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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Study of the Catalytic Dehydrochlorination of 1,2-Dichloropropane

Dzh. Yu. Nadzhafov

Azerbaijani State Oil Academy, Baku, Azerbaijan

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Abstract—Catalytic dehydrochlorination of 1,2-dichloropropane in the presence of γ-Al_2O_3, CaX, and haydite was studied. A relationship between the catalytic activity and acidity of the catalysts under study was revealed.

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Development of new high-efficiency techniques for production of C_3H_4 hydrocarbons will make it possible to master manufacture of a wide variety of organic compounds widely used in pulp-and-paper and medical industries, in production of vitamins and mixed fodder, and in chemical industry for manufacture of polymeric materials, including synthetic caoutchoucs, oil additives, and antioxidant agents [1–3].

However, industrial production based on allene and methyl acetylene has not found wide application, which is primarily due to the lack of economically feasible industrial methods for obtaining C_3H_4 hydrocarbons. The existing techniques for production of allene and methyl acetylene have such inherent disadvantages as low yield and selectivity with respect to target products, multistage technology and high process temperature [4, 5]. For example, the only way to obtain C_3H_4 hydrocarbons at present is by pyrolysis of hydrocarbon raw materials. However, their content in the pyrolysis gas does not exceed 0.2–2.0%, which hinders their isolation. In addition, the thus obtained C_3H_4 hydrocarbons contain approximately equal amounts of allene and methyl acetylene, which requires special conditions for their separation.

In [6], data on the activity exhibited in the reaction of dehydrochlorination of 1,2-dichloropropane (DCP) by a number of catalysts, such as industrial aluminosilicate cracking catalyst AS-37, magnesium oxide, sodium and calcium forms of type-X zeolites, and aluminum oxide in optimal conditions for each catalyst, were reported. It was found that γ-Al_2O_3, CaX zeolite, and haydite are the most selective and active catalysts for dehydrochlorination of 1,2-dichloropropane [7].

This communication report results of a comparative study of the gas-phase dehydrochlorination of 1,2-dichloropropane and intermediate reaction products in the presence of γ-Al_2O_3, CaX zeolite, and haydite and of the effect of water vapor on process parameters.

EXPERIMENTAL

As starting raw materials served 1,2-dichloropropane (94–98% purity) isolated by rectification from organochlorine waste formed in synthesis of allyl chloride and propylene chlorohydrin.

The process of catalytic dehydrochlorination of 1,2-dichloropropane and the fundamental aspects of the course of the reactions involved in a conventional flow-through installation with a 10-cm^3 integral reactor were studied. The flow-through installation comprised (Fig. 1) an integral reactor having the form of a quartz glass tube with a total length exceeding by 15–20 cm the furnace length. To make lower the temperature gradient and gradients of the concentrations of the starting raw materials and reaction products, the ratio between the reactor and catalyst grain diameters was 12–30. The reactor tube was equipped with inlet for delivery of gases and liquid reagents and was connected by a ground joint to a cooled receiver for a liquid catalyst. The temperature in the reaction zone was measured with a chromel–alumel thermocouple connected to a dc potentiometer. The thermocouple was preliminarily calibrated (with its cold junctions placed within a test tube in a Dewar vessel with ice). The catalytic reactor was heated with a tubular electric furnace with a temperature control system. The tube was charged with 5 ml of a catalyst placed in the reactor between two layers of quartz sand (particle size 3 mm). The end of the thermocouple pocket was in the middle of the catalyst bed. The reactor was carefully inserted into the furnace so that the catalyst bed was situated at that place of the furnace in which the temperature gradient is zero and then fixed in this position. The reactor was connected to the system for delivery of raw materials and removal of reaction products.

Liquid raw materials were delivered through an evaporator with an electromechanical syringe batching unit. The system for collection of liquid products comprised a trap and Dewar and Marriott vessels. The volume of gases being formed was determined from the volume of brine displaced from the Marriott vessel.

The experiments were performed in the vapor phase at temperatures in the range 300–500°C under atmospheric pressure. The starting raw materials and reaction products were analyzed by GLC. Gaseous reaction products were analyzed on a chromatograph with a heat-conductivity detector on a 6-m-long compound column: 4 m, with fixed TEGNM liquid phase supported in an amount of 20 wt % by INZ-600 Inza brick; and 2 m, with 3.0 wt % Vaseline oil on a tripoli powder from the Zikeevo open pit. The products were preliminarily neutralized and dried over activated aluminum oxide. Aluminum oxide sieved with 0.25–0.5-mm mesh was prepared by calcination at 750°C for 7 h and subsequent cooling in a desiccator to room temperature. Liquid reaction products were analyzed in the isothermal mode at 120°C an detector current of 110 mA on a 3-m column packed with tricresyl phosphate (18%) supported by N-AW Chromaton.

Products of the thermocatalytic conversion of 1,2-dichloropropane are a complex mixture of various organic (organochlorine) compounds, which are separated upon cooling to –10 to 0°C into two phases, liquid and gaseous.

The gas phase contains methane, ethylene, propane, propylene, allene, methyl acetylene, and

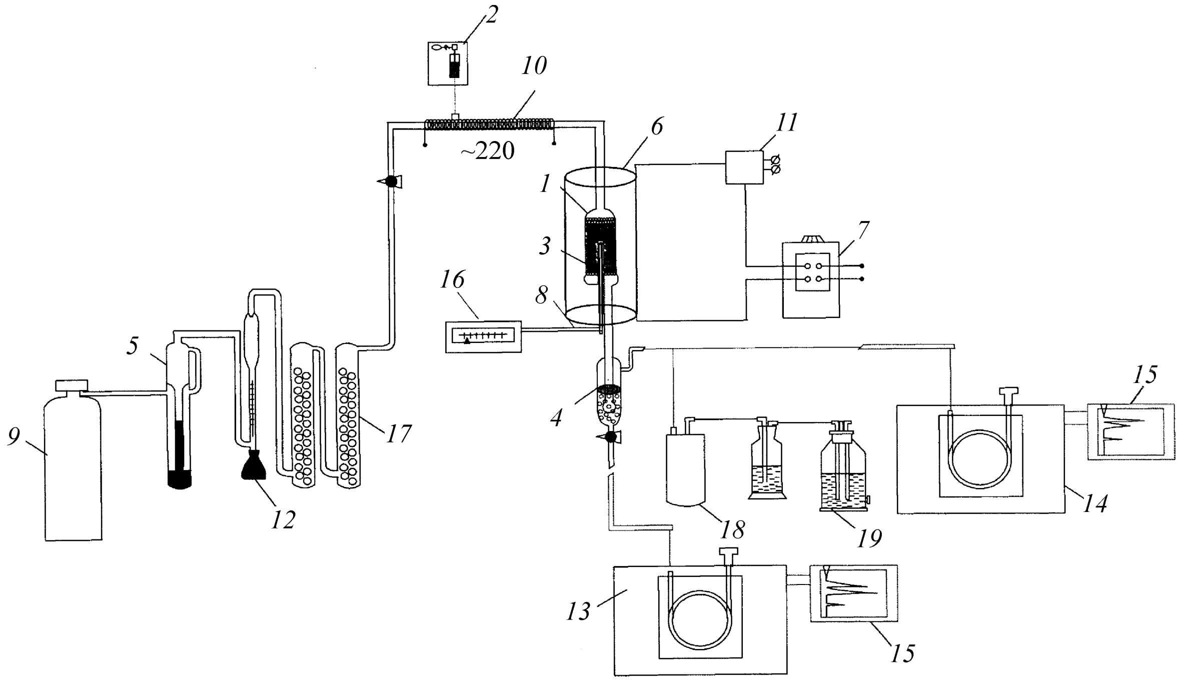

Fig. 1. Schematic of the flow-through catalytic installation. (*1*) Quartz reactor, (*2*) syringe batching unit for delivery of liquid products, (*3*) thermocouple pocket, (*4*) cooled ampule-receiver for liquid catalyzate, (*5*) rheometer, (*6*) electric furnace, (*7*) laboratory autotransformer or controlling potentiometer, (*8*) measuring thermocouple, (*9*) cylinder for supply of gases, (*10*) evaporator, (*11*) autotransformer, (*12*) foam meter of the gas flow rate, (*13*) liquid chromatograph, (*14*) gas chromatograph, (*15*) recording device, (*16*) dc potentiometer, (*17*) columns for drying and purification of gases, (*18*) Dewar vessel, and (*19*) Marriott vessel.

Table 1. Effect of temperature on the dehydrochlorination of 1,2-dichloropropane in the presence of γ-Al_2O_3 and CaX. Contact duration 7.4 s, raw material delivery rate 6.2 g h^{-1}

Reaction products	Content, wt %, at indicated temperature, °C		
	300	400	500
γ-Al_2O_3			
Composition (wt %):			
gas phase	4.2	8.9	10.1
liquid phase	78.5	73.0	66.7
hydrogen chloride	10.3	14.2	16.9
densification products	1.9	2.8	4.3
loss	5.1	1.1	2.0
Composition of the gas phase (mol %):			
methane	0.2	0.2	0.2
ethylene	20.1	26.8	15.9
propane	0.7	0.9	0.6
propylene	50.2	34.1	48.8
allene	3.4	5.6	4.9
methyl acetylene	19.7	28.5	25.3
ΣC_4	5.7	3.9	4.3
CaX			
Composition (wt %):			
gas phase	12.2	20.3	21.3
liquid phase	51.3	41.0	35.0
hydrogen chloride	23.5	25.6	31.4
densification products	8.5	9.7	11.2
loss	4.5	3.4	1.1
Composition of the gas phase (mol %):			
methane	0.2	0.4	0.2
ethylene	10.4	7.1	8.0
propane	1.0	1.2	1.3
propylene	57.0	48.8	53.9
allene	25.5	35.9	30.0
methyl acetylene	4.2	5.2	5.5
ΣC_4	1.7	1.4	1.1

C_4 hydrocarbons. The liquid phase concentrates unconverted raw materials, chloropene isomers, and trace amounts of macromolecular products. In discussion of the experimental data, changes occurring in the composition of the gaseous and liquid phases will be considered.

As follows from the data in Tables 1 and 2, the conversion of 1,2-dichloropropane and the redistribution of the reaction products in the liquid and gaseous phases depend on the nature of a catalyst.

The process on the γ-Al_2O_3 catalyst yields hydrocarbon gases in which about 80% are C_2–C_4 hydrocarbons (Table 1). In the thermocatalytic conversion of 1,2-dichloropropane at 30°C, the main products in the gas phase are ethylene, propylene, and the allene–methyl acetylene fraction whose contents are 20.1, 50.2, and 23.1%, respectively. As the process temperature is raised from 300 to 500°C, the amounts of ethylene and propylene decrease to 15.9 and 48.8%. The maximum content of allene and methyl acetylene in the gas phase, 34.1 mol %, is reached at a temperature of 400°C. In the temperature range under study, the process performed at 400°C yields the smallest amount of the liquid phase. On raising the process temperature to 500°C, the conversion of the starting raw material increases from 35.3 to 54%.

Experimental data on the temperature dependence of the dehydrochlorination of DCP in the presence of CaX are listed in Table 1. It can be seen that the conversion of the raw material and the volume of the resulting gas phase grow with increasing temperature. The temperature dependences of the conversion of DCP and of the concentration of the reaction products formed in steam conversion of DCP on CaX and γ-Al_2O_3 catalysts were found to be different. It should be noted that the process performed on CaX is characterized, in contrast to that on γ-Al_2O_3, by a comparatively high content of allene on the background of a lower content of methyl acetylene. The maximum yield of the allene–methyl acetylene fraction (41.1%) was reached in a process performed at 400°C. The fact that allene is predominantly formed in the presence of CaX suggests that the reaction of allene isomerization into methyl acetylene does not occur, i.e., differences in the nature of active centers in the CaX and γ-Al_2O_3 catalytic systems are manifested.

Table 2 presents experimental data on how the process temperature affects parameters of the reaction of DCP dehydrochlorination on haydite. The data are indicative of an extremal dependence of the yield of, and selectivity for allene and methyl acetylene on the process temperature. At 400°C, haydite shows the lowest activity and the conversion of raw materials does not exceed 35%. As the process temperature is raised to 450°C, the temperature dependence of the product yield somewhat changes, which leads to an increase in the yield of allene and methyl acetylene, with their total yield reaching the maximum value of 79%.

Raising the process temperature to 500°C results in that the yield of allene and methyl acetylene decreases on the background of a rise in the formation of ethylene, propylene, densification products, and hydrogen chloride. As a consequence, their relative amounts change in favor of destruction products. The fact that the ratio between allene and methyl acetylene in the gas phase is 7 : 1 indicates that no isomerization of allene into methyl acetylene occurs in the presence of haydite.

The results obtained give reason to believe that dehydrochlorination of DCP on the catalytic systems under consideration occurs by various pathways, with acid centers of varied nature involved. For example, mostly methyl acetylene is formed in the presence of aluminum oxide, and allene, on CaX and haydite. As follows from the data in Tables 1 and 2, the total yield of the allene–methyl acetylene fraction per the delivered raw material also differs from that per aluminum oxide. The yield of the target fraction in the presence of haydite substantially exceeds the amount of allene and methyl acetylene formed on CaX and aluminum oxide. Here, as also in the case of CaX, predominant formation of allene is observed (Table 2). On the basis of the experimental data obtained in conversion of 1,2-dichloropropane to give methyl acetylene, the catalysts under study can be arranged in order γ-Al_2O_3 > CaX > haydite.

For the reaction of 1,2-dichloropropane dehydrochlorination accompanied by the formation of allene, the sequence is different: haydite > CaX > γ-Al_2O_3.

The diagram in Fig. 2 presents the qualitative-quantitative hydrocarbon composition of the liquid phase, obtained in dehydrochlorination of 1,2-dichloropropane on γ-Al_2O_3, CaX, and haydite. The comparative results make it possible to arrange the catalysts under study in order of decreasing quantitative yield of the liquid phase as γ-Al_2O_3 > CaX > haydite.

A comparatively high content of 1,2-dichloropropane was observed when the process was performed on γ-Al_2O_3, and the lowest, on CaX. The contents of 1- and 2-chloropropene in the catalyzate are very close on all the catalysts. A different situation was observed for 3-chloropropene: it is hardly formed on γ-Al_2O_3, whereas on CaX and haydite, its content is 2.2 and 3.9%, respectively. Under the same conditions, the lowest yield of 2-propane was observed on γ-Al_2O_3 (1.28%) and reached values of 4 and 6.8% on, respectively, CaX and haydite.

Table 2. Effect of temperature on the dehydrochlorination of 1,2-dichloropropane on haydite. Contact duration 10.5 s, raw material delivery rate 6.2 g h^{-1}

Reaction products	Content, wt %, at indicated temperature, °C		
	400	450	500
Composition (wt %):			
gas phase	26.0	30.9	33.5
liquid phase	59.3	49.1	44.5
hydrogen chloride	13.2	18.3	20.1
densification products	1.0	1.3	1.4
loss	0.5	0.4	0.5
Composition of the gas phase (mol %):			
methane	8.5	5.5	4.8
ethylene	24.5	14.0	27.5
propane	–	–	–
propylene	1.4	1.5	1.8
allene	57.7	69.2	57.2
methyl acetylene	7.9	9.8	8.7
ΣC_4	–	–	–

These, to a certain extent ambiguous, results demonstrate that the reaction mechanism is rather intricate. To elucidate the mechanism by which hydrocarbons are formed from DCP on γ-Al_2O_3, and also on CaX zeolite and haydite, the conversion of intermediate dehydrochlorination products was studied: 2-chloropropane (**1**), 1-chloropropene-1 (**2**), 2-chloropropene-1 (**3**), and 3-chloropropene-1 (**4**) (Table 3).

The dehydrochlorination of the intermediate products (1-chloropropene-1, 2-chloropropene-1, and 3-chloropropene-1) on γ-Al_2O_3 is accompanied by unequal amounts of C_3H_4 hydrocarbons in the gas phase. The yield of methyl acetylene is the highest in conversion of 2-chloropropene-1. The main product in

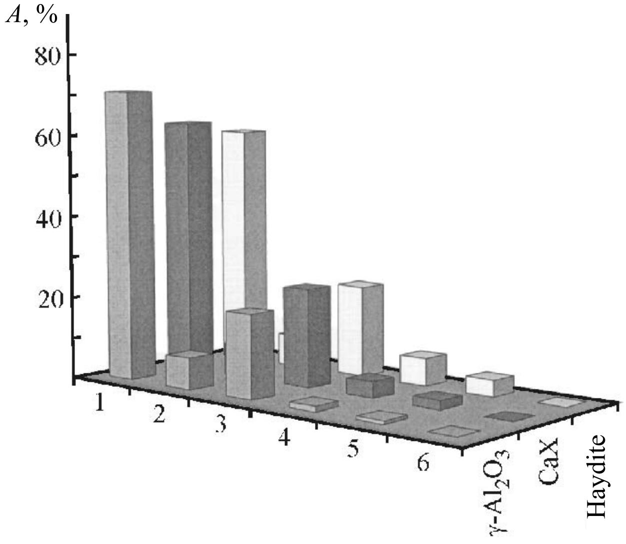

Fig. 2. Content of hydrocarbons in the liquid phase formed in dehydrochlorination of 1,2-dichloropropane on catalysts of varied nature under reaction cycle conditions. $T = 400°C$, contact duration 10.5 s, raw material delivery rate 6.2 g h^{-1}. (*A*) Yield of products, conversion. (1) 1,2-Dichloropropane, (2) 1-chloropropene, (3) 2-chloropropene, (4) 2-chloropropane, (5) 3-chloropropene, and (6) C_3H_6 oligomers + C_3H_4 oligomers.

the liquid phase in conversion of 2-chloropropane is 2-chloropropene-1; however, its yield is substantially lower than that in conversion of 1,2-dichloropropane (Fig. 2). The yield of the allene–methyl acetylene fraction in conversion of the intermediate chlorine-containing hydrocarbons on aluminum oxide is lower than that in conversion of 1,2-dichloropropane.

In dehydrochlorination of 2-chloropropanein the presence of CaX, as also in that of 1,2-dichloropropane, 2-chloropropene-1 is formed in the highest yield. The experimental data on dehydrochlorination of the intermediate products on CaX indicate that the yield of allene is the highest in conversion of 2-chloropropane; that of methyl acetylene, in the case of 1-chloropropene-1; predominant formation of propylene and ethylene in the gas phase is characteristic of 3-chloropropene-1.

A similar set of experiments was also performed in the presence of haydite. Their results demonstrate that 2-chloropropene-1 is the main source of allene formation on CaX and haydite, and 1-chloropropene-1, that of methyl acetylene. In contrast to the rest of the catalysts, allene is mostly formed from 2-chloropropane on γ-Al_2O_3, and methyl acetylene, from 2-chloropropene.

The dependence of allene and methyl acetylene formation in dehydrochlorination of the intermediate products (1-chloropropene-1, 2-chloropropene-1, 2-chloropropane, and 3-chloropropene-1) and the starting 1,2-dichloropropane on γ-Al_2O_3, CaX, and haydite confirms the rather good consistency of the process mechanism (Table 4). The largest allene : methyl acetylene ratio is characteristic of dehydrochlorination of 1,2-dichloropropane and 2-chloropropene on CaX and haydite (6.90 and 7.30, and 7.70 and 8.19, respectively), whereas on aluminum oxide, this parameter is substantially smaller and does not exceed 0.2, with the total content of the allene–methyl acetylene in the presence of this catalyst also being the lowest. In addition, irrespective of a raw material under study, the dehydrochlorination reaction in the presence of aluminum oxide mainly yields methyl acetylene and an insignificant amount of allene, which is, probably, a consequence of the allene–methyl acetylene isomerization at the catalyst surface. From the results of a thermodynamic calculation [7, 8] of the isobaric-isothermal potential of the reaction of structural isomerization of methyl acetylene into allene and of allene into methyl acetylene, depending on temperature, follows that the formation of methyl acetylene from allene must be spontaneous, whereas the rearrangement of methyl acetylene into allene has thermodynamic limitations. Thus, the experimental results obtained when performing dehydrochlorination of 1,2-dichloropropane and its chlorine-containing hydrocarbons in the presence of γ-Al_2O_3 are in good agreement with the theoretical predictions.

On the whole, the transformation of 1,2-dichloropropane and 2-chloropropene is characterized by the same type of conversion of raw materials and similar qualitative compositions of the reaction products for CaX and haydite. In the case of aluminum oxide, the composition is different and the process occurs under the active of surface active centers of a different nature [9].

In numerous heterogeneous catalytic reactions, e.g., in synthesis of hydrocarbons, the water molecule is regarded as a reactant or a reaction product. An insignificant amount of water can strongly affect the reaction selectivity as, e.g., in the catalytic hydrogenation of benzene over metallic ruthenium. The effect of water vapor on parameters of the dehydrochlorination of 1,2-dichloropropane was studied by its introduction into the reaction zone.

The formation of the allene–methyl acetylene

Table 3. Comparative reactivities in thermocatalytic conversion of chlorine-containing C3 compounds

Reaction products	Content, wt %, in the presence of indicated catalysts											
	1	2	3	4	1	2	3	4	1	2	3	4
	γ-Al_2O_3				CaX				haydite			
Composition (wt %):												
gas phase	43.6	29.1	38.6	20.2	52.8	36.0	43.2	19.4	53.4	44.4	48.0	40.00
liquid phase	38.3	40.7	31.9	52.8	30.4	31.3	23.5	46.4	35.3	30.1	26.6	39.6
hydrogen chloride	12.3	11.1	12.2	11.1	11.5	19.9	20.0	19.1	10.0	2.0	1.0	0.7
densification products	1.6	14.0	14.5	12.8	0.3	10.7	11.0	11.4	0.2	23.4	24.2	19.6
loss	1.1	5.1	2.4	3.1	5.0	2.1	2.3	3.7	1.1	0.1	0.2	0.1
Composition of the gas phase (mol %):												
methane	0.6	0.5	0.6	0.2	0.4	0.4	0.5	0.4	4.6	5.4	6.9	8.5
ethylene	24.8	25.3	24.5	37.2	6.6	7.2	6.9	12.5	9.0	22.1	20.7	19.6
propane	2.0	2.8	1.5	0.8	1.0	1.2	1.4	0.5	2.0			1.5
propylene	53.7	38.9	38.4	35.4	35.5	37.7	38.6	53.4	71.4	1.3	1.6	1.1
allene	4.3	3.6	3.5	2.3	43.4	5.9	43.9	17.8	7.0	14.8	63.1	56.1
methyl acetylene	11.6	24.3	26.9	16.2	11.3	43.4	5.7	13.4	6.0	56.4	7.7	13.2
ΣC_4	3.0	4.6	4.6	7.9	1.8	4.2	3.0	2.0	–	–	–	–
Composition of the liquid phase (mol %):												
1,2-dichloropropane	3.4	–	–	–	2.6	50.2	–	–	–	–	–	–
1-chloropropene	4.4	45.2	42.2	–	3.7	49.7	37.1	13.9	3.4	49.0	38.7	12.5
2-chloropropene	12.6	54.6	57.4	36.3	8.8	–	62.6	32.9	9.1	43.3	57.5	15.4
2-chloropropane	77.5	–	–	1.5	79.6	0.1	–	3.5	78.6	–	–	–
3-chloropropene	0.8	0.2	0.4	62.2	–	–	0.3	49.7	–	5.2	–	70.8
C_3H_4 oligomers	0.6	–	–	–	–	–	–	–	1.5	2.4	1.9	0.5
C_3H_6 oligomers	0.7	–	–	–	–	–	–	–	7.4	0.1	1.9	0.8

fraction may be due to presence of both basic and acid centers: however, the substantially higher content of methyl acetylene, compared with allene, results from the action of the stronger acid centers [10]. It is known that adsorption of water vapor on the surface of γ-Al_2O_3 in amounts of up to 8 mmol g^{-1} results in a strong increase in the concentration of basic centers and acid centers are transformed to become weaker. If it is assumed that acid-base active centers of moderate strength are involved in the dehydrochlorination of chlorine-containing C_3 hydrocarbons, then performing the reaction in the presence of water vapor must lead to a higher yield of dehydrochlorination products. The data in Table 5 demonstrate that, as expected, the yield of products in dehydrochlorination of chlorine-containing C_3H_4 hydrocarbons on aluminum oxide is higher in the presence of water, compared with that without water, which is, probably, due to appearance of additional

Table 4. Allene : methyl acetylene ratio in the reaction of catalytic dehydrochlorination

Composition of raw materials	Allene : methyl acetylene		
	γ-Al_2O_3	CaX	haydite
1,2-Dichloropropane	0.17	6.90	7.30
1-Chloropropene	0.15	0.14	0.26
2-Chloropropene	0.13	7.70	8.19
2-Chloropropane	0.37	3.80	3.58
3-Chloropropene	0.14	1.33	1.99

Table 5. Catalytic conversion of 1,2-dichloropropane in the presence of water vapor. Contact duration 7.4, water vapor : DCP molar ratio = 1 : 1, raw material delivery rate 6.2 g h^{-1}

Reaction products	Content, wt %		
	γ-Al_2O_3	CaX	haydite
Composition (wt %):			
gas phase	10.8	22.3	28.2
liquid phase	75.0	45.1	53.7
hydrogen chloride	11.6	23.0	14.0
densification products	1.7	8.7	3.5
loss	0.9	0.9	0.6
Composition of the gas phase (mol %):			
methane	0.1	0.3	7.8
ethylene	23.7	4.0	22.1
propane	0.4	0.7	–
propylene	29.3	50.1	2.1
allene	3.6	37.7	59.6
methyl acetylene	31.9	5.5	8.4
ΣC_4	8.0	1.7	–
Composition of the liquid phase (mol %):			
1,2-dichloropropane	43.9	51.2	54.2
1-chloropropene	11.3	8.8	8.2
2-chloropropene	34.9	26.4	21.7
2-chloropropane	9.2	9.7	9.6
3-chloropropene	0.1	3.5	6.3
C_3H_4 oligomers	0.6	0.2	–
C_3H_6 oligomers	–	0.2	–

basic centers on the catalyst surface and to weakening of the strength of the acid centers.

Introduction of water vapor into the reaction zone in dehydrochlorination of 1,2-dichloropropane in the presence of CaX and haydite hardly causes a redistribution of the reaction products.

An important specific feature of the catalysts under study is the simultaneous presence on their surface of Brønsted and Lewis acid centers, with no possibility of varying properties of centers of one type without changing those of the other type. Therefore, a study was performed in order to determine the nature and strength of all types of centers and acid-base interaction of starting reagents, reaction products, and water vapor with these centers. It is known that the acidity of catalysts can be determined by such methods as ion exchange, indicator technique, method of adsorption of volatile amines, and IR spectroscopy [11–14]. It was shown in the present study that the nature of acid centers on the surface can be determined under conditions close to real operation conditions of a catalyst (in situ). This technique consisted in the following: isomerization of butene-1 was performed on the surface of the starting catalyst sample, with analysis of the isomer composition of butenes-2; in the steady mode of the reaction of dehydrochlorination of 1,2-dichloropropane in the presence of water vapor, butene-1 was delivered into the reaction zone and changes in the concentration of the isomers, allene, and methyl acetylene in the reaction products were analyzed; as the reaction of dehydrochlorination was complete, isomerization of butene-1 was again performed on the catalyst surface. The uniqueness of this method is in that, being nonstationary, it enables studies under steady process conditions when the rates of all the reaction stages and the state of the catalyst remain invariable.

Butene-1 was isomerized on CaX, haydite, and γ-Al_2O_3 in the flow-through mode at a temperature of 350°C, atmospheric pressure, and volumetric flow rate of butene-1 equal to 120 h^{-1}. Butene-1 was produced by dehydration of *n*-butanol on aluminum oxide treated with 0.05 wt % KOH, which favored poisoning of strong acid centers and made it possible to obtain a product containing 94–95% butene-1.

Figure 3 presents data on properties of various acid centers of the catalysts, as determined by performing isomerization of butene-1 on their surface. The high yield of the *cis*-isomer on aluminum oxide is probably due to the large amount of Lewis acid centers and the possibility of co-existence of aluminum cations in different coordinations (CN = 6, 5, 4) predetermines their sufficiently high strength. It should be noted here that the formation of the *trans*-isomer, which mostly occurs on Brønsted acid centers, is not so intense because its yield is nearly two times lower than that of the *cis*-isomer.

The results of a study of the isomerization of butene-1 on CaX suggest that there are surface acid centers with nearly equal strengths. The higher yields of *trans*-butene-2, compared with those on aluminum oxide, can be attributed to structural bridge OH groups situated on the outer surface and on defects in zeolite crystals.

The Brønsted centers of haydite are also sufficiently

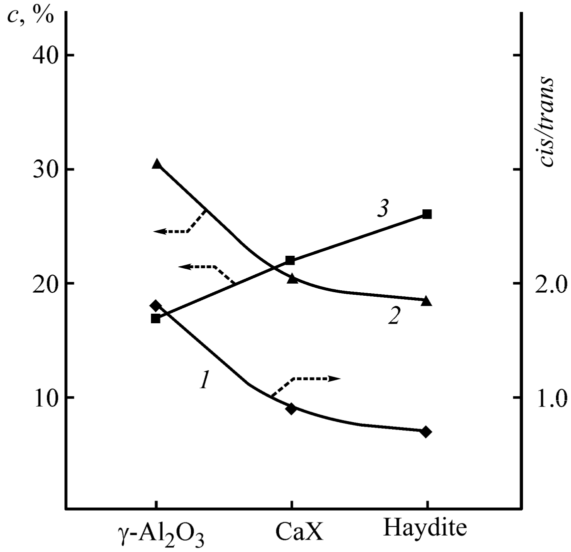

Fig. 3. Dependence of the isomer yield c on the catalyst nature. (*1*) *cis/trans*-butene-2 ratio, (*2*) *cis*-butene-2, and (*3*) *trans*-butene-2.

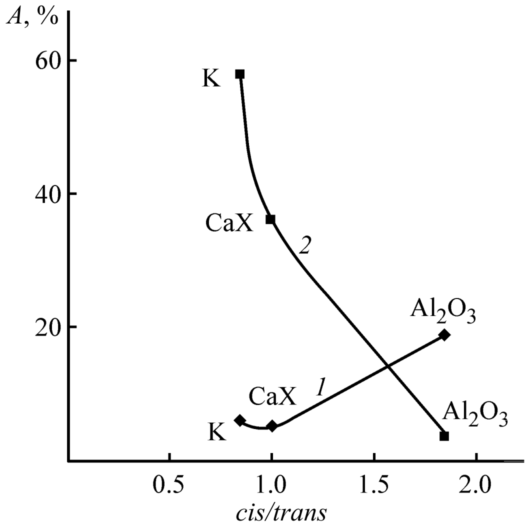

Fig. 4. Dependence of the yield *A* of products formed in joint dehydrochlorination of 1,2-dichloropropane and isomerization of butene-2 on the isomer ratio. (*1*) Methyl acetylene and (*2*) allene.

strong, with the strength of the centers substantially exceeding that for previously studied catalysts. The high Brønsted acidity is possibly a consequence of the formation of Al–O–Si and Fe–O–Si bridges in which SiOH enhances the overall acidity of iron–aluminum–silicon fragments on the periphery.

Figure 4 presents data on the yield of allene and methyl acetylene in dehydrochlorination of 1,2-dichloropropane in the presence of water and in joint isomerization of butene-1. Analysis of the target and isomeric reaction products reveals the following behavior: the small ratio between *cis* and *trans* isomers on CaX and haydite is characterized by a high yield of allene and low yield of methyl acetylene, whereas a large ratio between the isomers (in the case of aluminum oxide), by low yield of allene and more than four times higher yield of methyl acetylene. The so large ratio between the components of the allene–methyl acetylene fraction in the case of aluminum oxide assumes that structural isomerization occurs in the presence of Lewis acid centers. At the same time, introduction of water vapor into the reaction zone leads to dissociated adsorption of water molecules and to an increase in the strength of Brønsted acid centers, with partial blocking of Lewis acid centers, which causes, in the end, an overall decrease in the yield of the allene–methyl acetylene fraction.

Thus, a possible mechanism of the reaction of dehydrochlorination of 1,2-dichloropropane to give allene and methyl acetylene on γ-Al_2O_3, CaX, and haydite can be suggested. An analysis of possible correlations between the catalytic activity and the acidity of the catalysts demonstrated that allene is mostly formed on Lewis acid centers, whereas methyl acetylene is formed on Brønsted acid centers. The use of isomerization of butene-1 made it possible to reveal a number of fundamental distinctions between the acid centers on the surface of the catalysts under study. Performing the process in the presence of water hardly affects the redistribution of the reaction products. Possessing stronger Brønsted acid centers, haydite is the most active among other catalysts (CaX and aluminum oxide) for dehydrochlorination of 1,2-dichloropropane to give allene and methyl acetylene.

CONCLUSIONS

(1) The conversion of 1,2-dichloropropane and the formation selectivity of allene and methyl acetylene are affected both by the nature of a catalyst and by the temperature, partial pressure, and contact duration.

(2) Among the heterogeneous catalysts (γ-Al_2O_3, CaX, and haydite) used to obtain allene and methyl acetylene, haydite is the most promising because of the high rate of elimination of 1,2-dichloropropane, ready availability, and process selectivity. The optimal process conditions are found.

(3) The haydite catalyst remains unchanged in regeneration, is stable during no less than 20 min, and provides a 70.9% conversion of raw materials at a 22% yield of target products.

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