Effect of the composition of ZnO(Cu,Ag)/MgO(ZrO_2)-SiO_2 nanostructured systems on their catalytic properties in the ethanol-to-butadiene process

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INTRODUCTION 1,3-butadiene is one of the most important conjugated dienes and mainly used as an intermediate for synthesis of rubber, elastomers and polymer resins. Analysis of economic and environmental aspects of realization of ethanol (EtOH) or bioethanol conversion into 1,3-butadiene indicates that ethanol-to-butadiene (ETB) process is perspective for industry. A rather important problem in the development of catalysts for ETB process lies in the achieving of high activity and selectivity in the conversion of EtOH-aqueous mixtures. The development of the catalysts able to convert 50-80 vol% ethanol into 1,3-butadiene will provide some flexibility to the ETB-process. Moreover, two molecules of H_2O are formed with a single molecule of 1,3-butadiene in ETB process in accordance with the brutto-equation: $2\ C_2H_5OH \rightarrow C_4H_6 + H_2 + 2\ H_2O$ [1].

RESULTS AND DISCUSSION Three-component oxide samples of ZnO/MgO–SiO_2 with various MgO:SiO_2 ratios (1:3, 1:1, 3:1), also ZnO/MgO and ZnO/SiO_2 were characterized as catalysts for the conversion of aqueous ethanol into 1,3-butadiene (**Fig. 1**). The ZnO/MgO is characterized by the highest basicity; the number of medium and strong base sites of ZnO/MgO-SiO_2 system decreases as the MgO content decreases (**Fig. 2**). On the surface of two- and three-component catalytic systems there are Lewis acid sites of various nature: [Zn^{2+}-O-Si], [Mg^{2+}-O-Si]. Based on the OPTPD data of CO_2 and NH_3 after the probe molecule adsorption on the hydrated catalyst surface, it is qualitatively shown that the water adsorption leads to a change in the acid-base characteristics of the surface.

To evaluate water vapor effect on functional properties of the catalyst, water vapor adsorption/desorption over the surface, temperature programmed surface reaction of ethanol and isopropanol conversion reaction in the absence/presence of water vapor in the feed were performed. The results obtained indicate that the hydrophilicity of ZnO/MgO-SiO_2 is determined by the MgO:SiO_2 ratio, and the chemisorption of water occurs preferably on Mg-containing sites with the formation of Brönsted base sites. The presence of water in the initial reaction mixture leads to a decrease in the formation of C-C coupling products, probably due to the adsorption of H_2Oon active sites of aldol condensation of acetaldehyde. The hydrated sites formed in the interface of magnesia and silica remain active in C-C coupling reaction even in the presence of water in the reaction mixture. The selectivity of 1,3-butadiene formation > 60% is achieved in the conversion of ethanol-water mixture (80 vol% ethanol) in the presence of ZnO/MgO-SiO_2 catalysts with the ratio of MgO:SiO_2 = (1:1) and (3:1) [2].

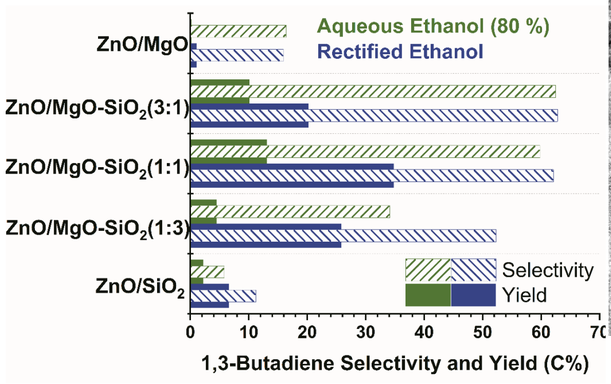
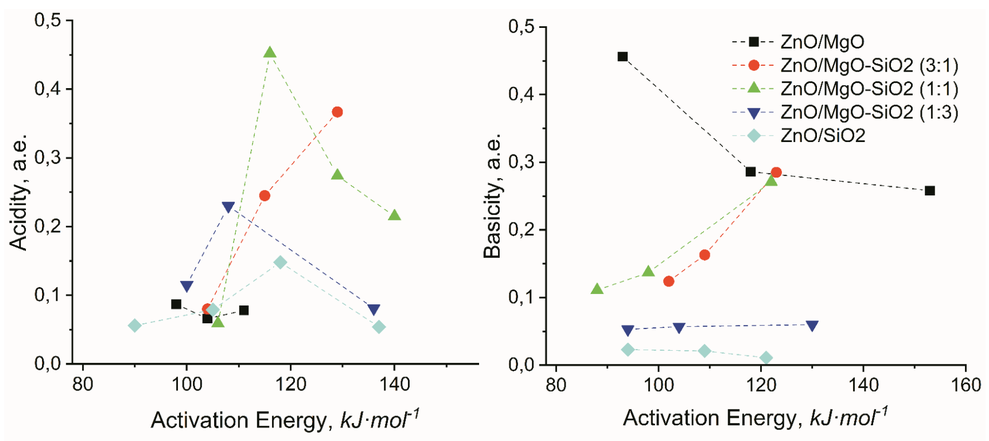


Figure 1. The selectivity and yields of 1,3-butadiene in the conversion of 96 and 80 vol% ethanol over ZnO/MgO-SiO_2 catalysts. Reaction conditions: WHSV = 1 $g_{EtOH}{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$, 648 K, time-on-stream = 1-5 h.

Figure 2. Acid-base characteristics of ZnO/MgO-SiO_2 samples investigated by one-pass temperature-programmed desorption of NH_3 and CO_2.



ZnLaZrSi oxide systems prepared with a silica (KSKG, A-175, A-380, SBA-15, MCM-41, MCM-48, MCF, dealuminated BEA zeolites) component of the different nature have been studied in 1,3-butadiene production from aqueous ethanol. The characteristics of the porous structure of the silica support, such as porosity, pore size distribution, specific and external surface areas, were found not to be critical parameters for achieving a high 1,3-butadiene yield during the EtOH-H_2O mixture conversion in the presence of ZnLaZrSi oxide catalysts. On the contrary, the quantity and strength of Lewis acid sites, which in turn differ depending on the choice of silica material, have a significant impact on 1,3-butadiene selectivity and yield. The highest values of the selectivity of 1,3-butadiene formation (up to 68 %) and yield as well as stability toward deactivation in the presence of H_2O were achieved over ZnLaZr–KSKG, ZnLaZr–SBA-15 and ZnLa–ZrSiBEA (dealuminated BEA zeoliteswith mononuclear isolated tetrahedral Zr(IV) species) [5].

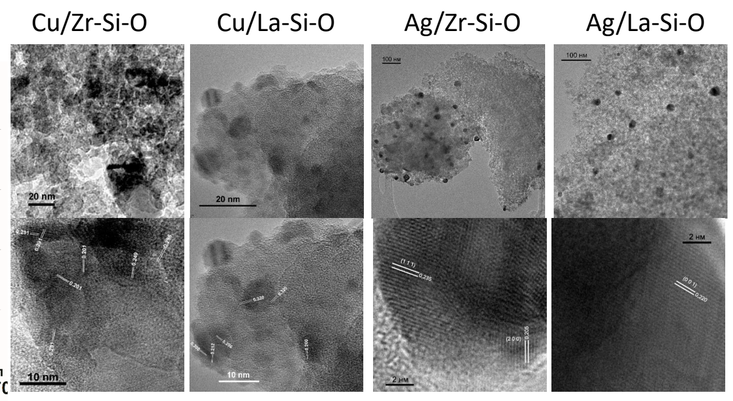
CONCLUSION The different nanostructured systems ZnO/MgO(ZrO_2)-SiO_2, included modified with Cu, Ag, La, have been studded in the ETB-process. The method of catalyst preparation significantly affects its dehydrogenation and acid–base characteristics. It has been shown that Lewis acid sites formed in the contact zones of catalyst components (MgO/SiO_2, ZrO_2/SiO_2, ZnO/SiO_2) play an important role in 1,3-butadiene synthesis from ethanol. The selection of a modifying additive is important to increase the dehydrogenation capacity of the catalyst. The dopant affects not only the redox properties of the catalytic system, but also the acid–base characteristics. Optimization of the number and strength of dehydrogenation sites and aldol condensation sites on the catalyst surface led to achieve a high yield of 1,3-butadiene.

Table 1. The indices of aqueous ethanol (80 vol.% EtOH) conversion into 1,3-butadiene in the presence of (Cu,Ag)/MgO-SiO_2 catalysts

Catalysts	T, K	Ethanol conversion, %	Product yield, C % (WHSV = 1 $g_{EtOH}{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$; TOS = 1-5 h)					
			1,3-Butadiene	Acetaldehyde	Ethylene	DEE	Butenes	Others
MgO-SiO_2	648	6.0	1.6	1.0	2.4	1.0	-	-
	673	16.0	4.8	1.4	7.1	2.2	0.2	0.2
	698	30.0	9.2	1.7	14.7	3.6	0.3	0.6
Cu/MgO-SiO_2	648	28.5	16.0	4.1	5.6	0.7	1.7	0.4
	673	40.0	21.2	3.6	11.2	1.0	2.6	0.4
	698	57.5	28.2	3.5	20.1	0.9	4.3	0.6
Ag/MgO-SiO_2	648	27.0	16.6	4.7	3.8	0.5	0.9	0.4
	673	39.0	22.8	5.1	7.8	0.8	2.0	0.6
	698	57.0	30.2	4.0	17.1	0.9	3.7	1.1

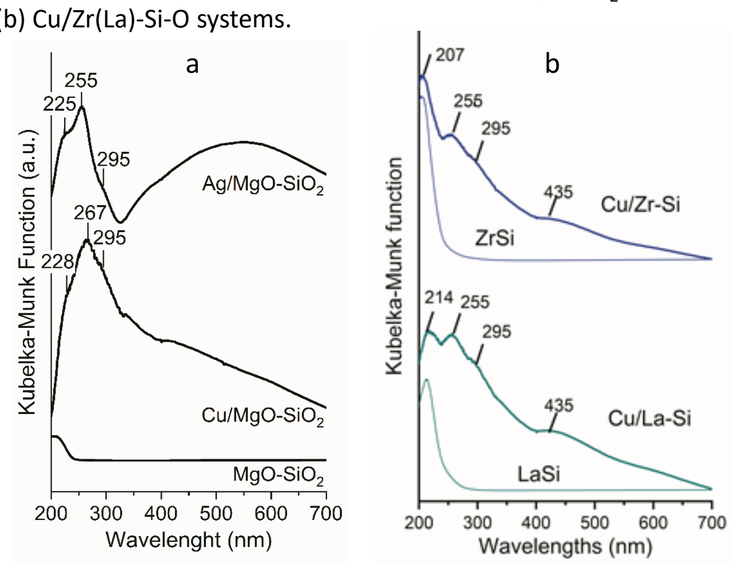
The modification of MgO-SiO_2 with copper and silver contributes to a significant increase in 1,3-butadiene yield, as well as the yields of ethylene, butenes and residual intermediate product, acetaldehyde (**Table 1**). This is caused by the formation of active sites for ethanol dehydrogenation and [Mg-O-Cu(Ag)] (**Fig. 3-a**) acid-base sites for the reactions of aldol-croton condensation of acetaldehyde with the formation of 1,3-butadiene and butenes, as well as ethanol dehydration [3].

Figure 3. HR-TEM images of studied catalysts.



HR-TEM and DR UV-Vis measurements, on the surface of Cu(Ag)/Mg(Zr,La)-Si-O metal-oxide systems copper and silver are concluded to be present in metallic and oxidized states like cations or subnanoclusters (**Fig. 3, 4**) [3, 4].

Figure 4. DR UV-vis spectra of studied samples recorded (after catalysis of ETB-process): (a) Cu(Ag)/MgO-SiO_2 systems; (b) Cu/Zr(La)-Si-O systems.



Three and four-component Cu(Ag)/Zr(La)-Si-O oxide systems are prepared and their acid-base characteristics and catalytic properties in aqueous ethanol conversion into 1,3-butadiene are studied (**Table 2**). In the catalyst, acid sites are shown to be preferentially formed with the participation of zirconium, and basic sites to be formed with the participation of lanthanum. The Cu/Zr-La-Si catalysts are characterized by high (≥65%) 1,3-butadiene selectivity during the conversion of both rectified and aqueous ethanol. Herewith, the catalyst activity depends on introduction order of the components, which is due to the difference in acid-base characteristics of the surface. According to NAP-XPS results, the positive effect of lanthanum addition into Cu/Zr-Si catalyst can be explained by the formation of lanthanum-containing base sites like [La–Ö–Si] and [La–Ö–H] being tolerant to the action of water. Therefore, a modification of the ETB-process catalysts with lanthanum increases their activity in aqueous ethanol conversion into 1,3-butadiene.

The differences in the mechanism of interaction of reaction intermediates with surface Zr- and La-containig sites were found out by C 1s NAP-XPS measurements, and the effect of H_2O on adsorption of carbon coke, ethoxy and MeCHO species over the catalyst surface was shown.

Table 2. Catalytic performance of the catalysts during aqueous ethanol (80 vol%) conversion (T = 598 K, WHSV = 0.42 $g_{EtOH}{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$, time-on-stream = 1-5 h.)

Catalysts	Ethanol conversion, %	Product Selectivity, C %			Product yield, C %
		1,3-Butadiene	Acetaldehyde	Ethylene+DEE	
Cu/Zr-Si-O	40.8	58.9	12.1	23.4	24.0
Cu/La-Si-O	33.4	47.0	14.3	29.9	15.7
Cu/Zr-La-Si-O	35.2	65.0	14.7	15.5	22.8
Ag/Zr-Si-O	50.0	48.0	9.0	38.0	24.0
Ag/La-Si-O	4.0	38.0	47.0	14.0	1.5

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