

Investigating Active Sites of Industrial Catalysts for the Oxidative Chlorination of Ethylene on a γ -Al₂O₃ Surface

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Abstract—Selecting the best catalyst for large-scale industrial processes of the oxychlorination of ethylene (OCE) is a practical task of great importance. In such processes, even a slight reduction in selectivity results in considerable losses of raw materials. The enhancement of selectivity requires knowledge of the structure of the catalysts' surfaces and the mechanism of the process of oxidative chlorination of ethylene into 1,2-dichloroethane (1,2-DCE). The structure of active sites of copper chloride catalysts on the surface of alumina was studied by physicochemical methods of IR spectroscopy and DTA. The structure was described for the active sites of catalysts for the oxidative chlorination of ethylene into (1,2-DCE) of two types, CuCl₂ and CuCl on γ -Al₂O₃: H1 (Harshow, United States) and OXYMAX-B (MEDC-B) (S d-Chemie Catalysts, Germany). It was ascertained that complex compounds with [CuCl₄]⁻² and [CuCl₂]⁻¹ are formed upon interaction between the active phase of the catalyst (copper chlorides CuCl₂ or CuCl), and the surface groups of the support γ -Al₂O₃ (\equiv Al–OH) (this observation does not fall into the known theory of their structure). In accordance with the results from our study, a method was elaborated for synthesizing a catalyst with the optimum properties for OCE, and a pilot setup for the detailed investigation of this process was built. The possibility of cutting ethylene losses in half during deep oxidation and eliminating the formation of side products by a factor of 1.5–2 was demonstrated by the industrial production of 1,2-DCE and vinyl chloride at OOO Karpatsnaftokhim in Kalusha. The method for producing 1,2-DCE is protected by a Ukrainian patent.

Key words: oxidative chlorination, ethylene, 1,2-dichloroethane, catalyst, structure, surface, group, copper chloride, deactivation, iron.

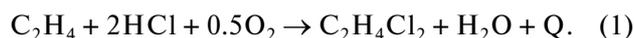
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INTRODUCTION

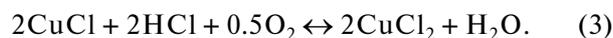
Selecting the best catalyst for large-scale industrial processes of oxychlorination of is of extreme importance, since even a slight reduction in selectivity can result in considerable losses of raw materials. Investigating the catalysts' surface structure and composition allows us to choose a theoretically substantiated method for producing a catalyst to enhance selectivity and stability toward catalyst deactivation, resulting in reduced losses of the target product.

An increase in conversion with respect to ethylene and hydrogen chloride, and an increase in the yield of 1,2-dichloroethane (1,2-DCE) and the enhancement of the total selectivity of oxidative chlorination of ethylene (OCE) toward the formation of 1,2-DCE with the use of catalysts based on CuCl₂ and CuCl supported onto γ -Al₂O₃ [1], is possible only after performing a more detailed investigation of the structure of the active sites at the catalysts' surface and of the mechanism of OCE. It is possible to vary the qualitative and quantitative compositions of OCE products by using different types of CuCl₂/ γ -Al₂O₃ catalysts (with copper chlorides supported onto an alumina surface and located in the internal pores of the support) [2].

The oxidative chlorination of ethylene is performed in a boiling catalyst bed, with a temperature in the reaction zone of 210–260°C and a pressure of 0.25–0.4 MPa [3]. The reaction of OCE in 1,2-DCE proceeds according to the equation



Todo et al. [4] believed that the following processes occur with the participation of copper catalysts:



The chemical interactions between the surface of γ -Al₂O₃ support and copper chlorides that were described in [5–7] are not ideal, since copper chlorides are not capable of catalyzing OCE without a support [8, 9]. The description of the mechanism of reactions (1–3) [10] without the participation of the surface groups of γ -Al₂O₃ is therefore not entirely reliable. Side products (up to 1–2% of the total amount of the resulting 1,2-DCE [11]) can be formed simultaneously with OCE. In this work, we investigated the composition of active sites of copper chloride catalysts on a γ -Al₂O₃ surface using IR spectroscopy and DTA.

EXPERIMENTAL

Five samples were studied:

(1) pure γ -Al₂O₃, as the support of the catalyst (Harshow, United States);

(2) H1-CuCl₂ industrial catalyst (Harshow, United States), supported from hydrochloric acid in aqueous solution onto a γ -Al₂O₃ surface. The catalyst contained 4.5–5 wt % of Cu (calculated for Cu^{+2,+1}) with a specific surface area of 100–120 m²/g, a bulk weight of 0.9–1.05 g/cm³, a pore volume of 0.3–0.4 cm³/g, and a content of particles having sizes (μ m) within the fractions 0.5 wt %, $d < 20$; 2.8 wt %, $d < 35$; 51.3 wt %, $d < 45$; 81.7 wt %, $d < 65$; 95.8 wt %, $d < 90$; 99.3 wt %, $d < 120$; and 0.1 wt %, $d > 120$;

(3) MEDC-B industrial catalyst (Süd-Chemie Catalysts, Germany) based on γ -Al₂O₃/CuCl₂ and containing 5 wt % of Cu^{+2,+1}, OXYMAX-B (MEDC-B), yellow-green; a mass fraction of copper chloride of 4.5–5.5 %; a bulk density of 0.95–1.05 g/cm³; a granulometric composition of <30 μ m less than 25 wt %; <40 μ m, 20–45 wt %; <50 μ m, 30–60 wt %; <80 μ m, 75–95 wt %; specific pore volume, 0.4 cm³/h; a specific surface area of 110–120 m²/h; and losses after 1–5 h of abrasion, 6–10 wt %;

(4) CuCl₂ · 2H₂O, crystalline hydrate of the catalysts' major component;

(5) CuCl₂ · 2HCl, hydrochloride of the catalysts' major component.

The composition of the samples' surface layer (in the form of powder preliminarily diluted with KBr) was determined by IR spectroscopy on a Thermo Nicolet Nexus FT-IR instrument over a frequency range of 4000–40 cm⁻¹, using a diffusion reflection attachment with a resolution of 4 and a scan number of 50.

To study the phase composition and phase transformations, a derivatographic analysis was performed on a Paulik–Erdey photorecording derivatograph as the temperature rose from 25 to 1000°C, following the standard procedure used at the Institute of Surface Chemistry, National Academy of Sciences of Ukraine.

The activities of the catalysts were tested in the laboratory on a specially designed pilot setup [23] and industrially in the OCE department of OOO Karpat-naftokhim [29].

RESULTS AND DISCUSSION

Studying the IR Spectra of the Investigated Samples of the Support, Catalysts, and Copper Chlorides in Order to Determine the Chemical Composition and Structure of the Surface Bed

The IR spectra of the γ -Al₂O₃ support, the Harshow catalyst (H1) – CuCl₂ supported onto the surface of γ -Al₂O₃, and the catalyst OXYMAX-B (MEDC-B) – γ -Al₂O₃ were interpreted. In the case of

γ -Al₂O₃, the intense characteristics of absorption of the surface groups were detected at 1377–1640 cm⁻¹. In the same region, triplet absorption bands emerge, characterizing the deformation vibrations of (–OH) groups of structural water in Al₂O₃ · nH₂O, Al(OH)₃ [12] at 1640 cm⁻¹ or CuCl₂ · 2H₂O. There are also deformation vibrations of groups (–OH) belonging to the surface compounds of γ -Al₂O₃ in Al⁺²OH at 1518 cm⁻¹ and Al⁺¹(OH)₂ at 1377 cm⁻¹, their intensities coinciding. However, there are almost no deformation vibrations of the hydroxyl (–OH) groups of surface compounds γ -Al₂O₃ (Al⁺²OH and Al⁺¹(OH)₂ at 1518 cm⁻¹ and 1377 cm⁻¹ in the samples of catalysts OXYMAX-B (MEDC-B) and H1). This supports our assumption as to possible interaction between the Al⁺²OH and Al⁺¹(OH)₂ surface groups and copper chlorides or its complexes [CuCl₄]^{-2,-1} [13].

Moreover, the residual intensity of absorption from the vibration of OH groups of type Al⁺¹(OH)₂ is observed on the sample of catalyst H1 at 1377 cm⁻¹, indicating that when CuCl₂ is applied onto the surface of type H1 γ -Al₂O₃, compounds of only two types are formed between Al⁺²OH and Al⁺¹(OH)₂ with [CuCl₄]^{-2,-1}. As for the sample of catalyst OXYMAX-B (MEDC-B), there is no absorption whatsoever at 1377 and 1518 cm⁻¹, demonstrating that groups Al⁺²OH and Al⁺¹(OH)₂ interact with the active phase of catalyst [CuCl₄]^{-2,-1} on their surface. However, a new characteristic absorption band not observed on the surface of the γ -Al₂O₃ support emerges at 1277 cm⁻¹ in the samples of catalyst OXYMAX-B (MEDC-B) and H1. This could indicate the rearrangement of the external surface bed of the catalyst, probably with the formation of new complexes of copper chlorides [CuCl₄]^{-2,-1} having γ -Al₂O₃ surface groups.

Based on the IR spectra of CuCl₂ · 2H₂O and CuCl₂ · 2HCl presented in Fig. 1, we may conclude that the stretching vibrations of hydrogen bonds H...Cl at 3230 and 3196 cm⁻¹ are the doublet bands characteristic of CuCl₂ · 2HCl. These bands are nowhere to be seen in the spectrum of CuCl₂ · 2H₂O; in contrast, hydrogen bonds are clearly seen in the latter compound at 3680 cm⁻¹.

The frequency of deformation vibrations of hydrogen bonds H...Cl can be seen in the IR spectrum of CuCl₂ · 2HCl at 1595 cm⁻¹, while the frequency of absorption of deformation vibrations of O...H bonds for CuCl₂ · 2H₂O is observed at 1620 cm⁻¹. Moreover, the characteristic frequency of vibrations for these two compounds emerges at 1277–1320 cm⁻¹; this can be ascribed to deformation vibrations of the H...Cl bond in H₂CuCl₄ or HCuCl₂ metal complexes. It is of interest that these compounds are identified on the surface of catalysts OXYMAX-B (MEDC-B) and H1 over the range of 1250–1277 cm⁻¹, attesting to the presence of these metal complexes on the surfaces of the catalysts

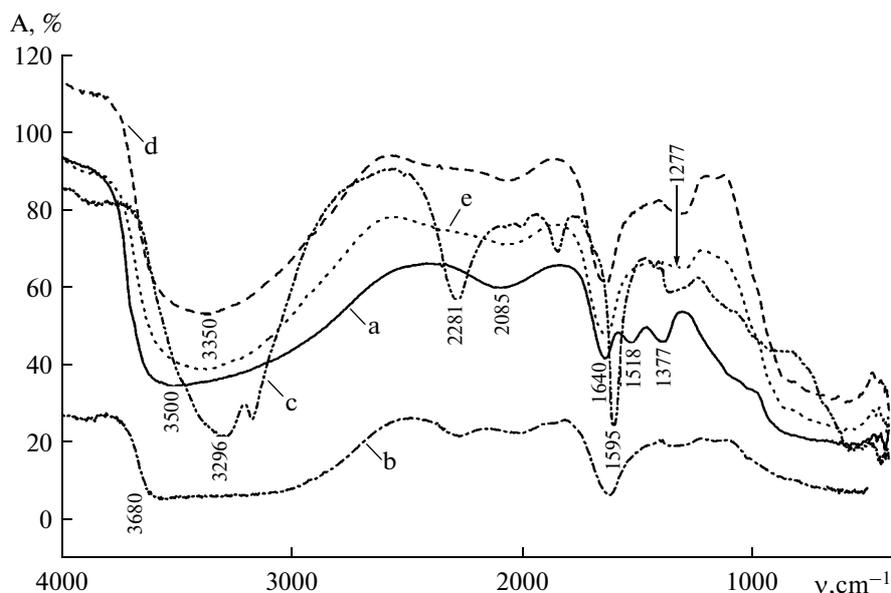
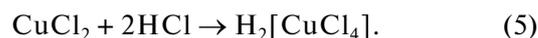


Fig. 1. IR spectra for samples of (a) the γ - Al_2O_3 support, (b) the main components of catalyst $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, (c) $\text{CuCl}_2 \cdot 2\text{HCl}$, and (d) industrial catalysts OXYMAX-B (MEDC-B) and (e) Harshow H1 as a function of wave number ν .

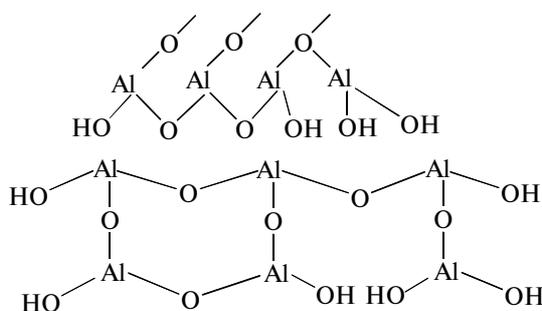
(which, due to interaction with the support, were shifted to the lower-frequency region of the IR spectrum). We may assume that metal complexes of copper (e.g., $[\text{CuCl}_4]^{-2}$ and $[\text{CuCl}_2]^{-1}$) exist on the surface of such OCE catalysts as OXYMAX-B (MEDC-B) and H1; this coincides with the data in [13].

We may assume these complexes are formed, since copper chlorides are known to form di- and tetracomplex copper chlorides in solutions of hydrochloric acid [14]:



In industrial use, copper chloride is applied to the surface of γ - Al_2O_3 from CuCl_2 solutions in hydrochloric acid as well [15].

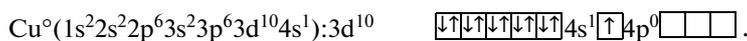
It is therefore copper tetra- and dichloride complex (rather than CuCl) that are applied to the surface of γ - Al_2O_3 [13]:



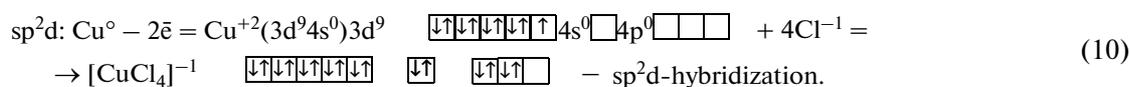
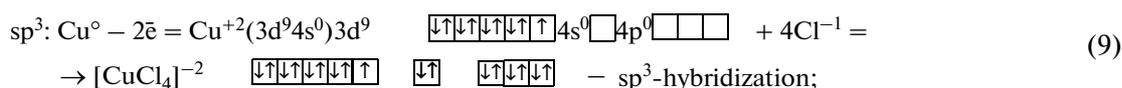
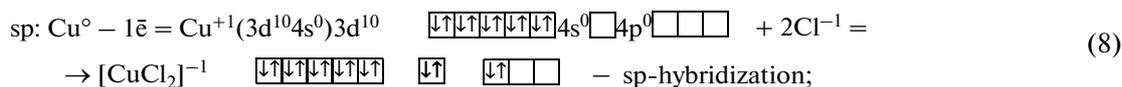
Copper tetrachloride $[\text{CuCl}_4]^{-1}$ complex has the structure of a planar square, while CuCl_2 has a linear structure and (according to [16]) can be located between the beds of an Al_2O_3 support inside the pores and on the surface of γ - Al_2O_3 , which may be coordi-

nated with it. The data obtained by Zipelli et al. [17] attest to the formation of coordination compounds between copper chlorides and oxychlorides and the surface of support γ - Al_2O_3 .

The unexcited state of a copper atom is:

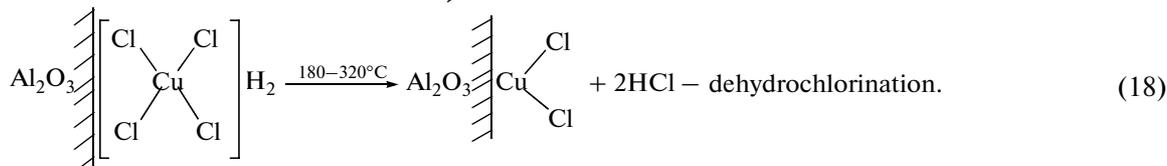
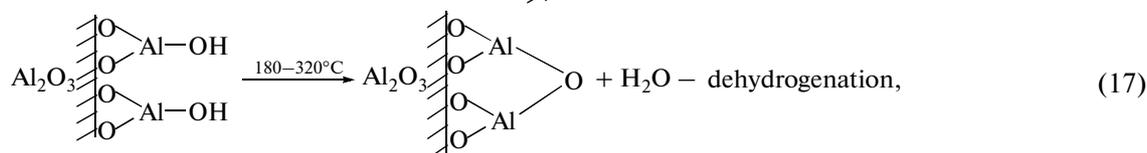
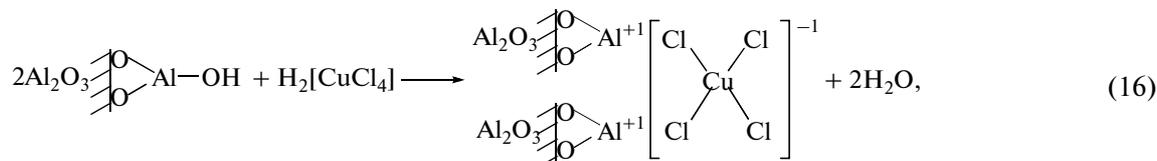
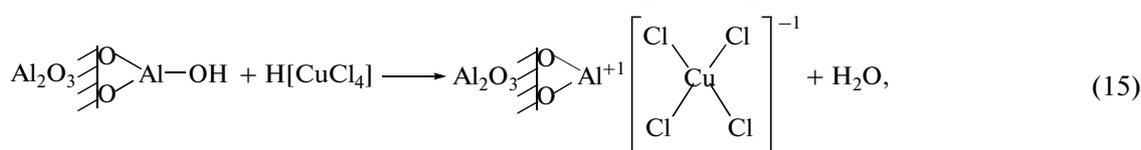
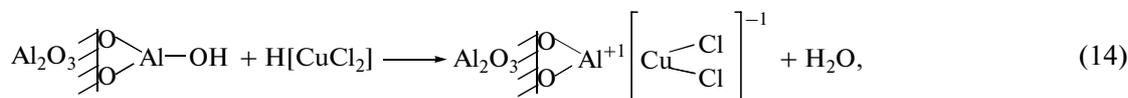
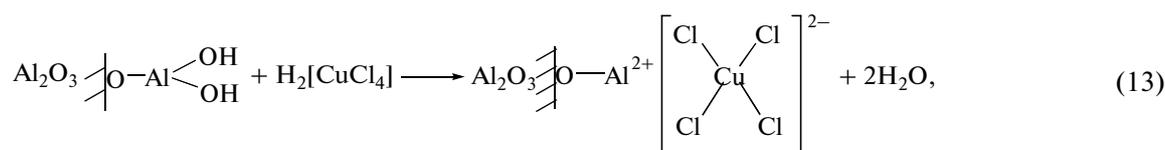
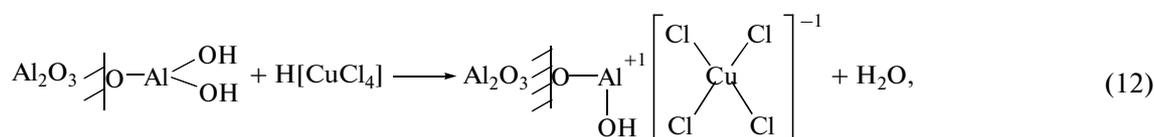
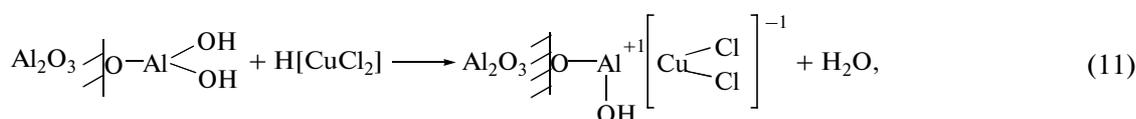


Copper tetrachloride and dichloride complex can be characterized by three types of hybridization:



Complexes sp (8) and sp³ (9) with external hybridization are paramagnetic, while complex sp³ has a tetrahedral configuration. The complexes with the external hybridization sp and sp³ are more reactive; while the complex with the internal hybridization sp²d is more stable and reacts at elevated temperatures only [18].

On the basis of the DTA and IR spectroscopy data shown in Fig. 2, we may conclude that the surface of the Al₂O₃ support is partially hydrated, yielding aluminohydroxyl groups. We assume that the reaction of coordination interaction can take place between the surface groups of the Al⁺²OH support and Al⁺¹(OH)₂, and the catalyst compounds H₂[CuCl₄] and H[CuCl₂]:



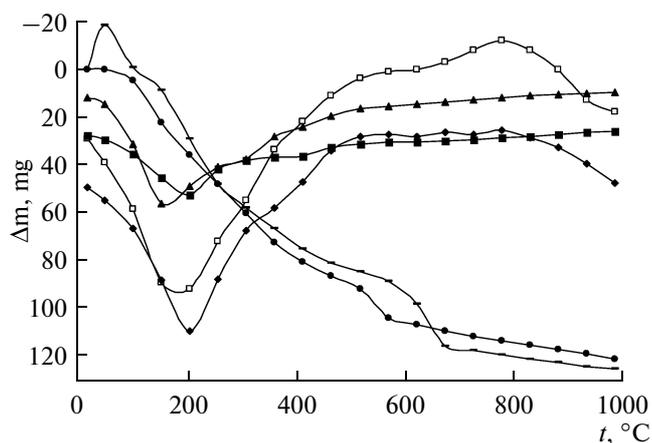


Fig. 2. Curves: —●— TG-H1, — — — TG-MEDC-B, —□— DTA-H1, —◆— DTA-MEDC-B, —▲— DTG-H1, —■— DTG-MEDC-B for samples of catalysts H1 and MEDC-B.

Three or four types of complexes between hydrated Al_2O_3 and copper complexes $[\text{CuCl}_4]^{-2}$, $[\text{CuCl}_2]^{-1}$, and $[\text{CuCl}_4]^{-1}$ are formed on the surface of the catalyst of oxidative chlorination of ethylene [reactions (11)–(16)] that cannot be identified by broad absorption bands at $1250\text{--}1277\text{ cm}^{-1}$. Meanwhile, the absorption frequencies of surface groups $\text{Al}^{+2}(\text{OH})_2 - 1578\text{ cm}^{-1}$ and $\text{Al}^{+1}\text{OH} - 1377\text{ cm}^{-1}$ in the infrared spectrum of the catalyst disappear.

We may assume the preparation of the catalysts by the coprecipitation or mechanochemical activation [8] of amorphous $\gamma\text{-Al}_2\text{O}_3$ and crystalline CuCl_2 during the formation of catalyst microparticles with diameters of $20\text{--}120\text{ }\mu\text{m}$, leading to the formation of complexes on the surface and inside the pores of the

catalyst [reactions (12), (13), and (16)]. In applying CuCl_2 from hydrochloric acid solution onto the surface of $\gamma\text{-Al}_2\text{O}_3$ solid particles (the H1 produced by Harshaw), $[\text{CuCl}_4]^{-2}$, 1 is adsorbed mainly on the surface of $\gamma\text{-Al}_2\text{O}_3$. Their interaction results in the formation of only partial surface coordination bonds between the support $\gamma\text{-Al}_2\text{O}_3$ (H1) and the supported catalyst (reactions (11), (14), and (15)); according to [19], there is some copper in the form of individual compounds of copper chlorides (reactions (6) and (7)). After 1–2 years of operation, industrial catalysts of the H1-supported type thus lose a considerable portion of their $[\text{CuCl}_4]^{-2,1}$ from the surface of the $\gamma\text{-Al}_2\text{O}_3$ support due to its mechanical abrasion and removal from the surface, reducing the efficiency of the OCE catalyst [20].

In contrast, the surface of catalyst OXYMAX-B (MEDC-B) produced by Sü d-Chemie Catalysts [22] is resistant to abrasion, which leads to mechanical deformation: thinning and shrinkage in the metal walls of industrial reactors in cooling pipes and cyclones. As a result, the thickness and durability of the metal walls in reactors and other equipment [23] are to be increased at a number of plants producing 1,2-DCE [21].

Differential Thermal Analysis of the Investigated Samples of Supports and Catalysts

In order to study the influence of the nature of active sites on the surface of objects under investigation in more detail, we studied derivatograms of samples of Al_2O_3 supports and H1 and OXYMAX-B (MEDC-B) catalysts (Fig. 2) [24]. Let us consider the DTA results (Table). For the $\gamma\text{-Al}_2\text{O}_3$ support, three regions of thermal transformations were identified in DTA curves upon heating. The first region of the dehydration of $\gamma\text{-Al}_2\text{O}_3$ lies at $25\text{--}50\text{--}120^\circ\text{C}$. The

DTA data for support and OCE catalyst samples

Sample	Temperatures of process onset/end, °C			Temperature of the maximum rate of the process, °C			Mean rate of the process, mg/min			Mass losses (Δm), %			$\Sigma\Delta m$, %	$\bar{V}_{\Delta m}^*$, mg/min
	DH	DH + DHC	D	DH	DH + DHC	D	DH	DH + DHC	D	DH	DH + DHC	D		
Al_2O_3 :														
2	25/120	120/200	200/590	120	200	480	2.27	1.65	0.34	4.31	2.64	2.64	12.8	0.65
3	50/120	120/250	250/610	120	250	470	2.41	1.81	0.3	3.59	5.02	2.33	11.7	0.28
@ Серед.	37/120	120/225	225/600	120	225	475	2.34	1.73	0.32	3.95	3.83	2.49	12.25	0.47
X1	20/180	180/250	250/550	150	250	525	2.23	2.31	1.97	5.72	2.6	9.49	20.55	1.31
OXYMAX-B (MEDC-B)	21/200	200/250	250/690	200	250	640	1.3	3.02	1.28	3.93	2.54	9.48	17.34	1.05

Note: DH denotes dehydration; DH + DHC, dehydrating and dehydrochlorination; D, destruction. *Mean rate of mass loss.

temperature of the maximum rate of the endothermic process, 120°C, is due to the elimination of adsorbed water from the surface of the dispersed support; the amount of water was approximately 4%. The rate of dehydration of γ -Al₂O₃ was approximately 2.34 mg/min. At $t > 120^\circ\text{C}$, the elimination of structural water from the γ -Al₂O₃ support and other dehydration processes start to occur (reaction (17)). It is clear that dehydration of the surface of γ -Al₂O₃ at these temperatures takes place due to the partial loss of $-\text{Al}(\text{OH})_n = 1, 2$ alumo hydroxyl groups (see Fig. 2). The rate of this process is lower than the dehydration rate of physically adsorbed water and is equal to 1.73 mg/min, while mass losses are equal to 3.83% (Table). Further heating to $>250^\circ\text{C}$ results in the rearrangement of the structure and the sintering of the γ -Al₂O₃ sample. The total mass loss for the γ -Al₂O₃ support below 950°C can be as high as 12%.

The temperature range of transformations varies for the samples of catalyst H1 with a γ -Al₂O₃ support and the active phase $[\text{CuCl}_4]^{-1,-2}$ applied onto its surface (see table). As can be seen from the DTA curves (Fig. 2, table), the dehydration of the sample of catalyst H1 can take place at 20–180°C [25]. The onset of the dehydration and dehydrochlorination process (reaction (18)) for catalyst H1 moves up to 180°C, and the process stops at 240°C, which is 20°C higher than the temperature of the maximum dehydration rate for the γ -Al₂O₃ support. Meanwhile, the rate of dehydration slows (2.23 gm/min), and the total dehydration rate increases appreciably, up to 2.31 mg/min.

The dehydration (reaction (17)) and dehydrochlorination (reaction (18)) of sample H1 occur within the range of 180–240 °C. The reaction that occurs could involve the rearrangement of the surface bed of γ -Al₂O₃ · $[\text{CuCl}_4]^{+2, +1}$. The losses upon the dehydration and dehydrochlorination of catalyst H1 can be as high as 5.72 and 2.6%, respectively. When sample H1 is further heated from 240 to 550°C, the destruction of the catalyst leads to a high loss of mass: 9.49%. The total mass loss when the sample of catalyst H1 is heated to 900°C grows to almost 20%. Meanwhile, the destruction rate above 550°C rises to 1.97 mg/min.

The difference between the fraction of the total mass loss for sample H1 (20.55%) and the fraction of mass loss due to dehydration, dehydrating, and dehydrochlorination below 350°C, is approximately 8.32%. This value corresponds to the greater portion of the active phase $[\text{CuCl}_4]^{-1,-2}$ supported on the surface of γ -Al₂O₃. At $t > 500^\circ\text{C}$, complex copper chlorides apparently decompose, leading to mass loss (within the range of 500–600°C). We may state that the stability of the active phase of copper chloride complexes on the surface of sample H1 is retained up to 180–240°C. Above 240°C, the structure of the active phase $[\text{CuCl}_4]^{-1,-2}$ changes, while at 320°C, CuCl₂

and CuCl decompose and oxychloride Cu₂(O)Cl₂ and oxide CuO are formed [12].

As follows from a comparison of the DTA and DTG results for catalysts MEDC-B and H1, the operating regime of dehydration and dehydrochlorination temperatures for sample H1 is 180–240°C ($\Delta t = 60^\circ\text{C}$), while for sample OXYMAX-B (MEDC-B), it is 210–250°C ($\Delta t = 40^\circ\text{C}$). The 20°C reduction in the range of operating temperatures for catalyst OXYMAX-B (MEDC-B) relative to H1 in the OCE reaction narrows the optimum regime of this catalyst's operation. The selectivity of oxidative chlorination of ethylene in 1,2-DCE on catalyst OXYMAX-B (MEDC-B) increases at these temperatures. On a supported-type catalyst (H1), the OCE reaction takes place at temperatures of 180 to 210°C. Such a broad regime of operation for the investigated catalyst samples on an industrial scale results in side processes of the oxidative chlorination of ethylene into trichloroethane, tetrachloroethane, and perchloroethylene, and combustion of ethylene.

The selectivity in the OCE reaction with respect to 1,2-DCE for the samples of H1-type supported catalyst does not exceed 96–97% while increasing to 98–98.5 % on samples OXYMAX-B (MEDC-B) [26]. It is known from industrial testing of the catalysts, however, that the deep oxidation and combustion of ethylene to CO and CO₂ falls to 1.5–2% on OXYMAX-B (MEDC-B) samples as compared to samples of catalyst H1, where the combustion of ethylene reaches 3–5% [27].

It follows from a comparison of the selectivities of the oxidative chlorination of ethylene into 1,2-DCE and the combustion of ethylene that the amount of impurities (side products of the process: trichloroethane, trichloroethylene, etc.) for catalyst OXYMAX-B (MEDC-B) does not exceed 1–1.5% while attaining 1.5–2.5% for samples H1. In the catalysts of the H1 type, the surface of γ -Al₂O₃ with non-uniformly distributed copper chlorides catalyzes processes of deep oxidation; this is attested to by an increase in the amount of deeply oxidized ethylene with the formation of CO and CO₂, as was observed for alumosilicates with an elevated alumina content [8]. The active phase of catalysts of a new type (OXYMAX-B (MEDC-B)), uniformly distributed over the γ -Al₂O₃ structure, however, reduces the influence of the support on the reaction of deep oxidation of ethylene. Flid et al. [3] demonstrated that these processes are catalyzed primarily by CuCl₂ fragments on the outer surface of the catalyst. It is the low content of these fragments in catalysts OXYMAX-B (MEDC-B) that reduces the combustion of ethylene and enhances the selectivity of the OCE process.

CONCLUSIONS

(1) The structure of the active sites of copper chloride catalysts on an alumina surface that determine the operation characteristics of the catalysts was investigated.

(2) The structure of active sites of two catalysts of CuCl_2 and CuCl types on $\gamma\text{-Al}_2\text{O}_3$ (H1 produced by Harshaw and OXYMAX-B (MEDC-B) produced by Süd-Chemie Catalysts) for the oxidative chlorination of ethylene into 1,2-DCE was examined.

(3) A description of the structure and mechanism of formation of surface compounds due to the interaction between the surface of support $\gamma\text{-Al}_2\text{O}_3$ and CuCl_2 , CuCl was proposed for the first time that explains the mechanism of contamination and deactivation of the catalyst with iron compounds through the interaction of these copper compounds with the walls of OCE reactors, yielding valuable recommendations when designing OCE reactors. It is assumed that when the active phase of catalyst CuCl_2 , CuCl interacts with the surface groups of $\gamma\text{-Al}_2\text{O}_3$ ($\equiv\text{Al-OH}$), complexes with $[\text{CuCl}_4]^{-2}$, $[\text{CuCl}_2]^{-1}$ are formed.

(4) A more detailed study of the mechanism of oxidative chlorination of ethylene with participation of the surface complexes that were under consideration will be performed by means of X-ray diffraction and mass-spectroscopy analysis.

(5) A method for synthesizing OCE catalyst with optimum properties was proposed on the basis of the obtained results [28], and a pilot setup for the thorough investigation of OCE catalyst under laboratory conditions was designed [23]. The possibility of cutting losses of ethylene by half during its deep oxidation and reducing the formation of side products by a factor of 1.5–2 were supported by the process for the industrial production of 1,2-DCE and vinyl chloride at OOO Karpatnaftokhim in Kalusha. The methods for the preparation of the catalyst and 1,2-DCE are protected by Ukrainian patents [29].

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