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Peculiarities of formation of the active surface of Cu-modified CrO_x/Al_2O_3 catalysts for dehydrogenation of isobutane to isobutylene

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Currently, the dehydrogenation of light paraffins is of importance for industry. This is connected with a growth in demand for olefins as the initial block for polymers and organic chemicals. In Russia, the microspherical chromia-alumina catalysts are widely used for dehydrogenation of paraffins in a fluidized bed catalytic process. However, these catalysts are characterized by high abrasive ability of microspheres, the formation of toxic catalytic dust, which pollutes the environment. The trend to complete refuse from microspherical catalysts is observed in foreign countries. As an alternative, CrO_x/Al_2O_3 catalysts in the fixed bed (processes Catofin and Catadiene) are used [1]. γ-Al_2O_3 is used as a support for these catalysts due to efficient porous structure and high thermal stability. The dehydrogenation process is carried out at high temperatures of 550-650 °C.

To increase the activity and selectivity of the catalysts different modifiers are used. The modifiers used represent alkaline and alkali-earth metals as well as metals of VIII (Fe, Co, NI) and Ib (Cu, Ag) groups are widely used to decrease the acidity of the catalysts and increase the mechanical stability of the catalyst granules. The Cu/Al_2O_3 materials are also used in the dehydrogenation of hydrocarbons as a heat-generating material [2]. However, an influence of copper on the CrO_x/Al_2O_3 catalysts for dehydrogenation of isobutane to isobutene had been poorly studied. Therefore, the investigation of the Cu addition on the state of the active component and catalytic properties in the dehydrogenation reaction is of importance. The present work is focused on the study of the effect of copper addition on the textural and redox properties of the modified alumina support and chromia-alumina catalysts on the basis thereof.

The pseudoboehmite was used as a precursor of the support (γ-Al_2O_3). The series of modified alumina supports (loading of Cu from 0 to 5 %wt.) were prepared by incipient wetness impregnation of boehmite by an aqueous solution of copper nitrate. Then the supports were dried at 120 °C for 12 hours and calcined at 750 °C for 6 hours. After calcination the modified supports were impregnated by an aqueous solution of chromium oxide (VI). The nominal loading of Cr_2O_3 in the catalysts was 4.5 %wt. Drying and calcination were carried out under the same conditions as for the supports. The structure of the prepared supports and catalysts as well as the states of Cu and CrO_x were studied by low-temperature nitrogen adsorption, TPR-H_2, XRD, UV-vis and Raman spectroscopy. The catalytic experiments were carried out in the quartz tubular reactor with a fixed catalyst bed at 540 °C. The experiment was carried out during 3 hours with a regeneration in air and reduction in H_2/N_2 [3].

The introduction of copper as a modifier was shown to change the textural characteristics of the supports and catalysts. An increasing of Cu loading to up to 2 %wt. results in increasing of the S_{BET} from 115 to up to 124 m^2/g along with decreasing of the mean pore size. Further increasing of Cu loading to up to 2.5 and 5 %wt. leads to decreasing of the S_{BET} to up to 102 and 95 m^2/g, respectively. The copper oxides were not detected by XRD, and only small amounts of $CuAl_2O_4$ phase was observed in the support and catalyst that indicates the formation of a layer of aluminates on the surface of the alumina support. The absence of the reflexes of chromium-containing phases in the XRD indicates the homogeneous distribution of CrO_x on the support surfaces. The TPR studies show that Cu promotes a reduction of chromia at low temperatures. The growth of the catalytic activity in the isobutane dehydrogenation to isobutylene is observed for Cu-modified catalysts. The optimal Cu content for this catalyst was 2 %wt.

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References

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