

# OXIDATIVE ACETOXYLATION OF PROPYLENE OVER METAL-CONTAINING ZEOLITE CATALYSTS

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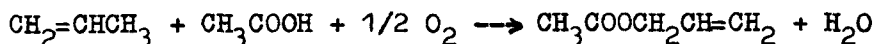
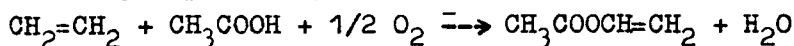
## ABSTRACT

The activity and the selectivity of the catalysts on the basis of A, X, Y, chabasite, erionite, mordenite, ZWM and ZWK type zeolites containing VIII group metals have been investigated in the reaction of oxidative acetoxylation of propylene to allylacetate. It was shown that among VIII group metals only Pd-containing catalysts are active in the allylacetate synthesis. The reaction of deep oxidation of propylene takes place in the case of another metal containing catalysts. The effect of transition metals on activity and selectivity of Pd-zeolite catalyst have been studied.

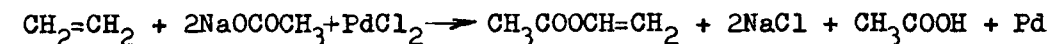
Using  $^{18}\text{O}$  labelled acetic acid it was shown that the mechanism of the reaction of propylene oxidative acetoxylation can include the formation of allyl alcohol as an intermediate with its etherization with acetic acid to allylacetate.

## INTRODUCTION

As is known the reaction of olefin oxidative acetoxylation can produce many important products such as vinylacetate and allylacetate.

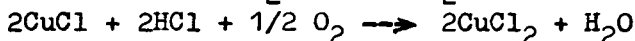
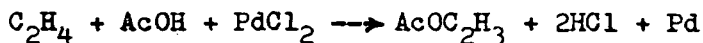


Allylacetate can be used as a starting compound for production of glycerine, glycidol, epichlorhydrine,  $\gamma$ -acetopropylacetate and other useful products [1]. Oxidative acetoxylation of olefins was discovered in 1960 when it was shown [2] that vinylacetate is formed from interaction of ethylene with sodium acetate in the presence of palladium chloride



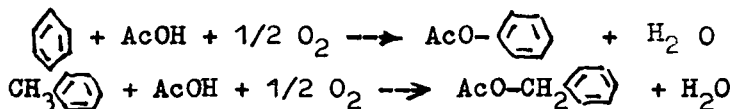
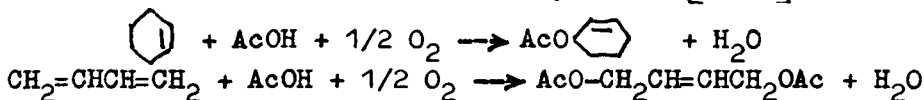
Since the process has been improved by using acetic acid instead of sodium acetate and by addition of cupric chloride to the reaction

mixture for palladium reoxidation



Later it was shown that this reaction could be carried out not only in homogeneous conditions but also in the gas phase using palladium or its compounds together with added different promoters (such as salts of transition metals) supported on alumina, silica gel, silica-aluminas, activated charcoal and other solids [4-11]. Besides palladium alkali acetate added up to 10-15 wt.% is a necessary component of the catalyst. It was suggested that alkali acetate may increase acetic acid adsorption on the catalyst surface, which may result in variation of the reaction kinetic order for acetic acid from 1 to 0 [12,13].

Different olefins, dienes and aromatics are shown to take part in the reaction of oxidative acetoxylation [14-22]



In addition to vinylacetate synthesis another important process is oxidative acetoxylation of propylene to allylacetate. This process is usually carried out in a gas phase at 140-200° under pressures of 1-10 atm 3. In these conditions together with the main reaction of allylacetate synthesis deep oxidation of propylene proceeds to give carbon dioxide and water but as a rule the selectivity of allylacetate formation is not lower than 90% [3].

The aim of this study is to investigate metal-containing zeolite catalysts in oxidative acetoxylation of propylene to allylacetate and elucidate the kinetics and mechanism of this process.

## EXPERIMENTAL

Catalysts were prepared using synthetic zeolites of types A (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=2.0), X(3.0), Y(4.8), K,Na-chabasite (5.0), K,Na-erionite (6.5), mordenite (11.9), ZWM (30-47) and ZWK (68-78). Active components (VIII group metals, promoters) were introduced into the zeolites by both ion exchange and impregnation. After reduction the zeolite catalyst was moulded without any bindings at a pressure of 100 atm. The fraction of the catalyst particles of 0.5-1.0 mm was used in the

experiments.

The catalytic experiments were carried out in a flow reactor at atmospheric pressure, 160-190° and a molar ratio of  $C_3H_6: CH_3COOH:O_2 = (2-6):1:(0.3-1.0)$ . The amount of the catalyst loaded into the reactor was 1-6 cc. The liquid reaction products were collected into the trap at 0° and analysed by GLC.

Labelled  $^{18}O$  acetic acid was prepared by interaction of  $CH_3COCl$  with  $H_2^{18}O$ . The products obtained from propylene oxidative acetoxylation and allyl alcohol etherization with acetic acid- $^{18}O$  were analysed by chromat-mass-spectrometry with a "Varian MAT-111" and "Kratos MS-70".

The temperature programmed reduction of the oxidized catalyst samples was carried out using chromatographic technique. The weight of the catalyst sample was 0.4 g. The catalyst sample was preoxidized by air or a mixture of air and helium (1:1) at 180 and 500°. The catalyst was reduced in a flow of a  $N_2$  and 10%  $H_2$  mixture at a rate of 30 cc/min. The temperature of the catalyst sample was increased linearly at a rate of 20 K/min. Changes in the hydrogen concentration at the reactor outlet was determined by a catarometer.

## RESULTS AND DISCUSSIONS

By analogy with liquid phase olefin oxidation [23] copper is sometimes added to Pd-catalysts for propylene oxidative acetoxylation as a promoter [7]. Therefore, first, we are to discuss the influence of the procedure of Pd,Cu-catalyst preparation on its activity and selectivity in allylacetate synthesis [24]. Results obtained are given in table 1. As is seen the type Y zeolites of Na- and H-forms as well as unreduced PdCuNaY and reduced ones are not active in oxidative acetoxylation of propylene to allylacetate. But over these catalysts acid catalyzed addition of acetic acid to propylene takes place with formation of isopropylacetate. Deep oxidation of propylene also takes place to a small extent over Pd,Cu-catalysts (samples 3 and 4). This is indicated by water formation in an amount of about 2%.

To prevent acetic acid addition to propylene zeolite acidic centers were neutralized in four different ways: 1.catalyst pretreatment with a sodium acetate solution, 2.catalyst pretreatment with a sodium chloride solution, 3.catalyst impregnation with a sodium chloride solution followed by calcination of the catalyst at 500°, 4.catalyst pretreatment with an alkaline solution. After pretreatment of the reduced catalyst with a sodium acetate solution (sample 5) the amount of isopropylacetate in the reaction products decreased to 4.3%. At

Table 1

Dependence of the properties of Pd,Cu-catalyst on the basis of NaY zeolite on the preparation procedure (1% Pd and 0.6% Cu were introduced by ion exchange). Process conditions: 180° atmospheric pressure,  $V_{\text{cat}} = 6 \text{ cc}$ ,  $V_{\text{CH}_3\text{COOH}} = 0,7 \text{ h}^{-1}$ ,  $\text{C}_3\text{H}_6:\text{CH}_3\text{COOH}:\text{O}_2 = 6:1:0.5$

No	Catalyst and preparation procedure	Product composition, %					Activity $\frac{\text{g-mole}}{\text{g.cat.h}} \times 10^3$	Selectivity %
		acetic acid	water	allyl-acetate	isopropylacetate	isopropyl alcohol		
1.	Starting NaY	98.3	1.2	-	0.5	-	-	-
2.	HY	90.3	0.6	-	9.1	-	-	-
3.	PdCuNaY unreduced	88.4	1.9	-	9.7	-	-	-
4.	PdCuNaY reduced	87.3	2.1	-	10.6	-	-	-
5.	PdCuNaY reduced and pretreated with 0.2 N $\text{CH}_3\text{COONa}$ (pH=9-10)	93.6	2.1	0.1	4.3	-	-	-
6.	PdCuNaY reduced and pretreated with 0,2 N NaCl (pH=9-10)	92.7	2.7	2.4	2.2	-	0.25	24.6
7.	PdCuNaY reduced impregnated with 0.2N NaCl and preheated at 500°	86.5	6.2	4.4	0.1	2.9	0.38	29.5
8.	PdCuNaY reduced and pretreated with 0.2 N NaOH	92.1	3.5	4.4	-	-	0.40	39.5

the same time formation of allylacetate as a product was observed. Catalyst pretreatment with a sodium chloride solution is more effective (sample 6). The amount of allylacetate in the reaction products was 2.4 %. This corresponds to catalyst activity of  $0.25 \times 10^{-3}$  g-mole/g.cat-h, with the reaction selectivity of 24.6%. However, with this catalyst pretreatment it is impossible to prevent isopropylacetate formation (2.2%). This suggests incomplete neutralization of zeolite acidic centers. Formation of isopropylacetate was excluded by impregnation of the catalyst with sodium chloride (sample 7), but in this case isopropyl alcohol occurred in the reaction products. The rate of allylacetate formation was  $0.38 \times 10^{-3}$  g-mole/g.cat.h, with the reaction selectivity of 29.5%. Catalyst pretreatment with an alkali solution was found to be the best procedure to neutralize the catalyst acidic centers (sample 8). By this method isopropylacetate formation was excluded completely and the catalyst activity and reaction selectivity were  $0.40 \times 10^{-3}$  g-mole/g.cat.h and 39.5%, respectively.

The effect of metal concentration on the catalytic properties of PdCuNaY catalysts have been also investigated (fig.1 and 2).

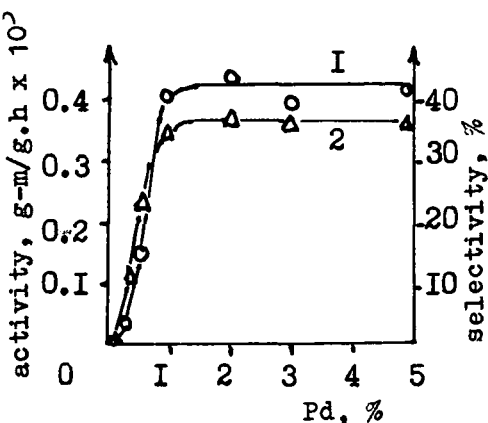


Fig. 1

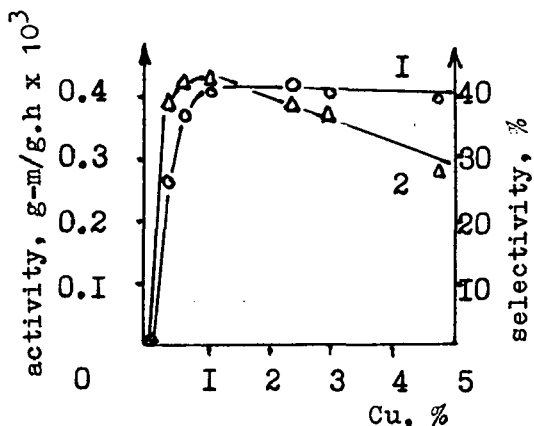


Fig.2

Fig.1. Dependence of the catalytic properties of PdCuNaY on Pd concentration (Cu contents 3%) 1-activity, 2-selectivity.

Fig.2. Dependence of the catalytic properties of PdCuNaY on Cu concentration (Pd contents 1%) 1-activity, 2-selectivity.

As is seen monometallic catalysts containing only Pd or Cu are inactive in propylene oxidative acetoxylation. As the metal concentration increased the catalyst activity and reaction selectivity also increased up to some extent. The catalyst containing 1% Pd and 0.6% Cu is found to be most efficient. This metal content corresponds to

atomic ratio Pd:Cu 1:1.

Next, the effect of different ways of metal introduction into the catalyst was studied. It is shown (table 2) that the most active ( $0.79 \times 10^{-3}$  g-mole/g.cat.h) and selective (52.8%) catalyst can be prepared by simultaneous ion exchange introduction of Pd and Cu from a solution of palladium tetraaminochloride and cupric chloride.

The influence of alkali cations on the properties of type Y zeolite based Pd,Cu-catalyst can be seen from the data presented in table 3. The catalytic activity slightly increases with an increase

Table 2

Influence of succession of metals introduction into NaY zeolite on its catalytic properties (1% Pd, 0.6% Cu). Reaction conditions are indicated in table 1

Succession of metals introduction	Activity, $\frac{\text{g-mole}}{\text{g.cat.h}} \times 10^3$	Selectivity %
1. Pd, 2. Cu	0.40	39.5
2. 1.Cu, 2. Pd	0.38	38.1
3. Pd+Cu simultaneously	0.79	52.8

Table 3

Catalytic properties of NaY zeolite with various alkali cations (1% Pd, 0.6% Cu). Reactions conditions are indicated in table 1

No	Zeolite	Activity, $\frac{\text{g-mole}}{\text{g.cat.h}} \times 10^3$	Selectivity, %
1.	LiY	0.34	36.1
2.	NaY	0.40	39.5
3.	KY	0.47	43.2
4.	CsY	0.51	9.6

of the metal atomic number, i.e. with transition from Li to Cs. This is confirmed by the influence of acetates of alkali metals on the Pd catalyst of olefins oxidative acetoxylation [12].

Copper is shown to be a promoter of zeolite NaY based Pd-catalyst only in the case of ion exchange metal introduction. But the ca

talyst is also active in the reaction, with no copper involved, provided it is prepared by zeolite impregnation with palladium chloride and alkaline metal acetate after its reduction (table 4). As is seen from the data presented the activity and selectivity of Pd-catalyst depend on the type of zeolite used. The catalysts on the basis of NaA and NaX zeolites are inactive in this reaction. In the case of low silica zeolites of Y, chabazite, erionite and mordenite type the catalyst activity is on the level of  $(0.2-0.4) \times 10^{-3} \frac{\text{g-mole}}{\text{g.cat.h}}$

Table 4

The effect of the type of zeolite on the properties of Pd-catalyst (1.5% Pd, 15% AcOK) at 180°, atmospheric pressure, C<sub>3</sub>H<sub>6</sub>: CH<sub>3</sub>COOH:O<sub>2</sub>=2:1:0.5, V<sub>cat</sub> = 2 cc, V<sub>CH<sub>3</sub>COOH</sub> = 2 h<sup>-1</sup>

No	Zeolite	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	Activity, $\frac{\text{g-mole}}{\text{g.cat.h}} \times 10^3$	Selectivity, %
1	NaA	2.0	0	0
2	NaX	2.9	0	0
3	NaY	4.8	0.35	35
4	KNa-chabazite	5.0	0.44	34
5	K,Na-erionite	6.5	0.15	100
6	Na-mordenite	11.9	0.19	26
7	ZWM-408	29.6	7.33	96
8	ZWM-364	47	7.43	94.3
9	ZWK-XI	68	5.52	87
10	ZWK-III	78	3.04	89

The catalysts on the basis of high silica zeolites of type ZWM (molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30-47) are most active. But an increasing in the ratio of silica to alumina in zeolites to 68-78 results in a decrease of the catalyst activity which may be accounted for by structural factors (transition from zeolite of type ZWM to zeolite of type ZWK). The reason for inactivity of Pd-catalysts on the basis of NaA and NaX zeolites is not clear and further investigations are needed. The fact that copper is an unnecessary component of the catalyst when it is prepared by impregnation could be explained by a large size of Pd-crystallites resulting from reduction of impregnated catalysts. Consequently the process of Pd reoxidation is facilitated. It is well known [13], that in the case of Pd-catalysts prepared by impregnation of nonzeolite carriers the activity passes through the maximum, which de-

depends on the size of metal crystallites on the surface.

According to the literature data [3-9] Pd with various promoters is usually used as a catalyst for the reaction of propylene oxidative acetoxylation. No information on the catalytic properties of other VIII group metals is available. The data we obtained show (table 5) that among VIII group metals only Pd is active in this reaction.

Table 5

Activity of monometal catalysts on the basis of zeolite of ZWM-408 type (metal content 1,5%, AcOK-15%). Reaction conditions are indicated in table 4

No	Metal	Product composition,%(wt)			Activity, $\frac{\text{g-mole}}{\text{g.cat.h}} \times 10^3$	Selectivity, %,
		acetic acid	water	allyl-acetate		
1.	Co	96.2	3.8	-	-	-
2.	Ni	95.2	4.8	-	-	-
3.	Ru	97.4	2.6	-	-	-
4.	Rh	96.6	3.4	-	-	-
5.	Pd	71.5	6.3	22.2	7.33	96
6.	Os	94.1	5.9	-	-	-
7.	Ir	97.1	2.9	-	-	-
8.	Pt	95.1	4.9	-	-	-
9.	Ag	96.5	3.5	-	-	-

Other VIII group metals as well as Ag, a typical catalyst for oxidative reaction, can effect only deep oxidation of propylene. This result is unique because in other oxidative type reactions all VIII group metals are more or less active. The cause of inactivity of VIII group metals, except Pd, in allylacetate synthesis may be either the absence of a necessary intermediate originating from a propylene molecule or a high rate of full oxidation of this intermediate.

Bimetal catalysts on the basis of Pd and a metal of group VIII or another transition metal have been investigated (table 6). As is seen from the table the activity and selectivity of Pd-catalyst depends on the type of the second metal component. In the case of such metals as Rh, Ag the activity of Pd-catalyst decreases up to zero. To explain the effect of transition metals on the activity of Pd-catalyst it is necessary to take into account, on the one hand, possible change in palladium dispersion on the surface of the carrier as well as specific catalytic activity and, on the other hand, possible chan



Table 6

Activity of bimetal Pd-catalyst on the basis of ZWM-408 zeolite (content of Pd 1.5%, content of second component 1.5% AcOK-15%). Reaction conditions are indicated in table 4

No	Second component	Product composition, (wt) %			Activity, $\frac{\text{g-mole}}{\text{g.cat.h}} \times 10^3$	Selectivity, %
		acetic acid	water	allyl-acetate		
1.	Fe	90.1	3.0	6.9	2.00	71.0
2.	Ni	73.2	17.2	9.6	3.42	26.5
3.	Ru	77.5	17.1	5.4	1.88	16.5
4.	Rh	81.0	19.0	-	-	-
5.	Os	66.2	18.3	15.5	5.75	36.4
6.	Ir	76.9	13.8	9.3	3.20	31.0
7.	Pt	73.7	19.3	7.0	2.52	18.0
8.	Mn	76.8	6.6	16.6	5.35	76.4
9.	Ag	96.8	3.2	-	-	-

ges in the rate of palladium oxidation. To answer the question which of these possibilities is prevalent further investigations are needed.

Studies of bimetal catalysts with copper and a metal of group VIII as its two components has also show that in this case only Pd containing catalyst are active in allylacetate synthesis (table 7).

Table 7

Activity of bimetal Cu-catalyst on the basis of ZWM-408 zeolite (Cu content 1.5%, content of the second component 1.5%, AcOK-15%). Reaction conditions are indicated in table 4

No	Second component	Product composition, (wt.) %			Activity, $\frac{\text{g-mole}}{\text{g.cat.h}} \times 10^3$	Selectivity, %
		acetic acid	water	allyl-acetate		
1.	Co	95.4	4.6	-	-	-
2.	Ni	96.3	3.7	-	-	-
3.	Ru	88.3	11.7	-	-	-
4.	Rh	96,7	3.3	-	-	-
5.	Pd	84.9	6.6	8.5	2.64	52.3
6.	Os	92.9	7.1	-	-	-
7.	Ir	94.9	5.1	-	-	-
8.	Pt	91.5	8.5	-	-	-

Other bimetal Cu-containing catalysts are active only in full oxidation of propylene.

To elucidate the mechanism of the reaction the kinetics of the process has been investigated using Pd,Cu-catalyst on the basis of a mordenite type zeolite [25]. The catalyst was prepared using ion exchange technique. The amounts of palladium and copper in the catalyst were 1.5 wt.% and 2.5 wt.%, respectively. After reduction of the catalyst it was pretreated with an alkaline solution to neutralize the acidic centers,

As is shown the reaction rate is proportional to the oxygen partial pressure (fig.3) and passes through a faint maximum in dependence on the propylene partial pressure (fig.4).

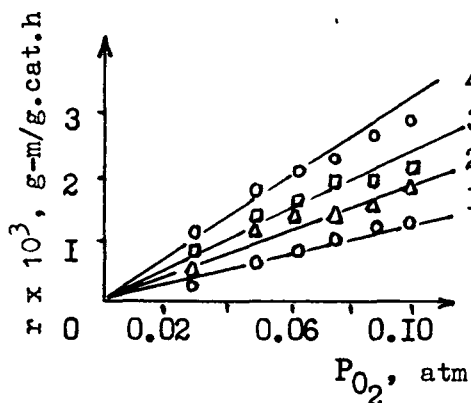


Fig.3

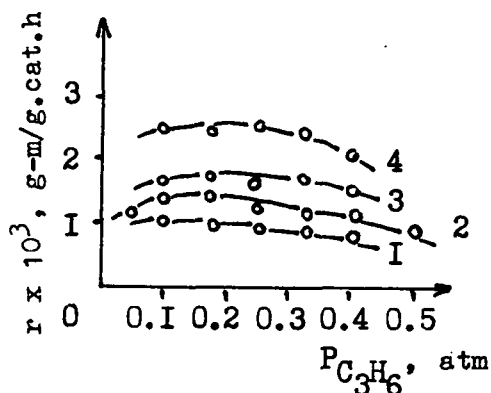


Fig.4

Fig.3. The dependence of allylacetate formation on the oxygen partial pressure at  $P_{C_3H_6} = 0.25$  atm,  $P_{CH_3COOH} = 0.1$  atm and temperatures: 1-160°, 2-170°, 3-180°, 4-190°.

Fig.4. The dependence of allylacetate formation on propylene partial pressure at  $P_{O_2} = 0.075$  atm,  $P_{CH_3COOH} = 0.1$  atm and temperatures: 1-160°, 2-170°, 3-180°, 4-190°.

Thus, according to the data obtained the following kinetic equation could be proposed

$$r = \frac{k \cdot P_{O_2} \cdot P_{C_3H_6}}{(1 + a \cdot P_{C_3H_6})^2} \quad (1)$$

The constants "k" and "a" were estimated by the graphical method at various temperatures and the values of the Arrhenius parameters of these constants ( $K_0$ ,  $E$ ,  $a_0$  and  $Q$ ) were also calculated. Next, using these values as the initial estimates of the parameters the minimization of the function  $F$  was done by means of a microcomputer "Iskra-

$$F = \sqrt{\frac{1}{n} \sum_{i=1}^n \left( \frac{r_{ie} - r_{ic}}{r_{ie}} \right)^2}$$

where  $n$  is the number of experiments,  $r_{ie}$  and  $r_{ic}$  are the experimental and calculated reaction rates. Initial and corrected values of the parameters are presented in table 8.

Table 8

The kinetic parameters corrected with a microcomputer  
"Iskra-1256"

No Parameters	$K_0$	$E, \frac{\text{cal}}{\text{mole}}$	$a_0$	$Q \frac{\text{cal}}{\text{mole}}$	F
1. initial	89	4090	0.392	2540	0.493
2. corrected	87.56	4258	0.397	2640	0.177

This table shows that the value of the minimized function decreases from 0.493 to 0.177 but the kinetic parameters vary insignificantly. This is indicative of a rather deep pit over the surface of the minimized function  $F$  within the parameters.

To determine the slow stage of the process the catalyst oxidation in air flow at various temperatures followed by temperature programmed reduction has been studied (fig.5). Hydrogen consumption

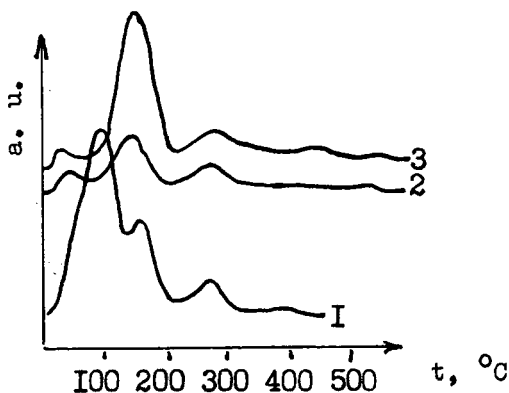


Fig.5. TPR profiles for Pd,Cu-catalysts pretreated at  $500^\circ$  in air flow for 1 hr  
1-1.55% Pd, 3.0% Cu  
2-0.1% Pd, 1.55% Cu  
3-0.1%Pd, 3.0% Cu

takes place in temperature ranges of  $40-100^\circ$ ,  $100-200^\circ$  and  $200-400^\circ$ . The first maximum of hydrogen consumption is due to reduction of palladium ions. This conclusion is confirmed by the fact that the area of the first peak increases with an increase in the Pd content in the catalyst from 0.1% (curves 2 and 3) to 1.55% (curve 1). It is well known from the literature data [26,27] that palladium cations are reduced into the atomic state in a temperature range of  $20^\circ$  to  $150^\circ$ .

Two other peaks in temperature ranges of  $100-200^{\circ}$  and  $200-400^{\circ}$  are assigned to reduction of copper ions [27,28] since an increase in the copper content of the catalyst results in an increase in the area of these peaks (curves 2 and 3).

As at a temperature as high as  $500^{\circ}$  metal atoms are oxidized not only on the surface of the metal crystallites but also in their volume the catalyst used to investigate the kinetics of the process was oxidized at the reaction temperature ( $180^{\circ}$ ). In this case the oxygen partial pressure in the oxidizing gas (a mixture of air and helium) was equal to 0.1 atm as it was in some catalytic runs (fig.6). As is seen from this figure hydrogen consumption at TPR of the catalyst oxidized at  $180^{\circ}$  is much lower than that for the catalyst oxidized at

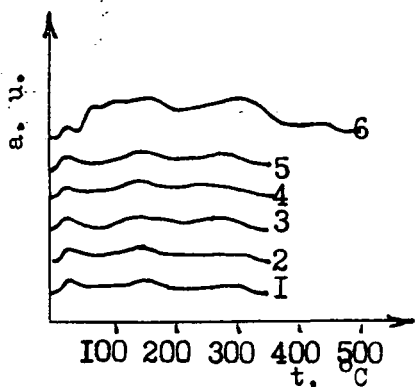


Fig.6

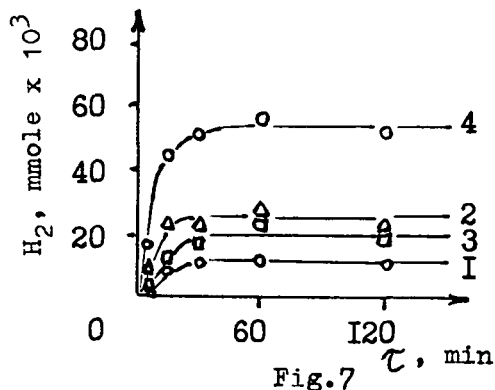


Fig.7

Fig.6. TPR profiles for Pd,Cu-catalyst oxidized at: 1.- $180^{\circ}$ ,  $Po_2=0.1$  atm,  $\tau=5$  min; 2- $180^{\circ}$ ,  $Po_2=0.1$  atm,  $\tau=15$  min; 3- $180^{\circ}$ ,  $Po_2=0.1$  atm,  $\tau=30$  min; 4- $180^{\circ}$ ,  $Po_2=0.1$  atm,  $\tau=60$ min; 5- $180^{\circ}$ ,  $Po_2=0.1$  atm,  $\tau=120$  min; 6- $500^{\circ}$ ,  $Po_2=0.2$  atm,  $\tau=60$ min.

Fig.7. The amount of hydrogen absorbed by the catalyst at its TPR in temperature ranges of  $40-100^{\circ}$ (1),  $100-200^{\circ}$ (2),  $200-300^{\circ}$ (3) and  $40-300^{\circ}$ (4) (total amount of  $H_2$ ) in dependence on the duration of catalyst oxidation at  $180^{\circ}$  and  $Po_2=0.1$  atm.

$500^{\circ}$ . It can be assumed that only atoms on the surface of metal crystallites would be oxidized at  $180^{\circ}$ .

From the data presented in fig.7 the amount of metal atoms oxidized at  $180^{\circ}$  could be estimated. For instance, the highest amount of Pd atoms is found to be 20-25% of the total content of Pd in the catalyst. The rate of Pd oxidation as determined by graphical differentiation of the kinetic curve (fig.7, curve 1) is equal to  $0.2 \times 10^{17}$  Pd at/g.sec. But the reaction rate of propylene oxidative acetoxylation

at 180° and  $P_{O_2}=0.1$  at, is equal to  $5 \times 10^{17}$  molec./g.sec. As Pd oxidation is the first stage of the process of propylene oxidative acetoxylation the rate of metal oxidation could be either higher than that of the overall process or the rates of metal oxidation and those of the process could be equal. It seems likely that a higher rate of the process of propylene oxidative acetoxylation we observed may be indicative of a higher rate of Pd oxidation in the reaction conditions, particularly, in the presence of acetic acid.

Experiments with labelled  $^{18}O$  acetic acid were carried out to identify the intermediate stages of the process of propylene oxidative acetoxylation. It can be assumed that this reaction proceeds through formation of allyl alcohol as intermediate species followed by their etherization with acetic acid to give allylacetate. This conclusion can be made from the fact that acrolein and allylacetate are formed upon propylene oxidation over a Pd,Cu-catalyst prepared on the basis of Na-form zeolite (table 9), whereas only deep oxidation of propylene takes place over a Pd,Cu-catalyst prepared on the basis of H-form zeolite. Acrolein would not form over this catalyst and it would not carry out the reaction of oxidative acetoxylation of propylene to allylacetate. Instead, simple addition of acetic acid to a propylene molecule takes place to form isopropylacetate. One can assume that upon propylene oxidation over Pd,Cu-catalyst on the basis of Na-form zeolite acrolein is formed as a secondary product during oxidation of allyl alcohol.

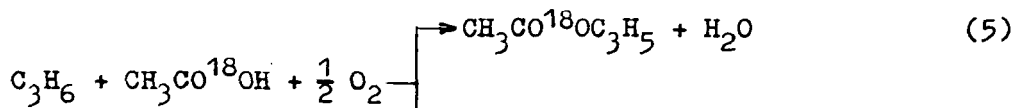
Table 9

Dependence of the products of propylene oxidative conversion on the catalyst composition

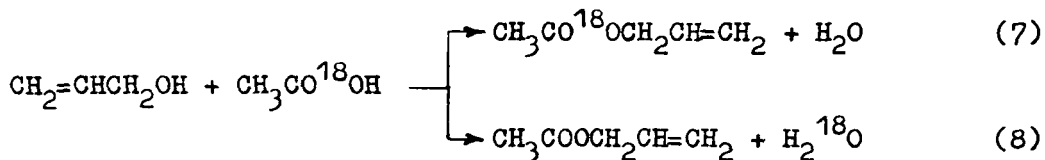
Catalyst	Products of propylene oxidative acetoxylation at 180°	Products of propylene oxidation at 200°
PdCu/HM	$CH_3COOCH(CH_3)_2$	$CO_2$
PdCu/NaM	$CH_3COOCH_2CH=CH_2$	$CO_2, CH_2=CHCHO$ <sup>⊠</sup> $CH_3COOCH_2CH=CH_2$

⊠ Total selectivity of acrolein and allylacetate formation is equal to 40% with propylene conversion up to 10%, but the portion of these products among the products of partial oxidation is equal to 80%.

If the reaction of propylene oxidative acetoxylation proceeds through formation of allyl alcohol followed by its etherization with acetic acid the labelled oxygen of the acetic acid  $\text{CH}_3\text{CO}^{18}\text{OH}$  would convert either into molecules of allylacetate or water



Which of these processes will take place depends on the mechanism of allyl alcohol etherization over the Pd,Cu-catalyst



The isotopic composition of the initial acetic acid and that of the acetic acid after the reactions of oxidative acetoxylation and etherization are indicated in table 10.

Table 10  
Isotopic composition of acetic acid (%)

Substance	Number of $^{18}\text{O}$ atoms in molecule			Specific concentration of $^{18}\text{O}$
	0	1	2	
Initial acetic acid	53.4	38.3	8.3	27.5
Acetic acid after oxidative acetoxylation	55.6	37.8	6.6	25.5
Acetic acid after etherization with allyl alcohol	77.7	18.2	4.1	13.2

It can be seen that there are 38.3% of molecules with one  $^{18}\text{O}$  atom and 8.3% of molecules, containing two  $^{18}\text{O}$  atoms in the initial acetic acid. The specific concentration of  $^{18}\text{O}$  in the initial acetic acid is equal to 27.5%. Approximately the same distribution of  $^{18}\text{O}$  was observed in the acetic acid after the reaction of propylene oxidative acetoxylation. But the specific concentration of  $^{18}\text{O}$  in the acetic acid after the reaction with allyl alcohol decreased approximately twice and was equal to 13.2%.

Mass-spectroscopy of the allylacetate obtained from the reaction of oxidative acetoxylation shows that the specific  $^{18}\text{O}$  concen-

tration is equal to  $\sim 28\%$  both in acyl and alcoxyl parts of the molecule. This implies that both oxygen atoms in the molecule resulting from this reaction originate from acetic acid and the reaction proceeds according to equation 5.

Allylacetate obtained from the reaction of allyl alcohol etherization with acetic acid on Pd,Cu-catalyst at  $180^\circ$  has been analyzed mass-spectroscopically using chemical ionization. The number of molecules containing no  $^{18}\text{O}$  atoms, and one or two  $^{18}\text{O}$  atoms is shown to be equal to 79.8, 16.9 and 3.3 %, respectively. Comparison of the isotopic composition of allylacetate obtained from the reaction of allyl alcohol etherization with that of acetic acid after this reaction (table 10) shows their good agreement. Isotopic exchange of oxygen between acetic acid and allyl alcohol makes difficult elucidation of the mechanism of etherization reaction. Calculations made show that the isotopic exchange proceeded up to 83% against the equilibrium. The presence of acetic acid and allyl alcohol with near equilibrium distribution of oxygen  $^{18}\text{O}$  will give allylacetate with the same specific  $^{18}\text{O}$  concentration independent of the way of its formation (equations 7 or 8). But simple calculations may show that oxygen  $^{18}\text{O}$  distribution in allylacetate will depend on the way of the etherization reaction (table 11).

Table 11

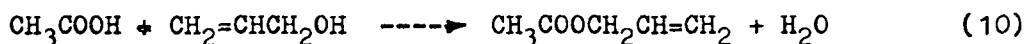
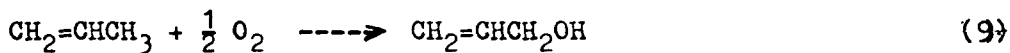
Isotopic composition of allylacetate for various mechanisms of allyl alcohol etherization

Number of $^{18}\text{O}$ atoms in allylacetate molecule	Content of isotopic molecules of allylacetate for the etherization scheme (%)	
	$\text{CH}_3\text{COOH} \left[ \begin{array}{c} \text{---} \text{---} \text{---} \\   \quad   \\ \text{---} \text{---} \end{array} \right] + \text{HO} \left[ \begin{array}{c} \text{---} \\   \\ \text{---} \end{array} \right] \text{CH}_2\text{CH}=\text{CH}_2$	$\text{CH}_3\text{CO} \left[ \begin{array}{c} \text{---} \text{---} \\   \quad   \\ \text{---} \end{array} \right] \text{OH} + \text{H} \left[ \begin{array}{c} \text{---} \\   \\ \text{---} \end{array} \right] \text{OCH}_2\text{CH}=\text{CH}_2$
0	77.7	74.4
1	18.2	23.7
2	4.1	1.9
Specific concentration of $^{18}\text{O}$	13.2	13.7

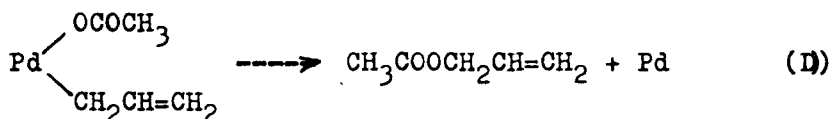
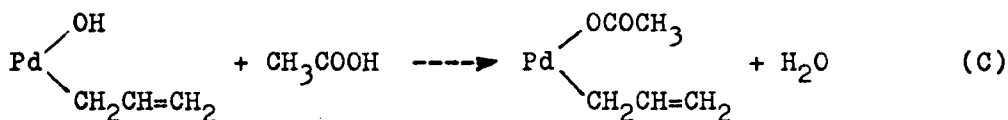
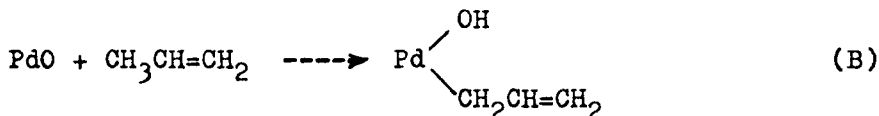
If a etherization reaction proceeds retaining completely the acetic oxygen in the allylacetate molecule the distribution of  $^{18}\text{O}$  in the reaction product will coincide with that in the acetic acid after reaction (table 10). In the case of inclusion of oxygen from allyl alcohol to allylacetate the amount of unlabelled ether molecules and

that with two  $^{18}\text{O}$  atoms would decrease but the content of isotopic ether molecules with one  $^{18}\text{O}$  atom would increase. Experimentally observed distribution of  $^{18}\text{O}$  in allylacetate molecules indicates that the etherization reaction proceeds according to equation 7, i.e. ether oxygen in allylacetate originates from acetic acid.

Hence, the results obtained do not contradict the mechanism of the reaction of propylene oxidative acetoxylation through allyl alcohol as an intermediate:



It can be assumed that allyl alcohol is in a chemisorbed state as a compound with palladium (type B) and scheme of allylacetate formation could be presented as follows:



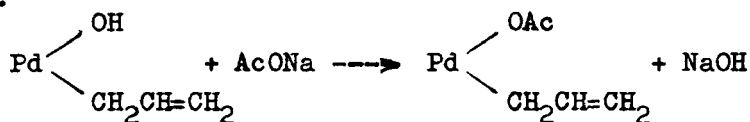
Thus the reaction of propylene oxidative acetoxylation considered in terms of traditional heterogeneous catalysis has a number of specific features. Firstly, only the catalysts on the basis of alkali forms of zeolites show activity in this reaction. If an H-form of zeolite is used in catalyst preparation addition of acetic acid to propylene with formation of isopropylacetate will take place instead of the reaction of oxidative acetoxylation. The cause is shown to be a change in the selectivity of propylene oxidation in the case of H-form zeolite (table 9). This is likely to be due to the fact that in the case of H-form zeolite catalysts it is not propylene molecules which are oxidized but propyl carbocations emerging on the acidic centers of the zeolite upon their interaction with propylene. Carbocation formation will not take place if zeolites contain alkali cations instead of protons. Another function of alkaline cations in



zeolites may be involvement into formation of alkaline metal acetate in the reaction conditions



which in this case will play a role similar to that in the catalysts on the basis of nonzeolites carriers [12,13]. There is some possibility that in the presence of alkaline metal acetate instead of stage (C) in the proposed reaction scheme the following reactions will take place:



Another specific feature of the reaction of propylene oxidative acetoxylation is that only palladium is active in allylacetate synthesis. In the case of other VIII group metals only the reaction of deep oxidation of propylene takes place. To answer the question what is responsible for this phenomenon further investigations are needed.

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