OLIGOMERIZATION OF ETHYLENE ON Pd-ALUMINOSILICATE CATALYSTS UNDER PRESSURE

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Impregnated Pd catalyst, which contain an amorphous aluminosilicate (AAS) and a zeolite of the X type [1, 2], are characterized by a high selectivity as regards the dimerization of ethylene at atmospheric pressure. The transformations of C_2H_4 on Pd-containing aluminosilicate catalysts at elevated pressure are studied in the present paper.

DISCUSSION OF RESULTS

As can be seen from Table 1, on the impregnated catalyst 3% Pd—AAS* the olefin conversion passes through a maximum, which is 14.1-15.2% at 10-15 atm, with increase in the pressure from 5 to 20 atm at an C_2H_4 space velocity (SV) of 900 h^{-1}. Here the selectivity of the process as regards dimerization shows little change. With increase in the temperature from 50 to 150°C the degree of ethylene conversion for a pressure of 15 atm is maximum at 100°, and the yield of butenes when based on reacted C_2H_4 is 93.5%. A decrease in the ethylene conversion with increase in the temperature above 100° is evidently related to the reduction of Pd(II) during experiment [3], and also to deactivation of the catalyst (blocking of the active centers) by the adsorbed hydrocarbons (23.2% at 150°).

The oligomerization of ethylene is affected by the SV of the reacting olefin. The C_2H_4 conversion at 15 atm increases with decrease in the SV from 900 to 300 h^{-1} and is 20.1% at 300 h^{-1}. Here the selectivity of the process as regards the formation of butenes decreases slightly.

In the experiments using pressure we used a zeolite-containing impregnated 2% Pd—CaNaX catalyst, which was characterized by a high selectivity as regards the dimerization of ethylene at atmospheric pressure [2], and low-percent ion-exchange and impregnated Pd catalysts based on zeolite CaNaY. From Table 2 it can be seen that on 2% Pd—CaNaX impregnated catalyst the C_2H_4 conversion at 100° passes through a maximum, corresponding to 10 atm and is 19.9% with increase in the pressure from 5 to 15 atm. Here both the yields of C_4H_8 (from 16.5 to 30.4%) and the amounts of hydrocarbons adsorbed on the catalyst (by 1.6 times) increase, while the yield of liquid C_6-C_8 hydrocarbons decreases from 43% to zero. The C_2H_4 conversion at 5-10 atm increases by 1.3-1.6 times with increase in the temperature from 25 to 100°, but the yield of C_4H_8 decreases from 30.9-35.2 to 16.5-19.3% due to the formation of large amounts of liquid hydrocarbons that are adsorbed on the catalyst.

The 0.1% Pd impregnated catalyst, deposited on zeolite CaNaY, exhibits at 10 atm and 100° approximately the same activity as the ion-exchange sample (Table 3). The ethylene conversion was 13-14%. The selectivity of the impregnated catalyst as regards dimerization was higher: the yield of butenes is 7.6%, while the amount of adsorbed hydrocarbons at 100° is 38.2%, which is nearly half of that obtained on the ion-exchange catalyst. Up to 76.1% of hydrocarbons that failed to desorb from the catalyst were formed on the latter. A triple increase in the SV failed to decrease their amount.

When the temperature is raised from 25 to 100°, the degree of C_2H_4 conversion on the impregnated zeolite increases from 3.2 to 13.4% while the yield of C_4H_8 increases from 1.8 to 7.6%. The amount of adsorbed higher hydrocarbons decreases at the same time. The proportion of the redistribution reactions of the hydrocarbons via both carbon and hydrogen

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*The impregnated catalysts are designated as Pd support, while the ion-exchange catalysts are designated as [Pd] support (support - AAS, zeolite).

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TABLE 1. Oligomerization of Ethylene on Pd-Aluminosilicate Catalyst under Pressure (SV = 900 h^{-1})

C_2H_4 pressure, atm	T, °C	C_2H_4 conversion, %	Yield when based on reacted ethylene, %				
			i-C_4H_{10}	α-C_4H_8	trans-β-C_4H_8	cis-β-C_4H_8	adsorbed hydrocarbons
3% Pd – AAS catalyst							
5	100	9,1	–	9,5	65,3	14,4	10,8
10	100	14,2	–	7,7	56,0	25,8	10,5
12	100	14,1	–	9,2	56,7	27,3	6.8
15	100	15,2	–	8,5	58,7	26.3	6,5
20	100	9,7	–	9,0	55,6	25,6	9,8
15	50	3,1	–	8,6	57,7	25,3	8.4
15	130	10,5	1,1	11,0	53,6	27,1	7,2
15	150*	6,5	1,2	7,3	37,7	18,4	22,3
15	100†	16,5	0,8	8,8	55,5	28,1	6.8
15	100‡	20,1	1,2	7,7	57,5	25,8	7,8
4% Pd – AAS catalyst							
–	100**	8,1	–	7,8	61,6	28,2	2,4

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*Yield of C_5–C_8 = 13.1%.

†SV = 600 h^{-1}.

‡SV = 300 h^{-1}.

**Atmospheric pressure.

increases with increase in the temperature, as is evidenced by an increase in the yields of C_3H_8, i-C_4H_{10}, and n-C_4H_{10} (see Table 3).

It is interesting to compare the properties of Pd-aluminosilicate catalysts in the oligomerization of ethylene at atmospheric and elevated pressures. Primarily it should be mentioned that the maximum C_2H_4 conversion at elevated pressure is greater than at atmospheric pressure. Thus, on impregnated 3% Pd–AAS catalyst at 100° and 15 atm the ethylene conversion was 15.2%, whereas at the same temperature and atmospheric pressure it was 8.1% on the 4% Pd–AAS catalyst (see Table 1). As was already mentioned, the selectivity of this catalyst at elevated pressure remains high. It should also be mentioned that both at atmospheric pressure [2] and a pressure of 15 atm the C_2H_4 conversion on the impregnated 3% Pd–AAS catalyst passes through a maximum at 100° when the temperature is raised.

On Pd-containing impregnated and ion-exchange zeolites the C_2H_4 conversion increases when going from atmospheric [2, 4] to elevated pressure, while the selectivity as regards dimerization decreases. On the impregnated 2% Pd–CaNaX catalyst the yield of high-molecular-weight hydrocarbons (when based on reacted ethylene), adsorbed on the catalyst, was 37.9-67.8% at 10-15 atm, whereas at atmospheric pressure it did not exceed 17.7-44.5% [2]. The degree of C_2H_4 conversion at atmospheric pressure and 100° on the same catalyst was 10.1%, while at 10 atm it increased to 19.9% (see Table 2). The selectivity as regards dimerization decreased due to the formation of trimers, tetramers, and other ethylene oligomers. The yield of C_4H_8 was 19.3%.

On the ion-exchange [0.1% Pd]CaNaY catalyst the C_2H_4 conversion at 10 atm and 100° was 3-5% higher than at atmospheric pressure, while the yield of ethylene dimers was lower: 3.5-4.2% under pressure and 31.7% at atmospheric pressure (see Table 3). On the impregnated 0.1% Pd catalyst the degree of C_2H_4 conversion at 10 atm and 100° was 13.4%, i.e., it was 3.3 times higher than at atmospheric pressure under these conditions (see Table 3).

The higher yields of adsorbed hydrocarbons at atmospheric pressure, and especially at elevated pressure, on Pd-zeolites when compared with the Pd–AAS, can apparently be explained by the intense formation of high-molecular-weight hydrocarbons, which under the reaction conditions remain in the zeolite cavities and are not removed when the catalyst is blown with N_2. At both atmospheric and elevated pressure the Pd-zeolites are superior in activity to the Pd–AAS catalyst with a close amount of Pd, but they are inferior to it in selectivity as regards the dimerization of ethylene.

TABLE 2. Oligomerization of Ethylene on Impregnated 2% Pd–0.48CaNaX Catalyst under Pressure (SV = 900 h^{-1})

C_2H_4 pressure, atm	T, °C	C_2H_4 conversion, %	Yield when based on reacted ethylene, %									
			C_3H_8	C_3H_6	i-C_4H_{10}	n-C_4H_{10}	α-C_4H_8	trans-β-C_4H_8	cis-β-C_4H_8	i-C_5H_{12}	C_6—C_8	adsorbed hydrocarbons
5	25	10,1	–	0,2	1,3	1,1	2,5	23,0	9,7	1,3	–	60,9
	100	13,2	–	0,2	1,2	0,6	3,4	8,0	5,1	0,6	43,0	37,9
10	25	12,3	0,2	0,3	3,1	1,6	3,5	18,9	8,5	2,6	15,1	46,2
	100	19,9	0,8	0,8	2,7	1,9	3,4	10,3	5,6	0,8	30,5	43,2
15	100	6,3	–	0,6	3,1	1,0	4,2	17,6	8,6	3,2	–	61,7
–	100 *	10,1	–	–	–	–	7,2	47,4	23,3	–	–	22,1

*Atmospheric pressure.

TABLE 3. Oligomerization of Ethylene on Pd-Zeolite Catalysts under Pressure (SV = 900 h^{-1})

C_2H_4 pressure, atm	T, °C	C_2H_4 conversion, %	Yield when based on reacted ethylene, %									
			C_3H_8	C_3H_6	i-C_4H_{10}	n-C_4H_{10}	α-C_4H_8	trans-β-C_4H_8	cis-β-C_4H_8	i-C_5H_{12}	C_6—C_8	adsorbed hydrocarbons
Impregnated 0.1% Pd – 0.75CaNaY catalyst												
10	25	3,2	1,3	–	2,6	1,3	Traces	1,8	Traces	0,2	–	92,8
	50	8,6	2,8	0,1	14,1	7,5	0,2	2,8	1,3	12,2	–	59,0
	100	13,4	2,5	0,1	16,7	8,0	0,8	4,5	2,3	10,2	16,7	38,2
–	100 *	4,0	–	–	2,5	–	5,3	24,2	12,4	–	–	55,6
Ion-exchange [0.1%Pd]0.75CaNaY catalyst												
10	100	14,2	4,2	0,2	9,2	4,2	0,8	2,2	1,2	5,3	–	72,7
	100 †	12,2	4,3	0,2	7,1	3,8	0,6	1,9	1,0	5,0	–	76,1
–	100 *	9,4 ‡	0,2	1,2	12,1	1,6	2,8	19,7	9,2		51,0	

*Atmospheric pressure.

†SV = 2700 h^{-1}.

‡Yield of C_2H_6 = 2.0, and of i-C_4H_8 = 0.2%.

EXPERIMENTAL

The experiments were run in a flow system under pressure in a 23-mm diameter steel reactor. The C_2H_4 feed rate was regulated with a rotameter under pressure. The liquid and gaseous reaction products were collected at atmospheric pressure and analyzed by the GLC method [2].

In both the amorphous aluminosilicate and zeolite 0.48CaNaX (SiO_2/Al_2O_3 = x = 2.5) the Pd was inserted by impregnation, while in zeolite 0.75CaNaY (x = 4.3) it was inserted by both impregnation and ion exchange. Aqueous $[Pd(NH_3)_4]Cl_2$ solution was used in both cases. Prior to the experiments the catalysts were activated in an air stream at 450-475° and a SV of 600-800 h^{-1}. The length of the experiments was 0.5-1 h. After the experiments the catalysts were blown with N_2 with increase in the temperature up to 200-250°. The hydrocarbons adsorbed on the catalyst, which represented C_2H_4 polymers, were determined during the regeneration of the catalysts with air, which was run under the same conditions as the activation.

CONCLUSIONS

1. At 100°, with increase in the pressure from 5 to 20 atm the degree of ethylene conversion on impregnated Pd—aluminosilicate and Pd—CaNaX catalysts passed through a maximum at 10-15 atm and was 15-20%.

2. Under pressure the impregnated Pd—aluminosilicate catalyst exhibits a high selectivity as regards ethylene dimerization. The yield of butenes when based on reacted ethylene reaches 93.5%.

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REACTION OF VINYL CHLORIDE WITH BROMOFORM AND RELATED COMPOUNDS IN THE PRESENCE OF COORDINATION INITIATORS BASED ON $Fe(CO)_5$

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The reaction of vinyl chloride (VC) with bromoform and related compounds is of interest as a path for the synthesis of pure polychlorobromoalkanes, which are important intermediates in organic synthesis. In [1] we described the telomerization of VC with bromoform and the partial transfer constants of the chain in the presence of benzoyl peroxide (BP). The relative ease of homolytically cleaving the C—Br bond in $CHBr_3$ makes possible a comparative study of the effect of theoretically different initiators and initiating systems on the reaction course.

In the present paper we studied the reaction of VC with $CHBr_3$ in the presence of $Fe(CO)_5$, $Fe(CO)_5$ + DMF, and $Fe(CO)_5$ + hexamethylphosphotriamide (HMPA). The experimental results are given in Table 1. For comparison we have included in the table the experiments run in the presence of BP. As can be seen from Table 1, the telomerization of VC with bromoform occurs in all cases to give telomer homologs of general formula $CHBr_2(CH_2CHCl)_nBr$

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