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Author(s)	MATSUZAKI, Isao; NITTA, Masahiro; TANABE, Kozo
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APPLICATION OF HAMMETT INDICATORS TO ESTIMATING COVERAGES OF ACID SITES OF SILICA-ALUMINA BY NITROGEN, ETHYLENE, WATER, ETHYL ALCOHOL, PYRIDINE AND *n*-BUTYLAMINE

By

Isao MATSUZAKI^{*}), Masahiro NITTA^{*})
and Kozo TANABE^{*})

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Abstract

Hammett indicators have been applied to estimate the coverages of acid sites of silica-alumina by nitrogen, ethylene, water, ethyl alcohol, pyridine and *n*-butylamine and to evaluate the relative pK_a values of their acidic forms under the conditions employed.

Four of Hammett indicators, dicinnamalacetone ($pK_a = -3.0$), benzeneazodiphenylamine ($pK_a = +1.5$), *p*-dimethylaminoazobenzene ($pK_a = +3.3$), and methyl red ($pK_a = +4.8$), were allowed to be adsorbed on acid sites of silica-alumina to color it in scarlet or purple, the colors of their acidic forms. The colored silica-alumina was exposed to the reagents in gas phase in the temperature range from -60 or 20 to 150°C and inspected for color change.

The points which have been revealed are: 1) neither nitrogen nor ethylene can be adsorbed; 2) water and ethyl alcohol can be adsorbed on acid sites of $pK_a \leq -1.7$ and of $pK_a \leq \sim -2$, respectively, but their concentrations in the adsorbed phase are small above 50°C ; 3) pyridine and *n*-butylamine would be densely adsorbed on acid sites of $pK_a \leq +5.3$ and of $pK_a \leq +10.6$, respectively.

Introduction

The estimation of coverage of active sites on catalyst surface during the progress of reaction is of importance for the study on heterogeneous catalysis but its determination is generally very difficult. One of us¹⁾ has recently estimated the coverage of catalyst surface by mono- and diadsorbed ethane in the nickel-catalyzed ethylene hydrogenation by making use of ortho- and para-hydrogen conversion and H_2 - D_2 equilibration. We have extended our interest in estimating the coverage to the field of catalysis by solid acids. This paper is concerned with the first phase of approach, dealing with an application of Hammett indicators for qualitative estimation of coverage of silica-alumina by

^{*}) Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan

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ethylene, water, ethyl alcohol, nitrogen, pyridine and *n*-butylamine, the first three of which are the components of hydration of ethylene to ethyl alcohol.

Hammett indicators²⁾ which are defined as uncharged bases capable of being converted to conjugate acids by transfer of one proton have been extensively used in cooperation with *n*-butylamine for the measurement of the acid strength and the number of acid sites on solid surfaces.³⁻⁶⁾ The pK_a value of conjugate acid of a Hammett indicator is used to specify the indicator in its basic form. The principle of the measurement consists in observing acid-base competitive reactions among acid sites, Hammett indicators and *n*-butylamine in which the pK_a values of reactants are the leading factor. Thus an acid site having a pK_a value of α is defined as one capable of converting any Hammett indicators, whose pK_a values are equal to and less than α , to their acid forms.

Silica-alumina has been widely used as solid acid and proved to have acid sites with pK_a values ranging from +6.8 to as low as below -8.2. On the other hand, all the reagents mentioned above have basic property: the pK_a values of H_3O^+ , $C_2H_5OH_2^+$, $C_5H_5NH^+$ and $n-C_4H_9NH_3^+$, *i. e.*, the conjugate acids of water, ethyl alcohol, pyridine and *n*-butylamine, are known⁷⁾ to be -1.7, ~ -2 , +5.3 and +10.6, respectively; the basic strengths of nitrogen and ethylene, though having not determined experimentally, might well be considered to be by far lower than that of ethyl alcohol, the weakest base of the four, since one might think that reactions $N_2 + H^+ = N_2H^+$ and $C_2H_4 + H^+ = C_2H_5^+$ would favor extremely the left hand sides.

Let us consider the interaction of silica-alumina with one of the six basic substances, *e. g.*, with water vapor at room temperature. Water will be adsorbed on those acid sites of $pK_a \leq -1.7$ with the concentration in adsorbed phase controlled by the thermodynamic nature of the equilibrium between the gas and adsorbed phases. This phenomenon of adsorption can be visualized when we use silica-alumina preliminarily colored with Hammett indicators: the silica-alumina colored with indicators of $pK_a > -1.7$ would remain unchanged in color by contact with water vapor, while the one colored with indicators of $pK_a < -1.7$ would change its color to that of the basic form, *the degree of color change being proportional to the concentration of water adsorbed.*

The above description illustrates the principle of our intended application of Hammett indicators to the estimation of coverage of active acid sites. For wide applicability of this principle, it is necessary as a sufficient condition that the temperature dependences of pK_a values of acid sites, Hammett indicators and adsorbates are small in a wide range of temperature. The possibility that this sufficient condition may be filled actually is suggested by the data,⁸⁾ though

limited in number, on the change of pK_a values of various acids in the range $0\sim 50^\circ\text{C}$.

Experimental

1. Materials used

1.1. Silica-alumina

The material used was "Silica-alumina catalyst N631(L)" of Nikki Chemical Co., in the form of pellet 6×6 mm, containing 13.6% alumina. It was crushed, sieved out to $5\sim 10$ mesh and calcined at 400°C for one hour for activation.

1.2. Hammett indicators

The Hammett indicators used are listed in Table 1. They were used as 0.1 wt % benzene solutions.

TABLE 1. The Hammett Indicators Used

Indicator No.	Substance	pK_a (of conjugate acid)	Supplier and grade
I	dicinnamalacetone	- 3.0 ³⁾	Tokyo Chemical Industry Co., guaranteed reagent
II	benzeneazodiphenylamine	+ 1.5 ⁹⁾	" , "
III	<i>p</i> -dimethylaminoazobenzene	+ 3.3 ¹⁰⁾	" , "
IV	methyl red	+ 4.8 ¹¹⁾	Wako Pure Chemical Industries, "

1.3. Reagents

The reagents used are listed below:

- (1) nitrogen ... cylinder nitrogen of 99.99% purity.
- (2) water ... deionized water, outgassed by boiling before use.
- (3) ethylene ... over 99.5% purity from Takachiho Chemical Industries Co.
- (4) ethyl alcohol ... extra pure grade from Kanto Chemical Co.
- (5) pyridine ... guaranteed reagent from Kanto Chemical Co.
- (6) *n*-butylamine ... guaranteed reagent from Wako Pure Chemical Industries.

2. Apparatus used

The apparatus used is shown schematically in Fig. 1. V is a vessel containing silica-alumina. EF is an electric furnace thermostated by means of a thermocouple fixed at the middle of the outer wall of the vessel. The

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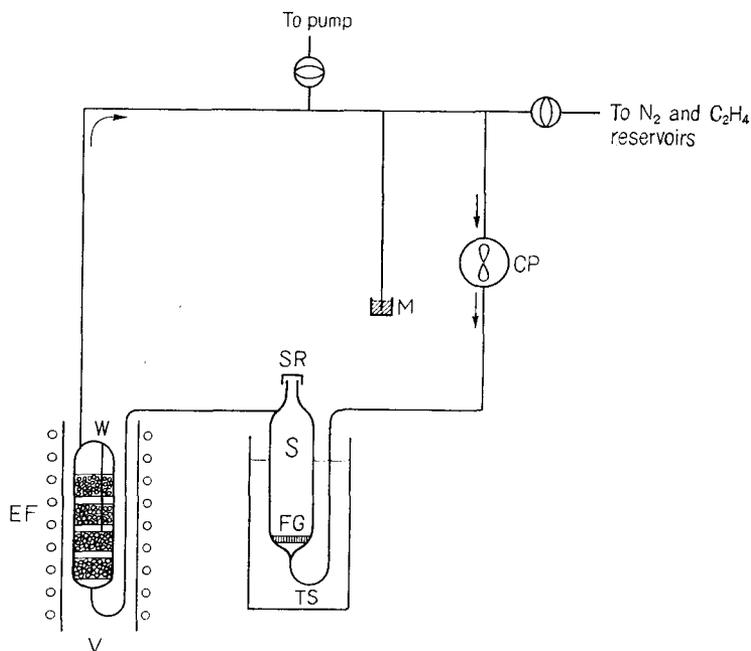


Fig. 1. Apparatus used

temperature of the silica-alumina was observed on a millivolt meter connecting to a thermocouple inserted in the well, W, of the vessel. When the vessel was needed to be cooled, the electric furnace was replaced by a methanol bath cooled with dry ice. S is a liquid vaporizer equipped with a fritted glass disk, FG, at the bottom and a silicone rubber disk, SR, at the top. TS is a water bath thermostated at 20°C. CP is a diaphragm-type gas circulation pump, the arrows indicating the direction of gas flow. M is a mercury manometer.

3. Procedure

3.1. Preparation and charging of colored silica-alumina

To 15 ml of benzene was added 3.5 g of the silica-alumina and then 0.1 ml of one of the indicator solutions. The indicator was adsorbed onto acid sites to color the silica-alumina in light purple or scarlet, the color of the acidic form of the indicator. After decanting out the benzene the colored silica-alumina was dried at 90°C. We had thus four kinds of silica-alumina each colored with one of the four indicators.

Each 1 g of the four colored silica-alumina was put in the vessel in layers using glass wool as plugs and inserts, evacuated at 50°C for 30 min and cooled to room temperature or -60°C.

3.2. Contact of reagents to colored silica-alumina

Nitrogen was introduced into the apparatus with the vessel kept at room temperature, circulated for 30 min and the silica-alumina was inspected by naked eye for any color change. The vessel was then inserted into the electric furnace and heated at a higher temperature under circulation of nitrogen. After keeping the vessel for 30 min at that temperature the electric furnace was removed and the color of the silica-alumina promptly inspected. In the same fashion color inspections were made at several temperatures up to 150°C. Ethylene was used in the same way as nitrogen except that -60°C was employed additionally.

In runs using the liquid reagents, the liquid vaporizer was used together with nitrogen as carrier gas: for example, water was injected via the silicone rubber disk into the liquid vaporizer through which nitrogen was being circulated, and after a while the vapor pressure of water reached the saturation value at the temperature of the water thermostat. Similar observations of color change were made at various temperatures ranging from 20 to 150°C.

When a series of observation was over for a reagent, the silica-alumina was evacuated at 150°C. After this evacuation, except for the cases with pyridine and *n*-butylamine, the colors of the four samples were the same as those of the unused ones, so that the set of the same charges was used successively. After runs with pyridine and *n*-butylamine the silica-alumina samples were renewed.

Results and discussion

The results obtained are shown in Table 2. The pK_a values, which we know for the indicators and reagents used, are those at room temperature and our knowledge on their temperature dependence is lacking almost completely. However, we might regard them as constant in the range 20~150°C, because the observed changes⁸⁾ in pK_a values of various acids in the range 0~50°C are so small and because there are no results in Table 2 against regarding the pK_a values constant. The latter reason can be well understood if we pay special attention to the phenomena that both pyridine ($pK_a = +5.3$) and *n*-butylamine ($pK_a = +10.6$) are capable of converting all the acidic forms of the indicators ($pK_a = -3.0 \sim +4.8$) to the basic irrespective of the temperature, and that both water ($pK_a = -1.7$) and ethyl alcohol ($pK_a = \sim -2.0$) are capable of converting the acidic form of the indicator I ($pK_a = -3.0$), but incapable of converting those of the other indicators ($pK_a > -1.7$). Therefore, we shall advance consideration in what follows on the basis of independence of pK_a upon temperature.

TABLE 2. Color Change of Hammett Indicator-Adsorbed Silica-Alumina by Contact with Reagents

Indicator No. (pK_a)	Color change <u>acidic</u> basic	Temp. °C	Color change or color when contacted with						
			N ₂ (600 mm)	C ₂ H ₄ (600 mm)	N ₂ (600 mm) +H ₂ O (25 mm)	C ₂ H ₄ (600 mm) +H ₂ O (25 mm)	N ₂ (600 mm)+ C ₂ H ₅ OH (38mm)	N ₂ (600 mm)+ <i>n</i> -butylamine (50 mm)	N ₂ (600 mm)+ pyridine (20 mm)
I (- 3.0)	<u>light scarlet</u> yellowish white	-60		none	yellowish white	yellowish white	yellowish white	yellowish white	yellowish white
		20	none	"	"	"	"	"	
		50	"	"	"	"	"	"	
		100	"	"	none	none	none	"	"
		150	"	"	"	"	"	"	"
II (+ 1.5)	<u>light purple</u> yellowish white	-60		none	none	none	none	yellowish white	yellowish white
		20	none	"	"	"	"	"	"
		50	"	"	"	"	"	"	"
		100	"	"	"	"	"	"	"
		150	"	"	"	"	"	"	"
III (+ 3.3)	<u>light scarlet</u> yellowish white	-60		none	none	none	none	yellowish white	yellowish white
		20	none	"	"	"	"	"	"
		50	"	"	"	"	"	"	"
		100	"	"	"	"	"	"	"
		150	"	"	"	"	"	"	"
IV (+ 4.8)	<u>light purple</u> yellowish white	-60		none	none	none	none	yellowish white	yellowish white
		20	none	"	"	"	"	"	"
		50	"	"	"	"	"	"	"
		100	"	"	"	"	"	"	"
		150	"	"	"	"	"	"	"

Neither nitrogen nor ethylene was capable of converting any acidic forms of the indicators. For these phenomena the following two different explanations are applicable: 1) the basic strengths of nitrogen and ethylene are too weak to replace even the acidic form ($pK_a = -3.0$) of the indicator I; 2) both nitrogen and ethylene can react with acid sites of a certain low range of pK_a values but their concentrations at adsorption equilibrium are too small to result in perceptible color change. Of these two, we are rather in favor of the first case, since the basic strengths of nitrogen and ethylene would be by far weaker than water, ethyl alcohol and dicinnamalacetone.

Water vapor could convert, at lower temperatures, nothing but the acidic form of indicator I whose pK_a value is less than that of H_3O^+ , as expected from the role of pK_a value in acid-base reactions. From the observed clear color change, it is concluded that at 20° and 50°C water is adsorbed densely on those acid sites of $pK_a \leq -1.7$. As seen from the table, rise in temperature caused the decrease in converting capacity of water for the acidic form of indicator I. This phenomenon means that the equilibrium concentration of water adsorbed on acid sites of $pK_a \leq -1.7$ becomes less with rise in temperature, in accordance with the general rule for adsorption.

The behavior of ethyl alcohol was almost the same as that of water, as expected from a small difference in pK_a of their conjugate acids. With pyridine and *n*-butylamine, adsorption was observed by far stronger than with water and ethyl alcohol, in parallel with the order of basic strengths.

When the mixture of ethylene and water was applied and there was therefore possibility of the hydration to ethyl alcohol taking place, the color change was quite the same as with water. The liquid in the vaporizer was analyzed by means of a gas chromatography with the result that nothing was formed at all. It is, therefore, concluded from comparison of the three color changes with ethylene, water and ethylene plus water, that the contact of silica-alumina with a mixture of ethylene and water will result in the predominant adsorption of water on the acid sites of $pK_a \leq -1.7$.

The hydration of ethylene to ethyl alcohol by solid acids proceeds in the range 200~300°C with a mixture of atmospheric ethylene and water vapor of about 20 mm. With respect to active acid sites and their coverages in this hydration, the above-mentioned findings permit us to draw a rough picture: 1) water and ethyl alcohol are capable of being adsorbed on acid sites of $pK_a \leq -1.7$ and of $pK_a \leq \sim -2$, respectively, but their concentrations in the adsorbed phase are small; 2) ethylene would be unable to be adsorbed on any acid sites.

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