CARBONYLATION OF ETHYLENE BY CARBON MONOXIDE ON METAL ZEOLITE CATALYSTS

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Carboxylic acids or their esters are obtained by a one-stage carbonylation of olefins by carbon monoxide, usually in the presence of homogeneous catalysts, e.g. complexes of metals of Group VIII [1, 2].

Because of difficulties in the preparation and separation of complexes from the reaction products, the use of heterogeneous catalysts appears to be promising for this reaction. In the carbonylation of ethylene, the high activity and selectivity of Pd catalysts deposited on SiO_2 and activated charcoal was established [3, 5]. Since zeolites are characterized by constancy of their physicochemical properties, and also since they are now produced on a large scale, it is very important to broaden their field of application, in particular as catalysts with regenerative catalytic properties. Attempts to use Pd-containing type X and Y zeolites were unsuccessful because of decomposition of the zeolite by organic acids formed and acetic acid used as a solvent.

It was desirable to use synthetic mordenite and superhigh silicon zeolites (HSZ), characterized by high acid resistance, as carriers. In the present work, we studied the catalytic properties of zeolites containing metals of Group VIII for carbonylation of ethylene. We studied the influence of the nature of metals, methods of preparation of the catalysts, their activation, and conditions for carrying out the reaction in the carbonylation process.

DISCUSSION AND RESULTS

The carbonylation of ethylene was carried out in acetic acid in the presence of metal zeolite catalysts and a promoter (ethyl bromide). Together with propionic acid, the main reaction product, ethanol, ethyl acetate, ethyl propionate, and small amounts of diethyl ketone are formed.

Table 1 shows that the nature of the group VIII metal is of decisive importance in the carbonylation of ethylene. The most active and selective is the Pd-zeolite catalyst. The conversion of ethylene on it reaches 83%, and the selectivity of transformation of ethylene into propionic acid is 96 mole %. With respect to conversion, the RH-catalyst is comparable with a palladium catalyst, but its selectivity is lower. The Ir-zeolite catalyst has low activity and selectivity, while zeolites containing Pt and Ru do not catalyze the carbonylation of ethylene. On Pt-catalyst, hydration of ethylene occurs and ethyl acetate is formed.

To clarify the optimal conditions of activation, the Pd catalysts were subjected to different types of preliminary treatment.

Impregnated Pd-zeolite catalysts, used without preliminary treatment, are less active than Pd catalysts treated with air or air and H_2 (Table 2). Contacts subjected to preliminary air treatment had lower selectivity with respect to formation of propionic acid than those treated first with air and then with H_2. The same regularities were also observed in ion-exchange Pd-zeolites. After being treated with air, the ion exchange Pd contacts, deposited on a NaM zeolite, showed low selectivity in the formation of propionic acid, and increased selectivity with respect to the formation of esters, i.e., ethyl acetate and ethyl propionate, whose content in the mixtures reached 20-36%.

The influence of the preliminary treatment of the catalysts on their properties that we observed can be explained by the fact that on heating in air, some of Pd introduced in the form of H_2PdCl_4 and $[Pd(NH_3)]_4^{2+}$ is converted into PdO. As shown in [5], the catalytically

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TABLE 1. Influence of Nature of Metal in HSZ-1 Zeolite on Course of Carbonylation of Ethylene [Catalyst — 1% of metal/HSZ-1 (170°C, 60 atm, 2 h); catalyst was treated with air, and then with H_2 at 350°C, 5 h, promoter C_2H_5Br, 5%)]

Metal	Conversion of C_2H_4, mole %	Selectivity of transformation of ethylene, mole %				
		propionic acid	ethanol	ethyl acetate	ethyl propionate	diethyl ketone
Pd	82.6	96.0	2.5	0,5	0,8	0,2
Rh	79.0	84.2	9.5	2.8	2,8	0,7
Ir	41.0	16.7	41.7	41.6	–	–
Pt	82.0	–	38.0	62,0	–	–
Ru	9.0	–	–	–	–	–

TABLE 2. Influence of Preliminary Treatment (350°C, 5 h) and Method of Preparation of Catalyst on Carbonylation of Ethylene [(170°C, 60 atm, CO/C_2H_4 = 1, promoter C_2H_5Br, 3%, 2 h)]

Catalyst	Treatment			Conversion of C_2H_4 mole %	Selectivity of transformation of ethylene				
	without treatment	with air	with hydrogen		propionic acid	ethanol	ethyl acetate	ethyl propionate	diethyl ketone
				Impregnated catalysts					
1% Pd/NaM	+	–	–	70,3	85,2	4,0	4,7	4,8	1,3
As above	–	+	–	81,6	67,7	10,5	10,5	8,8	2,5
»	–	+	+	76,0	89,6	1,5	4,2	3,9	0,8
1% Pd/HSZ-3	–	+	–	90,0	88,1	4,6	3,3	3,2	0,8
As above	–	+	+	100,0	88,9	3,7	3,7	3,0	0,7
0.5% Pd/HSZ-1	+	–	–	69,2	90,3	3,5	3,5	2,6	0,1
As above	–	+	–	63,9	86,3	5,4	5,9	1,8	0,6
»	–	+	+	82,0	85,1	3,9	5,5	4,7	0,8
1% Pd/HSZ-1	+	–	–	64,7	89,5	1,2	4,9	3,8	0,6
As above	–	+	–	80,0	77,0	7,5	7,5	6,0	2,0
»	–	+	+	82,6	96,0	2,5	0,5	0,8	0,2
				Ion-exchange catalysts					
1% Pd/NaM	–	+	–	67,0	52,0	3,2	3,8	33,0	8,0
As above	–	+	+	67,0	90,0	0,7	5,0	3,4	0,9
1% Pd/NaM	+	–	–	71,3	85,7	4,0	4,6	4,6	1,1
As above	–	+	–	79,4	71,5	5,3	10,5	9,9	2,8
»	–	+	+	79,0	84,2	2,0	5,2	7,6	1,0
0.5% Pd/HSZ-1	+	–	–	70,0	91,0	2,9	3,7	1,9	0,5
As above	–	+	–	78,6	82,7	6,6	6,0	4,0	0,7
»	–	+	+	77,0	91,8	0,5	3,6	3,6	0,5

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*Time of reaction 4 h.

TABLE 3. Influence of Duration of Experiment on Carbonylation of Ethylene [(170°C, 40 atm, CO/C_2H_4 = 1, promoter C_2H_5Br, 3%)]

Catalyst	Duration of experiment, h	Conversion of C_2H_4, mole %	Selectivity of transformation of ethylene, mole %				
			propionic acid	ethanol	ethyl acetate	ethyl propionate	diethyl ketone
1% Pd/HSZ-3	2	73,3	79,0	9,0	7,0	4,0	1,0
As above	4	90,0	88,9	3,7	3,7	3,0	0,7
1% Pd/HSZ-1	1	54,0	83,0	1,2	6,0	7,2	1,8
As above	2	77,0	84,1	7,3	5,6	2,2	0,8
»	4	86,0	83,4	6,8	5,0	3,8	1,0

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*Catalysts prepared by impregnation method.

active complex for the carbonylation reaction contains Pd(0). It is possible that PdO formed on the zeolite surface after air treatment is not completely reduced to Pd(0) under the reaction conditions (170°C, 10-40 atm CO), which leads to a decrease in the selectivity with respect to propionic acid and an appreciable increase in selectivity with respect to ethyl acetate, ethyl propionate and ethanol. As shown in [4], in the case of carbonylation of propylene, unreduced PdO passes partially into $Pd(OAc)_2$, which leads to the formation of the above side products of the process. Pd-Zeolite catalysts used in the reaction after drying at

TABLE 4. Influence of Temperature on Carbonylation of Ethylene on 1% Pd/HSZ-1 Catalyst* (40 atm, CO/C_2H_4 = 1, promoter C_2H_5Br, 3%, 2 h)

T., °C	Conversion of C_2H_4, mole %	Selectivity of transformation of ethylene, mole %				
		propionic acid	ethanol	ethyl acetate	ethyl propionate	diethyl ketone
140	43,4	60,4	10,1	26,1	2,7	0,7
150	55,7	73,1	13,0	10,5	2,7	0,7
160	56,0	78,1	10,5	8,2	2,6	0,6
170	77,0	84,1	7,3	5,6	2,2	0,8
180	74,0	78,4	9,9	6,7	4,0	1,0
190	75,3	69,9	16,2	9,3	3,7	0,9

*Prepared by impregnation method.

TABLE 5. Influence of Pressure on Carbonylation of Ethylene on 1% Pd/HSZ-1 Catalyst* (170°C, CO/C_2H_4 = 1, promoter C_2H_5Br, 3%, 2 h)

Initial pressure of mixture, atm	Conversion of C_2H_4, mole %	Selectivity of transformation of ethylene, mole %				
		propionic acid	ethanol	ethyl acetate	ethyl propionate	diethyl ketone
20	56,0	65,5	11,5	18,2	3,8	1,0
40	77,0	84,1	7,3	5,6	2,2	0,8
60	82,6	96,0	2,5	0,5	0,8	0,2
80	82,4	78,1	2,3	16,9	2,2	0,5

*Prepared by impregnation method.

140°C, i.e., without preliminary treatment, contain mainly H_2PdCl_4 or $[Pd(NH_3)]_4^{2+}$, which under the reaction conditions are also partially reduced by carbon monoxide to Pd(0) and are converted into the catalytically active complex. However, as can be seen from Table 2, the conversion of ethylene on these catalysts is lower than on air-treated catalysts.

The best results were obtained by successive treatment of zeolites containing H_2PdCl_4 or $[Pd(NH_3)]_4^{2+}$ by air, and then by H_2 to obtain maximum reduction to metal. The advantages of this treatment are evident from data in Table 2. Pd Contacts subjected to air–hydrogen treatment showed the highest activity and selectivity in the carbonylation of ethylene to propionic acid.

Increase in the duration of the reaction (Table 3) from 3 to 4 h in the presence of 1% Pd/HSZ-3 catalyst leads to an increase in ethylene conversion from 73.3 to 90.0% and increase in selectivity with respect to propionic acid from 79.0 to 88.9%. In the presence of 1% Pd/HSZ-1 catalyst, increase in the duration of the reaction from 1 to 4 h led only to an increase in the conversion of ethylene from 54.0 to 86.0%, but did not decrease the selectivity of ethylene into propionic acid (83-84%), which is apparently due to a different state of Pd in these zeolites varying in composition. The influence of the composition of HSZ-3 and HSZ-1 zeolites on the course of the process was confirmed by special experiments: In the presence of the former, ethanol and ethyl acetate, under the conditions of the carbonylation reaction, slowly transform into propionic acid, while on Pd/HSZ-1 ethanol and ethyl acetate do not react with CO.

We studied the influence of temperature and pressure on the carbonylation reaction on a Pd catalyst. Table 4 shows that the carbonylation of ethylene starts at 140°C. Increase in temperature to 170°C leads to increase in conversion of ethylene and selectivity of the process. Above 170°C, the conversion of ethylene remains practically constant and the selectivity decreases, mainly at the expense of hydration of ethylene into ethanol and formation of ethyl acetate. The carbonylation of ethylene in temperature range studied is not accompanied by the formation of H_2 and CO_2 (due to reaction with water gas) and ethane (as a result of hydrogenation of ethylene). Even at 180-190°C, the residual gas after the reaction has been carried out, contained not more than 1-2% of H_2 and CO_2.

Increase in the total pressure of the CO and C_2H_4 mixture (1:1) from 20 to 80 atm leads to increase in ethylene conversion from 56.0 to 83.0 (Table 5), and the highest selectivity

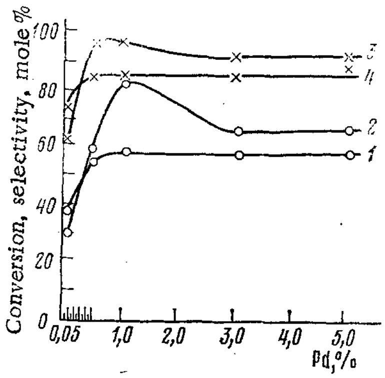

Fig. 1. Influence of Pd content in HSZ-1 zeolite on conversion of ethylene (1, 2) and selectivity of its transformation into propionic acid (3, 4), when the reaction is carried out for 1 h (1, 4) and 2 h (2, 3) (170°C, 60 atm).

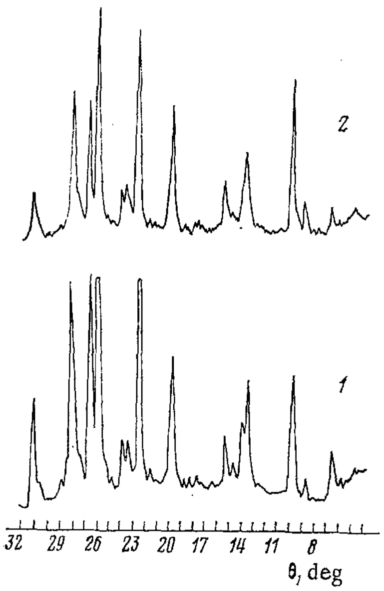

Fig. 2

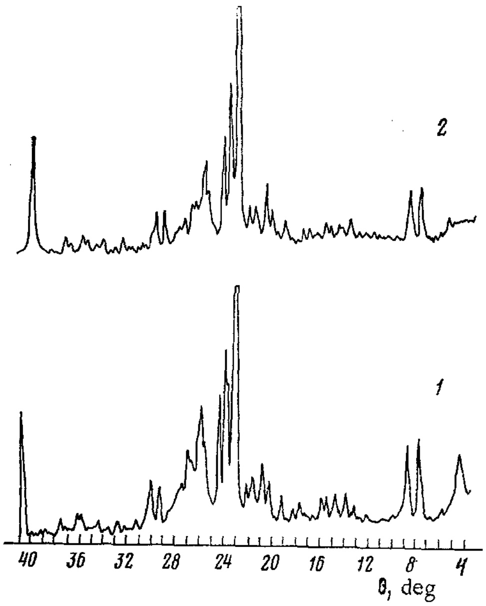

Fig. 3

Fig. 2. X-ray diffraction diagrams of Pd/NaM catalyst before (1) and after (2) carbonylation of ethylene by carbon monoxide. 170°C, 40 atm, 4 h.

Fig. 3. X-ray diffraction diagrams of Pd/HSZ-3 catalyst before (1) and after (2) carbonylation of ethylene by carbon monoxide (170°C, 40 atm, 4 h).

of transformation of ethylene into propionic acid is observed at an initial pressure of 40-60 atm.

We studied the influence of the Pd content in the HSZ-1 catalyst on the course of carbonylation of ethylene under optimal conditions of the process. Figure 1 shows that increase in Pd concentration in the zeolite from 0.05 to 1% leads to increase in the ethylene conversion to 56.0% after 1 h, and to 82.6% after 2 h of the reaction, while the selectivity of formation of propionic acid increased from 63 to 96%. Increase in Pd concentration in the catalyst from 1 to 5% led to a small decrease in activity and selectivity of the catalyst when the reaction was carried out for 2 h. We should note that at a low Pd content (<0.05%), the reaction products contained appreciable amounts of ethanol and ethyl acetate, which indicates the influence of the carrier on the process. Thus, 0.5-1.0% should be considered as the optimal content of catalysts based on HSZ-1 zeolite.

From the data of x-ray diffraction diagrams it is seen that after carbonylation of ethylene, the structure of NaM and HSZ-3 zeolites remained unchanged.

Thus, high-silicon zeolites can be used for the preparation of active, selective, and acid-resistant Pd-catalysts for carbonylation of ethylene into propionic acid.

EXPERIMENTAL

Acetic acid, c.p. brand, bp 118.0-118.1°C, n_D^{20} 1.3700, ethyl bromide, bp 38.4°C. n_D^{20} 1.4239; ethylene with a purity of >99.5%; carbon monoxide from a cylinder, with a purity of >99.7%, were used in the investigation. The mixture of CO and C_2H_4 was used in a ratio of 1:1.

The catalysts were prepared by impregnation and ion-exchange of NaM (SiO_2/Al_2O_3-10), HSZ-1, and HSZ-3 zeolites. Palladium was deposited on the zeolites from a hydrochloric acid solution of $PdCl_2$ in the form of H_2PdCl_4, followed by drying for 5 h at 350°C. For deposition of other metals on the zeolites, aqueous hydrochloric acid solutions of $Ru(OH)Cl_3$, $H_2Pt\cdot Cl_6$, H_2IrCl_6 or $RhCl_3$ were used.

Palladium was introduced into the zeolites by ion exchange from an aqueous solution of $[Pd(HN_3)_4]Cl_2$ and treated in the same way as the impregnated catalysts. After treatment of the catalyst with hydrogen, the residual hydrogen was removed by purging (350°C, 1 h).

Procedure for Carrying Out the Carbonylation Reaction. The experiments were carried out in a rotatory (60 rpm) stainless steel 0.15-liter autoclave. The autoclave was heated by an electric furnace and the heating was controlled by a thermocouple, using EPV1-01 apparatus. The accuracy of maintaining the temperature constant was ±1°C. The initial reaction mixture consisting of C_2H_5Br (0.6-1 g), AcOH (10-15 g), water (3-4 g), and 1 g of catalyst, was charged into a glass ampul, which was placed into the autoclave. The autoclave was closed, purged 3 times with a mixture of CO and C_2H_4 (1:1), pressure was produced by the above mixture, and the apparatus was heated to the working temperature. The reaction was carried out for 1-4 h. After the autoclave was cooled to ∿20°C, a probe of the gas was withdrawn for analysis, and the liquid reaction products were discharged.

Analysis of Reaction Products. The liquid products of the carbonylation reaction were separated from the catalyst by filtration, weighed and analyzed on a LKhM-8MD chromatograph with a flame ionization detector and built-in column (3 m × 3 mm and 1 m × 3 mm). The first part of the column was filled with chromatone N, treated with 3% H_3PO_4 (based on weight of carrier), and 10% poly(ethylene glycol adipate); the second part of the column was filled with porapaq Q. The components were identified by their retention times, and the quantitative content was determined by the calibration method using calibration coefficients. The analysis was carried out at 170°C, with He as gas carrier. The probe was introduced at 275°C.

The residual gas was analyzed on a chromatograph with a heat-conductivity detector on three columns connected by a three-way stopcock. The first column (4 m × 3 mm) was filled with Zikeevskii carrier tripolite with 5% mineral oil, and the gas was separated into narrow fractions. The fraction consisting of H_2, air, CH_4 and CO was separated on the second column (1 m × 3 mm) filled with CaA zeolite. The fraction consisting of C_2H_6, C_2H_4 and CO_2 was separated on a third column (2.7 m × 3 mm) filled with porapaq Q. The gas carrier was He. The analysis was carried out at ∿20°C.

The structural characteristics of the zeolites were determined on an x-ray diffractometer DRON-2.

CONCLUSIONS

1. Among metal zeolite catalysts containing palladium, rhodium, platinum, iridium, and ruthenium, palladium catalysts were found to be most active and selective in the carbonylation of ethylene by carbon monoxide.

2. By x-ray diffraction analysis it was found that the crystalline structure of high-silicon zeolites NaM and superhigh-silicon zeolites scarcely changes under the reaction conditions. There are thus new prospects for the preparation of new effective catalysts for the synthesis of carboxylic acids by carbonylation of olefins.

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SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN IN THE PRESENCE OF Co CATALYSTS CONTAINING HIGH-SILICON ZEOLITES

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Cobalt catalysts on carriers are used as catalysts in the Fischer–Tropsch synthesis [1-5].

We studied the synthesis of hydrocarbons from CO and H_2 in the presence of Co catalysts based on high-silicon zeolites of the pentasil type, obtained by using cobalt carbonate or carbonyl.

EXPERIMENTAL

All the carriers used for the preparation of the catalysts were first calcined for 5 h at 450°C. Some of the catalysts were prepared by mixing freshly prepared Co carbonate with the carrier in a ratio of 1:2. These catalysts were reduced for 4 h in an H_2 current at 450°C, and at a bulk speed (b.s.) of 100 h^{-1}. The carbonyl catalysts were prepared by impregnating the carrier with a dicobalt octacarbonyl $Co_2(CO)_2$ solution in n-hexane. The catalysts were then transferred in an Ar current into the reactor of a flow-type catalytic apparatus, and were treated in an H_2 current (b.s. 25 h^{-1}), while the temperature was raised from 25 to 150°C at a rate of 1 deg/min.

The synthesis of the hydrocarbons was carried out in a flow-type catalytic apparatus under the following conditions: $CO:H_2 = 1:2$, 170-200°C, b.s. = 100 h^{-1}. The liquid products were analyzed by GLC, and the heating was programmed from 60 to 250°C (10 deg/min). Column: 3% apiezone L on chromosorb P (3 mm × 3 m), katharometer.

The chemisorption of CO was studied by pulse chromatography method [6], and the forms of adsorption of CO were studied by the procedure described in [7].

DISCUSSION OF RESULTS

Table 1 shows that for the contacts not containing MgO, at 190°C, the contraction of the synthesis-gas (40%) and the total yield of the products (49 g/nm^3) are practically independent of the zeolite modulus, but the ratio of the liquid and gaseous products are thus not equal. Thus, with increase in the modulus from 42 to 109, the yield of liquid hydrocarbons decreases by a factor of 2, and the yield of the gaseous reaction products almost doubles.

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