

Catalytic Performance of CuO/ZnAl₂O₄-Al₂O₃ Catalysts in *n*-Hexanol Conversion

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A series of CuO/ZnAl₂O₄-Al₂O₃ catalysts with various CuO loading were prepared by an impregnation method. The effect of copper oxide addition for the reaction of *n*-hexanol was examined. The reactions were carried out at atmospheric pressure in a fixed bed reactor in the temperature range of 533–663 K. Experimental data show that the addition of copper oxide into studied catalysts does improve the activity in dehydrogenation of alcohol. Catalysts containing CuO have both dehydration and dehydrogenation properties, whereas ZnAl₂O₄-Al₂O₃ carrier only dehydrates alcohol. Obtained results indicate that the dehydrogenation of *n*-hexanol over CuO/ZnAl₂O₄-Al₂O₃ catalysts proceeds *via* carboxy intermediate.

Key words: hydrothermal synthesis, CuO/ZnAl₂O₄-Al₂O₃, *n*-hexanol, dehydration, dehydrogenation

The dehydration and dehydrogenation of alcohols over catalysts have been studied by many investigators. Some of catalysts particularly tend to promote dehydration, whereas others have mainly dehydrogenating effects. The selectivity for alcohol dehydration has long been used as a probe of the acid-base properties of catalysts surface. Dehydration of alcohols to olefins or ethers can be effected by most solid acid catalysts [1–3]. There was found that in the presence of catalysts with basic properties aliphatic alcohols of *n* carbon atoms can be readily converted to the esters of 2*n* carbon atoms and to symmetrical ketones of 2*n*-1 carbon atoms by vapor-phase contact. The ketonization of primary alcohols was studied in the presence of many metal oxides. The work of Komarewsky and Coley [4] indicated that over chromia *n*-hexanol underwent a reaction of dehydrogenation-condensation of two molecules of alcohol to form a symmetrical ketone and also direct dehydrocyclization took place with the formation of small amounts of phenols. Iron carbide and oxide catalysts dehydrogenate primary alcohol (C_{*n*}) to an aldehyde, which undergoes a secondary ketonization reaction to produce a symmetrical ketone [5]. Condensation of alcohols in the presen-

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ce of Fe-Si-Cr-K-O catalyst makes it possible to obtain ketones with a good yield [6,7]. They are also many other catalytic systems efficient in oxidative condensation of primary alcohols to esters and/or ketones, for example $\text{CeO}_2\text{-Fe}_2\text{O}_3$ [8], Sn-Ce-Rh-O [9], ZnO doped with alkali ions [10], CeO_2/MgO [11] *etc.*

Copper catalysts play a very important role in heterogeneous catalysis. They are widely used to produce linear or branched alcohols from synthesis gas. Cu/ZnO/ Al_2O_3 catalysts selectively form methanol from CO/ CO_2/H_2 mixtures at low pressure [12,13], and ketones in the presence of CO [14]. They are active also in the CO shift reaction [15], in the *ortho*-alkylation of phenols with alcohols [16]. Copper catalysts are very selective in isoamyl alcohol [17] and cyclohexanol [18] dehydrogenation.

Recently the growing interest in zinc aluminate applications as catalyst or a catalyst carrier has been observed. ZnAl_2O_4 is known to be active in the synthesis of methanol and selective reduction of NO_x , especially with copper addition [12,19,20]. It is active in dehydrogenation of alkanes [21], isomerization of cyclohexene [22], synthesis of indenenes and styrenes [23], production of esters from vegetables or animal oils and aliphatic alcohols [24] and in the alkylation of phenol with alcohols [25,26] and also in transformations of alcohols [27]. Zinc aluminate spinel is also a promising carrier for catalysts, such as Pt [28,29], Pt-Sn [30], Pt-Sn-Ga [31] (dehydrogenation processes [28,30,31] and high temperature combustion of *iso*-butene [29]) and Cu [12] (low-pressure synthesis of methanol). Zinc aluminate spinel or $\text{ZnAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ system can be obtained depending on hydrothermal synthesis conditions and reagents used. ZnAl_2O_4 is mainly active in dehydrogenation of alcohols, because of its basic properties, whereas $\text{ZnAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ system containing more acidic centers is active in dehydration.

The aim of presented work was to examine the influence of small amount of CuO (selective in dehydrogenation of alcohols [32–36]) on catalytic behavior of $\text{ZnAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ in reactions of *n*-hexanol transformations. It was interesting to know if CuO addition can generate a bifunctional catalyst with dehydration-dehydrogenation properties.

EXPERIMENTAL

Preparation of catalysts: The carrier used for this study was prepared as follows: Basic aluminium nitrate having the empirical formula $\text{Al}_2(\text{OH})_{6-x}(\text{NO}_3)_x$, wherein *x* was close to 1, was used as aluminium precursor for the hydrothermal preparation of carrier. Basic aluminium nitrate was obtained by digesting powdered aluminium metal in water solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 348 K for several days. Synthesis mixture was prepared by the controlled addition of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ to a water solution of the basic aluminium nitrate, wherein the molar ratio of Al:Zn was close 3:1. The obtained mixture was heated at 433 K in an autoclave with a constant rotation under pressure of 0.1 MPa for 3 h. After cooling the autoclave to room temperature, the prepared product was several times water washed and condensed following evaporation at the elevated temperature. The material obtained in this way was dried at 413 K, and finally calcined at 873 K for 4 h. The resulting carrier was crushed into particles of 0.6–1.2 mm in size.

Supported catalysts were prepared by wet impregnation method with Cu(NO₃)₂·3H₂O aqueous solution at room temperature. The CuO content (wt.%) was based on the concentration of Cu ions in the processing solution. After impregnation the catalysts were dried in air, first at room temperature (24 h) and next at 383 K for 8 h. All the catalysts were calcined by heating to 873 K and holding for 4 h at the final temperature before the reaction. The prepared catalysts contained finally 1, 3 and 5% of CuO.

Characterization of catalysts: The phase composition of carrier and CuO/ZnAl₂O₄-Al₂O₃ catalysts were determined using XRD method. The XRD was carried out using CuK_α (Ni-filtered) radiation on a DRON-3 powder diffractometer.

The specific surface area and porosity of samples (after calcination at 873 K) were measured from the corresponding nitrogen adsorption-desorption isotherms obtained at the temperature of liquid-nitrogen by BET equation by a standard volumetric procedure, using the Sorptomatic 1900 apparatus. The pore size distribution was analyzed following the Dollimore-Heal method [37].

The concentration of the Lewis and Brönsted acid centers on the carrier surface was measured by means of IR spectroscopy using pyridine as a test molecule. Acidity type and acidity strength distribution of the investigated material was evaluated by the temperature-programmed desorption of ammonia (NH₃ TPD) method. The procedures applied for measurements of acidity of ZnAl₂O₄-Al₂O₃ were the same like presented in our earlier paper [22].

Transformations of n-hexanol: The reactions of *n*-hexanol (commercial material of analytical grade) over these catalysts were carried out in gas phase using a standard down flow fixed-bed reactor. The reactor was made of a vertical quartz tube with an inside diameter of 8 mm. The reactor was heated by an electrical tubular furnace, and the temperature was controlled with thermocouple placed in the center of the catalytic bed. In each experiment 3 cm³ of catalyst was used. The catalyst was loaded in the reactor and reduced at 453 K for 1 h with methanol. After pretreatment, the catalytic reactions were carried out under atmospheric pressure with the load of 1.0 h⁻¹. No carrier gas was added. *n*-Hexanol was introduced through the top of the reactor to pre-heating zone by a syringe micropump. Experiments were started at 533 K and studied as a function of increasing temperature, where at pre-chosen temperatures, after the stationary equilibrium had set in, the proper experiments were carried out for *ca.* 1 h. The condensed products of reaction were identified by the comparison of their retention times to the standards and analyzed quantitatively with a gas chromatograph HP 6890 equipped with a FID detector and a capillary column HP-5. Helium was used as carrier gas.

RESULTS AND DISCUSSION

In Figure 1 the XRD patterns of the carrier (as prepared and after calcination at 873 K, and 1373 K) and catalyst with 5% CuO loading are shown. The as-prepared carrier was found to be semi-amorphous as shown in Fig. 1a. However, some amount of microcrystalline pseudoboehmite AlO(OH)·xH₂O together with fine ZnAl₂O₄ spinel were visible. The diffraction peaks of the ZnAl₂O₄ phase became more intense and narrower after the temperature treatment, because of growing particles in the sample (Fig. 1b and c). Al₂O₃ phase is well visible in the sample calcined at 1373 K (Fig. 1c). For catalysts with lower loading of CuO (1 and 3%) diffraction lines provide no evidence for that oxide. CuO crystallites were not detected, suggesting that the Cu component is well dispersed, either as small crystallites or as a solid solution within the carrier lattice. Only the sample containing 5% of CuO exhibited separate copper oxide phase (Fig. 1d).

The specific surface areas and pore volumes of samples of carrier and CuO/ZnAl₂O₄-Al₂O₃ with various loading of CuO changed with the change in copper oxide content as shown in Table 1.

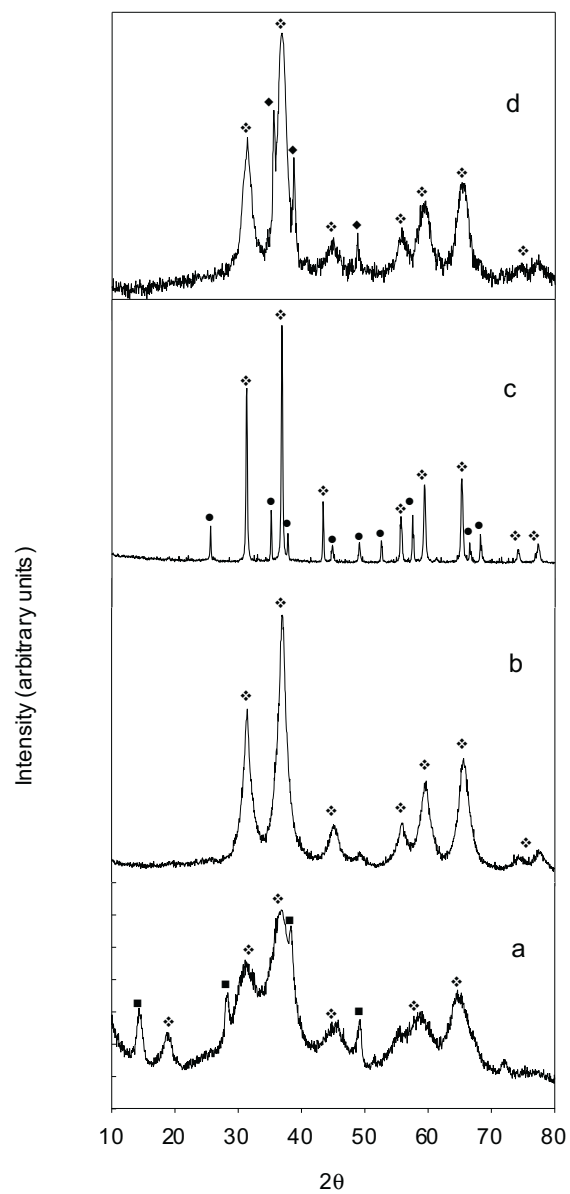


Figure 1. Powder X-ray diffraction patterns: a) ZnAl₂O₄-Al₂O₃ carrier (as prepared); b) ZnAl₂O₄-Al₂O₃ carrier calcined at 873 K; c) ZnAl₂O₄-Al₂O₃ carrier calcined at 1373 K; d) 5 wt.% CuO/ZnAl₂O₄-Al₂O₃. (◇) ZnAl₂O₄; (●) α-Al₂O₃; (■) pseudoboehmite; (◆) CuO.

Table 1. Textural properties of ZnAl₂O₄-Al₂O₃ carrier and CuO/ZnAl₂O₄-Al₂O₃ catalysts after calcination at 873 K.

	S _{BET} [m ² /g]	Total pore volume (at $p/p_0 = 0.95$) [cm ³ /g]	Mean pore radius [nm]
ZnAl ₂ O ₄ -Al ₂ O ₃	137	0.19	2.2
1%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃	125	0.17	2.2
3%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃	97	0.16	2.2
5%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃	91	0.13	2.1

By IR spectroscopy of adsorbed pyridine on carrier surface it was established that the carrier has Lewis acid sites to be equal 168 μmol Py/g. It does not indicate Brønsted acid sites. Total acidity of this sample evaluated by the NH₃ TPD measurements was 0.192 mmol NH₃/g. Contribution of acid centers of equal strength is as follows:

- 4.1% for desorption temperature of 473–523 K;
- 16.5% for desorption temperature of 523–573 K;
- 22.9% for desorption temperature of 573–623 K;
- 19.9% for desorption temperature of 623–673 K;
- 15.3% for desorption temperature of 673–723 K;
- 11.4% for desorption temperature of 723–773 K;
- 9.9% for desorption temperature of 773–823 K.

Investigated sample in main part is characterized by medium acid centers (T = 573–673 K).

Three catalysts containing 1, 3 and 5% CuO supported on hydrothermally obtained ZnAl₂O₄-Al₂O₃, and also pure carrier were tested in the transformation of *n*-hexanol. The carrier used showed different activity in studied reaction. ZnAl₂O₄-Al₂O₃ sample had dehydration activity and all copper catalysts exhibited both dehydration and dehydrogenation properties. The results obtained as a function of increasing temperatures are shown in Table 2. As may be seen from Table 2, the conversion of *n*-hexanol to the reaction products over ZnAl₂O₄-Al₂O₃ and CuO/ZnAl₂O₄-Al₂O₃ depends on the temperature at which the reaction was carried out. The conversion of *n*-hexanol in whole range of temperature studied was comparable for all catalysts containing copper. In the post-reaction mixtures, obtained over ZnAl₂O₄-Al₂O₃, only *n*-hexene and dihexyl ether were found at temperatures 588–603 K. In the case of catalysts containing CuO dehydrogenation is the main reaction as it may be seen in Table 3, which summarized data of selectivities to products of dehydration and dehydrogenation-condensation in all runs studied.

In the presence of copper catalysts *n*-hexanol was dehydrated to *n*-hexene and dihexyl ether and parallel dehydrogenation occurred at 533 K giving hexanal, which condensed to *n*-hexyl *n*-hexanoate according to Tishchenko reaction [38]:

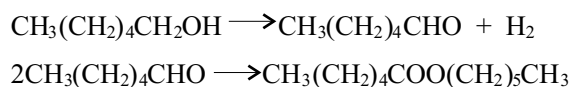


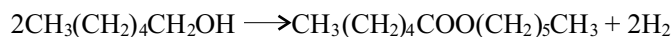
Table 2. Results of *n*-hexanol transformations over ZnAl₂O₄-Al₂O₃ and CuO/ZnAl₂O₄-Al₂O₃ catalysts at load = 1.0 h⁻¹.

Catalysts	ZnAl ₂ O ₄ -Al ₂ O ₃			1%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃				3%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃				5%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃			
	533	588	603	533	588	603	633	533	588	603	633	533	588	603	633
Reaction temp. [K]	533	588	603	533	588	603	633	533	588	603	633	533	588	603	633
Conversion [%]	36.0	100	97.8	45.3	75.9	82.5	91.0	60.8	86.0	90.6	96.0	49.1	81.0	89.2	93.8
Liquid products of reaction [%]:															
<i>n</i> -hexene	3.4	97.5	95.2	0.6	2.0	2.0	1.4	T	2.9	3.4	8.0	T	4.0	6.0	5.0
<i>n</i> -hexane	–	–	–	0.2	1.2	1.3	2.0	T	6.0	7.7	15.1	T	7.8	13.4	11.6
hexanal	1.2	–	–	20.1	36.0	40.0	39.5	16.8	24.9	26.5	26.9	22.9	34.2	32.6	36.0
<i>n</i> -pentanol	–	–	–	–	0.3	T	–	0.2	0.3	0.3	0.2	0.3	0.2	0.2	0.2
hexanoic acid	0.5	–	–	0.6	2.1	3.7	5.1	1.1	3.0	8.4	8.8	1.4	7.2	11.1	7.9
dihexyl ether	29.3	1.6	1.2	8.4	4.0	3.6	–	11.0	7.2	4.0	–	2.7	2.9	1.0	–
<i>n</i> -pentyl <i>n</i> -hexanoate	–	–	–	3.0	4.2	5.9	10.3	0.8	2.6	2.0	3.1	0.2	0.9	1.3	6.2
<i>n</i> -hexyl <i>n</i> -hexanoate	–	–	–	10.2	21.6	21.6	18.6	26.7	34.6	31.0	12.5	19.0	22.4	19.6	18.3
5-decanone	–	–	–	–	–	–	2.1	–	–	–	–	–	–	–	–
6-undecanone	–	–	–	–	–	–	6.5	–	–	4.0	15.7	–	–	2.7	7.5
others	1.6	0.9	3.6	2.2	4.5	4.4	5.5	4.2	4.5	3.3	5.7	2.6	1.4	1.3	1.1

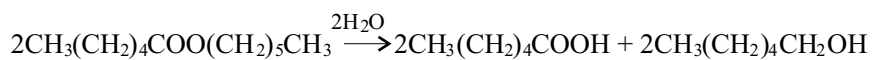
Table 3. Selectivity data for the reactions of *n*-hexanol over ZnAl₂O₄-Al₂O₃ and CuO/ZnAl₂O₄-Al₂O₃ catalysts.

		Selectivity of dehydration [%]	Selectivity of dehydrogenation and condensation [%]
ZnAl ₂ O ₄ -Al ₂ O ₃	533 K	90.8	3.3
	588 K	99.1	–
	603 K	98.6	–
1%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃	533 K	19.9	53.6
	588 K	7.9	81.4
	603 K	6.8	81.8
	633 K	1.5	84.6
3%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃	533 K	18.1	72.9
	588 K	11.7	72.2
	603 K	8.2	70.1
	633 K	8.3	60.6
5%CuO/ZnAl ₂ O ₄ -Al ₂ O ₃	533 K	5.5	85.7
	588 K	8.5	71.0
	603 K	7.8	63.0
	633 K	5.3	27.5

In parallel process alcohol condensed also to ester:



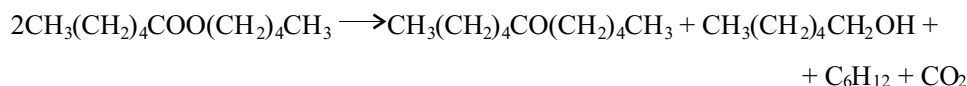
When *n*-hexanol was passed over studied copper catalysts, small amounts of *n*-pentanol and *n*-pentyl *n*-hexanoate were found in products. Also hexanoic acid was obtained and transformed to 6-undecanone according with below sequences:



At higher temperatures ester underwent direct transformation to 6-undecanone according to the equation:



or by Kagan process [39]:



Formation of 5-decanone from *n*-pentyl *n*-hexanoate can be explained in similar way.

In all experiments there were also obtained some other by-products, which have not been analyzed. Generally, the increase in the concentration of copper oxide up to 5% caused changes in decreasing of yields of dehydrated products and increasing of amounts of oxidized products.

CONCLUSIONS

Both $\text{ZnAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ and $\text{CuO/ZnAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ catalysts are active in transformation of *n*-hexanol. The promotion of $\text{ZnAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ with copper oxide was found to be effective for changing the acid-base properties of catalysts. The copper addition to $\text{ZnAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ system increased selectivity of dehydrogenation of catalysts and thus their basic character. $\text{CuO/ZnAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ systems behave as bifunctional catalysts with dehydration as well as dehydrogenation properties. Obtained results lead us to propose the general reaction pathways for transformations of *n*-hexanol over studied catalysts.

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