equil} = K_{12}/K_{21} = 0.084$$
$$\text{trans-2-butene/cis-2-butene} = 2.0$$

For the reaction paths of Fig. 9b that include the irreversible hydrogenation steps of 1-butene and 2-butene, as the reaction goes to completion, the actual ratio A_1/A_2 will be affected by the relative magnitudes of K_{32} and K_{31}. In fact it can be readily proved that the sign of $U_2 - K_{12}/K_{21}$, i.e., $U_2 - (A_1/A_2)_{equil}$, is solely dependent on the sign of $(K_{32} - K_{31})$. Therefore, it can be concluded that

$$\text{if } K_{32} > K_{31}, \text{ then } U_2 > (A_1/A_2)_{equil}$$
$$\text{if } K_{32} < K_{31}, \text{ then } U_2 < (A_1/A_2)_{equil}$$
$$\text{if } K_{32} = K_{31}, \text{ then } U_2 = (A_1/A_2)_{equil}$$

Fig. 10 is the mole fration ratio plot of butenes at 150 ℃. As seen, the mole fraction ratios approach the thermodynamic equilibrium values as the reaction advances. Therefore, it can be concluded that K_{32} is approximately equal to K_{31}.

To show that the observed experimental data are consistent with the proposed first-order scheme, elimination of t in Eq. (11a) and (11b) gives rise to

$$ln(A_1 - U_2A_2) = \frac{\lambda_1}{\lambda_2} ln(A_1 - A_2) + \left(\frac{\lambda_1}{\lambda_2} - 1\right) ln2 \qquad (14)$$

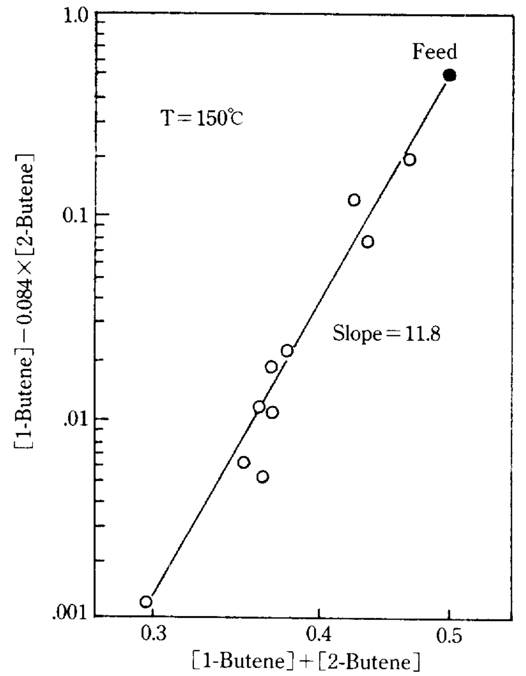

Fig. 11. Plot of butene hydrogenation data at 150°C according to Eq. (14).

Therefore, the plot of $ln(A_1 - U_2A_2)$ vs. $ln(A_1 - A_2)$ will give a straight line if the postulated reaction pathways are correct, the slope being equal to λ_1/λ_2. Fig. 11 is the plot of the 150℃ data, which agrees well with Eq. (14). The calculated slope from the figure is

$$\frac{\lambda_1}{\lambda_2} = 11.8$$

Furthermore, in terms of the rate constants, the ratio λ_1/λ_2 under the assumption of $K_{32} = K_{31}$, can be expressed as

$$\frac{\lambda_1}{\lambda_2} = 1 + \frac{K_{12}}{K_{31}} + \frac{K_{21}}{K_{31}} \qquad (15)$$

Since the value of K_{12}/K_{21} is 0.084, Eq. (15) yields

$$\frac{K_{21}}{K_{31}} = 0.84$$
$$\frac{K_{12}}{K_{31}} = 9.96$$

Thus all the relative values of rate constants can be determined from the data unambiguously. Furthermore, from Eqs. (9a) and (9b), we have

$$\frac{d(A_1 + A_2)}{dt} = -K_{31}A_1 - K_{32}A_2$$

$$= -K_{32}(A_1+A_2)$$

due to the fact that $K_{32}=K_{31}$. Hence, the hydrogenation of butene isomers should follow a first-order reaction, which is a convenient way of lumping isomers.

CONCLUSIONS

From the preceding discussions, it can be concluded that the analysis of experimental kinetic data in the composition space can provide meaningful kinetic informations even though the catalyst is subject to fouling during data acquisition. The methodology employed here can be extended to any complex reaction system such as catalytic reforming of naphtha. Modeling of commercial naphtha reforming has been attempted along this line [12].

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NOMENCLATURE

a : constant in Eq. (1) [gmol hr^{-1} gcat^{-1} MPa^{-2}]
A_1 : mole fraction of 1-butene [-]
A_2 : mole fraction of 2-butene [-]
A_3 : mole fraction of n-butene [-]
b : constant is Eq. (1) [MPa^{-1}]
c : constant in Eq. (2) [gmol hr^{-1} gcat^{-1} MPa^{-2}]
d : constant in Eq. (2) [MPa^{-1}]
E_3 : activation energy of propene hydrogenation [kJ/mol]
F_3 : molar flow rate of feed propene [gmol/hr]
F_4 : molar flow rate of feed 1-butene [gmol/hr]
F_t : molar flow rate of feed mixture including hydrogen [gmol/hr]
K_3 : first-order rate constant of propene hydrogenation defined in Eq. (3) [gmol hr^{-1} gcat^{-1} MPa^{-2}]
K_4 : first-order rate constant of butene hydrogenation defined in Eq. (4) [gmol hr^{-1} gcat^{-1} MPa^{-2}]
K_{ij} : pseudo-first-order rate constant for the reaction from j to i [hr^{-1}]
P_3 : partial pressure of propene [MPa]
P_{30} : partial pressure of propene at reactor inlet [MPa]
P_4 : partial pressure of butene [MPa]
P_{40} : partial pressure of 1-butene at reactor inlet [MPa]
P_H : partial pressure of hydrogen [MPa]
P_{H0} : partial pressure of hydrogen at reactor inlet [MPa]
P_t : reactor total pressure [MPa]
R_3 : rate of propene hydrogenation [gmol hr^{-1} gcat^{-1}]
R_4 : rate of butene hydrogenation [gmol hr^{-1} gcat^{-1}]
t : reaction time [hr^{-1}]
T : reaction temperature [K or ℃]
W : weight of catalyst [g]
X_3 : fractional conversion of propene [-]
X_4 : fractional conversion of butene [-]

REFERENCES

1. Wei, J. and Prater, C. D.: *Adv. Catal.,* **13**, 206 (1962).
2. Christoffel, E. G.: *Ind. Eng. Chem. Prod. Res. Dev.,* **18**(2), 143 (1979).
3. Pozzi, A. L. and Rase, H. R.: *Ind. Eng. Chem.,* **50**(7), 1075 (1958).
4. Gates, B. C., Katzer, J. R. and Schuit, G. C. A.: "Chemistry of Catalytic Processes", Chap. 5, McGraw-Hill, New York, NY (1979).
5. Satterfield, C. N.: "Heterogeneous Catalysis in Practice", Chap. 9, McGraw-Hill, New York, NY (1980).
6. Balois, J. M. and Beaufils, J. P.: *Reat. Kinet. Catal. Letters,* **3**(4), 355 (1975).
7. Lee, H. C. and Butt, J. B.: *J. Catal.,* **49**, 320 (1977).
8. Uchytil, J., Jakubickova, E. and Kraus, M.: *J. Catal.,* **64**, 147 (1980).
9. Kiperman, S. L.: "Catalytic Hydrogenation", Cerveny, L., editor, Chap. 1, Elsevier, New York, NY (1986).
10. Ellis, C.: "The Chemistry of Petroleum Derivatives, Vol. 2", Chap. 26, Reinfold, New York, NY (1937).
11. Reid, R. C., Prausnitz, J. M. and Poling, B. E.: "The Properties of Gases Liquids", 4th ed., McGraw-Hill, New York, NY (1987).
12. Ramage, M. P., Graziani, K. R. and Krambeck, F. J.: *Chem. Engg. Sci.,* **35**, 41 (1980).