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NOTES

Acetic Acid Esterification Catalyzed by Mordenite

In a recently published paper (*1*), the kinetic of the esterification reaction of acetic acid with ethyl alcohol, in vapor phase, catalyzed by decationized Y zeolite, is described. The advantages of performing this reaction, in vapor phase, have been largely described in a recently published patent (*2*). We observed that also mordenite, directly exchanged with hydrochloric acid, has a strong catalytic action in promoting esterification in mild temperature conditions (100–150°C) and without formation of by-products. We also observed that mordenite imposes a diffusion limitation in the mentioned esterification reaction, while decationized Y zeolite does not. The difference is mainly due to their crystallite sizes and, therefore, to their different intracrystalline diffusion coefficients. In the present note, these aspects will be examined and discussed both for the kinetic behavior of Y decationized zeolite and acidic mordenite.

The kinetic data related to Y zeolite are those obtained in the already mentioned paper (*1*), while kinetic runs related to mordenite have been performed on Zeolon, directly exchanged with hydrochloric acid. These runs were performed both on pellets of about 0.20 cm of equivalent diameter and on sieved particles of 30–60 mesh, by feeding the reagent in vapor phase. A set of runs were also made by feeding, on pellets the reagents in liquid phase. In all cases, flow rates were kept sufficiently high in order to prevent the influence of external diffusion on the reaction rates. The results obtained in a tubular differential plug flow reactor, are reported in Fig. 1, arranged in an Arrhenius type plot.

It can be observed, first of all, that the results do not depend much on whether the external phase is a vapor or liquid, in agreement with the very rectangular shape isotherms usually observed in the adsorption on zeolites. Therefore, reagents and products, inside the zeolite cavities can be considered in a condensed phase. In such a situation, the effect of the temperature on the kinetics can be carefully studied, in a broader range, without interference for the phase change of the reagents. Then, by observing Fig. 1, it can be also noted a strong influence of internal diffusion, when pellets of mordenite are used instead of particles, in the temperature range 120–150°C. The effect of the particle size on reaction rates is, of course, strictly related to the macropore diffusion coefficient that can be estimated in the usual way (*3*). On the contrary, by observing Fig. 1 it is not possible to evaluate, at once, the effect of intracrystalline diffusion on reaction rate. In fact, in order to evaluate the role of intracrystalline diffusion other information are needed. For this purpose, it is possible to apply the criterion suggested by Dogu and Dogu (*4*) that is based on the evaluation of a G parameter, representing the ratio between the characteristic time for the diffusion respectively in the crystall particles and in the pellets. The G factor can be expressed as

$$G = \frac{D_{\mathrm{Peff}}}{R_{\mathrm{p}}^2} \bigg/ \frac{D_{\mathrm{ceff}}}{R_{\mathrm{c}}^2} = \left(\frac{R_{\mathrm{c}}}{R_{\mathrm{p}}}\right)^2 \cdot \frac{D_{\mathrm{m}}}{D_{\mathrm{c}}} \cdot \frac{\tau_{\mathrm{c}}}{\theta_{\mathrm{c}}} \cdot \frac{\theta_{\mathrm{p}}}{\tau_{\mathrm{p}}}$$

being R_{c} and R_{p} the equivalent mean radius related respectively to the crystal particles (subscript c) and to the pellets (subscript p), D_{Peff} and D_{ceff} the effective diffusion coefficients respectively for the pellets and the particles. τ_{c} and τ_{p} are the tortuosity factors and θ_{c} and θ_{p} are the void fractions, always related respectively to the crystall particles and pellets. D_{c} is the intracrystalline diffu-

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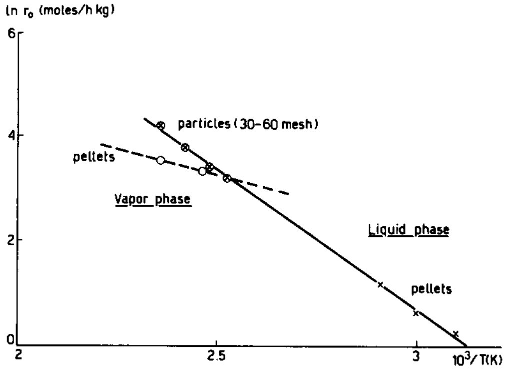

FIG. 1. Reaction rates for acetic acid esterification with ethyl alcohol on acidic mordenite. Data are arranged in an Arrhenius type plot. ×, Data obtained by using the reagents in liquid phase and the catalyst in pellets of equivalent radius 0.1 cm. ○, Data obtained by using the reagents in vapor phase and the catalyst in pellets of equivalent radius 0.1 cm. ⊗, Data obtained by using the reagents in vapor phase and the catalyst in particles (30–60 mesh).

sion coefficient, while D_m is the molecular diffusion coefficient.

When diffusion resistance in the micropores is negligible with respect to diffusion resistance in the macropore, the G factor approaches a zero value, on the contrary, when the G value is in the order of magnitude 0.1 or higher, diffusion resistance in the micropores cannot be neglected in evaluating the overall diffusion coefficients. By assuming, with a rough approximation, for both mordenite and Y zeolite that

$$\frac{\tau_c}{\tau_p} \cdot \frac{\theta_p}{\theta_c} = 1$$

we obtain for mordenite, at 150°C, $G = 2500$ on pellets ($R_p = 0.10$ cm) and $G = 40{,}000$ on particles ($R_p = 2.5 \times 10^{-2}$ cm) by taking $R_c = 5 \times 10^{-4}$ cm $D_c \simeq 10^{-9}$ cm^2/s (*5*) and $D_m = 0.10$ cm^2/s. For the liquid phase on pellets $G = 0.5$ by taking $D_m = 2 \times 10^{-5}$ cm^2/s. In the case of Y decationized zeolite, at 150°C, $G = 7.1 \times 10^{-2}$ for pellets of $R_p = 0.075$ cm, by taking the values $R_c = 2.0 \times 10^{-5}$ cm and $D_c \simeq 10^{-7}$ cm^2/s (*6*). The values of R_c have been estimated, in both cases by electron microscopy. On the basis of the obtained values of G it can be concluded that, in the case of mordenite, intracrystalline diffusion is always a rate-determining step. On the contrary, in the case of Y decationized zeolite the influence of intracrystalline diffusion upon reaction rate can be neglected. In fact, in the previously mentioned paper (*1*) it had been experimentally shown that macropore diffusion does not affect reaction rates in the adopted experimental conditions. Therefore, being the characteristic time for micropore diffusion lower than that for macropore one, it can be concluded that also intracrystalline diffusion has negligible effect in limiting reaction rates.

At last, kinetic data reported in Fig. 1 allow us to evaluate the activation energy for the intracrystalline diffusion coefficient by observing the slope of the continuous line, that is, 10.7 kcal/mol. This value is quite in agreement with the one reported in the literature (*5*), determined by employing other techniques.

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