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THE STRUCTURE OF TARTARIC ACID ADSORBED OVER NICKEL CATALYST OBSERVED BY FT-IRAS

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The structure of the L-tartaric acid adsorbed on the surface of a nickel metal catalyst with or without NaBr was studied by FT-IRAS. The carboxylic acid and carboxylate type adsorbed species were observed on nickel surface which was treated with only tartaric acid, while only one type of carboxylate ion was observed on the nickel surface which was treated with tartaric acid and NaBr.

1. Introduction

It is known that the enantio-selective hydrogenation proceeds over a nickel catalyst pretreated with amino acid or tartaric acid [1,2], and the structures of those adsorbed species and active sites over the catalysts were discussed [3,4]. Especially, the structure of amino acid adsorbed over the nickel surface has been studied by infrared spectroscopy [5–7].

The hydrogenation of methyl acetoacetate over the tartaric acid preadsorbed nickel catalyst proceeds enantio-selectively. When the catalyst was treated further with the second modifying reagent such as NaBr the enantio-selectivity increased markedly. Although the effect of the second modifier was previously discussed [3.4], the actual form of the adsorbed species on the nickel surface was not clear because of the difficulty of the investigation of the catalyst surface.

Recently, the infrared spectroscopic techniques have been developed and higher sensitive measurement can be performed by using Fourier transform infrared spectrometer. Especially, Fourier transform infrared reflection absorption spectroscopy (FT-IRAS) is one of the powerful techniques to observe the species adsorbed over metal surfaces in an atmospheric condition [8].

In this report, the structure of tartaric acid adsorbed over the nickel catalyst modified with or without NaBr was studied by means of FT-IRAS.

2. Experimental

A nickel (99.9% purity obtained from Nilaco) plate, 20 mm × 30 mm was polished thoroughly with α-Al_2O_3 powder, then rinsed with distilled water for several times to obtain a nickel mirror. Two kinds of samples were prepared, one was treated with L-tartaric acid (Kanto Chemical) solution (pH = ca. 3), and the other is further pretreated with a solution of NaBr (Kanto Chemical). The pretreatment of samples was performed in air at room temperature for 5 h. After the pretreatment, the nickel plate was washed with distilled water and then with methanol for several times as referred to the previous report [3]. The FT-IRAS spectrum was measured as soon as possible after the washing samples.

Infrared spectra of Ni tartrate, which was prepared from $NiCO_3$ (Wake Pure Chemical) and tartaric acid [3], sodium tartrate (Wako Pure Chemical) and tartaric acid were measured with KBr pellets.

FT-IRAS spectra were measured with a polarization modulation FT-IRAS instrument constructed with an FT-IR (JEOL JIR-100), a photoelastic modulator (Hinds) and reflection attachment [8]. FT-IRAS spectra were measured with 256 scans at 8 cm^{-1} resolution. The spectra of adsorbed species were obtained from the ratio spectrum of $(Ip - Is)/(Ip + Is)$, where Ip and Is are due to the intensities of the IR beam parallel and perpendicular to the plane of incidence respectively, and $(Ip - Is)$ contains the information of the surface species and background while $(Ip + Is)$ contains predominantly those of backgrounds [8].

3. Results and discussion

An FT-IRAS spectrum of tartaric acid adsorbed on the nickel surface is shown in fig. 1(a). Figure 1(b) shows the spectrum of tartaric acid and NaBr coadsorbed on nickel. These spectra were measured after washing the sample for three times with methanol. The intensity and the shapes of bands in these spectra did not change by further washing the samples. Therefore it is inferred that these spectra are due to the chemically adsorbed tartaric acid modified over nickel surface. The assignment of the spectra of tartaric acid adsorbed on nickel and related compounds are listed in table 1.

From fig. 1, it is found that the spectra were clearly changed by adding NaBr, especially for the bands attributed to –COOH group. For the spectrum of L-tartaric acid adsorbed on nickel, both bands due to the COOH group (1751, 1275 cm^{-1}) and COO^- group (1616, 1416 cm^{-1}) were observed. On the contrary for the sample of co-adsorption of tartaric acid and NaBr, the bands at 1635 and 1415 cm^{-1} of the COO^- group was observed as shown in fig. 1(b). Other bands due to C-O stretching, deformation of C-H and O-H were observed at almost the same wave numbers for all samples and reference materials. From these results, the states of two carboxylic groups of the tartaric acid over nickel surfaces were

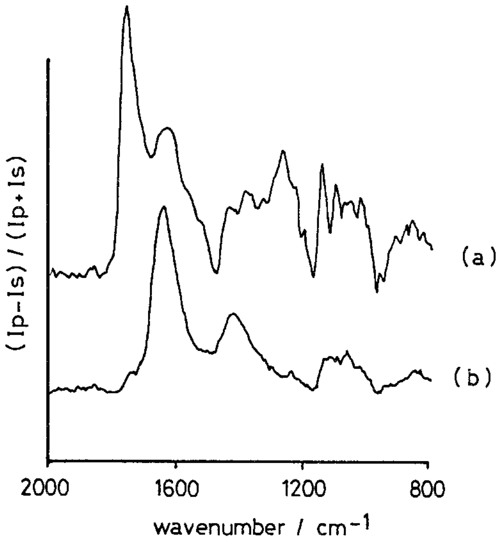

Fig. 1. IRAS spectra of tartaric acid adsorbed over Ni (a) by tartaric acid solution and (b) by tartaric acid solution with NaBr.

supposed to be as follows: for tartaric acid adsorbed on the nickel surface, the carboxylic group exists as carboxylate ion and carboxylic acid while for tartaric acid and NaBr coadsorbed on the nickel surface, those exist as carboxylate ions. The band position of ν_{as}(OCO) due to the carboxylate ion for nickel tartrate is much lower than that of sodium tartrate as shown in table 1. Compared to the band position of ν_{as}(OCO) of the tartaric acid on nickel at the two pretreatment conditions, that band for adsorbed tartaric acid is lower than that for coadsorbed tartaric acid and NaBr it suggests that sodium tartrate is mainly formed on the surface. The structure of tartaric acid adsorbed over Ni can be illustrated as shown in fig. 2.

Table 1
Infrared vibrational frequencies of tartaric acid

Adsorbed over Ni		Ni-Ta[b]	Na-TA[b]	TA[b]	assignment
TA[a]	TA and NaBr				
1751	–	–	–	1739	ν (C = O)
1616	1635	1594	1621	–	ν_{as} (OCO)
1416	1415	1419	1376	–	ν_s (OCO)
1257	–	1245	1241	1259	δ (CH), ν (CO)
1134	1122	1086	1112	1133	δ (OH)
1083	1060	1039	1066	1087	ν (CO)
1006	1010	1016	995	991	

[a] TA: tartaric acid.

[b] Measured with KBr pellets.

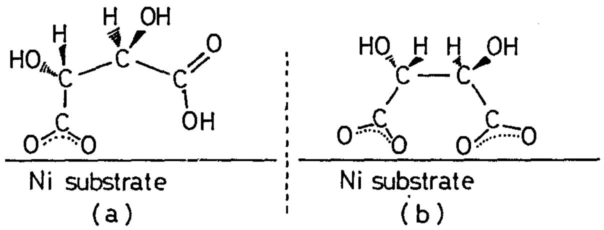

Fig. 2. Schematic view of the state for tartaric acid adsorbed over Ni; (a) by tartaric acid solution and (b) by tartaric acid solution with NaBr.

Harada and his coworkers reported [4] that the addition of NaBr to the tartaric acid preadsorbed nickel catalyst increases the optical yield of the hydrogenated compounds. These results were explained the inhibition of active sites, which did not have the ability for enantio-selective hydrogenation, by Br cation on the nickel catalyst. In the present study, it was found that by adding NaBr, tartaric acid adsorbed over the nickel surface to form completely tartarate.

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