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Deactivation of fixed-bed nickel hydrogenation catalysts by sulfur

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A series of fixed-bed nickel hydrogenation catalysts was tested in the dearomatization of hydrocarbon solvents. The mechanism of catalyst deactivation by aromatic sulfur compounds was studied in high-pressure micro-flow equipment by variation of the experimental conditions and the sulfur content of the feed. It is concluded that catalyst deactivation proceeds under mild but realistic conditions through formation of a surface sulfide which blocks the active surface. The rate of the disappearance of the active sites is a first-order process with rate constant $1.0 \times 10^{-3} \text{ (ppm S)}^{-1} \text{ h}^{-1}$. Under more severe conditions, more sulfide layers are formed, but bulk Ni_3S_2 was not observed even after full deactivation of the catalysts. The poisoning of the active sites in the latter case is no longer a first-order process. Consequently, under the circumstances investigated, the sulfur resistance of nickel catalysts is determined by the nickel surface area per unit weight of catalyst.

(Keywords: nickel catalysts; sulfur poisoning; aromatics hydrogenation)

A range of fixed-bed nickel hydrogenation catalysts has been prepared, aimed at applications in petroleum processing such as aromatics saturation in hydrocarbon solvents and white oils or selective diolefin removal in pyrolysis gasoline. The alumina-supported catalysts are characterized by relatively low nickel contents compared with conventional products used in the above-mentioned processes (typically 15 versus ~50 wt% Ni). In many application areas the activity of these catalysts has proved relatively high despite their low nickel loading. This can be ascribed to the high metal dispersion combined with large pore diameter.

However, as well as initial activity of nickel catalysts, their lifetime must be taken into account. Metallic nickel catalysts are mainly used to process relatively clean, pretreated feedstocks. As a result, poisoning by asphaltenes, metals or fouling does not occur. Consequently, chemical poisoning by coke and sulfur are the most relevant deactivation mechanisms. Carbon deposited on the supported nickel catalysts is removed by air treatment at e.g. 350°C, but the sulfur remains and intense sintering of the nickel crystallites is observed. Similar results are obtained after high-temperature treatment of deactivated catalysts with hydrogen. The fact that sulfur cannot be removed by classical regeneration methods means that the catalyst activity is not restored (see below).

This paper describes a study of the deactivation of fixed-bed nickel catalysts by sulfur during the dearomatization

of a hydrocarbon 'solvent' feedstock. Solvents, typically boiling between 100 and 315°C, are used for the manufacture of e.g. paints, inks, cosmetics, pharmaceuticals and products for household use. For some of these applications the aromatics content must be extremely low. Since solvents may contain up to 25 wt% aromatics, it is necessary to perform a hydrogenation step, for which fixed-bed nickel catalysts are quite suitable. The feed always contains ppm levels of sulfur, which to a large extent determines the lifetime of the catalyst.

As a result, it is of paramount importance to elucidate the underlying deactivation mechanism under more or less realistic conditions. Deactivation by bulk Ni_3S_2 formation would suggest the highest poison resistance for the highest nickel-containing catalyst, whereas a surface sulfidation pathway requires optimization of the nickel surface area per unit weight of catalyst.

Phase diagrams^{1,2} show that 1 ppmv S [$\log_{10}(P_{\text{H}_2\text{S}}/P_{\text{H}_2}) = -6$] and 250°C ($1000/T = 1.91 \text{ K}^{-1}$) are circumstances on the borderline between conditions where Ni_3S_2 or Ni metal is the more favourable species. It is also clear from the diagrams that at lower temperatures and higher sulfur levels (realistic conditions for petroleum processing), the sulfide becomes increasingly likely.

However, McCarthy and Wise³, calculating the relative energies of various modes of interaction of sulfur with nickel, concluded that sulfur adsorbed on a nickel surface is energetically the most favourable situation (a sulfur saturation coverage of 0.6 was reported) and that $\frac{1}{2}\text{Ni}_3\text{S}_2$ is less favourable. Bartholomew and Katzer⁴, comparing the heat of adsorption of sulfur on various forms of nickel ($\Delta H_{\text{ad}} = -150 \text{ kJ mol}^{-1}$) with bulk sulfide formation ($\Delta H_{\text{f}} = -75 \text{ kJ mol}^{-1}$), reached a similar conclusion.

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If indeed the surface sulfide is preferred over a bulk sulfide under realistic process conditions, it is nevertheless possible that diffusion of sulfur into the bulk, or of the nickel through the surface sulfide layer, occurs⁵. The situation of a surface sulfide might then be stable under conditions where Ni⁰ is predicted by the Ni–S phase diagram and unstable when NiS_{1-x} is the more stable phase. However, the initially formed surface sulfide could also be preventing migration of S into the bulk even under the latter conditions, in much the same way as the oxygen layer(s) in air-passivated metal catalysts do^{6,7}. Indeed, Mangnus *et al.*⁸ found that during temperature-programmed sulfidation of fixed-bed nickel catalysts, the surface sulfide is formed first at low temperature and bulk sulfidation occurs by diffusion of Niⁿ⁺ or Sⁿ⁻ on heating the sample.

Under realistic methanation conditions, surface sulfidation of nickel catalysts is indeed reported^{9,10} up to a saturation coverage of ~0.5–0.6. In this case however, the nickel–sulfur phase diagram prescribes Ni⁰ and not Ni₃S₂ formation.

To establish the mechanism of deactivation of fixed-bed nickel catalysts by sulfur during solvent dearomatization, investigations were conducted with a micro-scale high-pressure flow reactor by variation of process conditions and by doping the feedstock with various levels of dibenzothiophene (DBT).

EXPERIMENTAL

The analyses of the fixed-bed nickel catalysts studied are given in Table 1. The catalysts were prepared by impregnation of a preshaped support according to ref. 11. The commercial reference catalyst used during the activity test was an extruded nickel-on-alumina catalyst (55 wt% Ni). Nickel contents of all catalysts and sulfur contents after deactivation were measured by X-ray fluorescence, texture analysis by nitrogen physisorption,

nickel surface area by hydrogen chemisorption, and degree of reduction by the sulfuric acid method as described previously^{12,13}.

A commercially available hydrocarbon solvent feedstock was used. The main characteristics of the feed and dearomatized product are given in Table 2, showing little change other than saturation of the aromatics upon hydrogenative treatment.

Catalyst deactivation by sulfur was studied with a micro-reactor under the conditions given in Table 3. At the reactor diameter of 12 mm the extrudates had to be crushed to a particle size of 0.5–1.5 mm and diluted with <175 µm SiC to ensure proper fluid dynamics. During the first 2 d of the experiments, pure feed was processed without sulfur dopant, to reach a steady state (see Table 2). After this period, solvent feedstock was passed over the catalyst doped with various quantities of dibenzothiophene (DBT) as a source of aromatic sulfur, thus simulating the S-containing components under realistic conditions.

The sulfur levels in feed and product were measured using a Dohrmann Xertex analyser. Aromatics contents were analysed by ultraviolet spectrometry (at 267 nm). The u.v. method was calibrated by making dilutions and comparing the values obtained with those of the FIA method (ASTM D1319). Boiling ranges of petroleum fractions were performed by the ASTM D86 method.

RESULTS AND DISCUSSION

Micro-reactor experiments at 150°C

In the micro-reactor experiments the initial catalytic activity of a low-nickel sample (code 757, 12.1 wt% Ni, 159 m² g⁻¹ Ni_{tot}) was compared with that of a high-nickel reference catalyst (55 wt% Ni). Figure 1 shows that at this scale the temperature advantage of using the prototype catalyst over the reference at 90% conversion is ~25 K.

Table 1 Analysis of fixed-bed nickel catalysts

Catalyst code	Nickel content (wt%)	Nickel surface area (m ² g ⁻¹ Ni)	Degree of reduction (at%)	Crystallite diameter (nm)	Average pore radius (nm)
890	7.2	193	82	1.8	7.7
757	12.1	159	85	2.3	7.7
PM32	13.1	188	87	2.0	7.9
902	18.3	136	91	2.9	–
903	21.6	134	91	2.9	–

Table 2 Main characteristics of solvent feed and dearomatized product

	Feed	Product
Density (kg m ⁻³)	780	770
Boiling point (°C): initial	157	159
50%	174	175
90%	185	188
End	193	193
Flash point (°C)	42	40
Sulfur content (mg kg ⁻¹)	1	1
Aromatics content (vol%)	24	0.5
Viscosity at 25°C (mPa s)	0.85	0.92
Bromine index	150	100

Table 3 Test conditions for solvent dearomatization

Experiment
1. Solvent feed (2 days)
2. Spiked feed (4–30 mg/kg S as dibenzothiophene)
Test conditions
Temperature (°C) 150 or 200
Pressure (MPa) 4
H ₂ /oil ratio (v/v at s.t.p.) 175
LHSV ^a (h ⁻¹) 4.5
Micro-flow reactor with 6 g crushed extrudates ^b

^a Based on catalyst volume only

^b Diluted with <175 µm SiC; total bed volume 10 cm³

Figure 1 Solvent dearomatization activity as a function of temperature: comparison between catalyst 757 (■) and a commercial reference catalyst (●)

Figure 2 (a) Catalyst activity as a function of time with ~30 ppmw S as DBT added in the feed. Catalyst: ■, 890; X, PM32; ◆, 902; ★, 903. (b) Sulfur absorption as a function of time; conditions and symbols as in (a)

In Figure 2a a typical activity curve after dosing the feed with ~30 ppmw of sulfur as DBT is given for various catalysts as a function of time. It can be concluded from this plot that the sample containing 7 wt% Ni shows the lowest sulfur resistance. Catalyst 903, containing 22 wt% nickel, is the most resistant.

The measured difference between the amount of sulfur in the feed and the product represents the sulfur taken up by the catalyst. The sulfur absorption obtained in this way is plotted against time in Figure 2b. When these curves are extrapolated to zero sulfur uptake, the saturation levels of the various catalysts are obtained. Because of the similarity of the shapes of the activity and absorption curves, it can be concluded that this point in time corresponds to zero catalytic activity (compare Figures 2a and 2b). Integration of the absorption curves results in the total sulfur uptake of the various catalysts. These numbers together with some analysis data are given in Table 4, which shows that catalysts have been tested with nickel contents of 7–22 wt% and active surface areas ranging from 134 to 193 m² g⁻¹ Ni_{tot}. When it is also considered that the extrapolation described above leaves room for interpretation and that it is assumed that the reduction performed in the test reactor results in the same nickel surface area as the reduction procedure carried out in the chemisorption apparatus (or results in a constant systematic error), it is striking that the sulfur uptake for all the catalysts tested is constant (within 10%), i.e. 17 μmol S m⁻² Ni. This is a very strong argument in favour of the surface sulfidation pathway, the more so since the calculated atomic S/Ni_{surf} ratio derived from the saturation coverage mentioned above is 0.6, a figure reported frequently in the literature (see the introduction). The ‘bulk’ Ni–S compound calculated for samples 757 and 890 is approximately Ni₃S_{0.55}, i.e. by no means a stable Ni₃S₂ or Ni₆S₅ (bulk sulfide) phase.

By plotting the dearomatization first-order rate constant $k_r = -\ln(1 - X)$, where X = conversion, as a function of the fractional coverage of the nickel surface area, the well-known curves characteristic of selective poisoning are obtained (Figure 3a). This is most probably due to the breaking-up of active ensembles by adsorbed sulfur. However, a similar plot, although with more scatter of points, could be made depicting k_r versus cumulative sulfur uptake per unit weight of nickel in the catalysts. Therefore, in itself this figure would not allow a firm conclusion on the predominant deactivation pathway.

As an extra indication of the proposed mechanism, however, the first-order rate constants obtained during various runs were plotted against the clean nickel surface

Table 4 Sulfur uptake of fixed-bed nickel catalysts

Catalyst code	Nickel content (wt%)	Nickel surface area (m ² g ⁻¹)	Specific nickel surface area (m ² Ni g ⁻¹ cat)	Adsorbed sulfur ^a (μmol S m ⁻² Ni)	Total sulfur uptake ^b (wt%)
903	21.6	134	29	16	1.5
902	18.3	136	25	17	1.5
757	12.1	159	20	18	1.4 ^c
890	7.2	193	14	17	0.7 ^c
PM32	13.1	188	25	18	1.4

^a 17 μmol S m⁻² Ni = 10¹⁹ S atoms/1.6 × 10¹⁹ Ni atoms; S/Ni = 0.63

^b At zero activity

^c ‘Bulk’ ratio Ni₃S_{0.55}

Figure 3 (a) First-order rate constant as a function of fraction of the active nickel surface area poisoned by sulfur; conditions and symbols as in Figure 2. (b) Rate constant as a function of the unpoisoned nickel surface area to the third power; symbols as in Figure 2

Table 5 Sulfur uptake by nickel catalysts under various experimental conditions

Temperature (°C)	Feed S content (mg kg ⁻¹)	Situation at full deactivation
150	~30	surface sulfide
200	4	surface sulfide
200	28	1.7 monolayer S ^a

^a 'bulk Ni₃S'

area (assuming that full coverage, $\theta = 1$, is reached at zero activity). The best linearization was obtained when the fraction of the uncovered nickel surface to the third power, $(1 - \theta)^3$, was taken (Figure 3b). This suggests that the active ensemble for the reaction consists of three metal atoms¹⁰. The fact that the activity is somehow inversely proportional to the sulfur coverage obviously does not contradict the surface sulfidation mechanism.

Experiments at 200°C

The experiments described above were all conducted at 150°C with ~30 ppmw S from DBT in the feed. When the temperature of the reaction was increased to 200°C and the sulfur level lowered to 4.2 ppmw, the same 17 μmol of sulfur adsorbed per m² of nickel at full deactivation was found as shown in Table 4. This is a strong indication that under these (even more realistic) conditions the nickel catalyst tested (code PM 32) is still surface-sulfided.

On increasing the sulfur level to 28 ppmw at the same temperature as in the previous experiment, ~1.7 times the $S_{\text{ads}}/Ni_{\text{surf}}$ ratio corresponding to monolayer coverage

is measured at full catalyst deactivation (Table 5). This indicates that a different mechanism operates than during the previously described runs. The Ni/S bulk ratio at zero catalytic activity is 3. Consequently, 'Ni₃S' should be inferred if bulk sulfidation is assumed. This again is not a stable phase such as Ni₃S₂ or Ni₆S₅. Instead it is proposed that about two NiS surface layers are formed (as is observed for NiO in air-passivated nickel catalysts¹²) or, less probably, multilayers of sulfur are formed at the surface on top of each other. Prolonged exposure of the catalysts to sulfur may cause bulk sulfidation, but if so, this must be a very slow process, as it was observed that after twice the time necessary to reach zero activity, still only 2.2 monolayer equivalents of sulfur were taken up by the catalyst, corresponding to a theoretical bulk ratio of 'Ni₃S_{1.2}'. This once more is not yet bulk Ni₃S₂ and at this point no further sulfur absorption or adsorption could be measured. The 3150 catalyst volumes passed over the bed would translate to 2.2 years on-stream at a realistic 5 ppmw feed sulfur and an LHSV of 1 h⁻¹. This slow bulk sulfidation rate is in agreement with a solid-diffusion limitation model as suggested in ref. 8.

Modelling of the deactivation rate

The model proposed by Fowler and Bartholomew¹⁴ results in the following expression for the deactivation rate of heterogeneous catalysts by sulfur:

$$\ln[(s_0/s) - 1] = k_d n_i t - (k_d n_i + k_d s_0)(x/V)$$

where

t = time (h)

n_i = inlet concentration of poison (ppmw)

s_0 = number of sites at t_0

s = number of sites at t

V = average velocity (m h⁻¹)

x = catalyst bed height (m); x/V = LHSV⁻¹ or GHSV⁻¹

k_d = deactivation rate constant (h⁻¹ ppmw⁻¹).

The assumptions made are: uniform axial plug flow; strong non-uniform poisoning; very low Thiele modulus or very small poison concentration.

When $\ln[(s_0/s) - 1]$ is plotted as a function of time, a straight line should be obtained with slope $k_d n_i$. This has been done for the experiments performed at 150°C, 3 MPa and ~30 ppmw S (Figure 4). Straight lines are indeed obtained, indicating that the rate of the disappearance of the catalytically active sites is proportional to the amount of unpoisoned sites left (i.e. a first-order relation). The average deactivation rate constant is $\sim 1.0 \times 10^{-3} \text{ h}^{-1} \text{ ppmw}^{-1}$. The results for catalyst PM 32 are problematic, yielding a k_d value of $0.5 \times 10^{-3} \text{ h}^{-1} \text{ ppmw}^{-1}$. This could be due to experimental error, on the basis of the results obtained at 200°C and 4 ppmw S (see immediately below).

When a similar plot is made on the basis of the results obtained at 200°C, 2 MPa and 4 ppmw S, Figure 5 is obtained. This is again a straight line and k has exactly the same value as mentioned above ($0.97 \times 10^{-3} \text{ h}^{-1} \text{ ppmw}^{-1}$), suggesting that the same deactivation mechanism is operating.

However, when the procedure is repeated for the experiment performed at 200°C, 2 MPa and 28 ppmw S, a first-order relation is no longer observed (Figure 6).

Figure 4 Sulfur deactivation rate of nickel catalysts versus time at 3 MPa, ~30 ppmw S and 150°C; symbols as in Figure 2

Figure 5 Deactivation rate versus time at 2 MPa, 4 ppmw S and 200°C for catalyst PM32

Figure 6 Deactivation rate versus time at 2 MPa, 28 ppmw S and 200°C for catalyst PM32

Initially the deactivation rate is similar to those depicted in Figure 4, but it decreases gradually after ~50 h on-stream. This is in agreement with the observation above that no longer is a monolayer of sulfur adsorbed on the surface under these conditions (see Table 5), i.e. both approaches suggest that a different mechanism occurs under these more severe conditions.

Scope of the results obtained

It could be argued that end-of-run conditions during solvent dearomatization can be more severe than those applied in this study (e.g. 300°C and up to 10 ppmw S),

probably favouring bulk nickel sulfide formation. Furthermore, exposure times of 1 year could perhaps overcome the diffusion barrier formed by the surface sulfide layer, again leading to bulk sulfidation. The answer to these doubts must be first that at least in the early stages of the catalyst's life (mild conditions) the surface sulfide mechanism is operating. However, even under extremely severe conditions it is still relevant, because of the following.

Researchers at Leuna-Werke¹⁵ analysed a deactivated supported nickel catalyst used in the hydrogenation of cresol (hydroxytoluene) under relatively severe conditions (2.4 t catalyst, 1.5 MPa, 140–170°C, WSHV = 0.1–0.125 h⁻¹, 300–500 ppmw S mainly as thiophenol). Clearly the high sulfur level and its reactive nature would promote bulk sulfidation of the nickel catalyst. The authors analysed several samples of the spent catalyst taken from various heights in the reactor. Only in the sample taken closest to the reactor inlet was more than one surface sulfide layer formed (but not quite bulk Ni₃S₂). The samples taken from the bottom of the downflow reactor has not 'seen' any sulfur at all. The same profiles were observed along the axis of the individual catalyst pellets at mid-reactor level. Surface sulfide formation can be inferred from the (not quite complete) analysis data given for the core of mid-reactor pellets and over the full diameter of particles taken from the downstream part of the reactor.

This suggests that even under inlet conditions clearly promoting bulk sulfidation, the sulfur-trapping action of the nickel at the reactor inlet and at catalyst pellet edges will result in sulfur levels in the feed causing the surface sulfidation mechanism to prevail downstream. Furthermore, the diffusion barrier formed by the surface and subsurface nickel sulfides hinders complete bulk sulfidation even at the reactor inlet.

CONCLUSIONS

A fixed-bed catalyst containing 12 wt% nickel showed high initial solvent dearomatization activity compared with a conventional 55 wt% Ni commercial catalyst in a micro-reactor.

Under mild but realistic reaction conditions, aromatic sulfur compounds deactivate nickel catalysts during solvent dearomatization by the formation of a surface sulfide, thus blocking the active surface. The rate of disappearance of the active sites is a first-order process with an average rate constant of $1.0 \times 10^{-3} \text{ ppmw}^{-1} \text{ h}^{-1}$. Saturation coverage corresponds to $S_{\text{ads}}/\text{Ni}_{\text{surf}} \approx 0.6$ or $17 \mu\text{mol S m}^{-2} \text{ Ni}$.

Under more severe conditions, more sulfide layers are formed, but still no bulk sulfide even after full deactivation of the catalyst. This suggests a solid-diffusion-limited process. The poisoning of the active sites is no longer a first-order process under these circumstances.

The predominant mechanism, bulk versus surface sulfidation, is determined by the sulfur content in the feed and the operating temperature (other factors such as the nature of the sulfur compound were not investigated). Even under bulk sulfidation conditions, the sulfur-trapping action of part of the reactor load creates circumstances downstream causing the surface sulfidation mechanism to be relevant.

The consequence of the surface sulfidation mechanism is that under the experimental conditions used, the sulfur resistance of the nickel catalysts is determined by the nickel surface area per unit weight of catalyst.

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