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Catalysis Today 37 (1997) 267–275

CATALYSIS TODAY

Effect of nitrogen compounds on deactivation of hydrotreating catalysts by coke

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Abstract

A series of coked catalysts containing different levels of coke were prepared in a batch Autoclave by treatment of a sulfided CoMo catalyst with mixtures of vacuum gas oil (VGO) in mineral oil at 35 atm hydrogen and temperatures between 280°C and 370°C. A similar series of coked catalysts were prepared with acridine or carbazole added to the VGO mixture. After extraction with xylene and resulfiding, the coked catalysts were analyzed for C, N, pore volume and surface area, and tested for hydrogenation of naphthalene and carbon –nitrogen hydrogenolysis of indole. The presence of the nitrogen compound in the VGO mixture resulted in higher coke levels on the catalyst. All conversions decreased with coke content. However, for the same level of coke, the nitrogen-coked catalysts showed less deactivation as compared to the normal coked catalysts. This was attributed to strong adsorption of the nitrogen compounds on nonactive sites of the catalyst.

Keywords: Coking; Hydrotreating; Deactivation; Vacuum gas oil; Nitrogen compound

1. Introduction

Hydrotreating is one of the key processes in converting crude oil into valuable products. The aim of hydrotreating is to remove organic sulfur, oxygen, nitrogen, and metal-containing compounds from the feedstock. The catalyst life time is limited due to the deposition of coke and metals, which deactivate the catalyst. Coke is primarily responsible for the deactivation during the initial aging of the catalyst, while continued deactivation has been attributed to the deposition of metals [1,2].

Conventional research on catalyst coking basically focused on two areas. One is the characterization of the spent catalyst to determine the essential properties such as aromaticity of the coke, C/H ratio, absence or presence of heteroatoms, etc. Another is the study of correlation between coke and catalyst activity.

Coke is defined as the carbonaceous material deposited on the catalyst after extraction with a suitable solvent. The formation of these deposits on the hydrotreating catalysts has been attributed primarily to the presence of polynuclear aromatic compounds and asphaltenes [3,4]. There is general agreement that coke forms from condensation and dehydrogenation reactions involving the adsorbed species [5,6].

It has been suggested that adsorbed N-compounds act as coking precursors. In analyses of deactivation of hydrotreating catalysts, Furimsky [7,8] has noted a

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PII S0920-5861(97)00022-9

marked increase in C/N ratio in the coke deposits compared to the feedstock, suggesting preferential deposition of N-containing species. Choi et al. [9] have identified a series of quinolones and amides adsorbed on the catalyst surface. Satterfield et al. [10] observed that intermediates formed during HDN of quinoline leave some deposits on the catalyst surface. The formation of heavy species on the catalyst surface was also reported during HDN of indole and even aniline. Van Doorn et al. [11] found that conventional Soxhlet extraction did not remove quinoline completely. It was also noted by Speight [12] that organic nitrogen originally in the asphaltenes undergoes thermal reaction to remain in the nonvolatile coke. All of these observations support the concept that a substantial part of the deposits originates from N-containing species.

Zeuthen et al. [13,14] have reported two types of nitrogen on the catalyst in their TPO studies: a low-temperature form ascribed to adsorbed NH_x species, and a high-temperature form, attributed to strongly adsorbed organic-N species. They proposed that the high-temperature form of nitrogen consists of either strongly adsorbed organic-N species with a separate coke phase, or coke-N species, in which the coke covers the N-species. In either case, the nitrogen atom appears to be attached to the catalyst and is not in the coke itself. Recent work of Zeuthen et al. [15] showed that nitrogen adsorbs preferentially during the initial coke laydown.

The effect of N-compounds on coke formation and catalyst deactivation is not known. It is attributed to the strong adsorption of the N-compounds on the catalyst surface compared with other hydrocarbon structures present in the feed. With longer time on stream, the adsorbed species are converted to coke. Furimsky [8] suggested that the N-compound is initially adsorbed either by interaction of the nitrogen atom on Lewis sites via unpaired electrons on the nitrogen atom or by its ability to remove protons from the catalyst surface.

Muegge and Massoth [16], in their study of the comparison between hydrotreating catalyst deactivation by coking with vacuum gas oil (VGO) vs. anthracene (AN), found that hydrodenitrogenation was substantially lower for the VGO-coked catalysts compared to the AN-coked catalyst, which was partly attributed to nitrogen on the catalyst. It was also suggested that, in addition to deactivation by coke, nitrogen bound on the active sites from reaction with ammonia generated from reaction of the N-compounds present in the VGO could be the cause for the lower carbon–nitrogen hydrogenolysis (CNH) activities of the VGO-coked catalysts as compared to the AN-coked catalyst. Certain unreactive N-containing species in a given feed could cause excessive catalyst deactivation by selective poisoning of active sites. It was also found that the adsorption of N-containing compounds gave no significant loss in the HDS activity [4,16].

Thus far, work on direct comparison of the effects of the presence and absence of N-compounds on coke formation and catalyst deactivation have not been reported in the literature. Part of the reason is that there are various amounts and types of N-compounds in the feeds studied. The present research is an attempt to evaluate the presence of acridine and carbazole on coke formation by VGO and on deactivation of a $CoMo/Al_2O_3$ catalyst.

2. Experimental

The $CoMo/Al_2O_3$ catalyst (TK-550), containing 3.4% CoO and 14% MoO_3, was supplied by Haldor Topsøe A/S as 1/16 in. extrudates, which were crushed and sieved to 40–60 mesh size and calcined at 500°C overnight. Catalyst samples were sulfided at 400°C in a U-tube flow reactor at atmospheric pressure with 10% H_2S in H_2 for 2 h. After cooling in helium, the sulfided catalyst was rapidly transferred to a stainless steel basket and immediately immersed in mineral oil. The catalyst basket was placed into the spinning basket of an Autoclave reactor. About 320 ml of solution were charged to the reactor. The solution consisted of a mixture of VGO in mineral oil, to which 2–3 ml of CS_2 was added. In some runs, 3 wt% of acridine or carbazole was added to the solution. The VGO had the following properties: corrected boiling range 265–515°C; density (15°C) 0.924 g/ml; 2.86% S, 740 ppm N (200 ppm basic N), 0.1% Conradson Carbon, and 200 ppm asphaltenes.

Catalysts were coked for 8–24 h at temperatures between 280°C and 370°C, using various concentrations of VGO in order to obtain different amounts of coke. Coked catalysts were Soxhlet extracted with xylene, followed by an acetone wash, dried at 110°C, and subsequently resulfided at 400°C as before. The coked catalysts were analyzed for C and N by a commercial laboratory using a standard microcombustion technique. Surface area (BET) and pore volume data were obtained with a Micromeretics Analyzer. Coke density was determined from skeletal density measurements of the fresh sulfided catalyst (3.62 g/ml) and of coked catalyst D-6AC (3.11 g/ml), which gave a coke density of 1.6 g/ml according to the analysis presented by Espinat et al. [17].

Catalyst activity tests were carried out in a downflow, fixed-bed reactor under vapor-phase conditions at a hydrogen pressure of 35 atm. The reactor contained a preheating zone before the catalyst bed to vaporize the liquid feed. About 0.5 g of fresh or equivalent weight of fresh catalyst in aged catalyst (corrected for carbon content) was mixed with 5.5 g of 0.5 mm glass beads. The liquid feed was pumped into the top of the reactor, together with a flow of hydrogen. The model compound mixture used in the catalytic activity tests consisted of 2 wt% each of dibenzothiophene (DBT), naphthalene (NAP) for hydrogenation (HYD), and indole (IND) for CNH in *n*-heptane, containing 2–3 ml CS_2.

The catalyst was heated to 400°C in flowing helium and then sulfided in a 10% H_2S/H_2 stream for 2 h at atmospheric pressure. The reactor temperature was lowered to 350°C and the system pressure adjusted with hydrogen. The reaction solution was fed into the reactor at a flow rate of 10 ml/h with a hydrogen flow of 140 cc/min in order to age the catalyst. After 30 h on stream, liquid samples were taken and analyzed by gas chromatography. Major reaction products were: for DBT – biphenyl and cyclohexylbenzene; for NAP – tetralin; and for IND *ortho*-ethylaniline, ethylbenzene and ethylcyclohexane. In the latter case, a small amount of indolene was formed from a rapid equilibrium with indole [18], and was considered a reactant. Pseudo-first-order rate constants were calculated from conversions. For indole, the rate constant for CNH (of the first C–N bond rupture), was calculated from the disappearance of indole plus indoline. Relative activities (RAs) were calculated from the ratio of the rate constants of the coked catalysts to that of the fresh sulfided catalyst for each functionality. Due to the high conversions of DBT (>95%) at the test temperature, rate constants for HDS were not determined.

3. Results

3.1. Properties of coked catalysts

Table 1 presents carbon and nitrogen analyses of the coked catalysts. Some 2% C was obtained from the mineral oil itself. Generally higher carbon and nitrogen levels were observed with increasing temperature. Under comparable reaction conditions, the catalysts contained significantly more N when acridine (AC) or carbazole (CB) were present in the feed. Fig. 1 shows that at comparable conditions, higher coke levels were obtained when AC or CB was present. As shown in Fig. 2, the atomic N/C ratio on the aged catalysts decreased with increase in coke content, indicating that less N deposited than carbon as the coke level increased. This may be due to the higher temperatures used to achieve higher coke levels, whereby more of the nitrogen in the VGO may undergo HDN reaction. Thus, the presence of N-compounds appears to cause greater coking and greater retention of nitrogen under identical conditions.

Surface area and pore volume data for the coked catalysts are also given in Table 1. As expected, both properties decreased with increasing coke content. To assess pore plugging by coke, pore volume values were corrected for the weight and volume of coke present with the following equations:

$$W_c = 1.06\ (\%C/100), \tag{1}$$

$$V_c = W_c/1.6, \tag{2}$$

$$V^* = V^0(1 - W_c) - V_c, \tag{3}$$

where W_c and V_c are the weight (assuming $CH_{0.7}$) and volume of the coke, and V^* and V^0 are the corrected and sulfided catalyst pore volumes. A plot of pore volume vs. %C is shown in Fig. 3, where the upper line is the predicted value. It is seen that the experimental pore volume values are substantially below the predicted values, signifying some pore plugging. There appears to be no substantial difference between coked catalysts prepared with and without acridine or carbazole present, indicating that the higher N contents of the former have no effect on pore plugging.

Table 1
Preparation and properties of coked catalysts

Run[a]	Feed[b]	T (°C)	%C	%N	SA (m^2/g)	V_p (ml/g)
Fresh	—	—	—	—	203	0.591
J-5	1/3[c]	280	3.54	0.07	189	0.505
D-11	1/4	286	4.16	0.07	179	0.431
D-9	1/1	303	6.30	0.10	—	—
J-2	1/1	325	7.82	0.13	176	0.419
D-7	1/1	336	6.13	0.11	172	0.395
D-14	1/1	372	9.56	0.09	152	0.341
D-16AN	1/1	336	6.60	0.09	—	—
D-13AC	1/4	291	5.60	0.28	170	0.447
D-10AC	1/1	296	7.40	0.25	158	0.356
D-4AC	1/1[d]	336	10.20	0.35	—	—
D-8AC	1/1	336	8.19	0.27	160	0.406
D-6AC	1/1	372	11.82	0.34	135	0.298
J-9CB	1/1	327	8.38	0.26	163	0.349
D-17CB	1/1	336	7.02	0.32	—	—
J-4CB	1/1	353	10.38	0.30	173	0.376

[a] Runs marked with AC, CB or AN are with added acridine, carbazole or anthracene, respectively.
[b] Volume ratio of VGO to mineral oil; run duration 24 h, except where indicated otherwise.
[c] Run duration 8 h.
[d] Run duration 40 h.

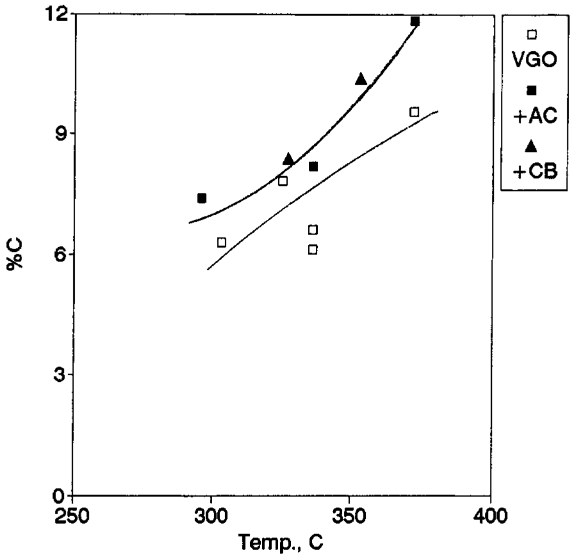

Fig. 1. Variation of %C deposition vs. temperature: Data for 1/1 VGO/mineral oil for 24 h reaction time.

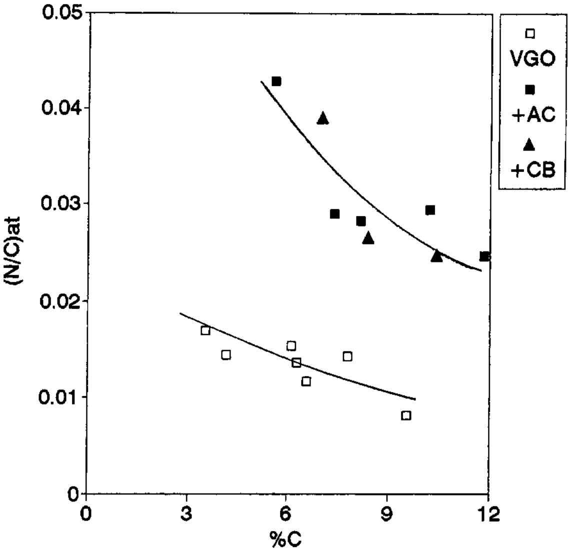

Fig. 2. (N/C) atomic ratio vs. total %C.

3.2. *Activities of VGO-coked catalysts*

Table 2 presents relative activity data for the various coked catalysts, while Figs. 4 and 5 present plots of relative activity of VGO-coked catalysts vs. %C for HYD and CNH, respectively. As expected, there is a regular decrease in activity with coke content in these plots. The HYD function is the less deactivated by coke than CNH. The general concave nature of these plots is typical for coke deactivation [16,19]. The data

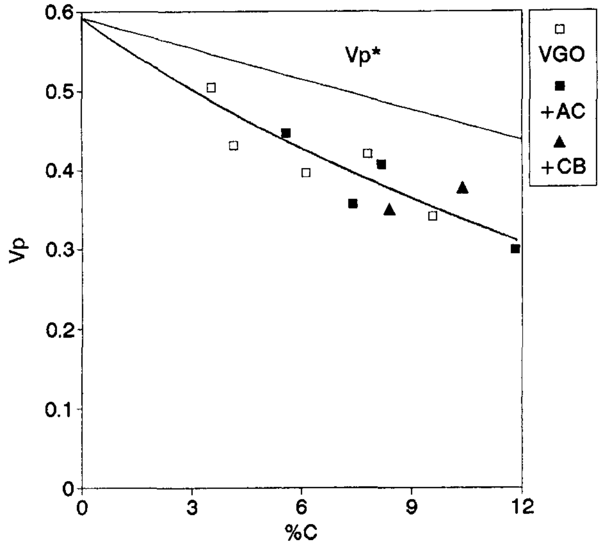

Fig. 3. Pore volume (V_p) vs. total %C. Solid curve is for the case of no pore plugging.

Table 2
Relative activities of coked catalysts

Run	%C	%N	RA	
			HYD	CNH
J-5	3.54	0.07	0.78	0.67
D-11	4.16	0.07	0.68	0.59
J-2	7.82	0.13	0.46	0.4
D-7	6.13	0.11	0.63	0.54
D-14	9.56	0.09	0.44	0.38
D-16AN	6.60	0.09	0.60	0.51
D-13AC	5.60	0.28	0.71	0.72
D-10AC	7.40	0.25	0.68	0.52
D-8AC	8.19	0.27	0.64	0.54
D-6AC	11.82	0.34	0.45	0.34
J-9CB	8.38	0.26	0.57	0.54
J-4CB	10.38	0.30	0.50	0.53

Table 3
Parameters for relative activity fits

	VGO		VGO+N-cpd	
	HYD	CNH	HYD	CNH
a	0.083	0.160	0.119	0.186
b	0	0	10.62	11.72
c	0.863	0.608	0.725	0.593

Eq: $RA^{*}=1-a(\%C-b\%N)^{c}$.

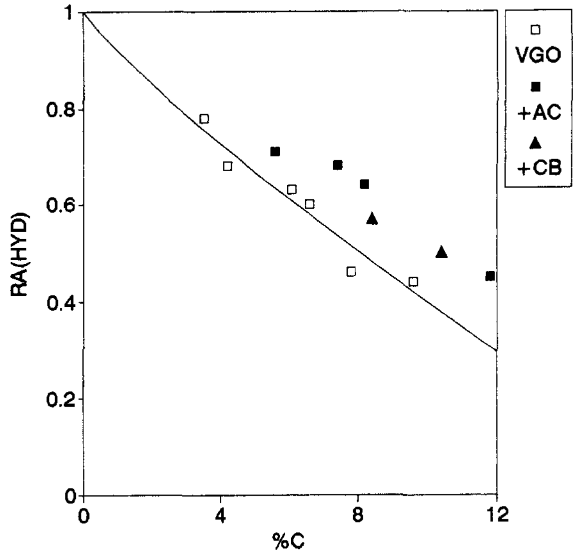

Fig. 4. Relative activity (RA) for HYD vs. %C.

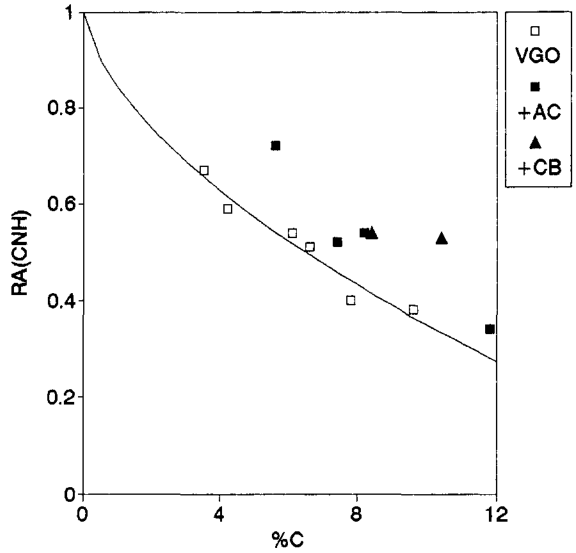

Fig. 5. Relative activiy (RA) for CNH vs. %C.

of Figs. 4 and 5 were fit to a power-law model [20] according to the equation

$$RA = 1 - a(\%C)^{c} \qquad (4)$$

with the values of *a* and *c* given in Table 3. The goodness of fit to the data is shown by the solid lines in Figs. 4 and 5.

3.3. Activities of VGO-coked catalysts in presence of N-compound

Figs. 4 and 5 show that relative activities are higher for these coked catalysts as compared to the VGO-coked catalysts at the same coke level. Surprisingly, for the same level of coke, the catalysts with added N-compound showed less deactivation than those without added N-compounds. This would appear to indicate that the presence of the extra N on the catalyst has promoted the activities. Such a phenomenon has not been reported in the literature and seems unreasonable in view of other findings that N-compounds in the feed depress catalytic activity [21].

An alternate explanation is that the N-compound did not adsorb on catalyst active sites, but rather on catalytically inactive adsorption sites. Thus, the added carbon due to the N-compound did not cause the expected additional deactivation. On this basis, a power law deactivation, corrected for the %C associated with the %N, was developed according to the following equation:

$$RA^* = 1 - a(\%C - b\%N)^c, \qquad (5)$$

where the term $b\%N$ represents the amount of %C not involved in deactivating the catalyst. The parameters a, b and c were determined by nonlinear least squares analysis using all the experimental RA data of Table 2. The parameter values are given in Table 3, and parity plots of RA^* vs. RA are shown in Figs. 6 and 7. The good correlations, demonstrate that Eq. (5) is a good representation for deactivation when both C and N are present on the catalyst.

4. Discussion

4.1. Effect of N-compound on catalyst properties

Under comparable preparation conditions, catalyst carbon contents were appreciably higher when acridine or carbazole was present in the VGO feed. Also, nitrogen contents were significantly higher (Fig. 2). Material balance calculations indicated that less than 1% of the added N-compound was deposited on the catalyst. The rest of the N-compound either remained intact or underwent HDN reaction to products. However, catalyst pore volume values depended only on the coke content, independent of the N content (Fig. 3). The relatively small loss in pore volume due to plugging of pores might have contributed to some additional catalyst deactivation at high coke level, but this was ignored.

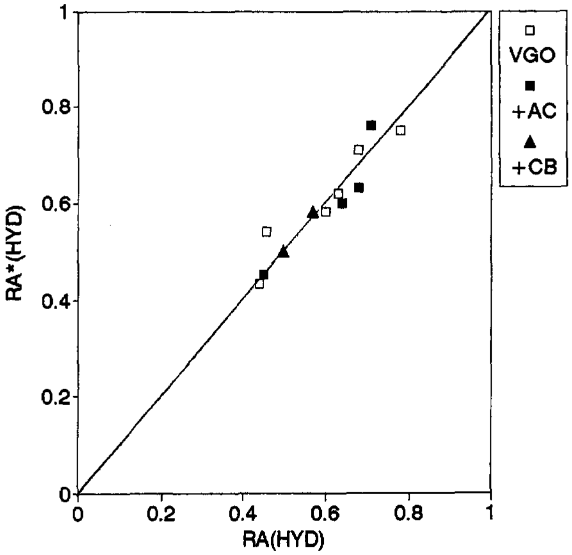

Fig. 6. Calculated relative activity (RA^*) vs. experimental relative activity (RA) for HYD with N-compound present.

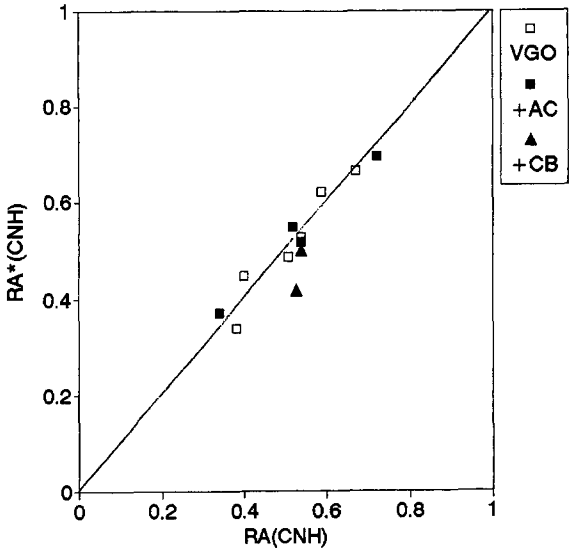

Fig. 7. Calculated relative activity (RA^*) vs. experimental relative activity (RA) for CNH with N-compound present.

In order to assess whether the increase in C and N content could be ascribed to adsorbed acridine, pairs of runs performed under comparable conditions with and without N-compound were analyzed by comparing increases in C and N with that expected for addition of acridine or carbazole. The following equations were used:

$$\%C = \%C_o + \mathrm{del}\%C^*, \tag{6}$$

$$\mathrm{del}\%C^*(AC) = 13 \times 12(\mathrm{del}\%N)/14, \tag{7}$$

$$\mathrm{del}\%C^*(CB) = 12 \times 12(\mathrm{del}\%N)/14, \tag{8}$$

$$\mathrm{del}\%N = \%N_o - \%N, \tag{9}$$

where del%C^* is the increase in %C expected based on the %N due to the adsorbed N-compound, and subscript o refers to data without the N-compound present. The results for each pair of runs are plotted in Fig. 8. As can be seen, the calculated data agree quite well with the experimental data, in line with the proposition of adsorbed N-compound. Thus, it appears that the increases in C and N obtained with the N-compound present can be ascribed to either N-compound being adsorbed intact, or to a polymer of the N-compound.

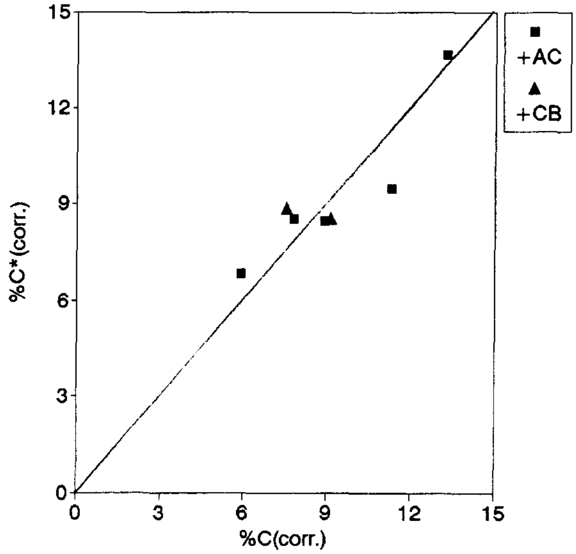

Fig. 8. Calculated %C^* vs. experimental %C. Values corrected to sulfide catalyst basis.

4.2. *Effect of N-compound addition on catalyst deactivation*

Surprisingly, for the same level of coke, the catalysts with added acridine or carbazole showed less deactivation based on total carbon content than those without the added N-compound (Figs. 4 and 5). On the basis that the coke deposit from the N-compound did not cover active sites, Eq. (5) was developed to account for this 'inert' coke. Using the parameter values of the VGO+N-compound sets of Table 3, three-dimensional plots of RA^* as a function of %C and %N were constructed for each functionality. The plots are shown in Fig. 9, where the increasing values of RA with %N at constant %C lines are evident.

The interesting aspect of the correlation of Eq. (5) is the values of parameter *b* of 10.6 for HYD and 11.7 for CNH (Table 3). These values are close within experimental error to the stoichiometric value expected for correction of %C due to %N in adsorbed N-compound, viz. $b(AC)=13\times12(\%N)/14=11.1$, and $b(CB)=12\times12(\%N)/144=10.3$. This result provides additional evidence for the proposition that acridine adsorbs on nonactive sites, i.e. the alumina support. Thus, the presence of the N-compound does not appear to affect coking from the VGO, that is, the two processes appear to be independent of each other.

5. Conclusions

1. Catalytic activities decreased monotonically with increase in coke derived from a VGO feed. CNH activity was slightly more deactivated than HYD activity.
2. Addition of acridine or carbazole to the VGO feed produced more carbon and nitrogen on the catalyst under comparable coking conditions. The added C and N deposits appeared to be due to adsorption of the N-compound intact, or as a polymer of the N-compound.
3. For the same level of coke, the coked catalysts treated with the N-compound showed less deactivation. This was attributed to deposition of the N-compound on inactive catalyst sites.
4. The evidence suggests that the deposition from the N-compound is independent of that from the VGO feed.

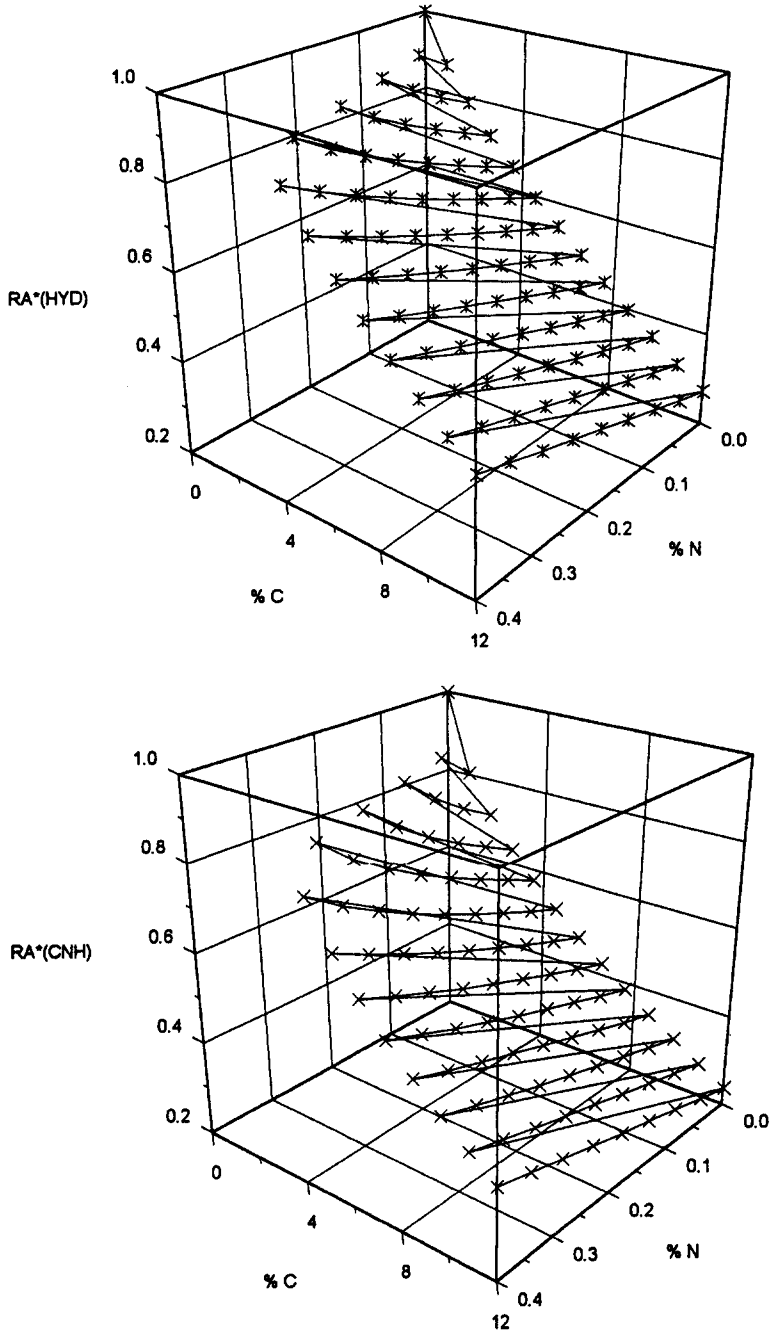

Fig. 9. Three-dimensional representation of relative activity for HYD (top) and for CNH (bottom) as a function of %C and %N. Lines connecting the points are for constant %C.

Acknowledgements

Support of this work by Haldor Topsøe A/C is greatly appreciated.

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