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On the Interaction of CrO_2Cl_2 Vapor with the Surface of γ-Al_2O_3 and the Formation of a Chromium Oxide Covering

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Samples of γ-Al_2O_3 containing different amounts of residual hydroxyl groups were obtained by thermal treatment. The possibility of interaction of the surface hydroxyl groups of γ-Al_2O_3 with chromyl chloride vapor was studied by IR spectroscopy. The hydrogen chloride evolved as a result of the reaction interacts with both strained Al–O–Al bridges and the surface OH groups. Different types of OH groups show different reactivities with respect to the interaction with CrO_2Cl_2. Bands at 3780 and 3700 cm^{-1} are due to OH groups which have a much higher reactivity than the OH groups responsible for bands at 3744 and 3733 cm^{-1}. Not all of the OH groups participate in the surface reaction. Decrease in their surface density results in increase in the reactivity. Modification of the γ-Al_2O_3 surface is achieved by reaction cycles consisting of treatment with CrO_2Cl_2 vapor and hydrolysis of the compounds obtained by water vapor. As a result, an increase in the chromium oxide amount on the surface of γ-Al_2O_3 is observed. This is ascribed to the "secondary" OH groups formed after the hydrolysis.

It is well known that chemical modification of the surface of Al_2O_3 with halogen compounds leads to essential changes in its acidic properties and catalytic activities. In the literature there are a number of studies using hydrogen halides,[1–4] halogenated hydrocarbons,[5,6] $SiCl_4$,[7] various silanes,[8] *etc.* as modifying agents. However, there are no investigations on reactions of the Al_2O_3 surface with vapors of valatile halides or halide oxides of transition metals, which are known to ensure a more uniform deposition of a transition metal and a halogen on the surface than the classical methods of catalysts preparation. In addition, hydrolysis of the surface compound obtained can proceed with formation of "secondary" OH groups, which in turn can interact with the vapor of the same or another halide. Thus, a possibility is found to perform controllable deposition of active components on the surface of supports and to prepare new types of catalysts.

The purpose of the present paper is to investigate the interaction of the surface of γ-Al_2O_3 with CrO_2Cl_2 vapor and the deposition of chromium oxide phases as a result of alternate treatment with chromyl chloride vapor and hydrolysis with water vapor.

Experimental

Samples of γ-Al_2O_3 (Leuna, GDR), with particle sizes of 0.25—0.64 mm, specific surface area of 190 m^2/g, and pore volume of 0.64 cm^3/g, were used for the experiments.

To obtain samples with different amounts of OH groups, the initial γ-Al_2O_3 was calcined for 3 h in air with a view to eliminating organic impurities, after which it was subjected to additional calcination for 3 h *in vacuo* (5×10^{-5} Torr) (1 Torr=133.322 Pa) at suitable temperatures.

The samples thus prepared were brought into contact with CrO_2Cl_2 vapor at an experimentally established temperature of 150 °C. It was found that at lower temperatures, 25 °C, physical adsorption proceeds to a great extent, whereas above 170 °C partial polymerisation of chromyl chloride occurs.[9] The weight gain as a result of chemisorption was determined with a McBain balance. With samples showing no weight change, the residual chromyl chloride vapor and the gaseous products were removed by evacuation for 1 h at 150 °C. The amount of OH groups was determined gravimetrically by assuming complete dehydration of the surface at 1150 °C.

Chromyl chloride was synthesized under laboratory conditions and used after redistillation.[10] Extraction of Cr and Cl^- from the sample was achieved by treatment with 2 M NaOH (1 M=1 mol dm^3). The Cr content was determined iodometrically, and that of Cl^-, by amperometric titration.

The specific surface area was determined by the BET method using low-temperature nitrogen adsorption.

Samples of γ-Al_2O_3 (10×30 mm) weighing 13—15 mg/cm^2 were studied by IR spectroscopy. They were obtained from fine Al_2O_3 powder under a pressure of 200 kg/cm^2. The thermal treatment, the surface modification by CrO_2Cl_2 and the hydrolysis with water vapor as well as the recording of spectra were carried out in a spectral vacuum quartz cell with NaCl windows. The spectra were taken at room temperature with a UR-20 (Carl Zeiss Jena, GDR) apparatus, an optical attenuator being placed in the reference beam.

Results

Table 1 contains data from thermogravimetric measurements of the amount of OH groups. The surface density of OH groups was calculated on the basis of specific surface area. Evidently, all the parameters shown in Table 1 decrease with increasing temperature of precalcination. It should be taken into account that the values of α_{OH} and ω_{OH} are approximate and higher than the real ones. This is indicated by preliminary IR spectroscopy studies. The latter confirmed works of other authors,[11,12] according to which within the above temperature range there is coordination water on the surface of the initial Al_2O_3. It can be assumed that above 400 °C the data on the hydroxyl coverage are real since the weight losses established are due only to dehydration of the surface at the expense of neighboring or favorably oriented OH groups.

Three samples precalcined at 250, 550, and 750 °C, respectively, were treated with CrO_2Cl_2 vapor. It was taken into account that at 250 °C there is still coordination water on the surface of Al_2O_3. At 550 and 750 °C there is no such water but the Al–O–Al bridges formed as a result of dehydration differ in number and stability. In addition, the temperature of 750 °C is limited for the γ-θ-transition of Al_2O_3.

The kinetics of the reaction of CrO_2Cl_2 with the surface of Al_2O_3 are illustrated by the gravimetric

TABLE 1. DEPENDENCE OF AMOUNT OF OH GROUPS (α_{OH}), THE SPECIFIC SURFACE AREA (S), AND SURFACE DENSITY OF HYDROXYL GROUPS (ω_{OH}) ON THE PRECALCINATION TEMPERATURE OF γ-Al_2O_3

	Temp/°C							
	170	250	350	450	550	650	750	850
$\frac{\alpha_{OH}\times 10^{-21}}{\text{numbers g}^{-1}}$	2.37	1.91	1.59	1.20	0.79	0.47	0.27	0.16
$S/m^2\,g^{-1}$	190	188	175	172	179	126	113	90
ω_{OH}/number nm^{-2}	12.49	10.20	9.09	7.00	4.44	3.63	2.35	1.74

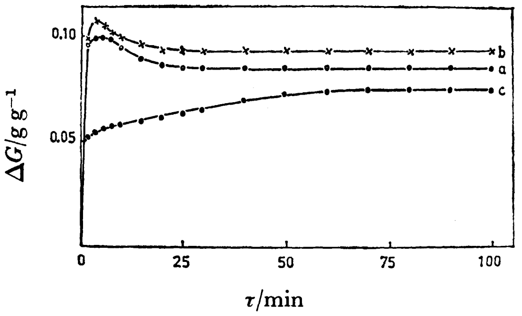


Fig. 1. Kinetic curves of CrO_2Cl_2 chemisorption at 150 °C on γ-Al_2O_3 precalcined at 250 °C (a), 550 °C (b), and 750 °C (c).

TABLE 2. DEPENDENCE OF THE Cl^- AND Cr CONTENTS AND THEIR RATIO ON THE PRECALCINATION TEMPERATURE OF γ-Al_2O_3

No.	Tem/°C	Numbers/10^{-20} g		Cl^-/Cr
		Cl^-	Cr	
1	250	1.93	3.49	0.55
2	550	2.77	3.67	0.75
3	750	2.65	2.35	1.13

curves presented in Fig. 1. The steep course of the curves in their initial portions indicates a rapid interaction. Contrary to the kinetic curves for samples calcined at 250 and 550 °C, the curve for the sample treated at 750 °C shows no maximum, which is probably due to differences in the diffusion of reaction products. After the initial portion of the curves there is a horizontal part indicating equilibrium. The data from chemical analysis (Table 2) show different contents of Cl^- and Cr, their ratios and the weight gain being presented by the kinetic curves. Obviously, the surface density of hydroxyl coverage affects the interaction which, however, is incomplete since the amounts of deposited Cl^- and Cr are much less than the theoretically calculated amounts needed for complete interaction of the available OH groups.

Figure 2 shows changes in IR spectra due to contact of the Al_2O_3 sample calcined at 550 °C with increasing CrO_2Cl_2 amount (the portions of 1.9 μmol).

The spectrum of the initial Al_2O_3 has absorption bands at 3780, 3744, 3733, and 3700 cm^{-1} which, according to the model of Peri,[1)] correspond to the srtetching vibrations of isolated OH groups. No bands are discernible in the low-frequency region. The bands at 3780 and 3700 cm^{-1} are not observed in the spectrum after the first portion of chromyl chloride vapor, whereas the bands at 3744 and 3733 cm^{-1} appear as a single band of lower intensity (spectrum 2). In addition, there is a broad band with a maximum at about 3580 cm^{-1}. According to literature data,[11)] this band is due to OH groups interacting by strong hydrogen bonds. Obviously, a chemical reaction with participation of the surface OH groups proceeds. The introduction of new CrO_2Cl_2 portions (spectra 3 and 4) leads to a more pronounced band at 3580 cm^{-1} which is broadened in the low-frequency region where three new bands appear at 1380, 1490, and 1580 cm^{-1}.

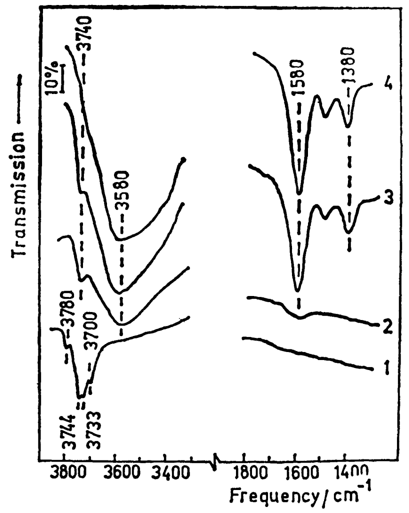


Fig. 2. IR spectra of initial γ-Al_2O_3 calcined for 3 h in air and outgassed in vacuum for 3 h at 550 °C (1), after successive interactions at 150 °C with 1.9 μmol CrO_2Cl_2 vapor (2), with 3.8 μmol CrO_2Cl_2 (3), and upon complete saturation (4).

To elucidate the nature of the first two bands, spectra of initial γ-Al_2O_3 were taken after its thermal treatment up to 500 °C. A gradual decrease in the intensity of these bands with increasing temperature was observed. At 500 °C they completely disappeared. This means that they are of the same nature and are in some way associated with the presence of coordination water on the γ-Al_2O_3 surface. In Refs. 14 and 15 the band at 1380 cm^{-1} is attributed to the overtone of the Al–OH stretching vibration, where the OH group vibrates as a whole and whose fundamental frequency should be at 660—700 cm^{-1}. In view of what has been mentioned above, the bands at 1380 and 1490 cm^{-1} could, according to our opinion, be the overtone of the coordination bond $>Al{:}OH_2$

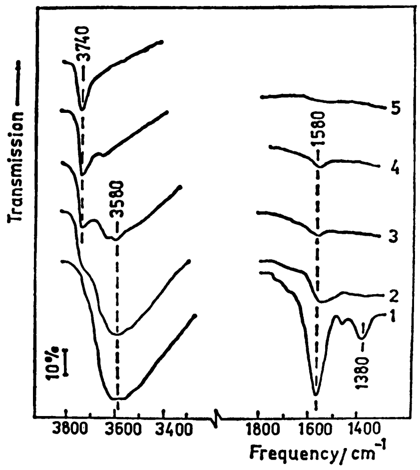


Fig. 3. IR spectra of γ-Al_2O_3 after its modification with CrO_2Cl_2 vapor at 150 °C (1), and after successive outgassing in vacuum and calcination 5 h at 250 °C (2), at 350 °C (3), at 450 °C (4), and at 550 °C (5).

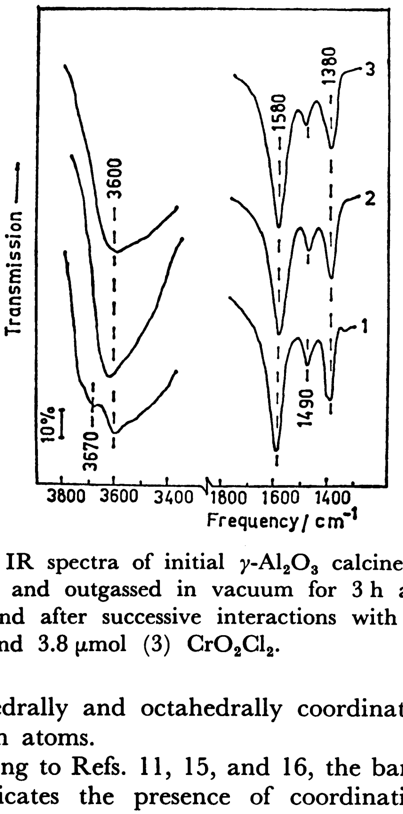


Fig. 4. IR spectra of initial γ-Al_2O_3 calcined for 3 h in air and outgassed in vacuum for 3 h at 250 °C (1), and after successive interactions with 1.9 μmol (2), and 3.8 μmol (3) CrO_2Cl_2.

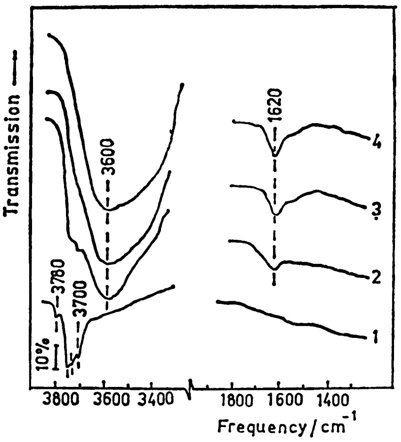


Fig. 5. IR spectra of initial γ-Al_2O_3 calcined for 3 h in air and outgassed in vacuum for 3 h at 750 °C (1), after successive interactions at 150 °C with 1.9 μmol (2), and 3.8 μmol CrO_2Cl_2 (3), and complete saturation (4).

in tetrahedrally and octahedrally coordinated surface aluminium atoms.

According to Refs. 11, 15, and 16, the band at 1580 cm^{-1} indicates the presence of coordination water. The IR spectra in Fig. 3 demonstrate its thermal stability. Spectrum 1 in Fig. 3 is identical with those given in Figs. 2—4. Evidently, with increasing temperature from 250 to 450 °C, the band at 1580 cm^{-1} gradually reduced its intensity and disappeared at 550 °C. A similar behavior is observed with the broad band at 3580 cm^{-1} which is shifted to higher frequences. Simultaneously, the composite band at 3740 cm^{-1} becomes more pronounced. Its presence may be attributed to (1) the formation of "secondary" OH groups as a result of the interaction of the evolved hydrogen chloride with Al–O–Al bridges; (2) the appearance of unreacted and "masked" OH groups; and (3) the hydrolysis of the Al–Cl bond by the coordination water during calcination. These assumptions are based on the investigations by Peri[1)] on the interaction of Al_2O_3 with hydrogen chloride and on our experimental data indicating an incomplete participation of the free OH groups in the chemical interaction as well as on the absence of chlorine in the samples after their calcination at 550 °C.

The spectrum of the sample preliminarily dehydrated and outgassed at 250 °C (Fig. 4. 1) has no pronounced characteristic bands of free OH groups due to the presence of coordination water (the bands at 1580 and 3600 cm^{-1}). Only a very weak band at 3670 cm^{-1} appears and is no more discernible after the introduction of the CrO_2Cl_2 vapor. The band at 1580 cm^{-1} preserves its intensity, which indicates that the coordination water does not interact with CrO_2Cl_2. The above spectra illustrate very well the behavior of the Al_2O_3 surface in the presence of coordination water and unambiguously confirm that the reaction between this surface and CrO_2Cl_2 leads to the formation of new OH groups and molecular water coordinatively bonded to the surface.

Figure 5 shows changes in the IR spectrum of a sample calcined at 750 °C after interaction with chromyl chloride vapor. The behavior of the bands at 3780 and 3700 cm^{-1} differs from that for the sample calcined at 550 °C. Contrary to the band at 3780 cm^{-1}, the one at 3700 cm^{-1} is also observed after the introduction of the first chromyl chloride portion. In addition, the band at 1620 cm^{-1} appears due to the OH deformation vibration and has a much lower intensity. The above facts confirm the assumption about certain variations in the mechanism of interaction between Al_2O_3 and CrO_2Cl_2 depending on the surface density of the hydroxyl groups.

From the spectra in Fig. 3 it is evident that part of the hydroxyl coverage on the support can be restored. This allows subsequent modification of the surface with CrO_2Cl_2 vapor with a view to increasing the amount of chromium oxide. This possibility is also ensured by the surface compounds with water vapor. For this reason, the following reaction cycle was carried out: treatment with CrO_2Cl_2 vapor of Al_2O_3 dehydrated at 550 °C; hydrolysis at 100 °C with water vapor of the surface compound obtained; calcination at 550 °C followed by a repetition of the above cycle. Table 3 shows data from chemical analysis of the samples obtained in this way. Here, ΔCr is the increase in Cr amount with each treatment cycle consisting of hydrolysis with water vapor, calcination at 550 °C, and modification with CrO_2Cl_2 vapor. Figure 6 presents changes in the IR spectra. Obviously, the chromium content increases with each treatment cycle. Simultaneously, the Cl^- amount and the $Cl^-/\Delta Cr$ ratio decrease, which is indicative of a hydrolysis process and a participation of the newly formed OH groups in the repeated modification. The spectra in Fig. 6 show a decreasing intensity of the composite band at 3740 cm^{-1} with increasing number of treatment cycles. In addition, the band due to strongly interacting OH groups is shifted from 3560 to 3600 cm^{-1}. It is noteworthy that after the second and subsequent treatments with chromyl chloride the bands at 3780 and 3700 cm^{-1} (coordination water) are not observed. Therefore, the amount of chromium oxides increases as a result of an interaction between chromyl chloride and OH groups giving rise to absorption bands at 3744 and 3733 cm^{-1}.

TABLE 3. DEPENDENCE OF THE AMOUNTS OF Cl^- AND Cr FIXED ON THE Al_2O_3 SURFACE AND $Cl/\Delta Cr$ RATIO ON THE NUMBER OF MODIFICATION CYCLES CONSISTING OF TREATMENT WITH CrO_2Cl_2 AND HYDROLYSIS WITH WATER VAPOR

Cycle No.	Numbers/10^{-20} g			$Cl^-/\Delta Cr$
	Cl^-	Cr	ΔCr	
I	2.77	3.67	3.67	0.75
II	1.45	6.75	3.08	0.47
III	0.54	8.19	1.44	0.38

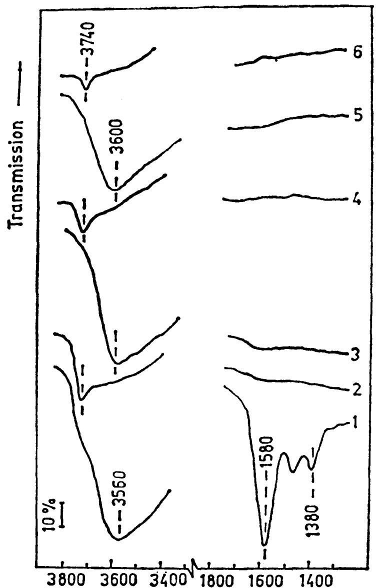
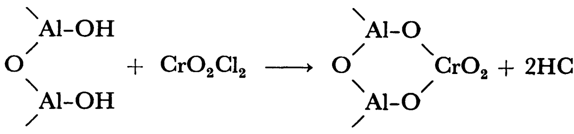


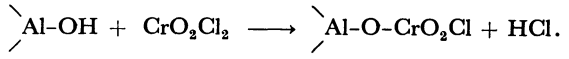
Fig. 6. IR spectra of γ-Al_2O_3 after successive treatments with CrO_2Cl_2 vapor at 150 °C (1, 3, and 5) and hydrolysis with water vapor at 100 °C and calcination at 550 °C (2, 4, and 6).

Discussion

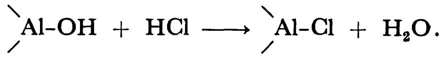
The data from IR spectroscopy indicate defferent chemical activities for the different types OH groups. The OH groups of the highest frequency (absorption band at 3780 cm^{-1}) appear to possess the highest reactivity. Next in reactivity come OH groups of the lowest frequency band (3700 cm^{-1}). After participating in an interaction, these OH groups cannot be restored by hydrolysis. This is evidence for sufficient stability of the Al–O–Cr bond formed. The OH groups responsible for the bands at 3744 and 3733 cm^{-1} are relatively less active. The absence of these bands in the spectrum after the treatment with higher CrO_2Cl_2 amounts should not be interpreted as the indication of complete consumption of these types of OH groups, but should rather be attributed to screening of the latter by the reaction products. As a result, their bands cannot be resolved and appear as one broader band.

The absence of bands at 3780 and 3700 cm^{-1} in the IR spectrum of Al_2O_3 treated with CrO_2Cl_2 and both the decrease in intensity of the bands at 3744 and 3733 cm^{-1} and the presence of Cr^{6+} alone (according to EPR data) indicate electophilic interaction of CrO_2Cl_2 and removal of a proton from the hydroxyl group:


$$\mathrm{O}\begin{matrix}\diagup \mathrm{Al{-}OH} \\ \diagdown \mathrm{Al{-}OH}\end{matrix} + \mathrm{CrO_2Cl_2} \longrightarrow \mathrm{O}\begin{matrix}\diagup \mathrm{Al{-}O} \diagdown \\ \diagdown \mathrm{Al{-}O} \diagup\end{matrix}\mathrm{CrO_2} + 2\mathrm{HCl}, \qquad (1)$$

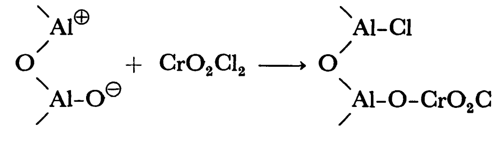

$$\rangle\mathrm{Al{-}OH} + \mathrm{CrO_2Cl_2} \longrightarrow \rangle\mathrm{Al{-}O{-}CrO_2Cl} + \mathrm{HCl}. \qquad (2)$$

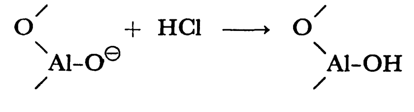
However, the reaction does not stop here. The appearance of a new absorption band at 1580 cm^{-1} indicates formation of water. This can occur only as a result of additional interaction of the hydrogen chloride with the surface OH groups according to the following scheme:


$$\rangle\mathrm{Al{-}OH} + \mathrm{HCl} \longrightarrow \rangle\mathrm{Al{-}Cl} + \mathrm{H_2O}. \qquad (3)$$

The investigation of Peri[1)] on the reaction of hydrogen chloride with Al_2O_3 confirms this scheme.

Since on the surface of Al_2O_3 strained Al–O–Al bridges occurred in addition to the groups, a nucleophilic addition of Cl^- to the surface aluminium atoms can also be expected:


$$\mathrm{O}\begin{matrix}\diagup \mathrm{Al}^{\oplus} \\ \diagdown \mathrm{Al{-}O}^{\ominus}\end{matrix} + \mathrm{CrO_2Cl_2} \longrightarrow \mathrm{O}\begin{matrix}\diagup \mathrm{Al{-}Cl} \\ \diagdown \mathrm{Al{-}O{-}CrO_2Cl}\end{matrix}, \qquad (4)$$


$$\mathrm{O}\begin{matrix}\diagup \mathrm{Al}^{\oplus} \\ \diagdown \mathrm{Al{-}O}^{\ominus}\end{matrix} + \mathrm{HCl} \longrightarrow \mathrm{O}\begin{matrix}\diagup \mathrm{Al{-}Cl} \\ \diagdown \mathrm{Al{-}OH}\end{matrix}. \qquad (5)$$

The fact that the first CrO_2Cl_2 portion (Fig. 2) leads to a gecrease in intensity of the bands characterizing the isolated OH groups and that a band of coordination water appears with the subsequent portions, shows that the first stage of the reaction proceeds according to Schemes 1 and 2. The hydrogen chloride evolved interacts first with the strained Al–O–Al bridges according to Scheme 5, which is confirmed by the band at 3680 cm^{-1} due to OH groups connected by hydrogen bonds. Only after this step the hydrogen chloride can interact with hydroxyl groups according to Scheme 3 and form water molecules which are coordinatively bound to the surface (the band at 1580 cm^{-1}). Herewith one answers the question about the constancy in intensity of the band at 1580 cm^{-1} after treatment with CrO_2Cl_2 of γ-Al_2O_3 calcined at 250 °C. The coordination centres of this sample are preliminarily occupied by water molecules and there is no possibility of additional coordination of the water formed as a result of the reaction. This type of reaction is confirmed by the spectra of the samples modified by calcination at 750 °C (Fig. 5). In this case, the band of coordination water is less pronounced due to the decrease in surface density of the hydroxyl groups and the larger amount of Al–O–Al bridges. Since dehydration at 750 °C leads to the formation of "isolated" OH groups alone, the interaction according to scheme 1 should be excluded. In view of the low density of OH groups on the surface (Table 1), the small amount of deposited chromium is quite natural. A comparison of the surface density of the hydroxyl groups with the amount of chromium per unit alumina surface leads to a conclusion that at 750 °C CrO_2Cl_2 interacts mainly according to Scheme 2. At lower temperatures the interaction proceeds partly according to Scheme 1. This is confirmed by the lower Cl^-/Cr ratio at these temperatures of precalcination.

The absence of maximum in the kinetic curve of the sample calcined at 750 °C and the much less pronounced band of deformation vibrations of water which is shifted to a higher frequency in this case, lead us to conclude that during dehydration the nucleophilic addition of Cl^- to the surface of Al_2O_3 is prevailing due to the evolution of hydrogen chloride.

The reaction according to Scheme 4 is not very propable since, in the case of the sample calcined at 750 °C and dehydrated to the highest degree so as to have the largest number of Al–O–Al bridges, the largest amount of chromium should be deposited, and the Cl^-/Cr ratio should be 2, which has not practically been observed. In addition, Scheme 4 shows no evolution of HC which would react according to Eq. 3 and lead to the band observed at 1620 cm^{-1} due to the presence of coordinatively linked water molecules.

The appearance of a band at 3740—3730 cm^{-1} upon hydrolysis or calcination of samples modified by CrO_2Cl_2 is indicative of restoration of part of the hydrate coverage on the carrier. This increase in the chromium amounts Table 3 as a result of successive cycles of halogenation and hydrolysis, which is accompanied by a decrease in intensity of the band at 3740—3730 cm^{-1}, confirms the formation of layers of chromium oxides on the Al_2O_3 surface. The absence of any bands at 3780 and 3700 cm^{-1} after hydrolysis of the samples, on the one hand, and of any band at 1580 cm^{-1} after the second and subsequent halogenations, on the other, confirms that the OH groups responsible for the appearance of the bands of highest and lowest frequencies have the highest reactivity. The OH groups giving rise to bands at 3744 and 3733 cm^{-1} and the eventually formed Cr–OH groups are probably responsible for the subsequent reactions of molecular deposition of chromium oxides. The bands caused by Cr–OH groups were not detected in the range investigated owing to too small an amount of deposited chromium oxide phase and the masking effect of the OH groups on the support.[17,18] The broad absorption band produced by the γ-Al_2O_3 skeleton, which appears in the range 800—1000 cm^{-1}, does not permit any observation of the characteristic band for the Cr–O bond.[17,19] We are of the opinion that the treatment with water vapor leads to hydrolysis of the structure obtained according to Eqs. 2, 3, and 5. Thus, repeated treatment with CrO_2Cl_2 vapor leads to both horizontal densification and vertical growth of the chromium oxide coverage. The continuous increase in the fixed chromium content and the decrease in amount of the chlorides with each cycle of treatment is very significant in this respect.

Conclusion

The surface OH groups of γ-Al_2O_3 react with CrO_2Cl_2 vapor, as a result of which hydrogen chloride is evolved. Part of the latter additionally interacts with the strained Al–O–Al bridges forming new Al–OH and Al–Cl groups. After the consumption of the strained Al–O–Al bridges the hydrogen chloride interacts with the Al–OH groups. As a result, water is formed which is coordinatively bound to the surface. On the sites where the halogen is bound to the surface, new "secondary" OH groups appear due to hydrolysis with water vapor or to calcination. They can interact again with the vapor of CrO_2Cl_2. The hydrogen chloride evolved does not interact with these surface hydroxyl groups. Successive reaction cycles consisting of treatment with CrO_2Cl_2 vapor and hydrolysis with water vapor may increase the amount of chromium oxides of the surface of γ-Al_2O_3.

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