Hydrocracking of *n*-heptane on a sulfided NiMo–Y zeolite catalyst: effect of the sulfidation method

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The activity and the selectivity of a bifunctional NiMo sulfides–Y zeolite catalyst for *n*-heptane hydrocracking depend very much on the sulfidation agent, namely hydrogen sulfide, or dimethyldisulfide in solution in *n*-heptane or *n*-decane. The presence of a hydrocarbon during the sulfidation lowers the acid activity of the catalyst because of coking of the zeolite acid sites, and also decreases the hydrogenating activity, due to a poorer sulfidation of the catalyst.

Keywords: hydrocracking catalysts; nickel–molybdenum sulfides; zeolite; *n*-heptane, hydrocracking of; sulfidation method

1. Introduction

Owing to its great versatility, hydrocracking is ever more used in petroleum refineries to produce gasoline or gasoils [1–5]. Hydrocracking catalysts are bifunctional, associating a hydro-dehydrogenating function with an acidic one. Since the feeds to be treated, such as vacuum gasoils, contain significant amounts of heteroatoms (in particular sulfur and nitrogen), the catalysts must resist to poisoning by hydrogen sulfide and ammonia [1,6].

That is why the hydro-dehydrogenating function of industrial hydrocracking catalysts is generally created by sulfides of group VI and VIII metals, nickel (or cobalt) and molybdenum. These catalysts are available in their oxidic form, and must be transformed into sulfides through an in situ pretreatment with a mixture of a sulfur-containing feed and hydrogen. The sulfidation process, and consequently the resulting activity of the catalyst depend most likely upon the nature of the sulfiding agent [7–9].

The aim of the present work was to determine the effect of the sulfiding feed on the activity of a sulfided NiMo/Y zeolite catalyst in hydrocracking of a model compound, *n*-heptane, under industrial conditions (high hydrogen pressure, presence of N- and S-containing compounds). Before reaction, the catalyst was sulfided in the reactor by dimethyldisulfide in *n*-heptane or *n*-decane, or by a H_2S/H_2 mixture. We also examined the effect of the nature of the sulfiding feed on the carbon and sulfur contents of the catalyst, as well as on its hydrogenating and acid activities using the *o*-xylene transformation model reaction: it has been previously demonstrated [10] that the rate of formation of the *m*- and *p*-isomers of *o*-xylene allowed to estimate the acid activity A_A of a bifunctional catalyst, the hydrogenating activity A_H being defined as the rate of formation of all the C_8 naphthenic compounds.

2. Experimental

The catalyst was prepared by the Institut Français du Pétrole. It contained 14 wt% Y zeolite mixed with NiMo on alumina ($NiO + MoO_3 = 16.8$ wt%).

Sulfidations by dimethyldisulfide: Dimethyldisulfide was dissolved either in *n*-heptane or in *n*-decane, to which aniline was added to generate NH_3. The feed was injected starting at 150°C, the temperature was then raised to 285°C (1 h stage), 325°C (1 h stage), 350°C (2 h stage) and finally to 380°C. Hydrocracking of *n*-heptane was then carried out at this temperature, under the same conditions as those used for the sulfidation: feed flow rate 3.5 $\ell\ h^{-1}$, hydrogen flow rate 10.7 $\ell\ h^{-1}$. The partial pressures were p(hydrocarbon) $= 0.285$ MPa, $p(H_2) = 5.7$ MPa, $p(H_2S) = 6.1$ kPa, $p(NH_3) = 5$ kPa, the total pressure was 6 MPa. The catalyst weight was 1.75 g.

Sulfidation by H_2S: Sulfidation was carried out at atmospheric pressure, with a 5 ml min^{-1} H_2S/H_2 flow rate. The mixture used contained 10 vol% H_2S in H_2. It was injected starting at room temperature, the temperature was then raised to 200°C (1 h stage), 300°C (1 h stage), and finally 380°C. After cooling down of the catalyst to 150°C under H_2S/H_2, this

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mixture was replaced by dimethyldisulfide and aniline in *n*-heptane, and the temperature was raised to 380°C according to the procedure described above for the sulfidation by dimethyldisulfide in *n*-heptane; the hydrocracking of *n*-heptane was then carried out.

At the end of the *n*-heptane hydrocracking experiment (6 h), the feed injection was stopped and the catalyst rapidly cooled in the reactor (room temperature was reached in 30 min). A slow hydrogen flow (3.5 ℓ h^{-1}, 5.7 MPa) was maintained in order to eliminate the feed remaining in the reactor. The carbon, sulfur and nitrogen contents of the catalyst were then measured by the Service Central d'Analyse du CNRS.

To characterize the acid and hydrogenating properties of the catalysts [10], 10 mol% of *o*-xylene were simply added to the hydrocracking feed (*n*-heptane +dimethyldisulfide + aniline).

All the reaction products were analyzed on-line by gas–liquid chromatography (Varian 3400) on a 50 m CP-Sil5 capillary column (Chrompack) with a temperature program from 45 to 55°C (2°C min^{-1}), then from 55 to 85°C (5°C min^{-1}).

3. Results and discussion

Whatever the sulfidation method, the catalyst exhibits a stable activity for *n*-heptane hydrocracking after about 2 h reaction. At steady state, the catalyst is 1.5 times more active after sulfidation by H_2S than after sulfidation by dimethyldisulfide in *n*-heptane, and 3 times more active than after sulfidation by dimethyldisulfide in *n*-decane (table 1).

n-heptane reaction products are mainly propane and butanes (iso and *n*-) in equimolar amounts (cracking C) and *n*-heptane isomers (isomerization I). Fig. 1 shows the effect of the sulfidation method on the isomerization/cracking (I/C) ratio of the catalyst, as a function of *n*-heptane conversion (the different *n*-heptane conversion values were obtained by changing the contact time on the stabilized catalyst). It can be observed that the I/C ratio normally decreases when the *n*-heptane conversion increases [11]. At the same *n*-heptane conversion, the I/C ratio is greater with the catalyst sulfided by H_2S than with the one sulfided by dimethyldisulfide in *n*-decane, and much greater than with the one sulfided by dimethyldisulfide in *n*-heptane. It has been demonstrated during a study of *n*-heptane transformation on a series of Pt/HY catalysts that the higher the ratio of the hydrogenating activity A_H to the acid activity A_A of the catalyst, the higher the I/C ratio [11]. Consequently, the differences observed between the I/C ratios according to the sulfiding feed indicate a modification of the hydrogenating and/or acid properties of the catalyst.

Table 1
Effect of the sulfidation method on the activity of the catalyst. $A_{(n\text{-}C_7)}$ = stabilized activity for *n*-heptane hydrocracking (10^{-3} mol h^{-1} g^{-1}), A_H = hydrogenating activity (10^{-4} mol h^{-1} g^{-1}) from *o*-xylene transformation, A_A = acid activity (10^{-4} mol h^{-1} g^{-1}) from *o*-xylene transformation, C, S, N = wt% on the spent catalyst

Sulfidation	H_2S–H_2	Dimethyldisulfide *n*-C_7	Dimethyldisulfide *n*-C_{10}
$A_{(n\text{-}C_7)}$	1.2	0.8	0.4
A_H	5.5	3.7	3.8
A_A	2.3	2.3	1.2
A_H/A_A	2.4	1.7	3.2
C	2.7	1.8	5.8
S	5.7	4.4	4.5
N	0.3	0.4	0.4

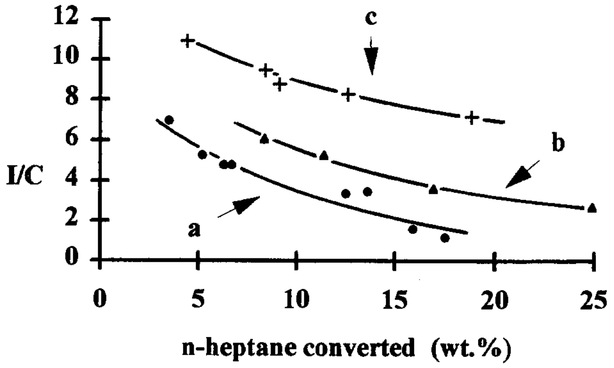

Fig. 1. Effect of the sulfidation method on the isomerization/cracking (I/C) ratio of the catalyst for *n*-heptane hydrocracking. (a) Dimethyldisulfide/*n*-heptane (●), (b) dimethyldisulfide/*n*-decane (▲), (c) H_2S/H_2 (+).

Table 1 gives the results obtained with the *o*-xylene model reaction, as well as the analyses of the C, S and N contents of the spent catalysts. If one compares first the catalyst sulfided by dimethyldisulfide in *n*-heptane to the one sulfided by H_2S, one can observe that the latter, probably because it is better sulfided (5.7 wt% S against 4.4 wt%), is much more active for hydrogenation (greater A_H value). This result contrasts with that reported by Leglise et al. [9] who measured a lower activity for *n*-heptane conversion on a NiMo/HY catalyst sulfided by H_2S, when compared to the catalyst sulfided by dimethyldisulfide in *n*-heptane/benzene. However, in this case, the Ni and Mo were impregnated directly on the zeolite, which is less efficient than our alumina support for the formation of the active phase [12]. This can also explain the low sulfuration level measured by these authors (less than 50%), whereas in our case it reaches 66% after sulfidation by dimethyldisulfide and 85% after sulfidation by H_2S. On the other hand, our results are in good agreement with those obtained by Prada Silvy et al. [7] or Gissy et al. [13]: these authors reported that alumina-supported sulfide catalysts exhibited higher hydrogenating properties after sulfidation by H_2S than after sulfidation in the presence of a hydrocarbon. They explained that the change in activity was due to an interaction between the hydrocarbon molecules and the reduced form of the catalyst, which yielded a poisoning of this catalyst through coking.

On the other hand (table 1), both catalysts have the same acid activity A_A, which can appear normal since the end of the sulfidation by H_2S is, actually, a sulfidation by dimethyldisulfide in *n*-heptane (see the experimental part). However, the coke content of the catalyst sulfided by H_2S is greater than that of the catalyst sulfided by dimethyldisulfide in *n*-heptane. It can be supposed that the catalyst obtained at the end of the H_2S treatment exhibits very strong hydrocracking properties, therefore is able to produce a great deal of olefins when contacting *n*-heptane at relatively low temperatures. These olefins would lead to a very significant coking of the strongest acid sites of the catalyst, which would normally be poisoned by ammonia produced by aniline decomposition. Moreover, it can be noted that the nitrogen content of the catalyst sulfided by H_2S is smaller than that of the catalyst sulfided by dimethyldisulfide in *n*-heptane or in *n*-decane (table 1). Therefore, the acid function of the catalyst would be poisoned to the same extent during both sulfidations (same A_A value), but not in the same manner: the acid sites are more poisoned by coke when the catalyst is sulfided by H_2S (2.7 wt% C) than when it is sulfided by dimethyldisulfide in *n*-heptane (1.8 wt% C), but they are more poisoned by nitrogen when the catalyst is sulfided by dimethyldisulfide in *n*-heptane (0.4 wt% N) than when it is sulfided by H_2S (0.3 wt% N). In any case, our results indicate that the sulfidation by pure H_2S is more efficient than the sulfidation by dimethyldisulfide in *n*-heptane. As a consequence, the A_H/A_A ratio is greater with the catalyst sulfided by H_2S than with the catalyst sulfided by dimethyldisulfide in *n*-heptane, which agrees with the change of the I/C ratio (fig. 1).

If one compares now the catalyst sulfided by dimethyldisulfide in *n*-heptane to that sulfided by dimethyldisulfide in *n*-decane (table 1), it can be seen that both catalysts have the same hydrogenating activity (A_H), and the same sulfur content. Therefore, the formation of the active sulfide phase is not sensitive to the nature of the solvent. If one refers to the interpretations of Gissy et al. [13], this means that *n*-heptane and *n*-decane have the same coking effect on the hydrogenating function. On the other hand, it is clear that the catalyst sulfided by dimethyldisulfide in *n*-decane exhibits weaker acid properties than the catalyst sulfided by dimethyldisulfide in *n*-heptane (smaller A_A value). This can be explained by a more significant carbon deposit on the catalyst (5.8 wt% against 1.8 wt%): indeed, the cracking of *n*-decane is more rapid than that of *n*-heptane [14], and thus more coke is produced since coking results from a secondary transformation of cracking products occurring mainly on the acid sites of bifunctional catalysts [11]. Consequently, the coking of the acid function depends on the nature of the hydrocarbon, in contrast to what was observed in the case of the hydrogenating function. Accordingly, the A_H/A_A ratio is greater with the catalyst sulfided by dimethyldisulfide in *n*-decane than with the catalyst sulfided by dimethyldisulfide in *n*-heptane, which agrees again with the change of the I/C ratio (fig. 1).

Lastly, it can be observed that the activity of the catalyst for *n*-heptane hydrocracking increases either when the hydrogenating activity increases or when the acid activity increases. This indicates that, under our experimental conditions, the rate limiting step of the hydrocracking reaction is not well-defined, and is neither the acid step nor the hydrogenating one. The same conclusion was already reached when studying *n*-heptane hydrocracking over catalysts containing different amounts of NiMo and/or zeolite [15].

4. Conclusions

The hydrogenating activity of a bifunctional NiMo sulfides–Y zeolite catalyst is higher after sulfidation by H_2S than after sulfidation by dimethyldisulfide in *n*-heptane or *n*-decane. This could be due to a smaller formation of the sulfide phase owing to some coking by the hydrocarbon, whatever it may be. On the other hand, the hydrocarbon is clearly responsible for the coking of the acid function of the catalyst during the sulfidation. This coking is all the more significant when the ability of the hydrocarbon to crack increases, from *n*-heptane to *n*-decane. Consequently, the nature of the sulfiding feed modifies deeply the ratio between the hydrogenating activity and the acid activity of the catalyst, which also modifies its activity and selectivity for the hydrocracking reaction.

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