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Influence of Heat Treatment Conditions on the Physicochemical and Catalytic Properties of a Chromium-Containing Catalyst for Tetrachloroethylene Hydrofluorination to Pentafluoroethane

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Abstract—The physicochemical properties of coprecipitated 95% Cr_2O_3–5% Al_2O_3 oxide systems obtained by heat treatment of the precursor in nitrogen and air between 110 and 600°C and their influence on the catalytic activity in tetrachloroethylene hydrofluorination were studied by thermal and X-ray diffraction analyses, diffuse reflectance spectroscopy, and specific surface are measurements. The $CrO_{1.9}$ compounds are more active than $CrO_{1.5}$, but their preparation in the finely divided state is difficult because of the high exothermicity of the oxidation stage, which results in the decomposition of the oxides $CrO_{1.9}$ and $CrO_{1.5}$ followed by the crystallization and sintering of the decomposition products. Fine-powder and highly active chromium-containing oxides with $CrO_{1.9}$ stoichiometry can be obtained by two-stage heating of hydroxides first in nitrogen and then in air at comparatively low temperatures.

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Halogenated hydrocarbons are widely used as refrigerants, foaming agents, aerosols, propellants, cleaners, etc. In recent years, the problem of synthesizing perfluorinated hydrocarbons has become urgent, since they exert a weaker destructive effect on the ozone layer than chlorofluorocarbons or chlorofluorohydrocarbons. According to the Montreal protocol of 1987, the production and consumption of chlorine-containing organic substances should be stopped in the nearest decade [1–3]. The most promising variants of their replacement are refrigerants of the ethane family, namely, 1,1,1,2-tetrafluoroethane $CH_2F–CF_3$ (refrigerant R-134a) and pentafluoroethane $CHF_2–CF_3$ (refrigerant R-125), which are produced by the gas-phase catalytic hydrofluorination of trichloroethylene $Cl_2C=CHCl$ and tetrachloroethylene $Cl_2C=CCl_2$, respectively. The main catalytic components of the fluorination catalysts are chromium compounds in the form of oxides, hydroxyfluorides, or fluorides, sometimes in combination with promoting and stabilizing admixtures of Al, Mg, Ni, Cr, Zn, Co, and others [3–17].

It is of great practical and scientific interest to study bulk or highly concentrated chromium-containing catalysts exhibiting high activity and selectivity in fluorination reactions [10, 12], which provide good models for investigation of formation of the main catalytic component without a complicating effect of the support. These catalysts are usually prepared by the precipitation of chromium hydroxides from solutions of Cr^{3+} salts and promoting elements followed by drying and calcination until the formation of oxide phases [5–8, 11–15]. The catalyst is finally formed under the action of fluorine-containing mixtures under conditions of a catalytic reaction or fluorinating preactivation. The properties of the resulting catalysts depend both on the fluorination conditions and on the properties of the oxide precursors [6–13]. However, information about the optimal properties of the oxide precursors and about the influence of preparation conditions on these properties is contradictory. For instance, according to [11–15], the chromium oxide precursors of fluorination catalysts should be amorphous and have a large specific surface area, but the recommended optimal specific surface area values vary in the wide range from 100 to 300 m^2/g. According to [11], the degree of crystallinity is a more important factor than the specific surface area. Fully crystalline chromium oxide is inactive in the fluorination of 1,1,1-trifluoro-2-chloroethane to 1,1,1,2-tetrafluoroethane. Contrary to this finding, it was shown [9] that crystalline samples are fairly active in this reaction, but the morphology of the crystalline particles is of significance.

The activity of the fluorination catalysts depends significantly on the oxidation state of chromium (n), whose optimal values lie in the range of $3 < n < 5$ [11, 12]. However, the conditions of formation of active oxides in high oxidation states remain unclear. The heat treatment of the precursor in air yields chromium oxides with chromium in oxidation states higher than 3 [16, 17]. Although these compounds have a smaller specific surface area, they are more active in fluorination than

those calcined in helium or hydrogen. Contrary to this, it was shown [6] that the samples heated in nitrogen at 350–380°C are more active than those heat-treated in air or hydrogen. However, it seems improbable that hydroxide calcination in an inert gas can yield chromium oxides with chromium in an oxidation state higher than 3.5.

The influence of the oxidation state of chromium on the activity of the chromium oxide fluorination catalyst was considered in detail [5–9]. The authors of those studies established a correlation between the activity of the chromium catalyst in the fluorination of 1,1,1-trifluoro-2-chloroethane and the redox properties of the chromium species of the catalyst, i.e., their ability to undergo reversible oxidation and reduction, measured by the temperature-programmed oxidation–reduction method [5–9]. It was found that chromium oxides with excess oxygen ($CrO_{1.7–1.9}$) are more active than Cr_2O_3 with the stoichiometric ratio $CrO_{1.5}$. This was explained by the high redox activity of chromium in these oxides. To ensure high activity, the oxide precursor should contain active oxygen readily exchanged for fluorine during pre-fluorination and under the catalytic reaction conditions [4, 18]. This results in the formation of active hydroxyfluorides containing rather weakly bound fluorine capable of exchanging halogens (replacement of Cl by F) in catalyzed reaction gases. For the samples examined in [5–9], heat treatment in nitrogen at 350–380°C yields a considerably larger amount of reversibly oxidizable and reversibly fluorinatable catalytic chromium species than heat treatment in air. However, for the causes and conditions of the formation of oxides with reversibly oxidizable chromium atoms were not studied in detail. The authors only assumed that these processes depend on the heat treatment, which determine the size and degree of crystallinity of the chromium oxide particles.

In this work, we studied the influence of the heat treatment conditions (temperature and gas phase composition) on the physicochemical and catalytic properties of highly concentrated aluminum–chromium catalysts.

EXPERIMENTAL

Preparation of Catalysts

Catalysts containing 95 wt % chromium oxide (on Cr_2O_3 basis) and 5 wt % Al_2O_3 were prepared by the addition of a mixture of $CrCl_3$ and $AlCl_3$ solutions (33–35 g (Cr + Al)/l) to a solution of ammonia (9%) at a constant pH ~7.5 and a temperature of ~75–80°C. The rate of addition of the solution of chromium and aluminum chlorides was 20–25 ml/min. After the completion of precipitation, the suspension was aged for 1 h at the same pH and temperature values, washed with distilled water, filtered, and dried in air at 110–120°C for 12 h. The resulting air-dry sample (VSG-110) was then heat-treated between 165 and 600°C using three different procedures: single-stage treatment in nitrogen or in air and two-stage heating first in nitrogen and then in air. The samples heat-treated in nitrogen or in air are designated by letters A and V, respectively, and a number indicating the calcination temperature. The samples preheated in nitrogen at temperature T_1 and then in air at temperature T_2 are designated AV-$T_1 + T_2$.

Investigation Methods

Thermal analysis (TA) was carried out using an STA-449-Jupiter instrument (NETZSCH). Samples (40 g) were heated from room temperature to 600°C at a rate of 5 K/min in flowing nitrogen or air (30 ml/min). Before measurements in nitrogen, the furnace space was evacuated two times. The samples were characterized by differential thermal (DTA), thermogravimetric (TG), and differential thermogravimetric (DTG) analyses.

X-ray diffraction analysis of the catalysts was carried out on an X'TRA diffractometer (Switzerland) using CuK_α radiation ($2\theta = 5°–70°$, 0.05° increments, counting time of 15–20 s per point). The phase composition of the chromium-containing samples was determined by comparing their experimental diffraction patterns with the diffraction patterns from the JCPDS database.

Specific surface area (S_{sp}, m^2/g) was derived from argon thermal desorption data using the Brunauer–Emmett–Teller (BET) method.

The electronic state of chromium was studied by diffuse reflectance spectroscopy (DRS) on a UV-2501 PC spectrophotometer (Shimadzu) with an ISR-240 A diffuse reflectance attachment. Samples with a grain size of 0.5–0.25 mm were placed in a quartz cell with am optical path length of 2 mm. The spectra were recorded relative to $BaSO_4$ as the reflection standard in the wavenumber range from 11000 to 54000 cm^{-1}. The DRS data are presented in the Kubelka–Munk function–wavenumber coordinates.

The catalytic activity of samples in the fluorination of tetrachloroethylene to pentafluoroethane was determined using a flow reactor with a fixed catalyst bed (grain size of 0.25–0.5 mm) in the kinetically controlled region at 320–370°C, 0.4 MPa, reactant molar ratios of HF : tetrachloroethylene = (10–20) : 1, and a residence time of 1–3 s. The activity was estimated in terms of the first-order reaction rate constant $K = -\ln(1 - X)/\tau$, where X is the tetrachloroethylene conversion (in mole fractions) at the residence time τ [19].

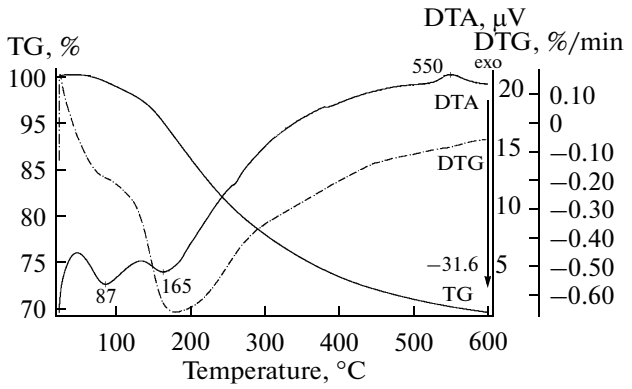

Fig. 1. Thermoanalytical profiles for the air-dry sample VSG-11 heated in flowing nitrogen.

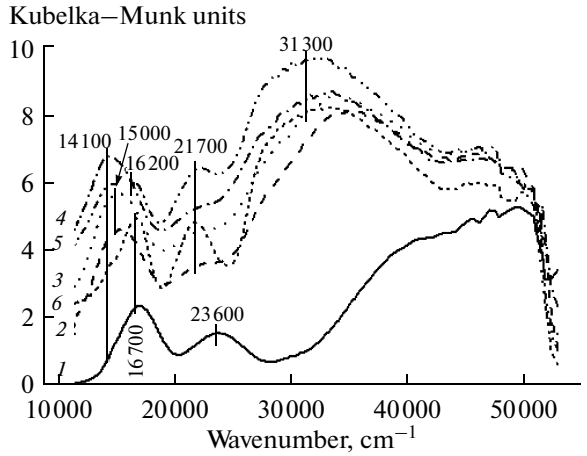

Fig. 2. Diffuse reflectance spectra of the Cr–Al samples heated in flowing nitrogen at various temperatures: (*1*) VSG-110, (*2*) A-280, (*3*) A-300; (*4*) A-370, (*5*) A-550, and (*6*) A-600.

RESULTS AND DISCUSSION

Properties of the Cr–Al Systems upon Single-Stage Heat Treatment in Nitrogen

Thermal analysis showed that, for the initial air-dry sample VSG-110, an increase in the temperature of heating in nitrogen from room temperature to 600°C leads to a continuous weight loss of the catalyst (Fig. 1). The total weight loss is 31.6%, indicating that the composition of the initial air-dry sample is $Cr_2O_3 \cdot 4.1H_2O$. An additional study by temperature-programmed desorption gave similar values of the weight loss (the TPD data are not presented), and a mass spectrometric analysis of the decomposition products showed that, as the sample is further heated in helium to 700°C, the major decomposition product is H_2O.

The dehydration process gives rise to endothermic peaks in the DTA curves. The peak positions are in agreement with the thermal behavior of precipitated chromium hydroxide in an inert medium [20–24]. The low-temperature endotherm at 87°C can likely be assigned to the elimination of physically adsorbed water. The DTA curve between 150 and 470°C contains several intense overlapped endotherms corresponding to the elimination of strongly bound water. According to the TG and DTG curves, ~75% of the total amount of water is eliminated at 300°C. The steady weight loss of the sample continues above 300°C, but at a lower rate and without well-defined maxima in the DTA and DTG curves, and ~90% of the total amount of water is removed at 450–470°C. At 550°C, dehydration is almost complete and an exotherm due to Cr_2O_3 crystallization is observed.

According to X-ray diffraction data, the samples heated in nitrogen in the range 120–500°C are amorphous to X-rays or contain traces of the fine crystalline Cr_2O_3 phase, whose presence is indicated by very broad halos near the main peaks of the Cr_2O_3 phase. The well-crystallized α-Cr_2O_3 phase is observed after calcination above the temperature of the exotherm (~550°C). No Al-containing phases are indicated by the diffraction patterns of the Cr–Al catalysts, which is probably due to the low aluminum content of the samples. The addition of small amounts of alumina stabilizes chromium oxide, increasing its crystallization and sintering temperatures.

The electronic state of chromium studied by DRS. It is well known [25] that for the octahedrally coordinated Cr^{3+} ion, there can be three absorption bands due to *d–d* transitions in the visible region of the diffuse reflectance spectrum, namely, a weak band at 13000–16000 cm^{-1} and two more intense bands at 15000–19000 and 21000–25000 cm^{-1}. For crystalline α-Cr_2O_3, two absorption bands are observed in the visible region near 460 and 600 nm (21700 and 16700 cm^{-1}, respectively) [26]. They are due to the *d–d* transitions of the Cr^{3+} ions in the octahedral oxygen environment. The more intense absorption in the UV region below 400 nm (above 25000 cm^{-1}) is due to the ligand-to-metal (O^{2-}–Cr^{3+}) charge-transfer bands.

The diffuse reflectance spectra of the chromium-containing samples heated at various temperatures in nitrogen are presented in Fig. 2. The bands in the regions mentioned above for the octahedral coordination of Cr^{3+} ions appear in the spectrum of the air-dry sample VSG-110 $Cr_2O_3 \cdot 4.1\ H_2O$: two absorption bands in the visible region at 16700 and 23600 cm^{-1} and a shoulder at 14100 cm^{-1} (Fig. 2, curve *1*). The bands in these regions persist as the treatment temperature is raised, and only the intensity and positions of their maxima change (Fig. 2, curves *2–4*). This can be explained by the dehydration of the initial sample occurring upon heating and coming to completion at ~550°C, according to the TA data, which is accompanied by the exothermic crystallization of the α-Cr_2O_3 phase. The diffuse reflectance spectra of the samples heated in nitrogen at 550 and 600°C (Fig. 2, curves *5*,

Influence of the temperature of heat treatment in nitrogen and air on the residual water content, H_2O : Cr ratio, specific surface area, and color of the catalysts samples according to TA data

T, °C	Residual water, wt %	$H_2O : Cr^{3+}$, mol/mol	S_{sp}, m^2/g	Color
Series A				
110	31.6	2.05	154	Gray-blue
165	29.7	1.90	160	"
220	26.5	1.63	160	"
280	16.0	0.85	180	"
300	10.4	0.50	190	"
340	7.8	0.38	230	"
370	6.3	0.30	250	Dark gray
400	4.7	0.22	270	"
420	3.9	0.18	280	"
450	3.0	0.14	285	"
470	2.7	0.13	260	"
500	2.3	0.10	270	"
550	1.0	0.05	143	Gray-green
600	<0.2	<0.01	98	Green
Series B				
110	33.5	2.05	154	Gray-blue
165	26.8	1.62	160	Blue + black
220	21.8	1.24	160	Black
280	13.4	0.70	160	"
300	11.6	0.60	160	"
340	8.6	0.42	160	"
370	6.9	0.33	160	Gray-green
400	3.9	0.18	130	"
420	0.6	0.03	90	"
450	0.5	0.02	68	"
470	0.5	0.02	63	"
500	0.4	0.02	52	Green
550	0.2	0.01	42	Bright green
600	<0.2	<0.01	34	"

6) are identical to the spectrum of well-crystallized α-Cr_2O_3 [26].

Thus, the main processes occurring during the heat treatment of the dry chromium-containing catalyst in nitrogen are the gradual dehydration without changes in the oxidation state of Cr^{3+} and the crystallization of α-Cr_2O_3 at a comparatively high temperature (550°C).

The data presented in the table and in Fig. 3 illustrate the influence of the temperature of heat treatment in nitrogen on the specific surface area and activity of the catalysts. It can be seen that the air-dry Cr–Al hydroxide sample (VSG-110) has comparatively high S_{sp} value (~150 m^2/g). As the temperature of heat treatment in nitrogen is increased, this sample undergoes gradual dehydration and, at ~300°C, when the residual water content decreases to ~10 wt % (~0.5 (mol H_2O/Cr^{3+}), S_{sp} begins to increase. At 400°C, the residual water content is 4.7% and S_{sp} is close to its maximum. As the temperature is raised to 500°C, S_{sp} remains approximately invariable (270–285 m^2/g). The increase in S_{sp} due to the dehydration of the sample is accompanied by an increase in catalytic activity. This is in agreement with the view that the thermolytic loss of hydroxyl groups results in the formation of coordinately unsaturated, catalytically active surface species (Cr^{3+} and O^{2-}) [27].

However, the enhancement of the activity lags somewhat behind the increase in the surface area. The maximum S_{sp} of the catalyst are reached at 370°C, when the residual water content of the catalyst is 4.7%, whereas the maximum activity is observed for the catalysts heat-treated at higher temperatures (~450–470°C), at which the water content decreases to 2.7%.

It is likely that residual water can block active sites. A similar adverse effect of water on the activity of the

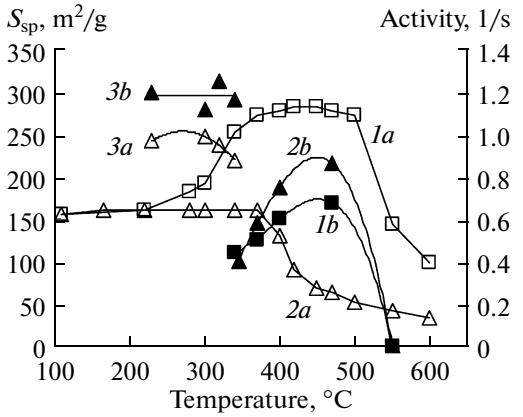

Fig. 3. Influence of the treatment temperature on the specific surface area and activity of the catalysts: (*1a*) S_{sp}, N_2; (*1b*) activity, N_2; (*2a*) S_{sp}, air; (*2b*) activity, air; (*3a*) S_{sp}, two-stage heat treatment in flowing nitrogen at 470°C and in flowing air at 230–340°C; and (*3b*) activity, two-stage heat treatment in flowing nitrogen at 470°C and in flowing air at 230–340°C.

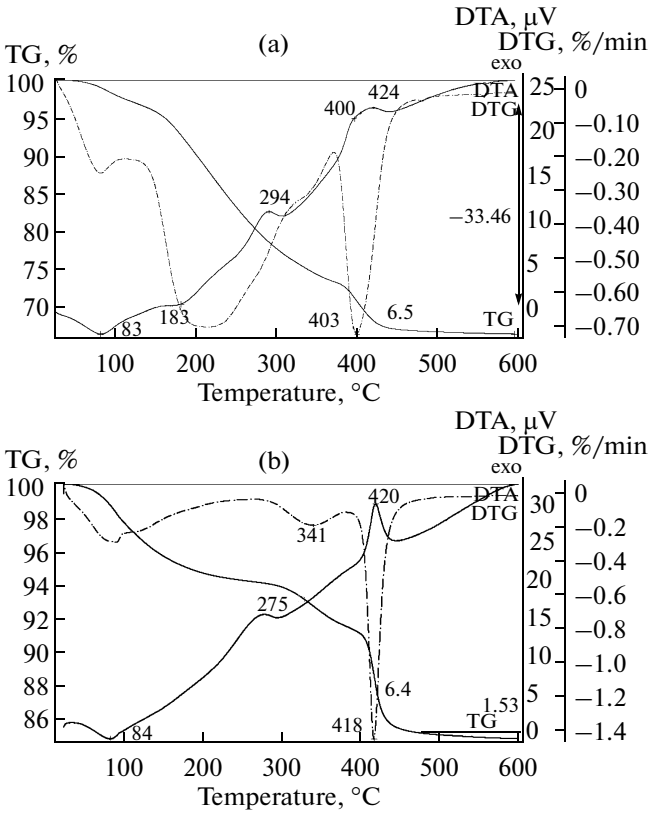

Fig. 4. Thermal analysis curves for (a) the air-dry sample VSG-110 heated in flowing air and (b) the sample A-470 pre-heated in nitrogen at 470°C.

chromium-containing hydrofluorination catalysts were observed by other authors [28]. Therefore, more complete dehydration is required for an increase in the activity. However, use of very high calcination temperatures for this purpose has limitations. As can be seen from Fig. 3, catalytic activity decreases sharply upon the heat treatment of the catalyst in nitrogen above 550°C. This can be due to the above-described crystallization of α-Cr_2O_3 and the considerable decrease in the specific surface area of the catalyst.

Properties of the Cr–Al Systems Subjected to Single-Stage Heat Treatment in Air

The TA studies showed that the primary heating of the initial hydroxide sample VSG-110 in air results in the appearance of a low-temperature endotherm at 83°C in the DTA curve (Fig. 4a). As for heating in nitrogen, this peak can be attributed to the elimination of physically adsorbed water. At higher temperatures, the thermal behavior of chromium hydroxide in air differs substantially from its behavior in the inert gas. In the temperature range from 150 to 400°C, intensive weight loss occurs and more complicated TG, DTG, and DTA profiles (compared to those for in nitrogen) are observed. This can be explained by of the endothermic dehydration of hydroxides and the exothermic oxidation of the resulting Cr^{3+} oxide occurring simultaneously. According to the published data [20, 29–31], when Cr^{3+} hydroxide is heated in an oxidative atmosphere in the temperature range from 140 to 350°C, it is oxidized to compounds of variable composition with the atomic ratio O : Cr = x, where $1.5 < x \le 2$. Therefore, compounds containing some amount (y) of overstoichiometric oxygen ($CrO_{1.5+y}$) are formed. At high temperatures, overstoichiometric oxygen is eliminated and $CrO_{1.5+y}$ turns into $CrO_{1.5}$. The temperature ranges and maximum rates of these processes can change, depending on the properties of the initial chromium hydroperoxide and on the conditions of its heat treatment [20].

In our case, the endotherm at ~220°C is replaced by an exotherm at 294°C (Fig. 4a). Simultaneously, the DTG curve indicates a less rapid weight loss. This can be due to the superimposition of the oxidation reaction $CrO_{1.5} \rightarrow CrO_{1.5+y}$, accompanied by a weight gain, on the dehydration processes, accompanied by a weight loss. At ~370°C, an intensive weight loss begins and a narrow intense peak is observed between 370 and 450°C with a maximum at 403°C. This peak can be attributed to the evolution of oxygen from the oxidized sample: $CrO_{1.5+y} \rightarrow CrO_{1.5}$. An exotherm with two maxima at 400 and 424°C, which can be assigned to the crystallization of Cr_2O_3, is observed in the DTA curve simultaneously with the decomposition of the oxidized sample. The bifurcation of the maximum of the exotherm is caused by the superimposition of two simultaneous thermal processes with opposite signs, specifically, the endothermic decomposition $CrO_{1.5+y} \rightarrow CrO_{1.5}$ and the exothermic crystallization of the resulting Cr^{3+} oxide. According to X-ray diffraction data, the samples are amorphous to X-rays below 420°C, while

above 450°C they contain the well crystallized phase α-Cr_2O_3.

The change in the color of the catalyst upon calcination in air is qualitative evidence of the change in the oxidation state of Cr^{3+} in the oxide. The oxidation of Cr_2O_3 to CrO_2 is accompanied by blackening of the sample [20, 21]. Under our conditions of heat treatment in air, the samples began to blacken already at 165°C; the black color became more intense at 220°C and persisted up to 340–350°C (table). Above 370°C, the samples began to change their black color to gray-green, and upon calcination in air at 500–600°C they acquired the bright green color characteristic of crystalline α-Cr_2O_3.

The diffraction pattern of the sample heated in air at 370°C contains broad halos near the main peaks of the Cr_2O_3 phase, indicating the presence of X-ray-amorphous or fine (<2 nm) crystalline particles of this phase. Well crystallized α-Cr_2O_3 appears as the temperature increases to 550°C.

The DRS studies revealed significant distinctions between the samples heated in air and in nitrogen. As was mentioned above, the spectrum of the initial dry sample VSG-110 exhibits absorption bands at 16700 and 23600 cm^{-1} (Fig. 5, curve *1*). As the temperature is raised to 165°C during heating in air, the bands become broader and less intense (Fig. 5, curve *2*) and the positions of their maxima change slightly. More significant differences appear after the treatment temperature of the initial VSG-110 samples is increased to 220–300°C (Fig. 5, curves *3*, *4*). According to the above TA data, dehydration is accompanied by Cr^{3+} oxidation into oxidized phases of variable composition from $CrO_{(1.5+y)}$ to $CrO_{1.90}$. Further evidence of the oxidation of Cr^{3+} is that the samples acquire the black color characteristic of Cr^{4+} [20, 21]. The diffuse reflectance spectra of the samples heated to 220 and 300°C exhibit a general rise of the absorption background and the absence of well-defined band maxima assignable to octahedrally coordinated Cr^{3+}, which were described in [25] and were observed by us for the samples heat-treated at 110 and 165°C. The rise of the general absorption background and the absence of resolved absorption maxima were explained by the oxidation of Cr^{3+} oxide to Cr^{4+} [32].

According to TA data, the oxidized compounds resulting from heat treatment in air at 200–300°C are unstable and, as the temperature is further increased above 370°C, both in air and in nitrogen the oxides with $CrO_{1.5+y}$ stoichiometry turn into oxides with $CrO_{1.5}$ stoichiometry, which is characteristic of Cr_2O_3. After that, the exothermic crystallization of α-Cr_2O_3 occurs immediately, which is confirmed by X-ray diffraction data. The increase in the heating temperature to 370°C and further to 550–600°C results in the appearance of well-resolved absorption maxima at 16700 and 21700 cm^{-1} in the diffuse reflectance spectra (Fig. 5, curves *5*, *6*), which correspond to those in the spectrum of well crystallized α-Cr_2O_3 [26].

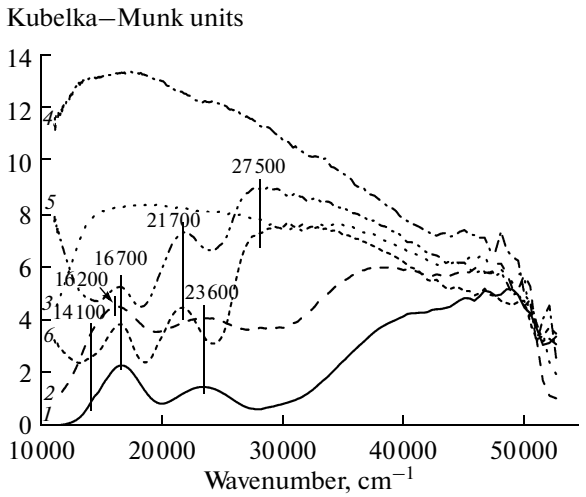

Fig. 5. Diffuse reflectance spectra of the Cr–Al samples heated in flowing air at various temperatures: (*1*) VSG-110, (*2*) V-165, (*3*) V-220; (*4*) V-300; (*5*) V-370, and (*6*) V-550.

As can be seen from the table and Fig. 3, on heating in air the values of S_{sp} observed throughout the temperature range examined are smaller than those for the samples heat-treated in nitrogen. Unlike heating in nitrogen, an increase in the temperature of heat treatment air from 165 to 370°C does not increase S_{sp}: it stays at the level observed for the initial hydroxide (150–160 m^2/g), whereas above 420°C it considerably decreases due to the crystallization of α-Cr_2O_3, which occurs at a substantially lower temperature than the same process in nitrogen. This can be due to the fact that, as the sample is heat-treated in air, the development of its surface during dehydration is complicated by the very exothermic oxidation of chromium oxide to $CrO_{1.5+y}$.

Since the oxidized compounds $CrO_{1.5+y}$ are unstable, the decomposition process $CrO_{1.5+y} \rightarrow CrO_{1.5}$ begins at a comparatively low temperature (~370°C) and the very exothermic crystallization of the resulting Cr_2O_3 occurs at 412°C. As a consequence, a marked decrease in its specific surface area takes place at a lower temperature than in nitrogen.

As can be seen from Fig. 3, the activity of the catalysts treated with air at 330–470°C is similar to, or slightly higher than, the activity of the samples heated at the same temperatures in nitrogen. This can be explained by the presence of more oxidized forms of chromium oxide, whose high activity counterbalances the lower activity of the low-temperature samples due to their smaller specific surface area and the presence of impurity Cl^- and OH^- anions. An increase in the calcination temperature above 470°C sharply decreases the catalytic activity, which can be due to the decomposition of highly active oxides with overstoichiometric oxygen ($Cr_{1.5+y}$) and the simultaneous decrease in S_{sp}.

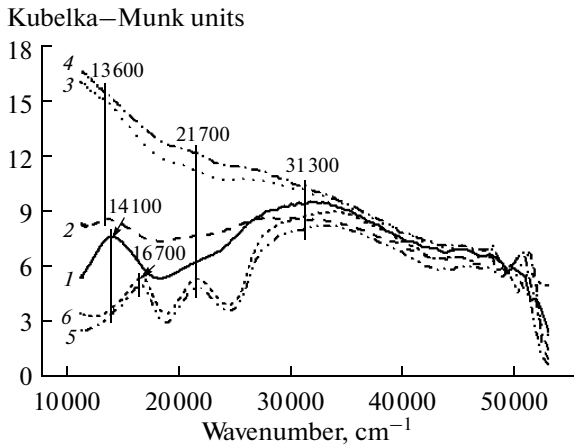

Fig. 6. Diffuse reflectance spectra of the Cr–Al samples heated in flowing nitrogen and then in flowing air at various temperatures: (*1*) A-470, (*2*) AV-470+230, (*3*) AV-470+300, (*4*) AV-470+340, (*5*) A-600, and (*6*) AV-600+280.

Due to the above processes occurring during heat treatment in air, the highly active catalysts form in a rather narrow temperature range and are poorly reproducible. The sample heats spontaneously by tens and hundreds of degrees (flash effect) due to the evolution of a large amount of heat in the oxidation of chromium oxide to $CrO_{1.5+y}$. This makes it is difficult to ensure the isothermicity of the catalyst bed and is responsible for strong effects of the following additional factors: catalyst bed volume, gas flow rate, heat removal conditions, etc. It is possibly due to these circumstances that the activity data reported by different authors for samples heat-treated in inert and oxidation media [6, 16, 17] are contradictory.

Properties of the Cr–Al Systems Subjected to Two-Stage Heat Treatment in Nitrogen and in Air

To optimize the heat treatment conditions, we carried out two-stage heating of hydroxide samples. Initially, the samples were heat-treated in nitrogen at comparatively high temperatures for more complete removal of water and foreign anions without reducing their high specific surface area. Next, they were heat-treated in air at comparatively low temperatures to prevent overheating and the decomposition of chromium oxides with overstoichiometric oxygen.

As can be seen from Fig. 3 (curve *3b*), the two-stage heat treatment first in nitrogen at 470°C and then in air at 230–340°C substantially increases the catalytic activity.

According to TA, X-ray diffraction, and DRS data, after heat treatment in nitrogen at 470°C (first stage), the sample is amorphous Cr_2O_3 with large S_{sp} (280 m^2/g) and a high degree of dehydration (~90%).

The TA data obtained after the additional heating in air of the sample pre-heat-treated in nitrogen are presented in Fig. 4b. The low-intensity weight loss events below 165°C can be attributed to the presence of molecular water adsorbed during the storage of the sample in air. Since the sample was pre-dehydrated, low-temperature dehydration events are almost absent from the DTA and DTG curves after the additional heat treatment of the sample in air. In other respects, its behavior is the same as the behavior of the air-dry sample heated in air (Fig. 4a). Between 150 and 340°C, the TG, DTG, and DTA curves indicate the exothermic oxidation $CrO_{1.5} \rightarrow CrO_{1.5+y}$. At >370°C, $CrO_{1.5+y}$ undergoes decomposition, which is manifested in the DTG curve as a narrow intense peak at 418°C, and the corresponding the weight loss is observed. This peak is immediately followed by the α-Cr_2O_3 crystallization exotherm in the DTA curve.

Since the pre-dehydrated sample was used, the weight loss (6.39 wt %) indicted by the TG curve in the 370–418°C range can be assigned to the elimination of overstoichiometric oxygen via the $CrO_{1.5+y} \rightarrow CrO_{1.5}$ transition. The composition of the overstoichiometric oxide formed below 370°C is $CrO_{1.9}$, as calculated from weight loss data. This is similar to the reported compositions of highly active samples ($CrO_{1.7–1.9}$) containing reversibly oxidized chromium [6–9]. The decomposition of the overstoichiometric oxide is followed by exothermic Cr_2O_3 crystallization at 420°C and by a decrease in S_{sp}.

The diffuse reflectance spectra of the sample heated only in nitrogen at 470°C (Fig. 6, curve *1*) and those of the samples that after heat treatment in nitrogen at 470°C were additionally oxidized with air at 230 to 340°C (Fig. 6, curves *2–4*) are compared in Fig. 6. It can be seen that the spectrum of the sample AV-470+230 (Fig. 6, curve *2*) resembles the spectrum of the sample A-470 heated in nitrogen. The difference is the slight decrease in the absorption intensity above 25000 cm^{-1} and the increase in the absorption background in the visible region, accompanied by a relative decrease in the intensity of the absorption bands at 14000 and 21700 cm^{-1}, which are due to the *d–d* transitions in the Cr^{3+} ion in the octahedral oxygen environment [25, 26, 32]. This indicates that the oxidized states exist already at relatively low temperatures.

Raising the additional oxidation temperature to 300 and 340°C makes the diffuse reflectance spectra (Fig. 6, curves *3*, *4*) qualitatively similar to the spectrum of the oxidized samples after primary treatment with air at 300°C (Fig. 5, curve *4*).

It is important that, for the samples preheated in nitrogen at 470°C, after additional treatment with air at 230–340°C S_{sp} remains high (220–240 m^2/g) and catalytic activity is well above the activity of the samples subjected to single-stage heat treatment in nitrogen or air (Fig. 3, curves *3a*, *3b*).

For the samples A-550 and A-600 pretreated in nitrogen at 550–600°C or in air above 370°C, additional heating in air at 230–340°C does not substantially change the diffuse reflectance spectrum, indicat-

ing the oxidation of Cr^{3+} (Fig. 6, curves *5*, *6*). These samples do not show high catalytic activity. Therefore, chromium is oxidized into the highly active nonstoichiometric compounds $CrO_{(1.5+y)}$ only if fine-particle amorphous Cr^{3+} oxide is subjected to additional heat treatment in air. Coarse α-Cr_2O_3 crystals contain no reversibly oxidizable chromium capable of forming the highly active nonstoichiometric oxides $CrO_{(1.5+y)}$.

Thus, the thermal behavior of the precipitated Cr–Al samples in nitrogen and air in the temperature range 110–600°C was studied by the TA, TPD, X-ray diffraction, BET, and DRS methods.

It is found that hydrated Cr^{3+} oxide is gradually dehydrated upon heating in nitrogen, which is accompanied by an increase in its specific surface area. At 400°C, when the degree of dehydration is ~85%, S_{sp} is close to its maximum, and it remains nearly constant (270–285 m^2/g) as the temperature is further increased to 500°C. The highest catalytic activity is achieved in a comparatively narrow treatment temperature range (470–500°C), where the samples have a large specific surface area and contain a small amount (2.3–2.7%) of residual water deactivating the active sites of the catalyst. At the treatment temperatures 550–600°C, chromium oxide is almost completely dehydrated, which is accompanied by its exothermic crystallization yielding coarse α-Cr_2O_3 crystals (S_{sp} < 100 m^2/g) and by a sharp decrease in catalytic activity.

The systems resulting from heating in air in the entire temperature range examined are coarser than those resulting from heat treatment in nitrogen. This can be explained by the following processes occurring in the oxidation medium:

$$CrO_{1.5}(am.) \xrightarrow{200-370^\circ C} CrO_{1.9}(am.)$$
$$\xleftarrow{370-403^\circ C} CrO_{1.5}(am.) \xrightarrow{412-420^\circ C} \alpha\text{-}Cr_2O_3(cr.).$$

The dehydration of chromium hydroxide and the highly exothermic oxidation of Cr^{3+} to oxides with $CrO_{1.9}$ stoichiometry occur in the temperature range from 200 to 370°C. Between 370 and 403°C, $CrO_{1.9}$ decomposes to less oxidized forms $CrO_{1.5}$. Very exothermic crystallization yielding coarse α-Cr_2O_3 crystals occurs at 412–420°C. The oxidation–decomposition processes $CrO_{1.5} \leftrightarrow CrO_{1.9}$ are reversible for noncrystallne fine-particle chromium oxides. Coarse α-Cr_2O_3 crystals contain no reversibly oxidizable chromium species that are the most active in the catalytic hydrofluorination of chloroalkanes. The oxides having reversibly oxidizable chromium exhibit high activity in hydrofluorination, but they are unstable and decompose readily to $CrO_{1.5}$ above 370°C.

The highly active catalyst should have a large specific surface area and low concentrations of deactivating impurity anions and water along with the optimal oxidation state of chromium. It is difficult to attain these properties by single-stage heat treatment in air because several intensive overlapping processes occur during the primary heating of the initial chromium hydroxide in air in a comparatively narrow temperature range (300–420°C): endothermic dehydration; exothermic oxidation, $CrO_{1.5} \leftrightarrow CrO_{1.9}$; and the endothermic decomposition of the oxidized phase to Cr_2O_3, which immediately undergoes exothermic crystallization and sintering at a lower temperature (400–420°C) than in nitrogen (550°C). The two-stage procedure involving heat treatment in nitrogen at comparatively high temperatures (450–470°C), which yields amorphous fine-particle Cr^{3+} oxides with a low concentration of foreign anions, and subsequent heat treatment in air at comparatively low temperatures (230–340°C), which ensures the formation of amorphous fine-particle oxidized phases $CrO_{1.9}$, proved to be an efficient way of enhancing the catalytic activity.

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