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The synthesis and investigation of the reforming catalysts for the reduced aromatics content gasoline obtaining

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Abstract

The paper presents the results of the carrier acidity impact studying on the Pt-Re/Al_2O_3 catalytic properties in gasoline reforming. The Pt-Re/Al_2O_3 catalyst preparation based on the superacidity carrier in consequence of the presence of promotor - the bayerite phase of aluminum hydroxide resulted in the н-C_7 predominat cracking to C_3-C_6 light paraffins. The obtained catalyst allows to produce the reduced aromatics content reformed gasoline (55%wt).

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Keywords: catalytic reforming; Pt-Re/γ-Al2O3 catalysts; surface acidity; aromatics

1. Introduction

A reduction in the aromatics content including benzol is considered to be an important task in the process of up-to-date engine fuels manufacturing [1]. Considering that a large amount of benzol contained in gasoline is accounted for reformat, the reduction in the aromatics especially in reformate without octane number loss becomes the high-priority task. The catalytic properties of the Pt/γ-Al_2O_3 system are determined by interacting force of the active component precursor with the carrier; the interaction depends not only on the precursor chemical composition but on the surface adsorption centers nature [2-8]. The γ-Al_2O_3 adsorption centers are represented by hydroxyl groups and Lewis acid sites (LAS). The relative oncentration of functional groups on the alumina surface and their force are identified to a great extent by the carrier phase homogeneity.

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The objective of this research is to study the carrier surface acidity impact on the catalytic properties of the Pt-Re/γ-Al_2O_3 reforming catalysts active phase.

2. Experimental

2.1. Carriers

The industrial aluminum hydroxide was obtained at the interaction of the $NaAlO_2$ and HNO_3 solutions by the continuous sedimentation method at the temperature of 33-35°C and pH 8.2-8.4 at ZAO "The Industrial Catalysts" of Rjazan (AlOOH-1) and at OAO "Angarsk Catalyst and Organic Synthesis Plant" (AlOOH-2). AlOOH-1 was used in the form of mass with humidity of 75%wt, AlOOH-2 hydroxide was additionally dried in the spray drying oven to obtain the powder having a humidity of 22%wt. The impurities content of aluminum hydroxide corresponds to Na_2O – 0,012 % wt and Fe_2O_3 – 0.004 %wt. The 0.3 % wt. Zr from $ZrO(NO_3)_2 \cdot 2H_2O$ was added into aluminum hydroxide at the peptizing stage by the acetic and oxalic acids (acid module and mole of acid/mole Al_2O_3 accordingly). The formed carrier was dried in the drying oven at the temperature of 120°C and was calcinated in the muffle furnace under dehumidified air supply at the temperature of 630°C.

2.2 Catalysts

The catalysts were prepared by H_2PtCl_6 and $HReO_4$ carrier impregnation by the procedure presented in the paper [9]. The amount and concentration of solutions were chosen on order to provide 0.25%wt Pt and 0.3 %wt Re content in the prepared catalyst. The catalysts were dried at the temperature of 120°C and calcinated for 5 hours in a glass reactor at atmospheric pressure in a flow of dry air upon temperature elevation to 500 °C and held at this temperature for 1 hour.

3. Methods

3.1. Thermogravimetric analysis (TGA)

The thermal decomposition process was studied by TGA method. The experiments were carried out on the STA-449C (Netzsch) thermal analyzer with a 10 %vol. O_2/Ar gas mixture up to the temperature of 1000°C. The heating rate corresponded to 10°C/min.

3.2. X-ray diffraction (XRD)

The XRD was carried out on the D8 Advance X-ray diffractometer in the monochromated Cu-k_α radiation. The obtained diffractograms interpretation was conducted by means of the ICDD database PDF-2 version of 2006. The diffraction spectra processing was performed using the EVA (Bruker) and Origin 6.0. Semi quantitative analysis was carried out with the help of the EVA. The given analysis is conducted using the relative intensities data and also using the alumina numbers values of the powder diffraction database cards. The a,b,c lattice parameters were estimated for pseudoboehmite by Rietveld method using the Pseudo-Voigt approximating function. The crystallite size was identified according to the Selyakov-Scherrer formula.

3.3. S_{BET}

Isotherms of nitrogen adsorption-desorption were obtained at 77.4 K on the Sorptomatic-1900 apparatus by CarloErba. The specific surface calculations were carried out in the range of nitrogen vapors equilibrium relative values at P/P_0 = 0.05-0.33 by the adsorption isotherm using the BET method (S_{BET}). The cumulative adsorption pore volume (ΣV) was defined by nitrogen adsorption value at P/P_0 = 0.996, the adsorbed nitrogen density was taken to be equal to the normal fluid density (the molar volume of the liquid N_2 reaches 34.68 sm^3/mole).