Oxidative addition of dihydrogen to the bimetallic sulfide catalysts: evidence by X-ray photoelectron spectroscopy

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Abstract

Reversible transformations Ni(IV) ↔ Ni(II) in alumina and Sibunit supported (Ni,Mo) sulfide catalysts were observed after in situ thermal treatment of catalysts in an X-ray photoelectron spectrometer chamber. The phenomenon is interpreted as a reductive elimination of occluded hydrogen under low pressure and high temperature, and oxidative addition of hydrogen after catalyst treatment with an $(H_2 + H_2S)$ mixture. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

One of the principal points for understanding the nature of active species in heterogeneous catalysts is the electronic structure of active metal atoms. X-ray photoelectron spectroscopy (XPS) is a direct experimental method to investigate the formal oxidation state of metals. The XPS study of inorganic and coordination compounds of transition metals has shown the binding energy (BE) of electrons on the internal levels of a central atom to be a complex function of metal oxidation state and of its first coordination sphere structure [1]. But this technique meets some restrictions when applied to the supported highly dispersed catalytic systems [2] including supported sulfide catalysts. Many studies aimed at obtaining information about the

chemical state of cobalt or nickel promoter atoms in the sulfided catalysts, so far the results appeared to be somewhat conflicting. Therefore, studies in this field were done mainly to reveal relationships between the activity and overall dispersion analyzing the XP-line intensities, because no chemical shifts of the spectra of both mono- and bimetallic sulfide catalysts were observed (see, e.g., Ref. [3] and references therein).

However, according to our studies [4–7], when supported sulfide catalysts are prepared using metal complex precursors, the observed chemical shifts in BEs of Ni or Co in bimetallic sulfide catalysts are essential if compared to highly dispersed binary sulfides of these metals. At the same time, position of Mo3d or W4f lines coincides well with that of both bulk MoS_2 (WS_2) and highly dispersed mono- and bimetallic sulfide catalysts. The explanation is that the electron density on the Ni (Co) atoms, entering

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the active component of the sulfide HDS catalysts, is reduced in comparison to that in the binary sulfides of these atoms. The probable reason is unusually high oxidation state of Ni(IV) and Co(III). In this paper, we shall try to explain the disagreements in the literature data. Moreover, we shall present experimental XPS evidences of the reversible transition Ni(IV) ↔ Ni(II), occurring in the bimetallic sulfide catalysts after their in situ thermal treatments in the spectrometer chamber.

2. Experimental

The X-ray photoelectron spectra (XPS) were recorded with an ESCA-3 spectrometer using AlK_α-radiation. The spectrometer was calibrated with respect to Au $4f_{7/2} = 83.8$ eV and Cu $2p_{3/2} = 932.4$ eV lines of the corresponding foils. BEs were calculated using C1s = 284.8 eV and Al2p = 74.5 eV lines as external stan-

dard. The accuracy of BE measurements was within ± 0.2 eV. Catalyst patterns were fixed onto the stainless-steel holder avoiding contact with air. Residual pressure in the spectrometer chamber did not exceed 5×10^{-9} Torr. All spectra were recorded at ambient temperature. Catalysts were in situ treated with hydrogen or $(H_2 + H_2S)$ mixture (vol. ratio is 9:1), total pressure being less than 1 Torr.

γ-Alumina and Sibunit with a surface area of 220 m^2/g were used as supports. Catalysts were prepared via «assembling in a solution» of the direct active component precursor followed by support impregnation and drying in air under IR-lamp [8]. The catalyst were sulfided ex situ in H_2S at 400°C for 2 h in a circulating set-up. Reaction products were frozen out in a trap cooled to -70°C. After vacuuming to residual 10^{-2} Torr at the sulfiding temperature and cooling to room temperature, the catalysts were sealed into glass ampoules without contact with air. The catalysts contained ~ 10 wt.% of
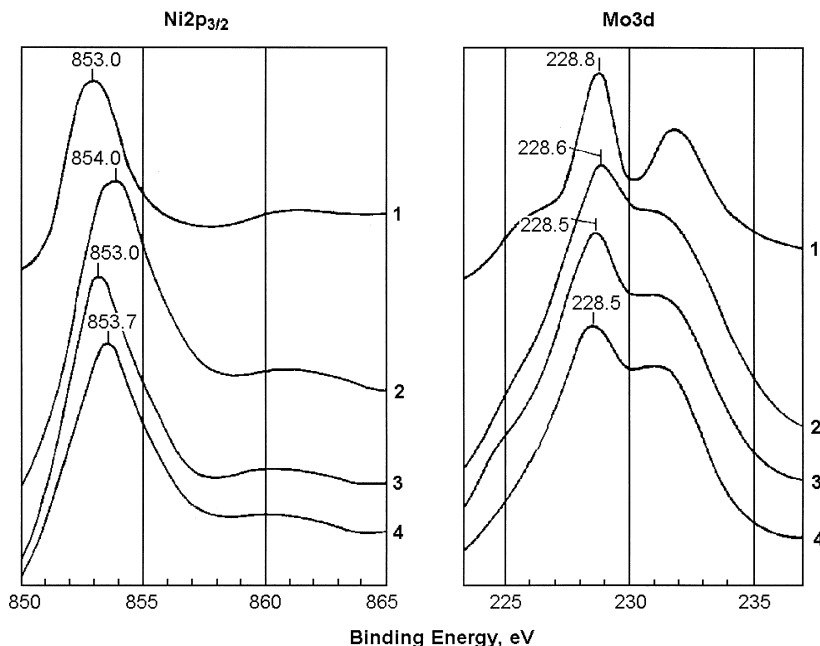

Fig. 1. XPS data on the electronic state of Ni and Mo in the active component composition of the sulfide (Ni,Mo)/Al_2O_3 catalysts. (1) NiS/Al_2O_3 catalyst and mechanical mixture ($MoS_2 + Al_2O_3$); (2) (Ni,Mo)/Al_2O_3 catalyst is sulfided ex situ at 400°C; (3) Previous pattern is evacuated in situ at 300°C until residual pressure of 5×10^{-9} Torr; (4) Previous pattern is sulfided in situ in $(H_2 + H_2S)$ at 300°C.

Mo and ∼ 3 wt.% of Ni. Mechanically mixed (MoS$_2$ + Al$_2$O$_3$) and highly dispersed NiS/Al$_2$O$_3$ catalysts served as references.

3. Results

In sulfide catalysts (Ni,Mo)/Al$_2$O$_3$ line Mo3d is characterized by a narrow poorly resolved doublet with BE (Mo3d$_{5/2}$) = 228.6 eV (Fig. 1B) exactly as in both bulk and highly dispersed MoS$_2$. This peak does not change after heating in the spectrometer chamber. For the Sibunit supported catalysts (Fig. 2B) this line is a well-resolved doublet, but its position is shifted towards higher BEs. As shown in Ref. [6], this shift seems to result from the epitaxial interaction of the active component with the support surface. It is important that line position does not change after in situ heating as well. The S2p line for both catalysts is characterized

by a narrow peak with BE = 162.7 ± 0.2 eV, and its position does not change after heating.

Line Ni 2p changes its position essentially (Fig. 1A, Fig. 2A). The Ni2p BEs in the freshly ex situ sulfided bimetallic catalysts are shifted by 1.0 eV upward with respect to the highly dispersed NiS/Al$_2$O$_3$. We observed this phenomenon many times with both bulk and supported bimetallic sulfide catalysts [4–7]. In the Sibunit supported bimetallic sulfide catalysts, this line is shifted upward even more (Fig. 2A). We believe that this effect also results from the chemical interaction of the active component with the support.

After sulfide catalysts vacuuming at 300–500°C to residual 10^{-10} Torr the Ni2p line is shifted by 1.0–1.2 eV downward for both catalysts. This considerably exceeds the BE measurements accuracy and corresponds to the Ni2p line position in the highly dispersed NiS. Note, that this line position does not change after
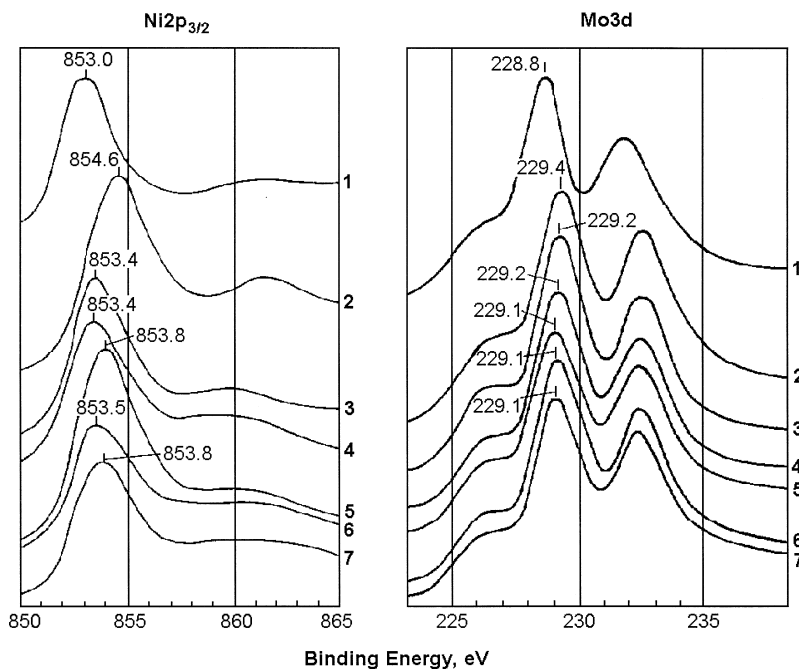

Fig. 2. XPS data on the electronic state of Ni and Mo in the active component composition of the sulfide (Ni,Mo)/Sibunit catalysts. (1) NiS/Al$_2$O$_3$ catalyst and mechanical mixture (MoS$_2$ + Al$_2$O$_3$); (2) (Ni,Mo)/Sibunit catalyst is sulfided ex situ at 400°C; (3) Previous pattern is evacuated in situ at 400°C until residual pressure of 5 × 10^{-9} Torr; (4) Previous pattern is reduced in situ in hydrogen at 300°C; (5) Previous pattern is sulfided in situ in (H$_2$ + H$_2$S) at 300°C. (6) Previous pattern is evacuated in situ at 300°C until residual pressure of 5 × 10^{-9} Torr; (7) Previous pattern is sulfided in situ in (H$_2$ + H$_2$S) at 300°C.
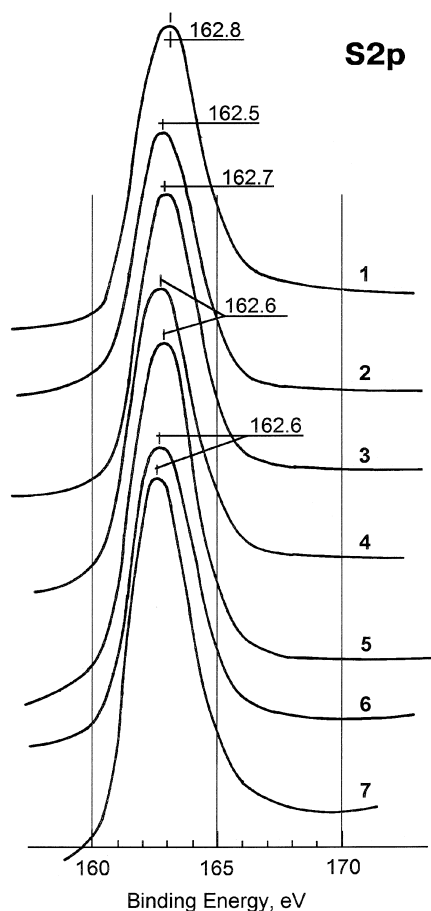
Fig. 3. XPS data on the electronic state of S in the active component composition of the sulfide (Ni,Mo)/Sibunit catalysts. (1) (Ni,Mo)/Sibunit catalyst freshly sulfided ex situ; (2) Previous pattern is evacuated in situ at 300°C until residual pressure of 5×10^{-9} Torr; (3) Previous pattern is reduced in situ in hydrogen at 300°C; (4) Previous pattern is sulfided in situ in $(H_2 + H_2S)$ at 300°C. (5) Previous pattern is evacuated in situ at 300°C until residual pressure of 5×10^{-9} Torr; (6) Previous pattern is reduced in situ in hydrogen at 300°C; (7) Previous pattern is sulfided in situ in $(H_2 + H_2S)$ at 300°C.

samples treatment with hydrogen at 300–400°C. Vacuumed samples treatment with the $(H_2 + H_2S)$ mixture at 300–450°C in the spectrometer chamber shifts BE by 0.5–07 eV back to higher values of BEs (Fig. 1A, Fig. 2A). This change in the Ni2p line position is reversible and is observed after repeated treatments (Fig. 2A). The line form and position of the S2p lines did not change after all treatments in the spectrometer chambers (Fig. 3).
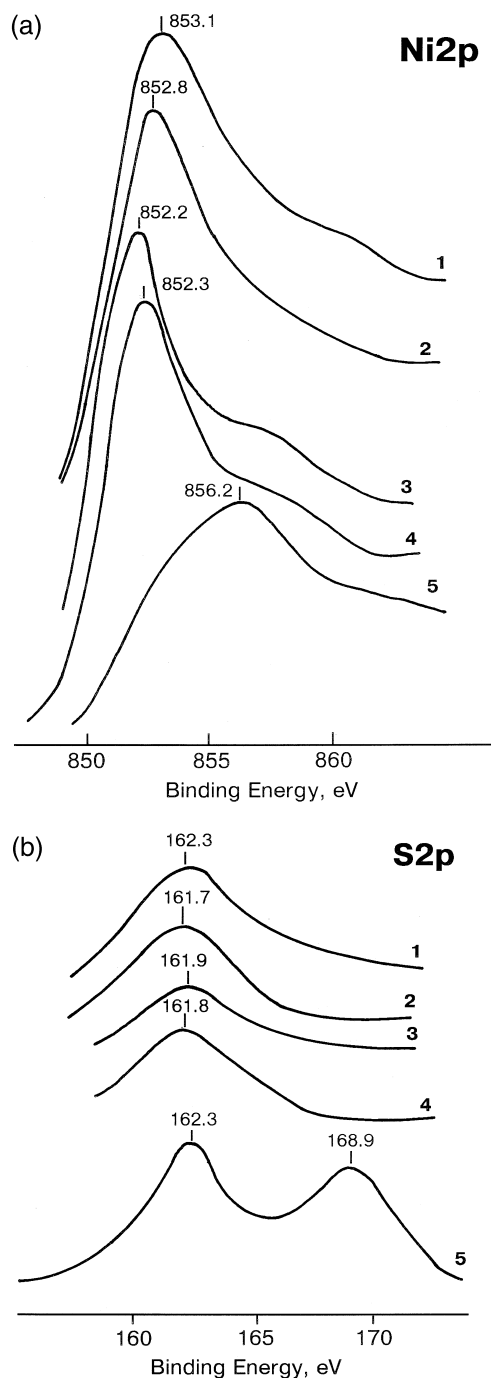
Fig. 4. XPS data on the electronic state of Ni and S in the active component composition of the sulfide NiS/ Al_2O_3 catalyst: (1) Initial form of the freshly ex situ sulfided catalyst; (2) Previous pattern is evacuated in situ at 300°C until residual pressure of 5×10^{-9} Torr; (3) Previous pattern is reduced in situ in hydrogen at 300°C; (4) Previous pattern is sulfided in situ in $(H_2 + H_2S)$ at 300°C.

Essential changes were observed in the Ni2p and S2p spectra of the ex situ sulfided NiS/Al$_2$O$_3$ catalysts (Fig. 4). After evacuating at 300°C, the Ni2p line is a little bit shifted downward, after hydrogen treatment at 300°C additional down shift is observed, but exposure of the catalyst to the (H$_2$ + H$_2$S) atmosphere at 300°C does not cause any changes in the spectra reduced catalyst. Evidently, the ultra dispersed metallic particles on Ni cannot transform the sulfide one under the given conditions. Expose of sulfide catalyst to air for several hours results in partial oxidation of Ni to the sulfate ions.

4. Discussion

Many papers describe XPS studies of sulfide catalysts (see, e.g., Ref. [3] and references therein). It has been found that in bimetallic sulfide catalysts the electron state of Mo (W) corresponds to that in the both bulk and supported MoS$_2$ (WS$_2$), while the state of Co (Ni) remains the subject of discussion. The main reason for these debates is a very complicated profile of the Co and Ni lines [9–12] caused by the heterogeneity of the surface species. Catalysts prepared from metal complex precursors are characterized by a more uniform composition of the active component [4]. Therefore, the Ni2p line in the XP-spectra is narrow (Figs. 1a, 2a) and its position may be interpreted more or less unambiguously. With this regard let us consider the data obtained in the following manner.

First, we must exclude the effect provided by the insufficient relaxation energy in small sulfide particles in supported sulfide catalysts. Sometimes changes in BEs and linewidth appear to characterize the photoionization phenomena in finely dispersed systems [13,14]. The relaxation energy changes are expected to shift the core level BEs to higher values, as the particle size decreases. At least four reasons can be contra forwarded.

(1) Active component in the alumina supported sulfide Mo and (Ni,Mo) catalysts of a metal complex origin by the size is practically identical to the MoS$_2$ and (Ni,Mo,S) species, which are not large than 10–15 Å [4]. Remember that (Ni,Mo,S) species are crystallized as molybdenite MoS$_2$ with Ni atoms being located on its edge plane. The size of NiS species in the alumina supported sulfide catalysts does not exceed 10 Å [15]. We do not observe any difference in the Mo 3d line position for mono- and bimetallic sulfide catalysts, but we observe a considerable shift of the Ni 2p line in the same sulfide catalysts. The lack of relaxation energy in the small particles of (Ni,Mo,S) species must result in synchronous changes in BEs of both metals, which is not so according to our data.

(2) The same chemical shift is observed for bulk Ni/MoS$_2$ and Ni/WS$_2$ catalysts [6], where single Ni ions are located at the periphery of a large disulfide macromolecule.

(3) Carbon support Sibunit is a conducting material, there must be no pattern charging under the X-ray radiation.

(4) After heating in the spectrometer chamber in vacuum, hydrogen or (H$_2$ + H$_2$S) mixture, the Mo3d line position does not change, but that of Ni 2p line is reversibly shifted.

Furthermore, we have to exclude the possible reversible segregation–aggregation process under thermal treating conditions because sulfides of transition metals are not volatile at these temperatures.

Therefore, the effect observed cannot be attributed to any physical action of radiation on the investigated pattern, but it is a chemical phenomenon, which must be attributed to the unusual electron state of Ni (or Co as well [4]).

The disagreement of our data with those obtained by other authors may be explained as follows.

(A) Sulfide catalysts, prepared from metal complex precursors, are characterized by a highly dispersed and uniform composition of the surface species in comparison to catalysts

prepared by impregnation [4]; therefore, the XP-spectra of the former are not widened allowing to obtain more reliable information.

(B) After exposure of freshly sulfided bimetallic catalysts to air for a long time (10 min and more) the XP-spectra of Ni show, that the Ni 2p line position coincides well with that for the highly dispersed NiS. Moreover, heating does not cause change XP-spectra of Ni after sample exposition to air. Besides, partial oxidation of the Ni sulfide to sulfate is observed for the highly dispersed NiS/Al_2O_3 catalyst after exposure to air (Fig. 4), and thermal treatments of the highly dispersed NiS in the spectrometer chamber resulted in irreversible reduction of Ni.

Therefore, the observed phenomenon is most likely caused by the unusually high formal oxidation state of Ni(IV). A possibility for the Ni(IV) with d^6 electronic configuration to form was demonstrated with ab initio investigations [16–18]. According to that Ni(II) with d^8 electronic structure (being in the square–planar environment of S atoms) transforms into Ni(IV) (d^6) in a square–pyramidal surrounding, when H_2S molecule adsorbs on Ni to the fifth coordination site [16]. The same situation is realized, when H_2S adsorbs on Ni in the sulfide bimetallic species [17]. In this case, electron density from Ni does not transfer to Mo, but localized on the S atoms bounded to Ni.

To explain the unusually high formal positive charge on Ni atoms we suggested an oxidative addition of dihydrogen to Ni to occur during catalyst sulfiding [19]. Ab initio calculations show that such oxidative addition is thermodynamically favorable stabilizing the Ni(IV) d^6 electronic state. The dihydrogen molecule is assumed to dissociate on the Ni atom yielding a «surface» H_s and an «occluded» H_o located under the Ni atom in the center of a trigonal sulfur prism. The H_2S adsorption on the active center helps the stabilization of the active Ni(IV) d^6 state [20].

The idea of oxidative dihydrogen addition allows the XPS data explanation [21]. Actually, ex situ sulfided catalyst vacuuming results in the *reductive elimination of hydrogen*. Therefore, we observe an Ni 2p line shift to lower BEs. Treatment with the $(H_2 + H_2S)$ mixture causes the *oxidative addition of dihydrogen.* Therefore, we observe the line shift to higher BEs. As freshly sulfided catalysts are exposed to air, the occluded hydrogen is oxidized, and we observe reduction Ni(IV) → Ni(II).

5. Conclusions

We believe that our XPS data indirectly prove the idea of oxidative dihydrogen addition to Ni atoms entering the active component of the sulfide HDS catalysts. Actually, a reversible shift of the Ni 2p line after the heating sulfide bimetallic catalysts in either vacuum or $(H_2 + H_2S)$ mixture seems to be a good argument in favor of this hypothesis: in vacuum hydrogen is removed (reduction of Ni(IV) to Ni(II)), and in $(H_2 + H_2S)$ mixture we observe hydrogen addition (and sulfur addition as well) resulting in the oxidation of Ni(II) to Ni(IV). Undoubtedly, we need the direct experimental proof of this idea.

Acknowledgements

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