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Effect of the binder content on the catalytic performance of beta-based catalysts

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Abstract

The influence of the amount of a clay binder (sodium bentonite) on the properties and performance of beta zeolite based catalysts for the hydroisomerization of *n*-octane was studied. The contribution of the bentonite to the total acidity of agglomerated catalysts was very low, although its presence could affect to the acidic properties. Experimental acidity values for the agglomerated catalysts did not match with those theoretically expected due to a solid-state ion exchange between protons of the zeolite and sodium of the clay during the calcination following the ion-exchange step. Metal dispersion values were in agreement with the specific surface area of the zeolite in the agglomerated catalysts, suggesting that the metal were mainly located into the zeolite.

Catalysts were tested in the hydroisomerization of *n*-octane. Concerning the agglomerated catalysts, the higher the strong acid site density per gram of zeolite was, the higher the *n*-octane conversion was observed. Non-agglomerated catalysts, even showing a higher strong acid site density per gram of zeolite, exhibited the lowest *n*-octane conversion. EFAL species were present on the agglomerated catalysts enhancing their acid strength through a synergetic effect that allowed them to be much more active for the hydroisomerization of *n*-octane.

Keywords: Binder; Zeolite; Hydroisomerization; *n*-Octane; EFAL

1. Introduction

Compared to other types of catalysts, zeolites exhibit exceptional properties with respect to both activity and selectivity because of their ability to adsorb and transform molecules in their inner pore volume. An important class of reactions performed by zeolites is the acid-catalyzed reactions. For that, the zeolite framework needs to contain protons which give rise to a high Brönsted acidity. This is exploited in many organic reactions, including oil cracking, isomerization and fuel synthesis.

Isomerization of long-chain alkanes appears to be an interesting alternative since provides branched molecules which possess higher octane number than linear ones [1]. 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 on the acid sites of the bifunctional catalyst whereas the metal provides hydrogenation–dehydrogenation capability [2].

In order to provide necessary mechanical strength and/or resistance towards attrition loss, most of industrial zeolite catalysts are prepared by embedding the zeolite crystallites in a matrix, using a binder: synthetic material, such as silica and alumina or natural clay, such as kaolin, bentonite, etc. [3]. The process of pellet formation of zeolite powders creates meso and macropores, thus modifying the diffusion characteristics of the molecules [4].

Also, the interaction between binder and zeolite can have a strong influence on the activity, selectivity and stability of the zeolite [3]. 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 [5,6]. Information regarding the influence of the binder on the acidity and

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catalytic performance of zeolite is, therefore, very important for the development of industrial catalysts.

Choudhary et al. [3] reported the influence of the addition of alumina or kaolin, as a binder, to H-Gallosilicate zeolite in propane aromatization. The catalyst deactivation and coke deposition on the zeolite were increased due to the alumina binder, but when kaolin binder was used, the coke deposition was not changed significantly. The role of sodium montmorillonite on bounded zeolite catalysts was studied by Cañizares et al. [7]. The binder gave the required resistance to the final catalyst, but influenced strong sites density due to partial solid state ion-exchange. Dorado et al. [5] reported the influence of the agglomeration with a clay binder on the activity of ZSM-5 and beta zeolite for the hydroisomerization of *n*-butane. A lower *n*-butane conversion was always obtained for the bounded catalysts, due to neutralization of some zeolite acid sites.

In earlier works [1,6], our research group reported, for the hydroisomerization of *n*-octane, the influence of the bentonite on the catalytic performance using three zeolite-based catalysts: mordenite, beta and ZSM-5. The *n*-octane conversion decreased when zeolites mordenite and ZSM-5 were agglomerated with bentonite as compared with that of non-agglomerated ones. However, the catalytic performance of catalysts based on zeolite beta was improved because the presence of extraframework aluminium species provided by the binder.

In this work, several catalysts consisting of zeolite beta agglomerated with different proportion of sodium bentonite were prepared. This proportion was optimized for the hydroisomerization of *n*-octane. The aim of this work is to select a suitable catalyst and to study the influence that the agglomeration process with different binder amounts can induce on both the catalyst acidity and the catalytic performance.

2. Experimental

2.1. Catalyst preparation

NH_4-BETA (Si/Al = 12.5) was supplied by Zeolyst International (CP 814E). The sample was calcined at 550 °C for 15 h in order to obtain the protonic form of the zeolite. The obtained sample was name to as HBETA.

Sodium bentonite was supplied by Aldrich Chemical Co. For the agglomeration process, the zeolite (protonic form) and the clay (sodium bentonite) were mixed together and suspended in water at 60 °C during 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, agglomerated zeolite was calcined at 550 °C for 15 h. Five samples were synthesized varying the binder amount (from 35 to 65 wt%).

After the agglomeration process, samples were ion-exchanged three times with 1 M NH_4Cl (30 ml g^{-1}), and calcined again at 550 °C for 15 h in order to obtain the acid form of the agglomerated zeolites.

The obtained samples were named as follows: first, the name of the zeolite is shown (HBETA). Then, the character B is related to the binder name (bentonite) and finally a number represents the amount of binder in the catalyst (wt%). For instance, HBETAB35 is a catalyst based on HBETA agglomerated with bentonite, and containing a proportion of clay in the final catalyst of 35 wt%.

A known volume of an aqueous H_2PtCl_6 solution was poured over all the catalysts. The solvent was removed by evaporation under vacuum. The metal concentration of the impregnating solution was calculated to yield a final platinum 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.

Bifunctional catalysts were named as above mentioned but including the symbol of the metal (Pt).

2.2. Catalyst characterization

To quantify the sodium content of each sample, atomic absorption measurements (AA) were performed using a SpectrAA 220FS spectrophotometer. Prior to measurement, the samples were dissolved in hydrofluoric acid and diluted to the interval measurement. The atomic absorption measurements had an error of ±1%.

Surface area was determined by using N_2 as the sorbate at 77 K in a static apparatus (Micromeritics ASAP 2010 adsorptive and desorptive apparatus). The samples were evacuated under a 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 ±3%.

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 method was described in earlier works [1,6]. The average relative error in the acidity determination was lower than 3%.

The chemisorption measurements were carried out using a dynamic pulse technique described in previous works [1,6]. The dispersion measurements with H_2 pulses had an error of ±5%.

Solid-state ^{27}Al NMR spectra were collected in a BRUKER Avance WB 400 spectrometer. The ^{27}Al NMR spectra were obtained at 12.5 kHz using 15° pulses and 1 s delay, a total of 5000 pulses being accumulated.

2.3. Catalytic experiments

Hydroisomerization of *n*-octane reactions were carried out in an Autoclave Engineers (BTRS-Jr) micro reactor that consisted of a tubular stainless steel reactor with vertical placing and downward flow. The liquid feed (*n*-octane) was performed by a HPLC pump. A backpressure regulator valve allowed high-pressure experiments. Experimental conditions were as follows: weight of catalyst, 1.5 g; temperature, 270–370 °C; total pressure, 10 bar; WHSV = 10 $g_{n\text{-C8}}$ h^{-1} $g_{\text{zeolite}}{}^{-1}$; and H_2/*n*-C_8 molar ratio, 14. All data were collected at 1 h on stream. Reaction products were analyzed with a HP 5890 Series II gas chromatograph equipped with a flame ionization detector and automatic valve for continuous analysis. The reactor effluent stream was sent for analysis through a heated line (about 180 °C) to the automatic valve. The gas chromatograph was equipped with a