

OBTAINING ACTIVE COMPONENTS (Ta, Re) OF BIMETALLIC CATALYSTS ON γ -Al₂O₃ AND TiO₂ MATRICES*

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R Tantalum methylete of general formula Ta₂(OMe)₁₀ was synthesized by electrochemical synthesis as a precursor for obtaining oxomethylete complexes of tantalum and rhenium. The complex is used to prepare catalysts in reactions of cross-condensation and reductive dehydration of alcohols. The catalysts are based on γ -Al₂O₃ and TiO₂. Ultradisperse and nanosized TiO₂ is obtained by the supercritical fluid technology. The sample is characterized by different methods (DTA, XRD, DSC). It is shown that annealing at 340°C allows obtaining anatase modification of TiO₂ with a specific surface of 27.3 sq.m/g which can serve as a matrix for drawing active components of catalysts. It is shown that the Ta-Re/Al₂O₃ catalyst allows transforming ethanol and mixtures of ethanol with glycerin into aliphatic hydrocarbons C₃-C₁₁. A technological scheme for obtaining active components of the catalysts for cross-condensation and reductive dehydration of alcohols is suggested.

Keywords: oxometalates complex tantalum and rhenium, electrochemical synthesis, cross-condensation, reducing the dehydration of alcohols, SAS-technology, alkoxide, methoxide of tantalum, titanium dioxide.

Introduction

Nowadays up to 84% of motor fuels are made from various hydrocarbons [1]. This situation will remain within the next decade. Estimates of hydrocarbon reserves suitable for industrial use significantly differ. However, in all cases such situation generates the need of involving renewable power sources in the sphere of industrial use [2].

Biomass is a promising renewable raw material. The total amount of biomass covering the earth is 800 bln t including renewable biomass of 200 bln t [3, 4]. One of the most widespread primary products of biomass decomposition is bioethanol, which cannot be used directly. In order to obtain required fuel hydrocarbons or petrochemical substrates from bioethanol by cross-coupling reactions and reductive dehydration of alcohols, nanocomposite catalytic materials are used [5]. Alcohols cross-coupling is a promising method for obtaining precursors of high-quality additives for motor fuel [6].

Complexes of d-elements and metals easily interact also with molecular hydrogen activating it for hydrogenation/dehydrogenation reactions. For this reason transition metals are used as catalysts in hydrogenation/dehydrogenation [7, 8]. Besides, the increased consumption of rhenium

as a catalyst makes it necessary to develop methods that would allow improving catalytic activity by introducing other metals into matrixes. One of the most promising directions for solving this problem is alkoxotechnology, within which it is possible to obtain materials with preset properties and structures [9, 10]. Alkoxides of transitional metals can be used as precursors for nanocomposite catalytic materials.

The purpose of this work is preparation of bimetallic rhenium-tantalum methylate followed by its application on γ -Al₂O₃ and on TiO₂ obtained by the SAS (supercritical anti-solvent) method for use as a catalysts in cross-coupling and reductive dehydration of alcohols enabling to obtain motor fuels or additives for them.

Experimental

Oxomethylate complex of tantalum and rhenium Ta₄O₂(OCH₃)₁₄(ReO₄)₂ was used as a precursor. It was obtained from tantalum methylate Ta₂(OMe)₁₀ and Re₂O₇.

Tantalum methylate was synthesized by the electrochemical method described in [11, 12] with the use of a cell without division of the anode and cathode spaces and electrodes: the cathode was platinum, the anode was tantalum. The following materials and reactants were used for methylates preparation: metal plates of tantalum (99.9% purity) and platinum (99.9% purity), metal chips of magnesium (95% purity), methanol (Merck KgaA, $\geq 99.5\%$ purity), aqueous ammonia (GOST 24145-80, high pure), lithium chloride (Merck KgaA, pure). Methanol was dried by heating with magnesium chips [13] because of methylates hypersensitivity to moisture. The final content of water was less than 0.01%. Lithium chloride for electrolysis in alcohol media was dehydrated by the technique described in [14]. Lithium chloride was deleted subsequently with hexane (TU 2631-006-29483781-2008, chemically pure).

Rhenium(VII) oxide was obtained from metallic rhenium powder (99.9% purity) by heating in a flow of oxygen at 400°C.

The oxomethylate complex of tantalum and rhenium Ta₄O₂(OCH₃)₁₄(ReO₄)₂ was synthesized in a "dry" boxing. Ta₂(OCH₃)₁₀ powder was dissolved in 25 ml of dehydrated toluene, and rhenium(VII) oxide powder was added to the obtained solution. The mass of Re₂O₇ powder was calculated for Ta:Re mass ratio 4:1. The mixture was kept at room temperature (21°C) for 5 min and at 35°C for 45 min at continuous stirring, and then refluxed for 8 min without stirring. The obtained complex was identified by X-ray phase analysis and IR spectroscopy [11, 15].

One of carriers was TiO₂ of two types obtained by the SAS (supercritical anti-solvent) method. Supercritical anti-solvent fluid precipitation was carried out in a laboratory system for dispergation, SAS-50 model (Thar Technologies, USA). Working pressure: 10–20 MPa; system temperature: 80°C, supercritical CO₂ flow rate: 5 g/min; solution feed rate: 45 ml/min [16, 17]. A

difference of the samples consisted in that the second sample was annealed at 340°C after preparation. The obtained samples were studied by thermogravimetric and X-ray phase analysis. Their composition was established by chemical elemental analysis, and their specific surface was measured.

A solution of tantalum and rhenium oxomethylate complex $\text{Ta}_4\text{O}_2(\text{OCH}_3)_{14}(\text{ReO}_4)_2$ in toluene was applied onto TiO_2 matrix by spraying.

Another carrier was $\gamma\text{-Al}_2\text{O}_3$, onto which the oxomethylate complex was applied by incipient wetness impregnation [18].

The Re–Ta catalyst tests on the $\gamma\text{-Al}_2\text{O}_3$ matrix were carried out at the Institute of Petrochemical Synthesis, RAS, in the flowing and circulating installation presented in Figure 1.

The content of C and H in TiO_2 was determined with the use of a Heraeus CHN-O-RAPID device. The metal content in tantalum alkoxide was determined by the gravimetric method [19]. Differential thermal analysis (DTA) [20] was carried out with the use of a Q-1500 D derivatograph of (F.Paulik, J.Paulik, L. Erdey; MOM, Hungary). X-ray phase analysis [21] was made with the use of a Shimadzu XDR 6000 diffractometer (radiation CuK_α , sample rotation, continuous (1 hail/min) and step-by-step (0.02° step, exposition 10 s) modes within the angle range 2θ 10–60°). In order to identify the phases ICDD – JCPDS card-index was used. IR spectra [22] of suspensions in vaseline oil between KBr plates were recorded with the use of an EQUINOX 55 Bruker Germany device. The TG-DSC of samples was carried out by means of a F1 Jupiter® STA 449 synchronous thermoanalyzer with a platinum furnace made by Netzsch-Geratebau GmbH, Germany. The analysis of the obtained data was carried out with the use of the Netzsch Proteus Analysis v.5.2.1 program.

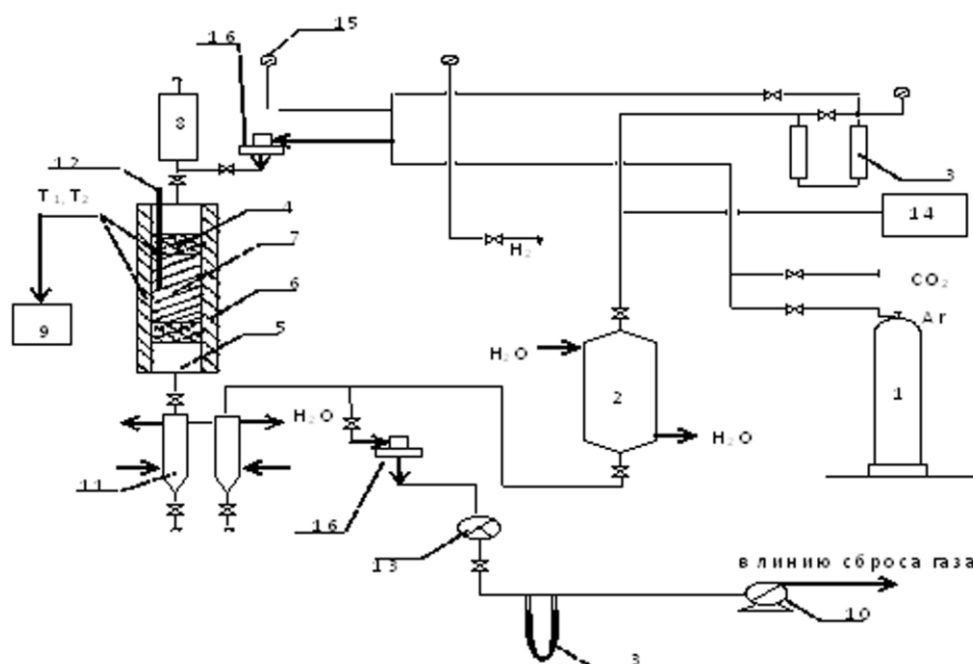


Figure 1. Scheme of flowing circulatory installation for studying recovery dehydration of alcohols: 1 – gas cylinder, 2 – gas circulation pump, 3 – flow meters, 4 – packed bed, 5 – reactor, 6 – electric furnace, 7 – catalyst layer, 8 – liquid pump, 9 – temperature regulator, 10 – gas meter, 11 – cooled gas separators, 12 – capillary with thermocouple, 13 – three-way tap, 14 – control unit, 15 – pressure sensor, 16 – pressure regulators.

[в линию сброса газа means to gas blowoff line]

Results and Discussion

Titanium dioxide was obtained with the use of SAS technology and studied by thermogravimetry and X-ray phase analysis. Figure 2 shows a thermogram of synthesized titanium dioxide. The presence of two endothermic ($T=35^{\circ}\text{C}$, $T=230^{\circ}\text{C}$) and one exothermic effects ($T=370^{\circ}\text{C}$) is found. The endothermic effects can be due to the dehydration process, as well as to the decomposition of organic components. The exothermic effect at 370°C is caused most likely by the process of crystallization of the obtained titanium dioxide. The mass loss of the sample is due to the decomposition of the organic phase that remained after the synthesis. The mass loss of the sample was 8.00% of the initial mass.

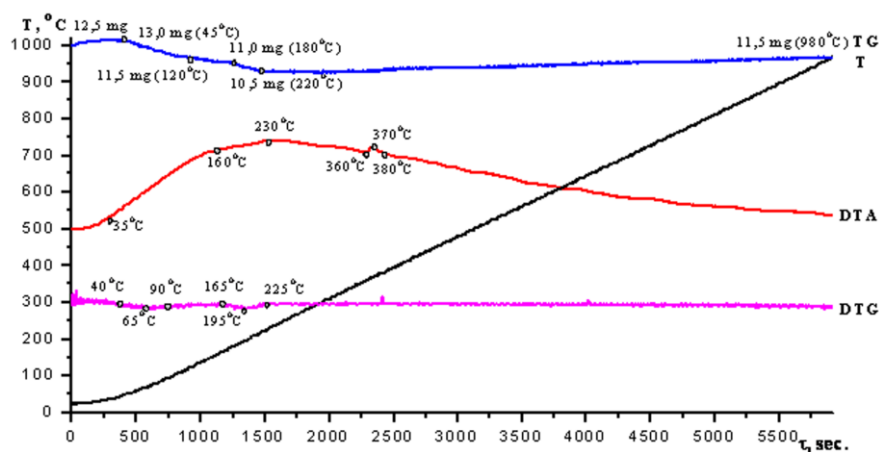


Figure 2. Thermogram of titanium dioxide obtained by the SAS method.

X-ray phase analysis showed that the synthesized titanium dioxide is mostly X-ray amorphous. Another sample of titanium dioxide obtained by the same method and under the same conditions was annealed at 340°C , and its X-ray pattern was recorded (Figure 3). Titanium dioxide modification is anatase with the following lattice parameters: $a = 3.785(3)$; $c = 9.484(3)$.

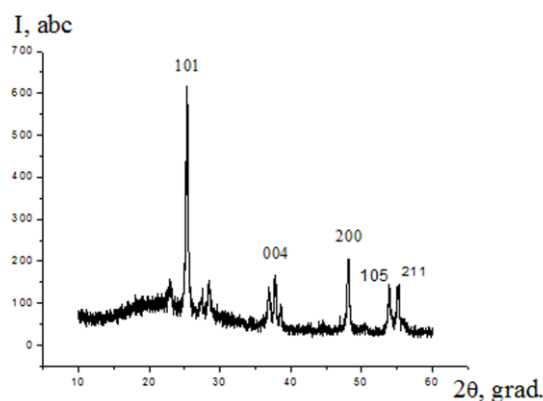


Figure 3. Results of X-ray phase analysis of titanium dioxide annealed at 340°C.

TG-DTG-DSC curves of titanium dioxide samples in the atmosphere of helium were recorded.

Two endothermic effects were found on the DSC curve in the temperature range 40–300°C due to evaporation of the adsorption moisture and the binding component. Further temperature increase in the range 400–450°C results in an exothermic effect due to titanium dioxide crystallization (Figure 4a).

The annealed example did not show thermal effects (Figure 4b).

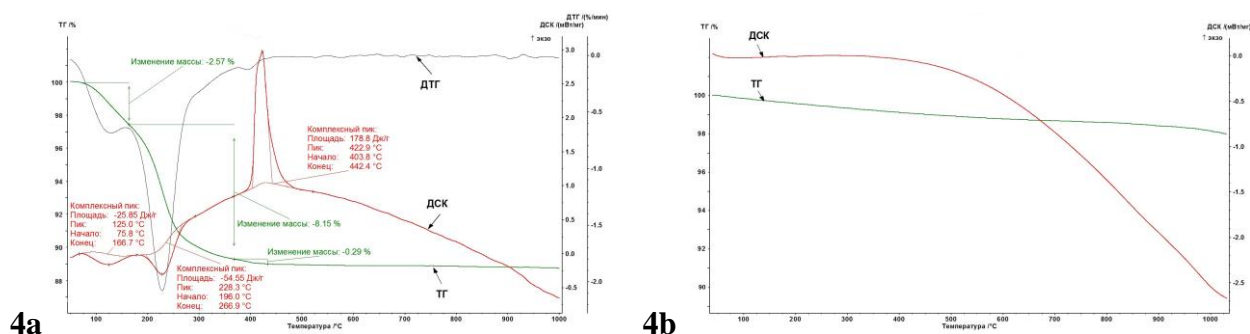


Figure 4. Results of X-ray phase analysis of titanium dioxide annealed at 340°C.

[ДТГ means DTG; ДСК means DSC; ТГ means TG; мин means in; мВт/мг means mW/mg; Температура means Temperature; Изменение массы means Mass change; Комплексный пик means Complex peak; Площадь means Area; Пик means Peak; Начало means Start; Конец means End]

Chemical analysis data: found for titanium dioxide obtained by the SAS method, % mass: 4.3 C, 0.85 N; for the sample annealed at 340°C, % mass: 3.9 C, 0.78 N.

The presence of carbon and hydrogen in the obtained oxides can be due to the presence of a minute quantity of the undecomposed precursor or due to the sorption of the reaction products and water vapor in the oxides.

The specific surface, the particle size and the pore volume of both samples were measured. The main characteristics are presented in Table 1.

Table 1. Characteristics of TiO₂ specific surface

Characteristics	Units of measurement	TiO ₂ samples	
		TiO ₂ obtained by the SAS method	TiO ₂ annealed at 340°C
Specific surface according to BET theory, A _{BET}	m ² /g	209.1	27.3
BET equation constant, C _{BET}	—	–62	43
Specific surface according to comparative method, A _{CM}	m ² /g	19.6	28.8
Nanopores volume (diameter less than 100 nm)	cm ³ /g	0.129	0.03
Ultrananopores diameter (diameter less than 2 nm)	cm ³ /g	0.075	0.007
Mean particle size	nm	27	18

A previously weighed carrier (in our case – titanium dioxide of two types: annealed and unannealed) was coated by spraying with a solution of the tantalum and rhenium oxomethylate complex in toluene. The unannealed and impregnated titanium dioxide sample is referred to hereafter as sample 1, and the annealed and impregnated one, as a sample 2.

After the spraying an increase in weight was observed: 0.0388 g in case of sample 2 and 0.0238 g in case of sample 1.

Thermogravigrams of titanium dioxide samples after applying the synthesized complex are shown in Figure 5.

In case of sample 1 exothermic effect is observed at 240°C due to the start of titanium dioxide crystallization (Figure 5a).

In case of sample 2 the same effect was observed at 335°C (Figure 5b).

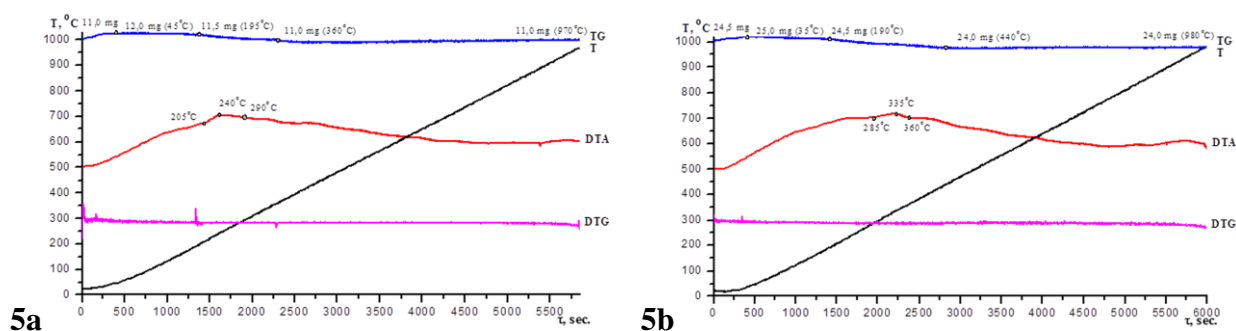


Figure 5. Thermogravigrams of titanium dioxide samples impregnated by the Ta and Re oxomethylate complex: a) TiO₂ – unannealed; b) TiO₂ – annealed at 340°C.

For both samples the specific surfaces were determined. In case of the sample in which titanium dioxide was annealed the specific surface was 3.3 m²/g at the first measurement and 3.7 m²/g at a repeated measurement. In case of the unannealed sample the first measurement gave 45.4 m²/g, and the second one, 45.2 m²/g.

The obtained data suggest that the tantalum and rhenium oxomethylate complex occupied free pores of titanium dioxide, which decreased the specific surface.

TG-DTG-DSC curves of the samples were recorded in the atmosphere of helium. Sample 1 showed three consecutive endothermic effects on the curve. Further heating resulted in an exothermic effect due to titanium dioxide crystallization. Further temperature increase gave an endothermic effect due to full removal of the organic component and the adsorbed water (Figure 6a).

In case of sample 2 three endothermic effects were found on the curve. The effects in the temperature ranges 70–155°C and 840–870°C are small and have no pronounced extremum (Figure 6b).

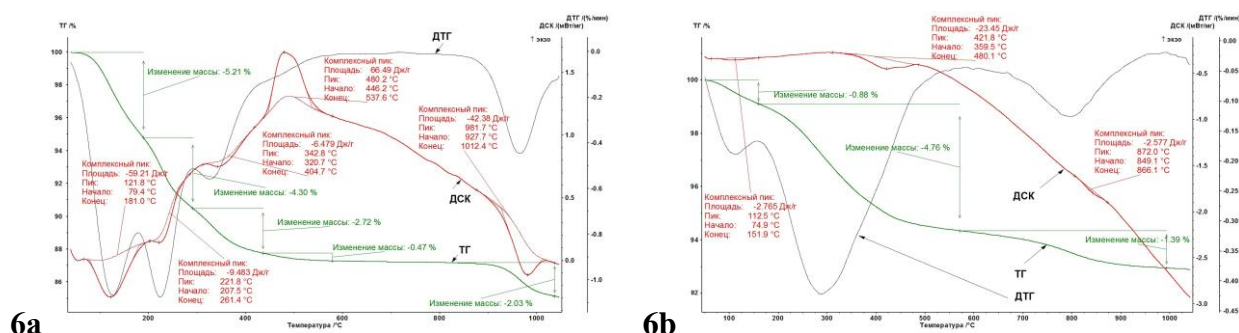


Figure 6. TG-DTG-DSC curves: a) TiO₂ sample not annealed and impregnated with the Ta and Re oxomethylate complex (sample 1); b) TiO₂ sample annealed and impregnated with the Ta and Re oxomethylate complex (sample 2).

[ДТГ means DTG; ДСК means DSC; ТГ means TG; мин means in; мВт/мг means mW/mg; Температура means Temperature; Изменение массы means Mass change; Комплексный пик means Complex peak; Площадь means Area; Пик means Peak; Начало means Start; Конец means End]

IR spectra of samples 1 and 2 were recorded, which confirmed the presence of the tantalum and rhenium oxomethylate complex in the titanium dioxide matrix. Thus, sample 2 shows absorption bands at 1169–1095 cm⁻¹ corresponding to Ta–O bond vibrations and bands at 493 cm⁻¹ corresponding to Re–O(R) bond vibrations. Sample 1 shows absorption bands at 1101 cm⁻¹ corresponding to Ta–O bond vibrations and absorption bands at 742 cm⁻¹ corresponding to Re–O bond vibrations.

Both samples show absorption bands at 3402 and 3389 cm^{-1} corresponding to the vibrations of the OH groups of water molecules. Absorption in the regions 1640 and 1625 of cm^{-1} is due to the deformation vibrations of the coordination water or adsorbed water molecules. Besides, there are absorption bands at 1007 cm^{-1} corresponding to Ti–O bond vibrations. There are also bands in the region 630–620 cm^{-1} typical of compounds with Ta–O bridge bonds forming "infinite chains" $\text{M–O}\dots\text{M}$ [13, 23].

In addition, X-ray patterns of the impregnated samples were recorded. Sample 1 is X-ray amorphous, as well as titanium dioxide obtained by the SAS (supercritical anti-solvent) method. However, intensity decreased in case of sample 1 due to the presence of other compounds as compared to the original sample. On the contrary, intensity increased in case of sample 2. Titanium dioxide modification was anatase with the following lattice parameters: $a=3.780(3)$; $c=9.483(3)$.

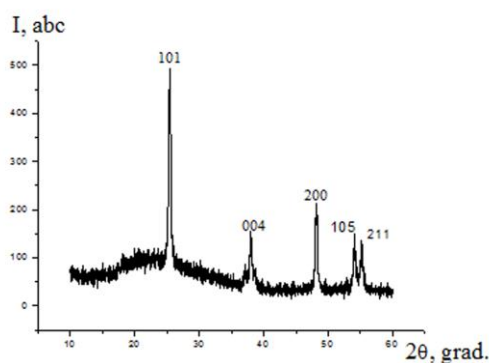


Figure 7. Results of X-ray phase analysis of TiO_2 sample annealed and impregnated with Ta and Re oxomethylate complex (sample 2).

Table 2 shows comparative analysis of annealed titanium dioxide vs annealed and impregnated, as well as a standard from ICCD-JCPDS base.

Table 2. Comparative table of TiO₂ X-ray data

No	Experimental data						ICCD-JCPDS data: TiO ₂ (anatase) – tetragonal crystal system (17560), cell parameters: <i>a</i> =3.785; <i>c</i> =9.5714.	
	TiO ₂ annealed at 340°C, cell parameters: <i>a</i> =3.785(3); <i>c</i> =9.484(3)			TiO ₂ annealed and impregnated with Ta and Re oxomethylate complex, cell parameters: <i>a</i> =3.780(3); <i>c</i> =9.483(3)				
	Intensit y, %	Bragg angle, 2θ°	Interplanar spacing, d, Å	Intensity, %	Bragg angle, 2θ°	Interplan ar spacing, d, Å	Bragg angle, 2θ°	hkl
1	100	25.37	3.511	100	25.42	3.504	25.32	101
2	25.1	37.91	2.373	22.5	37.98	2.369	37.83	004
3	35.1	48.11	1.891	44.7	48.15	1.89	48.09	200
4	19.2	54.11	1.695	21.7	54.08	1.696	53.93	105
5	20.5	55.06	1.668	22.7	55.18	1.665	55.09	211

The catalytic activity of the Ta–Re system applied onto γ -Al₂O₃ for transforming ethanol and its mixture with glycerin into aliphatic C₃–C₁₁ hydrocarbons was studied. The latter can be used as components of motor fuels or initial substances for a large number of petrochemical processes.

It was found that ethanol is transformed into methane, the ethane-ethylene fraction, C₃–C₈ hydrocarbons, oxygenates and water at a temperature of 350°C, a volume rate of raw materials supply of 0.6 h⁻¹ and a pressure of 5 at. (Ar) (Figure 8a, table 3). The yield of the target C₃–C₈ hydrocarbons fraction is 36% mass. calculated for the passed carbon. It can be seen from Figure 8 that the main products are hydrocarbons with even numbers of carbon atoms. The formation of a small amount of hydrocarbons with odd numbers of hydrogen atoms probably indicates the processes of cracking and metathesis of the formed hydrocarbons.

At present the production of bio-diesel fuel, mainly that of the first generation consisting of fatty acid methylates or ethylates, is being extensively developed. As a result, a large quantity of a by-product (glycerin) containing considerable amounts of interesterifying alcohol is formed. The

problem of isolating pure glycerin is very complex and expensive. Therefore, it is more perspective to use the glycerin-ethanol mixture for the production of an additional amount of fuel hydrocarbons by a single-step cross-condensation reaction proceeding at the same conditions as the above example of ethanol conversion.

Combined transformation of a mix containing 80% vol. of ethanol and 20% vol. of glycerin in the presence of the Re–Ta/Al₂O₃ catalyst provided 57.5% yield of the target fraction of C₃–C₁₁ hydrocarbons (Figure 8b, Table 4). This data shows that adding glycerin increases the yield of the target hydrocarbon fraction to 20% mass. and reduces the formation of the ethane-ethylene fraction by 40% mass. Probably, ethylene is formed on the acidic sites of the catalyst. As it was established earlier, it is a dead end product formed in the presence of metal oxide catalysts. Glycerin, in turn, is transformed into acrolein even at a temperature above 190°C. Acrolein can interact with ethylene formed on the catalyst surface. This assumption is supported also by the fact that the amount of hydrocarbons with an odd number of carbon atoms (Figure 8b) in the reaction products considerably increases. Thus, the process is exactly the cross-condensation of hydrocarbons of various substrates.

Note that combined processing of ethanol and glycerin gave 17% mass. of oxygenates. Their composition is shown in Table 4. The obtained compounds can be used without separation as diesel fuel components or after separation – as solvents or intermediate petrochemical products.

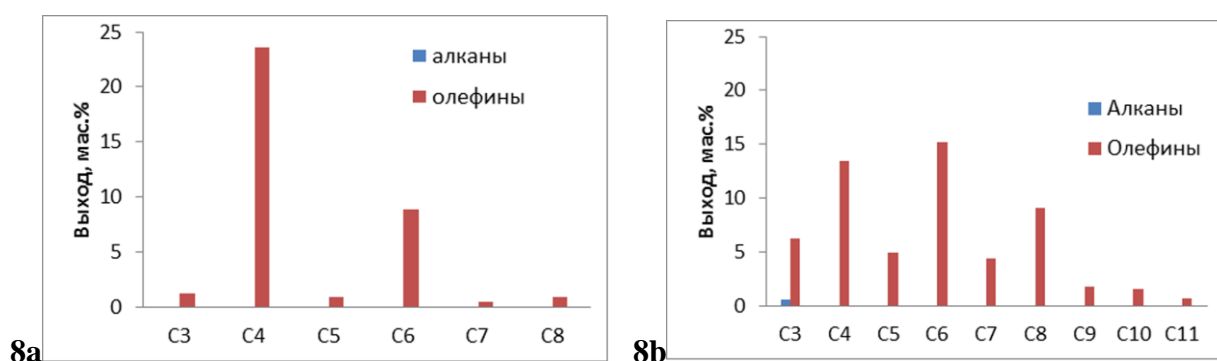


Figure 8. Yield of hydrocarbons in the presence of Re–Ta/Al₂O₃ catalyst (350°C, 5 at., Ar, 0.6 h⁻¹): a) ethanol transformation products; b) products of transformation of glycerin (20% vol.) and ethanol 80% (vol.) mixture.

[Выход, масс. means Yield, mass; алканы means alkanes; олефины means olefins]

Table 3. Yield of main products of transformation of ethanol and ethanol–glycerin mixture (80:20) in the presence of Re–Ta/Al₂O₃ catalyst (350°C, 5 at., Ar, 0.6 h⁻¹)

Yield of products	Raw materials	
	ethanol, % mass.	ethanol + glycerin, % mass.
methane	0.04	0.03
ethane + ethylene	59.78	19.83
C ₃ + hydrocarbons	35.90	57.42
oxygenates	4.13	16.54
aromatics	0.00	3.49
CO+CO ₂	0.00	2.57
H ₂	0.15	0.12
	100.00	100.00

Table 4. Composition of oxygenates obtained in the course of ethanol–glycerin mixture conversion

Oxygenates composition	Content, % mass.
acetaldehyde	1.87
diethyl ether	6.36
butanal	1.64
butanol	13.72
ethyl butyl ether	17.41
hexanol	10.17
ethyl acetate	9.55
butyl acetate	6.73
ethyl hexyl ether	11.12
hexanol	12.28
octanol	9.14
	100

In order to determine the optimum ethanol : glycerin ratio in the raw mixture a number of experiments with various initial concentrations of the reactants were performed. The results of ethanol (60%) – glycerin (40%) mixture conversion are shown below (Figure 9).

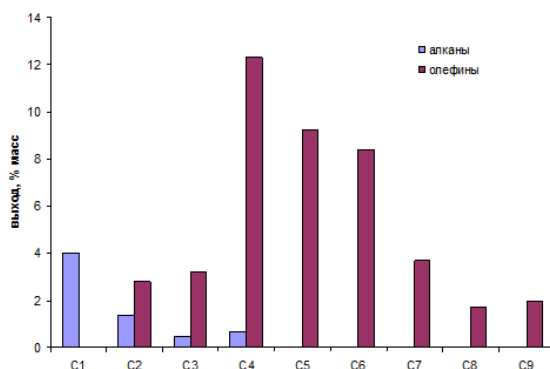


Figure 9. Yields of products of ethanol (60%) – glycerin (40%) mixture conversion.

[Выход, масс. means Yield, mass; алканы means alkanes; олефины means olefins]

The yield of the target C₃–C₉ hydrocarbon fraction was 44% mass. This is ~ 10% less than in the above example with 20% of glycerin. Increasing the content of glycerin in the initial glycerin–ethanol mixture mainly promotes the formation of oxygen-containing compounds. Their quantity increased practically by a factor of 2 (to 30% mass). Further increase of glycerin content in the initial mixture dramatically changes the reaction selectivity: aliphatic hydrocarbons practically do not form, but a mixture of oxygenates difficult to identify forms. Besides, tars form as a result of polymerization of acrolein (the product of glycerin thermal decomposition). Probably, when glycerin is in excess, the catalyst surface is filled with acrolein molecules and with products of their interaction. This prevents ethanol from penetrating with to the active centers and reduces the contribution of cross-coupling. This assumption is indirectly supported also by the presence of untransformed ethanol in the products of ethanol–glycerin (20% : 80%) mixture conversion.

Conclusions

TiO₂ samples were obtained and characterized by several methods (DTA, DSC, RPA). It was shown that annealing at 340°C allows obtaining TiO₂ (anatase) with specific surface 27.3 m²/g, which can serve as a matrix for applying active components of catalysts. The specific surface of TiO₂ impregnated with the tantalum–rhenium oxomethylate complex was 3.7 m²/g.

A difference of results in case of not annealed and annealed samples after carrying out DTA in oxygen and DSC in argon was found.

It was found that TiO₂ impregnated with the tantalum–rhenium oxomethylate complex does not change its lattice parameters, and, therefore, its structure.

Tantalum–rhenium methylate was obtained. It was used for obtaining γ-Al₂O₃-based catalysts for cross-condensation and reductive dehydration of alcohols.

The experiments showed that the presence of the catalyst (aTa–Re/Al₂O₃) in the reaction mixture promotes the transformation of ethanol and ethanol–glycerin mixtures into aliphatic C₃–C₁₁ hydrocarbons at yields up to 57% mass. It was established that the optimum content of glycerin is 20% vol., which enables reducing the dead-end ethane–ethylene fraction yield to 40% mass along with an increase of the target hydrocarbons fraction yield to 20% mass.

References:

1. Moiseev I.I. // Himija i zhizn' [Chemistry and Life]. 2015. № 8. P. 20–25.
2. Tsodikov M. V., Yandieva F.A., Chistyakov A.V., Gubanov M.A., Gekhman A.E., Moiseev I.I. // Doklady AN [Doklady Chemistry]. 2012. V. 447. № 5. P. 534–537.
3. Demirbas A. // Energy Edu Sci Technol. 2006. V. 16. P. 53–109.
4. Zharova P.A., Chistyakov A.V., Zavelev D.E., Kriventsov V.V., Yakimchuk E.P., Kryzhovets O.S., Petrakova O.V., Drobot D.V., Tsodikov M.V. // Izvestiya RAN (Ser. khim.) [Rus. Chem. Bull.]. 2015. № 2. P. 337–345.
5. Chistyakov A.V., Tsodikov M.V., Murzin V.Yu., Yandieva F.A., Zubavichus JA.V., Kozitsyna N.Yu., Gekhman A.E., Kriventsov V.V., Moiseev I.I. // Kinetika i kataliz (Kinetics and Catalysis). 2011. T. 52. № 2. P. 266–281.
6. Flid V.R., Leont'eva S.V., Efros I.E., Manulik O.S., Tsodikov M.V., Lakhman L.I. // Vestnik MITHT [Fine Chem. Tech.]. 2008. V. 3. № 4. P. 44–48.
7. Metallokompleksnyj kataliz v organicheskom sinteze i sinteze polimerov (Metal complex catalysis in organic synthesis and polymer synthesis) : <http://www.unn.ru/chem/neft/htmls/index.php?page=catalitic> (data obrashhenija 27.03.2014)
8. Tsodikov M.V., Chistyakov A.V., Gubanov M.A., Khadzhiev S.N., Gekhman A.E., Moiseev I.I. // Izvestiya RAN (Ser. khim.) [Rus. Chem. Bull.]. 2013. № 3. P. 819–828.
9. Drobot D.V., Shcheglov P.A., Nikishina E.E., Lebedeva E.N., Zimina G.V., Smirnova I.N., Fomichev V.V. // Vestnik MITHT [Fine Chem. Tech.]. 2006. V. 1. № 6. P. 5–15. (in Russ.).
10. Drobot D.V., Shcheglov P.A., Nikishina E.E., Lebedeva E.N. // Neorganicheskie materialy (Inorganic Materials). 2007. V. 43. № 5. P. 1–9. (in Russ.).
11. Shcheglov P.A. Mono-, bi- i trimetallicheskie oksoalkoksoproizvodnye (sintez, svojstva i primenenie) (Mono-, bi - and three-metallic oxoalkoxide (synthesis, properties and applications): abstracts of dissertation . . . Ph.D. (Chem.). Moscow, 2002. 25 p. (in Russ.).
12. Turova N.Ya., Korolev A.V., Tchebukov D.E., Belocon A.I., Yanovsky A.I., Struchkov Yu.I. // Polyhedron. 1996. V. 15. № 21. P. 3869–3880. (in Russ.).

13. Nakamoto K. *Infrakrasnye spektry neorganicheskikh i koordinacionnykh soedinenij* (Infrared Spectra of Inorganic and Coordination Compounds) : transl. from Engl. L.V. Hristenko / Ed. by. Yu.A. Pentin. M.: Mir, 1991. 536 p.
14. Hubert-Pfalzgraf L.G. // *J. Materials Chem.* 2004. V. 14. P. 3113–3123.
15. Gumerov F. // *The Chemical Journal.* October, 2008. P. 26–30.
16. Nikonova O.A., Seisenbaeva G.A., Kessler V.G., Shcheglov P.A., Drobot D.V. // *Rus. J. Inorgan. Chem.* 2007. V. 52. Iss. 11. P. 1687–1693. (in Russ.).
17. Smirnova K.A., Fomichev V.V., Drobot D.V., Nikishina E.E. // *Tonkie khimicheskie tekhnologii* (Fine Chemical Technologies). 2015. V. 10. № 1. P. 76–83 (in Russ.).
18. Chistyakov A.V. *Prevrashhenie spirtov v alifaticheskie uglevodorody v prisutstvii geterogennykh katalizatorov, sodержashhih nanorazmernye mono- i bimetallicheskie aktivnye komponenty* (The conversion of alcohols into aliphatic hydrocarbons in the presence of heterogeneous catalysts containing nanosized mono and bimetallic active components): dissertation Ph.D. (Chem.). Moscow, 2010. P. 6–20. (in Russ.).
19. Karpov Yu.A., Savostin A.P., Sal'nikov V.D. *Analiticheskij kontrol' v metallurgicheskom proizvodstve* (Analytical control in metallurgical production). M.: Akademkniga, 2006. 352 p. (in Russ.).
20. Topor N.D., Ogorodova L.P., Mel'chakova L.V. *Termicheskij analiz mineralov i neorganicheskikh soedinenij* (Thermal analysis of minerals and inorganic compounds). M.: MGU Publ., 1987. 188 p. (in Russ.).
21. Khabas T.A., Vakalova T.V., Gromov A.A., Kulinich E.A. *Rentgenofazovyj analiz: (X-ray analysis : guidelines)*. Tomsk: TPU, 2007. 40 p. (in Russ.).
22. Kim D.G., Vershinina E.A., Rybakova A.V., Frolova T.V. *Laboratornye raboty po organicheskoy himii* (Laboratory works on the organic chemistry: a tutorial). Chelyabinsk: Publ. Center YuUrGU, 2010. 230 p. (in Russ.).
23. Tarasevich B.N. *IK spektry osnovnykh klassov organicheskikh soedinenij. Spravochnye materialy.* (IR spectra of general classes of organic compounds). M.: MGU Publ., 2012. 54 p. (in Russ.).