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Synthesis of Supports for Reforming Catalysts

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Abstract—The formation of surface defects in γ-Al_2O_3 obtained by pseudoboehmite calcination and plasticized with monobasic, dibasic, and tribasic organic acids is reported. The efficiency of catalysts in reforming reactions depends on the defectivity of the support.

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The active phase or reforming catalysts forms via the strong interaction between the active component precursor and surface groups and defects of γ-Al_2O_3 [1]. These effects can be controlled by purposeful formation of surface defects in the crystal structure of alumina.

Here, we report the synthesis of highly defective γ-alumina with preset physicochemical properties as a support for reforming catalysts.

The defectivity of a finished support is predetermined by the aluminum hydroxide plasticization, modification, and calcination stages. Calcination is usually preceded by plasticization using mineral and/or organic acids. In this article, we report the effect of aluminum hydroxide plasticization with monobasic, dibasic, and tribasic organic acids on the defectivity of γ-Al_2O_3.

EXPERIMENTAL

Samples to be examined were prepared from pseudoboehmite obtained by continuous cold precipitation from a sodium aluminate solution with nitric acid. AlOOH was plasticized by treating it with solutions of acetic acid (sample 1), oxalic acid (sample 2), and citric acid (sample 3). The plasticized material was shaped into extrudates (d = 1.5 mm), dried at 120°C, and calcined at 520°C. The amount of acid taken for plasticization was 10 wt % of the calcined Al_2O_3. The reference sample was pure pseudoboehmite not treated with an acid (sample 0).

Next, calcined Al_2O_3 was loaded with 0.5 wt % platinum from an H_2PtCl_6 solution combined with dilute solutions of hydrochloric and acetic acids. The resulting catalysts were dried at 120°C and were calcined at 500°C in flowing dry air.

Thermogravimetric analyses were carried out on a Netzsch STA 449 C thermal analyzer in a flowing 20 vol % O_2 + Ar mixture at a heating rate of 10 K/min. The gaseous products were analyzed using a QMS 403 C Aeolos quadrupole mass spectrometer coupled with the thermal analyzer.

The effective helium density of the samples was measured with an AccuPyc 1330 automated helium pycnometer (Micromeritics). The accuracy of density measurements for the given set of samples was ± 0.002 g/cm^3.

X-ray diffraction patterns were obtained on a DRON-3 diffractometer using CuK_α radiation with a β filter.

The catalysts were tested in the model reaction of n-heptane reforming, which was carried out in an isothermal plug-flow reactor at an elevated hydrogen pressure, and the rate constants of the main reactions of n-C_7H_{16} (aromatization, k_{arom}; cracking, k_{crack}) were calculated. The aromatization selectivity (S) was determined as the $k_{arom}/k_{overall}$ ratio, where $k_{overall}$ is the overall rate constant of n-C_7H_{16} conversion. The integrated criterion of activity in the desired reaction was the average specific toluene formation rate ($g_{toluene}\ g_{Cat}^{-1}\ h^{-1}$) in the temperature range of 460–520°C.

RESULTS AND DISCUSSION

During acid plasticization, aluminum hydroxide decomposes partially to yield basic aluminum salts, which are likely located at the places of contact between primary pseudoboehmite particles on the surface [2].

The amount of an acid taken for plasticization was less than 2% of the stoichiometric amount necessary for the complete conversion of the hydroxide into basic salts. According to X-ray diffraction data, the noncalcined samples were the pure pseudoboehmite phase.

The oxidative calcination of the samples was performed under thermogravimetric conditions. Figure 1 presents the DTG curve and mass spectrometric CO, CO_2, and H_2O profiles for sample 2 (plasticized with oxalic acid). The DTG curve shows a minimum at

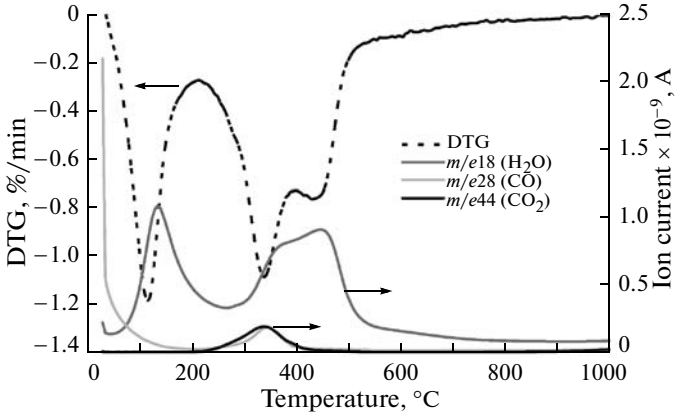

Fig. 1. DTG curve and mass spectrometric profiles of the heat treatment products of sample 2.

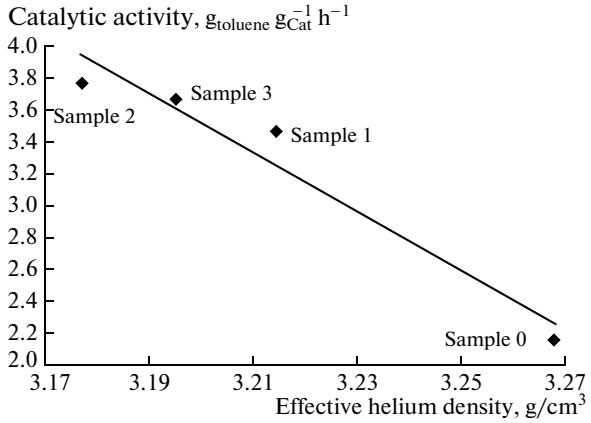

Fig. 2. *n*-Heptane reforming activity of the catalysts versus their effective helium density.

110°C, which is due to the release of adsorbed and capillary-condensed water, and two minima at higher temperatures. The first of them, occurring at 330°C, arises from the decomposition of organic aluminum salts yielding CO, CO_2, and H_2O. The second (430°C) is due to dehydration in the phase transition $AlOOH \longrightarrow Al_2O_3$ [3].

Thus, the oxidative treatment causes the complete decomposition of the organic salts on the surface of the primary aluminum hydroxide particles even at 520°C, yielding the pure γ-Al_2O_3 phase.

Under the thermohravimetric conditions, the oxide phase forms frontally, propagating from the periphery to the center of the primary particles. The order of the weight loss minima in the DTG curve indicates that the organic salts are localized mainly on the surface of the primary AlOOH particles. As a consequence, the "burnup" of the organic salts causes the formation of anionic vacancies and defects in the surface layers of alumina. The defects are likely pentacoordinated Al^{3+} ions, which are strong Lewis acid sites [4].

Earlier, we revealed the effect of the nature of the plasticizing acid on the effective helium density (ρ_{He}, g/cm^3) of alumina. This effect can be viewed as a qualitative criterion of the defectivity of the support [5]. It was hypothesized that there is a correlation between ρ_{He} and the strength of the plasticizing acid: the stronger the acid, the stronger the structural effect that it exerts [6].

As the defectivity of the Al_2O_3 crystallite surface increases, ρ_{He} decreases markedly. After the supporting of platinum, the defects serve as centers of the formation and stabilization of catalytic reforming sites [6, 7]. The strong interaction between the metal and the surface defects of γ-Al_2O_3 yields ionic platinum species, significantly enhancing the catalytic activity (Fig. 2).

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