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Hydrodesulfurization of gasoils over NiMo/Al_2O_3–H(or Ni)NaY zeolite hybrid catalysts

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Abstract

A series of hybrid catalysts constituted by NiMo/Al_2O_3 mixed with HNaY or Ni(1.45)NaY zeolite were prepared, and their activities in the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of an untreated gasoil and a commercially prehydrotreated gasoil were compared to those of conventional NiMo/Al_2O_3. The influence of HNaY zeolite loading on the activity of the hybrid catalysts was investigated with both untreated and hydrotreated feeds. The addition of increasing amounts of HNaY to NiMo/Al_2O_3 resulted in lower activities for the HDS and HDN of the untreated gasoil, being the decrease in HDS similar for all hybrid catalysts and in HDN proportional to the HNaY content. These catalysts have a very stable activity for HDS and decaying activity for HDN of the untreated gasoil. With the prehydrotreated gasoil, a small promoter effect (~20%) for initial HDS activity was observed with the addition of 5 wt.% of HNaY to NiMo/Al_2O_3, and then a marked decrease with further HNaY loading. However, all catalysts, included NiMo/Al_2O_3, suffered a rapid deactivation under the reactions conditions used, which was attributed to a desulfurization of the catalysts caused by the low conversion level obtained and, therefore, a low H_2S partial pressure in the reactor. The addition of Ni(1.45)Y zeolite to NiMo/Al_2O_3, decreased slightly the HDS and HDN of the untreated gasoil and increased by a factor of about three and nine times the initial and stationary, respectively, HDS of the prehydrotreated gasoil. Analysis of the relative distribution of sulfur species in products explains the observed synergy and the role of the Ni(1.45)NaY zeolite in the deep HDS over hybrid catalysts.

Keywords: Hydrodesulfurization; Hydrodenitrogenation; Gasoil; NiMo catalyst; Y zeolite

1. Introduction

Deep hydrodesulfurization (HDS) is an important and necessary process to improve the quality of the transportation fuels and to reduce the sulfur level to the low values implemented by environmental legislation [1,3]. To overcome this problem, new process design approaches and catalysts for performing deep HDS of diesel fuel are emerging [1–6]. The approach of combining conventional HDS catalysts and acidic zeolites has resulted very promising for deep HDS [4–17]. The zeolite-containing catalysts are more active for the HDS of the most refractory sulfur compounds in gasoils than the conventional Co(Ni)Mo/Al_2O_3 ones [7–13].

Despite the importance that composite zeolite-conventional hydrotreating catalyst have for industrial deep HDS, at present there is limited knowledge about the best method to incorporate the zeolite component into the conventional alumina-supported Co(Ni)Mo catalyst, and about the influence of parameters such as loading and nature of the incorporated zeolite on catalytic activity. In a previous work, we studied the effect of the preparation method of several HY zeolite-containing NiMo/Al_2O_3 catalysts on the HDS of dibenthothiophene (DBT) and 4,6-DMDBT [18]. It was found that the incorporation of 20 wt.% HNaY zeolite into the catalyst had practically no effect on catalytic activity in DBT HDS, while increased significantly the HDS of

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4,6-DMDBT over catalyst formulations in which the zeolite was mixed with the conventional NiMo/alumina catalyst.

In the present work, we report the influence of HNaY zeolite loading in a NiMo/Al_2O_3–HNaY hybrid catalyst and its substitution by a NiNaY zeolite on the HDS of real feeds. In order to examine the relationship between the catalytic functionality and the feed properties, two types of gasoil feeds, one unhydrotreated and other hydrotreated, were used for catalytic tests.

2. Experimental

2.1. Catalysts preparation

A series of NiMo/Al + HNaY(x) hybrid catalysts, x being the wt.% of HNaY zeolite, were prepared by physically mixing a conventional NiMo/Al_2O_3 catalyst and a HNaY zeolite in different proportions. The mixture was pressed into tablets without binder to avoid loss of zeolite microporosity and acidity [18], crushed and then sieved to a size of 0.25–0.15 mm. The conventional NiMo/Al_2O_3 catalyst (12 wt.% MoO_3, 3.45 wt.% NiO) was prepared by sequential (first Mo) pore volume impregnation of a γ-alumina with aqueous solutions of ammonium heptamolybdate and nickel nitrate. After each impregnation step, the catalyst was dried at 373 K for 4 h and then calcined in air at 773 K for 4 h. The HNaY zeolite was obtained by calcining at 723 K for 2 h a NH_4(59%)Y-form prepared by NH_4^+ ion exchange of a commercial NaY zeolite (Si/Al ratio 2.42) in ammonium nitrate solution. An additional NiMo/Al_2O_3 + Ni(1.45)NaY hybrid catalyst containing 20 wt.% Ni(1.45)NaY zeolite was prepared by similar physical mixing procedure as the NiMo/Al + HNaY(x) series using a Ni^{2+}-exchanged NaY sample containing 1.45 wt.% NiO.

2.2. Activity measurements

Catalytic activity tests were carried out in a high-pressure flow microreactor under the following conditions: temperature: 623 K; total pressure: 30 MPa; LHSV: 90 h^{-1}. Two type of feeds were used: (i) an untreated blend of atmospheric gasoil and heavy residual oil (1.87 wt.% S) enriched with 0.1 wt.% N in the form of pyridine; (ii) a commercially prehydrotreated gasoil (610 ppmw S, 150 ppmw N). Before catalytic measurements catalysts were presulfided in situ with a 7 vol.% CS_2/gasoil mixture at 2 MPa and 623 K for 4 h. The activity of the catalysts was evaluated in several separate runs over a total period of 8–16 h. Reactor liquid effluents were collected at regular intervals and analysed for total sulfur and nitrogen contents using an Antek sulfur/nitrogen analyser. In some experiments with the prehydrotreated gasoil additional analysis of sulfur compounds in reaction products were performed using a Varian CP 3800 chromatograph equipped with a pulsed flame fotometric detector (PFPD), a flame ionization detector (FID) and a DB-Petro105 m capillary column.

3. Results and discussion

3.1. HDS and HDN of untreated gasoil

The HDS and HDN activities of NiMo/Al + HNaY hybrid catalysts and their pure components after 2 h (initial) and 9 h (stationary) time-on-stream are compared in Fig. 1 The incorporation of 5 wt.% of HNaY zeolite in the hybrid catalyst resulted in about 25% decrease in the initial HDS activity as compared to conventional NiMo/Al_2O_3 catalyst. When higher HNaY zeolite contents were incorporated, practically the same decrease in initial HDS activity was obtained irrespective of the zeolite content. This catalytic behaviour is in accordance with previous results reporting that the conversion of DBT over the NiMo/Al + HNaY(20%) hybrid catalyst was slightly lower than on a conventional NiMo/Al_2O_3 catalyst [18] and the insignificant effect that the addition of acid function (silica–alumina or Y zeolite) to a sulfided NiMo on alumina had on the reactivity of DBT [16]. Furthermore, the HDS activity was stable during the first 12 h of reaction for all catalysts; there was not a significant deactivation of the HDS functionality, indicating that the acidic HNaY component has not a significant direct participation in the HDS of untreated gasoil. A different situation occurs for the HDN reaction. As observed in Fig. 1, increasing amounts of HNaY in hybrid catalysts decreased almost proportionally to the zeolite content the initial HDN activity of catalysts. Moreover, the NiMo/Al_2O_3 catalyst showed stable HDN activity, while zeolite-containing catalysts suffered strong deactivation of the HDN functionality.

These results indicate that the effect of HNaY loading on the catalytic behaviour of the hybrid catalysts is complex and also different for HDS and HDN reactions. Since pure HNaY zeolite was apparently almost inactive for both HDS

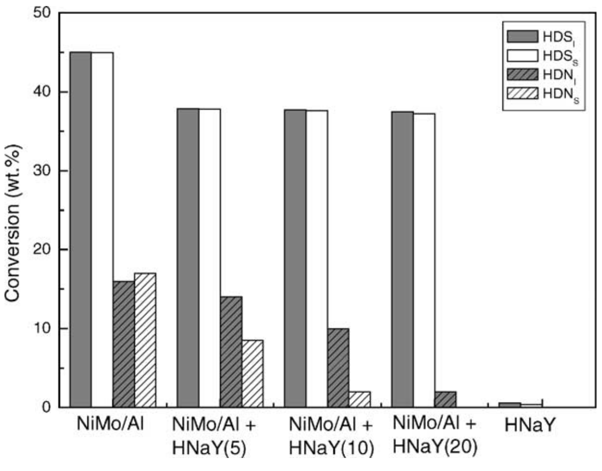

Fig. 1. HDS and HDN of untreated gasoil. Effect of HNaY loading on initial and stationary activities of NiMo/Al + HNaY(x) hybrid catalysts.

and HDN of untreated gasoil under the same reaction conditions as the NiMo/Al_2O_3 catalyst (Fig. 1), it would be expected that HNaY would behave as an inert diluent of the active NiMo/Al_2O_3 catalyst and, therefore, both HDS and HDN activities should decrease proportionally to the zeolite content in catalysts. This catalytic behaviour was really observed for HDN but not for HDS. However, the observation of a severe deactivation of the HDN function of zeolite-containing catalysts and, contrarily, that NiMo/Al_2O_3 catalyst did not suffer deactivation, suggests that HNaY affects the HDN reaction not only as a inert diluent of the NiMo/Al_2O_3 catalyst but also promoting the deactivation of the acid sites involved in HDN reactions. This additional effect of HNaY on HDN reactions is presumably caused by the adsorption of cracking products of the hydroconversion of gasoil over acidic HNaY zeolite and the subsequent coke deposition on the HDN active sites of conventional NiMo/Al_2O_3 catalyst. These cracking products do not seem to affect significantly the metal sulfide active sites of conventional NiMo/Al_2O_3 catalyst and, therefore, deactivation of their HDS functionality was not observed.

The fact that all hybrid catalysts containing HNaY exhibited practically the same HDS activity may be the result of two opposite effects of HNaY. One is the mentioned dilution of the NiMo/Al_2O_3 catalyst by HNaY incorporation. The other, positive effect of HNaY is its activity for cracking and isomerization of the refractory sulfur compounds into compounds which can subsequently be desulfurized over the NiMo component, and then could compensate the dilution effect. This possible explanation is supported by the activity tests of these catalyst with the prehydrotreated gasoil (vide infra) and the extensive hydrocracking observed in the HDS of 4,6-DMDBT over the NiMo/Al + HNaY(20%) hybrid catalyst, evidenced by the formation of significant amounts of cracking products like toluene benzene, ciclohexane and light products [18].

Fig. 2 illustrates the effect of Ni(1.45)NaY zeolite in NiMo/Al_2O_3 catalyst. It can be seen that the initial HDS and HDN activities of the NiMo/Al + Ni(1.45)NaY hybrid catalyst were about 23 and 64%, respectively, lower than those of conventional NiMo/Al_2O_3 catalyst. It is evident that the incorporation of 20 wt.% of Ni(1.45)NaY zeolite in the NiMo/Al_2O_3 catalyst caused also a dilution effect on activity, similar to that of the HNaY zeolite, because the Ni(1.45)Y-alone catalyst exhibited relatively very low activity for the HDS and HDN of the untreated gasoil, which is a feed containing large amounts of non-refractory sulfur compounds that desulfurize primarily through the direct desulfurization route [4,16,20 and references therein]. Note, however, that the catalytic performances of the Ni(1.45)NaY-alone catalyst and its hybrid catalyst were better (Fig. 2) than those of the HNaY zeolite counterparts. This relative improvement in catalytic activity and deactivation of the Ni(1.45)NaY-based catalysts in the HDS and HDN of the untreated gasoil is attributed to the higher hydrogenation properties and less acidity of the Ni(1.45)NaY zeolite.

Consequently, we can conclude that hybrid catalysts consisting in NiMo/Al_2O_3 mixed with zeolite HNaY or NiNaY may not be suitable for the HDS of untreated gasoil because the activity of the HNaY or Ni(1.45)NaY zeolite for the desulfurization of non-refractory sulfur compounds is very low compared to that of NiMo/Al_2O_3. This is understandable since HDS of non-refractory sulfur compounds proceeds mainly through the direct desulfurization route. The contribution of the acid or prehydrogenation route is minimum for HDS of these types of sulfur compounds.

3.2. HDS of prehydrotreated gasoil

To know about the performance of the hybrid catalysts with a more difficult feed, containing a greater proportion of refractory sulfur compounds, we evaluated the activity of the same catalysts using as feed a prehydrotreated gasoil. Fig. 3 shows the extent of HDS of prehydrotreated gasoil over the NiMo/Al + HNaY hybrid catalysts and their pure

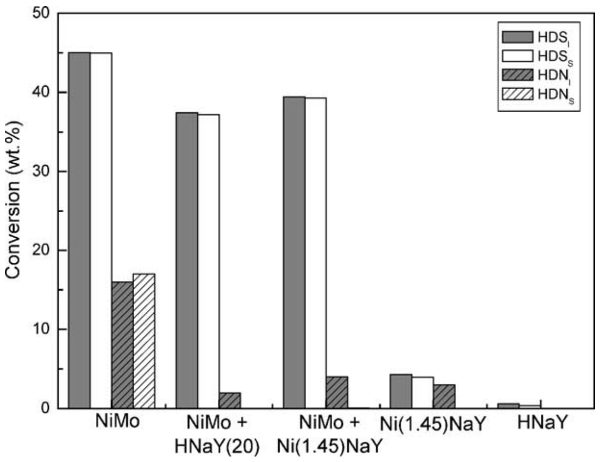

Fig. 2. HDS and HDN of untreated gasoil. Comparison of the activities of NiMo/Al + HNaY(20%) and NiMo/Al + Ni(1.45)NaY(20%) hybrid catalysts.

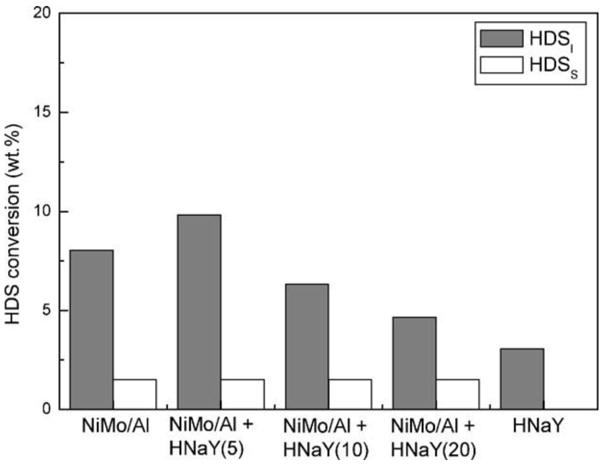

Fig. 3. HDS of prehydrotreated gasoil. Effect of HNaY loading on initial and stationary activities of NiMo/Al + HNaY(x) hybrid catalysts.

components. As expected from the much lower reactivity of the prehydrotreated gasoil, all catalysts had much lower levels of HDS activity than with the untreated gasoil, except pure HNaY that showed a definitely higher activity. It can be seen that, in contrast to the extremely low HDS activity observed with the untreated feed for HNaY, this catalyst exhibited a relatively high initial HDS activity, about one-third of that for the NiMo/Al_2O_3 catalyst, with the prehydrotreated gasoil. The 5 wt.% HNaY-containing hybrid catalyst exhibited about 20% higher initial HDS activity than conventional NiMo/Al_2O_3 catalyst. In this catalyst there is a small synergetic effect, which may be attributed to the prior modifications (demethylation, cracking and hydrogenation reactions) that this acidic HNaY zeolite induces in the refractory sulfur compounds, favouring so their posterior desulfurization [4,12,14]. However, at higher HNaY loading in hybrid catalysts, decreases of about 20 and 40% in initial HDS activity were observed as compared to the NiMo/Al_2O_3 catalyst. In these cases, although the effect of HNaY probably increased, the lower NiMo content of the catalysts reduced too much their HDS ability and, therefore, overall HDS activity decreased. Thus, an appropriate composition balance between conventional NiMo catalyst and acidic HNaY zeolite, as well as an adequate method of incorporating the zeolite [18], has to be used for improving the HDS of refractory sulfur compounds.

As shown in Fig. 4, these catalysts underwent a strong deactivation during the first 4 h on gasoil stream. The HDS activity of these catalysts decreased drastically with reaction time, being stabilized after about 6 h at a similar value (~1.7% conversion) for all catalysts, except for the HNaY catalyst, which was rapidly deactivated by extensive coke formation (Fig. 3). The observed remaining HDS activity of the hybrid catalysts seems to correspond exclusively to the contribution of the NiMo/Al_2O_3 component, and it largely reflects sulfur removal from DBT, and possibly the desulfurization also of a small amount from refractory sulfur compounds occurring probably through the hydrogenation route.

It should be noted that pure NiMo/Al_2O_3 catalyst, in contrast to the good stability shown with the untreated gasoil, with the prehydrotreated gasoil was subjected to strong deactivation (Fig. 4). Such a deactivation of conventional NiMo/Al_2O_3 was, however, not caused by coke deposition over the NiMo active sites. Catalytic tests on resulfided deactivated catalyst samples revealed (data do not shown) that most of the initial HDS activity recovered after the catalyst was subjected to a resulfiding treatment. These results demonstrated that deactivation of conventional NiMo/Al_2O_3 catalyst is mainly due to excessive desulfurization of the catalyst, as a result of the low HDS conversion reached under the reaction conditions used with this refractory feed and, consequently, the very low H_2S partial pressure existing over the catalyst bed. This is consistent with recent results reported by Vogelaar et al. [21]. They found that the major cause of deactivation for the NiMo/Al_2O_3 catalyst during thiophene HDS is a loss of sulfur atoms from the active phase caused by the high H_2 partial pressure under reaction conditions. So, the H_2S/H_2 ratio in the reactor must be kept above a minimum value to maintain adequate sulfidation of the active phase.

The HDS activities of prehydrotreated gasoil over pure Ni(1.45)NaY zeolite and its hybrid NiMo/Al + Ni(1.45)NaY catalyst are shown in Fig. 5 along with the activities of conventional NiMo/Al_2O_3 catalyst and the corresponding hybrid HNaY counterparts for comparison purposes. The initial HDS activity of Ni(1.45)NaY alone was remarkably

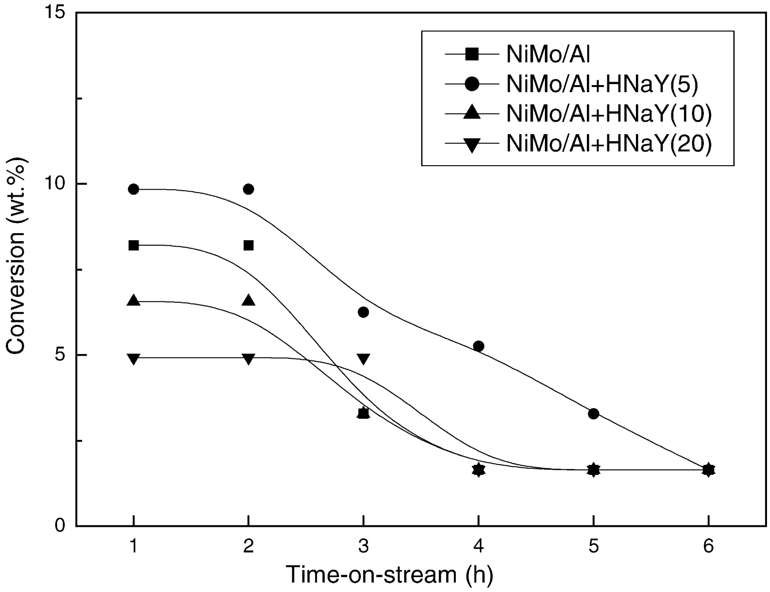

Fig. 4. Time-on-stream profiles for the HDS of prehydrotreated gasoil over conventional NiMo/Al and NiMo/Al + HNaY hybrid catalysts.

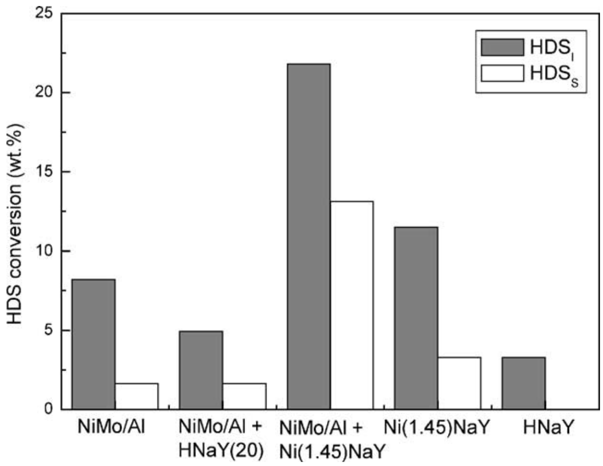

Fig. 5. HDS of prehydrotreated gasoil. Comparison of the activities of NiMo/Al + HNaY(20%) and NiMo/Al + Ni(1.45)NaY(20%) hybrid catalysts.

high compared to pure HNaY (about 3.5 times) and to conventional NiMo/Al_2O_3 catalyst (about 1.5 times); and after 6 h time-on-stream the differences were slightly higher, showing that the former catalyst deactivates slightly less than the other catalysts. The hybrid NiMo/Al + Ni(1.45)Y catalyst exhibited even much higher HDS activity (about 4.5 and 2.7 times) than its hybrid HNaY counterparts and than conventional NiMo/Al_2O_3 catalyst, respectively. Moreover, the deactivation of the NiMo/Al + Ni(1.45)NaY catalyst was substantially much lower (~25%) compared to that of NiMo/Al_2O_3 catalyst (~80%). The fact that the activity of the hybrid NiMo/Al + Ni(1.45)NaY catalyst was substantially higher than the sum of that corresponding to both the NiMo/Al_2O_3 and Ni(1.45)NaY individual components reveals an important promoting effect (a factor about 3) of the acidic Ni(1.45)Y zeolite on the activity of NiMo/Al_2O_3 catalyst in the HDS of prehydrotreated gasoil. A similar promoter effect was reported using a hybrid catalyst of NiHY zeolite and CoMo/alumina for the HDS of gasoil as well as for the conversion of 4,6-DMDBT [19].

In order to inquire on the nature of the promoter effect of Ni(1.45)NaY, sulfur species present in feed and products were analyzed. Chromatograms of sulfur compounds distribution of the prehydrotreated feed and its HDS products on the various catalysts are compared in Fig. 6. It can be seen that the relative distribution of sulfur compounds over conventional NiMo/Al_2O_3 catalyst was similar to that of the feed, being 4,6-DMDBT the compound with the highest concentration. In this case, only a slight decrease in concentration of all sulfur species and disappearance of DBT was observed. In contrast, the sulfur distributions obtained over HNaY and particularly on Ni(1.45)NaY and the hybrid NiMo/Al + Ni(1.45)NaY catalysts, were quite different from that over NiMo/Al_2O_3 catalyst. Over these zeolite-based catalysts, the concentration of di- and tri-MDBTs, and especially of the more refractory and major sulfur

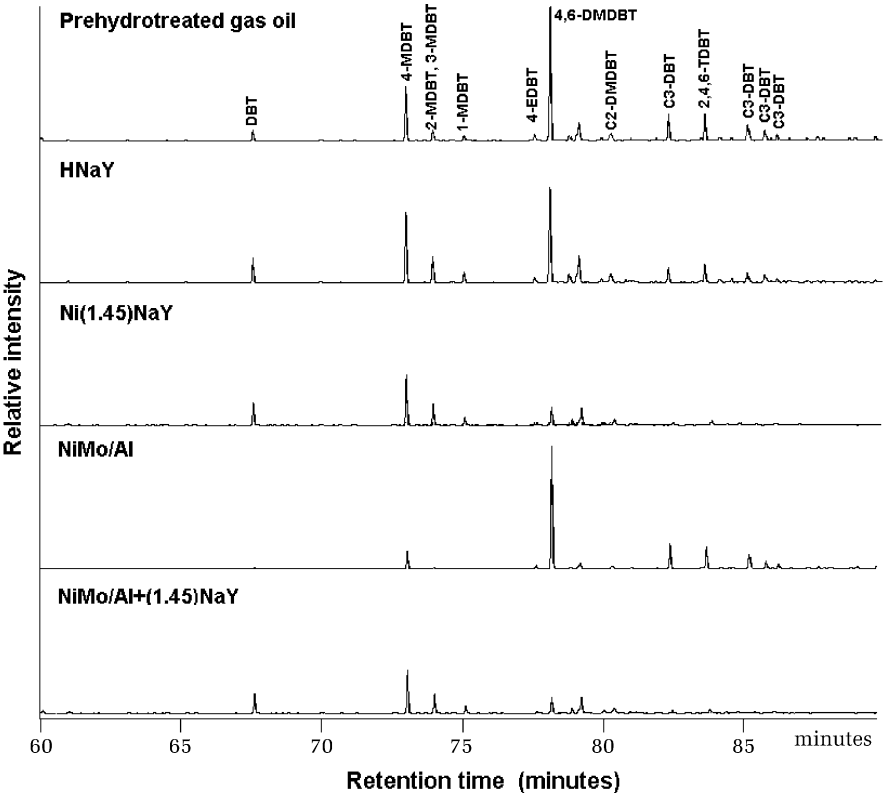

Fig. 6. Sulfur-specific chromatograms of prehydrotreated feed and after HDS over different catalysts: HNaY; Ni(1.45)NaY; NiMo/Al; and NiMo/Al + Ni(1.45)NaY.

component, 4,6-DMDBT, was significantly reduced in benefit primarily of 4-MDBT, other methyl-DBT isomers, DBT and 1,2,3,4-THDBT. Small amounts of compounds in a lower boiling range were also found, particularly over HNaY. As Fig. 6 shows, the extent of these changes in sulfur distribution increased in the order HNaY < Ni(1.45)NaY < NiMo/Al + Ni(1.45)NaY. These features of the sulfur distribution obtained from HDS of the prehydrotreated feed over HNaY, Ni(1.45)NaY and NiMo/Al + HNaY catalysts indicate that the mechanism of the HDS reaction is very similar for the three catalysts, proceeding predominantly through the demethylation and cracking route, in agreement with previous studies [4,12,14]. It is possible that isomerization reactions also occur, but to a minor extent since in the DMDBT fraction some non-identified sulfur species appeared.

From these results, it is concluded that the synergism and better performance observed over the hybrid NiMo/Al + Ni(1.45)NaY catalyst in the HDS of prehydroteated gasoil is essentially due to a cooperative action between Ni(1.45)NaY and NiMo/Al_2O_3. Ni(1.45)NaY transforms the refractory sulfur compounds mainly through demethylation and cracking reactions into others more reactive, which do not require prior hydrogenation to be desulfurized, and the NiMo/Al_2O_3 component desulfurizes then such sulfur compounds through the hydrogenolysis route.

Since HNaY and Ni(1.45)NaY zeolites give products with a similar sulfur distribution pattern, the lower HDS activity of HNaY and its hybrid catalyst seems to be due to the rapid deactivation of the acid sites of HNaY (see Fig. 2) by coke formation. This effect is diminished by the incorporation of Ni into zeolite, due to its enhanced hydrogenation activity.

4. Conclusions

The present hydrotreating results with real feeds confirm that hybrid catalysts based on physical mixtures of conventional NiMo/Al_2O_3 and an acidic HNaY zeolite are less active in hydrotreating of an untreated gasoil than the conventional NiMo/Al_2O_3 alone. The lower intrinsic activity of the HNaY zeolite for the HDS of non-refractory sulfur compounds through direct desulfurization and its tendency to suffer a rapid deactivation by coke deposition causes this component to behave as a diluent of NiMo/Al_2O_3 rather than as a promoter. Consequently, the addition of an acid zeolite to NiMo/Al_2O_3 is not useful for performing conventional hydrotreating of gasoils. The incorporation of a Ni^{2+}-exchaged Y zeolite, i.e. Ni(1.45)NaY, in NiMo/Al_2O_3 improves only slightly the catalyst performance for the hydrotreating of untreated gasoil.

In contrast to the HDS of untreated gasoil, in the HDS of a prehydrotreated gasoil (containing mostly refractory sulfur compounds), the hybrid catalyst containing 5 wt.% of HNaY exhibited initially a slightly higher activity than the conventional NiMo/Al_2O_3 catalyst. However, it suffered strong deactivation during the first 9 h of reaction. Catalysts with a higher HNaY loading were less active than NiMo/Al_2O_3 and were rapidly deactivated. However, the hybrid catalyst of NiMo/Al_2O_3 mixed with 20 wt.% Ni(1.45)NaY resulted to be initially about three times more active and has a slower deactivation than NiMo/Al_2O_3. This synergetic effect of Ni(1.45)NaY is attributed to the transformation of the refractory sulfur compounds in others more reactive through demethylation and cracking reactions on the acid sites of Ni(1.45)NaY, which seem to be preserved by the presence of the Ni hydrogenating function.

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