Synergistic Effect of Gold and Copper in the Catalytic Conversion of Ethanol to Linear α-Alcohols

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Abstract—The reaction features of the direct conversion of ethanol to butanol-1 and hexanol-1 in the presence of mono- and bimetallic active components based on Au and Cu supported on γ -Al₂O₃ have been studied. It has been found that under conditions providing the supercritical state of ethanol, the reaction rate and selectivity in the presence of the Au–Cu/Al₂O₃ catalyst abruptly increases. In addition, a synergistic effect is observed: the yield of desired products over the Au–Cu catalyst is 6 or 14 times that over the Au or Cu monometallic counterpart, respectively. Differences in the catalytic behavior of the Au–Cu, Au-, and Cu-based systems have been discussed taking into account their structural features and the reaction mechanism.

Keywords: gold, copper, nanoparticles, synergism, butanol, ethanol, catalysis **DOI:** 10.1134/S0965544116080120

The search for alternative sources of hydrocarbons and the development of methods for producing energy carriers and organic monomers are largely focused on the conversion of biomass products [1, 2]. The most available and common product derived from biomass is ethanol. In 2013, the production of ethanol was 85.3 million tons per annum [3]. Along with ethanol, other lower (C_1 and C_3-C_6) alcohols are being seen to have a rapid growth in production now. In the past decade, chemistry has been significantly enriched in novel reactions for conversion of ethanol and its homologues to hydrocarbons of various classes, which are important components of motor fuels and valuable petrochemical monomers and can be used as solvents and surfactant components [1-4]. A promising process, which is currently enjoying a surge of attention, is a direct catalytic reaction yielding higher alcohols owing to the condensation of the hydrocarbon skeleton of ethanol and/or the alkylation (cross-coupling) of ethanol with other lower alcohols [1-5]. However, it should be noted that the research in this area largely concerns homogeneous catalysis; therefore, the implementation of the research results in industry is complicated by the known difficulties of isolation and regeneration of catalyst systems.

Gold had long been disregarded as a catalytic metal—until 1989 when Japanese chemist M. Haruta showed that Au particles of a 2-5 nm size exhibit high

activity in the low-temperature oxidation of CO [6]. Later, it was found that Au nanoparticles are effective catalysts for other reactions: hydrogenation [7, 8], isomerization [9, 10], hydrodechlorination [11, 12], and hydrocarbon conversion [13, 14]. Recently, it has been reported that oxide-supported bimetallic composites of copper-promoted gold clusters exhibit high activity and selectivity in the steam reforming of methanol [15] and the reduction of *p*-nitrophenol to *p*-aminophenol [16]. Thus, the development of Au–Cu catalysts for ethanol conversion to linear α -alcohols seems to be extremely promising.

In this paper, we present the results of study of the basic features of the catalytic behavior of aluminasupported Au–Cu, Au, and Cu nanocomposites in the conversion of ethanol to butanol-1 and hexanol-1 under conditions providing the supercritical state of ethanol and under conventional subcritical conditions under which organic substrates are in the gaseous state.

EXPERIMENTAL

A Cu/Al₂O₃ catalyst containing 0.07 wt % Cu was prepared by incipient wetness impregnation of the support [17]. To this end, a calculated amount of Cu((NO₃)₂ · 6H₂O (Sigma-Aldrich, 98%) was dissolved in water. The resulting solution was added to γ -Al₂O₃ pellets calcined at 400°C for 3 h (AO Angarsk Catalysts and Organic Synthesis Plant, 160 m²/g, pellet diameter of 0.5 mm). After that, the wet pellets were dried at 25°C for 24 h and calcined at 400°C for 6 h.

An Au/Al₂O₃ catalyst containing 0.2 wt % Au was prepared by ion exchange [18, 19]. To this end, a calculated amount of HAuCl₄ (Sigma-Aldrich, 98%) was dissolved in water. The solution pH was adjusted to 7.0 using NaOH (Reakhim, 0.1 M); the solution was poured to Al₂O₃ pellets in water; the resulting mixture was stirred at 50°C for 1 h. After that, the pellets were separated from the mother liquor, washed with 4 L of water, dried at 25°C for 24 h, and calcined at 400°C for 3 h. After the first calcination, a portion of the Au/Al₂O₃ precursor was used to prepare an Au– Cu/Al₂O₃ catalyst; the remaining portion was calcined again at 400°C for 3 h to prepare an Au/Al₂O₃ catalyst.

An Au–Cu/Al₂O₃ catalyst containing 0.2 and 0.07 wt % of Au and Cu, respectively, was prepared by incipient wetness impregnation. To this end, a portion of the Au/Al₂O₃ precursor obtained after the first calcination at 400°C was impregnated with a copper nitrate solution in water, dried at 25°C for 24 h, and calcined at 400°C for 3 h.

The catalysts were tested on a Parr 5000 Series multireactor autoclave-type setup with the reactor volume of 45 mL. In a standard test on the conversion of ethanol in the supercritical state, the reactor was charged with 25 mL of ethanol and 5.6 g of the catalyst. The reactor was sealed and purged with argon to remove oxygen. Next, argon was pumped out to a residual pressure of 0.1 atm. The reaction was conducted at a temperature of 245, 275, and 295°C for 5 h. The reaction mixture was agitated with a magnetic stirrer (rotation speed of 1200 rpm). For the above conditions, the initial ethanol pressure in the reactor was 100 atm; during the experiment (5 h), the pressure was increased to 110–120 atm.

In a standard test on the conversion of ethanol in the subcritical state, the reactor was charged with 5 mL of ethanol and 1.1 g of the catalyst. The reactor was sealed and purged with argon; after that, argon was bled to a residual pressure of 0.1 atm. Next, the reactor was heated to 275° C and the stirring of the reaction mass was turned on. The reaction time was 5 h. For the above conditions, the initial ethanol pressure in the reactor was 50 atm; during the experiment (5 h), the pressure was increased to 55–60 atm.

Upon the completion of each catalytic test, the reactor was cooled with water to room temperature; the entire amount of the reaction gas was withdrawn into a gas holder to conduct qualitative and quantitative analyses of the gas mixture. After that, the reactor was unsealed to withdraw the liquid reaction mixture for analysis.

The gaseous reaction products were analyzed by gas chromatography using a Kristall-4000M instrument (flame ionization detector, HP-PLOT column) for gaseous C_1 – C_5 hydrocarbons and a Kristall-4000 chromatograph (thermal conductivity detector, SKT column) for CO, CO₂, and H₂. The qualitative composition of the liquid organic reactants was determined by gas chromatography-mass spectrometry on Agilent MSD 6973 (HP-5MS column) and Delsi Nermag Automass-150 instruments (CPSil-5 column) at EI = 70 eV. The quantitative determination of the liquid reactants was performedby gas-liquid chromatography on a Varian 3600 instrument (Chromatec column; SE-30; 0.25 × 250 cm; $D_{\rm f} = 0.3$ mm; 50°C (5 min); 10 °C/min; 280°C; $t_{inj} = 250$ °C; $P_{inj} = 1$ bar; split ratio, 1/200; flame ionization detector; internal standard, *n*-octane).

The metal loading of the catalysts was determined by atomic absorption spectrometry on a Thermo iCE 3000 instrument [17]. The relative error in the measurement of the metal content by this method does not exceed 1%. X-ray diffraction (XRD) patterns of the catalysts were recorded by XRD analysis on a Rigaku D/MAX2500 instrument using a CuK_{α} radiation source. Transmission electron microscopy (TEM) images of the catalysts were taken with a JEOL JEM 2100F/UHR instrument with a resolution of 0.1 nm. Prior to examination, 0.1 g of the sample was placed in 30 mL of C₂H₅OH and sonicated for 300 s. A droplet of the resulting mixture was placed on a standard carbon-coated TEM grid, dried for 1 h, placed under the microscope, and studied. Particle size was determined as the maximum linear size. The average particle size was determined by statistical processing of data on 250-300 particles. The chemical composition of the particles was determined by energy dispersive X-ray spectroscopy (EDS) analysis on a JED-2300 instrument.

RESULTS AND DISCUSSION

Features of Catalytic Behavior of Au–Cu, Au, and Cu Catalysts

At 275° C in the presence of the Au–Cu catalyst, ethanol in the supercritical state (partial pressure of 120 atm) is converted to butanol-1 and hexanol-1 with 2–3 times higher selectivities than those achieved in the conversion of gaseous ethanol (Table 1). It should also be noted that in this study, the product yield over the Au–Cu catalyst is an order of magnitude above that of the desired alcohols in the presence of other heterogeneous catalysts studied in [20–22].

Table 1 shows that the ethanol conversion and the alcohol selectivity over the Au–Cu catalyst significantly depend on temperature. The maximum selectivity for butanol-1 (74.4%) and hexanol-1 (17.8%) is achieved at 275°C. An increase in the reaction tem-

NIKOLAEV et al.

Table 1. Ethanol conversion and selectivity for desired products in the conversion of ethanol in the presence of mono- and bimetallic catalysts. The data are derived under conditions providing the supercritical state of ethanol (ethanol partial pressure in the reactor of 100-120 atm)

| Catalyst | Time h | T°C | EthanolSeleconversion, %butanol-1 | Selectivity, % | |
|---|----------|--------------|-----------------------------------|----------------|-----------|
| Catalyst | Time, ii | <i>I</i> , C | | butanol-1 | hexanol-1 |
| Au–Cu/Al ₂ O ₃ | 5 | 245 | 4.6 | 57.9 | 3 |
| Au-Cu/Al ₂ O ₃ | 5 | 275 | 33.4 | 74.4 | 17.8 |
| Au-Cu/Al ₂ O ₃ | 5 | 295 | 35.1 | 57.2 | 6.4 |
| Au-Cu/Al ₂ O ₃ * | 5 | 275 | 15.1 | 25.3 | 7.2 |
| Au-Cu/Al ₂ O ₃ ** | 50 | 275 | 32.9 | 75.1 | 17.5 |
| Cu/Al ₂ O ₃ | 5 | 275 | 11.5 | 0.2 | 0 |
| Au/Al ₂ O ₃ | 5 | 275 | 30 | 15.9 | 0.5 |

* Data for gaseous ethanol (ethanol partial pressure in the reactor of 50–60 atm). ** Data derived in ten consecutive 5-h catalytic cycles.

Table 2. Qualitative and quantitative composition of the ethanol conversion products over the Au–Cu catalyst under conditions providing the supercritical state of ethanol (ethanol partial pressure in the reactor of 100-120 atm)

| Temperature, °C | 245 | 275 | 295 | |
|----------------------------|------------------------|------|------|--|
| Ethanol conversion, % | 4.6 | 33.4 | 35.1 | |
| Substance | Product selectivity, % | | | |
| Acetaldehyde | 3 | 0 | 0 | |
| Butene | 4 | 0 | 5 | |
| <i>n</i> -Butane | 1 | 0 | 1 | |
| Diethyl ether | 5 | 1 | 16 | |
| Butanone-2 | 0 | 0 | 1 | |
| Butanol-2 | 0 | 0 | 1 | |
| Ethyl acetate | 5 | 0 | 2 | |
| $C_x H_y$ olefins (x = 6+) | 0 | 0 | 1 | |
| Butanol-1 | 58 | 74 | 57 | |
| 2-Butene-1-ol | 17 | 0 | 0 | |
| Ethyl butyl ether | 0 | 0 | 3 | |
| 2-Ethylbutanol-1 | 0 | 2 | 2 | |
| Hexanol-1 | 3 | 18 | 6 | |
| Ethyl hexyl ether | 0 | 1 | 0 | |
| Ethyl caproate | 2 | 1 | 1 | |
| The rest | 3 | 1 | 4 | |
| Σ | 100 | 100 | 100 | |

perature from 275 to 295°C leads to a slight increase in the ethanol conversion from 33.4 to 35.1% and a decrease in the selectivity for butanol-1 and hexanol-1 by 17.2 and 11.4%, respectively. Analysis of the ethanol conversion products (Table 2) shows that the decrease in selectivity at 295°C is primarily attributed to the development of both intramolecular and intermolecular alcohol dehydration reactions, which lead to an increase in the yield of olefins and ethers (primarily, diethyl ether). A decrease in temperature from 275 to 245°C leads to an abrupt decrease in the ethanol conversion and the selectivity for butanol-1 and hexanol-1 by 16.5 and 14.8%, respectively (Table 1). It is significant that, at 245°C, the products contain a fairly high amount of assumed intermediates of butanol-1 formation (scheme), such as acetaldehyde and 2-buten-1-ol (Table 2). Their accumulation in the reaction mixture suggests that the first two stages shown in the scheme rapidly occur and that, apparently, the rate-limiting



Fig. 1. Dynamics of change in the amounts of ethanol and butanol-1 during the reaction ($T = 275^{\circ}$ C, ethanol initial partial pressure of 100 atm). V_{cr^*} is the amount of ethanol in the reactor required to provide the ethanol pressure above the critical value (63 atm).

step of the entire process is the hydrogenation of 2butene-1-ol.



Scheme 1. Formation of butanol-1 from ethanol [1-3].

In ten consecutive 5-h tests, the activity and selectivity of the Au–Cu/Al₂O₃ system remain unchanged (Table 1). The high stability of the catalyst is apparently due to the stability of Au–Cu particles against sintering, as evidenced, in particular, by the small particle size preserved in Au–Cu/Al₂O₃ compared with the Au/Al₂O₃ monometallic counterpart (see Structural Features of the Catalysts).

Figure 1 shows the dynamics of change in the amount of consumed ethanol and butanol-1 produced in the reactor. It is evident from Fig. 1 that ethanol is consumed during the entire experiment; however, the amount of it is sufficient to maintain the supercritical state; that is, ethanol is actually in the fluid state throughout the experiment. It should be noted that the initial partial pressure of ethanol—100 atm—is equivalent to the total pressure in the system; during the experiment, the total pressure increases by 10-20 atm.

A kinetic study of ethanol conversion over the Au– Cu catalyst showed that the reaction is satisfactorily described by the first-order rate equation. Data processing in Arrhenius coordinates $(\ln(X)-1/T)$ in the range of 245–280°C showed that the apparent activation energy for ethanol conversion is 72 or 13 kJ/mol for ethanol in the supercritical or gaseous state, respectively. These values suggest that the increase in the ethanol conversion under supercritical conditions is due to weakening of diffusion limitations. According to [23, 24], another cause of the increase in the ethanol conversion can be an increase in the polarization of the O–H bonds and a decrease in the number of hydrogen bonds in supercritical ethanol, changes that facilitate ethanol adsorption and activation on the active sites of the catalyst.

The degrees of conversion and selectivities of the monometallic counterparts of the Au-Cu catalyst in the conversion of ethanol in the supercritical state are collated in Table 1. It is evident that at 275°C in the presence of the Cu/Al_2O_3 catalyst, the main product of ethanol conversion is diethyl ether. The ethanol conversion and the selectivity for the desired alcohol are 11.5 and 0.2%, respectively (Table 1). In the presence of the Au/Al_2O_3 catalyst, the ethanol conversion is 30% and the selectivities for butanol-1 and hexanol-1 are 15.9 and 0.5%, respectively (Table 1). Thus, the bimetallic catalyst exhibits significantly higher activity and selectivity in the ethanol conversion to linear α -alcohols. To determine the probable causes of the different behavior of the Au-Cu, Au, and Cu systems, the structural features of the mono- and bimetallic catalysts were studied by XRD, X-ray photoelectron spectroscopy (XPS), and TEM. The results are described below.

Structural Features of the Au-Cu, Au, and Cu Catalysts

The XRD patterns of the Au-Cu, Au, and Cu catalysts are shown in Fig. 2. Curve 1 in Fig. 2 shows that the XRD pattern of Cu/Al_2O_3 exhibits reflections at $2\theta = 32.5^{\circ}, 37.6^{\circ}, 39.5^{\circ}, 46.0^{\circ}, 61.1^{\circ}, and 66.8^{\circ}, which$ correspond to the reflections of the (220), (311), (222), (400), (511), and (440) faces of γ -Al₂O₃ [17]. The absence of reflections of copper-containing phases in the XRD pattern of Cu/Al₂O₃ is most probably attributed to the low copper concentration. The XRD pattern of Au/Al₂O₃ (Fig. 2, curve 2) exhibits, in addition to reflections of Al₂O₃, reflections at $2\theta =$ 38.1° , 44.4° , and 64.6° , which correspond to the reflections of the (111), (200), and (222) faces of gold crystallites [19]. In comparison with Au/Al₂O₃ (Fig. 2, curve 2), the diffraction peaks of gold in Au- Cu/Al_2O_3 are broadened (Fig. 2, curve 3); this finding indicates a higher dispersion of the Au-containing phase in $Au-Cu/Al_2O_3$.

Some examples of the formation of new phases composed of bimetallic alloys on the surface of Au– Cu, Au–Ni, and Pd–Ce catalysts were described in [25, 26]. The authors of the cited studies observed that the formation of the new alloys is accompanied by the occurrence of new reflections or by a shift of reflections of the supported phases of noble metals toward larger angles on a 2 θ scale. Our XRD data show that the diffraction patterns of the Au–Cu sample do not exhibit new reflections or shifts of Au reflections; this finding suggests that the formation of solid-solution alloys or intermetallic compounds with a regular structure can be excluded with a high degree of probability.

The electronic state of metals in Au, Cu, and Au–Cu catalysts was previously studied by XPS; the results are described in [17]. It was found that copper present on the surface of Cu/Al₂O₃ is in the form of CuO (80 at %) and Cu₂O (20 at %). Au/Al₂O₃ comprises gold in the form of Au^0 (100 at %). The electron binding energy of Au $4f_{7/2}$ in the XPS spectrum of $Au-Cu/Al_2O_3$ is 84.4 eV [17]. This result shows that, along with the originally zero-valent gold, Au(+n) cations $(0 \le n \le 1)$ are formed in Au–Cu/Al₂O₃. The Au(+*n*) content is low—on the order of 10-20 at %. Analysis of the Cu 2p core-level XPS spectra [17] suggests that, in $Au-Cu/Al_2O_3$, the fraction of surface oxide CuO decreases and the fraction of Cu₂O increases. The above results indicate that, in the Au-Cu catalyst, a contact between the Au(0) and CuO phases leads to electron transfer from the former to the latter. This process results in a partial reduction of CuO to Cu₂O; the evolved oxygen is bound to Au(+n) to form AuO_{v} . This model is consistent with the structural data on Au-Cu catalysts described in [27, 28].

Representative TEM micrographs of mono- and bimetallic catalysts are shown in Figs. 3a–3c. It is evident from Fig. 3a that the Cu/Al₂O₃ sample surface comprises regions of ordered atoms, which, according to EDS, correspond to Cu-containing particles with an average size of 3 ± 1 nm. The small size of the supported particles in Cu/Al_2O_3 , which was determined by TEM, is consistent with the X-ray amorphous state of the copper phases in Cu/Al₂O₃, which was revealed by XRD (Fig. 2, curve 1). The Au/Al₂O₃ surface comprises regions of ordered atoms, which, according to EDS, correspond to gold particles with an average size of 10 ± 2 nm (Fig. 3b). The formation of relatively large gold particles in Au/Al₂O₃ is attributed to the weak metal-support interaction, which leads to the sintering of noble metal particles during the calcination of the catalyst precursor [19].

The average particle size in Au–Cu/Al₂O₃ is smaller than that of Au/Al₂O₃: it is 5 nm (Fig. 3c). The shift of the average particle size in Au–Cu/Al₂O₃ suggests that copper oxides contribute to the stabilization of small Au particles on the surface of the support. An example of identification of the chemical composition of particles in the Au–Cu/Al₂O₃ catalyst is shown in Figs. 3c–3e. TEM–EDS analysis of a sample of 180 particles located both in particle clusters and at a considerable distance from each other showed that about 20% of particles in Au–Cu/Al₂O₃ are individual Au particles with a size of 12 nm and copper oxide particles with a size of 3 nm, while the remaining 80% are bimetallic composites consisting of copper oxide particles (3 nm) and small gold particles (5 nm).



Fig. 2. XRD patterns of (1) Cu/Al₂O₃, (2) Au/Al₂O₃, and (3) Au-Cu/Al₂O₃.

Causes of Different Behaviors of the Au–Cu, Au, and Cu Catalysts

TEM data suggest that the active phase in Cu/Al₂O₃ and Au/Al₂O₃ is represented by particles of 3 and 10 nm in size, respectively. It is known that the heat of adsorption of ethanol on the Cu surface is higher than that for Au [29]. It is also known that the heat of adsorption of alcohol abruptly increases with a decrease in the particle size from 4 to 1 nm [26]. Hence, it is reasonable to assume that the number of alcohol molecules strongly bound to the catalyst surface should be higher in Cu/Al₂O₃ and lower in Au/Al₂O₃. In addition, the deactivation of the alcohol-blocked active sites and a decrease in the ethanol conversion should occur. Comparison of the data on catalysis and morphology of active particles is consistent with this hypothesis: all other test conditions being equal, the ethanol conversion over Au/Al₂O₃ and Cu/Al_2O_3 is 30 and 11.5%, respectively.

The fact that the particle size in Au/Al_2O_3 is larger than that in Cu/Al_2O_3 provides an adequate explanation to the high selectivity for butanol-1 and hexanol-1. It is obvious that a high rate of growth of the hydrocarbon skeleton of the products should be observed in the case of coordination of two ethanol molecules on two free and closely spaced active sites (Scheme 1), the number of which should be larger in the 10-nm Au particles.

According to our reckoning, the increase in the ethanol conversion over $Au-Cu/Al_2O_3$ in comparison with the most active counterpart— Au/Al_2O_3 —is attributed to two factors. First, a contact between copper oxide and gold leads to an increase in the degree of



Fig. 3. Representative TEM micrographs of (a) Cu/Al_2O_3 , (b) Au/Al_2O_3 , and (c) $Au-Cu/Al_2O_3$. (d, e) EDS spectra of locations marked in (c). It is evident that the locations comprise either a bimetallic composite or individual metal particles.

dispersion of the gold clusters from 10 to 5 nm; therefore, at identical amounts of gold, the specific surface area of gold should be higher in $Au-Cu/Al_2O_3$. Apparently, the degree of dispersion of gold in the Au-Cu sample has not yet become sufficiently high to correspond to the case where the contribution of the mechanism of catalyst inhibition by hydrocarbon molecules strongly bound to the metal surface is a limiting factor for the entire process.

A certain contribution to the high activity of $Au-Cu/Al_2O_3$ can come from the formation of new

PETROLEUM CHEMISTRY Vol. 56 No. 8 2016

Au(+*n*) sites ($0 \le n \le 1$) in Au–Cu/Al₂O₃. The scheme shows that the growth of the hydrocarbon skeleton of the target alcohols passes through the dehydrogenation–hydrogenation stages. It is known that these processes over metal-containing catalysts are accompanied by a change in the oxidation state from M(*n*) to M(*n* + 2) [30]. For Au/Al₂O₃, changes in the oxidation state of the metal can be represented by the following cycle: Au(0) \rightarrow Au(+2) \rightarrow Au(0), which includes the oxidation state of (+2), which is not characteristic of gold. Therefore, the dehydrogenation–hydrogenation of hydrocarbons over zero-valent Au clusters in Au/Al₂O₃ should proceed at a relatively low rate. In fact, according to [30], zero-valent gold exhibits a low activity in the hydrogenation reaction. The formation of individual atoms in the oxidation state close to (+1)on the surface of the gold particles provides the occurrence of a high-rate cycle consisting of oxidation states characteristic of gold: $Au(+1) \rightarrow Au(+3) \rightarrow Au(+1)$. In this case, according to [19, 31], the presence of cationic gold leads to an increase in the activity of gold catalysts in acetylene hydrogenation and allylbenzene isomerization occurring through a dehydrogenationhydrogenation cycle. Therefore, it is reasonable to assume that the dehydrogenation-hydrogenation of hydrocarbons (and hence the formation of highmolecular-weight alcohols according to the scheme) over gold cations in Au–Cu/Al₂O₃ can also occur at a high rate. It is certainly necessary to take into account the presence of hydrogen in the reaction sphere and the relatively high reaction temperature; therefore, it would be only logical to expect the reduction of Au cations to Au⁰ and the subsequent decrease in the conversion to the level achieved over Au/Al₂O₃. However, the data on the stability of the Au-Cu catalyst suggest otherwise-the product yield does not change for at least the first ten cycles.

According to our reckoning, an increase in the selectivity for butanol-1 and hexanol-1 over Au– Cu/Al_2O_3 in comparison with the most selective counterpart—Au/Al_2O_3—can be attributed to a change in the morphology of the active site of the catalyst. Figure 3 shows that extended agglomerates of Au_n–Cu_n–Au_n–Cu_n clusters are formed in the bime-tallic catalyst. Apparently, these agglomerates contribute to the close coordination of a few ethanol molecules at once and, thereby, facilitate the growth of a more extended hydrocarbon skeleton of the alcohols. This hypothesis is supported by the fact that of all the tested samples, the Au–Cu catalyst alone provides the formation of trace amounts of a higher alcohol (octanol-1).

CONCLUSIONS

It has been shown that the Au–Cu/Al₂O₃ composite is an effective catalyst for the conversion of ethanol in the supercritical state to linear alpha-alcohols. It has been found that the Au–Cu/Al₂O₃ catalyst is characterized by the formation of nanosized bimetallic active components in which the concentration of Au⁺ⁿ (0 < n < 1) and Cu⁺¹ ions increases in comparison with monometallic catalyst counterparts (Au⁰/Al₂O₃ and Cu²⁺/Al₂O₃). Contacts between copper and gold in the Au–Cu/Al₂O₃ catalyst also lead to abrupt changes in the morphology of the supported particles: the average particle size decreases and agglomerates of Au_n–Cu_n– Au_n–Cu_n clusters are formed. These changes lead to a significant increase in the activity and selectivity for the formation of butanol-1 and hexanol-1 from ethanol under supercritical conditions over the Au-Cu catalyst. In this case, the supercritical state of ethanol apparently provides the most favorable conditions for the occurrence of the reaction because the ethanol conversion products formed under the experimental conditions transit into a gaseous state and thus facilitate the access to the surface active sites for ethanol fluids.

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REFERENCES

- Biomass Conversion: The Interface of Biotechnology, Chemistry and Materials Science, Ed. by C. Baskar, S. Baskar, and R. S. Dhillon (Springer, Berlin, 2012). doi 10.1007/978-3-642-28418-2
- S. N. Naik, V. V. Goud, P. K. Rout, and A. K. Dalai, Renew. Sustain. Energy Rev. 14, 578 (2010).
- 3. J. Sun and Y. Wang, ACS Catal. 4, 1078 (2014).
- 4. C. Angelici, B. M. Weckhuysen, and P. C. Bruijnincx, ChemSusChem 6, 1595 (2013).
- 5. A. Demirbas, Biofuels: Securing the Planet's Future Energy Needs (Springer, London, 2009). doi 10.1007/978-1-84882-011-1
- M. Haruta, N. Yamada, T. Kobbayashi, and S. Iijima, J. Catal. 115, 301 (1989).
- C. A. Nikolaev, N. A. Permyakov, V. V. Smirnov, et al., Kinet. Catal. 51, 288 (2010).
- S. A. Nikolaev and I. N. Krotova, Pet. Chem. 53, 394 (2013).
- V. V. Smirnov, S. A. Nikolaev, L. A. Tyurina, and A. Yu. Vasil'kov, Pet. Chem. 46, 289 (2006).
- V. V. Smirnov, S. N. Lanin, A. Yu. Vasil'kov, et al., Russ. Chem. Bull. 54, 2215 (2005).
- 11. M. A. Keane, S. Gomez-Quero, and F. Cardenas-Lizana, ChemCatChem 1, 270 (2009).
- M. O. Nutt, K. N. Heck, P. Alvarez, and M. S. Wong, Appl. Catal., B 69, 115 (2006).
- S. A. Nikolaev, A. Yu. Vasil'kov, V. V. Smirnov, and L. A. Tyurina, Kinet. Catal. 46, 867 (2005).
- S. N. Lanin, D. A. Pichugina, A. F. Shestakov, et al., Russ. J. Phys. Chem. A 84, 2133 (2010).
- 15. C. Pojanavaraphan, A. Luengnaruemitchai, and E. Gulari, Appl. Catal., A **456**, 135 (2013).
- 16. R. He, Y.-C. Wang, X. Wang, et al., Nat. Commun. 5, 1038 (2014).

- S. A. Nikolaev, E. V. Golubina, I. N. Krotova, et al., Appl. Catal., B 168/169, 303 (2015).
- 18. S. A. Nikolaev, A. V. Chistyakov, M. V. Chudakova, et al., J. Catal. **297**, 296 (2013).
- 19. S. Nikolaev, D. Pichugina, and D. F. Mukhamedzyanova, Gold Bull. **45**, 221 (2012).
- 20. T. Riittonen, E. Toukoniitty, D. K. Madnani, et al., Catalysts 2, 68 (2012).
- 21. S. Ogo, A. Onda, Y. Iwasa, et al., J. Catal. **296**, 24 (2012).
- 22. T. Tsuchida, S. Sakuma, T. Takeguchi, and W. Ueda, Ind. Eng. Chem. Res. 45, 8634 (2006).
- 23. J. Yang, Y. Zhang, Y.-X. Yu, and Y.-G. Li, J. Supercrit. Fluids **36**, 145 (2005).
- 24. D. Dellis, M. Chalaris, and J. Samios, J. Phys. Chem. B 109, 18575 (2005).

- 25. X. Liu, A. Wang, X. Wang, et al., Chem. Commun., p. 3187 (2008).
- 26. H.-L. Jiang and Q. Xu, J. Mater. Chem. 21, 13705 (2011).
- 27. F.-C. Duh, D.-S. Lee, and Y.-W. Chen, Mod. Res. Catal. 2, 1 (2013).
- 28. B. White, M. Yin, A. Hall, et al., Nano Lett. 6, 2095 (2006).
- 29. P. Tereshchuk and L. F. da Silva Juarez, J. Phys. Chem. C **116**, 24695 (2012).
- S. A. Nikolaev, L. N. Zanaveskin, V. V. Smirnov, et al., Russ. Chem. Rev. 78, 231 (2009).
- 31. D. A. Pichugina, S. A. Nikolaev, D. F. Mukhamedzyanova, et al., Russ. J. Phys. Chem. A **85**, 646 (2011).

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