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### IMPACT OF METAL CONTENT ON THE DEACTIVATION OF A BIFUNCTIONAL HYDROCRACKING CATALYST

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9 10

11 Keywords: deactivation, bifunctional catalyst, metal/acid balance, nitrogen poisoning,

12 hydrocracking.

#### 13 **ABSTRACT**

14 The catalytic performance of a hydrocracking bifunctional catalyst and, consequently, its activity 15 loss depends on the balance between the metal (M) and acid (A) functions. Commonly, the metal 16 function is reputed to stabilize catalyst activity and should, therefore, alleviate deactivation. In 17 order to test this hypothesis, this study aimed to assess the impact of the metal oxide  $(MoO_3)$ 18 content on the deactivation of a vacuum gasoil hydrocracking catalyst (a nickel-molybdenum 19 sulfide dispersed on a carrier containing USY zeolite). To do so, two bifunctional catalysts with 20 different metal oxide contents were submitted to specific operating conditions promoting catalysts 21 deactivation, i.e., high temperature (T=418°C) and high space velocity (LHSV=3 h<sup>-1</sup>). Experiments 22 were carried out in a pilot unit with a hydrotreated VGO feedstock containing 120 ppmw of organic 23 nitrogen. The loss in activity was measured by following the decrease of both the VGO conversion 24 (370°C<sup>+</sup>) and the apparent kinetic constants for the main hydrocracking reactions (cracking, 25 hydrodenitrogenation and aromatics hydrogenation) with time on stream. The aged catalysts, 26 sampled from three different reactor locations, were characterized by elemental, textural analysis 27 and thermogravimetry to investigate the quantity and nature of the coke deposits. To determine

28 the residual activity of the hydrogenation and acid catalyst functions, catalytic tests with different 29 model compounds (toluene and n-heptane) were carried out. It was observed that in the 30 hydrocracking of feedstocks with high nitrogen concentration, the decrease of the metal content 31 causes a substantial increase of the nitrogen compounds concentration in the catalytic bed. This 32 increase significantly reduces the available acid sites and, hence, the hydrocracking activity. But 33 at the same time, the M/A ratio is modified in favor of the metal function. The better balance of the 34 catalyst with low metal loading results in a lower coke deposition and, consequently, a lower 35 deactivation rate than with the catalyst with higher metal content.

#### 36 1 INTRODUCTION

37 The hydrocracking of vacuum gasoils (VGO) is a refining process to produce mainly middle 38 distillates (diesel and kerosene) <sup>1-3</sup>. This process employs bifunctional heterogeneous catalysts 39 that combine a (de)/hydrogenation and an acid function. Commonly the (de)/hydrogenation 40 function is provided by metal sulfides from group VIA (molybdenum, tungsten) and group VIIIA (nickel) <sup>4–6</sup>. Ultra-stable Y zeolites are widely used as acid components in hydrocracking catalysts 41 <sup>7</sup>. In the classical bifunctional hydrocracking mechanism <sup>8-11</sup>, the metal function serves to 42 43 dehydrogenate alkanes to the corresponding alkenes. These alkenes are desorbed from the metal 44 sites and diffuse to the acid sites, where they are protonated to carbenium ions. These 45 carbocations undergo skeletal isomerization and cracking; their products are desorbed as alkenes 46 which are finally hydrogenated to alkanes on metal sites. Thus, catalyst activity, stability and selectivity strongly depend on the balance between the metal and acid functions (M/A) <sup>12-14</sup>), the 47 distance between these functions (Weisz's intimacy criterion) 9,11,15 and on the characteristics of 48 49 the zeolite pores <sup>15,16</sup>.

50 Several authors have studied the balance between the metal and acid functions (M/A). For 51 bifunctional catalysts based on a noble metal (Pt) during the hydroisomerization and

hydrocracking reactions of n-heptane <sup>13,14</sup> and n-decane <sup>17</sup>, Guisnet et al. <sup>13,14,17,18</sup> found that at 52 53 low (M/A) ratios, the initial activity per acid site is low and increases with the increase of this ratio 54 until reaching a stable value, which corresponds to a bifunctional mechanism limited by the acid 55 sites. They also found that at low M/A ratio, the catalyst stability is poor because there is a fast 56 coke formation. For high M/A values, the catalyst is well balanced (i.e., acid-catalyzed reactions become the limiting step <sup>19</sup>) and the reaction follows the well-known ideal bifunctional 57 hydrocracking mechanism. Other works <sup>20,21</sup> also confirmed the relation between the metal loading 58 and catalyst activity. Degnan and Kennedy<sup>21</sup> evaluated the hydroisomerization of n-heptane on a 59 60 Pt catalyst and they found that an imbalance between the hydrogenation and the acid functions can even alter the apparent reaction network of the system. Denayer et al. <sup>22</sup> found a reduction in 61 62 activity with an increase of the (M/A) obtained by reducing the number of acid sites. The reduction 63 in activity is related to the decrease in acidity and consequently in cracking power.

For metal sulfide catalysts, Mendes et al. <sup>23</sup> quantified the amount of Brönsted acid sites available 64 65 in an ammonia atmosphere during the hydroconversion of cyclohexane and found that just around 1% of the acid sites remained available in the presence of ammonia. They noted that for two well-66 67 balanced NiMo catalysts with different Mo content, there is no difference in activity or selectivity independently of the ammonia content. Pirngruber et al. <sup>19</sup> compared the performance of metal 68 69 sulfided catalysts with different acidity levels on the hydroconversion of n-hexadecane. They found 70 that the inhibition of the acid sites by ammonia, in association with low zeolite contents, is 71 necessary to balance NiMo sulfide hydrocracking catalysts. They also observed a negative 72 correlation between catalyst selectivity to isomerization reactions and zeolite loading. The impact 73 of MoO3 loading on activity was guite small because it was mainly governed by the zeolite loading of the catalysts. In a similar work, Mendes et al. <sup>24</sup> confirm that ammonia helps to equilibrate the 74 75 metal-acid balance in NiMo catalysts. They also evaluated catalysts with different molybdenum 76 loadings in the n-hexadecane hydroconversion, but no noticeable evolution of the activity with Mo

loading and only a minor evolution of the maximal C16 isomer yield were observed. M.V. 77 Bukhtiyarova et al.<sup>25</sup> studied the effect of sulfosalicylic acid treatment on the properties of Beta 78 79 zeolite (BEA and BEA-SA) and the performance of NiW/Beta-Al<sub>2</sub>O<sub>3</sub> catalysts in hexadecane 80 hydrocracking. The total Brønsted and Lewis acid sites concentration decreased with an acid 81 treatment and as a result, the metal-acid balance of the catalyst shifted towards enhanced metal 82 function, providing the beneficial effect on hexadecane hydrocracking selectivity. I.G. Danilova et 83 al.<sup>26</sup> worked on the impact of rare earths on the acidity of high-silica ultrastable REY zeolites and 84 catalytic performance of NiMo/REY+Al<sub>2</sub>O<sub>3</sub> catalysts in VGO hydrocracking; they found that the 85 increase in  $RE_2O_3$  content led to a decrease in the strong acid site density, which suppresses 86 overcracking reactions and improves the selectivity to middle distillates.

87 The deactivation of bifunctional hydrocracking catalysts with VGO feeds is dominated by the poisoning involving organic nitrogen compounds and coke deposition <sup>27-29</sup>. N-compounds are 88 89 strongly adsorbed on the catalyst surface compared with other hydrocarbon structures present in the feed <sup>30–32</sup>. With a longer time on stream, the adsorbed species are converted to coke <sup>33–37</sup>. 90 91 Concerning deactivation by coke, two different mechanisms have been proposed to explain coke 92 formation on the metal and the acid sites of bifunctional catalysts. On metal sites, it is presumed 93 that coke results from successive dehydrogenation reactions leading to atomic carbon or partially hydrogenated intermediates that combine to form a graphitic coke <sup>38,39</sup>. On acid sites, it is accepted 94 95 that coke results from the polymerization of dehydrogenated intermediates generated on the metal 96 sites <sup>40</sup>.

97 The deactivation of bifunctional catalysts by coking has been the subject of numerous 98 investigations. Many of these studies were carried out on reforming catalysts, having a 99 hydrogenation–dehydrogenation function (Pt or Pt-Re) and an acid function ( $Al_2O_3$  or chlorinated 100  $Al_2O_3$ ). Barbier <sup>40</sup> analyzed the deposited coke on a spent reforming catalyst by temperature-101 programmed combustion and identified the presence of two peaks, one at around 300°C and the

102 other at around 450°C. It was established that the low-temperature (300°C) combustion was due 103 to the presence of coke on the metal phase. The results of Barbier determined that the amount of 104 coke deposited on the metallic function of a bifunctional catalyst always corresponded to a small 105 fraction of the amount of coke accumulated in the whole catalyst. Querini et al. <sup>41</sup> also analyzed 106 some industrial reforming catalyst, Pt/Al<sub>2</sub>O<sub>3</sub>, by thermal programmed oxidation (TPO) and found 107 that coke is deposited first on the metal and then on the acid sites. Coke on metal increases with 108 time initially and then remains constant, while coke on the acid sites increases during the whole run. The coke deposited on the metal is more dehydrogenated than the coke deposited on the 109 110 support <sup>42</sup>. Bartholomew <sup>30</sup> claimed that in the coke deactivation of reforming catalysts, coke 111 precursors might be formed on the metal sites via hydrogenolysis.

112 Most studies on the effect of the metal/acid sites ratio have been carried out using platinum 113 catalysts. In contrast, there is not much work with metal sulfide catalysts. To the best of our 114 knowledge, they all use different model molecules, especially alkanes, to evaluate the 115 hydroconversion reactions under conditions, not representative of the industrial process and 116 where there is no catalyst deactivation. Therefore, this work aims to evaluate the impact of 117 Molybdenum loading on the deactivation of a NiMo hydrocracking catalyst using a real feed. 118 Therefore, two bifunctional catalysts with different metal oxide contents were submitted to specific 119 operating conditions promoting catalysts deactivation in a pilot unit with a hydrotreated VGO, 120 according to the accelerated deactivation protocol developed in our previous work 43.

#### 121 **2 EXPERIMENTAL SECTION**

#### 122 **2.1 Feedstock**

The feedstock was a hydrotreated blend of 71% vacuum gasoil, 16% coker gasoil and 13% light
cycle oil on a weight basis. The main properties of this feed are shown in

Table 1. Dimethyl disulfide and aniline were added to the hydrotreated VGO to generate the hydrogen sulfide and ammonia partial pressures representative of the VGO mother feed. The mother feed contained a sulfur and a nitrogen content of 1.18 and 0.25 wt%, respectively.

Table 1. Feedstock properties.					
Properties		Feed			
Density @ 15°C	g/cm <sup>3</sup>	0.8679			
Refraction Index @ 70° C	-	1.4791			
Sulfur	wt%	0.016			
Nitrogen	ppmw	120			
Aromatics content	wt%	~42			
Yield of 370°C <sup>+</sup> fraction	wt%	64			
Initial boiling point (IBP)	°C	131			
T50 Boiling point	°C	397			
Final boiling point (FBP)	°C	554			

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#### 130 **2.2 Catalysts**

131 The reference catalyst consists of nickel-molybdenum sulfide particles dispersed on a carrier 132 containing USY zeolite. A series of catalysts with varying metal oxide content at a constant Ni/Mo 133 molar ratio was prepared to evaluate the impact of molybdenum content. Their molybdenum oxide 134 contents were 25%, 50% and 75% of the molybdenum oxide content related to the reference 135 catalyst. No modification was made to the zeolitic support. These fresh catalysts were used to 136 determine the activity of each function at different metal oxide contents. Based on these results, 137 the catalyst with 50% molybdenum was chosen to be subjected to the accelerated deactivation 138 conditions developed in our previous work <sup>43</sup> and compare its performance with that of the 139 reference catalyst.

140 The catalysts were synthesized by incipient wetness impregnation of the zeolitic support in 141 extrudates shape with a solution containing Ni and Mo precursors. After 1.5 hours of maturation, the solids were dried at 120°C for 12 hours and then calcined at 450 °C for 2 hours under air. No
additional information on catalyst properties is given for confidentiality reasons.

#### 144 **2.3 Experimental set-up**

145 The test runs were conducted in an up-flow fixed-bed pilot unit. Detailed information has been 146 reported elsewhere <sup>43</sup>. The pilot plant comprised two isothermal reactors in series, loaded with the 147 same hydrocracking catalyst diluted with inert carborundum (SiC). Thus, both reactors operate on 148 hydrocracking reactions. The unit has a liquid sampling system between the two reactors. The gas 149 and liquid phases from the total effluent were separated by a high-pressure separator installed downstream of the second reactor. The gaseous effluent was transferred to a gas flow meter and 150 151 then analyzed online by gas chromatography, while the liquid product was sent to a stripper and 152 finally to a storage vessel. The liquid products were characterized by density, refractive index, 153 nitrogen and sulfur contents and simulated distillation to daily track catalyst performance.

#### 154 **2.4 Experimental procedure**

155 At the beginning of the pilot unit tests, the catalyst was sulfided in situ with an atmospheric gasoil 156 spiked with 2% wt. (%/feed) of dimethyl disulfide (DMDS) and 2% wt. aniline (%/feed) at 350°C 157 and 14MPa. After this step, the deactivation conditions were imposed, i.e., 418°C, LHSV of 3 h<sup>-1</sup>, 158  $H_2/HC = 1500$  NL/L and P = 14 MPa, with the feedstock described in section 2.1. The catalyst 159 remained at the same conditions for 30 days. The density of the liquid effluent tracked the 160 stabilization of the catalyst. The performance was considered stable when the density variation 161 was lower than 0.0010 g/cm<sup>3</sup> for 24 consecutive hours. However, in those tests, the catalyst 162 immediately went into a deactivation regime at the conditions applied, barely showing stabilization. 163 Therefore, in the evaluation of the experimental results, the experimental points from the first two 164 days were not considered because the effects of the system stabilization and catalyst deactivation 165 can be superimposed at the beginning of the test. The unit was washed with atmospheric gasoil 166 at the end of the experiment. The catalyst was stripped and dried with hydrogen before being

unloaded. Catalyst samples taken at the end of each experiment were carefully collected to
 separate the particles from the inlet, middle and outlet of each catalytic bed. More information
 about specific experimental procedures can be found elsewhere <sup>43</sup>.

#### 170 2.5 Kinetic performance evaluation

171 The conversion of VGO (370°C<sup>+</sup>) (Equation 1) was monitored to assess the catalytic performance. 172 However, interpreting the raw conversion data can be misleading, especially when the conversion 173 is high. As the conversion increases, the reactant is depleted. Consequently, the differential 174 reaction rate decreases. A kinetic model must be established to do a rigorous analysis of reaction 175 rates, but for the complex reaction network of the VGO, this requires a significant amount of input 176 data <sup>43</sup>, which was not available in our case. Therefore, for simplicity's sake, power-law models 177 were used to calculate the apparent kinetic constants for the main reactions (cracking, 178 hydrodenitrogenation-HDN and aromatics hydrogenation-HDA). The inhibition and deactivation 179 were followed by the change in these constants during time on stream. The aim was to compare the different reaction rates for the two selected catalysts. A first-order <sup>43</sup> kinetics was assumed for 180 181 both N-containing and aromatic molecules <sup>43</sup> (Equation 2), i.e., for HDN and HDA, respectively. 182 To determine the apparent HDA kinetic constant, the amount of aromatic carbon was estimated 183 through the n-d-M method according to the standard ASTM D3238.

%Net Conversion=
$$\left(\frac{\text{mass}_{x \text{ feed}}\text{-mass}_{x \text{ product}}}{\text{mass}_{x \text{ feed}}}\right)$$
\*100 Equation 1

Where x is either the 370<sup>+</sup> mass fraction, the nitrogen content or the aromatic carbon content.

#### *k*=LHSV\*In(1-%NetConversion/100)

Equation 2

For reactions affected by catalyst deactivation, there is a dependence of the kinetic performance on deactivation. Therefore, an exponential decay model with three parameters (Equation 3) was assumed to dissociate both phenomena for cracking reactions. In this model, the catalyst deactivation depends on the deactivation constant and time on stream (TOS)  $^{43-45}$ . The alpha ( $\alpha$ ) 188 (1/time) parameter accounts for the activity loss rate by deactivation of the catalyst. Finally, the c

189 parameter represents the residual activity of the spent catalysts.

190 (A+c) corresponds to the kinetic constant of the fresh catalyst at time = 0.

#### 191 **2.6 Samples Characterization**

#### 192 2.6.1 Liquid Samples Characterization

Feed and liquid products (sampled every day) were characterized by a densimeter for determining
the density, by chemiluminescence for the nitrogen content, by X-Ray fluorescence spectrometry
for the sulfur content and gas chromatography for the simulated distillation.

#### 196 2.6.2 Catalyst Characterization

197 Before being characterized, the spent catalyst samples were submitted to extraction with toluene 198 in a soxhlet extractor at 250°C for 7 h and dried under vacuum at 120°C for 12 h. Then the following 199 analyses were carried out. The carbon, hydrogen and nitrogen contents were determined on a 200 Thermoscientific FlashSmart equipment. Nitrogen adsorption-desorption isotherms 201 measurements were performed in an ASAP Micromeritics apparatus to determine the catalyst 202 surface area and total pore volume. Additionally, the catalyst was analyzed by elemental 203 thermogravimetry on a thermobalance Mettler ToledoTGA-DSC1 coupled with a mass 204 spectrometer. The MoS<sub>2</sub> sheets were visualized and analyzed by transmission electron 205 microscopy with a JEOL JEM 2100F microscope to determine the slab length and promotion. The 206 TEM images were recorded in the bright field mode. The average dispersion of the MoS<sub>2</sub> particles 207 was calculated from the slab length distribution, assuming a hexagonal shape for the particles <sup>46</sup>. 208 Finally, the promotion degree of the MoS<sub>2</sub> particles was investigated by TEM-EDX detection, 209 leading to Ni/Mo ratio calculated for about 25 particles.

#### 210 2.6.3 Catalytic tests with model molecules

211 Catalytic tests with model compounds were carried out to characterize the activity of both catalytic 212 functions for the fresh and the spent catalysts. The hydrogenation activity was evaluated by 213 converting toluene to hydrogenated products. For fresh catalysts, the reaction was carried out in the presence of aniline (0.5 wt %) in order to moderate their activity. In the case of spent catalysts, 214 215 no aniline was used. The cracking function was determined by the hydroconversion of n-heptane 216 to isomerization and cracking products. The used methods are analogous to the one described 217 elsewhere <sup>47</sup>. The catalytic tests were carried out in a high-throughput fixed bed reactor unit in the 218 presence of H<sub>2</sub>S (generated by decomposition of DMDS) under hydrogen pressure. Catalysts 219 samples were sulfided in situ. The operating conditions for each experiment are presented in Table 220 2.

Table 2. Operati	Table 2. Operating conditions of the catalytic tests with model molecules.							
		Toluene Hydro	n-Heptane					
			Hydroconversion					
		Fresh catalyst	Spent catalyst	Fresh	and	spent		
				catalyst	S			
Concentration of reactant	wt %/feed	20*	20*		95.15			
DMDS concentration	wt %/feed	6	6		4.85			
Aniline concentration	wt %/feed	0.5						
Р	MPa	6	6		6			
LHSV	h⁻¹	2	2		4			
Т	°C	350	350	35	0/360/38	0		
H <sub>2</sub> /HC	NL/L	450	450		330			
	Concentration of reactant DMDS concentration Aniline concentration P LHSV T H <sub>2</sub> /HC	Table 2. Operating conditions         Concentration of reactant       wt %/feed         DMDS concentration       wt %/feed         Aniline concentration       wt %/feed         P       MPa         LHSV       h <sup>-1</sup> T       °C         H <sub>2</sub> /HC       NL/L	Table 2. Operating conditions of the catalytic termToluene HydroFresh catalystConcentration of reactantwt %/feed20*DMDS concentrationwt %/feed6Aniline concentrationwt %/feed0.5PMPa6LHSVh <sup>-1</sup> 2T°C350H <sub>2</sub> /HCNL/L450	Table 2. Operating conditions of the catalytic tests with model m Toluene HydrogenationToluene HydrogenationFresh catalystSpent catalystConcentration of reactantwt %/feed20*20*DMDS concentrationwt %/feed66Aniline concentrationwt %/feed0.5PMPa66LHSVh <sup>-1</sup> 22T°C350350H₂/HCNL/L450450	Table 2. Operating conditions of the catalytic tests with model molecules.Toluene Hydrogenationn-HeptaHydrocationFresh catalystSpent catalystFresh catalystSpent catalystFresh catalystConcentration of reactantwt %/feed20*20*DMDS concentrationwt %/feed66Aniline concentrationwt %/feed0.5PMPa66LHSVh <sup>-1</sup> 22T°C350350H₂/HCNL/L450450	Table 2. Operating conditions of the catalytic tests with model molecules.Toluene Hydrogenationn-HeptaneHydroc-nversionHydroc-nversionFresh catalystSpent catalystFreshConcentration of reactantwt %/feed20*20*MDDS concentrationwt %/feed66Aniline concentrationwt %/feed0.5PMPa666LHSVh <sup>-1</sup> 224T°C350350/360/38H2/HCNL/L450450330		

222 \*in cyclohexane as solvent

#### 223 **3 RESULTS**

To evaluate the impact of the  $MoO_3$  loading on catalyst performance, the results of the model molecule (Toluene, n-heptane) tests obtained with catalysts with different metal contents are firstly presented. These results serve as a basis for the interpretation of the VGO hydrocracking experiments under deactivation conditions for two catalysts with different metal content, which are reported in section 3.2. Subsequently, the characterization of the spent catalysts obtained in the pilot plant tests is shown in section 3.3.

#### **3.1** Model molecules tests for fresh catalysts with different MoO<sub>3</sub> contents

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In Figure 1a, the hydrogenation activity of the catalysts is presented as a function of their MoO<sub>3</sub> content; as expected, the conversion increased with the metal oxide content. Concerning the cracking function, the lower the amount of molybdenum, the lower the activity, although all catalysts had the same zeolite content (see Figure 1b). The strong dependence of the cracking activity on molybdenum loading is quite remarkable because it is more pronounced than reported in previous studies <sup>19,23,24</sup>. This indicates a strong limitation of the bifunctional mechanism by the initial dehydrogenation steps.



Figure 1. Catalytic activities evaluated by model molecules catalytic tests for fresh, dried catalyst
 samples with different MoO<sub>3</sub> contents a) Hydrogenation of toluene in the presence of aniline, b)
 Isomerization/cracking of n-heptane at 360°C.

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The selectivity to i-heptane is shown in Figure 2. The results indicate that the selectivity increases as the metal oxide content increases, for a given  $n-C_7$  conversion. This is sign of a better metal/acid (M/A) balance. As the metal content of the catalyst increases, the probability of an 247 intermediate i-C<sub>7</sub> olefin finding a metal site, before undergoing further isomerization and cracking





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Figure 2. Selectivity to i-C<sub>7</sub> Vs. n-C<sub>7</sub> conversion for fresh dried catalyst samples with different MoO<sub>3</sub>
 contents.

253 Once this simple screening of the molybdenum content was accomplished, the catalyst with 50 % 254 of the metal oxide content (designated as "0.5 MoO<sub>3</sub>") of the reference catalyst (designated as 255 "Reference") was selected to evaluate its loss of activity in the pilot unit under accelerated 256 deactivation conditions. The goal was to evaluate the impact of an important modification of the 257 M/A ratio on catalyst activity and deactivation.

#### 258 **3.2** Deactivation experiments with catalysts at different metal contents

- 259 3.2.1 Evolution of the apparent kinetic constants with time on stream
- 260 In the first place, the evolution of the net conversion (Equation 1) with time on stream is displayed
- in Figure 3 for both the first reactor and the whole system. The catalyst with the lower molybdenum
- 262 content presented a lower conversion for both reactors.



265

266 267

Figure 3. Net conversion as a function of time on stream for catalysts with different metal contents. Open symbols=First reactor effluent, Full symbols=Total effluent.

The evolution of the apparent kinetic constants for cracking, hydrodenitrogenation (HDN), and aromatic hydrogenation (HDA) reactions with time on stream (TOS) are shown in Figure 4, Figure 5 and Figure 6, respectively.

As was expected, the data indicate that the reduction in the amount of molybdenum (the component responsible for the hydrogenation activity) caused a decrease in the hydrogenation reactions of both aromatics and nitrogen compounds (Figure 5 and 6). Also, the cracking constants decreased by about 40%. This may be explained by two factors: (i) the limitation of bifunctional cracking by the metal function, as illustrated for n-heptane cracking in Figure 1b; (ii) the lower HDN activity, leading to a higher organic nitrogen concentration inside the reactor in the case of the 0.5MoO3 catalyst, which inhibits the cracking activity.

The kinetic rates for the mentioned reactions were lower in the first reactor than in the second one (HDA values are not shown for the first reactor since they are negligible). This result is explained by the organic nitrogen concentration profile along the system, that strongly inhibits both catalyst functions.



Figure 4. Global and first reactor kinetic constants as a function of time on stream for cracking
 reactions for catalysts with different metal contents. Open symbols=First reactor effluent, Full
 symbols=Total effluent.



Figure 5. Global and first reactor kinetic constants as a function of time on stream for HDN
 reactions for catalysts with different metal contents. Open symbols=First reactor effluent, Full
 symbols=Total effluent.



 293
 Image: O.5 MoO3
 Image: Reference

 294
 Figure 6. Global reactor kinetic constants as a function of time on stream for HDA reactions for catalysts with different metal contents.

#### 297 3.2.2 Activity loss

The data of the calculated rate constants as a function of time on stream were fitted to the exponential decay model (Supporting information, Figure S1 and Figure S2) presented in section 2.5 (Equation 3). The coefficients for both catalysts are presented in

301 Table 3. The reference catalyst had a higher residual activity (c value) than the  $0.5MoO_3$  catalyst. 302 But the exponential decay model also indicates that the relative activity loss was faster for the 303 catalyst with the stronger hydrogenation function and that the retained activity with respect to the 304 initial activity was lower for this catalyst (c/(A+c)). The inspection of the raw conversion data had suggested the opposite trend, i.e., a higher conversion loss for the 0.5MoO<sub>3</sub> catalyst (Figure 3). 305 306 However, as previously explained, it is more accurate to examine the evolution of the reaction rate 307 coefficients since the interpretation of the raw conversion data can be misleading because the 308 relationship between conversion and contact time is not linear. The higher the conversion, the 309 greater the contact time required to increase it (higher catalyst volume). So, in our case, it is not 310 the same to lose 25 points of conversion with the reference catalyst between 97 and 72 than to 311 lose 31 points with the catalyst of lower molybdenum content between 85 and 54 both of them during TOS from 94h to 838h. In other words, the fact that the conversion decreases from a high conversion (97%) implies the deactivation of a larger fraction of the catalytic bed than the fraction which is deactivated for the conversion to decrease from a value of 85%. This behavior is not reflected in the conversion curve but in the kinetic constants, so the comparisons at different conversion levels should be made based on these data. For the purpose of understanding, the analysis of the evolution of apparent velocity coefficients is more appropriate."

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Table 3. Activity loss rate coefficients (α) and residual activities (c) calculated with an exponential decay model for catalysts with different metal contents.
 321

Catalyst	α	Α	С	c/(A+c)
	(1/day)			
0.5 MoO₃	0.23	5.7	2.7	0.32
Reference	0.39	29	4.3	0.13

#### 322 **3.3 Spent catalysts characterization**

323 3.3.1 Elemental analysis

324 The carbon content of the spent samples is presented in Figure 7. Contrary to what was expected, 325 the carbon deposition was lower for the catalyst with lower metal content. This behavior can be 326 attributed to the higher nitrogen concentration (lower k<sub>HDN</sub> values) in the liquid phase with this 327 catalyst, which inhibits cracking reactions and, consequently, the polymerization reactions to form 328 coke. The values of the N/C ratio (Figure 8) as well as the nitrogen content in coke (Figure 9) 329 confirmed the latter. The nitrogen content was higher for the spent catalysts with lower 330 molybdenum loading. It means that the contribution to the overall coke formation from nitrogen 331 precursors plays a more important role for this catalyst in comparison with the reference catalyst. 332 For both catalysts, the carbon content along the reactor increased from the inlet to the outlet; 333 meanwhile, the N/C values decreased. Both facts agree with the nitrogen concentration profile, 334 which decreases along the length of the reactor. The preferential adsorption of the nitrogen

- 335 compounds on acid sites inhibits the polymerization of the dehydrogenated intermediates reducing
- the formation of coke deposits.
- 337
- 338





340Figure 7. Carbon contents of the spent catalysts with different metal contents. Samples taken at<br/>different reactor locations.

- 342
- 343



Figure 8. N/C ratio of the spent catalysts with different metal contents. Samples taken at different
 reactor locations.





348

Figure 9. Nitrogen content of the spent catalysts with different metal contents. Samples taken at different reactor locations.

351

Results of the H/C ratio of the coke in the spent catalysts are shown in Figure 10. A lower H/C ratio (indicating a more aromatic character of the coke deposit) was observed for the carbon deposits formed on the reference catalyst than for the 0.5MoO<sub>3</sub> catalyst. It can be related to the higher cracking rate of the reference catalyst, which enhances the polymerization reactions of the coke precursors, forming more condensed structures with lower H/C ratios and with more dehydrogenation reactions. The H/C ratio (Figure 10) diminished along the catalytic bed.



Figure 10. Hydrogen/Carbon ratio of the spent catalysts with different metal contents. Samples
 taken at different reactor locations.
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 362

Analysis of coke composition suggests that a proportion of the global coke originates from organic nitrogen species. However, as HDN proceeds through the reactor and nitrogen is removed, other mechanisms, such as aromatic coke formation, begin to play a more important role in catalyst deactivation. This corresponds to the results obtained in our previous work <sup>43</sup>.

#### 367 3.3.2 Textural Analysis

358

368 Catalysts were also analyzed by nitrogen adsorption-desorption isotherms. The surface area 369 (A<sub>BET</sub>) and pore volume (PV) with respect to the fresh catalyst are presented in Table 4. The area 370 and volume losses for each catalyst show a direct correlation with its carbon deposition. Thus, the 371 most significant modifications of the textural properties of the catalyst were found for the reference 372 catalyst. A more pronounced decrease of surface and pore volume happened at the bed outlet, 373 agreeing with the higher carbon content at this location. Table 4 also shows the ratio between the 374 hysteresis area of each spent catalyst and the corresponding fresh catalyst, following the methodology suggested by Sámano et al. <sup>48</sup>. The higher the value, the higher the extent of catalyst 375

- 376 deactivation. The data showed a higher deactivation with the reference catalyst than with the one
- 377 containing less molybdenum. The reactor outlet values were also higher than at the reactor inlet
- 378 for the two spent catalysts, consistent with the textural and the elemental results.

Table 4. Characterization of spent catalysts with different metal contents: Surface area (A<sub>BET</sub>), total
 pore volume (PV), micropore volume (μVol) and the ratio of hysteresis area (HA) of the spent
 catalyst relative to the fresh catalyst.

Catalyst	A <sub>BET</sub> /	ABETfresh	PV/PV <sub>fresh</sub>		μVol/μVol <sub>fresh</sub>		HA <sub>Spent Catalyst</sub>	
-	Bed	Bed	Bed	Bed	Bed	Bed	Bed	Bed
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
	(%)	(%)	(%)	(%)	(%)	(%)		
0.5 MoO <sub>3</sub>	82	78	85	79	68	63	1.13	1.28
Reference	82	71	78	69	61	65	1.33	1.49

#### 383 3.3.3 Thermo-gravimetric Analysis

TGA analyses were done to characterize the coke deposits on the spent catalysts. The first timederivative of weight loss as a function of temperature is illustrated in Figure 11. The first peak, around 100°C, corresponds to H<sub>2</sub>O desorption, the second one (280-330°C) corresponds mainly to SO<sub>2</sub> release and the last peak is associated with the combustion of the coke deposits <sup>49,50</sup>. In Table 5, the percentage of the weight loss within the range of temperature corresponding to coke deposits combustion is presented. These values agree with the carbon content from elemental analysis (see Figure 7).



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Figure 11. TGA profiles of bed inlet and bed outlet samples from the spent catalysts with different
 metal contents. Dotted line=First reactor effluent, continuous line=Total effluent.

The maximum weight loss temperature is an indicator of the nature of coke; the higher this temperature, the more difficult to combust the coke is. It is often associated with a lower H/C ratio of the coke deposits. However, the coke deposits on the catalyst with less metal concentration required a higher temperature to combust (Figure 11 and Table 5), although its H/C ratio is higher (Figure 10). This behavior suggests that the hightemperature peaks for this catalyst were related to the higher nitrogen content of its coke deposits (Figure 9). This is in agreement with the work of Zeuthen et al. <sup>35</sup>, who characterized some aged hydroprocessing catalysts by temperature-programmed oxidation and identified that the strongly adsorbed organic-nitrogen species are oxidized at temperatures around 500°C.

Catalyst	CO <sub>2</sub> weight loss (wt %)	Maximum Peak Temperature (°C)
0.5 MoO <sub>3</sub> Bed In	7.8	495
0.5 MoO <sub>3</sub> Bed Out	10.3	510
Reference Bed In	11.2	445
Reference Bed Out	16.6	440

405Table 5. Estimation of CO2 weight loss of the coke deposits and maximum peak temperature from406TGA profiles for spent catalysts with different metal contents.

#### 407 3.3.4 Model molecule tests

408 The residual activity of the (de)/hydrogenation and the acid functions of the spent catalysts were 409 characterized by toluene hydrogenation and n-heptane hydroconversion, respectively. Figure 12 410 illustrates the first-order rate constant of the spent catalysts relative to the corresponding fresh 411 catalyst ( $k_{Hydro}$  fresh) for both studied catalysts during toluene hydrogenation ( $k_{Hydro}$ ). These values 412 reveal that, despite its lower initial activity, the catalysts with the lower metal content retained more 413 hydrogenation activity than the reference catalyst, which lost around 80% of its original activity. 414 The reasons for this will be discussed in the next section. The activity loss of the metal function 415 increased along the catalytic bed for both samples.





420 Regarding the n-heptane cracking activity results (Figure 13), it was noticeable that it was severely 421 deactivated in both cases. All the residual activities were below 5%. Note that, as illustrated in 422 Figure 1b, the n-heptane cracking activity is not an exclusive measure of the acid function, but 423 rather presents the overall bifunctional hydrocracking activity of the catalyst. For the catalyst with 424 lower molybdenum content, the differences along the reactor were negligible. The reference 425 catalyst had a significantly higher residual cracking activity (in absolute and in relative terms) at 426 the bed outlet. This is attributed to the difference in nitrogen content of the carbon deposits. The 427 reference catalyst had a significantly lower N/C ratio at the bed outlet. It seems that the nitrogen 428 in the coke is the main cause of the decrease in residual cracking activity. We had already pointed 429 out in our previous work<sup>51</sup> that the residual acidity of the catalyst was decorrelated from the total 430 coke content and specifically related to nitrogen compounds.





- 436 The selectivity to i-heptane is presented in Figure 14. In contrast to the fresh samples, the 0.5
- 437 MoO<sub>3</sub> catalyst had a higher i-heptane selectivity, meaning that the ratio between the metal and

Figure 13. Residual catalytic cracking activity of the spent catalysts relative to the fresh catalyst,
 evaluated by isomerization/cracking of n-heptane at 360°C. Samples taken at different reactor
 locations.

acid sites (M/A) was better balanced for this catalyst. This is in line with the higher residual
hydrogenation activity (Figure 12) and the lower residual cracking (Figure 13) of the 0,5 MoO<sub>3</sub>
catalyst.



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442 443 444

Figure 14. Selectivity to i-C<sub>7</sub> Vs. conversion n-C<sub>7</sub>, obtained by n-heptane hydroconversion at different temperatures.

#### 445 **4 DISCUSSION**

Hydrocracking proceeds by bifunctional catalysis. This makes studying the deactivation very complex, because the deactivation of the overall hydrocracking activity depends on the deactivation of the metal and of the acid function as well as on the evolution of the balance between the two. We, therefore, started by evaluating the impact of metal/acid balance on the 450 activity of fresh catalysts in model reactions. As expected, on fresh catalysts, the hydrogenation 451 activity increased (almost proportionally) with the molybdenum content (Figure 1Figure 1a). The 452 decrease in the metal content also had a negative impact on the activity of the cracking function 453 (Figure 1b). This result agrees with other authors <sup>14</sup>, who established that at low metal/acid (M/A) 454 ratios, there is a limitation of the bifunctional mechanism by the (de)-hydrogenation steps. This 455 means that the metal sites are not sufficiently abundant to provide olefins for all the acid sites, so 456 the maximum activity of the cracking function cannot be exploited. A decrease in the overall activity 457 of the catalyst is then observed. The fact that the decrease is more pronounced than in some other 458 recent studies on sulfide hydrocracking catalysts <sup>19,23,24</sup> indicates that our catalysts covered a 459 range of lower M/A ratios than the works cited above.

460 During the pilot plant deactivation experiments, the following differences in the behavior of the 0.5
 461 MoO<sub>3</sub> catalyst with respect to the reference catalyst were observed in terms of reactivity:

• A lower cracking activity, but also a slower (relative) deactivation.

• A lower hydrodenitrogenation (HDN) and aromatics hydrogenation (HDA) activity.

464 In terms of characterization of the spent catalyst, it was observed that the 0.5 MoO<sub>3</sub> catalyst:

- Had a lower amount of coke, associated with a lower loss of surface area and pore volume.
- Had a higher nitrogen content (and, thus, a higher N/C ratio).
- Retained a higher percentage of its initial hydrogenation activity.

Retained a higher percentage of its initial cracking activity at the bed inlet, but a lower
 percentage at the bed outlet.

In the following discussion, we will try to rationalize these trends. In our earlier work, we had seen that the deactivation process is largely governed by the presence of organic nitrogen species, which in turn determines the metal/acid balance <sup>43</sup>. The lower the HDN activity, the higher is the nitrogen compounds' concentration along the catalytic bed. This higher concentration has a strong repercussion on the catalytic performance since nitrogen derivatives are known to be inhibitors of

the metal sites <sup>43,52–55</sup> and especially of the acid sites <sup>23,43</sup>, where they are strongly adsorbed <sup>56–59</sup>. 475 476 The inhibition of the acid and metal sites has two antagonistic effects with respect to coke 477 formation. On the one hand, the adsorbed nitrogen compounds may eventually be converted to 478 coke, permanently deactivating the acid sites. Moreover, the inhibition of the hydrogenation activity 479 of the metal sites leads to an increase in aromatics concentration along the reactor. If there are 480 sufficiently available acid sites, the aromatics undergo addition, dehydrogenation and hydrogen 481 transfer reactions to grow into large polyaromatic molecules, i.e., coke precursors <sup>3,60</sup>. On the other 482 hand, this coke deposition from aromatics is slowed down by the progressive inhibition of acid 483 sites by nitrogen compounds <sup>61</sup>. The data shown in this paper demonstrate that the latter effect 484 dominates over the former ones. Despite its lower HDN and HDA activity, i.e., despite of a higher 485 concentration of coke precursors, the 0.5 MoO<sub>3</sub> catalyst generated less coke. This must be related 486 to the lower availability of acid sites (i.e., a stronger inhibition by nitrogen compounds with respect 487 to the reference catalyst).

488 The spent catalyst samples with the lower molybdenum concentration presented higher nitrogen 489 contents and higher N/C ratios than the spent reference catalyst, especially at the bed inlet (Figure 490 8 and Figure 9), meaning that the contribution of nitrogen compounds to the overall coke formation 491 was higher for this catalyst. This result is linked to the more nitrogen-rich atmosphere in the reactor 492 when the 0.5 MoO<sub>3</sub> catalyst was used. The reference catalyst exhibited a higher amount of coke 493 with less nitrogen, i.e., a more significant contribution to the global coke formation came from 494 aromatic compounds (whose condensation reactions are catalyzed by the acid sites). This can 495 also explain the lower H/C ratio (Figure 10) of these samples.

496 Regarding the residual activities of the spent samples, it was observed that the loss of 497 hydrogenating activity was more pronounced for the reference catalyst (Figure 12). Since no 498 meaningful differences were observed in sintering or depromotion between the spent samples 499 (Supporting information table S1, TEM analysis), this behavior was attributed to a higher coke

500 build-up with the reference catalyst. In reference <sup>51</sup>, we had already observed a strong correlation 501 between the amount of coke formation and the loss of hydrogenation activity. The coke deposition 502 is determined by the metal/acid (M/A) balance. Figure 14 shows that the M/A balance was less 503 favorable for the spent reference catalyst (less metal sites vs. acid sites). This explains the higher 504 coke formation on this catalyst, which in turn leads to a strong deactivation of the metal function 505 (this feedback loop will be discussed later in the text).

The residual n-heptane hydrocracking activity was very low for both samples. The 0.5 MoO<sub>3</sub> catalyst had a lower cracking activity than the reference catalysts at the bed outlet (Figure 913). This is attributed to the higher nitrogen content of the coke on the 0.5 MoO<sub>3</sub> samples (Figure 9 because the nitrogen species are strongly adsorbed on the acid sites, deactivating them. As mentioned before, this catalyst exhibited a lower carbon deposition, which can be attributed to a more favorable M/A balance.

512 When making the link between the results of the model molecule tests and the VGO deactivation 513 experiments, we see that the 0.5 MoO<sub>3</sub> catalyst generated less coke and lost less VGO 514 hydrocracking activity (in relative terms, see Figure 4 and Table 3). The latter observation is 515 seemingly in contradiction with Figure 13, which shows that it lost, on average, a higher 516 percentage of its residual n-heptane cracking activity. In order to resolve this dilemma, we have 517 to make the hypothesis that the M/A balance does not have the same impact in n-heptane cracking 518 and in the VGO deactivation test. In n-heptane cracking, the fresh reference catalyst was fairly 519 well balanced, but became extremely badly balanced after deactivation (Figure 14). We 520 hypothesize that this did not strongly impact its n-heptane hydrocracking activity, but had strong 521 repercussions on its VGO hydrocracking activity. In order words, the stronger deactivation of the 522 reference catalyst would, after all, be mainly related to the stronger deactivation of its 523 hydrogenation function and not of its acid function. We admit, however, that this is just a 524 hypothesis for moment, which should be confirmed by complementary experimentation.

525 Let us finally come back to the above-mentioned negative feedback loop of deactivation. If we 526 have a hydrocracking catalyst with a strong hydrogenation function (our reference catalyst), it will 527 lead to a quick drop of the organic nitrogen profile in the reactor. This leads in turn to an imbalance 528 of the M/A ratio. This imbalance is the main cause of coke formation. Unsaturated coke precursors produced on the acid sites undergo polymerization reactions before being hydrogenated and 529 530 successive dehydrogenation reactions occurred on metal sites leading to partially hydrogenated 531 intermediates that combine to form coke. The formed coke deactivates both functions, but in a 532 more significant way the hydrogenation function <sup>51</sup>, since the cracking function is mainly affected 533 by the nitrogen compounds. This phenomenon leads to a negative feedback loop, which is 534 illustrated in Figure 15. When the hydrogenating function is deactivated by coke build up, the 535 nitrogen concentration increases progressively. Therefore, more acid sites are neutralized so that 536 the M/A balance tends to recover, and coke formation slows down. In other words, the coke 537 formation provides negative feedback on deactivation; thus, the deactivation rate slows down over 538 time.



# Figure 15. Schematic representation of the deactivation cycle of the acid and hydrogen functions of a bifunctional catalyst in a nitrogen-rich atmosphere. The hydrogenation function is represented by a blue rectangle, the cracking function by a green rectangle, coke on the metal function in black, the inhibited fraction of the cracking function in grey.

545

546 In general, our data show that the modification of the hydrogenation function of VGO 547 hydrocracking catalysts has two main consequences: a reduction of the HDN activity and a 548 reduction of the cracking activity. The balance between these two phenomena leads to 549 unexpected behavior with respect to deactivation in organic nitrogen-poor atmospheres. Current 550 literature states that a reduction in the hydrogenating function for samples with the same acid function, leads to more coke formation on the catalyst, which provokes rapid deactivation <sup>13,14,17</sup>. 551 552 However, this study showed that this does not hold true for nitrogen-rich reaction systems. In this 553 case, the decrease in the hydrogenating function causes an indirect decrease in the acid function 554 of the catalyst, due to a stronger inhibition by nitrogen compounds. This provokes a modification 555 on the M/A ratio, so the spent catalyst containing a lower Mo content actually shows a better 556 balance. Consequently, less coke generation was observed, with a lower aromatic character, but 557 with higher nitrogen content. Therefore, the deactivation was lower for the catalyst with a weaker 558 hydrogenating function.

We have seen that many of the deactivation phenomena that we observed are dictated by the behavior of the organic nitrogen compounds. It would be desirable to carry out a similar study with nitrogen-poor feeds, where inhibition effects play a smaller role. However, in practice, this is not easily reconciled with the ambition of an accelerated deactivation protocol: the high concentration of organic nitrogen allows us to operate at high temperatures, which enhances deactivation.

#### 564 **5 CONCLUSIONS**

The balance between the metal and the acid functions determines the rate-limiting step of the
 bifunctional reaction mechanism. In case of a significant reduction in the metal content, the
 initial (de)/hydrogenation reactions may become the rate limiting step of the mechanism.
 Therefore, the global catalyst activity decreases.

In hydrocracking of feedstocks with high nitrogen content, the decrease of the metal content
 of a bifunctional catalyst causes a substantial increase in the concentration of nitrogen
 compounds in the catalytic bed. This increase determines the performance of the catalyst by
 significantly reducing the available acid sites. Thus, there is a modification in the M/A ratio
 favoring a better balance of the spent catalyst resulting in a lower coke deposition and
 therefore, a lower deactivation rate.

575 The interplay between HDN and cracking in VGO hydroprocessing leads to perverse effects, 576 i.e., an improvement of the M/A balance when reducing the metal content, via the mechanism 577 explained above. The direct effect of the reduction of the metal content and its indirect 578 consequence, which is an increase in the acid sites inhibition by nitrogen, have an 579 antagonistic influence on the deactivation behavior. The balance between both effects is 580 expected to subtly depend on the properties of both the feed and the catalyst. This study 581 provides a methodology for studying this complex system and a framework for interpreting 582 the results, but one should be careful in generalizing the trends observed in this e, because

they may depend on the system under consideration. Therefore, for systems with lowernitrogen contents, a specific study should be carried out.

Our data also explains why deactivation slows down with time via an autoregulation phenomenon. A strong metal function in the fresh catalyst leads to a fast initial coke build up (by creating a M/A imbalance via the mechanism explained above). The coke builds up specifically deactivates the metal function, thereby restoring the M/A balance and coke formation slows down.

590

Supporting Information: Available as supporting information are the fits by the exponential decay
 model and the TEM analyses of the catalysts.

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## 766 TOC Graphic

