Brief Communications

XPS study of the surface composition of modified nickel—cobalt powder catalysts for enantioselective ethyl acetoacetate hydrogenation

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The surface cobalt concentration in the powder bimetallic Ni—Co catalysts (ratio Co/Ni ≈ 0.25) was shown by X-ray photoelectron spectroscopy to be 2—4 times that of the volume content. Both Ni and Co exist in mixed valent states, *viz.*, M^0 and M^{2+}, even after catalyst reduction. After ethyl acetoacetate hydrogenation, the cobalt content on the surface increases 16 times compared to that in the bulk. In addition, the metals are partially oxidized, and the amount of Ni^0 and Co^0 in the surface layers of the catalyst decreases 2—3 times. It was assumed that the increase in the cobalt content indicates an increase in the amount of cobalt complexes that involve the modifier, substrate, and reaction product, and which shield the nickel active sites. As a result, the enantioface differentiating ability of the catalyst decreases.

Key words: X-ray photoelectron spectroscopy, enantioselective catalytic hydrogenation, bimetallic Ni—Co catalysts, ethyl acetoacetate, modification, optically active ethyl hydroxybutyrate.

We have previously[1—4] found that the bimetallic powder Ni—Co catalysts and intermetallic LaNi—Co catalysts modified by *RR*-(+)-tartaric acid (HOOC—CH(OH)—CH(OH)—COOH) are active in the asymmetric hydrogenation of the C=O bond of ethyl acetoacetate (EAA) in (−)-ethyl β-hydroxybutyrate (EHB) with an optical yield of (*ee*) 41—54% (Scheme 1).

Therefore, it was of interest to use XPS and trace how the catalyst modification by *RR*-(+)-tartaric acid and EAA hydrogenation affects electronic states of nickel and cobalt on the catalyst surface.

Scheme 1
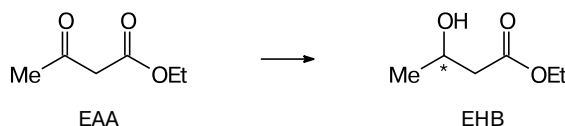
Experimental

The powder Ni—Co catalyst containing 20 wt.% Co and 80 wt.% Ni (atomic ratio Co/Ni ≈ 0.25) were prepared by evapo-

ration of a mixture of solutions of acetates and decomposition of salts at 450 °C followed by the reduction of oxides in a hydrogen flow at 350 °C and modification of the resulting catalysts with an aqueous solutions of RR-(+)-tartaric acid at pH 4.1. Procedures of preparation, reduction, and modification of the catalysts have been described earlier.[1] The procedure of catalyst preparation was specially selected in such a way that nickel and cobalt would be reduced incompletely, because published data[5,6] indicate that the presence of the non-reduced components along with the reduced ones increases the optical yield of EAA hydrogenation. The hydrogenation of EAA was carried out at 120 °C and a hydrogen pressure of 11 MPa. The chemical analysis of the reaction mixture after catalysis showed the absence of cobalt and nickel in the mixture.

X-ray photoelectron spectra were recorded on a KRATOS XSAM 800 spectrometer using Al-Kα radiation (1486.6 eV). The spectra were calibrated relative to the position of the C1s line with a bond energy (E_b) of 285.0 eV caused by the presence of adsorbed hydrocarbons of the oil in the diffusion vacuum pump.

The atomic ratios (Co/Ni) on the surface were determined from the relative intensities of lines of 2p-electrons of cobalt and nickel applying correction to the photoionization cross section, depth of free leakage of photoelectrons, and transmission factor of the analyzer.[7] The relative atomic concentrations of metallic cobalt and nickel (Co^0/Ni^0) in the surface layers with the thickness up to 30 Å analyzed by XPS were determined by spectra deconvolution according to the program of Gaussian peak synthesis. The intensity ratio of components of the Ni2p and Co2p doublets, spin-orbital splitting, and half-width of the components were maintained constant. The accuracy of bond energy determination was ±0.2 eV, and that of atomic ratios and parameters of unresolved lines was 10—20%.

X-ray photoelectron spectra of the Ni—Co catalysts before and after reduction and after modification and hydrogenation were recorded at room temperature.

Results and Discussion

The X-ray photoelectron spectra of the $Ni2p_{3/2}$ and $Co2p_{3/2}$ lines for the modified catalyst before and after EAA hydrogenation (solid lines) and results of their deconvolution (dotted lines) are shown in Figs 1 and 2.

The peak with E_b = 851.8 eV (see Fig. 1, a) is attributed to metallic nickel. The peak with E_b = 854.6 eV and its satellite with E_b = 860.2 eV are from Ni^{2+}. Similar values of the bond energy for Ni^0 and Ni^{2+} were obtained when studying the Ni/SiO$_2$ catalyst reduced at 300 °C.[8,9]

The peak with E_b = 777.4 eV corresponds to metallic cobalt (see Fig. 1, b). The peak with E_b = 780.1 eV and its satellite with E_b = 783.7 eV are assigned to Co^{2+}.

The peak with E_b = 851.7 eV is associated with metallic nickel (see Fig. 2, a). The peak with E_b = 857.0 eV and its satellite with E_b = 861.9 eV are due to Ni^{2+}. The peak with E_b = 777.4 eV corresponds to metallic cobalt (see Fig. 2, b). The peak with E_b = 781.6 eV and its satellite with E_b = 785.9 eV are ascribable to Co^{2+}.
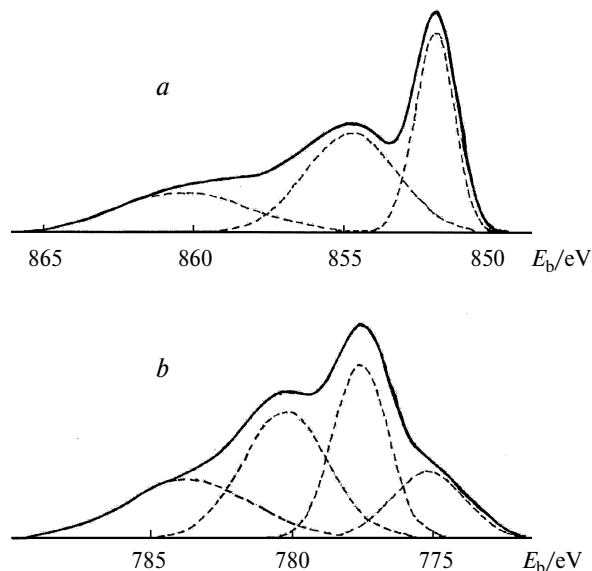
Fig. 1. X-ray photoelectron spectra for the $Ni2p_{3/2}$ (a) and $Co2p_{3/2}$ (b) lines of the Ni—Co catalyst (80 wt.% Ni, 20 wt.% Co) after modification with RR-(+)-tartaric acid (solid lines) and results of their deconvolution (dotted lines).
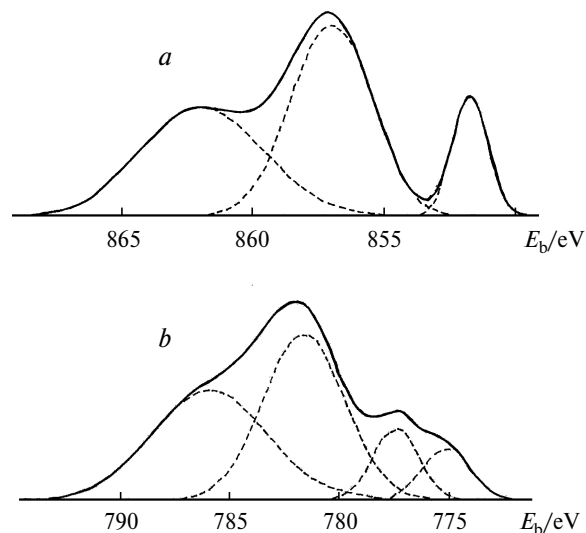
Fig. 2. X-ray photoelectron spectra for the $Ni2p_{3/2}$ (a) and $Co2p_{3/2}$ (b) lines of the Ni—Co catalyst (80 wt.% Ni, 20 wt.% Co) after EAA hydrogenation (solid lines) and results of their deconvolution (dotted lines).

The spectra of the $Co2p_{3/2}$ electrons (see Figs 1, b and 2, b) contain the Auger line of cobalt ($CoL_3M_{45}M_{45}$) from the side of lower binding energies.

The data on analysis of the electronic states of Ni and Co on the surface and the surface composition of the Ni—Co catalyst (initial, reduced, and modified, as well as the sample after EAA hydrogenation) are listed in Table 1. It is seen that the surface layer of the initial catalyst examined by XPS are considerably enriched in cobalt. The atomic Co/Ni ratio in the catalyst bulk is 0.25,

Table 1. Electronic states of the components and the surface composition of the Ni—Co catalyst (80 wt.% Ni, 20 wt.% Co; Co/Ni = 0.25)

Sample	Co/Ni (according to XPS data)	Bond energy/eV				Degree of reduction (%)			
		$Ni2p_{3/2}$		$Co2p_{3/2}$		Ni^0	Ni^{n+}	Co^0	Co^{n+}
		Ni^0	Ni^{n+}	Co^0	Co^{n+}				
Initial	0.99	851.8	855.0	777.5	780.2	27.9	72.1	30.9	69.1
Reduced	0.66	851.8	854.1	777.5	779.9	42.4	57.6	44.2	55.8
Modified	0.64	851.8	854.6	777.4	780.1	41.8	58.2	38.2	61.8
After catalysis	4.02	851.8	857.0	777.4	781.6	16.9	83.1	13.5	86.5

whereas on the surface this ratio is almost 4-fold higher (0.99). The reduction and modification of the catalyst decrease the cobalt content in the surface layers (Co/Ni = 0.66—0.64); however, the cobalt content exceeds the bulk content 2-fold and more. Hydrogenation results in a still greater enrichment of the surface layers in cobalt (Co/Ni = 4.02), *i.e.*, the cobalt content in the surface layers of the catalyst after the reaction is 16 times that in the bulk. These results differ considerably from the XPS data for the alloyed Ni—Co catalysts for which the compositions of the surface and volume are close.[10] It is most likely that for the alloyed catalysts cobalt segregation to the surface is substantially impeded compared to powder catalysts.

At the same time, as shown for the bimetallic powder Ni—Cu catalysts studied earlier,[5] the catalyst surface after both reduction and modification is enriched in nickel (atomic ratio Ni/Cu = 1.3—1.5).

As in the case of the Ni—Cu catalysts,[5] the both components on the surface of the Ni—Co catalyst (initial, reduced, modified, and after EAA hydrogenation) exist in the mixed (M^0 and M^{n+}) electronic state but their ratios on the surface differ strongly.

The initial Ni—Co catalyst contains approximately equal amounts of the metals in the M^0 state formed due to the decomposition of nickel (28%) and cobalt (31%) acetates. The degree of reduction of the both components in the surface layer of the catalyst after its reduction in H_2 is higher than that in the initial catalyst (Ni (42%), Co (44%)). Nevertheless, nickel and cobalt partly still exist in the oxidized state.

After the modification of the prepared catalysts by an aqueous solution of *RR*-(+)-tartaric acid, the metallic cobalt content somewhat decreases (38%). The hydrogenation reaction results in the further oxidation of a portion of Ni^0 and Co^0, and their contents in the surface layers decrease to 17 and 14%, respectively. Thus, the amount of Ni and Co existing in the metallic state in the surface catalyst layers decreases 2—3 times due to hydrogenation.

It has been shown previously[5] that in the Ni—Cu taken catalysts nickel and copper exist predominantly

as the metal. The amount of oxidized nickel does not exceed 10%. Just this catalyst allowed one to achieve the maximum optical yield of EHB.

In addition, the comparison of the X-ray photoelectron spectra of the Ni—Co catalyst before and after hydrogenation shows that E_b of the nickel and cobalt cations increases by 2.4 and 1.5 eV, respectively, *i.e.*, the electron density on the nickel and cobalt atoms decreases due to hydrogenation. This decrease in the electron density on the cations and the decrease in the content of metallic nickel and cobalt indicates, possibly, a strong interaction of the nickel and cobalt atoms with the electron-withdrawing sites of the substrate molecules. As a result, surface chiral centers are formed: complexes in which the substrate, metal (M^{n+}), and modifier interact tightly. This complex is [EAA($Ni^{n+}Co^{n+}$)Tart]. This conclusion is well consistent with the results of studies for the individual powder Ni catalysts,[11—13] two-component Ni—Cu catalysts,[5] and SiO_2-supported nickel catalysts[8]; their surface contain Co and Ni in both the reduced and oxidized states.

The X-ray photoelectron spectrum of C1s electrons recorded after the hydrogenation of EAA in the presence of the Ni—Co catalyst modified by *RR*-(+)-tartaric acid is presented in Fig. 3 (solid line). An analysis of the ex-
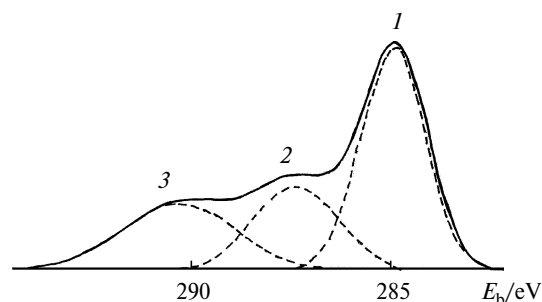
Fig. 3. X-ray photoelectron spectrum for the C1s line of the Ni—Co catalyst (80 wt.% Ni, 20 wt.% Co) after EAA hydrogenation: the C atoms of hydrocarbons from the pump oil and the hydrocarbon moiety of EAA molecules (*1*), C atoms of the COEt group (*2*), and C atoms of the C=O group (*3*). Dotted lines show the deconvolution results.

perimental spectrum indicates three peaks with $E_b =$ 285.0 (*1*), 287.4 (*2*), and 290.3 (*3*) eV with the intensity ratio equal to 2 : 1 : 1, respectively. The first peaks is caused by the presence of C atoms of hydrocarbons in the oil of the diffusion pump and to the C atoms of the hydrocarbon moiety of EAA. The second peak corresponds, probably, to the C atoms bound to the ethoxy group or hydroxyl. The third peak can be ascribed to the C atoms of the carbonyl group. The data obtained are close to the XPS data for methyl acetoacetate (MAA) adsorbed on the powder nickel surface.[11] Somewhat higher E_b values of the C1s electrons in the ethoxy group (or hydroxyl) and in the carbonyl group in the spectrum of the Ni—Co catalyst compared to the values in the spectrum recorded for the monometallic nickel catalyst are possibly due to the presence of cobalt.

The intensity ratio of peaks *2* and *3* (see Fig. 3) in the case, where the catalyst surface would contain only EAA in the keto form, should be 1 : 2. The observed equality of the intensities can be explained by the contribution of the OH groups of the reaction product EHB and/or by the fact that some adsorbed EAA molecules exist in the enol form and by the presence of tartaric acid. The data obtained agree with the IR spectroscopic studies of MAA adsorption on the Ni catalysts. The IR spectra exhibit the band of the C=C bond at 1530 cm^{-1}, indicating that MAA is partially adsorbed in the enol form.[11—13]

Thus, the study performed proved that the surfaces of the powder bimetallic Ni—Co catalysts are enriched in cobalt upon all treatments. This process occurs most intensely during the hydrogenation of EAA. The amount of cobalt in the near-surface layers of the catalyst after the reaction is 16 times that in the bulk (atomic ratio Co/Ni increase from 0.25 to 4.0). It can be assumed that results in an increase in the amount of the cobalt complexes that involve the modifier, substrate, and reaction product, which shield the active nickel sites. This decreases the enantioface differentiating ability of the catalyst (the optical yield of EAA hydrogenation on this catalyst is 45% instead of 65% for the nickel catalyst). According to available studies,[10] in the alloyed nickel—cobalt catalysts the surface is formed in a different manner with the surface composition close to the bulk composition. Therefore, these catalysts can exhibit other catalytic and enantioface differentiating properties as well. The alloyed catalysts based on nickel-containing intermetallic compounds are known[6] to manifest higher enantioselectivity in EAA hydrogenation upon cobalt introduction into these catalysts.

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