

Influence of the Support of CoMo Sulfide Catalysts and of the Addition of Potassium and Platinum on the Catalytic Performances for the Hydrodeoxygenation of Carbonyl, Carboxyl, and Guaiacol-Type Molecules

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The present work corresponds to part of a program aimed at upgrading oil obtained by pyrolysis of biomass by hydrotreatment (hydrodeoxygenation HDO). CoMo sulfide catalysts, nonsupported, supported on different supports (alumina, carbon, silica), or modified by K or Pt, were used. We used a model reacting mixture containing compounds representative of the molecules that must react to permit a primary stabilisation of the pyrolytic oil: 4-methylacetophenone (4-MA), diethylsebacate (DES), and guaiacol (GUA). In the reaction of the carbonyl group of the 4-MA it is shown that no important role is played by any acid–base mechanism; dispersion determines the activity. Acidity of the support influences the formation of active sites for decarboxylation and hydrogenation of the carboxyl group of DES. It was confirmed that guaiacol-type molecules lead to coking reactions. The role of acidity in the mechanism of these reactions is confirmed, but the modifications made in the catalysts in this work are still not sufficient to control coke deposition. The catalysts supported on carbon lead to the direct elimination of the methoxyl group of the guaiacol. Carbon, on the whole, seems to be a promising support. This work suggests that appropriate modifications of the hydrotreating catalysts can lead to a more effective process for stabilisation of the bio-oils by reaction with hydrogen. © 1995 Academic Press, Inc.

INTRODUCTION

One way of upgrading oils obtained by biomass pyrolysis (bio-oils) is catalytic hydrotreatment (1–4). This process, by eliminating oxygenated groups, leads to an improvement in the chemical stability of the bio-oils and an increase in the heating value. The thermal instability of bio-oils and the different reactivities of the oxygenated groups require that hydrotreatment be performed in two stages (5, 6): (i) a stabilisation stage, carried out at a

low temperatures (200 to 300°C), to eliminate the more reactive functions like ketones, carboxylic esters and acids, and guaiacol-type molecules; and (ii) a second stage executed at higher temperatures, aimed at deoxygenating mainly the phenolic-type molecules. Using the stabilisation stage alone, it would be possible to produce an oil which could be stored over long periods (5) for later processing or could be used immediately as low grade fuel. For this reason, this stabilisation stage is crucial for practical uses of bio-oil.

In previous studies (7, 8), we reported on the activity of traditional sulfided CoMo and NiMo catalysts for the hydrodeoxygenation of carbonyl, carboxylic, and methoxyl groups present in model compounds representative of the composition of bio-oils. Some of the corresponding molecules, because of their instability, are suspected to lead to coking reactions. They can be eliminated at temperatures ranging between 200 and 300°C. We also observed, as other authors did (9), a deficiency in the molar balance between guaiacol and reaction products; presumably, the reason for this is that guaiacol tends to form heavy compounds and coke under hydrotreating conditions. This coke formation tendency could render the low-temperature stabilisation of bio-oils more difficult and limit the life of the catalysts.

It is thus necessary to improve the performance of the catalytic systems. One possibility is to avoid the formation of polymerisation products by using a catalyst that is less active for that unwanted reaction; another is to find a catalyst that is more active for the deoxygenation reactions. This would permit work in a lower temperature range, where coking reactions do not take place or take place at a lower rate. A combination of these two solutions is understandably preferable.

Over CoMo and NiMo catalysts (7, 8), guaiacol reacts first to catechol by a demethylation reaction. Catechol is subsequently deoxygenated by a combination of C–O

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bond hydrogenolysis and hydrogenation reactions. The final products are benzene and cyclohexane. The γ -alumina support alone has a nonnegligible activity for the demethylation reaction but cannot deoxygenate the catechol produced. When alumina contains the active phase, the conversion is only slightly higher but the catalyst shows a better stability against deactivation. Hydrogenolysis and hydrogenation also occur.

Knowing from the literature the propensity of guaiacol and catechol to thermally form polycondensation products (9, 10) and the relatively strong interaction of these compounds with alumina (11–13), it is logical to assume that these reactions occur at the surface of the support. On the other hand, compounds containing a single oxygen function such as phenol have a much lower propensity for coking reactions (10). Taking these data into account, two objectives may be posited for the synthesis of superior catalysts: to prepare catalysts with a support that is less active for coke formation or to find a more active catalyst permitting a rapid conversion of dioxygenated molecules (guaiacol, catechol) into compounds containing only one oxygen (phenols). Both objectives were pursued in this work. Catalysts were prepared with neutral supports (silica and activated carbon) in order to evaluate their potential compared to alumina. Along the same line, an unsupported catalyst was also tested. To complete this study, the acid–base properties of a γ -alumina supported catalyst were modified by the addition of potassium. These experiments should shed some light on the mechanisms of guaiacol hydrodeoxygenation and suggest some tracks for the development of more adapted catalysts. The second objective, namely, to find a catalyst more active for the elimination of the first oxygenated group, was approached by testing a CoMo catalyst that was modified by the addition of platinum.

As in previous investigations, these catalysts were tested for their catalytic activity in the simultaneous hydrodeoxygenation of carbonyl, carboxylic groups, and guaiacol in order to get results reflecting to some extent the complicated interaction between reacting molecules which could occur with a pyrolytic oil. The decrease of the BET surface area due to the catalytic test and the quantity of carbon deposited were also determined.

EXPERIMENTAL

Reactor

A 570-ml stainless steel closed batch reactor was used for the tests. The solution of reactants occupied a volume of 170 ml. Under reaction conditions, the solution was vigorously agitated by means of a magnetically operated stirrer.

Catalysts

The CoMo catalysts were prepared by impregnation of the various supports with an aqueous solution of ammonium heptamolybdate (Merck) and cobalt nitrate (Merck). The alumina was obtained from Procatalyse (BET surface area S_{BET} , 240 m² g⁻¹ and pore volume V_p , 0.7 cm³ g⁻¹). The silica and carbon supports were from Kali-Chemie (AF 125, S_{BET} 260 m² g⁻¹, V_p 0.88 cm³ g⁻¹) and from Norit (RX 2 Extra, S_{BET} 1270 m² g⁻¹, V_p 0.68 cm³ g⁻¹), respectively. Pore volume impregnation was used with alumina and activated carbon. For the silica support, the wet method was used. A volume of water 5.5 times the pore volume was used and afterward this excess was evaporated in a rotavapor at 40°C. After impregnation, the solids were dried under a flow of air at 120°C for 16 h. Subsequently, the alumina- (CoMo/Al-1) and silica- (CoMo/Si) supported catalysts were calcined in air at 500°C for 4 h. and at 400°C for 3 h, respectively. The carbon-supported catalyst (CoMo/C) was activated directly before use in a H₂S/H₂ sulfidation mixture described later. The composition of the supported catalysts was 15% MoO₃ and 3% CoO. The unsupported CoMo catalyst (CoMo) was prepared according to the homogeneous sulfide precipitation (HSP) procedure (14, 15). The precipitate was dried in argon at 120°C and treated in the sulfidation mixture at 400°C for 4 h before use. This catalyst was prepared with atomic ratio Co/Co + Mo = 0.3.

The influence of the addition of potassium and platinum was studied by impregnating an industrial CoMo catalyst, Procatalyse HR-306, containing 14% MoO₃ and 3% CoO (CoMo/Al-2). Its BET surface area was 200 m² g⁻¹ and its pore volume was 0.46 cm³ g⁻¹. A wet impregnation method, with the solution of the precursors in a volume of water 10 times the pore volume, was used. Afterward, the excess water was eliminated in a rotavapor at 30°C. The precursors were potassium hydroxide (Janssen) and tetraaminoplatinum(II) nitrate (Aldrich). The impregnated solids were dried at 120°C and calcined at 500°C under air. The quantities used were calculated for obtaining contents of 1 wt% of K (CoMo/Al-K) and 0.5 wt% of Pt (CoMo/Al-Pt). As reported later, the actual contents were in good agreement with these values. Two samples of the CoMo catalyst were treated under the same pH conditions as the impregnations and served as references (unmodified catalysts). The pH was adjusted to 12.5 using a solution of ammonium hydroxide (CoMo/Al-S2) to be compared to CoMo/Al-K and to 6.2 using distilled water (CoMo/Al-S1) to be compared to CoMo/Al-Pt.

The catalysts were activated using a standard reduction–sulfidation procedure. It consisted of drying 1.2 g (unless otherwise stated in the results section) of catalyst under argon at 120°C for 1 h. The argon was then replaced

by a mixture of 15 vol% H₂S in H₂ at 100 ml min⁻¹. The temperature was increased to 400°C at 10°C min⁻¹. These conditions were maintained for 3 h. The solid was then cooled to room temperature under the same gaseous mixture. Finally, the gas was switched to argon in order to purge the reactor. The activation procedure was slightly different for the carbon-supported and unsupported catalysts. For these two catalysts the heating rate was 3°C min⁻¹ and the treatment time was 2 h. The catalysts were transferred into the reactant feed and, as much as possible, contact with air was avoided.

In another experiment, the activity of the alumina support alone was evaluated. The same standard procedure of drying, calcination, and reduction-sulfidation was used to prepare the corresponding sample.

A test using the catalyst HR-306 (CoMo/Al-2) and pure hexadecane served as a blank test to compare the content of coke after reaction.

Solution of Model Compounds

The model reactants were 4-methylacetophenone (0.232 mol liter⁻¹), diethylsebacate (0.116 mol liter⁻¹), and guaiacol (0.232 mol liter⁻¹). They were dissolved in hexadecane (3.03 mol liter⁻¹). Pentadecane (0.07 mol liter⁻¹) was added to this solution as an internal standard for the chromatographic analysis. CS₂ (0.025 mol liter⁻¹) was added as a precursor of H₂S.

In a separate experiment, guaiacol was used alone to study its specific influence on the formation of coke. The solution contained 8 wt% guaiacol in hexadecane. Carbon disulfide was added in the same proportion as in the standard mixture.

Reaction Procedure

The reactor was sealed immediately after the addition of the presulfurised catalyst to the reaction mixture. Air was evacuated by pressurisation-depressurisation cycles with nitrogen and subsequently with hydrogen. The mixture was then heated to 280°C at 4.5°C min⁻¹ under low hydrogen pressure (1 MPa) and slight agitation. After reaching the reaction temperature, the sampling line was purged by withdrawing 6 ml of the reactant solution. A first sample of 0.5 ml was then taken. It corresponded to the sample which was considered to correspond to time zero of the reaction. The concentrations of the reactants in this sample were conventionally considered to be 100%, neglecting the slight conversion reached at the end of the heating period. The pressure was increased to 7 MPa and the agitation was set at 1000 rpm. The starting time for agitation was taken as time zero. Liquid samples were taken every 10 min during the first hour of reaction and every 20 and 30 min in the second and third hours, respectively. The volume of liquid taken from of the reactor was

always measured. Hydrogen was added to maintain the pressure at 7 MPa when it was necessary. Prior to the chromatographic analysis, the liquid samples were diluted in one part benzene for one part sample (volume) in order to fully solubilise cathecol and phenol.

Analysis

The liquid samples were analysed in a Packard Model 428 gas chromatograph equipped with a split injector and a Flame Ionisation Detector (FID) both at 300°C. The different compounds were separated in a 25 m DB-5 capillary column. The electronic response of the detector was integrated by a Model 3308A HP integrator. The chromatographic peaks were identified by GC-MS analysis and by comparison of the retention times to those of known compounds. Response factors were determined and used in the calculation of the molar balances and selectivities.

After the tests, the used catalysts were recovered in isooctane in order to avoid any oxidation by air. The catalysts were subsequently extracted in a Soxhlet with hexane and acetone for 12 h before surface area and elemental composition analyses were carried out.

The BET specific surface areas of the various supports and catalysts were measured before and after reaction with an automated nitrogen adsorption instrument (Micromeritics ASAP 2000).

The elemental analyses (Co, Mo, Pt, K) were performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The sulfur and carbon contents were determined by automatic titration of the SO₂ and CO₂ formed, in a Ströhlein Coulomat 702 apparatus.

The acidity of sulfided catalysts was determined by TPD of NH₃. The same reduction-sulfidation procedure as described above was used before each measurement. The samples (0.3 g) were then flushed with He for 20 min. Ammonia was subsequently adsorbed at 100°C for 15 min. The temperature was increased at a rate of 10°C min⁻¹ to 500°C for pure alumina and alumina-supported catalysts, and 400°C for silica and carbon catalysts. This final temperature was maintained for 30 min. Desorbed ammonia was retained in a boric acid solution and afterward quantified by titration with sulfuric acid.

Expression of the Results

The reaction schemes of the hydrodeoxygenation of the reactants used in this work confirmed those established in a previous study (7). They are reported in Fig. 1.

The 4-methylacetophenone (4-MA) gives *p*-ethylmethylbenzene as the only product. The intermediates α ,4-dimethylbenzylalcohol and 4-methylstyrene were not observed under the standard reaction conditions due to the

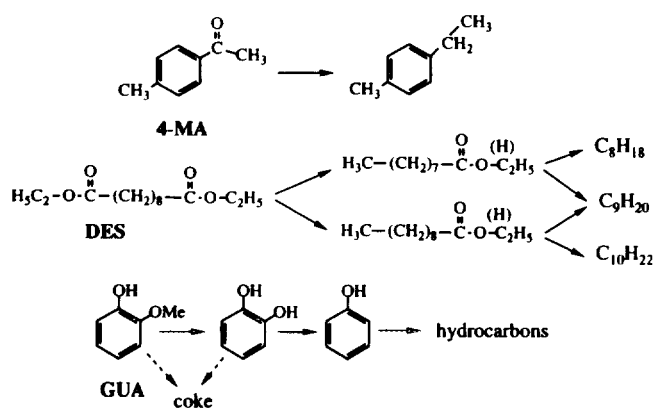


FIG. 1. Reaction schemes of the hydrodeoxygenation of 4-MA, DES, and GUA.

high activity of the CoMo catalyst for the conversion of these intermediate products.

The carboxylic groups of the diethylsebacate (DES) react following two paths. One is the reduction to a CH₃ group. With DES, the final product of that path is decane. The other path corresponds to the decarboxylation and leads finally to octane. A combination of these paths gives nonane. The carboxylic ester group may also react intermediately to a carboxylic acid group. This is represented schematically in Fig. 1 by an (H) situated above the ethyl group of the carboxylic ester. It has been shown in a previous study that a carboxylic acid group follows the same deoxygenation paths as a carboxylic ester group (7).

Concerning methoxyphenol (GUA), the first reaction is the hydrogenolysis of the methyl-oxygen bond leading to catechol. The subsequent reactions are the hydrogenolysis of the aromatic carbon-oxygen bonds followed by aromatic ring hydrogenation, giving benzene and then cyclohexane as final products.

The activity of the catalysts for the various reactions, as characterised by the disappearance of the reactants, will be reported as pseudo-first-order reactions with rate constants k . These are determined according to the equation used by Gevert *et al.* (16),

$$-\ln \frac{C_i}{C_0} = kWf(t/V), \quad [1]$$

where $f(t/V)$ is

$$f(t/V) = \sum_{i=1}^n \frac{t_i - t_{i-1}}{V_{i-1}}, \quad [2]$$

where C_i and C_0 are the reactant concentrations of sample i at time t and at time zero, respectively; k is the rate constant expressed in $\text{min}^{-1} \text{g-cat}^{-1} \text{cm}^3$; W is the catalyst

weight (g); t is the time in minutes; n is the number of samples taken; and V is the solution volume (cm^3). Specific rate constants were also calculated using the total surface area of the fresh catalysts. In this case they were expressed in $\text{min}^{-1} \text{cm}^3 \text{m}^{-2}$. The rate constants reported subsequently were generally determined using the first concentration data for which the linear relation was valid. It has been verified that this expression of the catalytic activity gives identical results, but it is more reliable (gives a better fit) than activities determined as initial reaction rates.

The selectivity for the deoxygenation of the carboxylic ester groups is expressed as a decarboxylation percentage. It is calculated using the concentrations of the final products octane, nonane, and decane according to the equation

$$S_{\text{decarb}} = \frac{(2 \times C_{\text{oct}} + C_{\text{non}})}{2(C_{\text{oct}} + C_{\text{non}} + C_{\text{dec}})} \times 100. \quad [3]$$

The activity of the catalysts for the hydrogenolysis of the carboxylic ester into a carboxylic acid group is approached by reporting the ratio of intermediate acids to intermediate esters (Eq. [4]). This ratio was almost constant over the conversion range studied. This factor will be called the deesterification ratio. It enables the qualitative comparison of the activity of the various catalysts for that reaction.

$$\text{Deesterification ratio} = \text{Deester} = \frac{(C_9 + C_{10})_{\text{acid}}}{(C_9 + C_{10})_{\text{ester}}}. \quad [4]$$

The selectivity in the conversion of guaiacol is reported as the ratio between phenol and catechol ($\text{phen/cath} \times 100$). It was calculated by linear regression using the first conversion points.

RESULTS

Influence of the Support on the Catalytic Activities and Selectivities

The catalytic activities and selectivities of the various modified catalysts are reported in Table 1.

For the hydrogenation of the carbonyl group of 4-MA, it is observed that the alumina-supported catalyst (CoMo/Al-1) is the most active, while the alumina support alone has a very low activity. The carbon-supported catalyst (CoMo/C) shows good activity but the silica-supported (CoMo/Si) and the unsupported catalyst (CoMoS) have a specific activity five to ten times lower than the alumina-supported catalyst.

Concerning the conversion of the carboxylic ester group, the differences in activity are less marked. The

TABLE 1

Pseudo-First-Order Rate Constants for the Conversion of 4-Methylacetophenone (4-MA), Diethylsebacate (DES), and Guaiacol (GUA), and Decarboxylation Selectivity, Deesterification, and phen/cat Ratios for the CoMo Catalysts Supported on the Different Supports, Unsupported CoMo Catalyst, and the Alumina Support

Catalyst	k_{4MA}		k_{DES}		S_{decarb} (%)	D_{eester} ratio	k_{GUA}		phen/cat (%)
	(*)	(**)	(*)	(**)			(*)	(**)	
γ -Al ₂ O ₃	0.15	0.06	0.32	0.14	(#)	(—)	0.35	0.15	~0
CoMo/Al-1	9.69	4.61	0.70	0.33	36	1.35	1.30	0.62	12.6
CoMo/Si	1.97	0.96	0.17	0.08	(#)	0.92	0.28	0.14	2.0
CoMo/C	7.79	1.10	0.83	0.12	22	0.34	0.22	0.03	89.3
CoMoS	0.82	4.32	0.77	4.05	(#)	(—)	0.39	0.21	8.0

Note. (*) $\text{min}^{-1} \text{g-cat}^{-1} \text{cm}^3$. (**) Specific constant rate in $\text{min}^{-1} \text{cm}^3 \text{m}^{-2} \times 10^2$. (#) Quantity of the products is insignificant.

alumina support alone has higher activity than the silica-supported catalyst (CoMo/Si). The alumina-supported (CoMo/Al-1), carbon-supported (CoMo/C), and the unsupported (CoMoS) catalysts have similar activities. The results of selectivity measurements indicate that the alumina-supported catalyst (CoMo/Al-1) has the highest decarboxylation and deesterification selectivities. The silica-supported catalyst (CoMo/Si) has a negligible decarboxylation selectivity but a relatively important deesterification selectivity. The carbon-supported catalyst (CoMo/C) displays a moderate decarboxylation selectivity and a low deesterification selectivity.

For the conversion of guaiacol (GUA), the alumina-supported catalyst (CoMo/Al-1) is the best. The other catalysts and the alumina support alone have activities three to six times lower.

The carbon-supported catalyst has a much lower activity for the production of catechol but produces phenol faster than the alumina-supported catalyst, as shown in Fig. 2. To have a comparable conversion of guaiacol, a large quantity of CoMo/C catalyst (2.5 g) was used for the test reported in Fig. 2. Another way of expressing

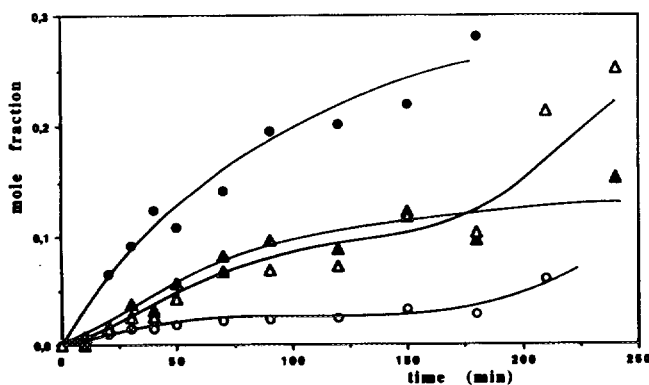


FIG. 2. Catechol and phenol production on carbon and alumina catalysts: (●) catechol on CoMo/ γ Al₂O₃; (○) phenol on CoMo/ γ Al₂O₃; (▲) catechol on CoMo/carbon; (△) phenol on CoMo/carbon.

this result is shown in Fig. 3. It shows data for the mole fraction of phenol as a function of the mole fraction of catechol for the catalysts supported on alumina and carbon. The selectivity in the conversion of guaiacol is very different. The carbon-supported catalyst produces more phenol than catechol. In addition, the phenol/catechol ratio is not constant but increases as the total conversion increases.

Influence of Pt and K on Catalytic Activities and Selectivities

The rate constants for the conversion of the different oxygenated groups and the selectivities for the Pt- and K- modified CoMo/Al₂O₃ catalysts together with those of the reference catalysts are reported in Table 2. The results show that the catalysts modified with platinum (CoMo/Al-Pt) and potassium (CoMo/Al-K) have higher activities for the conversion of 4-MA compared to those prepared in our laboratory. Compared with the reference samples (CoMo/Al-S1, CoMo/Al-S2), they are only marginally different. The DES conversion activity, decarboxylation selectivity, and ester to acid deesterification ratio are similar for all the catalysts except for those modified with potas-

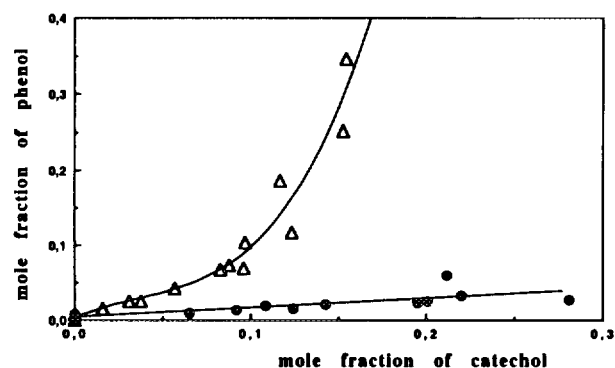


FIG. 3. Phenol/catechol ratio with catalysts supported on carbon (△) and alumina (●).

TABLE 2

Pseudo-First-Order Rate Constants for the Conversion of 4-Methylacetophenone (4MA), Diethylsebacate (DES), and Guaiacol (GUA), and Decarboxylation Selectivity, Deesterification, and phen/cat Ratios for the CoMo Catalysts Modified with Platinum and Potassium

Catalyst	k_{4MA} (*)	k_{DES} (*)	S_{decarb} (%)	D_{eester} ratio	k_{GUA} (*)	phen/cat (%)
CoMo/Al-2	9.55	0.73	38	1.16	0.70	13.7
CoMo/Al-Pt	11.95	0.73	34	1.11	0.65	12.4
CoMo/Al-S1	10.89	0.74	31	1.22	0.47	17.0
CoMo/Al-K	12.46	0.55	12	0.59	0.32	13.2
CoMo/Al-S2	10.39	0.77	34	1.37	0.43	13.3

Note. (*) $\text{min}^{-1} \text{g-cat}^{-1} \text{cm}^3$.

sium (CoMo/Al-K), for which the decarboxylation and deesterification selectivities are definitively lower. For the guaiacol conversion, the potassium-modified catalyst (CoMo/Al-K) shows a lower activity than the fresh (CoMo/Al-2) and platinum-modified (CoMo/Al-Pt) catalyst. Nevertheless, the effect of potassium is less marked when compared to the CoMo/Al₂O₃ sample treated under similar basic pH conditions (CoMo/Al-S2). The phenol/catechol ratio at low conversion is similar for all the catalysts.

Acidity of Catalysts

Table 3 shows the data on acidity for some catalysts and the alumina support.

The acidity of alumina-supported catalysts and the alumina support are three to four times higher than that of silica- or carbon-supported catalysts. The difference in acidity between potassium-modified catalyst (CoMo/Al-K) and CoMo/Al-2 (catalyst HR-306 without modification) is not significant. It is observed, in agreement with the literature (17, 18), that some acidity seems to be due to the presence of metal sulfides.

Influence of the Support and of the Presence of K and Pt on the Formation of Coke during HDO

Table 4 shows the elemental analysis of some catalysts before and after reaction, where the standard reacting mixture was used.

The carbon content of the CoMo catalysts supported on alumina was 8.95 wt% after reaction. This carbon content is slightly lower than that measured on the pure alumina support. In an independent experiment, a solution of guaiacol alone was used. The CoMo/Al-2 catalyst had a carbon content of 8.61 wt% after this test, indicating that guaiacol is mainly responsible for the coke formation. The carbon content of the catalyst CoMo/Al-2 (HR-306 without modification) used in the blank test with pure hexadecane was 1.8%.

The silica-supported catalyst shows a much lower propensity for coke formation than the alumina-supported catalyst. For the catalysts modified with potassium and platinum, the carbon content is not different from the carbon content on the unmodified catalyst.

The elemental composition of the active phase (Mo, Co, S) is very similar for all catalysts. It is not significantly modified after reaction, taking into account the carbon deposited. The industrial CoMo catalyst modified by the addition of Pt and K shows the same active metal proportion as the laboratory-prepared CoMo catalysts.

The influence of the test reaction on the textural properties of the catalysts on the various supports has also been studied. The results for the supported catalysts and the alumina support are reported in Table 5. The surface area for the unsupported catalyst was $19 \text{ m}^2 \text{ g}^{-1}$.

The HDO reaction causes a decrease in the specific surface areas and pore volumes of all the catalysts. The decrease is more significant for the carbon-supported catalyst, while it is very low for the silica-supported catalyst. The specific area diminution is approximately the same for the alumina-supported catalyst and the pure alumina support. The diminution of the pore volume is important for the alumina- and carbon-based solids.

DISCUSSION

In previous studies (7, 8), it has been shown that the catalytic functions required for the deoxygenation of the three model compounds were different. For this reason, it is logical to discuss the influence of the support and modifiers on the reactivity of each functional group separately. At the end of this paper, we also discuss the activity of the catalysts using the values of specific rate constants.

TABLE 3
Acidity for Catalysts and Alumina Support

Catalyst	CoMo/Al-2	CoMo/Al-K	$\gamma\text{-Al}_2\text{O}_3$	CoMo/Al-1	CoMo/Si	CoMo/C
Acidity μeq of NH_3/g	522.1	456.1	359.0	416.8	113.0	111.0

TABLE 4
Elemental Composition of Some CoMo Catalysts on Different Supports and Modified by Pt and K before and after the Standard HDO Test Reaction

Catalysts	C (wt%)	Mo (wt%)	Co (wt%)	S (wt%)	Pt (wt%)	K (wt%)
γ -Al ₂ O ₃ (before)	0.07	—	—	1.42	—	—
γ -Al ₂ O ₃ (after)	10.37	—	—	0.12	—	—
CoMo/Al-I (before)	0.06	8.18	2.16	5.69	—	—
CoMo/Al-I (after)	8.95	7.74	1.69	6.15	—	—
CoMo/Si (before)	0.05	7.73	1.89	5.40	—	—
CoMo/Si (after)	2.72	7.83	2.03	5.65	—	—
CoMo/C (before)	—	9.40	2.03	8.02	—	—
CoMo/C (after)	—	8.66	1.76	6.97	—	—
CoMoS (before)	0.05	41.20	11.70	36.10	—	—
CoMoS (after)	2.88	42.55	12.67	35.70	—	—
CoMo/Al-K (before)	0.05	7.67	2.21	—	—	0.83
CoMo/Al-K (after)	9.50	6.24	2.08	5.14	—	0.56
CoMo/Al-Pt (before)	0.05	7.26	2.24	—	0.46	—
CoMo/Al-Pt (after)	9.18	6.47	1.92	4.91	0.38	—
CoMo/Al-S1 (before)	0.05	6.87	2.49	—	—	—
CoMo/Al-S1 (after)	10.25	6.53	1.65	5.65	—	—

Carbonyl Group of 4-Methylacetophenone (4-MA)

The activities of the various catalysts for the hydrogenation of the carbonyl group of 4-MA are very different. A diminution in the activity by a factor of at least 10 is observed for the unsupported catalyst and the pure alumina support, when compared to alumina- and carbon-supported catalysts. With silica, the activity is five times lower than it is with alumina. Both CoMo/Al-I and CoMo/C are very active and even possess similar activities, in spite of the differences in acidity of their supports, alumina and carbon, respectively. It is well known that carbon is catalytically inert but promotes good dispersion of the cobalt and molybdenum sulfides. The differences must therefore be attributed to the differences in dispersion of the sulfide phases, and not to the acidic properties of the supports.

We have shown in previous publications (7, 8) that alcohol dehydration and olefin hydrogenation reactions are both very rapid on hydrotreating catalysts. This contradicts with the observations of Weisser and Landa (21), who considered the dehydration reaction the limiting stage. The present results confirm our initial observation. The succession of reactions, (i) carbonyl group hydrogenation, (ii) dehydration to olefin, and (iii) hydrogenation, is highly favoured in the presence of sulfide catalysts. This implies either that the active sites for these reactions are situated on the metal sulfides or that the reactions occur very rapidly on the support in our reaction conditions. For the first category of reaction, the dispersion of the sulfide phases is the main parameter. This is confirmed by the large difference between supported and unsupported catalysts. In principle the acidity of alumina should accelerate the dehydration step but this effect was not

TABLE 5
BET Specific Surface Area and Pore Volume of the Different Supported Catalysts before and after Reaction

Catalyst	Surface area (m ² g ⁻¹)				Pore volume (cm ³ g ⁻¹)			
	Before	After	Equiv. surf. ^a	Δ (%) ^b	Before	After	Equiv. vol. ^c	Δ (%) ^b
CoMo/Al-I	210	177	191	7.3	0.647	0.303	0.549	43.8
CoMo/Si	206	193	200	3.5	0.638	0.563	0.600	6.2
CoMo/C	711	469	—	—	0.405	0.266	—	—
γ -Al ₂ O ₃	239	197	214	7.9	0.681	0.435	0.552	21.2

Note. Volume of carbon deposit is calculated using a density of 1.8 g/cm³ for coke (19, 20).

^a Equiv Surf = surface of fresh cat \times (1-% carbon/100).

^b The % losses are calculated using the equivalent surface and pore volume respectively.

^c Equiv vol = Pore vol of fresh cat \times (1-% carbon/100)-vol of carbon deposit (ref. 19).

detected. In our experimental conditions (280°C), alcohol or olefin formed in the reaction are unstable, and 100% conversion to *p*-ethylmethylbenzene was obtained during the first minutes of reaction. Acidity, which is in principle responsible for the dehydration reaction, is not the crucial parameter. The low activity of the pure alumina support shows that the first step in the HDO of the ketone group is the rate-determining step.

It is generally reported that silica-supported catalysts are less active than alumina-supported catalysts (22, 23). Muralidhar *et al.* (23, 24) report an 87% decrease in hydrogenation activity. They also tested CoMo on silica–alumina supports of different compositions in HDS and HYD and found that activities decreased when the silica content increased in the support. Similar results indicating a decrease in hydrogenation activity were reported by Nishijima *et al.* (25, 26). This effect is due to the lower dispersion (27–30) of the sulfided phases on silica, and not to the lower acidity when compared to that of alumina. Earlier work in our group indeed showed that although the CoMoO_x oxide bilayer could be formed on silica, it was less stable, and reduction sulfidation led to a dramatic decrease in dispersion of the sulfided phases during the activating reduction–sulfidation procedure (27–30). Our conclusion is that the limiting stage in the reaction of 4-methylacetophenone (4-MA) is the hydrogenation of the carbonyl to a hydroxyl group.

Platinum clearly accelerates the reaction, although it is not possible to quantify this acceleration because of the limited accuracy of measurements in our autoclave reactor. This tendency agrees with those mentioned in the literature. Platinum has been reported to have high hydrogenating activity (31), and this activity is much increased in model catalysts containing noble metals associated with MoS₂ (32).

Activity changes due to potassium addition might be attributed to changes in molybdenum dispersion, a possibility supported by literature data dealing with the influence of modifiers on catalyst structure (33–36). Experiments at low temperatures are needed for more detailed data analysis and more precise conclusions.

Carboxylic Group of Diethylsebacate (DES)

Our discussion takes into account two types of data: (i) the variation of total conversion and (ii) the variation of selectivity, namely, the promotion of decarboxylation or hydrogenation reactions.

Concerning the conversion of the carboxylic ester group, the differences in activity are less marked than for the ketonic group. DES conversion activities are similar for all the catalysts except those supported on silica and the pure alumina support.

The selectivity results indicate that all the alumina-

supported catalysts have the highest decarboxylation and deesterification activities, except when modified with potassium. The silica-supported catalyst has a negligible decarboxylation selectivity but a relatively important deesterification selectivity. The carbon-supported catalyst displays a moderate decarboxylation selectivity and a low deesterification selectivity. The production of octane, nonane, and decane on the supported silica, unsupported catalysts, and the alumina support alone were insignificant.

The low decarboxylation selectivity and deesterification ratios for carbon- and silica-supported catalysts and potassium-modified catalysts, as compared with the ratios for alumina-supported catalysts, suggest a relation between support acidity and decarboxylation and deesterification reactions. This agrees with the higher acidic cracking activity of NiMo catalysts compared to that of CoMo catalysts that was reported by Ledoux *et al.* (37) for the case of decarboxylation. This was also supported by Laurent and Delmon (7), who found that a pure alumina support has some activity in the conversion of carboxylic ester to acid, and Knözinger *et al.* (38), who reported that activated aluminas were able to perform the nucleophilic addition of OH⁻ groups on electrophilic carbons.

In contrast, our results also show that our alumina supported and unsupported catalyst have no activity in the direct (primary) decarboxylation. Decarboxylation is also low or insignificant for catalysts that do not contain alumina, i.e., carbon or silica. Our conclusion is that active sites for decarboxylation could correspond to metal sulfides bound to the alumina support; they possibly correspond to Brönsted acid sites. The role of the Brönsted sites is suggested by the fact that the decarboxylation reaction is reported to be strongly inhibited by ammonia (8) and by our results obtained with the potassium-modified catalyst (Table 2).

Most catalysts give similar conversions of DES but some of them exhibit a low selectivity in decarboxylation. This implies a correspondingly higher activity of hydrogenation. This interpretation is not straightforward as dispersion effects, leading to higher overall activity, superimpose the effects on selectivity. Nevertheless, the high hydrogenating activity of the carbon-supported catalyst may be attributed to high dispersion and low acidity. The behaviour of the catalyst containing potassium can be satisfactorily explained by a depressed acidity, as compared to that of the nonmodified catalyst.

Reaction of Guaiacol (GUA)

The alumina support alone has a nonnegligible activity for guaiacol conversion, comparable to that of the other catalysts tested, except those supported on nonmodified alumina. Phenol is not present among the products, only

catechol was detected. On the other hand, coke formation was observed by Laurent and Delmon (8). We also verified this fact thanks to experiments with guaiacol as the only reactant using CoMo/ γ -Al₂O₃ catalyst.

The low amount of carbon deposited on silica-supported and unsupported catalysts compared with that on alumina and pure alumina clearly shows the relation between the presence of alumina and tendency of coke formation. Similar carbon contents (approximately 10%) and specific area diminutions are observed for alumina-supported catalysts and for the pure alumina support. This suggests that carbon deposition takes place on alumina. These results agree with the previously reported relation between support acidity and cracking and coke formation reactions (22, 39, 40) and confirm that coking during the reaction of guaiacol takes place on alumina acid sites. On the other hand, guaiacol conversion is lower for catalysts with weak acidity such as those supported on carbon or silica. This confirms that acid sites are involved. This is also confirmed by the facts that guaiacol conversion is highly inhibited by ammonia (8) and catalytic activity decreases for the potassium-modified catalyst (see Table 2). Acidity is thus involved both in the conversion of guaiacol to catechol and phenol and in the coke-forming side-reactions. The results in Table 2 show that our potassium-modified catalyst still possesses a substantial activity for guaiacol conversion. This is understandable, as the results of acidity measurements show that the quantity of potassium added (1%) was not enough to totally eliminate the acidity of alumina, and coke reactions were still comparable to those on the other alumina-supported catalysts.

The reaction scheme proposed to explain guaiacol HDO considers that the hydrogenolysis of the methyl-oxygen bond of the methoxyl group to form catechol and methane is the first stage, followed by a second stage leading to the elimination of one of the hydroxyl groups to produce phenol and H₂O (11, 13, 41). Bredenberg *et al.* (11) suggest that methyl-oxygen bond hydrogenolysis takes place on both support surface and metal sulfides, each by different mechanisms; on metals sulfides, a homolytic splitting, and on the support, a heterolytic scission would occur. These mechanisms suggest that catechol is the first reaction product, which is later transformed to phenol. Our results do not show this tendency in all cases. Table 1 and Fig. 3 show that the phenol/catechol ratio is not the same for all catalysts. In particular, the results for the carbon-supported catalyst are different; the phenol/catechol ratio is seven times higher than it is with the alumina-supported catalysts. This leads to an initial production of phenol that is equal to that of catechol (Fig. 2). These results might be interpreted as due to a direct elimination of the methoxyl group by the hydrogenolysis of the aromatic carbon-oxygen bond. Active sites for this reaction might be situated on metal sulfides, because carbon as such is an

inert material. The influence of carbon is only to increase metal dispersion. The possibility of this reaction is also considered in the literature (10, 41, 42) but no detailed studies to substantiate it have been made.

The Specific Rate Constants per Total Surface Area

Many attempts have made to relate the rate of reaction taking place on hydrotreating catalysts to their surface areas. In principle, it is presently still impossible to calculate this in a reasonably accurate way because there is no reliable method for evaluating the surface areas of the active phases, even if measurements using NO give widely different results according to the activating procedure and pretreatments of the catalysts (43, 44). In addition, it should be recalled that the active phase is mainly composed of two phases, MoS₂ (or CoMoS) and segregated Co₉S₈, which possess different functions. This makes it even more complicated to relate surface areas to catalytic activity. The only accessible value is the total surface area developed by the active phase and the support. Nevertheless we also present here the activity per total surface area for our catalysts (see Table 1).

As expected, the specific activities of the supported catalysts are generally much lower than the activity of the unsupported catalyst. For the reasons indicated above, the differences between the supported catalysts cannot be compared. Only for the silica-supported catalyst can the low activity observed be attributed to the lower dispersion of Co and Mo on this support compared with that on alumina.

One surprising result is that the activity for the 4-MA reaction is approximately the same as that for the unsupported and alumina-supported catalyst. We have no verified explanation for this. However, it can be recalled that some studies (45–50) showed that olefin bonds could be hydrogenated when adsorbed on alumina, provided that this alumina is irrigated by spillover hydrogen. We have shown that such a spillover takes place (51–55). We therefore speculate that alumina support plays a role in activating the hydrogenation of olefinic bonds during the succession of reactions of the 4-MA, thanks to the presence of spillover hydrogen.

CONCLUSIONS

The use of different supports and modifiers permits us to confirm or refine several conclusions concerning hydrodeoxygenation reactions on sulfided CoMo catalysts.

Acid-base mechanisms do not play an important role in the reaction of the HDO of the carbonyl group of the 4-MA. Dispersion of the sulfided phases constitutes the main factor determining activity.

The acidity of the support influences the formation of active sites for decarboxylation and hydrogenation of the carboxyl groups of DES. However, due to the role of acidity in dispersing CoMo sulfides on certain supports, the overall effect is complex.

Guaiacol-type molecules lead to coking reactions. Acidity plays a major role in the mechanism of these reactions. Although potassium, as an acidity modifier, does modify the reactions, the effect has yet to be optimised. Carbon gives a special selectivity to the CoMo catalysts.

As a whole the catalysts supported on carbon offer good perspectives for the HDO of pyrolysis oils.

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