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Ethanol Dehydrogenation on Copper Catalysts with Ytterbium Stabilized Tetragonal ZrO₂ Support

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Abstracts—The physicochemical and catalytic properties of Cu-containing crystalline zirconia, obtained via sol–gel synthesis in the presence of Yb³⁺ ions and polyvinylpyrrolidone, are studied. DTG/DSC, TEM, XRD and BET methods are used to analyze the crystallization, texture, phase uniformity, surface and porosity of ZrO₂ nanopowders. It is shown that increasing the copper content (1, 3, and 5 wt % from ZrO₂) raises the dehydrogenation activity in the temperature range of 100–400°C and lowers the activation energy of acetaldehyde formation. It is found that the activity of all Cu/t-ZrO₂ catalysts grows under the effects of the reaction medium, due to the migration and redispersion of copper.

Keywords: bioethanol, alcohol dehydrogenation, oxide catalysts, zirconia, copper-containing catalysts **DOI:** 10.1134/S0036024416120074

INTRODUCTION

Due to the continuing development of the hydrogen industry, the possibility of using biofuels (such as bioethanol) as stable and cost-effective sources of hydrogen was considered in [1, 2]. The production of bioethanol as a renewable, environmentally friendly and widely available natural resource is growing steadily. Catalytic conversion of an ethanol-water mixture at different temperatures proceeds via different mechanisms and gives a variety of products. Of great interest nowadays is studying methods of the catalytic steam reforming of ethanol to produce hydrogen-rich gas mixtures. One possible way of processing biofuels is the dehydrogenation of ethanol to acetaldehyde, which is an intermediate for the production of hydrogen with slight carbonization. This reaction is reversible and occurs at low temperatures [3-5]. Another possibility for the efficient conversion of ethanol is its conversion on acid catalysts to light olefins, which are used as a precursors for the production of chemicals and polymers [6, 7]. Acetaldehyde subsequently undergoes steam reforming to form mixtures of H_2 and CO [8, 9]. The preferred paths of ethanol conversion are mainly observed on supported catalysts, facilitating the adsorption of ethanol and its subsequent dehydrogenation. Developing efficient and stable catalysts for these processes is an important task.

Zirconia is currently attracting considerable interest as a support in a variety of catalytic processes [10– 13]. In addition to its established properties of strength, heat resistance, and radiation stability, the advantage of its use in catalysis is apparent in the interaction between the active phase and support (which affects the catalytic activity and selectivity), and in its high chemical inertness, compared to other known supports (Al_2O_3 , SiO_2) [14]. The surface of zirconia is characterized by a wide range of adsorption sites of different natures, and the ratio between these can change, depending on the conditions of sample preparation and pre-treatment [15].

The aim of this work was to synthesize and study the activity of copper catalysts, prepared from zirconia hydrogel containing structure-forming polymer and ytterbium to stabilize the t-ZrO₂ phase, in the vapor phase dehydrogenation of ethanol.

EXPERIMENTAL

Sample Preparation

Precursors of ZrO_2 powders were prepared from reagent grade $ZrOCl_2$ and $Yb(NO_3)_3$ using the sol-gel method. A diluted 25% NH₄OH solution (GOST 24147-80; KhimMed, analytical grade) was used as the precipitating agent. To regulate the structure of the powders, polyvinylpyrrolidone (PVP) (average molecular weight, 12000 g/mol, determined by viscometry) was introduced into the samples. PVP as an aqueous solution with a concentration of 0.1% was dissolved in the precipitant NH₃ × H₂O. The PVP content was 0.05 and 0.15 wt % by weight of the ZrO₂ final product. Next, a mixture of 1 M solutions of zir-



Fig. 1. Micrographs of ZrO₂ xerogel samples (a) without and (b) with structure-forming additive 0.05% PVP.

conium oxychloride and ytterbium nitrate was added (reverse synthesis) under continuous stirring into the precipitant with PVP and maintaining pH 9–10. The duration of liogel synthesis was 2 h at room temperature. The liogel was dried at 180° C for 2 h and then heat-treated at 500° C.

Sol-gel conditions of ZrO_2 synthesis were consistent with the stoichiometry of the hydrolysis-condensation reaction $ZrOCl_2 + 2NH_4OH = ZrO_2\downarrow + 2NH_4Cl + H_2O$.

The resulting hydroxide gel precipitate was washed with distilled water to remove NH_4^+ and Cl^- ions, dried with ethanol, and then heat-treated at 180°C for 2 h. The precipitate was then ground. The target product was a powder of zirconia $ZrO(OH_2)$ (xerogel) that contained ytterbium cations.

The crystal structure of zirconia forms at calcination temperatures of 500°C or higher. The final calcination temperature was 950°C.

Synthesized amorphous ZrO_2 containing 0.05 wt % PVP and crystalline ZrO₂ were characterized by means of DTG/DSC, XRD, TEM, and BET, and used in the preparation of Cu/ZrO₂ samples. The support was treated with a copper chloride solution with a concentration calculated to obtain copper contents of 1, 3, and 5 wt % by weight of ZrO_2 . For the deposition of copper, the ZrO₂ was held in the precursor solution in (CuCl₂ \cdot 2H₂O reagent grade) for 24 h at 25°C, dried at 60°C and subjected to heat treatment at 400°C for 3 h. Samples of CuCl₂/ZrO₂ were reduced in a hydrogen stream for 1 h at 300°C directly in the catalytic setup.

Physicochemical Characteristics of the Samples

The precipitated products were investigated via differential thermal analysis on a Netzsch STA 409 PC/PG unit equipped with an Aeolos mass spectroscopic analyzer (Germany) and specialized software. The process was conducted in air. The initial temperature was room temperature, the heating rate was 10-15 K/min, and the final temperature was 950° C.

The phase compositions of the samples were measured on an XRD-6000 diffractometer (Shimadzu) using Cu K_{α} radiation ($\lambda = 1.54$ Å) in the range of angles $2\theta = 22^{\circ}-56^{\circ}$ with a scanning step of 0.02°. The phases were identified using the international standards data bank (JCPDS). Exposure was ~1 s at each point. The average size of the powder particles' coherent scattering regions (CSRs) was calculated according to the formula

$$D=\frac{\lambda}{\beta\cos\theta},$$

where λ is the X-ray wavelength; β is the physical broadening, rad; and θ is the angle of X-rays reflection, degrees.

Low-temperature Brunauer–Emmett–Teller (BET) adsorption–desorption was used to measure the specific surfaces of the powders on a TriStar-3000 unit (Micromeritics, United States). The dependences of the pore volume distribution on their diameter in the mesopore region were obtained.

The distribution of the agglomerates in the synthesized powders was obtained using an Analisette-22 laser analyzer. The lower detection limit was 0.01 μ m.

Catalytic Experiments

A flow setup equipped with a Crystal Chromatec 5000 gas chromatograph (carrier gas, helium; separation column, Porapak-Q phase at a temperature of 125°C; detector, FID) was used to test catalytic properties. Alcohol vapor in a helium flow (rate, $1.2 \text{ L} \text{ h}^{-1}$) was fed from a bubbler into a glass reactor containing catalyst powder, a thin layer of which was distributed on wide-pore filter to avoid diffusion limitations. Before each experiment, the sample was heated in a helium flow at 400°C for 40 min. The catalytic exper-



Fig. 2. Differential scanning calorimetry: ZrO₂ precursor gel prepared (1) without and (2) with polyvinylpyrrolidone.



Fig. 3. Fragments of diffractograms of ytterbia-stabilized zirconia powders obtained at a temperatures of (a) 450 and (b) 950° C: F is (a) a solid solution with pseudocubic structure and (b) a solid solution with tetragonal structure.

iments were performed with gradual increase of the temperature in the range from 250 to 400°C, under the condition that a steady state was achieved at each temperature.

RESULTS AND DISCUSSION

Figure 1 shows photomicrographs of the xerogel samples of zirconia prepared with and without PVP. It can be seen that the powders have a hierarchical structure. Particles (~15%) with sizes of up to 100 μ m were found in the powder without the polymer additive, while smaller agglomerates about 3 μ m in diameter predominated in the samples with PVP.

BET dispersion analysis showed that the specific surface of ZrO_2 xerogels was $S_{sp} = 77 \text{ m}^2/\text{g}$ without PVP and ~200 m²/g with PVP. The average particle

diameter of the gel was reduced from 14 to 4-5 nm, so samples with PVP had micropores with diameters of 5 nm (total volume, 19 m³/g) that were not present in the samples without PVP. After crystallization, the specific surface area of the ZrO₂ + PVP particles was reduced to ~20 m²/g.

Using the results from the differential scanning calorimetry (DSC) of xerogel samples of zirconium oxides with different contents of PVP, it was found that the crystallization of amorphous zirconium oxide starts at 480°C (the location of the dominant exopeak, Fig. 2), which agrees with the literature data [16, 17]. In the temperature range of 0 to 250°C, there is a broad endothermic effect in the DSC curve that corresponds to the removal of adsorbed and bound water.

When the temperature was raised to 950°C, the development of zirconia crystalline structure was



Fig. 4. Micrographs of the sample and the particle size distribution of 5% Cu/ZrO₂ (a) before and (b) after catalysis.

observed and the samples' crystallinity grew. Introducing different amounts of PVP did not alter the diffraction patterns the ZrO_2 samples (Figs. 3a, 3b). The diffraction data (reflection angles, intensity and width at the half maximum of X-ray reflections) are given in Table 1.

The effect the concentration of polymer introduced at the synthesis stage (in this case PVP) had on the catalytic activity of the ceramic (calcined) zirconium oxide in the conversion of ethanol was studied.

2θ, deg	β	d, nm	Phase	2θ, deg	β	d, nm	Phase	
ZrC	Samj D ₂ with	ple 1: 0.05% I	PVP	Sample 2: ZrO ₂ with 0.15% PVP				
30.3	5	2.9	t	30.3	5	2.9	t	
34.6	6	2.4	t	34.6	5	2.9	t	
35.2	5	2.9	т	35.2	7.5	1.9	т	

Table 1. Zirconia diffraction data

On ZrO_2 , the dehydrogenation reaction proceeded with the formation of acetaldehyde. The maximum conversion of alcohol did not exceed 10%. Raising the concentration of PVP from 0.05 to 0.15% did not affect the activity of the zirconia in ethanol conversion. All samples were stable; the samples' activity did not change in the presence of the reaction medium. Note that dehydration reaction with the formation of ethylene also occurred on these samples, the conversion of ethanol by this way was less than 5%.

Figure 4 shows micrographs of 5% Cu/ZrO₂, obtained with a scanning electron microscope before and after catalysis. It can be seen that the particle size was 10 μ m and, compared to xerogel ZrO₂, the texture of the particles changed during the preparation of the copper-containing sample (the surface layer become less dense). Aggregation of the catalyst particles, and thus a reduction in specific surface area, was observed after catalysis.

On all copper-containing catalysts, the dehydrogenation reaction formed only acetaldehyde. The temperature dependences of the conversion of ethanol to

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Fig. 5. Temperature dependence of the conversion of ethanol to acetaldehyde at W% Cu/ZrO_2 , with different contents of copper in the (1) first and (2) repeated experiments.

acetaldehyde are shown in Fig. 5. The dehydrogenation reaction begins on the initial surface at $T = 250^{\circ}$ C. In the temperature range of $250-300^{\circ}$ C, the activity of the copper-containing sample remained unchanged and did not exceed 5%. The sample with the minimum copper content showed the highest activity in the temperature range of $300-360^{\circ}$ C, and its activity decreased. The maximum conversion of alcohol to acetaldehyde was observed on the sample with the maximum content of Cu (5%) at $T > 360^{\circ}$ C, and it reached 50% at 400°C. In a repeated experiment, the reaction occurred at a lower temperature: at T =

Table 2. Conversion of ethanol to acetaldehyde W, % on Cu/ZrO₂ catalysts at temperatures of 300 and 380°C: experimental activation energies of dehydrogenation E_a and logarithms of pre-exponential factor $\ln N_0$: (1) initial activity, (2) repeated experiment

No.	Cu, wt %	$W_{300}, \%$		W ₃₈₀ , %		$E_{\rm a}$, kJ/mol		$\ln N_0$	
		1	2	1	2	1	2	1	2
1	0	1	1	8	8	57	57	-5.1	-5.1
2	1	7	28	35	32	90	220	2.5	32.8
3	3	8	40	40	47	90	114	1.9	8.8
4	5	7	27	43	56	87	94	2.2	4.7
5	5*	_	—	17	58	76	134	-0.9	13.5
	C_2H_4			16	2	84	54	0.2	-7.8

 300° C, the conversion of ethanol to aldehyde was 30% on all samples. As in the experiment on the initial surface, however, the activity of the samples with 1 and 3% Cu decreased to 30% in the repeated test, starting at 340° C. As on the initial surface, the conversion of ethanol to acetaldehyde in the sample with 5% Cu, grew throughout the investigated range of temperatures in the repeated experiment. The catalytic properties of all of the studied samples are shown in Table 2.

Table 2 shows that during the preparation of copper-containing catalysts, dehydrogenation centers similar in nature form on the initial surface ($E_a \approx$ 90 kJ/mol), and the number of these centers is the same although the samples are of different compositions (close values of ln $N_0 \approx$ 2). Under the effect of the reaction medium (in the repeated experiments), new centers different in nature and quantity formed on the surface. With the growth of the copper content in the sample, the experimental activation energy of dehydrogenation falls linearly (Fig. 6), due to the formation of new centers on the samples with high contents of deposited copper.

To determine the effect preliminary reduction treatment had on copper-containing samples, we investigated the catalytic activity of the sample with a copper content of 5% that was not subjected to preliminary reduction (sample 5*). It was found that its activity was 2-3 times lower than that of preliminarily reduced samples. There was, however, considerable



Fig. 6. Effect of copper content in a sample on the characteristics of the catalytic activity in repeated experiments: E_a is the dehydrogenation activation energy (kJ/mol), W is the conversion of ethanol at $T = 380^{\circ}$ C (%), and $\ln N_0$ is the logarithm of the pre-exponential factor.

autoactivation during catalysis, due to the reduction of copper ions by reactive hydrogen, which is more efficient than molecular hydrogen (Fig. 7). Along with dehydrogenation, dehydration reaction with the ethylene formation occurred on this sample. On the initial surface, the conversion of alcohol to ethylene reached 16% at 380°C, and the selectivity toward dehydration at $T = 380^{\circ}$ C was 50%. In repeated experiments, the yield of ethylene did not exceed 2% of the total alcohol conversion. Copper ions deposited on

the surface of zirconia thus act as centers of both dehydration and dehydrogenation (the values of E_a for dehydration and dehydrogenation are similar: 84 and 76 kJ/mol, respectively). During the reaction, however, Cu²⁺ ions are partially/fully reduced, leading to the almost complete deactivation of the dehydration centers and a rise in the number of dehydrogenation centers (a rise in $\ln N_0$).

The nature of the dehydrogenation centers on the sample not reduced differed from those on the sample after preliminary reduction: the activation energy and number of dehydrogenation centers for sample 5* are lower than those of preliminarily reduced sample 5. The activation of the unreduced copper sample under the effect of the reaction medium was due to the formation of a large number of catalytic active sites (a rise in the exponential factor) with weaker bonding of the alcohol to the surface.

CONCLUSIONS

The deposition of copper on tetragonal zirconia allows us to improve its activity by 100–400%, and to alter the selectivity of the conversion of ethanol, depending on the pretreatment conditions. On reduced copper-containing Cu/ZrO₂ samples, only acetaldehyde is formed in the alcohol dehydrogenation reaction, while two products are formed on unreduced Cu²⁺/ZrO₂ samples: olefin and aldehyde. Close E_a values for Cu/ZrO₂ copper samples with different contents of copper, obtained for the initial surface of the catalysts, testify to the similar nature of the active sites that form during reduction treatment. During a catalytic reaction, the nature of the centers in samples



Fig. 7. Temperature dependence of the conversion of ethanol to aldehyde and olefin on unreduced Cu^{2+}/ZrO_2 on (1) the initial surface and (2) in the repeated experiment.

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with lower concentrations of copper changes, and the number of these centers grows.

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