METAL-CONTAINING ZEOLITE CATALYSTS FOR THE OXIDATIVE ACETOXYLATION OF PROPYLENE

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The catalytic oxidative acetoxylation of ethylene and propylene makes it possible to obtain the important intermediate products vinyl acetate and allyl acetate (AA) from readily available raw material in one stage, for example,

$$CH_2=CHCH_3 + CH_3COOH + \frac{1}{2}O_2 \rightarrow CH_2=CHCH_2OCOCH_3 + H_2O.$$
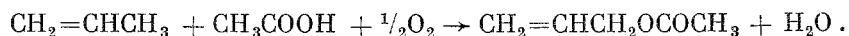
Extensive oxidation of propylene as a side reaction occurs at the same time

$$2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O.$$
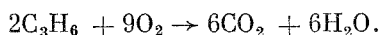
The acetoxylation of olefins was discovered in the case of the liquid-phase synthesis of vinyl acetate in the presence of palladium dichloride [1]. Subsequent investigations were directed toward modification of the liquid-phase process [2] and then to the development of the gas-phase acetoxylation of ethylene and propylene as a more promising process [3]. In all cases the catalysts are palladium compounds. According to [4-8], the best results are given by metallic palladium on various supports (activated carbon, titanium dioxide, zirconium dioxide, aluminum oxide, aluminosilicates, silicon carbide, silica gel [5-9]). The effectiveness of the catalyst is raised significantly by promoting additives and, in particular, by alkali-metal acetates [4, 5, 7, 9] and also by the compounds of metals with variable valence and copper salts, in particular [7, 10, 11]. The catalysts are prepared by impregnation of the supports with solutions of the palladium compounds and promoters; the palladium contents are 1-10%, and the promoter contents are up to 10-20%.

Acetoxylation is usually realized at 140-200°C and at a pressure of 5-10 atm. The yield of the product amounts on the average to 200-800 g/liter·h with up to 90-95% selectivity. A series of industrial vinyl acetate [8, 12] and, recently, allyl acetate [13, 14] products have been described.

Earlier we studied the catalytic characteristics of deposited palladium catalysts on aluminum oxide, silica gels, and aluminosilicates [11, 15, 16]. The aim of the present work was to investigate the possibility of preparing catalysts for oxidative acetoxylation of propylene on the basis of synthetic zeolites and to study the effect of the methods of preparation and the composition of the catalysts on the catalytic characteristics.

EXPERIMENTAL

The catalysts were prepared from industrial synthetic zeolites of the following types: NaY (SiO_2/Al_2O_3 = 5.0) K, Na-erionite (6.5), and Na-mordenite (11.9). As active components we used palladium and copper. The metals were introduced into the zeolites by ion exchange from aqueous solutions of palladium tetraaminochloride and copper acetate by the usual procedure [17]. The degree of exchange was determined from Na^+ contents of the mother solution and of the wash water by flame photometry. Before the experiment the samples were subjected to dehydration in a stream of air at 500°C and were reduced with hydrogen at 300°C.

Since investigations at atmospheric pressure were sufficient for a comparative study of the catalytic activity of the various samples, the catalytic experiments were carried out in

TABLE 1. Dependence of the Characteristics of the Catalysts Based on Zeolite NaY on the Methods of Preparation (1% Pd, 0.6% Cu)

Sample No.	Catalyst and method of preparation	Composition of catalysts product, %					Yield of allyl acetate, g/liter cat·h	Selectivity in C_3H_6, %
		CH_3COOH	H_2O	allyl acetate	IPAC	IPAL		
1	Initial NaY	98,3	1,2	0	0,5	0	0	—
2	Hydrogen form HY	90,3	0,6	0	9,1	0	0	—
3	PdCuNaY in ionic form	88,4	1,9	0	9,7	0	0	—
4	PdCuNaY reduced	87,3	2,1	0	10,6	0	0	—
5	CdCuNaY reduced, treated with 0.2 N CH_3COONa (pH 9–10)	93,6	2,1	Traces	4,3	0	0	—
6	PdCuNaY reduced, treated with 0.2 N NaCl (pH 9–10)	92,7	2,7	2,4	2,2	0	18,8	24,6
7	PdCuNaY reduced, impregnated with 0.2 N NaCl, calcined at 500°C in air	86,5	6,2	4,4	Traces	2,9	28,3	29,5
8	PdCuNaY reduced, treated with 0.2 N NaOH	92,1	3,5	4,4	0	0	30,0	39,5

a thermostated glass flow-type reactor at atmospheric pressure and 180°C with the ratio C_3H_6: $CH_3COOH:O_2$ = 6:1:0.5, a volume flow rate of 14 liters/h, and 6 cm³ of catalyst. We used air as source of oxygen. Before delivery to the reactor the initial gases were passed through columns filled with zeolite to purify them from contaminants and moisture. The liquid reaction products were collected in a receiver cooled to 0°C and were analyzed by chromatography.

Control tests on the catalytic activity of some samples were carried out in a metallic gradient-free reactor at a pressure of 6 atm with the previous process parameters.

The moisture content of the samples was measured on thermodesorption apparatus. The sample was first saturated with water in a stream of inert gas at 20°C. The peak for the water released was then recorded with linear increase in the temperature of the sample from 200 to 500°C. The amount of adsorbed water was determined from the area of the obtained peak and from calibrated desorption curves.

DISCUSSION OF RESULTS

The dependence of the catalytic characteristics on the method of preparation (Table 1) was studied on samples of NaY zeolite. As found, an essential stage in the production of the zeolite catalyst for acetoxylation is final neutralization of the protic acid centers of the zeolite, formed at the stage of reduction of the introduced metal ions. This feature distinguishes zeolites fundamentally from other supports. Without such treatment addition of acetic acid to propylene to form isopropyl acetate (IPAC) occurs on the zeolite catalyst. Such an effect is also observed on the zeolite containing palladium and copper in ionic form (Table 1, sample 3), since it also contains structural OH⁻ groups, while the reduction of the metals by propylene in the course of the reaction is accompanied by the formation of additional acid centers.

For comparison experiments were carried out on samples of zeolites without the metals. A small amount of IPAC is formed on the initial NaY zeolite, in which there are usually acid centers formed as a result of partial decationization (Table 1, sample 1). On the hydrogen form HY (sample 3), where the concentration of the OH⁻ groups is considerable, IPAC is formed at approximately the same rate as on the metal-containing zeolites.

The most effective method of neutralization is treatment of the reduced catalyst with an excess of 0.2 N solution of sodium hydroxide at 90–95°C for 2–3 h. This method completely eliminates the addition reaction (Table 1, sample 8). Milder treatments with alkaline solutions of acetate and sodium chloride do not give satisfactory results. In addition to AA the reaction products contain a considerable amount of IPAC (samples 5 and 6). If the catalyst is impregnated with a solution of sodium chloride and subsequently calcined in air at 500°C, another side product (isopropyl alcohol) appears in the catalysis product instead of IPAC. In addition, the selectivity of such a catalyst is appreciably lower than that of the catalyst
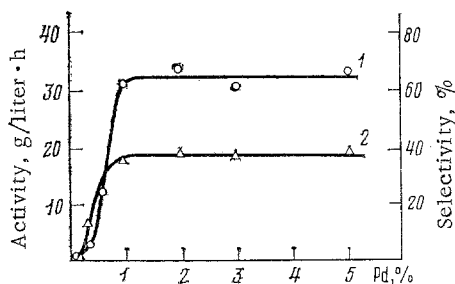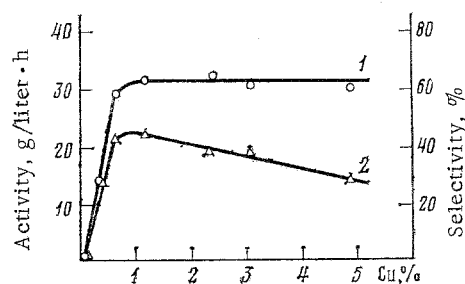
Fig. 1. Dependence of the catalytic characteristics of PdCuNaY on the concentration of Pd (with a constant Cu content of 3%): 1) activity; 2) selectivity in C_3H_6.

Fig. 2. Dependence of the catalytic characteristics of PdCuNaY on the concentration of Cu (with a constant Pd content of 1%): 1) activity; 2) selectivity in C_3H_6.

treated with a solution of alkali.

In addition to the bimetallic catalysts PdCuNaY, we tested individual metal-containing samples of PdNaY and CuNaY and also a mechanical mixture of the prepared individual forms. All the samples contained 1% each of Pd and Cu. According to data from the catalytic experiments, the zeolites containing each of the metals separately are practically inactive in the acetoxylation of propylene. Also inactive is their mechanical mixture. Activity in this reaction is only exhibited by the bimetallic catalyst containing palladium and copper introduced by ion exchange. In this case the reaction products are AA, CO_2, and water. The yield of AA under standard conditions amounts to 30 g/liter cat·h, and the selectivity calculated on the reacted propylene is ∿40%. The remainder of the propylene undergoes total oxidation. At a pressure of 6 atm the activity of the catalyst amounts 200 g/liter cat·h with ∿70% selectivity.

As a result of experiments with variation of the concentration and ratio of Pd and Cu in the NaY zeolite (Figs. 1 and 2) it was found that the maximum activity (32 g AA/liter cat·h with ∿40% selectivity, atmospheric pressure) is given by the catalyst with 1% Pd and 0.6% Cu added to the zeolite. In this case the atomic ratio of the metals contained in it is close to unity. Further increase in the concentration of palladium does not lead to an increase in activity, while increase in the copper content is accompanied by a reduction in selectivity on account of the accelerated total oxidation of propylene.

The effect of the order of introduction of the metals into the zeolite on its catalytic characteristics was established by testing samples of PdCuNaY prepared by successive and simultaneous ion exchange (Table 2). In the first case, after the introduction of one of the metals, the sample was calcined and reduced. Exchange was then realized from a solution of a salt of the other metal, and the calcination and reduction were repeated. In the second case exchange was realized from a solution containing palladium and copper salts simultaneously. The concentration of the metals was the same in all the samples. From Table 2 it follows that the activity of the catalyst obtained by simultaneous exchange is almost twice as high as the activity of samples prepared by successive exchange. The selectivity was also noticeably higher in the more active catalyst.

The results from tests on samples of zeolite of type Y containing various alkali-metal cations with the maximum degrees of exchange of sodium ions (Li ∿ 100%, K ∿ 100%, Cs ∿ 72% [18]), are given in Table 3. With increase in the atomic number of the number of the metal, i.e., in the transition from lithium to cesium, there is some increase in catalytic activity. These results are consistent with data obtained on nonzeolite catalysts with the same series of alkali-metal acetates as promoters [9]. On zeolites, however, the effect of the various cations of group I metals is significantly less clearly defined. It can be supposed that copper is the main promoter in the zeolite catalysts, while the alkali-metal cations entering into the composition of the zeolites and combined with their framework have a small additional promoting action, similar to the action of acetates. It should be noted that the zeolite with Cs^+ cation, unlike the others, showed very low selectivity on account of the very high degree

TABLE 2. Effect of the Order of Introduction of the Metals into the NaY Zeolite on Its Catalytic Characteristics (1% Pd, 0.6% Cu)

Method and order of ion exchange	Yield of allyl acetate g/liter cat·h	Selectivity in C_3H_6, %
Successive exchange 1) Pd. 2) Cu	30,0	39,5
Successive exchange 1) Cu, 2) Pd	28,8	38,1
Simultaneous exchange	59,5	52,8

TABLE 3. Catalytic Characteristics of Zeolites of Type Y with Various Alkali-Metal Cations (1% Pd, 0.6% Cu)

Initial zeolite	Composition of catalysis product, %			Activity, g/liter cat·h	Selectivity in C_3H_6, %
	CH_3COOH	allyl acetate	H_2O		
LiY	93,2	3,7	3,1	25,6	36,1
NaY	92,0	4,5	3,5	30,0	39,5
KY	91,5	4,9	3,6	35,6	43,2
CsY	71,8	5,2	23,0	38,4	9,6

TABLE 4. Dependence of the Catalytic Characteristics on the Type of Initial Zeolite (1% Pd, 0.6% Cu)

Initial zeolite	Reaction conditions	Yield of allyl acetate, g/liter cat·h	Selectivity in C_3H_6, %
NaY	Standard	30,0	39,5
K, Na-erionite	»	70,5	92,3
Na-mordenite	»	28,6	71,2
K, Na-erionite	Pressure 6 atm	450,0	95,4

of oxidation of the propylene.

Investigation of various types of high-silica zeolites as the basis of Pd—Cu catalysts for the acetoxylation of propylene showed that the type and structure of the initial zeolite are important factors which affect the catalytic characteristics (Table 4, Fig. 3). The catalyst based on mordenite, while having almost identical activity with the NaY zeolite, exhibits considerably higher selectivity. The most effective are catalysts prepared from K, Na-erionite. Their activity (70 g AA/liter cat·h) is more than twice the activity of zeolite of type Y, while the selectivity amounts to 92-95%. Tested under a pressure of 6 atm, this catalyst showed an activity of 450 g AA/liter cat·h with more than 96% selectivity. In addition, the catalysts based on erionite are distinguished by their higher stability with time. From Fig. 3 it is seen that after use for 8 h samples of PdCuNaM and PdCuK,NaE hardly change their initial activity at all. At the same time, on zeolite NaY there is a significant decrease in activity in a shorter time.

In order to check possible breakdown of the crystal lattice of zeolite NaY under the influence of the reaction medium experiments were carried out on the moisture contents of the initial zeolite and the freshly prepared and used catalysts. It was found that the moisture content of all the NaY zeolite samples was approximately the same (12.8-13.5%), and this indicates that the zeolite framework is stable under the reaction conditions. In addition, it proved possible to regenerate the use catalyst on NaY zeolite. After calcination in air at 500°C and subsequent reduction with hydrogen at 300°C the catalyst acquires its full initial activity, which again decreases according to the previous law in the course of the reaction. These data show that the reason for the reduction in the activity of catalysts based on NaY
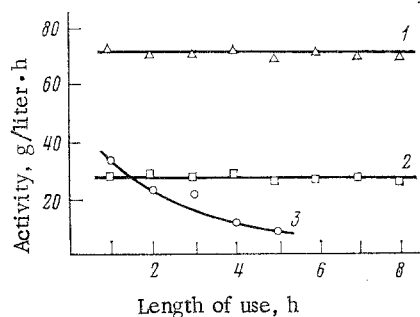
Fig. 3. Variation of the activity of Pd—Cu catalyst prepared from various types of zeolites with time: 1) K, Na-erionite; 2) Na-mordenite; 3) NaY.

is most likely poisoning of the catalyst by some reaction product, leading to a decrease in the specific surface area of the catalyst and to a reduction in the number of active centers.

The observed differences in catalytic activity, selectivity, and stability for the various types of zeolites are evidently due to the significant effect of the structure of the zeolite on external factors, which determine the ratio of the rates of the desired and side reactions. Such factors as the degree of dispersion and the distribution of the metals in the zeolite matrix, their possible interaction during preparation of the catalysts, the conditions for the formation of the active centers during the reaction, and the diffusion of the initial substances and reaction products in the various zeolites may form the subject of separate comprehensive investigation.

CONCLUSIONS

1. The possibility of obtaining metal-containing catalysts for the oxidative acetoxylation of propylene from synthetic high-silica zeolites was investigated. Activity is only exhibited by reduced bimetallic palladium—copper catalysts prepared by ion exchange.

2. In order to obtain the given catalytic characteristics it is necessary to add the acid function of the zeolite at the concluding stage of the preparation of the catalyst.

3. Best results with respect to the activity and selectivity are obtained on catalysts based on K, Na-erionite.

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MECHANISM OF RETARDATION OF OXIDATION REACTIONS BY METAL COMPLEXES.
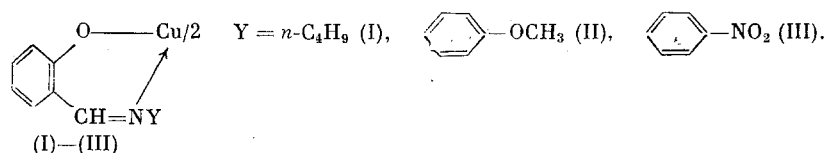
6.* KINETIC INVESTIGATION OF THE COORDINATION OF PEROXYL RADICALS BY COPPER COMPLEXES IN CHAIN TERMINATION EVENTS

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The retardation of the radical-chain oxidation of alcohols and aliphatic amines by metal complexes (ML_m) is based on one-electron transfer between ML_m and the peroxyl radicals [2, 3]. It can be supposed that the one-electron transfer between ML_m and the peroxyl radical, as in many other reactions of O-centered radicals with ML_m [2-5] is preceded by the formation of a complex.

In order to investigate the mechanism of antioxidative action of ML_m further and to obtain evidence for coordination of the peroxyl radicals on ML_m in the present work we investigated the kinetic relationships governing the inhibited oxidation of n-octanol (RH) in the presence of bis(salicylaldiminato)coppers (I)-(III):

$$O\text{———}Cu/2 \qquad Y = n\text{-}C_4H_9 \text{ (I)}, \quad \langle\!\!\bigcirc\!\!\rangle\text{—}OCH_3 \text{ (II)}, \quad \langle\!\!\bigcirc\!\!\rangle\text{—}NO_2 \text{ (III)}.$$

(I)—(III) CH=NY

EXPERIMENTAL

The complexes (I)-(III) were synthesized by the general method in [6] and were recrystallized from ethanol. The elemental analyses of the obtained compounds correspond to the formulas (I)-(III). The antioxidative characteristics of the complexes were investigated by initiated oxidation [7] at 115°C. The observed value of $k_p/k_t^{1/2} = W_0[RH]W_i^{1/2} = (3.3 \pm 0.1)\cdot10^{-3}$ (liter/mole·sec)$^{1/2}$ coincides with the oxidizability of the individual RH [8], where k_p and k_t are the rate constants of propagation and quadratic termination of the chains respectively [8]; W_0 is the rate of noninhibited oxidation, measured at $p_{O_2} = 0.3-1.0$ atm from the absorption of oxygen and independently from the accumulation of peroxy compounds; W_i is the rate of initiation of the chains by cumenyl peroxide. The initiation rate constant measured by the method in [8] is $k_i = (1.2 \pm 0.1)\cdot10^{-5}$ sec^{-1}, and when $[(II)] = (0.6-5.7)\cdot10^{-6}$ M, $k_i = (1.4 \pm 0.2)\cdot10^{-5}$ sec^{-1}. The similar value of k_i in the presence and in the absence

*For Communication 5, see [1].