Methylation of indole during catalytic tests for hydrodenitrogenation (HDN) reactions

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Abstract

Hydrodenitrogenation (HDN) is a catalytic process aimed at reducing the nitrogen content of petroleum crudes. We studied the reactivity of organic nitrogen compounds, aniline and indole, representative of those present in the crudes. The catalytic tests were carried out in the presence of H_2S in the reacting gas phase. It was generated in situ by adding sulphur compounds which decomposed easily to H_2S and hydrocarbon. The use of CS_2 as H_2S precursor led to the occurrence of side reactions: two methylindole isomers were identified in the indole reaction products. These side reactions were not observed with other H_2S precursors like dimethyldisulphide or diethyldisulphide. We established that the formation of the methylindole isomers results from a reaction between (undecomposed) CS_2 and the five-membered hetero-ring of indole or indoline and we proposed a two-step reaction mechanism.
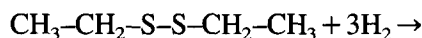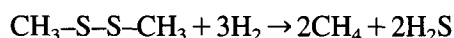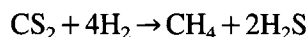
1. Introduction

Petroleum crudes contain heteroatoms impurities (sulphur, nitrogen and metals) [1] whose concentration must be reduced in order to enable the intermediate products stream to be processed more easily to produce stable and environmentally acceptable fuels. In particular, hydrodenitrogenation (HDN) is the process aimed at the reduction of the nitrogen content: the organic nitrogen compounds present in the crudes are reacted with hydrogen in the presence of a catalyst. The products of the reaction are hydrocarbons, nitrogen being eliminated in the form of ammonia.

This paper is part of a work aimed at studying the competition between aniline and indole (two compounds representative of the nitrogen compounds present in the crudes) for the active sites of a commercial HDN catalyst [2,3]. The catalytic tests were carried out in the presence of H_2S in the gas phase. The reason for doing so is that, at industrial level, HDN is applied to charges that also contain sulphur compounds. These sulphur compounds produce H_2S during their decomposition and it is well known that the H_2S partial pressure strongly influences activity and selectivity in HDN reactions [4–26]. Moreover, the HDN catalysts are normally used in a sulphided state. Thus another reason for adding H_2S is to ensure maintenance of the sulphided state of the catalyst.

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Indeed, a sulphided catalyst will slowly lose sulphur if used to process a sulphur free feedstock. This leads to a loss of activity which is not representative of the industrial process.

In the laboratory, compounds such as carbon disulphide (CS_2), dimethyldisulphide (DMDS) or diethyldisulphide (DEDS) are generally used to generate in situ H_2S, because these molecules decompose easily producing a constant H_2S partial pressure over a large range of reaction conditions. They decompose according to the following reactions [27]:

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

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

$$CH_3-CH_2-S-S-CH_2-CH_3 + 3H_2 \rightarrow$$

$$2CH_3-CH_3 + 2H_2S$$

We report in this paper unexpected results due to the use of CS_2 for controlling the H_2S partial pressure. When carrying out our catalytic test (competitive HDN of aniline and indole), we noticed the formation of two methylindole isomers. They were identified as 1-methylindole and 3-methylindole. These side reactions have never been reported before in the literature.

The experiments reported here were aimed at the elucidation of the mechanism of these side reactions. We studied the effect of different H_2S precursors (CS_2, DMDS and DEDS), we studied the influence of the H_2S level on the methylindole formation and we established whether CS_2 or CH_4 (product of the decomposition of CS_2) were involved in the formation of the methylated products. Finally, we compared the reactivity of CS_2 towards indole and indoline. As shown in Fig. 1, the first step of the indole reaction pathway is a hydrogenation equilibrium between indole and indoline. We established [3,34] that the equilibrium was reached in our reaction conditions. The experimental value of the molar ratio indoline/indole was 0.35. It corresponded to the value reported by Ho [35] and the same ratio was obtained whether indole or indoline were tested as reactant. We were interested in comparing the
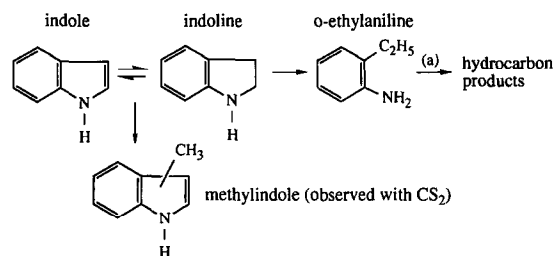

Fig. 1. Indole denitrogenation pathway.

[a] Recent results indicate that the obtention of the hydrocarbon products occurs essentially through the hydrogenation of indoline to octahydro-1H-indole. As this point does not interfere with the methylation reactions, we presented for simplicity the indole denitrogenation pathway generally reported in the literature [17,28–33]. A thorough discussion of the indole denitrogenation pathway can be found elsewhere [3,34].

reactivity of CS_2 towards indole with the reactivity of CS_2 towards indoline because of the difference in the nucleophilic character that the nitrogen atom has in these two compounds.

2. Experimental

The catalytic tests were performed in a bench-size continuous-flow reactor as described elsewhere [2,3]. 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 catalyst was in the oxide state (NiO, MoO_3) when introduced in the reactor. It was pretreated in situ according to a procedure which ensured an optimal catalyst sulphidation. The catalyst was first heated to 423 K under Ar and left at this temperature for half an hour. The activation gas – a mixture of H_2S(15 vol%)/H_2 – was introduced afterwards and the temperature rose, first up to 573 K where it remained half an hour, then up to 673 K where it remained one hour. During each step of the pretreatment procedure the heating rate was 0.17 K s^{-1} and the gas flow rate was 1.67×10^{-6} m^3 s^{-1}. At the end of the pretreatment, the catalyst was left under the H_2S-H_2 atmosphere and the temperature was dropped to 573 K before starting the reaction. The reaction conditions were:

– weight of catalyst: 8×10^{-4} kg
– temperature: 573 K

– total pressure: 5×10^6 Pa

– hydrocarbon feed flow rate to the reactor: 8.33×10^{-9} m^3 s^{-1} at STP

– H$_2$ flow rate to the reactor: 8.33×10^{-6} m^3 s^{-1} at STP.

The reacting gas phase resulted from the mixing of pure H$_2$ and a hydrocarbon feed. The hydrocarbon feed contained the two nitrogen model compounds (aniline and indole), a sulphur compound precursor of H$_2$S and a hydrocarbon solvent (n-heptane) which is inert in the reaction conditions. The comparison between the H$_2$S precursors (CS$_2$, DMDS and DEDS) was made on the basis of the same molar concentration of the sulphur compounds in the hydrocarbon feed. It gives rise to the same H$_2$S partial pressure in the reacting gas phase since, in each case, two moles of H$_2$S are produced per mole of sulphur compound. As an example, we reported in Table 1 the composition of the hydrocarbon feeds used for the first serial of tests. It consisted in comparing the effect of the three H$_2$S precursors at a sulphur concentration representative of the sulphur content of petroleum fractions. The reaction samples were analysed by temperature programmed gas chromatography using a Hewlett Packard (model 428) equipped with a 25 m capillary DB-5 column and a FID detector. The concentrations of reactants

and products were calculated using n-heptane as internal standard. The reaction products were identified by GC–MS analysis and the results of the identification were confirmed by the injection of the standard compounds. We expressed the reactivity of aniline by the percentage of conversion. This classical formulation is the difference between the initial concentration and the concentration after the reaction with respect to the initial concentration. This value corresponded to the percentage of aniline denitrogenation since the aniline products were hydrocarbons (cyclohexane and cyclohexene). For the evaluation of the indole reactivity, we reported three different expressions:

– the percentage of indole conversion;

– the percentage of 5-membered ring opening. Because of the easy interconversion between indole and indoline, indole reactivity is generally calculated taking into account indole and indoline as unconverted reactants [17,30,33]. In our case, we must take into account the formation of methylindole. The percentage of 5-membered ring opening was thus obtained by subtracting from the total indole conversion the percentage of indoline and methylindole namely the products of indole that still contained the five-membered ring.

Table 1
competitive aniline–indole HDN with different H$_2$S precursors

H$_2$S precursor	CS$_2$		DMDS		DEDS	
composition of the hydrocarbon feed (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	6.6857	heptane	6.6453	heptane	6.5959
% aniline conversion	19		17		20	
% indole conversion	66		60		59	
% nitrogen containing products of indole:						
3-methylindole	6		none		none	
1-methylindole	2		none		none	
indoline	11		12		11	
o-ethylaniline	22		21		19	
% 5-membered ring opening	47		48		48	
% indole denitrogenation	25		27		29	

- the percentage of indole denitrogenation: this value was calculated by subtracting from the total indole conversion the percentage of the different intermediate products of indole containing nitrogen namely methylindole, indoline and *o*-ethylaniline.

3. Results

Summarised in Table 1 are the results obtained with the three H_2S precursors. In each test, the sulphur compound was totally converted to H_2S. The variations in aniline conversion observed were within the experimental error. Concerning indole, a higher conversion was observed when CS_2 was used. The percentage of the different nitrogen products of indole is also reported in Table 1. No methylindole products were formed when DMDS or DEDS were used as H_2S precursor. The amount 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 observed with this sulphur compound. As a result, when indole reactivity was expressed not as indole conversion, but in terms of five-membered ring opening or in terms of indole denitrogenation, the results agreed closely with the three H_2S precursors (Table 1).

We further compared the effect of CS_2 and DMDS by varying the sulphur concentration in the hydrocarbon feed between 0 and 0.62 M. This gave rise to a H_2S partial pressure comprised between 0 and 132 kPa. The results are reported in Fig. 2 to 5. Aniline reactivity decreased as H_2S partial pressure increased (Fig. 2). No difference was observed between the two H_2S precursors. Fig. 3 compares the effects of CS_2 and DMDS on indole conversion. A higher conversion was observed with CS_2, the difference increasing with the H_2S level. This difference corresponded to the amount of methylindole formed and when the reactivity of indole was expressed in terms of 5-membered ring opening (Fig. 4) or in terms of
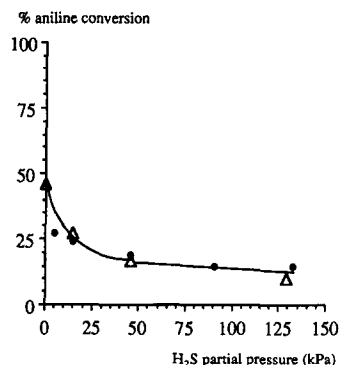

Fig. 2. Comparison of the effect of CS_2 and DMDS on aniline conversion. $\triangle$: DMDS as H_2S precursor; ●: CS_2 as H_2S precursor.
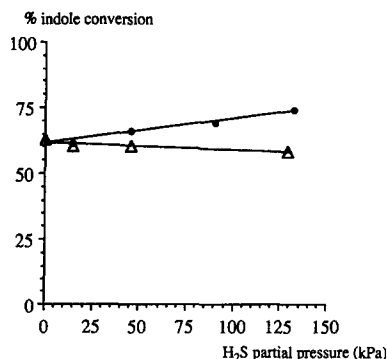
Fig. 3. Comparison of the effect of CS_2 and DMDS on indole conversion. $\triangle$: DMDS as H_2S precursor; ●: CS_2 as H_2S precursor.
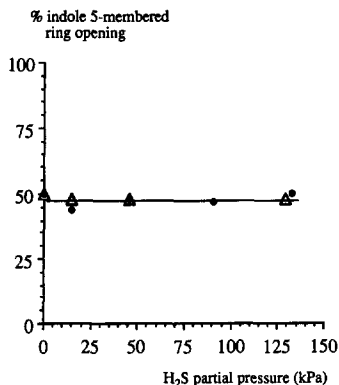
Fig. 4. Comparison of the effect of CS_2 and DMDS on indole 5-membered ring opening. $\triangle$: DMDS as H_2S precursor; ●: CS_2 as H_2S precursor.

indole denitrogenation, the results agreed with the two H_2S precursors. Fig. 5 reports the influence of the H_2S level on the amount of the two methylindole isomers formed. The percentage of 3-methylindole was proportional to the H_2S level. The percentage of 1-methylindole remained lower or equal to 2%.
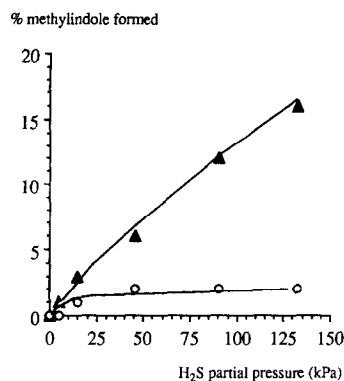
% methylindole formed

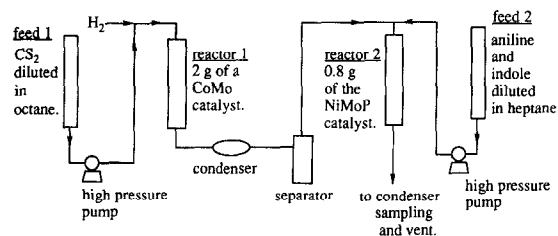Fig. 5. Influence of the H₂S level on the methylindole formation. ▲ : 3-methylindole; ○: 1-methylindole.

Fig. 6. Two stage reaction.

The side reactions leading to the formation of methylindole isomers were found to be specific to the use of CS_2 as H_2S precursor: no methylindole formation was observed neither in the absence of sulphur compound in the hydrocarbon feed nor when DMDS or DEDS were used as H_2S precursors. It was verified that these reactions were catalytic (no conversion was found in the absence of catalyst) and that CS_2 was not converted by a purely thermal reaction before coming into contact with the catalyst bed. An additional experiment was made to test the hypothesis that CS_2 was

responsible for the methylation reactions. This test is described in Fig. 6. It consisted in 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. This experiment excluded methylindole formation arising from a reaction between indole and methane (formed by the decomposition of CS_2). Moreover, if such a reaction did happen, we would expect methylindole formation when using DMDS as H_2S precursor since, in that case, methane is also formed in the gas phase. This was not observed (Table 1). The two results are thus in agreement, they demonstrate the direct involvement of CS_2 in the methylation reactions.

We compare in Table 2 the methylated product distribution observed when indole and indoline were respectively tested as reactant. More methylated products were formed with indoline. The analysis of the product distribution shows that it was due to the larger amount of products methylated in position 1 (1-methylindole and 1-methylindoline). The fact that a marked difference was found between the two tests indicates that the methylation reactions were at least as fast as the interconversion indole–indoline. When indoline is tested as starting compound, the amount of products methylated in position 1 is such that the molar ratio 1-methylindoline/ 1-methylindole can be calculated. This ratio (0.30) is close to the

Table 2
CS₂ reactivity towards indole and indoline

Reactant tested	Indole		Indoline	
composition of the hydrocarbon feed (molar concentration)	aniline	0.02461	aniline	0.0246
	indole	0.0504	indoline	0.0504
	CS₂	0.2167	CS₂	0.2167
	heptane	6.6857	heptane	6.6448
percentage of methylated compounds found in the products of the reaction:				
3-methylindole	6		3	
1-methylindole	2		10	
1-methylindoline	none [a]		3	

[a] 1-methylindoline was found in negligible amount.

molar ratio indoline/indole (0.35). It can thus be assumed that the hydrogenation equilibrium between the methylated products is reached as we established it for the couple indole–indoline [3,34].

Fig. 8. Mechanism of 1-methylindoline formation.

4. Discussion

Three experimental results were taken into account for the consideration of a reaction mechanism:

1– The methylation reaction is due to a reaction between (undecomposed) CS_2 and indole or indoline.

2– When indole is the starting compound, the methylation occurs mainly on position three (Fig. 5 and Table 2)

3– When indoline is the starting compound, products methylated on position one are essentially obtained (Table 2).

The mechanism proposed for the methylation of indole is reported in Fig. 7. The first step of the reaction would be the nucleophilic attack of the carbon in position three on the carbon atom of CS_2. This step can also be considered as an electrophilic aromatic substitution of indole by CS_2. The thioacid intermediate compound formed would then be reduced to methylindole under the condition used in our experiments (high H_2 partial pressure). The mechanism of indoline methylation is presented in Fig. 8. In that case the nucleophilic attack would involve the nitrogen atom of indoline (position one). The thioacid would then be reduced to 1-methylindoline. The reaction between CS_2 and the five-membered ring of indole or indoline thus would stem from the electrophilic character of the carbon atom of CS_2. In the case of indoline, the free electron pair of the nitrogen atom is not involved in the aromaticity of the heterocycle and the nitrogen atom has a strong
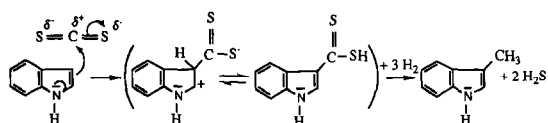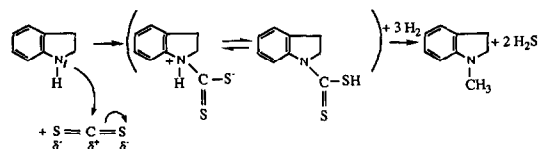

Fig. 7. Mechanism of 3-methylindole formation.

nucleophilic character. This explains the high affinity of the nitrogen atom of indoline for CS_2. As a result, a higher amount of methylated products is observed when indoline is tested as reactant. In the case of indole, the free electron pair of the nitrogen atom is involved in the aromaticity of the heterocycle. In consequence, the nucleophilic character of the nitrogen atom is not marked and the delocalisation of the electronic pair of the nitrogen atom confers a nucleophilic character on the carbon in position three. The mechanisms reported in Figs. 7 and 8 are similar to the mechanism of the Kolbe–Schmitt reaction (formation of salicylic acid by carboxylation of phenolates with carbon dioxide).

The methylated product distribution observed in these experiments (Table 2 and Fig. 5) can be rationalized follows.

When indole is the starting compound, the methylation occurs essentially on position three by the mechanism proposed in Fig. 7. To explain 1-methylindole formation two possibilities can be considered: the dehydrogenation of 1-methylindoline and the methylation on the nitrogen atom of indole. Although the nitrogen atom of indole has a low nucleophilic character, the latter interpretation remains possible. *When indoline is the starting compound*, the amount of 1-methylindole obtained arises from the dehydrogenation of 1-methylindoline formed by the mechanism reported in Fig. 8. Some 1-methylindole could also be obtained by the dehydrogenation of indoline preceding the methylation on position one but it is not the main mechanism, since in that case, no difference of reactivity towards CS_2 would have been observed between indole and indoline. The attack on the position three of indoline is not possible and the obtention of 3-methylindole must be explained by the dehydrogenation of indoline preceding the methylation on position three.

The percentage of methylindole formed in the presence of CS_2 corresponds to the additional conversion of indole observed with this sulphur compound (Table 1 and Fig. 3). Concerning aniline, no side reactions are observed. It is thus possible to take into account the side reactions for the interpretation of the results and, by comparing different H_2S precursors, we confirmed the results initially obtained with CS_2 [3,36], namely:

- an inhibiting effect of H_2S on aniline reactivity (Fig. 2). This is due to the inhibiting effect that H_2S exerts on the hydrogenation function of the catalyst, aniline reactivity being controlled by the rate of aniline hydrogenation to cyclohexylamine [3,33];
- a neutral effect of H_2S on the overall indole reactivity as expressed by the indole 5-membered ring opening (Fig. 4). This result was explained considering that the indole HDN pathway proceeds by two parallel paths [3,33]: the first path is a C–N bond cleavage reaction and is promoted by H_2S, the second path is a hydrogenation reaction and is inhibited by H_2S.

5. Conclusion

The conclusions to be drawn from these experiments are:

1– The use of CS_2 as H_2S precursor leads to the occurrence of side reactions which consist in the methylation of the 5-membered hetero-ring of indole or indoline. These side reactions are specific to the use of CS_2 and are not observed with other H_2S precursors like DMDS or DEDS.

2– The *first step* of the methylation reactions would be a nucleophilic attack on the carbon atom of CS_2. The attack occurs essentially on position three with indole and exclusively on position one with indoline. The *second step* would be the reduction of the thioacid function to methyl.

3– It is possible to take into account these side reactions for the interpretation of the experimental results since the percentage of the methylated products formed corresponds to the conversion observed with CS_2, coming in addition to the reactions of interest when studying the denitrogenation of indole.

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