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Kinetics of Aldolic Reactions in the Gaseous Phase on Solid Catalysts of Basic Character

S. MALINOWSKI AND S. BASIŃSKI

From the Polish Academy of Sciences, Institute of Organic Synthesis, Warsaw Institute of Technology, Chemical Department

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A series of basic catalysts, prepared by saturating silica gel with aqueous solutions of sodium hydroxide in quantities of 0.187 to 1.875 mmole/g gel, has been tested. For testing the basicity of the catalyst surface the standard reaction of acrolein with acetaldehyde and formaldehyde was investigated kinetically. A fitting kinetic equation was found and, for the individual catalysts, the apparent reaction rate constants and the activation energies were calculated on the basis of the results obtained in an integrating reactor at 275° and 300°C. At both these temperatures and for sodium concentrations from 0.003 to 0.81 mmole/g gel the apparent reaction rate constant was found to be linearly dependent on the sodium concentration in the catalyst. The numerical values for the coefficients of this relation were determined. It was also established that the apparent activation energy of the reaction for all the catalysts containing 0.187 to 1.875 mmole sodium/g gel is equal (10–12 kcal/mole). This allows the conclusion that the reaction is accelerated by identical sodium-containing centers, probably Si–O–Na groups, whereas the different values of the reaction rate constants result from the varying number of these centers.

Studies of the structure of solid catalysts can be effected in two ways: (1) by physicochemical methods; (2) by kinetic investigations of the model reaction accelerated by catalysts.

In one of our preceding papers (*1*) physicochemical investigations of a series of solid catalysts with a basic character are described. These catalysts consisted of silica gel impregnated with various quantities of Na ions. The present report is devoted to studies on the kinetics of the model reaction in the presence of various catalysts of this kind.

The group of solid catalysts possessing centers of a basic character on their surfaces is but little known. Research on solid catalysts of a basic character has so far been devoted to studies of reactions catalyzed by them, however, more fundamental works such as studies on the kinetics of these reactions, or studies treating on the basicity of catalysts are still lacking.

Solid catalysts of a basic character have been investigated by Pines (*2–5*) in relation to various reactions of hydrocarbons (isomerization, alkylation).

The notion of basicity of surfaces of solids has so far not been precisely defined. The basicity of the surface of the solid seems to depend on two factors: the number of basic centers and their specific strength (basicity).

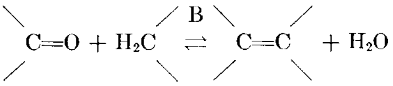
The aim of this work was to test the first of these factors, namely, the influence of basic centers on the activity of the catalyst. A series of silica–sodium catalysts, differing by the $SiO_2:Na_2O$ ratio, was examined. These catalysts were prepared using as a base silica gel almost free from alkali metals. From this gel a series of catalysts was prepared by saturating the silica gel with various quantities of sodium hydroxide-water solution.

The method of kinetic investigation of the model reaction of aldolic type was applied.

The kinetic method of examining the

catalysts and their features has the advantage over others in that it allows selective measurement of the quantity and strength of only those, e.g. basic, active centers which actually catalyze the reaction studied, also allows discovery of resemblances and differences of the structure of the basic centers, which directly influence their catalytic activity.

As a model of an ionic reaction catalyzed by bases we have chosen a reaction of aldolic type



$$>C{=}O + H_2C< \overset{B}{\rightleftharpoons} >C{=}C< + H_2O$$

(I) (II)

which occurs between the carbonyl (I) group and the compound containing the acidic hydrogen (II). We have established in our previous work (*6, 7*) that the rate of this type of reaction is directly proportional: to the acidity of hydrogen, K_{II}, in compound (II) and to the basicity, X_B, of the surface. The basicity seems to depend

$$V \approx K_{II}X_B$$

on two factors: the number of active basic centers and the basicity of every center.

In this work we have applied the same model reaction, therefore, $K_{II} = \text{const.}$, and the reaction rate depends on X_B. In the present work the condensation of acetaldehyde with formaldehyde to acrolein and water, carried out in the gas phase, served as the model reaction.

$$HCHO + CH_3CHO \rightleftharpoons CH_2{=}CH{-}CHO + H_2O$$

(III) (IV) (V)

This reaction proved convenient, because, as stated in our previous paper (*8*), it is accelerated by solid catalysts with a surface exhibiting a basic character; it runs selectively (quantity of by-products not exceeding 2%) and occurs with good yield in the range 200–350°C.

For all the catalysts the dependence of conversion on the actual contact time at two temperatures, 275° and 300°C, was determined in the reaction studied. On the basis of these results the form of the kinetic equation was determined, and the apparent reaction rate constants were calculated as well as the apparent activation energy.

Establishment of the Kinetic Area of the Reaction

The absence of the exterior and interior diffusion influence was verified by the method of Dowden and Bridger (*9*). For this purpose the dependence of conversion upon contact time was determined for two different quantities and two particle diameters of the catalyst impregnated with 0.250 mmole Na/g. The points marked on Fig. 1 lie almost on one line, this indicating that, under the given conditions, the reaction runs in the kinetic area.

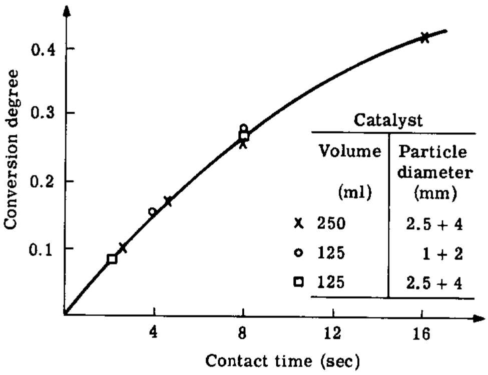


FIG. 1. Dependence of conversion degree upon contact time for various catalyst volumes and particle diameters.

Definition of the Kinetic Equation Form

We assume that during the reaction the acetaldehyde molecules undergo adsorption and react with formaldehyde molecules from the gaseous phase (by analogy to the mechanism in the liquid phase). Then the kinetic equation for the reaction

$$A + B = R + S$$

takes the following form:

$$v = k' \cdot \frac{p_A p_B - (1/K) p_R p_S}{1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_I p_I} \quad (1)$$

The reaction rate was defined as the change of the pressure of the product during the time of reaction;

$$v = dp_R/dt \quad (2)$$

Since both aldehydes (III) and (IV) were used in stoichiometric quantities, and taking into account that the starting mixture contained water deriving from the formaline, the equation, on transformation, takes the simple form:

$$\frac{dx}{dt} = \frac{k' \cdot [(1-x)^2 - (1/K)x(x+3.24)]}{A + Bx} \quad (3)$$

where x is the degree of conversion.

After integration and further mathematical transformations the following equation was obtained:

$$\frac{1}{2\sqrt{(b/2)^2 - c}} \cdot \frac{1}{\tau} \cdot \log\left[\frac{\beta(x-\alpha)}{\alpha(x-\beta)}\right] = \frac{B}{2A}\left\{-\frac{1}{\tau}\log\left(\frac{x^2 - bx + c}{c}\right) - \frac{1}{\tau} \cdot \frac{b}{2\sqrt{(b/2)^2 - c}} \cdot \log\left[\frac{\beta(x-\alpha)}{\alpha(x-\beta)}\right]\right\} + \frac{1}{2.303c} \cdot \frac{k'}{A} \quad (4)$$

in which the coefficients b, c, α and β depend on the reaction equilibrium constant K according to the formulas:

$$b = \frac{2K + 3.24}{K - 1} \qquad \alpha = \frac{b}{2} + \sqrt{\left(\frac{b}{2}\right)^2 - c}$$

$$c = \frac{K}{K - 1} \qquad \beta = \frac{b}{2} - \sqrt{\left(\frac{b}{2}\right)^2 - c}$$

(The reaction equilibrium constants, calculated on the basis of the thermodynamic potential of reaction are, at 275°C, 200, and at 300°C, 160).

On the basis of the experimental results obtained at 275°C using silica gel saturated with 0.250 mmole sodium hydroxide/g, from Eq. (4) were calculated:

$$k'' = k'/A = 0.045 \text{ sec}^{-1}$$

and

$$B/2A = -0.066$$

The low value of the coefficient $B/2A$ allows the assumption that in Eqs. (3) and (4) $B = 0$. In view of this the integrated kinetic equation takes the form:

$$\frac{2.303c}{2\sqrt{(b/2)^2 - c}} \cdot \log\frac{\beta(x-\alpha)}{\alpha(x-\beta)} = k'' \cdot \tau \quad (5)$$

This equation indicates that the logarithm of the algebraic function of the conversion degree, x, should be directly proportional to the contact time. The validity of this dependence, verified for the catalyst containing 0.250 mmole Na/g silica gel, is proof that Eq. (5) rightly describes the experimental results (Fig. 2). The apparent reaction rate constant at 275°C calculated on the basis of this equation amounted to 0.0455 sec^{-1} and differed only slightly from the constant calculated from Eq. (4).

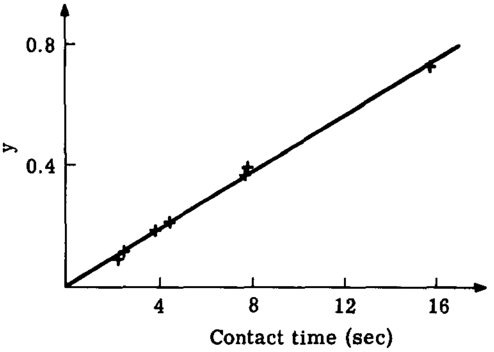


FIG. 2. Dependence between

$$y = \frac{2.303\, c}{2\sqrt{(b/2)^2 - c}} \cdot \log\frac{\alpha(x-\alpha)}{\beta(x-\beta)}$$

function and contact time.

The results obtained on the other catalysts containing other quantities of Na have also been described by Eq. (5). By means of this equation, on the basis of the experimental results, the apparent reaction rate constants were calculated for the remaining catalysts at 275° and 300°C.

Figure 3 shows the dependence of the apparent reaction rate constant on the quantity of Na in the catalysts.

As seen from this diagram, the apparent reaction rate constant, for quantities of sodium not exceeding 0.81 mmole/g gel

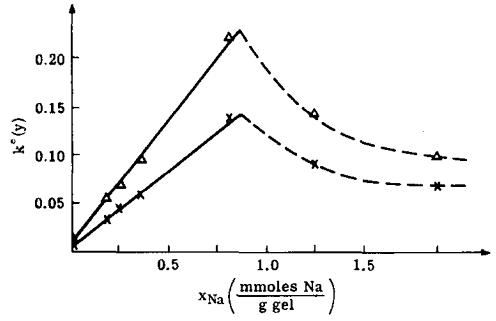


FIG. 3. Dependence between apparent reaction rate constant, and sodium concentration in silica catalyst.

shows a linear dependence on the quantity of sodium contained in the catalyst:

$$k'' = m \cdot x_{\mathrm{Na}} + n \qquad (6)$$

The numerical value of the coefficients m and n in Eq. (6) was calculated by the method of least squares of relative deviations from the straight line.*

The corresponding values are:
for 275°C

$$k'' = 0.165 \cdot x_{\mathrm{Na}} + 0.00275$$

for 300°C

$$k'' = 0.265 \cdot x_{\mathrm{Na}} + 0.00285$$

(k'' in sec^{-1}, x_{Na} in mmoles Na/g silica gel).

The existence of a linear dependence between the apparent reaction rate constant and sodium concentration in the silica catalysts allows the conclusion that on the silica gel saturated with sodium hydroxide there exist two kinds of active centers accelerating the aldolic reaction under study: (1) "sodium" centers occurring in the sodium-containing catalysts; (2) "sodium-free" centers not associated with the presence of alkali metals in the silica gel.

From this conclusion a physical sense can be attributed to the coefficients in Eq. (6): m is the specific apparent reaction rate constant of the sodium centers and n is the apparent reaction rate constant of the sodium-free centers.

The catalytic reaction rate depends on two factors: the number of active centers on the catalyst surface and the specific activity of the individual active centers. This activity is manifested in the activation energy of the reaction. In order to ascertain whether the nature of the basic centers changes with sodium concentration in the silica catalyst, the activation energy of the reaction was computed on the basis of the calculated apparent reaction rate constant. The results are presented in Fig. 4 where the dependence of the activation energy on the amount of Na on the catalyst is given.

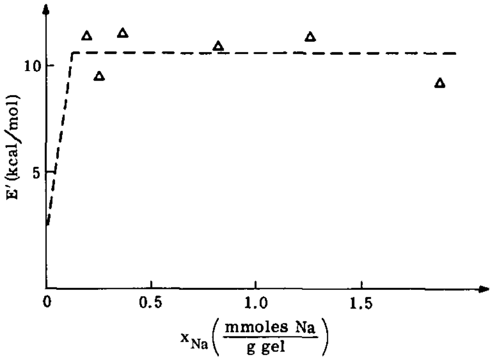


FIG. 4. Relationship between the apparent activation energy for acrolein formation, and sodium concentration on silica catalyst.

The sodium–silica catalysts containing sodium in quantities from 0.187 to 1.875 mmole/g gel are characterized by activation energies of the order of 10–12 kcal/mole. The activation energies may be assumed as equal and their dispersion as the result of an error in measurements. The activation energy of the reaction carried out on pure silica gel (containing sodium

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* The equations which we used, derived for this purpose were:

$$b = \frac{\sum(x_{\mathrm{Na}}/k'') \cdot \sum[1/(k'')^2] - \sum(1/k'') \cdot \sum[x_{\mathrm{Na}}/(k'')^2]}{\sum[x_{\mathrm{Na}}{}^2/(k'')^2] \cdot \sum[1/(k'')^2] - [\sum x_{\mathrm{Na}}/(k'')^{242}}$$

$$a = \frac{\sum[x_{\mathrm{Na}}{}^2/(k'')^2] \cdot \sum(1/k'') - \sum[x_{\mathrm{Na}}/(k'')^2] \cdot \sum(x_{\mathrm{Na}}/k'')}{\sum[x_{\mathrm{Na}}{}^2/(k'')^{24} \cdot \sum[1/(k'')^2] - [\sum x_{\mathrm{Na}}/(k'')^2]^2}$$

and potassium in a quantity of 0.003 mmole/g) is, however, different and amounts to 3 kcal/mole.

The above-mentioned results confirm the previously deduced conclusion as to the existence of two kinds of active centers on sodium-containing silica gel. At the same time they prove that the active centers formed as the result of activating silica gel with sodium of varying concentrations (0.187 ÷ 1.875 mmole/g) are identical. Consequently the reaction rate depends on the number of sodium centers. The initial linear growth of the reaction rate with increasing sodium quantities would indicate that the number of active sodium centers increases up to a sodium concentration of 0.81 mmole/g.

At sodium concentrations of 1.25 ÷ 1.875 mmole/g gel, the number of active centers accessible to the reacting molecules seems to diminish.

The last conclusion finds support in the observation that at higher concentrations of the sodium hydroxide with which the silica gel is saturated partial destruction of the silica gel structure optically perceivable occurs, causing a diminution of the gel's specific surface.

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