n-Pentane hydroisomerization on Pt-promoted acid zeolites

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ABSTRACT

Hydroisomerization of n-pentane over platinum promoted acid zeolites was studied. The effect of structure and strength of acid sites of the support was investigated on the reaction carried out under atmospheric pressure at 300 °C. In order to accomplish the above purpose, some zeolitic catalytic systems were studied, which have the same structure but different acidity and with similar acidity but different structure.

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1. Introduction

Light straight run (LSR) gasoline consists of the C_5–88 °C fraction of the naphtha cuts from the atmospheric crude still. The octane number of the LSR naphtha can be improved using an isomerization process to convert the normal paraffins to their branched isomers. It results in a significant octane number increase because n-pentane has an unleaded research octane number (clear RON) of 61.7 and iso-pentane has an average of 92.3. The isomerization of LSR is successfully carried out in the presence of hydrogen and it is referred as hydroisomerization. An atmosphere of hydrogen is used to minimize carbon deposits on the catalyst but hydrogen consumption is negligible [1,2].

In the development of the alkane isomerization process, four catalyst generations were developed and used in succession. The first two ($AlCl_3$ and metal on aluminosilicates) are no longer used. For the catalyst currently in use, $Pt/chlorinated$ Al_2O_3 (the third generation) and Pt/zeolites (the fourth generation), ratio between the acid and the metallic site has a determining role in the performance of the process [2]. The zeolites have the advantage of a well-defined porous structure, which allows one to select the suited structure for the process. Several reports have investigated the skeletal isomerization of hydrocarbons C_4–C_7 in the presence of hydrogen over Pt o Pd/BEA [3–6], MOR zeolite [7,8], Y-zeolite [6,9,10], ZSM-5 zeolite [11,12], and heteropolyacid catalysts [12,13].

The bifunctional mechanism has been accepted for catalysts of platinum supported over zeolites [14–16]. This mechanism requires the dehydrogenation of alkanes on the metallic sites, and the produced olefins protonate on the Brønsted acid sites to the corresponding alkylcarbenium ions. These carbenium ions can undergo to skeletal rearrangement and β-scission followed by de-protonation and hydrogenation over metal sites to produce the isomerization and cracking products. In this mechanism, it is very important to minimize the secondary reactions and to ensure a satisfactory reaction rate. For this requirement, it is necessary to have a defined ratio between the metal and acid sites. It is established that the selectivity to iso-paraffins depends on the balance between metal and acid functions [17,18]. Some authors [19,9] have reported optimal values of the ratio metallic site/acid site for the isomerization of lower n-alkanes (C_5–C_7). Other studies confirm the occurrence of physical adsorption of reactants and products inside the zeolite structure and their chemisorption at the reaction sites [2]. It could explain the influence of the zeolites structure on the results of the hydroisomerization process and the attention to the use of zeolites having specific structures for catalyst preparation.

In a previous work [20], we have compared the activity and selectivity for hydroisomerization of n-pentane over platinum promoted acid zeolites, with the aim to evaluate the role of the acidity and to structure upon the selectivity and catalytic activity. In the present work, it was tried to study separately these two effects. In order to accomplish the above purpose, we have studied zeolites-based catalysts with the same structure and different acidity and with similar acidity and different structure.

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2. Experimental

2.1. Preparation and characterization of catalysts

The bifunctional catalysts used consisted of HZSM-5, HBEA, HDBEA, and HDMOR as the acid function and Pt as the metal function.

ZSM-5 was synthesized hydrothermally using tetrapropylammonium bromide (TPABr) [21,22]. Solid silica (99.9 wt% from VENESIL), and aluminium sulphate ($Al_2(SO_4)_3 \cdot 12H_2O$) from Aldrich were used as Si source and Al source, respectively. Concentrated sulphuric acid was added to adjusting gel pH, and TPABr was used as template. To prepare synthesis gel, an aqueous sodium hydroxide solution was firstly prepared. Then, solid silica was added to this solution with continuous stirring until a homogenous dispersion was obtained to get the mixture A. On the other hand, aluminium sulphate was dissolved in water, and then TPABr was added to get the solution B. The solution B was added to the mixture A under continuous stirring. After completing the addition, the mixture was stirred for at least one hour to obtain a homogeneous mixture. Then, concentrated H_2SO_4 (from Aldrich) was added to adjust mixture pH between 9 and 10. The composition of the resulting mixture, expressed as mole ratios of components was the following: $SiO_2/Al_2O_3 = 100$; $Na_2O/SiO_2 = 0.26$; $H_2O/SiO_2 = 20$ and $TPABr/SiO_2 = 0.08$. The mixture was transferred to a stainless-steel autoclave and heated to 190 °C for 24 h. The solids recovered by filtration were washed with demineralised water and dried at 80 °C overnight. The removal of organic template was carried out at 550 °C for 6 h under air, to obtain ZSM-5 zeolite.

Mordenite and Beta zeolites were dealuminated by acid treatment of the hydrogen forms of a commercial Union Carbide sample designated LZM-5, and a commercial Süd Chemie sample designated Naβ, respectively. Some characteristics of commercial samples are included in Table 1. The ZSM-5, MOR, and BEA zeolites were ion exchanged for 3 h with a 3 M ammonium acetate solution, with continuous stirring at 60 °C using 20 mL of solution per gram of zeolite. The ammonium forms of zeolites were calcined in flowing air at 550 °C for 4 h to obtain the samples HZSM-5, HMOR, and HBEA. Then, HMOR and HBEA were treated with 1 M HCl. The acid treatment for HMOR was carried out under reflux for 3 h, and for HBEA was carried out at room temperature for 8 h, using 10 mL of solution per gram of zeolite in both cases. After the acid treatment, the samples were washed free of chloride, dried overnight at 80 °C and calcined at 550 °C under air for 15 h. These products were named as HDMOR and HDBEA.

The Pt-promoted catalysts were prepared by impregnating the calcined solids with $[Pt(NH_3)_4Cl_2]$ (from BDH, reagent grade) using the wet impregnation method with excess solution, to reach 0.5 wt% of Pt. In order to decompose the Pt complex, the catalysts were calcined under a stream of dry air (30 ml/min), the temperature was increased up to 150 °C (5 °C/min), and kept by a 2 h period. Then, the temperature was increased to 300 °C keeping it on that value by 16 h.

X-ray diffractograms (XRD) of the solids were recorded with a Philips diffractometer PW 1730 Phillips using Cu Kα radiation operated at 30 kV and 20 mA, and scanning speed of 2° 2θ/min. The relative crystallinity (%Cryst) of the zeolite samples were estimated by summing the peak intensities of diffraction lines between 8° and 30° 2θ/min, and normalizing to 100% with respect LZM-5 (Union Carbide) for HDMOR and Naβ (Süd Chemie) for HBEA and HDBEA [23]. HZSM-5 was taken as 100% crystalline. Chemical analysis for Al, P, and Si of the calcined samples were performed using atomic emission spectroscopy with a source of plasma inductively coupled. Samples were previously fused with lithium metaborate and dissolved in dilute nitric acid before analyses. Nitrogen adsorption–desorption isotherms were measured at −196 °C using a Micromeritics ASAP 2000 instrument. Before the measurements, the samples were evacuated for 12 h at 350 °C. The Langmuir equation was used to calculate the specific surface ($S_{Langmuir}$) from the adsorption data obtained at P/P_0 between 0.05 and 0.2. In order to compare with most reports on zeolites in the literature, the Brunauer–Emmet–Teller (BET) equation was also used to calculate the apparent surface area (S_{BET}). Micropore volume (V_{micro}) and the external surface (S_{ext}) were calculated from t-plot method [24].

The total acidity and the acid strength distribution of the acid zeolites were measured by temperature programmed desorption of ammonia (TPDA), using a Micromeritics TPD/TPR 2900 analyzer. 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. It was a convenient way to categorize the acid strength distribution obtained by this method.

The chemisorption measurements were carried out by using a dynamic pulse technique with an argon flow and pulses of H_2. In order to calculate the metal dispersion, and adsorption stoichiometry of metal/H = 1 was assumed. The equipment used was a Micromeritics TPD/TPR 2900 analyzer.

2.2. Catalytic test

n-Pentane transformation was carried out under atmospheric pressure in a continuous fixed-bed reactor at 300 °C, feeding n-pentane by the gas flow saturation method. The feeding gas mixture consisted of H_2 (12 ml/min) with a partial pressure of n-pentane of 0.26 atm. To reach this pressure, H_2 was passed through a glass vessel with n-pentane kept to 0 °C in an ice bath. The mass of catalyst was about 0.3 g (weight hourly space velocity WHSV = 2.5 h^{-1}). Before the reaction test, the metallic phase was reduced by a hydrogen flow (30 ml/min) at 450 °C for 2 h. The product analysis was done after 30 min by on-line chromatography using a Hewlett-Packard 5890A. A fused silica KCl/Al_2O_3 column was used for separation purposes. Product analysis was done each 30 min with a total time on stream of 3 h.

The total conversion (X) of n-pentane was calculated according to Eq. (1)

$$X = \frac{\sum A_i - A_{n\text{-pentane}}}{\sum A_i} \times 100 \tag{1}$$

where A_i is the corrected chromatographic area for a particular compound.

Table 1
Specific surface area, micropore volume, proportional crystallinity, and Si/Al ratio of zeolites.

Sample	S_{BET} (m²/g)	$S_{Langmuir}$ (m²/g)	S_{ext} (m²/g)	V_{micro} (cm³/g)	% Cryst.	Si/Al (molar)	% Cryst.
HZSM-5	338	538	27	0.11	100	52	100
Naβ	439	588	190	0.114	100	14	100
HBEA	490	707	211	0.146	94	16	94
HDBEA	451	650	200	0.131	93	64	93
LZM-5	42	55	34	0.015	100	5	100
HDMOR	321	469	53	0.140	75	25	75