KINETICS AND MECHANISM OF ACETONE HYDROGENATION ON NICKEL AND PALLADIUM CATALYSTS

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Kinetic studies of the gas-phase hydrogenation of acetone and IR spectroscopic investigations of the adsorption of acetone and propanol-2 on a Ni-catalyst have been performed. A mechanism consistent with the experimental data is suggested.

Исследована кинетика газофазного гидрирования ацетона, а также (методом ИК-спектроскопии) адоорбция ацетона и пропанола-2 на Ni-катализаторе. Обоснован механизм каталитической реакции, согласующийся с экспериментальными данными.

Hydrogenation reactions of carbonyl organic compounds and, in particular, of acetone are of a great practical importance /1/. The aim of the present study was to examine the kinetics and mechanism of gas-phase hydrogenation of acetone on nickel and palladium catalysts.

Reaction kinetics was studied by a flow-circulation technique at temperatures ranging from 333 to 363 K when the reverse reaction can be neglected. Supported Ni and Pd catalysts were reduced by H_2 at 573 and 453 K for 10 and 5 h, respectively. Ni surface area measured like in Ref. /2/, was 48.8 m^2/g. Experiments were performed in the kinetic region on samples with $(0.25-0.5) \times 10^{-3}$ m grains. Products were analyzed chromatographically. IR spectra of adsorbed acetone were recorded on a "Zëiss" UR-20 spectrophotometer. Catalyst samples were prepared by compacting (P = 4.9 mPa) finegrained powders in thin pellets to ensure sufficient transmittance in the 1100–2000 cm^{-1} region.

The pellets were placed into a cell with windows made of CaF_2. The construction of the cell permits "in situ" reduction of the samples by H_2 and thermal treatment and the elimination of the effect of the gas phase on the spectrum of the adsorbed acetone /3/.

In kinetic measurements the partial pressures of components were varied within a wide range. The dependence of the rate on the partial pressure of acetone P_{ac} was established with a great excess of H_2 in the mixture.

The selectivity of the process with respect to propanol-2 is independent of the contact time of reagents with the catalyst and is practically 100%. Under the given
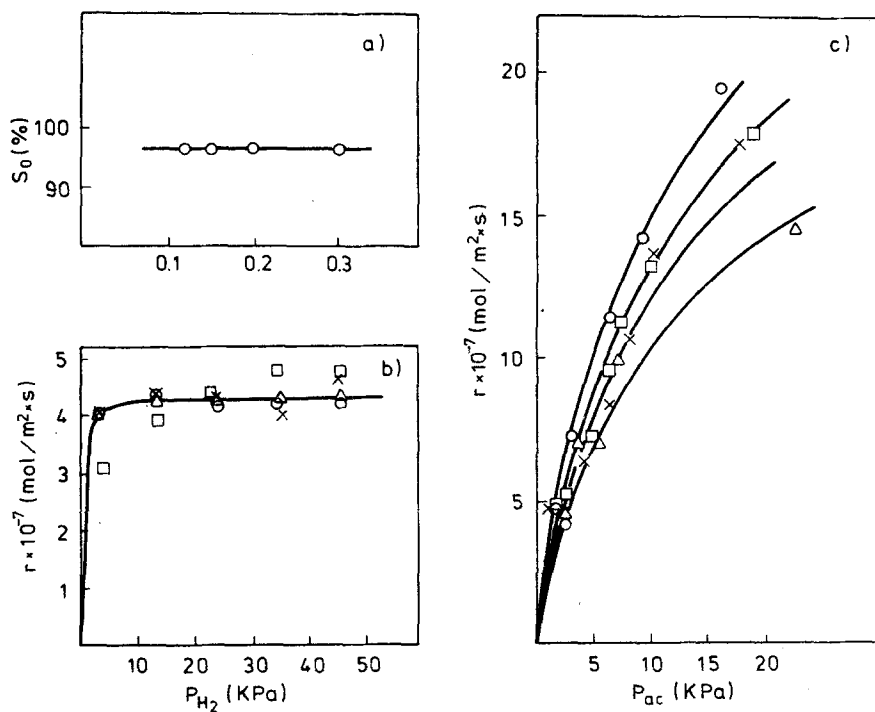
Fig. 1. Selectivity with respect to alcohol (a) and reaction rate vs. partial pressures of hydrogen (b) and acetone (c). $\triangle$ — 333 K, x — 340 K, $\square$ — 348 K, $\circ$ — 363 K
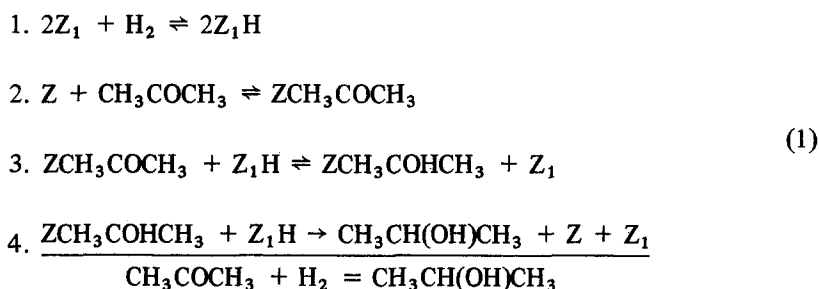
conditions, the rate of the overall process r is independent of the partial pressure of hydrogen and increases with an increase in P_{ac} (Fig. 1). The total kinetic reaction order with respect to acetone and alcohol is ~ 0.6—0.7.

Dissociative adsorption of hydrogen on Ni is known /4/ to occur rapidly with the formation of various chemisorbed hydrogen forms depending on the reaction temperature and the degree of surface coverage. Scarce data on the adsorption of acetone on nickel /5/ were obtained under conditions far from catalytic. Therefore, the adsorption of acetone was studied by IR spectroscopy at T = 353 K. The band with a maximum at 1620 cm^{-1} indicates that during the acetone adsorption an acyl structure of the type is formed

$$\begin{array}{c} CH_3 \\ \diagdown \\ C=O, \\ \diagup \quad \vdots \\ CH_3 \quad \vdots \\ Z \end{array}$$
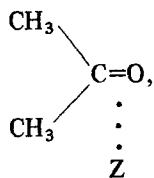
where Z is the adsorption center. It is obvious that in this case a dative band is formed and metal electrons are localized on antibonding π^*-orbitals of the CO-group. The observed shift of the band maximum ($\Delta = 20$ cm^{-1}) corresponding to the vibrations of the carbonyl group (1750 cm^{-1}) indicates the formation of a chemisorption bond between the latter and the catalyst surface. Bands with maxima at 1240, 1390 and 1460 cm^{-1} are assigned to the symmetric and asymmetric vibrations of the acetone methyl groups /6/.

The data obtained are, as a whole, consistent with the mechanism suggested previously /7/ for acetone hydrogenation on nickel involving the adsorption of the initial substances on various active centers. However, unlike in Ref. /7/, it should be assumed that the reaction product (propanol-2) does not adsorb on the catalyst. It is evidenced by the fact that under the given conditions the IR spectrum exhibits no respective absorption bands upon admitting alcohol to the catalyst. Therefore the reaction mechanism can be represented as:

$$1.\ 2Z_1 + H_2 \rightleftharpoons 2Z_1H$$

$$2.\ Z + CH_3COCH_3 \rightleftharpoons ZCH_3COCH_3$$

$$3.\ ZCH_3COCH_3 + Z_1H \rightleftharpoons ZCH_3COHCH_3 + Z_1$$

$$4.\ \frac{ZCH_3COHCH_3 + Z_1H \rightarrow CH_3CH(OH)CH_3 + Z + Z_1}{CH_3COCH_3 + H_2 = CH_3CH(OH)CH_3}$$

(1)

Hydrogen is assumed to be bound with adsorption centers Z_1, and acetone and its semihydrogenated form with centers Z. The first three steps are quasi-equilibrium and the rate-determining step is the addition of the second hydrogen atom to the semihydrogenated form of acetone.

The kinetic equation corresponding to scheme (1) is:

$$r = k_4\ \frac{K_3 b_{ac}P_{ac}\ \sqrt{b_{H_2}P_{H_2}}}{1 + b_{ac}P_{ac} + K_3 b_{ac}P_{ac}\ \sqrt{b_{H_2}P_{H_2}}} \cdot \frac{\sqrt{b_{H_2}P_{H_2}}}{1 + \sqrt{b_{H_2}P_{H_2}}} \qquad (2)$$

where k_4 is the rate constant of the rate-determining step, k_3 is the equilibrium constant of the third step, b_{H_2} and P_{H_2} are the adsorption coefficient and the hydrogen partial pressure, respectively, b_{ac} and P_{ac} are the same parameters for acetone.

Equation (2) describes well the experimental data obtained. Curves in Fig. 1 (c) were calculated from this equation. The activation heat of the rate-determining step determined from the temperature dependence of the constant k_4 is 11 kJ/mol. The b_{ac} value according to its physical sense decreases with the increase in the temperature. The temperature dependence of this value was used to calculate the heat of acetone adsorption (19 kJ/mol).

A standard change of entropy in the acetone adsorption, ΔS^o_{ac}, determined from the experimental data is $- 42$ J/(mol $\cdot$ K) (P $= 1.01 \times 10^5$ Pa, the acetone coverage of the surface $\Theta = 0.5$), whence it follows that in the course of adsorption acetone loses one degree of freedom of its translational motion.

Thus IR spectroscopic and thermodynamic characteristics indicate fairly high surface mobility of the acetone adsorbed on the Ni catalyst.

Studies of the acetone hydrogenation on a Pd catalyst at temperatures ranging from 333 to 363 K indicate no catalytic activity of the catalyst in this reaction. This can be attributed to the fact that acetone is not adsorbed on the Pd catalyst as evidenced by IR spectroscopic data.

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