X-Ray Photoelectron Spectra of Adsorbed Methyl Acetoacetate and Coordinated Tartaric Acid, Aspartic Acid and Alanine on the Nickel Surface

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Synopsis. The adsorption of methyl acetoacetate and the coordination of tartaric acid, aspartic acid, and alanine on the nickel surface were studied by means of X-ray photoelectron spectroscopy. The adsorbed methyl acetoacetate was partly in the enol-form, and the amino acids were coordinated with the surface through COO^- and NH_2 groups in a manner similar to the corresponding nickel chelate complexes, whereas the interaction of OH groups of tartaric acid with the surface was rather weak.

In the study of asymmetric hydrogenation catalyzed by metals modified with optically active molecules, it is of particular importance to ascertain not only the surface conditions of metals, but also the adsorbed states of the modifiers and reacting molecules. Few attempts have so far been made to analyze the surfaces from a physicochemical point of view. By using X-ray photoelectron spectroscopy (XPS), we previously studied nickel metals coordinated with tartaric acid and characterized the surface states of nickel responsible for the enantioface-differentiating hydrogenation.[1] In this work, we extended the XPS study to reveal the structures of the tartaric acid, aspartic acid, and alanine modifiers adsorbed on the Ni surface and to investigate the effect upon their stability of heat treatments in a hydrogen atmosphere. The adsorbed state of the reactant, methyl acetoacetate, was also studied.

Experimental

The X-ray photoelectron spectra were recorded at room temperature on a Hewlett-Packard 5950A ESCA spectrometer using monochromatized Al *Kα* exciting radiation. The nickel powder catalyst was prepared by decomposing nickel formate of an extra pure grade *in vacuo* and by then reducing with H_2 at 573 K. The modifications of the catalysts with (2*R*,3*R*)-tartaric acid, (*S*)-aspartic acid or (*S*)-alanine were performed in a manner analogous to those used in the previous studies.[1,2] The unmodified Ni catalyst used as a reference was also prepared similarly except for the absence of these optically-active modifiers. The catalysts were subjected to the *in situ* treatment in the preparation chamber of the spectrometer. The C 1s peak due to contaminant carbons, 285.0 eV, was taken as standard. For the experiments on the adsorption of methyl acetoacetate, a nickel foil of a 99.99% purity, obtained from the Material Research Co., was employed after being cleaned by an argon-ion bombardment following oxidation-reduction treatments.

Results and Discussion

Figure 1 (a) compares the C 1s photoelectron spectrum of tartaric acid adsorbed on Ni with the spectra of nickel tartrate, sodium tartrate, and tartaric acid. Two peaks with almost the same intensity appeared apart from Peak I due to contaminant carbons; Peak II at 286.8 eV is assigned to the carbon atom combining with a hydroxyl group, whereas Peak III, 288.8 eV, is assigned to the carbon atom in the carboxyl group. These binding energy values were closer to those from nickel tartrate (286.7 and 288.7 eV) and sodium tartrate (286.6 and 288.6 eV) than to those for tartaric acid (287.3 and 289.7 eV). Figure 1(b) shows the O 1s spectra. The peak of the adsorbed tartaric acid appeared at the higher binding-energy side of a broad peak of nickel tartrate and was lower by 0.6 eV than that of tartaric acid. The broad O 1s peak of nickel tartrate is due to the characteristic structure of the complex; oxygen atoms in the carboxyl and hydroxyl groups undergo strong interactions with central nickel ions.[3] The close similarity on the C 1s level, while there is a difference in the O 1s level between the complex and the adsorbate, suggests that the adsorbed tartaric acid is linked to a surface Ni atom through a carboxyl group by dissociating hydrogen atoms, whereas the hydroxyl groups have little interaction with the surface atoms. Such a description of the adsorbed structure agreed substantially with the model proposed previously.[1]

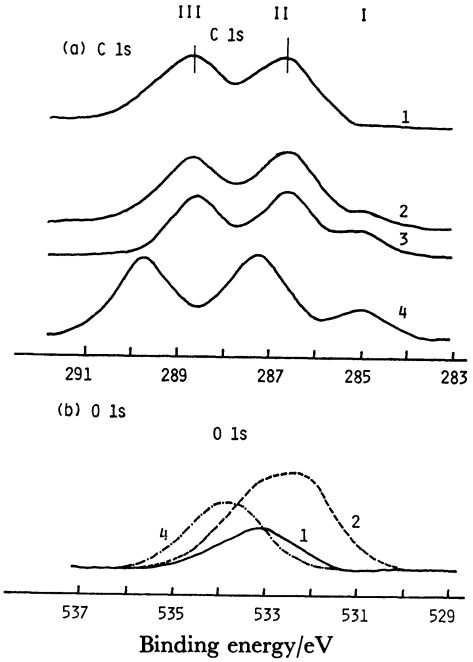

Fig. 1. X-Ray photoelectron spectra in the C 1s (a) and O 1s (b) regions.
1: Difference spectrum between unmodified nickel and tartaric acid-modified nickel(pH=5), 2: nickel tartrate, 3: sodium tartrate, 4: tartaric acid.

The doublet peaks in the C 1s region, due to the adsorbed tartaric acid, remained almost unchanged with heat treatments in a H_2-atmosphere up to 353 K,

indicating that the adsorbed modifier retains its original structure. By a treatment at 383 K, the peak intensity was considerably attenuated but the doublet structure still existed. Further heating at 603 K changed the doublets to a single peak appearing at 284.4 eV, indicating that the adsorbed tartaric acid underwent decomposition to produce a carbonaceous deposit by this treatment, corresponding to a complete loss of the enantioselective capacity of this surface. The O 1s and Ni $2p_{3/2}$ spectra showed that the modification of Ni catalysts in air, as an ordinary procedure, gave rise to the oxygen peaks associated with NiO and Ni_2O_3 oxides, but the subsequent H_2-treatment at 353 K resulted in an almost complete removal of both oxides. The corresponding oxygen species with binding energies of 529.3 and 531.5 eV were reproduced by exposing to a O_2-atmosphere at room temperature and were then again reacted off with H_2 at 353 K. Such high reactivity suggests that the catalyst surfaces, even though they were modified in air, were readily changed to be oxide-free under the conditions of hydrogenation at 323—373 K.

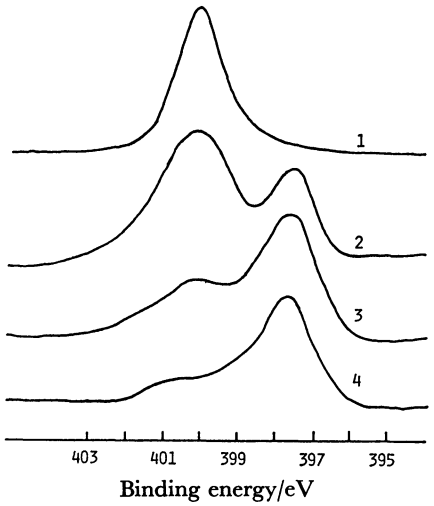

Fig. 2. Nitrogen 1s photoelectron spectra of adsorbed amino acids.
1: Aspartic acid, evacuated at room temperature, 2: aspartic acid, exposed to 6 Torr of H_2 at 363 K, 3: alanine, exposed to 10 Torr of H_2 at 373 K, 4: aspartic acid, exposed to 6 Torr of H_2 at 553 K.

Figure 2 shows the N 1s spectra of the adsorbed amino-acids. A single peak appeared at 400.1 eV by the coordination of aspartic acid; the binding-energy value was lower by 0.8 eV than that of aspartic acid (which is in the form of a zwitter ion, NH_3^+ and COO^-) and was close to that of the nickel ammine complex, *e.g.*, 400.0 eV for N atom in $[Ni(NH_3)_6]Cl_2$. The C 1s peak in the carboxyl group, 288.7 eV, was virtually identical with Peak III for the adsorbed tartaric acid. A similar correspondence was observed between the adsorbed alanine and the nickel–alanine complex. These spectral coincidences confirm a model[4] in which the amino acid is linked to a surface Ni atom through both amino and carboxyl groups. The heat treatment at 373 K gave rise to an additional N 1s peak at 397.5 eV (Spectra 2 and 3). Since such a low binding energy is characteristic of a nitride-like species,[5] it is evident that a part of the adsorbed amino acids was decomposed to produce nitrogen atoms.

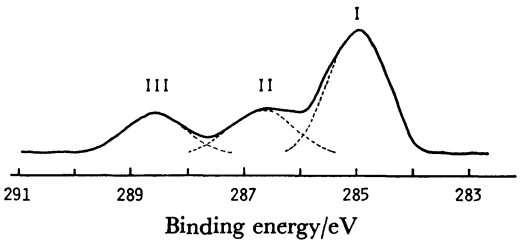

Fig. 3. Carbon 1s photoelectron spectrum of methyl acetoacetate adsorbed at room temperature on nickel surface.

As is shown in Fig. 3, the adsorption of methyl acetoacetate on a clean Ni surface provided three peaks in the C 1s region; they appeared at 285.0 (Peak I), 286.6 (Peak II) and 288.6 (Peak III) with an intensity ratio of 2.7 : 1 : 1. Peak III can apparently be assigned to C atoms in the carbonyl groups, whereas Peak I is associated with C atoms of hydrocarbons. Peak II is due to the carbon atom in the methoxy group, and its binding energy is close to that of a carbon atom combining with a hydroxyl group.[6] The appreciably higher intensity of Peak I, relative to the other two peaks, is partly due to contaminant carbons accumulated during prolonged evacuation following the adsorption. As for Peaks II and III, the original keto-form of methyl acetoacetate should provide the intensity ratio of 1 : 2, and it is to be noted that the observed equal intensity is derived on the basis of the assumption that about a half of the adsorbed species is in the enol-form. This finding is in line with the conclusion obtained from the tracer and IR spectroscopic studies.[1]

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References

1) I. Yasumori, Y. Inoue, and K. Okabe, "Catalysis, Heterogeneous and Homogeneous," ed by B. Delmon and G. Jannes, Elsevier, Amsterdam (1975), pp. 41—50; I. Yasumori, *Pure Appl. Chem.*, **50**, 971 (1978).
2) Y. Izumi, *Angew. Chem.*, **23**, 956 (1971).
3) J. Bolard, *J. Chim. Phys.*, **62**, 900 (1965).
4) J. A. Groenewegen and W. M. H. Sachtler, *J. Catal.*, **33**, 176 (1974); A. Hatta, Y. Moriya, and W. Suetaka, *Bull. Chem. Soc. Jpn.*, **48**, 3441 (1975).
5) C. R. Brundle, *J. Vac. Sci. Technol.*, **13**, 301 (1976); K. Kishi and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **47**, 2532 (1974).
6) U. Gelius, P. F. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Noldling, and K. Siegbahn, *Phys. Scripta*, **2**, 70 (1970).