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Hydroisomerization of *n*-octane over platinum catalysts with or without binder

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Abstract

The catalytic performance for the hydroisomerization of *n*-octane (conversion, selectivity and yield) of sets of bifunctional catalysts based on mordenite, beta and ZSM-5 zeolites with or without a binder (bentonite) were compared. As hydrogenating–dehydrogenating function, platinum supported by impregnation (1 wt.%) was used. It was found that the activity decreased in the following order: ZSM-5 > beta > mordenite-based catalysts. A decrease in the activity of agglomerated samples, because of the neutralization of the acid sites by the binder, was expected. The activity decrease was significantly high for ZSM-5 zeolite but the opposite effect was observed for beta zeolite. The presence of aluminium extraframework (EFAL) species in the beta agglomerated sample should be the responsible of this behaviour because of a synergetic effect between these EFAL species and the structural Brönsted acid sites causing an increase of the acid strength.

The octane isomers selectivity for the agglomerated mordenite and beta samples was very similar to that in the non-agglomerated ones. ZSM-5 agglomerated sample yielded higher isomer selectivity than the non-agglomerated one. The higher neutralization of the acid sites by the binder was the responsible to that because leads to a higher concentration of carbenium ions, which provide the octane isomers. Also, the binder provided meso and macropores to the zeolite where the metal was likely located avoiding a possible pore partial blockage, with the consequently lower diffusional constraint of the reactants.

Keywords: Zeolites; Hydroisomerization; Binder; *n*-Octane

1. Introduction

The current environmental requirements are giving rise to a general reduction in both reid vapour pressure and aromatics, alkenes, sulphur and methylterbutylether (MTBE) contents, which will have a negative impact on the octane number of the gasoline pool [1]. Isomerization of long-chain *n*-alkanes appears to be an interesting alternative since provides branched molecules which possess higher octane number than linear ones. Several studies have been made in C_4–C_7 isomerization processes [1–6], however the multibranched C_8 alkanes are the most useful isomers because of their high octane number.

Many bifunctional catalysts commercially used to isomerize alkanes contain a zeolitic component in combination with a noble metal, which provides the hydrogenating–dehydrogenating function. Several investigations have been carried out to evaluate the most suitable combination of acidic and metallic components to improve catalytic activity, selectivity and stability of the catalysts [7,8].

Zeolites like mordenite, beta and ZSM-5 have shown to be very promising as far as the hydroisomerization is concerned [1,2,7]. As the hydrogenating–dehydrogenating function, it has been demonstrated that platinum can remove coke precursors by hydrogenation, increasing the catalyst stability, and promotes the production of alkenes, allowing

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to set up the bifunctional mechanism characteristic of the alkane hydroisomerization [9]. Zhang and Smirniotis [10] reported the *n*-octane hydroisomerization results over some zeolites like mordenite and beta, and using platinum as hydrogenating function. With beta zeolite, a branched octane selectivity of 80% was obtained at conversion lower than 60%. Using mordenite as acid function and platinum as metallic one, Grau and Parera [11] reported selectivities of 54% with a conversion of 85%.

Most of the authors have investigated the role of acid site density [10], and the zeolite pore dimension [7] on the activity and selectivity of different catalysts, in their powder form, for the alkane hydroisomerization reactions.

However, if a zeolite-based catalyst is to be used in an industrial level, it must be pelletized with a binder in order to obtain larger and more resistant particles, and to avoid an extremely high-pressure drop in fixed-bed reactors [1]. Despite of that, the effect of the binder on the catalytic performance of the zeolites for the alkane hydroisomerization is rarely studied. Some studies have been developed in *n*-butane hydroisomerization with agglomerated catalysts, using ZSM-5 and beta zeolites as acid function and palladium as metallic one. Dorado et al. [1] reported an increase in the *iso*-butane selectivity (around 30%) when ZSM-5 zeolite was agglomerated with a binder, whereas they observed a decrease in the selectivity (around 5%) of beta zeolite when it was agglomerated with the same binder.

Bentonite is a laminar and expandable clay with wet binding properties and widely available throughout the world. The dispersability of clays in aqueous suspensions is the reason for their agglomeration properties: zeolite particles are surrounded by clay laminae and, when the water is removed, a solid phase is achieved in which the zeolite particles are bound by the clay. It has been shown that the sodium form of a bentonite (and not the acidic one) has binding properties [12]. However, because zeolites are mainly used as acid catalysts, further transformation of the bound zeolite to the acid form is required.

In this work, several acid catalysts based on mordenite, beta and ZSM-5 zeolites agglomerated with a clay (bentonite) were prepared. As hydrogenating–dehydrogenating function, platinum was used because of its high activity and good selectivity [10]. The aim of this work was to evaluate the influence of the binder on the catalyst acidity and how this factor can affect the catalytic activity and selectivity for the *n*-octane hydroisomerization reaction.

2. Experimental

2.1. Catalyst preparation

The parent zeolites mordenite (Si/Al = 10.4), beta (Si/Al = 13.0) and ZSM-5 (Si/Al = 15.6) were supplied in the ammonium form by Zeolyst International. To obtain the protonic form, zeolites were calcined at 550 °C for 15 h. Bentonite was supplied by Aldrich Chemical Co. Mordenite, beta and ZSM-5 samples on the protonic form were named to as HMOR, HBETA and HZSM-5, respectively.

Zeolite (35 wt.%) and bentonite (65 wt.%) were mixed and suspended in water at 60 °C for 2 h. The suspension was then dried at 120 °C for 12 h. After grinding and sieving, particles with an average particle size of 0.75 mm were obtained. Finally, the bound zeolite was calcined at 550 °C for 15 h. After the agglomeration process, the bound mordenite and ZSM-5 zeolites were ion-exchanged with 0.6N HCl (35 ml g^{-1}) whereas for the bound beta zeolite, the ion-exchange process was carried out three times with 1 M NH_4Cl (30 ml g^{-1}). Then, all the ion-exchanged samples were calcined again at 550 °C for 15 h in order to obtain their acid form.

A known volume of an aqueous H_2PtCl_6 solution was poured over all the catalysts (with or without binder). The solvent was removed by evaporation under vacuum. The metal concentration of the impregnating solution was calculated to yield a final Pt content in the catalysts of 1 wt.%.

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.

Non-agglomerated mordenite, beta and ZSM-5 samples containing both acid and metallic functions were named to as PtMOR, PtBETA and PtZSM-5, respectively.

Agglomerated catalysts were named to as with “Bent” following the name of the non-agglomerated zeolite (PtMOR, PtBETA and PtZSM-5). For example, PtBETA/Bent corresponds to an HBETA zeolite agglomerated with bentonite, subsequently re-incorporation of the acid function and finally, metal incorporation.

2.2. Catalyst characterization

Pores size distribution and BET surface area were determined by adsorption and desorption data acquired on a 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, whereas specific total pore volumes were evaluated form N_2 uptake at a relative pressure (P/P_0) of N_2 equal to 0.99. The Horvath-Kawazoe method was used to determine the microporous surface area and micropore volume [13]. The Barret, Johner and Halenda (BJH) method was used to determine the distribution of the mesopores [14]. Surface area measurements have an error of ±3%.

The concentration of the acid sites was measured by temperature programmed desorption of ammonia (TPDA) using a Micromeritics TPD/TPR 2900 analyzer. The sample was first heated from room temperature to the calcination temperature at 15 °C min^{-1} under a flow of helium. This temperature was held during 30 min. After reducing the catalyst under a hydrogen flow, the system was cooled to