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Effect of H_2S on the stability of $CoMo/Al_2O_3$ catalysts during hydrodeoxygenation

T.-R. Viljava*, R.S. Komulainen, A.O.I. Krause

Department of Chemical Technology, Helsinki University of Technology, PO Box 6100, FIN-02015 HUT, Helsinki, Finland

Abstract

The effect of H_2S addition on the activity and the stability of CoMo catalyst during hydrotreating of phenol and anisole was studied. The presence of H_2S strongly decreased the HDO activity of the sulfided catalyst, and the ratio of the HDO reaction pathways depended on the H_2S concentration. The hydrogenolysis route to aromatics was suppressed, whereas the conversion of the hydrogenation–hydrogenolysis route to alicyclics at moderate H_2S concentrations remained the same as in the absence of H_2S. This clearly supports the presence of two types of active sites for HDO on the catalyst. Sulfidation of the catalyst was not a prerequisite for demethylation of anisole to phenol, though it increased the activity of the catalyst. Demethylation proceeded effectively even on the acidic sites of the Al_2O_3 support and on the sulfhydryl groups formed on CoMo catalyst in the presence of H_2S. In addition to desulfurization and changes in the structure of the active sulfided catalyst, the formation of coke and high molecular weight compounds on the catalyst decreased its activity but did not affect the selectivity of HDO.

Keywords: H_2S; $CoMo/Al_2O_3$ catalyst; Hydrodesulfurization; Hydrodeoxygenation; Sulfiding agents; Catalyst deactivation

1. Introduction

Interest in the development of renewable raw materials for fuel and chemical production has greatly increased during the last decades. Biomass is, environmentally, a very attractive substitute for oil due to its CO_2 neutrality and low sulfur and metal content. Furthermore, biomass is also available in many countries, which lack fossil raw material resources.

The composition of liquefied biomass is complex and varies with the raw material and the liquefaction method used [1]. Typically, these liquids contain high amounts of oxygen-containing compounds, and a reduction in the oxygen content is required to improve the properties of the liquids as well as to ensure their stability during storage. Hydrodesulfurization (HDS) has been an essential process in oil refining for a long time. A similar hydrotreating process (hydrodeoxygenation, HDO) can be used for upgrading biomass-based oils. Catalysts containing Mo as an active element and Co or Ni as a promoter on Al_2O_3 support have most often been used in HDS processes [2,3]. The catalysts are active in their sulfided form. These sulfide catalysts have also been observed to catalyze HDO [2,3].

Few investigations on HDO have been reported in the literature compared to HDS and hydrodenitrogenation (HDN) studies. HDO of phenols, typical representatives of the oxygen-containing compounds in liquefied biomass, is generally accepted to proceed via two parallel reaction pathways: the bond between the oxygen atom and the aromatic carbon can be broken giving aromatic products (direct hydrogenolysis route), or the aromatic ring can be hydrogenated before the rupture of the oxygen–carbon bond (com-

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* Corresponding author. Fax: +358-9-451-2622.
E-mail address: viljava@polte.hut.fi (T.-R. Viljava)

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bined hydrogenation–hydrogenolysis route) [3–5]. In the latter route, alicyclic products are formed and the corresponding alicyclic alcohols are probably formed as short-lived intermediates. Due to the ever-tightening environmental legislation, a decrease in the concentration of aromatics in liquid fuels is nowadays desired. For biomass-based raw materials, this makes the prehydrogenation pathway of HDO more advantageous in fuel production in spite of the higher H_2 consumption of the route.

The two reaction paths of HDO have been proposed to proceed on different kinds of active sites on the sulfided $CoMo/Al_2O_3$ catalyst [2,3,5–7]. These active sites have been presented to be associated with the molybdenum sulfide phase, but they differ in the degree of reduction. The hydrogenolysis sites have been suggested to have a higher affinity for electrons [6,7]. Interconversion of these active sites due to changes in the H_2S–H_2 ratio in the gas phase has been suggested in some papers [6–9]. In addition, acidic sites of the Al_2O_3 support, as well as sulfhydryl groups, play a role in the overall reaction pathways on $CoMo/Al_2O_3$ catalysts [2,10].

The effect of sulfur on HDO is, however, far from clear [2,3,11]. Though proved as an inhibitor of HDO, some H_2S is believed to be necessary during HDO to maintain the sulfidation level of the catalyst. The H_2S addition during the HDO of biomass-based liquids may be critical for the stability of the catalyst and for the selectivity of the process, since these liquids do not usually contain sulfur compounds capable of acting as resulfiding agents for the catalyst. One possibility to maintain the catalyst in its sulfided form during HDO could be simultaneous hydrotreating of biomass-based feeds with traditional oil-based feedstocks. However, on the basis of several studies in laboratory scale, competition between sulfur and oxygen removal decrease noticeably the efficiency of hydrotreating in that kind of operation [3,4,11].

The presence of H_2S strongly affects the selectivity of HDO and HDS [4,5,11–15]. Gevert et al. [5] have reported the hydrogenolysis route of HDO of methyl phenols on $CoMo/Al_2O_3$ catalyst to be more inhibited by H_2S than the hydrogenation–hydrogenolysis route. Our earlier studies [11] also revealed changes in the reaction selectivity when anisole was hydrotreated in the presence of small amounts of CS_2. Though the conversion of anisole to phenol increased with CS_2 added to the reactor, further HDO of the phenol intermediate was strongly inhibited. The experiments were, however, carried out in a batch reactor and the stability of the catalyst could not be examined.

It is obvious that more information is required about the role of sulfur compounds in HDO reactions and about the necessity of sulfiding agents for the stability of the catalyst. Therefore, we have studied the effect of the addition of H_2S on the presulfided CoMo catalyst during hydrotreating of oxygen-containing feeds to find out if an optimum concentration of H_2S in the feed can be found under which both the activity and the stability of the catalyst could be improved. The reactions were carried out in a flow reactor, and phenol and anisole were used as oxygen-containing model compounds. Though phenol is a very simple model compound for the oxygen-containing components of biomass-based liquids, its reactions give unambiguous information concerning the effect of reaction conditions on the reaction selectivity of HDO. In hydrotreating of anisole, the presence of the methoxy group causes an increase in the number of reaction paths typical for HDO of real feeds.

2. Experimental

The catalyst was a commercial HDS catalyst (Ketjenfine 742-1.3Q, Akzo Chemie) containing 4.4 wt.% of CoO and 15 wt.% of MoO_3 on γ-Al_2O_3. The catalyst was crushed and sieved to a fraction of 0.5–0.75 mm.

The catalyst (0.5 g) was packed into a flow reactor (ID=10 mm, L=380 mm) between two layers of silicon carbide. The catalyst was calcined *in situ* at 400°C under N_2 for 2 h. After calcination, the catalyst was either used as such in the reaction tests or presulfided with 5% H_2S/H_2 (flow-rate 2.5 l/h (NTP)) at 400°C for 4 h. The temperature of the catalyst layer was decreased to the reaction temperature, 200–300°C, and the total pressure was adjusted to 1.5 MPa. The liquid feed containing 3 wt.% of phenol (J.T. Baker, lab. grade) or anisole (methyl phenyl ether, Merck, >99%) in *m*-xylene (Merck, >99%) was introduced to the reactor at a rate of 10 g/h. The gas feed rate was 2 l/h (NTP). H_2S was added to the gas feed of the reactor in different concentrations during HDO or 5% H_2S/H_2 was added for 1 h between HDO periods, or CS_2 was added to the liquid feed as a precursor of H_2S during HDO. Addition of the sulfiding agents was studied at 250°C. Reactions of the oxygen-containing compounds on the sulfided catalyst were compared with those proceeding on the oxide form of the catalyst in the presence and absence of sulfiding agents, and also with those on γ-Al_2O_3 support (Akzo, γ-Al_2O_3 001/1.5 E). For anisole, the reactions were also tested in the absence of catalyst.

Liquid sampling was started after 2 h of liquid feed. The samples were taken at intervals of 30 min and they were analyzed by gas chromatography using with a flame ionization detector (HP 6890 A). The capillary columns were DB-1 and HP-1. Response factors for the reactants and the products were determined, and frequently tested against model solutions of known concentration, using cumene as an internal standard. The accuracy of the response factor was within ±2%. After the reaction, the catalysts were washed with *m*-xylene, dried under air at 150°C for 2 h and analyzed for sulfur and carbon content using a Leco SC-444 analyzer.

3. Results and discussion

3.1. Reactions of phenol and anisole in the absence of sulfur in the feed

Both temperature and time-on-stream influenced the conversion and the stability of the catalyst in the reactions of phenol. As reported earlier [15], the HDO

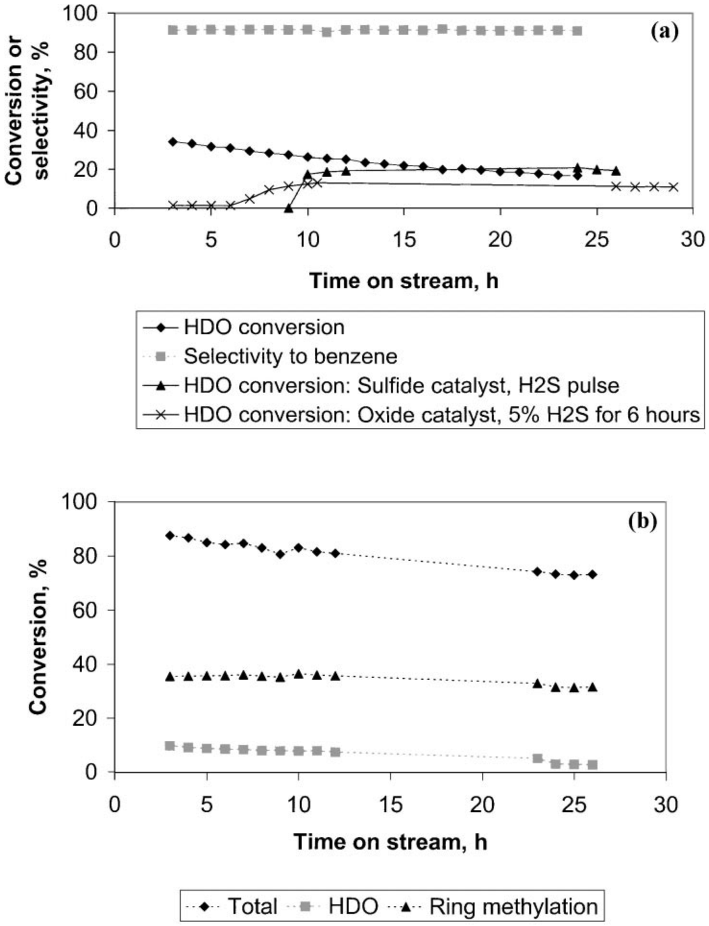

Fig. 1. Stability of the sulfided CoMo catalyst: (a) conversion and reaction selectivity of phenol; (b) conversion of anisole at 250°C.

Table 1
Initial conversion and reaction selectivity of phenol and anisole on the sulfide catalyst

	Phenol			Anisole			
Reaction temperature (°C)	250	300	250	250	300	250	250
Form of the catalyst[a]	Sulfided[b]	Sulfided	Oxide[b]	Sulfided	Sulfided	Oxide	γ-Al_2O_3
Conversions (%)[c]							
Total	36.4	71.9	0.12	88.2	96.8	63.3	47.9
HDO	36.4	71.9	0.12	10.4	48.5	0	0
Methyl transfer to benzene ring	–	–	–	36.8	24.4	32.0	25.8
Product selectivity (%)[d]							
Phenol	–	–	–	48.4	40.8	50.0	48.0
Benzene	92.9	86.4	100	7.5	22.8	0	0
Cyclohexane and cyclohexene	7.1	13.6	0	0	4.3	0	0
Toluene	–	–	–	4.0	9.7	0	0
Ortho-cresol	–	–	–	24.7	12.2	29.7	30.0
Ortho-methylanisole	–	–	–	1.4	0	5.4	6.9
2,6-Xylenol	–	–	–	10.8	3.7	14.4	15.1
Catalyst analysis[e]							
S (%)	7.2 (24 h)	7.2 (7 h)	0.7 (6 h)	6.9 (26 h)	6.9 (7 h)	0.5 (7 h)	–
C (%)	4.3 (24 h)	6.6 (7 h)	5.3 (6 h)	6.9 (26 h)	5.6 (7 h)	7.0 (7 h)	–

[a] Pretreatment of the catalyst — sulfided: presulfided with H_2S, oxide: oxide form after calcination under N_2.

[b] From [15].

[c] Approximated on the basis of the conversion trendline for fresh catalyst.

[d] Selectivities of the identified reaction products (average values of the samples, 2–4 h).

[e] Catalyst analyzed after the reaction. Presulfided catalyst: sulfur content 8.2%. The time-on-stream of the catalyst mentioned.

conversion of phenol on the sulfided CoMo/γ-Al_2O_3 catalyst decreased from 36 to 26% in 10 h at 250°C when no sulfur was added to the reactor after presulfiding (see Fig. 1a). At 300°C, the initial phenol conversion of 72% decreased to 52% in 6 h. On the other hand, for phenol, conversion of only 0.1% was detected at 250°C on the oxide form of the catalyst, indicating that the sulfided forms of the active metals are required for the HDO reaction.

Examples of the initial product distributions of phenol at 250 and 300°C are presented in Table 1. Benzene was formed via the direct hydrogenolysis route and cyclohexane and cyclohexene via the combined hydrogenation–hydrogenolysis route. No other reaction products were detected. Under the conditions studied, the direct hydrogenolysis route was strongly favored over the combined hydrogenation–hydrogenolysis route. The selectivity of HDO reactions was not affected by the time-on-stream (see Fig. 1a) [15], but depended slightly on temperature. This indicates that either these two HDO paths are proceeding on the same active site or two different active sites are involved which deactivate at the same rate.

The total conversion of anisole on the presulfided CoMo/γ-Al_2O_3 catalyst decreased from 88 to 73% and the HDO conversion from 10 to 3% in 24 h at 250°C (see Fig. 1b). At 300°C, the initial conversion was only slightly higher, 97%, and no clear decrease in the total conversion was detected in 7 h. HDO conversion, however, decreased noticeably, from 49 to 20% in 7 h at 300°C. The initial total conversion of anisole at 250°C was as high as 63% on the oxide form of the catalyst, and even on the plain γ-Al_2O_3 support it was 48%. In the absence of the catalyst or the support material, no reaction of anisole was detected. The activity of the oxide catalyst remained approximately constant for 7 h, but the total conversion of anisole on the γ-Al_2O_3 support decreased to about 37% in the same period. No HDO products were formed on these catalysts and only the formation of phenol and shifts in the position of the methyl group were detected. Examples of the initial hydrotreating product of anisole are included in Table 1. These results further support

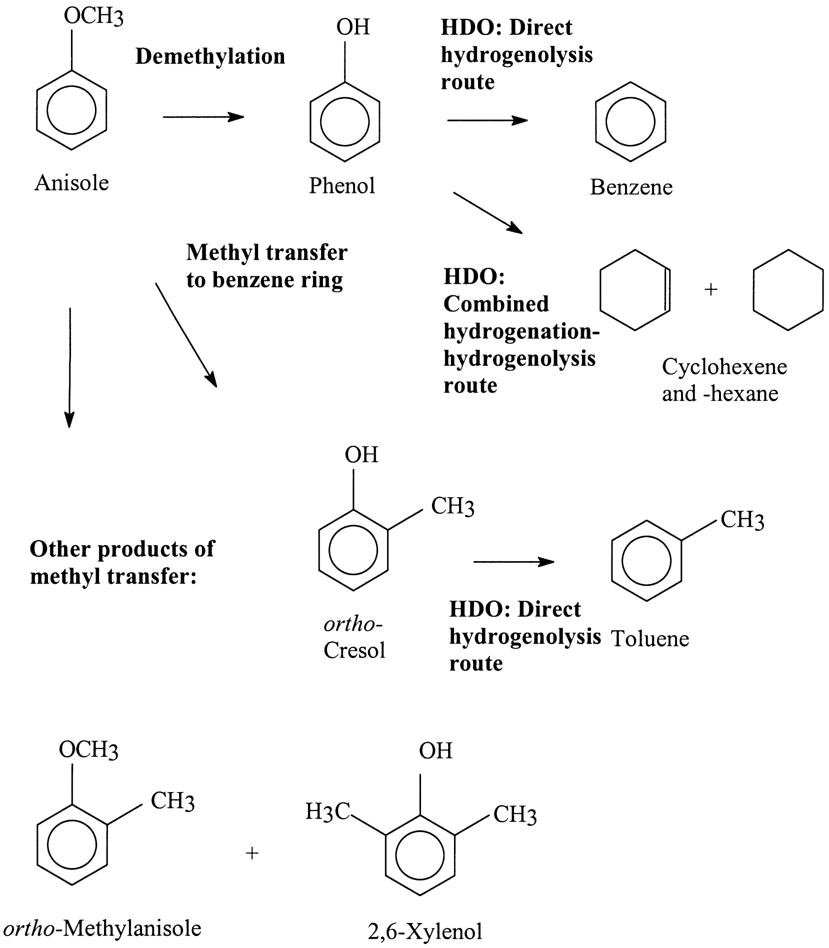

Fig. 2. Simplified formation routes for the identified reaction products of anisole.

the assumption that a sulfided catalyst is needed for the HDO reactions and, on the other hand, the cleavage of the bond between the aliphatic carbon and the oxygen atom proceeds quite effectively even on the acidic sites of the catalyst support.

At 225°C, benzene was the only oxygen-free product of anisole on a presulfided CoMo/γ-Al_2O_3 catalyst. Aromatic HDO products, benzene and toluene, were formed at 250°C. Hydrogenated HDO products, cyclohexane and cyclohexene, were only detected at 300°C. Conversion of anisole to ring-methylated products was noticeable, being about 37 and 24% at 250 and 300°C, respectively. Toluene probably formed via the direct hydrogenolysis route of HDO from *ortho*-cresol. Likely due to the reaction conditions used, the formation of hydrogenated HDO products from *ortho*-cresol was not detected. In the conversion values presented in Table 1, toluene is included as a product for both HDO and for methyl transfer reactions. The simplified reaction network for the hydrotreating of anisole to the identified reaction products is presented in Fig. 2. Ring-methylation was more pronounced in the flow reactor than in a batch system at 7 MPa, in which only *ortho*-cresol was formed as a product of ring-methylation [11]. In the flow reactor, *ortho*-cresol and 2,6-xylenol were formed as the major products and *ortho*-methylanisole and toluene as the minor products.

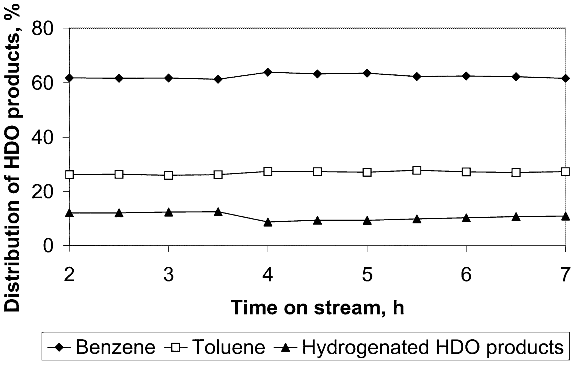

Fig. 3. Distribution of HDO products in hydrotreating of anisole at 300°C in the absence of added sulfiding agents.

The product distribution of anisole at 250°C was naturally affected by the time-on-stream due to suppression of HDO. At temperatures high enough for the hydrogenation–hydrogenolysis route of HDO to proceed, the ratio of the HDO products, however, remained practically constant (see Fig. 3). This suggested that the active sites for the HDO routes deactivated at the same rate as was in the case of phenol.

3.2. Effect of added sulfiding agents on HDO of phenol

In order to study more precisely the deactivation of the catalyst and the role of sulfur, experiments were carried out with sulfur compounds, either H_2S or CS_2, added into the HDO feed. The addition of H_2S predictably decreased the initial activity of the catalyst in the HDO reactions of phenol [3–7]. The effect of the addition of CS_2 on the HDO reactions was similar to the effect of H_2S. More accurately, the conversion of the direct hydrogenolysis route of phenol to benzene was strongly suppressed, even in the presence of the lowest amount of H_2S studied, 0.0125% H_2S. On the other hand, the conversion of the combined hydrogenation–hydrogenolysis route to alicyclics remained with the H_2S concentrations up to 2.5% the same as in the absence of H_2S. Only at the H_2S concentration typically used in presulfidation of the catalyst, 5% H_2S, did this conversion decline. The effect of H_2S on the selectivity of HDO can be clearly seen in Fig. 4. The selective inhibition of the direct hydrogenolysis route of the HDO reactions by H_2S clearly indicates the presence of at least two kinds of active sites on the catalyst, and the sites differ in their sensitivity towards sulfur. H_2S adsorbs preferentially on the active sites of the direct hydrogenolysis route probably due to the higher electron affinity of these sites compared to the hydrogenation sites [6,7]. No increase in the rate of the hydrogenation–hydrogenolysis route in the presence of H_2S, which would indicate the interconversion of the active sites of the catalyst observed in the studies of Laurent and Delmon [6,7] and Delmon [8,9], was detected under the conditions used. The selective inhibition of one of the parallel

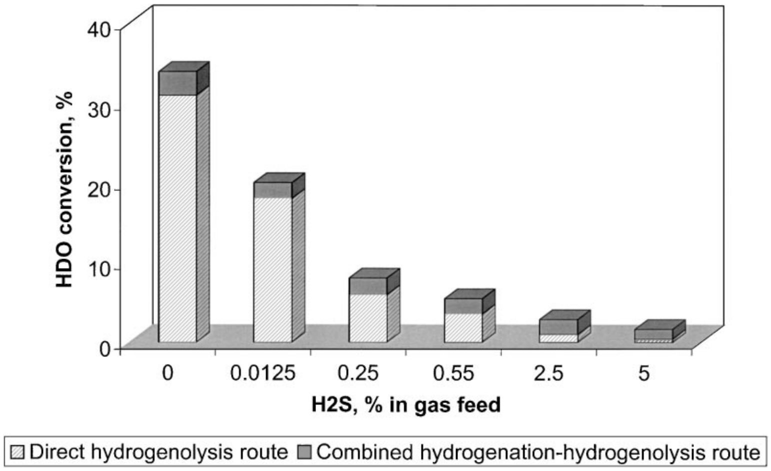

Fig. 4. Effect of H_2S on the HDO routes of phenol.

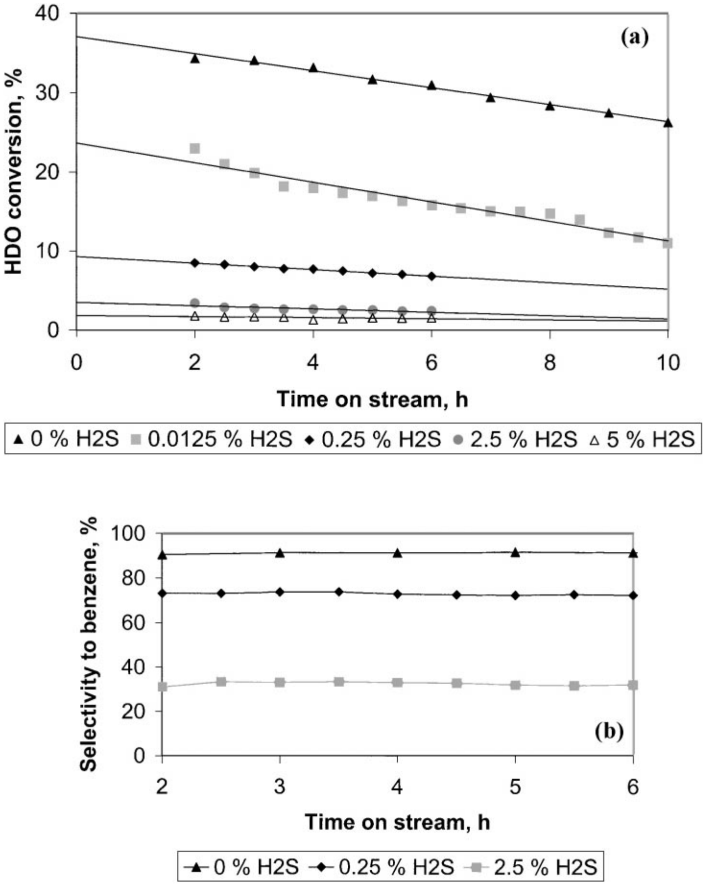

Fig. 5. Stability of the sulfided CoMo catalyst in hydrotreating of phenol in the presence of H_2S: (a) conversion; (b) selectivity of the catalyst.

reaction paths by H_2S can potentially be used to control the selectivity of HDO reactions on a process scale to favor the alicyclic reaction products. Unfortunately, it seems that the selectivity adjustment can only be carried out at the cost of the total HDO conversion.

From the stability point of view, the addition of H_2S to the HDO feed had neither a clear positive nor a negative effect on the activity of the catalyst in HDO reactions of phenol: the total HDO conversion gradually decreased with time-on-stream as it did in the absence of H_2S (see Fig. 5). The selectivities of the two reaction routes remained nearly constant with time-on-stream, showing that the active sites for hydrogenolysis and hydrogenation deactivated at approximately similar rates. A slight positive effect on the activity of the catalyst was, however, achieved when the sulfided catalyst was flushed with 5% H_2S/H_2 for 1 h after an HDO period of 8 h. When the HDO was started again, the HDO conversion increased and stayed about 4% units higher than without an H_2S treatment after 24 h on oxygen-containing feed. Thus, it seems that the active form of the sulfided catalyst cannot be maintained during HDO by continuous adding of sulfiding agents to the feed. Nevertheless, a pulse of H_2S has a positive effect on the activity of the catalyst.

In our previous study [15], it was not possible to activate the oxide form of the catalyst by the addition of sulfiding agents continuously to the HDO feed. In this study, we added 5% of H_2S/H_2 to the HDO feed on the oxide catalyst for 6 h and then removed H_2S from the feed (see Fig. 1a). The activity of the catalyst gradually increased after the removal of H_2S but stayed at a lower level than on the sulfided catalyst at the same time on oxygen-containing feed.

In summary, the continuous addition of H_2S to the feed in HDO of phenol decreases the initial conversion level of HDO and determines the ratio of the reaction products, but it does not noticeably prevent deactivation of the sulfide catalyst. H_2S acts as an inhibitor especially for the hydrogenolysis route of HDO. This inhibition effect disappears, however, when H_2S is removed from the HDO feed. Reactivation of the HDO catalyst by resulfidation seems to be more reasonably carried out with a separate sulfiding cycle in the absence of the oxygen-containing feed.

3.3. *Effect of added sulfiding agents on the reactions of the methoxy group*

The total conversion of anisole on the sulfided catalyst was slightly increased in the presence of H_2S but the HDO reactions were strongly suppressed, and oxygen-free products were formed in small amounts only at the lowest H_2S concentrations studied (see Fig. 6). Under higher concentrations of H_2S, methyl transfer to the benzene ring also diminished to some extent and some unidentified products were detected. The simultaneous enhancement of the demethylation reaction of anisole to phenol and the suppression of the HDO reactions suggests that these reactions proceed, at least partially, on different active sites of the catalyst. As mentioned before, demethylation and ring-methylation of anisole were also noticeable on the oxide form of the catalyst and on the γ-Al_2O_3 support, indicating that the sulfide form of the catalyst is not a prerequisite for these reactions. Acidic sites of Al_2O_3 are probably involved in the demethylation reactions. However, the addition of 0.55% H_2S to the feed on the oxide catalyst increased the conversion of anisole to phenol from 32 to 50%, thus emphasizing the role of sulfur in the demethylation reaction. Possibly this positive effect of sulfur originates from sulfhydryl groups formed on the catalyst. These sites have been presented to give rise to Brønsted acidity of the catalyst [2]. In addition, H_2S may to some extent act as a reactant molecule and capture the methyl group from anisole. We suggested this kind of reaction pathway for the reaction network of anisole in the presence CS_2 in our previous paper [11] as an explanation for the observed change in the activation energy of the primary reaction of anisole to phenol. With the gas chromatographic analysis method used, formation of methyl sulfides could not be detected.

Under the conditions studied, the presence of H_2S did not improve the stability of the sulfide catalyst in the hydrotreating of anisole either. It is possible that stability improvements could be seen at higher reaction temperatures in which the inhibiting effect of H_2S has shown out to be lower [14] and the resulfiding effect is expected to be stronger. In this study higher reaction temperatures were, however, avoided to

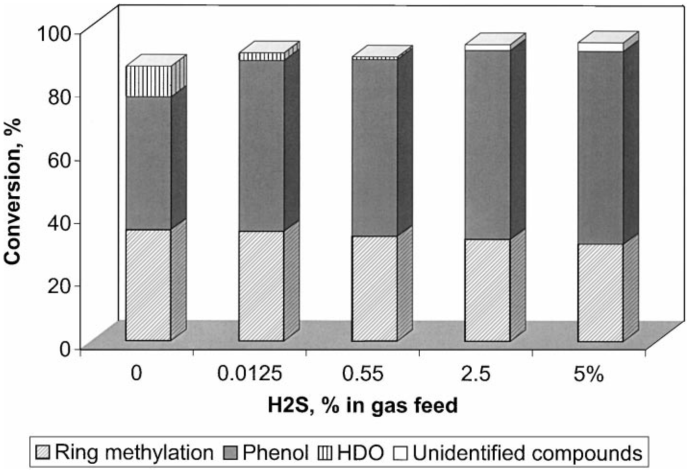

Fig. 6. Effect of H_2S on the reaction routes of anisole.

minimize the formation of coke and high molecular weight reaction products.

3.4. Deactivation of the catalyst

Deactivation of the sulfided CoMo/Al_2O_3 catalyst during hydrotreating of oxygen-containing feeds has in the literature been presented to be caused by coke and high molecular weight reaction products formed from the oxygen-containing compounds and by the replacement of the catalytic sulfur with oxygen [1,8,16]. In addition, water formed in the HDO reactions has turned out to be a weak inhibitor for HDO [8].

In our study, the mass balance of phenol on the sulfide catalyst was >97% at 250°C. At 300°C, a discrepancy of about 8% was observed, suggesting the formation of high molecular weight reaction products and coke. In fact, faster deactivation of the catalyst was observed at higher temperatures. The measured mass balance in the anisole experiments was of the same order than in the phenol experiments under the same reaction conditions. The carbon contents of the catalysts after reaction were 4–8 wt.%, depending on the reaction temperature and the time-on-stream (see Tables 1 and 2). The observed deactivation of both the hydrogenolysis and the hydrogenation sites at equal rates is likely, at least partially, caused by blocking of these sites with the high molecular weight compounds and coke. However, the effect of sulfur on the deactivation cannot be completely ruled out.

The sulfur content of the presulfided catalyst decreased during hydrotreating of phenol at 250°C in the absence of sulfiding agents by about 12% in 24 h. The corresponding decrease in the sulfur content was 16% in 26 h in hydrotreating of anisole. A similar desulfurization of the sulfided catalyst was seen even when low molecular weight sulfiding agents were added to the HDO feed (see Table 2). The decrease observed is clear when compared to the decrease, 2%, observed during HDS of benzothiophene on the same catalyst [15]. This suggests that the decrease was caused by the presence of the oxygen-containing molecule. It is possible that in addition to this decrease in the total sulfur content of the catalyst, the structure of the active sulfide catalyst partially changes during HDO deactivating the catalyst further. The methods to test the changes in the sulfide structure were not available in this study. As mentioned before, no indication of the interconversion of the active sites was, however, detected.

The sulfur content of the oxide catalyst markedly increased during hydrotreating of phenol and anisole in the presence of sulfidation agents (see Table 2). Thus, sulfidation of the oxide catalyst proceeded to some extent also in the presence of the oxygen-containing feed but HDO was inhibited by the sulfiding agents, H_2S and CS_2, and proceeded only after the removal of the sulfur compounds from the feed. Similarly, in our previous studies in a batch reactor [4,11,17], HDO reactions were suppressed by the presence of organic sulfur compounds until the HDS conversion was

Table 2
Effect of added sulfiding agents on the final sulfur and carbon content of the catalysts in hydrotreating at 250°C and 1.5 MPa

Reactant	Form of the catalyst[a]	Concentration of the sulfiding agent[b]	Total time on HDO feed (h)	S (%)	C (%)
Phenol	Oxide [15]	5% H_2S	12	7.8	6.4
	Oxide [15]	0.13% CS_2	7	3.7	5.1
	Oxide	5% H_2S for 6 h	10	5.6	5.8
	Oxide	5% H_2S for 6 h	29	4.5	7.6
	Sulfide	2.5% H_2S	6	7.1	6.1
	Sulfide	5% H_2S	6	7.4	6.6
	Sulfide	5 % H_2S (pulse 1 h)	26	6.5	7.5
Anisole	Oxide	0.55% H_2S	7	3.1	6.4
	Sulfide	0.55% H_2S	7	7.5	6.3
	Sulfide	2.5% H_2S	7	7.4	6.9
	Sulfide	5% H_2S	7	7.6	6.5

[a] Pretreatment of the catalyst — sulfided: presulfided with H_2S, oxide: oxide form after calcination under N_2.
[b] Concentration of H_2S (vol.%) in the gas feed or CS_2 (wt.%) in the liquid feed.

almost complete. The activity of the catalyst after the removal of the sulfiding agents from the feed was lower than the activity of the presulfided catalyst after the same time on oxygen-containing feed. This difference in the activity is likely due to the reaction temperature that is markedly lower than the temperature used for presulfidation of the catalyst. It is, however, possible that the formation of the active sulfide structure is prevented by the presence of the oxygen-containing molecules. Therefore, sulfidation of the catalyst for HDO is more efficiently carried out as a separate cycle in the absence of oxygen-containing feed. In that case, deactivation of the catalyst by coke and high molecular weight compounds can also be avoided.

4. Conclusions

The addition of sulfiding agents to the feed during HDO strongly decreases the initial activity of a sulfided CoMo/Al_2O_3 catalyst and determines the ratio of the HDO reaction products. It does not, however, prevent catalyst deactivation with time on oxygen-containing feed. The direct hydrogenolysis route of HDO to aromatics is suppressed by the addition of H_2S, whereas the conversion of the combined hydrogenation–hydrogenolysis route to alicyclics remains the same as in the absence of H_2S up to H_2S concentrations typically used in presulfidation of the catalyst. Thus, two types of active sites for the HDO reactions are present on the sulfided catalyst. On the other hand, demethylation of the methoxy group in anisole to phenol is enhanced in the presence of H_2S, but the further HDO reactions are suppressed. For demethylation, sulfidation of the catalyst is not required and the reaction proceeds also quite effectively on the acidic sites of the γ-Al_2O_3 support. Sulfidation of the catalyst, however, increases the conversion of demethylation due to formation of sulfhydryl groups on the catalyst.

As a result, the addition of sulfiding agents to the feed during hydrotreating of oxygen-containing compounds does not solve the deactivation problem of sulfided CoMo/Al_2O_3 catalysts. In addition to desulfurization and changes in the structure of the active sulfided catalyst, the formation of coke and high molecular weight compounds on the catalyst decrease the activity of the catalyst. The selective inhibition of one of the parallel HDO reaction paths by H_2S may, however, be used under favorable conditions to adjust the selectivity of hydrotreating on a process scale to favor alicyclic reaction products, but only at the cost of the total HDO conversion.

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