

Effect of hydrogen sulphide on the hydrodeoxygenation of aromatic and aliphatic oxygenates on sulphided catalysts

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Abstract

A sulphiding agent added to maintain catalyst activity affects hydrodeoxygenation (HDO) of bio-oils. Aromatic compounds are dominant oxygenates in wood-based biofuels, and aliphatic oxygenates in vegetable oils and animal fats. The effects of H₂S on the HDO of aromatic and aliphatic oxygenates on sulphided NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃ catalysts were compared in liquid and gas phases.

Direct hydrogenolysis and hydrogenation reactions played a major role in the HDO of phenol. H₂S suppressed these reactions on the NiMo catalyst and mainly direct hydrogenolysis on the CoMo catalyst, inhibiting thereby the HDO of phenol. The inhibition by H₂S was attributed to the competitive adsorption of phenol and H₂S. The effect was in contrast to the promoting effect of H₂S on the HDO of aliphatic oxygenates, in which acid-catalysed and hydrogenation reactions predominate. The differences were attributed to the different reaction mechanisms due to the distinct molecular and electronic structures of aromatic and aliphatic oxygenates. Phenol was found to be less reactive than aliphatic oxygenates. Further, the NiMo catalyst exhibited lower activity for the HDO of phenol than did the CoMo catalyst, while the reverse was the case for the HDO of aliphatic oxygenates.

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Keywords: Biofuel; Hydrodeoxygenation; Aromatic oxygenate; Aliphatic oxygenate; Hydrogen sulphide; Sulphided catalyst

1. Introduction

The target set by the European Union for increasing the share of biofuels in traffic fuels to 2% by the end of 2005 was not achieved [1,2]. Research and development efforts aimed at producing cost-competitive biofuels on large scale need to receive substantial support if the new technologies are to succeed.

Wood, vegetable oils and animal fats are possible raw materials for the production of biofuels. The next generation biofuels will involve the conversion of the raw material to liquid followed by an upgrading process. Biofuels contain high content of oxygen (10–50 wt.%), present in both aromatic and aliphatic structures, which vary with the origin of the oil [3,4]. For example, wood-based biofuels contain mainly aromatics like phenolic and furanic compounds. Vegetable oils and animal fats comprise triglycerides. High oxygen content leads to deleterious properties such as high viscosity, thermal and chemical instability, and

immiscibility with hydrocarbon fuels [3–5]. The oxygen content of biofuels needs to be reduced, therefore.

The traditional hydrotreating processes used in oil refining can provide a solution for the upgrading of bio-oils [3,5]. As the heteroatom to be removed from the oil is oxygen, and the oxygen is eliminated in the form of water in the presence of hydrogen, the process is called hydrodeoxygenation (HDO). The typical catalysts, such as alumina-supported nickel-molybdenum or cobalt-molybdenum, are more active in sulphided form than in oxide form, and oxygenates present in bio-oils affect the sulphide structure negatively. Moreover, since the sulphur content of bio-oils is low, a sulphiding agent must be added to the feed to maintain the sulphidation degree of the catalyst [4]. Various studies have indicated that sulphiding agents affect the HDO process differently depending on feed composition and process conditions. For example, the addition of a sulphiding agent to a bio-oil has generally been found to suppress the HDO of phenolic and furanic compounds on sulphided NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts [6–10], but a promoting effect has been demonstrated in HDO studies with aliphatic oxygenates, such as esters and carboxylic acids on similar catalysts [11,12].

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Considerable attention has been paid to the HDO of phenolic and furanic compounds, but the results from different studies have not been mutually consistent because of differences in the experimental conditions. It is important therefore to clarify the HDO reactions of different bio-oil components and the effect of sulphiding agents on the reactions in order to allow optimisation of the HDO process conditions for a particular feed and product quality. In the present study, we explored the effects of sulphiding agents on the HDO performance of aromatic oxygenates. Phenol was selected as the model for aromatic oxygenates, and its reactions on sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts were studied in liquid and gas phases with batch and flow reactors, respectively. The effect of H₂S on the reactions of phenol was determined by adding H₂S at various concentrations. Additional experiments were carried out with benzene, cyclohexanone and cyclohexanol. To further elucidate the effect of sulphiding agents, the results were compared with our previous findings regarding the HDO of aliphatic oxygen-containing compounds under similar conditions [12,13].

2. Experimental

Commercial NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ hydrotreating catalysts were crushed and sieved to a fraction of 0.59–0.75 mm and used in presulphided form.

The batch reactor was a 50 ml autoclave equipped with a fixed catalyst basket and a magnetic stirrer. A batch of catalyst (0.5 g) was packed into the catalyst basket and activated in situ at 350 °C under atmospheric pressure, as described previously [13]. The reactants and their concentrations in the reaction mixture (volume 16 ml) are listed in Table 1. Experiments were carried out at 250 °C under 7.5 MPa pressure. Liquid samples for analysis were withdrawn from the bottom of the reactor. No hydrogen was added to the reactor during the runs, and a maximum of five samples were removed in each run in order to avoid excessive pressure and volume changes in the reactor. The vapour–liquid phase equilibrium was assumed to be unaffected by sampling, and the results are discussed on the basis of the liquid-phase compositions.

Table 1
Origin and concentration of chemicals used in the HDO experiments

Chemical	Supplier	Composition (wt.%)	
		Batch reactor ^a	Flow reactor ^b
Reactant^c			
Phenol	J.T. Baker, lab. grade	3	3
Cyclohexanone	Fluka, >99%	–	3
Cyclohexanol	Aldrich, 99%	2	3
Benzene	Fluka, >99.5	1	–
<i>n</i> -Decane (standard)	Sigma, >99%	1	–
<i>m</i> -Xylene (solvent)	Merck, >99%	96–98%	97%

^a Composition in the reaction mixture.

^b Composition in the liquid feed.

^c Only one reactant was present in the feed.

For the gas-phase experiments, the catalyst was packed between two layers of silicon carbide (1–3 mm) in a tubular flow reactor made of stainless steel (i.d. 10 mm, length 380 mm), and the catalyst was activated at 400 °C under atmospheric pressure, as explained elsewhere [13]. Experiments were carried out at 250 °C under 1.5 MPa pressure. The concentration of H₂S (0–24,000 ppm) was adjusted by feeding pure hydrogen (AGA, 99.999%) and either 0.25 or 5 vol.% H₂S/H₂ mixture (AGA, 99.999%) at various flow rates by keeping the total gas flow rate constant at 2 l/h (NTP). The liquid feed, whose composition is presented in Table 1, was fed at a rate of 10 g/h (NTP). Liquid samples were removed at regular intervals for analysis.

The liquid samples from the reactors were analysed with a gas chromatograph (HP6890, flame ionisation detector, HP-1 column of dimensions 60 m × 0.25 mm and 1 μm film thickness). In addition, a few liquid samples were analysed qualitatively by GC/MS for identification of trace compounds. The gas outlet stream of the flow reactor was qualitatively analysed during the runs with an online gas chromatograph (HP5890A, thermal conductivity detector, HP-PLOT/U column of dimensions 30 m × 0.32 mm and 10 μm film thickness). The sulphur and carbon contents of catalysts were determined after the experiments with a sulphur-carbon analyser (LECO, SC-444).

Conversions, selectivities and yields were calculated on molar basis. Total conversion of a reactant was calculated as the ratio of the converted reactant to the reactant fed, and the HDO conversion was the fraction of the reactant converted to hydrocarbons. The selectivity was calculated as the ratio of a product to the converted reactant, and the reaction yield was defined as the product of the total conversion and the selectivity.

3. Results and discussion

Repeated experiments in both flow and batch reactors showed the conversion and selectivity values to vary within ±2 percentage units, indicating good reproducibility of the experimental data.

3.1. Reactions of phenol on sulphided catalysts

Reaction products of phenol detected in the liquid samples from batch and flow reactors included aromatic and alicyclic hydrocarbons and a few oxygen-containing compounds. The HDO products of phenol were benzene, cyclohexane and cyclohexene, while oxygen-containing compounds were cyclohexanone and diphenyl ether. In addition, in the presence of H₂S, a sulphur-containing compound, cyclohexanethiol, was detected. The oxygen- and sulphur-containing compounds were formed in trace amounts.

Concentration profiles of the hydrocarbons as a function of time (Fig. 1) indicated that benzene and alicyclic hydrocarbons were formed in two parallel reactions in which benzene and cyclohexane appeared as the end products, as described earlier [6–8,14]. The formation of an intermediate, cyclohexanol, from phenol in trace amounts via hydrogenation of the aromatic ring before rupture of the C–O σ-bond has been reported [6,10], but we did not detect cyclohexanol in the liquid sam-

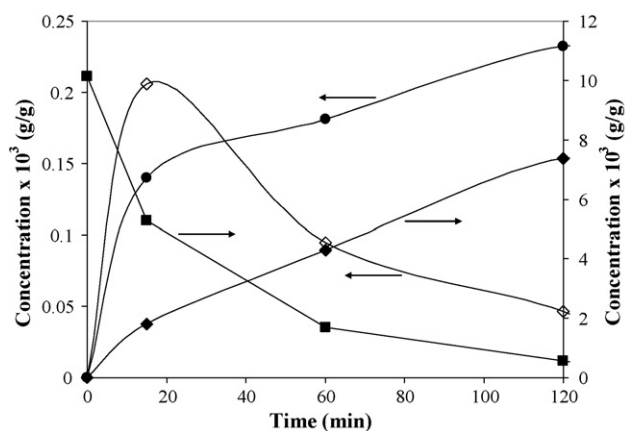


Fig. 1. Concentration profiles of phenol (■), benzene (●), cyclohexane (◆) and cyclohexene (◇) in the absence of H_2S at $250^\circ C$ under 7.5 MPa pressure in the batch reactor studies with $NiMo/\gamma-Al_2O_3$.

ples. Nevertheless, the formation of cyclohexanone suggested hydrogenation of the aromatic ring before the formation of alicyclic hydrocarbons. Cyclohexanone contains a $C=O$ π -bond, and a hydrogenation step before the elimination of the oxygen atom and the formation of cyclohexanol as intermediate would be expected. Experiments with cyclohexanone and cyclohexanol were performed in order to determine whether these oxygenates were intermediates in routes to both aromatic and alicyclic hydrocarbons. Since cyclohexane and cyclohexene were the only HDO products of cyclohexanone and cyclohexanol, we concluded that cyclohexanone and cyclohexanol are possible intermediates in the formation of alicyclic hydrocarbons but not in the formation of benzene. The conversions of both cyclohexanone and cyclohexanol were complete in gas-phase experiments, indicating the high reactivity of these compounds on the sulphided catalysts under the studied conditions. In the batch reactor studies, the concentration profiles for cyclohexane and cyclohexene produced from cyclohexanol as a function of time (Fig. 2) suggested that the formation of cyclohexene from cyclohexanol is followed by the formation of cyclohexane.

Reactions of benzene on the sulphided catalysts were studied in the batch reactor. The formation of cyclohexane and cyclohexene in trace amounts was detected on both catalysts, indicating the hydrogenation of benzene. However, the conversion of ben-

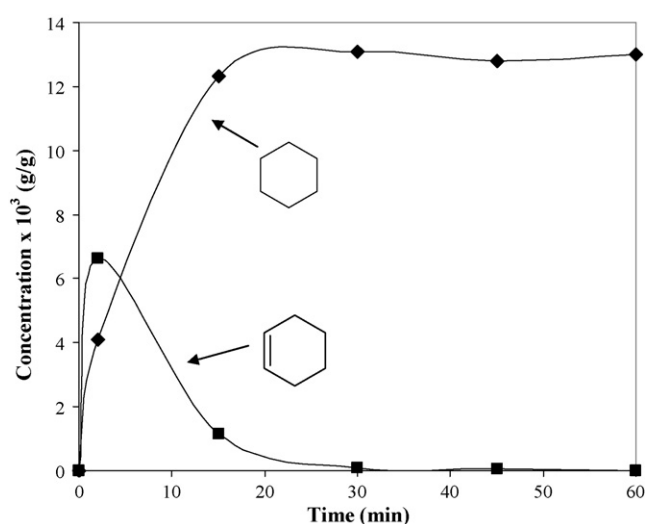


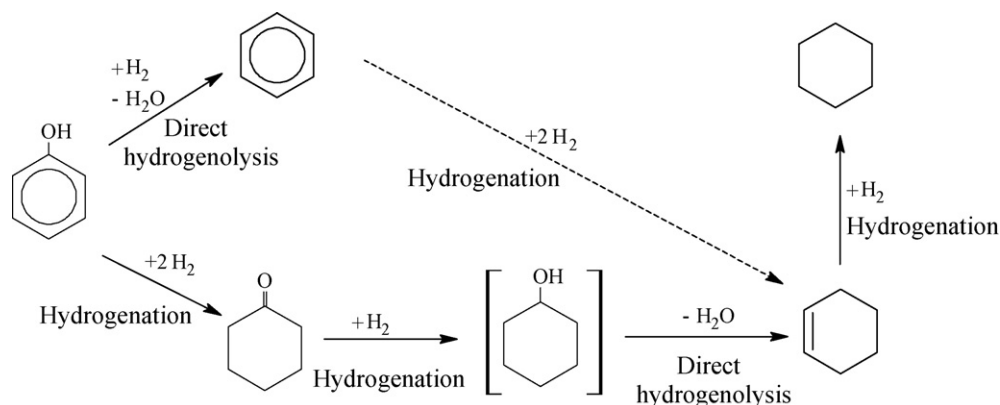
Fig. 2. Concentration profiles of cyclohexane and cyclohexene in the reactions of cyclohexanol on $NiMo/\gamma-Al_2O_3$ catalyst at $250^\circ C$ under 7.5 MPa pressure in the batch reactor.

zene to alicyclic hydrocarbons at the end of a 60 min run was less than 1.5%, and the hydrogenation of benzene was concluded to be negligible under the studied conditions.

A reaction scheme for the HDO of phenol was proposed on the basis of these findings (Scheme 1). The reaction scheme is in good agreement with the results of previous studies in our laboratory [6,7,15]. In the present work, however, the formation of cyclohexanone as intermediate before the formation of alicyclic hydrocarbons was revealed. The hydrogenation of benzene is shown in Scheme 1 with a dashed reaction arrow since it was insignificant under the studied conditions. The reaction scheme and formation of cyclohexanethiol are discussed below where the effect of H_2S on the product distribution is of interest.

3.2. Effect of H_2S on the reactions of phenol

In both the absence and presence of H_2S in the flow reactor, the main products of HDO of phenol under the studied conditions were cyclohexane on the $NiMo$ catalyst and benzene on the $CoMo$ catalyst, and the yield of cyclohexene never exceeded 2% on either catalysts. The predominant formation of



Scheme 1. Reaction scheme for the HDO of phenol on sulphided catalysts.

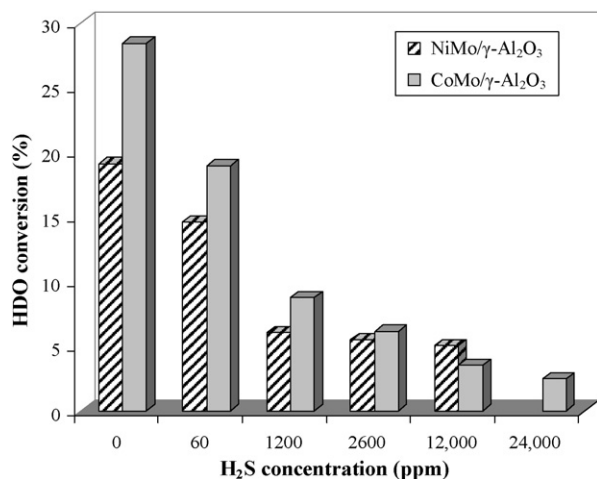


Fig. 3. Effect of H₂S on the HDO conversion of phenol on sulphidated catalysts at 250 °C under 1.5 MPa pressure in the flow reactor.

cyclohexane on the NiMo catalyst is in good agreement with the high hydrogenation activity of this catalyst [16]. When no H₂S was added, the HDO conversions of phenol in the gas-phase experiments were 19% on the NiMo catalyst and 28% on the CoMo catalysts, revealing the lower activity of the former than the latter catalyst for the HDO of phenol. On both catalysts, the HDO conversion of phenol decreased with increasing H₂S concentration in the feed, as seen in Fig. 3, and as a result the yields of both aromatic and alicyclic hydrocarbons dropped, as seen in Fig. 4. The results clearly indicate that H₂S has an inhibiting effect on the routes to both aromatic and alicyclic hydrocarbons. The degree of inhibition can be better understood by evaluating the molar ratios of aromatic to alicyclic hydrocarbons. The addition of sulphiding agent reduced these ratios. The decrease was minor with the NiMo catalyst, indicating that the degrees of inhibition of the routes to aromatic and alicyclic hydrocarbons were about the same. With the CoMo catalyst, the molar ratio was above 9.0 in the absence of H₂S and dropped to below 1.0 in the presence of 24,000 ppm H₂S. Clearly, H₂S strongly suppressed the route to benzene on the CoMo catalyst. It has been reported earlier that the addition of sulphiding agents suppresses the formation of both aromatic and alicyclic

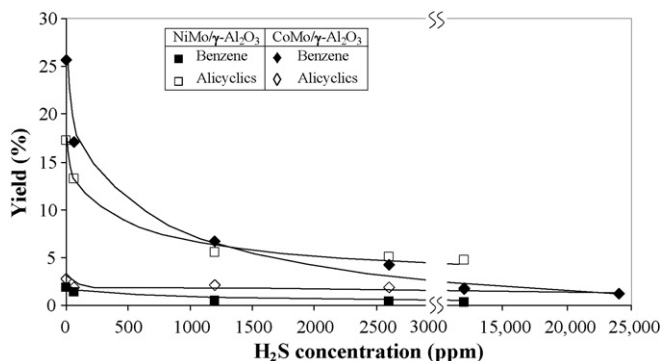


Fig. 4. Effect of H₂S on the yields of benzene and alicyclic hydrocarbons in the reactions of phenol on sulphidated catalysts at 250 °C under 1.5 MPa pressure in the flow reactor.

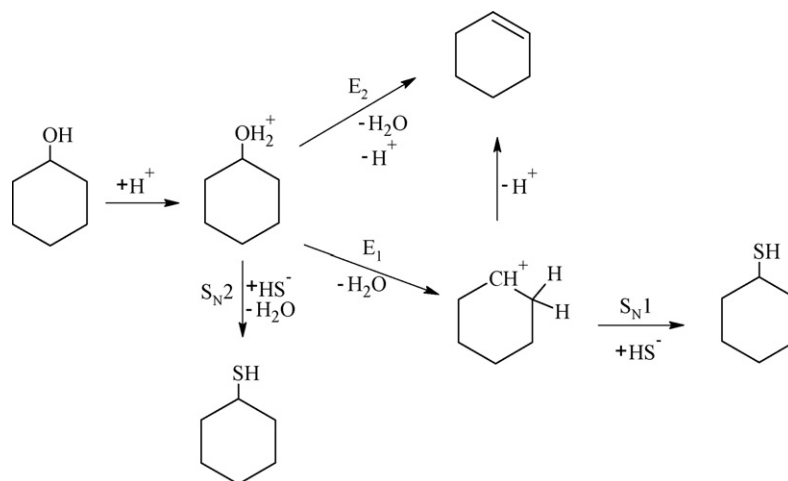
hydrocarbons from phenol and mono- and dimethyl-substituted phenols on sulphidated NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts [6–8,10]. Further, the effect on the formation of alicyclic hydrocarbons has been reported to be stronger with the NiMo than the CoMo catalyst.

Since the catalysts are more active in sulphidated form than in oxide form, the degree of sulphidation is likely an important factor for the catalyst performance. Further, coke formation can deactivate catalysts [17]. The sulphur and carbon contents of the catalysts before and after the reactions were of interest, therefore. The sulphur content of the catalysts after presulphidation was 7.0 ± 0.3 wt.% in the flow reactor and 5.8 ± 0.3 wt.% in the batch reactor. In both the absence and presence of H₂S, the sulphur content was almost unchanged after the reactions. Meanwhile, the carbon content in the flow reactor studies increased up to 5.0–6.0 wt.% independently of the H₂S concentration.

As presented above, two HDO paths lead to the formation of hydrocarbons (Scheme 1): one yields benzene directly from phenol and the other alicyclic hydrocarbons after hydrogenation of the aromatic ring of phenol. In principle, rupture of the C–O σ-bond can occur by dehydration reaction and by direct hydrogenolysis reaction, involving simultaneous oxygen cleavage and hydrogenation. However, the dehydration reaction, which is an acid-catalysed elimination reaction, can take place only if both α- and β-carbon atoms with respect to the oxygen atom are saturated [18]. Since neither of these atoms is saturated in the phenol molecule, benzene could not be formed by the dehydration reaction.

Coordinatively unsaturated sites (CUS) associated with MoS₂ phase, i.e. sulphur anion vacancies, on sulphidated catalysts are generally accepted to be the active sites for hydroprocessing reactions [4,16]. Similarly, these sites might be the catalytic centres for the direct hydrogenolysis reaction, in which adsorption of phenol on CUS through its oxygen atom is followed by simultaneous C–O σ-bond cleavage and hydrogenation, yielding benzene and water. Thus, the inhibiting effect of H₂S can be interpreted in terms of the competitive adsorption of phenol and H₂S on the catalytic sites.

Since both α- and β-carbon atoms with respect to the oxygen atom are saturated in alicyclic oxygen-containing compounds, alicyclic hydrocarbons can be formed not only by the direct hydrogenolysis reaction but also by the dehydration reaction, which may occur by E₁ and E₂ elimination mechanisms, as shown in Scheme 2. Additional experiments with cyclohexanol in the absence and presence of a sulphiding agent were carried out to determine the contribution of dehydration and direct hydrogenolysis reactions to the formation of alicyclic hydrocarbons. In the batch reactor, the addition of 3800 ppm sulphiding agent to a reaction mixture containing 2 wt.% cyclohexanol caused the HDO conversion of cyclohexanol to decrease by about 7 percentage units at the end of a 60 min run. Clearly, the formation of alicyclic hydrocarbons was suppressed by the presence of sulphiding agent, as was the formation of benzene from phenol. We conclude that the direct hydrogenolysis reaction plays a major role in the formation of alicyclic hydrocarbons, and further that the same catalytic sites are involved in the formation of aromatic and alicyclic hydrocarbons.



Scheme 2. Formations of cyclohexene and cyclohexanethiol by elimination and nucleophilic substitution reactions, respectively.

Cyclohexanethiol can be formed by acid-catalysed S_N1 and S_N2 nucleophilic substitution reactions, as shown in Scheme 2, and it may react very quickly to cyclohexene via elimination of H_2S . The SH^- groups present on the catalyst surface may act as nucleophiles. Since the concentration of the nucleophile is a governing factor in acid-catalysed nucleophilic substitution reactions [19], the increased concentration of the nucleophiles in the presence of H_2S could be expected to allow the formation of cyclohexanethiol. This may explain why the thiol was detected only in the presence of sulphiding agent.

To determine the effect of H_2S on the hydrogenation reactions occurring in the HDO of phenol, we plotted the molar ratio of cyclohexane to cyclohexene in the flow reactor experiments as a function of H_2S concentration. As shown in Fig. 5, the addition of H_2S reduced the molar ratio of cyclohexane to cyclohexene on the NiMo catalyst. The ratio was above 9.0 in the absence of H_2S and dropped to below 2.0 in the presence of 12,000 ppm H_2S . On the CoMo catalyst, in contrast, the molar ratio was not noticeably affected by the addition of H_2S (Fig. 5). Similar results were obtained in the experiment with cyclohex-

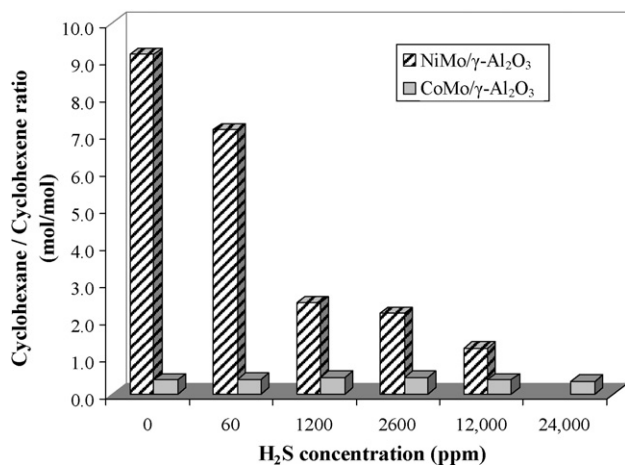


Fig. 5. Effect of H_2S on the molar ratios of cyclohexane to cyclohexene in the reactions of phenol on sulphided catalysts at 250 °C under 1.5 MPa pressure in the flow reactor.

anol in the absence and presence of the sulphiding agent. The conversion of cyclohexanol on the NiMo catalyst in the flow reactor experiments was complete in both absence and presence of 24,000 ppm H_2S in the feed. In the absence of H_2S , the main product was cyclohexane, and the addition of 24,000 ppm H_2S shifted the main product to cyclohexene. Evidently, the hydrogenation reactions were inhibited on the NiMo catalyst, but were not appreciably on the CoMo catalyst. Similarly, H_2S has been reported to inhibit the hydrogenation reactions in the case of sulphided NiMo/ Al_2O_3 catalysts and to have an insignificant effect in the case of sulphided CoMo/ Al_2O_3 catalysts [6,9,20–22].

3.3. HDO of aromatic versus aliphatic oxygenates

We have earlier carried out extensive studies on the HDO of methyl heptanoate, ethyl heptanoate, heptanol and heptanoic acid under the same conditions as employed in the present study [12,13]. Comparison of the HDO of phenol and these aliphatic oxygen-containing compounds reveals a clear difference in the reactivity on the sulphided catalysts. In both the absence and presence of sulphiding agent, the HDO conversion was noticeably higher for the aliphatic oxygenates than phenol, indicating a higher reactivity of the aliphatic oxygenates than the aromatic oxygenate on sulphided catalysts. In illustration of this, Fig. 6 compares the HDO conversions of methyl heptanoate and phenol. Fig. 6 also shows that, in both the absence and presence of H_2S , the NiMo catalyst is more active for the HDO of the methyl ester than is the CoMo catalyst. The opposite situation prevails for phenol HDO, showing, as noted also above, the difference in catalyst activities for the HDO of aromatic and aliphatic oxygenates.

The catalytic site for cleavage of the oxygen from the aliphatic oxygenates was concluded to be sulphur anion vacancies [12]. Since the same sites were proposed to catalyse the direct hydrogenolysis reactions, H_2S could be expected to have similar effects on the HDO of phenol and the aliphatic oxygenates. The different effects of the sulphiding agent on the HDO of aromatic and aliphatic oxygenates may be explained as follows. Hydrogenation reactions and acid-catalysed reactions

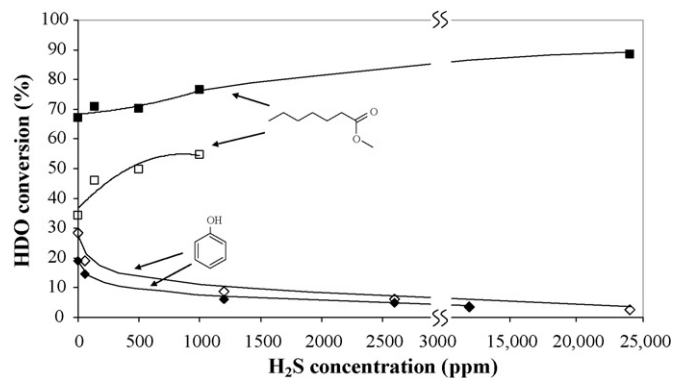


Fig. 6. Effect of H₂S concentration on the HDO conversions of methyl heptanoate and phenol on NiMo/γ-Al₂O₃ (■, ◆) and CoMo/γ-Al₂O₃ (□, ◇) catalysts in the gas phase at 250 °C under 1.5 MPa pressure. Data for the methyl ester was taken from ref. [12].

(hydrolysis, dehydration, esterification, E₂ elimination and S_N2 nucleophilic substitution) play a major role in the HDO of the aliphatic ester, alcohol, and carboxylic acid compounds [13]. The Brønsted acid sites were concluded, on the basis of the effects of H₂S, to be of importance for the acid-catalysed reactions. Several studies have shown that the dissociative adsorption of H₂S on sulphided catalysts increases the acidity of the catalysts [23–25]. Correspondingly, the promoting effect of H₂S was attributed to the increased catalyst acidity in the presence of H₂S [12]. The formation of hydrocarbons by direct hydrogenolysis reactions in the HDO of phenol is not, however, directly related to catalyst acidity but rather to the availability of the vacancy sites and hydrogen. Consequently, the divergent effects of the sulphiding agent on the HDO of the aromatic and aliphatic oxygenates were concluded to arise from the different reaction mechanisms, which are essentially influenced by the molecular and electron structures of aromatic and aliphatic oxygenates.

In the HDO of aliphatic oxygenates, the addition of H₂S was found to suppress the hydrogenation reactions on the NiMo catalyst and not to affect them on the CoMo catalysts [12]. Thus, the hydrogenation reactions were affected similarly in the HDO of phenol and aliphatic oxygenates.

The formation of sulphur-containing compounds, such as dimethyl sulphide, diheptyl sulphide, hexanethiol and heptanethiol, even in the absence of sulphiding agents in the feed were discovered in the HDO of aliphatic oxygenates [13]. This observation suggested a possible role of reactive sulphur species on the catalysts in the formation of sulphur-containing compounds. The situation was, however, not the same in the HDO of phenol, and a sulphur-containing compound was detected only when sulphiding agent was added to the reactor.

4. Conclusions

The results revealed that, under identical conditions, phenol is less reactive on the sulphided catalysts than are aliphatic oxygen-containing compounds such as ester, alcohol and carboxylic acid. Further, contrary to the activity for the HDO of aliphatic oxygenates, the activity for the HDO of phenol was higher with the CoMo catalyst than the NiMo catalyst. The

effect of the sulphiding agent on the HDO of phenol was opposite to its effect on the HDO of the aliphatic oxygenates. The addition of sulphiding agent enhanced the acid-catalysed reactions of aliphatic oxygenates such as dehydration and hydrolysis, while it suppressed the direct hydrogenolysis reaction of phenol due to competitive adsorption. Thus, the opposite effects can be explained in terms of the different reaction mechanisms for the elimination of oxygen, a difference that is related to the different molecular and electron structures of aromatic and aliphatic oxygenates.

In conclusion, this work indicates that the performance of the HDO process and the effect of the sulphiding agent added to the HDO feed to maintain catalyst activity and stability are dependent on the composition of the bio-oil feed. Addition of sulphiding agent to a wood-based HDO feed, which contains mainly phenolic compounds, will probably affect the total HDO negatively. In contrast, a promoting effect is likely for vegetable oils and animal fats, which contain mainly aliphatic oxygenates.

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