



Optimal process conditions for the isomerization–cracking of long-chain *n*-paraffins to high octane isomerizate gasoline over Pt/SO₄²⁻–ZrO₂ catalysts

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ABSTRACT

An assessment of the process conditions for the isomerization–cracking of long-chain *n*-paraffins over commercial Pt/SO₄²⁻–ZrO₂ catalysts was made. Pretreatment and reaction conditions were optimized with a focus on the maximization of the yield of short, high octane branched paraffins for the gasoline pool. While selectivity was an important issue attention was also paid to the reduction of the yield to gases (C₁–C₄). Therefore cracking had to be modulated to produce the correct molecular size adjustment without scission to too much smaller fragments. Skeletal isomerization was to be maximized. The activity in both acid-catalyzed reactions had to be tuned while keeping a stable activity level.

The only pretreatment condition assessed was the calcination temperature (screened in the 600–800 °C range). Calcination at 600 °C produced the highest activity level while 700 °C was convenient from the point of view of selectivity. The optimum temperature coincided with the production of the highest concentration of Brønsted acid sites.

Regarding the reaction conditions, increasing temperature values augmented the conversion but also increased the cracking. Therefore optimum values were found at a moderate temperature, 225 °C, given the high reactivity of the feed. Space velocity values were analyzed with attention to the liquid C₅₊ yield, the selectivity to branched isomers and the stability of the catalysts. Best yields to branched naphtha products were obtained at WHSV = 18 h⁻¹. The H₂/hydrocarbon molar ratio was a function of the catalyst coking rate. A value of 10 was enough to attain a stable conversion value. 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 Brønsted acid sites and hence the activity while high pressures enhanced hydrocracking and decreased the liquid yield. The optimal pressure value was 20 atm.

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1. Introduction

Isomerization–cracking of long-chain normal paraffins has lately attracted the interest of academy and industry researchers because of its potential impact on augmenting the throughput of middle distillates by means of the processing of low-grade waxy feed stocks coming from the dewaxing of lubes, the recycling of some plastics and the separation of Fischer–Tropsch waxes and heavy paraffins. Most scientific studies have concentrated on the production of naphtha cuts while applications for producing the full range of middle distillates can be found in the patents literature. The catalysts employed in isomerization–cracking are bifunctional. They comprise a metal function supplied by tiny Pt or Pd metal particles and an acid function supplied by the support. Many examples can be found in the literature of catalyst supports for this reaction. They are amorphous aluminosilicates [1–3], zeolites of uni- or

multi-directional channels like β, mordenite, L, Y, ZSM-5, ZSM-12, ZSM-22 [4–11], silica alumina phosphates (SAPO) [12,13], mesoporous materials like Al-MCM-41 [14] and oxoanion promoted zirconia, SO₄²⁻–ZrO₂ WO₃–ZrO₂ and SO₄²⁻–WO₃–ZrO₂ [15–21]. A review on the available catalysts for hydroisomerization of long-chain normal paraffins has been recently published [22].

Researchers were early confronted with the fact that conventional hydrocracking catalysts like silica-alumina or β and L zeolites, were not appropriate for the treatment of highly paraffinic feed stocks. Too much cracking on these catalysts produced a high yield of low-value light gases with a consequent decrease of the liquid yield and the fuel throughput of the process.

Especially when the desired products are gasoline compounds the requirements on the catalysts become stringent. For producing a gasoline product the molecules of the feed must be more or less severely cracked to the C₅–C₁₂ range and skeletally isomerized to produce a maximum of branches. Skeletal branching is closely related to the antidetonating capacity of the gasoline. Both skeletal isomerization and cracking are acid-catalyzed reactions, i.e. they proceed over acid sites.

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The first catalytic issue is therefore the correct distribution of acid strength of these catalysts. Acidity requirements grow inversely proportional to the length of the chain with the general understanding that the longer the chain the higher the reactivity of the paraffin. Cracking is always more demanding than skeletal branching. This is one reason why cracking can sometimes proceed after skeletal branching has taken place on a same acid site. The consequences of an inappropriate acid strength distribution are easily foreseen. If the acid sites are too strong extensive cracking occurs with the combined disadvantages of low liquid yield and premature catalyst coke fouling. If the acid sites are too weak isomerization might occur but cracking will be highly disfavored. As a consequence inconveniently long isomers of low volatility and low octane number are obtained.

In the search for a correct isomerization–cracking catalyst both common isomerization and cracking catalysts have been tried. While cracking catalysts have proved not to provide adequate liquid yield and selectivity, isomerization catalysts have been more suitable (see Table 1).

High liquid yields and high selectivity to branched isoparaffins can notably be obtained over oxoanion promoted zirconia catalysts. These catalysts, tungsten–zirconia ($\text{WO}_3\text{-ZrO}_2$) and sulfate–zirconia ($\text{SO}_4^{2-}\text{-ZrO}_2$) have outstanding properties of high activity and selectivity at low temperatures. Many reports have been published on the catalytic properties of these two catalysts for the isomerization and cracking of medium and long paraffins. These reports have unfortunately concentrated on the study of a few synthesis or reaction variables. A comprehensive study on the influence of the full range of variables needed for running a hydrocracking process is still lacking.

A comprehensive assessment of reaction variables for the isomerization–cracking of long paraffins over commercial $\text{SO}_4^{2-}\text{-ZrO}_2$ is done in this work using n-hexadecane as a model compound. Reaction, pressure, hydrogen-to-hydrocarbon molar ratio and spatial velocity are screened in the convenient ranges in order to optimize the relevant merit figures of the process: octane properties of the isomerizate, liquid yield, appropriate stability of the catalyst, etc. A pretreatment variable related to the activity and selectivity of the catalyst was also screened, the calcination temperature of the support. No other pretreatment was deemed necessary since only available commercial catalysts are used and calcination temperature is the variable that affects the most the final acidity distribution.

In order to correctly focus the development of the work a previous discussion on the relation of molecular features, thermodynamics, octane number and overall gasoline quality issues was inserted in the beginning of the Results and discussion section. Such recalling of

concepts seems necessary to correctly perform the optimization procedure.

2. Experimental

2.1. Catalysts preparation

A commercial $\text{SO}_4^{2-}\text{-ZrO}_2$ support (MEL Chemicals) in the form of a powdery sulphate doped hydroxide gel (Grade XZO 1249/01, 7 wt.% SO_3 on ZrO_2 basis, 5 microns average particle size, $>300 \text{ m}^2 \text{ g}^{-1}$, $>0.3 \text{ ml g}^{-1}$) was used. This powder was first pressed and shaped into cylindrical pellets using a die and a hydraulic press (8 Tn cm^{-2}). Then the pellets were ground and sieved to 35–80 meshes. Samples were taken and were subjected to calcination in static air (3 h) in a muffle at several calcination temperatures (T_c), 600, 700 and 800 °C in order to see the influence of this variable on acidity, crystal structure, catalytic activity and selectivity. In each calcination treatment the catalyst was first heated from room temperature to 180 °C at $2 \text{ }^\circ\text{C min}^{-1}$ in air and this value was held for 1 h. Then the temperature was increased in 1 h to the desired value of T_c (600, 700, 800 °C) and held for another 2 h. The sample was then cooled down to room temperature and unloaded. The obtained $\text{SO}_4^{2-}\text{-ZrO}_2$ crystalline solid was named SZ^{T_c} .

SZ^{T_c} was then impregnated with chloroplatinic acid by the incipient wetness method. The amount of solution was regulated in order to obtain 0.5% Pt in the final catalyst. This Pt load was chosen in attention to some previous reports on the influence of the Pt content on the performance of the catalyst [23]. Once impregnated the sample was kept 24 h at room temperature. Then it was put in a stove and the temperature was raised slowly from room temperature to 110 °C. Finally it was dried at this temperature overnight. The dried material was then calcined in static air (3 h) in a muffle at 500 °C and cooled down in nitrogen. The metal phase was reduced by placing the sample in a hydrogen stream (80 ml.min^{-1}) and heating at 300 °C for 1 h. The thus obtained samples were called PtSZ^{T_c} . The temperature of reduction was chosen in accord with previous studies of TPR of Xu and Sachtler [24] that indicated the ranges of sulfate decomposition. In order to match the temperatures of possible sulfur decomposition and metal sintering, the maximum temperature of reaction (300 °C) was made to coincide with the temperature of the reduction step.

2.2. Catalysts physicochemical characterization

The catalysts were characterized by means of element chemical analysis, X-ray diffraction (crystallinity and crystal phase), nitrogen

Table 1
Results related to the hydrocracking of long paraffins over different catalysts.

Catalyst	T [°C]	Feed	H ₂ /Feed [mole ratio]	PH ₂ [atm]	WHSV [h ⁻¹]	X [%]	S _{iso} [%]	S _{C1-C4} [%]	Ref.
0.6Pt/MSA	285	n-C ₁₀	4	29.6	1.46	50.0	79.0	–	[3]
0.5Pt/CaY	275	n-C ₉		2.2	1.00	76.4	87.8	12.2	[9]
0.5Pt/H-USY	290	n-C ₈	16	6.8	0.42–112 ^a	55.7	92.6	6.9	[5]
0.5Pt/H-β	290	n-C ₈	16	6.8	0.42–112 ^a	47.6	77.1	20.1	[5]
0.5Pt/H-LTL	290	n-C ₈	16	6.8	0.42–112 ^a	49.7	72.4	26.2	[5]
0.3Pt/H-MOR	300	n-C ₈	6	14.8	4.00	67.9	24.2	71.6	[10]
0.5Pt/H-MOR	235	n-C ₁₃₋₂₀	12	19.7	3.00	62.9	37.8	25.0	[13]
H-MOR+Pt/Al ₂ O ₃	300	n-C ₈	6	14.8	4.00	79.3	61.6	67.4	[10]
Pt/H-MOR+Al ₂ O ₃	300	n-C ₈	6	14.8	4.00	50.4	55.0	52.3	[10]
0.5Pt/H-ZSM-5	280	n-C ₉	6	1.9	1.00	98.5	18.9	–	[11]
0.5Pt/H-ZSM-12	290	n-C ₈	16	6.8	0.42–112 ^a	50.5	66.8	27.5	[5]
0.5Pt/H-ZSM-22	290	n-C ₁₂	7	59.2	1.04	93.0	90.0	–	[6]
0.5Pt/SAPO-11	371	n-C ₁₃₋₂₀	12	9.9	3.00	79.7	58.0	22.2	[13]
0.5Pt/WO ₃ -ZrO ₂	230	n-C ₁₆	2	20.4	1.00	85.9	83.1	–	[15]
0.5Pt/WO ₃ -ZrO ₂	300	n-C ₁₀	6	0.99	1.00	98.0	55.3	36.7	[20]
0.5Pt/SO ₄ -ZrO ₂	150	n-C ₁₆	2	20.4	1.00	76.7	19.8	–	[15]
1.0Pt/SO ₄ -ZrO ₂	300	n-C ₁₀	6	14.8	4.00	89.3	38.7	39.1	[21]
Pd/Al-MCM-41	350	n-C ₁₃	6.5	34.5	1.50	60.2	86.5	–	[14]

PH₂: hydrogen partial pressure; X: conversion; S_{iso}: selectivity to isoparaffins; S_{C1-C4}: selectivity to light gases; ^a: range varied in order to obtain approximately 50% conversion.

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