Supercritical Ethanol and Isopropanol Conversion into Chemicals over Au-M Catalysts

Polina A. Zharova[*a], Andrey V. Chistyakov[a,b], Mark V. Tsodikov[a,b], Sergey A. Nikolaev[c], Francesco Rossi[d,e], Flavio Manenti[d]

[a]Topchiev Institute of Petrochemical Synthesis RAS, Leninskii pr. 29, Moscow 119991, Russia
[b]Semenov Institute of Chemical Physics RAS, Kosygina str., 4, Moscow 119991, Russia
[c]Moscow State University, Leninskie Gory 1, Moscow 119991, Russia
[d]Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Piazza Leonardo da Vinci, 32, 20133 Milano, Italy
[e]Purdue University, Forney Hall of Chemical Engineering, 480 Stadium Mall Drive, West Lafayette, IN 47907-2100, United States
zharova@ips.ac.ru

This study is the first to investigate the catalytic performance of Au-Cu catalysts in the direct alkylation of ethanol with isopropanol. Alcohols and ketones containing 5 or 7 carbon atoms were suggested as aim products of the reaction. For example depending on catalyst composition and reaction conditions pentanol-2 selectivity was 30-40%. To describe the differences between the structure of supported metals in catalysts, energy dispersive X-ray (EDX) analysis and transmission electron microscopy (TEM) were performed. Structural investigations of Au-Cu/Al_2O_3, Au/Al_2O_3 and Cu/Al_2O_3 catalysts were conducted via X-ray photoelectron spectroscopy (XPS).The relationships between a compound's structure, activity and mechanistic aspects are discussed to clarify the factors that may affect the synergetic effect in the presence of the Au-Cu catalyst.

1. Introduction

The first reference to gold as a catalyst dates back to 1906 when Bone and Wheeler observed oxidation of hydrogen on a heated gold gauze (Bone and Wheeler, 1906). A number of papers dealing with catalytic hydrogenation of alkenes on gold films and impregnated gold catalysts were reviewed by Yolles et al. (1971) and Bond and Sermon (1973). In 70's however, the original breakthrough in the catalysis by gold should be linked with Haruta et al. (1987), who demonstrated in 90's that gold can be an excellent catalyst when supported on metaloxides in a dispersed state. The recent progress in heterogeneous catalysis resulted in remarkable investigations that showed the high activity of gold nanoparticles in the conversion of alcohols to synthetic hydrocarbons (Nikolaev et al., 2013), selective oxidation of propene (Feng et al., 2014), synthesis of hydrogen peroxide (Hutchings et al., 2012), water gas shift reaction (Tabakova et al., 2013), hydrogenation of alkenes (Nikolaev et al., 2010), isomerisation (Simakova et al., 2010), and hydrodechlorination (Gómez-Quero et al., 2013).

The conversion of ethanol into n-butanol over purely heterogeneous catalysts has been reported in several publications and patents (Sun et al., 2014). Generally, the reaction temperature varies from 200 up to 450°C with a relatively low conversion (e.g., 10%–20%) and a selectivity approaching 70%. Hydroxyapatites have been shown to be the most active and selective catalytic systems for higher alcohols production (Ogo et al., 2012). In a plug flow reactor, the highest n-butanol selectivity was found to be 76.3% at 14.7% conversion of ethanol (Tsuchida et al., 2006) and 81.2% at 7.6% conversion of ethanol (Ogo et al., 2012). The study of a batch reactor process showed that a 20% Ni/Al_2O_3 catalyst manufactured by Crossfield produces the highest selectivity of 80% at a conversion of approximately 25% after 72 h (Riittonen et al., 2015). Isopropanol condensation generally leads to ketones formation due to its higher rate of acetone alkylation compared to Guerbet condensation. Over hydrotalcite-derived mixed oxide (Mg₃AlOₓ), the primary products are diacetone

alcohol, phorone and isophorone (Ordóñez et al., 2011). The Guerbet reaction of supercritical isopropanol into a small amount of 3,3,5-trimethylcyclohexanolwas observed in a study of the decomposition of epoxy resin with KOH (Jiang et al., 2010). The self-coupling of 2-propanol occurred with a heterogeneous Ni/CeO_2 catalyst (Shimura et al., 2013) (>200°C) and various coupling products, including methyl isobutyl ketone (21%),4-methyl-2-pentanol (19%), diisobutyl ketone (21%) and 2,6-dimethyl-4-hexanol (9%), were obtained in comparable yields to previous studies (Torres et al., 2007). Several examples are shown to describe acetone-butanol-ethanol (ABE) fermentation products conversion in comparison to Guerbet type catalysts (Sreekumar et al., 2014). In both catalytic systems studied in these works, the formation of ketones C_7–C_{19} was observed, which indicates that no interaction between the ethanol and acetone occurred. The formation of 2-pentanon occurred only in the presence of Pd-hydrotalcite catalyst, and its yield did not exceed 10% from other C_7–C_{11} ketones (Sreekumar et al., 2014). The fermentation mixture of the IBE conversion also did not lead to C_5 product formation. The alkylation of secondary alcohols with primary alcohols thus effectively catalysed by homogeneous base and homogeneous/heterogeneous transition metal systems (Wang et al., 2013) but never a pure heterogeneous catalytic system.

Recently was found that $Au-Ni/Al_2O_3$ catalysts are prospective for heterogeneously catalyses isopropanol alkylation with ethanol (Zharova et al.,2016). This study scope is the investigation of ethanol and isopropanol cross-coupling process peculiarities. The relationships between a compound's structure, activity and mechanistic aspects are discussed to clarify the factors that may affect the synergetic effect in the presence of the Au-Cu catalyst.

2. Materials and Methods

Analytical grade ethanol (96%) and isopropanol (96%) were used without further purification. In typical alkylation experiment initial mixture contains equal volumes of alcohols (13 ml). Both ethanol and isopropanol loading for individual alcohol conversion test were 25 ml. Gamma Al_2O_3 with S=160 m^2/g was used as a support for metal nanoparticles. Au/Al_2O_3 catalysts were produced by deposition-precipitation and Au-Cu/Al_2O_3, Cu/Al_2O_3 produced by impregnating as described by Nikolaev et al. (2013).

The metal content of the catalysts was determined by atomic absorption on a Thermo iCE 3000 AA spectrometer. Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis of catalysts were carried out on a JEOL JEM 2100F/UHR microscope and a JED-2300 X-ray spectrometer, respectively. XPS analysis of the catalysts was performed on a Kratos Axis Ultra DLD spectrometer using AlK radiation (1486.6 eV). The alkylation of alcohols was performed in a 45 mL high pressure Parr autoclave equipped with magnetic stirring under argon. The reactor was heated up to 275°C with a heating rate of 20 °C/min. Reaction conditions were chosen on the base of previous works (Chistyakov et al., 2017). Gaseous reaction products were analyzed by the GC. Liquid reaction products were analyzed by the GC and GC-MS.

3. Results and Discussion

First, we tested the activity of the 0.2Au-0.07Cu, 0.2Au and 0.07Cu catalysts for the self-condensation of ethanol and isopropanol (Table 1). The bimetallic 0.2Au-0.07Cu catalyst showed the highest yield of condensation products, such as butanol-1, hexanol-1 and octanol-1 with a total selectivity of 92.2% at 33.4% conversion of ethanol. Conversely, the 0.07Cu system primarily catalysed the dehydration of ethanol to provide diethyl ether and ethylene, and dehydrogenation to provide acetic aldehyde. The conversion and selectivity to linear alcohols in the presence of Cu catalyst does not exceed 11.5 and 0.2%, respectively. An Au analogue was then used to catalyse the conversion of ethanol primarily into butanol-1 but produced a low conversion (30%) and low selectivity (16.4%).

Next, the scope of isopropanol for self-condensation using 0.2Au-0.07Cu, 0.2Au and 0.07Cu catalysts was investigated. The results of this study show that isopropanol undergoes no self-condensation. The primary products were acetone and propane over 0.2Au-0.07Cu and 0.2Au catalysts (Table 1). The 0.07Cu system catalysed the isopropanol dehydrogenation into acetone and dehydration into propene, as shown in Table 1. Alumina based systems typically catalyse the dehydrogenation of secondary alcohols to provide corresponding ketones as primary products (Jenck, 2004). Study of active components content in bimetallic systems effect at alkylation selectivity showed that gold concentration increase from 0.2 to 0.5 wt.% results in selectivity of pentanol-2 increase from 30 to 41% (Table 2). However, the total selectivity of alkylation products changes slightly (about 5%). In the presence of 0.2Au-0.07Cu catalyst steps of hydrogenation of ketones into alcohols (4 → 5b, 6b → 7b) occur less intensively. This phenomenon probably can be explained by structural effect - smaller particles is less effective in the hydrogenation process than bulk particles. Varying the content of copper in the catalysts does not seem to change the selectivity.

Table 1. Conversion of individual alcohols (ethanol and isopropanol). (T = 275°C; P = 150 atm, 5 h).

| Catalyst	0.2Au-0,07Cu		0.2Au		0.07Cu	
Substrate	EtOH	iPrOH	EtOH	iPrOH	EtOH	iPrOH
Conversion (%)	33.4	31.2	30	27.4	11.5	13.1
Selectivity (%)						
Butanol-1	74.4	-	15.9	-	0.2	-
Hexanol-1	17.8	-	0.5	-	-	-
Propane	-	12.7	-	17.9	-	4.8
Acetone	-	83.2	-	76.4	-	56.7
Others	7.8	4.1	83.6	5.7	99.8	38.5

Table 2. Products formation selectivity and conversions of ethanol and isopropanol mixture (275 °C, 150 atm, 5 h on stream)

Catalyst	0.2Au-0.07Cu	0.5Au-0.32Cu	0.5Au-0.8Cu	0.2 Au
total selectivity of alkylation products, %	63.8	69.5	66.7	33.8
ethanol conversion, %	64.6	50.6	46.16	46.7
isopropanol conversion, %	49.3	46.9	42.23	56.40
product	Selectivity. %			
propane	1.5	1.4	-	-
acetic aldehyde	0.1	-	1.5	2.9
acetone	6.7	8.3	10.6	13.6
butenes	0.6	0.4	0.2	2.7
butane	0.3	0.1	0.8	1.6
ethyl isopropyl ether	1.5	-	-	-
diethyl ether	2.5	3.3	1.6	33.0
ethylacetate	0.8	0.7	0.1	0.8
butanol-1	12.3	14.5	17.3	8.0
pentenes	2.0	-	-	
pentanone-2	13.1	16.5	16.9	10.3
pentanol-2	30.6	41.1	41.4	19.0
hexanol-1	1.4	-	-	-
butyl ethyl ether	0.4	-	-	-
butylacetate	0.6	-	-	0.1
ethyl butyrate	0.2	-	-	-
heptanone-4	8.8	1.5	0.1	0.0
heptanone-2	1.7	0.6	0.6	0.1
heptanol-4	5.6	9.0	6.9	0.2
heptanol-2	2.8	0.9	0.8	2.8
nonanone-4	1.0	-	-	-
nonanol-4	0.2	-	-	-
other	5.2	1.8	1.2	4.8
Σ	100.0	100.0	100.0	100.0

Probable pathways of alkylation of ethanol with isopropanol are shown in Scheme 1, 2. Feeding alcohol conversions that are approximately equal may indicate the equable filling of the active surface with chemisorbed substrates and its equable activity. The total selectivity of alkylation products is shown to be 63.8-69.5%; the primary byproducts are diethyl ether (S=2.5-3.3%), butanol-1 (S=12.3-14.5%) and acetone (S=6.7-8.3%). Thus ethanol takes part in two parallel reactions: alkylation with isopropanol; and self-aldonyzation, leading to butanol-1 formation. In the reaction products, only traces of acetic aldehyde were found, indicating the equable activity of the substrates with regard to dehydrogenation with the formation of acetic aldehyde and acetone (Scheme 1). Acetic aldehyde and acetone exhibit markedly different activities: acetic aldehyde rapidly converts into butanol-1 or interacts with isopropanol with pentanol-2 formation, while acetone is less active and has a tendency to accumulate in the reaction products. The primary product of the interaction of ethanol and isopropanol is pentanol-2, whose selectivity reaches 30.6-41.1%. The selectivity of pentanone-2 is 13.1-16.5%, which indicates the low efficiency of steps 4 and 5α shown in Scheme 2. However, in the reaction products, there are no unsaturated alcohols or ketones (3,6α, 8b). Thus, the Au-Cu/Al$_2$O$_3$ catalyst shows the highest efficiency during the dehydrogenation and hydrogenation of unsaturated

C-C bonds steps. Based on Scheme 1, 2 and Table 2, pentanol-2 during interaction with acetic aldehyde primarily converts intoheptanone-4, followed by hydrogenation into heptanol-4. The primary byproduct of this step (4→8α) is heptanone-2, which undergoes hydrogenation into heptanol-2 (6b→7b) or interacts with acetic aldehyde molecule forming nonanone-4 and/or nonanol-4. Alcohols containing more than nine carbon atoms in its carbon skeleton were not observed among reaction products.
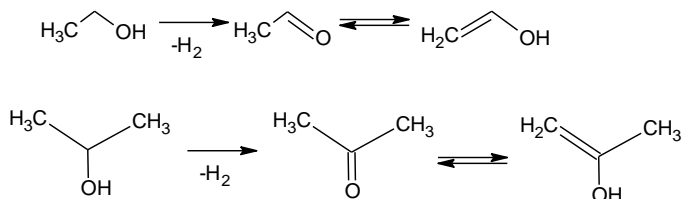
Scheme 1. Reagent activation
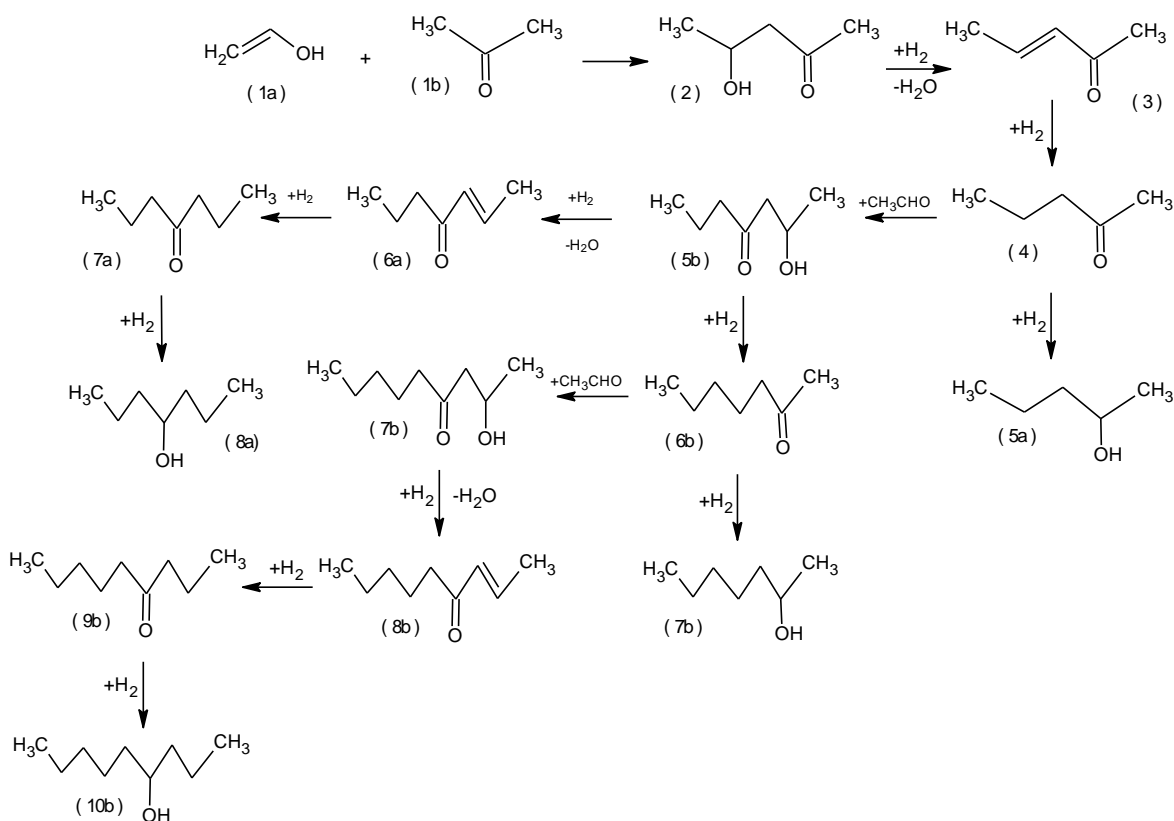
Scheme 2. Schematic presentation of the alkylation of ethanol with isopropanol

Should be noticed, that alkylation process was carried out under rather sever conditions (275°C, 150 atm, 5 h, batch mode). Supported metals in catalysts could interact with alcohols and/or be washed out from the surface of catalysts by organic media under these conditions. This process results in a decrease of the concentration of active components and deactivation of catalyst. To verify this hypothesis the concentration of Au and Ni after 50 h of time-on-stream was tested with atomic absorption spectroscopy and the results show metals concentration after 50 h on stream corresponds to the initial concentration of copper and gold with certainty instrument error. The TEM image of the $Au-Cu/Al_2O_3$, Au/Al_2O_3 and Cu/Al_2O_3 catalyst is presented in Fig. 1. For Au/Al_2O_3 a broad spherical particles size distribution with the mean size of 1-15 nm was observed. Cu/Al_2O_3 sample was characterized by spherical copper particles of 1-11 nm with the average size of 4 nm. The histogram of particle size distribution for $Au-Cu/Al_2O_3$ catalyst show the absence of particles with a size of 9 nm or more (Figure 1). The average particle size is 2.5 nm. The morphological features of impregnated particles in the $Au-Cu/Al_2O_3$ catalyst indicate that the presence of copper species prevents gold clusters from sintering. According to TEM-EDX analysis, about 80% of particles is presented as bimetallic composites

consisting of copper oxide particles and small gold particles. Au-Cu/Al$_2$O$_3$ catalyst contains about 71% of spherical and 29% of non-spherical bimetallic composites. The presence of non-spherical particles in the Au-Cu/Al$_2$O$_3$ catalyst may be caused by distortion of spherical gold clusters situated near Cu$_x$O$_y$ species upon sintering of gold during catalyst calcination.
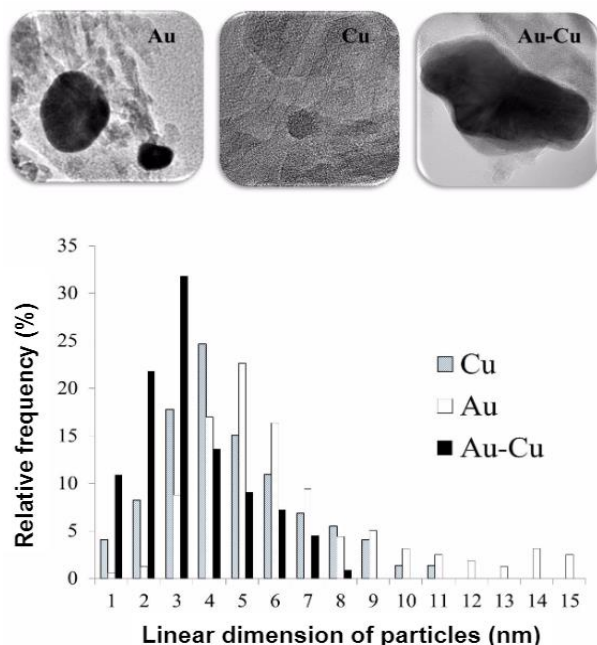

Figure 1. Size and shape of supported particles in Au/Al$_2$O$_3$, Cu/Al$_2$O$_3$ and Au-Cu/Al$_2$O$_3$ and particle size distribution for this catalysts

Au/Al$_2$O$_3$ comprises gold in the form of Au^0 (100 at.%) (Fig. 2). The electron binding energy of Au 4$f_{7/2}$ in the XPS spectrum of Au–Cu/Al$_2$O$_3$ is 84.4 eV. This result shows that, along with the originally zero-valent gold, Au($+n$) cations (0 < n < 1) are formed in Au–Cu/Al$_2$O$_3$. The Au($+n$) content is low—on the order of 10–20 at.%.
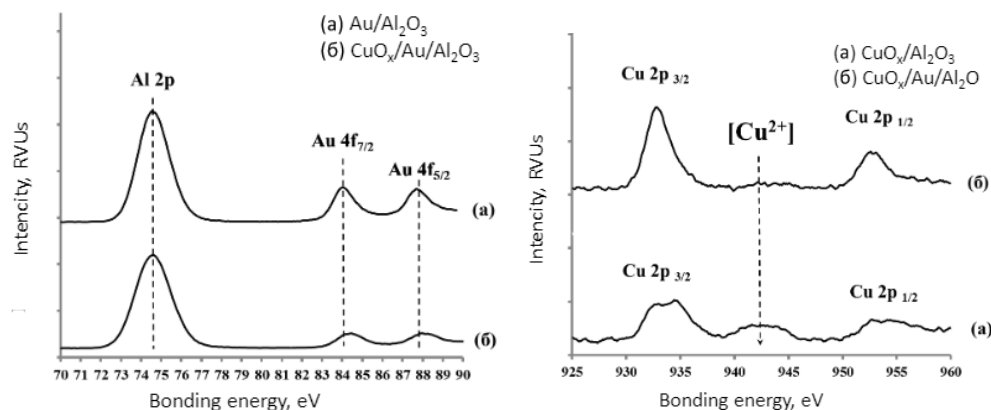

Figure 2. Al 2p, Au 4f and Cu 2p XPS spectra for mono- and bimetallic catalysts: Au/Al$_2$O$_3$, CuO$_x$/Au/Al$_2$O$_3$ and CuO$_x$/Al$_2$O$_3$.

In order to analyze the oxidation states of the supported metal species in the catalysts, XPS techniques was applied and the results are presented in Figs. 2. The Cu 2p spectrum of the Cu/Al$_2$O$_3$ catalyst exhibits a doublet of two spin orbit components: Cu 2p$_{3/2}$(932.5 eV) and Cu 2p$_{1/2}$ (952.6 eV). These binding energies can be attributed to Cu$_2$O and/or Cu^0 species (He, 2011). A peak at 944 eV was observed for the Cu/Al$_2$O$_3$ catalyst. This satellite is the unique feature of CuO spectrum and is absent in XPS spectra of Cu$_2$O and/or Cu^0 species (Biesinger, 2010). The precise quantification of Cu^0, Cu$^+$, and Cu^{2+} contents is a rather difficult task due to over-lapping of XPS signals from Cu^0, Cu$^+$, and Cu^{2+} electrons in the Cu 2$p_{3/2}$ and Cu 2p$_{1/2}$ regions.

Nevertheless, the $([Cu^0] + [Cu^+])/[Cu^{2+}]$ ratio can be roughly estimated. Biesinger et al. reported that the area of Cu^{2+} satellite is twice lower than the area of Cu $2p_{3/2}$ peak for the Cu^{2+} species (Biesinger, 2010). Bearing this in mind, the $([Cu^0] + [Cu^+])/[Cu^{2+}]$ ratio for the Cu/Al_2O_3 catalyst should be about 1/7. Cu 2p XPS spectra for bimetallic $Au-Cu/Al_2O_3$ catalyst contains peaks at 932.5, 944 and 952.6 eV. Analysis of these peaks intensities permits to estimate the $([Cu^0] + [Cu^+])/[Cu^{2+}]$ ratio for the $Au-Cu/Al_2O_3$ catalyst as 1/4.

4. Conclusions

This study shows that the $Au-Cu/Al_2O_3$ catalysts containing 0.2-0.5 wt.% of gold and 0.07-0.8 wt.% of copper are efficient systems for ethanol condensation into 1-butanol and 1-hexano. $Au-Cu/Al2O3$ systems were used for the heterogeneous catalysed alkylation of ethanol with isopropanol into pentanol-2. $Au-Cu/Al_2O_3$ produced the highest pentanol-2 selectivity of 30–41% at 275°C. The combined selectivity of alkylation products (i.e., alcohols and ketones C_5, C_7, C_9) was found to be 63%–70%. It has been found that the $Au–Cu/Al_2O_3$ 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 (Au^0/Al_2O_3 and Cu^{2+}/Al_2O_3). Contacts between copper and gold in the $Au–Cu/Al_2O_3$ 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 alcohols alkylation products.

Reference

Biesinger M.C., Lau L.W.M., Gerson A.R., Smart R. St.C., Appl. Surf. Sci., 257, 2010, 887–898.
Bond G.C., Sermon P.A., Gold Bull., 6, 1973, 102–105.
Bone W.A., Wheeler R.V., Phil. Trans. R. Soc. A, 206, 1906, 1–67.
Chistyakov A.V., Zharova P.A., Nikolaev S.A., Tsodikov M.V., Catalysis Today, 279, 2017, 124–132
Feng X., Duan X., Qian G., Zhou X., Chen D., Yuan W., J. Catal., 317, 2014, 99–104.
Gómez-Quero S., Cárdenas-Lizana F., Keane M.A., J. Catal., 303, 2013, 41–49.
Haruta M., Kobayashi T., Sano H., Yamada N., Chem. Lett., 16, 1987, 405–408.
He Z., Lin H., He P., Yuan Y., J. Catal. 277, 2011, 54–63.
Hutchings G.J., Edwards J.K., Front. Nanosci., 3, 2012, 249–293.
Jenck J.F., Agterberg F., Droescher M.J., Green Chem., 6, 2004, 544–556.
Jiang G., Pickering S.J., Lester E.H., Warrior N.A., Ind. Eng. Chem. Res., 49, 2010, 4535–4541.
Nikolaev S.A., Smirnov V.V., Vasil'kov A. Yu, Podshibikhin V.L., Kinet. Catal., 51, 2010, 375–379.
Nikolaev S.A., Chistyakov A.V., Chudakova M.V, .Kriventsov V.V., Yakimchuk E.P., Tsodikov M.V., J. Catal., 2013. V. 297. P. 296–305.
Ogo S., Onda A., Iwasa Y., Hara K., Fukuoka A., Yanagisawa K., J. Catal., 296, 2012, 24–30.
Ordónez S., Dhaz E., Leyn M., Faba L., Catal. Today, 167, 2011, 71–76.
Riittonen T., Eranen K., Maki-Arvela P., Shchukarev A., Rautio A.-R., Kordas K., Kumar N., Salmi T., Mikkola J.-P., Renew. Energ., 74, 2015, 369–378.
Simakova I.L., Solkina S. Yu., Moroz B.L., Simakova O.A., Reshetnikov S.I., Prosvirin I.P., Bukhtiyarov V.I., Parmon V.N., Murzin D. Yu., Appl. Catal. A, 385, 2010, 136–143.
Shimura K., Kon K., Siddiki S.M.A.H., Shimizu Ken-ichi, Appl. Catal. A: Gen., 462–463, 2013, 137–142.
Sreekumar S., Baer Z.C., Gross E., Padmanaban S., Goulas K., Gunbas G., Alayoglu S., Blanch H.W., Clark D.S., Toste F.D., ChemSusChem, 7, 2014, 2445–2448.
Sun J., Wang Y., ACS Catal., 2014, Vol. 4, №. 4, 1078-1090.
Tabakova T., Ilieva L., Ivanov I., Zanella R., Sobczak J.W., Lisowski W., Kaszkur Z., Andreeva D., Appl. Catal. B: Environ., 136–137, 2013, 70–80.
Torres G., Apesteguia C.R., Cosimo J.I.D., Appl. Catal. A, 317, 2007, 161–170.
Tsuchida T., Sakuma Sh., Takeguchi T., Ueda W., Ind. Eng. Chem. Res., 45, 2006, 8634–8642.
Yolles R.S., Wood B.J., Wise H., J. Catal., 21, 1971, 66–69.
Wang D., Guo X.-Q., Wang Ch.-X., Wang Ya-N., Zhong R., Zhu X.-H., Cai L.-H., Gao Z.-W., Hou X.-F., Adv. Synth. Catal., 355, 2013, 1117–1125.
Zharova P.A., Chistyakov A.V., Tsodikov M.V., Nikolaev S.A., Corbetta M., Manenti F., Chemical Engineering Transaction, 50, 2016, 295-300.