

Effect of the metal loading in the hydroisomerization of *n*-octane over beta agglomerated zeolite based catalysts

Antonio de Lucas, Paula Sánchez, Fernando Dorado,
María Jesús Ramos*, José Luis Valverde

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

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Abstract

The hydroisomerization of *n*-octane over catalysts containing palladium and/or platinum as the hydrogenating-dehydrogenating function and beta agglomerated zeolite as the acid function was studied. A slight decrease in the strong acid density of monometallic catalysts with increasing metal content, mainly on platinum samples, was observed due to the acid sites to be partially covered by metal particles. The diameter of the metal particles in bimetallic catalysts was higher than that corresponding to the monometallic ones with the same metal content.

Catalytic results showed that the reaction scheme is influenced by the hydrogenating/acid balance. It was observed that the octane isomer yield increased with the hydrogenating/acid balance (defined as the ratio between the number of hydrogenating sites and the strong acid ones, nPd/nA and nPt/nA), then remaining constant at $nPd/nA > 0.15$ and $nPt/nA > 0.20$. In this last situation, the isomerization reaction over the acid sites was the limiting step of *n*-octane transformation, since the octane isomer yield does not depend on the metal content. *n*-Octane conversion was lower in the bimetallic catalysts than that observed in monometallic ones with the same metal content. The different conversion values would be attributed to the different interaction between the two metals in the bimetallic catalysts. A decrease of the multibranched isomers formation was observed when the palladium content increased in the bimetallic catalysts. Platinum present in these catalysts did not promote the methane and ethane formation, because its possible interaction with palladium in a bimetallic particle.

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1. Introduction

Due to a heightened awareness of the environmental problems worldwide, there is a need of gasoline containing small quantities of aromatics and olefins. As a consequence, an increase in the percentage of *iso*-alkanes with a high octane number in gasolines is required.

Isomerization of alkanes is carried out over bifunctional catalysts consisting of an acid function, provided by solid acids; i.e., zeolites, and a metallic function (noble metals). Isomerization takes place in the acid sites of the bifunctional catalyst whereas the metal provides hydrogenation–dehydrogenation capability. Both acid and metal site density are

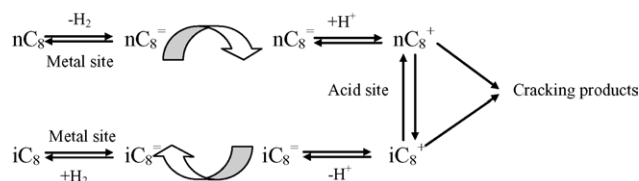
important and their proper balance is critical in determining the activity of the catalyst.

Several zeolites like mordenite, ZSM-5 and beta have been tested in alkane hydroisomerization [1–3]; however, the latter has a great industrial interest because its acidity and particular pore system: three-dimensional and interconnected channel system with 12-membered elliptical openings having mean diameters of 0.64×0.76 nm [4].

Due to the high-pressure drops caused by powder catalysts in industrial reactors, it would be necessary to pelletize the zeolite with a binder in order to obtain larger and more resistant particles and avoid meaningful pressure drops [5,6].

As the hydrogenated–dehydrogenated function in alkane hydroisomerization, several metals have been tested [2,3,6]. The metal phase dehydrogenates the alkanes into alkenes,

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

Scheme 1. Mechanism of *n*-octane isomerization.

which are protonated at the acid sites yielding carbenium ions. After rearrangements and/or scissions, these carbenium ions desorb from the acid sites as alkenes and, then, they are hydrogenated at the metal phase to yield the different reaction products [7]. This isomerization mechanism is presented in Scheme 1.

An ideal mechanism is characterized by the control of the acid function; the hydrogenation–dehydrogenation activity of the catalyst is enough to balance the acidity [8]. At high metal contents, the hydroisomerization reactions proceed through successive mono-, di- and tribranched intermediates, being cracking a secondary reaction. A catalyst exhibiting this consecutive mechanism is considered to be in balance and, in this way, an equilibrium between saturated and unsaturated species can be established. If the metal content is too high, reaction exclusively catalyzed by the metallic function like hydrogenolysis would become the main reaction [9]. In an extensive study, Guisnet [10] reported the benefits that platinum produces in zeolites. With high values of the metal/acid balance, the platinum acid zeolites are very stable, because the metal avoids deactivation by coke.

Additionally, catalytic performance of a metal catalyst may be influenced by the addition of a second metal. Lee and Rhee [11] found that Pd–Pt bimetallic interaction gives rise to enhanced sulfur tolerance while maintaining activity for the isomerization of pure *n*-hexane similar as that of monometallic Pt/H-Beta and Pd/H-Beta catalysts. Ali et al. [12] reported that the incorporation of Ir, Rh or Re enhances the activity of Pt/Al₂O₃ catalyst for the hydroconversion of alkanes.

In this work, it was investigated the hydroisomerization of *n*-octane on beta agglomerated zeolite based catalysts, containing both platinum and/or palladium. The aim was to study the influence of the metal content and how the combination of these metals in the same catalyst modified the catalytic performance in the hydroisomerization of *n*-octane.

2. Experimental

2.1. Catalyst preparation

The bifunctional catalysts used in this work consisted of H-Beta as the acid function, Pt and/or Pd as the metal function, and sodium bentonite as the binder. The physicochemical characteristics of the bentonite (Bent), H-Beta (HB), H-Beta agglomerated with bentonite (HBBent) and two bifunctional catalysts impregnated with 1.00 wt.% of metal (Pd and Pt) were given in Table 1.

Beta zeolite (Si/Al = 12.5) was supplied in the ammonium form by Zeolyst International. Calcination at 550 °C for 15 h yielded the acid form of the zeolite (HB). Sodium bentonite was supplied by Aldrich Chemical Co.

H-Beta was bound with sodium bentonite (35/65 w/w) by preparing a homogeneous aqueous suspension of both materials, under continuous agitation, and heating at 60 °C for 2 h. Then, the suspension was dried at 120 °C overnight. After grinding and sieving, particles with 0.75 mm average particle size were obtained. Finally, the agglomerated zeolite was calcined at 550 °C for 15 h.

The acid form of the zeolite was obtained by exchanging three times the Na⁺ with 1 M NH₄Cl (30 ml g⁻¹) under agitation at 80 °C for 12 h and calcined again at 550 °C for 15 h.

Metal incorporation was carried out by an impregnation technique: the sample was placed in a glass vessel and kept under vacuum at room temperature for 2 h in order to remove water and other compounds adsorbed on the zeolite. A known volume of an aqueous metal precursor solution was then poured over the zeolite. As metal precursor, H₂PtCl₆ or Pd(NO₃)₂ were used because they are commonly used in bibliography [13,14] and in the case of the palladium precursor, the use of ammoniated ion precursors could show more calcination difficulties [2,15]. Next, the solvent was removed by evaporation under vacuum. The metal content added to the catalyst was controlled by measuring the metal concentration in the impregnating solution. In this way, catalysts with 0.25, 0.50, 0.75 and 1.00 wt.% of metal were synthesized. In the case of bimetallic catalysts, a simultaneous impregnation with both precursors was employed with a total metal content of 1.00 wt.%.

After metal incorporation, 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.

Table 1
Characterization data of the raw materials and two representative samples

Catalyst	Surface area (m ² g _{cat} ⁻¹)	D _{H₂} (%)	Total acidity (mmol NH ₃ g _{cat} ⁻¹)	Weak acidity (mmol NH ₃ g _{cat} ⁻¹)	Strong acidity (mmol NH ₃ g _{cat} ⁻¹)
Bent	37		0.038	0.038	–
HB	636		0.626	0.129	0.497
HBBent	241		0.250	0.090	0.160
1.00PdBBent	233	25	0.240	0.090	0.150
1.00PtBBent	237	73	0.264	0.093	0.171

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