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Influence of clay binder on the liquid phase hydroisomerization of *n*-octane over palladium-containing zeolite catalysts

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Abstract

The influence of the clay binder on the properties and performance of palladium-containing zeolite catalysts in the liquid phase hydroisomerization of *n*-octane was studied. Three different framework zeolites with similar Si/Al ratio were used as catalysts: USY, mordenite and beta with or without binder. In all cases, a decrease in the catalytic activity of agglomerated samples, because of the modification of the acidity and the porosity of the zeolites by the binder, was observed. The decrease in the acidity after the agglomeration could be attributed to solid-state ion exchange between zeolite protons and clay sodium during the calcination of the catalyst. Moreover, the aluminium extraframework species (EFAL) created during the agglomeration process could cause a partial blocking of the micro-pore mouths, which would lead to an increase in the length of the effective diffusional pathway. After the agglomeration process, the monobranched isomers selectivity increased for all the samples while the multibranched isomers selectivity decreased. Due to the high pressure in the liquid phase, a significantly higher isomers selectivity was obtained as compared to vapour-phase conditions, and cracking became important only at relatively high average conversions.

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

1. Introduction

Recently, alkanes and fundamentally *iso*-alkanes are being used as an alternative to other gasoline compounds like lead, aromatics, alkenes and others considered harmful to the environment or the public health. The reduction in the content of these adverse compounds will have a negative impact on the octane number of the gasoline pool. The octane number of *iso*-alkanes is higher than that corresponding of the linear ones. The former compounds may be obtained via two processes: an alkylation process, where light alkenes are alkylated with lower *iso*-alkanes or a hydroisomerization process, in which linear alkanes are converted into the corresponding branched ones [1].

The hydroisomerization of C_7 and C_8 has been widely studied [2–7], the multibranched C_8 alkanes obtained from this process are the most useful isomers because of their high octane number. However, no industrial hydroisomerization process exists for C_7 and C_8 paraffins due to their high tendency to crack [8,9].

Under the classical bifunctional process, the rate-limiting step of hydroconversion of *n*-alkanes is assumed to be the carbenium ion rearrangement with and without β-scission on the acid sites. Both the balanced metal/acid content and the effective transport between metal and acid sites are required to obtain the desired isomerization yield in *n*-alkane conversion [10,11].

Most industrial hydroisomerization catalysts are based on zeolites, which provide the acid function. As the hydrogenating–dehydrogenating function, several metals have been tested including Pt, Pd, Rh, Ir, Ru, Re and Ni, mostly associated with mordenite or CaY. However, palladium, although rarely studied, was shown to be the most selective in the *n*-butane hydroisomerization [12,13]. Bifunctional catalysts, with both hydrogenating–dehydrogenating and isomerization function have shown high efficiency in alkane hydroisomerization. Noble metal-zeolite catalysts especially Pt or Pd loaded Y, mordenite and beta possess a high activity and selectivity for hydroisomerization of *n*-alkanes [11]. Zeolite beta presents a three-dimensional 12-MR structure and has shown to have a

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higher selectivity in isomerization and conversion than the one-dimensional 12-MR mordenite [11,14]. Y zeolite catalysts have been used because Y zeolite has the largest pore system among the crystalline alumino-silicates [15]. Both acid and metal site density are important and their proper balance is critical in determining the activity, stability and product selectivity of the catalyst [16].

On the other hand, most industrial zeolite based catalysts require the zeolite to be pelletized with a binder in order to improve the mechanical properties of the catalyst particles, thus avoiding extremely high-pressure drops in fixed-bed reactors [17]. It has been demonstrated that the binder is not active as a catalyst but could change the acid properties of a zeolite as a result of changes in the proton-exchange efficiency, trapping by the binder of coke precursors, and/or blocking of zeolite channels during the pelletization process [17,18]. Some authors have studied the influence of different binders on the catalytic performance of zeolites [19–21], even though bentonite has not been widely studied.

Bentonite is a laminar and expandable clay with wet binding properties and widely available throughout the world. The scientific interest of bentonite is due to its physical and chemical properties as well as its low price. Consequently, the industrial application of bentonite is an attractive process. 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 with the zeolite particles are agglomerated by the clay. It has been shown that the acid form of clays does not have binding properties and that their sodium forms exhibit better properties [22]. Because zeolites are mainly used as acid catalysts, further transformation of the agglomerated zeolite to the acid form is required [17].

Furthermore, for experimental reasons, most of academic studies on hydroisomerization are performed in vapour phase using a hydrogen pressure below 10 bar [23], being very scarce the existing literature about the process in liquid phase.

Recently, our research group [24,25] has reported that depending on the zeolite studied, the binder (bentonite) influenced the activity for the hydroisomerization of *n*-octane in the vapour phase. The agglomeration process caused a decrease in the activity of ZSM-5 and mordenite catalysts. However, beta improved its catalytic activity when it was agglomerated.

In this work, several acid catalysts based on USY, mordenite and beta zeolites agglomerated with a clay (sodium bentonite) were prepared. As hydrogenating–dehydrogenating function, palladium was used. The aim of this work was to evaluate the influence of the binder on the catalytic activity and selectivity for the *n*-octane hydroisomerization reaction.

2. Experimental

2.1. Catalyst preparation

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

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. With this size, no internal diffusion limitations in the catalytic runs were detected. Finally, the agglomerated zeolites were calcined at 550 °C for 15 h. In order to re-incorporate the acid function in the zeolite, the agglomerated catalyst was ion-exchanged with 0.6N HCl (35 ml g^{-1}) in the case of mordenite. The ion-exchange for the USY and beta zeolites was carried out three times with 1 M NH_4Cl (30 ml g^{-1}). The ion-exchanged samples were subsequently calcined again at 550 °C for 15 h in order to obtain the acid form of the zeolites.

A known volume of an aqueous $Pd(NO_3)_2$ 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 Pd content in the resulting 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 450 °C for 4 h.

Non-agglomerated USY, mordenite and beta samples containing both acid and metallic functions were named to as PdUSY, PdMOR and PdBETA, respectively. Agglomerated catalysts were named to as with “Bent” following the name of the non-agglomerated zeolite. For example, PdUSY/Bent corresponds to a palladium USY zeolite agglomerated with bentonite.

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 from N_2 uptake at a relative pressure (P/P_o) of N_2 equal to 0.99. The Horvath–Kawazoe method was used to determine the microporous surface area and micropore volume. The Barret, Johner and Halenda (BJH) method was used to determine the distribution of the mesopores. 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 firstly heated from room temperature to the calcination temperature at 15 °C min^{-1} under a flow of helium, holding this temperature during 30 min. After reducing the catalysts under a hydrogen flow, the system was cooled to 180 °C. Ammonia was then flowed over the sample for 15 min. Later, the sample was purged with helium for 1 h in order to eliminate physisorbed species. The temperature was ramped at 15 °C min^{-1} from 180 to 560 °C