



Effect of acidity, hydrogenating phases and texture properties of catalysts on the evolution of asphaltenes structures during residue hydroconversion



Guillaume Magendie^a, Bertrand Guichard^{a,*}, Didier Espinat^b

^a IFP Énergies Nouvelles-Établissement de Lyon, Catalysis and Separation Division, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

^b IFP Énergies Nouvelles-Établissement de Lyon, Physics and analysis Division, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

ARTICLE INFO

Article history:

Received 8 August 2014

Received in revised form 3 October 2014

Accepted 12 October 2014

Available online 15 November 2014

Keywords:

NiMo catalysts

Acidity

Cracking

Hydrogenation

Asphaltenes

Ring-opening

ABSTRACT

The aim of this work was to investigate vacuum residues hydroconversion using acid-modified catalysts. To achieve this goal, silicon was incorporated by a grafting procedure. The catalysts with different silicon amounts in the support or hydrogenating active phases were evaluated performing hydrotreatment of a Safaniya vacuum residue at 370 °C. A multi-techniques set of analyses was used, in order to characterize both the sulphided active phase and acidity. It can be concluded from this study that acidity is beneficial for conversion of asphaltenes but the hydrogenation active phase does not seem to be the main way to improve the transformation. The proposed mechanism is the following: with short reaction time, acidity promotes cracking of naphthenic and alkyl units but hydrogenation is not completed. Then, with longer reaction times, asphaltenes reveal a loss of aromatic rings which demonstrates that the hydrogenation pathway is enhanced and a significant loss of molecular weight is observed. This new way of transformation opens the way to a complete change of reactivity over the whole HDT processes. If used as a pretreatment of petroleum residues, this type of catalyst could drastically improve the conversion yield of heavy feeds in order to develop sustainable refining processes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Refining heavy or extra heavy oil is still a challenge for researchers in the fields of hydroprocessing technologies. It appears even more attractive since the worldwide trend indicates a decline of light conventional crude oil availability, the latest being gradually replaced by heavier non conventional resources that contain asphaltenes and high concentrations of nitrogen and sulfur compounds. The associated specific operation is named conversion and consists in the transformation of heavy compounds, i.e. boiling at temperature higher than 540 °C (Vacuum Residue) or higher than 370 °C (Atmospheric Residue) into lighter ones, i.e. boiling at lower temperature (transportation fuels). In parallel, stringent regulation and speciation on polluting agent in fuels (like sulfur compounds) highlights the need of improve the existing processing yield and the final quality of products [1].

Petroleum residues conversion can be achieved by two different routes [2,3]. In the specific case of heavy feedstock containing high

metal (Ni, V) and asphaltenes loadings, ebullated bed technology is particularly suitable to convert up to 80 wt.% of the 540 °C [4,5]. The reaction is usually performed at high temperature (>410 °C) and pressure (>15 MPa), with continuous addition and withdrawal of catalyst. Nevertheless, improvement of such processes needs to overcome a tricky limitation due to the instability of effluents leading to sediment formation and causing severe operability issues as well as catalyst deactivation [6,7]. Indeed, at high temperature, in thermal cracking conditions, cracking pathway is mainly assumed to take place by radical way [8,9]. Moreover, hydrogenation reactions are not thermodynamically promoted, which leads to increase the global aromaticity of effluents and enhance the instability of compounds [10–12]. For this reason, heavy feedstock residues, with lower metal concentration, can also be hydrotreated using fixed bed units at lower temperatures (370–410 °C) [13]. It allows producing very low sulfur oils, as well as products that can be further upgraded in a Residue Fluid Catalytic Cracker (RFCC).

HDM and HDS catalysts are generally composed of sulphided NiMo or CoMo active phases supported on alumina carrier in order to perform hydrogenation reactions on the feed [14]. The support properties have a key impact in the process. A compromise must be done on porosity, in order to maximize specific surface area for

* Corresponding author. Tel.: +33 4 37 70 23 08.

E-mail address: bertrand.guichard@ifpen.fr (B. Guichard).

high dispersion of active phase, and also allow bulky asphaltene molecules to diffuse till the catalytic sites [15,16]. A higher porosity also prevents for deactivation by pore mouth plugging with metal and coke deposition after conversion [7,17,18]. The support can also be used in order to provide an increased acidity to the catalyst and enhance hydrocracking reactions [19–21] by promoting hydrogenolysis reaction pathway [22].

Three different approaches are described in literature in order to improve acidity on catalyst for processing heavy oils. It can be obtained by modifying the support: using zeolites [19,23–25] or mixed oxides [26–32]. The last method consists in using acidic doping agent (such as halogen) [23,33–36].

Many developments were carried out in the middle distillates field, but the use of zeolite is probably more limited for heavy oil conversion because of its small pore diameter and the difficulty of mixing them with amorphous matrix [37]. Thus accessible external surface of zeolite crystallites represents a small portion of the total catalyst surface [23].

In the last decade, mixed oxides have also been applied to hydroconversion system using heavy Maya crude oil in a fixed bed reactor, particularly by Ancheya et al. [26–32]. First CoMo(P) and NiMo(P) were investigated supported on mixed TiO₂ or SiO₂ alumina support [26,27,38]. They were prepared by coprecipitation of salts by urea hydrolysis method which did not allow to carefully monitoring the support porous distribution. Moreover it was observed that quality/quantity of sulphided metal active phase is affected by high level of silica, which is coherent with the poor affinity of Mo and Ni with this element. IR results [32] also highlight that supports and catalysts acidity can be enhanced by using silica. As a matter of fact, only weak improvements of metal (HDM) and asphaltènes (HDA₇C₇) removal activities were reported. No definitive conclusions were raised concerning TiO₂ or SiO₂ presence.

Concerning doping agent method, TiO₂ using titanium isopropoxide in different routes or SiO₂ from Rhodorsil® emulsion have also been incorporated on catalyst by pore volume impregnation [23,29] and also lead to a drastic decrease in the amount of “NiMoS” active phases [30,32]. As a consequence, these catalysts were less active in purification reactions (HDS; HDN; HDA₇C₇) but also achieve no more conversion. Other acidic doping agents (F, P, V) have also been studied to improve residues hydrotreatment/hydroconversion catalysts [23,33–36]. F doped NiMo catalyst shows higher HDS, HDN and HDA₇C₇ activities at low and high temperatures, but this result can no longer be strictly attribute to acidity, as catalysts have both a better acidic and hydrogenating power (revealed by the sulphided species analysis [23,33]). Surprisingly, no variations in mass distribution or asphaltene structures are noted using fluorine. It also has been observed that vanadium has a synergic effect on acidity and hydrogenating active phase, which can also improve HDA₇C₇ and HDM activity [34].

Consequently it is suspected, regarding to literature, that acidity should improve residue hydrotreatment and/or hydroconversion, particularly at low temperature, in absence of thermal contribution. This work aims to get some additional comprehension on the role of such acidity by studying catalysts exhibiting independent variations in textural features, hydrogenation rates and acidity using a Safaniya residue hydroconversion tests. It is suspected that some improvements can be achieved providing a well-balanced hydrogenation-acidity as for the VGO hydrocracking [22]. To achieve this goal, NiMoP catalysts supported on mixed Al₂O₃–SiO₂ were prepared. Silica was introduced by using grafting procedures, described in literature [39–43]. After a brief description of the catalysts preparation, a detailed characterization of textures, acidity and hydrogenating active species is presented. Then catalytic performances on model molecules as well as on vacuum residue are summarized. Finally, all these results allow us to discuss the impact of acidity in the hydroconversion mechanism. A

molecular model is proposed to describe the asphaltene evolution in working conditions.

2. Experimental

2.1. Alumina grafting (carrier preparation)

Mesoporous monomodal aluminosilicate carriers were obtained by grafting silica on the alumina surface as described elsewhere [44,45] (see Table 1). Trilobal alumina extrudes obtained by coprecipitation of aluminum sulfate and sodium aluminate were used. In order to increase the silica amount grafted over the support, the complete grafting process can be repeated two or three times, from pretreating to calcination steps. It allows us to obtain silica-alumina carriers up to 2.3 wt.% of silicon.

2.2. Catalyst preparation

The catalysts prepared for this study were obtained from the incipient wetness impregnation with a NiMoP solution into the previous mentioned aluminosilicate supports. The NiMoP catalyst prepared from the raw alumina support is selected as reference. The solution containing Ni, Mo and P was prepared under reflux at 90 °C using respectively Ni(OH)₂; MoO₃ and H₃PO₄ as precursors. Impregnation is followed by a maturation step in a water saturated atmosphere, for 24 h at room temperature. Then, a drying step was performed for 24 h at 120 °C followed by calcination under air for 2 h at 450 °C. In some impregnated solutions EDTA was added to improve the active phase dispersion [46–50]. The molar ratio EDTA/Ni was set to 1.0 mol/mol.

The target concentration of active phase for all catalysts is 14.5 wt.% MoO₃ with the following molar ratio Ni/Mo=0.4 and P/Mo=0.5. The XRF analysis reveals that the concentration is in agreement with the previous mentioned values (Table 1). The catalysts will be noted NiMoP X, where X stands for the number of grafting steps. The same number of grafting steps may have led to some differences in the silica amount (see Table 1). Two additional catalysts were prepared from a three-step grafted alumina aiming 18 wt.% MoO₃ with the same molar ratio Ni/Mo/P (NiMoP 3 18%) or replacing molybdenum by tungsten (NiWP 3 23.4%).

2.3. Catalyst activation and evaluation (Vacuum resid)

Before catalytic evaluation in batch reactor or characterization, the catalysts were sulphided in gas-phase at atmospheric pressure. Catalysts were introduced in a glass reactor and heated from room temperature to 350 °C at 5 °C min⁻¹ followed by 2 h at this temperature, under a 15:85 v/v H₂S/H₂ gas mixture flow at 2 NL g_{catalyst}⁻¹ h⁻¹. This gas flow insures a large excess of sulfur in relation to MoS₂ stoichiometry. At the end of the sulfidation, the reactor was cooled down to room temperature and the H₂S/H₂ flow was replaced by argon flow up to 15 min. Afterwards, reduced pressure was applied into the glass reactor (~100 Pa) and it was sealed to prevent the sample from reoxidation. This operation, in particular reduce pressure, is only applied to seal easily the glass cell and so to obtain a long term sample, catalytic evaluation being only carried out some days after sulfidation.

The composition of Safaniya Vacuum Residue (VR) is reported in Table 2. It contains large amounts of metals and asphaltene. The catalytic test was carried out in an isothermal stainless steel 300 mL batch reactor operated. The catalyst is introduced inside a stationary perforated basket with a hollow stirrer placed in the center. A catalyst volume of 15 mL (sulphided ex-situ) was used for treating 90 mL of feedstock. The reactor is first purged with hydrogen, then pressurized to 4.2 MPa and heated up, from room

Download English Version:

<https://daneshyari.com/en/article/53605>

Download Persian Version:

<https://daneshyari.com/article/53605>

[Daneshyari.com](https://daneshyari.com)