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NOTE

X-Ray Photoelectron Spectroscopy Studies on Nickel–Tungsten Mixed Sulfide Catalysts

Among hydrodesulfurization (HDS) catalysts, which generally combine a Group VIA metal sulfide (MoS_2 or WS_2) with a Group VIII metal (Co or Ni) considered to be the promoter, the Co–Mo system has so far been the most studied as it has the optimum activity in HDS (*1*). However, for other reactions, e.g., hydrodenitrogenation or aromatic and olefin hydrogenation, other couples may have a considerable interest, and among them the Ni–W system.

For the unsupported or supported Co–Mo catalysts, a well-defined Co–Mo–S phase was evidenced by Topsøe *et al.* (*2*) by using various techniques, including Mössbauer emission spectroscopy (MES) which is very suitable for determining the cobalt environment. This Co–Mo–S phase is composed of small MoS_2 patches with a MoS_2-like structure and the cobalt ions are located at the edge positions ("edge decoration"). A geometrical model has recently been developed (*3*) to correlate the shape and size of these supported patches with catalytic activity measurements: it can be deduced that only the edge sites, unpromoted or promoted by Co or Ni, are active in hydrogenation and in HDS. This type of phase has been proved to occur in other sulfide systems such as Fe–Mo and Co–W (*2, 4*).

In a combined study by X-ray photoelectron spectroscopy (XPS) and MES, Alstrup *et al.* (*5*) showed that, by a careful determination of binding energy differences and by comparison of peak shapes, different cobalt phases can be distinguished. In particular, the cobalt 2*p* binding energy in the Co–Mo–S phase, the presence of which is proved by MES, is ≃0.5 eV higher than that found in bulk Co_9S_8. In this study, which deals with the surface characterization of nickel–tungsten mixed sulfides, we will describe our attempts to apply the XPS technique to determine (a) a chemical shift between Ni in bulk nickel sulfide with nickel in intimate contact with WS_2 (Ni decorating WS_2) and (b) the surface composition with respect to bulk composition.

EXPERIMENTAL

Catalyst Preparation

Two sets of mixed Ni–W sulfides with various atomic composition α [α = Ni/(Ni + W)] have been prepared.

Mixed oxide sulfidation (*MOS*). Mixed Ni–W oxides have been obtained by precipitation, at pH 8, of a solution containing ammonium tungstate as $H_2W_{12}O_{42}^{10-}$ and nickel nitrate (from Prolabo) in various proportions with ammonia. After washing with distilled water, drying and calcination (air, 400°C, 4 h), a part of the solids is converted into sulfides by reaction with a H_2–H_2S (90–10) mixture at 400°C for 4 h. The remaining part is used for the oxide characterization.

Homogeneous sulfide precipitation (*HSP*). The second series was obtained by a procedure relatively similar to that used by Candia *et al.* (*6*) in the preparation of unsupported Co–Mo sulfides. Ammonium sulfide $(NH_4)_2S$ is rapidly added to a hot (60°C) solution of a mixture of nickel nitrate and acidified ammonium tungstate with a predetermined Ni/W ratio. After vigorous stirring for 15 h, the black precipitate formed in this hot mixture is filtered off and the remaining water is evaporated (80–

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100°C). Then a treatment with H_2–H_2S (90–10) at 400°C is performed for 4 h. The sulfides obtained by MOS and HSP are always kept under dry N_2 before any XPS analysis. The Ni–W sample composition was obtained from elemental analyses performed at the "Laboratoire Central d'Analyse du CNRS."

XPS Measurements

The samples were analyzed in a AEI ES 200 B spectrometer equipped with a Al X-ray source. Binding energies (BE) were referenced to the C 1*s* level coming from *in situ* contamination at 285.0 eV. Since this reference level is sometimes considered to be unreliable, we have checked on the compounds containing W that the S 2*p*–W $4f_{7/2}$ separation is constant whatever the examined samples, and have found it to be 129.55 (±0.15) eV. This corresponds to S 2*p* at 162.7 eV (HSP) or 163.0 eV (MOS). This small difference between the two series could be due to a certain inaccuracy in the calibrant level.

The sulfide samples were pressed on an indium foil in a nitrogen drybox attached to the spectrometer and then transferred to the XPS chamber without exposure to atmospheric oxygen. To check if reoxidation occurs during this transfer, we have also recorded the O 1*s* region. In general, only a weak and broad feature at ≃533 eV was detected and assumed to be caused by some water contamination in the spectrometer as already observed on bulk MoS_2 and WS_2 samples. No typical O 1*s* and Ni $2p_{3/2}$ BE corresponding to nickel oxide or hydroxide was detected. Therefore we shall assume when discussing the results that reoxidation does not occur on either series of samples. The atomic ratios were calculated by using integrated peak areas for each of the detected elements (Ni $2p_{3/2}$ including the multiplet and shake-up structures up to ≃13 eV apart from the peak maximum and W 4*f* doublet) and the XPS sensitivity factors deduced from Scofield cross sections (*7*) and assuming that (i) the transmission factor of the analyzer is proportional to the kinetic energy E_k, and (ii) the mean free path of the photoelectrons is proportional to $(E_k)^{0.8}$.

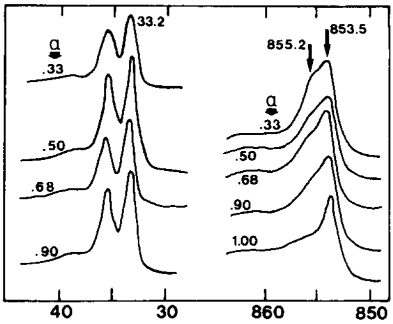

FIG. 1. W $4f_{5/2-7/2}$ and Ni $2p_{3/2}$ spectra of HSP samples with various α values (BE in eV).

RESULTS AND DISCUSSION

Binding Energy Analysis

In Table 1, the W $4f_{7/2}$ and Ni $2p_{3/2}$ binding energy results are summarized. The values for the mixed oxides, not discussed in detail in this report, will be used only as a comparison with those obtained on the sulfides. Note only that the Ni–W–O system, which is widely discussed in Ref. (*8*), appears to be very similar to the Ni–Mo–O series (*9*) prepared in the same way.

W $4f_{5/2-7/2}$ doublet. For both series of sulfides, the W 4*f* doublet is well resolved (see Fig. 1 for samples of the HSP series) and is undoubtedly to be assigned to W in a WS_2-like structure. The very small W $4f_{7/2}$ BE variations (less than 0.2 eV) along the series are within the limits of the accuracy of BE determinations as discussed in the Experimental section. From a rough decomposition of the W 4*f* doublet using symmetrical peak shapes, it appears that ≃90% of W is sulfided in the MOS samples whereas W is completely sulfided (100% $W^{(IV)}$) in the HSP samples.

Ni $2p_{3/2}$ in pure nickel MOS and HSP compounds (α = *1*). These compounds are obtained at too low a temperature to produce well crystallized samples. However, by X-ray diffraction, in addition to broad

TABLE 1

Binding Energies (eV)

Samples	W $4f_{7/2}$	Ni $2p_{3/2}$
Oxides		
$\alpha = 0$ (WO_3)	35.8	—
$\alpha = 1$ (NiO)	—	854.3 856.0 $\approx 863^a$
$0 < \alpha < 1$	35.7 (±0.2)	856.2 to 855.0, $\approx 863^a$ (when α increases)
$NiWO_4$ (Commercial)	35.5	856.2, $\approx 863^a$
Sulfides from MOS		
$\alpha = 0$ (Commercial)	33.5	
$\alpha = 0$	33.5	—
$\alpha = 1$	—	853.7, FWHM^b = 1.9 eV
$0 < \alpha < 1$	33.3 (±0.2)	853.7 854.7 ± 0.3 FWHM^b = 3.0 eV
Sulfides from HSP		
$\alpha = 0$	33.2	—
$\alpha = 1$	—	853.5, FWHM = 1.9 eV
$0 < \alpha < 1$	33.2 (±0.1)	853.5 855.0 ± 0.2 FWHM $\approx$ 3.0 eV

[a] A shake-up satellite is always present on the high-energy side of the Ni $2p_{3/2}$ level in the oxides.

[b] FWHM = full width at half maximum.

lines which can be assigned to NiS, Ni_3S_2 is detected. The XPS Ni $2p_{3/2}$ peak shape and position (853.7 eV for the MOS sample and 853.5 eV for the HSP sample) are completely different from those observed on NiO. The shake-up satellite structure, present on the oxide (pure or mixed) at ≈863 eV is absent, which signifies (almost) complete transformation into nickel sulfide. A shoulder on the high-BE side (see Fig. 1), which can be due to a multiplet splitting effect, broadens the peak (FWHM = 1.9 eV). These BE values can be compared with literature results: Ng and Hercules (*10*) reported 854.1 and 854.9 eV for, respectively, Ni_3S_2 and NiS; for nonstoichiometric NiS, the value 853.2 eV was obtained (*11*). Recently, for Ni_3S_2 and NiS prepared under well-defined conditions, Broutin *et al.* (*12*) found, respectively, 853.9 and 854.2 eV. The high shift (0.7 eV) reported by Ng and Hercules (*10*) between Ni_3S_2 and NiS compared to the values of Ref. (*12*) could be due to sample preparation. In the work of Ng and Hercules, no structural controls were performed. Thus, considering that the Ni_3S_2–NiS shift is small according to Broutin *et al.* (*12*), the Ni $2p_{3/2}$ BE values we are reporting are really representative of Ni in bulk Ni sulfides such as Ni_3S_2 and/or NiS.

Mixed Ni–W sulfides. X-Ray diffraction does not give evidence of the presence of a new phase but only those already detected (WS_2, Ni_3S_2, and probably NiS). More interesting is the presence of another nickel peak at ≈855 eV when WS_2 is present (see Fig. 1). As a matter of fact, the FWHM of the Ni $2p_{3/2}$ peak is higher (≈3 eV) when WS_2 is present. Decomposition of the spectra into two components or reliable peak difference construction with respect to composition are difficult because of the shoulder and tail on the high-BE side. For α

= 0.33 samples, the proportion of the ≃855.0 eV species appears higher in HSP than in MOS preparations. This high-BE species cannot be due to the presence of some remaining oxide as it was observed on both series, in particular on the HSP samples for which the calcination in air has not been performed and also because the strong shake-up structure is absent. Therefore we assign this nickel species at about 855 eV to nickel ions in intimate contact with WS_2. The presence of two different bulk nickel sulfide phases is improbable despite the values of Ng and Hercules (*10*) already discussed. The origin of this BE shift compared to bulk nickel sulfides (Ni_3S_2 and NiS) can be due to initial state effects (chemical effect), final state effects (screening, relaxation), or both. Choosing among these effects is not straightforward but our results are comparable to the findings of Alstrup *et al.* (*5*) on the Co 2*p* BE in the Co–Mo–S phase about 0.5 eV higher with respect to Co in bulk Co_9S_8 and to those of Zaikovskii *et al.* (*13*) who observed a higher BE (≃1 eV) for Ni in contact with WS_2 with respect to bulk NiS. Hence, it appears reasonable to consider the nickel location as being at the edges of the anisotropic WS_2 layers similar to the cobalt ions of the Co–Mo–S phase "decorating" MoS_2. This view somewhat resembles the earlier description of Voorhoeve and Stuiver (*14*) on the pseudointercalation of Ni at the sides of the WS_2 crystallites.

In another study (*15*), it was found that the nickel species interacting with MoS_2 have a Ni $2p_{3/2}$ binding energy (853.9 eV) lower than that determined under the same experimental conditions on NiS (854.6 eV) or Ni_3S_2 (854.1 eV). This result appears rather surprising but experimental conditions such as washing the samples with acidic solutions to eliminate nickel sulfides may have modified the nickel species interacting with MoS_2.

Surface Composition

The surface composition $Ni/(Ni + W)_{XPS}$ deduced from the W 4*f* and Ni $2p_{3/2}$ peaks plotted against the bulk composition α is reported in Fig. 2. For the oxide precursors of the series MOS (Fig. 2a), the experimen-

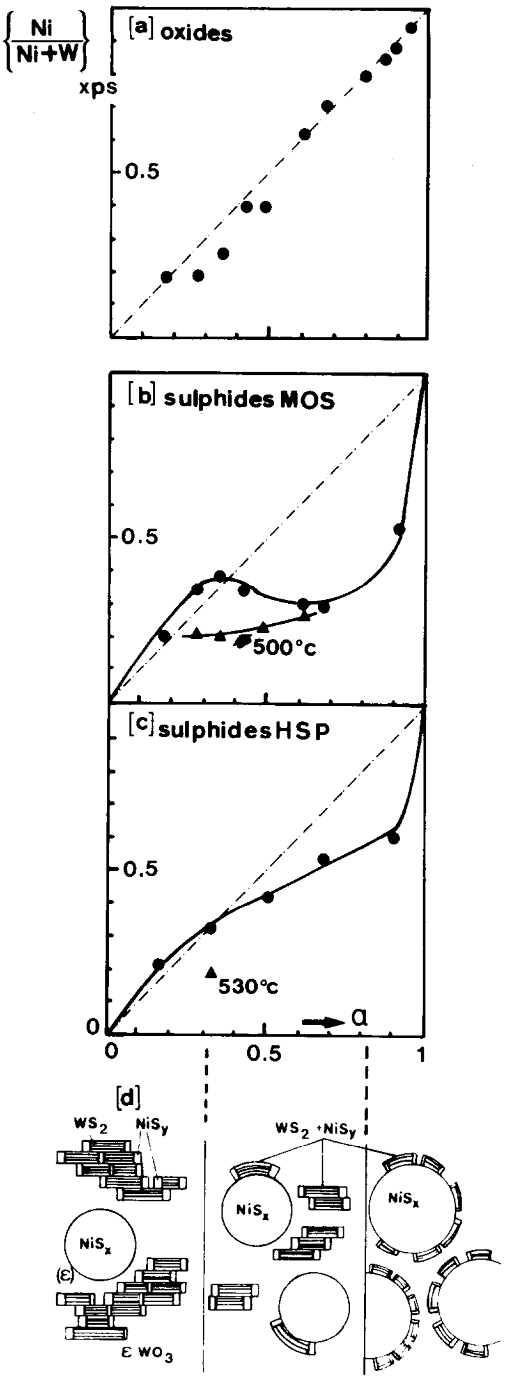

FIG. 2. The concentration ratio Ni/(Ni + W), from XPS intensities, as a function of α: (a) oxides, (b) MOS samples, (c) HSP samples, and (d) modeling of the mixed Ni–W sulfides.

tal values, close to the straight line of slope 1, are symptomatic of a homogeneous composition within the analyzed depth.

By sulfidation at 400°C, deviation from this straight line is observed when α is higher than 0.30 to 0.35 (Fig. 2b). This effect, more pronounced when the sulfidation stage is carried out at 500°C, is indicative of a relative nickel depletion in the surface layers. A similar behavior, less pronounced however, is detected on the mixed HSP sulfides (Fig. 2c). Once again, when the final sulfidation step is carried out at temperatures higher than 400°C, the $Ni/(Ni + W)_{XPS}$ ratio is much less than expected for homogeneous samples.

Modeling of the Surface Composition of the Mixed Ni–W Sulfides

We can propose the following model (Fig. 2d):

(i) The more positive Ni species ($BE \simeq 855$ eV) forming the Ni–W–S phase are well dispersed within all the slabs of WS_2 and a correct Ni–W composition is obtained by XPS.

(ii) The Ni species forming the bulk NiS_x sulfide (we do not, for the moment, define an exact stoichiometry x) are partly not detected if the crystallite size is higher than the mean free path of the Ni photoelectrons.

(iii) For $\alpha < 0.3$, the surface composition being close to the bulk composition, we can assume that a large part of Ni belongs to the Ni–W–S phase. In addition some WO_3 may remain in the MOS series and WS_2 crystallites without nickel may also be found in the two series.

(iv) When $\alpha > 0.3$, or when the temperature of sulfidation is higher than 400°C, the NiS_x phase begins to grow. For samples prepared at 400°C, the BET surface area slightly increases when α increases ($\alpha < 1$). However, when higher temperatures are used, the surface area decreases and WS_2 sintering may be an alternative explanation. Some of these particles can support WS_2 layers partially or completely decorated by Ni, depending on the WS_2 patch size and on α. As the Ni content increases, the number and/or the size of the NiS_x particle increases and the WS_2 crystallites become less stacked. At the limit $\alpha \simeq 0.8$ we propose that all the WS_2 phase is supported as small patches on the NiS_x crystallites. Depending on the nickel composition α, the patches will have a maximum Ni decoration.

CONCLUSION

In a comparison of the dibenzothiophene desulfurization activity on various metal sulfides, Chianelli (*16*) pointed out that the primary influence in HDS performance is the electronic effect. Considering the phases of WS_2 and NiS_x in the curves he reported (*16*), one can observe that these sulfides are not the best for HDS. However, more recently, Harris (*17*) showed from theoretical calculations that transition metals such as Co or Ni act as promoter when a charge transfer occurs from the promoter to the MoS_2 (WS_2) slabs. Conversely, a poisoning or inhibiting effect (i.e., Cu) accounts for the reverse effect. In this report, we have shown that the Ni $2p_{3/2}$ BE is really modified when Ni is in intimate contact (probably in decoration position) with WS_2 by reference to bulk nickel sulfides. Although observed chemical shifts do not always originate in a modification of the electronic distribution, we suggest that the shift we observed in these mixed sulfides is mainly due to a charge transfer from Ni to W through sulfur which causes an electronic deficiency at the nickel ions. Such an explanation could also be applied to cobalt in the Co–Mo–S phase (*5*).

The second point which emerges from this study is the possible role as carrier played by bulk nickel sulfide when investigating unsupported mixed sulfides. Such a conclusion was already mentioned by Sanders and Pratt (*18*) and confirmed by Garreau *et al.* (*19*) from electron microscopy studies on mixed Ni–Mo sulfides. In this case, a maximum HDS activity was found from samples of α about 0.6 to 0.8 (*18, 20*).

The anisotropic WS_2 crystallites, stacked along the *c* axis when no or few particles of NiS_x are present, can be well dispersed as a thin skin on this nickel sulfide carrier.

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