

Cr₂O₃/Al-Al₂O₃ Composite Catalysts for Hydrocarbons Dehydrogenation Prepared from Aluminum Nanopowder

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Abstract. Aluminum nanopowder (10–150 nm) was treated hydrothermally in mild conditions (60–95 °C, at atmospheric pressure), and an aluminum-alumina composite with high porosity and specific surface area was obtained. Cr₂O₃/Al-Al₂O₃ catalysts were prepared using the aluminum-alumina composite by impregnation techniques and tested in dehydrogenation of C₄-hydrocarbons. It was shown that aluminum-alumina composites had high chemical and phase purity, specific surface area of 150–350 m²/g and the average pore size of 8–13 nm, that is favorable for application as support for catalysts. Cr₂O₃/Al-Al₂O₃ catalysts had high activity and selectivity in dehydrogenation of n- and i-butane (conversion of 44–80 mol.% and selectivity >85% at temperatures of 540–610 °C), that is comparable ones for commercial catalysts for CATOFIN, STAR processes.

INTRODUCTION

Unique properties of aluminum oxide define its wide application in different fields of production, in particular, as catalyst supports for hydrocarbon raw material reprocessing [1, 2]. As of today, there are a large number of methods of preparation of aluminum oxide: acidic precipitation of aluminates of alkali metals [3, 4]; thermochemical activation of aluminum trihydroxide [5] and others. A lot of existing approaches are technologically complex, multistage and energy consuming. In this case the obtained alumina supports should be of a phase-homogeneous character and should possess certain acid-base properties of the surface [2]. For the efficient and stable functioning of the applied catalyst the support should possess a certain homogeneous and stable structure, a phase constitution, high specific surface area and pore-size distribution providing the efficient reagent supply to active sites of the catalyst and product removal from the catalyst surface.

A new approach to obtaining aluminum oxides with preset properties consists in the use of the aluminum nanopowder (ANP), having differing dispersion and subjected to hydrothermal treatment [6–10], as a precursor. Herewith, the characteristics of alumina supports, obtained from ANP, depend on a number of factors: an ANP particle size, temperature and pressure during hydrothermal treatment, the Al:H₂O ratio, equipment used and etc. Thus, during hydrothermal treatment of industrial aluminum powders “PA-1” and “PA-2” (Russian grade, the particle sizes are 450–630 and 250–450 μm, correspondingly) in the presence of hydrogel of aluminum hydroxide followed by reactive sintering in the microwave field, alumina supports having specific surface area of ~98–182 m²/g and pore volume of 0.43–0.59 cm³/g are obtained [7]. For dehydrogenation catalyst C₃–C₄ of paraffins the authors [8] used the support based on the powder-like metallic aluminum “PA-4” (Russian grade, the average size of particles is 20–22 μm) and the product of thermochemical activation of gibbsite (the size of the particles is 9 μm) in different ratios.

Such support has specific surface of 28.6–135.7 m²/g, total pore volume of 0.26–0.91 cm³/g, at that, the pore volume of less than 0.1 μm amounts to 0.03–0.31 cm³/g. In papers [9, 10] it was suggested that dispersed aluminum should be mixed with powder-like ZrFe (the average size of the particles is 375 μm) and subsequently the mixture should be loaded into a mold and subjected to hydrothermal synthesis at 100–250 °C and corresponding pressure of the water steam. However, it has been noted that the reduction of particle sizes by an order of magnitude does not lead to a substantial increase in catalytic activity of catalysts. In most cases in order to conduct hydrothermal synthesis high temperatures and high pressures are required, owing to which the search of the methods of obtaining aluminum oxides with preset properties in milder conditions is urgent.

The use of aluminum powder having the particle size of 10–500 μm due to its higher reactivity as a precursor is of particular interest when obtaining an alumina support for heterogeneous catalysts. Earlier it was shown that during hydrothermal treatment of ANP at temperature of 60–65 °C without using autoclave equipment, that is, at atmospheric pressure, aluminum oxides-hydroxides, containing residual quantities of metallic aluminum in their structure and having specific surface of 178–328 m²/g, pore volume of 0.53–0.78 cm³/g, the average pore size of 8.6–14.8 μm [11], can be obtained, which is of particular interest in case they are used as catalysts supports. The studies in the field of application of powder-like metallic aluminum of differing dispersion for obtaining composite Al-Al₂O₃ materials of broad spectrum application are urgent and remain open. The purpose of the present paper was to study active sites and acid-base properties of the surface of aluminum oxides-hydroxides obtained by means of hydrothermal treatment of the aluminum nanopowder and subjected to subsequent thermal treatment in the temperature range of 25–1300 °C, as well as the research of the activity of chrome catalysts prepared on the basis of Al-Al₂O₃ of the composite support in dehydrogenation of C₄ paraffin hydrocarbons.

METHODS AND MATERIALS

Materials

Industrial ANP obtained by the method of electrical explosion of conductors (CJSC “Novosibirskiye nanomaterialy”, Novosibirsk), having such characteristics as the average particle size of 54±10 μm, specific surface area of $S_{sp} = 11.2 \pm 0.6$ m²/g, the pore diameter of $d_{pore} = 2-5$ μm, was used in the study.

Hydrothermal Synthesis of Aluminum Nanopowder

Aluminum oxides-hydroxides were obtained during hydrothermal treatment of ANP consisting in preparation of an ANP suspension in the distilled water, preliminary heated up to 60–65 °C, in the mass ratio of H₂O:Al=25 [12]. The prepared suspension was continuously stirred. After a certain induction period (3–5 min) ANP oxidation took place, which was accompanied by the process of spontaneous heating of the suspension up to $T = 92-97$ °C accompanied by intensive hydrogen release. After reaction the water excess was removed by the decantation method, and the reaction products were dried up in the air at room temperature. Thermal treatment of aluminum oxides-hydroxides was conducted in the muffle furnace in the air in the temperature range of 150–1300 °C at a heating rate of 10°C/min and subsequent soaking of the sample at a preset temperature during one hour.

Preparation of Cr₂O₃/Al-Al₂O₃ Catalysts

A chrome-alumina catalyst was prepared by the method of incipient wetness impregnation of the preliminary molded Al-Al₂O₃ support with the solution of chromic acid (chemically pure, Vecton, Russia) and potassium nitrate (chemically pure, Vecton, Russia). The estimated amount of the components amounted to 2 % wt. of K₂O and 20 % wt. of Cr₂O₃. The impregnated granules were dried at 95 °C during 4 h and calcined at 700 °C during 4 h.

Characterization of the Support and the Catalyst

Thermal analysis (Differential scanning calorimetry and thermogravimetric analysis) was conducted using the device of synchronic thermal analysis “STA 449 F1 Jupiter” conjugated with the gas mass-spectrometer “QMS 403 Aeolos” (NETZSCH-Geraetebau GmbH, Germany) when heating the sample in the air at a heating rate of 10 K/min. The study by the method of scanning electron microscopy (SEM) was conducted using the system “Quanta 200”

having electron and focused beams. The study of the porous structure of samples was carried out by the method of low-temperature nitrogen adsorption using the “TriStar 3020” analyzer (Micromeritics, USA). Fourier-transform infrared spectroscopy (FTIR) of the obtained products of hydrothermal synthesis was conducted using the IR-Fourier spectrometer “Nicolet 6700” (Thermo Scientific), in the mode of attenuated total reflection (ATR) in the range from 400 to 4000 cm^{-1} . Acid-base properties of the samples’ surface were measured by the method of pH-metry by means of the ion meter “ITAN” when using the suspension of aluminum oxides-hydroxides in the distilled water (pH=5.6–6.0).

Catalytic activity of catalysts was studied under dehydrogenation of n-butane (99.9 vol.%) and isobutene (99.9 vol.%) at 540–610°C in a fixed-bed quartz reactor with the inside diameter of 16 mm. The weight of the sample was 1 g. A chromia-alumina catalyst of the 1–2 mm fraction size was mixed with quartz glass of the same fraction in the ratio equal to 1:1. Tests were carried out at atmosphere pressure in the mixture of 22% n-butane or isobutane and nitrogen at a mixture flow rate of 44.3 ml/min (space velocity of 2670 h^{-1}). The catalytic reaction was carried out by cycles in the following sequence: dehydrogenation – 12 min, with the product gas sampled at 10th min; inert-gas flushing – 5 min; regeneration in air flow – 15 min; inert-gas flushing – 5 min, and then the cycle was repeated. The gaseous products of the reaction were analyzed on ChromatecCrystall5000.2 gas chromatograph (Chromatec, Russia) with a thermal conductivity detector, two flame ionization detectors, and a Varian Capillary Column CP Al₂O₃/Na₂SO₄ capillary column (50 m) at 130°C.

RESULT AND DISCUSSION

Characterization of the Al-Al₂O₃ Composite

As a result of hydrothermal treatment of aluminum nanopowder, we obtained loose white-colored powder, representing ~7.7 μm sized aggregates, which consist of finer particles ($d_{\text{ave}}=1 \mu\text{m}$, $\sigma_d=0.5 \mu\text{m}$) of a different shape (Fig. 1, a). The microstructure of synthesized samples is characterized by a porous cell structure having open pores (Fig. 1, b). According to the data of XRD analysis, the products of hydrothermal synthesis are: γ -AlOOH (γ -AlOOH (boehmite), Al(OH)₃), Al(OH)₃ (gibbsite) and residual metallic aluminum (Table 1).

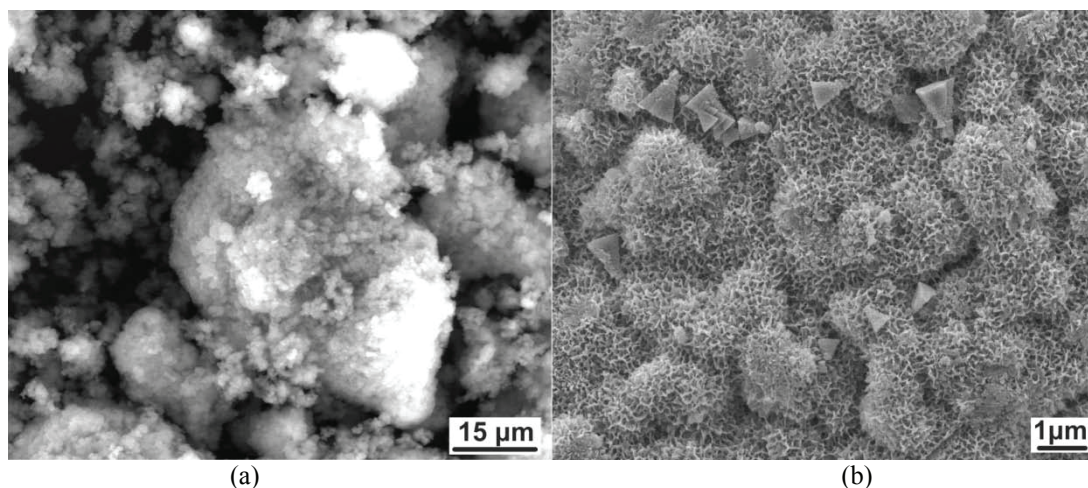
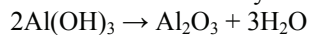


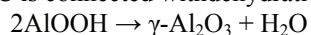
FIGURE 1. SEM images of aluminum oxide-hydroxide composite.

Figure 2 shows data obtained during the study of the products of hydrothermal treatment of the aluminum nanopowder by the method of thermal analysis when heating up to 1000 °C at a heating rate of 10 deg/min in the air flow (40 ml/min) during monitoring sample mass loss (TG-signal), heat effects (DSC-signal), as well as during mass-spectrometer monitoring of decomposition products and phase transformations. In the temperature range of 50–230 °C there is mass loss (11.8 %), accompanied by endothermic spike with maximum at temperature of 94 °C. In this temperature range the elimination of physically adsorbed water was detected by gas mass-spectrometer ($m/z=18$ signal). In the temperature range of 230–460 °C there is sample mass loss by 12.5 % accompanied by two

endothermic effects with maximums at 264 and 417 °C, as well as by the water elimination. The first of the two spikes is associated with the phase transformation of aluminum trihydroxide (gibbsite) into aluminum oxide:



A broader peak with maximum at 417 °C is connected with dehydration of pseudo-boehmite into $\gamma\text{-Al}_2\text{O}_3$:



The presence of phases of $\text{Al}(\text{OH})_3$ and AlOOH in the products of hydrothermal treatment of ANP was also revealed by the XRD analysis (Table 1).

TABLE 1. Properties of Al- Al_2O_3 composite

Sample	Temperature of calcination (°C)	Phases	Volume percent (%)	S_{BET} (m ² /g)	V_{pore} (cm ³ /g)	pH _{lis}	ΔpH
Al-25	25	Al	40	243	0.53	5.9	0.16
		$\gamma\text{-AlOOH}$	59				
		$\text{Al}(\text{OH})_3$	~1				
Al-150	150	Al	50	251	0.56	5.9	0.11
		$\gamma\text{-AlOOH}$	49				
		$\text{Al}(\text{OH})_3$	~1				
Al-250	250	Al	15	297	0.65	6.0	0.02
		$\gamma\text{-AlOOH}$	85				
Al-400	400	Al	7	328	0.78	6.1	0.35
		$\gamma\text{-Al}_2\text{O}_3$	93				
Al-700	700	Al	5	256	0.76	6.4	0.37
		$\gamma\text{-Al}_2\text{O}_3$	95				
Al-900	900	Al	4	152	0.67	6.6	0.56
		$\delta\text{-Al}_2\text{O}_3$	96				
Al-1300	1300	Al	3	6.5	0.23	7.8	1.91
		$\alpha\text{-Al}_2\text{O}_3$	97				

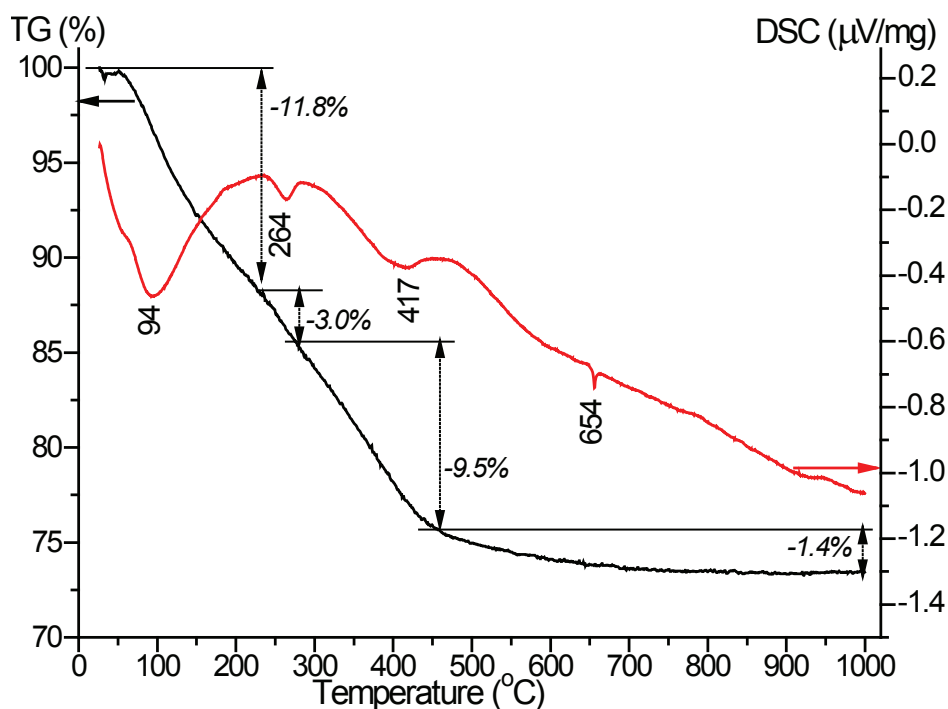


FIGURE 2. Results of thermal analysis of Al- Al_2O_3 composite.

In the temperature range of 450–1000 °C there is merely trivial loss of sample mass – 1.4 %. At temperature of 654 °C there is an endothermal effect conditioned by aluminum melting which agrees with XRD data and confirms the presence of the residual number of metallic aluminum in the structure of the oxide material. Due to intensity of this spike the calculation was conducted, according to which the content of metallic aluminum in the product of hydrothermal treatment of aluminum nanopowder amounts to ~ 2 %, which is in good agreement with the data of XRD analysis.

Specific surface area and pore volume for prepared samples are presented in Table 1. The increase of both S_{BET} and pore volume takes place with the increase in the temperature of calcinations from 25 to 400 °C. Decrease of S_{BET} from 328 to 256 and 152 m²/gis observed with increasing temperature of calcination up to 700 and 900 °C, respectively. The sample, treated at 1300 °C, has S_{BET} of 6.5 m²/g, which is associated with the presence of α -Al₂O₃ in the structure of the sample.

Acid-base properties of the surface of Al-Al₂O₃ composite, calcined at different temperatures, were determined by the pH measurements and FTIR. In Fig. 3a there are time variation curves of pH of the aqueous suspension of synthesized samples. It is visible that the most dramatic change of pH is observed in the initial period (initial 60 seconds) of the contact of water with the sample surface. As to samples, subjected to thermal treatment at 25 and 150°C, there is not any significant variation of pH of the suspension, which is connected with predominance of the boehmite phase in their structure. The most drastic change of pH of a basic nature is observed in samples containing aluminum oxide modifications, the formation of which is in the temperature range of 400–1300 °C. This fact indicates that acid-base properties of the systems of Al-400, Al-700, Al-900 and Al-1300 samples are defined by Lewis centers able to interact with water followed by its dissociation.

During the first minute of contact of water with the sample, significant changes of pH take place; proceeding from this time of contact of water with the sample surface, when it is possible to fix pH of the solution quite reliably, the first 70 seconds were chosen. The change of pH of the aqueous suspension during kinetic curves processing were represented as the following difference: $\Delta\text{pH}_{70} = \text{pH}_{70} - \text{pH}_{\text{H}_2\text{O}}$ (Table 1).

A subsequent trend of the curves is the evidence of a smooth change of pH of the systems under study up to establishment of the sorption-electrochemical equilibrium characterized by the pH magnitude, corresponding to pH of the isoionic state (pH_{iis}) of samples' surface. During interaction of water with the surface of aluminum oxides-hydroxides, pH_{iis} of the suspension changes from the average acidic value ($\text{pH}=5.9\text{--}6.1$), through the subacid one ($\text{pH}=6.4\text{--}6.6$) up to the weak-basic one ($\text{pH}\sim 7.8$) (Table 1). Hence, with the increase of the temperature of calcination, the suspension acidity and, consequently, the surface acidity of samples, calcined at different temperatures, reduces.

According to the results of FTIR two basic regions of absorption are revealed in the sample spectra: low-frequency and high-frequency. Oscillations of the Al-O bond correspond to a low-frequency region of 480–830 cm⁻¹ [13-15]. A high-frequency region of 3100–3740 cm⁻¹ responds to oscillations of surface OH-groups and oscillations of OH-groups of the water adsorbed on Lewis acidic centers representing incompletely coordinated aluminum atoms. On the obtained spectra of all samples under study an absorption band (a.b.) of ~ 3740 cm⁻¹, justifying the presence of isolated OH-groups on the surface, was discovered.

Absorption bands of 3661 cm⁻¹, 3330 cm⁻¹, 3100 cm⁻¹, present on spectra of Al-150 and Al-250 samples, belong to oscillations of OH-groups [15]. An OH-group connected with one cation of Al³⁺ was discovered in the spectrum of the Al-1300 sample. Absorption bands of 840 cm⁻¹, 735 cm⁻¹, 620 cm⁻¹, 480 cm⁻¹ correspond to oscillations of the Al-O bond [13-15]. The analogy of absorption bands in spectra of Al-150 and Al-250 samples is explained by the presence of the same phases in the composition. Al-400, Al-700 and Al-900 samples have absorption bands of 550 cm⁻¹ and 830 cm⁻¹ in their spectra indicating the presence of the Al-O bond on the sample surface. An absorption band of 3530 cm⁻¹ present in the spectra of Al-400, Al-700 and Al-900 samples corresponds to the oscillation of the bond of OH-groups undisturbed by a hydrogen bond.

It was determined that at low temperatures of aluminum oxides-hydroxides calcination (up to 400 °C) acidic centers prevail on sample surface; as far as the calcination temperature rises, the ratio of acidic and basic centers changes towards basic ones. As shown in Fig. 3b, the intensity of absorption bands of surface OH-groups reduces with the rise of calcination temperature in the whole range of temperatures under study. IR-spectra of samples ranging from Al-400 to Al-1300 differ significantly from spectra of Al-150 and Al-250 samples owing to a different phase composition [11]. In comparison with Al-150 and Al-250 samples, Al-400, Al-700, Al-900 and Al-1300 samples do not have an absorption band of 1070 cm⁻¹ responsible for deformation oscillation of the Al-OH bond (Fig. 3, b).

When comparing acid-base properties of the surface among obtained modifications of aluminum oxide, it was revealed that Al-400 and Al-700 samples, which contain a γ -Al₂O₃ modification in their composition, display

predominantly acidic properties. Time variation curves of pH of the aqueous suspension of Al-4 and Al-5 samples are evident of predominant presence of Lewis acidic centers representing incompletely coordinated aluminum atoms formed during dehydration. Thus, aluminum atoms, located on the surface of oxides, accept electron pairs from hydroxyl groups of water molecules, thus saturating the aqueous suspension with protons, which, in their turn, condition the increased acidity. As is seen from Table 1, the most dramatic change of pH_{susp} from faintly acid to faintly basic is characteristic for the Al-1300 sample. Thus, the structural-phase transformation leads to transition of Lewis acids to Bronsted bases leading to an increase of a coordination number of aluminum and a change of the crystallographic type of the lattice.

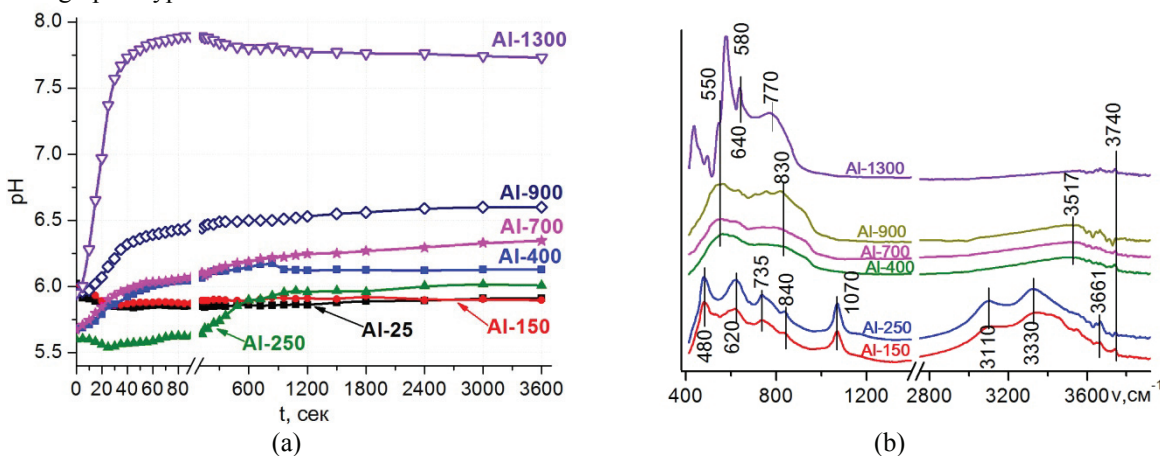


FIGURE 3. pH measurements of aqueous suspension of Al-Al₂O₃ composite (a) and IR-spectra of Al-Al₂O₃ (b) composite, calcined at different temperatures.

Characterization of the Cr₂O₃/Al-Al₂O₃ Catalyst

The Al-700 sample was chosen as a support for the synthesis of a chrome-alumina catalyst, since the γ -Al₂O₃ phase is dominant in its structure; in addition, this support possesses optimal texture characteristics (S_{BET} , pore volume and pore size distribution) to be used as a support. The isotherms of N₂ adsorption-desorption and pore size distributions for the Al-Al₂O₃ support and the Cr-containing catalyst are presented in Fig. 4. The presence of a hysteresis loop on isotherms of N₂ adsorption-desorption for both the support and the catalyst is indicative of a mesoporous structure. The Al-Al₂O₃ composite support has pores of 3–20 nm with maximum of pore size distribution at ~8 nm (Fig. 4, b). The Cr₂O₃/Al-Al₂O₃ catalyst has S_{BET} =122 m²/g, the pore volume of 0.38 cm³/g and the same pore size distribution, which indicates homogeneous distribution of an active component on the support surface.

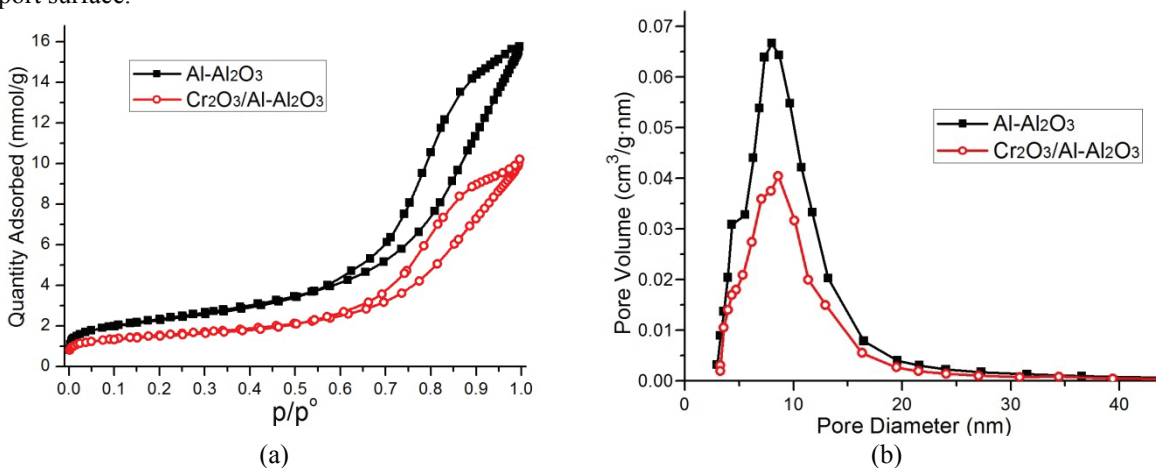


FIGURE 4. Isotherms of N₂ adsorption-desorption (a) and pore size distributions (b) for Al-Al₂O₃ composite support and Cr₂O₃/Al-Al₂O₃ catalyst.

Catalytic Properties

The catalytic properties of a catalyst at 540–610 °C are presented in Fig. 5. Catalytic activity was studied in conditions comparable to [16]. The conversion of n-butane increases from 46.1 to 77.5 % with the temperature rise from 540 to 610 °C, while a decrease of selectivity of corresponding olefins from 95.8 to 82.5 % takes place. In this temperature range the yield of butylenes and butadiene is 44–64 %. The activity of the $\text{Cr}_2\text{O}_3/\text{Al}-\text{Al}_2\text{O}_3$ catalyst in dehydrogenation of isobutane is same. The increase of conversion from 44.1 to 81.6 % takes place with the temperature rise from 540 to 610 °C. The yield of isobutylene is 43.2–74.4 %, which is higher in comparison with that of dehydrogenation of n-butane. It is associated with high selectivity of this catalyst during dehydrogenation of isobutane into isobutylene of 91.5–97.2 %. Comparison with catalytic results from [16] is shown in Fig. 5. The prepared catalyst has high activity and selectivity in dehydrogenation, which is comparable with that of industrial catalysts [16, 17].

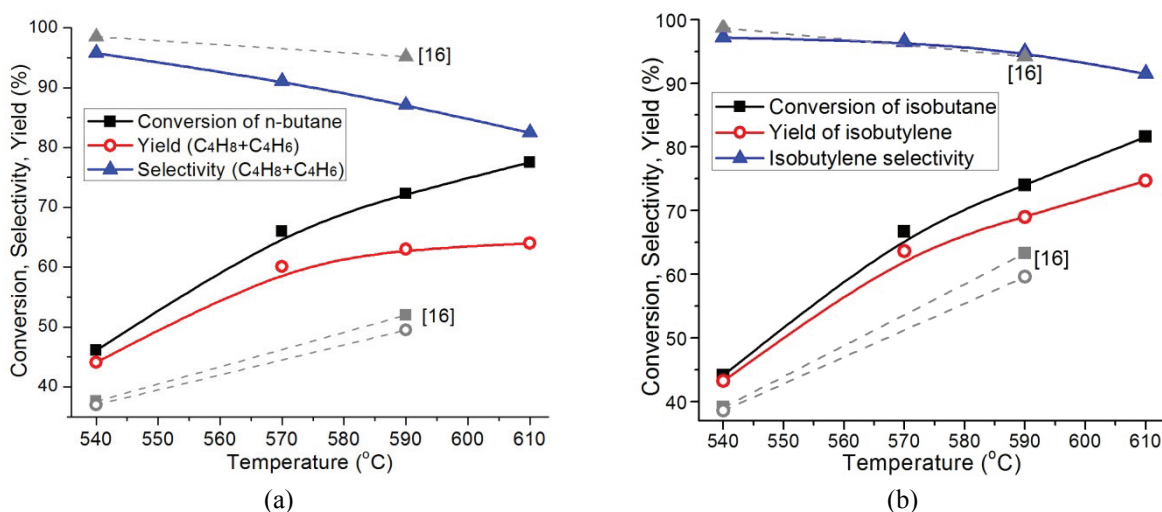


FIGURE 5. Catalytic properties of $\text{Cr}_2\text{O}_3/\text{Al}-\text{Al}_2\text{O}_3$ catalysts and catalyst from [16] in dehydrogenation of n-butane (a) and isobutane (b).

CONCLUSION

Thus, the method of thermal analysis has shown that in order to obtain an alumina support the temperature of thermal treatment is to be not less than 450 °C, that is, the temperature sufficient for completion of main phase transitions of aluminum hydroxides into alumina. The method of thermal analysis and XRD prove the presence of the residual metallic aluminum in the structure of synthesized aluminum oxides-hydroxides. According to the data of pH measurements and FTIR it is established that predominantly acidic properties are revealed by $\text{Al}-\text{Al}_2\text{O}_3$ composite at treatment temperature of 400–700 °C, which contain the $\gamma\text{-Al}_2\text{O}_3$ modification in its composition and have predominantly Lewis acidic centers on the surface. The studies of the catalytic activity of catalysts in dehydrogenation of n- and isobutane have shown that catalysts are characterized by high activity and selectivity.

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