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Secondary Effects in Catalytic Tests for Hydrodenitrogenation Reactions Due to Side Reactions with Sulphur Compounds

CoMo and NiMo catalysts used for hydrodesulphurization and hydrodenitrogenation of petroleum fractions are normally used in a sulphided state. Laboratory tests must thus be conducted in conditions such that the catalyst remains sulphided. If an insufficient amount of sulphur compounds is present in the feed to ensure maintenance of the sulphided state of the catalyst, additional sulphur must be added in some way. However, mechanistic studies require the use of only a limited number of molecules in the reacting mixture in order to make unequivocal analysis possible. Therefore, it would be advantageous for such studies if this additional sulphur were to be in the form of a simple sulphur compound. In the laboratory, the introduction of H_2S in medium or high pressure equipment (5×10^6 Pa or more) is inconvenient. Compounds such as CS_2, dimethyldisulphide (DMDS) or diethyldisulphide (DEDS) are often used instead, because these compounds produce H_2S very easily before or in the very first catalyst layers at the inlet of the reactor. For example, the hydrogenation reaction for CS_2 is (*1*)

$$CS_2 + 4\ H_2 \rightarrow 2\ H_2S + CH_4,$$

CH_3SH being a reaction intermediate.

It is known that H_2S partial pressure strongly influences activity and selectivity in hydrodenitrogenation (HDN) reactions (*2–17*). Therefore, it is necessary to maintain a well controlled H_2S concentration in the reactor to study HDN reactions under conditions relevant to the hydrotreatment of petroleum fractions.

We report in this note unexpected results due to the use of CS_2 for controlling the H_2S partial pressure in HDN reactions. Our aim was the study of the competitive HDN of aniline and indole over a commercial NiMo P/γ-Al_2O_3 hydrotreating catalyst (*18*). We noted the formation of several isomers of methylindole, which appeared to increase with higher CS_2 levels in the feed. The purpose of this work was to establish whether CS_2 was involved in the formation of these methylated products. Catalytic tests were performed using other H_2S precursors, namely, dimethyldisulphide (DMDS) and diethyldisulphide (DEDS). It is known that the decomposition of these compounds to H_2S is practically as easy as that of CS_2 (*1*):

$$CH_3{-}S{-}S{-}CH_3 + 3\ H_2 \rightarrow 2\ CH_4 + 2\ H_2S.$$

$$CH_3{-}CH_2{-}S{-}S{-}CH_2{-}CH_3 + 3\ H_2 \rightarrow 2\ CH_3{-}CH_3 + 2\ H_2S.$$

We compared the effect of these three sulphur compounds on the reactivities of aniline and indole when tested in competition.

The catalytic tests were performed in a bench-scale-size continuous-flow reactor as described elsewhere (*18*). The catalyst tested was a commercial NiMoP catalyst supported on γ-alumina (composition 2.9 wt% Ni, 12.6 wt% Mo, 2.9 wt% P). The oxide form was pretreated *in situ* by a mixture of H_2S (15 vol%)–H_2 at 673 K (final temperature). The experimental conditions were:

—catalyst weight	0.8 g.
—temperature	573 K.
—total pressure	5×10^6 Pa.
—liquid flow rate to the reactor	30 ml h^{-1}
—H_2 flow rate to the reactor	30 liter h^{-1} at STP

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TABLE I

Competitive Aniline–Indole Hydrodenitrogenation with Different H_2S Precursors

H_2S precursor	CS_2		DMDS		DEDS	
Composition of the model feed tested (molar concentration)	Aniline	0.0246	Aniline	0.0246	Aniline	0.0246
	Indole	0.0504	Indole	0.0504	Indole	0.0504
	CS_2	0.2167	DMDS	0.2167	DEDS	0.2167
	Heptane	6.6867	Heptane	6.6453	Heptane	6.5959
% Aniline conversion	19		17		20	
% Indole conversion	66		60		59	
% Nitrogen-containing products of indole						
Methylindole	8		None		None	
Indoline	11		12		11	
o-Ethylaniline	22		21		19	
% Indole denitrogenation[a]	47		48		48	
% Five-membered ring opening[b]	25		27		29	

[a] The percentage of indole denitrogenation was calculated by subtracting from the total conversion the percentage of the different products of indole containing nitrogen, namely, methylindole, indoline, and *o*-ethylaniline.

[b] The percentage of indole five-membered ring opening was calculated by subtracting from the total conversion the percentage of the different products of indole that still contain the five-membered ring, namely, methylindole and indoline.

The feed compositions are given in Table 1. Under the reaction conditions used, the liquid feed was completely vaporized in the reactor. The same sulphur level was used in all experiments, corresponding to a H_2S/H_2 molar ratio of 0.011.

The results of the catalytic tests are summarised in Table 1. In each test, the sulphur compound in the feed was totally converted to H_2S. The variations in aniline conversion observed were within the experimental error. However, with indole, a higher conversion was observed when CS_2 was used.

For the HDN of indole, the reaction pathway generally reported in the literature consists of a sequential reaction including several steps (*2, 19–24*), as shown in Fig. 1. The first step is a hydrogenation reaction leading to an equilibrium between indole and indoline. In a second step, *o*-ethylaniline is produced by the breaking of the bond between the nitrogen and the carbon in po-

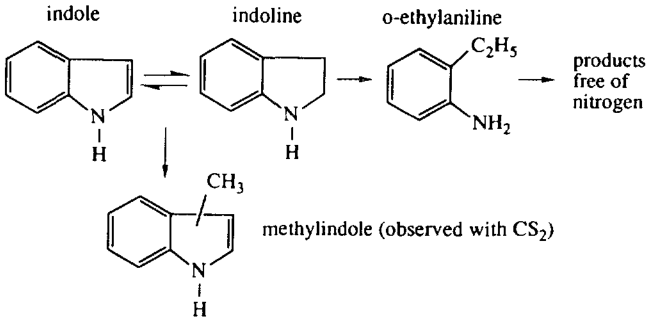

Fig. 1. Indole hydrodenitrogenation pathway.

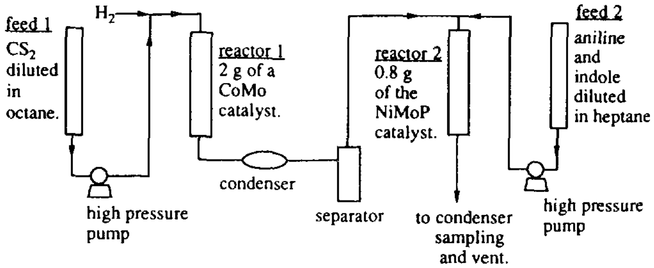

FIG. 2. Two-stage experimental arrangement.

sition 2 of the indoline. The last step is the denitrogenation of *o*-ethylaniline, which gives essentially ethylcyclohexane. The formation of methylindole observed in our experiments has been included in this pathway.

The percentages of the different nitrogen products of indole are also reported in Table 1. No methylindole was formed when DMDS or DEDS were used as H_2S precursor. The percentage of indoline and *o*-ethylaniline formed were similar for the three sulphur compounds. It is noteworthy that the percentage of methylindole formed in the presence of CS_2 corresponded to the additional conversion of indole found with this sulphur compound.

The side reaction leading to the formation of methylindole thus appeared to be specific to the use of CS_2 as H_2S precursor. It was verified that this reaction was catalytic (no conversion was found in the absence of catalyst) and that CS_2 was not converted by a purely thermal reaction before coming in contact with the catalyst bed. An additional experiment was made to test the hypothesis that CS_2 was responsible for the unexpected methylation reaction: the setup is illustrated in Fig. 2. The experiment consisted of decomposing CS_2 to H_2S and methane in a first reactor before injecting the nitrogen model compounds to be reacted in the second reactor. It was verified that CS_2 was completely reacted after the first reactor. Under the conditions of this experiment, the formation of methylindole was not observed.

Under the competitive HDN conditions used in this work, the conversion of aniline was similar for all three sulphur compounds tested. In contrast, the conversion of indole was higher when using CS_2 in comparison with DMDS or DEDS. The analysis of the indole product distribution showed that the higher conversion of indole observed with CS_2 as the source of sulphur was due to the occurrence of a side reaction leading to the formation of methylindole. However, when the reactivity of indole is expressed, not as disappearance of indole, but in terms of five-membered ring opening or in terms of indole denitrogenation, the results agree closely in the three sets of experiments (Table 1).

The methylation of indole was due to a catalytic reaction between indole and CS_2. It is suggested that such a reaction is an acid–base catalyzed mechanism. The reaction could involve the electrophilic carbon of CS_2 (Lewis acid) and the nucleophilic carbon of indole (3 position) which is a Lewis base. Further experiments are currently being carried out to elucidate the mechanism of this side reaction.

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