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Influence of Regeneration Conditions on the Activity of the Catalyst for Oxidative Chlorination of Ethylene

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Abstract—The possibility of thermochemical regeneration of an industrial batch of a spent and partially deactivated catalyst to improve its activity and selectivity in oxidative chlorination of ethylene to give 1,2-dichloroethane was studied.

In the existing process for manufacture of vinyl chloride by a balanced scheme, 1,2-dichloroethane 1,2-$C_2H_4Cl_2$ is produced by direct and oxidative chlorination of ethylene. The oxidative chlorination process uses as a catalyst $CuCl_2$ supported by γ-Al_2O_3 [1]. The reaction requires a slight excess of C_2H_4 and occurs in accordance with the overall equation [2]

$$C_2H_4 + 2HCl + 0.5O_2 \rightarrow C_2H_4Cl_2 + H_2O + Q. \quad (1)$$

The main reaction is accompanied by side reactions: complete and incomplete combustion of C_2H_4 to give CO and CO_2 [3]:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O, \quad (2)$$

$$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O. \quad (3)$$

Other possible side reactions yield CCl_4, chloral, trichloroethane, trichloroethylene, etc. (a total of up to 2% relative to 1,2-$C_2H_4Cl_2$ obtained) [4].

In the course of the process, redox reactions may occur on the catalyst surface [5]:

$$C_2H_4 + 2CuCl_2 \rightarrow C_2H_4Cl_2 + 2CuCl, \quad (4)$$

$$2CuCl + 0.5O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O. \quad (5)$$

The appearance of iron in the catalyst can be accounted for by the following reactions between the reactor walls and the catalyst:

$$Fe + CuCl_2 \rightarrow FeCl_2 + Cu, \quad (6)$$

$$4FeCl_2 + O_2 + 4HCl \rightarrow 4FeCl_3 + 2H_2O, \quad (7)$$

$$2FeCl_3 + 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 6HCl. \quad (8)$$

EXPERIMENTAL

The study was performed on the newly created experimental laboratory installation that operates on real process gases (taken from the stage of ethylene oxychlorination at a shop of Lukor Private Company, Kalush) and adequately models the industrial process.

After two years of operation, the characteristics of the catalyst changed, which led to a decrease in its activity in oxychlorination. Therefore, our goal was to study the possibility of regenerating the oxychlorination catalyst and to analyze methods of such a regeneration under the conditions maximally similar to those used in the industry.

Experiments on catalyst regeneration were performed in two ways: by thermal treatment of the catalyst in a fluidized bed in oxygen-rich gas mixture or in air and by washing the catalyst in dichloroethane. In addition, the physicomechanical properties of catalyst samples before and after regeneration were studied.

The regeneration was performed in two modes: in air with heating to 180, 210, and 250°C and at increased oxygen content (20, 30, and 40 vol %) and nitrogen content of 80, 70, and 60 vol %, respectively. Simultaneously, analyses for the content of copper(I, II, total) chloride and iron(III) in the catalyst were made, with the bulk weight m_b, specific surface area S_{sp}, and pore volume V in the catalyst determined before and after regeneration. The data obtained are listed in the table.

In addition, the table lists data on washing of the catalyst to remove iron(III) chloride by extraction into dichloroethane and describes changes in the physicomechanical properties of the catalyst.

Physicomechanical properties of the catalyst for oxychlorination of ethylene before and after its regeneration in the air and oxygen-rich gas mixture. Regeneration duration 8 h

Catalyst	Cu(I, II) content	Fe(III) content	V, cm^3 g^{-1}	S_{sp}, m^2 g^{-1}	m_b, g cm^{-3}	Color
	wt %					
Fresh	4.2	0.12	0.36	140.0	1.02	Green
Without regeneration	4.15	0.30	0.26	74.5	1.31	Brown
After regeneration:						
180°C	4.10	0.30	0.26	78.5	1.29	Dark green
210°C	4.51	0.301	0.276	85.0	1.28	Green
250°C	4.585	0.30	0.286	99.0	1.27	Lettuce-green
Extraction in dichloroethane:						
80°C	4.75	0.254	0.276	101.2	1.12	Dark green
60°C (agitation)	4.58	0.255	0.269	100.0	1.12	Green
After regeneration with O_2/N_2, vol %:						
210°C 30/70	4.18	0.31	0.27	100.5	1.27	″
210°C, 40/60	4.76	0.275	0.28	105.0	1.26	Light green
250°C, 40/60	4.77	0.26	0.32	108.0	1.25	Green

As the concentration of oxygen in the regenerating gas increases, the bulk weight of the catalyst decreases from 1.3 to 1.27–1.25 g l^{-1}, which is due to partial removal of by-products formed in the oxychlorination. This may be confirmed by a simultaneous increase in the pore volume in the catalyst, with this dependence being more pronounced at 250°C.

Gradually raising the temperature from 180 to 250°C in regeneration leads to a considerable increase in the pore volume from 0.25 to 0.3–0.33 cm^3 g^{-1}, and this dependence is stronger at increased concentrations of oxygen, compared with the regeneration in air.

As seen from the table, the content of Fe(III) in the catalyst remains, on the whole, unchanged when the temperature is raised in air and decreases from 0.3 to 0.26 wt % in the case of regeneration in the oxygen-rich gas mixture. The best results, as regards the decrease in the amount of Fe(III), were obtained in extraction washing of the catalyst in boiling dichloroethane. In this case, the content of Fe(III) in the catalyst decreased to 0.25 wt %. Apparently, dichloroethane can dissolve $FeCl_3$ [1], which makes it possible to use this method to partly diminish the amount of Fe(III) formed on the oxychlorination catalyst and poisoning it.

After regeneration for 8 h at a prescribed temperature, the activity and selectivity of the regenerated catalyst in oxidative chlorination of C_2H_4 was studied in the standard operation mode: 225°C, $C_2H_4 : HCl : O_2 = 1.07 : 2 : 0.7$, flow rate of the circulation gas (60% CO_2) 72–80 l h^{-1}, temperature of the quenching column 87–100°C, pressure in the system 7–12 kPa, total flow rate of exhaust gases 76–86 l h^{-1}, and experiment duration 1 h. Additionally, the circulation gas was analyzed for the content of CO, CO_2, C_2H_4, and O_2 in the course of an experiment. After the experiment, the weight of the dichloroethane formed was determined, its purity and the content of microimpurities were analyzed chromatographically, and the content of unchanged HCl was measured. After that, the conversion in terms of hydrogen chloride and C_2H_4 and the yield of dichloroethane in percent relative to the theoretical value before and after regeneration in air and in oxygen-rich gas mixture were calculated.

Figure 1 (curves *1, 2*) shows that the conversion of hydrogen chloride remains unchanged (~98.5%) upon regeneration of the catalyst in air and O_2. At the same time, the conversion of C_2H_4 upon regeneration (curves *3, 4*) grows from 89 to 94–95% as the content of O_2 in the regenerating gas increases from 20 to 40%, with this trend being particularly pronounced at 250°C.

Figure 2 shows how the combustion of C_2H_4 on the catalyst subjected to regeneration depends on the content of O_2 in the regenerating gas at 210 and 250°C.

After regeneration of the catalyst, the combustion of C_2H_4 in synthesis of 1,2-dichloroethane (Fig. 2)

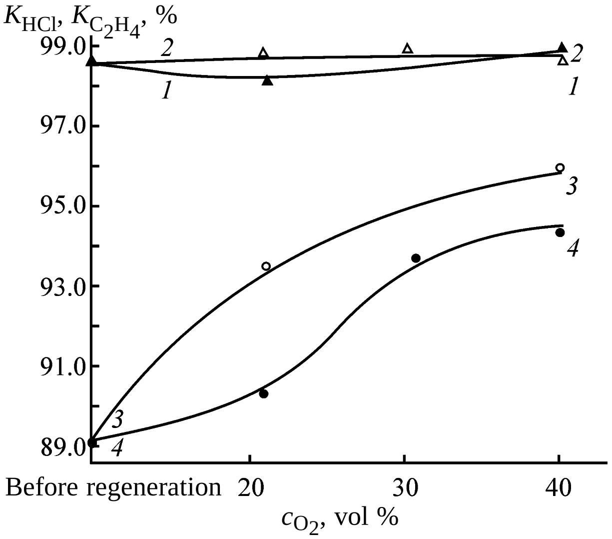

Fig. 1. Conversion of (*1, 2*) HCl (K_{HCl}) and (*3, 4*) C_2H_4 ($K_{C_2H_4}$) on a regenerated catalyst vs. the content of oxygen, c_{O_2}, in the regenerating gas. Temperature, °C: (*1, 3*) 210 and (*2, 4*) 250.

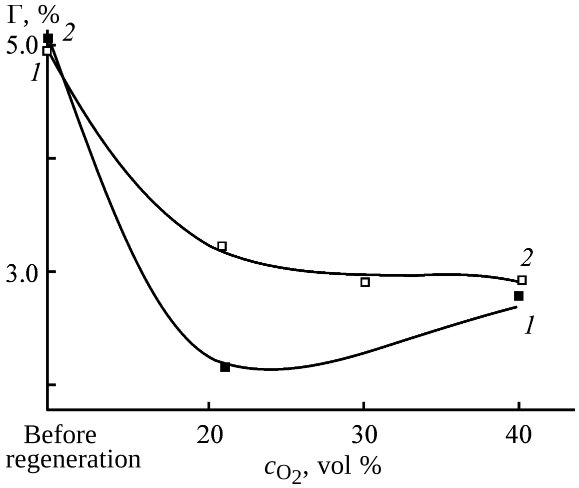

Fig. 2. Combustion Γ of C_2H_4 on a regenerated catalyst vs. the content of oxygen, c_{O_2}, in the regenerating gas. Temperature, °C: (*1*) 250 and (*2*) 210.

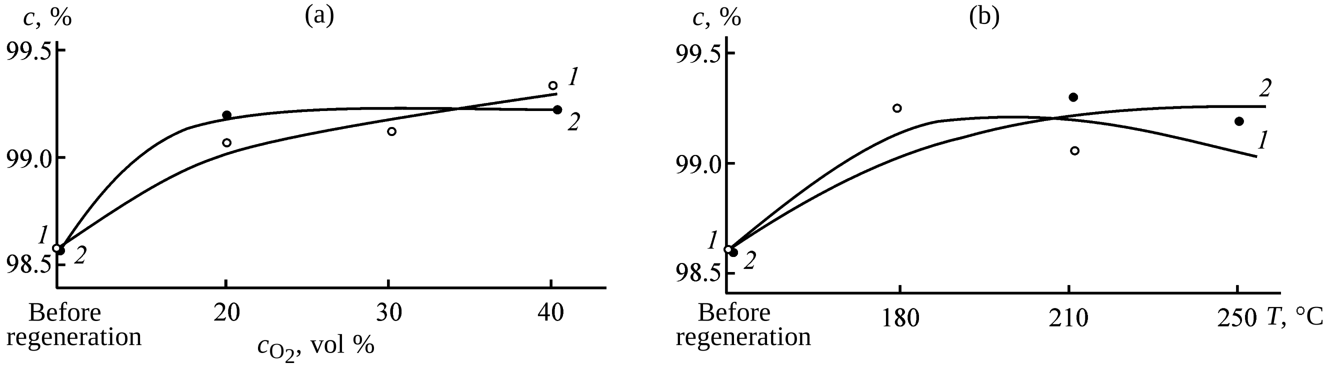

Fig. 3. Purity *c* of dichloroethane obtained on a regenerated catalyst vs. (a) content of oxygen, c_{O_2}, in the regenerating gas and (b) temperature *T* of the catalyst regeneration. (a) Temperature, °C: (*1*) 210 and (*2*) 250. (b) Medium: (*1*) air and (*2*) 40 vol % oxygen; the same for Fig. 4.

decreases from 5 to 2.5–3% in proportion to an increase in the content of O_2 in the regenerating gas. The same trend is observed on raising the regeneration temperature from 180 to 210 and 250°C.

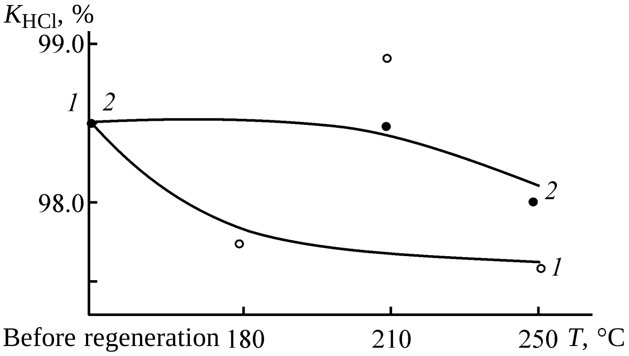

Fig. 4. Conversion of HCl, K_{HCl}, on a regenerated catalyst vs. the temperature *T* of catalyst regeneration.

Figures 3a and 3b show how the purity of dichloroethane in synthesis of 1,2-dichloroethane depends on the content of O_2 in the regenerating gas and on the temperature of catalyst regeneration. It can be seen that the purity of dichloroethane grows from 98.6% before regeneration to 99.5% after regeneration as the temperature is raised or the content of O_2 in the regenerating gas is made higher. In this case, the tendency toward an increase in the purity of dichloroethane is more pronounced when the regeneration is performed in an oxygen-rich gas mixture (Figs. 3a, 3b; curves *2*).

Figure 4 shows how the conversion of HCl in the catalytic synthesis of 1,2-dichloroethane depends on the temperature of the catalyst regeneration in air and in an oxygen-rich gas mixture (Fig. 4, curves *1, 2*). It can be seen that the conversion of HCl decreases

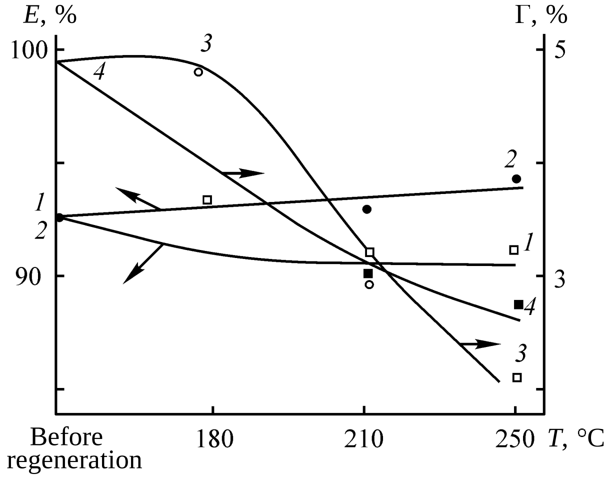

Fig. 5. (*1, 2*) Efficiency *E* of C_2H_4 conversion and (*3, 4*) C_2H_4 combustion Γ on a regenerated catalyst vs. the temperature *T* of catalyst regeneration. Medium: (*1, 3*) air and (*2, 4*) oxygen-rich gas mixture; the same for Fig. 6.

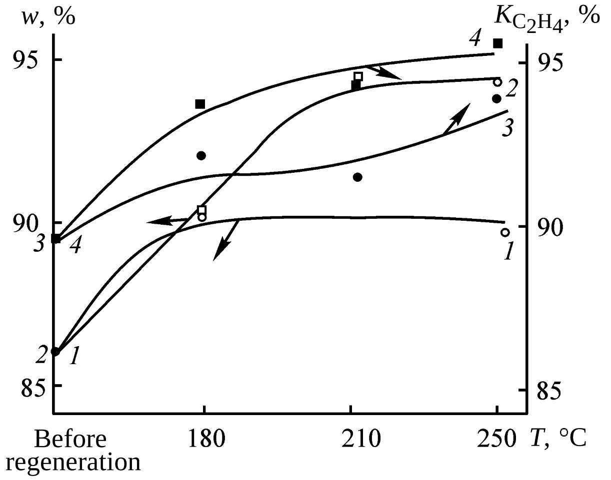

Fig. 6. (*1, 2*) Yield *w* of dichloroethane (relative to the theoretical value) and (*3, 4*) C_2H_4 conversion $K_{C_2H_4}$ on a regenerated catalyst vs. the temperature *T* of catalyst regeneration.

from 98.5 to 97.5–98%. This decrease is more pronounced in the case of regeneration in air, compared with that in the oxygen-rich gas mixture.

The increase in the conversion of C_2H_4 and decrease in its combustion after regeneration is understandable, because they are associated with partial restoration of the structure and activity of the catalyst after its thermochemical treatment in an O_2 atmosphere, which is due to oxidation of the catalyst surface and removal of tar and carbon black therefrom. This is, in turn, confirmed by the improvement of the physicomechanical properties of the catalyst, namely, by an increase in the specific surface area and pore volume and decrease in the bulk weight (see table).

Figure 5 shows how the efficiency of C_2H_4 conversion (curves *1, 2*) and C_2H_4 combustion (curves *3, 4*) in synthesis of 1,2-dichloroethane on a regenerated catalyst depend on the temperature of catalyst regeneration in air and an oxygen-rich gas mixture. It can be seen that the efficiency of C_2H_4 conversion into dichloroethane grows from 92.5 to 93–94% as the regeneration temperature increases from 180 to 250°C in the oxygen-rich has mixture (Fig. 5, curve *2*). Simultaneously, the combustion of C_2H_4 decreases from 5% before regeneration to 2–2.5% after regeneration as the temperature of catalyst regeneration is increased to 250°C.

Additionally, we calculated the yield of dichloroethane in synthesis of 1,2-dichloroethane (relative to the theoretical value) and its dependence on the temperature of catalyst regeneration (Fig. 6, curves *1, 2*). These data are compared with the dependence of the ethylene conversion in synthesis of 1,2-dichloroethane on the temperature of the catalyst regeneration (Fig. 5, curves *1, 2*) in the air and oxygen-rich gas mixtures. Figure 5 shows that the C_2H_4 conversion and yield of dichloroethane relative to the theoretical value tend to increase on a regenerated catalyst as the temperature of catalyst regeneration is raised. In this case, the C_2H_4 conversion increases by 5–7% upon regeneration, the yield of dichloroethane also grows by 5–7%. This confirms once more the fact that the catalyst activity in C_2H_4 conversion into dichloroethane increases after regeneration. The yield of by-products, trichloroethane, trichloroethylene, and others, does not increase in the case of a partly regenerated catalyst, and the combustion of C_2H_4 is suppressed.

CONCLUSIONS

(1) A partly deactivated catalyst for C_2H_4 oxychlorination can be regenerated. The regeneration in an oxygen-rich gas mixture (30–40 vol % O_2) is more effective than that in air (20 vol % O_2) under the same treatment conditions (180–210–250°C, 8 h).

(2) The regeneration improved the physicomechanical properties of the catalyst, namely, increased the pore volume and the specific surface area (by 10–20%) and decreased the bulk weight, and thus enhanced the activity and selectivity of a regenerated catalyst in oxychlorination of ethylene into 1,2-dichloroethane.

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