STUDY OF MECHANISM OF OXIDATION OF ACROLEIN ON A VANADIUM–MOLYBDENUM OXIDE CATALYST

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Received July 7th, 1978

The mechanism of the incorporation of oxygen into the products of acrolein oxidation has been studied by a microcatalytic pulse technique with vibrating catalyst bed. It was found that acrylic acid is formed as the product of partial oxidation by stepwise redox mechanism and that in addition to the catalyst oxygen, also oxygen from the gas phase participates in carbon dioxide formation.

According to patent literature, one of the most efficient and selective catalysts for gas phase oxidation of acrolein to acrylic acid is based on a mixture of vanadium and molybdenum oxide. A few data about mechanism of this industrially important reaction have been reported so far[1] and data about mechanism of this reaction effected with a vanadium–molybdenum oxide catalyst are still lacking. The aim of the present work was to contribute to the elucidation of this problem.

EXPERIMENTAL

Catalyst. Vanadium–molybdenum catalyst deposited on Aerosil (30% by weight of the active component) with V : Mo = 1 : 5 ratio was prepared by the procedure elsewhere[2]. The total specific surface of the catalyst was 57 m^2/g (by BET method).

Aparatus. A pulse microcatalytic apparatus with vibrating catalyst bed, represented schematically in Fig. 1, was used in the present study. It consisted of three parts: the device for preparing and feeding gases, the reactor and finally of the analytical part. Helium was purified by passing through three columns. The first one *4*, containing a molecular sieve, served for removal of water traces, the second, filled with a nickel–chromium catalyst *5*, removed oxygen. Further purification of the gases from oxygen up to 0·002% content (v/v) was made on a short column packed with a NaX molecular sieve *6* and cooled by liquid nitrogen. The apparatus was thermostatted to 160°C. The glass reactor *15* was placed into a tubular oven and was connected to the system of metal valves *via* steel cappillaries. Electromagnetic saw served as the source of vibrations of the reactor (50 Hz frequency, 2—3 mm amplitude). The apparatus can work in two regimes, pulsion and flow. The switch of one to another regime was realized by means of two metal valves. *10*, *12*).

Analytical part of the apparatus consisted of a feeding loop *13* (20 cm^3 volume), two cooling traps for condensation of reaction products *16*, *17* and two chromatographs, of which one was equipped with a thermal conductivity detector and the other with a flame-ionisation detector *20*. Starting or reaction mixtures passed through two cooling traps *16*, *17*. The first one, cooled by liquid nitrogen, trapped acrolein, acrylic acid, carbon dioxide and water. The second was filled with a molecular sieve and removed oxygen and carbon dioxide. At low acrylic acid concentrations its analysis was carried out on the chromatograph equipped with a flame-ionisation detector, using two samples; one was used to determine O_2, CO, CO_2, H_2O and C_3H_4O the other to analyse C_3H_4O, $C_3H_4O_2$, O_2 and CO. One analysis took 18—20 min. Condensation time in cooling traps was 20 min.

Calculations. From the results of chromatographic analysis we calculated material balances of carbon and oxygen (B_C, B_O), acrolein conversion (x, %), selectivities $S(C_3H_4O_2)$, $S(CO_2)$) specific rates of formation of acrylic acid and carbon dioxide ($w(C_3H_4O_2)$, $w(CO_2)$), the degree of the reduction of catalyst surface on introducing the reduction mixture to the catalyst in stationary state(Q)

$$B_C = \frac{A'(C_3H_4O) + A(C_3H_4O_2) + A(CO_2)}{A(C_3H_4O)}\,100\,, \qquad (1)$$

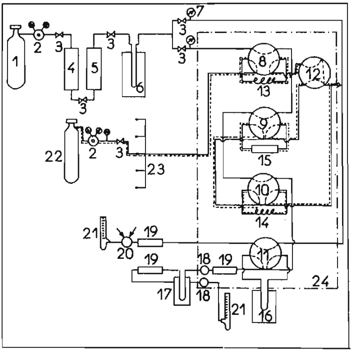
where $A(C_3H_4O)$ is the amount of acrolein in the pulse in the inlet port of the reactor (in mol), $A'(C_3H_4O)$ is the amount of acrolein in the pulse in the outlet port of the reactor (mol) $A(CO_2$ is the amount of CO_2 formed during the flow of one pulse through the reactor (mol) and $A(C_3H_4O_2)$ is the amount of acrylic acid in one pulse (mol). For calculation of material balance of oxygen the following stoichiometric equations were used:

$$C_3H_4O + 1/2\,O_2 = C_3H_4O_2 \qquad (A)$$

FIG. 1

Schematic Diagram of Apparatus

1 Cylinder with helium, 2 reductors, 3 valves, 4 column with molecular sieve, 5 column with a Ni–Cr catalyst, 6 column with molecular sieve, 7 manometer, 8—11 six-way metal valves, 12 four-way metal valve, 13 feeding loop, 14 loop for analysis in flow regime, 15 reactor, 16 cooling trap for reaction products, 17 cooling trap filled with molecular sieve for freezing reaction products, 18 thermal conductivity detector, 19 chromatographic columns packed with Polysorb, Porapak and molecular sieve, 20 flame ionisation detector, 21 rheometer, 22 cylinder with gaseous mixture, 23 distribution system for individual gaseous mixtures, 24 air thermostat.



$$C_3H_4O + 3{\cdot}5\,O_2 = 3\,CO_2 + 2\,H_2O\,. \qquad (B)$$

Conversions x and selectivities S were calculated from relations (*2*) and (*3*):

$$x = \frac{A(C_3H_4O) - A'(C_3H_4O)}{A(C_3H_4O)}\,100 \qquad (2)$$

$$S = \frac{A_i}{A(C_3H_4O) - A'(C_3H_4O)}\,100 \qquad (3)$$

$$A_i = A(C_3H_4O) \quad \text{or} \quad A(CO_2)\,.$$

The reaction rate was determined from Eq. (*4*) where G is the weight amount of the catalyst (g), S_p is the specific surface of the catalyst (m^2/g) and τ is the time needed to pass the pulse through the reactor.

$$w_i = (A_i/GS_p\tau)\,10^{-4} \quad [\text{mol cm}^{-2}\,\text{s}] \qquad (4)$$

On calculating the degree of the reduction of the catalyst surface we assumed that the area corresponding to one oxygen atom is 7·8 $Å^2$. In this case the coverage of 1 m^2 of the surface by the oxygen monolayer corresponds to 0·238 mol of molecular oxygen, *i.e.* to $1{\cdot}28\,.\,10^{19}$ oxygen atoms.

RESULTS AND DISCUSSION

Mechanism of acrolein oxidation was investigated at 260 and 280°C. Experiments were carried out with gaseous mixtures of the following compositions: 0·06% C_3H_4O + 0·12% O_2 + 99·82% He (reaction mixture), 0·06% C_3H_4O + 99·94% He (reduction mixture) and 0·12% O_2 + 99·88% He (oxidation mixture). Individual mixtures were prepared in advance in steel cylinders on the basis of partial pressures.

It is known that under stationary conditions of the reaction two mechanisms of the incorporation of oxygen into the molecule of the compound undergoing oxidation are possible: stepwise redox mechanism and associative mechanism[3]. With the aim to estimate the relative importance of each of these routes we compared the rates and selectivities of the interaction of acrolein with vanadium–molybdenum catalyst in stationary state during catalysis (pulse of the reaction mixture), reduction (pulse of the reduction mixture) and reoxidation (pulse of the oxidation mixture). The stationary state was achieved by treating the catalyst with pulses of the reaction mixture. Fig. 2 shows the dependence of the rates of acrylic acid and carbon dioxide formation, material balance of carbon, acrolein conversion and the selectivity on the number of pulses of the reaction mixture for one run at 280°C, when the mixture contained 0·1% C_3H_4O and 0·2% O_2 (v/v). Analogous dependences were obtained also for all the other experiments in which the catalyst was in stationary state.

As evident from Fig. 2, for first pulses only low material balance of acrolein is achieved (*c.* 50%). The balance increases with increasing number of pulses and on approaching stationary state it equals to 100% (in 10th pulse). Incomplete balance indicate that in first pulses acrolein binds strongly and irreversibly on the surface. Establishment of stationary state is accompanied by the increase in the rate of acrylic acid formation and by the decrease in the rate of carbon dioxide formation, which reflects also in the selectivity of the reaction. Such a change in the rates of these reactions is obviously connected not only with the removal of weakly bound oxygen, which accounts for the rate decrease in carbon dioxide formation, but also with the changed catalyst surface (concerning its chemical composition and the oxidation state of vanadium and molybdenum ions).

After stationary state on the catalyst was established, pulses of reaction, reduction and oxidation mixtures were successively introduced. In Table I are presented the rates of acrylic acid and carbon dioxide formation, the degree of conversion, the selectivity, the degree of the reduction of the catalyst, along with the ratio of the

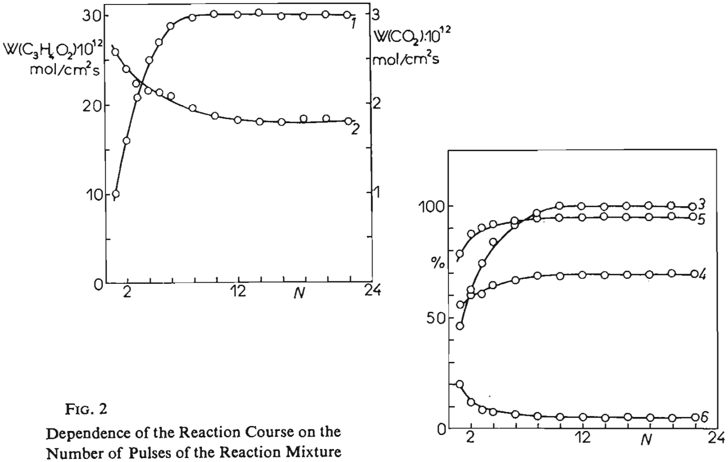


FIG. 2

Dependence of the Reaction Course on the Number of Pulses of the Reaction Mixture

a *1* Rate of acrylic acid formation, *2* rate of carbon dioxide formation; ; *b* *3* Change in the balance of carbon, *4* acrolein conversion, *5* selectivity with respect to acrylic acid, *6* selectivity with respect to carbon dioxide, *N* number of pulses.

TABLE I

Results of Experiments with Pulses of Different Composition

Regime	Temperature °C	$w(C_3H_4O_2)$	$w(CO_2)$	x %	$S(C_3H_4O_2)$	$S(CO_2)$	B_c %	Q %	w_{cat}/w_{red}	
		pmol cm^{-2} s^{-1}			%				$C_3H_4O_2$	CO_2
Catalysis	280	1·45	1·87	51·0	93·5	6·6	97·5	—	—	—
Reduction		0·72	1·80	51·0	96·0	4·0	92·0	0·58	1·04	1·96
Catalysis		1·51	1·86	57·0	93·5	6·5	98·0	—	—	—
Reduction		0·74	1·80	50·0	96·0	4·0	93·0	0·60	1·03	2·02
Reoxidation		0·94	—	—	—	—	—	—	—	—
Catalysis	260	0·71	1·64	51·5	96·0	4·0	94·0	—	—	—
Reduction		0·54	1·72	45·5	97·5	2·5	92·0	0·59	0·96	1·3
Reoxidation		0·27	—	—	—	—	—	—	—	—

rate during catalysis to that observed during reduction. By one pulse of the mixture, 0·005 – 0·006 parts of the oxygen monolayer was removed from the surface. As follows from the Table, during this process, stationary state of the catalyst remained unchanged (rates in experiments 1 and 3 are identical). From this Table it is also evident that the same result is obtained in both reduction and in catalysis, the major product being acrylic acid. The rates of acrylic acid formation in catalysis and in reduction are very similar to each other. This similarity shows that oxygen of the catalyst participates in acrylic acid formation, *i.e.* the acid is produced by stepwise redox mechanism. The rate of carbon dioxide formation during catalysis is faster than that during reduction. This means that oxygen from the gas phase takes part in its formation. In accordance with this, the amount of carbon dioxide corresponding to the difference in the amount of carbon dioxide was also obtained after one pulse of oxygen (oxidation mixture) was introduced into the reactor, likely due to the oxidation of strongly adsorbed acrolein. Carbon monoxide was present among reaction products only in trace amounts.

The comparison of the rates of the reactions proceding during catalysis and reduction just discussed allow us to conclude that in the oxidation of acrolein on vanadium–molybdenum oxide catalyst the product of partial oxidation, acrylic acid, is formed by stepwise redox mechanism and that in addition to the catalyst oxygen also oxygen from the gas participates in formation of the products of total oxidation. It seems likely that oxygen from the gas phase causes the decomposition of strongly bound surface structures, in agreement with the associative mechanism of CT type (ref.[4]).

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Translated by J. Hetflejš.