

N-HEXANE ISOMERIZATION OVER Pt, Pd CATALYSTS SUPPORTED ON MIXES of HY+ γ -Al₂O₃

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Received Date: July 22, 2014

Abstract

In this study, a decationized form of faujasite zeolite HY and mixes of this zeolite with alumina γ -Al₂O₃ of various ratios have been used as carriers for catalysts 0.35 wt.% Pt and 0.80 wt.% Pd. Physico-chemical characteristics of the obtained catalysts were determined by methods of BET, SEM, EDS, TEM, XRD, TPR, H₂ pulse chemisorption (HPC), and TPD. Activity of the catalysts for n-hexane isomerization was tested at the temperature range 225-450°C and two values of pressure 0.1 and 0.7 MPa. In feed flows the molar ratio hydrogen: hydrocarbon was 5.92 with the concentration of n-hexane as 9.2 mol.%. It has been found that the value of optimal ratio γ -Al₂O₃: HY was 2.5:1. The effect of the mixed carriers is included in the reduction of acidity and metal crystallites, increase of metal dispersity and reducibility of catalyst and the improvement of catalyst stability. At 0.7 MPa the activity, selectivity, and stability of catalysts have been shown to be significantly higher than those obtained at 0.1 MPa.

Keywords: HY, Mixed Carrier, N-Hexane Isomerization, Pd, Pt, γ -Al₂O₃+HY

Introduction

Currently, the standardized criteria play an important role in the orientation of the petroleum refining toward not only the product usages but also the environmental impacts. The Euro-4 and Euro-5 standards require the significant reduction of aromatics and the maximum benzene concentration of 1 vol. % in gasoline. The United States and Europe define the limit of aromatic hydrocarbons in gasoline not to exceed 25 vol.%, and from the beginning of 2011, when the standard Mobile Source Air Toxics (MSAT II) is effective, the concentration of benzene must be limited to 0.62 vol.% [1].

The problem becomes more trouble when lead containing additives, the most effective and cheap ones, have been completely eliminated, and MTBE and other oxygenated compounds also have been shown to belong to poisoning substrates and their utilization either is forbidden or must be reduced significantly. Thus in the present petroleum refinery the task of increasing octane number of gasoline lies on catalytic processes, such as cracking, reforming, alkylation, and isomerization. However, to reduce the content of aromatic hydrocarbons, reaction of light paraffin isomerization process must play an important role because by this way octane number of gasoline can be increased without rising up the concentration of aromatic hydrocarbons. In this aspect, the isomerization process should be considered as a modern and progressive industrial one.

Various generations of isomerization catalysts have been developed. The first generation was liquid Lewis acid; the following generation was included in solid acids (amorphous and crystalline silica-alumina), and at present time in utilization one have mainly bi-functional catalysts containing noble metals supported on various acidized (chlorinated) carriers, including zeolites. The advantage of the last kind of catalysts is

included in the balance between acidic and red-ox functions. Pt/zeolites catalysts are able to be operated at high temperatures (525 - 575 K) with good stability and long lifetime [2]. Catalysts Pt on chlorinated alumina express high activity at low temperatures (400 - 450 K), but very sensitive to impurities (poisons) [3]. Pt is a very expensive and scarce metal. Therefore, more and more current studies have been taken in order either to decrease Pt content or to replace it in industrial catalysts.

Palladium is an interesting alternative to platinum. Palladium is cheaper than platinum and the choice of Pd as active component is determined on the basis of its performance and stability. Pd-H₄SiW₁₂O₄₀ supported on SiO₂ and Pd-WO₃/ZrO₂ was found to be active in skeletal isomerization of alkanes [4].

Pore size of zeolite contributes part to defining the selectivity of catalysts on reaction products. For zeolite HY its pore size is favorable for forming two-branched molecules of iso-hexane from n-hexane [5]. Nevertheless, with high acidity, zeolite HY also enhances the cracking process leading to the reduction of reaction efficiency. Aluminum oxide is a good carrier for isomerization reaction, but it expresses relatively weak acidity. It is hopeful that the combination of two types of the mentioned above carriers could create good carriers characterized by appropriate properties for the reaction. Mixed carriers should be characterized by mild acidity, high value of specific surface area, and appropriate pore size for isomerization of low n-paraffin to branched iso-paraffins with high octane number.

The purpose of this work is to study the influence of mixed carriers γ -Al₂O₃+HY on physico-chemical properties and activity of Pt, Pd-supported catalysts in order to create highly active contacts for n-hexane isomerization at normal pressure and at 0.7 MPa.

Experimental

Aluminium oxide was prepared by precipitating 5% solution of ammonia with solution of Al(NO₃)₃·9H₂O up to pH 8-9. The precipitate was aged 12 h and the product Al(OH)₃ then was washed by distilled water, dried and calcined at 500 °C to receive γ -Al₂O₃. Mixed carriers were obtained by mechanical mixing of Al(OH)₃ with HY, then calcined at 500 °C for 6 h. Active phases 0.35 wt.% Pt and 0.80 wt.% Pd were supported on the carriers by impregnation method, then dried, calcined at 400 °C for palladium and 500 °C for platinum catalysts during 3 h. The procedure of catalyst preparation was described in detail in articles [6, 7]. Before reaction, the platinum catalysts were reduced at 500 °C, and palladium catalysts were reduced at 400 °C during 2 h in a hydrogen flow. Catalysts were assigned as follows: Pd/Al-HY(3:1) means 0.8 wt.% Pd on mixed carrier γ -Al₂O₃+HY with ratio Al₂O₃: HY = 3:1. By the same way Pt/Al-HY(2.5:1) means 0.35 wt.% Pt on mixed carrier γ -Al₂O₃+HY with ratio Al₂O₃: HY = 2.5:1.

Physico-chemical properties of the catalysts were characterized by some modern methods. Specific surface area of catalyst was obtained by Brunauer, Emmett, and Teller (BET) using Nova Station A with the lower limit is 0.01 m²/g, N₂ as the adsorption gas, saturated vapor pressure of 765 mmHg, temperature of the chamber is 77.35K, and volume of cylinder is 0.07645 cm³. The morphology and elementary distribution on the catalyst's surface were discovered by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) using FE-SEM Jeol 7401. Transmission Electron Microscopy (TEM) was utilized not only to analyze the morphology but also to measure the metal cluster on the surface and inside the pores with high resolution. The X-ray Diffraction (XRD) patterns of the catalysts were carried out using a Bruker D8 Advance at 35 kV, 30 mA, and CuK _{α} radiation. The XRD measurements were carried out at 2 θ from 5° to 40°. The red-ox property was investigated by Temperature-Programmed Reduction (TPR). The dispersity and metal cluster size were studied by Hydrogen pulse chemisorption (HPC). Both TPR and HPC were conducted using Altamira Ami-200. The Temperature

Programmed Desorption (TPD) of adsorbed ammonia on the acid sites was carried out using nitrogen as a purge gas.

Activity of the studied catalysts was tested in a micro-flow reactor at following conditions: temperature range 225 - 450 °C; pressure 0.1 MPa and 0.7 MPa; mol ratio of H₂:n-hexane 5.92; n-hexane concentration in feed 9.2 mol%; feed flow 7.5 l/h; catalyst weight 1.5 g. The reaction mixture was analyzed on the GC Agilent Technologies 6890⁺ with a FID detector, and DB 624 column with 30 m of length and 0.32 mm of outer diameter were used.

Result and Discussion

The XRD pattern of sample Pd/ γ -Al₂O₃ (line 1, Fig. 1a) contains very weak peaks indicating the existence of amorphous state of γ -Al₂O₃. XRD patterns of Pd- and Pt-containing catalysts on zeolite HY and on mixed carriers are similar, containing characteristic peaks of zeolite HY at 2 θ = 6.5; 10.5; 12; 16; 19; 21; 24; 27.5; 32 degrees. Compared to catalyst Pd/HY, characteristic peaks of HY in mixed carriers are weaker. As seen in Table 1, the value of HY crystals size calculated according Scherrer formulae [8] at peak at 2 θ = 6.5° varied in interval 28-34 nm. It is interesting to notice that in XRD patterns of all the samples any characteristic peaks of Pt, Pd, or other phases were not observed.

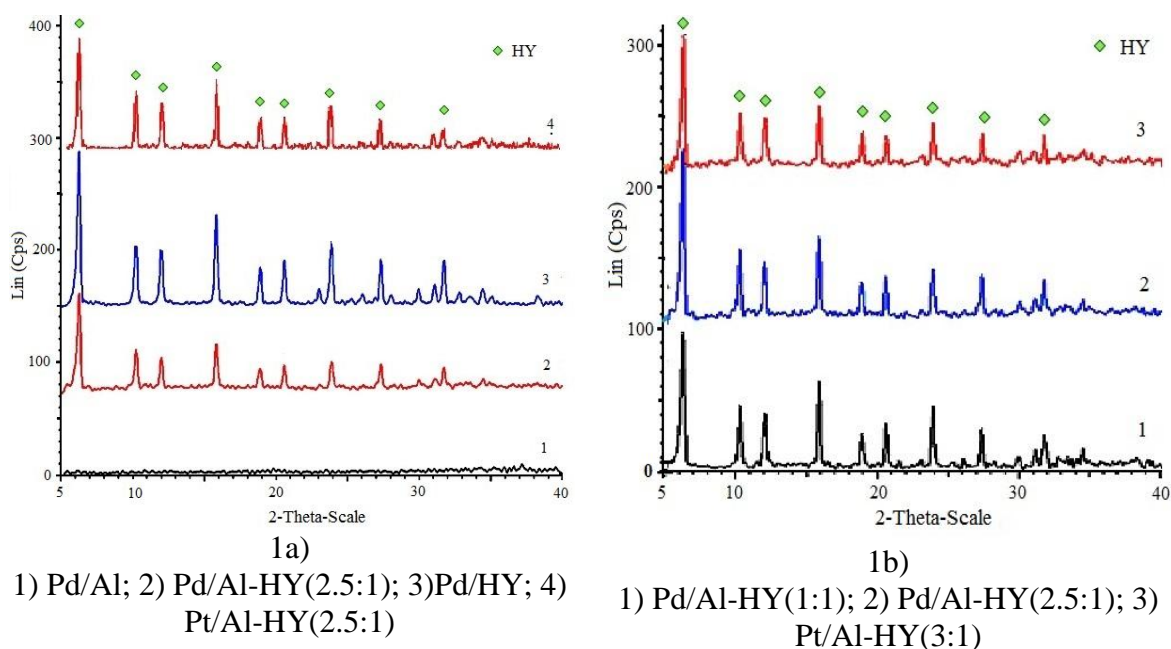


Figure 1. XRD patterns of catalysts

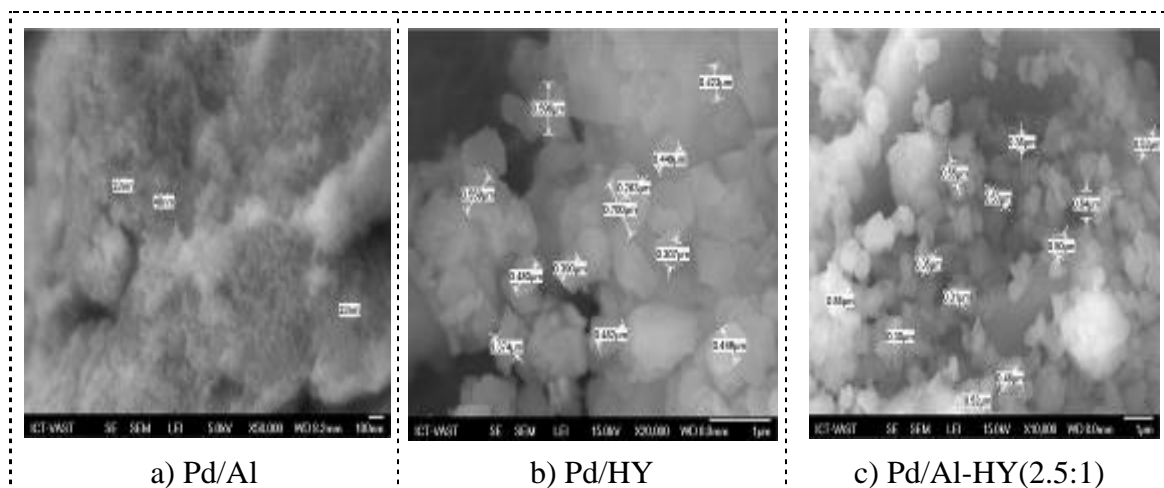


Figure 2. SEM of catalysts

SEM images (Fig. 2a) indicates that aluminium oxide in catalyst Pd/Al exists in form of fine porous cotton with particle size in the range of 200-460 nm. In catalyst Pd on HY (Fig. 2b) and on mixed carrier (Fig. 2c) zeolite crystallites are seen in the form of rectangular cube with dimension of 350 nm x (500-700) nm and 300 x (550-850) nm. In mixed carriers HY crystallites are distributed on the surface of aluminium oxide with dimension of 300 x (350-550) nm and small particles (54-80 nm).

EDS pattern (not shown) indicated that on the surface of Pd/Al₂O₃ and Pd/HY catalysts the distribution of the elements is more uniform, while on Pd/Al-HY their distribution is less uniform. Elemental composition on the surface of the catalysts are presented in Table 1.

On Pd/Al sample surface concentration of Pd has been found very high (13.4 atom%), but as it seen from Table 1 the value of cluster size of Pd was the biggest and the dispersity was the lowest. On the surface of sample Pd/HY the value of ratio Si:Al = 3, closed to that in zeolite HY (the original zeolite was (Na₈₆ [(AlO₂)₅₆.(SiO₂)₁₃₆].260 H₂O). On this catalyst the surface concentration of Pd was found sufficiently low (1.24 atom%). It is possible to distinguish three regions of the surface for sample Pd/Al-HY. In the first region the concentration of aluminium reaches 75.69 atom% and the concentration of silicon only 1.33 atom%. No palladium was seen in this region. In the second region the values of Al and Si concentrations were found 60 and 14 atom% respectively (ratio Al:Si > 4). In this region Pd has very low concentration, only about 0.73 atom%. In the third region the values of concentrations of Al and Si were found identical, approximately 33-36 atom%, and concentration of Pd in this region is about 3 atom%. From the above analysis it shows that, on the mixed carrier, Pd seems to be concentrated on the Si-rich surface, means on zeolite. It can be assumed that, in the mixed carrier, zeolite located on the surface of alumina, as confirmed by SEM data.

On TEM images (Fig. 3) the Pd and Pt dispersed particles on the surface of catalysts could be observed. The values of agglomerates size of Pd and Pt determined by measuring on TEM images and by hydrogen pulse chemisorption are identical. As seen in Table 1, the dispersity of Pd on mixed carriers is better than that on zeolite HY and particle dimension of Pd reduced and Pd dispersion improved with zeolite content. On Pd/HY the values of Pd agglomerates size and Pd dispersity are 7.3 nm and 16 % correspondingly, but on Pd/Al-HY these values are 4.2 – 6 nm and 18.69 – 27.57 %, respectively. Also on mixed carriers agglomerates size and dispersity of Pt have been determined as 2 nm and 70 %, correspondingly.

