# Hydrodesulfurization

## III. Relation between Pretreating Conditions and Hydrodesulfurization Activity of Co–Mo–Al$_2$O$_3$ Catalyst

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Hydrodesulfurization (HDS) experiments were carried out over a commercial Co–Mo–Al$_2$O$_3$ catalyst in a continuous-flow reactor at atmospheric pressure and temperatures of 250 and 350°C. The reactants were hydrogen and benzothiophene (BT) dissolved in *n*-dodecane. The effects of pretreating conditions on catalytic activity were investigated by following BT conversion as a function of run time. It was shown that stationary activities differed notably with pretreatment conditions and temperature. Contrary to the results at 400°C, prereduction at 250°C was inadequate to promote rapid HDS activity. Presulfiding at 250°C (following prereduction or not) led to formation of a highly active catalyst. Presulfiding at 350°C or processing at 350°C gave lesser activities than in the same pretreating conditions at 250°C. The results are explained in terms of the poisoning phenomena of active sites by hydrocarbon molecules and the role of catalyst presulfiding, which at the same time causes an increase of HDS activity as well as a protecting effect against poisoning, is discussed.

## INTRODUCTION

Having assessed in Part II (*1*) the importance of the nature of the catalytic surface during the activation procedure, especially with respect to the reaction network, benzothiophene (BT) hydrodesulfurization (HDS) was further investigated on a commercial Co–Mo–Al$_2$O$_3$ catalyst, the aim being to examine catalyst pretreatment effects on BT hydrogenolysis with respect to H$_2$S and hydrocarbon compound formation during the initial stages of catalyst activation. In commercial applications Co–Mo–Al$_2$O$_3$ catalysts are usually presulfided with hydrogen sulfide/hydrogen or another sulfiding agent. In the absence of presulfiding, HDS catalysts normally become sulfided by the sulfur compounds contained in the feedstock. Presulfiding

produces higher HDS activity, but the reason is not entirely clear (*2, 3*).

Recent works have tried to elucidate the nature of the Co and Mo species in oxidic catalyst or formed during reduction and sulfiding [see references in the review of Massoth (*4*) and the more recent papers on spectroscopic measurements, e.g., X-ray photoelectron spectroscopy (ESCA) (*5–8*), infrared (*9*), electron spin resonance (ESR) (*10*), laser Raman (*11*), and Mössbauer spectroscopy (*12*)]. Only a few works have attempted to draw some correlation between state of pretreated catalyst and HDS activity (*13–16*). De Beer *et al.* (*17*) followed thiophene HDS at atmospheric pressure, at 400°C and under different sulfiding conditions. Blidisel *et al.* (*18*) studied the hydrogenolysis of thiophene dissolved in benzene at 20 atm pressure, at 300°C, over an oxidic, prereduced or presulfided Ni–Mo–Al$_2$O$_3$ catalyst. With respect to BT,

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Kilanowski *et al.* (*19*) carried out HDS experiments with reactant solutions prepared with a 50-wt% *n*-heptane in *n*-dodecane, over a sulfided Co–Mo–$Al_2O_3$ catalyst in a pulse microreactor at atmospheric pressure and temperatures of 350 to 450°C. On the other hand Daly performed BT HDS study at 1250 psig, with a stirred-batch minireactor at 250°C, over presulfided, prereduced, and unactivated Co–Mo–$Al_2O_3$ catalysts (*20*).

The present work deals with HDS of BT *n*-dodecane mixture at atmospheric pressure in a continuous-flow reactor at 250 and 350°C. The effects of (pre)treatment (reduction or sulfiding) were followed by measurements of BT hydrogenolysis as a function of run time. The rate of attainment and the level of the steady states were used to demonstrate the significant effects of reduction, sulfidation, temperature, and paraffinic solvent on the activation of a Co–Mo–$Al_2O_3$-type catalyst.

### EXPERIMENTAL

For this investigation the commercially manufactured catalyst Girdler CoO–$MoO_3$–$Al_2O_3$ type G 35 was used. According to the manufacturer, the catalyst has a specific surface area of 311 $m^2g^{-1}$ ($\frac{1}{16} \times \frac{3}{16}$ in.) and contained 3.1 wt% CoO, 11.7 wt% $MoO_3$, and 1.7 wt% $SiO_2$. The atomic ratio Co/(Co + Mo) was 0.37.

The fixed-bed-type reactor was similar to that described in Part 1 (*21*). Benzothiophene was dissolved in *n*-dodecane (0.3 wt% sulfur) and its hydrogenolysis was followed under continuous flow, i.e., 0.03191 mole *n*-dodecane $h^{-1}$ + 0.0001218 mole BT $h^{-1}$ and 0.07812 mole hydrogen $h^{-1}$ at STP.

Liquid reaction products (4 ml sample) were collected periodically and analyzed chromatographically using pseudocumene as an internal standard. The glc apparatus was supplied by Intersmat, Model IGC 12, equipped with a thermal conductivity detector. The columns (2 m length and 0.125 in. diam.) were 10% Apiezon L on 80 to 100-mesh HMDS-treated chromosorb W. The injector, column, and detector were, respectively, held at 300, 140, and 250°C and the hydrogen carrier gas had an inlet pressure of 1.5 kg/$cm^2$. The $H_2S$ content of the noncondensable gas was analyzed by absorption in KOH solution followed by iodometric titration.

The catalyst samples (2 g) were pretreated *in situ* prior to contacting the vaporized charge of *n*-dodecane–BT at 250 or 350°C. Oxidized, prereduced, or presulfided catalysts were tested:

(i) In the oxidized case, the catalyst samples were simply heated *in situ* for about 3 h to the desired reaction temperature (250 or 350°C).

(ii) In the prereduced case, reduction was carried out in the standard $H_2$ flow (0.07812 mole $h^{-1}$ at STP). The temperature was increased over about 3 h from room temperature to the reduction temperature (250 or 400°C). The reduction conditions were either 1 and 10 h at 250°C or 1 h at 400°C, after which the reactor was cooled to reaction temperature in the same flow of $H_2$.

(iii) In the presulfided case, sulfidation was performed at atmospheric pressure with a mixture of 6 vol% $H_2S$ in the standard flow of $H_2$ and applied for 1 h on catalyst samples which had been pretreated according to procedure (i) at 250 and at 350°C or procedure (ii) (reduction at 400°C, then sulfidation at 250°C).

The reaction products were ethylbenzene (EB) and $H_2S$. Styrene was not detected as it was in Part II (*1*). BT conversion was calculated from the amount of EB produced and the amount of unconverted BT. Since the former value corresponds fairly well to the BT reacted, it was possible to follow catalyst sulfiding, taking into account the $H_2S$ evolved in the gas phase. Thus for each 4-ml feed sample (containing 2.82 × $10^{-4}$ mole BT), the sulfur held by the catalyst was the mole balance between EB formed and $H_2S$ iodometrically titrated. In lapses of time where no successive samples were
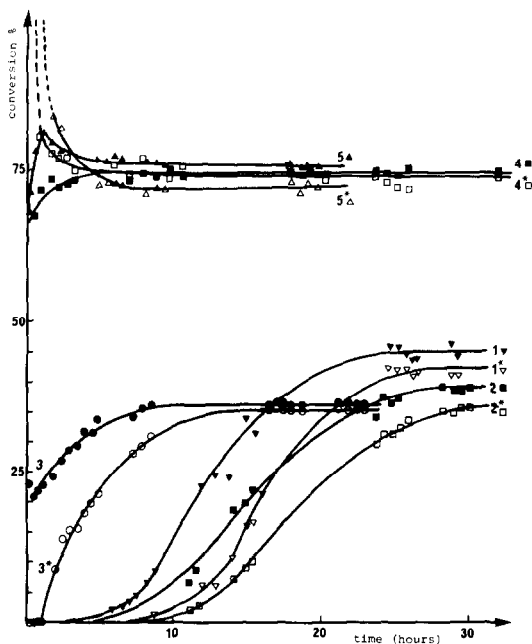
FIG. 1. Conversion of benzothiophene as a function of run time, at 250°C. Conditions of pretreatment: 1. initially oxidic, 2. prereduced 10 h at 250°C, 3. prereduced 1 h at 400°C, 4. prereduced at 400°C, then presulfided at 250°C, 5. presulfided at 250°C. Curves with asterisks: molar ratio (%) between $H_2S$ evolved into gas phase and BT supplied.

collected (overnight), these values were estimated from experimental data.

### RESULTS

The variations in BT conversion as a function of run time at 250 and 350°C are depicted in Figs. 1 and 2, respectively. Catalyst samples which were in the original oxidized state or which had been prereduced in hydrogen or presulfided in $H_2S$–$H_2$ were subsequently exposed to an $n$-dodecane–BT–$H_2$ stream. It is shown that in most cases a steady state of BT conversion is achieved usually before 30 h on stream. Thus for tests performed at 350°C as well for runs 3, 4, or 5 at 250°C, the curve corresponding to BT conversion became confused within the experimental error with the curve showing the level of $H_2S$ release. This attests that each BT-reacted molecule gives one $H_2S$ molecule and that the lack of $H_2S$ initially observed corre-

sponds to catalyst sulfiding. This also implies that $H_2S$ dissolution in the $n$-dodecane liquid sample is negligible in the conditions applied. For runs 1 and 2 at 250°C, i.e., for catalyst initially oxidic and hydrogen prereduced, a discrepancy (about 6% relative) between activity based on BT conversion and $H_2S$ production is observed and it may be that catalyst sulfiding is not completely achieved at 30 h run time. If this is the case, the sulfur uptake (see Table 1) would be slightly underestimated, but the changes during catalyst activation are quite significant and in agreement with the results of Massoth and Kibby (22), viz., the least prereduced catalyst is the most active at the steady state.

### Catalyst Behavior at 250°C

Initially no BT hydrodesulfurization is observed for the oxidic catalyst at 250°C (Curve 1, Fig. 1). After 6 h on stream, BT conversion is noticed, as deduced from the appearance of ethylbenzene. However,
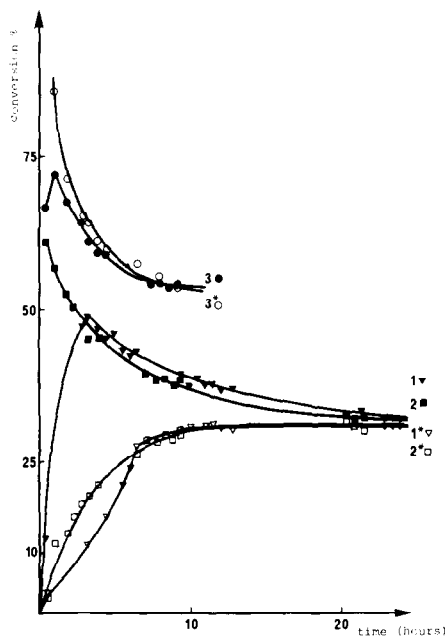


FIG. 2. Conversion of benzothiophene as a function of run time, at 350°C. Conditions of pretreatment: 1. initially oxidic, 2. prereduced at 400°C, 3. presulfided at 350°C. Curves with asterisks: molar ratio (%) between $H_2S$ evolved into gas phase and BT supplied.

TABLE I

Correlation between Effect of Pretreatment on Degree of Sulfiding and BT Conversion

| Catalyst pretreatment[a] | Temperature of test (°C) | BT conversion at steady state (%) | Atomic ratio[b] $S/(Co + Mo)$ | Degree of sulfiding[c] $S/S_{max}$ |
|---|---|---|---|---|
| 1. Initially oxidic | 250 | 45 | 0.43 | 0.26 |
| 2. Prereduced at 250°C | 250 | 39 | 0.34 | 0.21 |
| 3. Prereduced at 400°C | 250 | 36 | 0.26 | 0.16 |
| 4. Prereduced at 400°C then presulfided at 250°C | 250 | 75 | — | — |
| 5. Presulfided at 250°C | 250 | 75 | — | — |
| 6. Initially oxidic | 350 | 32 | 0.54 | 0.33 |
| 7. Prereduced at 400°C | 350 | 32 | 0.54 | 0.33 |
| 8. Presulfided at 350°C | 350 | 54 | — | — |

[a] Prereduction: 1 h, 400°C, 0.07812 mole $H_2$ $h^{-1}$ at STP except for catalyst 2, 10 h, 250°C.

[b] $8.273 \times 10^{-4}$ at. g Co + $16,255 \times 10^{-4}$ at. g Mo in 2 g catalyst sample. $S$: mole balance between EB formed and $H_2S$ iodometrically titrated up to steady state.

[c] S content of the catalyst relative to maximum sulfur (100%) for complete conversion to $MoS_2$ and $Co_9S_8$.

$H_2S$ is evolved into the gas phase only 2 h later. HDS activity increased during about 20 h reaching a nearly steady activity level of 45% BT conversion. $H_2S$ is achieved in concentrations increasing with degree of catalyst sulfiding as well as with its HDS activity.

The same behavior is found with a catalyst which was $H_2$ pretreated during 1 h, and therefore overnight reduction (10 h) was performed; this is in agreement with the results of Ripperger and Saum (23) who reported that catalyst reduction for 4 h is not appreciable up to 250°C. Curve 2, Fig. 1, shows no basic difference with the foregoing catalyst except that HDS activity appeared later and increased at a slower rate than before.

The behavior of catalyst prereduced at 400°C is quite different: HDS activity increased this time in a fast way, as soon as the feed was delivered. After about 10 h on stream a steady state is obtained at 36% conversion, which is still lower than before. Thus, an initially high activity leads to a steady conversion lower than that obtained for the oxidized or mildly reduced catalyst. Similarly to what was reported for $MoO_3$–$Al_2O_3$ catalysts (22), our data show that the least prereduced catalyst was the most ac-

tive which after line-out was that with the greatest sulfur level (see Table 1).

Prereduction at 400°C and subsequent sulfiding at 250°C afford a high steady conversion level which is obtained in a few hours. The situation is contrary to the previous one, as the catalyst released in a decreasing way an excess of sulfur (as $H_2S$), while BT conversion increased from 67% (in the first sample collected after 33 min of run) to nearly 75%. These results are in agreement with those of De Beer et al. (17, 24) who reported a substantial activity increase with catalyst presulfiding. Sulfiding without $H_2$ prereduction at 400°C (Curve 4, Fig. 1) yielded similar HDS activity, with the only difference that a slight maximum at 80% conversion is depicted before steady-state establishment at nearly 75%.

*Catalyst Behavior at 350°C*

Initially oxidic catalyst showed an averaged activity of 12.5% for the first 4-ml sample (Fig. 2). This value increased to a maximum of 48.5% at 3 h on stream, then slowly decayed to a level of 32% during a period of 16 h. It should be noted that this ultimate HDS activity is lower at 350 than at 250°C.

Prereduction in $H_2$ at 400°C led to a relatively high initial activity; nevertheless, conversion decreased progressively from 61 to 32% after about 20 h on stream. Such a marked initial difference between oxidic and prereduced catalyst has already been reported by De Beer *et al.* (*17*) during Co–Mo–$Al_2O_3$ catalyst activation for thiphene HDS at 400°C.

Presulfiding with $H_2S/H_2$ led to an initial conversion of 66%. However, after a maximum at 1 h of run, the conversion level dropped to about 54%, in a fashion similar to that of the two earlier catalysts which were either initially oxidic or prereduced, but nevertheless comparatively to a smaller extent. It should be noted that a large fraction of the sulfur taken up by the catalyst is evolved into the gas phase during an initial period of about 1 h, the level of $H_2S$ release progressively reaching the BT conversion level a few hours later.

As can be seen in Table 1, the total sulfur uptake of Co–Mo–$Al_2O_3$ is significantly higher at 350 than at 250°C, although HDS activity levels are lower.

Most of our data can be ascribed to poisoning phenomena due to the effect of *n*-dodecane on the reduced metallic species (see Discussion). In order to prove this point, other solvents have been tested, using a pulse reactor at atmospheric pressure and 350°C (*29*). Thus, the hydrocarbon solvent was injected continuously (3 ml h$^{-1}$) through a buret and a Beckmann pump into the tube reactor (5 mm diam., 130 mm length), mixed with $H_2$ carrier gas (70 ml min.$^{-1}$) then passed over 250 mg of powdered prereduced Co–Mo–$Al_2O_3$ catalyst. HDS tests were performed with a standard mixture of 5 wt% thiophene, 5 wt% heptane in 90 wt% hexane, which was injected into the reactor by a syringe (5 $\mu$l pulse) every 80 min, while the hydrocarbon (*n*-dodecane) supply was cut off for chromatographic analysis. When hexane or cyclohexane was delivered from the pump, thiophene HDS remained at a steady state (30% conversion) during a period of 11 h;

on the other hand HDS activity decreased slowly to about 15% level while *n*-dodecane was streamed over the catalyst. The drop of thiophene HDS was even much more pronounced with dodecene-1 because the catalyst was totally inactive after 20 min on stream.

## DISCUSSION

Reduction of Co–Mo–$Al_2O_3$ catalyst in hydrogen causes a loss of oxygen and a lowering of the Mo valence. Using ESCA, Patterson *et al.* (*25*) simultaneously observed $Mo^{6+}$, $Mo^{5+}$, and $Mo^{4+}$ species in a ratio depending on reduction temperature and time. With respect to the effect of Co on the ease of Mo reducibility, total disagreement exists between various investigators (*4*). However, it has been demonstrated in our laboratory that Co promotes Mo oxide reduction when Mo has an inhibitory effect on the reduction of cobalt oxide to metallic cobalt (*26*).

When the catalyst is sulfided, some terminal oxide anions are replaced by sulfide anions and some others are removed, forming vacancies. According to Massoth (*4*), vacancies generated by reduction or sulfiding are considered to be the active sites for adsorption of sulfur compounds and surface sulfide (and oxide) for adsorption of hydrogen. For Co–Mo–$Al_2O_3$ catalyst, the role of Co appears to increase the $Mo^{3+}$ concentration (the presumed active site for HDS) either by increasing catalyst reducibility (*15*) or by forming intercalated $CoMoS_2$ (*27*). Two other reports have recently been presented which advocate the involvement of $Mo^{3+}$ in HDS, namely, those of Delvaux *et al.* (*8*) for the contact synergism model and Duben on the interpretation of ESCA experiments on sulfided Co–Mo catalysts (*28*).

According to our results, the catalyst in the initially oxidic state has no HDS activity. The really active form is created as the catalyst is reduced or reduced and sulfided. When catalyst is prereduced at 400°C substantial BT desulfurization takes place ini-

tially as expected from the higher reduction level. On the other hand, the catalytic activity developed at the steady state is smaller than after a smoother prereduction, showing that contact of the catalyst with hydrogen at high temperature lowers efficiency, as reported in the literature (3, 18). Assuming that no additional reduction of the catalyst prereduced at 400°C occurs in the reaction with BT–H₂ at 250°C, it appears that the activity increase during the transient stage results from catalyst *sulfiding*. Despite a higher initial sulfiding rate clearly due to the higher HDS activity, the catalyst sulfur level is lower than in the case of a catalyst which is initially oxidic or mildly reduced. This is in agreement with the findings of De Beer *et al.* (17), namely, that a correlation exists between sulfur compound conversion at the steady state and the degree of catalyst sulfiding. However, the question arises as to why an initially high HDS activity gives rise to the poorest steady activity level. We believe that changes of HDS activity during activation of the prereduced catalyst up to the steady state can reasonably be explained by a poisoning phenomenon of active sites. This poisoning could be due to some interaction between the hydrocarbon molecules of *n*-dodecane and the reduced metallic species (presumably anion vacancies) with formation of coke precursors and ultimate coke deposits. This view is supported by pulse experiments on thiophene, which has been injected over a catalyst having previously contacted a stream of *n*-dodecane in hydrogen (29). Thus long-chain saturated hydrocarbons like *n*-dodecane suffer on the reduced catalyst a set of reactions, leading finally to coke lay-down, which cause partial catalyst deactivation on start-up. Dodecene-1 behavior shows that this phenomenon should be explained by a standard bifunctional catalysis. One can suppose, for example, that *n*-dodecane suffers some dehydrogenation on reduced sites (particularly on vacancies); the olefin thus formed through the medium of the acidity of the

support gives rise to a carbocation which can undergo various modifications, leading to more or less polymerized products.

A much higher HDS activity arises when the catalyst is presulfided, as generally reported in the literature. Our initial HDS increase means adjustment of the H₂S presulfided surface to the BT reaction environment, namely, desorption of excess H₂S which competes with BT for the same sites (17). The small maximum of conversion achieved thereafter may be due to some poisoning effect, which arises when the catalyst is discharged from too much sulfur. Such a maximum is not observed when the catalyst is reduced prior to sulfiding (Curve 4) and activity is initially lower, possibly because a prereduced catalyst sulfides to a lesser extent than a catalyst that has only been fired (25), giving fewer sulfided anion vacancies (16) and consequently lower HDS activity, taking into account the correlation between sulfur content and HDS activity (17).

Thus catalyst presulfiding causes at the same time an increase of HDS activity as well as a protecting effect against poisoning. These two phenomena are perhaps interrelated and it is possible that sulfided species next to reduced species favor both hydrogenolysis of sulfur compounds and hydrogenation of coke precursors. This leads us to consider that catalyst sulfiding brings the necessary complement for proper working of reduced species. It is therefore possible that the activity increase after sulfidation is connected with a combination of reduced and sulfided species in a ratio and in a distribution which are optimal on the catalyst surface. Presulfiding should allow one to obtain the greatest number of such associations and one can even suppose that a part of the well-known promoting role of Co consists of aiding their formation.

At the steady state the HDS activity is controlled by a distribution between sulfided, reduced, poisoned, and oxidic sites and one may assume that sulfided sites

are numerous enough and sufficiently well distributed on the catalyst surface to ensure a good protection against ulterior poisoning. Therefore the effect of presulfiding which is frequently carried out in industrial operation units would be to protect the catalyst against poisoning during the reactor start-up.

Experiments performed at 350°C (Fig. 2) emphasize this harmful solvent effect as appreciable decay of HDS activity is observed initially either on prereduced or on presulfided catalyst. These results are very similar to the data presented by De Beer et al. (17) relating to HDS of 6 vol% thiophene in $H_2$ at 400°C over prereduced or presulfided Co–Mo–$Al_2O_3$ catalyst. This implies that thiophene, like the hydrocarbon solvent, leads to a similar poisoning effect, possibly through intermediate products such as butadiene (30) or diacetylenic species (31) which are known to be coke precursors. Such a behavior of thiophene has been checked in our laboratory in experiments (to be reported as Part IV) where catalysts were presulfided with $H_2$–thiophene instead of $H_2$–$H_2S$ (32).

Comparison of Figs. 1 and 2 shows two marked effects, i.e., (a) whatever the temperature, *presulfiding* affords the initially highest conversion due undoubtedly to a greater concentration of HDS sites, (b) whatever the pretreatment, runs performed at higher temperature give rise to lesser HDS activity levels. This latter effect is reported in the literature in only two papers to our knowledge, i.e., by Kilanowski et al. (19) in a work where reactant pulses (0.5 μl) including dibenzothiophene dissolved in 50 wt% n-heptane + n-dodecane were injected between 350 and 400°C over a freshly sulfided Co–Mo–$Al_2O_3$ catalyst and by Sotani (33) in a study on thiophene HDS over unsupported $MoO_3$ at 350, 375, and 400°C.

We suggest that this apparent inconsistency may be explained in the following way: temperature increase from 250 to 350°C enhances rates of reactions, but if the rate of catalyst sulfiding is increased, the

TABLE 2

Comparison with Data for Extent of Catalyst Sulfiding

| Reference | $S/S_{max}$ | Conditions |
|---|---|---|
| Ahuja et al. (36) | 0.65 | 350°C, 60 kg/cm² pressure thiophene dissolved in hc. |
| Patterson et al. (25) | 0.62 | 400°C, atmospheric pressure $H_2S/H_2$ |
| De Beer et al. (17) | 0.59 | 400°C, atmospheric pressure, $H_2S/H_2$ |
| | 0.53 | 400°C, atmospheric pressure, thiophene |
| Takatsuka et al. (37) | 0.55 | 350°C, 100 kg/cm², Khafjii G.O. |
| | 0.64 | 350°C, 100 kg/cm² $H_2S$ dissolved in product oil |
| Saum (23) | 0.326 | 300°C, 5 atm, thiophene 0.2% in isooctane |
| | 0.24 | 300°C, 5 atm, Straight-run gas oil S = 0.45% |
| Present work | 0.26 | 250°C, 1 atm, BT 0.3% in n-dodecane |
| | 0.16 | 250°C, 1 atm, BT 0.3% in n-dodecane |
| | 0.33 | 350°C, 1 atm, BT 0.3% in n-dodecane |

reactions responsible for its poisoning through the feed must be increased still further (34).

Finally, it should be noted that the sulfur levels of our prereduced and initially oxidic catalyst are relatively low compared to data generally reported (see Table 2), which concern experiments performed under higher pressures or at higher temperatures in the absence of hydrocarbon solvent. One remarkable exception is the work of Ripperger and Saum (23), who achieve values comparable to ours at 300°C and 5 atm with a feed which was either a solution of 0.2% thiophene in isooctane or a straight-run gas-

oil (0.45 wt% S). Taking into account that desulfurization activity of Co–Mo–Al$_2$O$_3$ catalyst increased with pressure for sulfiding with feedstock (35), our results point to better activation procedures under higher hydrogen partial pressure especially when some H$_2$S contacted the catalyst initially. This conclusion is moreover in accordance with the results of Daly (20), which demonstrate that prereduced or presulfided catalyst show equal activities when BT hydrogenolysis is performed at 250°C and under 1250 psig pressure.

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