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Modelling product distribution of pyrolysis gasoline hydroprocessing on a Pt–Pd/HZSM-5 catalyst

A. Gutierrez, P. Castaño*, M.J. Azkoiti, J. Bilbao, J.M. Arandes

University of the Basque Country, Faculty of Science and Technology, Chemical Engineering Department (Leioa, Group CPWV), 48080-644 Bilbao, Spain

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ABSTRACT

The hydrocracking of pyrolysis gasoline (70 wt% of aromatics) has been studied using an integral fixed bed reactor with a Pt–Pd/HZSM-5 (0.2 wt% Pt, 0.48 wt% Pd; $SiO_2/Al_2O_3 = 19$) catalyst over a wide range of experimental conditions: 350–450 °C; 20–50 bar; $P_{PyGas} = 1$ bar, H_2:PyGas molar ratio (n_{H_2}), 20–49; WHSV, 2.7–32 h^{-1}; Under these experimental conditions the deactivation is negligible and therefore data in the stationary state have been reported. Based on previous models for the hydrocracking of model compounds (methylcyclohexane and toluene), we have proposed a kinetic diagram and kinetic equations that satisfactorily describe the product distribution under the experimental conditions studied. The experimental data have been fitted to the proposed model and its parameters have been estimated. The kinetic model is used for reactor simulation and optimization.

1. Introduction

The upgrading of secondary interest streams is one of the challenges in the refineries, given that market requirements are more demanding concerning the quality of automotive fuels. The pyrolysis gasoline (PyGas) is a by-product of the steam cracking of naphtha with a boiling point in the 40–120 °C range, which usually contains C_5–C_{12} hydrocarbons with high octane number, high content of aromatics, such as benzene, toluene and xylene (BTX), and unsaturated components, such as mono- and di-olefins [1]. The PyGas has been used either as high-octane blending component for motor gasoline fuel or as high-aromatic feedstock for aromatic extraction [2]. Furthermore, an increase in the production of PyGas is foreseen as a consequence of olefin production intensification in steam cracking units to face the increasing olefin demand [3].

PyGas composition is not suitable for direct use in internal combustion engines, given that its mono-aromatic components are involved in the formation of polyaromatic hydrocarbons (PAH) and solid particles, whereas olefins and styrene are gum agents [4]. In order to improve stability and composition, PyGas is subjected to a two-stage heterogeneous catalytic hydrogenation [5,6]. In the first stage, very reactive species (mono-olefins, di-olefins and styrene) are selectively removed using Pd or Ni catalyst supported on Al_2O_3 at mild temperature and pressure conditions. The second stage is carried out under more severe conditions and using $CoMo/Al_2O_3$ catalyst in order to remove sulphur and avoid additional olefin hydrogenation.

The hydrogenated PyGas has a higher aromatic content than that allowed by the more and more restricted legislations that regulate the quality of automotive fuels. A more severe hydroprocessing leads to more interesting products: isoalkanes as a blending component for the gasoline pool, or C_{2+} *n*-alkanes as a feed of the steam-cracking unit itself. Isoalkanes have a higher octane number than cycloalkanes and contribute to improving the quality of the gasoline and, consequently, the hydrogenation of aromatics (leading to cycloalkanes) must be followed by ring-opening [7]. Given that C_{2+} *n*-alkanes are fed to the steam-cracking unit, they intensify the production of olefins [8]. The hydrogenation and ring opening may be carried out in series or simultaneously by using bifunctional catalysts. The latter process in a single step (hydrocracking) has advantages due to a faster aromatic conversion kinetics. This result is due to the simultaneous hydrogenating-cracking capacity of the bifunctional catalyst, which avoids the thermodynamic limitations of the hydrogenation–dehydrogenation steps [9].

A bifunctional catalyst is required for PyGas hydrocracking. The more active metallic functions for hydrogenation are noble metals (Pt and Pd) [7]. Furthermore, the use of zeolites with suitable shape selectivity as supports allows tailoring product distribution. Thus, HZSM-5 zeolites perform well as supports in the intensification of C_{2+} *n*-alkane selectivity [10–12]. Castaño et al. [13] has proven a better performance of the bi-metallic Pt–Pd function than that of monometallic functions, concerning activity, selectivity and stability (thioresistance) of the catalysts. The same authors [14,15] have assessed the effect of HZSM-5 support acidity and the nature

* Corresponding author. Tel.: +34 94601 8435; fax: +34 94601 3500.
E-mail address: pedro.castano@ehu.es (P. Castaño).

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Nomenclature

E	activation energy, kJ mol^{-1}
k_1–k_9	kinetic constants for the steps of PyGas hydrocracking. Units in Table 2
$k_i\|_{T_{ref}}$	kinetic constant at the reference temperature. Units in Table 2.
m_j, m_{PyGas}	mass flow rate of j lump, and of PyGas, g$_j$ h^{-1}.
R	gases constant, kJ (mol K)$^{-1}$
T, T_{ref}	temperature and reference temperature, K
x_j	mass fraction of j lump, g$_j$ g$_{tot}^{-1}$

Greek letters

α, β	reaction orders with respect to hydrogen, dimensionless
τ	space time, g$_{cat}$ h g$_{PyGas}^{-1}$

Subscripts

A, C, H	aromatics, cycloalkanes, and hydrogen
I, M, O, P	isoalkanes, methane, olefins, and paraffins (alkanes)

Superscripts

i, o	inlet and outlet

of the interaction between the active phases in the bifunctional Pt/HZSM-5 catalyst in the aromatic ring opening of PyGas under hydrocracking conditions.

This paper studies the kinetic modelling of PyGas hydrocracking on a Pt–Pd/HZSM-5 bifunctional catalyst. The background of the study is the kinetic modelling of the hydrogenation steps of toluene used as model compound [16] and of methylcyclohexane (toluene hydrogenation product) ring-opening [17] and the kinetic modelling of toluene hydrocracking [18]. The complex composition of PyGas and of the product streams makes advisable to group the components into lumps, as was the case in the kinetic modelling of the aforementioned reactions.

2. Experimental

2.1. Catalyst

The Pt–Pd/HZSM-5 catalyst has been prepared by ion exchange at 60 °C using $Pt(NH_3)_4(NO_3)_2$ (Alfa Aesar) and $Pd(NH_3)_4(NO_3)_2$ (Stem Chemicals) as precursors. The support used is a HZSM-5 zeolite (Si/Al = 19, Akzo Nobel-Albemarle) supplied in ammonic form. Prior to the incorporation of the metallic phase, the calcination of the zeolite (2 h at 550 °C) has been carried out in order to obtain its acid form. The volume of the solution needed for obtaining the required metallic charge has been added drop-by-drop on the calcined zeolite suspended in deionized water. The suspension (containing the zeolite and the precursor) is stirred for 24 h and the water is removed by vacuum at 80 °C. Subsequently, it is dried at 120 °C for 24 h. The catalyst obtained is sieved ($0.15 < d_p < 0.30$ mm) and calcined at 450 °C for 4 h. This temperature is reached following a ramp of 5 °C min^{-1}.

The main properties of the catalyst are set out in Table 1. The metallic content has been determined by ICP-AES in a Perkin Elmer Optima 3300DV, subsequent to dissolving the sample in HF at 90 °C. The surface properties have been determined from the adsorption–desorption isotherms of N_2 at −196 °C in a Micromeritics ASAP 2010. Prior to the analysis, the sample is subjected to vacuum at 250 °C for 18 h. The metallic surface has been determined by CO selective chemisorption at 35 °C in a Micromeritics ASAP 2010C. Previously, the sample is subjected to reduction in a H_2 flow (Alphagaz) for 2 h at 400 °C, followed by a treatment under vacuum (5 h, 10^{-8} bar). As observed in Table 1, Pd is more efficiently deposited on the acid function than Pt. Nevertheless, high dispersion of the metallic phase on the catalyst is observed. Furthermore, the incorporation of the metallic phase does not decrease the BET surface area of the support, given that they maintain a relatively high value.

Table 1
Catalyst properties.

Support	Zeolite HZSM-5
SiO_2/Al_2O_3	19
Pt (wt%)	0.202 ± 0.01
Pd (wt%)	0.482 ± 0.05
Sg (m^2 g$_{cat}^{-1}$)	313
$V_{P/P_o} = 0.2$ (cm^3 g$_{cat}^{-1}$)	89
V_{pore} (cm^3 g$_{cat}^{-1}$)	0.21
$V_{micropore}$ (cm^3 g$_{cat}^{-1}$)	0.109
d_{pore} (nm)	2.7
Dispersion (%)	54
$A_{Metallic}$ (m^2 g$_{met}^{-1}$)	198
$A_{Metallic}$ (m^2 g$_{cat}^{-1}$)	2.58
d_p^M (nm)	1.68
B:L 1453 cm^{-1} (150 °C)	5.87
B:L 1448 cm^{-1} (150 °C)	0.99
Total acidity (μmol$_{NH_3}$ g$_{cat}^{-1}$)	506
Weak (150–280 °C)	60 (12%)
Medium (280–420 °C)	296 (58%)
Strong (420–550 °C)	150 (30%)
Average acid strength (J mmol$_{NH_3}^{-1}$)	117

The total acidity and the distribution of the acid strength have been measured by temperature programmed desorption (TPD) of NH_3 (Union Carbide, purity: 99.4%), which is adsorbed at 150 °C [19,20]. The apparatus used is a TG-DSG Setaram 111 calorimeter provided with a Harvard syringe for NH_3 injection. Prior to NH_3 adsorption (30–40 mL min^{-1}), the sample is heated at 550 °C for 30 min to remove possible impurities. Once the sample has been saturated, the NH_3 desorption is monitored in a mass spectrometer (Balzers Quadstar 422) on-line with the calorimeter. The catalyst has a total acidity of 506 μmol g^{-1}, with 12% corresponding to weak acidity, 58% to medium acidity and 30% to strong acidity, according to a previously established classification [15].

The nature of the acid sites has been determined by Fourier transform infrared spectroscopy (FTIR) of pyridine adsorbed in a Nicolet 740 SX provided with SPECAC transmittance cell connected to a vacuum pump. The pellet containing approximately 30 mg of sample with KBr (transparent to IR radiation) is introduced into a cell and subjected to vacuum at 300 °C for 30 min. Subsequently, temperature is decreased to 150 °C and pyridine adsorption is carried out until sample saturation, which provides the spectrum. The calculation of the Brønsted/Lewis site ratio (0.99) has been carried out from the areas of FTIR vibration bands at 1547 cm^{-1} (interaction of pyridinium group with Brønsted acid sites) and 1455 cm^{-1} (interaction of pyridinium group with Lewis acid sites), using the molar extinction coefficients $\emptyset_B = 1.67$ cm μmol^{-1} and $\emptyset_L = 2.22$ cm μmol^{-1} provided elsewhere [21].

2.2. Kinetic runs

PyGas hydrocracking reactions have been carried out in a fixed bed reactor of descending flow under the following experimental conditions: WHSV = 2.7–32 g$_{PyGas}$ h^{-1} g$_{cat}^{-1}$; 350–450 °C; 20–50 bar; P_{PyGas} = 1 bar and H_2:PyGas molar ratio (n_{H_2}), 20–49. Previously, the catalyst diluted in 1 g of CSi (0.5 mm) is reduced under atmospheric pressure in a stream of H_2:N_2 (vol. ratio 1:2) with a flow rate of 90 mL min^{-1}, by increasing the temperature to 400 °C and main-