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# The Kinetics of Ethylene Polymerization in Nickel-Y Zeolite

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The polymerization of ethylene in NiY zeolite is preceded by a rapid sorption and diffusion of $C_2H_4$ molecules in the solid. The respective rates of both processes can be experimentally distinguished. The influence of intracrystalline mass transport on the rate of dimerization has been investigated; the rate of this reaction in terms of the local concentration of reactant in the solid and its true activation energy have been determined.

## I. INTRODUCTION

The question whether the concepts of surface catalysis are applicable in the case of intracrystalline catalytic reactions in zeolites was already raised in one of the first publications that dealt with the subject (*1*). The locus of catalytic activity of zeolites is the bulk volume of the crystalline solid phase, whereas in surface catalysis the reaction takes place at the phase boundary of a solid. The term "surface" is used in the present context only in the sense of a phase boundary, which is a well-defined macroscopic concept. "Internal surfaces" can be visualized in the crystal structures of zeolites, but these cannot be measured unambiguously, and they do not constitute phase boundaries. Since the sorption in zeolites must be regarded as the formation of solid solutions (*2*, *3*), a catalytic reaction in a zeolite can be considered as a homogeneous reaction in a solid, coupled with the transfer of reactants and products from the gas into the solid and vice versa.

The different steps of this composite process can be distinguished experimentally in the polymerization of $C_2H_4$ in Y zeolite containing nickel ions. The catalytic polymerization of $C_2H_4$ by zeolites has been described by Jones and Landis (*4*). The present investigation is concerned with the kinetics of this reaction at relatively low pressures of reactant.

### NOMENCLATURE

| | |
|---|---|
| $D$ | diffusion coefficient of $C_2H_4$ in the zeolite |
| $k_2$ | rate coefficient of bimolecular intracrystalline reaction in terms of concentration in the solid [Eq. (6)], per unit mass of zeolite |
| $k'_2$ | apparent rate coefficient of bimolecular reaction in terms of partial pressure in the gas phase [Eq. (2)], per unit mass of zeolite |
| $m$ | concentration of sorbed species in the zeolite in moles per gram |
| $m_0$ | $m$ at the phase boundary |
| $n$ | number of moles in the gas phase |
| $p$ | pressure |
| $R$ | radius of spherical particles, characterizing average linear dimension of zeolite crystals |
| $s$ | total amount of $C_2H_4$ sorbed per gram of zeolite |
| $t$ | time |
| $\eta$ | dimensionless modulus, dependent on $\varphi$, characterizing the degree of catalytic utilization of the intracrystalline space [see Refs. (*7–10*)] |

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$\varphi$ $= R\left(\frac{k_2 m_0}{D}\right)^{1/2}$, dimensionless modulus characterizing ratio between rate of intracrystalline reaction and rate of intracrystalline diffusion [see Refs. (*7–10*)].

## II. EXPERIMENTAL METHODS

Equilibria and rates of sorption were measured by recording the change of pressure ($p$) in a constant volume of 1.10 liter, which was kept at 25°C and was opened at time zero to a much smaller volume of 0.050 liter that contained the zeolite sample at the desired temperature. Pressures and pressure changes were measured with 1% accuracy by a differential capacitance manometer (Granville-Phillips). The system was evacuated by a mercury diffusion pump with liquid nitrogen trap to pressures below $10^{-5}$ Torr. The interaction of $C_2H_4$ and the zeolites at 350°C was studied in a circulation apparatus. The gas (2 liter by volume) was circulated continuously over the solid in a heated reactor. The pressure and thereby the number of moles in the gas was continuously recorded; its composition was determined intermittently by gas chromatography.

The synthetic zeolite Y in the Na form (designated NaY) had the water-free composition $NaAlO_2(SiO_2)_{2.7}$ and consisted of crystallites of about 1-μm diameter. The nickel zeolite (designated NiNaY) was obtained from this material by exchanging 62% of the $Na^+$ ions against $Ni^{2+}$. The solids were calcined in air at 400°C for 10 hr, weighed in dry form, transferred to the apparatus and evacuated at 360°C for at least 5 hr, then cooled in vacuum to the temperature of measurement.

Ethylene was C.P. grade; it was purified from permanent impurities by condensation and stripping at −195°C.

## III. RESULTS

The sorption isotherm of $C_2H_4$ in unreduced NiNaY at 25°C is shown in Fig. 1. The isotherm practically coincides with the isotherm obtained for the parent NaY material, which is also shown in Fig. 1. The sorption is reversible in both solids at this temperature.

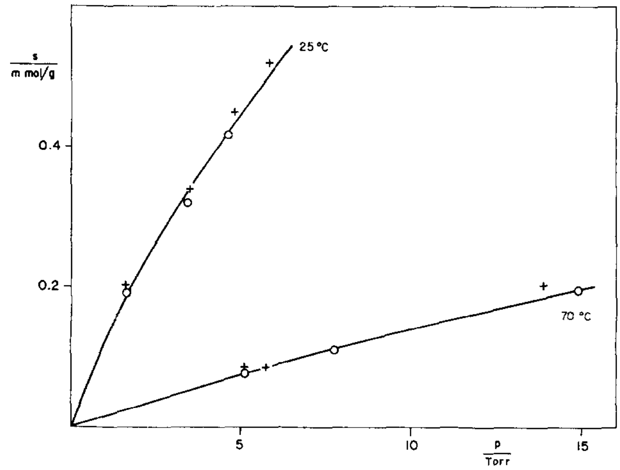

FIG. 1. Sorption isotherms of $C_2H_4$ in NiNaY (+) and NaY (○) at 25 and 70°C. The points for NiNaY at 70°C represent only the reversible fraction of the sorption.

The rate of sorption is controlled by diffusion (see Fig. 3). The rate of diffusion into spherical particles of radius $R$ can be characterized by a time constant $R^2/D$, where $D$ is the diffusion coefficient. The time constants $R^2/D$ were evaluated from the observed sorption kinetics at different levels of saturation on the basis of the integral of the diffusion equation for spherical geometry. The procedure is described in detail elsewhere (*5, 6*). At 25°C

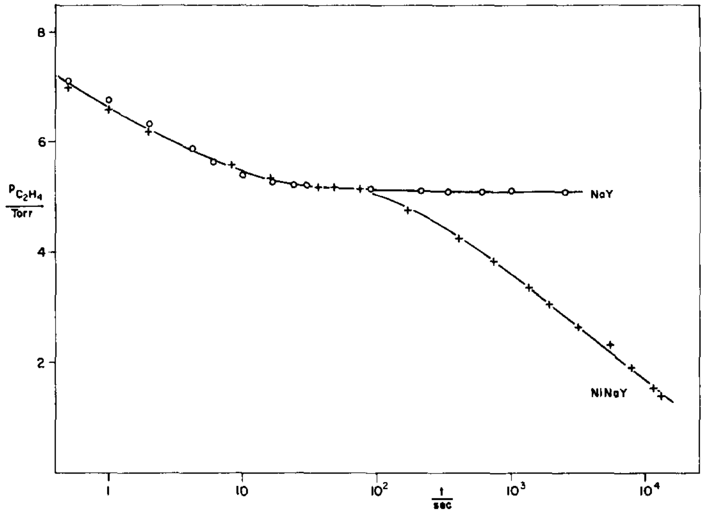

FIG. 2. $C_2H_4$ uptake into NiNaY (+) and into NaY (○) at 70°C. The pressure in the closed system of constant volume is plotted on a logarithmic time scale.

the following values of $R^2/D$ were obtained:

| Sorbed amount (mmoles/g) | | $R^2/D$ (sec) | |
|---|---|---|---|
| Initial | Final | NiNaY | NaY |
| 0 | 0.2 | 650 | 260 |
| 0.2 | 0.35 | 650 | 330 |
| 0.35 | 0.45 | 850 | 320 |

The rate of sorption slows down more strongly than should be expected on the basis of the diffusion equation towards the end of the sorption process—particularly in NiNaY.

At 70°C an initial rapid uptake of $C_2H_4$ was observed in NiNaY and in NaY, but only in NiNaY is this rapid sorption followed by a much slower process that consumes more $C_2H_4$ than the rapid sorption and that did not reach equilibrium within 3 hr. Figure 2 shows the observed decrease in $C_2H_4$ pressure over both zeolites (1.84 g of NiNaY; 1.98 g of NaY) on a logarithmic time scale. Whereas the rapid sorption process is essentially terminated after 15 sec for both solids and no further sorption is then observed in NaY, a much slower uptake of $C_2H_4$ follows the rapid sorption in NiNaY. The two processes in NiNaY can clearly be distinguished, because of the different time constants. Only the rapid sorption in NiNaY is reversible, as is the uptake in NaY. The equilibrium isotherm in NaY for 70°C is also shown in Fig. 1, together with the reversible rapid uptake into NiNaY. The isotherm relating the concentration ($m$) of reversibly sorbed $C_2H_4$ in moles per gram of either zeolite to the equilibrium pressure ($p$) has the slope

$$\left(\frac{dm}{dp}\right)_{\text{equ}} = 1.6 \times 10^{-5} \text{ mole g}^{-1} \text{ Torr}^{-1}, \text{ at } 70°\text{C}. \quad (1)$$

The kinetics of the rapid reversible part of the uptake into NiNaY and the kinetics of sorption in NaY at 70°C are shown in Fig. 3 as a function of the square root of time. The rapid sorption process appears to be controlled by diffusion in the solid; the time constant is for both zeolites

$$R^2/D = 85 \text{ sec} \pm 15\% \text{ at } 70°\text{C}.$$

The rate of the subsequent slow uptake into NiNaY, which is observed after the rapid reversible sorption has reached equilibrium, is not proportional to the $C_2H_4$ pressure but, rather, to its second power, as shown in the second order plot in Fig. 4. The rate of the slow $C_2H_4$ uptake from the gas phase can be represented by

$$-\frac{dn_{C_2H_4}}{dt} = k'_2 \cdot (p_{C_2H_4})_2, \quad (2)$$

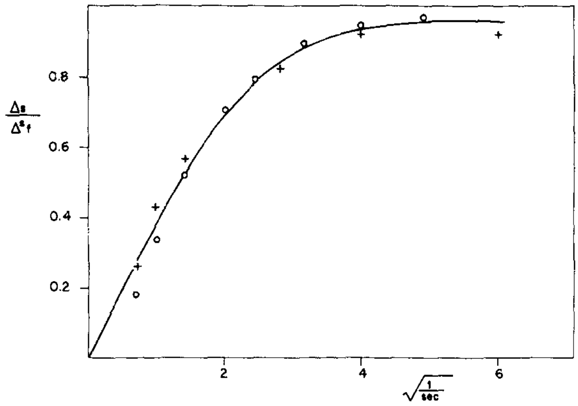

FIG. 3. Kinetics of $C_2H_4$ sorption in NaY (○) and of rapid sorption in NiNaY (+) at 70°C: $\Delta s$ = amount sorbed from $t = 0$ to time $t$; $\Delta s_f$ = amount sorbed from $t = 0$ to equilibrium.

with $k'_2 = 7 \times 10^{-8}$ mole g$^{-1}$ Torr$^{-2}$ min$^{-1}$ at 70°C.

At 210°C, the initial rate of sorption in NiNaY follows the second order law, Eq. (2); the following values of $k'_2$ were calculated from the observed rates:

at $p_{C_2H_4}$ = 6.6 Torr: $k'_2 = 4.2 \times 10^{-7}$ mole g$^{-1}$ Torr$^{-2}$ min$^{-1}$;

at $p_{C_2H_4}$ = 4.2 Torr: $k'_2 = 3.8 \times 10^{-7}$ mole g$^{-1}$ Torr$^{-2}$ min$^{-1}$.

No distinct initial rapid sorption step was observed at this temperature at pressures up to 8 Torr.

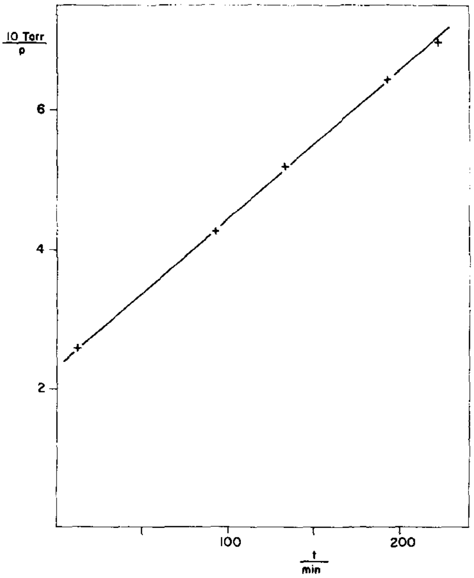

FIG. 4. Second order plot of $p_{C_2H_4}$ over 1.84 g of NiNaY at 70°C.

At 350°C, values of

$k'_2 = 1.2 \times 10^{-6}$ mole g$^{-1}$ Torr$^{-2}$ min$^{-1}$ at $p_{C_2H_4}$ = 50 Torr,

$k'_2 = 0.8 \times 10^{-6}$ mole g$^{-1}$ Torr$^{-2}$ min$^{-1}$ at $p_{C_2H_4}$ = 200 Torr,

were obtained for the fresh NiNaY in the circulation reactor. No reaction was observed with NaY. At temperatures above 200°C the $C_2H_4$ uptake in the solid—following a second order rate law—is initially the dominant reaction. The rate of this process decreases, however, as the solid approaches saturation and desorption of products (mainly $C_4H_8$) occurs. The system reaches finally a steady state that has not been investigated in detail.

In summary we observe in the system NiNaY/$C_2H_4$, (a) a reversible sorption of $C_2H_4$, following the isotherm

$$\left(\frac{m_{C_2H_4}}{p_{C_2H_4}}\right)_{equ} = 8 \times 10^{-11} \cdot \exp\left\{\frac{8.3\ \text{kcal}}{RT\ \text{mole}}\right\} \text{mole g}^{-1}\ \text{Torr}^{-1} \quad (3)$$

at small pressures, the rate of sorption being controlled by diffusion in the solid with

$$\frac{R^2}{D} = 1.6 \times 10^{-4} \cdot \exp\left\{\frac{9\ \text{kcal}}{RT\ \text{mole}}\right\} \text{sec.} \quad (4)$$

(b) A second order reaction of $C_2H_4$ in the solid, following eq. (2) with

$$k'_2 = 5 \times 10^{-7} \cdot \exp\left\{\frac{-4.1 \text{ kcal}}{RT \text{ mole}}\right\} \text{mole g}^{-1} \text{ Torr}^{-2} \text{ sec}^{-1}. \quad (5)$$

The sorption of *trans*-2-butene in NaY has also been investigated at 25°C, where it is reversible and the equilibrium can be described by a Langmuir isotherm

$$m_{C_4H_8} = m^{\infty} \frac{p_{C_4H_8}\, b}{1 + p_{C_4H_8}\, b},$$

with $m^{\infty} = 2.5 \times 10^{-3}$ mole $g^{-1}$; $b = 14.3$ $\text{Torr}^{-1}$. The rate of sorption of $C_4H_8$ in NaY at 25°C corresponds to $R^2/D \leq 100$ sec; the rate of desorption is much smaller, it can be characterized by a first order rate constant of $10^{-3}$ $\text{sec}^{-1}$.

## IV. Discussion

The behavior of $C_2H_4$ towards NiNaY and NaY can be explained as reversible sorption in the Y lattice—which is rather unspecific with respect to the cation—being followed by a chemical reaction between two $C_2H_4$ molecules in the case of NiNaY. The products of this reaction are essentially not desorbed at 70°C and small pressures of reactant. This observation can be explained by the intracrystalline dimerization of $C_2H_4$, in agreement with earlier results of Jones and Landis (*4*). These authors found that $C_2H_4$ polymerizes in faujasite zeolites containing nickel ions, the reaction product consisting mainly of the dimers $C_4H_8$.

This reaction exemplifies the sequence,

sorption/diffusion/reaction/desorption,

that has to be expected for any catalytic reaction in a zeolite. If we consider the polymerization to gaseous products, then the last step in the sequence—that is, the desorption—is clearly rate determining. This condition is most obvious at 70°C, where the ethylene dimerizes with a finite rate to a product that remains then sorbed in the solid. At 350°C the rate of $C_2H_4$ consumption is initially much greater than the rate of $C_4$ desorption. The solid reaches a steady state, finally, where it is saturated with polymerized material and where the desorption of reaction products limits the rate of further $C_2H_4$ consumption and thus the rate of the overall process.

In the case of a zeolite catalyst, desorption means the transfer of a sorbed molecule from the solid into the gas phase, that is, the penetration of a phase boundary. For *trans*-2-butene, the rate of sorption in NaY at 25°C is 100 times faster than the rate of desorption; despite the high mobility of $C_4H_8$ *in* the crystal, its rate of desorption is relatively small.

The analysis of the system NiNaY/$C_2H_4$ can be carried further because the rates of sorption and diffusion, on the one hand, and chemical reaction, on the other hand, can be experimentally distinguished.

Under the conditions of the measurements at 70 and 210°C, the solid contained only negligible amounts of polymerization products (less than 3% of its capacity) and the degree of saturation with reversibly sorbed $C_2H_4$ was less than 4%.

There will be a concentration gradient of $C_2H_4$ in the zeolite crystal if the reaction is fast enough to compete with the supply of reactant by diffusion in the solid. The kinetic principles that apply to a system where mass transport in a condensed phase is coupled with a chemical reaction are well established (*7, 8*); methods to estimate the depletion of reactant towards the center of the solid particles from the time constant of diffusion ($R^2/D$) and from the observed rate of reaction have been described by Wagner (*9*) and by Weisz and Prater (*10*).

It is directly obvious from the experimental data obtained at 70°C (Fig. 2) that at this temperature no concentration gradient of reactant persisted in the solid when the dimerization was observed because sorption equilibrium with $C_2H_4$ is established before the dimerization becomes noticeable. At elevated temperatures (210 and 350°C) the amount of reversibly sorbed $C_2H_4$ is too small to be observed directly, but we can estimate if a significant concentration gradient of $C_2H_4$ is necessary to sustain the observed rate of reaction, since we know the order of magnitude of $R^2/D$. Following the procedure described by Weisz and Prater *(10)* and using their notation, we obtain the dimensionless moduli $\eta\varphi^2$ and $\eta$ for the conditions *in* the zeolite crystals. For example, we have at 70°C and $p_{C_2H_4} = 5$ Torr: for the rate of reaction per unit mass of solid from Eq. (2)

$$\frac{dn}{dt} = -3 \times 10^{-8} \text{ mole g}^{-1} \text{ sec}^{-1};$$

for the concentration of reactant ($C_2H_4$) in the solid at the phase boundary from Eq. (1)

$$(m)_0 = 8 \times 10^{-5} \text{ mole g}^{-1};$$

for the time constant of diffusion of $C_2H_4$

$$R^2/D = 85 \text{ sec}.$$

We obtain with these values

$$\eta\varphi^2 = \frac{R^2}{D} \cdot \frac{1}{m_0} \cdot \left|\frac{dn}{dt}\right| = 3.2 \times 10^{-2};\ \eta > 0.99.$$

In the same way we find, for the remaining temperatures and partial pressures, where $k'_2$ was determined,

| Temp (°C): | 70 | 210 | 350 | | |
|---|---|---|---|---|---|
| $p_{C_2H_4}$ (Torr): | 5 | 5 | 5 | 50 | 200 |
| $\eta\varphi$ | 0.03 | 0.14 | 0.27 | 2.7 | 5.4 |
| $\eta$ | 0.99 | 0.98 | 0.95 | 0.85 | 0.7 |

Thus the observed rate coefficient $k'_2$ was not influenced by mass transport up to 210°C; even at 350°C the influence is insignificant as far as the order of magnitude is concerned. The observed rate coefficients $k'_2$ and $k'_2/\eta$ are shown as a function of temperature in Fig. 5, the straight line in Fig. 5 corresponds to Eq. (5).

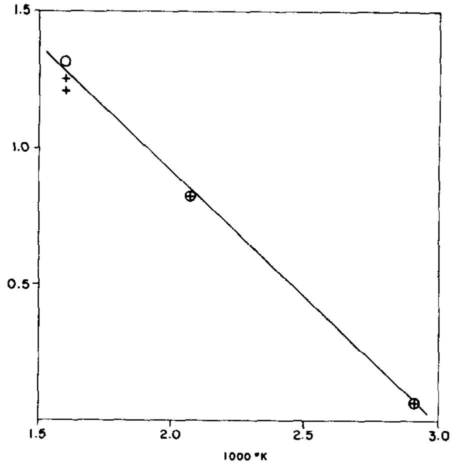

FIG. 5. Temperature dependence of the rate coefficient $k'_2$ (mole Torr$^{-2}$ g$^{-1}$ sec$^{-1}$): Ordinate: (+) $\log_{10}(10^9 \cdot k'_2)$; (○) $\log_{10}(10^9 \cdot k'_2/\eta)$.

The rate coefficient $k'_2$ in Eq. (2) is only an apparent rate constant, characterizing the rate of the reaction in terms of the partial pressure of reactant in the gas phase, whereas the reaction occurs between $C_2H_4$ molecules in the solid. The rate equation can also be written in terms of the concentration of $C_2H_4$ in the solid ($m_{C_2H_4}$, in moles per gram of solid), which then defines a rate constant $k_2$ for the intracrystalline reaction:

$$-\frac{dn_{C_2H_4}}{dt} = k_2 \cdot m^2_{C_2H_4}. \tag{6}$$

By combining Eq. (2) with Eq. (6),

$$k_2 = k'_2 \cdot \left(\frac{m}{p}\right)^{-2}_{C_2H_4}, \tag{7}$$

we obtain $k_2$ in the temperature-dependent form from Eqs. (3) and (5):

$$k_2 = 10^{14} \cdot \exp\left\{\frac{-21 \text{ kcal}}{RT \text{ mole}}\right\} \text{ g mole}^{-1} \text{ sec}^{-1}. \tag{8}$$

This quantity has to be divided by the density of the zeolite (1.4 g cm$^{-3}$) to obtain $k_2$ in the alternate unit (cm$^3$ mole$^{-1}$ sec$^{-1}$). The rate constant $k_2$ characterizes the rate of reaction in the solid, undisguised by the preceding sorption and diffusion of reactant; its temperature coefficient gives a "true" activation energy of 21 kcal/mole.

The rate coefficient that determines the intracrystalline Thiele modulus $\varphi$ is, of course, the coefficient in terms of the concentration *in* the solid, that is, $k_2$ and not the apparent rate constant $k'_2$. This consideration was implied in the evaluation of the product $\eta\varphi^2$ because the observed rate was normalized by the concentration in the solid at the phase boundary.

We have analyzed the first two steps in the sequence (sorption/diffusion) + (reaction/desorption) quantitatively, but we have excluded the last one (desorption). It seems that the desorption controls the overall rate of formation of *gaseous* products. At 350°C and $p_{C_2H_4} \geq 50$ Torr, the solid is first saturated with polymers, while at steady state a slow desorption of $C_4H_8$ and other hydrocarbons controls the rate of further ethylene consumption, despite the high mobility of $C_4H_8$ in NaY. With respect to desorption, the situation in a zeolite is different from the condition in a macroporous solid. Whereas in the macroporous system the gas phase extends into the pore structure, a discontinuity exists at the phase boundary of a zeolite catalyst, since reactants or products enter or leave the force field of the solid at the phase boundary. The transfer from the solid into the gas phase (desorption) will be associated with an activation energy that is at least equal to the value of the heat of sorption. A complete analysis of the system, including the rate coefficients of desorption of the individual products, appears to be rather difficult in the present case because a large variety of polymers is generated in the solid.

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