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Influence of Internal Diffusion in 1-Butene Isomerization over Alumina at High Temperatures

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INTRODUCTION

The publication of a paper concerning the 1-butene isomerization over γ-alumina (*1*) aroused the interest of some researchers, mainly it is for that which concerns the reported conclusions. Particularly E. A. Lombardo and W. K. Hall in a private communication exposed some doubts about the role that diffusion could play in the reaction kinetics. Such observations have been taken into account, and these observations stimulated us to a further thorough examination of both the experimental and theoretical part of the work. Some of the observations made by Lombardo and Hall have been in the meanwhile published (*2*).

The two observations were the following: (a) a relatively low value of activation energy had been reported (about 6.9 kcal/mole); and (b) the *cis/trans*-2-butene ratio was at equilibrium from the very beginning of the reaction. Such observations could generate the doubt that the kinetic treatment we developed, based on the Langmuir–Hinshelwood (L.–H.) model, could be incorrect, since the process would appear diffusion-limited. If this would be true, the conclusions that we deduced about the change in catalyst activity with temperature could be incorrect.

To verify if the reaction could be significantly diffusion-limited, some calculations were made of the value of the modified Thiele modulus Φ_s (*3*). The obtained values in a rough approximation were close to unity and in agreement with the ones reported by Hall. According to the usual criterion for simple reactions, these values correspond to a value of the effectiveness factor of the catalyst close to unity. Actually, since the reaction rate found for the isomerization reaction is expressed by a L.–H. model reflecting inhibition, the criterion for simple reaction could not be valid and a deeper analysis must be performed. In order to take into account the effect of the inhibition on the effectiveness factor, the method given by Roberts and Satterfield (*4*) has been applied. Such a method was derived for catalyst slabs, but it can be applied also to our problem, because our purposes are mainly comparative. Since the values of the internal diffusion coefficients of the three butenes are quite close, on the basis of the rate equation obtained in (*1*), it derives that the values of the parameter $KP_{1\Delta}$ mentioned in (*4*) can be evaluated. Some typical values of such a parameter are $KP_{1\Delta} = 0.44$ ($T = 550°\text{C}$ and $\tau = 2.4$ g hr/mole) and $KP_{1\Delta} = -0.13$ ($T = 530°\text{C}$ and $\tau = 2.4$ g hr/mole). Such values are sufficiently low to justify that the employment of a first-order reaction rate equation is suitable for describing the effect of internal diffusion.

It has been emphasized that the evaluation of the modulus, Φ_s, is affected by an uncertainty due to the determination of the tortuosity factor. Such an uncertainty around an almost unitary value of Φ_s can significantly affect the value of the effectiveness factor.

To avoid such an uncertainty, some experiments have been planned and performed to verify if in our experimental conditions the kinetics of the process would be or not diffusion-limited.

EXPERIMENTAL

The same Alcoa F-110 alumina of the previous work (*1*) has been employed as catalyst. Such alumina has been crushed and sieved to obtain fractions of catalyst with a well-defined range of particle dimensions. With all these catalyst samples the experimental runs have been made in the same conditions of (*1*). First, two series of runs have been made at 530°C at two different contact times. Successively, to confirm the conclusions derived from these experiments, a new series of runs has been done at 550°C. The experimental conditions and data are reported in Table 1. The inert gas was nitrogen, 99.999% pure, and the 1-butene was drawn from the same batch of the previous work (*1*). The analysis of reagents and products was also done in the same way. The specific surface area of the catalyst, determined by the BET method, was the following:

Catalyst particle dimensions	Specific surface area (m²/g)
¼-in. balls	167
3.2–10 mesh	169
20–30 mesh	170
30–40 mesh	170
50–60 mesh	171
60–80 mesh	176

The specific pore volume, determined by the mercury penetration technique, was 0.225 ml/g. These values are slightly differ-

TABLE 1
EXPERIMENTAL CONDITIONS AND RESULTS

T (°C)	$P_{1\Delta}$ (atm)	$\tau = W/F$ (g hr/ moles)	Catalyst particle		Outgoing gas molar fractions (Ref. to 1 mole of fed olefin)			
			Weight (g)	Dimensions (mesh)	1Δ	*t*2Δ	*c*2Δ	ΔΔ
531	0.249	6.06	0.6061	¼-in. balls	0.8639	0.0747	0.0606	0.0008
530	0.250	6.11	0.5989	¼-in.–3.2	0.8293	0.0954	0.0741	0.0011
531	0.249	6.01	0.6007	3.2–10	0.6696	0.1886	0.1395	0.0022
530	0.248	6.28	0.6030	10–20	0.5574	0.2555	0.1844	0.0027
530	0.248	6.23	0.6039	20–30	0.3986	0.3490	0.2493	0.0031
530	0.249	6.18	0.6060	30–40	0.3250	0.3915	0.2800	0.0035
530	0.246	6.19	0.6068	50–60	0.3222	0.3840	0.2899	0.0039
530	0.253	6.25	0.6060	60–80	0.3222	0.3918	0.2825	0.0035
530	0.238	2.43	0.2823	¼-in. balls	0.9696	0.0152	0.0148	0.0004
530	0.242	2.26	0.2733	3.2–10	0.8726	0.0660	0.0606	0.0008
530	0.245	2.14	0.2842	20–30	0.6836	0.1776	0.1380	0.0008
530	0.248	2.32	0.2834	30–40	0.5613	0.2508	0.1867	0.0011
530	0.246	2.33	0.2841	50–60	0.4978	0.2921	0.2090	0.0011
530	0.245	2.35	0.2842	60–80	0.5017	0.2879	0.2092	0.0012
551	0.253	2.39	0.2971	¼-in. balls	0.9130	0.0445	0.0413	0.0012
550	0.250	2.44	0.2959	3.2–10	0.8693	0.0731	0.0551	0.0024
550	0.252	2.40	0.2957	20–30	0.5477	0.2592	0.1885	0.0046
550	0.248	2.46	0.2956	30–40	0.4661	0.3087	0.2204	0.0047
551	0.250	2.44	0.2952	50–60	0.4390	0.3268	0.2293	0.0041
550	0.251	2.43	0.2961	60–80	0.4413	0.3236	0.2308	0.0042

ent from the ones taken from Alcoa technical bulletins, and given in the previous work.

INTERPRETATION

The effectiveness of a catalyst is given, by definition, by the ratio of the actual reaction rate r_e and the rate obtainable if all of the catalyst surface were available to the reaction, r_t:

$$\eta = \frac{r_e}{r_t}.$$

Actually our experimental data are integral conversion and not reaction rate data. To calculate the catalyst effectiveness from such results, we can observe that, in our case, we can write:

$$\eta = \frac{r_e}{r_t} = \frac{M^*[x(1+R) - R]}{M[x(1+R) - R]} = \frac{M^*}{M} = \frac{k^*}{k}, \tag{1}$$

where

$$M^* = \frac{k^* b_\Delta P_\Delta}{1 + b_\Delta P_\Delta},$$

$$M = \frac{k b_\Delta P_\Delta}{1 + b_\Delta P_\Delta},$$

and x is the 1-butene conversion. R was defined in (*1*), and k^* and k are the effective reaction rate constant and the reaction rate constant when all of the catalyst surface is available, respectively. At constant hydrocarbon partial pressure, the 1-butene conversion can be obtained by integrating the reversible pseudo-first-order kinetic equation:

$$-\frac{dx}{d\tau} = M[x(1+R) - R]\cdot$$

For the same value of time factor τ we obtain:

$$\frac{k^*}{k} = \frac{\ln[(R+1)x^* - R]}{\ln[(R+1)x - R]},$$

where x^* is the actual conversion of the reacting substance, and x is the conversion obtainable if all of the surface would be available. The experimental data show that, for catalyst particle dimensions smaller than 50–60 mesh, the conversion is independent from particle size, and then we can assume such a datum as the conversion value obtainable when all of the catalyst surface is available. Then, substituting the values of x and x^* in Eq. (1), we can calculate the ratio k^*/k and hence η.

The plot of η vs catalyst particle dimensions is shown in Fig. 1. We can see that in our working conditions, provided that the reverse reaction is taken into account, the value of η is independent of the time factor τ at the same temperature and from temperature to temperature.

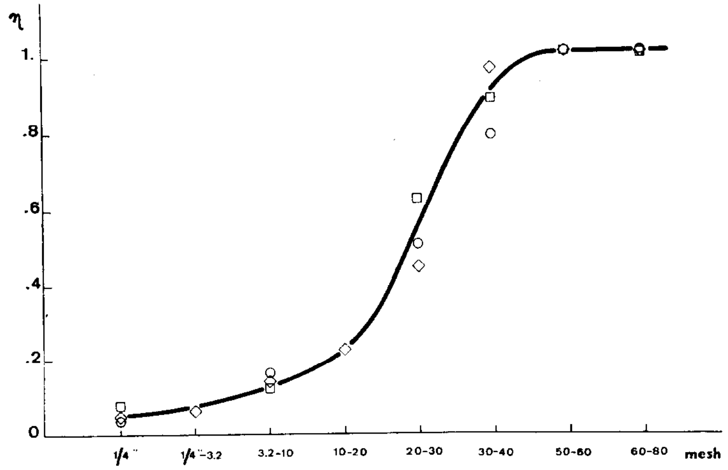

FIG. 1. Effectiveness factor vs catalyst particle dimensions. (◇) 530°C and $\tau \simeq 6$; (○) 530°C and $\tau \simeq 2.3$; (□) 550°C and $\tau \simeq 2.4$.

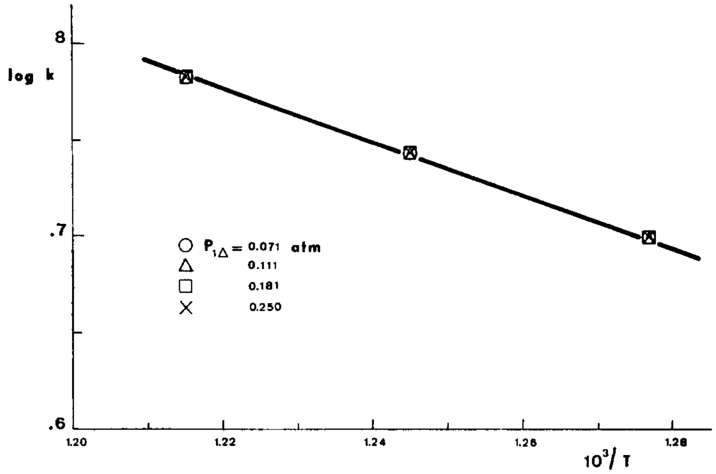

FIG. 2. Independence of activation energy from 1-butene partial pressure.

Concerning the given value of activation energy, about 6.9 kcal/mole, we can point out that it does not represent the apparent, but a value very close to the true activation energy value, calculated by the L.–H. model. The difference is only due to the fact that the effectiveness factor is just a little lower than unity. Besides this value is not affected (Fig. 2) by the 1-butene partial pressure, as it could happen if the reaction would be significantly diffusion-limited. In fact the kinetic runs of the previous work (*1*) were performed with a mean particle size corresponding to an effectiveness factor value of the order of 0.8 at any temperatures.

The apparent activation energy is bound to the true activation energy as follows:

$$E_a = E_t - Q,$$

where Q is the heat of adsorption of the reagent (—10.46 kcal/mole) (*1*). It follows that:

$$E_a = 6.9 + 10.46 = 17.36 \text{ kcal/mole}.$$

This value is comparable with those reported by other authors (*5–7*), which employed a pseudo-first-order reaction rate scheme, despite they worked in a different temperature range and with preactivated alumina.

Finally, from an observation of the data reported in Table 1, we can see that the *cis/trans*-2-butene ratio is constant and equal to the equilibrium value for the smallest particle dimensions, and tends to be slightly lower with increasing particle diameter. Such a phenomenon, connected to the observed decrease of effectiveness factor value in the same conditions, could be attributed to the increase of diffusion limitation and to a slight difference in the diffusion coefficients of the two isomers in such conditions, but the low deviations of the *cis/trans*-2-butene ratio from equilibrium values with ¼-in. balls can not be entirely explained on the basis of such an effect.

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