Conversion of ethanol and glycerol to olefins over the Re- and W-containing catalysts

P. A. Zharova,^a* A. V. Chistyakov,^a D. E. Zavelev,^a V. V. Kriventsov,^b E. P. Yakimchuk,^b O. S. Kryzhovets,^c O. V. Petrakova,^c D. V. Drobot,^c and M. V. Tsodikov^a

 ^aA. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 633 8520. E-mail: zharova@ips.ac.ru

^bG. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 5 prosp. Akad. Lavrent 'eva, 630090 Novosibirsk, Russian Federation.

Fax: +7 (383) 330 8056

^cMoscow State University of Fine Chemical Technologies named after M. V. Lomonosov, 86 Vernadsky prosp., 119571 Moscow, Russian Federation. Fax: +7 (495) 936 8825

Fax: +7 (495) 930 8825

The catalytic conversion of a mixture of ethanol and glycerol over the Re–W/Al₂O₃ catalysts was studied. The Re–W binary system exhibits a non-additive cocatalytic effect in the conversion of ethanol and its mixture with glycerol into the fraction of olefins C_4 – C_9 . The non-additive increase in the catalytic activity is associated with the specific structure of the binuclear metallocomplex precursors, due to which the supported metals are arranged in the immediate vicinity from each other on the support surface and intensively interact to form Re⁷⁺. The study of the combined conversion of ethanol and glycerol made it possible to find an optimum ratio of the reactants in the initial mixture. The yield of target hydrocarbons attains 50 wt.% based on the amount of carbon passed through the reactor.

Key words: ethanol, glycerol, heterogeneous catalysis, tungsten, rhenium, EXAFS spectroscopy, XANES spectroscopy.

Biomass attracts significant attention of many researchers as renewable and sustainable raw materials that can be considered as an alternative source of hydrocarbons produced from oil. Ethanol is one of the primary biomass products and its annual production in 2013 attained 103.3 • 10⁶ m³ and continuously increases.¹ Ethanol is used most widely as a solvent² but in recent times it is added to motor fuels in many countries.³ Ethanol as a fuel is characterized by a lower energy capacity than traditional types of motor fuels. Its high hygroscopicity can result in an increase in corrosion activity and separation of gasoline-ethanol mixtures and eventual failure of engines. In addition, ethanol is aggressive toward general mechanical rubber goods applied as compressors and pipe lines, which also impedes its use in internal combustion engines.4

Ethanol is also used for the transesterefication that converts triglycerides of fatty acid in vegetable oils into biodiesel. Considerable amounts of glycerol along with ethanol as a transesterification agent are formed in this process. These mixtures have not found use yet and their separation and utilization significantly increase the cost of the final product.⁵

A more rational method for using ethanol is its processing to fuel hydrocarbons or petrochemical substrates. The combined conversion of ethanol and glycerol seems to be especially promising.

It was found earlier that the direct conversion of ethanol⁶ and its analogs to hydrocarbons of various classes can efficiently occur in the presence of the industrial alumina platinum catalyst,⁷ intermetallic compounds,⁸ and a series of bimetallic systems characterized by the non-additive effect of active components.⁹

Synergic catalysts $M_1 - M_2$ /support represent a promising basis for the design and synthesis of new nanocomposites which show very high activity, selectively, and stability of operation.¹⁰

Tungsten—rhenium alloys have been known long ago¹¹ and are widely used for the production of thermocouples, thermistors, and filaments for mass spectrometers.¹² The rhenium- and tungsten-containing bimetallic systems exhibit pronounced synergetic effects active in enhancing the catalytic activity in hydrocarbon conversion,¹³ due to which they are attractive for use in the direct transformation of ethanol and its mixtures with glycerol to aliphatic hydrocarbons.

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 2, pp. 0337-0345, February, 2015.

^{1066-5285/15/6402-0337 © 2015} Springer Science+Business Media, Inc.

Experimental

Rhenium oxomethylate $\text{Re}_4\text{O}_2(\text{OMe})_{12}$ and tungsten oxomethylate $[WO(\text{OMe})_4]_2$ were synthesized by anodic dissolution in methanol according to known procedures.^{14,15} The bimetallic complex $\text{Re}_{4-x}W_x\text{O}_6(\text{OMe})_{12}$ (Fig. 1) was obtained by the anodic dissolution of rhenium in methanol in the presence of dissolved $[WO(\text{OMe})_4]_2$.¹⁶

Industrial γ -Al₂O₃ (spherical granules with the sphere size 2.0–3.0 mm, specific surface area \geq 190 m² g⁻¹, pore volume 0.65 cm³; weight fractions of impurities: iron \leq 0.14 wt.%, sodium \leq 0.1 wt.%; sorption capacity with respect to sulfur hexafluoride \leq 0.01 wt.% and that with respect to hydrogen (deuterium) fluoride \leq 0.007 wt.%) was used as a support for catalyst preparation.

Metals were supported by the impregnation to incipient wetness method from methanol solutions of the corresponding precursors. The supported samples were dried for 5 h at 80 °C in a vacuum oven and calcined for 5 h in a muffle furnace at 500 °C in argon. Prior to catalytic tests, the catalysts were treated in a hydrogen flow (450 °C, 10 h, 10 L h⁻¹, 50 atm).

The metal content in the samples of the synthesized catalysts was determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) on an EMAL-2 instrument.

Ethanol (analytical grade, GOST 5964-93) was used without preliminary purification. Ethanol conversion was studied on a PID Eng&Tech microcatalytic batch setup with the stationary catalyst bed¹⁷ in the reactor volume (10 cm³ volume) (9.12 mm internal diameter, 153 mm length). The catalyst samples of 10 cm³ were used. Ethanol conversion was studied under optimum conditions⁸: in argon at a pressure of 5 atm, temperature 330 °C, and space velocity of the substrate 0.6 h⁻¹.

Gaseous reaction products were analyzed on-line on a gas chromatograph, and hydrocarbon gases C_1 — C_5 were analyzed on a Kristall-4000M chromatograph (flame-ionization detector, HP-PLOT/Al₂O₃) column). The content of CO, CO₂, and H₂ was determined on a Kristall-4000 chromatograph (thermal conductivity detector, CKT column). and low CO concentrations (<0.4 vol.%) were determined using a Riken Keiki gas analyzer with the IR cell (model RI-550A).

Liquid organic reaction products in the aqueous and organic phases were identified by the MS/GC method using MSD 6973 (Agelent) and Automass-150 (Delsi Nermag) instruments with



Fig. 1. Structure of bimetallic complex $\text{Re}_{4-x}W_xO_6(\text{OMe})_{12}$.

an ionization energy of 70 eV and a sample volume of 1 μ L. The quantitative content of organic substances was determined by GLC on a Varian 3600 instrument. The content of ethanol in the aqueous phase was determined using MS/GC from the ratio of integral signals of alcohol and water by the absolute calibration method.

The acid properties of the catalyst were studied by the TPD NH3 method. The X-ray photoelectron spectra were detected at room temperature on an XSAM-800 spectrometer (Kratos) using non-monochromatic Mg-K α radiation with the power ≤ 90 W. The spectra were recorded in the mode of constant relative energy resolution. Photoelectron spectra were detected with an increment of 0.1 eV. The measurements were carried out in a chamber evacuated at a pressure of $\sim 5 \cdot 10^{-8}$ Pa. The analyzed spectra were approximated by the Gaussian profile or their sum, and the background caused by secondary electrons and photoelectrons experienced energy losses were approximated by a straight line. The EXAFS and XANES (W-L₃, Re-L₃) spectra were recorded on an EXAFS spectrometer at the Siberian Center of Synchrotron Radiation (SCSR, Novosibirsk, Russia) using the transmission procedure at an electron energy of 2 GeV and an average current in the integrator during measurement of 80 mA. A Si(111) crystal split monoblock was used as a monochromator.

The percent conversion (X) of ethanol was determined from the equation $X = (1 - v[EtOH]_t/v[EtOH]_0) \cdot 100\%$, where $v[EtOH]_t$ is the content of ethanol in the reaction products (mol), and $v[EtOH]_0$ is the amount of alcohol passed through the catalyst bed (mol). The catalyst activity (A) was calculated according to the equation $A = \Sigma v(C_{3+x}H_{6+y})v(M)^{-1}\tau^{-1}$, where $\Sigma v(C_{3+x}H_{6+y})$ is the total amount (mol) of hydrocarbons C_{3+} formed within the reaction time τ , and v(M) is the content of supported metal in the catalyst weighed sample.

Results and Discussion

Study of the catalytic properties of the rhenium—tungsten catalysts. In the presence of the Re- and W-containing catalysts, ethanol is converted to alkane and olefin hydrocarbons C_1-C_{10} , liquid oxygenates, and water. The yields of the major products of conversion of 700 mmoles of ethanol in the presence of the γ -Al₂O₃-supported monoand bimetallic catalysts are presented in Table 1.

The γ -Al₂O₃ support is slightly active in hydrocarbon chain condensation. In the presence of γ -Al₂O₃, the yield of hydrocarbons C₃₊ is 2.09 mmoles (see Table 1) or 0.45 wt.% (Fig. 2) at the 60% initial alcohol conversion. The major product of ethanol conversion on γ -Al₂O₃ is ethylene formed with the selectivity >80%. Oxygen-containing products, mainly diethyl ether, are also formed in insignificant amounts. The modification of alumina with rhenium (5 wt.%) decreases ethanol conversion to 40% and changes the selectivity of the process. The products contain predominantly oxygenates consisting of 95 wt.% diethyl ether and minor amounts of acetaldehyde and ethyl butyl ether. In the presence of the W/Al₂O₃ catalyst containing 5 wt.% of the supported component, the ethanol conversion increases to 100%, and the yield of the target

Product	Y/mmol								
	Al ₂ O ₃	Re/Al ₂ O ₃	W/Al ₂ O ₃	Re-W/Al ₂ O ₃					
H ₂	8.74	48.57	6.51	3.84					
cõ	0.00	0.00	0.00	0.00					
CO_2	0.00	0.00	0.00	0.00					
CH_4	0.92	3.21	0.08	0.90					
C_2H_6	4.21	4.28	3.14	27.27					
$\tilde{C_2H_4}$	336.31	4.26	289.98	112.10					
$\tilde{C_3H_8}$	0.00	1.08	0.00	0.73					
C ₃ H ₆	0.12	1.38	6.73	0.95					
C_4H_{10}	0.14	12.71	16.87	6.23					
C ₄ H ₈	1.83	5.77	13.18	32.13					
C5H10	0.00	0.65	0.00	1.28					
C ₅ H ₁₂	0.00	0.00	0.56	1.51					
C_6H_{14}	0.00	0.00	0.40	2.05					
$C_{6}H_{12}$	0.00	0.00	6.79	8.24					
C7H16	0.00	0.00	0.00	0.29					
C ₇ H ₁₄	0.00	0.00	1.22	1.75					
C ₈ H ₁₈	0.00	0.00	0.00	0.42					
$C_{8}H_{16}$	0.00	0.00	3.10	2.83					
C_9H_{20}	0.00	0.00	0.00	0.00					
C ₀ H ₁₈	0.00	0.00	0.00	0.00					
C10H22	0.00	0.00	0.00	0.08					
C ₁₀ H ₂₀	0.00	0.00	0.00	0.13					
$R_x H_y O_z$	5.35	148.65	19.23	20.22					

Table 1. Yields (Y) of the products of conversion of 700 mmoles of ethanol in the presence of the studied catalysts*

* Catalytic parameters of the process: in the presence of Al_2O_3 , Re/Al_2O_3 , W/Al_2O_3 , and $Re-W/Al_2O_3$, conversion X = 60, 40, 100, and 100%, respectively; the activity(*A*) of Re/Al_2O_3 , W/Al_2O_3 , and $Re-W/Al_2O_3$ is 267.65, 599.41, and 721.18 h⁻¹, respectively.

fraction of hydrocarbons C_{3+} is 48.86 mmoles (see Table 1), or 19.61 wt.% (see Fig. 2). With the unmodified support, a significant yield of ethylene (289.98 mmol) is observed.

In contrast to the monometallic systems, the Re–W/ Al_2O_3 bimetallic catalyst obtained by supporting the heteronuclear alkoxide precursors on γ -Al₂O₃ shows the



Fig. 2. Yields (*Y*) of the fraction of aliphatic hydrocarbons C_3-C_{10} produced by converting ethanol in the presence of the studied catalytic systems (350 °C, 5 atm Ar, 0.6 h⁻¹).



Fig. 3. Yields (*Y*) of the products for ethanol conversion on the Re–W/Al₂O₃ catalyst (350 °C, 5 atm Ar, 0.6 h⁻¹): alkanes (*1*), olefins (*2*), oxygenates (*3*), and aromatic compounds (*4*).

non-additive increase in the yield of the fraction of aliphatic hydrocarbons $C_3 - C_{10}$ in the conversion of ethanol (see Fig. 2). The yield of the target fraction was 58.60 mmoles (see Table 1), or 30.5 wt.% (see Fig. 2) at 100% ethanol conversion. Among the formed hydrocarbons, the structures with an even number of carbon atoms prevail (Fig. 3). The reason is that the process proceeds predominantly via aldol condensation followed by the hydrogenolysis of the formed oxygenates.13 Carbon mono- and dioxide are absent from the reaction products. This means that all the carbon fed into the reactor is consumed by the formation of aliphatic and oxygen-containing compounds. The yield of the oxygenates attains 20 wt.% (see Fig. 3). The major components of the oxygenate fractions are diethyl and ethyl butyl ethers (Table 2) formed on the acid sites of the catalyst. As shown earlier,⁷ diethyl ether similarly to ethanol is converted to the fraction of aliphatic hydrocarbons, which makes it possible to increase the yield of the target fraction by oxygenate recirculation.

Resource tests were carried out to assess the time-on stream behavior of the most active bimetallic Re–W-con-

Table 2. Composition of the oxygenates obtained by the conversion of ethanol (I) and an ethanol(80 vol.%)—glycerol(20 vol.%) mixture (II) in the presence of the Re–W/Al₂O₃ catalyst

Component	Content (wt.%)					
of oxygenates	Ι	II				
Acetaldehyde	2.35	1.87				
Diethyl ether	72.34	6.36				
Butanals	_	1.64				
Butanols	_	13.72				
Ethyl butyl ether	25.32	17.41				
Hexanols	_	22.45				
Ethyl acetate	_	9.55				
Butyl acetate	_	6.73				
Ethyl hexyl ether	_	11.12				
Octanols	_	9.14				
Sum	100.00	100.00				

taining catalyst. It was shown that the yield of the main fractions of ethanol conversion remains nearly unchanged after 3 and 72 h of reaction (Fig. 4). The analysis of the reaction products shows that the composition of hydro-carbons formed over this period of time remained unchanged.

The production of biodiesel, especially biodiesel of the first generation, is being pursued extensively with the main products represented by esters (methylates or ethylates) of fatty acids. As a result, a large amount of the accompanying product (glycerol) containing significant amounts of the esterification agent is formed. The isolation of pure glycerol is very complicated and expensive process. Therefore, it seems more promising to use a mixture of glycerol and ethanol for the production of an additional amount of fuel hydrocarbons by the one-step cross-condensation that occurs under the conditions identical to those of ethanol conversion.

A series of experiments on the combined conversion of ethanol and glycerol was carried out with different ratios of initial reagents. The highest total vield of the target fraction (49 wt.%) was obtained with a mixture consisting of 20 wt.% glycerol and 80 wt.% ethanol. Moreover, the addition of glycerol decreases the yield of the ethaneethylene fraction from 35 to 6 wt.% (Fig. 5, *a*). Probably, ethylene formed on the acid sites of the catalyst and, as found earlier, ¹³ does not undergo further transformations in the presence of the metal oxide catalysts. In turn, glycerol is converted to acrolein already at temperatures >190 °C, and acrolein can interact with ethylene formed on the catalyst surface. This assumption is also favored by the fact that the amount of hydrocarbons with an even number of carbon atoms increases significantly in the reaction products (see Fig. 5). This indicates the cross-condensation of hydrocarbon frameworks of various substrates. Carbon mono- and dioxide are found in the reaction products, and their overall yield did not exceed 5 wt.%. Carbon monoxides are probably formed due to the thermal decomposition of a portion of the initial glycerol.



Fig. 4. Yields (Y) in 3 (a) and 72 h (b) of the major products for ethanol conversion on the Re–W/Al₂O₃ catalyst during the resource tests (350 °C, 5 atm Ar, 0.6 h⁻¹): olefins (1), alkanes (2), and oxygenates (3).



Fig. 5. Yields (*Y*) of the products produced by converting mixtures ethanol(80%)—glycerol(20%) (*a*) and ethanol(60%)—glycerol(40%) (*b*) on the Re–W/Al₂O₃ catalyst (350 °C, 5 atm Ar, 0.6 h⁻¹): alkanes (*1*), olefins (*2*), oxygenates (*3*), and aromatic compounds (*4*)

The combined treatment of a mixture of 80 vol.% ethanol and 20 vol.% glycerol gave the products containing 28.6 wt.% oxygenates with the compositions presented in Table 2. These compounds can be used without separation as components of diesel fuel or after separation as solvents or intermediate petrochemical products. In addition, aromatic compounds (4.5 wt.%) were found among the reaction products, indicating the probability of intensification of formation of condensation products formation and, as a consequence, coking of the catalyst surface.

When the glycerol content in a mixture with ethanol is increased to 40 wt.%, the yield of the target fraction of hydrocarbons C_4 — C_{10} decreases to 38 wt.%, which is ~10% lower than that in the presence of 20% glycerol additive (Fig. 5, b). An increase in the glycerol content in the initial mixture with ethanol favors the formation of oxygen-containing compounds, the amount of which is nearly doubled. The yield of aromatic hydrocarbons also increases twofold. Evidently, a deficient of hydrogen and/or coreactant appears in the system and, for this reason, the dehydrocyclization of intermediate products proceeds easily. The selectivity of the reaction drastically changes with the further increase in the glycerol fraction in the initial mixture. Almost no aliphatic hydrocarbons are formed, but a poorly identifiable mixture of oxygenates and resins yielded by the polymerization and dehydrocyclization of acrolein, product of thermal decomposition of glycerol, are formed.

Probably, the thermal decomposition of glycerol and acrolein occurs first in the combined processing of glycerol and ethanol. Acrolein molecules become thermodynamically unstable under the conditions of the process. Therefore, they react with each other to form mainly oxygenates or condensation products. It is most likely that target hydrocarbons are formed in the reactions of acrolein with the products obtained from ethanol. A decrease in the yield of the ethane-ethylene fraction in the presence of glycerol can indicate that ethylene interacts with glycerol. It seems also possible that the reactants, primarily, glycerol, are selectively adsorbed on the catalyst surface and prevent ethanol from interaction with the acid sites, thus decreasing the contribution of dehydration. In favor of the second variant indirectly indicates the presence of a considerable amount of unconverted ethanol in the conversion products of a mixture of 20 vol.% ethanol and 80 vol.% glycerol. The high content of ethanol in the reaction products can also be attributed to its probable formation from glycerol during the reaction. It is known¹⁸ that glycerol undergoes dehydroxylation on the Ni-containing catalysts supported on Al₂O₃ in the presence of hydrogen, and significant amounts of ethanol are formed in some cases. However, the dehydroxylation of glycerol under inert atmosphere conditions is unlikely.

Study of the structure of the rhenium-tungsten catalysts. Study of the acid properties of the surface of the rhenium-tungsten catalysts. The study of the acid properties of the catalyst and support surfaces by temperature-programmed desorption of ammonia showed that γ -Al₂O₃ contain acid sites of weak and medium strength in an approximately equal ratio (Fig. 6). Depositing rhenium oxide on alumina does not enhance the acidic properties. When tungsten oxide is deposited on the support, the number of acid sites increases but not the acidity strength. At the same time, supported Re-W heterometallic complex shows a noticeable (nearly twofold) increase in the concentration of acid sites of moderate strength (see Fig. 6), which probably indicates the formation of tungsten and rhenium heteropolyacids on the alumina surface. It is not excluded that the cocatalytic effect of W and Re during ethanol conversion can be related to the formation of moderately strong acid sites that appear in maximum concentrations of medium-strength acid sites on the surface clusters of the mixed oxide.

The W4f spectrum (Fig. 7, *a*) can be decomposed into two peaks $W4f_{7/2}$ and $W4f_{5/2}$ with bond energies of 36.1 and 38.2 eV corresponding to the W⁶⁺ state. For a similar description of the Re4f spectrum, the full width of this



Fig. 6. Acidity spectra of the studied catalysts obtained by the temperature-programmed desorption of ammonia: Re–W (1), W (2), Re (3), and Al_2O_3 (4); w is the desorption rate.

function at the half-height is ~1.5 times higher than those of the $W4f_{7/2}$ and $W4f_{5/2}$ peaks. Based on this, the Re4f spectrum can be presented by the sum of two doublets



Fig. 7. Photoelectron W4f (*a*) and Re4f (*b*) spectra for the Re–W/Al₂O₃ catalyst; E_b is the bond energy.

Re4f_{7/2}—4f_{5/2} with characteristic values of spin—orbit splitting and Re4f_{7/2}/Re4f_{5/2} ratio (Fig. 7, *b*). The positions of the Re4f_{5/2} peaks in the bond energy scale (45.6 and 46.4 eV) correspond to the Re⁶⁺ and Re⁷⁺ states, respectively. The ratio of their intensities is 69/60.

The data obtained suggest that a portion of rhenium enters into the structure of the complex oxide, thus modifying its surface. The modifying components are arranged, as a rule, on the surface layer of structure-forming oxide and do not penetrate deep into the structure. According to the structural analysis data (EXAFS and XANES), supported WO₃ interacts with the Al₂O₃ surface to form mixed surface compounds W—O—Al. In the case of the bimetallic catalyst, Re partially substitutes W in these compounds (W–O–Al) to form clusters of the presumable structure AlRe_{0.5}W_{0.5}O₄. Another portion of Re forms the surface phase Re₂O₇. As it is known, Re₂O₇ is a catalyst of olefin disproportionation and, therefore, it can be the active phase contributing to the selectivity of hydrocarbon formation. It is most likely that the synergetic effect of increased selectivity in hydrocarbon formation is induced by the contribution of two sites active in this reaction: AlRe_{0.5}W_{0.5}O₄ and Re₂O₇.

XAFS study of the structure of the rhenium—tungsten catalysts. The results of the EXAFS study of the local environment of tungsten and rhenium in the studied W/Al_2O_3 and Re/Al_2O_3 samples are presented in Tables 3 and 4, respectively.

Table 3. Results of the EXAFS study of the local environment of tungsten in the studied samples and reference compounds^a

Sample		W/	Al ₂ O ₃		Re–W/Al ₂ O ₃				WO ₃		$Al_2(WO_3)_4$		AlWO ₄	
	Model 1 ^b		Model 2 ^c		Model 1 ^b		Model 2 ^c		(see Ref. 8)		(see Ref. 13)		(see Ref. 14)	
	R	N	R	N	R	N	R	N	R	N	R	N	R	N
W-0	1.73	2.5	1.73	2.5	1.73	2.3	1.73	2.4	1.75-2.21	6	1.72-1.76	4	1.89	6
	2.25	1.1	2.27	1.2	2.25	1.0	2.26	1.2	_	_	_	_	_	_
W-Al	3.04	1.0	3.36	1.2	3.02	1.1	3.38	1.3	_	_	3.29-3.72	4	3.42-3.62	8
	_	_	3.65	1.3	_	_	3.70	1.7	_	_	_	_	_	_
W—W	3.60	1.1	_	_	3.59	1.6	_	_	3.65-3.86	6	4.36-4.93	6	2.61-3.09	2
	_	_	_	_	_	_	_	_	4.91-5.14	6	—	_	4.54	4

^{*a*} Here and in Table 4, R is the distance Å and N is the coordination number.

^b Structural model based on tungsten oxide and the additional averaged short W—Al distance (vacancy) in addition to a longer W—W distance (tungsten oxide).

^c Structural model based on tungsten oxide and only several different W—Al distances from the structures of the aluminoxide compounds.

 Table 4. Results of the EXAFS study of the local environment of rhenium in the studied samples and reference compounds

Sample	Re/Al ₂ O ₃		Re–W/Al ₂ O ₃		ReO ₃ (see Ref. 10)		Re ₂ O ₇ (see Ref. 11)		ReO ₂ (see Ref. 12)		NH ₄ ReO ₄ (see Ref. 13)	
	R	N	R	N	R	N	R	N	R	N	R	N
Re—O	1.75	4.3	1.75	4.6	1.87	6	1.65—2.16 1.71—1.85	6.0(0.5) 4.0(0.5)	1.94	4	1.74	4
									2.11	2		
Re-Al	3.02	~1.0	3.03	~1.1	_	_	_	_	_	_	_	_
Re—Al (model 1)	3.32	~1.0	3.34	~1.1	_	—	_	—	_	—	_	—
Re—Re (model 2)	3.26	~0.9	3.25	~1.0	_	-	—	_	—	_	_	-
Re-Re	_	_	_	_	3.72-3.75	6	3.68—3.78 3.65—3.78	4	2.61	2	_	_
								2	3.68-3.71	8		
	_	_	_	_	5.24—5.28	12	4.58—5.06	4	4.61—4.96 5.25—5.45	6 8	_	_

The XANES spectra of the monometallic samples containing tungsten and rhenium closely resemble the spectra of tungsten(+6) and rhenium(+6) oxides. However, all spectra of rhenium and tungsten have a minor shoulder (marked by arrow) indicating that some Re and W atoms are tetrahedrally coordinated by oxygen atoms,¹⁹ and rhenium contributes more substantially to the spectrum of this state (Figs 8 and 9).

Three significant peaks are observed in the range of distances <4 Å: the first most intense peak (in a range of $\sim 1-2$ Å) was assigned to the distances from tungsten to oxygen, the second peak (at $\sim 1.9-3$ Å) was attributed to possible distances from tungsten to oxygen and aluminum, and the third peak (in a range of $\sim 2.9-3.9$ Å) was ascribed to the distance from tungsten to aluminum and/ or tungsten. A comparison of the radial distribution curves of atoms for the W/Al₂O₃ and Re/Al₂O₃ samples shows that the local environments of tungsten and rhenium are of different types, because there are substantial differences in the number and amplitudes of the M—O and M—M peaks (M = W, Re; see Tables 3 and 4).

It is known that at ~20 °C WO₃ is the most stable when it adopts the low-symmetry monoclinic and triclinic modifications²⁰ rather than a more symmetrical tetragonal modification.²¹ Several possible positions were established for the first two modification of tungsten²² (from two to six), and each position has intrinsic, somewhat different from other set of W–O and W–W distances in a sufficiently wide range, namely: $R_{W-O} \approx 1.75-2.21$ Å, N = 6;



Fig. 8. XANES spectra (W-L₃ edge) for the W/Al₂O₃ (1) and Re–W/Al₂O₃ (2) samples.



Fig. 9. XANES spectra (Re-L₃ edge) for the Re/Al₂O₃ (1) and Re–W/Al₂O₃ (2) samples.

 $R_{W-W} \approx 3.69-3.86$ Å, N = 6; $R_{W-W} \approx 4.91-5.14$ Å, N = 6. Therefore, it can be expected that the peak amplitudes in the radial distribution curve for the atoms of similar modifications will be underestimated and the peaks themselves are broadened compared to those observed for more symmetrical structures.^{23,24} This fact should also explain in part the available differences in the local structures of W and Re, since rhenium oxide ReO₃ is stable in the highly symmetrical cubic modification.

It is known that there are individual mixed W—Al oxide compounds, structures of which are fairly well studied by the diffraction methods.^{25,26} Assuming additionally localization over the cationic vacancies, it should be taken into account that alumina contains the following distances characteristic of regular octahedral ($R_{Al-O} \approx 2.0$ Å, $R_{Al-Al} \approx 2.8$ Å, $R_{Al-Al} \approx 3.2$ Å) and tetrahedral ($R_{Al-O} \approx 2.0$ Å, ≈ 1.64 Å, $R_{Al-Al} \approx 3.2$ Å, $R_{Al-Al} \approx 3.4$ Å) cationic positions.²⁶

Only two significant peaks are observed for the Re/Al_2O_3 and $Re-W/Al_2O_3$ samples in the range of distances <3.2 Å. The first high-amplitude peak (in a range of ~1–2 Å) was attributed to the distances from rhenium to oxygen, and the second peak (in a range of ~2.4–3.1 Å) is considerably lower in amplitude compared to the first peak and it can be assigned to the distances from rhenium to aluminum and/or rhenium (see Table 4). The positions of the first and second peaks almost coincide for the studied catalysts; however, on going from the rhenium and

rhenium—tungsten samples, the peak amplitudes somewhat increase.

Fitting procedure showed that the best coincidence of the model curve with the experimental curve $k^3\chi(k)$ could be achieved upon the introduction of additional Re–W distances. The following set of distances and coordination numbers was obtained for the rhenium sample: $R_{\text{Re}-0} \approx 1.75 \text{ Å}$, $N \approx 4.3$; $R_{\text{Re}-\text{Al}} \approx 3.02 \text{ Å}$, $N \approx 1.0$ and $R_{\text{Re}-\text{Al}} \approx 3.32 \text{ Å}$, $N \approx 1.0$. The variant $R_{\text{Re}-\text{Re}} \approx 3.26 \text{ Å}$, $N \approx 0.9$ is possible for the third sphere. A very similar set of values was also calculated for the tungsten—rhenium sample: $R_{\text{Re}-0} \approx 1.75 \text{ Å}$, $N \approx 4.6$; $R_{\text{Re}-\text{Al}} \approx 3.03 \text{ Å}$, $N \approx 1.1$ and $R_{\text{Re}-\text{Al}} \approx 3.34 \text{ Å}$, $N \approx 1.1$; the variant $R_{\text{Re}-\text{Re}} \approx 3.25 \text{ Å}$, $N \approx 1.0$ is possible for the third sphere.

It is known²⁵ from the X-ray diffraction analysis (XRD) data that the high-symmetry structure of cubic oxide ReO₃ has the following set of distances and coordination numbers: $R_{\text{Re}-\text{O}} \approx 1.86$ Å, N = 6; $R_{\text{Re}-\text{Re}} \approx 3.72$ Å, N = 6; $R_{\text{Re}-\text{Re}} \approx 5.26$ Å, N = 16.

A comparison of the obtained values with the results of analysis of cubic oxide indicates that bulk oxides of the ReO₂ and Re₂O₇ types are not formed.^{27,28} The calculated Re—O distances (~1.75 Å, $N \approx 4.5$) best correspond to the structure of (NH₄)ReO₄,²⁹ in which Re⁷⁺ exists in the tetrahedral oxygen environment (see Table 4). The low coordination numbers (see Table 4) assumes that monomer (ReO₄) can be formed on the support surface, and the monomer can form several modifications that intensely interact, most likely, with the support. A similar result was obtained^{30–33} by Raman and EXAFS spectroscopy.

The supported tungsten and rhenium oxides very strongly interact with the Al_2O_3 support during syntheses of all studied catalysts. This interaction results in a significant disordering and dispersion of the formed surface oxide and aluminoxide structures in the monometallic samples of the WO_x , ReO_y , W-O-Al, and Re-O-Al types, as well as of the W-Re-O and Al-W-Re-O types in the bimetallic catalyst Re-W/Al_2O_3. The formation of the mixed active component Re-W is accompanied by competitive sorption. It is most likely that the Re-containing alkoxide precursor is mainly sorbed on the catalyst surface. It can be assumed that all possible sites on the support surface are filled first, and then near-surface phases are formed accompanied by a probable increase in the contribution of distorted oxide and aluminoxide phases.

Thus, the combined conversion of ethanol and glycerol gives products in which the fraction of olefins C_4-C_9 makes up 50 wt.%. The non-additive cocatalytic effect of the Re- and W-containing systems was observed during the conversion of ethanol and its mixtures with glycerol: the yield of hydrocarbons C_4-C_9 increases considerably (20-25 wt.%). Probably, the observed effect of increased catalytic activity is due to the mutual influence of the metals. Owing to the structure of the binuclear complexes, the Re and W atoms are linked by the oxygen bridges and are separated by a distance of the sum of their van der Waals radii. Such a neighborhood makes the formation of tetracoordinated Re^{7+} feasible and induces synergism of the catalytic properties of the supported metals. The sublimation temperature of bulky rhenium oxide corresponding to the charge state Re^{7+} is lower than the reaction temperature, although in the studied systems Re^{7+} was stable at 450 °C, probably, due to the vigorous interaction with the support.

The support in the rhenium-containing systems is involved in chemical interactions with dispersed metal particles and, hence, the catalytic processes of these systems are determined not only by the active metal but the whole chemical metal—support system; these properties depend on the nature of the support and the character of its interaction with metal.

References

- 1. World Ethanol and Biofuels Report, 2014, www.agra-net.net/ agra/world-ethanol-and-biofuels-report.
- V. N. Stabnikov, I. M. Roiter, T. B. Protsyuk, *Etilovyi spirt* [*Ethyl Alcohol*], Pishchevaya Prom-st´, Moscow, 1976, 272 pp. (in Russian).
- A. Demirbas, Biodiesel: A Realistic Fuel Alternative for Diesel Engines, Springer, London, 2008, 208 pp.
- S. D. Varfolomeev, I. I. Moiseev, B. F. Myasoedov, Vestn. RAN [News of Russian Academy of Sciences], 2009, 79, No. 7, 595–607 (in Russian).
- 5. I. I. Moiseev, Russ. Chem. Rev., 2013, 82, 616-623.
- M. V. Tsodikov, V. Ya. Kugel', F. A. Yandieva, G. A. Kliger, L. S. Glebov, A. I. Mikaya, V. G. Zaikin, E. V. Slivinskii, N. A. Plate, A. E. Gekhman, I. I. Moiseev, *Kinet. Katal.*, 2004, 45, 904–916 [*Kinet. Catal. (Engl. Transl.*), 2004, 45, No. 6].
- F. A. Yandieva, M. V. Tsodikov, A. V. Chistyakov, V. Ya. Kugel', Ya. V. Zubavichus, A. A. Veligzhanin, L. E. Kitaev, V. V. Yushchenko, A. E. Gekhman, I. I. Moiseev, *Kinet. Katal.*, 2010, 51, 572–582 [*Kinet. Catal.* (*Engl. Transl.*), 2010, 51, No. 4].
- A. V. Chistyakov, A. E. Gekhman, F. A. Yandieva, I. I. Moiseev, V. Ya. Kugel, M. V. Tsodikov, *Catal. Lett.*, 2008, 121, No. 3–4, 199–208.
- A. V. Chistyakov, M. V. Tsodikov, V. Yu. Murzin, F. A. Yandieva, Ya. V. Zubavichus, N. Yu. Kozitsyna, A. E. Gekhman, V. V. Kriventsov, I. I. Moiseev, *Kinet. Katal.*, 2011, 52, 266–281 [*Kinet. Catal. (Engl. Transl.*), 2011, 52, No. 2].
- T. N. Rostovshchikova, E. S. Lokteva, S. A. Nikolaev, E. V. Golubina, S. A. Gurevich, V. M. Kozhevin, D. A. Yavsin, V. V. Lunin, in *Catalysis: Principles, Types and Applications*, Ed. M. Song, Nova Sci. Publ., New York, 2011, 483 pp.
- E. M. Savitskii, M. A. Tulkina, S. I. Ipatova, E. I. Pavlova, Metallovedenie i temperaturnaya obrabotka metallov [Physical Metallurgy and Temperature Treatment of Metals], 1960, No. 9, 20–25 (in Russian).
- F. Brot, Chem. Eng. News Am. Chem. Soc., 2003, 1-2; http://pubs.acs.org/cen/80th/rhenium.html.
- A. Chistyakov, M. Tsodikov, M. Chudakova, A. Gekhman, I. Moiseev, *Chem. Eng. Trans.*, 2011, 24, 175–180.

- 14. N. Ya. Turova, Russ. Chem. Rev., 2004, 73, 1041-1064.
- D. V. Drobot, P. A. Shcheglov, E. E. Nikishina, E. N. Lebedeva, *Neorg. Mater.*, 2007, 43, No. 5, 1–9 [*Inorg. Mater.* (*Engl. Transl.*), 2007, 43, No. 5].
- G. A. Seisenbaeva, A. V. Shevelkov, J. Tegenfeldt, L. Kloo, D. V. Drobot, V. G. Kessler, J. Chem. Soc.. Dalton Trans., 2001, 2762–2768.
- 17. http://www.pidengtech.com/thereference.html.
- Yu. A. Korolev, A. A. Greish, L. M. Kozlova, L. M. Kustov, Kataliz v promyshlennosti [Catalysis in Industry], 2010, No. 4, 34–38 (in Russian).
- A. Kuzmin, R. Kalendarev, J. Purans, Proc. SPIE, 2003, 5122, 79–85.
- 20. E. Salje, Acta Crystallogr., 1977, 33, 574-577.
- ICSD Collection Code 27961 tetragonal WO₃; http:// icsd.ill.eu/icsd/details.php?id[]=27961.
- 22. ICSD Collection Code 14332, 80057 monoclinic WO₃; 80053, 1620 — triclinic WO₃; http://icsd.ill.eu/icsd/details.php?id[]=14332; http://icsd.ill.eu/icsd/details.php?id[]=80057; http://icsd.ill.eu/icsd/details.php?id[]=80053; http://icsd.ill.eu/icsd/details.php?id[]=1620.
- J. Purans, A. Kuzmin, C. Guery, Proc. SPIE, 1997, 2968, 174–179.
- 24. A. Kuzmin, J. Purans, Ph. Parent, *Physica B*, 1995, 208–209, 45–46.
- ICSD Collection Code 4164 AlWO₄; http://icsd.ill.eu/ icsd/details.php?id[]=4164.

- 26. ICSD Collection Code 2134, 73878, 73879, 36069 Al₂(WO₃)₄; http://icsd.ill.eu/icsd/details.php?id[]=2134; http:// icsd.ill.eu/icsd/details.php?id[]=73878; http://icsd.ill.eu/ icsd/details.php?id[]=73879; http://icsd.ill.eu/icsd/ details.php?id[]=36069.
- ICSD Collection Code 68771 γ-Al₂O₃; http://icsd.ill.eu/ icsd/details.php?id[]=68771.
- ICSD Collection Code 16810, 201875 ReO₃; http:// icsd.ill.eu/icsd/details.php?id[]=201875; http://icsd.ill.eu/ icsd/details.php?id[]=16810.
- ICSD Collection Code 15217 Re₂O₇; http://icsd.ill.eu/ icsd/details.php?id[]=15217.
- ICSD Collection Code 24060 ReO₂; http://icsd.ill.eu/ icsd/details.php?id[]=24060.
- International Tables of X-ray Crystallography, Vol. 3, Kynock Press, Birmingham, 1962, p. 281, ICSD Collection Code 1394, 1395 – (NH₄)ReO₄.
- 32. F. D. Hardcastle, I. E. Wachs, J. A. Horsley, G. H. Via, J. Mol. Catal., 1988, 46, No. 1–3, 15–36.
- M. Rønning, D. G. Nicholson, A. Holmen, *Catal. Lett.*, 2001, 72, No. 3–4, 141.

Received February 13, 2014; in revised form June 26, 2014