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LETTERS TO THE EDITORS

Comment on 1-Butene Isomerization over Alumina at High Temperatures

Recently, Forni *et al.* (*1*) reported the results of a study of the isomerization of 1-butene over Alcoa F-110 alumina between 510 and 550°C. Their data suggested to us that the reaction was diffusion limited under their experimental conditions, a possibility which they did not consider. The experimental fact which attracted our attention was that the *cis/trans* ratio was at equilibrium, even at very low conversion. This behavior is symptomatic of diffusion limitation because, when the residence time inside the pore system is long compared with the time of half reaction, the molecules may achieve equilibrium before diffusing back into the bulk gas phase. This picture is in agreement with the mathematical treatment of a similar system given by Wei (*2*).

Recently, Hightower and Hall (*3*) summarized the data in the literature and reported initial *cis/trans* ratios for alumina varying between 1.3 and 6.0. Included were data for many different aluminas and catalytic techniques, and for a wide range of temperatures (23–300°C). All these results contrast strikingly with those of Forni *et al.* (*1*).

Sometimes a reaction system may be mathematically tested for diffusion limitation. Several workers developed appropriate criteria for systems of various degrees of complexity (*2*, *4*), but a rigorous test could not be made for the experiments of Forni *et al.* (1) because insufficient data were given. Instead, an approximate treatment, based on the criterion first introduced by Wagner (*5*) and developed by others (*4*), was used. In this, it was assumed that early in the reaction the system could be adequately represented by a first order irreversible process, i.e.,

$$A \rightarrow B$$

where A represents 1-butene and B, the 2-butenes.

A modified Thiele modulus, Φ_s, may be defined (*4*) for a spherical particle as

$$\Phi_s = \frac{R^2}{C_g D_e}\left(-\frac{1}{V}\frac{dn}{dt}\right), \qquad (1)$$

where R (cm) is the average particle radius, C_g (mol cm^{-3}) is the reactant concentration in the gas phase, D_e (cm^2 sec^{-1}) is the *effective* diffusion coefficient and $-(1/V)(dn/dt)$ is the observed reaction rate per unit volume of catalyst particles (mol sec^{-1} cm^{-3}). Bulk diffusion outside the pores was neglected. It is not usually significant for gas-phase reactions unless intraparticle diffusion is highly rate limiting, but in that event, it will contribute further to the falsification of the kinetics. Thus, C_g was taken to represent the concentration at the pore mouths. The criterion to be applied is that diffusion effects are negligible when

$$\Phi_s \leqslant 1.0$$

The principal problem is to estimate D_e. Data given in Ref. (*1*) include: surface area, 180 to 280 m^2 g^{-1}; internal porosity, 0.272 and particle size, 20 to 40 mesh. No information concerning the pore size distribution was given, but data for another batch of F-110 alumina was obtained from the files of the Gulf Research & Development Company.* The distribution determined with the original ⅛-in. balls, was

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* Courtesy of Dr. O. A. Larson.

broad; it could not be accurately described as mono- or bimodal. Pore radii ranged from 15 to 300 Å, but only 25% of the pore volume was in the pores having radii larger than 100 Å and only 10% of the area was contributed by these pores. About half the pore volume and over 70% of the area was in pores having radii less than 50 Å. This material differed from that of Forni *et al.* (*1*) in that it had a higher porosity (0.34 $cm^3\ g^{-1}$) and a lower surface area (150 $m^2\ g^{-1}$). Hence, the Gulf sample had larger pores (estimated from ratio of pore volume to surface area), on the average than that of Forni *et al.* (*1*). Thus, of the two samples, the Gulf material should be the *less* affected by diffusion effects. Therefore, we tested for diffusion limitation using the Gulf data with the knowledge that whatever the result, Forni's catalyst (*1*) should have a higher value of Φ_s.

In order to ascertain the regime of diffusion within the pores, the bulk diffusivity, D_{12}, was calculated using a well-known formula based on modern kinetic theory (*4*); the result was $D_{12} = 0.55$ cm²/sec. The lower limit of the transition region (the maximum radius for which Knudsen diffusion applies) was calculated from the criterion, $D_k = 0.1D_{12}$ (D_k is the Knudsen diffusivity); a radius of 150 Å was obtained. Despite the fact that the Gulf sample had 11% of its pore volume with radii larger than 150 Å, it was assumed that Knudsen diffusion applied to the entire pore system. This assumption led to the calculation of a smaller value of Φ_s than the real one.

Because of the broad pore size distribution, the average pore radius ($\bar{r}$) was calculated using the following formula (*4*),

$$\bar{r} = \frac{\int_{V_1}^{V_2} r\,dv}{V_2 - V_1}; \tag{2}$$

here, $V_2 - V_1$ is the entire pore volume between the limits 300 and 7 Å, respectively. The resulting average radius, $\bar{r}$, was 74 Å. In the same vein, the tortuosity factor, τ, was taken equal to unity, a choice which again increased D_e above its probable value and thus minimized Φ_s. The result at 510°C was

$$D_e = 1.4 \times 10^{-2}\ \mathrm{cm^2/sec}.$$

The rate of reaction was calculated from the data given in Table 2 of Ref. (*1*) for 1-butene isomerization at a partial pressure of 0.25 atm at 510°C. These conditions were those for which the effect of diffusion would be the *least* important of the eight cases reported. We find for the initial rate of reaction

$$\left(-\frac{1}{V}\frac{dn}{dt}\right) = \frac{k_1 bP}{1 + bP}\cdot\frac{\rho_p}{3600}$$
$$= 1.5 \times 10^{-4}\ \mathrm{moles/sec\ cm^3},$$

where $k_1 = k_{12} + k_{13}$, is the rate constant for 1-butene going to the 2-butenes, b is the adsorption equilibrium constant, P is the initial partial pressure of 1-butene, ρ_p is the particle density of the catalyst and $C_g = 3.9 \times 10^{-6}$ moles/cm³ is the concentration of 1-butene in the gas phase at 510°. The kinetic form is equivalent to a reaction rate between first- and zero-order with respect to reactant.

Using these data, and the smallest size of the catalyst particles (40 mesh = 0.021 cm radius), a value for Φ_s was calculated, i.e., $\Phi_s = 1.2$. This value indicates that even under those circumstances which tend to minimize the effects of diffusion, the best that can be done is to reduce the value of Φ_s to about unity. In the real case, Φ_s will be much larger for the following reasons: (i) Data for the Gulf sample were used; the sample of Forni *et al.* (*1*) apparently had a smaller average pore radius; (ii) The tortuosity factor was taken as unity; Satterfield (*4*) suggested that when τ is unknown, typical values between 2 and 6 may be used; for example, Fejes *et al.* (*6*) reported $D_e = 0.27 \times 10^{-3}$ cm²/sec, calculated from direct kinetic measurement of a highly diffusion-limited isomerization of *n*-butenes, at 150°C, over silica–alumina. Since the diffusion was in the Knudsen regime, the value of the tortuosity factor could be estimated at $\tau \simeq 8$; (iii) The smallest particle size was used, whereas a better choice would have been to use an average particle radius; and (iv) The lowest ratio of rate to reactant concentration was used; higher values of Φ_s would have been obtained for all other experiments reported (*1*). For a given value of Φ_s, the effectiveness factor is lowered if reversibility of reaction is considered, but is raised if the kinetics are less than first-order (*4*). The two effects tend to counterbalance.

To estimate a more likely value of Φ_s, nothing can be done concerning the first factor. However, choosing $\tau = 4$, taking the *average* particle radius as 0.03 cm, and using the observed reaction rate for 530° and 0.111 atm, a value of 18 was obtained. Therefore, from the available data, it may be concluded that the reaction is probably diffusion limited.

It would have been interesting to compare the value of the apparent activation energy with other values reported in the literature to see if it has been lowered, as expected (*4*), by diffusion limitation. Hightower and Hall (*3*), Ogasawara and Cvetanovic (*7*) and Brouwer (*8*) reported values in very close agreement (12.0–12.5 kcal/mole), using different aluminas and catalytic techniques and covering a wide range of temperatures (0–200°C). Unfortunately, it is not possible to make this comparison because Forni *et al.* (*1*) activated their alumina *in situ* at different temperatures while the other workers did so beforehand at a constant temperature.

Forni *et al.* (*1*) derived an endothermic heat of adsorption for the *n*-butenes from their kinetic data. This unusual result may be quite significant if their treatment is correct. Before this conclusion can be accepted, however, it will be necessary to evaluate the effects of diffusion experimentally.

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REFERENCES

1. FORNI, L., ZANDERIGHI, L., AND CARRÁ, S., *J. Catalysis* **12**, 298 (1968).

2. WEI, J., *J. Catalysis* **1**, 526 (1962).

3. HIGHTOWER, J. W., AND HALL, W. K., *J. Phys. Chem.* **71**, 1014 (1967).

4. SATTERFIELD, C. N., "Mass Transfer in Heterogeneous Catalysis," M. I. T. Press, Cambridge, Mass., 1969.

5. WAGNER, C., *Z. Phys. Chem.* **A193**, 1 (1943).

6. FEJES, P., KALLÓ, D., AND SCHAY, G., *Congr. Catalysis, 4th, Symp. 3,* Paper No. 24.

7. OGASAWARA, S., AND CVETANOVIC, R. J., *J. Catalysis* **2**, 45 (1963).

8. BROUWER, D. M., *J. Catalysis* **1**, 22 (1962).

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