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Screening of optimal pretreatment and reaction conditions for the isomerization-cracking of long paraffins over $Pt/WO_3–ZrO_2$ catalysts

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ABSTRACT

Pretreatment and reaction conditions for the isomerization-cracking of long paraffins over commercial $Pt/WO_3–ZrO_2$ catalysts were screened. Optimal conditions were seeked for the production of short, high octane branched paraffins for the gasoline pool. n-C_{16} was used as a model molecule. The reaction over the acidic catalyst was used to adjust the size of the molecules to the boiling range of gasolines and to add branching in order to increase the octane number of the product. These adjustments had to be done while minimizing the production of light gases and getting a stable activity level.

With respect to the pretreatment it was confirmed that the best calcination temperature of the tungstate oxoanion promoted hydroxides was 800 °C. Optimality was mostly related to the activity level. The optimum temperature coincides with the appearance of small WO_3 crystallites which are thought to be center for creation of Brönsted acid sites in the presence of platinum and hydrogen.

Regarding the reaction conditions, increasing temperature values augmented the conversion but also increased the cracking. Therefore optimum values were found at moderate temperature given the high reactivity of the feed. Space velocity values were analyzed with attention to the liquid C_{5+} yield, the selectivity to branched isomers and the stability of the catalysts. Best yields to branched naphtha products were obtained with $Pt/WO_3–ZrO_2$ at WHSV = 18 h^{-1}. The catalyst coking rate was a function of the H_2/hydrocarbon ratio. A value of 6 was enough to attain a stable conversion value on $Pt/WO_3–ZrO_2$. The values of liquid yield as a function of pressure displayed a volcano pattern that was rationalized in terms of a non-classical bifunctional mechanism of reaction.

High pressure values increased the concentration of Brönsted acid sites and hence the activity. Too high pressures enhanced hydrocracking and decreased the liquid yield.

The results indicate that in general terms $Pt/WO_3–ZrO_2$ at moderate reaction conditions transforms a paraffinic heavy cut into a branched isomerizate that can be added to the gasoline pool to improve the quality properties. It was however found that under some conditions the octane gain is inversely proportional to the yield of light gases indicating that a high RON isomerizate can only be got at the expense of the liquid yield.

1. Introduction

Gasoline is a hydrocarbons mixture used as a fuel of motors of spark ignition. The composition of this mixture has greatly evolved in the last decades to accommodate two fundamental restrictions: (i) quality, mainly determined by the limit of minimum RON (Research Octane Number); (ii) toxicity, as measured by the set of values of concentration of compounds with noxious effects on the environment and the human life.

A virgin naphtha cut is composed of normal paraffins and naphthenes of five to eight carbon atoms and has an approximate RON value of 68 points. This value must be raised to 95–98 in order to satisfy the requirements of modern motors.

This article is devoted to the study of the transformations of long paraffins on a high acidity catalyst, $WO_3–ZrO_2$. In order to understand the necessary transformations long paraffins should undergo to become a high quality isomerizate some concepts about octane rating should be revised. Octane number measures the antiknocking capacity of a fuel and depends on the chemical nature of its components. Some general trends can be deduced by analyzing large RON data sets, like those published by API [1]. Fig. 1 shows the variation of the RON of different chemical families: normal paraffins, isoparaffins, aromatics, naphthenes and olefins, as a function of their carbon number. Aromatic compounds display the highest RON, followed by naphthenes, olefins and isoparaffins. Normal paraffins have negligible RON. It can also be seen that for isoparaffins RON increases with the branching and for molecules of equal chemical nature (aromaticity, branching, substitution) it decreases with carbon number. It can also be deduced

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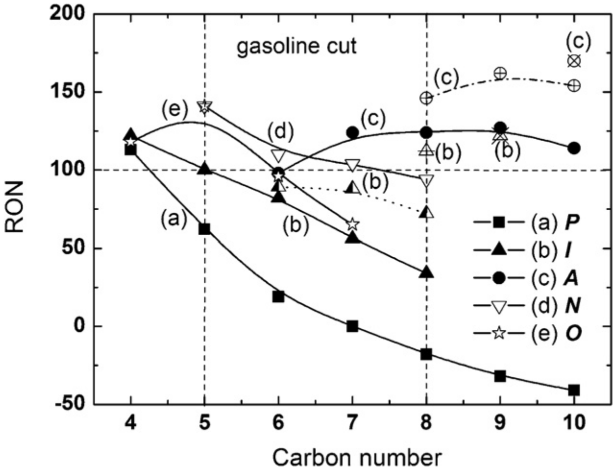

Fig. 1. RON of different chemical families as a function of the molecule carbon number. (a) Paraffins; (b) isoparaffins; (c) aromatics; (d) naphthenes; (e) olefins.

that RON is increased by the presence of tertiary and quaternary carbons.

According to the previous discussion and the insight of Fig. 1, isomerization-cracking of long paraffins should produce molecules in the C_5–C_8 range with the highest possible branching. From a thermodynamic point of view branching is a function of temperature and molecular size. Some long chain branched compounds, like 2,2,3-trimethyl-pentane have a high octane number (RON = 100) but they are in thermodynamic equilibrium with other isoparaffins of same carbon number and much lower RON. Therefore branched C_5–C_6 cuts are to be preferred to heavier cuts. The challenge to refiners is to maximize the quality and throughput of isomerizate while getting a stable operation and a minimum yield of light gases.

The most desirable features of the isomerizate are intimately linked to the choice of the catalyst. In this sense oxoanion promoted zirconia catalysts, Pt/SO_4^{2-}–ZrO_2 (Pt/SZ) and Pt/WO_3–ZrO_2 (Pt/WZ), have attracted the interest of researchers in the last decade due to their high activity at low temperatures. Catalysts based on Pt/SZ are indeed the base of the Par-Isom process (UOP) for isomerization of C_5–C_6 virgin naphtha.

A more recent and less studied application of oxoanion promoted zirconia catalysts has been the isomerization-cracking of long paraffins, Fischer–Tropsch waxes and plastics to produce short branched paraffins for the gasoline pool. In previous reports Pt and other noble metals (Ni, Pd, etc.) have been impregnated over SZ and WZ supports and their activity in isomerization-cracking of long paraffins has been assessed [2–5]. All reports conclude that Pt provides the most convenient metal function because it produces more active and stable catalysts. For this reason in this work only Pt/WZ catalysts are studied. Though many reports on the isomerization-cracking of long paraffins exist no single work focuses on the optimization of reaction conditions for obtaining a high RON isomerizate. Such focus is taken in this work.

Commercial WZ supports, a fixed content of Pt (0.5%) and a fixed Pt reduction temperature (300 °C) are used. All other pretreatment and reaction parameters are varied (activation temperature, reaction temperature, total pressure, H_2/hydrocarbon ratio).

Some studies on the hydrocracking of long paraffins are worth to be referenced. Deldari [6] studied the hydroisomerization of n-hexadecane over bifunctional catalysts, such as silica–aluminas, zeolites, tungsten and sulphate promoted zirconias and MCM-41 mesoporous materials. Wang et al. [7] studied modified and unmodified zeolites using dodecane as test molecule. Their results suggest that the catalysts with the highest concentration of Brönsted acid sites of medium strength are the most active in isomerization. Other works compare the activity and selectivity of Pt/WZ catalysts in the hydrocracking of n-hexadecane against other bifunctional catalysts based on USY zeolites and amorphous silica–alumina [8]. Walendziewski et al. [9] reported results of mechanical mixtures of zirconia catalysts (WZ and SZ) with alumina for the reaction of hydroisomerization and hydrocraking of waxes.

The only pretreatment variable studied in this work is the temperature of calcination of the support as this determines the total amount and the strength distribution of the acid sites. Its influence on the performance of the catalysts is specially studied because of its impact on the rates of isomerization and cracking.

2. Experimental

2.1. Catalysts preparation

A WO_3–ZrO_2 support with 15% W was supplied by MEL Chemicals in the form of a powdery hydroxide gel. This was first pressed into the form of pellets using a die and an hydraulic press. Then it was ground and sieved to 35–80 meshes. Several calcination treatments were performed in order to find the best temperature. The catalyst was calcined at 2 °C min^{-1} in air from room temperature to 180 °C and then this value was held for 1 h. Then the temperature was increased in h to the desired value (600, 700, 800 °C) and held for another 2 h. The sample was then cooled down to room temperature and unloaded. The obtained crystalline solid was then impregnated with chloroplatinic acid by the incipient wetness method. The amount of solution was regulated to obtained 0.5% Pt in the final catalyst. Once impregnated the sample was kept 24 h at room temperature and then dried slowly in a stove. The temperature was raised slowly from room temperature to 110 °C in order to prevent the solvent carrying over the metal precursor to the pore mouths. The dried material was then calcined in air in a muffle at 500 °C and cooled down in nitrogen. The metal phase was reduced by placing the sample in a hydrogen stream (30 $cm^3\,min^{-1}\,g^{-1}$) and heating at 300 °C for 1 h. The thus obtained samples were called Pt/WZ_{T_c}, where T_c is the calcination temperature (in Celsius degrees).

2.2. Catalysts characterization

The physicochemical characterization of the catalyst was done using element chemical analysis, X-ray diffraction (crystallinity and crystal phase), nitrogen adsorption (specific surface area and pore volume distribution), pyridine adsorption (acidity) and n-hexane test batch reaction (activity, selectivity). The metal phase was studied by CO chemisorption and test reaction of cyclohexane dehydrogenation.

The chemical analysis of the Pt content of the solids was determined by atomic emission spectroscopy (ICP-AES) using an ARL model 3410 equipment. The solids were dissolved in a digestive pump with a mixture of 1 ml sulphuric acid, 3 ml chlorohydric acid and 1 ml nitric acid. The W content was determined by X-ray fluorescence.

X-ray diffraction spectra were measured in a Shimadzu XD-1 equipment with CuKα radiation filtered with Ni. The spectra were recorded in the 2θ range between 20° and 65° and with a scanning rate of 1.2 min^{-1}. The percentage of tetragonal phase of the samples was calculated using Eq. (1) [10]. The peaks located at $2\theta = 28°$ and $2\theta = 31°$ were attributed to the monoclinic phase of zirconia and those located at $2\theta = 30°$ to the tetragonal phase. The peaks located at $2\theta = 23$–$25°$ were attributed to WO_3 crystals.

$$X_t\ (\%) = \frac{100\,\alpha I_t}{I_m + \alpha I_t} \qquad (1)$$