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How does an acidic support affect the hydrotreatment of a gasoil with high nitrogen content?

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KEYWORDS: hydrodenitrogenation, hydrodesulfurization, gasoil, acidity, MoS₂, silica-alumina

Abstract

Two NiMo sulfide catalysts, supported on Al₂O₃ and silica-alumina, respectively, were compared in the hydrotreating of a mixture of straight-run and coker gasoil. Experiments were conducted in a continuous fixed bed reactor, at 623-643K and 5 MPa. The Al₂O₃-supported catalyst proved to be slightly more active in HDN and significantly more active in HDS than its silica-alumina analogue. The activity trend was attributed to the inhibition provoked by the strong adsorption of basic nitrogen species. Earlier work had shown that the adsorption (and thus the inhibition) was significantly stronger on an acidic support. Our data further showed that the reactivity of neutral (pyrrole benzologues) and basic nitrogen compounds was

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3 different. The basic fraction was converted in a gradual fashion, while the large majority of
4 neutral species was converted very quickly, except for a small fraction, which remained
5 practically inert to hydrotreating.
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10 11 12 **1. Introduction**

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14 Hydrotreatment catalysts usually consist of Ni- or Co-promoted MoS₂ nanoparticles
15 supported on alumina. Alumina is the preferred support material because of its advantageous
16 textural properties and its mechanical stability. In some cases, silica-alumina is used instead.
17 Many reports in the literature suggest that the acidity of the silica-alumina has a beneficial
18 effect on the HDN activity of NiMo-type sulfide catalysts. For example, Miranda *et al.* ¹
19 found a linear correlation between the content of Brønsted acid sites and the HDN rate of
20 piperidine (amorphous silica alumina supports with different Si/Al ratio). Prins and co-
21 workers compared the activity of alumina and of silica-alumina supported catalysts in the
22 HDN of o-toluidine and of methylcyclohexylamine; in both cases, the silica-alumina
23 supported catalysts were more active ^{2,3}. Murti *et al.* ⁴ observed the same result in the
24 hydrotreatment of coal derivate liquid. Introducing acidity into an alumina support by grafting
25 of silica also improved the HDN activity in the hydroconversion of Safaniya vacuum residue
26 ⁵. Fluorination of the support also has a positive effect on the HDN activity ⁶. The positive
27 impact of support acidity on HDN activity has also been observed with industrial catalysts.
28 Minderhoud and van Veen ⁷ reported that silica-alumina supported catalysts were more active
29 in the HDN of Vacuum Gas Oil than alumina-supported catalysts.
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51 This beneficial effect of support acidity on HDN activity was explained by different theories:
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3 (i) Kozai and co-workers⁸ proposed that acid sites of amorphous silica-alumina (ASA)
4 are directly involved in the breaking of the C-N bond in methyl-cyclohexylamine to form
5 methyl-cyclohexene.
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10 (ii) The interaction of MoS₂ with an acidic support modifies the electronic properties of
11 sulfide phase^{6,9-11}. It induces an electron deficiency in the sulfide phase, *via* a transfer of
12 electrons to the support. This modification is expected to influence the reactivity and the
13 adsorption properties of the sulfide slabs.
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18 (iii) Prins and co-workers^{2,3,12} reported that the adsorption constants of o-methyl-aniline,
19 methylcyclohexylamine and cyclohexene over NiMo/ASA were systematically higher than
20 over NiMo/Al₂O₃. The stronger adsorption contributes to a higher activity of the ASA-
21 supported catalysts for certain reactions in the HDN network.
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27 (iv) Compared to an alumina support, silica-alumina modifies the dispersion (*i.e.* slab
28 size and stacking) of the sulfide nanoparticles. Yet, due to the large diversity of silica-alumina
29 materials, literature provides conflicting evidence: some report that the incorporation of silica
30 into the support deteriorates dispersion,¹³ whereas in other studies the impact on slab length
31 was negligible^{14,15}.
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39 (v) Hensen *et al.*¹⁶ showed that the acidity of the support leads to a higher sulfur
40 tolerance, *i.e.* the active sites are less sensitive to inhibition by H₂S. This means that silica-
41 alumina supports should be especially attractive for high pressure applications, in a sulfur rich
42 environment. This is in line with the observation that silica-alumina is a good support for
43 VGO hydrotreating.
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52 We recently reported a detailed comparison of the behavior of alumina and silica-
53 alumina supported NiMo catalysts in the HDN of two model molecules, *i.e.* quinoline¹⁷ and
54 indole¹⁸. Comprehensive kinetic modeling allowed us to distinguish the influence of support
55 on adsorption and intrinsic rate constants. The studies showed that the support acidity indeed
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3 enhanced the intrinsic rate constants of the rate-limiting hydrogenation steps in the HDN
4 network of quinoline, presumably due to the modification of the electronic properties of the
5 sulfide slabs. At the same time, the adsorption of reactants and intermediates on the active
6 sites was also stronger, which led to a strong self-inhibition of quinoline, *i.e. in fine* a negative
7 effect on catalytic activity. The silica-alumina support also modified the concentration of
8 promoted NiMoS sites at the edges of the MoS₂ slabs. In our specific case, it decreased, but
9 this conclusion should not be generalized since the concentration of promoted sites strongly
10 depends on the preparation method. Overall, the combination of the three above-mentioned
11 factors (adsorption, intrinsic rate constant and concentration of promoted sites) led to a
12 decrease of the HDN activity (vs. an alumina supported catalyst) in the HDN of quinoline and
13 a similar activity of both catalysts in the case of indole. Yet, it is not straightforward to
14 extrapolate the behavior with model molecule to real feeds, because they are very complex
15 mixtures for which mutual inhibition effects between HDS and HDN are hard to predict. In
16 the present study, which is based on Chapter 5 of the PhD thesis of M. T. Nguyen ¹⁹, we
17 therefore compared the performance of the alumina and silica-alumina supported NiMo
18 catalysts in the hydrotreatment of a gasoil mixture. Since our focus was on evaluating HDN,
19 we chose for this purpose a mixture of straight run gasoil and coker gasoil leading to a feed
20 with high nitrogen content and a wide variety of N compounds.

2. Materials and methods

2.1 Catalysts

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The NiMo(P)/Al₂O₃ and NiMo(P)/ASA (Amorphous Silica-Alumina) catalysts were identical to those described and characterized in our previous works ^{17,18}. Their main characteristics are compiled in **Table 1**. The metal content of the two catalysts were selected so as to obtain the same volumetric activity in the hydrogenation of toluene ¹⁷. The reasoning behind this

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3 approach was that HDN reactions necessarily imply the hydrogenation of aromatic rings. By
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5 choosing two catalysts with the “same” hydrogenation activity for benzene rings, differences
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7 in HDN can be attributed to specificities in the adsorption and activation of nitrogen
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9 containing rings.
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13 The acidity of the ASA catalyst was characterized *via* its activity in the isomerization of
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15 cyclohexane: it was at least four times more active than its Al₂O₃ counterpart¹⁷. The detailed
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17 characterization of the acidity of the ASA support was already carried out in previous work²⁰.
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19 Our ASA support is similar to the Si30Al70 sample in the before-mentioned reference.
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24 Table 1: Properties of the NiMo(P)/Al₂O₃ and NiMo(P)/ASA catalysts¹⁷
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	NiMo(P)/Al ₂ O ₃	NiMo(P)/ASA
% wt MoO ₃	18.6%	14.0%
% wt NiO	3.84%	2.97%
% wt P ₂ O ₅	4.93%	3.84%
Compacted bulk density, g/cm ³	0.77	0.93
Average MoS ₂ slab length / nm	6.1	6.6
NiMoS site density, (mmol NiMoS/cm ³)	0.424	0.318

2.2 Gasoil feed mixture

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42 The gasoil feed was a mixture of 50 wt% of straight run gasoil and 50 wt% of coker gasoil.
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44 Properties of individual gasoils and gasoil mixture are given in **Table 2**. A more detailed
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46 analysis of the nitrogen and sulfur species at a molecular level was performed by GCxGC
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48 either with a sulfur or nitrogen specific detector (SCD or NCD), respectively (see appendix
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50 for details).
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Table 2: Properties of straight run gasoil, coker gasoil and their mixture

	Straight Run GO	Coker GO	Gasoil feed blend
Total nitrogen (wppm)	96± 5	1320 ± 99	703 ± 53
Basic nitrogen (wppm)	47.9	569	290 ± 23
Total sulfur (wt %)	0.44	2.38	1.44
Density at 15°C (g/ml)	0.849	0.882	0.865
Boiling point range (5-95%) (°C) ^a	187-390	193-402	190 - 397
Kinematic viscosity at 20°C (mm ² /s)	6.2	6.1	6.2
Kinematic viscosity at 40°C (mm ² /s)	3.8	3.7	3.8

^a determined by simulated distillation (ASTM D2887)

2.3 Catalytic tests in fixed-bed continuous reactor and analysis of effluents

Catalytic tests were performed in a three phase fixed-bed reactor in up-flow mode. A detailed description of the setup is provided in the supporting information.

1 cm³ of catalyst was loaded into the reactor in the form of ground particles (sieve fraction 80 and 125 µm). The hydrotreatment reactions were performed at a pressure of 5 MPa. A value of temperature was fixed during each run, *i.e.* 350, 360 or 370°C. Conversion was varied by adjusting the LHSV in the range of 2-6 h⁻¹ (starting at a high LHSV and going to low a LHSV). The inlet H₂/hydrocarbon ratio was fixed at 400 NL/L. Deactivation was evaluated by returning to the initial LHSV at each temperature. In order to quantify catalytic activity, apparent rate constants were calculated from $r = k.C^n$ rate law (see supporting information).

The liquid reactor effluent was analyzed by UV Fluorescence to determine total sulfur content and by chemiluminescence (ANTEK 9000NS) to determine the total nitrogen content. The basic nitrogen content was measured by potentiometric titration (ASTM D2896). The global evolution of the different molecular families was followed by mass spectroscopy. The MS method, which is derived from ASTM D2425, is described in detail in ref. ²¹. It quantifies twelve groups in wt% according to their stoichiometric formula: paraffins (C_nH_{2n+2}), non-

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3 condensed naphthenes (C_nH_{2n}), condensed two and three ring-naphthenes (C_nH_{2n-2} and C_nH_{2n-4}), seven aromatic families (from C_nH_{2n-6} to C_nH_{2n-18}), which were regrouped in mono-, di- and triaromatics in our analysis, as well as benzothiophene and dibenzothiophenes. The contribution of each group-type is determined by the sum of the molecular peaks M^+ and/or fragment peaks $(M-H)^+$, weighed by the average response coefficient and corrected for the contribution of the other group-types.

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17
18 At the end of experiment, the catalyst was unloaded and sieved by a molecular sieve in order to remove SiC particles contaminants (particle size smaller than 50 μm). The catalysts were then washed with Soxhlet apparatus using heptane as a solvent at 85°C during 24 hours. Finally, the catalysts were then dried under vacuum (10 mPa) at 100°C for 24 hours. The content of deposited carbon and nitrogen on the used catalysts was measured by CHNS analysis.

31
32 In order to make sure that the catalytic tests measured actual chemical kinetics and not mass transfer rates, we estimated the characteristic times of external and internal mass transfer (see supporting information). The characteristic time of external mass transfer was in the order of 0.03 s, the one of internal transfer was less than 1 s, *i.e.* both were negligibly small compared to the characteristic time of chemical kinetics (> 1h).

3. Results

3.1 Analysis of the gasoil feed mixture

51 Our study uses a mixture of straight run gasoil (SRGO) and coker gasoil (CGO) (50/50 wt %). The straight run gasoil has low nitrogen content (~100 ppm). At the sulfur levels of Ultra Low Sulfur Diesel (ULSD), HDN of a SRGO is complete and the HDN activity of catalysts is considered as not to be critical for such “easy” feeds. We, therefore, chose to mix the SRGO

with a more difficult feed, coming from coking of a vacuum residue. This CGO has a very high nitrogen content of 1300 ppm, and in contrast to Light Cycle Oils (LCO) coming from FCC processes, a large fraction of the organic nitrogen belongs to basic nitrogen species (43%), which are known to be the strongest inhibitors²².

Analysis of sulfur compounds in gasoil mixture by GCxGC-SCD provided the distribution of refractory sulfur compounds in the feed. The gasoil mixture contained a large amount of alkylated dibenzothiophenes (DBT) compounds, especially C₃⁺-DBT (10.6%). These compounds are well known to be refractory compounds towards the HDS reaction^{23–28}.

Figure 1 shows the distribution of families of sulfur compounds in the feed.

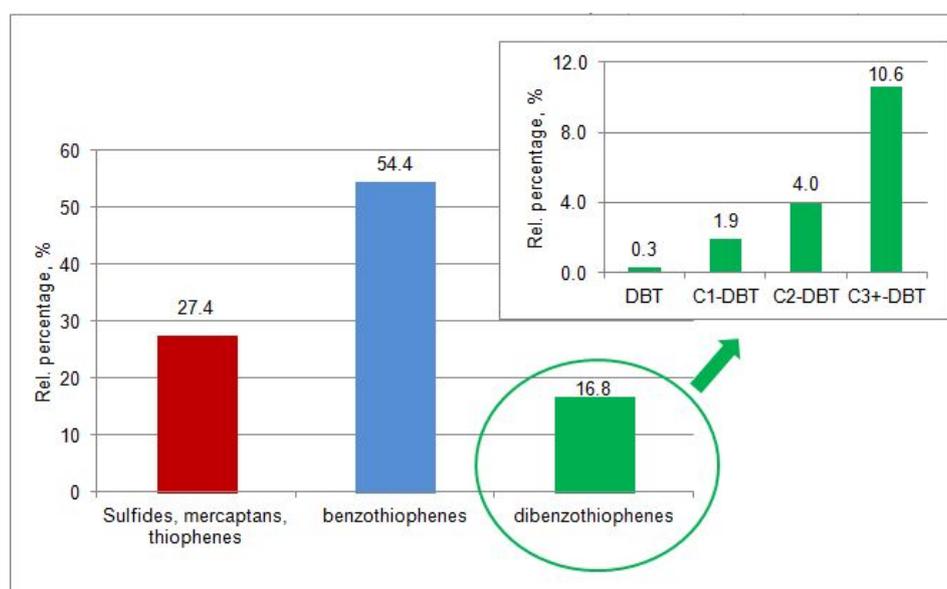


Figure 1: Family analysis of sulfur compounds in the gasoil mixture by comprehensive gas chromatography coupled with sulfur Chemiluminescence detector.

The distribution of nitrogen organic compounds in the gasoil mixture was obtained from GCxGC-NCD. The identification of each family was carried out thanks to a standard mixture and GCxGC/MS characterization^{29,30}. The GCxGC-NCD chromatogram is given in **Figure 2**.

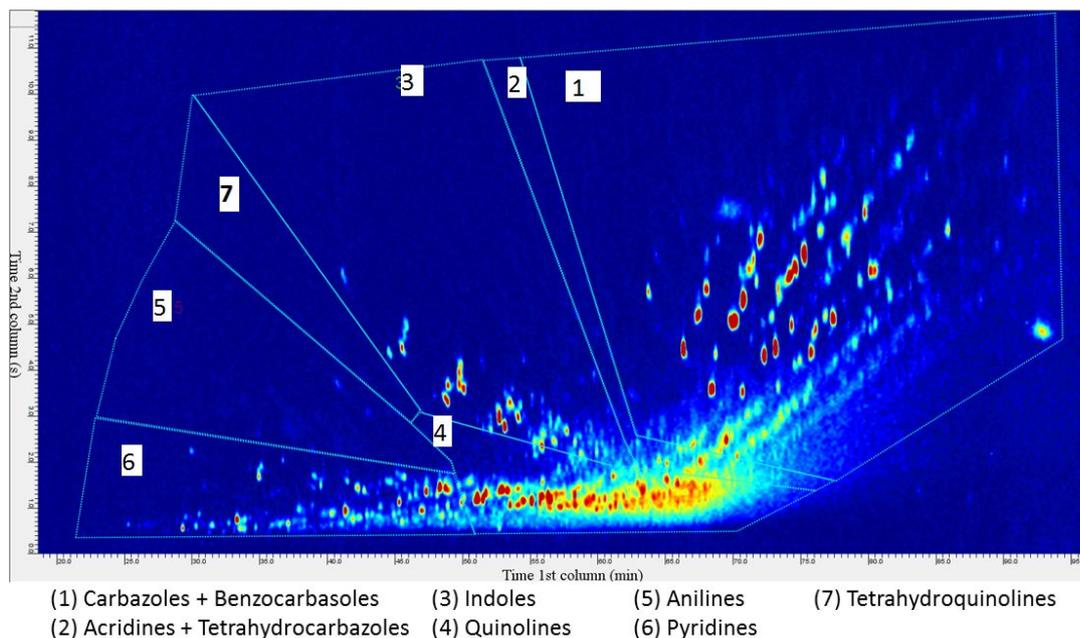


Figure 2: Semi-quantitative analysis by comprehensive gas chromatography coupled with nitrogen chemiluminescence detector of nitrogen compounds in the gasoil mixture

In **Figure 2**, we can see the speciation in several families of N-compounds in the gasoil feed mixture. Semi-quantification was carried out by calculating the ratio of peak volume of each family as compared to total peak volume. The relative percentage of each family of N-compounds is given in **Figure 3**. An overlap between several families such as alkyl-pyridine and alkyl-quinoline, alkyl-acridine and alkyl-carbazole did not allow a precise quantification. Moreover, alkyl-carbazole and alkyl-benzocarbazole were eluted in the same zone in the chromatogram.

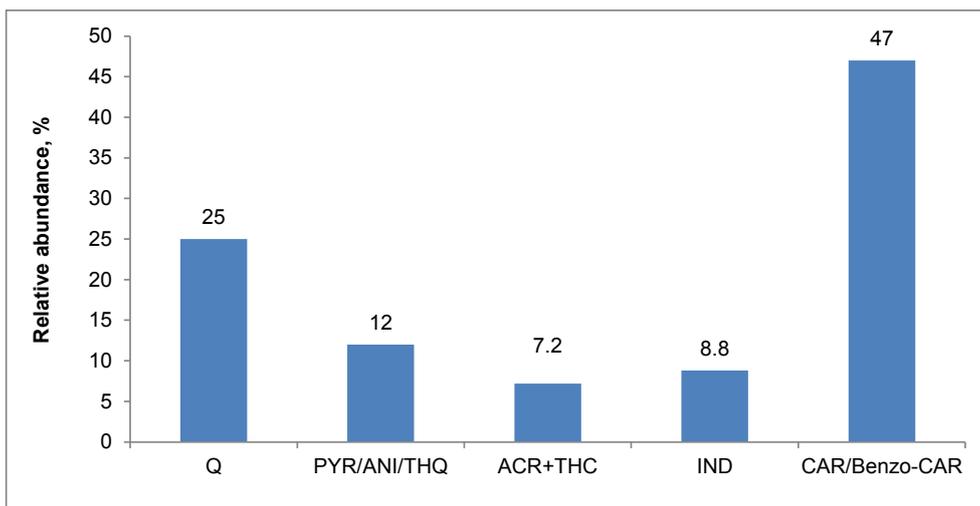


Figure 3: Distribution of N-compound families from GCxGC-NCD analysis

(In this figure: Q: quinoline-, PYR: pyridine-, ANI: aniline-, THQ: tetrahydroquinoline-, ACR: acridine-, THC: tetrahydrocarbazole-, IND: indole- and CAR: carbazole- type compounds)

Figure 3 indicates that the gasoil mixture contained mainly carbazole and benzocarbazole type compounds, which are well known to be highly refractory towards hydrotreating reactions. There was also a significant amount of (basic) quinoline type compounds (25%). The relative percentage of all basic N-compounds families (quinoline-, PYR/ANI/THQ-, and acridine-type compounds) represented 44% of the total N-compounds. This result is very close to 41% of basic nitrogen obtained by potentiometric titration (Table 2).

3.2 Catalytic conversion of the SRGO + CGO mixture

3.2.1. Global evolution of the GO composition during hydrotreating

The MS analysis allows us to follow globally the evolution of different molecular families during hydrotreating. We show the results obtained with the ASA-supported catalyst, the trends for the Al_2O_3 -supported sulfide catalyst were similar.

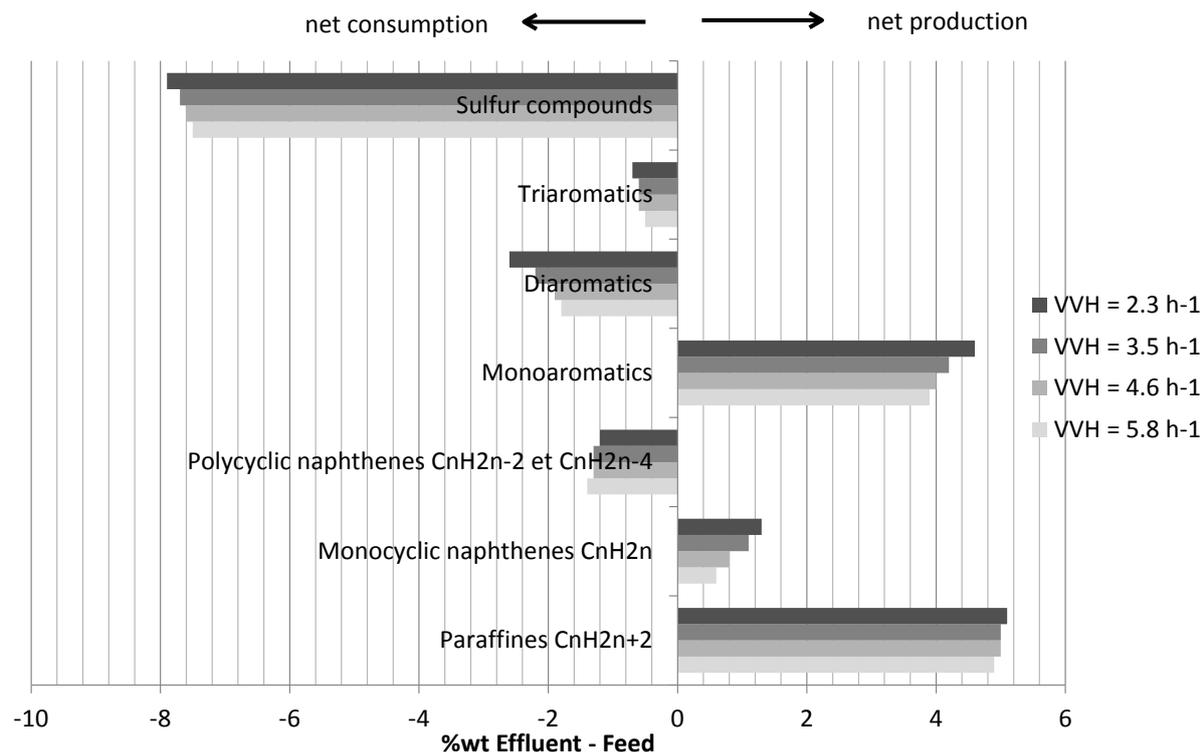


Figure 4: Change in composition between feed and effluent: decrease/increase in the mass percentage of paraffines, non-condensed naphthenes, condensed naphthenes, monoaromatics, diaromatics, triaromatics and sulfur compounds upon hydrotreatment over the ASA-supported catalyst.

The shifts in composition of the gasoil (Figure 4) were mainly due to the conversion of sulfur compounds and of aromatics. The increase in the concentration of paraffines could be attributed to the desulfurization of sulfides, mercaptanes and thiophenes in the feed. Monoaromatics were formed by direct desulfurization of benzo- and dibenzothiophenes as well as by hydrogenation of diaromatics. At high residence time, the monoaromatics were further converted into monocyclic naphthenes. The decrease of polycyclic naphthenes at short residence time was tentatively attributed to ring opening reactions. With increasing residence time the concentration of these compounds slightly increased again. This was ascribed to the slow hydrogenation of bi-phenyl compounds, which had been formed by direct desulfurization of dibenzothiophenes. The remaining sulfur compounds were benzo- and dibenzothiophenes.

3.2.2. HDS and HDN conversion

Figure 5 shows the HDS and HDN conversion as a function of residence time for the two catalysts. The HDS conversions were in the range of 90 to 98%. This corresponds to a residual sulfur concentration in the range of 200 to 700 ppmw, *i.e.* not yet at ultra-low sulfur diesel levels. This is the conversion range where mainly the most refractive sulfur compounds, *i.e.* the dibenzothiophenes, which represent 16% of the sulfur compounds in the feed (Figure 2), are converted.

The alumina-supported catalyst was significantly more active in HDS. This result is in line with Couman's work¹⁵; he already found that the silica-alumina supported NiMo catalysts were less active in HDS of DBT than alumina-supported ones. The alumina-supported catalyst also showed a higher HDN activity, but the difference between the two catalysts was less pronounced than in HDS. The ratio of the apparent rate constants at 350°C (Al_2O_3 vs. ASA) was equal to 1.1, *i.e.* close to ratio obtained for quinoline HDN, which was equal to 1.2¹⁷. The difference of the HDS rate constants was significantly higher (factor of 1.7 in favor of Al_2O_3).

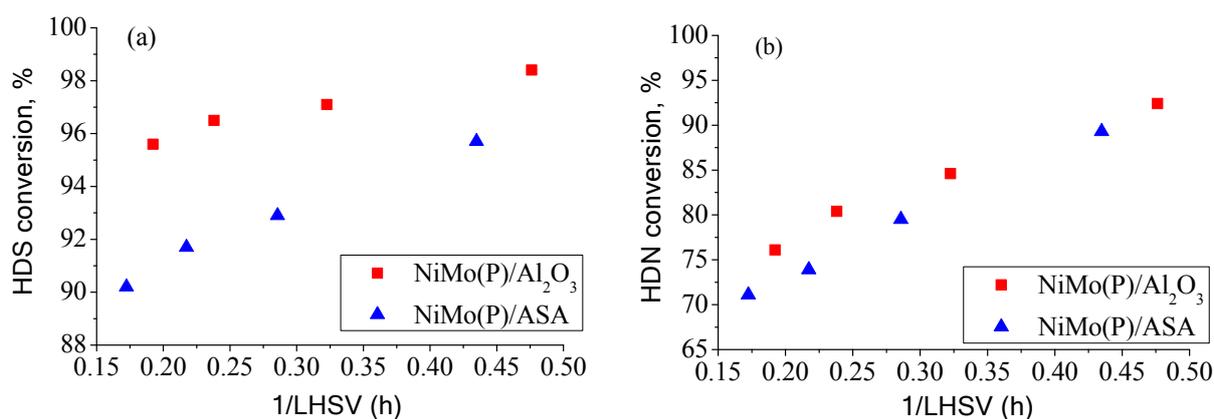


Figure 5: HDS (a) and HDN (b) conversion activity of the two catalysts at 360°C

3.2.3. Deactivation

As mentioned in the experimental section, the deactivation of the catalysts was evaluated by returning to the initial reaction conditions at the end of the run at each temperature. A comparison of the rate constant at the end of the run with the rate constant at the beginning of the run allowed evaluating the extent of deactivation. The loss of HDS activity was between 13 and 15% for both catalysts. The deactivation of HDN was less pronounced for the alumina supported catalyst (5%) than for the silica-supported catalyst (10%). The stronger deactivation of the silica-alumina supported catalyst was already observed in the HDN of quinoline and indole. The carbon and nitrogen contents in used NiMo(P)/Al₂O₃ were 5.0 +/- 0.02 and 0.37 +/- 0.06 wt%, respectively. The corresponding values for used NiMo(P)/ASA were 5.3 +/- 0.04 and 0.47 +/- 0.04 wt%, respectively. The carbon contents were close, but the nitrogen content was significantly higher on silica-alumina, due to the stronger adsorption of basic nitrogen species on this support. The stronger irreversible adsorption of nitrogen probably explains the stronger deactivation.

3.2.4. Basic and neutral nitrogen species

The behavior of neutral pyrrole benzologues and basic nitrogen species in hydrotreatment is quite different. It is, therefore, interesting to follow the evolution of the two families as a function of residence time. **Figure 6** shows the concentration profiles for the NiMo(P)/ASA catalyst. The results for the alumina-supported catalyst were qualitatively similar. We can see that the concentration of neutral nitrogen species dropped rapidly and then remained constant. The decrease of the basic nitrogen concentration was a lot more gradual.

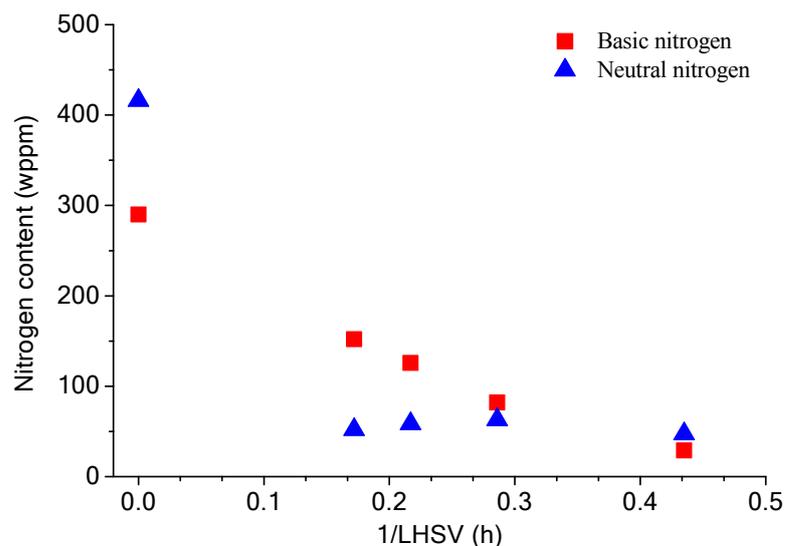


Figure 6: Evolution of neutral and basic nitrogen content as a function of residence time, over NiMo(P)/ASA catalyst at 360°C.

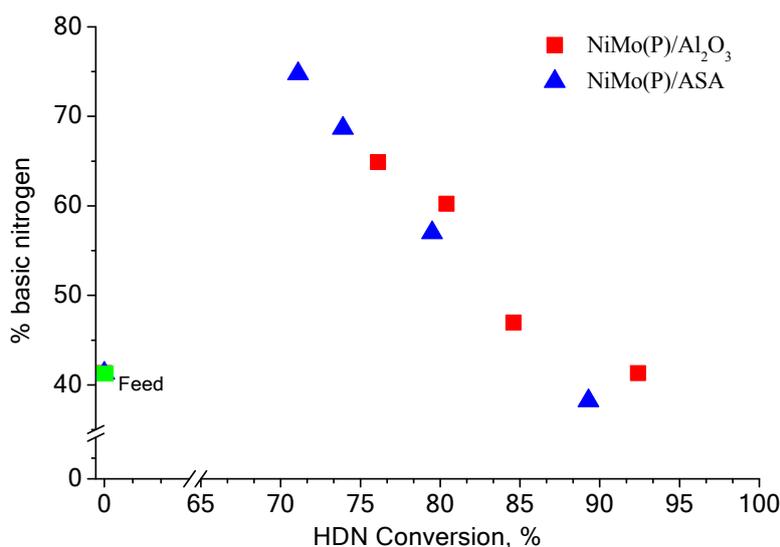


Figure 7: Relative percentage of basic nitrogen content in the feed and effluents at 360°C as function of HDN conversion

Figure 7 shows how the fraction of basic nitrogen species evolves as a function of HDN conversion for the two catalysts. At high HDN conversion, the fraction of basic nitrogen species was slightly lower on the ASA-supported catalyst, which suggests that the acidic support has a small preference for the conversion of the basic species. In other words, the HDN of neutral species is more inhibited by the competitive adsorption of basic species on

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3 the more acidic catalyst; hence the relative abundance of neutral nitrogen was slightly higher
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5 on the ASA catalyst.
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10 **4. Discussion**

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12 In the hydrotreating of nitrogen rich gasoil feed with a high concentration of basic nitrogen
13 species, the HDN activity of a silica-alumina supported catalyst was lower than that of an
14 alumina supported catalyst. This matches the behavior observed in the HDN of quinoline ¹⁷.
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16 We assume that, as in the case in quinoline, the strong adsorption of the basic nitrogen species
17 leads to auto-inhibition and, hence, reduces the catalytic activity of ASA vs. Al₂O₃. For the
18 sake of clarity we note that when we speak about adsorption, we refer to adsorption on the
19 active sites and not to adsorption on the support; the adsorption constants in our earlier work
20 were obtained from kinetic modelling, *i.e.* adsorption on sites, which do not participate in
21 catalysis, was not accounted for.
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34 The majority of the neutral species was converted very quickly (Figure 6). The hydrogenation
35 of the aromatic rings in a neutral nitrogen species creates a basic reaction intermediate. One
36 could, therefore, imagine that the neutral nitrogen species are not really HDN-converted, but
37 simply transferred to the basic nitrogen pool. However, model molecule studies with
38 carbazole derivatives or indole showed that the basic intermediate is rarely detected because it
39 undergoes C-N bond scission very quickly ^{18,31,32}. We can, therefore, assume that this rule also
40 applies to gasoil feeds.
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51 While the majority of neutral nitrogen species was very reactive and rapidly HDN-converted,
52 there was a certain fraction, which was extremely refractory (Figure 6). Its concentration
53 hardly decreased even at the highest HDN conversions reached in this study. Analysis of the
54 effluent by mass spectrometry showed that the refractory pyrrole benzologues were mainly
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3 carbazole and tetrahydrocarbazole-species, in agreement with the literature ^{33–35}. A more
4 detailed discussion of the molecular level analysis of the effluents is, however, beyond the
5 scope of the present contribution and will be presented in a separate paper.
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11 Another observation that merits a brief discussion is that the gap in the HDS activity of the
12 two catalysts is much bigger than the difference in HDN activity. In our model molecule
13 study on quinoline, we had identified that the support acidity had two antagonistic effects: it
14 enhanced the intrinsic reaction rate for hydrogenation reactions, but it also led to auto-
15 inhibition because of a very strong adsorption of the intermediates. The enhancement of the
16 intrinsic hydrogenation activity moderated the auto-inhibition effect. At the moderate HDS
17 levels that we are dealing with in this study, we can presume that the direct desulfurization
18 pathway (which does not involve hydrogenation of the aromatic rings) contributes to a large
19 share of the overall activity. Hence, HDS does not benefit as much as HDN from the
20 enhanced intrinsic hydrogenation activity of the acidic support, but it is negatively impacted
21 by the stronger inhibition (due to the stronger competitive adsorption of basic nitrogen
22 species). We believe that this phenomenon can explain the mediocre HDS activity of the
23 ASA-supported catalyst. More extensive coking on the ASA support might also play a role,
24 but the CHNS of the used catalysts indicates that the carbon content of both catalysts is not
25 very different. Thus, enhanced coke formation is probably not the major cause of the lower
26 HDS activity.
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49 The discussions above are based on the data obtained with a SRGO + CGO feed. We verified
50 whether the trends also apply to other types of gasoil, in particular to LCO feeds, which have
51 a very low fraction of basic nitrogen species. The results of hydrotreating tests with a SRGO
52 + LCO feed are described in the supporting information. Globally the same trends were
53 observed: the alumina-supported catalyst was more active in HDS and also in HDN. Recent
54 papers showed that indole and quinoline were both strong inhibitors of HDS of an SRGO; the
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3 inhibiting effect of the quinoline was only marginally stronger than that of indole^{36,37}. We,
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5 therefore, presume that our hypotheses expressed above also apply to LCO feeds: the bad
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7 performance of the ASA support is mainly attributable to the stronger inhibition by nitrogen
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9 species, even if the large majority of them are pyrrole benzologues.

13 5. Conclusions

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17 An ASA-supported NiMo catalyst and an alumina-supported NiMo catalyst, both having the
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19 same the activity in toluene hydrogenation, were compared in the hydrotreating of SRGO +
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21 CGO and of SRGO + LCO. In both cases, the ASA-supported was less active in HDN and
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23 HDS than its Al₂O₃-supported analogue. We presume that the activity difference can be
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25 mainly attributed to inhibition by basic, but also by neutral nitrogen species, which are more
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27 strongly adsorbed on the ASA-catalyst^{17,18}.

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31 Concerning the behavior of neutral (pyrrole type) and basic nitrogen species in the CGO-
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33 containing feed, our study suggests that deep HDN levels are achieved by pushing the
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35 conversion of the residual basic nitrogen species. Neutral nitrogen species show two extreme
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37 behaviors: either they are converted very quickly or they remain inert up to very high
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39 conversion levels. The refractory pyrrole benzologues are alkylated carbazole and
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41 tetrahydrobenzocarbazole species, as will be demonstrated in a separate paper.

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46 **Supporting information:** GC analysis methods, evaluation of mass transfer in the catalytic
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48 tests, results of catalytic tests with an LCO + SRGO feed.

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