Influence of Method of Introduction of Cu- and Zn-Based Modifiers on the Properties of Chromia–Alumina Catalysts¹

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Abstract—Three methods of introduction of modifiers based on Cu and Zn compounds into the CrO_x/Al_2O_3 catalysts for dehydrogenation of light paraffin hydrocarbons are considered: Introduction from sol, introduction using successive impregnation technique and introduction of modifiers by impregnation along with precursor of chromium oxide. The obtained samples are studied by a complex of physical-chemical methods (XRD, UV-Vis spectroscopy, temperature-programmed reduction with hydrogen (TPR-H₂), X-ray fluorescent (XRF) spectrometry, low-temperature N₂ sorption). The catalytic properties of the samples are studied in kinetic mode in isobutane dehydrogenation. Cu- and Zn-modifiers are shown to influence on the peculiarities of reduction of Cr^{6+} and, hence, specify the state of active surface of CrO_x/Al_2O_3 catalysts formed in the reductive reaction medium. Not only do the states of modifiers influence on the initial activity of the catalyst, but also on its activity after oxidative regeneration. Introduction of modifiers by successive impregnation method results in formation of copper and zinc aluminates or defective spinels on the Al_2O_3 surface. When the active component is introduced, the modified surface of the support promotes formation and stabilization of Cr^{6+} sites that can undergo reversible reduction—oxidation and provide high activity and selectivity towards formation of isobutylene (>98%).

Keywords: CrO_x/Al_2O_3 catalysts, modification method, Cu- and Zn-based modifiers, state of active component, isobutane dehydrogenation **DOI:** 10.1134/S0023158418020118

INTRODUCTION

 $CrO_{y}/Al_{2}O_{3}$ catalysts are widely used in industry to produce valuable monomers for chemical synthesis [1. 2]. In the literature a number of methods for preparation of chromia-alumina catalysts was proposed: mechanical mixing [3], incipient wetness impregnation [4-6], deposition from solution of precursor salts of active component and support [7], one-pot synthesis [8], sol-gel synthesis [9], hydrothermal synthesis [10, 11], etc. The choice of the preparation method is determined by specified characteristics of the catalyst, such as structural-mechanical properties, porous structure, chemical composition, state of active component, and the opportunity to synthesize it in industry [12]. To increase the activity, selectivity and stability of CrO_x/Al₂O₃ catalysts different modifiers based on compounds of potassium [13], calcium [14], VIII group metals (first of all, iron, cobalt, nickel) [15], etc., are widely used. Special interest is brought by the modifiers based on copper [16–18] and zinc [19, 20] compounds. Simultaneous introduction of copper and zinc, including their application as active components, is used in catalytic dehydrogenation of organic compounds [21, 22]. However, the influence of Cuand Zn-based compounds on the surface structure and state of active component of chromia–alumina catalysts for isobutane dehydrogenation into isobutylene has been poorly studied.

In this work, the effect of method of introduction of Cu and Zn modifying compounds into $CrO_{x}/Al_{2}O_{3}$ catalysts on the state of active component and, as a consequence, on the catalytic properties of the formed chromium oxide sites in isobutane dehvdrogenation were considered. The impregnation by sol or the solution of modifiers followed by deposition of Cr-containing active component as well as the method of simultaneous impregnation from solution containing both the modifiers and chromium oxide precursor were studied. When choosing the methods of support preparation and introduction of Cu- and Zn-based modifiers, we took into account the widespread use of incipient wetness impregnation method in the industry [3-5] as well as the opportunity to reduce the synthesis time (one-pot impregnation) [8, 23] and formation of highly disperced phases of the modifiers (solgel synthesis) [24].

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EXPERIMENTAL

Synthesis of Supports and Catalysts

Pseudoboehmite was used as a γ -Al₂O₃ precursor and obtained by precipitation of sodium aluminate by the solution of sulphuric acid at pH 7–9 followed by washing-off from sodium. Cu(NO₃)₂ · 3H₂O (chemically pure) and Zn(NO₃)₂ · 6H₂O (chemically pure) in amounts of 2.5 wt % in catalysts calculated with respect to Cu and Zn, respectively, were used as precursors of the modifiers.

The catalysts were synthesized by three various methods, with variation of the method of modifier introduction. The first catalyst (hereinafter $CrO_x/Cu-Zn/Al_2O_3$) was prepared by incipient wetness impregnation of the support with precursors of the modifiers and then with a precursor of the active component. Pseudoboehmite was impregnated by water solution of copper and zinc nitrates followed by drying at 170°C for 12 h and calcination at 500°C for 6 h. To obtain the modified CrO_x/Al_2O_3 catalysts with Cr_2O_3 and K_2O contents of 4.5 wt % and 0.85 wt % respectively, the support was impregnated with the aqueous solution of CrO_3 (chemically pure) and KNO₃ (used as a source of alkali metal) and then dried at 120°C and calcined in air at 700°C for 2 h.

The second catalyst had the same chemical composition (hereinafter CrO_x -Cu- Zn/Al_2O). The catalyst was synthesized by impregnation of pseudoboehmite with water solution simultaneously containing the precursors of modifiers and active component. After that the catalyst was dried and calcined under the same conditions as for the previous sample.

The third catalyst was prepared by introduction of the modifiers by impregnation of pseudoboehmite with sol of copper and zinc hydroxides. The sol was prepared by controllable hydrolysis of the corresponding nitrates at 70°C in the solution of ethylene glycol at pH 1–2 [25]. The catalyst was hereinafter referred to as **Sol**. The mixture obtained was dried using the rotation steamer at 90°C and a 0.5 atm during 4 h. The modified support was dried in the air flow at 170°C for 12 h and calcined during 6 h at 500°C. After that it was impregnated with water solution of CrO₃ and KNO₃ with the given composition, and then the catalyst was dried and calcined under the same conditions as in the previously two samples.

Characterization of Supports and Catalysts

Chemical analysis of the catalysts was carried out using sequential X-ray fluorescence (XRF) wavelength-dispersive spectroscopy (XRF-1800) (Shimadzu, Japan). Porous structure of the samples was studied by low-temperature (-196° C) N₂ sorption (TriStar 3020 analyzer, Micromeritics, USA). The specific surface area was determined using the multipoint BET method, isotherms of adsorption were leveled off in the range of relative pressures P/P_0 from 0.05 to 0.30. To plot the curves of pore size distribution the BJH-Desorption method was used and accompanied by the analysis of desorption branches of the nitrogen adsorption-desorption isotherms. Prior to the measurements, the sample weighs (100–120 mg) were outgassed in vacuum at 200°C for 2 h.

The chemical states of chromium and phase composition of the catalysts were studied using diffuse reflectance UV-vis spectroscopy (DRS) on the Evolution 600 spectrometer (Thermo Scientific, USA) using a base line spectrum of freshly precipitated BaSO₄ and powder X-ray diffraction (XRD) on the Miniflex 600 diffractometer (Rigaku Corporation, Japan) using a monochromatic Cu K_{α} radiation ($\gamma =$ 1.5418 Å). The phase composition was detected using the PCPDFWIN database.

To evaluate the peculiarities of reduction of copper and chromium compounds in the catalysts the temperature-programmed reduction with hydrogen (TPR-H₂) was used. The measurements were carried out using the ChemiSorb 2750 chemisorption analyzer ("Micromeritics," USA) with a thermal-conductive detector (TCD-signal) at a heating rate of 10°/min and a flow rate of argon-hydrogen mixture (10 vol % H₂) of 20 mL/min.

Testing of Catalytic Properties of the Samples

Catalytic properties of the samples were investigated in isobutane dehydrogenation into isobutylene in accordance with technique described in [26]. The experiments were carried out in the kinetic mode in a fixed-bed tubular quartz reactor at 540°C. A weigh of catalyst (500–600 mg) with the particle sizes of 0.1– 0.25 mm was mixed with the inert diluent (quartz) in the volumetric ratio of 1 : 2. The reaction mix of 15% *i*-C₄H₁₀ in N₂ was passed through the fixed catalyst bed with a rate of 9 L/h. The testing duration was 3 h and included air regeneration (rate flow 3 L/h) and reduction in a flow of H₂ + N₂ (0.53 and 3 L/h, respectively).

RESULTS AND DISCUSSION

Characterization of Catalysts

The porous structure of the catalysts was studied using low-temperature adsorption of nitrogen. In Fig. 1 the adsorption-desorption isotherms of nitrogen and pore size distributions are presented for the synthesized catalysts and the Al₂O₃ sample taken as a result of thermal treatment of the initial pseudoboehmite at 500°C. The presence of a hysteresis loop for P/P_0 of 0.5–1.0 in all isotherms (Fig. 1a) indicates that the synthesized catalysts and alumina support have mesoporous structures. In Fig. 1b it can be seen that the pores within the samples possess the sizes between 2 and 20 nm, with the maximum of distribution being at 6-10 nm.

A comparison of the characteristics of the prepared catalysts and supports allow tracing how the porous structure transforms depending on the method of introduction of modifiers and the active component. In the isotherm for the Sol catalyst based on the support modified by sol of copper and zinc hydroxides, a loop of hysteresis was shifted towards higher values of P/P_0 as compared to isotherms for Al₂O₃ support. This suggests decreasing the share of mesopores with sizes below 5 nm and increasing the share of mesopores with sizes above 5 nm (Fig. 1b). This can be associated with localization of particles of sol in the fine pores of the support.

Adsorption-desorption isotherms for catalysts are located below the one of the support (Al_2O_3) in all range of relative pressures, both for catalysts obtained by successive introduction and co-introduction of active components and modifiers. This evidences on the uniform distribution of the modifiers and active component inside the support pores. In the curves of pore size distribution, the volume of pores with size of 2–10 nm in the catalysts is less than in the alumina obtained by pseudoboehmite calcination at 700°C.

In Table 1 some parameters of porous structure and results of chemical analysis of chromia–alumina catalysts and alumina calcined at 500°C is shown. The surface area of the catalysts is lower as compared to the one of alumina that is connected both with localization of active component and modifiers in the pores of the support and also with higher calcination temperature of the catalysts (700°C). The sample obtained by introduction of modifiers through impregnation with sol has the maximal volume of pores, which is caused by the increase of the width of the latter (Fig. 1b).

Results of X-ray fluorescence analysis show that the catalysts have similar chemical composition. Some elevated level of content of individual components can be connected with their concentration on the surface of the sample, which makes them more available for X-ray beam.

The phase composition of the catalysts, state of active component and modifiers supported on the sur-



Fig. 1. Isotherms of nitrogen adsorption-desorption (a) and pore size distribution (b) for support and chromia-alumina catalysts.

face of alumina were investigated by XRD and UV-vis spectroscopy (DRS). In Fig. 2a XRD patterns for modified catalysts and alumina calcined at 500°C are

Sample	$T_{\text{calcination}}, ^{\circ}\text{C}$	<i>S</i> , m²/g	Pore volume, cm ³ /g	Pore size, nm	Composition of elements, wt %						
					Al	0	Cr	K	Cu	Zn	Σ
Al ₂ O ₃	500	207	0.30	5.7	56.2	43.5	_	_	_	_	99.7
$CrO_x/Cu-Zn/Al_2O_3$	700	138	0.28	9.1	49.1	36.9	3.6	0.8	3.4	3.6	97.4
$CrO_x - Cu - Zn/Al_2O_3$	700	131	0.28	8.5	44.9	41.7	3.7	0.9	2.9	3.0	97.1
Sol	700	141	0.37	8.6	49.1	38.3	3.5	0.8	3.8	4.0	99.5

 Table 1. Characteristics of porous structure of alumina and chromia–alumina catalysts

Dashes mean the absence of corresponding elements in composition of sample.

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Fig. 2. XRD patterns (a) and UV-vis spectra (b) of Al_2O_3 support and synthesized catalysts.

presented. For all samples, reflexes of γ -Al₂O₃ phase typically present and are associated with the use of pseudoboehmite as a precursor. The absence of expressed reflexes of Cr-containing phases points at stabilization of chromia in a highly-dispersed amorphous state. Reflexes of phases of Cu and Zn oxides are not also observed, which evidences on their high dispersion or incorporation into the support structure. However, a comparison of X-ray patterns for alumina and modified catalysts shows that the intensity of reflexes of the catalysts at $2\theta = 31.3^{\circ}$ and 36.9° as well as at 60.5° and 66.6° differ from the intensity of reflexes for Al₂O₃ and, according to database PCPDFWIN and data of [27], are assigned to phases of copper and zinc aluminates. Besides, the parameter of cubic lattice, *a*, of γ -Al₂O₃ phase (Table 2) increases with introduction of the modifiers. This allows suggesting that Cu and Zn form solid solutions with alumina with cubic structure and spinel phase. The above described reflexes are more intensive in the spectra of CrO_x/Cu–Zn/Al₂O₃ and Sol catalysts, which can be caused by stabilization of the main part of modifiers as defective spinel. In the sample prepared by co-introduction of modifiers and the active component, copper and zinc, hypothetically, form joint phases with alumina support as well as with active component.

In the UV-vis DR spectra (Fig. 2b) of all the catalysts the adsorption bands with maximums at 270 and 370 nm are observed, which can be caused by electron transfer $O \rightarrow Cr^{6+}$ with tetrahedraly coordinated chromium in the strongly- and weakly bonded forms as well as the band with low intensity with maximum at 445 nm that is typical for dichromates [28–30]. These absorption bands are the most marked in the spectrum of the Sol catalyst. Besides, in the spectra for all catalysts, absorption bands in the range of 200–245 nm are presented and related to electron transfer $O \rightarrow Cu^{2+}$ (ligand-to-metal charge transfer) [9, 31].

It is noteworthy that in the spectrum of the Sol catalyst absorption bands in the range of 500–600 nm, which is more expressed than in the spectra of other catalysts, is observed and corresponds to Cr^{3+} state [29]. The absorption band in the range of 700–800 nm can be attributed to formation of mixed oxides of Cu(I) and Cu(II) in the Sol sample. Similar bands were found in Ref. [31] during the investigation of Cu/Al₂O₃.

Thus, based on the data of XRD and UV-vis spectroscopy, it can be concluded that the active component is in a highly-dispersed amorphous state on the surfaces of the prepared catalysts, mainly in a Cr^{6+} state. The modifiers are also weakly crystallized and, in particular, comprise the aluminates of $CuAl_2O_4$ and $ZnAl_2O_4$. The Sol sample contains an active component in the Cr^{3+} state. Besides, copper and zinc can be presented in the form of dispersed oxide. This confirms that both modifiers and active component change their state under conditions of sol impregnation.

The peculiarities of reduction of modified supports and chromia–alumina catalysts on the basis thereof, were investigated by TPR-H₂. The appearance of TPR profiles (Fig. 3) shows that hydrogen consumption basically occurs in a range of 200–430°C. The H₂ consumption for CrO_x –Cu– Zn/Al_2O_3 catalyst obtained by simultaneous introduction of modifiers and active component into the high-temperature range (the peak with a maximum at 367°C) can be caused by formation of mixed phases of copper and chromium, presumably as copper chromates. The presence of lowtemperature shoulder in the TPR profiles of the CrO_x/Cu – Zn/Al_2O_3 and Sol catalysts at 257 and 255°C, respectively, probably indicates successive

Catalysts	a* Å (XRD)	H_2 consumption**, µmol/g					
Cuturysts	<i>u</i> , <i>H</i> (<i>H</i> (D))	supports	freshly prepared sample	sample after reaction			
$CrO_x/Cu-Zn/Al_2O_3$	7.9254	269	802	584			
CrO_x - Cu - Zn / Al_2O_3	7.9381	0 (Al ₂ O ₃)	889	665			
Sol	7.9407	243	1171	539			
CrO_x/Al_2O_3	7.9030	0 (Al ₂ O ₃)	493	163			

Table 2. Lattice parameter (*a*) of γ -Al₂O₃ phase and amount of hydrogen consumed by the supports and catalysts investigated

* Determined by XRD method.

** Determined by TPR-H₂ method.

reduction of copper compounds (easily reducible component) from the oxide state [32], and then the chromium reduction from high valence state, i.e., $Cr(VI) \rightarrow Cr(III)$ transformation [33]. Reduction peaks with maximum at 325 and 342°C in the TPR profiles of the supports are referred to reduction of copper from a highly dispersed phases of surface aluminate as it was shown in Ref. [34]. Comparison of peak areas of hydrogen consumption by the supports and catalysts shows that impact of hydrogen that is consumed for the reduction of oxidized forms of copper is 20-34% (Table 2). Thus, one can assume that in accordance with the results of UV-vis spectroscopy from 40 to 80% of chromium in the catalysts are presented as Cr⁶⁺. Different location of TPR peaks and different shape of these hydrogen consumption peaks for two above noted catalysts can indicate the reduction of Cr(VI) particles with various sizes from the same phases [34] or about various interaction of copper and zinc with the support surface [35]. Smaller reduction temperature for the Sol sample is attributed to low-temperature reduction of copper (peak at 255°C), which makes further reduction of Cr^{6+} easier [36].

Comparison of the amount of hydrogen consumed by the catalysts before and after the catalytic experiment (two cycles of isobutane dehydrogenation followed by re-oxidation in air at 700°C) (Fig. 3, Table 2) shows that for all catalysts a narrowing of H₂ consumption peak is observed that can result from redistribution of modifiers and chromium on the surface of catalysts with formation of more stable species. Temperatures of TPR peak maximums differ after catalytic cycles over all three catalysts. Probably, this is caused by different form of chromium interaction with the support or different Cr⁶⁺ species. Chromium is still reduced at low temperature (peak at 305°C) in the Sol catalyst that can be a result of stabilization of copper in the form of separate oxide phase. Reduction of this phase (a shoulder at 225°C) simplifies the reduction of active component. Mechanism of action of modifiers in the $CrO_x/Cu-Zn/Al_2O_3$ and $CrO_x-Cu-Zn/Al_2O_3$ catalysts is different than for the Sol catalyst. Probably, a stabilization of modifiers in the surface structure of

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alumina occurs for these two samples that leads to changing of the nature of interaction of chromium with the support.

The amount of hydrogen consumed decreases after dehydrogenation reaction for all catalysts investigated. This suggests partial stabilization of chromium sites in the Cr³⁺ state (probably, α -Cr₂O₃) that are not subjected to re-oxidation in the selected regeneration conditions. As shown in TPR profile of the CrO_x-Cu-Zn/Al₂O₃ catalyst, this sample consumes maximum amount of hydrogen. This evidences on the keeping of larger amount of redox forms of copper and chromium. In the Sol catalyst, the amount of such forms decreases considerably after its placement into redox conditions of the catalytic reaction of isobutane dehydrogenation.



Fig. 3. TPR-H₂ profiles for catalysts (a) $CrO_x/Cu-Zn/Al_2O_3$, (b) $CrO_x-Cu-Zn/Al_2O_3$, (c) Sol: (*1*) supports, (*2*) freshly prepared catalysts on the basis thereof, (*3*) same catalysts, after 2 cycles of isobutane dehydrogenation and after regeneration cycle.



Fig. 4. Dependence of isobutane conversion and selectivity towards isobutylene formation on time of dehydrogenation for the prepared chromia-alumina catalysts at 540°C.

Catalytic Properties of Samples in Isobutane Dehydrogenation

Figure 4 shows isobutane conversion (X) and selectivity (S) towards isobutylene formation depending on the time of isobutane dehydrogenation over the prepared modified chromia-alumina catalysts as well as on the catalyst, obtained by impregnation of Al_2O_3 support by water solution of CrO₃ and KNO₃ which was used as a reference sample. The CrO_{y}/Cu - Zn/Al_2O_3 and $CrO_r-Cu-Zn/Al_2O_3$ catalysts show comparable activity during the first 18 min of reaction. Furthermore, isobutane conversion increases that indicates changing of the state of the active surface under the influence of reductive reaction mixture and formation of more active sites. As opposed, the isobutane conversion for the Sol catalyst decreases during these 18 min. This can be caused by significant changing of the state of active component, for example, its aggregation accompanied by formation of low active α -Cr₂O₃ phase [1], which is consistent with the TPR data, or with formation of carbon deposits resulting in blocking of the main part of active sites [37]. However, high selectivity towards isobutylene formation (98-99%)is achieved for all catalysts. This evidences on low probability of formation of carbon deposits at 540°C.

The catalytic properties change after regeneration of the samples in the air flow followed by reductive activation. The isobutane conversion for the Sol catalyst decreases that indicates sample deactivation. In comparison with the first 18 min, the isobutene conversion for the CrO_x -Cu-Zn/Al₂O₃ catalyst is much lower. This confirms significant changing of its surface state under the influence of oxidative and reductive treatments. After slight increase of isobutene conversion at this step, the catalyst activity gradually decreases.

The $\text{CrO}_x/\text{Cu}-\text{Zn}/\text{Al}_2\text{O}_3$ catalyst obtained by successive introduction of modifiers and active component, rapidly increases its activity after oxidative and reductive treatment (isobutane conversion increases from 10.8 to 13.8%). Then the conversion increases to up to 14.3%, and then, at the end of dehydrogenation cycle it decreases to up to ~12%. The selectivity of isobutylene formation over this catalyst is also higher than the one over other catalysts.

It is noteworthy that the activity (isobutane conversion) and selectivity over the catalysts modified by copper and zinc compounds are higher than those for the CrO_x/Al_2O_3 catalyst. Thus, the introduction of the modifiers makes positive impact on the catalyst activity, but the activity increase depends on the introduction method.

Relatively low conversion and fast deactivation of the sample prepared by introducing the modifiers from the sol can be connected with the fact that the active component is present in the form of Cr_2O_3 as shown by UV-vis and TPR methods (Fig. 2b and Table 2). An increase of the reduction temperature of chromium oxides (shift of peak maximums from 284 to 305°C) and significant decrease of the TPR peak area after isobutene dehydrogenation over the Sol catalyst can be a result of relatively low stability of deposited chromium oxides that leads to rapid deactivation of the sample due to aggregation of active component.

The sample prepared by one-step introduction of modifiers and chromium $(CrO_x-Cu-Zn/Al_2O_3)$ shows higher activity than the Sol catalyst, which can be attributed to elevated concentration of "strongly bound" Cr^{6+} sites, according to the data of UV-vis spectroscopy (absorption band at 370 nm in Fig. 2b). After oxidative regeneration and reductive activation the surface state of these catalysts change, and this leads to sharp fall of conversion.

The $CrO_x/Cu-Zn/Al_2O_3$ catalyst prepared by successive impregnation is the most active. High values of conversion and selectivity of isobutylene formation for this sample are explained by stabilization of active component predominantly in the form of redox Cr^{6+} sites (reduction peak at 337°C in Fig. 3a) as well as the absence or lower content of Cr_2O_3 (Fig. 2b). The activity of this catalyst in the dehydrogenation process increases in the first cycle of dehydrogenation and significantly rises after the redox cycle. This is caused by "favorable" distribution of modifiers, mainly in the form of surface aluminates that promote stabilization of active component in the form of redox Cr^{6+} sites.

CONCLUSION

Thus, the modifying additives of copper and zinc compounds increase the activity and selectivity of chromia-alumina catalysts in isobutane dehydrogenation independently on the method of their introduction. The method of introduction of modifiers (from sol or by successive or joint addition of the active component with the precursors) influences on their distribution and state in the catalysts obtained, and also determines the state of active component (chromium oxides), reactivity and catalytic properties of the sample. The catalyst prepared by successive introduction of Cu- and Zn-containing modifiers and chromium precursor using impregnation method shows the highest activity in isobutane dehydrogenation and high selectivity towards isobutylene formation (98.9%).

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