

OXIDATION OF ACROLEIN TO ACRYLIC ACID ON VANADIUM MOLYBDENUM OXIDE CATALYST; THE REACTION KINETICS

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The oxidation kinetics of acrolein have been studied in gas phase in the presence of vanadium molybdenum oxide catalyst. Using a through-flow apparatus with integral reactor, the effect has been studied of concentration of individual reaction components, *i.e.* acrolein, oxygen, steam and acrylic acid, on conversion degree of acrolein. The measurements have been carried out at atmospheric pressure. For evaluation of the kinetic data measured an equation has been suggested expressing dependence of the oxidation rate on the mentioned parameters.

In our previous paper¹ we studied properties of vanadium molybdenum oxide catalyst on Aerosil in gas-phase oxidation of acrolein to acrylic acid. With the use of micro-catalytic pulse technique it was possible to prove redox mechanism of the reaction². IR study of interaction of acrolein with surface of the catalyst revealed³ that the aldehyde is adsorbed in the form of the acrylate which is stable even at the temperatures of the catalytic reaction but can be easily removed from the catalyst surface by action of steam. The present communication deals with kinetics of oxidation of acrolein on the said catalyst.

EXPERIMENTAL

Acrolein. The acrolein sample used for the reaction was of *p.a.* purity grade (Fluka Bush, Switzerland). Acrolein of lower purity than 97 per cent was purified by distillation in argon flow before use. Purity of acrolein was checked by chromatographic analysis, by bromide-bromate method and by measurement of vapour pressure with isoteniscope.

Catalyst. The vanadium molybdenum oxide catalyst (atomic ratio Mo : V = 4.7) was prepared as follows: Solution A — 31 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ of *p.a.* purity grade was dissolved in 220 cm³ distilled water. Solution B — 4.34 g NH_4VO_3 of *p.a.* purity grade was dissolved in 200 cm³ distilled water at 60°C, and 7.5 g freshly distilled ethylenediamine was added after cooling. Solution C — 57 g Aerosil 380 (Elektroschmelzwerk, Kempten, Germany) was dispersed in 500 cm³ distilled water with intensive stirring. The solutions A and B were mixed and added to C with intensive stirring. The obtained mixture was evaporated in a turbine drier A/S NA (Denmark) at 90°C to give the catalyst powder which was calcinated at 180°C 6 h and finally annealed in air in a tube furnace at 300°C 6 h. Specific surface of the catalyst was determined by the BET method from adsorption of nitrogen, and its value was 57 m²/g. Its composition was

determined by chemical and spectral analyses: 64% SiO₂, 17.25% Mo, 1.92% V. X-Ray diffraction analysis using a URS-50 1M apparatus (U.S.S.R) showed that the catalyst is amorphous.

Apparatus. The oxidation kinetics were studied in a standard through-flow apparatus with integral reactor which was described in our previous communication¹ along with the procedure of analysis of the reaction gas mixture.

RESULTS AND DISCUSSION

The oxidation kinetics of acrolein on vanadium molybdenum oxide catalyst was studied at 300°C at atmospheric pressure. Influence of partial pressures of acrolein, oxygen, steam, and acrylic acid on conversion degree of acrolein was investigated. The individual acrolein conversion degrees at a chosen initial composition of gaseous reaction mixture were attained by suitable choice of time factor, *i.e.* ratio of the catalyst weighing and volume flow rate of the gaseous mixture. From preliminary experiments it could be concluded that, for the chosen catalyst grain diameter 0.4 to 0.6 mm and total flow rate of the gaseous reaction mixture 3 cm³ s⁻¹, the measured values of acrolein conversion are not distorted by internal and external diffusion. At the chosen ratio (10) of the reactor tube diameter and the catalyst grain diameter it can be presumed that temperature gradient across the catalyst bed and distribution of flow velocities in the cross section of the catalyst layer will not depreciate the results of measurements⁴. Height of the catalyst bed was adjusted at values above 1 cm by dilution of the catalyst with silicon carbide of the same grain size with the aim of minimization of effect of longitudinal diffusion. The used semi-automatic temperature controller Zeparis (ZPA, Trutnov) enabled a reliable temperature control in the reactor with the accuracy of $\pm 2^\circ\text{C}$. The temperature drop along the catalyst bed measured with an iron-constantan thermocouple had the maximum value of 3°C. Service life of the catalyst was proved by a continuous experiment of 100 h length.

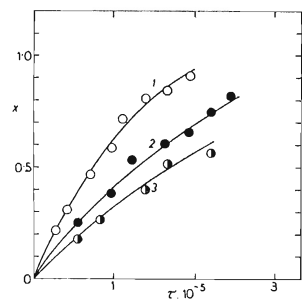
Composition of the initial reaction gas for the proper kinetic measurements was chosen with variable concentrations of acrolein (4 to 7 per cent by vol.), oxygen (3.5 to 12 per cent by vol.), steam (2 to 25 per cent by vol.), and acrylic acid (0 to 2 per cent by vol.). The measurements were divided into several series in which gradually one concentration was varied at constant concentrations of the remaining components. The obtained data on conversion of acrolein into acrylic acid at the stationary state are given in Fig. 1.

The experimental reaction products contained always small amounts of carbon dioxide and acetic acid besides unreacted acrolein and the acrylic acid produced. In the whole range of measurement, yields of carbon dioxide and acetic acid did not exceed 4 and 2 per cent, respectively. The experimental technique used allowed to determine the acrolein conversion with an accuracy better than 5 per cent.

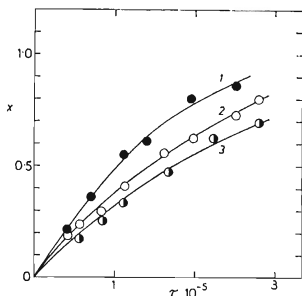
For selection of the reaction schemes and discussion of plausibility of the corresponding rate equations we used preliminary evaluation of the kinetic data and con-

TABLE I
Results of verification of the suggested rate equation with the experimental data

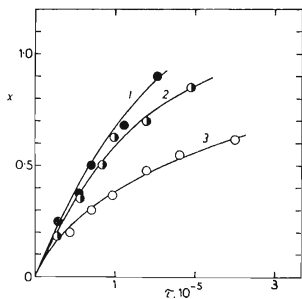
Constants	Values of constants	
	linear regression	non-linear regression
$k, \text{ mol s}^{-1} \text{ g}^{-1} \text{ Pa}^{-0.5}$	$1.35 \cdot 10^{-7}$	$1.4 \cdot 10^{-7}$
K_1	0.75	1.4
$K_{11}, \text{ Pa}$	5	4.5



a



b

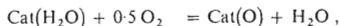
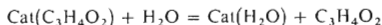


c

FIG. 1

Dependence of acrolein conversion x on time factor τ [g s dm^{-3}] (all the percentages by vol.): a 1 4% $\text{C}_3\text{H}_4\text{O}$, 7% O_2 , 17% H_2O ; 2 6.4% $\text{C}_3\text{H}_4\text{O}$, 7% O_2 , 17% H_2O ; 3 7% $\text{C}_3\text{H}_4\text{O}$, 7% O_2 , 17% H_2O , 2% $\text{C}_3\text{H}_4\text{O}_2$, N_2 as inert gas; b 1 7% $\text{C}_3\text{H}_4\text{O}$, 12% O_2 , 17% H_2O ; 2 7% $\text{C}_3\text{H}_4\text{O}$, 7% O_2 , 17% H_2O ; 3 7% $\text{C}_3\text{H}_4\text{O}$, 5% O_2 , 17% H_2O ; c 1 4% $\text{C}_3\text{H}_4\text{O}$, 7% O_2 , 25% H_2O ; 2 4% $\text{C}_3\text{H}_4\text{O}$, 7% O_2 , 10% H_2O ; 3 4% $\text{C}_3\text{H}_4\text{O}$, 7% O_2 , 2% H_2O

clusions of the former communications. It was found that (i) steam affects positively the oxidation rate, (ii) the acrylic acid formed retards the reaction, (iii) results of the measurements using the microcatalytic pulse technique suggest participation of oxygen from the catalyst surface in the reaction², (iv) IR spectroscopic findings on the adsorption of acrolein³ support the presumption that steam accelerates desorption of acrylic acid. The observed dependences resulted in the following choice of the reaction scheme:



where $\text{Cat}(\text{O})$ means the oxidized positions of the catalyst, and $\text{Cat}(\text{OC}_3\text{H}_4\text{O})$, $\text{Cat}(\text{C}_3\text{H}_4\text{O}_2)$, and $\text{Cat}(\text{H}_2\text{O})$ stand for the catalyst positions occupied by acrolein, acrylic acid, and water, resp.

Assuming that the slowest (rate limiting) step of the oxidation of acrolein to acrylic acid is reoxidation of the catalyst, the following kinetic equation can be derived by the known procedure⁵:

$$r = kP(\text{O}_2)^{1/2} (1 + K_1P(\text{C}_3\text{H}_4\text{O}_2)/P(\text{H}_2\text{O}) + K_{11}P(\text{C}_3\text{H}_4\text{O}_2)/P(\text{C}_3\text{H}_4\text{O}) P(\text{H}_2\text{O}))^{-1}.$$

Introduction of this relation into definition equation for rates of chemical reactions in flow, integration, and linearization allowed to calculate, at first, the values of constants by means of linear regression. The correlation coefficient 0.989 served as a criterion of correctness. To make the calculation more precise, we used further the Fletcher method of non-linear regression⁶. Table I gives the result of mathematical treatment of experimental data with the use of standard program⁷. Fig. 1 confronts the recomputed values of acrolein conversion with experimental data.

The experimental data were also used for verification of the rate equation derived under the assumption that the slowest step of the suggested scheme is desorption of acrylic acid and for verification of the rate equation suggested in the paper by Erenburg and coworkers⁸. In both the cases the experimental and the recomputed data showed no satisfactory agreement.

As far as formal reaction kinetics allows, the mentioned analysis of experimental kinetic data suggests the following mechanism of the studied oxidation. Acrolein is adsorbed rapidly and strongly at the catalyst surface. Interaction of the adsorbed

acrolein with lattice oxygen results in formation of acrylic acid whose desorption is accelerated by steam. The final step of the whole catalytic process is reoxidation of the catalyst by oxygen from gas phase. With respect to the reaction order in oxygen being $\frac{1}{2}$, it can be presumed that the slowest step of the reoxidation is entry of oxygen into the vacancies⁹. This step can be negatively affected by adsorption of water vapour.

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