Determination of acid strength of solid superacids by temperature programmed desorption using pyridine

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Acid strength of solid superacids was determined by temperature programmed desorption using pyridine. An approximately linear relationship exists between the acid strengths of solid acids determined by the Hammett method and the termination temperature of pyridine desorption. The acid strength of colored superacids versus temperature relationships practically fell on the linear line.

Keywords: solid superacid; TPD; pyridine; acid strength

In recent years, we reported that the solid superacids of metal oxides were synthesized by treating oxides of Fe, Ti, Zr, Sn, and Al with the oxo-anions of SO_4^{2-}, WO_4^{2-}, and MoO_4^{2-} [1,2]. With the colorless superacids, the acid strengths, indicated by the Hammett function (H_0), were determined by color change of the Hammett indicators. However, the Hammett method could not be applied to the colored superacids such as SO_4^{2-}/Fe_2O_3 and MoO_3/ZrO_2. Very recently, Lin and Hsu used a method of temperature-programmed desorption (TPD) using benzene for estimating the superacid strength [3]; isomerizations of *n*-butane and *n*-propane at low temperatures were also reported to be probe reactions for measuring the strength [4]. TPD using pyridine as a desorption molecule is a useful method to estimate the acid strength of solid surface. The synthesized superacids were prepared by calcining at 723–1123 K; thus structures of superacid sites are not maintained when the materials are heated at temperatures above those of calcination. It is expected that pyridine adsorbed on the superacid sites should be completely desorbed before the programmed temperature reaches at calcination temperature for preparation. The basicity of pyridine is low ($pK_a = 5.18$) in comparison with that of NH_3 ($pK_a = 9.25$), which is generally used [5]. In this study, we report that an approximately linear relationship exists between the acid strengths of solid acids determined by the Hammett method and the termination temperature of pyridine desorption. Moreover, the acid strength of colored superacids was estimated by the relative activity of the catalysts, and the strength versus temperature relationships practically fell on the linear line.

TPD experiment was performed on 16 solid acids with different acid strength, the H_0 values of those acid strengths being in the range of $H_0 \leqslant -5.6$ to $H_0 > -16.12$. Prior to the TPD experiment, the samples were heated in vacuum at 443–773 K and suspended in dried pyridine for half an hour at room temperature. After that, excess pyridine was removed by evaporation and evacuated for half an hour. The TPD experiment was carried out with thermal gravimetrical and differential thermal analyses (TG-DTA). The sample was heated in He stream (60 ml min^{-1}) with temperature programmed rate at 10 K min^{-1}. The termination temperature of pyridine desorption was determined by the measurement of TG.

SiO_2–Al_2O_3 (JRC-ASL-2) was a reference catalyst supplied by Catalysis Society of Japan. Most of the solid acids, SO_4^{2-}/ZrO_2, SO_4^{2-}/SnO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/Fe_2O_3, SO_4^{2-}/Al_2O_3, WO_3/ZrO_2 [1], WO_3/TiO_2 [2], ZrO_2–TiO_2 (mole ratio = 1 : 3, 1 : 1, and 3 : 1) [6], and Al_2O_3 [7] were prepared by the reported methods. B_2O_3/ZrO_2 [8] and B_2O_3/Al_2O_3 were obtained as follows: metal hydroxides were impregnated with H_3BO_3 solution followed by evaporating water, drying, and calcining in air at 773 K (B_2O_3/ZrO_2) or 873 K (B_2O_3/Al_2O_3). SiO_2–ZrO_2 was prepared by hydrolysis of $ZrO(NO_3)_2 \cdot 2H_2O$ and $Si(OC_2H_5)_4$ dissolved in ethanol, the hydrolysis was carried out using an excess amount of distilled water with a drop of HNO_3. The precipitate of mixed hydroxide was dried and calcined in air at 773 K for 3 h.

Examples of temperature-variation of the pyridine desorption are shown in figs. 1 and 2, where the catalysts are SiO_2–Al_2O_3 and WO_3/ZrO_2. After loss of water from the original, untreated samples is subtracted from the observed TPD, the obtained curves (C) come to ends at 701 and 859 K, which are termination temperatures of the pyridine desorption. In most cases the termination temperature did not exceed the calcination temperatures of catalysts; otherwise it could be diffi-

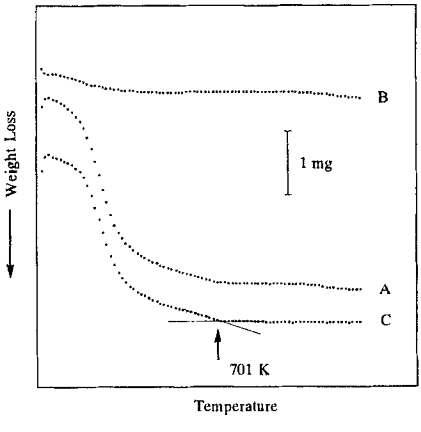

Fig. 1. TG weight loss curves of SiO_2–Al_2O_3 samples. (A) Pyridine adsorbed, (b) untreated, (C) A − B.

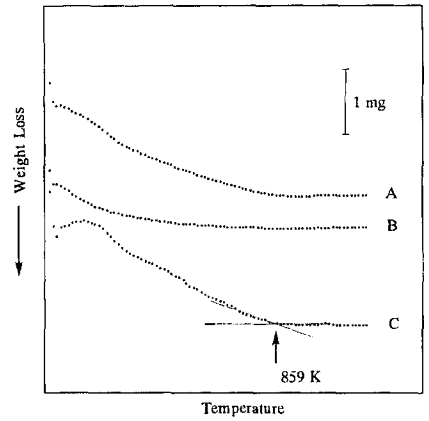

Fig. 2. TG weight loss curves of WO_3/ZrO_2samples. (A) Pyridine adsorbed, (B) untreated, (C) (A − B) × 2.

cult to determine between pyridine desorption and loss of hydroxyls or weight decrease based on the sulfate decomposition for the sulfate-supported superacids.

Fig. 3 shows a relation between the H_0 values of highest acid strength ($H_{0,\max}$) determined by the Hammett method or estimated by a catalytic activity and the termination temperatures of pyridine desorption. In the cases of Al_2O_3, ZrO_2–TiO_2 (1 : 3, 1 : 1, and 3 : 1), B_2O_3/Al_2O_3, SiO_2–ZrO_2, SiO_2–Al_2O_3, SO_4^{2-}/Al_2O_3, SO_4^{2-}/TiO_2, WO_3/ZrO_2 and SO_4^{2-}/ZrO_2, the $H_{0,\max}$ values determined by the Hammett method are proportional to the temperatures of pyridine desorption terminated. The measured values were plotted between two lines drawn in the figure except that of SO_4^{2-}/SnO_2. In the TPD experiment of SO_4^{2-}/SnO_2, exothermic reac-

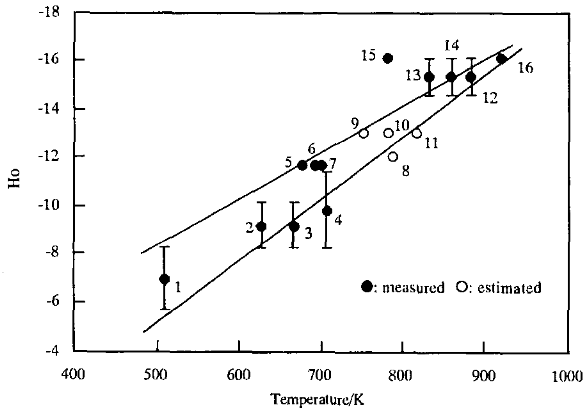

Fig. 3. The relation between $H_{0,\max}$ and termination temperature of pyridine desorption. (1) Al_2O_3, (2) ZrO_2–TiO_2(1 : 3), (3) ZrO_2–TiO_2(3 : 1), (4) B_2O_3/Al_2O_3, (5) ZrO_2–TiO_2(1 : 1), (6) SiO_2–ZrO_2, (7) SiO_2–Al_2O_3, (8) B_2O_3/ZrO_2, (9) MoO_3/ZrO_2, (10) WO_3/TiO_2, (11) SO_4^{2-}/Fe_2O_3, (12) SO_4^{2-}/Al_2O_3, (13) SO_4^{2-}/TiO_2, (14) WO_3/ZrO_2, (15) SO_4^{2-}/SnO_2, (16) SO_4^{2-}/ZrO_2.

tion was observed at temperature below that expected from the acid strength by the Hammett method; oxidation of the adsorbed pyridine occurred on the SO_4^{2-}/SnO_2 surface. From the results, it is shown that TPD using pyridine is useful to determine the highest acid strength of the solid superacids. In addition, $H_{o,max}$ of other superacids, which were estimated by catalytic activities, could be plotted between the lines, the estimation of acid strength of those superacids was practically correct.

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