The kinetics of transformation of isopentenols in the presence of the Nafion-H catalyst

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The kinetics of transformation of 3-methyl-1-buten-3-ol in the presence of the Nafion-H catalyst was studied. A comparison between the data obtained and those for the reaction catalyzed by sulfuric acid showed that under the same conditions, the macroscopic acidic properties of Nafion-H correspond to the catalytic activity of 8—15% sulfuric acid.

Key words: kinetics, catalysis, solid acids, acidity.

The increasing interest in the use of solid acids as catalysts gives rise to the problem of establishing their catalytic activity. The acidity of solid catalysts is usually established by the indicator method under the assumption that the ionization mechanisms of the indicator and reagent are similar. This makes it possible to compare their ionization constants (including protonation constants). When this approach is used, the acidity function H_0 changes for protonation processes.

The use of the indicator methods, which is well substantiated for the determination of the acidity of solutions, meets several objections in the case of solid acids. When the acidity of the catalyst is studied, the ionization of the indicator should consist of one equilibrium stage of protonation, and there should be a possibility of measuring the ratio of concentrations of the neutral and protonated forms C_B/C_{BH^+} of the indicator (indicator ratio). These conditions are often not fulfilled. For example, the use of *p*-aminoazobenzene for the determination of the acidity of the Nafion-H catalyst[1] is incorrect, since the ionization mechanism of this compound in solutions of acids is complex and includes six equilibrium stages.[2] The use of anthraquinone as the indicator[1] is also unreasonable,[3] since it is impossible to determine exactly the indicator ratios from the UV spectra, because the curve of absorption of the neutral form of anthraquinone is not retained when the acid concentration increases. However, the above errors can be easily eliminated in measurements of the acidity of solid acids, whereas it is very difficult to avoid the principal methodological error which is often met in attempts to estimate quantitatively the acidity of the solid catalyst. The fact is that the acidity function H_0 is determined from Eq. (1):

$$H_0 = \log(C_B/C_{BH^+}) + pK_{BH^+}, \qquad (1)$$

where H_0 is the acidity function; pK_{BH^+} is the negative logarithm of the basicity constant (basicity indicator) of the indicator, which allows H_0 to be measured; and C_B/C_{BH^+} is the indicator ratio. The indicator ratio in a solution that is in phase equilibrium with the solid acid is measured to estimate the acidity of the solid catalyst. The pK_{BH^+} value for an aqueous solution of the acid is usually used for the calculation of H_0 by Eq. (1); however, this is invalid, since pK_{BH^+} depends strongly on standardization of the magnitude measured. An infinitely dilute solution of acid in the solvent, in which C_B/C_{BH^+} of a series of indicators for the determination of H_0 are measured, is accepted as the standard state. Therefore, when this procedure is ignored, the results of the indicator measurements of the Nafion-H and other solid acids differ by 5—6 units.[1,4,5] Quantitative comparison of the acidity functions H_0 even in liquid acid—solvent systems is a very difficult task.

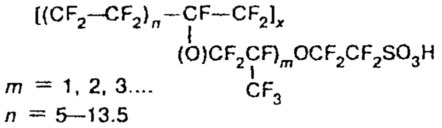
The kinetic method proposed in this work for the determination of the effective (macroscopic) acidity has no disadvantages inherent in the indicating method. The method is the following. In the presence of an acid catalyst with an unknown acidity, the kinetic curve is measured when the reaction mechanism is well known and the rate constants of elementary stages are known. If the rates of this reaction depend on the acidity of the medium, the latter can be estimated when the effective rate constant is determined. In the study of the catalytic activity of solid catalysts, the effective acidity measured by the catalytic method can include, along with the acidity of active sites, the parameters associated with transport of reagents to the acidic sites and removal of the reaction products from these sites. If the contribution of the transfer processes is ruled out, for example, by pulverization of the solid catalyst, its acidity can be determined. The influence of the transfer processes is a disadvantage of the method, but it allows one to obtain, in certain cases, additional information on the accessibility of acidic sites in solid catalysts with different modifications.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2090—2093, October, 1998.

As in the indicator method, the same mechanism of the chemical reaction for the model and processes studied should be the necessary condition for correct application of the kinetic method. When the equilibrium methods for measuring the acidity are used, the retention of the ionization mechanism on going from the indicator to the substrate can be postulated, whereas in the kinetic method, the retention of the shape of the kinetic curve is a necessary (but not sufficient) condition for the retention of the reaction mechanism.

The most comprehensive information on the acidity of solid catalysts can be obtained when the equilibrium (including the indicating method) and kinetic methods are used in combination.

In this work, some possibilities of the method for the determination of the acidity were shown for the perfluorinated ion exchange resin Nafion-H with active sulfuric groups and inert basis. The Nafion-H resin has the formula



$$[(\mathrm{CF_2{-}CF_2})_n{-}\mathrm{CF{-}CF_2}]_x$$
$$\qquad (\mathrm{O})\mathrm{CF_2}\underset{\mathrm{CF_3}}{\mathrm{CF}})_m\mathrm{OCF_2CF_2SO_3H}$$

m = 1, 2, 3....

n = 5—13.5

with molecular weight 950—1800. In this case, the reaction of transformation of unsaturated alcohols 3-methyl-1-buten-3-ol and 3-methyl-2-buten-1-ol is a convenient process for the study of the acidity. The kinetics of transformation of these alcohols were studied in detail in aqueous solutions of sulfuric and perchloric acids.[6,7]

In solutions with moderate concentrations of H_2SO_4 (7—35 wt.%), isomerization of the first alcohol to the second of the aforementioned alcohols, dehydration of the equilibrium mixture of these alcohols to isoprene, and hydration of isopentenols occur. The rates of all reactions under study depend on the acidity of the medium.

In addition to the concepts presented above, the choice of the Nafion-H catalyst is due to its wide use in the syntheses of esters and cyclic ethers,[8] dimethylacetals,[9] and in hydration of alkynes[10] and epoxides.[11] The acidic properties of Nafion-H make it possible to carry out the process without a solvent, and the products of transformation of the starting alcohol 3-methyl-1-buten-3-ol are well dissolved in the alcohol itself. These conditions for the process are close to those of real practical syntheses.

Experimental

3-Methyl-1-buten-3-ol (purity 99.9%) was the starting reagent. Catalysts of two types were used: powdered Nafion-H[1] and crystalline Nafion-H.[12] Experiments were carried out in a thermostatted reactor with a sampling outlet and a magnetic stirrer. The quantity of the starting alcohol was 3 mL in all experiments, and the amount of the catalyst was varied from 0.1 to 1.0 g.

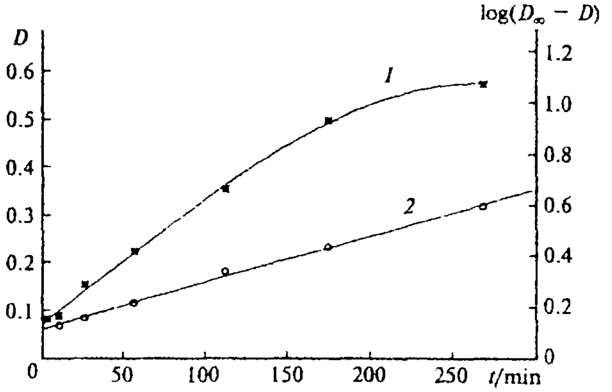


Fig. 1. Kinetic curve of formation of isoprene (*1*) and its logarithmic anamorphosis (*2*) at 25 °C. D is the current optical density, and D_∞ is the optical density at the end of the reaction; λ = 217 nm.

During the reaction, 50 mL of the reaction mixture was taken and introduced into a 100-mL flask filled with twice distilled water. After stirring of the solution, its spectrum in the 205—230 nm range was recorded in a quartz cell with the absorbing layer thickness of 10 mL. The molar absorption coefficients of the alcohols and isoprene for this UV spectral region were taken from the known work.[13] Only isoprene absorbs at 225 nm, its absorption coefficient being $1.54 \cdot 10^4$ L mol^{-1} cm^{-1}.

The kinetic curve of formation of isoprene at 25 °C is described by a first-order equation (Fig. 1), which coincides with the dependence for the H_2SO_4—H_2O system.

Results and Discussion

The effective rate constants k_{eff} for dehydration of 3-methyl-1-buten-3-ol in the presence of the Nafion-H catalyst of different types at 25 °C are presented in Table 1.

The a value (see Table 1) is proportional to the number of active acidic sites of the Nafion-H catalyst per mass unit of the starting alcohol.

Table 1. Effective rate constants of dehydration of 3-methyl-1-buten-3-ol

Type of catalyst Nafion-H	Weight of catalyst/g	a*	$k_{eff} \cdot 10^3$ /min^{-1}
Powdered	0.1	0.004	1.3
Powdered	0.3	0.13	2.6
Powdered	0.6	0.25	5.8
Powdered	1.0	0.41	8.5
Powdered from another batch	0.6	0.24	5.0
Granular, cylindrical	1.2	0.48	3.4

* a is a quantity equal to the mass ratio of the catalyst and starting alcohol.

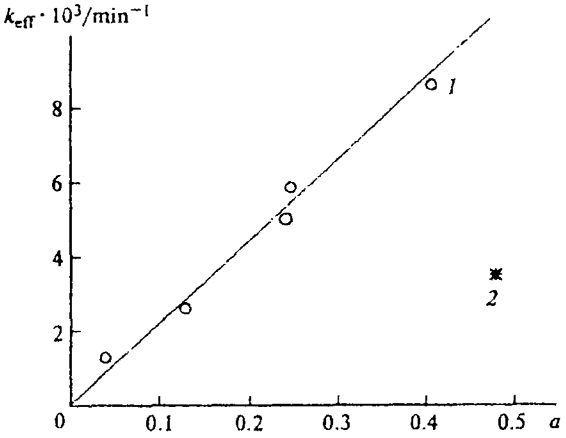


Fig. 2. Dependence of the effective rate constant of formation of isoprene from the equilibrium mixture of isopentenols on the *a* parameter (the mass ratio of the Nafion-H catalyst to the starting alcohol): *1*, powdered samples; *2*, granular cylindrical sample.

The dependence of the effective rate constant on the *a* value is presented in Fig. 2. The straight line in Fig. 2 indicates that the transfer of the reagents to the acidic sites (external diffusion) is not a limiting stage. The points on the line correspond to the separately prepared and dried samples of the powdered catalyst. In addition, as can be seen in Fig. 2, granular Nafion-H possesses a considerably lower catalytic activity, which is probably related to the influence of transfer processes.

Comparison of the effective constants k_{eff} for the dehydration of the equilibrium mixture of 3-methyl-1-buten-3-ol and 3-methyl-2-buten-1-ol in the H_2SO_4—H_2O and Nafion-H—isopentenol systems shows that the macroscopic acidic properties of Nafion-H in the interval studied (0.1—1.0 g in 3 mL of alcohol) correspond to the change in H_0 in the range of 8—15 wt.% sulfuric acid. The acidity function H_0 changes from −0.3 to −0.8.[3] This value is considerably lower than those presented in the works published previously,[1,5] although the samples studied contain no water, whose presence decreases the acidity of the catalysts of the Nafion-H type.[5]

The authors thank B. V. Mislavskii for the catalyst samples.

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Received February 6, 1998;
in revised form May 13, 1998