Journal of Catalysis **198,** 47–55 (2001)
doi:10.1006/jcat.2000.3103, available online at http://www.idealibrary.com on IDEAL®

Influences of the Hydrogen Sulfide Partial Pressure and of a Nitrogen Compound on the Hydrodeoxygenation Activity of a CoMo/Carbon Catalyst

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Received June 13, 2000; revised October 2, 2000; accepted October 30, 2000; published online February 7, 2001

The influences of the hydrogen sulfide partial pressure and of a basic nitrogen compound (diaminopropane) on the activity of a sulfided CoMo/carbon catalyst in hydrodeoxygenation were studied from 10 to 150 kPa H_2S, under a total pressure of 7 MPa, at 270 and 200°C in the transformation of a mixture of guaiacol, ethyldecanoate, and 4-methylacetophenone in *p*-xylene. It is likely that three different active sites are responsible for hydrogenolysis, hydrogenation, and acid-catalysed reactions. An increase in hydrogen sulfide partial pressure decreases the average degree of reduction and uncoordination of the active sites and inhibits the hydrogenolysis and hydrogenation pathways, the first being affected to a larger extent. This accounts for the decrease of guaiacol dehydroxylation and the increase of 4-methylacetophenone conversion. The reactions catalysed by acid sites located on the metal sulfide, namely decarboxylation and alcohol dehydration, are promoted by hydrogen sulfide. The addition of diaminopropane strongly inhibits the conversion of guaiacol and ethyl decanoate. The decarboxylation selectivity is decreased as well. © 2001 Academic Press

Key Words: **hydrodeoxygenation; hydrogen sulfide; sulfided catalyst; carbon support.**

1. INTRODUCTION

Liquids derived from the pyrolysis of biomass, such as bio-oils (1), should be upgraded to enable storage, transportation, and use. Hydrodeoxygenation (HDO) could be adequate for this purpose (2, 3). The reactions involved are quite similar to those occurring in the hydrotreating of petroleum fractions.

The present work deals with the influences of the hydrogen sulfide partial pressure and of the addition of a basic nitrogen compound, i.e., diaminopropane, on the HDO activity of a carbon-supported sulfided CoMo catalyst.

As biomass-derived liquids do not contain sulfur compounds (4, 5), a partial pressure of hydrogen sulfide is needed to preserve the sulfided catalyst from oxidation by oxygenated compounds and water (6–8), or reduction of the sulfided phase by hydrogen, depending on the operating conditions.

HDO reactions are deeply influenced by hydrogen sulfide. In the conversion of 4-methylphenol the direct hydrogenolysis of the $C_{aromatic}$–O bond is more strongly inhibited than the hydrogenation of the aromatic ring followed by hydrogenolysis (9–11). In the simultaneous hydrodesulfurization(HDS) and HDO of phenol and mercaptophenol (12, 13) the HDO of a hydroxyl group was suppressed by the presence of a mercapto group either in the same or in a separate molecule.

Depending on the origin of biomass, bio-oils are characterised by a nitrogen content between 0.2 and 1 wt% (4, 5). Nitrogen-containing molecules, like ammonia or amines, are strong inhibitors of hydrogenation (HYD) (14–16) and HDS (17, 18) reactions. They can interact with incompletely coordinated molybdenum atoms, or with –SH acid sites. HDO reactions are also affected by nitrogen compounds. The HDO of phenols is inhibited by quinoline, *o*-ethylaniline (19), and indole (20). Ammonia, generated by decomposition of ammonium carbonate (10), or diaminopropane (9) inhibits the HDO of 4-methylphenol.

A double objective will be pursued in this work: to improve the understanding of HDO reactions and to investigate the modifications of the active sites occurring under different reaction conditions. Our results will be supported by comparisons with previous work performed in the same field (9, 21, 22). The use of activated carbon instead of alumina as support should make interpretation easier, because there is no longer a contribution of the support acidity to the conversion of the reactant. The role of the sulfhydryl groups should be more easily understood.

2. EXPERIMENTAL

2.1. The Catalyst

The catalyst was prepared using a commercial activated carbon, BKK-100 (particle size diameter between 0.3 and

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0021-9517/01 $35.00

0.5 mm, specific surface area 1100 $m^2 g^{-1}$, pore volume 0.7 $cm^3 g^{-1}$). The support was impregnated with aqueous solutions of ammonium heptamolybdate and cobalt nitrate, using the incipient wetness method. Molybdenum was impregnated first. After each impregnation, the sample was dried overnight at 130°C and then at 400°C for 3 h under an argon flow. The composition of the catalyst was 15 wt% of MoO_3 and 3 wt% of CoO. This catalyst has been extensively characterised by N_2 physisorption, XPS, and SEM (23). The textural characteristics of the catalyst were specific surface area, 677 $m^2 g^{-1}$, and pore volume, 0.4 $cm^3 g^{-1}$.

2.2. The Catalytic Tests

The tests were carried out in a fixed-bed continuous-flow tubular reactor (internal diameter, 1.75 cm; length, 70 cm). A 1.5 g portion of catalyst (particle diameter between 0.3 and 0.5 mm) was diluted with glass spheres (diameter between 0.2 and 0.45 mm) to reach a volume of 18 cm^3. The catalytic bed (8 cm height) was loaded in the reactor between two plugs of glass wool. The rest of the reactor was filled with 1 mm diameter glass spheres.

Prior to the reaction, the catalyst was dried at 130°C overnight, under nitrogen flow. The sulfidation mixture, 15 vol% H_2S in H_2, was then introduced, with the pressure set at 0.3 MPa and the flow at 150 ml min^{-1}; after a 30 min stabilisation period, the temperature was increased to 400°C (3°C min^{-1}). These conditions were held for 3 h. The temperature was subsequently decreased to 270°C, the gas switched to pure hydrogen, and the liquid feed introduced. The pressure was progressively raised to 7 MPa in 1 h. The liquid feed rate was 45 ml h^{-1} and the hydrogen flow rate 24 l h^{-1}. The tests were performed at a total pressure of 7 MPa. This procedure was also followed for the experiments performed without catalyst.

The decomposition of the hydrogen sulfide precursor, dimethyl disulfide (DMDS), in the absence and in the presence of the catalyst (thermal and catalytic reaction of DMDS, respectively) was first investigated. We also studied the reaction of the oxygenated model compound mixture in the absence of the catalysts. For the study of the thermal and catalytic reactions of DMDS, the liquid feed contained DMDS (7.2 wt%, 0.67 mol l^{-1}) and pentadecane (2 wt%, 0.082 mol l^{-1}) as internal standard for the chromatographic analysis; *p*-xylene was used as solvent.

For the study of the HDO reactions, the composition of the mixture of oxygenated model compounds was as follows: guaiacol (GUA), 3 wt%, 0.21 mol l^{-1}; ethyl decanoate (ED), 3 wt%, 0.13 mol l^{-1}; 4-methylacetophenone (MA), 3 wt%, 0.20 mol l^{-1}; and pentadecane, 2 wt%, 0.082 mol l^{-1} in *p*-xylene. DMDS was added as a precursor of H_2S; its concentration depended on the hydrogen sulfide partial pressure required for the test. For the test done with diaminopropane (DAP), its concentration was 0.29 wt%, 0.034 mol l^{-1}, and the concentration of DMDS was 1.8 wt%, 0.17 mol l^{-1}.

Three series of experiments were done to study the influence of hydrogen sulfide. In the first series, four tests were performed at different hydrogen sulfide partial pressures (50, 75, 100, and 150 kPa), using a fresh catalyst for each test. In the second, called "P_{H_2S} increase", the test was done at increasing hydrogen sulfide partial pressures (10, 25, 35, 50, 75, and 150 kPa) without changing the catalyst and always waiting 24 h before modifying the operating conditions (temperature and hydrogen sulfide partial pressure). Finally, after the activity was measured at a hydrogen sulfide partial pressure of 150 kPa, this pressure decreased to 10 kPa and the activity was measured again. The last point at which the initial conditions were restored is indicated as 10 kPa bis. In the third series of experiments, called "P_{H_2S} decrease," the test was done at decreasing hydrogen sulfide partial pressures (150, 100, 50, and 25 kPa) without changing the catalyst and waiting 24 h before modifying the operational conditions. Finally, after the activity was measured at 25 kPa, the hydrogen sulfide partial pressure was increased back to 150 kPa (150 kPa bis) for a last series of product analyses.

Two reaction temperatures were used for the test: 270°C in order to evaluate the reactivity of GUA and ED and 200°C in order to evaluate the reactivity of MA.

Liquid samples, collected before the back pressure regulator every hour, were analysed by using a gas chromatograph equipped with an FID detector and a capillary column (stationary phase CP-Sil-8CB; length, 25 m).

Conversion, yield, and selectivity data reported here were obtained in the period corresponding to 18 to 24 h of reaction, where conversion and selectivities are nearly constant. The error in the experimental values of the conversion and selectivity was estimated at 10–15%.

The HDO pathways of the model compounds are reported in Fig. 1.

3. RESULTS

3.1. Preliminary Tests

The thermal decomposition of DMDS starts at a temperature above 200°C and is completed at 300°C. DMS appears only at 270°C. The catalytic decomposition of DMDS (Fig. 2) starts at a much lower temperature and at temperatures higher than 180°C the decomposition is complete. Methylmercaptan is formed at 150°C.

The conversion of ED and MA at 270°C without the catalyst is always lower than 1%, while the conversion of GUA is 1.5%. The conversion of MA at 200°C is lower than 1%.

3.2. Influence of the Hydrogen Sulfide Partial Pressure

The GUA conversion was not affected by hydrogen sulfide and almost similar values were obtained in the three series of experiments. An important molar balance deficit was observed; the sum of the product yields calculated on

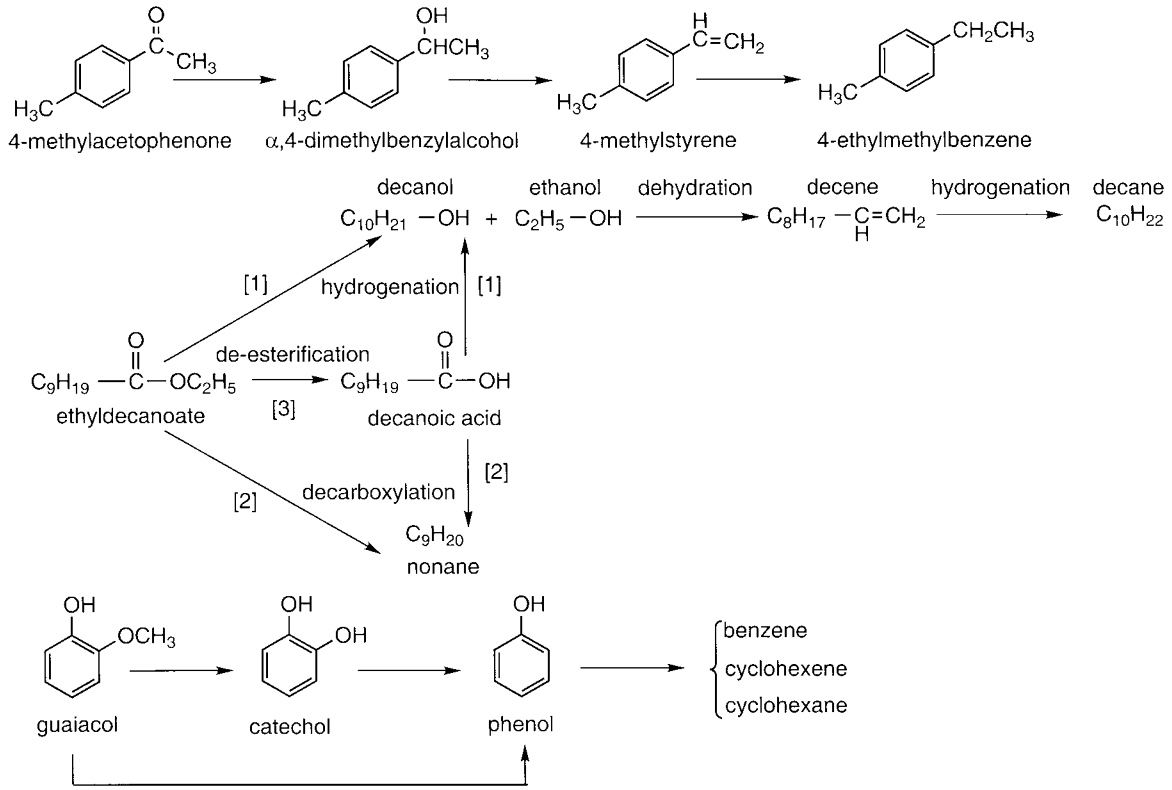

FIG. 1. Hydrodeoxygenation pathways of 4-methylacetophenone, ethyl decanoate, and guaiacol.

the basis of gas chromatographic analyses corresponded to 60–80% of the reactant conversion. Actually, when the liquid samples were withdrawn from the reactor, a white dense unidentified phase was observed. It is known that phenolic compounds with two oxygenated substituents are often involved in condensation reactions (24, 25). The gas phase, which could contain aromatic and alicyclic compounds, such as benzene, cyclohexene, and cyclohexane, was not analysed.

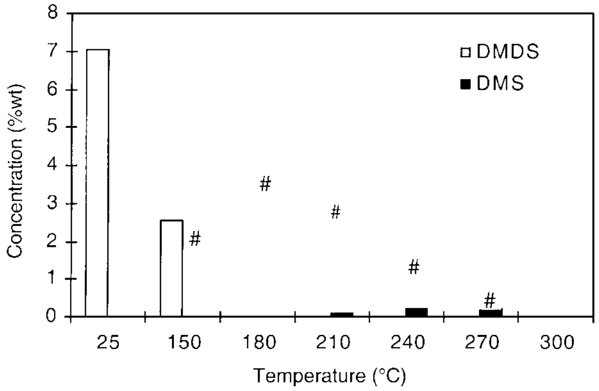

FIG. 2. Evolution of the DMDS and DMS concentrations in the liquid phase in the catalytic decomposition of DMDS. The presence of MM is also indicated (#), but a quantification of this product was not done. Total pressure, 7 MPa.

For the first series of tests performed with a fresh catalyst for each P_{H_2S}, we report in Table 1 the conversion, molar balance, and product yields after 2 h of reaction, as well as the mean values obtained from the analysis of three

TABLE 1

GUA Conversion, Molar Balance, and Yields of C6 Hydrocarbons (Benzene, Cyclohexene, Cyclohexane), Phenol, and Catechol, for the First Series of Tests, Performed at Different P_{H_2S}. (Total Pressure, 7 MPa; Temperature, 270°C)

P_{H_2S}		Conv GUA (%)	Molar balance (%)	Yield (%)		
				C6	Ph	Cat
50 kPa	2 h	20	82	5.0	4.6	7.0
	Nearly constant state	19	67	4.5	3.9	4.3
75 kPa	2 h	22	76	4.5	4.4	6.8
	Nearly constant state	19	67	4.8	3.8	4.0
100 kPa	2 h	23	68	4.4	3.8	7.4
	Nearly constant state	21	57	4.2	3.0	4.8
150 kPa	2 h	20	88	4.2	3.9	9.6
	Nearly constant state	17	83	3.7	2.9	7.4

Note. The values of conversion and yield were measured after 2 h of reactions and at a nearly constant state.

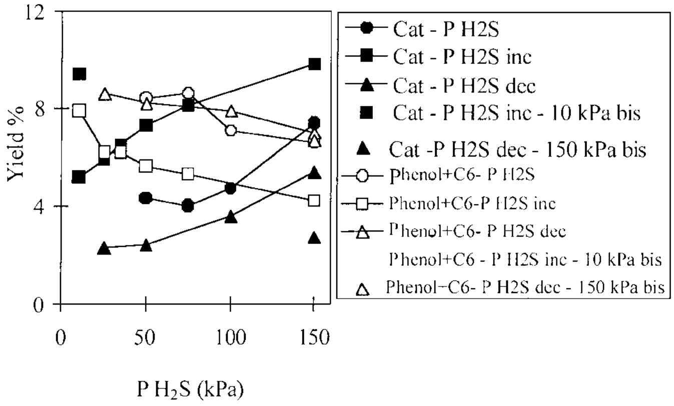

FIG. 3. Evolution of catechol and phenol + C6 yields as a function of P_{H_2S} for the three series of experiments. Reaction temperature, 270°C. Total pressure, 7 MPa.

samples withdrawn in the period between 18 and 24 h (nearly constant state).

The evolution of the yields in catechol and the sum of phenol and C6 (which includes benzene, cyclohexene, and cyclohexane) as a function of P_{H_2S} is shown in Fig. 3. For the three series of experiments, phenol and C6 yields decrease with increasing P_{H_2S}, while catechol yields increase. As a consequence, the phenol + C6-to-catechol ratio decreases with increasing P_{H_2S} (Fig. 4). In the case of the "P_{H_2S} increase" series, higher ratios are obtained than in the other two test series. Only for the "P_{H_2S} increase" series is this ratio lower than 1. For the two other series, the phenol + C6 amount is higher than that of catechol, except at high P_{H_2S} (150 kPa). In the "P_{H_2S} increase" series, the phenol + C6-to-catechol ratio after 300 h of reaction (10 kPa bis) is lower than the one observed at the beginning of the test (10 kPa). In contrast in the "P_{H_2S} decrease" series, this ratio, after 200 h of reaction (150 kPa bis), is higher than that at 150 kPa; in this case, the catechol yield is lower at 150 kPa bis than at 150 kPa.

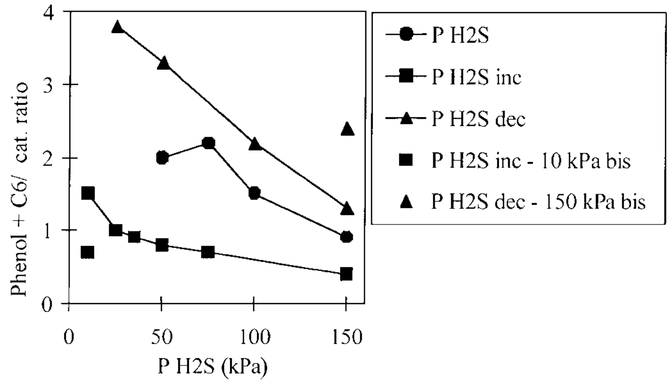

FIG. 4. Evolution of the phenol + C6-to-catechol ratio as a function of P_{H_2S} for the three series of experiments. Reaction temperature, 270°C. Total pressure, 7 MPa.

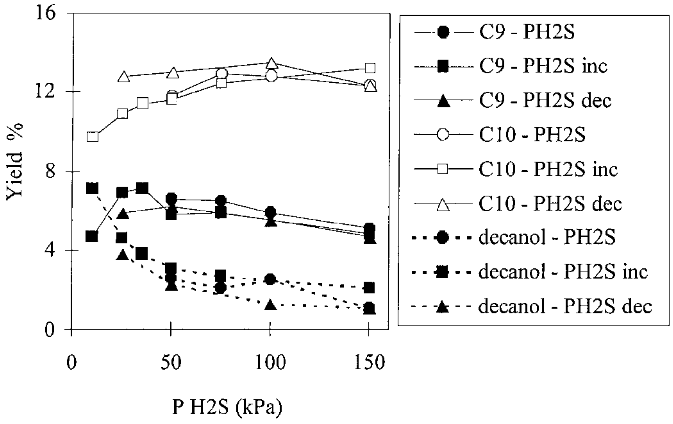

FIG. 5. Evolution of C9 (nonane), C10 (decane + decene), and decanol yields as a function of P_{H_2S} for the three series of experiments. Reaction temperature, 270°C. Total pressure, 7 MPa.

The conversion of ED was not affected by hydrogen sulfide. The sum of the product yields always corresponded to 95% (±5%) of the ED conversion. The evolution of the yields in nonane, decanol, and molecules containing 10 atoms of carbon (C10), as a function of P_{H_2S}, is represented in Fig. 5. In the "P_{H_2S} increase" series, nonane yields increase at low P_{H_2S}; for P_{H_2S} higher than 50 kPa they are constant. For the two other test series, the yields in decarboxylated products are almost constant with the increase of hydrogen sulfide. C10 yields increase, while decanol yields decrease with the increase of P_{H_2S}. With the increase of P_{H_2S} the dehydration of the alcohol is favored. This behavior is more evident for the "P_{H_2S} increase" series and at low hydrogen sulfide partial pressure.

The product yields and the decarboxylation selectivity are reported in Table 2. In the "P_{H_2S} increase" series, a higher nonane yield is observed at 10 kPa bis than at 10 kPa; this results in a higher value for the decarboxylation

TABLE 2

Nonane (C9), Decane + Decene (C10), and Decanol Yields and Decarboxylation Selectivity for the Conversion of ED for the "P_{H_2S} Increase" and "P_{H_2S} Decrease" Series (Reaction Temperature, 270°C; Total Pressure, 7 MPa)

	Yield (%)			
H_2S partial pressure	Nonane	Decane + decene	Decanol	Decarboxylation S (%)
10 kPa	4.7	9.2	7.1	22
10 kPa bis	6.3	9.6	6.8	28
150 kPa	4.7	12.7	1.1	26
150 kPa bis	3.4	13.9	1.0	19

TABLE 3

MA Conversion at Different P_{H_2S} (Reaction Temperature, 200°C; Total Pressure, 7 MPa)

H_2S partial pressure	First series	Second series, "P_{H_2S} increase"	Third series, "P_{H_2S} decrease"
25 kPa		31% (2)	34% (4)
35 kPa		28% (3)	
50 kPa	22%	23% (4)	26% (3)
75 kPa	19%	21% (5)	
100 kPa	19%		18% (2)
150 kPa	12%	15% (6)	12% (1)
150 kPa bis			12% (5)

selectivity. In the "P_{H_2S} decrease" series a lower nonane yield is observed at 150 kPa than at 150 kPa.

The results for the conversion of MA are reported in Table 3. The hydrogenation of the carbonyl group of MA was always inhibited by hydrogen sulfide. The sum of the product yields always corresponded to 95–100% (±5%) of the reactant conversion. The selectivities in 4-ethylmethylbenzene and α,4-dimethylbenzyl alcohol, as a function of the hydrogen sulfide partial pressure, are represented in Fig. 6; they show different tendencies for the three series of tests. In the tests performed with a fresh catalyst for each hydrogen sulfide partial pressure, the 4-ethylmethylbenzene selectivities are almost constant, while the selectivity in the alcohol does not show any clear trend. For the "P_{H_2S} increase" series, the 4-ethylmethylbenzene and the α,4-dimethylbenzyl alcohol selectivities are constant. In the "P_{H_2S} decrease" series the 4-ethylmethylbenzene selectivity increases, while the selectivity in α,4-dimethylbenzyl alcohol decreases as a function of P_{H_2S}. Comparing the "P_{H_2S} increase" and the "P_{H_2S} decrease" series, higher 4-ethylmethylbenzene selectivities are observed in the first case.

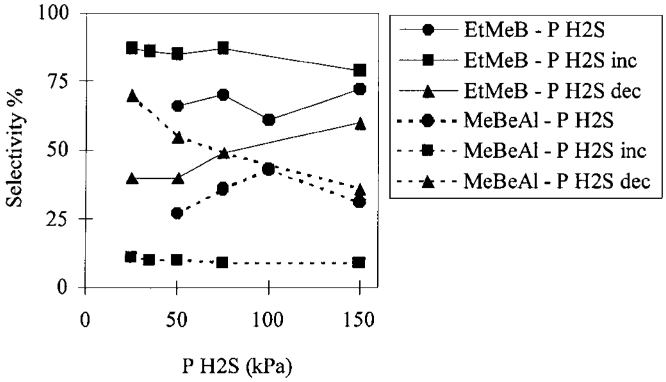

FIG. 6. Evolution of 4-ethylmethylbenzene (EtMeB) and α,4-dimethylbenzyl alcohol (MeBeAl) selectivities as a function of P_{H_2S} for the three series of experiments. Reaction temperature, 200°C. Total pressure, 7 MPa.

TABLE 4

GUA Conversion, Molar Balance, Phenol + C6 and Catechol Yields, and Phenol + C6/Cat Ratio in the Absence and in the Presence of DAP (P_{H_2S}, 100 kPa; Reaction Temperature, 270°C; Total Pressure, 7 MPa)

DAP concentration	Conv GUA (%)	Molar balance (%)	Yield (%) Phenol*	Yield (%) Catechol	Ph*/Cat ratio
0 mol l^{-1a}	21	57	7.1	4.7	1.5
0 mol l^{-1}	23	62	10.1	4.1	2.5
0.034 mol l^{-1}	12	32	2.8	1.1	2.5

[a] Results obtained with a catalyst with the same composition, but prepared at a different time and used in the series of tests for the study of the influence of the hydrogen sulfide partial pressure.

3.3. *Influence of a Basic Nitrogen Compound: Diaminopropane (DAP)*

The GUA conversion and the molar balance deficit sharply decreased (by about 50%) when DAP was added (Table 4). The phenol + C6 ratio did not seem to be affected. ED conversion decreased when DAP was added (Table 5). Decanoic acid yields were not affected, but the decarboxylation selectivity strongly decreased. The conversion of MA increased when DAP was added (Table 6), but the molar balance was largely deficient and some unidentified peaks appeared in the chromatogram. However, even if identified, they cannot account for the molar balance deficit as their area is very small.

4. DISCUSSION

4.1. *Thermal and Catalytic Reaction of DMDS*

In the literature, it is reported that disulfides decompose easily (26). DMDS decomposes more easily than DMS in the presence of hydrogen, under atmospheric pressure on hydrotreating catalysts, producing primarily methylmercaptan at a temperature as low as 170°C; the maximum yields reach 70% at 220°C while hydrogen sulfide production starts at about 200°C. Under pressure, the decomposition of DMDS into Methylemercaptan can start even at lower temperature (27). Our results confirm that in the presence of a sulfided CoMo/C catalyst the decomposition of DMDS starts below 150°C and we calculated the P_{H_2S} values considering that DMDS completely decomposes into H_2S.

4.2. *The Influences of the Hydrogen Sulfide Partial Pressure and of the Presence of Diaminopropane on the HDO Activity: Identification of the Active Sites Involved in HDO Reactions*

We will compare our results with those obtained with alumina-supported catalysts, presented previously (9, 21, 22).

TABLE 5

ED Conversion, Molar Balance, Nonane, Decane + Decene, Decanol, and Decanoic Acid Yields, and Decarboxylation Selectivity in the Absence and in the Presence of DAP (P_{H_2S}, 100 kPa; Reaction Temperature, 270°C; Total Pressure, 7 MPa)

DAP concentration	Conv ED (%)	Molar balance (%)	Yield (%)				Decarboxylation S (%)
			Nonane	Decane + decene	Decanol	Decanoic acid	
0 mol l^{-1a}	23	96	5.9	12.5	2.5	2.5	28.3
0 mol l^{-1}	27	102	5.4	16.1	3.6	2.1	21.4
0.034 mol l^{-1}	8	88	0.3	3.7	1.0	2.2	5.8

[a] Results obtained with a catalyst with the same composition, but prepared at a different time and used in the series of tests for the study of the influence of the hydrogen sulfide partial pressure.

4.2.1. Guaiacol. The conversion of GUA initially involves the breaking of the O–methyl bond (demethylation) to give catechol. The reaction then proceeds through hydrogenolysis of the $C_{aromatic}$–O bond (dehydroxylation), first to phenol and then to benzene, cyclohexene, and cyclohexane (21, 28, 29). Phenol can also be directly formed from guaiacol by a demethoxylation reaction (hydrogenolysis of the $C_{aromatic}$–O bond) (30). In our experiments the main products were catechol, phenol or cyclohexene, and cyclohexene.

Previous results indicated that the HDO of 4-methylphenol to toluene over sulfided CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts is strongly inhibited by hydrogen sulfide (9) whereas the demethylation of GUA was not affected by hydrogen sulfide, nor by water. These results tend to exclude the participation of Brønsted acid sites. Actually it is reasonable to expect that Brønsted acidity increases by adsorption of water and especially hydrogen sulfide. In contrast, a strong inhibition by ammonia, combined with the fact that alumina alone had some activity for GUA conversion (about half that of the sulfided CoMo catalyst), giving catechol as single product, indicated that the acid sites of the alumina support (C_S sites) were mainly responsible for demethylation. Compared to alumina, carbon-supported catalysts are less active for the breaking of the O–methyl bond, but more active for the $C_{aromatic}$–O bond hydrogenolysis. With the CoMo/C catalyst, the total GUA conversion is constant, but the formation of dehydroxylated products, phenol and C6, decreased with increasing the hydrogen sulfide partial pressure. A molar balance deficit was always observed and not influenced by the increase of the hydrogen sulfide partial pressure. A previous work (24) showed that phenolic-type molecules with two or more oxygenated substituents are the major cause of coke formation during HDO of bio-oils on alumina-supported catalysts. The mechanism involved would be similar to that responsible for the synthesis of phenol–formaldehyde resins.

TABLE 6

MA Conversion, Molar Balance, and 4-Ethylmethylbenzene and α,4-Dimethylbenzyl Alcohol Yields in the Absence and in the Presence of DAP (P_{H_2S}, 100 kPa; Reaction Temperature, 200°C; Total Pressure, 7 MPa)

DAP concentration	Conv MA (%)	Molar balance (%)	Yield (%)	
			EtMeB	MeBeAl
0 mol l^{-1a}	21	99	12.3	8.6
0 mol l^{-1}	13	108	8.4	5.5
0.034 mol l^{-1}	45	36	15.5	0.8

[a] Results obtained with a catalyst with the same composition, but prepared at a different time and used in the series of tests for the study of the influence of the hydrogen sulfide partial pressure.

As for the formation of dehydroxylated products, it is logical to consider possible analogies between the breaking of the C–O and C–S bonds. Hydrogenolysis reactions are always more inhibited than hydrogenation ones. The cleavage of the $C_{aromatic}$–O bond thus seems to correspond to a hydrogenolysis reaction and it would take place on strongly reduced molybdenum atoms with a high degree of coordinative unsaturation (B sites). Upon increasing the hydrogen sulfide partial pressure, the average degree of reduction and the coordinative unsaturation of the active sites decrease and the hydrogenolysis of $C_{aromatic}$–heteroatoms bonds is consequently inhibited. Two different hypotheses about the reaction and the active sites involved may be proposed. If demethylation is considered as the first reaction step and only a consecutive pathway is assumed for the transformation of GUA to catechol and then to phenol, it must be excluded that this reaction involves "classical" hydrogenation or hydrogenolysis sites (A or B sites), or acid sites on the metal sulfide (C_M sites). In the first case the conversion would be inhibited by an increase of hydrogen sulfide, while in the second case it would be enhanced. In the case of carbon-supported catalyst, as nonoxidized carbon contains very low amounts of phenolic and carboxylic acid groups (31) and the the overall acidity in the support (the total number of acid sites is less than 5.3 mequiv/g of which 90% correspond to weak acid sites) is very low, we assume there is no contribution to the activity from the support. A first speculative interpretation would be that the breaking of the O–methyl bond is a sort of hydrocracking reaction, involving H^+ and H^- species, generated by a heterolytic scission of hydrogen on the sulfided phase. The positively charged H^+ would attack the O atom of the methoxy group, which carries a partial negative charge. The H^- would attack the carbon, which is partially positively charged.

A second possible interpretation of the results is to consider that parallel pathways are operating in the conversion of GUA: the demethylation to catechol and the demethoxylation to phenol occurring at the same rate on the carbon-supported catalyst (30). Even if the breaking of the O–methyl bond should be easier than the hydrogenolysis of the $C_{aromatic}$–O bond, several authors have supposed that the direct demethoxylation can take place even on alumina-supported catalysts (28, 29). However, in that case, Lewis acid sites on the support would be much more numerous than the demethylation and demethoxylation sites on the sulfided phase. The dominant effect would be that of the support acidity, with no notable influence of hydrogen sulfide on GUA conversion. When alumina is replaced by carbon, Lewis acidity is not present any more, and all the reactions take place on the sulfided phase. As the support does not contribute to the activity, distinction between sites responsible for the demethoxylation and dehydroxylation would be possible. In this case the most coherent hypothesis would be that demethylation involves H^+ and sulfhydryl groups (C_M), while demethoxylation, like dehydroxylation, takes place on highly reduced, uncoordinated molybdenum atoms. At increasing P_{H_2S}, hydrogen sulfide would adsorb on molybdenum vacancies, with the formation of H^+ and sulfhydryl groups; the demethylation reaction would consequently be enhanced, while the cleavage of the $C_{aromatic}$–O bonds is inhibited. The GUA conversion would thus be approximately constant, while the phenol + C6/catechol ratio would decrease.

The addition of DAP decreases both the demethylation and the demethoxylation/dehydroxylation reactions. This is logical, as this basic compound can poison sulfhydryl and H^+ species as well as reduced, uncoordinated molybdenum atoms. With increasing hydrogen sulfide partial pressure an adsorption or reaction of hydrogen sulfide takes place on the hydrogenolysis sites; uncoordinated sites would be progressively transformed into blocked sites. When the hydrogen sulfide partial pressure is abruptly decreased, the hydrogenolysis activity is only partially recovered. The formation of the incompletely coordinated sites is a relatively slow process. When the hydrogen sulfide partial pressure is decreased stepwise from 150 to 25 kPa, hydrogenolysis sites are progressively generated; the more reductive atmosphere could render them more stable. These observations confirm that sulfided catalysts are very flexible and can adapt to different reaction conditions.

4.2.2. Ethyl decanoate. The effect of hydrogen sulfide on ED conversion is less marked than that observed on alumina-supported catalysts (22). At low P_{H_2S} the amount of decarboxylated products slightly increases and the dehydration of decanol to decene and decane is favoured. The hydrogenation of the carboxylic group into alcohol is almost constant; the sum of decanol, decene, and decane is unchanged.

In principle, the de-esterification should be an acid-catalysed reaction (C_M sites), while the hydrogenation of the carboxylic group to alcohol should involve hydrogenation sites (A sites). It is astonishing that hydrogen sulfide does not inhibit this reaction as does the conversion of MA. A compensation between an increase of acid sites (sulfhydryl species, C_M) and a decrease of hydrogenation sites (uncoordinated molybdenum atoms, A) due to hydrogen sulfide could result in an overall constant ED conversion and hydrogenated products yield. The promotion effect of hydrogen sulfide on the transformation of decanol into decene and decane and the weak increase of nonane would indicate that acid sites, present on the metal sulfides as–SH groups, are involved (C_M) in these reactions.

The inhibition effect of diaminopropane also confirms that acid sites are involved in the conversion of ED. The decarboxylation reaction would take place on more electrophilic sites than the hydrogenation one as it is more strongly inhibited.

Using the same kind of arguments as for the reaction of GUA, it could be speculated that an increase of the hydrogen sulfide partial pressure would relatively rapidly enhance the acidity of the sulfided phase by adsorption of hydrogen sulfide and formation of sulfhydryl groups.

4.2.3. 4-Methylacetophenone. The inhibition by hydrogen sulfide could have been interpreted as the participation of partially reduced sites, located on incompletely coordinated molybdenum atoms. The fact that ammonia had almost no influence on this reaction suggested that the ketonic group does not adsorb on electrophilic sites. It was shown (9) that uncoordinated sites have an electrophilic character and that they are even more strongly inhibited by ammonia than by hydrogen sulfide. Two mechanisms were therefore proposed by Laurent and Delmon (22), involving the participation of nucleophilic species. According to the first, the carbonyl group could adsorb through the carbon atom on a nucleophilic sulfur atom, and the reaction would proceed through the addition of a proton on the negative oxygen atom and subsequently the addition of a hydrogen atom on the carbon. This second hydrogen atom would be nucleophilic like a sorbed hydrogen species or a hydrogen atom bonded to molybdenum (hydride species). The second possible mechanism supposed that the carbonyl group

TABLE 7

Four Kinds of Active Sites have been Tentatively Identified: (A) Three-Fold Coordinatively Unsaturated Mo Atoms (Hydrogenation), (B) Three-Fold Coordinatively Unsaturated Mo Atom with a Sulfhydryl Group (–SH) Neighbour (Hydrogenolysis Sites, Cleavage of the Heteroatom–Carbon Bonds), (C_S) Acid Sites of the Support, and (C_M) Acid Sites on the Metal Sulfide, Sulfhydryl Groups (–SH)

	$CoMo/Al_2O_3$–$NiMo/Al_2O_3$		CoMo/C	
	NH_3 (0–200 kPa)	H_2S (0–400 kPa)	DAP	H_2S (25–150 kPa)
4-Methylphenol hydrogenation	↓ (A)	↓ (A)		
4-Methylphenol hydrogenolysis	↓↓ (B)	↓↓ (B)		
GUA Conv	↓	=	↓	=
Catechol	Not reported	↓ (C_S)	↓	↑ (C_M)
Phenol + C6	Not reported	↓↓ (B)	↓	↓ (B)
Phenol + C6/Cat ratio	Not reported	↓	=	↓
DES or ED conv	↓	↑	↓	=
Decarboxylation *S*	↓	↑	↓	↑ =
C-10	↓	↑ (A)	↓	= (↑) ($A + C_M$)
C-9	↓↓	↑↑ (C_M)	↓↓	↑ = (C_M)
MA Conv	=	↓	(?)	↓ ($A + C_M$)

might react in a "pre-adsorbed" state with an activated hydride species. The effect of hydrogen sulfide would have been to modify the ability of the active phase to form hydride species and thus to inhibit the conversion.

Decanol is more easily dehydrated into decene and decane at increasing hydrogen sulfide partial pressure. With the increase of P_{H_2S}, hydrogen sulfide would adsorb on hydrogenation sites (partially reduced and uncoordinated molybdenum atoms): the first hydrogenation step of the carbonyl group into the alcohol would be inhibited (sites A), with a decrease of MA conversion, while the dehydration of the alcohol would be favored by the acidity of the sulfhydryl groups (sites C_M) (32).

With regard to the influence of diaminopropane, the high increase of the conversion and the large molar balance deficit, which is unusual for the reaction of MA, suggest that side phenomena take place. Diaminopropane could interact with the decomposition products of dimethyl disulfide and form amine polysulfides (33).

The results are summarised in Table 7 and allow us to compare carbon and alumina support catalysts. Arrows indicate whether the mentioned conversion or selectivity increases (↑) or decreases (↓) when a parameter is modified.

A full agreement exists among the results of the different investigations concerning the inhibition by hydrogen sulfide of the reactions involving the cleavage of $C_{aromatic}$–O bond and on the hydrogenation of the carbonyl group of MA. The role of coordinatively unsaturated molybdenum atoms, probably differing in the degree of reduction and uncoordination, has been confirmed and explained.

5. CONCLUSIONS

The activity of sulfided CoMo/C catalyst is deeply affected by modifications of the hydrogen sulfide partial pressure; when the initial conditions are restored the catalyst is able to regain, at least in part, its activity.

Hydrogen sulfide does not affect the activity of the CoMo/C catalyst for the overall conversion of GUA. With regard to the products, hydrogen sulfide inhibits the direct hydrogenolysis of the $C_{aromatic}$–O bond, and the phenol + C6-to-catechol ratio is consequently decreased. Highly reduced, coordinatively unsaturated sites, located on the metal sulfides, are very likely responsible for the hydrogenolysis of the $C_{aromatic}$–O bond. The decrease of the H_2/H_2S ratio decreases the average degree of reduction of the active sites; phenol production is consequently inhibited. Acid species that can be located on the sulfide phase as well as generated by heterolytic dissociation of hydrogen would be responsible for the demethylation of GUA to catechol.

For ED, the conversion is not influenced by hydrogen sulfide, and the selectivity in hydrogenated and decarboxylated products is slightly changed. Diaminopropane decreases both the ED conversion and the decarboxylation selectivity. Hydrogenation and acid sites located on the metal sulfides are involved in these reactions; parallel and consecutive pathways are simultaneously possible, and thus the overall effect of hydrogen sulfide is not very marked.

MA is the only reactant molecule whose conversion is inhibited by hydrogen sulfide. Reduced and incompletely coordinated molybdenum atoms are likely involved in the hydrogenation of the carbonyl group, while sulfhydryl acid species would be responsible for the dehydration of the alcohol.

ACKNOWLEDGMENTS

This work was carried out as part of the UE project JOR3-CT95-0025. We also acknowledge the FRNS (Belgium) for financial support.

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