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OXIDATIVE ACETOXYLATION OF PROPYLENE IN THE PRESENCE OF PALLADIUM

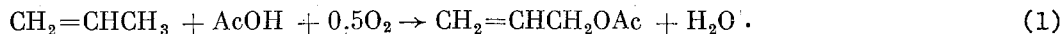
CATALYSTS.

I.* CATALYTIC COMPOSITION

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UDC 541.128:542.943:542.951.1:547.313.3

By the catalytic oxidative acetoxylation of olefins and aromatic compounds in the presence of Pd catalysts, such important products as the vinyl, alkylphenyl, benzyl, and allyl esters of acetic acid can be prepared in a single stage from the available raw material; for example, allyl acetate (AA) [2] can be obtained by the reaction



The most promising processes are the gas-phase oxyacetoxylation of olefins [3], with the majority of investigations in recent years being concentrated on their development. The gas-phase oxyacetoxylation of ethylene is the basis of an industrial method of obtaining vinyl acetate [4]; the development and successful experimental-industrial testing of a process for AA synthesis by the joint oxidation of propylene and AcOH in the gas phase on a Pd catalyst has been reported [5].

The mechanism of the oxidative acetoxylation of propylene and other olefins has been little studied. The few publications are mainly concerned with the kinetics of ethylene acetoxylation and the kinetic equations introduced differ substantially [6, 7].

Our present work has been carried out on propylene, which contains both vinyl and allyl H atoms, and our aim has been to study the general principles of the oxidative acetoxylation of olefins, to clarify the nature of active centers, and to establish the most probable mechanism for the process. We have also investigated the effect of the catalytic composition and the support structure on the main parameters of this process.

EXPERIMENTAL

The kinetic studies were carried out on an apparatus which in essence was an improved version of the nongradient stainless-steel reaction vessel as described by Korneichuk [8]. The assembly of this vessel is shown in Fig. 1. Heat transfers in the reaction vessel between the catalyst layer and the circulating liquid coolant occurred directly across the metal wall. The original propylene, O₂, and inert gas (mainly N₂) mixture was prepared in a cylinder

*For preliminary article, see [1].

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 Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1479-1484,
 July, 1981. Original article submitted February 5, 1981.

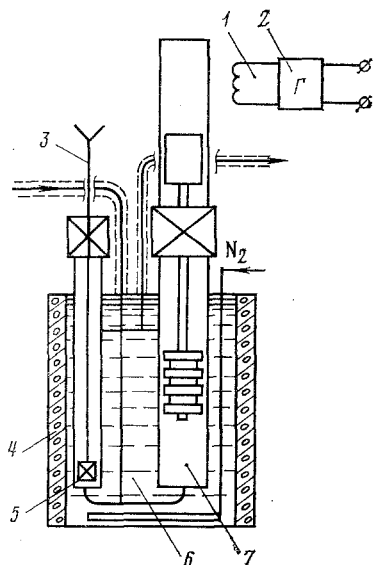


Fig. 1. A scheme of the reaction vessel: 1) electromagnetic drive; 2) thyristor impulse generator; 3) thermocouple; 4) electric furnace; 5) bucket with catalyst; 6) oil bath; 7) nongradient reaction vessel.

TABLE 1.* Results Obtained for the Nongradient Operation of the Reaction Vessel (carrier-gas helium, input gas nitrogen, reaction vessel volume 0.3 liter, circulation rate 170 liters/h at NTP)

v , liters/h	$\frac{\Delta l g \epsilon}{\Delta \tau}$	K_T	δ , rel. %
2,89	1,26	1,13	11,50
4,80	2,10	1,87	12,30
9,00	3,58	3,51	2,60
18,50	6,97	7,21	3,30
29,50	9,08	11,50	21,00

* v is the carrier gas input; ϵ is the relative N_2 peak height; τ is the registration time;

$$K_T = \frac{0,434 \cdot v}{V_R}; V_R \text{ is the reactor volume; and } \delta = \left| \frac{\frac{\Delta l g \epsilon}{\Delta \tau} - K_T}{K_T} \right| \times 100\%.$$

and was left until it was completely homogenous.

The experiments were carried out in the temperature interval 50-250°C; the charge volume was ≤ 6 ml. The gradient-free operation of the reaction vessel was determined by the method described in [9], taking into account the data in [10]. As seen from Table 1, nongradient conditions are retained when the general input of the gas mixture is ≤ 20 liters/h and the circulation rate is 170 liters/h (deviation from nongradient conditions ≤ 10 rel. %). As seen from Table 2, the effect of internal diffusion is insignificant when the catalyst grain diameter is < 5 mm.

The catalyst was prepared by applying $PdCl_2$ from an acidified HCl solution onto an amorphous carrier ($\gamma-Al_2O_3$ and amorphous aluminosilicates containing 0.4-10% of Al_2O_3), and then by reducing it with hydrazine hydrate after Cl^- ions had been removed by washing, the catalyst was impregnated with the alkali-metal acetate.

Chromatographic analysis was carried out on an LKhM-8MD (model 5) chromatograph on columns: a) 1000 \times 3 mm with 5% polyethylene glycol sebacinate on Polychrome 1 at 125°C [H_2O + AA + allylidene diacetate (ADA)]; b) 2000 \times 3 mm with silica gel KSK-2 at 70°C (C_3H_6 + air + CO_2); or c) 1000 \times 3 mm with zeolite NaX at 20°C (O_2 + N_2).

TABLE 2. The Dependence of the Rate (W_2) and Selectivity (S) of Propylene Acetoxylation on the Catalyst Grain Diameter [volume of catalyst Sl, 1.7 ml; 190°C; 6 atm; space velocity 5000 h⁻¹; molar ratio of reactants C₃H₆:AcOH:O₂:N₂ = 9.7-9.5:1.5-1.3:1:3.3]

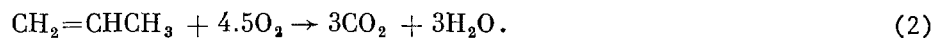
Granule size, mm	$W_1 \cdot 10^3$,* moles AA/g cat·h	S, † %
≥5	10,7	89,8
<5-3	12,3	91,6
3-2	12,1	92,0

* W_1 = mole % AA·q/P, where P is the catalyst weight, g; q is the cataly-
zate weight g/h.

†S = $\mu_{AA} \cdot 100\% / \mu_{AA} + 0.33\mu_{CO_2}$, where μ
is the amount of substance² in the
reaction products, mole/h; S is also
calculated with respect to the water
content of the reaction products.

DISCUSSION OF RESULTS

The oxidative acetoxylation of propylene in the temperature interval 120-250° and at a pressure of 1-20 atm in the presence of a Pd-AcOK/amorphous aluminosilicate catalyst proceeded solely according to Eq. (1). Products containing an AcO group in the vinyl position were absent. Together with allyl acetate (AA) formation, there occurred the thorough oxidation of propylene and (or) the allyl fragment of AA



Under acetoxylation conditions, AcOH is apparently little oxidized (the AcOH balance in all experiments was close to 100%). Typical acetoxylation data are presented in Table 3.

As Table 3 shows, AA is subjected to further acetoxylation to allylidene diacetate according to the overall reaction



ADA is possibly also formed directly from propylene by the mechanism proposed for benzyli-
dene diacetate formation during the liquid-phase acetoxylation of toluene [11].

The relationship between the rates of reactions (1) and (2) depends on the reaction conditions, and on the composition and state of the catalyst. As follows from the data in Table 4, a catalytic composition Pd-AcOK/ γ -Al₂O₃ is adequately active and selective. Lithium and sodium acetates are significantly less effective than AcOK as promoters. Synergism was not observed when mixtures of AcOK, AcOLi, and AcONa were used.

TABLE 3. The Oxidative Acetoxylation of Propylene (experimental conditions are given in Table 2)

Molar ratio of reactants C ₃ H ₆ :AcOH:O ₂ :N ₂	Composition of liquid products, %				$W_1 \cdot 10^3$, moles AA/g cat·h	S, %
	AA	H ₂ O	AcOH	ADA		
9,6:2,1:1:3,8	37,4	8,7	53,3	0,60	17,3	96,3
9,6:1,95:1:3,8	35,8	10,9	52,7	0,60	16,1	94,8
9,6:1,3:1:3,8	28,9	8,4	62,4	0,30	12,0	92,0
9,6:1,9:1:5,4	33,3	9,1	57,2	0,40	13,9	93,6
9,6:0,7:1:7,8	36,7	13,8	49,3	0,20	4,4	86,3

TABLE 4. The Effect of Alkali-Metal Acetates on the Activity and Selectivity of the Catalytic Composition (support S1, Pd content 1.5%; experimental conditions are given in Table 2)

Content, %			$W_1 \cdot 10^3$, moles AA/g cat·h	S, %
AcOK	AcONa	AcOLi		
15	0	0	12.08	92.0
0	15	0	2.86	72.0
0	0	15	2.29	69.6
7.5	7.5	0	7.77	72.8
7.5	0	7.5	3.17	65.0
0	7.5	7.5	0.47	39.0
5	5	5	2.97	70.4
0	0	0	0.12	7.6

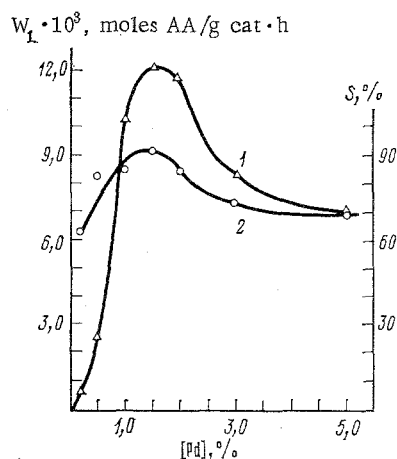


Fig. 2

Fig. 2. The dependence of activity (1) and selectivity (2) on the palladium content in the catalytic composition (AcOK content 15%, support S1).

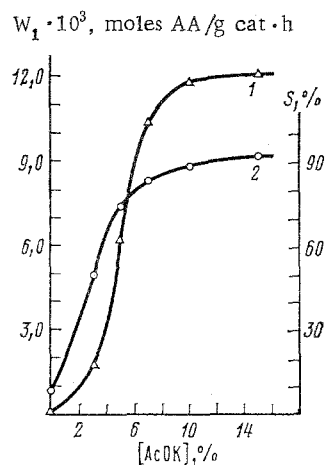


Fig. 3

Fig. 3. The dependence activity (1) and selectivity (2) on the AcOK content in the catalytic composition (Pd content 1.5%, support S1).

As the Pd content of the catalytic composition increased, the rate of reaction (1), as Fig. 2 shows, increased at first, reaching a maximum in the presence of 1.5% Pd, and then fell sharply. The selectivity changed in parallel to the rate. Apparently, when the Pd content is >1.5%, aggregates begin to form and only the external surface of these is accessible to the reactants.

The rate and selectivity of propylene acetoxylation increased as the AcOK content in the catalyst increases to ~15% (Fig. 3), and afterwards remained almost constant. This type of dependence of W_1 and S on AcOK can be explained as follows. At 180°C, AcOK is known to form a melt with AcOH, containing ~50 mole % AcOK [12, 13]. This melt acts as a liquid microphase in the support pores, in which medium, as we previously reported [1], the reaction between oxygen, propylene, and AcOH, in contact with metallic Pd takes place. Apparently, the maximum volume of the microphase is reached in the presence of 15% AcOK and a further increase in AcOK content does not affect the rate and selectivity of oxyacetoxylation. The variation in selectivity as the AcOK content increases indirectly confirms that reactions (1) and (2) take place in different phases of the catalytic composition. This is illustrated particularly clearly by the dependence of selectivity on rate (Fig. 4); although these are kinetic characteristics and are independent [14], the direct proportionality observed indicates that an increase in volume of the liquid phase, in which the selectivity of acetoxylation is close to

TABLE 5. The Effect of the Chemical Composition and the Structural Characteristics of the Aluminosilicate Support on the Activity of the Catalytic Composition (Pd 1.5%, AcOK 15%; experimental conditions are given in Table 2)

support	Al ₂ O ₃ content, %	Bulk density, g/ml	Pore volume, ml/g	Specific surface, m ² /g	Main fraction of pores		Content, g/ml (pore)		W ₁ · 10 ³	
					pore radius, Å	% total pore volume	Pd	AcOK	moles AA/ml (pore) · h	moles AA/ml (pore) · h
S1	100	0,49	0,65	134	50-460	69	0,0188	0,1875	12,08	18,60
S2	10,3	0,70	0,46	200	30-50	100	0,0329	0,329	9,4	20,45
S3	10,3	0,72	0,44	120	40-63	97			9,04	20,55
S4	10,3	0,70	0,46	120	50-80	86			9,31	20,23
S5	10,3	0,70	0,40	75	60-120	88			8,18	20,45
S6	10,3	0,70	0,44	62	80-150	83			9,00	20,45
S7	10,3	0,71	0,44	46	100-200	80			8,74	19,86
S8	5,7	0,52	0,81	520	30-60	51	0,0185	0,185	14,33	17,70
S9	5,7	0,56	0,82	290	30-50	89			14,68	17,90
S10	5,7	0,54	0,83	180	62-90	80			13,45	16,20
S11	5,7	0,53	0,82	110	100-130	72			14,19	17,30
S12	5,7	0,53	0,80	90	160-250	66			15,12	18,90
S13	5,7	0,54	0,80	75	145-260	64			14,00	17,50
S14	1,1	0,47	0,94	390	30-50	61	0,0162	0,162	16,36	17,40
S15	1,1	0,48	0,94	120	100-160	80			16,04	17,06
S16	1,1	0,48	0,93	62	80-150	89			15,16	16,30
S17	1,1	0,48	0,93	50	120-200	62			14,60	15,70
S18	1,1	0,46	0,92	40	250-380	75			15,27	16,60
S19	1,1	0,46	0,92	32	310-790	82			14,72	16,00
S20	0,40	0,60	0,68	90	90-130	66	0,0231	0,231	13,33	19,60
S21	0,40	0,60	0,65	50	110-170	75			12,60	19,40
S22	0,40	0,63	0,64	49	170-270	66			12,42	19,40

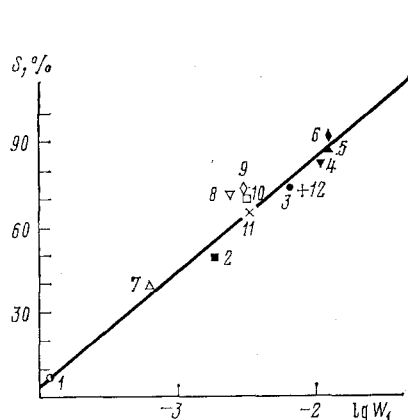


Fig. 4

Fig. 4. The dependence of selectivity of log W₁ (Pd content 1.5%, support S1); the content of alkali-metal acetates, %: 1) 0 AcOK; 2) 3.0 AcOK; 3) 5.0 AcOK; 4) 7.0 AcOK; 5) 10.0 AcOK; 6) 15.0 AcOK; 7) 7.5 AcONa and 7.5 AcOLi; 8) 15.0 AcOLi; 9) 15.0 AcONa; 10) 5.0 AcOK; 5.0 AcONa and 5.0 AcOLi; 11) 7.5 AcOK and 7.5 AcOLi; 12) 7.5 AcOK and 7.5 AcONa.

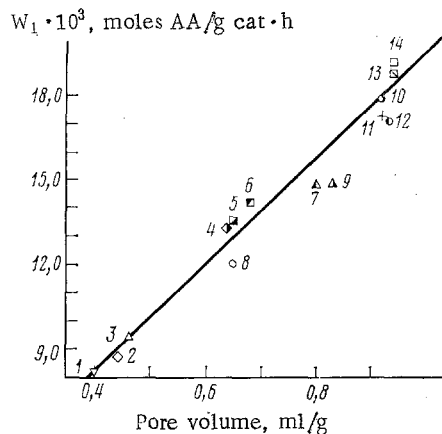


Fig. 5

Fig. 5. The dependence of W₁ on the support pore volume [Pd 0.0329 g/ml (pore), AcOK 0.329 g/ml (pore)]: 1) S5; 2) S7; 3) S2; 4) S22; 5) S21; 6) S20; 7) S13; 8) S1; 9) S11; 10) S18; 11) S19; 12) S17; 13) S15; 14) S14.

100% [1], leads to reduction of the solution surface not covered by the melt, where reaction (2) is taking place, i.e., to an increase of both the rate and the selectivity of oxyacetylation.

The data in Table 5 confirm that reaction (1) takes place in the liquid microphase. These

data show that the reaction rate depends neither on the chemical composition of the support nor on its specific surface in the range 30-520 m²/g, nor on the pore radius in the interval 40-790 Å. W₁ depends only on the total pore volume and on the Pd and AcOK concentrations in this volume, according to the data in Figs. 2 and 3. When the contents of these two components per unit pore volume are identical, the rate of reaction (1), as shown by Fig. 5, is directly proportional to the total pore volume, and under these conditions, W₁, expressed in moles AA/ml (pore)·h, remains constant and equal to ~20.45·10⁻³ (see Table 5).

Our data show that the catalytic composition Pd-AcOK/amorphous aluminosilicate ensures an adequately high rate and selectivity for the gas-phase oxidative acetoxylation of propylene. The rate of this process does not depend on the chemical composition, nor on the structural characteristics of support over the investigated range, but depends on the total pore volume and on the pore concentration of Pd and AcOK.

Propylene acetoxylation is carried out in the liquid microphase, i.e., the AcOH-AcOK melt, which fills the support pores, and is directed exclusively onto the allyl position. The side reaction of the thorough oxidation of propylene takes place mainly on the solid catalyst surface, not covered by the liquid microphase.

CONCLUSIONS

1. The catalytic composition Pd-AcOK/amorphous aluminosilicate is highly active and selective for the oxyacetoxylation of propylene in the gas phase; the rate of this process does not depend on the support chemical composition, the pore diameter in the range 40-790 Å, nor the specific surface in the interval 30-520 m²/g.

2. The acetoxylation of propylene takes place in the liquid microphase which fills the support pores and is in the form of an AcOH-AcOK melt; the side reaction of the thorough oxidation of propylene occurs mainly on the solid catalyst surface which is not covered by the liquid microphase.

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