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Abstract

Full Text

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CHEMISTRY

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INVESTIGATION OF THE REGULARITIES OF THE SYNTHESIS OF ORGANIC COMPOUNDS FROM CO AND H_2 ON CATALYSTS WITH A LOW IRON CONTENT

Previously we established the possibility of using, in the synthesis from carbon monoxide and hydrogen, iron catalysts with a metal content one to two orders of magnitude lower than in commonly used catalysts. The study of the regularities in the behavior of these catalysts may provide additional information on the mechanism of synthesis from CO and H_2. However, even determining the kinetic parameters of the process presents considerable difficulties. First of all, this is connected with the complexity of the process, as a result of which a multicomponent mixture of products is formed.

Table 1

Dependence of the temperatures of equal activity on the iron content in the catalysts

Iron content, wt. %	Synthesis temp., °C	CO conversion, %
0.1	493	63.6
0.2	340	68.2
0.5	325	69.7
1.0	306	67.8
5.0	277	67.4
10.0	262	65.0

In connection with the above, we undertook an attempt to determine the activation energy of the process by an indirect route, without establishing the kinetic equation. For this purpose the dependence of the observed activity of the catalyst on the iron content was used. The results obtained are presented in the present work.

The method of investigation and the methods of catalyst preparation do not differ from those described in (^{1}).

Catalyst samples were prepared by impregnating talc ($S_g = 60$ m^2/g), containing about 2 meq/100 g of exchange bases, with a solution of iron nitrate, followed by precipitation of iron hydroxide with ammonia, drying, and calcination.

Experiments to determine the activity of the catalyst in the synthesis from carbon monoxide and hydrogen were carried out in a flow apparatus at a pressure of 30 atm, a space velocity of 200 hr^{-1}, and a CO:H$_2$ ratio in the starting gas of 1:1.

The activity of the catalyst samples was characterized by the process temperature at which, at identical catalyst charges (~60 g), a specified degree of conversion of carbon monoxide (65-70%) was achieved. The procedure described was used in order to exclude the influence of changes in the concentration of the reacting gases along the catalyst bed, allowance for which is difficult because of the absence of a kinetic equation for the process. The desired value of the process temperature was recorded in all cases after 2-3 days of steady operation of the catalyst. Catalyst samples with an iron content from 0.1 to 10 wt. %* were used. The results obtained are given in Table 1.

To process the results obtained, let us consider certain regularities of the process, taking into account the research method used.

* The maximum iron content in the samples (10 wt. %) corresponds to surface coverage of the order of a monolayer.

The observed reaction rate W can be determined in the form:

$$W = f(C_i) C_{\mathrm{Fe}} S_g g k_0 e^{-E/RT}, \tag{1}$$

where C_i are the concentrations of the components of the reaction mixture; C_{Fe} is the surface concentration of iron on the support (the number of iron atoms per unit surface area); S_g and g are the specific surface area and the catalyst charge, respectively; k_0 is the pre-exponential factor; E is the apparent activation energy; T is the temperature of the process at which the given sample exhibits standard activity in the synthesis.

We shall assume that the activity of a single center, at a not excessively high concentration of iron on the support, does not depend on the iron content. The possibility of such an assumption for samples containing 0.2-0.5 wt.% iron was confirmed experimentally. In experiments with samples containing 0.2 and 0.5 wt.% iron, carried out at the same temperature ($354 \pm 1°$), the activity of the catalyst, characterized by the amount of CO converted, was, under identical

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Fig. 1. Determination of the activation energy from the temperatures of equal activity of the samples

Figure 1: Fig. 1. Determination of the activation energy from the temperatures of equal activity of the samples

conditions, 23 and 65 arbitrary units, respectively. Thus, when the iron content was changed by a factor of 2, the catalyst activity changed by a factor of 2.8.

Fig. 1. Determination of the activation energy from the temperatures of equal activity of the samples

When the surface is incompletely filled with deposited iron, the surface concentration of iron C_{Fe}, to a first approximation, is proportional to the iron content in the sample (q)

$$C_{\mathrm{Fe}} = aq. \tag{2}$$

Expression (1) can now be rewritten in the form:

$$W = f(C_i) S_g g a k_0 q e^{-E/RT}. \tag{3}$$

In equation (3), the quantities W, $f(C_i)$, S_g, g, a, and k_g do not change for different samples and, consequently, one may write

$$q e^{-E/RT} = \mathrm{const}$$

or

$$\ln q - \frac{E}{RT} = \mathrm{const}. \tag{4}$$

It follows from (4) that, from the results of the experiments described, the value of the apparent activation energy of the synthesis process can be determined. At the same time, the applicability of equation (4) may be regarded as evidence for the correctness of the approach described.

We shall now use equation (4) to process the results obtained. The experimental data in the coordinates of equation (4) are presented in Fig. 1.

As can be seen from the figure, the experimental points in the range of iron contents in the samples from 0.2 to 10 wt.% lie on a straight line. The point corresponding to the sample with an iron content of 0.1 wt.% deviates, which may be a manifestation of a more complete chemical interaction of the iron with the substance of the silicate support (2).

On the basis of the foregoing, the data in the figure make it possible to determine the magnitude of the apparent activation energy E. The slope of the straight line is $7.2 \cdot 10^3$ deg^{-1}. Hence $E = 33$ kcal/mol.

The value obtained substantially exceeds the apparent activation energy for promoted precipitated iron catalysts, which is 20–25 kcal/mol (^{3}), which is apparently connected with the influence of the promoters, as well as with some difference in the mechanism of the process on the indicated catalysts. However, this question requires special consideration.

Thus, the decrease in the activity of iron catalysts for synthesis from CO and H_2 as the iron content is reduced, which occurs in the transition from concentrated to dilute catalysts, was also observed in the series of catalysts studied, in which the coverage of the support surface by the active component was expressed in fractions of a monolayer. It is important to note that the value of the apparent activation energy is constant at least over the range of iron contents in the samples from 0.2 to 10 wt. %, although it differs considerably from the value characteristic of precipitated iron catalysts.

The method used here for determining the apparent activation energy (and, correspondingly, the temperature coefficient) has the advantage that it does not require knowledge of the kinetics of the process and is therefore of interest for determining the activation energy of complex processes whose kinetic equations have not been established.

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Note: Figure translations are in progress. See original paper for figures.

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