Surface Acidity of Cesium Hydrogen Salts of 12-Tungstophosphoric Acid Characterized by Low-Temperature CO Adsorption

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The surface acidity of cesium hydrogen salts of 12-tungstophosphoric acid, $Cs_xH_{3-x}PW_{12}O_{40}$ (Csx; x = 2 - 3), has been characterized by FT-IR measurements of the low-temperature adsorption of CO. In the region of the CO stretching, CO adsorbed on H^+ (2165 cm^{-1}) and CO on Cs^+ (2154 cm^{-1}) were distinguished. The relative intensity of 2165 cm^{-1} band to 2154 cm^{-1} band increased linearly with the formal H^+/Cs^+ ratio, (3-x)/x. The integrated intensity of 2165 cm^{-1} changed in parallel with the catalytic activity for the surface-type reactions.

Heteropoly compounds are efficient catalysts for a wide variety of reactions.[1] Cesium hydrogen salts of $H_3PW_{12}O_{40}$ in the solid state, $Cs_xH_{3-x}PW_{12}O_{40}$ (denoted hereafter by Csx), particularly x ~ 2.5, show very high activities for various acid-catalyzed reactions.[2] The catalytic activity sharply rises from nearly zero at x = 2 and drops to zero at x = 3, showing a high maximum at x = 2.5. It was previously presumed that this remarkable change reflected the surface acidity.[1,3] Therefore, the confirmation of the surface acidity is of great concern. According to thermal desorption of NH_3 and pyridine,[1,3,5] calorimetric titrations with NH_3,[6,7] and an indicator test,[4,8,9] both $H_3PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are very strong acids. These measurements, however, involve strong interactions between the surface and the probe molecules, so that the surface reaction other than acid-base interaction may be involved.[10,11] In addition, the basic molecules are often absorbed into the bulk of heteropolyacids,[1,3,4] so that the surface acid sites can not be measured separately. Recently, the adsorption of CO has been used to measure the acidity of the hydroxyl groups of zeolites[12-15] and sulfated zirconia.[16-18] CO is a very weak base and its interaction with the surface acid sites is moderate.[10,11]

In the present study, the surface of the cesium hydrogen salts was characterized by IR measurements of the low-temperature adsorption of CO to confirm the anticipated correlation between the surface acidity and the catalytic activity. It has been shown that the Cs^+ and H^+ on the surface can be distinguished from each other by the IR bands of the adsorbed CO, and that the numbers of H^+ on the surface thus measured varied in parallel with the catalytic activity.

Cesium hydrogen salts, Csx (x = 2 - 3), were prepared by the titration of an aqueous solution of $H_3PW_{12}O_{40}$ with an aqueous solution of Cs_2CO_3, as in the previous works.[2-4] Csx (ca. 20 mg) dispersed in water was spread on a Si plate and dried. The sample was set in an *in-situ* cell and evacuated at 423 K for 1 h to remove adsorbed water. Then, it was cooled to about 100 K, and a predetermined amount of CO was introduced. IR spectra were recorded at 100 K with a JASCO FT-IR 550 spectrometer.

Figure 1 shows the IR spectra of CO adsorbed on Cs2.5 and Cs3 measured at 100 K. According to the previous study, Cs2.5 has a large number of H^+ and Cs3 contains no H^+.[1] No peak was observed for Cs3 in the region of OH stretching (3000 -3700 cm^{-1}), showing that no residual H^+ exists (spectrum a). Broad peaks at 3600, 3150, and 1620 cm^{-1} were observed for Cs2.5 before evacuation, and the peaks at 3600 and 1620 cm^{-1} disappeared by evacuation at 423 K (spectrum c). According to the TG analysis, the adsorbed (or absorbed) water of Cs2.5 desorbs below 423 K.[19] Actually after the evacuation at 423 K, there was no peak around 3600 and 1620 cm^{-1}, which correspond to adsorbed water. The broad peak around 3150 cm^{-1} shifted to around 2400 cm^{-1} by H-D exchange by the use of D_2O. Thus, the broad peak must be due to the OH group of the Brønsted acid site (BAS). Judging from the position and the broad band shape, a strong interaction exists between H^+ and neighboring oxygen or OH group.

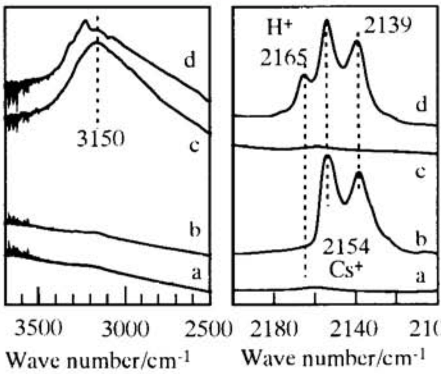

Figure 1. IR spectra of CO adsorbed on heteropolyacids.
(a) Before and (b) after adsorption of CO on $Cs_3PW_{12}O_{40}$.
(c) Before and (d) after adsorption of CO on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.
CO introduced was (b) 1.5 and (d) 2.2 molecules per bulk-anion at 100 K.

When 1.5 molecules of CO per anion in the bulk was introduced to Cs3 at 100 K, two peaks at 2154 and 2139 cm^{-1} appeared (spectrum b). No peak was observed in this region in the case of the Si plate alone. When the amount of CO introduced was large, the peak due to CO in the gas phase with rotational bands were observed. The peak at 2154 cm^{-1} is assigned to the CO adsorbed on Cs^+, since the same band has been observed with Cs-ion exchanged mordenaite and ZSM-5.[14,20,21] The peak at 2139 cm^{-1} is usually attributed to physisorbed or liquid-phase like CO.[10,11] No peak was observed in the region of OH vibration before and after CO adsorption.

IR spectrum of CO adsorbed at 100 K on Cs2.5 is shown in Figure 1, d. Other cesium hydrogen salts (Cs2, Cs2.3, Cs2.75, and Cs2.8) showed essentially the same peaks. When 2.2 molecules of CO per bulk-anion was introduced to Cs2.5 at 100 K, three peaks at 2165, 2154, and 2139 cm^{-1} appeared. The latter two bands are assigned as in the case of Cs3. Since the peak at 2165 cm^{-1} observed for Cs2 - Cs2.8 was not detected for Cs3, this was assigned to CO adsorbed on BAS. This assignment is supported by the fact that the IR band of CO adsorbed on the BAS is observed at 2168 - 2175 cm^{-1} in the case of zeolites,[10,11] and further confirmed by the following observation.

With the adsorption of CO, the broad peak, especially in the

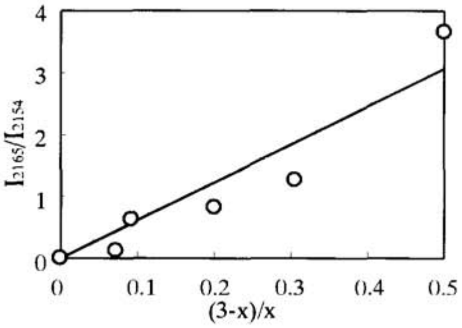

Figure 2. Plots of the relative peak intensity, I_{2165}/I_{2154}, against (3-x)/x, where the x is the Cs content of the solid bulk.

3000 - 3100 cm^{-1} region (assigned toBAS in the above), decreased in intensity. The decrease was also obvious in other samples but Cs3. It was confirmed that these decreases in the OH region were in proportion to the increases in the peak intensity at 2165 cm^{-1}. This supports the assignment of this peak to CO adsorbed on BAS. A new small band increased at around 3230 cm^{-1} with the decrease in the broad band at 3150 cm^{-1}, which may correspond to the stretching mode of BAS CO adsorbed.

The three peaks at 2165, 2154, and 2139 cm^{-1} were deconvoluted by assuming Lorentzian function for 2139 cm^{-1}, and Gaussian function for 2165 and 2154 cm^{-1}. When the deconvoluted peak areas are plotted against the CO pressure, they showed Langmuir-type adsorption in the low CO pressure range (0 - 40 Pa). The leveled-off peak intensities in the Langmuir-type isotherms were taken as full CO coverage of each site. The relative intensities of the 2165 cm^{-1} peak versus that of the 2154 cm^{-1} peak, I_{2165}/I_{2154}, at high CO pressures are plotted against the (3-x)/x in Figure 2. Here x is the Cs content in the bulk, so that (3-x)/x is the H$^+$/Cs$^+$ ratio of the salt. It is noted that I_{2165}/I_{2154} increased approximately in proportion to (3-x)/x for x = 2 - 3. It was previously indicated on the basis of ^{31}P-NMR that Csx's are nearly uniform solid solutions of $H_3PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$ and the surface H$^+$/Cs$^+$ ratio reflects the ratio in the bulk. The change of the peak intensity with x shown in Figure 2 supports the previous conclusion.

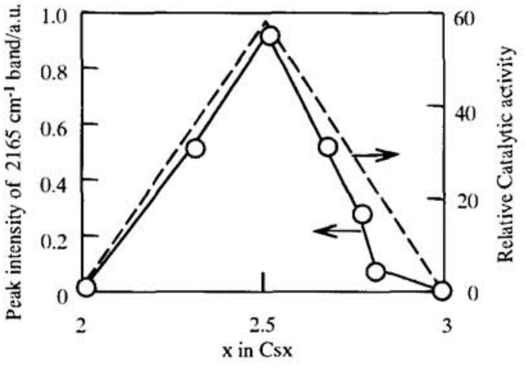

Figure 3. Changes of the peak intensity of the 2165 cm^{-1} band with the bulk Cs content, x, as compared with the catalytic activity. The peak intensity; this work. The catalytic activity; the rate of alkylation of 1,3,5-trimethylbenzene by cyclohexane at 353 K.[20] Both are normalized to catalyst weight.

Figure 3 shows the change of the intensity of the 2165 cm^{-1} band (CO on BAS, normalized by the catalyst weight) and the catalytic activity with the Cs content, x. The changes in the amount of CO adsorbed and catalytic activity[22] in the range of x 2 - 3 are very close. The trends agree also with the number of surface H$^+$ estimated previously from the surface area and the chemical formulas.[3] The excellent agreement clearly shows the usefulness of the present method for the measurement of the surface acid sites of Csx and confirms the previous conclusion that the catalytic activity of Csx (x = 2 - 3) is governed by the surface acidity.

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