OXIDATION OF ETHANOL ON Sn–Mo OXIDE CATALYSTS

Magdy A. WASSEL[a], Nalla K. ALLAHAVERDOVA[b] and Tofki G. ALKHAZOV[b]

[a] *Chemistry Department, Faculty of Science, Al-Azhar University, Egypt*
[b] *Institute of Oil Chemistry, Baku 370601, C.I.N.*

Received April 4, 1991
Accepted August 9, 1991

To determine the acidic and basic properties of the title catalysts, the adsorption of NH_3 and SO_2 was compared using pulse method. It was found that this characteristics undergoes changes when the Sn–Mo catalyst is treated with aqueous potassium hydroxide solutions of different concentrations. The catalyst treated with the more concentrated KOH solution possesses mainly properties of a base. When studying the oxidation of ethanol it has been found that the $\alpha CO_2/\alpha$ aldehyde conversion ratio increases with the time of contact of the mixture with the catalyst while the $\alpha CO_2/\alpha$ acid ratio is not affected. The study of two alcohols deuterated either in OH group (C_2H_5OD) or in the alkyl group (C_2D_5OH) has shown that the substitution of C—H for C—D bond enhances the stability of the primary oxidation procuct, deuterated ethanal, so that it is not transformed further to acetic acid.

From patent literature and publications it becomes evident that ethanol as a raw material for the preparation of ethanoic acid, ethanal, ethyl esters and other derivatives attracts ever increasing attention[1–4]. IR spectra of the surface of several catalysts upon adsorption of ethanol show absorption bands at 1 450, 1 540, 1 400, 1 050 and 1 095 cm^{-1} which indicate formation of the aldehyde via carbonate and carboxylate structures[5]. Other bands at 1 540 and 1 400 cm^{-1} may indicate the presence of the oxidation products on catalyst surface. Their presence was confirmed by weight changes of the catalyst. The carbonate and carboxylate structures are considered to be responsible for the formation of deep oxidation products[6]. The present work reports on the gas phase catalytic oxidation of ethanol. Our purpose was to determine the effect of several process parameters on the rate of ethanol conversion for the Sn–Mo oxide catalyst with Sn : Mo molar ratio 9 : 1.

EXPERIMENTAL

The catalyst was prepared by co-precipitation of aqueous solutions of tin tetrachloride and ammonium paramolybdate with aqueous ammonia. The obtained mixtures were evaporated, the precipitates were dried at 120°C and then sintered at 300°C for 3 h and then at 500°C for 10 h.

Diffraction and IR spectroscopic measurements made on DRON-05 and IR-20 (Zeiss, Jena) instruments showed that the catalyst with Sn : Mo ratio 9 : 1 was the solid solution of Mo^{6+}

in SnO_2. From the Mo^{6+} ion radii ($r = 0{\cdot}065$ nm and $r = 0{\cdot}064$ nm) the formation of the solid solutions can be inferred. As shown by EPR, the introduction of the molybdate ions into tin dioxide results in formation of two types of Mo^{5+} ions having narrow EPR signals with the parameters $g_1 = 1{\cdot}951$, $g_2 = 1{\cdot}926$ and $g_3 = 1{\cdot}8991$. Furthermore, the substitution of Sn^{4+} for Mo^{6+} ions leads to formation of a cation vacancy owing to which the Mo^{5+} ions are stabilized.

RESULTS AND DISCUSSION

During adsorption measurements, NH_3 or SO_2 were fed into a stream of helium flowing through a microcatalytic reactor. Their adsorption properties were estimated from their chromatographic peaks after passing the gases through the reactor filled with the catalyst (S_{cat}) compared to the peak areas obtained after NH_3 or SO_2 had passed through the reactor filled with quartz (S_q) which does not adsorb these gases. Before feeding NH_3 or SO_2, the catalyst was heated in the reactor in a stream of helium at 300°C. The results of these measurements at different temperatures are presented in Table I. Data show that on increasing potassium hydroxide content in the catalyst, the S_{cat}/S_q ratio increases for NH_3, indicating decreasing NH_3 adsorption. This finding can be due to the reduction of Sn–Mo oxide catalyst acidity by KOH. This decreases both the total number and strength of acid centers. This is confirmed by the fact that the great amount of ammonia ($S_{cat}/S_q = 0{\cdot}7$) is adsorbed on the untreated catalyst at 200°C while the catalyst treated with KOH adsorbs ammonia very little ($S_{cat}/S_q = 0{\cdot}95$, $0{\cdot}97$).

The oxidation of ethanol was studied using the reactors of two types. One was tubular of several different diameters, the catalyst being placed on its wall and the other was a quartz flow reactor with a section of diameter 25 mm to which granulated catalyst of particle size 1·5–2·5 mm was placed.

TABLE I

Acidic and basic properties of Sn–Mo oxide catalysts (catalyst volume 0·1 cm^3, NH_3 and SO_2 pulse volumes 1 cm^3)

KOH, wt. %	S_{cat}/S_q for NH_3			S_{cat}/S_q for SO_2		
	25°C	100°C	200°C	25°C	100°C	200°C
0	0·06	0·52	0·70	0·97	1·00	1·00
0·1	0·22	0·58	0·86	0·94	1·00	1·00
0·5	0·35	0·80	0·95	0·92	0·96	1·00
1·0	0·50	0·82	0·97	0·90	0·91	0·94

The reaction mixture containing gaseous ethanol, oxygen water vapour and nitrogen was fed into the reactor. The volume of the catalyst varied from 0·5 to 7 cm^3. The composition of the reaction mixture, its flow rate and temperature inside the reactor were maintained constant automatically. The reaction products were analyzed by GLC. Ethanol adsorbed on the Sn–Mo oxide catalyst at 220 to

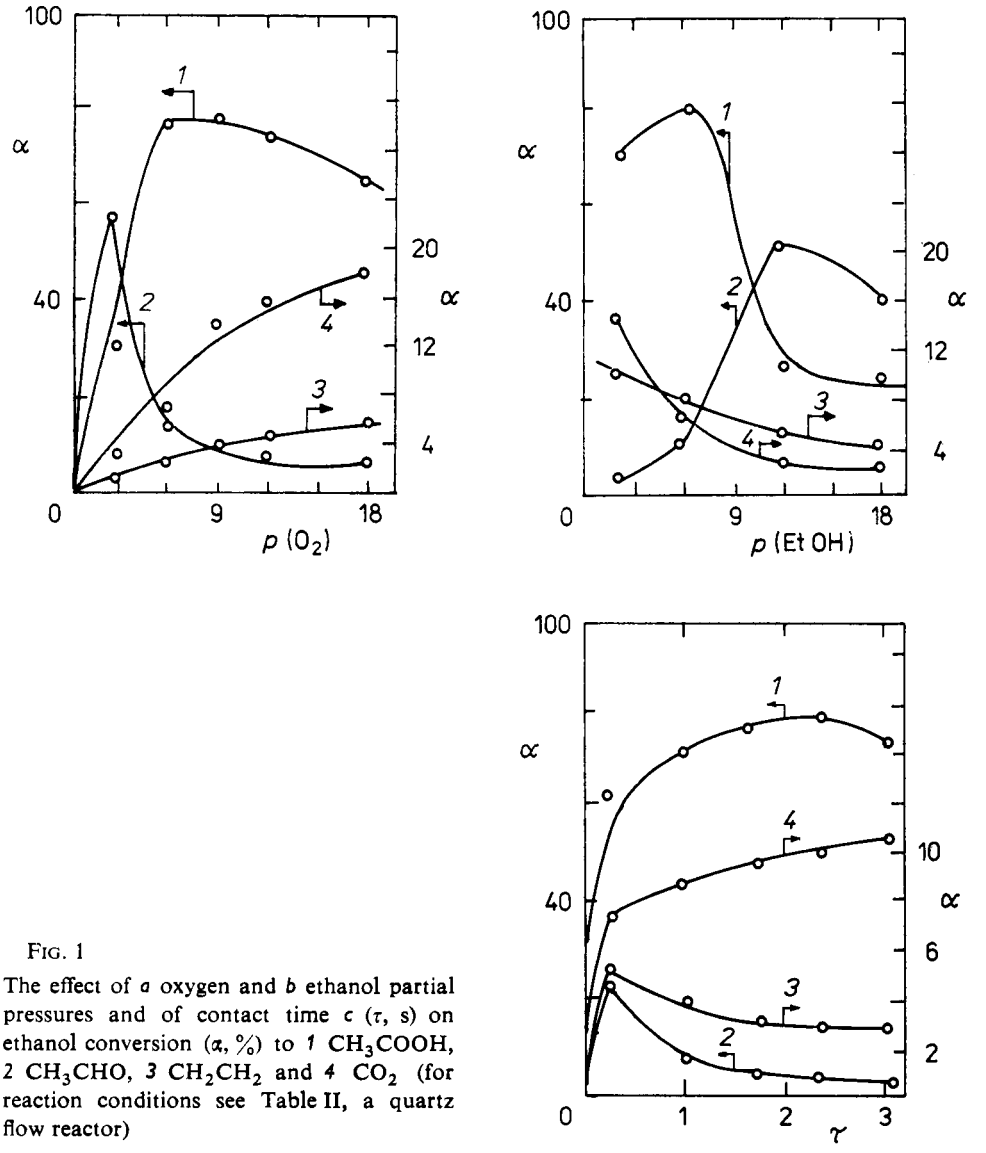

FIG. 1

The effect of *a* oxygen and *b* ethanol partial pressures and of contact time *c* (τ, s) on ethanol conversion (α, %) to *1* CH_3COOH, *2* CH_3CHO, *3* CH_2CH_2 and *4* CO_2 (for reaction conditions see Table II, a quartz flow reactor)

260°C is converted into ethanal, ethanoic acid, CO_2, water and ethylene. On increasing reaction temperature ethanol and ethanoic acid outputs pass through maxima and CO_2 and ethylene formation increases.

The influence of water vapour is more complex as it participates in the formation of CO_2 and ethanoic acid. In its absence the output is very low while with high water content the decrease in conversion is observed. Figure 1 documents the effect of contact time on the conversion of ethanol into oxidation products on the granulated

TABLE II

Oxidation of ethanol and its oxidation products on the Sn–Mo oxide catalyst (catalyst volume 0·1 cm^3, NH_3 and SO_2 volumes 1 cm^3, $W = 2\,070\ h^{-1}$, 220°C, $C_2H_5OH : H_2O : O_2 : N_2 = 1 : 10 : 6 : 5$ v/v)

Substance	Conversion %	Output, %			
		CH_3CHO	CH_3COOH	C_2H_4	CO_2
Ethanol	96	23·6	68·2	0·2	6·0
Ethanal[a]	70	0	52·9	0	14·4
Ethylene	20	0	0	0	17·4

[a] Ethanoic acid does not react.

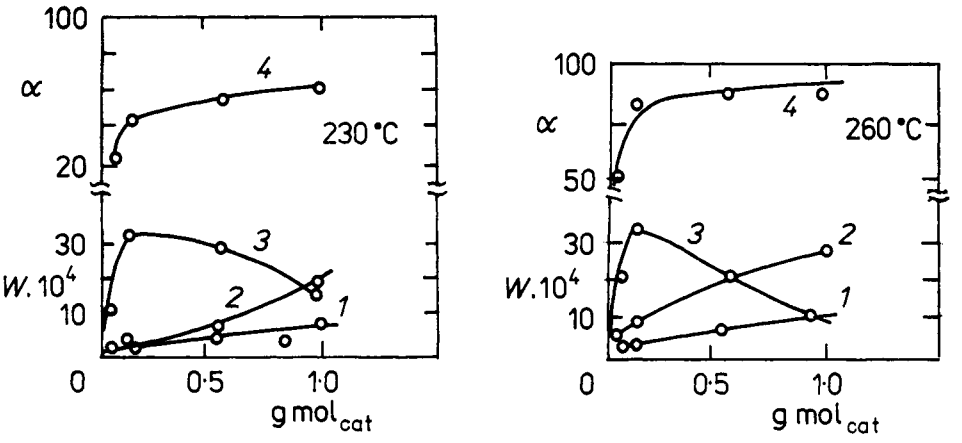

FIG. 2

The dependence of the rate of product formation upon catalyst amount (a tubular reactor, W in mmol per h, pO_2 and p(EtOH) are partial pressures in kPa). For designation of curves see Fig. 1

catalyst (the change was observed by changing the catalyst volume). The output of ethanoic acid increases with contact time while ethanol formation decreases. In a narrow tubular reactor without the catalyst there proceeds homogenous oxidation of ethanol with oxygen which becomes detectable at 140°C (up to 6%).

As shown in Fig. 2, the catalyst layer on the tubular reactor wall surface induces ethanal formation, the rate of which increases with the amount of the catalyst similarly as does ethanoic acid and CO_2 formation. From these data one can deduce that ethanal is the intermediate product of the ethanol oxidation into ethanoic acid and that not all the oxidation products are formed on the catalyst surface, some of them being formed in bulk. This means that ethanol is oxidized to give ethanal both by homogenous and heterogenous processes.

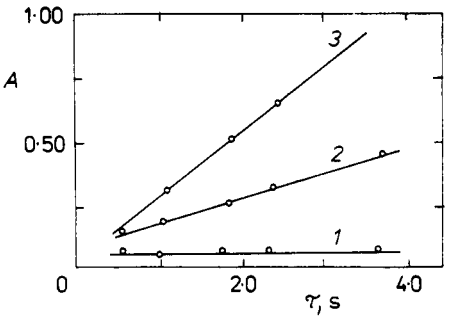

FIG. 3

The dependence of $\alpha CO_2/\alpha CH_3CHO$ (line 2, 220°C and line 3, 240°C) and $\alpha CO_2/\alpha CH_3COOH$ (line 1, 220°C) upon contact time τ (in s). For reaction conditions see Table II

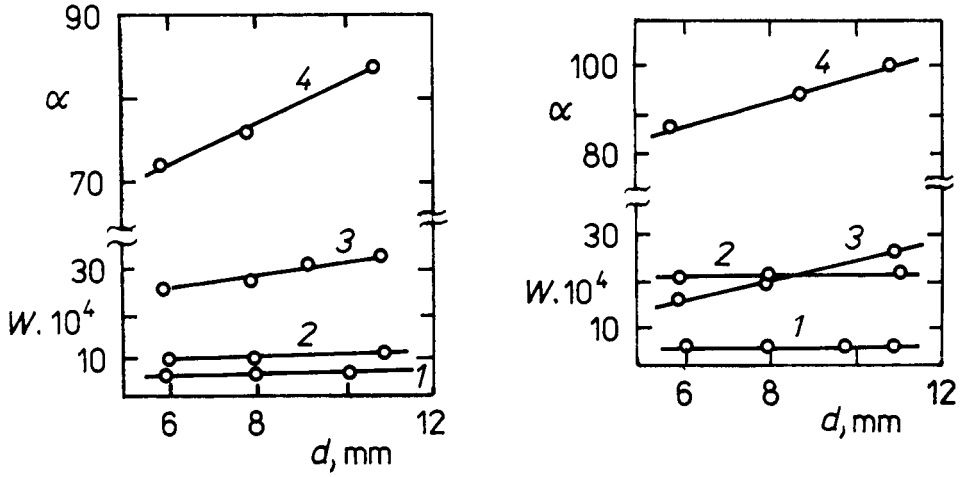

FIG. 4

The effect of tubular reactor diameter (d in mm) on the rate of product formation at 230 (a) and 260°C (b). For designation of curves see Fig. 1

To shed some light on the modes of ethanol transformation, the conversion of ethanal, ethanoic acid and ethylene was studied under conditions of ethanol oxidation. In the course of these tests, the reaction mixtures in which ethanol was replaced by the equivalent amount of the corresponding reaction product were fed into the reactor filled with the granular catalyst. The obtained results are presented in Table II and lead to the following conclusions:

a) Ethanoic acid is formed from ethanol; *b*) ethylene does not play a role in the formation of ethanal and ethanoic acid and it is only source of CO_2; *c*) ethanoic acid is stable product and does not undergo further oxidation under reaction conditions; *d*) ethanal is converted readily into ethanoic acid and CO_2. This conclusion is confirmed by experimental data shown in Fig. 3. The above mentioned facts allow us to propose the following scheme for ethanol oxidation:

$$\begin{array}{ccccc} C_2H_5OH & \longrightarrow & CH_3CHO & \longrightarrow & CH_3COOH \\ \downarrow & & \downarrow & & \\ C_2H_4 & \longrightarrow & CO_2 & & \end{array}$$

Taking into account the results obtained in the empty reactor, one can suppose that ethanol is readily formed also in bulk. The effect of the reactor tube diameter (with catalyst quantity on its walls being 0·5 grammole) on the output of ethanol oxidation confirms this supposition (Fig. 4). The increase of the free volume of the reactor tube influences CO_2 and to the less extent also ethylene formation while that of ethanal is practically constant.

At the same time, in the case of the ethanoic acid feed IR spectra of the catalyst show the bands corresponding to carbonate and carboxylate structures (1 450, 1 540 and 1 400 cm^{-1}). However, from Table II it follows that ethanoic acid is not

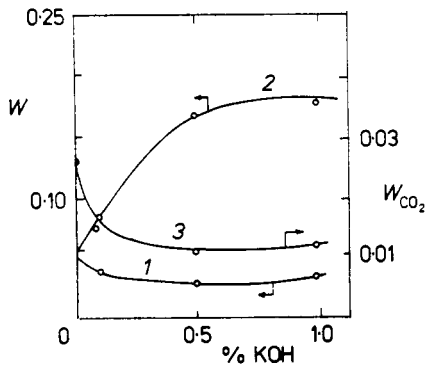

FIG. 5

Effect of KOH (wt. %) in the Sn–Mo oxide catalyst on formation of *1* CH_3COOH, *2* CH_3CHO and *3* CO_2 (*W* in mmol per h, 230°C, a quartz flow reactor, the alcohol: air volume ratio 1 : 15, flow rate 3 420 h^{-1})

TABLE III

Oxidation of ethanol on the Sn–Mo oxide catalyst (catalyst volume 0·1 cm^3, $W = 2\,070\ h^{-1}$, 300°C, $C_2H_5OH : H_2O : O_2 = 1 : 10 : 12$ v/v)

Compound	Output, %			
	CH_3CHO	CH_3COOH	C_2H_4	CO_2
C_2H_5OH	28·4	38·6	4·4	26·8
C_2H_5OD	28·2	40·1	2·1	26·0
C_2D_5OH	44·7	4·8	7·1	37·9

oxidized to CO_2. This indicates that a product deposited on the catalyst surface is the main source of CO_2.

An additional information was obtained by the oxidation of two alcohols deuterated in OH (C_2H_5OD) or alkyl group (C_2D_5OH). The results are presented in Table III. The substitution of the hydrogen of hydroxylic group for deuterium does not influence CH_3COOH and CH_3CHO outputs, indicating that the loss of hydroxylic group hydrogen is not likely the limiting step of formation of these products. The substitution of C_2H_5 hydrogens for deuterium leads to the decrease in CH_3COOH formation as well as an increase in CH_3CHO and CO_2 outputs.

Figure 5 shows that the rate of oxidation products formation depends upon the amount of KOH. The small amount supresses ethylene formation. The rate of the deep oxidation reaction leading to CO_2 is decreasing too.

The above data allow to conclude that ethanal is formed by both homogenous and heterogenous processes, while CH_3COOH and CO_2 are formed from CH_3CHO on the catalyst surface.

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