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Catalysis Today 65 (2001) 257–264

CATALYSIS TODAY

www.elsevier.com/locate/cattod

CoMo/carbon hydrodeoxygenation catalysts: influence of the hydrogen sulfide partial pressure and of the sulfidation temperature

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Abstract

This work concerns the influence of the hydrogen sulfide partial pressure and the sulfidation temperature on the hydrodeoxygenation activity and selectivity of a CoMo catalyst supported on activated carbon. An attempt is made to identify the active sites involved in the reaction of different oxygenated molecules: guaiacol demethylation and dehydroxylation, ethyldecanoate hydrogenation and decarboxylation, 4-methylacetophenone hydrogenation.

Keywords: Hydrodeoxygenation; Carbon support; Sulfided cobalt–molybdenum

1. Introduction

Hydrodeoxygenation reactions are studied with the aim of upgrading biomass derived liquids, often called bio-oils. These liquids are characterised by a high oxygen content (O = 26–47 wt.%) which is prejudicial to their thermal stability, fluidity and energetic content. In order to enable the storage, transportation and utilisation of bio-oils, partial or total oxygen removal is necessary [1]. In former works [2,3], typical hydrodesulfurisation catalysts, such as sulfided NiMo/Al_2O_3 or CoMo/Al_2O_3, were found to be active for HDO reactions, but they were rapidly deactivated by coke deposition due to the acidity of the alumina support. This tendency to coke formation was found to be particularly due to oxygen substituted phenolic compounds like guaiacol and catechol [4,5]. The utilisation of a neutral support, such as activated carbon, has been shown to limit the formation of condensation products acting as coke precursors and to facilitate the elimination of oxygen from the molecules involved in coke formation. In hydrotreating, in general, catalysts supported on activated carbons have received much attention in the last years [6].

It is known that the surface of CoMo sulfided catalysts is extremely dynamic and flexible. It gets modified and reconstructs during its life cycle. Starting with its formation as oxide, proceeding with the sulfidation pretreatment, it undergoes modifications following the changes of the experimental conditions. It can adapt to different conditions of temperature, hydrogen and hydrogen sulfide partial pressure, to different feedstock compositions, as well as to the presence of coke and metal deposits. During all these changes, in different states of the active phase dispersion and with variable sulfur content, it keeps its ability to facilitate numerous reactions via several different mechanisms [7]. It is now generally accepted that the metal sulfides of CoMo catalysts possess three kinds of active sites [8–11]. They depend on the surface coordination and reduction state of MoS_2. Hydrogenation sites likely are threefold coordinatively unsaturated Mo atoms. Hydrogenolysis sites, responsible for the cleavage of the heteroatom–carbon bonds, would be created under more severe reduction

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PII: S0920-5861(00)00559-9

conditions. They would be constituted of a threefold coordinatively unsaturated Mo atom with a sulfhydryl (–SH) or hydride (–H) group neighbour. Acid sites, located on the alumina support (Lewis acidity) and on the sulfided phase as –SH groups (Bronsted acidity), are also present. These sulfhydryl groups can be generated by adsorption of H_2S on the sulfur vacancies associated with the MoS_2 phase. Anyway, except for a few cases, the respective role of acid sites located on MoS_2 and those located on the support is not clear.

As biomass derived liquids do not contain sulfur compounds, a partial pressure of H_2S is required to create the catalytic sites and to preserve the sulfided phase from oxidation by oxygenated compounds and water or reduction by hydrogen, according to operating conditions. The variation of the H_2S partial pressure can strongly modify the active sites existing on the MoS_2 phase, their relative amount and consequently the catalytic activity.

Hydrotreating catalysts are generally available with the metals in the oxide state. Before the reaction, the catalyst undergoes a reducing and sulfiding treatment (activation) with a mixture of a sulfur source and hydrogen. Cobalt and molybdenum oxides are transformed into sulfides, which are the active form for hydrotreating processes. The activation step is crucial for the physico-chemical properties of the catalysts (nature, composition and dispersion of the active phase) and consequently for the activity and selectivity. In particular, the temperature used in this step can deeply affect the degree of reduction and sulfidation, as well as the dispersion of the active phase.

By following the conversion of the various oxygenated molecules and the product selectivities, as a function of the H_2S partial pressure and of the sulfidation temperature, we will try to make or refine some hypotheses about the kind of active sites responsible for the HDO of various oxygenated functions.

A double objective will be pursued in this work. Firstly, to improve the understanding of HDO reactions on carbon supported catalysts, secondly, by means of the HDO reactions themselves to investigate the modifications of the active sites under different reaction and activation conditions. As the role of different active sites is concerned, the use of activated carbon support instead of alumina should make interpretation easier, because there is no more contribution of the support acidity to the conversion of the reactant. Consequently, the role of the sulfhydryl groups should be more easily understood.

2. Experimental

The catalyst was prepared using a commercial activated carbon, BKK-100 (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 and cobalt second. After each impregnation, the sample was dried under argon flow at 130°C overnight and at 400°C for 3 h. The composition of the catalyst was 15 wt.% of MoO_3 and 3 wt.% of CoO.

Prior to XPS analyses, the catalysts were sulfided in a glass reactor at atmospheric pressure with a mixture of 15 vol.% H_2S in H_2 at different temperatures: 250, 300, 350, 400 and 440°C. After sulfidation, the samples were transferred and stored into flasks containing *iso*-octane, avoiding any contact with air.

The XPS analyses were performed on an SSX 100/206 spectrometer. The general spectrum and the peaks of C_{1s}, O_{1s}, S_{2p}, Mo_{3d} and $Co_{2p3/2}$ were recorded. Binding energies were calculated by reference to the binding energy of the C–(C,H) component of C_{1s} fixed at 284.2 eV. Peak intensities were converted into atomic percentage using the sensitivity factors given by the manufacturer.

XRD analyses were performed on a Siemens D500 diffractometer using the $K\alpha1,2$ emission of Cu ($\lambda = 1.54\,Å$) for 2Θ angles varying from 5 to 60°. The sulfided samples were analysed without any protection from air.

Prior to the reaction tests, 1.5 g of catalyst was dried at 130°C overnight, under nitrogen flow. The sulfidation mixture, 15 vol.% H_2S in H_2, was then introduced, the pressure set at 0.3 MPa and the flow at $150\,ml\,min^{-1}$; after a stabilisation period of 30 min, the temperature was increased to the desired value. The catalysts for the study of the H_2S partial pressure were sulfided at 400°C, while for the study of the sulfidation temperature the catalyst was sulfided at 250, 300, 350, 400 or 440°C. The final conditions were maintained for 3 h. The temperature was subsequently decreased to 270°C. The gas was switched to pure hydrogen and the liquid feed introduced. The liquid feed rate was 45 ml h^{-1} and the hydrogen flow rate 24 l h^{-1}. The tests were done at a total hydrogen pressure of 7 MPa. For the study of the H_2S partial pressure, four tests were performed at P_{H_2S} equal to: 50, 75, 100 and 150 kPa. For the study of the sulfidation temperature, all the tests were made with P_{H_2S} equal to 100 kPa. H_2S was generated by the decomposition of dimethyldisulfide. In addition to this compound, the liquid feed contained a mixture of oxygenated model compounds: guaiacol (GUA), ethyldecanoate (ED) and 4-methylacetophenone (MA). Two reaction temperatures were used for the tests: 270°C to evaluate the reactivity of GUA and ED, and 200°C to evaluate the reactivity of MA. Feed composition as well as the reaction pathways have been detailed in a previous work [14].

3. Results

3.1. Influence of the hydrogen sulfide partial pressure on the catalytic activity

The conversion data concerning GUA, ED and MA are reported in Table 1. GUA and ED conversion are not affected, while the hydrogenation of the carbonyl group of MA is inhibited by hydrogen sulfide.

Only the products obtained from the conversion of GUA are affected by the variation of H_2S. The evolution of the yields in catechol and phenol* (Ph* includes the yields in phenol, benzene, cyclohexene and cyclohexane) as a function of P_{H_2S} are shown in Fig. 1. Phenol and C_6 yields decrease, while catechol yields increase with the increase of P_{H_2S}. As a consequence the phenol* to catechol ratio decreases.

Table 1
GUA, ED and MA conversion at different P_{H_2S}

H_2S partial pressure (kPa)	GUA conversion (%)	ED conversion (%)	MA conversion (%)
50	19	23	22
75	19	23	19
100	18	23	19
150	17	23	12

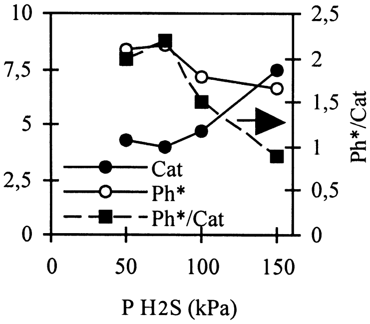

Fig. 1. Evolution of catechol and phenol* (Ph* = phenol + benzene + cyclohexene + cyclohexane) yields and of the phenol* to catechol ratio as a function of P_{H_2S}.

3.2. XPS and XRD results for samples sulfided at different temperatures

Using the XPS results, various surface atomic ratios were calculated for the catalyst before and after reaction, in order to put in evidence the presence of different molybdenum and sulfur species as a function of the sulfidation temperature.

The Mo^{6+}/Mo_{tot}, Mo^{5+}/Mo_{tot} and Mo^{4+}/Mo_{tot} ratios are reported in Fig. 2a. Mo^{6+} species are present in almost all the samples analysed. They could be due to non-sulfided MoO_3, or to partially sulfided, but not reduced molybdenum oxysulfides ($MoO_{3-x}S_x$), or to sulfate $Mo(SO_4)_3$, or to Co–Mo mixed oxides ($CoMoO_4$). It is known that the latter does not easily undergo sulfidation. The presence of $CaMoO_4$ (due to calcium impurity in the activated carbon) also contributes to Mo^{6+}. The Mo^{6+}/Mo_{tot} ratio decreases when the sulfidation temperature increases and after the reaction test. Mo^{5+} species never represent more than 20% of the total molybdenum. They only slightly decrease with the sulfidation temperature and they could be due to sulfided, but only partially reduced, or to partially reduced but non-sulfidable species. Mo^{4+} species are always more abundant than Mo^{5+} or Mo^{6+}. Their relative amount increases with the sulfidation temperature. Only a weak increase (especially for the catalyst pretreated at 250 and 300°C) is observed for the samples after catalytic test.

In literature, the sulfidation degree is often discussed in terms of S^{2-}/Mo^{4+} ratio [15–17]. Theoretically, it should be equal to 2, even if lower values

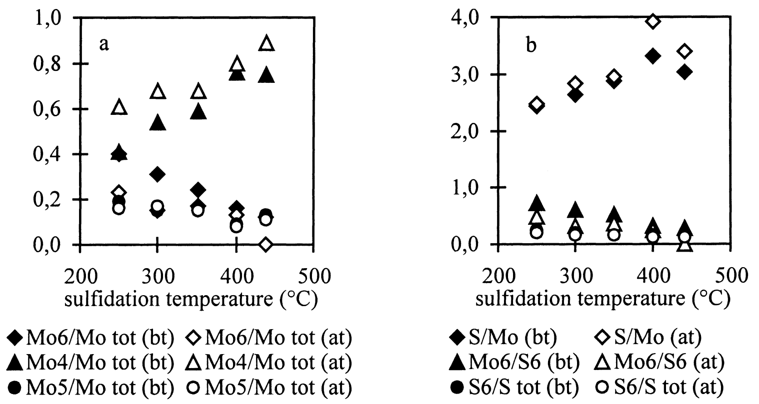

Fig. 2. (a) Mo^{6+}/Mo_{tot}, Mo^{4+}/Mo_{tot} and Mo^{5+}/Mo_{tot} atomic ratios for the catalyst before (bt) and after (at) test. (b) S_{tot}/Mo_{tot}, Mo^{6+}/S^{6+} and S^{6+}/S_{tot} atomic ratios for the catalyst before (bt) and after (at) test.

could be observed due to the existence of sulfur vacancies at the surface of MoS_2. In our case, the system is too complex and no significant values could be calculated for this ratio. Only a rough evaluation of the overall sulfidation degree is possible using the S_{tot}/Mo_{tot} values (Fig. 2b). This ratio is always higher than 2 and slightly increases with the sulfidation temperature. This can be interpreted as a weak increase of the sulfidation degree [17]. The formation of sulfates (S^{6+}/S_{tot} ratio) (Fig. 2b) seems to be not much affected by the pretreatment of the catalyst. S^{6+} species are probably due mainly to a re-oxidation of sulfide ions during storage and/or preparation of the samples for analysis. Oxygen dissolved in the liquid paraffins which protect the catalyst, or accidental contact with outside atmosphere would cause some re-oxidation. The evolution of the Mo^{6+}/S^{6+} ratio should indicate whether Mo^{6+} species are related to re-oxidation during the preparation of the samples for the analyses, or to an incomplete reduction–sulfidation of molybdenum, which would depend on the sulfidation procedure itself. The fact that the S^{6+}/S_{tot} ratio is almost constant while the Mo^{6+}/S^{6+}, Mo^{6+}/Mo_{tot}, Mo^{5+}/Mo_{tot}, Mo^{4+}/Mo_{tot} ratios are dependent on the sulfidation temperature indicates that the amount of Mo^{6+} species mainly depends on the sulfidation procedure.

Only a short comment will be made about the XRD analyses. The catalyst in the oxide state and two samples sulfided at 250 and 440°C, respectively, were analysed. The pattern of the sample sulfided at 440°C shows a peak at $2\Theta = 14°$ and very small ones at $2\Theta = 39.5, 49$ and $58.5°$; these peaks can be attributed to MoS_2 phase (JCPDS standard file 37-1492) [18], even if a small shift of $\Delta 2\Theta = +0.25°$ is observed with respect to the standard pattern.

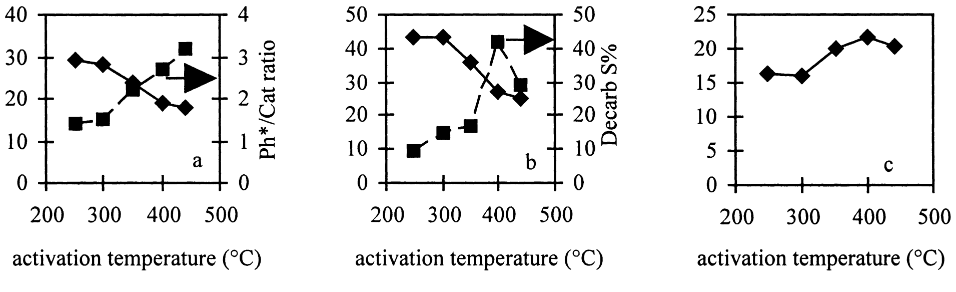

Fig. 3. (a) GUA conversion and phenol* to catechol ratio; (b) ED conversion and decarboxylation selectivity; (c) MA conversion as a function of the activation temperature.

3.3. Influence of the sulfidation temperature on the catalytic activity

The conversion of GUA decreases with the increase of the sulfidation temperature, while the Ph*/Cat ratio increases (Fig. 3a). The conversion of ED decreases and the selectivity in decarboxylated products increases (Fig. 3b). Only in the case of MA, a modest increase of the conversion is observed for the catalysts sulfided at higher temperatures (Fig. 3c).

4. Discussion

In what follows, we discuss at first the influence of the hydrogen sulfide partial pressure. We will present a comparison of our results about the HDO of GUA, ED and MA over the CoMo/C catalyst with those previously obtained on alumina supported catalysts [3,12,13]. An attempt to identify the active sites responsible for the reaction of the different oxygenated functions will be made. In a second part, we shall focus more on the changes of the catalyst physico-chemical characteristics as a function of the sulfidation temperature. On the basis of the existence and formation of different active sites, a correlation with the catalytic activity will be made.

4.1. Influence of the hydrogen sulfide partial pressure: identification of the active sites

The conversion of GUA initially involves the breaking of the O–methyl bond (demethylation) to give catechol. Then the reaction proceeds through the hydrogenolysis of the $C_{aromatic}$–O bond (dehydroxylation) to phenol first and further to benzene, cyclohexene and cyclohexane [3]. Phenol can also be directly formed from guaiacol by a demethoxylation reaction (hydrogenolysis of the $C_{aromatic}$–O bond).

With our CoMo/C catalyst, the total GUA conversion is constant, but the formation of dehydroxylated products, phenol, benzene, cyclohexene and cyclohexane, decreases with the increase of the H_2S partial pressure. It is logical to consider that similarities exist between the breaking of the C–O and C–S bonds. The inhibition by H_2S in the dehydroxylation of methylphenol [13] and GUA ([12], the present work) is in agreement with numerous data concerning C–S hydrogenolysis activity in HDS [11]. Such 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 complex sites involving strongly reduced molybdenum atoms with a high coordination unsaturation. Upon increasing the H_2S partial pressure, the average degree of reduction and the coordination unsaturation of the active sites decrease; the hydrogenolysis of $C_{aromatic}$–heteroatoms bonds is consequently inhibited. As for the constant conversion of GUA and the increase of catechol yield, a possible interpretation can be based on the existence of two parallel pathways, proceeding at the same rate for the demethylation to catechol and the demethoxylation to phenol. In the case of alumina support, Lewis acid sites would be responsible for the major part of demethylation, while when activated carbon is used, both demethylation and demethoxylation or dehydroxylation would take place on the sulfided phase. As the carbon support does not contribute to the activity, the distinction between sites responsible for the cleavage of the O–methyl and $C_{aromatic}$–O bonds is possible in principle. The most coherent hypothesis would be that demethylation involves H^+ and sulfhydryl groups, 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 and the cleavage of the $C_{aromatic}$–O bonds inhibited, as discussed above. The GUA conversion would thus be constant, while the Ph*/Cat ratio would decrease.

Three main reactions have been identified for the conversion of the carboxylic ester group. Hydrogenation gives saturated alcohols and subsequently, by dehydration, unsaturated and saturated hydrocarbons containing 10 carbon atoms. Decarboxylation produces hydrocarbons with nine carbon atoms. Decanoic acid formed by de-esterification is an intermediary product which can be further transformed through the hydrogenation or the decarboxylation pathways. In a previous work [12] done with sulfided $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts, H_2S promoted the conversion of diethylsebacate. It was suggested that both hydrogenation and acid sites, located on the metal sulfides, were responsible for the reaction of the carboxylic group. In the case of our CoMo/C catalyst, the effect of hydrogen sulfide on ED conversion is less marked. The increase of H_2S partial pressure does not significantly influence the conversion of ED and the product yields. From our experiments, it is not possible to clearly distinguish the role of the different active sites for the hydrogenation and decarboxylation of the ester.

In the reaction of MA, the conversion of the carbonyl group proceeds through the hydrogenation to α,4-dimethylbenzylalcohol, which is dehydrated to 4-methylstyrene and finally hydrogenated to 4-ethylmethylbenzene. In agreement with the results of Laurent and Delmon [12] on alumina supported catalysts, we have shown that MA conversion is inhibited by H_2S. The participation of hydrogenation sites located on incompletely coordinated molybdenum atoms would account for these results. With the increase of P_{H_2S}, hydrogen sulfide would adsorb on partially reduced and uncoordinated molybdenum atoms and the hydrogenation of the carbonyl group would be inhibited.

4.2. The influence of the sulfidation temperature: catalyst characteristics

4.2.1. Physico-chemical characterisation

XPS measurements show that the degree of reduction of molybdenum increases with the sulfidation temperature (decrease of the Mo^{6+}/Mo_{tot} ratio and increase of the Mo^{4+}/Mo_{tot} ratio); Mo^{4+} represents more than 50% of all the molybdenum species for temperatures higher than 300°C. However, relatively large amount of Mo^{6+} has been found. Mo^{6+} species are probably in relation with four different aspects or phenomena which simultaneously exist in our samples.

A first part of Mo^{6+} is certainly related to the presence of $CaMoO_4$ due to calcium impurities in the support. Another part of Mo^{6+} is likely due to the presence of cobalt–molybdenum mixed oxides. The latter are more easily formed on carbon than on alumina as a consequence of the weaker interactions of molybdenum with carbon than with alumina. A third reason for the presence of Mo^{6+} can be found in the experimental procedure for the preparation of the sulfided samples for XPS analyses. A partial, accidental surface re-oxidation during the preparation and storage of the samples may take place. However, these three aspects would account only for a part of the Mo^{6+} species and they do not explain the increase of reduced Mo^{4+} with the sulfidation temperature. It can reasonably be supposed that in the range of temperature studied, neither $CaMoO_4$ nor $CoMoO_4$ can get sulfided. Moreover, the decrease of the Mo^{6+}/S^{6+} ratio with the sulfidation temperature indicates that there is no strict relation between the Mo^{6+} and S^{6+} species. The reduction–sulfidation degree of molybdenum mainly depends on the activation temperature. We have shown that the dispersion of molybdenum-containing species is relatively low and non-homogeneous [19]. This explains why non-reduced, non-sulfided molybdenum oxides and oxysulfides are still present after sulfidation at low temperature; more complete reduction–sulfidation would take place only at high temperature.

The S_{tot}/Mo_{tot} ratio is always higher than 2 and only slightly increases with the sulfidation temperature. The S^{6+}/S^{tot} or the S^{2-}/S_{tot} ratios are constant. There are no reasons to believe that the total amount of molybdenum (Mo_{tot}) detected by XPS is not constant, thus our results would indicate that the total sulfur level only slightly increases with the sulfidation temperature. However, its variation would be less important than the increase of the reduction degree of molybdenum. This suggests that the S^{2-}/Mo^{4+} ratio decreases with the increase of the sulfidation temperature.

After catalytic test, the Mo^{6+}/Mo_{tot} ratio decreases, while the Mo^{4+}/Mo_{tot} ratio increases. The increase of the reduction degree of molybdenum after 36–48 h of reaction can be attributed to the stronger reduction conditions (high pressure) compared to the activation performed before XPS analyses [20], or to a different sulfidation role of DMDS, rather than to the longer contact with sulfiding agents. Actually samples sulfided for longer times (non-published results) do not show significant differences, neither concerning the Mo^{4+}/Mo_{tot} ratio nor the catalytic activity. XRD analyses show that MoS_2 crystallites grow with increasing the sulfidation temperature.

4.2.2. The catalytic activity and the active sites

From the physico-chemical characterisation of the CoMo/C catalyst sulfided at different temperatures, it can be concluded that two phenomena take place simultaneously: the increase of the reduction degree of molybdenum and the increase of MoS_2 crystal size.

The modification of these two aspects should be related to the changes in catalytic activity and selectivity and to the formation of different active sites [21].

With the increase of MoS_2 crystal size and the corresponding decrease of the active phase dispersion, the number of active sites decreases. This would account for the decrease of GUA and ED conversion. At the same time, the reduction degree of molybdenum increases: this would explain the higher selectivity in deoxygenated products. The strongly reduced, coordinatively unsaturated sites, responsible for the cleavage of $C_{aroamtic}$–O bond are probably located at the edges of MoS_2 crystals, as those responsible for the breaking of C–S bonds [7,22]. As the reaction of MA is concerned, the study of the influence of H_2S partial pressure indicated that the hydrogenation of the carbonyl group would take place on reduced molybdenum sites. The increase of MA conversion with the sulfidation temperature and with the reduction degree of molybdenum is in agreement with this first hypothesis. But, it is surprising that the decrease of the active phase dispersion does not have a negative effect on this reaction.

5. Conclusions

The activity of sulfided CoMo/C catalyst is deeply affected by modifications of the H_2S partial pressure during reaction and by the sulfidation temperature during the activation step.

H_2S does not affect the activity of the CoMo/C catalyst for the overall conversion of GUA. As regards the product, H_2S inhibits the direct hydrogenolysis of the $C_{aromatic}$–O bond and the phenol* to catechol ratio is consequently decreased. Highly reduced coordinatively unsaturated sites located on the metal sulfides are very likely responsible for the hydrogenolysis of $C_{aromatic}$–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 which can be located on the sulfide phase would be responsible for the demethylation of GUA to catechol. As for ED, the conversion and the products yield are not influenced by hydrogen sulfide. Both hydrogenation sites and acid sites located on the metal sulfides could be involved in these reactions, as previously proposed. However, due to the complex reaction pathway, more precise interpretations seem to be difficult. Reduced and incompletely coordinated molybdenum atoms are likely to be involved in the hydrogenation of the carbonyl group of MA.

The reduction–sulfidation of our CoMo/carbon catalysts is a very complex process. The reduction degree of molybdenum and the crystallinity of MoS_2 simultaneously increase with the increase of the sulfidation temperature. The most important parameter to affect GUA and ED conversion seems to be the dispersion of the active phase. The increase of the reduction–sulfidation degree of molybdenum has a positive effect on the formation of deoxygenated products from GUA and on the hydrogenation of MA. As previously shown, reduced, coordinatively unsaturated molybdenum atoms are very likely responsible for these reactions.

It is interesting to note that the use of a carbon supported catalyst avoids the interference of the support acidity with that of the sites carried by the sulfide phase. This allows to clarify the behaviour of the latter.

Acknowledgements

The financial support of the European Union (JOR3-CT95-0025) is gratefully acknowledged.

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