CATALYTIC PROPERTIES OF A $PdCl_2 \cdot CuCl_2$/ZEOLITE SYSTEM IN THE OXIDATION OF C_2-C_4 OLEFINS TO CARBONYL COMPOUNDS

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Zeolites containing Pd^{2+} and Cu^{2+} cations are highly effective in the vapor-phase oxidation of lower olefins to carbonyl compounds [1-3]. In the present work we studied the dependence of the catalytic properties of the $PdCl_2 \cdot CuCl_2$/zeolite systems [3] obtained by the impregnation method on the composition and structure of the lattice of crystalline aluminosilicates and conditions for their use in the reactions of C_2-C_4 olefins with atmospheric oxygen. The results were compared with the data for similar catalysts prepared from aluminum oxide, silicon dioxide, and amorphous aluminosilicate (AAS).

EXPERIMENTAL

The catalysts were prepared by impregnating zeolites of types A ($SiO_2/Al_2O_3 = x = 2.0$), X ($x = 2.5$), Y ($x = 4.4$ and 4.9) and mordenite (M) ($x = 11.9$), γ-Al_2O_3, SiO_2, and AAS (12% Al_2O_3) with ammoniacal solutions of Pd and Cu chlorides. Before use, they were activated for 2 h in air current at 350°C. According to the data of chemical analysis and IR spectroscopy, the activation led to complete removal of NH_3 from the contacts. Under these conditions, NH_4Cl and HCl were liberated from the catalysts based on Al_2O_3, SiO_2, and AAS, in contrast to the case with zeolite catalysts. The highest loss of Cl (about 20% of the initial content) was observed for the $PdCl_2 \cdot CuCl_2$/AAS system. The initial ethylene (with an admixture of 0.9 vol.% of C_2H_6), propylene (0.7 vol.% of C_3H_8), and a fraction containing 46.9% of cis-2-butene, 49.6% of trans-2-butene, and 3.5% of C_4H_{10} were dried over calcined $CaCl_2$. The air serving as the source of O_2 was passed through columns with activated carbon, Al_2O_3, and 4A zeolite. The main products of the oxidation of C_2H_4, C_3H_6, and C_4H_8 were acetaldehyde (AcH), acetone, and methyl ethyl ketone (MEK), respectively. The side products were mainly CO_2; in the case of C_3H_6, small amounts of propanol were obtained; no chlorine-containing organic compounds were detected. The procedures for carrying out the catalytic experiments, analysis of products, and IR spectroscopic measurements are described in [2].

DISCUSSION OF RESULTS

The formation of the carbonyl compounds was observed only on catalysts containing both Pd and Cu (Table 1). On $PdCl_2$/NaY ($x = 4.4$) at 115°C the maximal conversion of C_2H_4 to AcH was only about 5%,

TABLE 1. Oxidation of Ethylene and Propylene on $PdCl_2 \cdot CuCl_2$/Carrier Catalysts Containing 0.66% Pd and 3.98% Cu [115°C, olefin : H_2O: air = 1 : 2 : 5 (molar), $v = 800\ h^{-1}$]

Carrier	Ethylene		Propylene		
	yield of AcH, %	selectivity (S), %	yield of C_3H_6O (CH_3-$COCH_3 + C_2H_5CHO$), %	S, %	content of C_2H_5CHO in C_3H_6O, %
NaA (x=2,0)	4,4	91,7	0,15	99,9	–
NaX (x=2,5)	14,4	99,3	10,1	99,9	0,62
NaY (x=4,4)	32,3	98,3	27,0	99,7	0,64
NaY (x=4,4) *	17,7	98,8	–	–	–
NaY (x=4,9)	23,3	98,1	–	–	–
NaM (x=11,9)	5,1	99,2	1,1	99,9	1,6
SiO_2	5,1 †	99,9	3,0 †	99,9	1,6
Al_2O_3	15,1 †	78,2	3,1 †	89,1	0,43
AAS*	6,1 †	92,5	–	–	–

* Content of Pd and Cu 0.33 and 2.0%, respectively.

† After 1 h of operation.

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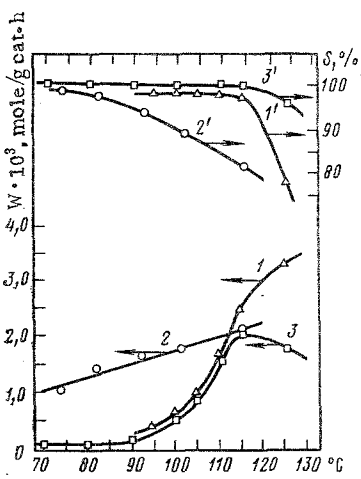

Fig. 1. Dependence of rate (W) and selectivity of formation (S) of carbonyl compounds during oxidation of C_2H_4 (1, 1', 2, 2') and C_3H_6 (3, 3') on $PdCl_2 \cdot CuCl_2/NaY$ (x = 4.4) on temperature: 1, 1', 3, 3') olefin : H_2O : air = 1 : 2 : 5 (molar), v = 800 h^{-1}; 2, 2') C_2H_4 : H_2O : air = 1 : 0.14 : 5 (molar), v = 614 h^{-1}.

and after 30 min, the conversion fell to zero. In the presence of $CuCl_2/NaY$ (x = 4.4), in general, no conversion of C_2H_4 took place under these conditions. If the data in Table 1 are compared with those obtained in [2] on PdCu zeolites, it is seen that the $PdCl_2 \cdot CuCl_2$/zeolite catalysts are not inferior in activity to the corresponding ion-exchange-produced catalysts with the same content of Pd and Cu. The characteristic feature of the impregnated catalysts is their higher selectivity (S), which reaches 98-99% and does not change with time. They are also characterized by operational stability: the conversion of the olefins remains constant, even in the longest experiments (15 h). Under the same conditions, the yield of the carbonyl compounds (A) in the presence of PdCu zeolites obtained by ion exchange rapidly decreased with time, and oxidative heat treatment of the samples at 300-350°C after catalysis did not restore their initial activity [2]. For example, during oxidation of C_2H_4 on PdCuNaY (x = 4.4) under conditions of Table 1, A decreased after 5 h from 30-33% to 7.5% at S with respect to AcH of 70-80%, and after regeneration the activity of the catalyst was half that of a fresh sample. It is probable that Cl^- ions present in the impregnated catalysts stabilize their activity. This action of the halide ions is known for homogeneous PdCu oxidizing systems of olefins, and is due to the value of the Pd^0/Pd^{2+} and Cu^{2+}/Cu^+ redox potentials established during the formation of halide complexes of transition metals and facilitation of the oxidation of Pd^0, formed during the reaction, to Pd^{2+} by the action of Cu^{2+} cations [4].

The coordination reaction between the Cl^- ions and M^{2+} cations (M = Pd, Cu) may be one of the reasons for the high selectivity of the $PdCl_2 \cdot CuCl_2$/zeolite catalysts, since the M^{2+} cations may be the active centers of side reactions. The products of intensive oxidation are formed, probably, mainly from carbonyl compounds, and not from the initial olefins. This is indicated by the following experimental data. The selectivity of the oxidation of C_3H_6 to acetone on the zeolite catalysts is higher than the S of the conversion of C_2H_4 to AcH (see Table 1 and [2]), which may be the result of a higher reactivity of AcH with respect to reactions of further oxidation, condensation, etc. It is known [5] that in air–vapor mixtures on Pd/Al_2O_3, intensive oxidation of AcH takes place more readily than the oxidation of acetone, and the reactions proceed already at 100°C. At the same time, intensive oxidation of lower olefins on zeolites containing transition-metal cations takes place at temperatures > 150°C [6], whereas on PdNaY, under the same conditions, the rate of the reaction for C_3H_6 is 50 times as high as for C_2H_4 [7].

Another reason for the high selectivity of the impregnated catalysts is that their H^+ acidity is lower than that of ion-exchange-produced catalysts. In particular, the IR spectra of $PdCl_2 \cdot CuCl_2/NaY$ (x = 4.4), treated in an air current at 100-400°C, in contrast to PdCuNaY (x = 4.4) [8], do not contain absorption bands of acidic OH groups. As found in [8], an increase in the concentration of the latter in the ion-exchange-produced PdCu-faujasite leads to a decrease in its activity, selectivity, and stability during the oxidation of C_2H_4 to AcH. The absence of protonated OH groups in $PdCl_2 \cdot CuCl_2/NaY$ is clearly due to the method of preparation (impregnation of the zeolite by a solution of Pd and Cu salts), which, in contrast to the ionic exchange of Na^+ for the

TABLE 2. Dependence of Yields of AcH (A) and Selectivity of Its Formation (S) in Oxidation of C_2H_4 on $PdCl_2 \cdot CuCl_2/NaY$ (x = 4.4; 0.66% Pd; 3.98% Cu) on Conditions of the Process

Expt. No.	T., °C	v, h^{-1}	$C_2H_4 : H_2O$: air (molar)	A, %	S, %
1	95	614	1 : 0,14 : 5	20,9	91,1
2	95	662	1 : 0,62 : 5	25,0	97,5
3	95	700	1 : 1 : 5	18,5	97,0
4	95	800	1 : 2 : 5	5,5	97,0
5	115	614	1 : 0,14 : 5	26,7	82,2
6	115	662	1 : 0,62 : 5	35,1	88,4
7	115	700	1 : 1 : 5	40,2	91,3
8	115	800	1 : 2 : 5	32,3	98,2
9	115	1000	1 : 4 : 5	17,5	99,5
10	115	1050	1 : 2 : 7,5	25,0	93,9
11	115	1300	1 : 2 : 10	24,4	90,5
12	115	1600	1 : 2 : 13	23,2	88,7

double-charged Pd^{2+} and Cu^{2+} cations, does not lead to the appearance in the faujasite structure of S_{II} sites, free of metal cations, where protons are localized. These usually appear during the hydrolysis of M^{n+} in heat treatment of the catalysts before they are used in the catalysis [9].

Of the $PdCl_2 \cdot CuCl_2$/zeolite systems studied (see Table 1), the most active are the catalysts prepared from widely porous zeolites of the faujasite type, as in the case of the catalysts produced by ion exchange [2]. This indicates localization of the active centers in the catalysts of the two types, mainly in the voids of the crystalline aluminosilicates. $PdCl_2$ and $CuCl_2$ may penetrate into the voids of the zeolites during the preparation and activation of the catalysts, and thus systems are clearly formed similar to the zeolite–salt adducts described in [10].

An appreciable contribution to the stabilization of the PdCu catalysts is introduced also by the aluminosilicate lattice. This conclusion is based on comparison of the properties of the catalysts based on zeolites, Al_2O_3, SiO_2, and AAS, containing equal amounts of Pd and Cu (see Table 1). In activity, the nonzeolite catalysts are appreciably inferior to $PdCl_2 \cdot CuCl_2/NaY$ (x = 4.4), and the yield of the carbonyl compounds obtained on them rapidly decreases with time. After oxidation treatment at 250-350°C, the initial activity of the samples is not restored. $PdCl_2 \cdot CuCl_2/Al_2O_3$ and $PdCl_2 \cdot CuCl_2$/AAS systems are characterized by relatively low (80-90%) selectivity of oxidation of C_2H_4 to AcH. To stabilize the catalysts based on SiO_2 and Al_2O_3, it was suggested that HCl be added to the reaction mixture [11], but this appreciably decreases the practical value of the catalysts. Our results show that zeolite is an important component part of the PdCu catalysts for oxidation of olefins to carbonyl compounds, and apparently plays the role not only of a carrier or "solid solvent" dispersing $PdCl_2$ and $CuCl_2$ in its voids, but also of a macromolecular ligand stabilizing the Pd^{2+} and Cu^{2+} cations.

The dependence of the catalytic properties of the impregnated catalysts on the conditions of use was studied for the example of $PdCl_2 \cdot CuCl_2/NaY$ (x = 4.4). At a molar ratio olefin : H_2O : air = 1 : 2 : 5 (content of H_2O vapors 25 vol.%), the catalyst begins to show activity in the reactions of C_2H_4 and C_3H_6 at a temperature higher than 90°C (Fig. 1). In the 90-125°C range, the rate of oxidation (W) of ethylene increases, and S with respect to AcH is retained at a high level up to 115°C, and only at 125°C does it decrease to 78%. In the case of C_3H_6, W is maximal at 115°C and S is practically independent of temperature.

Decrease in the content of H_2O vapors in the initial mixture appreciably changes the temperature dependence of W (see Fig. 1). At a ratio $C_2H_4 : H_2O$: air = 1 : 0.14 : 5 (molar) (2.3 vol.% of H_2O vapors), the catalyst has considerable activity already at 70-90°C, although S is lower than in the experiments with a mixture containing 25 vol.% of H_2O vapors. It is probable that because of the high absorbability of type Y zeolite, the amount of H_2O required for the reaction to take place is ensured in the catalysis zone. Water is a necessary component of the catalytic process [12] and can influence the adsorptional–desorptional equilibrium established in the catalyst–reaction mixture system.

According to the data on the rate of oxidation of C_2H_4 to AcH on $PdCl_2 \cdot CuCl_2/NaY$ (x = 4.4) in the 80-125°C range (see Fig. 1), the apparent activation energy of the process (E_a) is ~ 96 and ~ 21 kJ/mole at 25 and 2.3 vol.% of H_2O vapors in the reaction mixture, respectively. This strong influence of the H_2O content on the temperature dependence of W can be explained by considering the above-mentioned diversity in the role of H_2O in catalysis on the PdCu systems. At a considerable amount of H_2O in the initial mixture of reagents (25 vol.%), the sharp increase in W with increase in temperature (E_a ~ 96 kJ/mole) is apparently due to the re-

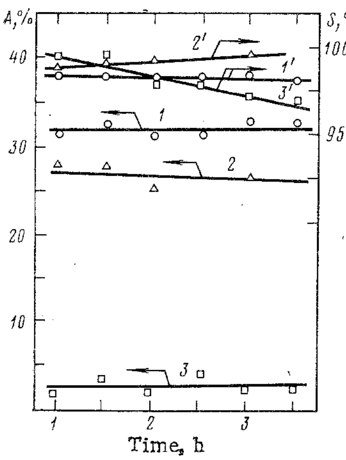

Fig. 2. Time-dependent change in yields of carbonyl compounds (A) (1-3) and selectivity (S) (1'-3') during oxidation of ethylene (1, 1'), propylene (2, 2'), and butenes (3, 3') on $PdCl_2 \cdot CuCl_2/NaY$ (x = 4.4). Conditions are given in Table 1.

moval from the catalyst, for example from the intercrystalline volume, of some of the H_2O condensed below 100°C, which may form a "film" and prevent access of the reacting molecules to the Pd^{2+} and Cu^{2+} cations. In experiments with an initial mixture containing a small amount of H_2O vapors (2.3 vol.%), increase in temperature probably leads to decrease in the amount of H_2O in the zeolite voids where catalysis takes place. We should note that for the $PdSO_4$/activated carbon catalyst, whose ability to absorb H_2O is considerably lower than that of crystalline aluminosilicates, the E_a of the oxidation of C_2H_4 in the 95-155°C range was found to be negative (−75.3 kJ/mole) even at a $C_2H_4 : H_2O : O_2$ ratio = 2 : 3 : 1 (molar) [13]. After the impregnation of this catalyst with H_2SO_4 (up to 10%), which increased the hydrophilicity of the catalyst, the E_a increased to 35.6 kJ/mole [13].

The optimal $C_2H_4 : H_2O$ ratio depends on reaction temperature (Table 2). A comparison of the results of experiments 1-4 and 5-9, shows that the maximal activity of $PdCl_2 \cdot CuCl_2/NaY$ at 95 and 115°C is observed of at $C_2H_4 : H_2O$ ratios = 1 : 062 and 1 : 1, respectively. With increase in temperature, larger amounts of H_2O must be introduced into the reaction zone; this is also necessary to ensure the selective operation of the catalyst (see Table 2). The influence of the space velocity of feed of the reaction mixture on the yield of AcH, when the content of H_2O vapors is varied (experiments 5-9), is greater than in experiments 8, 10-12 with different C_2H_4 : air ratios. In general, the highest values of A and S on PdCu catalysts obtained by ion exchange [2] and by impregnation are attained at the same temperature and composition of the initial mixture.

The results listed in Table 1 and Fig. 1 show that the reactivities of C_2H_4 and C_3H_6 with respect to oxidation to carbonyl compounds on the $PdCl_2 \cdot CuCl_2$/zeolite catalysts are similar (this is also observed in the case of the ion-exchange-produced PdCu catalysts [2]). During oxidation of C_3H_6, acetone is mainly formed, and the content of propanol in the C_3H_6O obtained does not exceed 1.6% (see Table 1). The degrees of conversion of C_2H_4 and C_3H_6 to carbonyl compounds are comparable under equal conditions, but the yield of methyl ethyl ketone during oxidation of C_4H_8 is much lower, and at 115°C it is ~2.5% (Fig. 2). In the 115-140°C range, the conversion of butenes increases inappreciably, while the S decreases. The sharp decrease in the reactivity of olefins on transition from C_2H_4 and C_3H_6 to C_4H_8 also confirms the similarity of the oxidation mechanisms of C_nH_{2n} compounds on PdCu zeolites in solutions of Pd and Cu salts, for which a similar dependence is observed [4]. The lower oxidation rate of butenes under conditions of homogeneous catalysis is due to the character of the complex formation of the C_4H_8 molecules with Pd^{2+} cations, and to the fact that butenes are less soluble than C_2H_4 and C_3H_6 in aqueous solutions [4].

CONCLUSIONS

1. Characteristic features of the catalytic action of the $PdCl_2 \cdot CuCl_2$/zeolite systems obtained by the impregnation method were studied during the oxidation of C_2-C_4 olefins to carbonyl compounds. In activity, selectivity, and stability, systems based on synthetic faujasites are superior to both the $PdCl_2 \cdot CuCl_2/Al_2O_3$ (SiO_2; amorphous aluminosilicate) and the ion-exchange-produced PdCu zeolites already studied.

2. Conditions were found ensuring a 98-99% selectivity of the conversion of C_2H_4 to acetaldehyde, and C_3H_6 to acetone.

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COTELOMERIZATION OF ETHYLENE AND ISOBUTYLENE WITH METHYL ISOBUTYRATE

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A study of telomerization and cotelomerization of various monomers with telogens, which react by rupture of the C—Cl bond, shows that the polar properties of the growing radicals and reacting molecules exert a considerable influence on the distribution of the reaction products. In this connection the most significant results are obtained when monomers containing substituents with different polarities, e.g., propylene and vinyl chloride, are used in cotelomerization [1]. Reactions with methyl isobutyrate in which a C—H bond is ruptured are considerably less sensitive to the polar properties of the reactants. In this case the course of the reaction is determined mainly by the structure of the growing radicals (primary, secondary) from the point of view of its effect on their ability to join onto a monomer and participate in a chain-transfer reaction with a telogen. The results of telomerization of ethylene and propylene with methyl isobutyrate showed that the yield of both homo- and cotelomers having ethylene as the last monomer unit is greater by a factor of 2.5-3 than compounds containing a propylene monomer unit at the end. This is due to the greater difficulties in the growth and chain-transfer stages in the latter [2]. It seemed interesting to compare, in cotelomerization with methyl isobutyrate, the monomers ethylene and isobutylene, which differ in structure still more. In the last, the growing radicals are tertiary and sterically hindered, which should cause a reduction in their capability for chain transfer

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