Full Length Article

Coke from SARA fractions in VGO. Impact on Y zeolite acidity and physical properties

Jayson Fals, Juan Rafael García, Marisa Falco, Ulises Sedran*

Instituto de Investigaciones en Catálisis y Petroquímica INCAPE (UNL – CONICET), Colectora Ruta Nacional 168 km 0 – Paraje el Pozo, (3000) Santa Fe, Argentina

ABSTRACT

The impact of the composition of the various hydrocarbon fractions in a conventional VGO (saturated SF, aromatic AF and resin RF) and the whole VGO on the coke formed in their catalytic cracking was evaluated over two Y zeolites with different degree of mesoporosity. The parent zeolite was in its protonic form, Si/Al relationship of 30 and the modified sample was desilicated by alkaline treatment. The fractions were separated from the VGO by means of ASTM D2007-11 method. The catalytic conversion experiments were performed in a batch, fluidized bed laboratory Riser Simulator reactor at 500 °C in the 0.7–3.0 s reaction time range, with a zeolite mass of 0.2 g and a zeolite/reactant mass of 1. Independent of zeolite, fraction SF was the easiest to crack. In the case of the AF fraction, the modified zeolite, with the highest intracrystalline mesoporosity, was more active than the parent zeolite. Gasoline was always the main product, with selectivities from 60 to 70%. All the feedstocks produced more coke on the modified zeolite; however, in spite of the higher coke yields, this zeolite suffered a lower loss of total acidity. As expected, a negative change in both acidity and textural properties (specific surface area and pore volume) were observed as a consequence of the formation of coke. The reactivity of VGO over both zeolites differed from that of fraction SF, even though it was the major fraction (68%). This behavior could be the consequence of interactions between the various fractions composing VGO.

1. Introduction

The catalytic cracking of hydrocarbons in transport fluidized bed reactors (FCC) is a well established process which converts low value, heavy molecular weight hydrocarbons, particularly vacuum gas oils (VGO) and also some residual cuts, into high value products such as gasoline, middle distillates, liquefied petroleum gas (LPG) and petrochemical olefins [1]. Conversions higher than 75 wt% are achieved in very short contact times [2]. Among many other issues, the characteristics of the feedstock are key factors in determining the overall process performance and the distribution of products [3,4].

Different hydrocarbon fractions can be distinguished in crude oils and their various constituting cuts. According to the solubility in diverse solvents with different polarities, at least four fractions can be separated from VGOs: saturated, aromatic, resin and asphaltenes, thus reflecting the SARA composition [5,6]. Paraffinic and naphthenic molecules with small amounts of heteroatoms mainly constitute the saturated fraction. It includes non-polar compounds such as linear, branched and cyclic hydrocarbons. The aromatic fraction is formed by aromatic cyclic hydrocarbons with one or more rings and moderate concentration of heteroatoms (particularly sulfur). Resins are, together

with the asphaltene fraction, the heaviest fractions in crude, with high polarity and condensed aromatic structures. Particularly, asphaltenes comprise highly polar hydrocarbons, with condensed aromatic rings and alkenic side chains, plus heteroatoms such as sulfur, nitrogen, oxygen and metals included in the main structure [7,8].

The most used laboratory method to separate the SARA hydrocarbon fractions in a heavy feedstock is ASTM D2007-11 standard, which is performed over two chromatographic columns packed with clay and silica gel. Besides this classic method, there exist more sophisticated techniques, such as high performance liquid chromatography [9] and thin layer chromatography combined with flame ionization detection (FID) [7,10]. These methods are faster and consume lower amounts of solvents, as compared to chromatographic columns packed with silica and clay, but they are not completely reproducible [7].

FCC catalysts are composed, the main component being the Y zeolite, present in fresh catalysts from about 15 to 40 wt%, supported on a matrix (either active or inactive). Their acidity, considering amount, nature and strength, together with their textural properties are key factors in determining activity and selectivity in these catalysts. In that sense, it is important that reactant molecules diffuse as easily as

---

possible through the catalyst pore system until reaching the active sites which are to catalyze the chemical reactions through carbocation mechanisms [11]; obviously, products are subjected to the same diffusion circumstances.

Even though Y zeolite has been used through decades given its excellent activity, selectivity and hydrothermal stability, the microscopic nature of its pore system imposes severe diffusion restrictions to bulky reactants and products, which condition their interaction with acidic active sites [12–14]. A possible solution to this fact could be provided by the generation of intracrystalline mesoporosity in the zeolite, alkaline lixiviation being a simple technique which selectively removes silicon atoms from the crystalline network, thus producing a partial destruction of the network leading to interconnected mesopores [15–19].

An additional issue, intrinsic to acidic zeolites facing hydrocarbons at high temperatures, is derived from the fast deactivation the catalysts must tolerate from the deposition of coke. The complex set of chemical reactions taking place in FCC inevitably leads to coke deposition, which has a twofold impact: active acid sites are covered and pore blocking is also observed [20–22]. Both coke yield and nature (H/C relationship, condensation degree) will depend on the composition of the feedstock, the catalyst properties and process conditions. Thus, they could affect the delicate heat balance of the commercial units, based on the combustion of coke in the regeneration section to provide the heat consumed by the overall endothermic set of reactions in the riser [23].

Ibarra et al. [24] studied coke deactivation mechanisms during the catalytic cracking of different feedstocks under FCC conditions, using various techniques such as Fourier transformed infrared (FTIR) spectroscopy, temperature programmed oxidation coupled with FTIR spectroscopy and mass spectrometry (TPO-FTIR and TPO-MS), ^{13}C coupled polarized magic angle spinning nuclear magnetic resonance (CP-MAS NMR), X-ray photo spectroscopy (XPS), Raman spectroscopy and matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS). They digested the inorganic portion of the samples to obtain two coke fractions, respectively soluble and insoluble in dichloromethane, and further analyzed them. Two main types of coke were observed, one of them with strong aromatic character and low H/C relationship, constituted by condensed aromatic rings, the other one showing olefinic nature, constituted by species with conjugated double bonds [24].

Given feedstock, catalyst and process conditions, it is important to know the reactivity of the VGO, which certainly reflects that of its constitutive SARA fractions, to recognize, and ideally predict and understand, their impact on the process yields and product quality, as well as on catalyst performance. It is the objective of this study to crack a VGO feedstock and the fractions constituting it over Y zeolites with different degree of intracrystalline mesoporosity in order to estimate their individual impact on the catalyst properties after coke formation. As already mentioned, FCC catalysts are compound, with Y zeolite exclusively contributing the micropore specific surface area and most of the acidic function in the particles, while the matrix usually plays important roles such as support, heat carrier, and zeolite dilution media [12,25]. Given that the main aim in this work is to evaluate the impact of coke formation on the deactivation of the zeolite component in FCC catalyst (both losses in acidity and changes in textural properties), the catalytic activity was observed only in the steamed zeolites, to avoid the influence of the matrix and binder. Moreover, the dilution effect could be significant.

2. Experimental

2.1. SARA VGO fractioning

A paraffinic vacuum gas oil was fractionated into its SARA fractions by means of ASTM D2007-11 standard [26]. The properties of the parent VGO are shown in Table 1.

Initially, the asphaltene fraction was precipitated with n-pentane

Table 1
VGO properties.

°API	22.94
Aniline point (°C)	80.1
CCR (wt.%)[a]	0.11
Distillation curve (°C)[b]	
Initial	199
10% vol.	345
30% vol.	405
50% vol.	438
70% vol.	465
90% vol.	495
Final	512
Nickel (ppm)	0.10
Vanadium (ppm)	0.73
Sodium (ppm)	0.38
Iron (ppm)	2.36
Copper (ppm)	< 0.02
Sulphur (wt.%)	0.39

[a] ASTM D-4530.
[b] ASTM D-1160.

(Merck, > 99.5 wt%), and the remaining oil was further passed through glass chromatographic columns using a series of solvents with increasing polarities. Two columns were used in series, each having 310 mm length and 44 mm diameter. The upper column was loaded with 50–500 μm Attapulgite clay particles to adsorb polar compounds and resins (resin fraction, RF). The lower column was loaded with 63–200 μm silica gel particles (Merck, Silica gel 60, code number 107734) which is aimed at retaining the aromatic fraction. The columns were swept with n-pentane to elute the saturate fraction (SF) and then separated. The upper column, containing the RF fraction was washed with a acetone:toluene 50:50 vol mixture to remove resins from the bed. The lower column was rinsed with toluene and aromatic compounds (AF fraction) were collected. All the fractions were dried with anhydrous CaCl$_2$ (Merck, > 99.9 wt%) and finally the solvents in each fraction were removed in a rotatory vacuum evaporator at 40 °C and 417 Torr. The complete removal of solvent in each fraction after treatment was confirmed by means of GC analysis.

2.2. Alkaline treatment of Y zeolite

Two Y zeolites with different degrees of intracrystalline mesoporosity were used. The parent zeolite was a commercial Y zeolite (CBV 760, Zeolyst International, protonic form). The modified sample was the result of the following alkaline treatment on the parent zeolite [14,27–29]. 10 g of zeolite were suspended in 300 mL of a NaOH solution (0.10 M) and the suspension was stirred during 15 min at room temperature. Then, a 1.00 M HCl solution was added to the suspension to reach a final pH of 2.00 in order to quench the alkaline leaching. The thus desilicated zeolite was separated from the solution by filtration and submitted to three cycles of ion exchange using 5 mL of 0.50 M NH$_4$Cl solution per gram of zeolite. The ion-exchanged zeolite was then thoroughly washed using deionized water, dried in an oven during 16 h at 110 °C and finally calcined in a muffle oven during 4 h at 550 °C in order to obtain the zeolite in its acid form. The parent and desilicated zeolites were named Y-00 and Y-10, respectively. Both the modified and untreated zeolites were hydrothermally stabilized by steaming during 5 h at 788 °C (100% steam). The steamed zeolites were named Y-00-S and Y-10-S, respectively, in concordance with their parent zeolites.

2.3. Physicochemical characterization

The textural properties of the zeolites, both before and after reaction (coked samples), were assessed by means of nitrogen adsorption at −196 °C using a Micromeritics ASAP 2020 sorptometer. Before analysis, the samples were degassed under vacuum during 3 h at 300 °C.