

Hydroisomerization of a refinery naphtha stream over platinum zeolite-based catalysts

María Jesús Ramos^{a,*}, Juan Pedro Gómez^b, Fernando Dorado^a,
Paula Sánchez^a, José Luis Valverde^a

^a *Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avd. Camilo José Cela s/n, 13071 Ciudad Real, Spain*

^b *Centro Tecnología Repsol-YPF, Ctra. Nnal. V, km 18, 28931 Móstoles, Spain*

Received 5 July 2006; received in revised form 28 August 2006; accepted 28 August 2006

Abstract

In this paper, the hydroisomerization of a C7–C8 stream obtained by distillation of a refinery naphtha stream using platinum zeolites (mordenite, beta and ZSM-5) agglomerated with a binder was performed. Catalysts based on beta and ZSM-5 zeolites were more active than that based on mordenite one. With this catalyst, the catalyst activity was likely controlled by the accessibility to the active sites. The aromatics compounds present in the feed were totally converted to naphthenic compounds. In this sense, their contribution to the estimated research octane number was lower than that obtained in palladium based catalysts, where the aromatics compounds were not totally converted. Nevertheless, the estimated research octane number of the product fraction obtained using platinum catalysts was higher than that reported for palladium ones. In platinum catalysts, branched products and naphthenic compounds contributed in a higher extent to the estimated research octane number of the product fraction. © 2006 Elsevier B.V. All rights reserved.

Keywords: Hydroisomerization; Naphtha; Zeolites; Agglomeration; Catalysis; Petroleum

1. Introduction

Due to a heightened awareness of the environmental problems worldwide, there is a need of gasoline containing small quantities of compounds considered harmful to the environment or the public health such as aromatics and oxygenated compounds. Reductions of aromatics have a negative effect on the octane number that has to be compensated by other means [1].

Isomerization of long-chain *n*-paraffins appears to be an interesting alternative since provides branched molecules which possess higher octane number than linear ones. Isomerization is one of the several reactions occurring in the reforming of naphthas, which is undertaken to upgrade low octane naphtha to a higher octane effluent. Under the process conditions of reforming, other reactions could occur like aromatization (or dehydrocyclization), and dehydrogenation, with some cracking [2].

The reduction imposed on the aromatics content has a negative effect on the reforming units that use fundamentally heavy

naphtha in the range C7–C10, providing greater quantities of aromatics. Isomerization reaction constitutes the most important alternative due not only to the production of branched paraffins with high octane number but also to the fact that ring-opening reactions of aromatics compounds from reformer feedstocks are yielded. For example, cyclohexane, a benzene precursor, can be rearranged over commercial paraffin isomerization catalysts to a mixture of branched paraffins.

The industrial processes of *n*-paraffins hydroisomerization need the presence of bifunctional catalysts, which present two kinds of active or functional sites: (i) an acid function provided by zeolites, and (ii) a hydrogenating–dehydrogenating function provided by a noble metal [3–6].

The performance of this kind of catalysts has been confirmed almost exclusively by using either powders or tablet-shaped catalysts formed by simple compressing and hardening of zeolite powders. However, the high-pressure drops caused by powder catalysts in industrial reactors require that catalysts are shaped for industrialization, improving the crush strength to prevent the catalyst from breaking down into powder-like materials in commercial use. In this sense, materials like clays, oxides, etc., have been used as binders. Information regarding the influence of

* Corresponding author. Tel.: +34 926 29 53 00; fax: +34 926 29 53 18.
E-mail address: MariaJesus.Ramos@uclm.es (M.J. Ramos).

the binder on the acidity and catalytic performance of zeolites is very important for the development of industrial catalysts. Some authors have studied the influence of different binders on the catalytic performance of zeolites [7–10]. In previous works [3,4], the advantages of the bentonite as a binder were reported.

Concerning the hydroisomerization reactions, hydrocarbon binary and ternary mixtures have been tested [5,6,11]. Jiménez et al. [6] studied the hydroisomerization of a hydrocarbon feed containing *n*-hexane, *n*-heptane and cyclohexane over zeolite catalysts. Tests involving binary mixtures of these three hydrocarbons revealed that *n*-heptane was the main source of cracking products. Gopal et al. [5] reported the hydroisomerization of C5–C7 alkanes and simultaneous saturation of benzene over Pt/H-ZSM-12 and Pt/Beta. Although Pt/Beta was much more active and had better sulfur resistance, the capability of Pt/H-ZSM-12 to provide a significantly higher yield of isomers made it an attractive catalyst. In a previous work, the use of palladium containing zeolites for the hydroisomerization of a C7–C8 complex feedstock was studied [12].

The aim of this work was to study the hydroisomerization of a C7–C8 stream, obtained by distillation of a refinery naphtha stream, by using catalysts based on the following zeolites: mordenite, beta and ZSM-5, all of them agglomerated with a binder (bentonite) and impregnated with platinum. The influence of the zeolite structure was investigated and the results were compared to those previously reported for palladium catalysts [12].

2. Experimental

2.1. Catalyst preparation

Commercial ammonium zeolites, mordenite (Si/Al = 10.4), beta (Si/Al = 13.0) and ZSM-5 (Si/Al = 15.6) were supplied by Zeolyst International. The samples were calcined at 550 °C for 15 h in order to obtain the protonic form of the zeolite. The obtained samples were named to as HMOR, HBETA and HZSM-5, respectively.

Bentonite was supplied by Aldrich Chemical Co. For the agglomeration process, the protonic form of the zeolite (35 wt.%) and bentonite (65 wt.%) were mixed together and suspended in water at 60 °C for 2 h. The suspension was then dried at 120 °C overnight. After grinding and sieving, particles with an average particle size of 0.75 mm were obtained. Finally, the agglomerated zeolite was calcined at 550 °C for 15 h.

After the agglomeration process, agglomerated beta zeolite samples were ion-exchanged three times with 1 M NH₄Cl (30 ml g⁻¹). The samples with mordenite and ZSM-5 zeolites were ion-exchanged with 0.6N HCl (35 ml g⁻¹). Then, all the samples were calcined again at 550 °C for 15 h.

All the catalysts were impregnated with an aqueous H₂PtCl₆ solution. The metal concentration of the impregnating solution was calculated to yield a final Pt content of 1 wt.% in the resulting catalysts. After the impregnation process, the catalysts were calcined at 400 °C for 4 h and reduced *in situ* under a hydrogen flow of 190 ml min⁻¹ g⁻¹ at 410 °C for 4 h.

The final catalysts were firstly identified with the symbol of the metal (Pt), following by the name of the zeolite (MOR, BETA

and ZSM-5). The term “Bent” originates from the name of the binder (bentonite).

2.2. Catalysts characterization

Surface area was determined by using N₂ as the sorbate at 77 K in a static apparatus (Micromeritics ASAP 2010 adsorptive and desorptive apparatus). The samples were evacuated under vacuum of 5×10^{-3} Torr at 350 °C for 15 h. Specific total surface areas were calculated using the BET equation. Surface area measurements had an error of $\pm 3\%$.

In order to quantify the total amount of metal incorporated in the catalysts, atomic absorption (AA) measurements were performance using a SpectrAA 220FS spectrophotometer. The error of these measurements was of $\pm 1\%$.

The total acid site density and the acid strength distribution of the catalysts were measured by temperature programmed desorption of ammonia (TPDA), using a Micromeritics TPD/TPR 2900 analyzer. The samples were housed in a quartz tubular reactor and pretreated in flowing helium ($\geq 99.9990\%$ purity) while heating at 15 °C min⁻¹ up to the calcination temperature of the sample. After reducing the catalysts under a hydrogen flow, the samples were cooled to 180 °C and saturated for 15 min in an ammonia stream ($\geq 99.9990\%$ purity). The catalyst was then allowed to equilibrate in a helium flow at 180 °C for 1 h. Next, ammonia was desorbed by heating at a rate of 15 °C min⁻¹. Temperature and detector signals were simultaneously recorded. The total acidity was obtained by integration of the area under the curve. This curve was fitted using two peaks, which were classified as weak and strong acidity depending on the desorption temperature. The use of these peaks was not based on any peak assignment to a specific Brønsted or Lewis acid sites but it was a convenient way to categorize the acid strength distribution obtained by this method. The average relative error in the acidity determination was lower than 3%.

The chemisorption measurements were carried out by using a dynamic pulse technique with an argon flow of 50 ml min⁻¹ and pulses of H₂ ($\geq 99.9995\%$ purity). In order to calculate the metal dispersion, an adsorption stoichiometry of Pt/H = 1 was assumed [13]. The apparatus used was the same as that described for the TPDA. Dispersion measurements with H₂ pulses were carried out at 60 °C to avoid the spill over phenomenon [14]. Previously, the sample was pretreated by heating at 15 °C min⁻¹ in argon flow up to 250 °C and kept constant at this temperature for 20 min. Then, the sample was reduced *in situ*. Next, the hydrogen was removed by flowing argon for 30 min, the temperature being 10 °C higher than the reduction temperature. Finally, the sample was cooled to the experiment temperature in an argon gas flow. The dispersion measurements with H₂ pulses had an error of $\pm 5\%$.

2.3. Distillation procedure

A naphtha stream supplied by the company REPSOL-YPF (from Spain) was the feed to a pilot plant distillation unit (a scheme was depicted in [12]). Table 1 shows the naphtha stream composition. In order to define a specific stream to develop the

Download English Version:

<https://daneshyari.com/en/article/153795>

Download Persian Version:

<https://daneshyari.com/article/153795>

[Daneshyari.com](https://daneshyari.com)