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Inhibiting effects in hydrodesulfurization of 4,6-diethyldibenzothiophene

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Abstract

This study addresses some of the inhibiting aspects of the hydrodesulfurization (HDS) of 4,6-diethyldibenzothiophene on a sulfided $CoMo/Al_2O_3–SiO_2$ catalyst at relatively low hydrogen pressures. It is shown that thermodynamic equilibrium does not play a significant role in inhibiting sulfur removal at 2.17 MPa hydrogen pressure at least up to 370 °C. Both 3-ethylcarbazole and naphthalene inhibit the HDS rate, with the former being far more potent. Other electron-rich or electron-deficient substituted carbazoles are also strong inhibitors, suggesting that the substituent-induced electronic effect is not a factor governing the poisoning potency of the carbazole family. Operating at high temperatures is more effective in mitigating the inhibiting effect than operating at high hydrogen pressures. A strong inhibiting effect can lead to falsification of the overall HDS kinetics.

1. Introduction

The importance of hydrodesulfurization (HDS) in petroleum refining needs no special elaboration. Suffice it to say that future sulfur specifications in diesel fuels may go down below 10 wppm or less. To develop catalysts and processes in this ultradeep HDS regime requires the desulfurization of refractory sulfur heterocycles whose sulfur heteroatom is sterically hindered. With conventional MoS_2-based catalysts under most conditions of practical interest, the HDS of such refractory sulfur compounds relies heavily on the hydrogenation pathway [1–4]. As a result, the reaction is hydrogen intensive and its rate may possibly be inhibited by thermodynamics at very low hydrogen pressures and very high temperatures [3,5].

A more important inhibiting effect in the HDS of middle distillates (200–350 °C boiling range) arises from competitive adsorption of indigenous nitrogen compounds and aromatics [1–4,6]. Prior studies of the inhibiting effect of nitrogen compounds are mostly restricted to six-membered heterocycles such as quinoline and pyridine [1–4,6,7]. For six-membered nitrogen compounds, there appears to be a good correlation between adsorption equilibrium constants and proton affinities, except for sterically hindered nitrogen compounds [8,9]. It seems, then, that the initial mode of adsorption for six-membered nitrogen compounds is through the nitrogen heteroatom, either by donating its unpaired electron to the Lewis site or by interaction with the proton of a Brønsted site.

As significant as these prior studies are, one must recognize that the majority of the nitrogen compounds in many hard-to-desulfurize middle distillates (e.g., light catalytic cycle oils) are five-membered heterocycles such as carbazoles [10–12]. This class of nitrogen species is nonbasic in that the extra pair of electrons in the nitrogen heteroatom is involved in the π cloud of the ring and is therefore not readily available for interacting with acids. Moreover, the nitrogen atom in the pyrrolic ring acts as an electron source. As such, a pyrrole ring is relatively richer in electrons (π-excessive) compared with a benzene ring [13]. The initial contact of nonbasic nitrogen heterocycles with the catalyst surface most likely favors a side-on configuration involving the aromatic ring (parallel to the catalyst surface) rather than the nitrogen heteroatom. That is, the adsorption mode for carbazole compounds is similar to that for polynuclear aromatics such as naphthalene. So five-membered nitrogen heterocycles and aromatics are likely to be more harmful to the hydrogenation pathway than to the hydrogenolysis pathway. It follows that the HDS of refractory sulfur species should be more vulnerable to nonbasic nitrogen and aromatic poisons than that of reactive sulfur species such as dibenzothiophene (DBT). Indeed, this is the case with aromatic poisons [14].

The present study aims to understand better some of the inhibiting effects in the ultradeep HDS regime by study-

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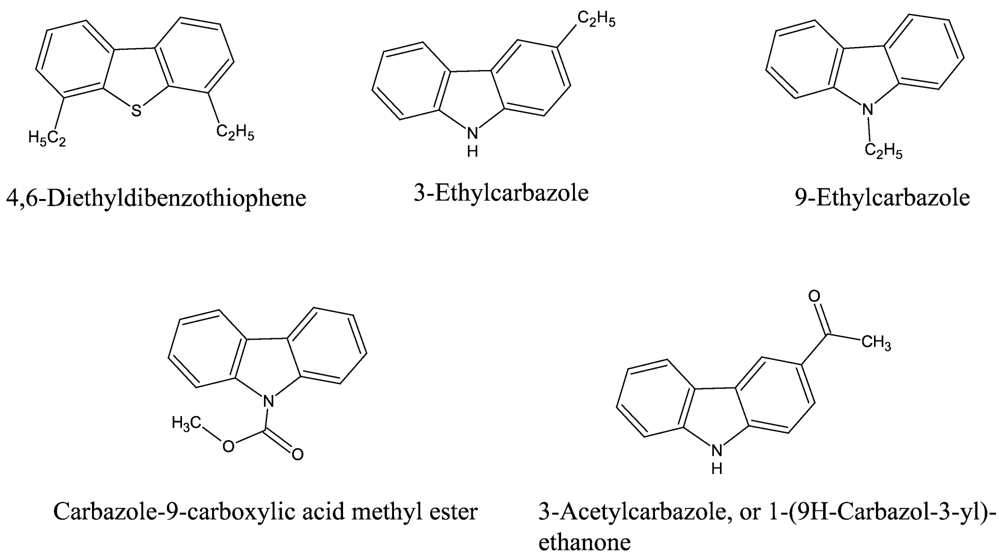

Fig. 1. Structures of some of the heterocyclic sulfur and nitrogen compounds used in this study.

ing the HDS of 4,6-diethyldibenzothiophene (46DEDBT), a probe molecule more refractory than 4,6-dimethyldibenzothiophene [15]. The catalyst used is a commercial sulfided $CoMo/Al_2O_3–SiO_2$. The work begins with the determination of the overall HDS kinetics in the absence of any inhibitor under conditions free of thermodynamic effect. We then study the extent to which the HDS rate may be inhibited by the thermodynamically limited hydrogenation at high temperatures. Following this, both steady-state and transient experiments are conducted to follow the manner in which the HDS rate is inhibited by 3-ethylcarbazole (3ECBZ) and naphthalene at 1.83 MPa (250 psig) hydrogen pressure and 265 °C. For comparison, the inhibiting effect of 3ECBZ on the HDS of DBT is examined to see if DBT HDS is indeed less vulnerable to 3ECBZ poisoning. Similar experiments are conducted with other substituted carbazoles to explore the possibility of mitigating the inhibiting effect by modifying the electronic properties of carbazoles. Specially designed experiments are carried out to ascertain the relative effects of temperature and hydrogen pressure on the poisoning process. Finally, we show that a strong inhibiting effect can falsify the overall apparent HDS kinetics. These results, taken together, should shed some light on the catalytic chemistry and kinetics of ultradeep HDS of refractory middle distillates.

2. Experimental

2.1. Materials

The gases used were cylinder hydrogen of electrolytic grade (99.95%) and cylinder 10% $H_2S–H_2$ mixture. Dodecane, naphthalene, 9-ethylcarbazole (9ECBZ or *N*-ethylcarbazole), and DBT were all analytic pure grade. Compounds obtained through external custom synthesis include 46DEDBT, 3ECBZ, 3-acetylcarbazole (3ACBZ) [or 1-(9*H*-carbazol-3-yl)-ethanone], and carbazole-9-carboxylic acid methyl ester (CBZ9ME). Fig. 1 shows the structures of some of the compounds. The stabilities of 9ECBZ, 3ACBZ, and CBZ9ME were tested in batch tubing bomb experiments at 1.83 MPa hydrogen pressure and 265 °C overnight. No decompositions of these compounds were observed. The solubility of 3ECBZ in paraffinic solvents is much higher than that of carbazole [13]. The commercial $CoMo/Al_2O_3–SiO_2$ catalyst, in the form of 1/16-inch extrudates, was crushed and sieved into 20–40 mesh granules. It was sulfided at 400 °C for 1 h at atmospheric pressure with a 10% H_2S-in-H_2 mixture.

2.2. Reactor and procedures

The experiments were conducted in two parallel isothermal, cocurrent fixed-bed reactors (3/8-inch o.d. 316 stainless-steel pipe) in a common heated box. Each reactor, operated in upflow mode to avoid incomplete catalyst wetting and bypassing, has a feed burette, pump, gas–liquid separator, and product collector. Glass beads were charged in the fore and aft zones to achieve vapor–liquid equilibrium. Typically, the catalyst required many hours to equilibrate its activity after each condition change. To minimize the axial dispersion effect, 3 g catalyst was uniformly mixed with an equal amount of glass beads in the reactor central zone [16]. Comparative experiments showed that the diluted bed indeed gave a higher conversion than the undiluted bed.

Table 1 lists the compositions of the 10 feed mixtures (A to J) used in this work, with the balance being dodecane. Compounds in the liquid effluents were identified by GC/MS and quantified with a HP gas chromatograph using a 75% OV-1/25% Supelo wax 10 capillary column. The total nitrogen was analyzed by combustion and chemiluminescence using the Antek analyzer. The product gases were

Table 1
Compositions (wt%) of feeds A to J[a]

Compound	A	B	C	D	E	F	G	H	I	J
46DEDBT	0.8	–	0.8	0.8	–	0.8	0.8	0.8	0.8	0.8
DBT	–	1.5	–	–	1.5	–	–	–		
Naphthalene	–	–	10.0	–	–	–	–	–		
3ECBZ	–	–	–	0.112	0.112	0.007	–			
9ECBZ	–	–	–	–	–	–	0.007			
CBZ9ME	–	–	–	–	–	–	–	0.0081		
CBZ9ME	–	–	–	–	–	–	–		0.032	
3ACBZ	–	–	–	–	–	–	–			0.0075

[a] Balance is dodecane.

vented through a caustic scrubber followed by a wet test meter.

All the experiments were carried out at a treat gas rate of 116 cc H_2/cc liquid feed (650 standard cubic feet hydrogen per barrel of liquid feed). The first set of experiments was done to determine the HDS kinetics (feed A, 1067 ppm sulfur) at 1.83 MPa hydrogen pressure and 265 °C over a range of WHSVs (liquid weight hourly space velocity, cc liquid feed/(g_{cat} h)). Under these conditions, the reaction is not diffusion limited.

The sequence of the poisoning experiments is as follows. Each reactor started with a poison-free feed (feed A or B) giving the base-case data at 265 °C and 1.83 MPa. Following this, a poison-containing feed (feeds C to J) replaced the poison-free feed at time zero to slow down the HDS rate under the same conditions. The state of the reactor was monitored by intermittently analyzing the liquid effluents over the entire run. After the reactor reached a new steady state, the original poison-free feed was put back on stream to strip the reversibly adsorbed poison off the catalyst, thus recovering all or part of the lost HDS activity. The liquid products were analyzed during the stripping period until the catalyst lined out its activity again.

Besides H_2S, the main HDS products were identified to be diethylcyclohexylbenzenes (C4CHB), diethylbiphenyls (C4BP), ethylcyclohexylbenzenes (C2CHB), ethylbiphenyls (C2BP), ethylbenzenes (C2BZ), and ethylcyclohexanes (C2CH). These products, each having many isomers, accounted for more than 98% of 46DEDBT converted. Trace amounts of diethylbicyclohexyl, ethylbicyclohexyl, biphenyl (BP), and cyclohexylbenzene (CHB) were noted under some conditions. Virtually no partially hydrogenated 46DEDBTs (e.g., tetra- or hexa-hydro-DEDBT) were observed. Tetralin and decalin were the main products of naphthalene hydrogenation and accounted for more than 99% of naphthalene converted. Hence side reactions such as ring opening were neglected. The principal products from the HDS of DBT were BP and CHB. Due to their low concentrations, individual hydrodenitrogenation (HDN) products were not measured. The carrier solvent dodecane was essentially inert under the reaction conditions studied.

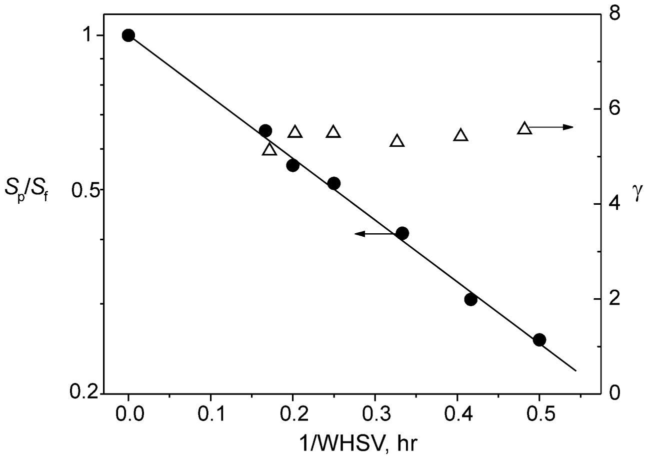

Fig. 2. Overall HDS kinetics of 46DEDBT HDS: ln(S_p/S_f) (●) and γ(Δ) vs 1/WHSV; 1.83 MPa, 265 °C, 116 cc H_2/cc liquid feed. The solid line is model prediction.

3. Results and discussion

3.1. Overall HDS kinetics and selectivity

Fig. 2 plots ln(S_p/S_f) vs 1/WHSV at 1.83 MPa and 265 °C, where S_p and S_f are the total sulfur contents (wt%) in the liquid product and feed, respectively. The straight line (solid circles) indicates that the HDS rate is pseudo-first order. This suggests that the sulfur coverage on the catalyst surface may be low even in the absence of any poison. The apparent rate constant obtained from regression is 2.73 ± 0.05 cc liquid feed/(g_{cat} h), including the hydrogen concentration term because of its insignificant variation across the reactor. The fit is good, with $\chi^2 = 1.9 \times 10^{-4}$, as also indicated by the solid line. Note that here the kinetics is for the overall sulfur removal; detailed HDS network and mechanistic kinetics are beyond the scope of this work.

Fig. 2 also shows that interconversion between C4BP and C4CHB is insignificant because of the approximate constancy of the mass ratio γ defined as

$$\gamma = \frac{\text{wt\% C4CHB in product}}{\text{wt\% C4BP in product}}. \tag{1}$$

As shown in Fig. 2, $\gamma \sim 5.5$ over a wide range of WHSVs, indicating that the hydrogenation pathway dominates the sulfur removal process. Under the conditions

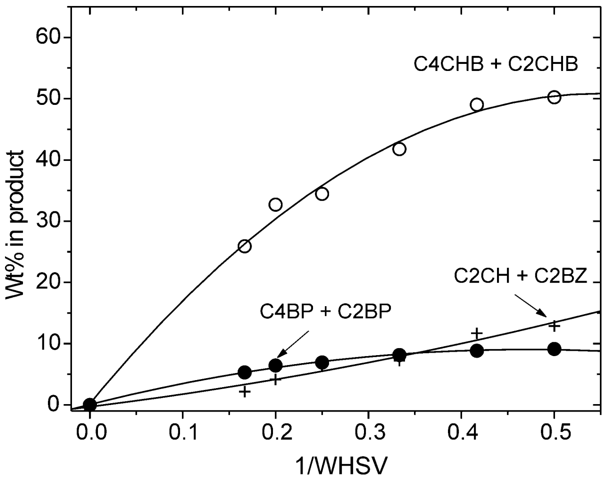

Fig. 3. Weight percents of various HDS product lumps (C4CHB + C2CHB, C4BP + C4BP, and C2CH + C2BZ) in the total liquid effluents (including unconverted 46DEDBT) vs 1/WHSV at 1.83 MPa, 265 °C, and 116 cc H_2/cc liquid feed.

tested, the concentrations of C2CHB and C2BP are far lower than those of C4CHB and C4BP. The mass ratio C2CHB/C2BP is also approximately constant (~ 4.5) over a wide range of HDS levels (not shown).

Fig. 3 shows the concentrations (wt%) of major product lumps versus space time (1/WHSV) at 1.83 MPa and 265 °C. The major hydrocarbon product lumps are C4CHB+ C2CHB, C4BP + C2BP, and C2BZ + C2CH. The C2BZ + C2CH product lump most likely results from link cleavage in C4CHB rather than in C4BP because the link between the two phenyl groups in C4BP is much tougher to break.

3.2. Possible thermodynamic inhibition

While the intent of this work is not to define the HDS network, it is helpful for the present discussion to propose a rather simplified lumped HDS network as shown in Fig. 4. The lumps of C2CHB and C2BP are not shown because they are minor products and their reaction pathways are unclear. The primary desulfurization pathway appears to be 46DEDBT $\rightleftharpoons$ “hydro-46DEDBT” $\rightarrow$ C4CHB, with “hydro-46DEDBT” being the aggregate of all partially hydrogenated 46DEDBT. This aggregate, being an ultraactive intermediate, is essentially unobservable under the conditions used. The reversible character of the 46DEDBT hydrogenation step may affect HDS because of the thermodynamically mandated low concentration of “hydro-46DEDBT” at low hydrogen partial pressures and high temperatures. However, if the “drainage” reaction “hydro-46DEDBT” $\rightarrow$ C4CHB becomes sufficiently fast at high temperatures (i.e., it has a high activation energy), the overall HDS rate may not suffer and may actually increase. The HDS rate may also increase if the direct hydrogenolysis 46DEDBT $\rightarrow$ C4BP accelerates appreciably at high temperatures. The possibility that some hydrogenation sites may transform into hydrogenolysis sites at high temperatures may not be ruled out with certainty. At very high temperatures, dehydrogenation of C4CHB to C4BP may occur. The result of all this is that γ should be a strong decreasing function of temperature.

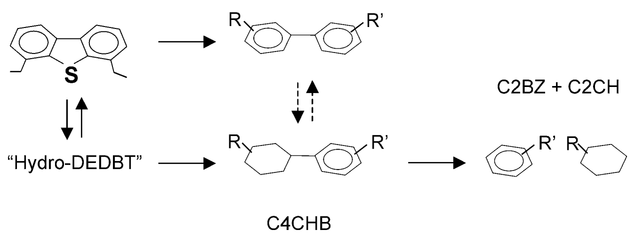

Fig. 4. Portion of lumped 46DEDBT HDS network at 265 °C and 1.83 MPa H_2 pressure. “Hydro-DEDBT” is the lump of all hydrogenated 46DEDBTs (e.g., tetra- or hexa-hydro-DEDBT). The total number of carbon atoms in R and R' is 4.

The foregoing discussion is qualitative. Let us see the data obtained with feed A at 2.17 MPa hydrogen pressures and 1.5 WHSV (6 g catalysts charge). The reaction temperature was incrementally raised from 265 to 370 °C at the same WHSV. As can be seen from Fig. 5, the HDS level increases with increasing temperature and essentially attains 100% at 280 °C and maintains at this level at least up to 370 °C.

Fig. 6 shows the weight percents of C4CHB, C4BP, and C2CH + C2BZ in the total liquid effluents (including unconverted 46DEDBT). At a low temperature of 265 °C, the concentration of C4CHB is much higher than that of C4BP ($\gamma \sim 5.5$). Increasing temperature speeds up the formation of C2CH + C2BZ from C4CHB, resulting in a rapid decline in the C4CHB concentration. In contrast, the C4BP level remains low and fairly constant, suggesting that there is little net interconversion (hydrogenation–dehydrogenation) between C4BP and C4CHB. Here γ decreases with increasing temperature mainly due to the decline in C4CHB. Although not shown in Fig. 6, the behavior of C2CHB and C2BP is similar to that of C4CHB and C4BP. Thus, the picture here is that while increasing temperature may inhibit the formation of “hydro-46DEDBT,” the sulfur removal process

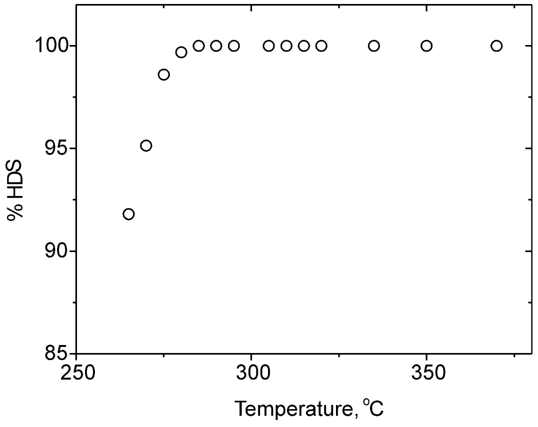

Fig. 5. Percentage 46DEDBT HDS vs temperature at 2.17 MPa H_2 pressures; feed A, 1.5 WHSV, 116 cc H_2/cc liquid feed.

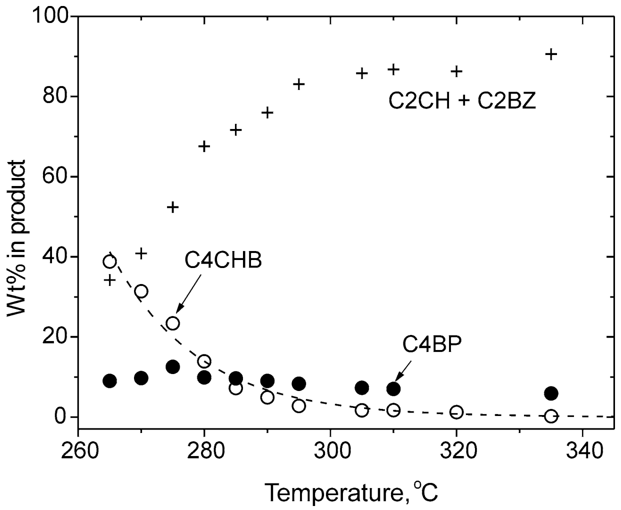

Fig. 6. Weight percents of C4CHB (○), C4BP (●), and C2CH + C2BZ (+) in the total liquid effluents (including unconverted 46DEDBT) at 2.17 MPa, 1.5 WHSV, and 116 cc H_2/cc liquid feed.

is essentially driven by the pathway "hydro-46DEDBT" → C4CHB → C2CH + C2BZ under the conditions tested.

3.3. Inhibition by 3ECBZ and naphthalene

We now turn to inhibition due to nitrogen and aromatic compounds. Fig. 7 shows the percentage HDS vs h-on-stream obtained from the sequential off-poison and on-poison experiments at 1.83 MPa and 265 °C. The HDS level is about 70% with neat 46DEDBT (feed A). Note that the initial off-poison experiment was run for 400 h before switching over to a poison-containing feed (in the figures to follow, the elapsed hour after introducing the poison-containing feed is plotted). As can be seen from Fig. 7, upon feed switching the extent of sulfur removal drops and eventually reaches a new steady state. With 80 wppm feed nitrogen (as atom) added as 3ECBZ (feed D), HDS diminishes to less than 10%. Apparently, the majority of the catalytically active sites are taken over by nitrogen compounds (3ECBZ and its hydrogenated derivatives), with an overall HDN level of about 58% (not shown). In contrast, the damage caused by naphthalene (feed C) is relatively minor; HDS drops from 70 to 53%. Hence a significant fraction of the active sites remain immune to naphthalene poisoning, even though the feed naphthalene concentration (10 wt%) is orders of magnitude higher than that of 3ECBZ.

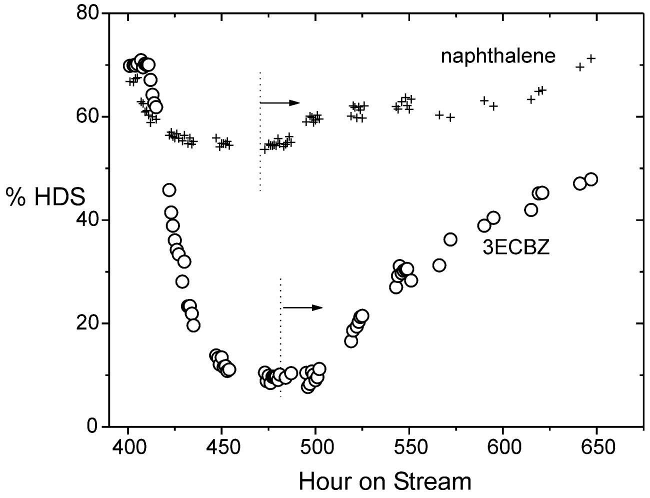

Fig. 7. Percentage 46DEDBT HDS vs elapsed hour after introduction of feeds C (○) and D (+) at the 400th hour; 1.83 MPa, 265 °C, 2.4 WHSV, 116 cc H_2/cc liquid feed; the vertical lines indicate the beginning of the stripping experiments using feed A.

The difference between the two inhibitors can further be seen from subsequent stripping experiments. After switching back to feed A (indicated by the dashed vertical lines and arrows in Fig. 7), the recovery of the HDS level in the naphthalene case appears to be a two-step process. The loosely adsorbed species are stripped off the catalyst surface followed by the removal of strongly adsorbed species. The lost HDS activity can almost be fully recovered. In contrast, the HDS activity recovery in the 3ECBZ case appears to be a one-step process with a progressively slower recovery rate. Fig. 7 strongly suggests that complete recovery of the lost HDS activity may not be achievable even after a long time. This may have much to do with the propensity of nitrogen heterocycles to polymerize and may eventually go on to form coke [7,13,17,18].

To sum up, 3ECBZ is a far more potent inhibitor than naphthalene under the conditions used. Consistent with this, the proton affinity, boiling point, and molecular size of 3ECBZ are all higher than those of naphthalene [19]. Also, 3ECBE's shape is similar to that of 46DEDBT; both molecules presumably take the side-on configuration as the preferred adsorption mode. In this regard, we point out that fluorene is a stronger inhibitor than anthracene and phenanthrene in the HDS of 4,6-dimethyldibenzothiophene possibly due to its molecular shape [20]. Finally, the hydrogenation of 3ECBZ would produce more basic nitrogen species that are presumably more poisonous than 3ECBZ [13].

Before proceeding further, it is worth pausing to look at how 3ECBZ affects the HDS of DBT, a relatively reactive sulfur compound that takes hydrogenolysis as its principal HDS pathway.

3.4. Effect of 3ECBZ on DBT HDS

The experiment started with the 1.5 wt% DBT-in-dodecane feed (feed B) at 265 °C, 3 WHSV, and 1.83 MPa. These conditions gave a 95% HDS with a low CHB/BP ratio of about 0.34 vs $\gamma \sim 5.5$ shown in Fig. 2. The reactor was subsequently switched to feed E containing both DBT and 3ECBZ (80 ppm total nitrogen). As Fig. 8 indicates, the HDS level dropped to 63.5% at the new steady state, indicating that a large fraction of the active sites survived after nitrogen breakthrough.

Comparison of Figs. 7 and 8 shows that 46DEDBT HDS is more sensitive to poisoning by 3ECBZ than DBT HDS,

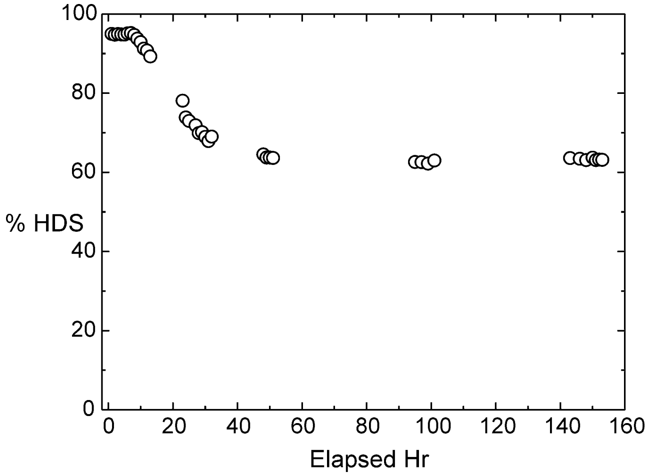

Fig. 8. Percentage DBT HDS vs elapsed hour after introduction of feed E; 1.83 MPa, 265 °C, 3 WHSV, 116 cc H_2/cc liquid feed.

thus confirming our earlier supposition. A possible explanation may be that 46DEDBT HDS, being a high hydrogen intensity reaction, requires hydrogenation sites involving specific multiplets of adjacent sulfur vacancies (or coordinatively unsaturated sites). Such multiplets are sites on which 3ECBZ can easily and selectively adsorb. This, if true, means that it does not take much 3ECBZ to break up the multiplets, making 46DEDBT HDS very sensitive to 3ECBZ. This is not the case with DBT HDS for which the site requirements are much less stringent and hence a low sensitivity to 3ECBZ poisoning. To further test this proposition, we perform poisoning experiments with a feed containing a trace amount of 3ECBZ.

3.5. Sensitivity to 3ECBZ concentration

With feed F (5 ppm total nitrogen) at 265 °C and 1.83 MPa hydrogen pressure, the extent of HDS drops to 40.5%, indicating that the damaging effect of 5 ppm nitrogen is even greater than that of 10 wt% naphthalene (cf. Fig. 7). This is entirely consistent with the proposition that even an exceedingly small amount of 3ECBZ can break up the multiplets. In this case the liquid effluent is virtually free of organonitrogen within the detection limits. This says that HDN is nearly completed at some point in the reactor; downstream of which the catalyst bed remains essentially unpoisoned (NH_3 is much less poisonous than organonitrogen). It is this unpoisoned part of the catalyst bed that accounts for the majority of the residual HDS level. A practical implication of this result is that in order to boost HDS activity by separating out indigenous nitrogen compounds in petroleum distillates, one has to remove them to a very low level.

3.6. Temperature vs pressure effects

Having witnessed the poisoning power of 3ECBZ, we now want to see the extent to which 3ECBZ's poisoning effect can be mitigated through process conditions. With feed F (5 ppm total nitrogen), the dual-reactor system was used to ascertain the relative effects of temperature and pressure on the poisoning process. To mitigate the poisoning effect, one may consider either a high-temperature or a high-pressure operating strategy. The former may suppress the adsorption of nitrogen compounds, whereas the latter may help HDS through enhanced HDN, for HDN in general is highly sensitive to hydrogen pressure [13]. To provide a common base for comparing these two strategies, we begin the poisoning experiments with the same HDS level, as detailed below. It is relevant to point out that in practice the refiner adjusts process conditions to maintain a constant HDS level dictated by the sulfur specification.

We first desulfurize 46DEDBT in feed A to the same extent (90% HDS) under two different sets of conditions: one at 280 °C and 1.83 MPa, the other at 270 °C and 3.38 MPa. The WHSV and hydrogen treat rate are the same for both cases. Thus, prior to the arrival of 3ECBZ, the two catalyst beds have similar sulfur profiles but in very different environments. One is under high temperature, while the other under high hydrogen pressure. After switching over to the nitrogen-containing feed, the two environments would generate different nitrogen profiles in the reactor unless by chance HDS and HDN have the same pressure response and the same activation energy. Fig. 9 shows the HDS declines observed in the subsequent poisoning experiments with feed F. As can be seen, the environment does matter: the high-temperature operation is more effective for combating the poisoning effect than the high-pressure operation. Besides weakening the adsorption of nitrogen compounds, the high-temperature environment presumably accelerates the reaction "hydro-46DEDBT" → C4CHB → C2CH + C2BZ. A recent study [21] has shown that HDS is more sensitive to temperature than HDN in tests with a light catalytic cycle oil.

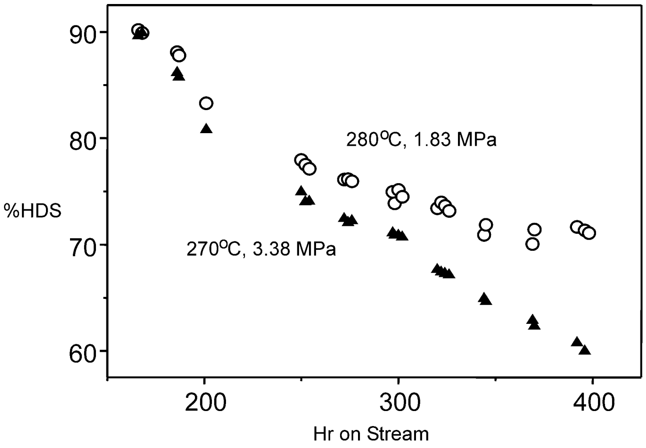

Fig. 9. Percentage 46DEDBT HDS vs elapsed hour under two different conditions: 1.83 MPa and 280 °C (○); 3.38 MPa and 270 °C (▲); 116 cc H_2/cc liquid feed, 2.5 WHSV (feeds A and F).

3.7. Effects of substituents

Given the high poisoning potency of 3ECBZ, a natural question then is: Can the poisoning potency of carbazole compounds be significantly weakened by modifying their structures? If the ability of carbazole compounds to donate electrons to the active sites is a controlling factor for catalyst poisoning, it might be possible to mitigate the poisoning effect by changing carbazoles' electronic properties. In this regard, we note that Geneste, Moreau, and co-workers [22–24] observed a significant substituent effect on the hydrogenation rates of substituted benzenes over a sulfided Ni–Mo/Al_2O_3 catalyst. They rationalized the results in terms of a substituent-induced electronic effect that changes the π-adsorption strength of various benzene derivatives.

To pursue the idea, we perform poisoning experiments with the following carbazole derivatives: 3ACBZ, 9ECBZ, and CBZ9ME. Each of these derivatives was added to the 46DEDBT feed to give 5 wppm total nitrogen. The electron-donating ethyl group in 3ECBZ and the electron-withdrawing acetyl group in 3ACBZ are both attached to the benzene ring. With carbazole as the reference molecule, the benzene ring in 3ECBZ is electron rich, whereas that in 3ACBZ is electron deficient. Fig. 10 shows the expected trend in that 3ACBZ (feed J) is a weaker inhibitor than 3ECBZ (feed F), although the difference is small.

Let us look at 9ECBZ in which the electron-releasing N-ethyl group would enrich the electron density of the pyrrole ring. This inhibitor (feed G) is slightly more potent than 3ECBZ, as Fig. 11 shows. This result also suggests that the adsorption of carbazole compounds should be side on for otherwise 3ECBZ would be more potent.

The carboxylate group in CBZ9ME is electron withdrawing, with the result that the pyrrolic ring in CBZ9ME is electron deficient compared with that in 9ECBZ. Fig. 12 indicates that the poisoning power of CBZ9ME (feed H) is similar to that of 3ECBZ (and hence weaker than that of 9ECBZ). Thus, directionally, electron withdrawing seems to have a small beneficial effect. However, this electron-deficient nitrogen species is still very destructive. As an example, Fig. 13 shows that with just 20 ppm total nitrogen as CBZ9ME (feed I), the majority of the catalytic sites for 46DEDBT HDS are shut off. For perspective, the HDS decline resulting from 5 ppm nitrogen as CBZ9ME is shown in Fig. 13 as well. Figs. 12 and 13 suggest that the presence of the bulky carboxylate group does not appear to introduce additional complexities that fundamentally change the adsorption characteristics of the carbazolic structure.

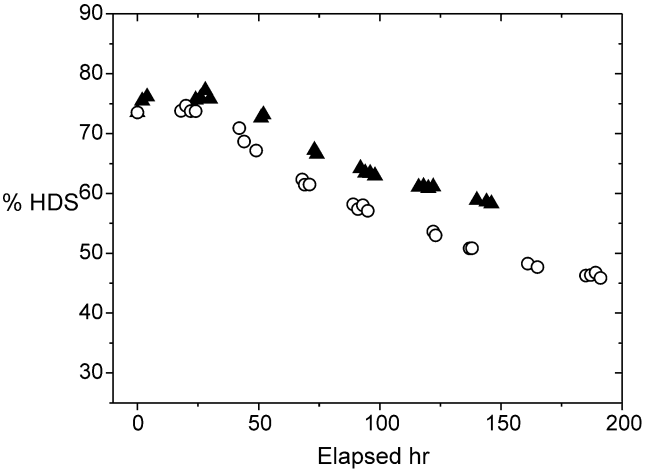

Fig. 10. Percentage 46DEDBT HDS vs elapsed hour. Comparison of poisoning power of 3ECBZ (○, feed F) and 3ACBZ (▲, feed J); 1.83 MPa, 265 °C, 2.1 WHSV, 116 cc H_2/cc liquid feed.

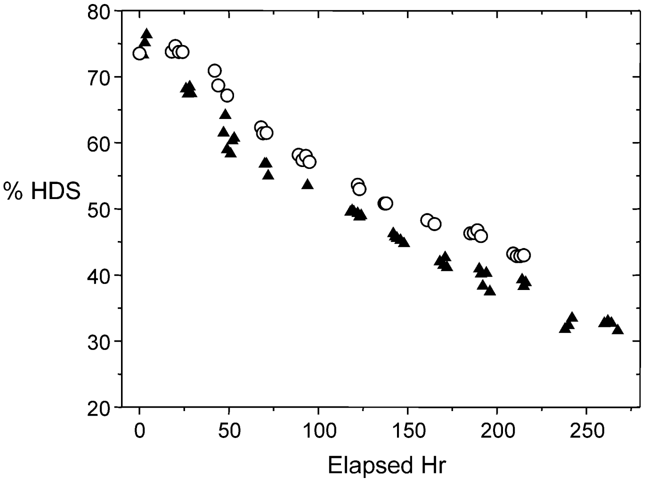

Fig. 11. Percentage 46DEDBT HDS vs elapsed hour. Comparison of poisoning power of 3ECBZ (○, feed F) and 9ECBZ (▲, feed G); 1.83 MPa, 265 °C, 2.1 WHSV, 116 cc H_2/cc liquid feed.

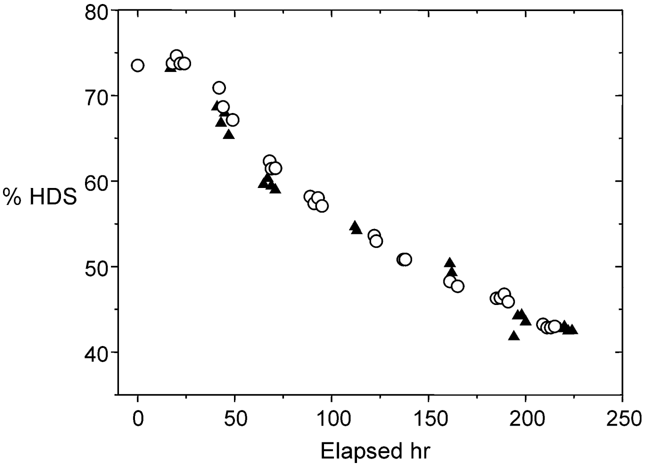

Fig. 12. Percentage 46DEDBT HDS vs elapsed hour. Comparison of poisoning power of 3ECBZ (○, feed F) and CBZ9ME (▲, feed H); 1.83 MPa, 265 °C, 2.1 WHSV, 116 cc H_2/cc liquid feed.

Summarizing, the adsorptivity of carbazole species may vary due to a substituent-induced electronic effect, it is still far greater than that of 46DEDBT. In other words, the very nature of the carbazolic structure is the overriding factor governing the poisoning potency. Another factor not considered here is that the high poisoning potency of carbazole

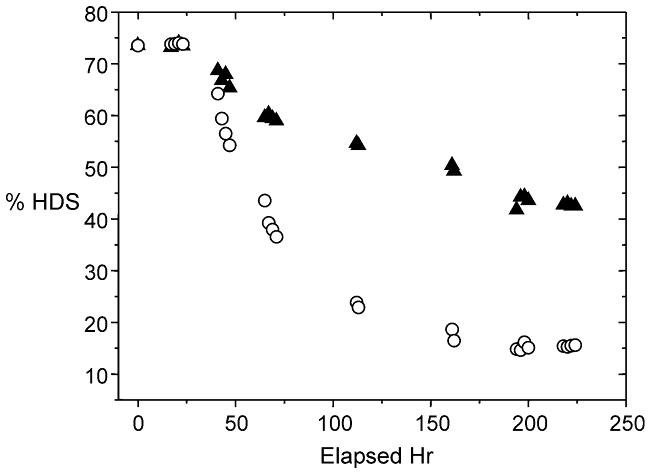

Fig. 13. Percentage 46DEDBT HDS vs elapsed hour. CBZ9ME as poison at 5 ppm (▲, feed H) and 20 wppm (○, feed I) N in feed; 1.83 MPa, 265 °C, 2.1 WHSV, 116 cc H_2/cc liquid feed.

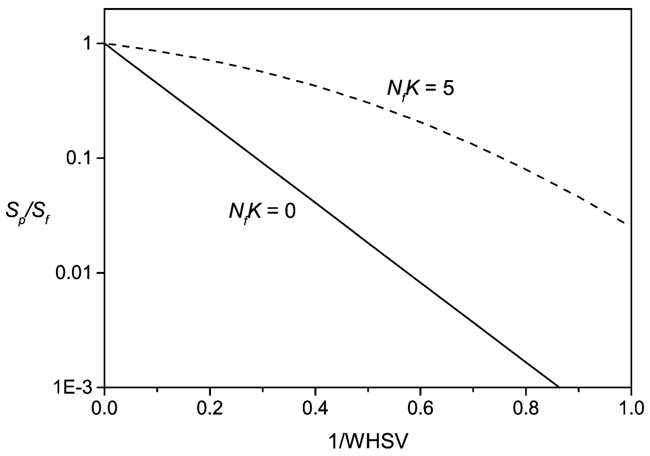

Fig. 14. Poisoning-falsified overall HDS kinetics, $\ln S_p/S_f$ vs 1/WHSV; $n = 1$, $k_{HDS} = 8.0$ l/h, and $k_{HDN} = 2.85$ l/h.

compounds may also have much to do with the formation of partially hydrogenated organonitrogen species which may be more poisonous than the parent molecule.

3.8. Poisoning-disguised HDS kinetics

Adsorption-disguised kinetics is a well-known phenomenon arising from strong adsorption of self-produced reaction intermediates. The purpose of this section is to show how catalyst poisoning by foreign species such as 3ECBZ and its hydrogenated derivatives can lead to falsification of the overall HDS kinetics.

The overall HDS kinetics for a single sulfur species in most cases is pseudo-first order [1–4, and this work]. The collective behavior of a large number of first-order reactions usually gives the appearance of a higher-than-first-order reaction [25]. Thus, the overall HDS kinetics for a petroleum feedstock can be viewed as the sum of a vast number of first-order reactions subject to competitive adsorption. It has long been observed in practice that the $\ln S_p$ vs space time curve is concave upward, implying a higher-than-first-order apparent kinetics. Typically, the overall order is between 1.5 and 2 for most middle distillates, the wider the rate constant spectrum, the higher the overall order. What goes on is that as space time increases, reactive sulfur species desulfurize rapidly and the mixture becomes progressively more refractory, thus giving rise to a higher overall order. The analysis to follow shows how poisoning may disguise the overall, apparent HDS kinetics.

Consider an isothermal, steady-state plug-flow reactor. Let S and N be the concentrations of total sulfur and nitrogen (both as atom) at any point in the reactor, respectively. Then $S = S_o + S_h$ and $N = N_o + N_h$. The subscript o signifies that the heteroatom (sulfur or nitrogen) in question is contained in a parent molecule (e.g., 46DEDBT or 3ECBZ), whereas the subscript h denotes the same heteroatom contained in the hydrogenated parent molecule (e.g., hydro-DEDBTs or hydro-3ECBZs). Since $S_h \ll S_o$, we can safely assume that $S \approx S_o$. Other simplifying assumptions are as follows: (A) The Langmuir–Hinshelwood model is applicable. (B) The feed nitrogen species (e.g., 3ECBZ) and all its hydrogenated derivatives have the same adsorption equilibrium constant K. (C) The adsorption equilibrium constants for sulfur species, homocyclic species (HDS and HDN products such as C4CHB), H_2S, and NH_3 are all much smaller than K. (D) The extent of HDN is low, so $N = N_o + N_h \approx N_f$, where N_f is the feed nitrogen concentration. Although some of the assumptions are untenable in certain situations, they give simple, closed-form results that reveal the essential point we wish to convey. Extension of the present model to more realistic situations is straightforward if done numerically.

Assuming an nth-order HDS rate (with k_{HDS} as apparent rate constant) in the absence of nitrogen poisoning, we write the mass balance equations for total sulfur and nitrogen as

$$\mathrm{WHSV}\frac{\mathrm{d}S}{\mathrm{d}\tau} = -\frac{k_{HDS}S^n}{1+KN}, \tag{2}$$

$$\mathrm{WHSV}\frac{\mathrm{d}N}{\mathrm{d}\tau} = -\frac{k'_{HDN}N}{1+KN}, \tag{3}$$

where τ is the dimensionless space time, with $\tau = 1$ corresponding to the reactor outlet. For nitrogen removal, by virtue of assumption D, we neglect the variation of $1 + KN$ along the reactor length, so Eq. (3) becomes

$$\mathrm{WHSV}\frac{\mathrm{d}N}{\mathrm{d}\tau} = -\frac{k'_{HDN}N}{1+KN} \approx -\frac{k'_{HDN}N}{1+KN_f} = -k_{HDN}N. \tag{4}$$

That is, the self-inhibition effect is lumped into the effective rate constant k_{HDN}. However, we do not invoke this assumption for Eq. (2) because sulfur removal is sensitive to even a small variation in N.

The boundary conditions are $\tau = 0$, $S = S_f$, and $N = N_f$. Integration of Eq. (4) gives $N = N_f \exp(-k_{HDN}\tau/\mathrm{WHSV})$ that can then be substituted into Eq. (2) to yield S analytically. For a single sulfur species, the HDS kinetics is generally pseudo-first-order $(n = 1)$. The results give a compact expression for S_p/S_f as follows:

$$n = 1, \quad \frac{S_p}{S_f} = \exp\left[-\frac{k_{HDS}}{WHSV}(1-f)\right], \tag{5}$$

$$n \neq 1, \quad \frac{S_p}{S_f} = \left[1 + \frac{(n-1)k_{HDS}(1-f)}{S_f^{1-n}WHSV}\right]^{1/(1-n)}, \tag{6}$$

where

$$f = \frac{WHSV}{k_{HDN}} \ln\left[\frac{1 + KN_f}{1 + KN_f \exp(-k_{HDN}/WHSV)}\right] \tag{7}$$

and N_fK may be called poisoning intensity. Hence, the net effect of a poison is to decrease the effective reactor length (or contact time) by a dimensionless factor f. That f depends on WHSV means that poisoning can falsify the apparent kinetics. Moreover, f is a function of k_{HDN} and N_fK. When either $N_fK \to 0$ or $k_{HDN} \to \infty$, $f \to 0$ as it should. As $k_{HDN} \to 0$, $f \to N_fK/(1 + N_fK)$.

One can do some thought experiments with the above model. In catalyst exploratory studies, one may rank experimental catalysts in HDS tests using a single sulfur compound (e.g., 46DEDBT). Let us consider the $n = 1$ case. Suppose that the activity test is done in the absence of a nitrogen poison ($N_fK = 0$), one then uses first-order kinetics to quantify the catalyst activity, as shown by the straight line in Fig. 14 where $\ln(S_p/S_f)$ is plotted against 1/WHSV for $k_{HDS} = 8.0$ l/h and $k_{HDN} = 2.85$ l/h. However, if one adds a nitrogen species to the feed so $N_fK = 5$, then the catalyst gives the appearance of a fractional or negative-order kinetics (dashed line in Fig. 14). That is, the HDS rate becomes progressively faster as nitrogen species get removed with increasing space time. Since the tolerance of different experimental catalysts for nitrogen poisons can vary widely (varying K for different catalysts), catalyst ranking must be done with care.

For a petroleum fraction, we set $n = 1.5$ with no loss of generality. So Eq. (6) gives

$$\frac{S_p}{S_f} = \frac{1}{[1 + \frac{k_{HDS}\sqrt{S_f}}{2WHSV}(1-f)]^2}. \tag{8}$$

Now consider a hypothetical cases where a catalyst is tested with a very high-quality feed so that N_fK is very small, say $N_fK = 0.5$. The behavior of the catalyst for all practical purposes can be described as 1.5 order kinetics, as shown as the solid curve in Fig. 15 for $S_f = 1.72$ wt%, $k_{HDS} = 19$ l/(h wt%$^{1/2}$), and $k_{HDN} = 2.85$ l/h. Suppose now that one switches to a different feed that has the same sulfur compound distribution and total sulfur concentration. The only difference is that the new feed has a higher $N_fK = 5$. As the dashed curve in Fig. 15 shows, the decay of S_p/S_f with this feed gives the appearance of a first-order reaction. As N_fK increases, the disparities among the sulfur species become smaller because the fast-reacting sulfur species are hurt more than the slow-reacting ones. As a result, the mixture appears more homogeneous, yielding an overall order close to unity.

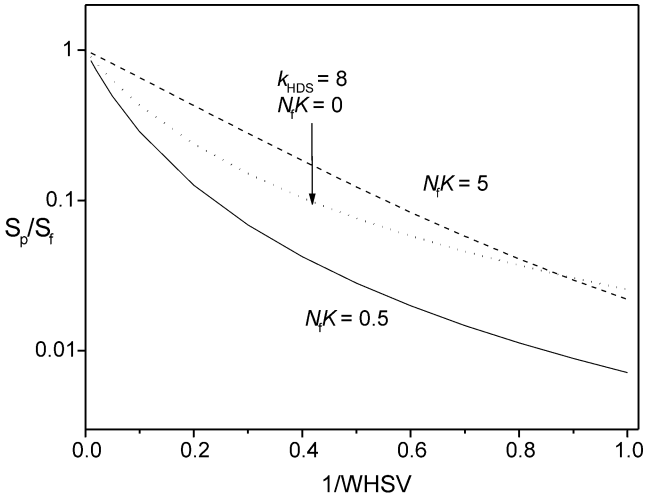

Fig. 15. Poisoning-falsified overall HDS kinetics, $\ln S_p/S_f$ vs 1/WHSV; $n = 1.5$, $S_f = 1.72$ wt%, $k_{HDS} = 19$ l/(h wt%$^{1/2}$), and $k_{HDN} = 2.85$ l/h.

Alternatively, one may view the above result as an example of separating out nitrogen species to boost HDS activity. The dashed curve ($N_fK = 5$) may be viewed as the HDS behavior of a high-nitrogen feed. Once the nitrogen compounds get removed (e.g., via adsorption) from the feed, one sees a rather different apparent kinetics (solid curve $N_fK = 0.5$) that gives a much higher sulfur reduction.

Now suppose that there is another catalyst that is less active, with $k_{HDS} = 8$ l/(h wt%$^{1/2}$). But it is so resistant to nitrogen poisoning that $N_fK \to 0$. The behavior of this nitrogen-resistant catalyst is shown as the dotted line in Fig. 15, giving the appearance of an activity crossover.

4. Concluding remarks

Despite their low basicity, carbazole species are strong poisons to the HDS of refractory sulfur compounds over commercial HDS catalysts. And the poisoning process may not be fully reversible. Changing the electron density around the nitrogen atom or in the aromatic ring has relatively little effect on the poisoning potency of carbazole species. For the same HDS level, a high-temperature operation can somewhat mitigate the poisoning effect. A strong inhibiting effect can disguise the overall apparent HDS kinetics. It is worthwhile to gain more insights into the poisoning process by developing a mathematical model that quantifies the interactions among sulfur compounds, carbazole poisons, and the catalyst surface. This should be a subject of future research.

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