SORPTION OF ACETIC AND PROPIONIC ACIDS AND PROPANAL ON A MOLYBDENUM-VANADIUM OXIDE CATALYST

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It has been found by gas chromatography that the equilibrium adsorption of propanal, propionic and acetic acids on molybdenum-vanadium oxide catalyst can be described by the Langmuir adsorption isotherm. The existence of carboxylates on the catalyst surface has been proved by IR spectroscopy.

Because of its good conservation effects, propionic acid has broad applications in agrochemistry. Moreover, it is used for preparation of its esters and other special substances. It is almost not found in nature and is formed in small amounts during fermentation processes. Industrially it is produced by catalytic oxidation of hydrocarbons and by carbonylation of ethene.

Our first paper[1] dealt with possibilities of obtaining propionic acid by catalytic oxidation of propanal in gas phase. It was found that on a Mo-V oxide catalyst propionic acid is formed with acetic acid and carbon dioxide as the side products. In order to contribute to understanding of the reaction mechanism, we have studied the equilibrium adsorption of the components, i.e. propanal, propionic acid and acetic acid (inclusive the estimation of the nature of their interactions with the catalyst surface) using IR spectroscopy. The present communication summarizes the results of these experimental studies.

EXPERIMENTAL

The oxide catalyst with mol. ratio Mo : V = 4.7 : 1 (coated on Aerosil) had the specific surface of 57 m^2 g^{-1}. Its preparation and properties were described elsewhere[2]. The gas chromatographic method was used to study the equilibrium reversible adsorption. All measurements were carried out on a Chrom 42 apparatus equipped with a thermal conductivity detector; the conditions are given in Table I. The catalyst grain size was 0.4 – 0.6 mm, helium was used as the carrier gas. The chromatograms were evaluated in a conventional way[3] by the method of the peak maximum.

The character of interaction of propanal, acetic and propionic acids with the surface of molybdenum-vanadium oxide catalyst was studied by IR spectroscopy. The spectra were measured with a two-beam Perkin–Elmer 684 spectrophotometer using thin catalyst plates (10 mg cm^{-2}) which exhibit sufficient transmittance in the region from 1 300 to 2 000 cm^{-1} to enable monitoring of both the sorption and desorption.

Before each experiment the catalyst was heated at 300 °C in vacuum (5 . 10⁻³ Pa) for 2 h. Then the studied substance was sorbed on the catalyst from gas phase at room temperature and, subsequently, thermally desorbed at temperatures gradually increasing from 100 to 250 °C in vacuum. IR spectrum was measured after each desorption. All the operations were performed in a glass vessel with NaCl windows.

RESULTS AND DISCUSSION

The adsorption isotherms obtained are successfully described by the Langmuir equation. The values of constants of this equation are presented in Table I along with the values of isosteric adsorption heat. The constants were calculated by linear regression and the correlation coefficient was always higher than 0.95.

The sorption of both acetic and propionic acids proceeds in almost the same way. The acids are sorbed on the catalyst surface by donor–acceptor interaction, which is manifested by distinctly lowered values of $v(C=O)$ (1 715 cm⁻¹ for acetic acid, 1 725 and 1 714 cm⁻¹ for propionic acid[4]). However, already at room temperature there takes place a distinct acid-base reaction of the acids sorbed on the catalyst surface to give the corresponding carboxylates. This fact is connected with formation of new intense bands around 1 540 cm⁻¹ ($v_{as}(COO)$) and 1 420 cm⁻¹ ($v_s(COO)$). With respect to the very small wavenumber difference between these bands, the bonding to the catalyst surface can be formulated as bidentate[5]. On heating to 100 °C, most of the molecules of acids disappear from the catalyst surface, and the spectrum practically exhibits the carboxylate bands only, the more marked band being that at 1 680 cm⁻¹ (which partly

TABLE I
Equilibrium adsorption data $a = L Kp / (1 + Kp)$

Quantity	Adsorbate		
	propanal	propionic acid	acetic acid
Pulse of adsorbate, mol	1.39 . 10⁻⁴	1.34 . 10⁻⁴	1.75 . 10⁻⁴
He flow rate, m³ s⁻¹	1.09 . 10⁻⁶	0.96 . 10⁻⁶	0.96 . 10⁻⁶
Cat. weight, g	1.65	1.36	1.56
L^a, mol kg⁻¹	0.265	0.192	0.222
Langmuir equation-constants $K . 10^4$, Pa⁻¹	2.00 (356 K)	8.97 (455 K)	2.77 (433 K)
	1.03 (368 K)	6.28 (470 K)	2.27 (445 K)
	0.89 (381 K)	5.10 (485 K)	1.74 (470 K)
	0.53 (393 K)	3.13 (501 K)	1.52 (491 K)
Ads. enthalpy, kJ mol⁻¹	−46	−56	−33

^{a} The number of active centres.

overlapps with the $\nu(CO)$ band of the acid). Most likely this band can be ascribed to the $\nu_{as}(COO)$ vibration of the carboxylate molecule bound monodentately[5]. On further increasing the desorption temperature, the bands of carboxylates are diminished in same way as the amount of the sorbed substances is decreased. At 250 °C the desorption of propionic acid is practically complete. Actetic acid is completely desorbed at a rather high temperature (~300 °C).

The sorption of propanal on the catalyst surface is immediately followed by oxidation, and only the presence of the acid and the corresponding carboxylate can be observed. The nonreacted propanal can be found if the sorption proceeds in the presence of water vapour. Under such conditions, the most active centres of the catalyst are blocked, and it is possible to observe $\nu(CO)$ of propanal as a close pair of bands at 1 699 and 1 681 cm^{-1}. The $\nu(CO)$ value is lowered by about 40 cm^{-1} as compared with that of the free propanal which is caused by donor–acceptor interaction with the catalyst surface[4]. These bands disappear on heating at 100 °C in vacuum.

The technique adopted allows effective monitoring of the influence of water vapour on the behaviour of propionic acid on the catalyst surface. The sorbed propanal is oxidized to propionic acid which is partially transformed into the carboxylate. The desorption at 100 °C removes predominant part of the acid which is indicated by the intensity decrease of the bands at 1 715 and 1 730 cm^{-1}, the amount of carboxylate being not markedly changed.

A simultaneous adsorption of water vapour and propanal is accompanied by a drastic lowering of the carboxylate bands at about 1 530 and 1 420 cm^{-1} and by a distinct increasing of the acid content, which is caused probably by a shift of the equilibrium to the right (Eq. (A)).

$$A^- + H_2O \rightleftharpoons HA + OH^- \quad (A^- = \text{carboxylate}) \qquad (A)$$
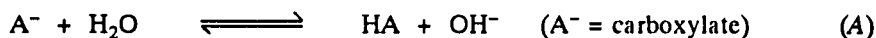
Then the subsequent desorption markedly lowers the total amount of the acid sorbed on the catalyst surface.

The spectral manifestations of acetic and propionic acids are practically identical in the region available (the spectrum of propionic acid and propionate exhibits the additional band of $\delta(CH_2)$ at 1 468 cm^{-1}. Hence the results obtained give no evidence concerning the reaction step in which acid is formed.

The validity of the Langmuir equation and the constant value of isosteric adsorption heat suggest that the equilibrium reversible adsorption takes place at energetically equivalent centres. The presence of water and/or surface hydroxyl group accelerates the transformation of carboxylates into acids and their subsequent desorption. The comparison of results of measurements from both the techniques shows that the reversible adsorption of propanal proceeds in two forms, viz. the non-activated and the activated ones. The former leads to desorption of propanal and the latter to desorption of propionic acid. In all the cases it was observed that a part of the adsorbate is bound irre-

versibly. According to literature data[5] it can be presumed that this part is responsible for the destruction of surface structures into carbon dioxide (which was observed among the oxidation products) at the reaction temperatures, i.e. 300 °C.

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