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Hydrodesulfurization

IV. The Effects of the Feed Components on Co–Mo–Al_2O_3 Catalyst Activation

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Benzothiophene dissolved in *n*-dodecane was used to investigate the hydrodesulfurization (HDS) activation procedure of Co–Mo–Al_2O_3 catalyst. Prereduced samples were submitted to various treatments prior to contacting with standard feed, namely, (a) by varying the sulfur compounds (H_2S or thiophene) in the *n*-dodecane–H_2 mixture, (b) by changing the molecule type which contacts the freshly prereduced catalyst (*n*-dodecane, H_2S, or thiophene), and (c) by sulfiding with H_2S–H_2 before, during, or after *n*-dodecane treatment. It is shown that presulfiding with H_2S gives better HDS activity than presulfiding with thiophene, owing to the coke precursor which may be formed in the hydrogenolysis of thiophene. *n*-Dodecane leads to some catalyst coking especially when sulfided species are absent on the catalytic surface or when they are reduced by the H_2 flow. Although presulfiding with H_2S enhances hydrocracking activity, catalyst poisoning by *n*-dodecane is not a problem, providing that enough sulfur species are still held on the catalyst, allowing good hydrogenation activity toward coke precursors. It appears that both H_2S and benzothiophene play a protecting role against catalyst poisoning, the former by forming quickly sulfided sites and the latter by preventing too great a desulfurization of the catalytic surface as well as by competing favorably with *n*-dodecane adsorption. For optimal activation care has to be taken to secure good hydrogenation activity, notably during the initial stages of feed supply. This points to better HDS activity under higher sulfiding pressure, especially when "sulfurized" feedstock is used.

INTRODUCTION

Hydrorefining of petroleum fractions on catalysts of Co–Mo–Al_2O_3 type is mainly performed for hydrodesulfurization (HDS) which involves hydrogenolysis of sulfur-containing compounds with formation of hydrocarbons and hydrogen sulfide. Hydrogenation of reactive olefinic bonds and of some aromatic compounds is carried out at the same time and partial hydrocracking can take place depending upon the operating conditions. Hydrocracking is a complex process of consecutive and parallel reactions which involve carbonium ion formation and transformation of *n*-paraffins into isoparaffins and lower paraffins.

HDS catalysts of Co–Mo–Al_2O_3 type have to be sulfided to provide optimum activity. Under industrial conditions the sulfiding is carried out either by means of an H_2S/H_2 mixture or by a feed containing an easily decomposable sulfur compound, e.g., CS_2 or CH_3SSCH_3. According to McKinley (*1*) presulfiding is not essential for conventional HDS catalysts, since the oxide form is converted into the sulfide form rather quickly during the reaction. In the same way Ternan and Whalley (*2*) reported that catalyst presulfiding using the hydrocarbon feedstock in a bottom-feed liquid-phase reactor is equivalent to presulfiding with CS_2 or H_2S. On the other hand, elsewhere it is not recommended that the sulfiding stage be avoided by direct treatment with the raw material containing a sulfur compound (*3*).

It is therefore apparent that there is no general agreement about the best activation procedure. Most studies dealing with the correlation between pretreating conditions and HDS activity were performed with thiophene–hydrogen mixtures without a hydrocarbon solvent (*4–8*). Only a few

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studies have been concerned with model systems in which sulfur compounds are dissolved in a hydrocarbon solvent. Thus Daly (*9*) reported HDS of benzothiophene (BT) dissolved in decalin using presulfided, prereduced, or unactivated Co–Mo–Al_2O_3 catalyst. Ripperger and Saum (*10*) showed the influence of reduction temperature on catalytic activity in HDS of thiophene–isooctane. Blidisel *et al.* (*11*) found that prereduced Ni–Mo–Al_2O_3 catalysts gave lower activity than presulfided or initially oxidic catalyst in HDS of thiophene–benzene mixture.

We have shown in Part III (*12*) that BT conversion at the steady state strongly depends on the nature of the catalyst pretreatment and that the differences could be ascribed to some poisoning during transient stage, subsequent at least partially to some interaction between a reduced form of the catalyst and the molecules of feed (*n*-dodecane).

To amplify these conclusions, we have undertaken a study of the effect of various pretreatments on a prereduced catalyst, involving each component of the reaction mixture, i.e., *n*-dodecane, BT, H_2S, and H_2, but excepting ethylbenzene which had no effect in the concentrations formed.

The whole activation of catalyst samples can be depicted as follows:

$$\begin{array}{l} \text{Prereduction in hydrogen flow} \\ \text{Pretreatment during 1 h} \\ \begin{array}{l}\text{Standard} \\ \text{feed supply}\end{array} \left\{\begin{array}{l}\text{transient stage} \\ \text{steady state}\end{array}\right. \end{array}$$

EXPERIMENTAL

A commercially manufactured Girdler Co–Mo–Al_2O_3-type G_{35} catalyst was used. It contained 3.1 wt% CoO, 11.7 wt% MoO_3, 1.7 wt% SiO_2 and its specific surface area was 311 $m^2\ g^{-1}$ ($\frac{3}{16} \times \frac{3}{16}$ in.). The apparatus and method employed for BT HDS activity measurements (continuous flow) were similar to those described earlier (*13*). The catalyst samples (2.00 ± 0.01 g) were prereduced *in situ* in a stream of H_2 with a flow rate of 0.07812 mole h^{-1}. Each sample was heated from room temperature to 400°C over about 3 h, maintained at this temperature for one additional hour, then cooled to 250°C over a period of 3 h, under the standard H_2 flow. One of the following types of pretreatment was then applied:

(i) sulfiding with H_2/H_2S (6 vol%) with (run 2) or without (run 1) simultaneous *n*-dodecane supply (0.03191 mole h^{-1} STP);

(ii) sulfiding with H_2/thiophene with (run 8) or without (run 7) simultaneous *n*-dodecane supply;

(iii) *n*-dodecane supply with the standard flow of H_2 before (run 3) or just after (run 4) sulfiding with H_2/H_2S.

Sulfiding with thiophene was effected by leading the standard flow of H_2 through a vessel containing thiophene located near the entry of the reactor: this corresponds to a thiophene content in the hydrogen gas of about 10% by volume at 20°C.

Each pretreatment was applied over a period of 1 h, except sulfiding with thiophene, which required 5 h to attain optimum catalyst sulfiding, as was verified by titrimetric analysis of the H_2S evolved.

The effect of each particular pretreatment was followed by measuring the benzothiophene (BT) conversion and H_2S evolution as a function of run time. The standard mixture used was 0.07812 mole H_2 h^{-1}, 0.03191 mole *n*-dodecane h^{-1}, and 0.0001218 mole BT h^{-1} (0.300 wt% sulfur). As the BT conversion levels achieved after prereduction on the one hand and presulfiding on the other hand appear more differentiated at 250 than at 350°C (*12*), the former lower temperature was selected for estimating most significantly the *n*-dodecane effect on the activation procedure. As initial activity for BT HDS is needed, catalysts have to be prereduced at higher temperature (400°C). For runs 5 and 6 it was possible to follow the sulfiding of the catalysts: for each 4-ml feed sample, the sulfur held by the catalyst sample was the mole balance between the ethylbenzene (EB) formed and the H_2S iodometrically titrated.

For overnight operation, where no successive liquid samples were collected, the sulfur uptake was estimated from the experimental curves (Fig. 1). Gas–liquid chromatographic analysis of the liquid samples collected revealed a weak hydrocracking of *n*-dodecane, especially in the first sample of each run: about 20 peaks connected with products lighter than *n*-dodecane and which we have not tried to identify appeared on the chromatogram. These reactions decreased with time on stream and became negligible at the steady state. On the contrary, when H_2S was supplied together with *n*-dodecane (run 2), the magnitude of hydrocracking products could be estimated to be about 1–2%. The same behavior was observed when H_2S was supplied together with the standard feed (Fig. 3).

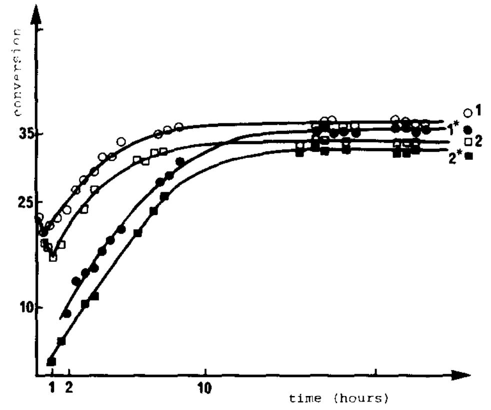


FIG. 1. Benzothiophene conversion versus run time, 1. without pretreatment (except hydrogen prereduction at 400°C) 2. after *n*-dodecane pretreatment. Curves with asterisks: molar ratio (%) between H_2S evolved into gas phase and BT supplied. Reaction conditions: 250°C, 2 g catalyst; standard feed: 0.03191 mole *n*-dodecane h^{-1}, 0.07812 mole hydrogen h^{-1}, and 0.0001218 mole BT h^{-1}.

RESULTS

EFFECT OF *n*-DODECANE, H_2S AND THIOPHENE PRETREATMENT

To check the extent to which interactions between the reduced catalyst and *n*-dodecane, H_2S, or thiophene gases affected initial and steady-state BT conversion, several pretreatments were performed, using each sulfur compound (H_2S or thiophene) either with *n*-dodecane or without, together with the standard flow of H_2. Data for these runs are shown in Table 1.

1. Pretreatment with H_2 + n-Dodecane (Run 6): Solvent Effect on Prereduced Catalyst

Applied for 1 h this pretreatment lowers BT conversion (3% absolute) from start-up and during the entire activation stage com-

TABLE 1

HDS ACTIVITY AS A FUNCTION OF PRETREATMENT

Run	Pretreatment[a] of Co–Mo–Al_2O_3 previously H_2 reduced at 400°C, 1 h	Percentage BT conversion at steady state[b]
1	H_2 + H_2S	75
2	H_2 + H_2S + *n*-dodecane	58
3	H_2 + *n*-dodecane, then H_2 + H_2S	50
4	H_2 + H_2S, then H_2 + *n*-dodecane	45
5	Without pretreatment	36
6	H_2 + *n*-dodecane	33
7	H_2 + thiophene	43
8	H_2 + thiophene + *n*-dodecane	28

[a] Conditions of pretreatment: 0.07812 mole H_2 h^{-1} STP (H_2/H_2S 6 vol%), 0.03191 mole *n*-dodecane h^{-1}, temperature 250°C, duration 1 h, except runs 3–4 (2 h) and 7–8 (5 h).

[b] Value observed for 10 h after BT conversion had reached a steady state.

pared to run 5, where standard feed contacts the prereduced catalyst directly (Fig. 1). After an initial decay of BT conversion, possibly due to irreversible BT adsorption at the beginning of the experiments [see Zdrazil (*17*)], a similar activity increase is observed while the catalyst is sulfided and H_2S is evolved into the gas phase progressively up to a steady level. The extent of catalyst sulfiding S/S_{max} (where S is the mole balance between the ethylbenzene formed and the H_2S evolved up to the steady state and S_{max} is the maximum sulfur (100%) for complete conversion to MoS_2 and Co_9S_8) after 20 h on stream was 12.9% for run 6 (33% BT conversion) and 14.4% for run 5 (36% BT conversion). This observation, viz., that the catalyst with the lowest sulfur content appears less active, has already been reported (*7, 8, 12*).

2. *Pretreatment with H_2 + n-Dodecane Followed by H_2 + H_2S (Run 3): Solvent Effect on a Prereduced Catalyst Prior to Sulfiding*

With (Fig. 2, curve 3, run 3) or without (curve 1, run 1) *n*-dodecane pretreatment, the same transient behavior is observed, as the catalyst initially releases an excess of H_2S in a decreasing way, while BT conversion increases from the first sample to a steady level in a few hours. However, the steady HDS level is much lower after solvent treatment, being 50% and 75%, respectively.

3. *Pretreatment with H_2 + H_2S Followed by H_2 + n-Dodecane (Run 4): Solvent Effect on Presulfided Catalyst*

When applied to a presulfided catalyst which gives otherwise the best HDS activity (run 1), *n*-dodecane treatment led surprisingly to a BT conversion of only 45% (Fig. 2, curve 4, run 4). The same result was achieved in a second identical run. It is interesting to note that if the feed *n*-dodecane + H_2 holds BT molecules when it is delivered immediately after H_2–H_2S pretreatment, the best activity level is achieved.

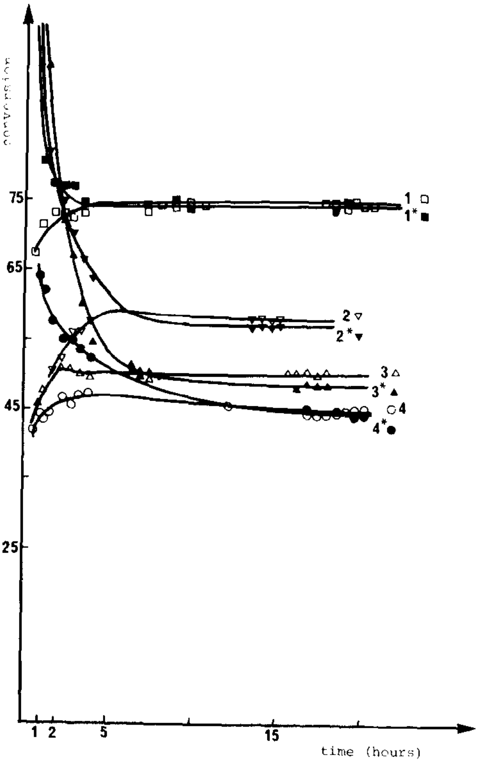


FIG. 2. Benzothiophene conversion versus run time after different pretreatments: 1. H_2 + H_2S, 2. H_2 + H_2S + *n*-dodecane, 3. H_2 + *n*-dodecane followed by H_2 + H_2S, 4. H_2 + H_2S followed by H_2 + *n*-dodecane. Curves with asterisks: molar ratio (%) between H_2S evolved into gas phase and BT supplied.

4. *Pretreatment with H_2 + H_2S + n-Dodecane (Run 2): Solvent Effect during Catalyst Sulfiding*

Appreciable hydrocracking was observed (see Experimental) by glc for the two liquid samples collected during this pretreatment. The amount of *n*-dodecane so "hydrocracked" can be roughly estimated to be no more than 1–2%, not taking into account the quantity not evolved into the gas phase and thus adsorbed on the catalyst presumably as coke. The level of the GC peaks then decreases markedly (one order of magnitude) until the BT conversion steady state is achieved.

5. *Pretreatment with H_2 + Thiophene (Run 7)*

Sulfiding with H_2 + thiophene is slow, since about 5 h was necessary to acheive a steady release of H_2S at the reactor exit. This is in accordance with the results of De Beer *et al.* (*6*), who reported that optimum sulfiding with H_2 + thiophene took longer overall than with H_2 + H_2S. Subsequent standard feed supply leads to increased BT conversion which leveled rapidly at 43%. This value was retained during more than 15 h on stream.

6. *Pretreatment with H_2 + thiophene + n-Dodecane (Run 8)*

Simultaneous supply of *n*-dodecane during 5 h to the H_2 + thiophene stream gives rise to the lowest HDS activity (28% BT conversion).

EFFECT OF H_2S ON BT CONVERSION AT STEADY STATE

To check the effect of H_2S on a catalyst which has reached a steady state of activity, a run was performed over a catalyst which was pretreated according to the procedure of run 3 and which already showed 50% BT conversion after 45 h on stream. This long time on steady level demonstrates that catalyst fouling is a slow process and may be negligible after line-out. H_2S, at about 6 vol% in H_2, was led into the *n*-dodecane–BT stream for 1 h, giving rise to appreciable hydrocracking of *n*-dodecane. An extensive drop of BT conversion is observed (Fig. 3), showing that H_2S competes successfully with BT adsorption. However, when the H_2S supply is turned off, HDS activity is rapidly and fully restored. This demonstrates that H_2S inhibits reversibly the HDS rate while enhancing the hydrocracking of *n*-alkanes. It must be emphasized that no apparent poisoning effect accompanies this hydrocracking.

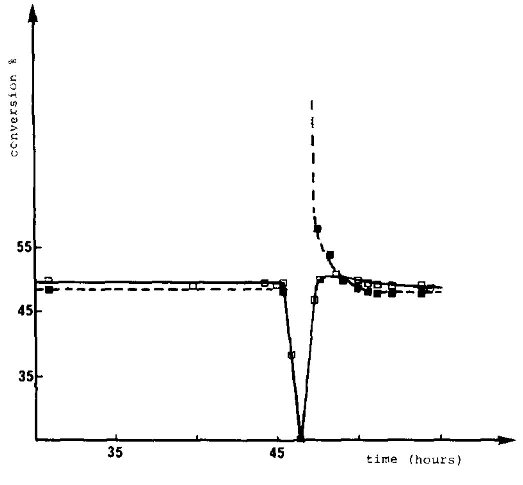


FIG. 3. Effect of an additional H_2S supply on benzothiophene conversion (open symbols). Broken line: molar ratio (%) between H_2S evolved into gas phase and BT supplied (filled symbols).

EFFECT OF AN INTERRUPTION OF FEED SUPPLY ON THE STEADY LEVEL OF BT CONVERSION

This run was performed over a catalyst presulfided with H_2 + H_2S, giving 75% conversion (run 1). The feed supply was turned off after 7 h on stream, leaving only the standard flow of H_2 passing over the catalyst during about 12 h. Upon readmitting *n*-dodecane + BT, it appears (Fig. 4) that the catalyst has been reduced by the H_2 flow, as some part of the sulfur that issued from the BT hydrogenolysis was used in catalyst resulfiding: the amount of H_2S evolved during about 5 h is found to be effectively below the quantity formed by the BT hydrogenolysis. It is interesting to note that BT conversion increases with catalyst resulfiding, but the level never completely reaches the previous steady state. This demonstrates that the catalyst which has been reduced (desulfided) through the H_2 flow gives rise to irreversible poisoning.

DISCUSSION

The experiments reported above were performed to study the effect of H_2S, *n*-dodecane, and thiophene on the activation of prereduced Co–Mo–Al_2O_3 catalysts for the HDS of benzothiophere.

As can be seen, the best activation proce-

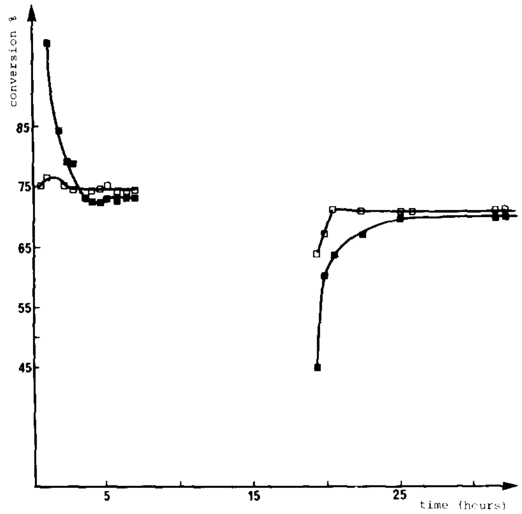


FIG. 4. Effect of cutting off the feed supply for 12 h on catalyst HDS activity. Open symbols: BT conversion. Filled symbols: molar ratio (%) between H_2S evolved into gas phase and BT supplied. Reaction conditions as in Fig. 1.

dure involves presulfiding with H_2–H_2S mixture (run 1). The hydrocarbon solvent, *n*-dodecane, shows a rather harmful effect during this activtion (run 2), an effect which is even more marked when *n*-dodecane treatment is carried out before or after the catalyst presulfiding (runs 3 and 4). As a rule, better HDS activities are achieved on a presulfided (runs 1 to 4) than on a prereduced catalyst (runs 5 and 6).

Discrepancies between initial BT conversions observed after the various pretreatments as well as those achieved at steady state can at least be partly explained in terms of catalyst poisoning by harmful reactions developed between some reduced catalytic species and *n*-dodecane (*12*). Considering the catalysts which are in a reduced state just when standard feed is supplied, it is shown (Fig. 1, runs 5 and 6) that HDS activity increases at the same rate with or without *n*-dodecane pretreatment. The same discrepancy along the transient period means obviously that it is during the initial *n*-dodecane treatment that some potential HDS sites have been poisoned. The lower sulfur uptake after line-out, viz., S/S_{max} = 12.9% and S/S_{max} = 14.4%, respectively, is also relevant in this regard. This poisoning effect during the *n*-dodecane pretreatment (run 6) may result from dehydrogenation of *n*-dodecane over reduced Mo species (*20*) and subsequent hydrocracking at a rate too rapid for the hydrogenation component of the catalyst to saturate the activated species effectively; this will therefore lead to carbonaceous deposits on some potential HDS sites. It is clear that this harmful effect can be operative during the entire activation period (10 h) where sulfur is added to the catalyst from BT–HDS. This is consistent with literature data which report either initially high coke deposition when hot hydrogen contacts the fresh catalyst (*14, 21, 24*) or carbonaceous residue formation over catalyst with low sulfur content (*15*). Relevant to this behavior is also the experiment depicted in Fig. 4, where catalyst deactivation is achieved on a surface which has been depleted from some sulfur by the standard flow of hydrogen.

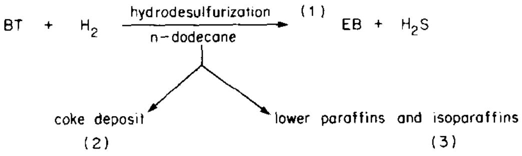
On the other hand, H_2S-presulfided catalysts always give better HDS activities, but it should be noted that these activities are markedly conditioned by the procedure used. Presulfiding with H_2S and simultaneous *n*-dodecane supply (run 2) leads to lower activity than with H_2S + H_2 alone, obviously because *n*-dodecane initially contacts a catalyst which is mainly in a reduced state, which allows some poisoning as shown previously.

In fact our results demonstrate that presulfided catalysts are more resistant toward poisoning for HDS activity, although it is generally observed that hydrocracking reactions are enhanced just when a large excess of H_2S gas contacts the catalyst together with solvent molecules. It is indeed well known (*16*) that excess (nonstoichiometric) sulfur influences the acidic properties of the surface (due to a large proton concentration on S) and increases acidic hydrocracking (*22*). Keeping in mind that the H content of sulfided catalyst is appreciably higher than for a comparable reduced catalyst (*23*) it seems reasonable to consider that hydrogenation rates are fast enough to prevent any coke formation. This is supported by the experiment of Fig. 3, where the H_2S supply together with the standard feed does not lead to any drop of HDS activity after cutting off the H_2S flow and leveling.

Considering runs 1 and 4, it appears that the absence of BT molecules in the feed, which contact the presulfided catalyst at the very first stage, allows considerable deactivation, as only 42% BT conversion is observed in the product sample (compared to 67% for run 1, Fig. 2). Subsequent increase of HDS activities is obviously connected with H_2S removal from the surface and formation of sites active in BT HDS. It is thus expected that fast desorption of excess H_2S allows fast increase of HDS activity, a behavior also depicted in Fig. 3. Run 4 clearly shows the slowest BT conversion on start-up (Fig. 2), probably because the greatest part of H_2S was already evolved during the foregoing H_2 + *n*-dodecane treatment. This implies that a catalyst, although it has been thoroughly presulfided, can be deactivated when it is submitted to reduction by the hydrogen flow (see also Fig. 4). The presence of *n*-dodecane during this S removal favors harmful effects, especially in the absence of BT molecules which can no longer compete successfully for adsorption of the solvent molecules (*17*). Subsequent standard feed supply emphasizes this solvent effect on a catalyst rather depleted in sulfur (see Fig. 2, curve 4*), as the transient stage (curve 4) now shows the lowest increase in HDS activity up to the steady state. On the contrary, when standard feed contacts a freshly H_2S-sulfided catalyst (run 3), which was already previously poisoned by *n*-dodecane, BT conversion increases more rapidly despite a high H_2S concentration (Fig. 2, curve 3*). As a result, H_2S as well as BT molecules play a protective role against catalyst poisoning, the former by forming sulfided sites rather quickly and the latter by preventing too great a desulfiding of the catalytic surface as well as by competing favorably with solvent adsorption.

In addition, the rate at which catalyst is sulfided seems to influence markedly the activation procedure: thus in our experimental conditions sulfiding by H_2S in the presence of *n*-dodecane during 1 h (run 2) gives 58% conversion, compared to 33% by the BT feed. This is consistent with the finding of Laine *et al.* (*25*), who recently verified that HDS activity of an Ni–Mo–Al_2O_3 catalyst is increased by adding, for instance, H_2S to thiophene during the activation procedure.

The following scheme summarizes the main features observed:



Process (1) is favored on sulfided catalysts.

Process (2) poisons potential HDS active sites, especially on H_2-prereduced catalysts.

Process (3) is important on freshly reduced catalysts (accompanied by coke deposit) and also on sulfided catalysts, especially in H_2S atmosphere (but not accompanied by coke deposit).

Presulfiding with H_2 + thiophere is slow and gives a lower HDS activity (43%) than with H_2 + H_2S (75%), a result in agreement with the findings of De Beer *et al.* (*6*). The fivefold sulfiding time obviously allows higher catalyst deactivation by the thiophene hydrocarbon skeleton: thus primary products in thiophene hydrogenolysis would be either butadiene (*18*) or diacetylenic species (*19*), i.e., coke precursors which would be likely to poison the active surface, especially under the low H_2 partial pressure used. As expected, presulfiding with H_2 + thiophene and a simultaneous supply of n-dodecane gives rise to the poorest HDS activity combining the harmful effects of a hydrocarbon solvent and a carbonaceous sulfiding agent during catalyst activation.

Thus HDS catalyst activation is a function of several parameters, namely, the nature of the presulfiding agent, the rate of presulfiding, and the presence of hydrocarbon feedstock. Presulfiding with $H_2 + H_2S$ appears to be the best activation procedure, provided that the catalyst sulfur uptake is adequate at the point when the sulfurized feed is supplied.

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