INTRODUCTION

Chromia-alumina (CA) catalysts are used in industrial processes of the dehydrogenation of light hydrocarbons with the formation of olefins. At present, light olefins are derived from oil stock by the steam and catalytic cracking of naphtha. However, these processes can no longer supply the growing global demand for these products; at the same time, there are large quantities of light hydrocarbons that are used insufficiently and very ineffectively.

The dehydrogenation of light alkanes is an endothermic reaction; therefore, high temperatures are necessary to obtain the desired yields of olefins. For example, temperatures of 520–700°C are used in industrial processes of propane dehydrogenation. In addition, the rates of side reactions of stock cracking and coke formation increase. The accumulation of coke in a catalyst leads to its deactivation. The catalyst must therefore be frequently subjected to oxidative regeneration. Under severe reaction conditions, the requirements for the operational performance of catalysts are more rigorous. Along with high levels of activity and selectivity, they must exhibit high mechanical and thermal stability and withstand frequent oxidative regeneration.

Even though the activity of CA catalysts in the dehydrogenation of light alkanes was first recognized more than 70 years ago, studies aimed at improving such catalysts are now being performed. Thanks to these comprehensive studies, SPS, a wear-resistant and highly active CA catalyst was prepared at OAO NII Yarsintez [1, 2] and is now used in a plant for the dehydrogenation of isobutene in Saudi Arabia. Its high stability and resistance to mechanical destruction were achieved by switching from the so-called coagulation structure (catalyst IM-2201, designed at the Research Institute of Monomers for Synthetic Rubber) to the crystallization structure (SPS). Researchers at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, developed a highly active and selective catalyst on a crucially new Al2O3/Al ceramic–metal support, cermet [3, 4]. It was subsequently modified with a product of the thermochromic activation of gibbsite, and a new modification of CA catalyst was derived that exhibits higher activity than the industrial IM-2201 catalyst, high abrasion resistance (no less than 94–96%), high thermal stability, and resistance to coke deactivation [5, 6].

The nature of the active forms of the catalyst, the conditions of their formation, and the mechanism of their deactivation have been studied in many works [7, 8]. It
has been shown that the conditions of catalyst mass preparation affect the composition of the surface forms of chromium, the strength of their bonds with the support, and the acidity of the surface (all of which govern the catalytic activity and selectivity of the catalyst), along with the catalyst’s resistance to coke formation and stability over time. The methods and conditions for preparing CA catalysts that are currently known and used can be divided into three main groups: (1) impregnation of the support with a chrome salt solution and subsequent thermal decomposition with the formation of chromium oxides; (2) codeposition, in which hydroxides of aluminium and chromium are simultaneously formed, then dried and subjected to a high-temperature treatment in air (calcination); and (3) the epitaxy of atomic layers, in which Al₂O₃ is saturated with vapors of chromium acetylacetonate, and the resulting surface complex is treated with air at 600°C to remove acetylacetonate ligands [9].

In this work, we used a modified method of codeposition from aqueous solutions of chromium and aluminium nitrates at pH = 9.5–10 [10] for the preparation of the CA catalyst. This was simpler than conventional codeposition, since some stages were excluded. In developing this method of preparation, the authors considered that the most active catalysts are obtained from thermodynamically unstable deposits derived under conditions far from equilibrium [11]. This applies in our method too, since the stages of the filtration, washing, and drying of the deposit were excluded from the process of CA catalyst preparation, and the suspension of chromium and aluminium hydroxides was subjected to high-temperature treatment at 550°C; as this takes place, the evaporation, drying, and interaction of chromium and aluminium oxides proceed at a high rate.

In this work, we studied the chemical and phase composition, the texture of the catalyst, and the activity in the dehydrogenation of propane and discuss the similarities and differences of its properties in comparison to known CA catalysts.

**EXPERIMENTAL**

**Catalyst Preparation**

A mixture of water-soluble salts of chromium and aluminium (reagent grade) was heated to a temperature of 80–90°C and treated with a saturated ammonia solution to pH = 9.5–10. The resulting suspension of chromium and aluminium hydroxides was placed in a muffle furnace and held at 550°C for 75 min. It was then cooled to room temperature, triturated, and sieved to a fraction with grains of 0.2–0.4 mm.

The ratios of chromium and aluminium salts in the original samples were selected so as to obtain samples with chromium contents of 2.8, 5.5, 9.0, and 11.3 wt %.

The samples were calcined at 650 and 900°C for 1 h.

**Chemical Analysis**

Determining the total content of chromium. We placed a weighed portion of the catalyst sample in a quartz crucible and added 10 g of potassium pyrosulphate K₂S₂O₇. The crucible was heated in a muffle furnace to 700°C and held for 30 min (to obtain a fusion cake). After that, it was cooled, dissolved in 20 ml of diluted H₂SO₄ (1 : 1), and heated to dissolve the fusion cake; upon cooling, it was transferred with distilled water into a graduated flask with a volume of 100 ml. An aliquot of the resulting solution was admixed with 10 ml of H₂SO₄ (ρ = 1.84 g/cm³), diluted with distilled water to 200 ml, and heated to boiling. Next, we poured 10 ml of 0.25% solution of AgNO₃, diluted with water to 300–400 ml, added 3–5 g (NH₄)₂S₂O₈, and heated to decompose ammonium persulfate. After cooling, the solution was titrated using 0.0125 N standard solution of Mohr’s salt Fe(NH₄)₂(SO₄)₂ ⋅ 6H₂O. The relative error of the analysis did not exceed 2.0%.

Determining the content of Cr⁶⁺. A weighed portion of the sample (0.1–0.3 g) was dissolved in 10 ml of dilute sulfuric acid (1 : 1) with heating. Upon cooling, an aliquot of the resulting solution was titrated using 0.0125 N standard solution of Mohr’s salt Fe(NH₄)₂(SO₄)₂ ⋅ 6H₂O. The relative error of the analysis did not exceed 3.0%.

Determining the content of Cr³⁺. This was done according to the difference between the total content of chromium and the content of Cr⁶⁺.

**X-ray Diffraction Analysis**

XRD was performed using an ADP-2-01 diffractometer (CuKα, radiation, Ni filter) equipped with software to automate data acquisition, processing, and analysis.

The specific surface area and pore distribution in the samples were determined by low-temperature nitrogen adsorption. Adsorption isotherms were obtained using an Autosorb-1 instrument (Quanchrome, United States). The samples were pre-evacuated at 280°C for 1 h. The measurement error for specific surface area and pore volume was 5–7%.

**Hydrogen Temperature-Programmed Reduction (TPR)**

Hydrogen TPR was used to control the amount of reduced forms of chromium in the catalyst over the temperature range under study. The measurements were performed using an Autosorb-1C instrument. The samples were preheated in a stream of He (30 ml/min) at 140°C for 1 h and then cooled in a stream of He to room temperature. The samples were then reduced with a mixture of 5.5 vol % H₂ + 94.5 vol % N₂ in the mode of programmed temperature rise at a rate of 10°C/min in a range of 50–750°C; the flow rate of the gas mixture was 40 cm³/min; the sample weight was 1.0 g. The