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## THE EFFECT OF MOISTURE ADSORPTION ON THE ACIDITY DISTRIBUTION OF ACID SITES OF SILICA-ALUMINA

By

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### Abstract

The effect of the title was investigated for the purpose of obtaining an experimental support for the conclusion of the preceding investigation<sup>1)</sup> that the  $pK_a$  value of the conjugate acid of water vapor interacting with acid sites on solid surface might well be considered to be  $-1.7$  which is the  $pK_a$  value of free  $H_3O^+$ .

Moistened samples of silica-alumina with various contents of adsorbed water up to 1% of the original weights were prepared by moistening at 20°C in 42 and 90% relative humidity bath for varied lengths of time and subjected to the measurement by the Johnson method<sup>2)</sup> for the acidity distribution of acid sites using three Hammett indicators, dicinnamalacetone ( $pK_a = -3.0$ ), benzeneazodiphenylamine ( $pK_a = 1.5$ ) and 4-benzeneazo-1-naphthylamine ( $pK_a = 4.0$ ).

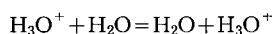
The result was that moisture adsorption had no effect on the acidity at  $H_0 \leq 4.0$  with a small decreasing effect on that at  $H_0 \leq 1.5$ , while it caused a pronounced decrease in that at  $H_0 \leq -3.0$ , which favors the conclusion mentioned above.

### Introduction

Water vapor is involved in a number of gas-phase catalyses by solid acids such as olefin hydration, phenol alkylation by alcohol, alcohol dehydration, etc. It is therefore important to determine the basic strength of water vapor interacting with acid sites of solid acids. Our preceding experiment<sup>1)</sup> has led to a conclusion that the basic strength of water vapor might well be considered as such that the  $pK_a$  value of its conjugate acid is  $-1.7$  which is the  $pK_a$  value of free  $H_3O^{+*}$ . The present investigation was undertaken

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<sup>\*\*)</sup> From the reaction



the  $pK_a$  value of  $H_3O^+$  is calculated as:

$$\begin{aligned} pK_a(H_3O^+) &= -\log ([H_3O^+][H_2O]/[H_3O^+]) = -\log [H_2O] \\ &= -\log (1000/18) = -1.7 \end{aligned}$$

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to get an experimental support for this conclusion.

The acidity distribution of acid sites of solid acids is measured by the JOHNSON<sup>2)</sup> or BENESI<sup>3)</sup> method, both of which make use of competitive acid-base reactions among acid sites, Hammett indicators<sup>4)</sup> and *n*-butylamine where the acid and basic strengths of the reactants are the leading factor. When a moistened sample of solid is subjected to the measurement by the JOHNSON or BENESI method, we deal with competitive acid-base reactions among the above three reactants plus water and hence the difference in measured distributions of acid sites between dry and moistened samples ought to have close connection with the basic strength of water vapor. While several investigators<sup>2,5,6)</sup> have observed that samples of solid acids, when exposed to moisture, give distributions of acid sites different from those of dry samples, no survey has been made on the change in the acidity distribution of acid sites by moisture adsorption with a view of estimating the basic strength of water vapor. It is under these circumstances that the present investigation was focused on the effect of the title.

### Experimental

"Silica-Alumina Catalyst N631(L)" of the Nikki Chemical Co., in the form of 6×6-mm pellet, containing 13% alumina was adopted as the source material for silica-alumina. The material was crushed, sieved out to below 100 mesh and calcined at 400°C for 3 hr for activation. After cooling the calcined powder in a desiccator, the container was sealed and stored there; throughout handling of the powder a great deal of care was taken not to expose it to moist air.

About 0.5 g of the powder was scooped into a weighing bottle and placed in a constant-humidity bath for a measured length of time; the bottle was then weighed for the amount of water adsorbed and all the powder poured into 10cc benzene in a 50-cc ERLLENMEYER'S flask to measure the acidity distribution by the JOHNSON method. Two constant humidity baths were employed, one was maintained at 42% relative humidity at 20°C by means of saturated aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ <sup>7)</sup> and the other at 90% relative humidity at 20°C by means of saturated aqueous solution of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ <sup>7)</sup>. The Hammett indicators used are dicinnamalacetone ( $pK_a = -3.0$ <sup>3))</sup>\*, benzene-azodiphenylamine ( $pK_a = 1.5$ <sup>8)</sup>), and 4-benzeneazo-1-naphthylamine ( $pK_a = 4.0$ <sup>5)</sup>) supplied from the Tokyo Chemical Co., guaranteed reagent, which were each used as 0.1 wt % benzene solution. The titration of the sample suspension

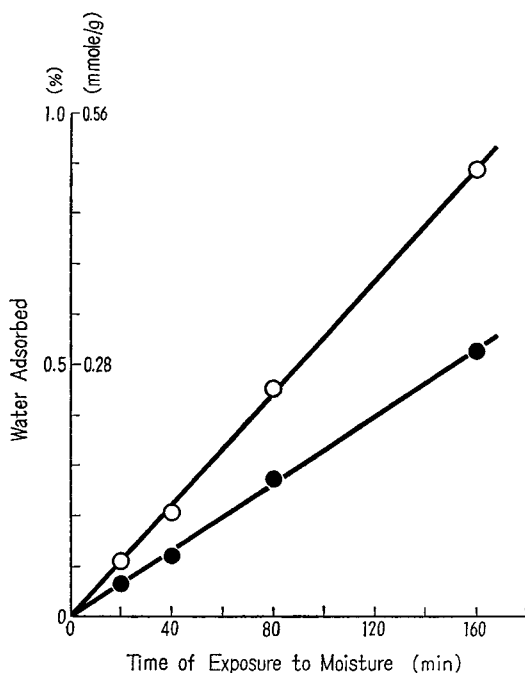
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\*) The  $pK_a$  values in the parentheses following the names of Hammett indicators or chemicals are for their conjugate acids.

in benzene with 0.1N *n*-butylamine benzene solution was controlled so as to take about 3 hr to reach the completion, 0.3 ml of each of the three indicator solutions being added.

### Results and Discussion

Fig. 1 shows the moisture adsorptions of silica-alumina under 42 and 90% relative humidities at 20°C. It is seen from Fig. 1 that the rate of moisture adsorption is roughly proportional to the partial pressure of moisture and that even 42% relative humidity at 20°C, which is generally considered



**Fig. 1.** Moisture adsorptions of silica-alumina of below 100 mesh under 42 and 90% relative humidities at 20°C. (Humidity: ○ 90%; ● 42%).

a drying atmosphere, exerts moistening influence on silica-alumina. It follows that it is not always adequate to prepare powdered samples for the acidity measurement by calcination of materials followed by grinding and sieving in open air. A simple countermeasure against this moistening effect of air is to calcine powdered materials as in our present experiment.

Fig. 2 shows the changes with moisture adsorption in the acidities in the ranges of  $H_0^{4)} \leq -3.0$ ,  $\leq 1.5$  and  $\leq 4.0$ . The phenomena of Fig. 2 are

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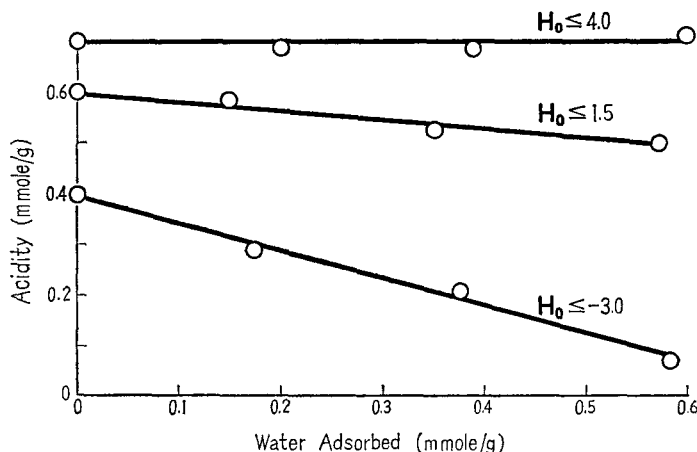


Fig. 2. Changes with moisture adsorption in the acidities of silica-alumina in the ranges of  $H_0 \leq -3.0$ ,  $\leq 1.5$  and  $\leq 4.0$ .

characterized by the following points:

- (1) The acidities at  $H_0 \leq \alpha$  ( $\alpha \geq 1.5$ ) are almost uninfluenced by moisture adsorption, whereas that at  $H_0 \leq -3.0$  is influenced pronouncedly.
- (2) The decrease in the acidity at  $H_0 \leq -3.0$  is less than the amount of the water adsorbed.

Let us see to what extent these salient phenomena can be accounted for on the basis of the premise that water vapor behaves as a base so that the  $pK_a$  value of its conjugate acid is  $-1.7$ . When the sample is dry and dicinnamalacetone ( $pK_a = -3.0$ ) is used as indicator, the indicator molecules are adsorbed on the acid sites of  $H_0 \leq -3.0$  and the butylamine ( $pK_a = 10.6$ ) molecules take part concurrently in the following three reactions:

- 1) adsorption on the acid sites of  $H_0 \leq 10.6$
- 2) replacement of the adsorbed indicator molecules
- 3) migration of the once adsorbed molecules to stronger acid sites

Thus at the end of the titration all the acid sites of  $H_0 \leq -3.0$  have been neutralized by butylamine<sup>\*</sup>). When the sample is moistened, the water molecules are adsorbed on the acid sites of  $H_0 \leq -1.7$ , the dicinnamalacetone molecules adsorbed on those of  $H_0 \leq -3.0$  and the butylamine molecules take part concurrently in the above three reactions plus

- 4) replacement of the adsorbed water molecules

<sup>\*</sup>) It has recently been found that at the end of the titration the acid sites of  $-3.0 < H_0$  are also partially neutralized, but this over-neutralization is neglected here for the sake of brevity.

Thus at the end of the titration a considerable amount of the water molecules adsorbed on the acid sites of  $H_0 \leq -3.0$  remain unreplaced by butylamine because of the greater basic strength of water than dicinnamalacetone, resulting in the above-mentioned phenomena (1) and (2).

The phenomena that little influence results from moisture adsorption when the other indicators than dicinnamalacetone are used, can be accounted for easily. In the case, for example, of 4-benzeneazo-1-naphthylamine, because of the greater basic strength of the indicator than water, all the adsorbed water molecules will be replaced by butylamine before all the adsorbed indicator molecules have been replaced, thus resulting in no influence.

The above inference is based on neglect of the observed gradual decrease in the acidity at  $H_0 \leq 1.5$  and so far as moisture adsorption is less than 1%, the premise we have assumed with respect to the basic strength of water vapor might well be taken to be semiquantitatively valid. WALLING<sup>6)</sup> observed that Florisil, acidic to benzeneazodiphenylamine, became basic to it and acidic to *p*-dimethylaminoazobenzene ( $pK_a = 3.3$ ) when exposed to moist air to pick up water by 8% of the original weight and that Socony Vacuum catalyst, acidic to *p*-nitrophenylazo-(*p'*-nitro)-diphenylamine ( $pK_a = 0.43$ ), became basic to it and partially acidic to benzeneazodiphenylamine upon picking up water by 5.4%. These phenomena are in harmony with the observed gradual decrease in the acidity of  $H_0 \leq 1.5$  and suggest that the basic strength of water vapor should become greater up to  $pK_a = 1.5$  with increasing degree of moisture adsorption.

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