Influence of Water in the Deactivation of a Sulfided NiMo/γ-Al₂O₃ Catalyst during Hydrodeoxygenation

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Water and oxygenated compounds are generally viewed as highly detrimental to the stability of sulfided hydrotreating catalysts. In this paper, a sulfided NiMo/γ-Al₂O₃ catalyst was treated in a batch reactor under typical hydrotreating conditions with or without water vapor. Changes of the HDO activity, composition, and texture of the various catalyst samples were further evaluated. Catalyst samples used in the HDO of organic oxygenated compounds were also characterized by XPS for modifications of the chemical surface composition.

Water caused a decrease of the catalytic activity to one-third the activity of the fresh catalyst but did not change the hydrogenation–hydrogenolysis selectivity. Water was also the cause of a small loss of the specific surface area conjugated to some crystallization of the γ-alumina support in a hydrated boehmite phase. On the other hand, the metal content, the dispersion, and the sulfidation state were not specifically affected by water. The deactivation would rather be related to the appearance of oxidized nickel species. The observations can be interpreted as resulting from the formation of an inactive nickel sulfate layer covering the active sulfide phases or from the formation of nickel aluminate. Otherwise, the oxidation of the molybdenum sulfide phase by water or oxygenated compounds in reaction conditions is very limited. © 1994 Academic Press, Inc.

INTRODUCTION

Energy supply is often cause for concern. Other important pending questions deal with environmental problems and the progressive creation of a greenhouse effect. In both contexts, biomass is an attractive source of energy. In particular, agricultural and agro-forestral lignocellulosic biomasses can potentially constitute a significant part of the energy market (1, 2). For an efficient energetic use, the raw solid biomass must be transformed into liquids or gases. Thermochemical processes were developed for this purpose. Of special interest are oils produced by fast pyrolysis of biomass, because the process is relatively simple and liquids are produced with high yields (3, 4). Nevertheless, liquids from biomass have the common characteristic of retaining a high quantity of oxygen both in the structure of the organic molecules they contain and as dissolved water (5, 6). Consequently, the properties of these bio-oils are hardly comparable to those of petroleum-derived products, and an upgrading step is required if the objective is not just burning in furnaces, but rather, for example, producing transportation fuels.

Hydroprocessing of bio-oils using sulfided cobalt molybdenum or nickel molybdenum catalysts was successfully tested by several groups (7–9). Pure hydrocarbon products were obtained through hydrodeoxygenation reactions. The process is closely related to the processes of petroleum hydrodesulfurization and hydrodenitrogenation as similar reaction conditions and catalysts may be used. Nevertheless, the composition and properties of the biomass-derived feeds have to be carefully considered for the technical development of the hydrodeoxygenation route. Potential problems to face are related, for example, to the thermal instability (polymerization tendency) of the oils, the diversity of the chemical groups, the high heteroatom content, and the high water content. One particularly important aspect of these problems is the fact that catalysts need to be highly resistant to deactivation. However, there has been, until now, nearly no focus on the catalyst stability during bio-oil hydrotreating. It was reported only recently that hydrotreatment tests of fast pyrolysis oils could not last more than 7 days because of reactor plugging (10).

In this paper, we concentrate on the potential deactivating role of water. The influence of organic oxygenated compounds on chemical modifications of the catalysts is also approached.

Water and oxygen-containing compounds may affect the activity of sulfided hydrotreatment catalysts in different ways. A direct perturbation may occur by competitive adsorption on active sites. In this case, inhibition is a function of the adsorption strength. It was reported in previous papers (11–15) that the inhibition by oxygenated compounds is moderate. Water caused only very weak inhibition on the hydrodeoxygenation of phenolic (11, 13), ketonic, and carboxylic groups (12). This indicated a low

281

adsorptivity of water on the sulfide phases responsible for the reactions. As a whole, water was much less poisoning than other small molecules like hydrogen sulfide or ammonia (11). On the other hand, water may adsorb relatively strongly on γ-alumina and perturb reactions occurring on this support, such as hydrolysis of carboxylic esters (12). For organic oxygenated compounds, the adsorption strength and inhibiting action are similar to sulfur-containing compounds (11, 14, 16) and substantially weaker than nitrogen-containing compounds (11, 15, 16).

But water or oxygen-containing compounds may also deactivate sulfided hydrotreatment catalysts by acting on their structure or chemical composition. The present paper focuses on this aspect. Although it was very seldom considered in the literature, the general consensus is that sulfided catalysts may be deactivated due to the oxidation of active phases by oxygenated compounds during the hydrotreating of low sulfur content feeds (17–22). Furimsky (17) observed that, during the hydrodeoxygenation of tetrahydrofuran in the absence of sulfur compounds, sulfided catalysts lost sulfur, which was supposed to be replaced by oxygen. Nishijima et al. (18) and Yoshimura et al. (19, 20) studied the deactivation occurring during the hydrotreating of low-sulfur-containing coal-derived feed stocks (which contain molecules similar to those of biomass-derived oils). They observed by XPS the oxidation of molybdenum sulfide to Mo^{6+}, of nickel sulfide to unspecified oxidized nickel species (Ni^{++}), and of sulfidic sulfur to sulfate anions. The extent was a function of the oxygen and sulfur content of the feeds (18, 20). On the base of thermodynamical phase diagrams, they deduced that molybdenum and nickel have a much higher affinity for oxygen than for sulfur (M–$O \gg M$–S) and that molybdenum has a higher affinity for sulfur or oxygen than nickel (Mo–$X \gg Ni$–X) (20).

Concerning more specifically water, it is generally considered that it plays a deactivating role but strong evidence is still lacking (20–22). Vogelzang et al. (22) reported that water (added as methanol) caused a rapid decrease of the catalytic activity for the conversion of naphthol. This observation was interpreted as due to structural modifications of the catalyst, especially oxidation by water. On the other hand, Yoshimura et al. observed that the deactivating and oxidizing strength of water was very weak in comparison to benzofuran and molecular oxygen (20).

Besides chemical modifications, water could be the cause of other deactivation phenomena. In particular, sulfate species formed even in low quantities would be quickly dissolved in water, thus rapidly decreasing the metal content. On the other hand, there is a danger of structural changes of the alumina support due to the action of water.

The present paper reports, for the first time, on the deactivation and modifications induced by the action of water in the absence of other oxygenated compounds. A sulfided nickel molybdenum catalyst was subjected to typical hydrotreating conditions in a closed batch reactor during a 5-day period with or without added water. Catalyst samples withdrawn were characterized for their BET surface area, crystallinity (XRD), bulk composition (elemental analysis), and surface chemical composition (XPS). The catalytic activity of samples subjected to each treatment condition was evaluated. The XPS spectra of catalysts having been used in batch reaction tests in the presence of various oxygenated compounds were also recorded and compared to those of the catalysts treated in the presence of water.

METHODS

Catalyst

An industrial nickel molybdenum catalyst supported on γ-alumina (Procatalyse HR 346) was used throughout this study. The size of the catalyst particles (obtained by crushing extrudates) was between 0.315 and 0.5 mm. Prior to use, the catalyst in its oxide form (as delivered) was activated by a standard laboratory sulfidation procedure in an all-glass reactor at atmospheric pressure. The operation consisted in drying the catalyst at 120°C under a flow of 100 ml/min of argon for 1 h. The gas was then switched to a mixture of 15% H_2S/85% H_2 at 100 ml/min. The temperature was raised at a rate of 10°C/min to a final temperature of 400°C which was maintained for 5 h. After that period, the reactor was cooled rapidly (30 min) to room temperature under the same mixture. Finally, the pretreatment gas was switched back to argon for 30 min.

Treatments

1. Catalyst Exposed to Water in Simulated Reaction Conditions

Twenty grams of sulfided catalyst were exposed to three different conditions for studying the effect of water: a blank test in an inert solvent dodecane alone (Blank run $_{(x)}$), the solvent plus water ($H_2O_{(x)}$), and the simultaneous addition of water and hydrogen sulfide (H_2O-$H_2S_{(x)}$). The conditions of treatment and the nomenclature are presented in Table 1.

The experimental procedure was the following: the activated catalyst was quickly poured into a 0.57-dm^3 batch reactor containing 170 ml dodecane. Ten ml water and 0.25 ml CS_2 (which is quickly decomposed in H_2S under treatment conditions) were added, depending on the experiment. The reactor was sealed and air was carefully evacuated. The temperature was increased to 360°C under vigorous mechanical stirring and mild hydrogen pressure. The total pressure was then fixed at 70 bars by adding hydrogen. These conditions were maintained for about

TABLE 1

Nomenclature of the Treated Catalyst Samples and Corresponding Treatment Conditions

Acronym	Feed
Conditions: total pressure, 7 MPa; temperature, 360°C; treatment time, 1 to 5 days	
Blank run $_{(i)}$[a]	170 ml dodecane
H₂O $_{(i)}$[a]	170 ml dodecane + 10 ml distilled water
H₂O–H₂S $_{(i)}$[a]	170 ml dodecane + 10 ml distilled water + 0.25 ml CS₂
Conditions: total pressure, 7 MPa; temperature, 340°C; treatment time, 150 min	
H₂O $_{(150)}$	170 ml dodecane + 7.8 ml H₂O + 0.25 CS₂
4MP $_{(150)}$[b]	13.6 wt% 4-methylphenol in dodecane + 0.25 CS₂
DBF $_{(150)}$[c]	13.6 wt% dibenzofuran in dodecane + 0.25 CS₂
Dodec $_{(150)}$	170 ml dodecane + 0.25 CS₂
Dodec $_{(150)}$–air	Dodec $_{(150)}$ + let freely under air during 3 days

[a] The subscript $_{(i)}$ is the sample number from 1 to 5 and corresponds to the number of days of treatment.

[b] The conversion of 4-methylphenol at the end of the test was 100%.

[c] The conversion of dibenzofuran at the end of the test was 53%.

12 h. The heating was then stopped and the reactor cooled overnight. The day after, the reactor was opened and approximately 2 g of catalyst were sampled. Care was taken that the catalyst did not come in contact with air by keeping it wetted by dodecane during sampling and pouring it immediately in isooctane. The catalyst particles were washed three times with isooctane. In the experiment with added CS₂, 0.25 ml was introduced in the reactor after each sampling operation. The reactor was then closed, and the whole cycle realized again. The operation was repeated five times (5 days). The calculated pressure of H₂S was 1.1 bar. The water pressure, determined experimentally, was around 25 bars under treatment conditions. Note that the saturation pressure of water is around 170 bars at the treatment temperature.

2. Catalyst Used in HDO Reaction Tests

In another set of experiments, the sulfided catalyst was used over a shorter period (150 min) in batch reaction tests with a reacting mixture containing different oxygenated compounds. These were water (H₂O $_{(150)}$), 4-methylphenol (4MP $_{(150)}$), and dibenzofuran (DBF $_{(150)}$). The practical work and treatment conditions were similar to those described above except the temperature, which was fixed to 340°C. The different feeds, reaction conditions, and sample nomenclature are reported in Table 1. After a test, the catalyst particles were placed in isooctane and analyzed by XPS. One experiment was performed in the presence of the solvent dodecane

alone (Dodec $_{(150)}$). In this experiment, a fraction of the spent catalyst was not recovered in isooctane. It was separated from dodecane by filtration and let to stand freely under ambient air for 3 days before XPS analysis (Dodec$_{(150)}$ + AIR).

Catalytic Activity of Treated Catalysts

Some of the catalyst samples recovered in the experiments dealing with the influence of water were further subjected to a standard reaction test in batch reactor. The catalyst particles, protected from air by isooctane, were poured into the reactor containing a standard reaction mixture composed of 4-methylphenol, 2-ethylphenol, and dibenzofuran, each at 4.5 wt%, in dodecane. Additionally, 0.25 ml CS₂ was added. The tests were performed at 340°C and 70 bars. Liquid samples were taken at various times during the tests and analyzed by gas chromatography. More details about the reaction procedure may be found in Ref. (11). The catalyst was quantitatively recovered after the reaction, washed with acetone, dried, and weighed. The concentration-time data were satisfactorily fitted to a first-order kinetic equation provided that samples with a conversion higher than 60% were not considered. The activities are arbitrarily reported as pseudo-first-order rate constants for the conversion of one of the reactants, 4-methylphenol. The conversion proceeds through two parallel pathways, one being the hydrogenation of the aromatic ring, the other being the direct elimination of the OH group (hydrogenolysis). The selectivity is expressed as the ratio of corresponding products, methyl cyclohexane to toluene (MCH/TOL) (Fig. 1). The standard deviation of the rate constants and selectivities was estimated as ±7% and ±10%, respectively.

Chemicals

The organic chemicals were from Janssen, and all had a purity of 99⁺%. The gases used in the pretreatments, treatments, or reaction tests were argon N46, nitrogen A28, and hydrogen N30 from L'Air Liquide, and all
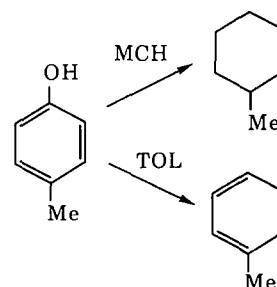

FIG. 1. Simple reaction scheme of 4-methylphenol hydrodeoxygenation.

were used as received. Their reported maximum oxygen contents are 3, 3, and 10 ppm, respectively.

Physicochemical Characterizations

The recovered catalyst particles were never crushed before physicochemical characterization in order to avoid contamination by atmospheric oxygen. Isooctane was generally evacuated by passing a flow of argon at 130°C for 3 h, except for the XPS analysis.

The BET surface area of the catalysts was determined using an automated nitrogen adsorption apparatus Micromeritics ASAP 2000. Prior to measurement, the catalysts were outgassed under a minimum vacuum of 4×10^{-3} Torr (1 Torr = 133.3 Nm^{-2}) at 100°C for approximately 5 h.

The X-ray diffraction spectra were recorded on a Philips PW-1130/90 apparatus working at 40 kV and 40 mA. The X-ray radiation was $CuK\alpha$ (λ = 1.5405 Å).

The nickel and molybdenum content in the last sample recovered in the experiments dealing with the influence of water (blank test $_{(5)}$, H_2O $_{(5)}$, H_2O-H_2S $_{(5)}$) and in the freshly sulfided catalyst was determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). The sulfur content of these catalysts was measured with an automated Ströhlein Coulomat 702 apparatus. The catalyst samples were equilibrated in atmosphere previous to measurement.

The XPS analyses of the catalyst samples were performed on a Surface Science Instruments spectometer (SSX 100) with a resolution (FWHM Au $4f_{7/2}$) of 1.0 eV. The residual pressure during the analysis was between 1 and 5×10^{-9} Torr. The X-ray beam was monochromatized $AlK\alpha$ radiation (1486.6 eV). It was focalized and lighted an elliptical surface of 1.74 mm on 1.37 mm. Charging effects were avoided thanks to the isolation of the samples and the utilization of a charge neutralizer (flood gun) adjusted at an energy of 10 eV. Binding energies were referenced to the binding energy of C_{1s} considered to be at 284.8 eV. Quantitative intensity results were obtained using C_{1s}, O_{1s}, Al_{2p}, $Mo_{3d5/2}$, S_{2p}, and Ni_{2p} peaks. The intensities were estimated by calculating the integral of each peak after "S-shaped" background subtraction and, when required, multicomponent deconvolution. Atomic concentration ratios were calculated by correcting the intensity ratios with the theoretical sensitivity factors based on Scoffield cross sections.

Care was taken to avoid exposure of the catalyst samples to atmospheric oxygen. The catalyst particles were pressed on 4-mm diameter stainless steel holders while keeping them continuously immersed in isooctane. When introducing the samples in the XPS machine, a meniscus of isooctane was present over the solids until

TABLE 2

Activity and Selectivity for the Hydrodeoxygenation of 4-Methylphenol of the Freshly Sulfided Catalyst and Catalysts Treated in the Presence of the Solvent Alone (Blank run $_{(5)}$), Added Water (H_2O $_{(5)}$), and Water Plus Hydrogen Sulfide ($H_2O-H_2S_{(1)}$, $H_2O-H_2S_{(3)}$, $H_2O-H_2S_{(5)}$)

	Rate constant (cm³ min⁻¹ gcata⁻¹)	Selectivity MCH/TOL	BET surface area (m²/g)
Fresh	2.65	20.0	181[a]
Blank run $_{(5)}$	2.30	20.5	172
H_2O $_{(5)}$	0.90	19.0	133
H_2O-H_2S $_{(1)}$	1.43	23.3	170
H_2O-H_2S $_{(3)}$	0.82	19.5	156
H_2O-H_2S $_{(5)}$	0.92	23.0	150

[a] The BET surface area of the fresh catalyst corresponds to the catalyst in its oxide form.

they were in contact with the nitrogen stream sweeping through the outgassing chamber.

RESULTS

Catalytic Activity of Treated Catalysts

The activity and selectivity of the freshly sulfided catalyst and several catalyst samples treated in the presence of the solvent dodecane alone (Blank run $_{(5)}$), added water (H_2O $_{(5)}$), and water plus hydrogen sulfide ($H_2O-H_2S_{(1)}$, H_2O-H_2S $_{(3)}$, $H_2O-H_2S_{(5)}$) are reported in Table 2.

The activity of the catalysts treated in the presence of water vapor for approximately 60 h (($H_2O-H_2S_{(5)}$) and (H_2O $_{(5)}$)) is almost three times lower than that of the freshly sulfided catalyst. The catalyst H_2O-H_2S lost 46% of its initial activity after 12 h of treatment ($H_2O-H_2S_{(1)}$). The activity does not change significantly after 36 h of treatment, indicating that a stabilization occurred between 12 and 36 h of treatment. The presence of hydrogen sulfide during the treatment has practically no influence on the overall activity. The catalyst treated in dodecane alone retains a large part of the activity of the fresh catalyst. The difference is barely significant compared to the standard deviation. The selectivity for hydrogenation of the aromatic ring relative to direct elimination of phenolic OH group (hydrogenation/hydrogenolysis) does not vary significantly for any catalyst.

Surface Area

The BET surface areas of the tested catalysts are presented in the same Table 2 as the catalytic activity results.

The surface area of the catalysts treated in the presence of water shows a tendency to decrease as a function of the treatment time (series H_2O-H_2S). The loss at the longest
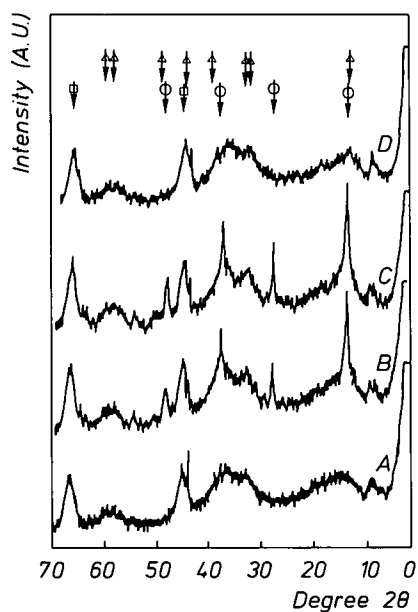
FIG. 2. XRD spectra of (A) the freshly sulfided catalyst, (B) catalyst (H_2O–H_2S (5)), (C) catalyst (H_2O (5)), and (D) catalyst (Blank run (5)). Arrows indicate the position of the diffraction lines of (△) MoS_2, (□) γ-alumina, and (○) boehmite.

X-Ray Diffraction

The X-ray diffraction spectra of the freshly sulfided catalyst and of the samples treated at the longest time in the presence of the solvent alone (Blank test (5)), added water (H_2O (5)) and water plus hydrogen sulfide (H_2O–$H_2S_{(5)}$) are shown in Fig. 2. The diffraction patterns of the fresh and dodecane-treated catalysts (A and D) do not present any sharp diffraction lines except a peak at $2\theta = 44.6°$. Broad diffraction lines corresponding to molybdenum disulfide (theoretically at 14.4, 32.7, 33.5, 39.5, 44.1, 49.8, 58.3, 60.1°) and γ-alumina (45.8, 66.9°) are visible and are indicated by arrows. The other diffraction peaks observed in the catalyst samples treated by water (B and C) appear at 2θ values of 14.6, 28.3, 38.4, 49.2°. Their position and relative intensity correspond to the diffraction lines reported for the hydrated alumina called boehmite (23). This hydrated alumina phase is produced continuously as a function of the treatment time (not shown).

treatment time for the catalysts treated in the presence of water plus hydrogen sulfide or water alone is 17 and 26%, respectively (relative to the surface area of the oxidic catalyst). It is substantially less if we compare it to the sulfided catalyst treated with dodecane alone. The surface area of this catalyst stays relatively constant. Experimental values of the samples in this series fluctuate between 170 and 176 m^2/g.

Elemental Analysis

The weight content of nickel, molybdenum, sulfur, and the atomic ratios S/(Mo + Ni) and Ni/(Mo + Ni) of the freshly sulfided catalyst and catalyst samples having been treated five days in the presence of the solvent alone (Blank test (5)), with added water (H_2O (5)), and with water plus hydrogen sulfide (H_2O–$H_2S_{(5)}$) are reported in Table 3.

The catalyst samples treated in the presence of water have a slightly lower nickel, molybdenum, and sulfur content than the fresh and dodecane-treated catalysts. The sulfidation state of the catalysts (ratio S/(Mo + Ni)) is maximum for the freshly sulfided catalyst. It is slightly lower for the catalysts treated with water and even lower for the catalyst treated in dodecane alone. The Ni-to-total-metal-content ratio (Ni/Mo + Ni) does not vary, indicating that the various treatments did not lead to a selective removal of one of the two metals.

Surface Composition

The S_{2p}, $Ni_{2p3/2}$, and Mo_{3d} XPS spectra of the (H_2O–$H_2S_{(x)}$) catalyst samples series are presented in Figs. 3, 4, and 5, respectively. The $Ni_{2p3/2}$ spectra of catalyst samples (Blank test (x)) are shown in Fig. 6. For the attribution of the XPS peaks, pure nickel sulfide (α-NiS), nickel sulfate ($NiSO_4$), and the oxidic nickel molybdenum catalyst were also analyzed. Their S_{2p} and $Ni_{2p3/2}$ spectra are presented in Figs. 7 and 8, respectively. The spectra of the freshly sulfided NiMo catalyst and the catalyst exposed to air (Dodec (150) + AIR) are also added in these figures.

1. XPS Peaks Attribution

S_{2p}. Sulfidic sulfur corresponds to a binding energy of 161.8 eV (NiS and freshly sulfided catalyst, A and B in Fig. 7). The peak of sulfur as sulfate is present at 168.7 eV ($NiSO_4$ and air-exposed catalyst, C and D). Note that

TABLE 3

Weight Percentage of Nickel, Molybdenum, and sulfur, and Atomic Ratios Sulfur to Metal and Nickel to Metal of the Freshly Sulfided Catalyst and Catalyst Samples Treated in the Presence of Water and Hydrogen Sulfide (H_2O–$H_2S_{(5)}$), Water (H_2O (5)), and Dodecane (Blank run (5))

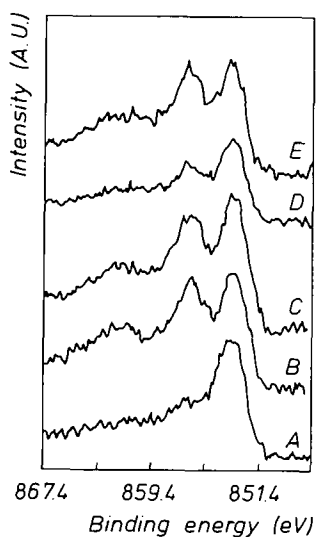|	Ni	Mo	S	S/(Mo + Ni)	Ni/(Mo + Ni)
Fresh	2.25	8.71	8.18	1.98	0.30
Blank run (5)	2.42	9.36	7.40	1.66	0.30
H_2O (5)	2.16	8.21	7.05	1.79	0.30
H_2O–H_2S (5)	2.03	7.73	6.90	1.87	0.30

FIG. 9. $Ni_{2p3,2}$ spectra of (A) $Dodec_{(150)}$, (B) $H_2O_{(150)}$, (C) $4MP_{(150)}$, (D) $DBF_{(150)}$, and (E) $Dodec_{(150)}$ + air.

DISCUSSION

Representativity of the Experimental Conditions

The partial pressure of water vapor in a typical hydro-treatment of pyrolytic oils can be estimated assuming a pyrolysis oil containing 20% of water and a weight content of organic oxygen of 30%, a liquid hourly space velocity of 0.5, a total pressure of 100 bars (1 bar = 100,000 Nm^{-2}), and a hydrogen flow rate corresponding to 10 times the stoichiometry for a complete deoxygenation. Such a calculation indicates that water vapor pressures around 7 and 16 bars would exist at the entrance and exit of the reactor, respectively. The water pressure could be higher with some fast pyrolysis oils containing even more oxygen. The water pressure used in this study was around 25 bars. It is thus representative of the conditions that could exist in the hydrotreatment of highly oxygenated bio-oils. However, it is much higher (from 10^2 to 10^3 times) than the water pressure that would ever exist in the hydrotreating of petroleum-derived feeds. In the treatment in the presence of hydrogen sulfide and water, the ratio H_2S/H_2 was similar to the ratio existing in typical HDS processes. On the other hand, the treatment time (around 60 h) was limited in comparison to the normal life of an industrial catalyst.

Influence of Water

The treatment of the NiMo catalyst in the presence of water vapor induces a diminution of its activity to one-third the activity of the fresh catalyst independently of the presence of hydrogen sulfide during the treatment. The deactivation appears relatively quickly in the first hours of treatment. The decrease of catalytic activity must be attributed to a permanent modification (in the sense that the activity is not restored in the presence of hydrogen sulfide within the time of a batch reaction test when water was removed).

The presence of water vapor causes a partial crystallization of the γ-alumina support to boehmite. This process continues during the whole experiment and is in agreement with the literature which indicates that γ-alumina is metastable under hydrothermal conditions (32) and transforms into boehmite in the temperature range 140–380°C. The boehmite phase that appears during our hydrothermal treatments of the NiMo catalyst is relatively well crystallized as evidenced by the sharpness of the diffraction peaks. The small decrease of the BET surface area may be attributed to this crystallization phenomenon. In addition, the formation of the hydrated alumina phase induces a small increase of the catalyst specific weight, which may also contribute to the observed decrease of specific area.

It may be expected that these structural and textural

as for both series of catalysts treated in the presence of water. The sulfate peak is slightly more intense in the catalyst exposed to air. No oxidation of molybdenum disulfide into molybdenum trioxide can be clearly observed except in the catalyst having been in contact with air, but the proportion of Mo^{6+} relative to Mo^{4+} remains very low.

3. Influence of Water on the Dispersion of S, Ni, and Mo

The XPS atomic ratios are presented in Table 4.

One limitation of the present measurements is that the analyses were made on the catalyst particles without additional crushing to fine powder. In such conditions, the X-ray beam had a size comparable to that of the particles. A certain scattering of the values ensues, due to inhomogeneities in catalyst preparation.

The ratios O/Al, Mo/Al, and S/Al do not show any clear change as a function of the various treatments. Comparing these to the value for the freshly sulfided sample, no clear evolution of these ratios as a function of the treatment time can be deduced. The Ni/Al ratio seems lower for the treated samples than for the fresh catalyst, but no evolution as a function of the treatment time is observed. The ratio Ni/(Mo + Ni) of the fresh catalyst is close to the bulk ratio (0.28 compared to 0.30). It is always lower for the treated catalysts when compared to the fresh catalyst. The ratio S/(Mo + Ni) is around two and is not influenced by the treatment conditions.

TABLE 4

XPS Atomic Ratios of the Freshly Sulfided and Treated Catalysts

	C/Al	O/Al	Ni/Al	Mo/Al	S/Al	Ni/(Mo + Ni)	S/(Mo + Ni)
Fresh	1.08	1.93	0.026	0.068	0.18	0.28	1.91
Blank run (1)	1.11	1.93	0.021	0.063	0.16	0.25	1.97
Blank run (2)	1.21	1.87	0.015	0.066	0.16	0.19	1.99
Blank run (3)	1.00	1.82	0.020	0.069	0.15	0.22	1.75
Blank run (4)	0.88	1.93	0.022	0.079	0.21	0.22	1.83
H₂O (1)	0.65	1.95	0.015	0.053	0.13	0.22	1.88
H₂O (2)	0.60	1.93	0.015	0.059	0.15	0.20	2.07
H₂O (3)	0.60	1.82	0.016	0.063	0.14	0.20	1.80
H₂O (4)	0.75	1.88	0.023	0.073	0.19	0.24	2.01
H₂O (5)	0.59	1.95	—	0.081	0.17	—	—
H₂O–H₂S (1)	0.60	2.02	0.023	0.061	0.18	0.27	2.14
H₂O–H₂S (2)	0.55	2.02	0.023	0.065	0.16	0.26	1.82
H₂O–H₂S (3)	0.64	2.08	0.023	0.069	0.18	0.25	1.96
H₂O–H₂S (4)	0.61	2.06	0.020	0.071	0.19	0.22	2.06
H₂O–H₂S (5)	0.54	2.02	0.017	0.068	0.17	0.21	2.00

modifications of the alumina support could occur during the hydrotreatment of bio-oils and would contribute to their long-term deactivation. Nevertheless, in our experiments, the observed deactivation cannot be entirely attributed to these modifications. Indeed, the decrease in activity is much higher than the decrease in surface area. Some other effects must occur.

In principle, the observed deactivation could be due to a decrease of the quantity of active metals. The elemental analysis shows that the samples treated in the presence of water have a slightly lower molybdenum and nickel content (Table 3). The difference compared to the fresh or dodecane treated catalyst is, on average, 10%. The decrease of the bulk concentration could simply be due to a difference in the hydration level of the catalyst samples which were equilibrated in atmosphere before weighing. This would be supported by the fact that the ratio Ni/(Ni + Mo) is not modified although a higher solubility of nickel could be expected. Also, this decrease of the content of molybdenum and nickel does not correspond to a similar decrease at the catalyst surface, as observed by XPS (Table 4). Indeed, the dispersion of molybdenum stays, on average, at the same level as that of the fresh catalyst. The dispersion of nickel is lower in all the spent-catalyst samples when compared to the freshly sulfided catalyst. Rather than a loss, this very likely indicates a sintering of nickel atoms when equilibrating the fresh catalyst under reaction conditions. But these observations cannot be linked to the lower activity of the water-treated samples in comparison to the solvent-treated samples.

Another cause of catalyst deactivation could, a priori, be the loss of sulfur which could result in an overreduction

of the active molybdenum and nickel sulfide phases. This is why, when using sulfur free feeds (model HDO or HDN feeds), a sulfur compound is generally added in low quantity. In the spent-catalyst samples, the sulfur to metal atoms ratio decreases slightly when compared to the freshly sulfided sample (Table 3). But it is unlikely that such a small decrease could be responsible for the deactivation we observed. This conclusion is substantiated by the fact that the sulfur content is the lowest in the sample treated in dodecane alone, which retains most of its activity. This also suggests that water might not be implicated in the loss of sulfur. The decrease can be interpreted as resulting from the elimination of some labile sulfur as hydrogen sulfide. This elimination was more extensive in the dodecane-treated sample because the hydrogen pressure was the highest in the corresponding treatment.

The deactivation could, according to the literature (17–22), originate from an oxidation of the sulfide phases by water. No oxidation of the molybdenum disulfide phase was discerned in our experiments. The oxidation of sulfidic sulfur into sulfate was always limited. These observations agree with the results of Yoshimura et al. (20). They observed practically no additional oxidation of a NiMo catalyst upon addition of water during a short hydrotreating test of a coal liquid when compared to the situation without added water. The thermodynamic phase diagram presented by Yoshimura et al. (20) indicates that, when converting oxygen pressure in water pressure assuming the equilibrium $H_2 + \frac{1}{2}O_2 = H_2O$, no oxidation of MoS_2 and NiS_x has to be expected in practical water-pressure conditions.

However, an oxidation of the nickel sulfide species is

observed when water is present during the treatment. Oxidized nickel species are observed in the XPS spectra in proportions close to that of sulfide species, and remain almost constant as a function of the treatment time. These species cannot receive a specific attribution by comparison to known compounds. Their appearance is not hindered by the presence of a pressure of 1.1 bar of H_2S. A large part of the deactivation of the water-treated catalysts should be attributed to this modification. Two interpretations may be proposed. The first is that nickel sulfide is oxidized in nickel sulfate and that these species form an inactive layer at the surface of nickel sulfide particles, and maybe also molybdenum sulfide particles. Nickel species decorating the edge plane of the MoS_2 particles (which possess the active sites) could be especially sensitive. As a consequence, access to the active sites would be hindered and/or their quantity reduced, resulting in the observed lower activity. This interpretation is supported by the observations of Yoshimura et al. (33) that, during TPO (temperature programmed oxidation) of a sulfided NiMo catalyst, sulfate nickel species cover bulk sulfides and protect them from further oxidation. Formation of oxidized nickel species covering nickel sulfide was also reported by Montes et al. (34) and Lichtman et al. (35). Conceptually, this interpretation would also be valid supposing that the oxidized nickel species are nickel hydroxides or oxides.

A second possible explanation could be that the oxidized nickel species correspond to nickel aluminate. The effect of water would be to favor the migration of nickel atoms into the alumina lattice (or the hydrated alumina lattice). A positive effect of water for the formation of cobalt aluminate during regeneration of a CoMo catalyst was reported by Arteaga et al. (36). This phenomenon would result in a decrease of the concentration of active nickel species. The observed deactivation would originate from a decrease of the catalytic synergy between nickel and molybdenum phases due to modification of the optimum Ni/Mo ratio.

Influence of Oxygenated Compounds

When oxygenated compounds (dibenzofuran and 4-methylphenol) were reacted, no significant modifications of the XPS spectra were observed compared to the catalyst treated with added water alone, indicating that these compounds are not more oxidizing than water. This observation contrasts strongly with the results obtained by Yoshimura et al. (20) in conditions not much different from ours. It is difficult to interpret the difference on the basis of available information. The difference of partial pressures of hydrogen sulfide may be an explanation but seems insufficient, as no effect was observed in our experiments. One possibility might be that insufficient care was taken

in the experiments of Yoshimura et al. to avoid exposure of the catalysts to oxygen, especially at high temperature, but this cannot be clearly evaluated from the description of their experimental procedure.

CONCLUSIONS

The presence of water under hydrotreating conditions is responsible for the loss of two-thirds of the initial activity of a sulfided NiMo catalyst in less than 60 h, but the hydrogenation–hydrogenolysis selectivity was not affected. The presence of hydrogen sulfide had no effect on the deactivation phenomenon. Water vapor caused a partial crystallization of the γ-alumina support into a hydrated boehmite phase. A small decrease of the specific surface area accompanied this phenomenon. On the other hand, water vapor did not modify significantly the content, dispersion, and sulfur content of the molybdenum and nickel phases. No oxidation of the molybdenum sulfide phase was observed. However, water caused a partial oxidation of the nickel sulfide phase into oxidized nickel species. The decrease of catalytic activity due to water may be attributed to that structural modification. It could result from the formation of inactive nickel species, either a sulfate layer over nickel and molybdenum sulfide phases, or trapped nickel atoms in the alumina lattice. On the other hand, the oxygenated organic compounds we tested do not lead to deeper oxidation of the sulfide phases than water.

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