Oxidation of acrolein on a multicomponent oxide catalyst

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Catalytic oxidation of acrolein to acrylic acid has been studied and the optimum composition of the multicomponent catalyst $Mo_aV_bCu_cFe_dO_x$ has been found. The reaction kinetics has been measured.

Keywords: Acrylic acid; oxidation; mixed oxides; acrolein

The gas phase catalytic oxidation of acrolein to acrylic acid is known [1,2] to proceed with high selectivity in the presence of molybdenum vanadium oxide catalyst. This two-component catalyst attains an acceptable activity at temperatures above 570 K, i.e. in a region where the heterogeneous catalytic reaction can be accompanied by undesirable homogeneous gas phase radical oxidation. Therefore, industrial processes adopt multicomponent catalysts exhibiting satisfactory activities at about 520 K. The present paper gives the results of experimental studies of properties of a four-component oxide catalyst type $Mo_aV_bCu_cFe_dO_x$. These results include the optimum composition of the catalyst and basic information about the corresponding reaction kinetics.

In order to find the optimum composition of the catalyst, we used the statistical approximation method of Fabian [3]. The following procedure [4] was used for preparation of the catalyst: Solution A was prepared by stepwise dissolution of hexaammonium heptamolybdate and ammonium metavanadate in distilled water. Solution B was prepared by stepwise dissolution of copper(II) nitrate, iron(III) nitrate, and tartaric acid in distilled water. The molar ratios of the metals and the corresponding weights of the starting substances were chosen according to Fabian's procedure. Both solutions were mixed, and the pH was adjusted to 7.5–8 by addition of aqueous ammonia (26%). The clear blue-green solution was concentrated with constant stirring at 340 K to obtain a paste which was then dried at 400 K for 5 h, calcinated at 430 K for 2 h and at 450 K for 6 h, and finally annealed at 573 K for 5 h and at 623 K for 5 h.

Table 1
Tests of the catalysts

Catalyst	Conversion C_3H_4O (%)	Yield $C_3H_4O_2$ (%)	Selectivity $C_3H_4O_2$ (%)	Yield CO_2 (%)	Selectivity CO_2 (%)
$Mo_{11}V_2Cu_1Fe_1$	77	71	92.2	6	7.8
$Mo_{12}V_4Cu_1Fe_1$	69	65	94.2	4	5.8
$Mo_{12}V_2Cu_3Fe_1$	43	40	93.0	3	7
$Mo_{12}V_2Cu_1Fe_{1.5}$	81	73	90.1	8	9.9
$Mo_{12}V_{2.25}Cu_{1.25}Fe_{0.875}$	73	68	93.1	5	6.8
$Mo_{12}V_{2.5}Cu_{1.5}Fe_{0.75}$	66	63	95.5	3	4.5
$Mo_{12}V_{2.75}Cu_{1.75}Fe_{0.625}$	61	59	96.1	2	3.2
$Mo_{12}V_3Cu_2Fe_{0.5}$	59	58	98.3	1	1.7
$Mo_{12}V_{3.25}Cu_{2.25}Fe_{0.375}$	52	49	94.2	3	5.8

Table 2
Kinetics data

Reaction mixture (vol%)	Catalyst weight (g)	Time factor $\times 10^{-5}$ (g s mol^{-1})	Yield $C_3H_4O_2$ (%)
5.4 C_3H_4O	7.00	20.91	79.3
6.4 O_2	5.00	17.92	69.5
34 H_2O	5.00	14.93	59.2
54.2 N_2	4.00	11.95	50.6
	3.00	8.96	41.8
	1.50	4.48	18.5
	2.40	7.17	29.4
	3.75	11.2	45.0
4 C_3H_4O	0.80	3.23	18.1
6.4 O_2	1.40	5.64	30.6
34 H_2O	2.10	8.47	40.3
55.6 N_2	2.80	11.29	53.2
	3.80	15.32	65.5
	5.00	20.16	84.8
	5.30	21.37	87.5
	3.50	14.11	62.5
4 C_3H_4O	6.80	19.58	87.3
8 O_2	6.30	18.14	85.4
34 H_2O	6.00	17.28	81.2
54 N_2	4.50	13.53	69.5
	3.80	10.94	62.3
	3.00	8.64	52.9
	2.30	6.62	40.5
	1.80	5.18	36.6
	1.40	4.03	27.7
	1.10	3.16	24.8

The catalysts obtained were tested in a flow apparatus with integral reactor [1] at constant conditions: reaction temperature 523 K, catalyst weight 1 g, catalyst grain size 0.4–0.6 mm, flow rate of reaction mixture 5 $dm^3\ h^{-1}$, composition of reaction mixture (vol%) 4% C_3H_4O, 7% O_2, 17% H_2O, 72% N_2. Acrolein in the reaction product was estimated polarographically according to Moshier [5], acrylic acid was estimated titrimetrically with 0.01 M NaOH (phenolphthalein), and carbon oxides were estimated by gas chromatography; the last method also revealed that the yield of acetic acid did not exceed 1% rel. The catalysts were evaluated on the basis of the acrolein conversion values, yields of acrylic acid and carbon dioxide, and the oxidation selectivity for acrylic acid as defined by Sachtler [6]. The results of tests are presented in table 1.

From table 1 it follows that the highest selectivity of oxidation of acrolein to acrylic acid is attained on the oxide catalyst $Mo_{12}V_3Cu_2Fe_{0.5}O_x$. The properties of this catalyst were verified at higher values of acrolein conversion. With 3 g of the catalyst adopted at the above-given conditions of 100% conversion of acrolein the yield of acrylic acid was 96%. The specific surface of the catalyst determined from adsorption of nitrogen is 8.5 $m^2\ g^{-1}$.

Using the catalyst $Mo_{12}V_3Cu_2Fe_{0.5}O_x$ we investigated the kinetics of acrolein oxidation. The kinetic region of measurements was given by the choice of the catalyst grain size 0.4–0.6 mm, the flow rate of gaseous reaction mixture 5 $dm^3\ h^{-1}$, and height of the catalyst bed more than 1 cm. The oxidation proceeded with high selectivity. In the whole range of measurement the yield of side products, i.e. acetic acid and carbon dioxide, did not exceed a sum of 3% rel. which is within experimental error. Therefore, the values of acrolein decrease rate and acrylic acid formation rate can be considered comparable. The data measured are presented in table 2.

From evaluation of the kinetic data it follows that the rate of formation of acrylic acid can satisfactorily be described by

$$r = kp_{O_2} \tag{1}$$

with the value of rate constant $k = 6.9 \times 10^{-11}$ mol $s^{-1}\ g^{-1}\ Pa^{-1}$ at 503 K, determined with an accuracy of 4.5%.

Using the microcatalytic pulse technique, Popova et al. [7] showed that the oxidation of acrolein on molybdenum vanadium oxide catalyst proceeds by the redox mechanism. Our kinetic measurements indicate that, at high concentration of water vapour in the feed, the slowest, i.e. rate-limiting, step of the reaction consists in the reoxidation of the catalyst with molecular oxygen from the gas phase.

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