THE INDIVIDUAL AND COMPETITIVE HYDROGENATIONS OF ETHYLENE AND PROPYLENE IN A STIRRED SLURRY REACTOR

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The hydrogenation of ethylene and propylene was studied in the presence of a 5% Pt/carbon catalyst suspended in water. In the hydrogenation of the respective olefin, the rate-controlling steps affecting the overall reaction rate were first examined. As for the results, the hydrogenation rates were found to be predominantly controlled by the mass transfer of olefin from the gas phase to the catalyst particles in the region of excess hydrogen, while in the region of excess olefin they were influenced not only by the mass transfer but also by the combination of the chemical reaction and the pore diffusion. For the latter region, an intrinsic kinetic expression was derived assuming the adsorption of molecular hydrogen as the rate-determining step.

For the competitive hydrogenation of both olefins, the selectivity, defined as the ratio of the reaction rate of propylene to that of ethylene, was examined on the basis of the results obtained in the hydrogenation of the individual olefin.

Introduction

A number of catalytic hydrogenations of gaseous unsaturated hydrocarbons may usually be carried out in fixed bed operations. However, slurry reactors, in which finely divided catalysts are suspended in an inert solvent, appear to offer some advantages in respect to the heat controls in the case of exothermic reactions. Koelbel *et al.*⁴⁾ and Farkas and Sherwood⁸⁾ have studied the hydrogenation of ethylene over a Raney nickel catalyst using a bubble column as a slurry reactor. The hydrogenation of acetylene has also been studied by Heck and Smith³⁾ in this type of the reactor. However, it seems that the kinetics of the intrinsic reaction has not satisfactorily been accounted by them. On the other hand, the use of a stirred slurry reactor allows one to analyze the chemical kinetics readily because the bubbles can be regarded as being well mixed¹¹⁾ as well as the slurries, and likewise to examine the mass transfer characteristics between the gas and the liquid, and the liquid and the particle.

In this work, the hydrogenation of ethylene and propylene on a 5% Pt/carbon catalyst suspended in water is described for the use of a stirred reactor. The resistances to the gas-liquid and liquid-particle

mass transfer of the reactants are first evaluated, and the intrinsic kinetic expressions are then derived. For the competitive hydrogenation of both olefins, further interest is focused on how the selectivities are influenced by some operating factors.

1 Experimental

A glass stirred reactor, 75 mm in I.D. by 180 mm high, with four baffle plates was used. The agitation device consisted of glass impellers with four flat turbine blades. The stirring speed was kept constant at 1800 rev/min throughout the experiments. A nozzle for gas supply was placed at the level of 1 cm above the bottom of the reactor. The catalyst used was a 5% Pt-carbon powder (particle diameter $d_p = 6 \mu$, particle density $\rho_p = 1 \text{ g/cm}^3$, porosity $\theta = 0.5$) manufactured by Nippon Engelhard Co., which was suspended over the range of the catalyst loading of 0.1 to 0.5 g/l in distilled water. Commercial hydrogen and nitrogen were used without further purification. A gas mixture which comprised hydrogen, ethylene and/or propylene (and nitrogen for dilution, if necessary) was fed at a total flow rate of 400 cm³/min. Hydrocarbon impurities were detected by chromatographic analysis to be less than 0.02% in the ethylene and to be less than 0.4% in the propylene.

Runs were made at temperatures of 5, 20 and 35°C under atmospheric pressure. A steady state was achieved in an hour after the hydrogenation was initiated, and the conversion of olefin was determined

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Fig. 1 Hydrogenation rates of ethylene

Fig. 2 Evaluation of resistances to mass transfer of ethylene

Fig. 3 Evaluation of resistances to mass transfer of hydrogen

by gas chromatography. The separation was obtained in a 4 m column filled with 0.2% squalane on active alumina. The reaction rate was calculated from the conversion, and the composition of each reactant in the gas phase was set equal to that in the effluent gas including the vapour of the solvent and the product.

2 Individual Hydrogenation of Ethylene and Propylene

2.1 Evaluation of mass transfer resistances

On the steady-state hydrogenation of olefin in a stirred slurry reactor, the rate of gas-liquid mass transfer of reactant i must be equal to the rate of liquid-particle mass transfer, and both of these rates must be equal to the rate at which reactant i is consumed by chemical reaction within the particles. Such a generally accepted concept^{6,9)} lead to the following expression for the overall reaction rate of reactant i :

$$\frac{C_{i4}^*}{r_i} = \frac{1}{k_{li}a_g} + \frac{1}{a_c} \left(\frac{1}{k_{ci}} + \frac{C_{si}}{\eta_i k_i f_i} \right) \quad (1)$$

It can be seen from this equation that the total resistance is made up of three separate resistances in series. The plots of C_{i4}^*/r_i vs. $1/a_c$ based on Eq. (1) may be useful for evaluating the magnitudes of the three resistances with the aid of the calculative approaches even in the absence of an *a priori* knowledge of the intrinsic kinetics.

In Fig. 1 the overall reaction rates, which were observed by varying the ethylene fraction in the gas feed, α_4 , during the hydrogenation of ethylene, are shown as a function of the partial pressure of ethylene p_4 . The maximum rates are attained with p_4 of 0.1 to 0.2 atm at the three temperature levels. As will be seen in Fig. 4, these pressures of ethylene $p_{4,max}$ correspond to the conditions where the saturated concentration of ethylene are almost comparable to those of hydrogen, because the solubilities of ethylene are usually 5 to 9 times larger than those of hydrogen. This suggests that the catalyst surface is primarily occupied by excess hydrogen under the conditions of $p_4 < p_{4,max}$, and by excess olefin under the conditions of $p_4 > p_{4,max}$. Therefore, it may be preferable to evaluate the mass transfer resistances for olefin in the region of excess hydrogen and those for hydrogen in the region of excess olefin. From this point of view, C_{i4}^*/r_4 at $\alpha_4 = 0.125$ and C_{i2}^*/r_2 at $\alpha_4 = 0.5$ are plotted against $1/a_c$ in Figs. 2 and 3, respectively. The linear relationships shown by these plots contain the possibility either of first order kinetics in reactant i ($f_i C_{\infty si}$) or of negligible reaction resistance ($C_{si}/\eta_i k_i f_i \approx 0$).

Calculation of volumetric liquid-phase mass transfer coefficients The volumetric liquid-phase mass transfer coefficients of olefins and hydrogen can be determined from the intercepts with the ordinate in Figs. 2 and 3. The secured values of $k_{li}a_g$ at 1800 r.p.m. are summarized in Table 1.

Evaluation of liquid-particle mass transfer coefficients Since the slopes of the straight lines shown in Figs. 2 and 3 involve a sum of the liquid-particle resistance and the reaction resistance, these two re-

Table 1 Evaluation of mass transfer characteristics
($N=1800$ r.p.m., $F_T=400$ cm³/min)

Temp. [°C]	$k_{i2}a_g$ [min ⁻¹]	$k_{i4}a_g$ [min ⁻¹]	$k_{i6}a_g$ [min ⁻¹]	$(1/k_{ei}^*)/(1/k_{ei} + C_{si}/\eta_i k_i f_i)$			k_{e2} [cm/min]	k_{e4} [cm/min]	k_{e6} [cm/min]
				H ₂	C ₂ H ₄	C ₃ H ₆			
5	3.72	2.38	1.54	0.36	1.47	1.50	13.8	3.82	2.10
20	4.65	3.47	2.68	0.46	1.50	1.43	19.7	5.86	3.33
35	6.12	4.86	—	0.68	1.76	—	29.1	8.44	—

distances cannot be determined separately. But it is possible to compare the slope of the straight line with the conservative value of the liquid-particle resistance $1/k_{ei}^*$ for a sphere settling at its terminal velocity. The Sherwood number corresponding to k_{ei}^* was estimated to be essentially 2 from the correlation of Brian and Hales¹⁾. The straight lines with the slopes of $1/k_{ei}^*$ are shown by broken lines in Figs. 2 and 3. Harriott²⁾ found the ratio of the actual liquid-particle mass transfer coefficient for agitated system to that for free settling sphere, k_{ei}/k_{ei}^* , to fall generally between 1 and 4. For the mass transfer of olefin, as shown in Table 1, the ratio of $1/k_{ei}^*$ to the slope of the straight line is approximately 1.5 regardless of the three different temperatures. This value, being in the range found by Harriott, gives a reasonable evidence that in the region of excess hydrogen the overall rates are possibly controlled by the mass transfer of olefin. Therefore, the liquid-particle mass transfer coefficients of olefin can be determined directly from the slopes of the straight lines in Fig. 2. On the other hand, for the mass transfer of hydrogen the slopes in Fig. 3 are larger than the estimated values of $1/k_{ei}^*$, and therefore it follows that the reaction resistance cannot be ignored in the region of excess olefin. For such a situation, there is no obvious way to separate the two resistances. However, as the ratio k_{ei}/k_{ei}^* in the low Sherwood number region is of minor influence on the Schmidt number of diffusing substance in the light of the form of Ranz-Marshall's correlation, the liquid-particle mass transfer coefficients of hydrogen k_{e2} are estimated by multiplying k_{e2}^* by a factor of 1.5 obtained for the mass transfer of olefin. The values of k_{ei} thus determined are also summarized in Table 1.

2.2 Hydrogenation rates in the region of excess hydrogen

The overall reaction rates in this region are assumed to be controlled by the mass transfer of olefin. The chain lines in Fig. 1 represent the calculated lines with the evaluated values of $k_{i4}a_g$ and k_{e4} .

2.3 Hydrogenation rates in the region of excess olefin

For the rate expression in this region, as it is necessary to account for the reaction resistance, the surface concentration of reactant i must be calculated from the equation,

Fig. 4 Concentration profiles throughout three-phase, relative importance of reaction resistance for reactant i and catalytic effectiveness factor in hydrogenation of ethylene at 5°C

Fig. 5 Effects of surface concentration of ethylene and hydrogen on reaction rates

$$C_{si} = C_{li}^* - (1/k_{i4}a_g + 1/k_{ei}a_c)r_i \quad (2)$$

In Fig. 4, the concentration profiles and relative importance of reaction resistance C_{si}/C_{li}^* calculated throughout the three-phase system are depicted for the typical hydrogenation of ethylene.

Fig. 5 shows the dependence of the hydrogenation rates of ethylene on the surface concentration of ethylene and hydrogen. The reaction rates are found to be of first order in hydrogen and of slightly negative order in olefin. Such tendencies have been

Fig. 6 Arrhenius plots of kinetic parameters

Fig. 7 Selectivities for competitive hydrogenation in the region of excess hydrogen

Fig. 8 Reaction rates of competitive hydrogenation in the region of excess olefin

encountered by many workers^{7,10)} who have dealt with the gas-phase hydrogenations of lower olefins in the kinetic regime.

However, the catalytic effectiveness factors for the present experimental data, estimated from the estab-

lished method by Satterfield and Roberts^{5,6)}, were within the range of 0.3 to 0.6 to imply the existence of the pore diffusion resistance. Therefore, the conservation equation for the reactant i within the particles is set up rigorously as follows:

$$\frac{D_i \theta}{\tau} \left(\frac{d^2 C_i}{dx^2} + \frac{2}{x} \frac{dC_i}{dx} \right) = \frac{\rho_p}{w} k_i a_c f_i \quad (3)$$

with the boundary conditions

$$x=0, \quad dC_i/dx=0 \quad (4)$$

$$x=d_p/2, \quad C_i=C_{si} \quad (5)$$

The tortuosity factor τ is postulated as 4, which is generally acceptable value for porous solid materials.

A discrimination among the intrinsic kinetic expressions (determination of f_i), which are presumed on the basis of Langmuir-Hinshelwood forms, are performed by means of a nonlinear least squares method. In the course of iterative procedure, Eqs. (3)–(5) are numerically solved to give the catalytic effectiveness factor. As a result of fitting the various data, the following equation was selected for the hydrogenation of ethylene.

$$r_4 = k_4 a_c \eta_4 f_4 = \frac{k_4 a_c \eta_4 C_{s2}}{1 + K_4 C_{s4}} \quad (6)$$

Similarly, for the hydrogenation of propylene,

$$r_6 = k_6 a_c \eta_6 f_6 = \frac{k_6 a_c \eta_6 C_{s2}}{1 + K_6 C_{s6}} \quad (7)$$

These equations suggest the adsorption of molecular hydrogen to be a rate-determining step. The temperature dependency of the rate parameters are shown in the form of Arrhenius type plots in Fig. 6, and the catalytic effectiveness factors estimated for the hydrogenation of ethylene at 5°C are shown in the lower half of Fig. 4. The solid lines in Fig. 1 represent the calculated lines from Eqs. (3)–(6).

3 Competitive Hydrogenation of Ethylene and Propylene

3.1 Selectivities in the region of excess hydrogen

Under the conditions of excess hydrogen, the hydrogenation rates are controlled only by the mass transfer of both olefins. Then the selectivity, defined as the ratio of the reaction rate of propylene to that of ethylene, may be given by the ratio of the mass transfer rates of both olefins as follows:

$$S = \frac{r_6}{r_4} = \frac{1/k_{l4} a_g + 1/k_{c4} a_c}{1/k_{l6} a_g + 1/k_{c6} a_c} \frac{C_{l6}^*}{C_{l4}^*} \quad (8)$$

Fig. 7 shows that the selectivity r_6/r_4 , observed by varying the relative fraction of the respective olefins in the total olefin feed of $\alpha_o=0.125$, exhibits a linear relation to the ratio of the concentration of both olefins.

3.2 Selectivities in the region of excess olefin

Fig. 8 shows the plots of r_4 vs. C_{s4} and r_6 vs. C_{s6}

observed for the total olefin feed of $\alpha_o=0.5, 0.625$ and 0.7 . Under these conditions, as the reaction resistance contributes to the overall process, it is of interest to see how the selectivity is affected by the intrinsic kinetic behaviour of the competitive hydrogenation or by the pore diffusion effect.

If the adsorption of molecular hydrogen is the rate-determining step as assumed for the individual hydrogenation, the consumption rate of hydrogen may be written as,

$$r_2 = k_{r4} a_c \eta_4 \theta_2 \theta_4 + k_{r6} a_c \eta_6 \theta_2 \theta_6 = k_a a_c \eta_2 (1 - \theta_4 - \theta_6) C_{s2} \quad (9)$$

Solving for θ_2 and with the assumption of equilibrium adsorption of olefins, one gets the following expressions for the reactions of ethylene and propylene, respectively.

$$r_4 = \frac{k_a a_c \eta_4 K_4 C_{s4} C_{s2}}{\{K_4 C_{s4} + (k_{r6}/k_{r4}) K_6 C_{s6}\} (1 + K_4 C_{s4} + K_6 C_{s6})} \quad (10)$$

$$r_6 = \frac{k_a a_c \eta_6 (k_{r6}/k_{r4}) K_6 C_{s6} C_{s2}}{\{K_4 C_{s4} + (k_{r6}/k_{r4}) K_6 C_{s6}\} (1 + K_4 C_{s4} + K_6 C_{s6})} \quad (11)$$

Eqs. (10) and (11) reduce to Eq. (6) for ethylene and Eq. (7) for propylene when another olefin concentration approaches zero. From the ratio of Eq. (11) to (10), it follows that the selectivity should change in proportion to the surface concentration ratio C_{s6}/C_{s4} when both olefin molecules are competitively adsorbed on the catalytic sites. As shown in Fig. 9, however, the selectivity deviates from the linear relationship with C_{s6}/C_{s4} , and also it seems to be affected by α_o . To clarify such experimental aspects, the pore diffusion effects were first examined on the basis of the combination of Eqs. (3)–(5), (10) and (11). As a result, it was proved that the selectivities were little influenced by the pore diffusion, *i.e.*, $\eta_4 \simeq \eta_6$. Therefore, it is suspected that the change in the selectivity may be due to the intrinsic kinetic behaviour. An additional assumption is to consider two kinds of sites, *viz.* (1) active site to which ethylene molecule alone is adsorbed, and (2) active site available for the competitive adsorption of both olefin molecules. Then the rate expression for the reaction of ethylene is rewritten as:

$$r_4 = \frac{k_a a_c \eta_4 K_4 C_{s4} C_{s2}}{\{K_4 C_{s4} + (k_{r6}/k_{r4}) K_6 C_{s6}\} (1 + K_4 C_{s4} + K_6 C_{s6})} + \frac{k'_a a_c \eta_4 C_{s2}}{(1 + K'_4 C_{s4})} \quad (12)$$

The solid lines in Figs. 8 and 9 show the calculated curves from Eqs. (3)–(5), (11) and (12) with the values of $k_a=2.66$, $k'_a=0.78$, $k_{r6}/k_{r4}=5.31$, $K_4=350.0$, $K'_4=0.0$, $K_6=48.0$ and $\eta_4 \simeq \eta_6=0.6-0.7$ which are estimated by a nonlinear least squares method. The values of K_4 and K_6 are rather close to the values at 5°C in Fig. 6 which were obtained in the individual hydrogenation of olefin.

Fig. 9 Selectivities for competitive hydrogenation in the region of excess olefin

Conclusions

The hydrogenations of ethylene and propylene were studied over a 5% Pt/carbon catalyst suspended in water by use of a stirred slurry reactor. On the hydrogenation of the individual olefin, the reaction rates in the region of excess hydrogen were found to be controlled by the gas-liquid and liquid-particle mass transfer of olefin. In the region of excess olefin the intrinsic reaction resistance and the pore diffusion resistance could not be ignored. Therefore, the intrinsic kinetic expression was derived assuming the adsorption of molecular hydrogen as the rate-determining step, and the catalytic effectiveness factor was estimated.

On the competitive hydrogenation of ethylene and propylene, the selectivity in the region of excess hydrogen was determined solely by the ratio of the mass transfer rate of propylene to that of ethylene. For the expression of the intrinsic reaction rate in the region of excess olefin, a model assuming two kinds of sites, which consisted of the active sites available for the adsorption of ethylene alone and those available for the competitive adsorption of both olefins, was appropriate. Thus, the selectivity in this region could be correlated to the ratio of Eq. (11) to (12) being subjected to some pore diffusion effects.

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Nomenclature

a_c	= specific external area of catalyst	$[\text{cm}^2/\text{cm}^3]$
C_{ii}	= concentration of reactant <i>i</i> in bulk liquid	$[\text{mol}/\text{l}]$

C_{li}^*	= concentration of reactant i on gas-liquid interface (calculated from Henry's law)	[mol/l]
C_{si}	= concentration of reactant i on catalyst surface	[mol/l]
D_i	= molecular diffusivity of reactant i	[cm ² /min]
d_p	= mean diameter of catalyst particle	[cm]
F_T	= total feed rate of gas mixture	[cm ³ /min]
f_i	= function of adsorption constants and concentration of reactants	
K_4, K_6, K'_4	= adsorption constants of ethylene and propylene	[l/mol]
k_a, k'_a	= adsorption rate constants of hydrogen	[cm/min]
k_4, k_6	= reaction rate constants of ethylene and propylene	[cm/min]
k_{ci}	= liquid-particle mass transfer coefficient of reactant i	[cm/min]
k_{ci}^*	= liquid-particle mass transfer coefficient of reactant i for free settling sphere	[cm/min]
$k_{li}a_g$	= volumetric gas-liquid mass transfer coefficient of reactant i	[min ⁻¹]
k_{r4}/k_{r6}	= ratio of surface reaction rate constant of olefin	[—]
N	= agitation rate	[r.p.m.]
p_4	= partial pressure of ethylene	[atm]
r_i	= reaction rate of reactant i	[mol/l·min]
S	= selectivity defined as r_6/r_4	[—]
w	= catalyst loading	[g/cm ³], [g/l]
x	= distance	[cm]
α_i	= relative fraction of reactant i in gas feed	[—]
η_i	= catalytic effectiveness factor	[—]
θ	= porosity of catalyst particle	[—]
θ_4, θ_6	= surface coverage of ethylene and propylene	[—]

ρ_p	= apparent density of catalyst particle	[g/cm ³]
τ	= tortuosity factor of catalyst	[—]
<Subscripts>		
c	= catalyst particle	
g	= gas-phase, or bubble	
i	= reactant (2=hydrogen, 4=ethylene, 6=propylene, o =olefins)	
l	= bulk liquid phase	
s	= catalyst surface	
$*$	= gas-liquid interface	

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