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Decomposition of Chlorinated Hydrocarbons on Iron-Group Metals

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Abstract—The decomposition of 1,2-dichloroethane and chlorobenzene on nickel–alumina, cobalt–alumina, and iron–alumina catalysts at 400–600°C was studied. Thermodynamic calculations demonstrated that the susceptibility of metals to chlorination under exposure to HCl increases in the order Ni < Co < Fe. The addition of hydrogen to the reaction mixture was found to dramatically decrease the rate of carbon deposition in the decomposition of 1,2-dichloroethane because of the intense hydrogenation of intermediates that are graphite precursors. Two fundamentally different reaction paths were found in the degradation of 1,2-dichloroethane: decomposition via a carbide-cycle mechanism with the formation of carbon as the main product (under conditions of a deficiency of hydrogen) and 1,2-dichloroethane hydrodechlorination accompanied by methanation of the formed carbon (under conditions of an excess of hydrogen). The degradation of chlorobenzene diluted with hydrogen in a molar ratio of 1 : 50 was not accompanied by carbon formation on the catalyst. A comparison between the selectivity for reaction products on nickel–alumina and cobalt–alumina catalysts indicated that the former catalyst is more active in the rupture of C–C bonds and in the methanation reaction of deposited carbon, whereas the latter is more favorable for hydrodechlorination. The optimum conditions and thermal regime for efficient and stable operation of the catalysts were found.

INTRODUCTION

A study of the decomposition of chlorinated hydrocarbons on iron-group metals is of interest both from the standpoint of fundamental science and for the development of a procedure for neutralizing these compounds, which are industrial waste constituents. The catalytic conversion of chlorinated hydrocarbons has been described in a number of Russian and foreign publications [1–5].

It is well known that hydrocarbons are decomposed on iron-group metals by a carbide-cycle mechanism [6–12]. According to this mechanism, a hydrocarbon initially undergoes adsorption and decomposition on a metal particle to form unstable surface carbides. The carbides are decomposed to release atomic carbon, which diffuses through the bulk metal particle to the sites at which a graphite phase is formed. Thus, carbon and hydrogen are formed in the decomposition of chlorine-free hydrocarbons on iron-group metals. This decomposition of hydrocarbons by a carbide-cycle mechanism lent impetus to a study of the behavior of chlorinated hydrocarbons under the above conditions. We examined the decomposition of chlorinated aliphatic and aromatic hydrocarbons, namely, 1,2-dichloroethane and chlorobenzene. We found that these compounds also decomposed with the formation of carbon and hydrogen, whereas chlorine, which is a constituent of the molecules, was bound to hydrogen and was removed as HCl.

This work was devoted to studying the decomposition of chlorinated hydrocarbons on iron-group metals in order to develop a new procedure for neutralizing these compounds.

EXPERIMENTAL

Four different catalysts based on iron-group metal catalysts were synthesized. Three of these catalysts were prepared by the coprecipitation of nickel (cobalt, iron) and aluminum nitrates at a constant pH of the solution. The nickel–alumina (Cat 1), cobalt–alumina (Cat 2), and iron–alumina (Cat 3) catalysts were prepared by coprecipitation at pH 10, 9, and 10, respectively. The precipitates were allowed to stand in the mother liquor for a day; thereafter, they were washed with a tenfold volume of distilled water, dried, and calcined at 330°C for 1 h. The fourth catalyst (Cat 4) was prepared through mechanical activation of a mixture of nickel oxide and hydrargillite (in a proportion of 3.6 g of NiO to 0.6 g of hydrargillite); the activation time was $\tau = 5$ min. The samples were mechanochemically activated in an ARO-2 planet-centrifuge mill (power of 800 W; sample weight of 10 g; rotational speed of cylinders of 10 s^{-1}).

Figure 1 demonstrates a schematic diagram of the flow reactor with a McBain balance. A catalyst sample was placed in quartz basket *12*, which was suspended on graduated quartz spring *7* by quartz filament *10*. The extension factor k of the coil was equal to 100 mm/g.

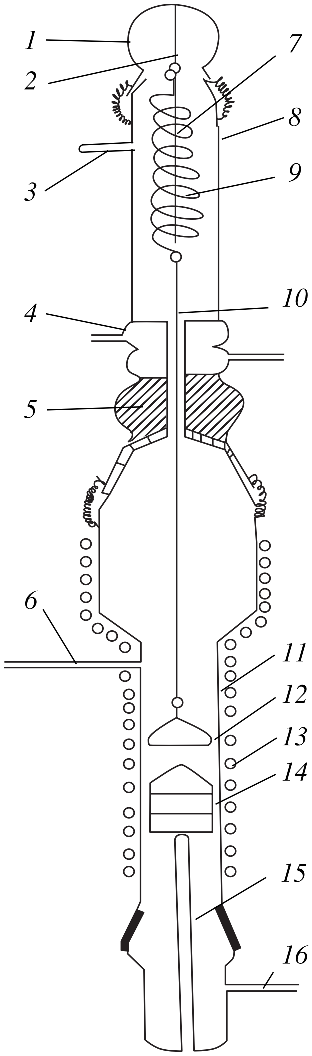

Fig. 1. Schematic diagram of the reactor with a McBain balance: (*1*) stopper, (*2*) hook, (*3*) argon supply tube, (*4*) condenser, (*5*) asbestos insulating lining, (*6*) reactant supply tube, (*7*) quartz spring, (*8*) jacket, (*9*) reference point, (*10*) quartz filament, (*11*) reactor body, (*12*) basket, (*13*) voltage winding, (*14*) stack, (*15*) thermocouple well, and (*16*) gas vent.

The extension of the spring was measured with a cathetometer to within 0.01 mm using reference point *9*. The sensitivity of the McBain balance was 1×10^{-4} g. This procedure allowed us to monitor changes in sample weight immediately in the course of the experiments and to study the kinetics of carbon deposition on catalysts [13]. To prolong the time of contact between a catalyst and a gas and, hence, to increase the conversion of a chlorine derivative, we constructed so-called stack *14*. The stack consisted of three identical quartz baskets, which were joined to each other at a spacing of 1.1 cm to form a single system. This system was mounted on thermocouple well *15* in a temperature plateau zone of the reactor.

The catalyst weight varied from 0.1 to 0.7 g. Before each experiment, the catalyst was reduced *in situ* in a hydrogen flow either at a constant temperature of 300°C for 30 min or by gradually heating the reactor to a reaction temperature of 400–600°C for 1.5–2 h. The completeness of catalyst reduction was monitored with the McBain balance: a constant mass of the sample was indicative of its complete reduction.

A chlorine-containing test compound was supplied to the reactor by passing a gas (argon or hydrogen) through a bubbler filled with 1,2-dichloroethane of chlorobenzene. The bubbler was thermostatted at 20°C. The amount of test compound supplied to the reactor was determined by the change in bubbler weight. The weight of the bubbler filled with a chlorine derivative was 60–70 g; the consumption of chlorobenzene or 1,2-dichloroethane was 0.8–2.4 or 2.1–6.3 g depending on the reaction time. The consumption of the chlorine derivatives was monitored by chromatography. The concentrations of the test compounds in gas mixtures were determined to within ±0.1%. The consumption was additionally controlled by weighing the bubbler in an analytical balance before and after experiments. The measurement error varied from 0.2 to 2% depending on the experimental conditions. The gas flow rate through the bubbler was varied from 2 to 10 l/h. The reaction products were also analyzed by chromatography. The purity of 1,2-dichloroethane and chlorobenzene was no lower than 99.9%.

The total experimental error, which primarily resulted from errors in the trapping and titration of HCl, was as high as 10%.

Hydrogen chloride formed in the course of reaction was trapped in a saturator containing a sodium hydroxide solution. The amount of released HCl was determined by acid–base titration (methyl red indicator).

RESULTS AND DISCUSSION

The decomposition of 1,2-dichloroethane on Cat 4 was performed in an argon atmosphere at 400–550°C. Figure 2 demonstrates the rate of carbon buildup as a function of the temperature of decomposition of 1,2-dichloroethane diluted with argon in the molar ratio Ar : $C_2H_4Cl_2$ = 9 : 1 at 450–550°C. At 450 and 475°C (curves *1* and *2*), the catalyst was deactivated; however, beginning at 500°C, the amount of carbon increased almost linearly and the operation of the catalyst stabilized. At 550°C (curve *5*), the rate of carbon formation reached a maximum and the reaction was even accelerated. This can be associated with the dispersion of nickel particles in the course of catalyst carbonization. It is likely that the catalyst was deactivated because the active surface of metal particles was poisoned with hydrogen chloride formed in the decomposition of dichloroethane. In this context, we thermodynamically evaluated the stability of iron-group metals under exposure to HCl. For this purpose, we calculated thermodynamic parameters as functions of the temperature of the metal chloride reduction with hydrogen:

$$MCl_2 + H_2 \rightleftarrows M + 2HCl, \qquad (I)$$

where M = Ni, Co, or Fe.

The equilibrium constant K_p for each of the metals is determined by the equation

$$K_p = [HCl]^2/[H_2] = \exp[-\Delta G_T^\circ/RT],$$

where ΔG_T° is the change in the Gibbs free energy. Figure 3 shows the K_p–T plots for different metals. It follows from Fig. 3 that K_p = 1 atm for nickel and cobalt at 430 and 570°C, respectively, whereas the equilibrium constant for iron is as low as 0.1 atm even at 700°C. Thus, the thermodynamic calculation suggests that the nickel–alumina catalyst exhibits the highest stability in the decomposition of chlorinated hydrocarbons.

The experiments on 1,2-dichloroethane decomposition in an argon atmosphere demonstrated that the cobalt–alumina and iron–alumina catalysts were deactivated by hydrogen chloride at 400–600°C. This fact is consistent with the results of the thermodynamic analysis. A metal chloride phase was detected in a deactivated catalyst sample by X-ray diffraction analysis; this fact indicates that the chlorination of a metal surface is responsible for deactivation.

To achieve effective and stable operation of catalysts in the decomposition of 1,2-dichloroethane, we added hydrogen to the reaction mixture $C_2H_4Cl_2$ + Ar, because an excess of hydrogen shifts the equilibrium of reaction (I) to facilitate metal surface purification. In this case, the rate of carbon deposition on the catalyst dramatically decreased (Fig. 4, curve *2*). This can be explained by the fact that hydrogen, which is adsorbed on the nickel surface, hydrogenates the intermediate products of the catalytic decomposition of 1,2-dichloroethane and, hence, decreases the rate of carbon deposition.

Table 1 summarizes the amounts of carbon formed in the decomposition of 1,2-dichloroethane on catalyst Cat 4 in a temperature range of 475–550°C at various $C_2H_4Cl_2 : Ar : H_2$ ratios. It can be seen in Table 1 that the rate of carbon deposition increased with temperature and decreased with the mole fraction of hydrogen in the reaction mixture.

Next, nickel–alumina catalyst Cat 1 was tested in the decomposition of 1,2-dichloroethane in an argon atmosphere at 500–600°C and in a hydrogen atmosphere at 350–600°C. Tables 2 and 3 summarize the results and specify the compositions of gas, the amounts of carbon deposited in the reaction over 3 h, and the conversions of 1,2-dichloroethane. An analysis of the results demonstrated that, in an excess of hydrogen, the rate of carbon deposition dramatically decreased and vinyl chloride was absent from the reaction products; however, ethane appeared and the amount of formed methane increased by a factor of 5–10. The last-mentioned circumstance is due to the intense methanation of carbon deposited on the catalyst in the course of decomposition. Thus, we can conclude that the decomposition of 1,2-dichloroethane can proceed via two independent routes. Under conditions of a deficiency of hydrogen, a carbide-cycle mechanism [9–12, 14] is predominant and the process can be described by the following reaction scheme:

$$4Ni + C_2H_4Cl_2 \longrightarrow 2[Ni–C] + 2[Ni–Cl] + 2H_2,$$

$$[Ni–C] \longrightarrow Ni + C,$$

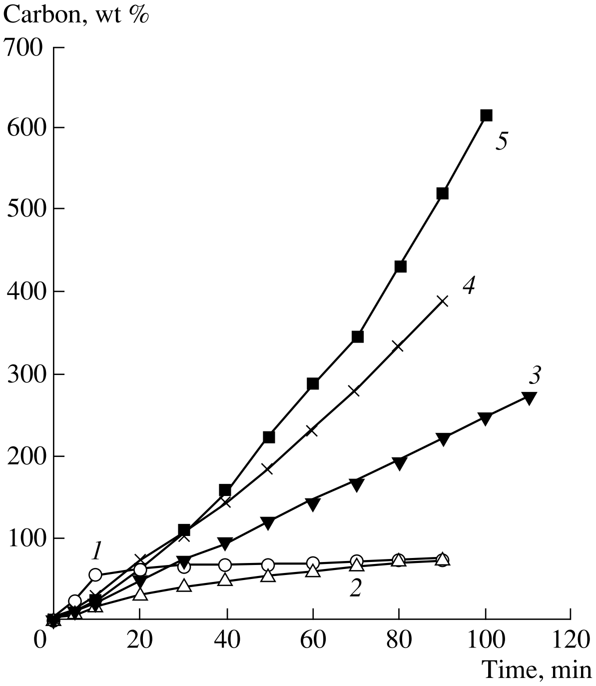

Fig. 2. Carbon formation from 1,2-dichloroethane diluted with argon in the molar ratio Ar : $C_2H_4Cl_2$ = 9 : 1 on a nickel–alumina catalyst at temperatures of (*1*) 450, (*2*) 475, (*3*) 500, (*4*) 525, and (*5*) 550°C.

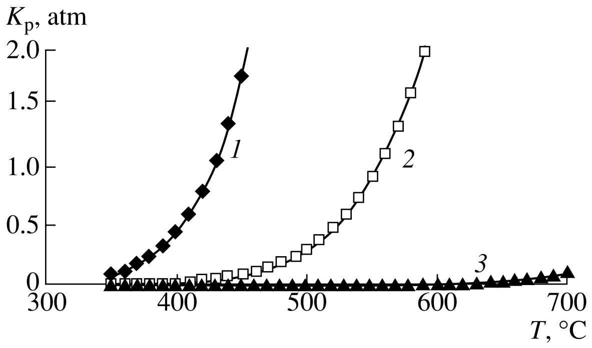

Fig. 3. Temperature dependence of the equilibrium constant of the reaction $MCl_2 + H_2 = M = 2$ HCl, where M = (*1*) Ni, (*2*) Co, or (*3*) Fe.

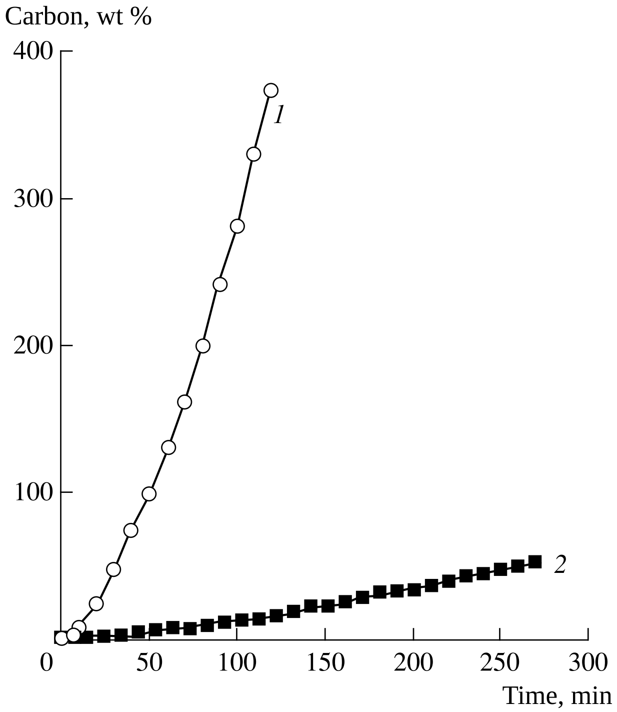

Fig. 4. Carbon formation on catalyst Cat 4 at 550°C in argon and hydrogen atmospheres: (*1*) Ar : $C_2H_4Cl_2$ = 9 : 1 and (*2*) H_2 : Ar : $C_2H_4Cl_2$ = 50 : 9 : 1.

$$2[\mathrm{Ni{-}Cl}] + H_2 \longrightarrow 2\mathrm{Ni} + 2\mathrm{HCl}.$$

The 1,2-dichloroethane molecule is adsorbed on a nickel particle; there after, the C–Cl bonds, as the weakest bonds in the molecule [15], are ruptured. Hydrogen released in the course of decomposition binds chlorine on the surface of nickel to form HCl and partially hydrogenates the surface carbide to form CH_4. In this case, the process primarily proceeds via the formation of carbon.

Table 1. Decomposition of 1,2-dichloroethane diluted with argon and hydrogen on catalyst Cat 4 (reaction time of 100 min)

Space velocity, l/h			*T*, °C	Amount of carbon, % of Cat weight
$C_2H_4Cl_2$	Ar	H_2		
1	9	–	550	630.9
1	9	2	550	350.1
1	9	5	475	25.5
1	9	5	500	131.5
1	9	5	550	325.4
1	9	10	550	238.8
1	9	20	550	86.3
0.2	1.8	10	550	13.0

Under conditions of an excess of hydrogen, hydrodechlorination is the predominant process:

$$\begin{aligned} &C_2H_4Cl_2 + 2\mathrm{Ni} \xrightarrow{H_2} 2[\mathrm{Ni{-}C}] + 2\mathrm{HCl} + H_2,\\ &[\mathrm{Ni{-}C}] + 2H_2 \longrightarrow \mathrm{Ni} + CH_4\\ &\;\downarrow\\ &\mathrm{C} + 4\mathrm{H} \longrightarrow CH_4. \end{aligned} \qquad \mathrm{(II)}$$

The hydrogenation of deposited carbon (reaction (II)) is also catalyzed by nickel. Thus, the surface carbide and the formed carbon are almost completely hydrogenated by hydrogen and the C–Cl bond is subjected to hydrogenolysis. In this case, methane is the main reaction product (except for HCl). At 350–450°C, the formation of ethane in considerable amounts was also observed (Table 3).

The dilution of 1,2-dichloroethane with hydrogen in a ratio of 1 : 9 provided the stability of the cobalt–alumina catalyst (Cat 2) in a temperature range of 500–600°C. We found that the decomposition of 1,2-dichloroethane on this catalyst under conditions of an excess of hydrogen also proceeded primarily via the hydrodechlorination path. Table 4 summarizes data on the selectivity for the products of 1,2-dichloroethane decomposition on catalysts Cat 1 and Cat 2 on dilution with hydrogen at the molar ratio $H_2 : C_2H_4Cl_2 = 9 : 1$. The amount of methane formed on the cobalt–alumina catalyst was smaller than that on the nickel–alumina catalyst at the same temperature, and the reverse is true of the amount of ethane. The conversion of 1,2-dichloroethane at 550°C was higher than 99% on both of the catalysts.

At the same time, the dilution of 1,2-dichloroethane with hydrogen had no effect on the stability of iron–alumina catalyst Cat 3: it was also deactivated at 400–600°C. This can be explained by the fact that, of Group VIII metals, iron is most susceptible to chlorination (Fig. 3).

We also examined the activity and selectivity of catalysts Cat 1 and Cat 2 in the hydrodechlorination of chlorobenzene over a temperature range of 350–500°C at a ratio between the reactants $H_2 : C_6H_5Cl = 50 : 1$. In this case, chlorobenzene was more highly diluted with hydrogen because the volatility of chlorobenzene is lower than that of 1,2-dichloroethane. Carbon was not deposited on the catalysts at this high hydrogen content of the reaction atmosphere because coke was completely hydrogenated to methane. Table 5 indicates that, in addition to hydrogen chloride, only benzene and methane were present in the reaction products. The selectivity for benzene on cobalt was noticeably higher than that on nickel. It seems likely that this fact can be explained by a lower activity of cobalt in the carboniza-

Table 2. Composition of the products of 1,2-dichloroethane decomposition on catalyst Cat 1 upon dilution with argon (Ar : $C_2H_4Cl_2$ = 9 : 1; reaction time, 3 h)

T, °C	Composition of products, vol %			Amount of carbon, % of Cat weight	Conversion, %
	CH_4	vinyl chloride	H_2		
500	3.0	2.2	2.0	139.9	83.0
550	2.8	4.0	0.8	202.1	95.1
600	2.5	5.2	0.5	213.1	98.8

Table 3. Composition of the products of 1,2-dichloroethane decomposition on catalyst Cat 1 upon dilution with hydrogen (H_2 : $C_2H_4Cl_2$ = 9 : 1; reaction time, 3 h)

T, °C	Composition of products, vol %			Amount of carbon, % of Cat weight	Conversion, %
	CH_4	C_2H_6	C_3H_8		
350	9.9	7.3	–	6.2	97.3
400	16.5	4.0	~0.1	10.5	98.7
450	18.8	2.2	0.2	9.6	99.3
500	22.0	0.8	0.3	11.9	99.7
550	23.7	–	0.7	14.0	100
600	23.3	–	0.5	16.8	100

Table 4. Selectivity for the products of 1,2-dichloroethane decomposition on nickel–alumina and cobalt–alumina catalysts in an excess of hydrogen (H_2 : $C_2H_4Cl_2$ = 9 : 1)

Catalyst	*T*, °C	Selectivity, %				Conversion, %
		CH_4	C_2H_6	C_3H_8	Carbon	
Cat 1	450	29.6	69.7	0.2	0.5	99.4
	500	37.5	60.2	0.3	2.0	99.5
	550	57.3	28.9	0.6	13.2	99.9
Cat 2	500	14.4	78.5	0.3	6.8	98.8
	550	24.6	59.0	0.6	15.8	99.5

Table 5. Selectivity for the products of chlorobenzene decomposition on nickel–alumina and cobalt–alumina catalysts in an excess of hydrogen ($H_2 : C_6H_5Cl = 50 : 1$)

Catalyst	*T*, °C	Selectivity, %		Conversion, %
		CH_4	C_6H_6	
Cat 1	350	0.5	99.5	99.0
	400	19.1	81.9	99.4
	500	87.7	12.3	99.9
Cat 2	350	0.3	99.7	78.9
	400	2.0	98.0	90.3
	500	50.4	49.7	99.5

tion of chlorobenzene and benzene, which results from hydrodechlorination.

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