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# Activated Aluminium Oxide: New Aspects of the Formation and Application of the *in situ* Synthesis of Aluminium Chloride Catalysts for Hydrocarbon Conversion

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## Abstract

Using the methods of Auger electron spectroscopy and the transmission electron microscopy, the process of aluminium activation by liquid metal alloy Ga–In was investigated. It was demonstrated that the components of the Ga–In alloy penetrate across the “biographical” aluminium oxide film to spread over the surface of aluminium metal. The activated aluminium interaction with *tert*-butyl chloride in liquid isobutene was investigated. It was revealed that the interaction takes place in three stages: the formation of aluminium chloride ionic complexes and aluminium chloride, the decomposition of *tert*-butyl chloride *in situ* obtained aluminium chloride systems, the formation of stable molecular aluminium chloride complexes with *tert*-butyl chloride, which complexes block the further interaction between chloroalkanes and activated aluminium. The aluminium chloride complexes obtained were studied for the case of isobutane alkylation by butenes.

**Key words:** activated aluminium oxide, liquid metal alloy Ga–In, *tert*-butyl chloride, isobutane, butylenes, alkylation, Auger electron spectroscopy, transmission electron microscopy, ATR infrared spectra

## INTRODUCTION

Aluminium metal is considered a promising material in the field of alternative power engineering and catalysis. Thus, oxidizing aluminium [1] or its activated alloys with copper, nickel, cobalt or zinc by water with further calcination the precipitate formed, one obtains adsorbents [2] and catalyst carriers for various processes, in particular for CO oxidation [3]. When water is used as an oxidant, one could simultaneously obtain such a valuable energy carrier as hydrogen [4–6].

The most interesting field of aluminium metal applying for catalysis consists in an *in situ* synthesis of the catalyst due to the action of the reaction medium. The first attempts to perform such a synthesis were connected with the process of electrochemical aluminium dissolution in the reaction medium (acylhalides with aromatic compounds) [7]. Within the last few years it was found that the direct interac-

tion of aluminium metal with organic chlorine compounds results in the conversion of hydrocarbons. Thus, the authors of [8] using aluminium metal powder activated by iodine vapour and polyhalogenomethanes (CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CHBr<sub>3</sub>, CH<sub>2</sub>Br<sub>2</sub>), performed the conversion of cyclohexane into dimethyldecals under mild conditions. The authors of [9] reported the oligomerization of dec-1-ene when metal aluminium exposed to different alkyl chlorides and the chlorides of some transition metals. These authors noted a high rate of the interaction between aluminium metal and *tert*-butyl chloride, allyl chloride as well as benzyl chloride.

However it is known that the action of the environment results in the fact that “biographically” formed oxide layers appear on the surface of aluminium thus in order to transfer it to the reactive state, researchers use special receptors for activation. At the same time, no proper attention was taken into account in the literature to the formation of the active surface of aluminium.

Our studies [10] demonstrated that the oxide layers on the surface of aluminium metal destroyed under the influence of the liquid metal alloy (LMA) Ga–In, and obtained so activated aluminium oxide (Al\*) reacted with *tert*-butyl chloride (TBC) to form ionic and molecular aluminium chloride complexes  $[\text{AlCl}_4]^-$ ,  $[\text{Al}_2\text{Cl}_7]^-$  and  $\text{AlCl}_3$ . As a result, a wide range of products was obtained, whose distribution reflects the basic direction of so-called coupled oligomerization reaction of intermediate isobutene formed [11]. Of particular interest are the potentialities to use of such aluminium chloride complexes as catalysts in the reaction of isobutane alkylation by butene. In this case, the complexes should be *in situ* formed in the environment of isobutane.

This paper presents the results of studies concerning the formation of the active surface of aluminium and its interaction with TBC in the medium of isobutane at different temperature molar ratio values, as well as the results of performing the reaction of isobutane alkylation by butenes on the *in situ* formed aluminium chloride complexes.

## EXPERIMENTAL

In this work we investigated the samples of analytical grade (ch. d. a) aluminium metal, trademark AD-1 and AMg-6. As an activator we used LMA Ga–In containing 76 mass % of gallium. The activation of aluminium samples was carried out at a room temperature and contact time ranging within 24–36 h *via* applying a drop of LMA onto the surface of initial aluminium metal [12]. We used TBC (Aldrich), liquid isobutane and butenes (Sinteticheskij Kaucuk OJSC, Russia).

The determination of morphological, phase and crystallographic characteristics of  $\text{Al}_2\text{O}_3$  film samples obtained from molten analytical grade aluminium and AMg-6 was carried out at the temperature equal to 1073 K, whereas the investigation of their interaction with LMA Ga–In was performed with the use of transmission electron microscopy (TEM), microscope JEM 2100 Jeol (the accelerating voltage equal to 200 kV, the resolution of the crystal lattice being of 0.14 nm) with INCA-250 energy dis-

persion X-ray spectrometer (Oxford Instruments). Lamellar aluminium samples with juvenile surface containing only portions of oxide film (*i. e.*, with no metal base), were obtained using the method described in [13]. These areas were transparent when viewed in transmitted light; their size was 1 mm or less. Preliminary choosing the area of the sample surface was carried out using an optical microscope.

For the investigation by means of the Auger electron spectroscopy (AES) we used AD-1 aluminium metal. In order to obtain the most fine and smooth oxide film on the juvenile surface of aluminium the specimens were melted and then poured onto a heated steel platform. The size of the samples was  $10 \times 10 \times 1$  mm. The activation of aluminium samples was carried out in the chamber of the Auger spectrometer at a residual pressure approximately equal to  $10^{-4}$  mm Hg and at the temperature of 293 K. For performing the experiments on changing the chemical composition depending on the depth of surface etching for the aluminium alloy AD-1 being in contact with LMA Ga–In (*in situ* investigation) we used Shkhuna-2 AES (Electron Co., Ryazan, Russia), equipped with an ion gun ( $\text{Ar}^+$ ) in order to etch the surface layers of the sample. The sample was brought into contact with a drop of LMA Ga–In, whose amount was equal to about 20  $\mu\text{L}$ . The sample chamber was evacuated and the investigation began in about 15–20 min after starting of the eutectic contact with aluminium. The size of the probe zone was  $50 \times 50 \mu\text{m}$ . The rate of ion etching was equal to 1–4 nm/min.

The kinetic studies were carried out using an autoclave with stirring [14] within the temperature range of 300–353 K, at Al\* : TBC 1 molar ratio from 1 : 0.03 to 1 : 14 and the pressure equal to 1.5–2.0 MPa. The activated Al\* was placed into the autoclave, after preliminary-mechanical cleaning in argon from the products of interaction with oxygen. Then in the autoclave were successively added a calculated amount of TBC and about 40 g of isobutane. The composition of the reaction mixture was monitored using a gas liquid chromatography with sampling once in an hour. The gas chromatography analysis was performed with the use of HP 5890 Series II and GC-1000 Chromos gas chromatographs equipped with capillary columns and a flame ionization detector.

The catalytic testing in the reaction of isobutane alkylation by butenes was carried out at 300 K within the pressure range of 1.5–2.0 MPa. Butenes were fed in the autoclave with aluminium chloride pre-formed in the isobutane environment with a mass rate of 10 g/g of Al\* per hour. The duration of the experiment was equal to 1 h. After the reaction was finished, the unreacted Al\* was purified from resinous products in acetone and weighed. The resinous reaction products were hydrolyzed with an aqueous solution of NaCl at a concentration of 0.1–0.2 g/mL and extracted then with *n*-hexane. The extract obtained was analyzed by means of gas chromatography-mass spectrometry (GC-MS) employing 6890/5973N chromatograph (Agilent Technologies). The analysis was carried out using HP-5ms non-polar capillary chromatography column. For the ionization we used electron impact ionization energy equal to 70 eV. The identification obtained mass spectra were performed with the use of NIST MS SEARCH 05 library.

The resinous reaction products were applied onto the crystal for the attenuated total reflection (ATR) made of ZnSe; the IR spectrum was registered with respect to a pure crystal with the spectra accumulation number and the resolution equal to 32 and 4 cm<sup>-1</sup>, respectively, within the range of 4000–400 cm<sup>-1</sup>. All the spectra were recorded using a Nicolet 5700 spectrometer (Thermo Electron Corp.) with a deuterated triglycerine sulphate detector.

## RESULTS AND DISCUSSION

### *Formation of aluminium activated state*

As it follows from the analysis of the TEM data, the structure of the oxide film obtained from molten analytical grade aluminium is not uniform. There were areas of the film observed consisting of crystals with the size ranging within 4–10 nm dispersed in an amorphous matrix. In addition, there are areas of the film with structural formations (with the sizes up to 30–50 nm) those possess the layers of crystal lattice with a period of 0.24 nm, which may correspond to the planes (311) of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Electron diffraction patterns of the mentioned sample

correspond to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase with interplanar distance (*d<sub>i</sub>*), nm: 0.239, 0.198, 0.139, *etc.* (PDF 10-0425).

The structure of the oxide film obtained from melt AMg-6 aluminium is similar to the above mentioned data for the sample of analytical grade aluminium. The analysis of the TEM data allows us to conclude that the most prominent feature of the oxide film of this sample consists in the presence of several types of structures: the crystal structure close to the structure of MgAl<sub>2</sub>O<sub>4</sub>, MgO like structure, and amorphous, relatively thin structure.

Thus, these results confirm the literature data [15] that the admixture of magnesium (more than 1 mass %) promotes the formation of magnesium oxide film on the surface of aluminium alloys.

When applying a drop of LMA Ga–In of 20  $\mu$ L in volume onto an aluminium plate sample we registered emerging dark dull spots on the surface spreading radially from the centre of the drop. After 50–60 min the dark areas were spread over a surface area at a distance of 10–15 mm from the border of the LMA Ga–In drop. Similar changes were observed on the reverse of the aluminium plates.

The electron microscopy and X-ray analysis data corresponding to the dark areas of aluminium sample surface, located at a distance of 5–10 mm from the border of LMA drops, indicate the presence of the alloy components, both in a localized form as spherically shaped particles, and in the form of morphologically immature particles. Figure 1, a demonstrates LMA Ga–In particles located on the oxide film. Figure 1, b demonstrates a part of the oxide film, where the LMA Ga–In particles were not observed in an explicit form, but the X-ray spectra (see Fig. 1, c) obtained from this exhibit peaks of Ga and In alongside with area the peaks inherent in Al and O. According to X-ray microanalysis the concentration of In and Ga exhibit deviation from the stoichiometry of the LMA reflected in an increasing the Ga/In ratio. To all appearance, this could be due to a higher diffusion mobility of Ga as compared to In in the course of spreading over the surface and penetration into the bulk of Al.

In such a way the LMA components spread over the surface and diffuse through the

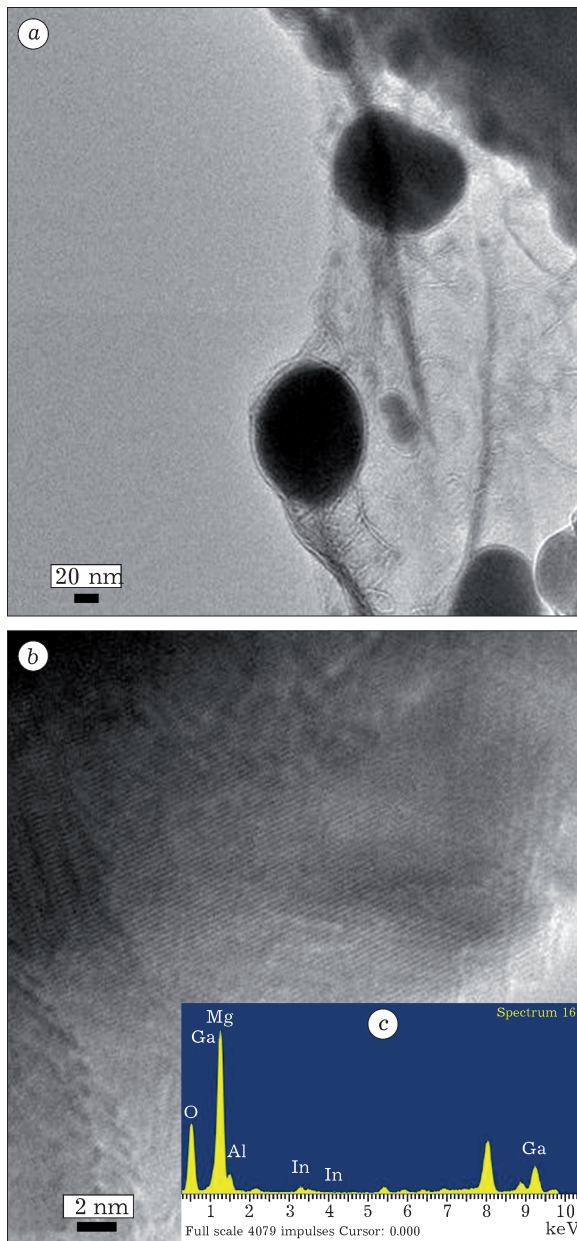


Fig. 1. Areas of the oxide film obtained from the melt of AMg-6 grade aluminium after the activation of LMA Ga-In: *a* – the area of the oxide film whereon the particles of LMA Ga-In are located; *b* – the portion of oxide film where no particles of LMA Ga-In are observed; *c* – X-ray spectrum obtained from the area demonstrated in Fig. 1, *b*.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub>, MgO films into the bulk of aluminium foil. At the first stage, the LMA penetration occurs along the boundaries of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles, the defects in the structure of the crystalline and amorphous phases of the oxide film, as well as through the vacancies in the octahedral positions of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure. The

same picture was observed for the aluminium-magnesium alloys with MgAl<sub>2</sub>O<sub>4</sub> or MgO film on the surface.

Figure 2 demonstrates the results of the investigation concerning the elemental composition of the surface layers of AD-1 aluminium performed by means of the AES. Analyzing the spectral data, we could conclude that under the vacuum conditions ( $\sim 10^{-4}$  mm Hg) and at the temperature of 293 K the components of LMA diffuse through the aluminium oxide layer at the place of contacting between LMA droplet and aluminium, then spread under the film over the surface and into the bulk of the sample. According to AES, the concentration of Ga and In under the oxide film does not always correspond to the stoichiometry of LMA. To all appearance, this is connected with local structural heterogeneity of the analyzed surface areas [10], which results in differences in the diffusion rates of LMA components.

Earlier, we studied the features of the activation process for aluminium and its alloys by LMA Ga-In with the use a complex of X-ray spectral and electron microscopy methods. [16] As the result of analyzing the past and current investigations, the following stages of the formation of the activated aluminium state could be distinguished:

1. The diffusion of LMA Ga-In components through the aluminium oxide layer.
2. Spreading the LMA Ga-In over the surface of aluminium.
3. The destruction of the surface oxide film.

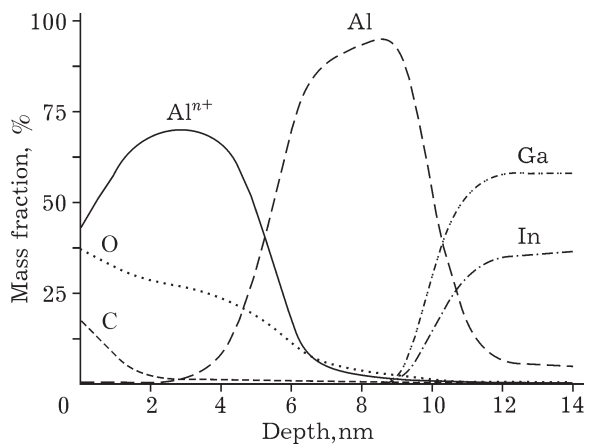
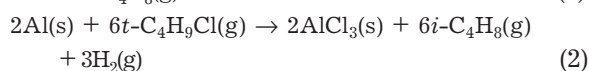
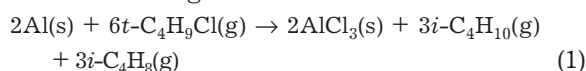


Fig. 2. Results of AES analysis on the surface of the sample of alloy AD-1 at a distance of 0.4 mm from the initial boundary of LMA Ga-In drop. The activation time being equal to 1.5 h.

4. The oxidation of the aluminium surface.
5. The penetration of LMA Ga–In components along the grain boundaries of polycrystalline aluminium.
6. Ga bulk diffusion into aluminium grains.

**Interaction of activated aluminium with *tert*-butyl chloride in the environment of isobutane at different temperature values**

According to the data of [17, 18], the aluminium metal can interact with TBC according to the following two reactions:



Both reactions are thermodynamically allowed under the standard conditions in the gas phase. Judging by the form of equations (1) and (2), it is expected that the reaction should run according to the first order with respect to TBC. It should be noted that for the conversion of 1 mol of Al it is required to spend 3 mol of TBC and 1 mol of TBC else in order to form the aluminium chloride complex.

In our experiments, the formation of isobutane and isobutene was first observed, which indicates the reaction running according to equation (1). Figure 3 demonstrates the kinetic curves of TBC consumption depending on time. Conventionally, the curves can be divided into three parts: 1) a part caused by the induction

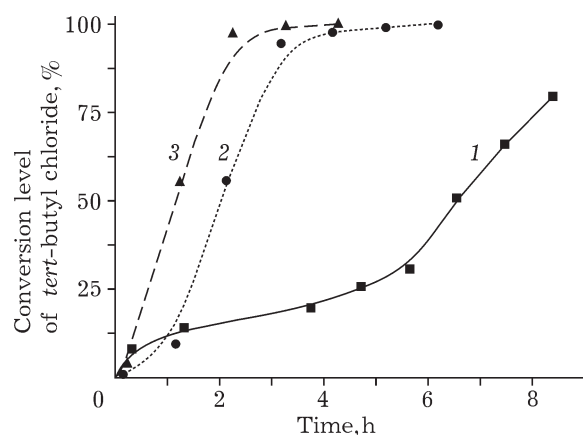
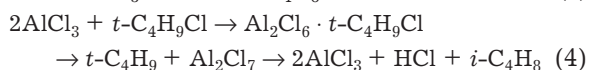
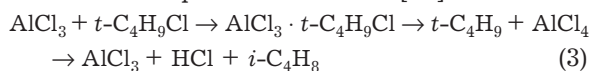


Fig. 3. Kinetic curves for the consumption tert-butyl chloride with time at different temperatures (the molar ratio activated aluminium oxide/*tert*-butyl chloride being equal to 1 : 4); temperature, K: 313 (1), 333 (2), 353 (3).

period, 2) a part described by the first order kinetic equation, and 3) a part described by the second order kinetic equation.

The presence of the induction period we mentioned earlier. The performing of repeated experiments in some cases demonstrated unsatisfactory reproducibility of this part of the kinetic curve. In the kinetics of heterogeneous reactions [19], the induction period is connected with the nucleation of a new phase and with its propagation through the interface area between solid and liquid reactants. Taking into account the mass of unreacted activated aluminium and the results of calculation according to the equation of chemical reaction (1) one can see that the amount of TBC required for the stoichiometry is consumed within the induction period, *i. e.*, the formation of aluminium chloride complex is observed just during this period. It should be noted that with increasing the temperature the induction period ceases to be a rate-determining factor to disappear almost completely by 353 K.

On the other hand, the appearance of aluminium chloride in the system should result in a rapid decomposition of TBC at the temperature values higher than 250 K [20], according to one of the possible schemes [21]:



The overall equation should look like a direct decomposition of TBC, *i. e.*, the first-order reaction, which is just displayed in Fig. 3 after the induction period. The obtained values of the reaction rate constants observed correspond to a linear dependence in Arrhenius coordinates ( $r^2 = 0.94$ ). The apparent activation energy and pre-exponential factor calculated from the dependence were found to be equal to 30.9 kJ/mol and  $7 \cdot 10^5 \text{ h}^{-1}$ , respectively.

According to equations (3) or (4) the decomposition of TBC by aluminium chloride formed in the course of the induction period results in the formation of isobutene, whereas its interaction with isobutane gives trimethylpentanes. The appearance of the reaction products within the induction period indicates the formation of aluminium chloride complexes at very beginning of the interaction between  $\text{Al}^*$  and TBC,

which confirms the mentioned above. During the period of time corresponding to the decomposition of TBC, an increase in the percentage of  $C_8$  hydrocarbons is observed, but only to a point. Thereby, with increasing the temperature, a decrease in the time period, when these hydrocarbons prevail. The further yield of hydrocarbons, predominantly  $C_5$ – $C_7$  ones, is connected with the consumption of isobutane equal to the mass of isobutane necessary for their formation, *i.e.*, there is no TBC decomposition observed, although the TBC concentration decreases. The kinetic curve of spending TBC within this period of time (see Fig. 3) corresponds to the second order kinetic equation. The only possible products, according to equations (3) and (4) could be presented by molecular or ionic complexes.

The formation of molecular complexes is indicated by the IR ATR spectroscopy data. The IR ATR spectra (Fig. 4, curves 1 and 2) exhibit an absorption band (a. b.) at 497 and a shoulder at  $529\text{ cm}^{-1}$  against the background of intense a. b. at  $549\text{ cm}^{-1}$ , those earlier [11] were attributed to  $AlCl_4^-$  and  $Al_2Cl_7^-$  ions, respectively. Unfortunately, the only work whose the authors investigated the molecular complexes [21] is available from the literature. According to this work, the a.b. at  $549\text{ cm}^{-1}$  corresponds to the molecular complexes such as  $AlCl_3 \times mt-C_4H_9Cl$ , where  $m = 1, 2$ . Other absorption bands those

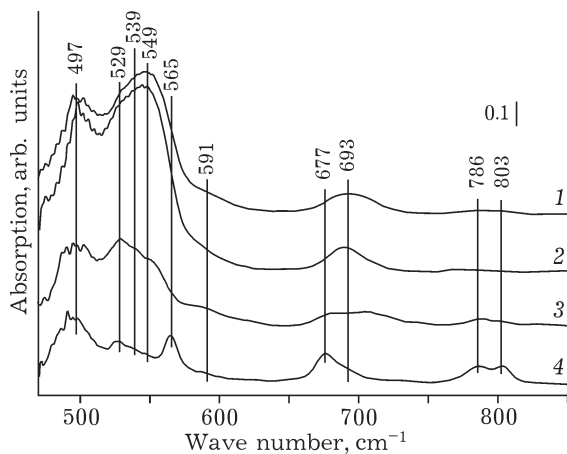


Fig. 4. IR ATR spectra of resinous reaction products resulted from the interaction of aluminium activated by *tert*-butyl chloride among isobutane at different molar ratios between activated aluminium oxide and *tert*-butyl chloride and at the temperature values: 1 – 1 : 4, 313 K; 2 – 1 : 4, 333 K; 3 – 1 : 1, 313 K; 4 – 1 : 0.25, 313 K.

correspond to these molecular complexes are overlapping with the a. b. of ions, being not resolved in the spectrum. The authors noted that the molecular complexes exist within the temperature range 80–120 K, but they could be stabilized either under the conditions of aluminium chloride deficiency, or by means of inert components (*n*-octane and other hydrocarbons) at the temperature values amounting up to 200 K. Within the temperature range 300–353 K under our use the molecular complexes are stable. To all appearance, under the reaction conditions any structures are formed those increase their stability. After the hydrolysis of resinous products, no oxygen compounds formed were registered by means of CMS, those anyway could indicate the structure of the cation, however cyclopentadiene-1,3 and cyclohexadiene-1,3 derivatives were found. To all appearance, in composition with aluminium chloride and hydrogen chloride, these compounds form an ionic adduct, wherein the molecular complexes of aluminium chloride with TBC could be stable.

Thus, at the  $Al^*/TBC$  molar ratio equal to 1 : 4, there are undesirable reactions observed such as the chloroorganic compound decomposition and the formation of molecular complexes stable under the reaction conditions, which prevents  $Al^*$  from complete conversion.

#### *Interaction of activated aluminium with tert-butyl chloride in the environment of isobutane at different molar ratio values*

The complete conversion of  $Al^*$  is observed at the molar ratio equal to 1 : 14. In this case, because of a high concentration of TBC within the first 4 h, a zero kinetic order reaction is observed with respect to the chloroorganic compound. Further we registered the kinetic order, which indicates the TBC decomposition by aluminium chloride formed. To all appearance, the complete dissolution of the solid reagent is promoted by a partial dissolution of the aluminium chloride in the reaction medium. At  $Al^*/TBC$  molar ratio values  $< 1 : 4$ , the interaction could be judged qualitatively, since the most part of the TBC converted during 1–2 h. With decreasing the  $Al^*/TBC$  molar ratio,  $C_8$  hydrocarbons are prevailing among the liquid products.

Figure 4 (curves 3, 4) demonstrates IR ATR spectra of resinous products formed at Al\*/TBC molar ratio values equal to 1 : 1 and 1 : 0.25, and at the temperature amounting to 333 K. The IR spectra exhibit absorption bands at 497, 529 and 549  $\text{cm}^{-1}$ , earlier attributed to  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$  and molecular complexes  $\text{AlCl}_3 \times m\text{t-C}_4\text{H}_9\text{Cl}$  ( $m = 1, 2$ ), respectively. The emergence of a low-intensity shoulder at 539  $\text{cm}^{-1}$  against the background a. b. at 529  $\text{cm}^{-1}$ , as well as the presence of a. b. at 591  $\text{cm}^{-1}$  indicate the formation of polynuclear ion  $\text{Al}_3\text{Cl}_{10}^-$  [21, 22]. The authors of [21], studying the interaction between aluminium chloride and TBC at the temperature ranging within 80–120 K, attributed the absorption bands at 537 and 587  $\text{cm}^{-1}$  to the vibrations inherent in this ion. The investigation of emission IR spectra resulted from the melts of alkali metal chloroaluminates and the application of the theory of normal vibration modes by the authors of [22] demonstrated that the absorption at 533  $\text{cm}^{-1}$  corresponds to ion  $\text{Al}_3\text{Cl}_{10}^-$ . The appearance of an intense absorption band at 565  $\text{cm}^{-1}$  in the experiment with Al\*/TBC molar ratio equal to 1 : 0.25, indicates that there is possible formation of polynuclear species such as  $\text{Al}_n\text{Cl}_{3n+1}^-$ , where  $n > 3$  [22]. The authors of this paper observed an absorption band at 567  $\text{cm}^{-1}$ . Unfortunately, there is no other information available from the literature about polynuclear species with composition  $\text{Al}_n\text{Cl}_{3n+1}^-$  ( $n > 3$ ).

The formation of polynuclear ions is observed at a high concentration of aluminium chloride. The cause of the formation of these ions, in the opinion of the authors of [23, 24], might consist either in the dissociation of the existing  $\text{AlCl}_4^-$  ion or in the solvation of aluminium chloride under formation by this ion [25]. This question represents the subject of a separate investigation and is not connected with the goal of this paper.

With a decrease in the molar ratio Al\*/TBC down to 1 : 0.03, aluminium chloride phase nucleation is observed, which phase moves on the surface of the activated aluminium plate in certain direction. This new phase forms spherical nuclei of about 50  $\mu\text{m}$  in diameter. It can be assumed that as the molar ratio increases these nuclei should grow in size and grow over the

surface of the plate Al\* to form a continuous layer that would react violently with TBC to involve isobutane in the interaction. According to [19], it should be expected that there is some Al\*/TBC molar ratio value observed to prevent the formation of the nuclei of a new phase and, as a consequence, its interaction with TBC.

Thus, at the Al\*/TBC molar ratio equal to 1 : 14, there is a complete dissolution of Al\* in the reaction medium observed, and the reaction exhibits zero order with respect to the chloroorganic compound at the initial moments of time. As it is for aluminium chloride observed, a decrease of the molar ratio results in the formation of polynuclear species. With decreasing the molar ratio down to 1 : 0.03, the only nuclei of aluminium chloride phase are observed to form on the surface of the Al\* plate.

#### *Alkylation of isobutane by butenes on the formed aluminium chloride complexes*

The use of aluminium chloride complex formed at a molar ratio Al\*/TBC equal to 1 : 0.25, and at the temperature of 333 K, in the alkylation reaction of isobutane provides an almost complete conversion of butenes (about 97 %). The yield of liquid hydrocarbons with respect to converted butylenes reaches 1.7 g/g. This value is lower than the stoichiometric value for the alkylation reaction (2.04 g/g), however it is in a good agreement with the data for the reaction of solid aluminium chloride published in [26]. The composition of the resulting alkylate includes TBC, which confirms the formation of molecular complexes those, to all appearance are decomposed with adding butylenes to the reaction medium. The mass fraction of hydrocarbons  $\text{C}_8$  is equal to 60 %, which is in a good agreement with the results of the works, where aluminium chloride and diethyl ether complexes [27], and a 1-butyl-3-methylimidazolium chloride – aluminium chloride ionic liquid [28] were used.

#### **CONCLUSION**

Thus, the diffusion of Ga–In LMA components through the oxide film and their distribution over the surface of aluminium result in

the destruction of the oxide film thus the bulk diffusion of Ga in aluminium grain promotes the formation of the active surface of activated aluminium oxide. The latter being under the influence of *tert*-butyl chloride in the isobutane environment is able to form aluminium chloride complexes of different composition active in the reaction of liquid phase isobutane alkylation by butenes.

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