Ultraviolet Study for the Adsorption of Acetylacetone on D-Tartaric Acid Preadsorbed Nickel Film

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(Received April 2, 1970)

The ultraviolet spectra of β-diketones adsorbed on evaporated metals have been studied in order to clarify the chemical bonding of the chemisorbed species and the electronic properties of the metal surfaces.[1] The exposure of the metal films to acetylacetone vapor gives absorption peaks which can be assigned to the π–π^* transition of adsorbed acetylacetonate.

α-Amino and α-hydroxy acids function as chelating agents to metal ions. These acids are used as modifying reagents for hydrogenation catalysts, which then catalyze the asymmetric hydrogenation reaction of β-diketones.[2] The ultraviolet spectra of adsorbed β-diketones on the acid preadsorbed metal will, then, give important information shedding light on the mechanism of the modifications of catalysis and, in general, the corrosion mechanism of metal surfaces.

In the present communication, the adsorption of acetylacetone on evaporated nickel film pretreated with D-tartaric acid is studied.

The experimental apparatus shown in a previous paper[3] was improved for use here. The evaporation and other procedures have been described in the previous paper. After the nickel had been evaporated onto the quartz windows in a vacuum, a D-tartaric acid solution previously degassed was gently introduced into a quartz cell through a break-off seal broken by a glass-coated magnet. After treating the metal film with the acid solution for 30 min at 0°C, the solution was poured out from the quartz cell and the solvent water was completely removed by vacuum-distillation. Then acetylacetone was introduced, and the ultraviolet spectra of the adsorbed species were recorded on a Hitachi EPS-2 spectrophotometer.

The D-tartaric acid solutions had concentrations of 2% and were adjusted to various pH's, such as 2.0, 5.0, and 9.0, by a 1N NaOH aqueous solution. The results are shown in Fig. 1.

In the treatment of the metal at pH 2.0, a weak, broad band was observed around 280 mμ after a 30 min adsorption of the acetylacetone. After 18 hr, the band maximum shifted to a longer wavelength.

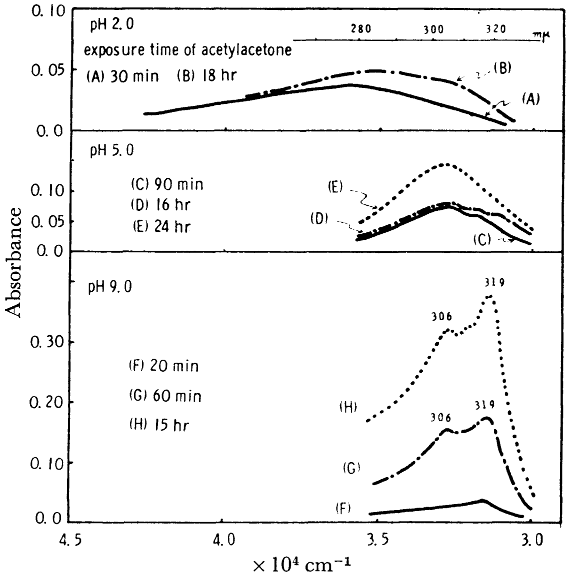

Fig. 1. Ultraviolet spectra of acetylacetone adsorbed on nickel film with preadsorbed D-tartaric acid at pH 2.0, 5.0 and 9.0.

In the case at pH 5.0, absorption peaks were obtained at 306, 316, and 322 mμ after 16 hr, and only one peak, at from 303 to 306 mμ, after 24 hr.

Figure 1 also shows the spectra obtained after the adsorption of acetylacetone on the metal film treated with the pH 9.0 solution. An absorption band was observed at 318 mμ after 20 min. After 15 hr, three intensive bands (about ten times that after 20 min) were obtained at 306, 313, and 319 mμ.

The adsorption of acetylacetone on nickel film without preadsorbed D-tartaric acid gives a band at 303 mμ which can be assigned to the π–π^* transition of adsorbed acetylacetonate.[1] In the cases with the preadsorbed acid, the absorption spectra of the adsorbed species are considerably different from that with no preadsorption procedure; furthermore, the spectra depend very significantly on the pH condition of the acid solution. By the way, the IR spectrum of D-tartaric acid adsorbed on the nickel film has been obtained, and the UV spectrum of adsorbed acetylacetonate on the nickel film treated with NaOH is different from the above spectra.

The elucidation of the relation between the spectral variation and the modification mechanism of the catalyst is now in progress.

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