

## TPD-MS AND SPECTROSCOPIC STUDIES OF Cr(acac)<sub>3</sub> BINDING AT SILICA AND ALUMINA SURFACE

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*The mechanism of binding of Cr(acac)<sub>3</sub> molecules at active sites of the surface of silica and alumina supports has been studied by temperature programmed desorption mass spectrometry (TPD-MS), UV-vis and IR spectroscopy. It has been found out that surface hydroxyl groups are responsible for binding of Cr(acac)<sub>3</sub> molecules only in the case of silica support due to hydrogen bonding with acetylacetonate ligand. In contrast, the binding of Cr(acac)<sub>3</sub> molecules at the alumina surface can be due to donor-acceptor interaction of  $\pi$ -electrons of acetylacetonate ligands with Al<sup>3+</sup> sites.*

### Introduction

The binding of chromium acetylacetonate Cr(acac)<sub>3</sub> with the surface of silica [1-6], alumina [3, 7-9] and silica-alumina [6, 10, 11] was widely discussed in connection with the synthesis of supported heterogeneous catalysts. Two mechanisms of binding of Cr(acac)<sub>3</sub> at surface active sites of the supports are contradictory. Molecular Cr(acac)<sub>3</sub> may bind to the surface due to the formation of hydrogen bonds with hydroxyl groups [3-6, 8, 10, 11] or donor-acceptor interaction with coordinatively unsaturated Al<sup>3+</sup> sites [8, 10]. The chemical interaction of Cr(acac)<sub>3</sub> molecules with surface active sites may also result in the formation of Cr(acac)<sub>x</sub> (x<3) species at the support surface [2, 3, 5-7, 9, 11]. Therefore, the binding of Cr(acac)<sub>3</sub> molecules at the support surface should be reasonably considered as the first step of the formation of Cr(acac)<sub>x</sub> species.

Although IR spectroscopy was widely used to study the binding of Cr(acac)<sub>3</sub> molecules at the surface of oxide supports [2-6, 8, 10, 11] the details of interaction of acetylacetonate ligands with surface active sites are not clear yet. This concerns, first of all, the supports which differ in the nature and chemistry of surface sites.

The possibility of hydrogen bonding of Cr(acac)<sub>3</sub> molecules with hydroxyl groups of alumina surface was supposed earlier [8] but was not proved experimentally unlike the case of silica surface.

The ligand substitution reaction between the hydrogen bonded Cr(acac)<sub>3</sub> molecules and hydroxyl groups of silica surface that occurs upon thermal activation was reported [2, 5]. It resulted in covalent bonding of chromium acetylacetonate species  $\equiv\text{SiO}-\text{Cr}(\text{acac})_2$ . The release of acetylacetone molecules was assumed by Haukka et al. [2] and later confirmed by Hakuli et al. [5]. The amount of the evolved acetylacetone is proportional to the hydrogen bonded Cr(acac)<sub>3</sub> molecules whose loading depends on the reaction temperature.

The combination of UV-vis and IR spectroscopy and temperature programmed desorption mass spectrometry can be used to clarify the details of interaction of Cr(acac)<sub>3</sub> with surface active sites on the molecular level. First, the energy of electron transitions of Cr(acac)<sub>3</sub> and the frequencies of the vibrations in acetylacetonate ligands are sensitive to their involvement into molecular interactions. Second, the release of acetylacetone upon the thermal activation of Cr(acac)<sub>3</sub> at the support surface can help to detect the hydrogen bonded molecules.

The aim of this work was to study the mechanism of the interaction of Cr(acac)<sub>3</sub> molecules

with active sites of silica and alumina surface.

## Experimental

Decoration of the surface of fumed silica (Aerosil 200, Evonik Degussa AG, particle size 12 nm, 200 m<sup>2</sup>/g) and alumina (Aeroxide Alu C, Evonik Degussa AG, particle size 13 nm, 100 m<sup>2</sup>/g) nanoparticles with Cr(acac)<sub>3</sub> (Aldrich, 97%) was performed according to the procedure described by Babich et al. [4, 8]. The supports were compacted by pressing, crushed and sieved (the fraction of particle size of 0.25-0.50 mm was used). The supports were calcined at 673 K for 2 h prior decoration procedure. The loading of chromium in silica and alumina samples decorated with Cr(acac)<sub>3</sub>, denoted hereinafter as Cr(acac)<sub>3</sub>/SiO<sub>2</sub> and Cr(acac)<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, was 0.69 and 0.78 at/nm<sup>2</sup>, respectively. The acac/Cr molar ratio of 3 indicated the binding of the intact Cr(acac)<sub>3</sub> molecules at the surface of both supports [4, 8].

The reference samples with chromium loading of 0.69 Cr/nm<sup>2</sup> and 0.78 at/nm<sup>2</sup>, denoted hereinafter as Cr(acac)<sub>3</sub> ~ SiO<sub>2</sub> and Cr(acac)<sub>3</sub> ~ Al<sub>2</sub>O<sub>3</sub>, were prepared by dry blending of Cr(acac)<sub>3</sub> with the preliminary calcined silica and alumina, respectively.

The encapsulation of Cr(acac)<sub>3</sub> into silica matrix was performed by sol-gel technique. First, tetraethylorthosilicate (TEOS) (Aldrich, 98%) was pre-hydrolysed for 2 h at room temperature to form the primary siloxane species terminated with hydroxyl groups (the reactant molar ratio was 1.0 TEOS : 0.05 HCl : 3.82 H<sub>2</sub>O). Then the resulting composition was diluted with 0.037 M ethanol solution of Cr(acac)<sub>3</sub> in the proportion 1:3 per volume. To complete gelation, the composition was left in the closed vessel at room temperature for 6 months and dried in air at room temperature for 1 week. The synthesised silica gel with encapsulated Cr(acac)<sub>3</sub> is denoted hereinafter as Cr(acac)<sub>3</sub>-SiO<sub>2</sub>.

UV-vis diffuse reflectance spectra were recorded within 190 - 1100 nm with resolution of 1 nm by means of a Lambda 35 UV-vis spectrometer (Perkin-Elmer) equipped with a Labsphere RSA-PE-20 diffuse reflectance and transmittance accessory. The background correction was performed using certified reflectance standard Spectralon (Labsphere) supplied with the spectrometer. Kubelka-Munk function for infinitely thick samples was used to convert the reflectance measurements into equivalent absorbance spectra. The conversion was performed using UV Winlab Advanced Spectroscopy Software supplied with the spectrometer.

IR reflectance spectra of the powdered samples were recorded within 400 - 4000 cm<sup>-1</sup> with resolution of 4 cm<sup>-1</sup> by means of a Nexus Nicolet Fourier Transform Infrared spectrometer (Thermo Scientific) equipped with a Smart Collector reflectance accessory. The background correction was performed using KBr (Merck, for IR spectroscopy) as a diffuse reflectance standard. The samples were diluted with KBr in the proportion 1:10 per weight before IR spectrum recording. The bulk Cr(acac)<sub>3</sub> and Al(acac)<sub>3</sub> (Aldrich, 99%) were diluted in the proportion 1:25 per weight.

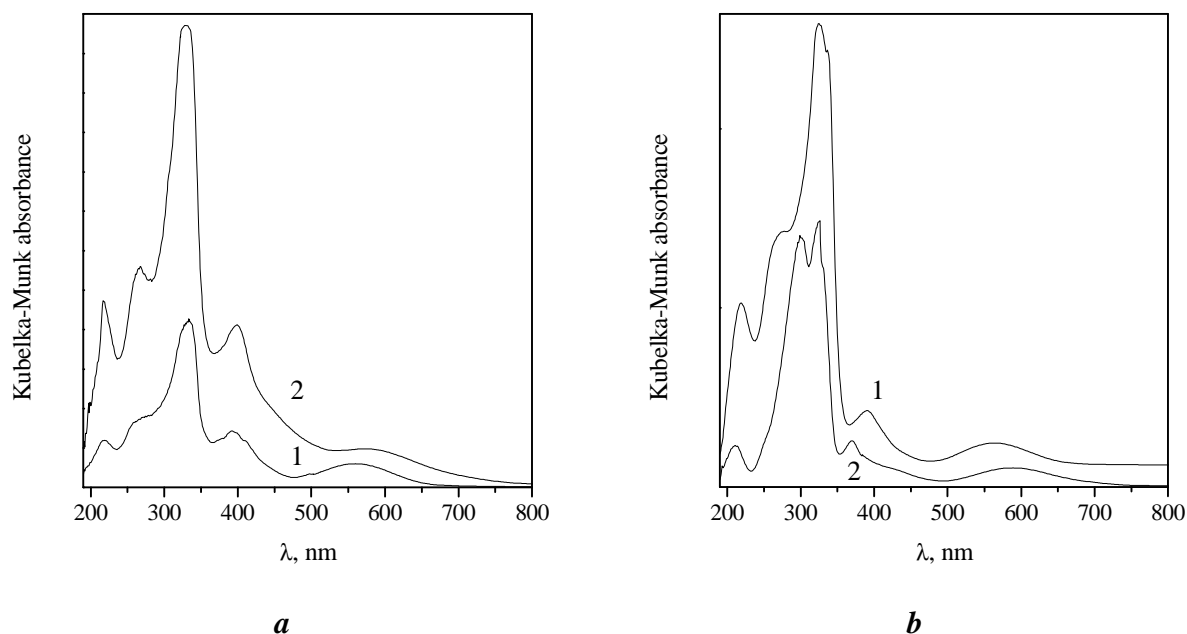
The temperature programmed desorption mass spectrometric (TPD-MS) study was performed under vacuum (10<sup>-6</sup> Pa) in the temperature range of 303 – 1073 K with a heating rate of 10 K/min. The release of acetylacetone upon thermal activation of Cr(acac)<sub>3</sub> at silica and alumina supports was controlled by means of quadrupole mass spectrometer MX 7304A (Selmi, Ukraine). Electron ionisation mass spectra of volatile products in the range of *m/z* 12 – 200 were recorded continuously upon the increase of temperature.

## Results and discussion

The colour of Cr(acac)<sub>3</sub>/SiO<sub>2</sub> and Cr(acac)<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> samples was found to be green while bulk Cr(acac)<sub>3</sub>, Cr(acac)<sub>3</sub> ~ SiO<sub>2</sub> and Cr(acac)<sub>3</sub> ~ Al<sub>2</sub>O<sub>3</sub> are magenta. Since the initial magenta colour of

bulk  $\text{Cr}(\text{acac})_3$  turned green upon decoration of the supports, this indicates the interaction of  $\text{Cr}(\text{acac})_3$  molecules with silica and alumina surface.

UV-vis spectra of  $\text{Cr}(\text{acac})_3 \sim \text{SiO}_2$ ,  $\text{Cr}(\text{acac})_3/\text{SiO}_2$ ,  $\text{Cr}(\text{acac})_3 \sim \text{Al}_2\text{O}_3$  and  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  are shown in Figure 1. The positions of the absorbance bands in the spectra of  $\text{Cr}(\text{acac})_3 \sim \text{SiO}_2$  and  $\text{Cr}(\text{acac})_3 \sim \text{Al}_2\text{O}_3$  correlate with the reported data for ethanol solution and gaseous  $\text{Cr}(\text{acac})_3$  [12] and makes it possible their assignment (Table 1).



**Fig. 1.** UV-vis spectra of a)  $\text{Cr}(\text{acac})_3 \sim \text{SiO}_2$  (1) and  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  (2), b)  $\text{Cr}(\text{acac})_3 \sim \text{Al}_2\text{O}_3$  (1) and  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  (2) samples.

**Table 1.** Band positions and assignments in UV-vis spectra of  $\text{Cr}(\text{acac})_3 \sim \text{SiO}_2$ ,  $\text{Cr}(\text{acac})_3/\text{SiO}_2$ ,  $\text{Cr}(\text{acac})_3 \sim \text{Al}_2\text{O}_3$  and  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  samples

$\text{Cr}(\text{acac})_3 \sim \text{SiO}_2$	$\text{Cr}(\text{acac})_3 / \text{SiO}_2$	$\text{Cr}(\text{acac})_3 \sim \text{Al}_2\text{O}_3$	$\text{Cr}(\text{acac})_3 / \text{Al}_2\text{O}_3$	assignment [12]
220	220	219	211	$\pi_3(e) \rightarrow \pi_4(a_1)$
*	267	*	301	$\pi_3(e) \rightarrow \pi_4(e)$ ; $\pi_3(a_2) \rightarrow \pi_4(a_1)$
330	330	327	326	$d(e_t) \rightarrow \pi_4(a_1)$ ; $d(e_t) \rightarrow \pi_4(e)$
392	398	391	370	$S \rightarrow T$
560	573	563	589	${}^4A_2 \rightarrow {}^4A_2 + {}^4E$

The  $\text{Cr}(\text{acac})_3 \sim \text{SiO}_2$  sample exhibits the absorbance bands which correspond to different electron transitions in  $\text{Cr}(\text{acac})_3$  molecule at 220, 330, 392, and 560 nm. The  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  exhibits a similar UV-vis spectrum with absorbance bands located at 220, 267, 330, 398 and 568 nm. This can mean only minor changes of  $\text{Cr}(\text{acac})_3$  molecules during their binding at silica surface.

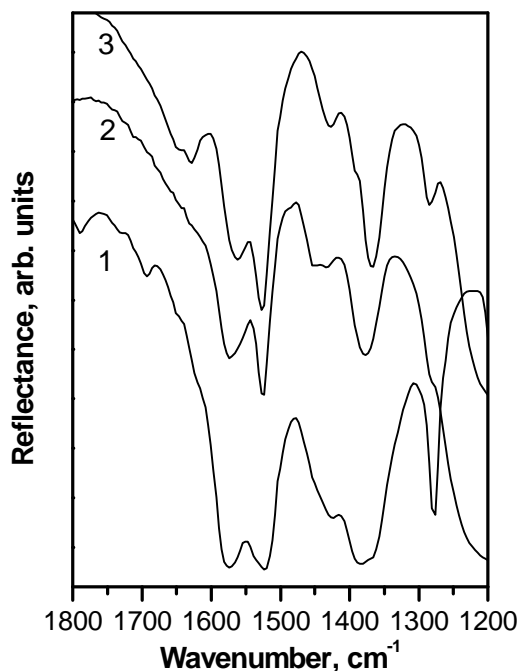
The  $\text{Cr}(\text{acac})_3 \sim \text{Al}_2\text{O}_3$  sample exhibits the absorbance bands which correspond to the electron transitions in  $\text{Cr}(\text{acac})_3$  molecule at 219, 327, 391, and 563 nm. The  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  exhibits a UV-vis spectrum with absorbance bands located at 211, 301, 326, 370 and 589 nm. One can

conclude stronger influence of alumina surface on  $\text{Cr}(\text{acac})_3$  molecules that is reflected in more substantial shift of the band positions as well as in variation of relative intensity of bands.

The red shift of bands of  $S \rightarrow T$  and  ${}^4A_2 \rightarrow {}^4A_2 + {}^4E$  electron transitions in  $\text{Cr}(\text{acac})_3$  molecule was observed upon silica decoration. While in the case of alumina support the red shift of band of  ${}^4A_2 \rightarrow {}^4A_2 + {}^4E$  transition and substantial blue shift of bands of  $\pi_3(e) \rightarrow \pi_4(a_1)$  and  $S \rightarrow T$  electron transitions in  $\text{Cr}(\text{acac})_3$  molecule was observed. This indicates to the difference in the mechanism of binding of  $\text{Cr}(\text{acac})_3$  molecules at silica and alumina supports and to the distinct influence of alumina on acetylacetonate ligands of  $\text{Cr}(\text{acac})_3$  if compared with silica support. The observed change of magenta colour of bulk  $\text{Cr}(\text{acac})_3$  to green upon decoration of silica and alumina surface may be explained by the red shift of the band of  $d \rightarrow d$  electron transition in UV-vis spectra by 13 and 26 nm, respectively.

IR spectroscopic study was performed to clarify the changes of  $\text{Cr}(\text{acac})_3$  molecules during their binding at silica and alumina surface.

IR spectra of bulk  $\text{Cr}(\text{acac})_3$ ,  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  and  $\text{Cr}(\text{acac})_3\text{-SiO}_2$  samples in the region of  $1250\text{--}1650\text{ cm}^{-1}$  characteristic for the vibrations of acetylacetonate ligand are shown in Figure 2. The position of the observed bands and their assignment [13-15] are summarised in Table 2. The



**Fig. 2.** IR spectra of bulk  $\text{Cr}(\text{acac})_3$  (1),  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  (2) and  $\text{Cr}(\text{acac})_3\text{-SiO}_2$  (3).

the involvement of  $\text{C} = \text{O}$  groups in interaction with silica network.

The IR spectra of bulk  $\text{Cr}(\text{acac})_3$ ,  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  and bulk  $\text{Al}(\text{acac})_3$  in the region of  $1250\text{--}1650\text{ cm}^{-1}$  are shown in Figure 3. In contrast to bulk  $\text{Cr}(\text{acac})_3$  for which the bands at  $1278$ ,  $1522$  and  $1577\text{ cm}^{-1}$  are typical (Fig. 3, curve 1),  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  exhibits the bands at  $1286$ ,  $1527$  and  $1582\text{ cm}^{-1}$  (Fig. 3, curve 2) that indicates the involvement of acetylacetonate ligands into interaction with alumina surface sites. The position of the observed bands and their assignment are summarised in Table 2.

bands of  $\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{O})$ ,  $\nu(\text{C}=\text{C}) + \nu(\text{C}-\text{C})$  and  $\nu(\text{C}=\text{O})$  vibrations of acetylacetonate ligand are taken for the detailed consideration.

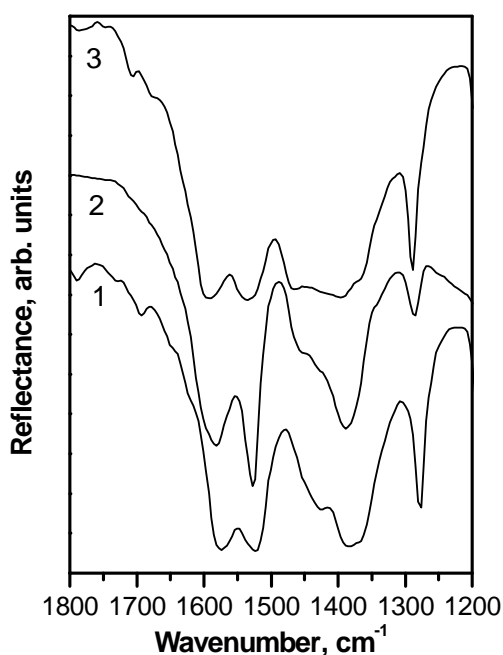
The bulk  $\text{Cr}(\text{acac})_3$  exhibits the bands at  $1278$ ,  $1522$  and  $1577\text{ cm}^{-1}$  (Fig. 2, curve 1). The corresponding bands in the spectrum of  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  (Fig. 2, curve 2) are slightly different and located at  $1282$ ,  $1526$  and  $1573\text{ cm}^{-1}$ , respectively. The difference in the position of the bands in IR spectra of bulk  $\text{Cr}(\text{acac})_3$  and  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  is within the spectrometer resolution and can hardly be used to attribute it to the particular interaction of  $\text{Cr}(\text{acac})_3$  with surface active sites.

IR spectrum of  $\text{Cr}(\text{acac})_3\text{-SiO}_2$  is shown in Figure 2 (curve 3). The positions of the considered bands at  $1284$ ,  $1527$  and  $1562\text{ cm}^{-1}$  differ from those in the spectrum of bulk  $\text{Cr}(\text{acac})_3$  (Table 2). A substantial difference in the position of  $\nu(\text{C}=\text{O})$  vibration band in IR spectra of bulk and encapsulated  $\text{Cr}(\text{acac})_3$  at  $1577$  and  $1562\text{ cm}^{-1}$ , respectively, can indicate

**Table 2.** Band positions and assignments in IR spectra of bulk  $\text{Cr}(\text{acac})_3$ ,  $\text{Cr}(\text{acac})_3/\text{SiO}_2$ ,  $\text{Cr}(\text{acac})_3\text{-SiO}_2$ ,  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  and bulk  $\text{Al}(\text{acac})_3$

Band assignment	Band position, $\text{cm}^{-1}$				
	$\text{Cr}(\text{acac})_3$	$\text{Cr}(\text{acac})_3/\text{SiO}_2$	$\text{Cr}(\text{acac})_3\text{-SiO}_2$	$\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$	$\text{Al}(\text{acac})_3$
$\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{O})$	1278	1282	1284	1286	1289
$\delta(\text{C}-\text{H})$	1320-1470	1320-1470	1320-1470	1320-1470	1320-1470
$\nu(\text{C}=\text{C}) + \nu(\text{C}-\text{C})$	1522	1526	1527	1527	1535
$\nu(\text{C}=\text{O})$	1577	1573	1562	1582	1593

The positions of the bands in IR spectrum of bulk  $\text{Al}(\text{acac})_3$  at 1289, 1535 and 1593  $\text{cm}^{-1}$  are very close to those in  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$ . Therefore it is not possible to detect correctly the surface  $\text{Al}(\text{acac})_x$  species which can be formed from acetylacetonate evolved upon covalent bonding of  $\text{Cr}(\text{acac})_3$  at the alumina surface.



**Fig. 3.** IR spectra of bulk  $\text{Cr}(\text{acac})_3$  (1),  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  (2) and bulk  $\text{Al}(\text{acac})_3$  (3).

One should consider in detail the position of the band which correspond to  $\nu(\text{C}=\text{O})$  vibration of acetylacetonate ligand in different surrounding. In IR spectra of bulk  $\text{Cr}(\text{acac})_3$  this band is located at 1577  $\text{cm}^{-1}$ . For  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  this band is shifted to 1573  $\text{cm}^{-1}$ . For  $\text{Cr}(\text{acac})_3\text{-SiO}_2$  further shift to 1562  $\text{cm}^{-1}$  is observed. Such behaviour of vibration of  $\text{C}=\text{O}$  group can be explained by its interaction with active sites either on silica surface or inside silica matrix. In the latter case, somewhat stronger interaction should be observed for steric reasons that results in more substantial band shift. In contrast, for  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  the opposite band shift to 1582  $\text{cm}^{-1}$  is observed. Therefore, it reasonable to assume the difference in the mechanism of the binding of  $\text{Cr}(\text{acac})_3$  molecules at silica and alumina supports that agrees with the results of UV-vis spectroscopic study.

To discuss the molecular binding of metal acetylacetonates  $\text{M}(\text{acac})_n$  at the support surface (silica, alumina, titania etc), one should consider two alternative ligand structures. First, the ligand can be postulated mostly as the system with delocalised  $\pi$ -electrons [16] responsible for interaction (scheme 1, a). Second, the irregular distribution of the electron density in acetylacetonate cycle may be supposed (scheme 1, b) and binding is expected to realise *via* definite group rather than a whole  $\pi$ -electron system. Furthermore, the acetylacetonate ligand possesses  $\text{C}=\text{O}$  and  $\text{C}-\text{H}$  groups which differ in chemical properties [17] and the ability to be involved in interaction with surface sites.



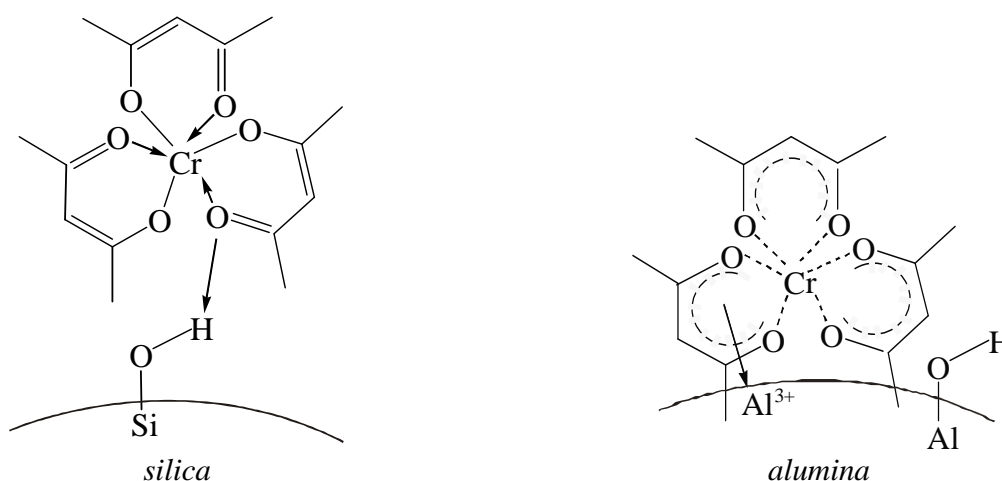
**Scheme 1.** Alternative structures of acetylacetonate ligand in metal acetylacetonates  $M(acac)_n$ .

Köhler et al. [3] proposed the mechanism of bonding of  $Pt(acac)_2$  molecules with hydroxyl groups of silica surface. The possibility of the formation of hydrogen bonds with participation of both delocalised  $\pi$ -electrons of acetylacetonate ligands and oxygen free electron pairs was assumed.

The observed behaviour of acetylacetonate ligand vibrations for  $Cr(acac)_3/Al_2O_3$  can be explained by interaction of its  $\pi$ -electrons with alumina surface active sites.

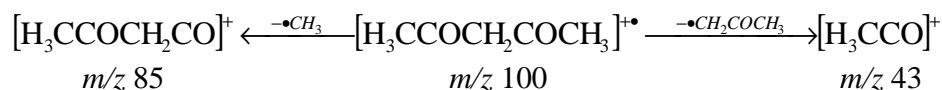
It is also necessary to take into account the dependence of the loading of the deposited  $Cr(acac)_3$  on the concentration of surface hydroxyl groups of silica [4]. This indicates the involvement of  $C=O$  groups in hydrogen bonding with hydroxyl groups of silica network. This conclusion agrees with earlier reported results on quantum chemical simulation of interaction of  $Cr(acac)_3$  with silanol groups  $\equiv Si-OH$  [18]. The formation of hydrogen bonds via the oxygen atom of acetylacetonate ligand and the hydrogen atom of  $\equiv Si-OH$  was found out to be most energetically favourable. The binding of  $Cr(acac)_3$  molecules at  $Al^{3+}$  sites of alumina surface was supposed since the concentration of surface hydroxyl groups on the alumina surface did not influence the  $Cr(acac)_3$  loading [8].

The scheme 2 illustrates the possible mechanism of binding of  $Cr(acac)_3$  molecules at active sites of silica and alumina surface.



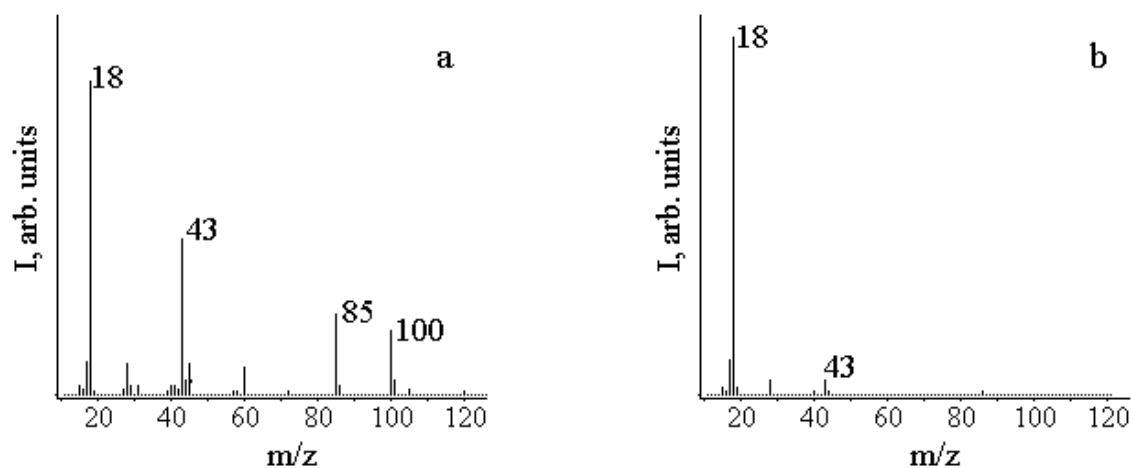
**Scheme 2.** Binding of  $Cr(acac)_3$  molecule at active sites of silica and alumina surface.

The proposed mechanism of binding of  $Cr(acac)_3$  molecules at the active sites of silica and alumina surface was proved by TPD-MS technique. The desorption of acetylacetonate could be controlled by its molecular ion ( $m/z$  100). The fragment ions  $[H_3CCOCH_2CO]^+$  and  $[H_3CCO]^+$  with  $m/z$  85 and 43 (scheme 3) are also characteristic for acetylacetonate [19, 20].



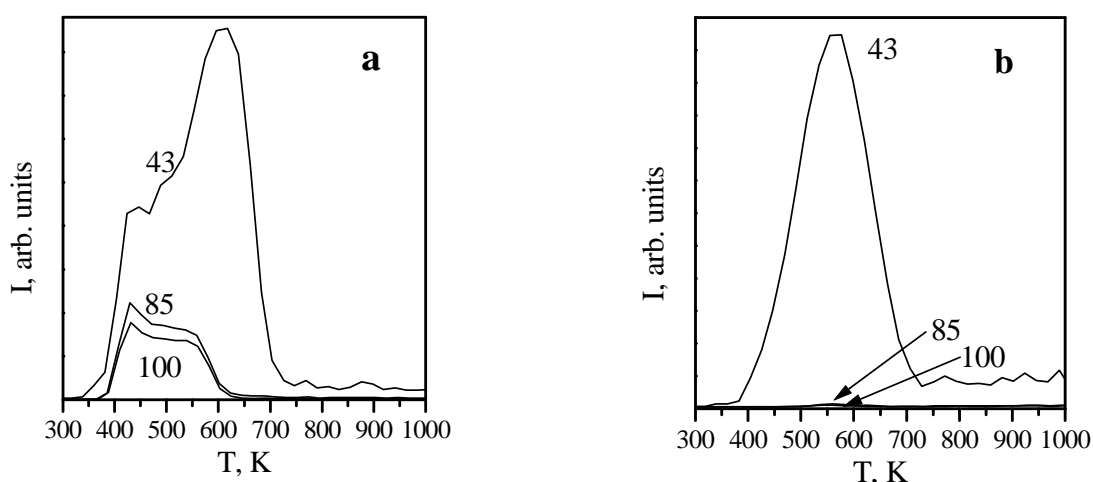
**Scheme 3.** Fragmentation of cation-radical of acetylacetone.

The mass spectra of the volatile products desorbed from  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  and  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  at 435 K are shown in Figure 4. The peak at  $m/z$  18 corresponds to water desorbing from the surface of both samples. The acetylacetone related peaks at  $m/z$  43, 85 and 100 dominate in the case of  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  (Fig. 4, a). In the case of  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  (Fig. 4, b), the molecular ion ( $m/z$  100) as well as fragment  $[\text{H}_3\text{CCOCH}_2\text{CO}]^+$  ( $m/z$  85) are not detected.



**Fig. 4.** Mass spectra of the products desorbed from  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  (a) and  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  (b) at 435 K

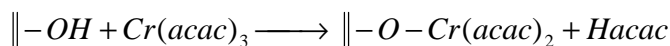
TPD-MS patterns of  $m/z$  43, 85 and 100 for  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  and  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  are shown in Figure 5.



**Fig. 5.** TPD-MS patterns of  $m/z$  43, 85 and 100 for  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  and  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$

TPD-MS of  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  (Fig. 5, a) exhibits the pattern of the molecular ion ( $m/z$  100) in

the region of 400-600 K. This means the release of acetylacetonate molecules which can originate from  $\text{Cr}(\text{acac})_3$  molecules hydrogen bonded to surface hydroxyl groups. Upon thermal activation, a substitution of acetylacetonate ligands with surface hydroxyl groups occurs that results in the formation of the covalently bonded chromium acetylacetonate species (scheme 4).



**Scheme 4.** Substitution of acetylacetonate ligand of  $\text{Cr}(\text{acac})_3$  with surface hydroxyl group.

From Figure 5, a one can see that above 600 K the intensity of signal of the molecular ion ( $m/z$  100) is negligible while the fragment ion  $[\text{H}_3\text{CCO}]^+$  ( $m/z$  43) demonstrates the intense peak at 610 K. The predominant release of the fragment ion  $[\text{H}_3\text{CCO}]^+$  in the absence of the molecular ion indicates the thermal decomposition of those acetylacetonate ligands in  $\text{Cr}(\text{acac})_3$  molecule which are not in hydrogen bonding with the silica surface.

The obtained results are in agreement with the observations of Hakuli et al. [5] who reported the reaction of  $\text{Cr}(\text{acac})_3$  with hydroxyl groups of silica surface within 433-473 K and the formation of  $\equiv\text{SiO}-\text{Cr}(\text{acac})_2$  surface species at 473 K. The partial decomposition of acetylacetonate ligands in surface chromium acetylacetonate species was observed within 493-513 K.

The TPD-MS patterns of  $m/z$  43, 85 and 100 for  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  are shown in Figure 5, b. In contrast to TPD-MS of  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  (Fig. 5, a), the TPD-MS of  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  exhibits only negligible intensity of the molecular ion ( $m/z$  100) in the region of 400-600 K while the intense signal of the fragment ion  $[\text{H}_3\text{CCO}]^+$  ( $m/z$  43) is observed within 400-750 K. Since the molecules of acetylacetonate are not released it is reasonable to suppose the thermal decomposition of acetylacetonate ligands which are not in hydrogen bonding with the alumina surface.

## Conclusions

The TPD-MS of  $\text{Cr}(\text{acac})_3/\text{SiO}_2$  sample exhibits the pattern of the molecular ion ( $m/z$  100) in the region of 400-600 K. This means the release of acetylacetonate molecules which can originate from  $\text{Cr}(\text{acac})_3$  molecules hydrogen bonded to surface hydroxyl groups.

The TPD-MS of  $\text{Cr}(\text{acac})_3/\text{Al}_2\text{O}_3$  sample exhibits only negligible intensity of the molecular ion ( $m/z$  100) in the region of 400-600 K while the intense signal of the fragment ion  $[\text{H}_3\text{CCO}]^+$  ( $m/z$  43) is observed within 400-750 K. Since the molecules of acetylacetonate are not released, the thermal decomposition of acetylacetonate ligands which are not in hydrogen bonding with the alumina surface predominates.

The surface hydroxyl groups are responsible for binding of  $\text{Cr}(\text{acac})_3$  molecules only in the case of silica support due to hydrogen bonding with C = O group in acetylacetonate ligand. In contrast, the binding of  $\text{Cr}(\text{acac})_3$  molecules at the alumina surface can be due to donor-acceptor interaction of  $\pi$ -electrons of acetylacetonate ligands with  $\text{Al}^{3+}$  sites.

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## ИССЛЕДОВАНИЕ Cr(acac)<sub>3</sub> НА ПОВЕРХНОСТИ ОКСИДОВ КРЕМНИЯ И АЛЮМИНИЯ МЕТОДАМИ ТПД–МС, УФ И ИК СПЕКТРОСКОПИИ

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*Методами температурно–программируемой десорбционной масс–спектрометрии (ТПД–МС), УФ и ИК спектроскопии исследован механизм взаимодействия молекул Cr(acac)<sub>3</sub> с активными центрами поверхности оксидов кремния и алюминия. Установлено, что в случае оксида кремния поверхностные гидроксильные группы взаимодействуют с Cr(acac)<sub>3</sub> с образованием водородных связей с ацетилацетонатными лигандами. В случае оксида алюминия реализуется донорно–акцепторное взаимодействие π–электронов ацетилацетонатных лигандов молекул Cr(acac)<sub>3</sub> с координационно–ненасыщенными центрами Al<sup>3+</sup> поверхности.*

## ДОЛІДЖЕННЯ Cr(acac)<sub>3</sub> НА ПОВЕРХНІ ОКСИДІВ КРЕМНІЮ ТА АЛЮМІНІЮ МЕТОДАМИ ТПД–МС, УФ ТА ІЧ СПЕКТРОСКОПІЇ

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*Методами температурно–програмованої десорбційної мас–спектрометрії (ТПД–МС), УФ та ІЧ спектроскопії досліджено механізм взаємодії молекул Cr(acac)<sub>3</sub> з активними центрами поверхні оксидів кремнію та алюмінію. Встановлено, що у випадку оксиду кремнію поверхневі гідроксильні групи взаємодіють з Cr(acac)<sub>3</sub> з утворенням водневих зв'язків з ацетилацетонатними лігандами. У випадку оксиду алюмінію реалізується донорно–акцепторна взаємодія π–електронів ацетилацетонатних лігандів молекул Cr(acac)<sub>3</sub> з координаційно–ненасиченими центрами Al<sup>3+</sup> поверхні.*