The Study of CrOₓContaining Catalysts Supported on ZrO₂, CeO₂, and CeₓZr(1–x)O₂ in Isobutane Dehydrogenation¹

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Abstract—Olefin hydrocarbons are valuable raw materials for petrochemical and polymer manufacturing. Highly effective, but toxic chromium-containing catalytic materials are the most widely used catalysts to obtain olefins in industry. In this regard, the urgent challenge to increase the efficiency of oil processing is to develop the catalysts with low content of harmful active component. In the present study, the catalysts with low chromium content (1 theoretical monolayer = 5 Cr atoms per nm² of support) were synthesized by incipient wetness impregnation of the supports (Al₂O₃, ZrO₂, CeO₂, and CeₓZr(1–x)O₂). The samples obtained were characterized by low-temperature nitrogen adsorption, X-ray diffraction and H₂-temperature-programmed reduction methods. The catalytic properties of the catalysts were tested in isobutane dehydrogenation reaction. It was shown that the state of chromium on the surface is different over different supports. For the CrOₓ/CeO₂ catalyst, the formation of Cr₂O₃ particles with low activity in the dehydrogenation reaction was observed. For other samples, a highly disperse X-ray amorphous state of chromium was characteristic. The catalyst based on CeₓZr(1–x)O₂ was the most active in isobutane dehydrogenation reaction due to possible stabilization of chromium as Cr(V) state.

Keywords: Cr-containing catalysts, ZrO₂, CeO₂, CeₓZr(1–x)O₂, isobutane dehydrogenation
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INTRODUCTION

Olefin hydrocarbons (ethylene, propylene, isobutylene, etc.) are valuable chemical compounds for the production of polymers, dyes, rubbers, fibrous materials, etc. They are mainly formed as by-products in the processes of steam cracking of naphtha and catalytic cracking of heavy oil fractions. These alkenes are also produced in a large scale by dehydrogenation of the corresponding alkanes. At present, the catalytic nonoxidative dehydrogenation (DH) of paraffinic hydrocarbons is of great industrial importance and is a large-scale petrochemical process. The most widely used catalysts for DH of C₃–C₅ alkanes are those containing Pt–Sn or CrOₓ supported on Al₂O₃ [1–3]. However, the use of such systems is limited due to high cost of platinum and the toxicity of chromium oxides. Thus, various types of supported and bulk oxides (indium [4], vanadium [5, 7], gallium [8, 9] and molybdenum [10] oxides) are studied to obtain alternative catalysts for hydrocarbon dehydrogenation possessing comparable properties to Pt- and Cr-containing ones. Nevertheless, in the review by Sattler J.J.H.B. et al. [11] concerning modern state of research of such systems (namely, deposited gallium, vanadium and molybdenum oxides) for oxidative and non-oxidative dehydrogenation of hydrocarbons, the authors concluded that these catalysts are significantly inferior to chromium- and platinum-containing systems, rapidly deactivate and lose activity after the regeneration stage. Carrying out the oxidative dehydrogenation in the presence of O₂ and/or CO₂ leads to the partial and deep oxidation of hydrocarbons and selectivity loss. Therefore, the development of chromium-containing systems with high catalytic activity even at low content of the active component is the up-to-date direction of scientific research.

γ-Al₂O₃ [12–14], SiO₂ [15, 16], ZrO₂ and TiO₂ [5, 17, 18], zeolites [19], MgO [20], ordered mesoporous materials [21, 22], etc., were studied as supports for chromium-containing catalysts. It is known that the state of active component in the catalyst and its efficiency are determined by support properties, conditions of catalyst synthesis and the addition of modifiers/promoters of various nature. The change of some parameter allows controlling the state of active phase. γ-Al₂O₃ is widely used as a support for chromium-containing systems. CrOₓ catalysts based on ZrO₂ even with low content of the active component are the most active in the dehydrogenation of hydrocarbons [23, 24]. However, their use is limited by high price of zirconium compounds, the complexity to

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obtain a support with a developed specific surface area and sintering at high temperatures [25]. Chromium-containing systems may differ in terms of the amount of chromium introduced as well as the nature of the precursor, composition, conditions of preparation and subsequent treatment, and the state of the oxide support surfaces. Nevertheless, on the surfaces of both alumina and zirconia, a significant part of chromium is in a highly dispersed Cr(VI) state due to possible strong interaction of chromium ions with the surface of ZrO$_2$ or Al$_2$O$_3$ that prevents their segregation into the low-active phase of α-Cr$_2$O$_3$. Zirconia and other oxides (SiO$_2$, La$_2$O$_3$, etc. [26–29]) are also used as modifiers in CrO$_x$/Al$_2$O$_3$ catalysts. According to the literature data, it is possible to estimate the state of chromium oxides on the surface of various supports and approach the understanding of the mechanisms of active phase formation. Nevertheless, despite increasing attention to CeO$_2$, CeO$_2$–containing materials and mixed oxides of Ce$_x$Zr$_{1-x}$O$_2$ as catalysts, modifiers and supports for various applications, the studies focused on application of cerium-containing materials in dehydrogenation processes are limited mainly by reactions in the oxidative mode [30]. However, the systems that contain ceria as a modifier or support can be of interest because of the ability of CeO$_2$ to increase the dispersion of the active component (in particular, Cr, W, V oxides) in calcined samples by forming surface states M–O–Ce [31–33].

The purpose of the present work was to study the state of chromium deposited on CeO$_2$ and Ce$_x$Zr$_{1-x}$O$_2$, in comparison with Al$_2$O$_3$– and ZrO$_2$–based catalysts and the catalytic properties of the obtained model chromium-containing samples in the isobutane dehydrogenation reaction.

**EXPERIMENTAL**

**Synthesis of Supports and Catalysts**

γ-Al$_2$O$_3$, ZrO$_2$, CeO$_2$ and Ce$_x$Zr$_{1-x}$O$_2$ were used as supports. Aluminum, cerium and zirconium oxides were obtained by thermal decomposition of AlO(OH), Ce(NO$_3$)$_3$·6H$_2$O and ZrO(NO$_3$)$_2$·H$_2$O, respectively, at 600°C for 4 h. Since γ-Al$_2$O$_3$ is a classical and the most commonly used support for chromium-containing catalysts, it was used for comparison with the catalysts based on other supports. Mixed Ce$_x$Zr$_{1-x}$O$_2$ oxide was synthesized by co-precipitation method. The calculated amounts of Ce(NO$_3$)$_3$·6H$_2$O and ZrO(NO$_3$)$_2$·H$_2$O (Ce : Zr molar ratio = 1 : 1) were dissolved in distilled water, and then an aqueous solution of ammonia NH$_3$·nH$_2$O (2 mol/L) was added dropwise. The precipitate was dried at 90°C for 12 h and calcined at 500°C for 4 h.

Model Cr-containing catalysts were prepared by incipient wetness impregnation of the obtained supports with an aqueous solution of CrO$_3$ (reagent grade). The chromium content corresponded to one monolayer (5 Cr atoms per nm$^2$ of support) [23] that was 2–8 wt % of Cr. The synthesized catalysts were dried at 95°C for 12 h, calcined in air atmosphere at 600°C for 4 h.

**Characterization of Supports and Catalysts**

The measurement of porous structure characteristics of the materials was carried out by low-temperature nitrogen adsorption at −196°C using TriStar 3020 automated gas adsorption analyzer (Micromeritics, USA). The specific surface area was determined by the multipoint BET method via linearization of the adsorption isotherm in the $P/P_0$ range from 0.05 to 0.30. The Barrett–Joyner–Halenda method (BJH-Desorption) with an analysis of the desorption branch of the nitrogen adsorption–desorption isotherm was used to plot the pore size distribution. The samples (100–120 mg) were degassed in vacuum at 200°C for 2 h prior to the measurements.

Diffuse reflectance spectroscopy (DRS or UV-vis spectroscopy) and X-ray diffraction (XRD) methods were used to study the chemical state of chromium and the phase composition of the catalysts. Diffuse reflectance spectra were recorded on a Cary spectrometer (Varian, Australia) with DRA-CA-30I attachment (Labsphere, USA) in the wavelength range of 250–800 nm. MgO was used as a standard sample. XRD patterns were obtained on a MiniFlex 600 diffractometer (Rigaku, Japan) using monochromatic CuK$_\alpha$ radiation ($\lambda$ = 1.5418 Å) with a scanning rate of 0.2 deg/min, step size of 0.2 deg and 2θ = 10°–90°. The phase composition of the catalysts was determined using the PCPDFWIN database and the POWDER CELL 2.4 full profile analysis software.

Temperature-programmed reduction with hydrogen (TPR-H$_2$) was carried out using ChemiSorb 2750 chemisorption analyzer (Micromeritics, USA) equipped with thermal conductivity detector (TCD). The experiments were carried out at a heating rate of 10°C/min using a 10 vol % H$_2$/Ar mixture with a flow rate of 20 mL/min.

To calculate the amount of weakly bound Cr(VI), the catalysts were boiled in distilled water according to the method described in [34]. Chromium amount in soluble form was determined by inductively coupled plasma mass spectrometry (ICP-MS) method using Agilent 7500c spectrometer (Agilent, USA).

**Catalytic Tests**

The activity of the prepared catalysts was investigated in the reaction of isobutane dehydrogenation in a tubular quartz flow reactor with a fixed catalyst bed at 540°C. The reaction mixture (15% i-C$_4$H$_9$/N$_2$) was passed through the catalyst bed ($V_{cat} = 0.75$ mL, particle size was 0.25–0.5 mm) diluted with quartz glass...