Study of Nickel Oxide-Kieselguhr Catalyst. IV. The Effect of Temperature upon the Initial Rate of Polymerization and the Amount of Initial Adsorption of Propylene[1,2]

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(Received May 10, 1957)

In a previous paper[3] it was reported that the course of catalytic polymerization of propylene over the nickel oxide-kieselguhr catalyst at 0°C obeyed the Zeldowitch type equation[4]

$$-\frac{\mathrm{d}P}{\mathrm{d}t}=ae^{-\alpha(P_0'-P)} \qquad (1)$$

where P is the observed pressure of propylene at time t and a, α and P_0' are empirical constants; "the initial rate" $R_0\equiv a$ was found to vary linearly with the amount v of "the initial adsorption", i. e. the amount of propylene corresponding to the pressure difference P_0-P_0', as

$$R_0=k(v-v_0) \qquad (2)$$

where P_0 is the pressure of propylene, which would be observed, if expanded in the dead space at $t=0$ without interaction with the catalyst and k or v_0 is a constant. This initial rate law 2 was established at 0°C irrespective of the catalyst composition, the ineffective amount v_0 increasing almost linearly with the nickel oxide content, and the rate constant k increasing with decreasing nickel oxide.

The present paper reports results obtained in other series of experiments at higher temperatures which were performed to see whether the initial rate law 2 still holds and to determine the activation energy and the heat of initial adsorption respectively from k and v.

Experimental Results

The catalyst employed is a different species from the previous one and contains nickel oxide of about twenty per cent. The course of the over-all reaction was followed by the measure-

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[1] Presented before the tenth Annual Meeting of the Chemical Society of Japan held at Tokyo, April 1957.

[2] Part 3 appeared in *Catalyst*, **12**, 72 (1955) (in Japanese).

[3] S. Kawaguchi, *J. Phys. Chem.*, **61**, 394 (1957).

[4] H. A. Taylor and N. Thon, *J. Am. Chem. Soc.*, **74**, 4169 (1952); P. T. Landsberg, *J. Chem. Phys.*, **23**, 1079 (1955).

ment of pressure decrease at constant volume. The apparatus and the experimental procedure including the catalyst preparation were previously reported[5]. Experiments were made at 0, 20, 80, 100, 110.6 and 140°C. The higher reaction temperatures were maintained constant by means of vapor baths of benzene, water, toluene and *m*-xylene, respectively.

Eq. 1 was applied to each pressure-time curve. The rate equation can reproduce data for more than four hours at 0 and 20°, but only for the first several ten minutes at higher temperatures. Numerical value of the constant α decreases with increasing initial pressure at all temperatures as shown in Fig. 1, but increases as the temperature rises from 0 to 80°. Usually α decreases with increasing temperature[6] and is considered theoretically to be proportional to the reciprocal of absolute temperature[7]. However such an anomalous temperature dependence as in this case has also been reported in other systems[6]. Data of α at 100, 110.6 and 140° fall on the same curve as those at 80° within the experimental error.

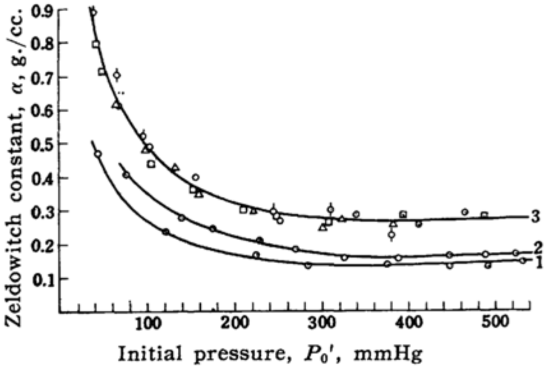

Fig. 1. Dependence of Zeldowitch constant, α, upon the initial pressure, P_0', when applied to the catalytic polymerization of propylene over a nickel oxide-kieselguhr catalyst. Curve 1: 0°, curve 2: 20°, curve 3: 80° (⊙), 100° (◬), 110.6° (▣), and 140° (⦶).

The isotherm of the initial adsorption v of propylene at each temperature is shown in Fig. 2. Isotherms at 0 and 20° obey the B. E. T. equation at the higher relative pressure than 0.05, giving monolayer volumes $v_m=11.63$ and 11.57 cc. (STP)/g. cat., and energy factors $c=49$ and 37, respectively. At 80° and higher temperatures, the pressure range examined is lower than the relative pressure 0.05 and the B. E. T. equation does not hold. Langmuir equation can not fit the data, either.

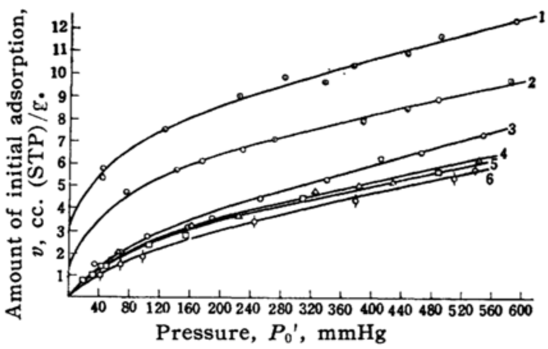

Fig. 2. Isotherm of the initial adsorption of propylene on a nickel oxide-kieselguhr catalyst at 0° (curve 1), 20° (curve 2), 80° (curve 3, ⊙), 100° (curve 4, ◬), 110.6° (curve 5, ▣), and 140° (curve 6, ⦶).

The pressure dependence of the initial rate R_0 of over-all reaction is plotted in Fig. 3. The initial rate markedly increases as the temperature rises from 0 to 20 and 80°, but curves at higher temperatures lie closely near to that at 80°. Plotting the logarithm of the initial rate against the logarithm of the initial pressure, the following empirical pressure exponents are obtained.

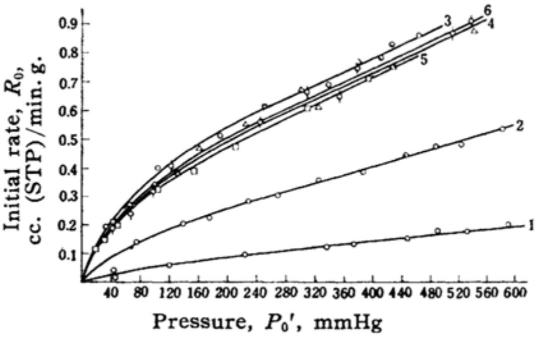

Fig. 3. Pressure dependence of the initial rate of propylene polymerization over a nickel oxide-kieselguhr catalyst at 0° (curve 1), 20° (curve 2), 80° (curve 3, ⊙), 100° (curve 4, ◬), 110.6° (curve 5, ▣), and 140° (curve 6, ⦶).

$$\begin{aligned} R_0 &= kP^x \\ x &= 0.75 \text{ at } 0^\circ \\ &\ 0.68 \text{ at } 20^\circ \\ &\ 0.58 \text{ at } 80\sim140^\circ \end{aligned}$$

When initial rates are plotted directly against amounts of initial adsorption, straight lines are obtained as shown in Fig. 4. The rate equation 2 holds too in this case, the constant v_0 however vanishing at temperatures above 20°C in accordance with the rate law as shown in Table I.

Activation energy determined from values of the rate constant, k, at 0 and 20° is 8.7 kcal./mole, and that obtained from the Arrhenius plot (Fig. 5) for data at higher temperatures is 0.86 kcal./mole.

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[5] S. Kawaguchi and H. Kihara, *J. Inst. Polytech., Osaka City Univ.*, **4C**, 202 (1953).

[6] H. A. Taylor and N. Thon, *J. Am. Chem. Soc.*, **74**, 4169 (1952).

[7] M. A. Cook and A. G. Oblad, *Ind. Eng. Chem.*, **45**, 1456 (1953); I. Higuchi, T. Ree and H. Eyring, *J. Am. Chem. Soc.*, **77**, 4969 (1955).

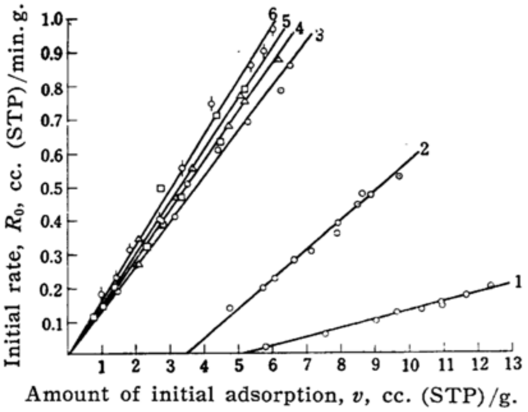

Fig. 4. The initial rate of polymerization vs. the amount of initial adsorption of propylene at 0° (line 1), 20° (line 2), 80° (line 3, ⊙), 100° (line 4, ◬), 110.6° (line 5, ▣), and 140° (line 6, ⊙).

TABLE I

CONSTANTS OF THE INITIAL RATE LAW, $R_0=k(v-v_0)$

Reaction temp. °C	Rate const., k min.$^{-1}$	Ineffective amt. of adsorpn. v_0, cc. (STP)/g.
0	0.029	5.1
20	0.087	3.4
80	0.133	0
100	0.145	0
110.6	0.149	0
140	0.159	0

From isotherms of the initial adsorption in Fig. 2, the isosteric heat of propylene adsorption was calculated by means of the Clausius-Clapeyron equation, and is illustrated in Fig. 6 as the function of the amount of adsorption. The heat of adsorption obtained between 0 and 20° is 7 to 8 kcal./mole for the range of surface coverage examined, while that obtained at higher temperatures shows a very remarkable drop at low surface coverage down to 1.9 kcal./mole at the higher coverage region.

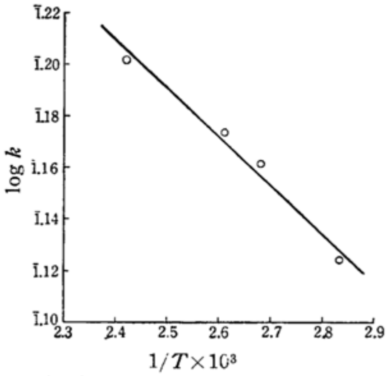

Fig. 5. Arrhenius plot of the first-order rate constant of the initial rate law for the catalytic polymerization of propylene over a nickel oxide-kieselguhr catalyst.

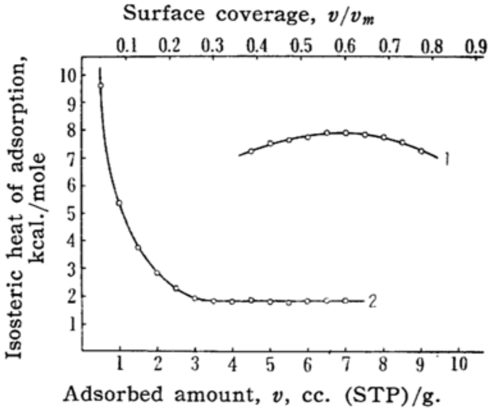

Fig. 6. Isosteric heat of the initial adsorption of propylene on a nickel oxide-kieselguhr catalyst. Curve 1: 0—20°, curve 2: 80—140°.

Discussion

The appearance of a distinct break in the Arrhenius plot of the over-all initial rate of propylene polymerization was previously reported[2)] upon experimental results performed with similar initial pressure at various temperatures. The difference between activation energies at lower and higher temperature ranges is now clarified by the present systematic investigation. The change of activation energy with temperature has occasionally been reported on various systems, and Ozaki[8)] also obtained apparent activation energies of 7 and −2 kcal./mole in the ranges of reaction temperature of −70∼−10° and 40∼150°, respectively, for the near-initial rate of ethylene polymerization over a nickel oxide-acid clay catalyst which was pretreated at 400°.

The change in the activation energy may indicate the change of the elementary step whose velocity is measured as the initial rate of the over-all reaction. The course of the over-all reaction at 0° was previously assumed[3)] to correspond primarily to chemisorption of the propylene molecule from van der Waals layer onto the active site. If the chemisorption were so rapid as the physical adsorption at higher temperatures and attains equilibrium in the initial several minutes, the initial rate which is determined by the extrapolation of pressure data beyond ten minutes would correspond to the addition step of pro-

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8) A. Ozaki, *Catalyst*, [illegible], [illegible] ([illegible]).

pylene. In this case the initial rate could be represented by Eq. 2, if it were assumed that the chemisorbed amount is constant in the pressure range examined and the addition step proceeds between the chemisorbed monomer and the physically adsorbed one. If this were the case, the time course of the over-all reaction at higher temperatures should be represented by a rate law taking into account the superposition of addition steps or desorption of products. However previous theoretical treatment[2] showed that a rate law derived assuming the superposition of monomer chemisorption and dimerization can reproduce the kinetic data from 70 minutes to 6 hours at higher temperatures. Furthermore the fact that the heat of adsorption also changes remarkably with temperature suggests the possibility that the change in the activation energy is merely due to the change in the heat of adsorption.

The value of 7 to 8 kcal./mole appears slightly great as the heat of physical adsorption, however the system of propylene-nickel oxide also shows the isosteric heat of adsorption of 5 to 6 kcal./mole at the similar surface coverage[9]. The large and rapid decrease of the heat of adsorption at low surface coverage as depicted in Fig. 6 seems to indicate the existence of rapid chemisorption at higher temperatures, while the constant value of about 1.9 kcal./mole at the higher coverage suggests the physical adsorption. The remarkable change of the heat value between the two temperature ranges can not be unequivocally interpreted. It may be due to the a priori heterogeneity of the catalyst surface.

Summary

The catalytic polymerization of propylene over a nickel oxide-kieselguhr catalyst was studied at constant volume and at 0, 20, 80, 100, 110.6 and 140°C. The pressure-time curve was analyzed by means of the Zeldowitch type equation. The initial rate law, $R_0=k(v-v_0)$, can again represent the data at 0 and 20°, but the ineffective amount of initial adsorption, v_0, becomes zero at higher temperatures, resulting in a simple first-order rate law, $R_0=kv$. The activation energies obtained between 0 and 20°, and among higher temperatures are 8.7 and 0.86 kcal./mole, respectively. The isosteric heats of initial adsorption are 7—8 and 1.9 kcal./mole in the respective temperature regions. The elementary process whose initial rate was measured is considered again to be slow chemisorption of propylene from the van der Waals layer onto the active site of the catalyst.

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[9] To be published.