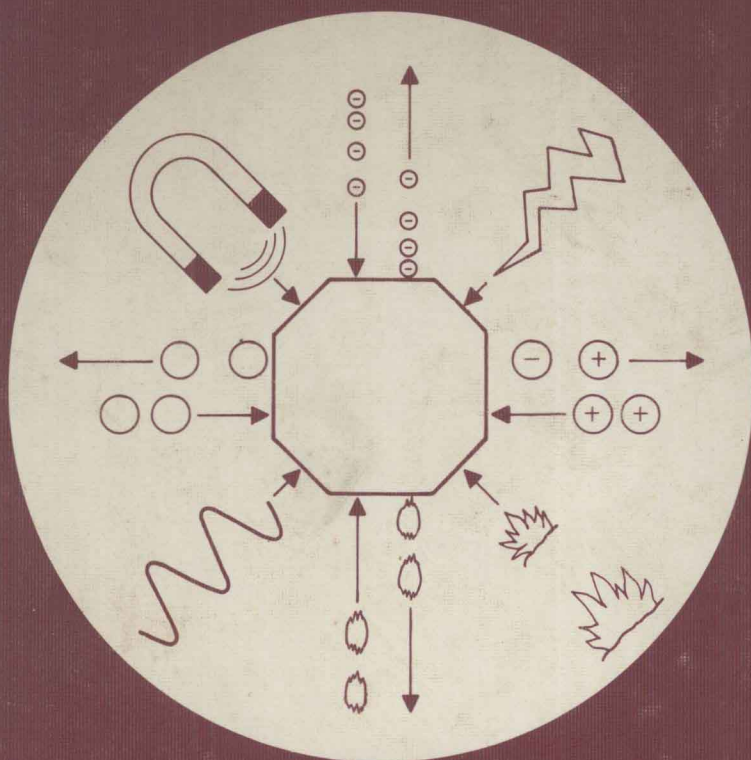


studies in surface science and catalysis



51

NEW SOLID ACIDS AND BASES

THEIR CATALYTIC PROPERTIES

K. Tanabe
M. Misono
Y. Ono
H. Hattori

Studies in Surface Science and Catalysis

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NEW SOLID ACIDS AND BASES

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by

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Studies in Surface Science and Catalysis 51

NEW SOLID ACIDS AND BASES
their catalytic properties

Preface

Nineteen years have passed since the monograph "Solid Acids and Bases" was published in 1970. During this period many new kinds of solid acids and bases have been found and synthesized. The surface properties (in particular, acidic and basic properties) and the structures of the new solids have been clarified by newly developed measurement methods using modern instruments and techniques. The characterized solid acids and bases have been applied as catalysts for diversified reactions, many good correlations being obtained between the acid-base properties and the catalytic activities or selectivities. Recently, acid-base bifunctional catalysis on solid surfaces is becoming an ever more important and intriguing field of study.

It has been recognized that the acidic and basic properties of catalysts and catalyst supports play an important role even in oxidation, reduction, hydrogenation, hydrocracking, etc. The effect of the preparation method and the pretreatment condition of solid acids and bases on the acidic and basic properties, the nature of acidic and basic sites and the mechanism regarding the generation of acidity and basicity have been elucidated experimentally and theoretically. On the basis of the accumulated knowledge of solid acids and bases, it is now possible to design and develop highly active and selective solid acid and base catalysts for particular reactions.

Moreover, the chemistry of solid acids and bases is being related to and utilized in numerous areas including adsorbents, sensors, cosmetics, fuel cells, sensitized pressed papers, and others.

In the present volume, the great progress in solid acids and bases made over the past two decades is summarized and reviewed with emphasis on fundamental aspects and chemical principles.

We wish to express our gratitude to Ms. Cecilia M. Hamagami and Mr. I. Ohta of Kodansha Scientific Ltd. for their invaluable assistance of the preparation of the English manuscripts which comprise this book.

Summer 1989

Kozo TANABE
Makoto MISONO
Yoshio ONO
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Definition and Classification of Solid Acids and Bases

In general terms, a solid acid may be understood to be a solid on which the color of a basic indicator changes or a solid on which a base is chemically adsorbed. More strictly, following both the Brønsted and Lewis definitions, a solid acid shows a tendency to donate a proton or to accept an electron pair, whereas a solid base tends to accept a proton or to donate an electron pair. These definitions are adequate for an understanding of the acid-base phenomena shown by various solids, and are convenient for a clear description of solid acid and base catalysis.

TABLE 1.1 Solid Acids

1. Natural clay minerals: kaolinite, bentonite, attapulgite, montmorillonite, clarit, fuller's earth, zeolites (X, Y, A, H-ZSM etc), cation exchanged zeolites and clays
2. Mounted acids: H_2SO_4 , H_3PO_4 , $\text{CH}_2(\text{COOH})_2$ mounted on silica, quartz sand, alumina or diatomaceous earth
3. Cation exchange resins
4. Charcoal heat-treated at 573 K
5. Metal oxides and sulfides : ZnO , CdO , Al_2O_3 , CeO_2 , ThO_2 , TiO_2 , ZrO_2 , SnO_2 , PbO , As_2O_3 , Bi_2O_3 , Sb_2O_5 , V_2O_5 , Cr_2O_3 , MoO_3 , WO_3 , CdS , ZnS
6. Metal salts : MgSO_4 , CaSO_4 , SrSO_4 , BaSO_4 , CuSO_4 , ZnSO_4 , CdSO_4 , $\text{Al}_2(\text{SO}_4)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CoSO_4 , NiSO_4 , $\text{Cr}_2(\text{SO}_4)_3$, KHSO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Zn}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, CaCO_3 , BPO_4 , AlPO_4 , CrPO_4 , FePO_4 , $\text{Cu}_3(\text{PO}_4)_2$, $\text{Zn}_3(\text{PO}_4)_2$, $\text{Mg}_3(\text{PO}_4)_2$, $\text{Ti}_3(\text{PO}_4)_4$, $\text{Zr}_3(\text{PO}_4)_4$, $\text{Ni}_3(\text{PO}_4)_2$, AgCl , CuCl , CaCl_2 , AlCl_3 , TiCl_3 , SnCl_2 , CaF_2 , BaF_2 , AgClO_4 , $\text{Mg}(\text{ClO}_4)_2$
7. Mixed oxides : $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-SnO}_2$, $\text{SiO}_2\text{-ZrO}_2$, $\text{SiO}_2\text{-BeO}$, $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-CaO}$, $\text{SiO}_2\text{-SrO}$, $\text{SiO}_2\text{-ZnO}$, $\text{SiO}_2\text{-Ga}_2\text{O}_3$, $\text{SiO}_2\text{-Y}_2\text{O}_3$, $\text{SiO}_2\text{-La}_2\text{O}_3$, $\text{SiO}_2\text{-MoO}_3$, $\text{SiO}_2\text{-WO}_3$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-ThO}_2$, $\text{Al}_2\text{O}_3\text{-MgO}$, $\text{Al}_2\text{O}_3\text{-ZnO}$, $\text{Al}_2\text{O}_3\text{-CdO}$, $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-ThO}_2$, $\text{Al}_2\text{O}_3\text{-TiO}_2$, $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$, $\text{Al}_2\text{O}_3\text{-MoO}_3$, $\text{Al}_2\text{O}_3\text{-WO}_3$, $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Mn}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$, $\text{Al}_2\text{O}_3\text{-NiO}$, $\text{TiO}_2\text{-CuO}$, $\text{TiO}_2\text{-MgO}$, $\text{TiO}_2\text{-ZnO}$, $\text{TiO}_2\text{-CdO}$, $\text{TiO}_2\text{-ZrO}_2$, $\text{TiO}_2\text{-SnO}_2$, $\text{TiO}_2\text{-Bi}_2\text{O}_3$, $\text{TiO}_2\text{-Sb}_2\text{O}_5$, $\text{TiO}_2\text{-V}_2\text{O}_5$, $\text{TiO}_2\text{-Cr}_2\text{O}_3$, $\text{TiO}_2\text{-MoO}_3$, $\text{TiO}_2\text{-WO}_3$, $\text{TiO}_2\text{-Mn}_2\text{O}_3$, $\text{TiO}_2\text{-Fe}_2\text{O}_3$, $\text{TiO}_2\text{-Co}_3\text{O}_4$, $\text{TiO}_2\text{-NiO}$, $\text{ZrO}_2\text{-CdO}$, ZnO-MgO , $\text{ZnO-Fe}_2\text{O}_3$, $\text{MoO}_3\text{-CoO}$, $\text{Al}_2\text{O}_3\text{-MoO}_3$, $\text{NiO-Al}_2\text{O}_3$, $\text{TiO}_2\text{-SiO}_2\text{-MgO}$, $\text{MoO}_3\text{-Al}_2\text{O}_3\text{-MgO}$, heteropoly acids

TABLE 1.2 Solid Bases

1.	Mounted bases: NaOH, KOH mounted on silica or alumina; Alkali metal and alkaline earth metal dispersed on silica, alumina, carbon, K_2CO_3 or in oil; NR_3 , NH_3 , KNH_2 on alumina; Li_2CO_3 on silica; <i>t</i> -BuOK on xonotolite
2.	Anion exchange resins
3.	Charcoal heat-treated at 1173 K or activated with N_2O , NH_3 or $ZnCl_2-NH_4Cl-CO_2$
4.	Metal oxides: BeO, MgO, CaO, SrO, BaO, ZnO, Al_2O_3 , Y_2O_3 , La_2O_3 , CeO ₂ , ThO ₂ , TiO ₂ , ZrO ₂ , SnO ₂ , Na ₂ O, K ₂ O
5.	Metal salts : Na_2CO_3 , K_2CO_3 , $KHCO_3$, $KNaCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$, $(NH_4)_2CO_3$, $Na_2WO_4 \cdot 2H_2O$, KCN
6.	Mixed oxides: SiO_2-MgO , SiO_2-CaO , SiO_2-SrO , SiO_2-BaO , SiO_2-ZnO , $SiO_2-Al_2O_3$, SiO_2-ThO_2 , SiO_2-TiO_2 , SiO_2-ZrO_2 , SiO_2-MoO_3 , SiO_2-WO_3 , Al_2O_3-MgO , $Al_2O_3-ThO_2$, $Al_2O_3-TiO_2$, $Al_2O_3-ZrO_2$, $Al_2O_3-MoO_3$, $Al_2O_3-WO_3$, ZrO_2-ZnO , ZrO_2-TiO_2 , TiO_2-MgO , ZrO_2-SnO_2
7.	Various kinds of zeolites exchanged with alkali metal or alkaline earth metal

TABLE 1.3 Solid Superacids

Group	Acid	Support
1a	SbF_5	$SiO_2-Al_2O_3$, SiO_2-TiO_2 , SiO_2-ZrO_2 , TiO_2-ZrO_2
1b	SbF_5	$Al_2O_3-B_2O_3$, SiO_2 , SiO_2-WO_3 , $HF-Al_2O_3$
2	SbF_5 , TaF_5	Al_2O_3 , MoO_3 , ThO_2 , Cr_2O_3 , Al_2O_3-WB
3	SbF_5 , BF_3	graphite, Pt-graphite
4	BF_3 , $AlCl_3$, $AlBr_3$	ion exchange resin, sulfate, chloride
5	SbF_5-HF SbF_5-FSO_3H	metal (Pt, Al), alloy (Pt-Au, Ni-Mo, Al-Mg), polyethylene, SbF_3 , AlF_3 , porous substance ($SiO_2-Al_2O_3$, kaolin, active carbon, graphite)
6	$SbF_5-CF_3SO_3H$	F- Al_2O_3 , $AlPO_4$, charcoal
7	Nafion (polymeric perfluororesin sulfonic acid)	
8	$TiO_2-SO_4^{2-}$, $ZrO_2-SO_4^{2-}$, $Fe_2O_3-SO_4^{2-}$	
9	H-ZSM-5 zeolite	

In accordance with the above definitions, a summarized list of solid acids and bases is given in Tables 1.1 and 1.2. The first group of solid acids in Table 1.1 includes naturally occurring clay minerals. The main constituents are silica and alumina. Various types of synthetic zeolites such as zeolites X,Y,A, ZMS-5, ZSM-11, etc. have been reported to show characteristic catalytic activities and selectivities. The well-known solid acid, synthetic silica-alumina, is listed in the seventh group, which also includes the many oxide mixtures which have recently been found to display acidic properties and catalytic activity. In the fifth and sixth groups are included many inorganic chemicals such as metal oxides, sulfides, sulfates, nitrates, phosphates and halides. Many have been found to show characteristic selectivities as catalysts.

Of the solid bases listed in Table 1.2, special mention should be made of the alkaline earth metal oxides in the fourth group and mixed metal oxides in the sixth group, whose basic properties and catalytic action have been recently found to be striking and interesting. A solid superacid is defined as a solid whose acid strength is higher than the acid strength of 100% sulfuric acid. Since the acid strength of 100% sulfuric acid expressed by the Hammett acidity function, H_0 , is -11.9 , a solid of $H_0 < -11.9$ is called a solid superacid. The kinds of solid superacids are shown in Table 1.3. The groups 1 through 6 include acids supported on various solids.

On the other hand, a solid superbases is defined as a solid whose base strength expressed by the basicity function, H_- , is higher than $+26$. The basis of the definition has been described in the literature.¹⁾ The kinds of solid superbases are shown in Table 1.4 together with their preparation method and pretreatment temperature.

TABLE 1.4 Solid Superbases

	Starting material, Preparation method	Pretreatment temp. K	H_-
CaO	CaCO ₃	1173	26.5
SrO	Sr(OH) ₂	1123	26.5
MgO-NaOH	(NaOH impregnated)	823	26.5
MgO-Na	(Na vaporized)	923	35
Al ₂ O ₃ -Na	(Na vaporized)	823	35
Al ₂ O ₃ -NaOH-Na	(NaOH, Na impregnated)	773	37

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Determination of Acidic and Basic Properties on Solid Surfaces

A complete description of acidic and basic properties on solid surfaces requires the determination of the acid and base strength, and of the amount and nature (Brønsted or Lewis type) of the acidic and basic sites.

2.1 ACIDIC PROPERTY

2.1.1 Strength and Amount of Solid Acid

When measuring the strength of a solid acid or base, it should be recognized that activity coefficients for species on the solid are unknown. Therefore, acidity and basicity functions for the solid are not properly defined thermodynamically. Nevertheless, the acidity and basicity functions are clearly valuable in a relative sense, while the absolute values are also useful provided the above limitations are recognized and numerical accuracy is not overstated.

The acid strength of a solid is defined as the ability of the surface to convert an adsorbed neutral base into its conjugate acid. If the reaction proceeds by means of proton transfer from the surface to the adsorbate, the acid strength is expressed by the Hammett acidity function H_0 ,¹⁾

$$H_0 = pK_a + \log [B] / [BH^+], \quad (1)$$

where $[B]$ and $[BH^+]$ are, respectively, the concentrations of the neutral base (basic indicator) and its conjugate acid and pK_a is pK_{BH^+} . If the reaction takes place by means of electron pair transfer from the adsorbate to the surface, H_0 is expressed by

$$H_0 = pK_a + \log [B] / [AB], \quad (2)$$

where $[AB]$ is the concentration of the neutral base which reacted with the Lewis acid or electron pair acceptor, A.

The amount of acid on a solid is usually expressed as the number or mmol of acid sites per unit weight or per unit surface area of the solid, and is obtained by measuring the amount of a base which reacts with the solid acid. This is also sometimes loosely called "acidity".

For the determination of strength and amount of a solid acid, there are two main methods: an amine titration method using indicators and a gaseous base adsorption method.

A. Amine Titration Method Using Indicators

The color of suitable indicators adsorbed on a surface will give a measure of its acid strength: if the color is that of the acid form of the indicator, then the value of the H_0 function of the surface is equal to or lower than the pK_a of the conjugate acid of the indicator. Lower values of H_0 correspond to greater acid strength. Thus, for indicators undergoing color changes in this way, the lower the pK_a , the greater the acid strength of the solid. For example, a solid which gives a yellow coloration with benzalacetophenone ($pK_a = -5.6$), but is colorless with anthraquinone ($pK_a = -8.2$), has an acid strength H_0 which lies between -5.6 and -8.2 . A solid having $H_0 \leq -16.04$ will change all indicators in Table 2.1 from the basic to the acidic colors, whereas one which changed none of them will have an acid strength of $H_0 > +6.8$.

The experimental details of the acid strength determination are described in earlier publications.^{2,3} The acid strength of a solid superacid which is very sensitive to moisture can be determined by observing the color change of an indicator whose vapor

TABLE 2.1 Basic indicators used for the measurement of acid strength

Indicators	Color		pK_a ^{†1}	$[H_2SO_4]^{†2}/\%$
	Base-form	Acid-form	pK_a	
Neutral red	yellow	red	+ 6.8	8×10^{-8}
Methyl red	yellow	red	+ 4.8	—
Phenylazonaphthylamine	yellow	red	+ 4.0	5×10^{-5}
<i>p</i> -Dimethylaminoazobenzene	yellow	red	+ 3.3	3×10^{-4}
2-Amino-5-azotoluene	yellow	red	+ 2.0	5×10^{-3}
Benzeneazodiphenylamine	yellow	purple	+ 1.5	2×10^{-2}
Crystal violet	blue	yellow	+ 0.8	0.1
<i>p</i> -Nitrobenzeneazo- (<i>p</i> '-nitro-diphenylamine)	orange	purple	+ 0.43	—
Dicinnamalacetone	yellow	red	— 3.0	48
Benzalacetophenone	colorless	yellow	— 5.6	71
Anthraquinone	colorless	yellow	— 8.2	90
2,4,6-Trinitroaniline	colorless	yellow	—10.10	98
<i>p</i> -Nitrotoluene	colorless	yellow	—11.35	^{†3}
<i>m</i> -Nitrotoluene	colorless	yellow	—11.99	^{†3}
<i>p</i> -Nitrofluorobenzene	colorless	yellow	—12.44	^{†3}
<i>p</i> -Nitrochlorobenzene	colorless	yellow	—12.70	^{†3}
<i>m</i> -Nitrochlorobenzene	colorless	yellow	—13.16	^{†3}
2,4-Dinitrotoluene	colorless	yellow	—13.75	^{†3}
2,4-Dinitrofluorobenzene	colorless	yellow	—14.52	^{†3}
1,3,5-Trinitrotoluene	colorless	yellow	—16.04	^{†3}

^{†1} pK_a of the conjugate acid, BH^+ , of indicator, B, ($=pK_{BH^+}$)

^{†2} wt. percent of H_2SO_4 in sulfuric acid solution which has the acid strength corresponding to the respective pK_a

^{†3} The indicator is liquid at room temperature and acid strength corresponding to the indicator is higher than the acid strength of 100 percent H_2SO_4 .

is adsorbed on a solid sample through a breakable seal in a vacuum system at room temperature.⁴⁾ The indicators used for the determination are included in Table 2.1.

The amount of acid sites on a solid surface can be measured by amine titration immediately after determination of acid strength by the above method. The method consists of titrating a solid acid suspended in benzene with *n*-butylamine, using an indicator. The use of various indicators with different pK_a values (see Table 2.1) enables us a determination of the amount of acid at various acid strengths by amine titration. The experimental details such as the effects of titration time, volume of added indicator, pore size, and moisture on measured acid amount are given in Reference 2.

As an example, the acid strength and amount of ZnO–Al₂O₃ having different compositions as well as those of ZnO and Al₂O₃, when calcined at 773K in air, are shown in Fig. 2.1.⁵⁾ The maximum acid amounts were observed when the content of ZnO was 10 mol% at any acid strength. Many examples of good correlations between acid amount and catalytic activity have been reported. An example is shown in Fig. 2.2, where the catalytic activity of various binary oxides increases linearly with increasing acid amount at acid strength $H_0 \leq -3$ of the catalysts.⁶⁾

The amine titration method gives the sum of the amounts of both Brønsted and Lewis acid, since both proton donors and electron pair acceptors on the surface will react with either the electron pair ($-\ddot{N}=$) of the indicator or that of amine ($\equiv N:$) to form a coordination bond. This method is rarely applied to colored or dark samples where the usual color change is difficult to observe. However, the difficulty can be minimized by mixing a white substance of known acidity with the sample or by employing the spectrophotometric method.^{2,7)} Calorimetric titration of a solid acid with amine is also available for the estimation of the acid amount of a colored or dark sample.^{2,7-9)} Recently, Hashimoto *et al.* developed a method to measure the acid strength

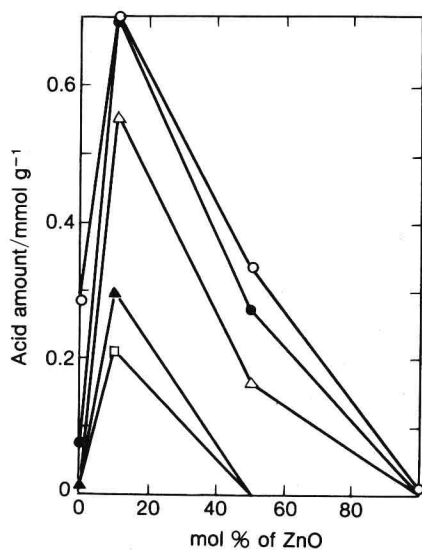


Fig. 2.1 Acid amounts at various acid strengths of ZnO–Al₂O₃ vs. mol % of ZnO.
 —○—; $H_0 \leq 4.8$, —●—; $H_0 \leq 3.3$, —△—; $H_0 \leq 1.5$, —▲—; $H_0 \leq -3.0$, —□—;
 $H_0 \leq -5.6$

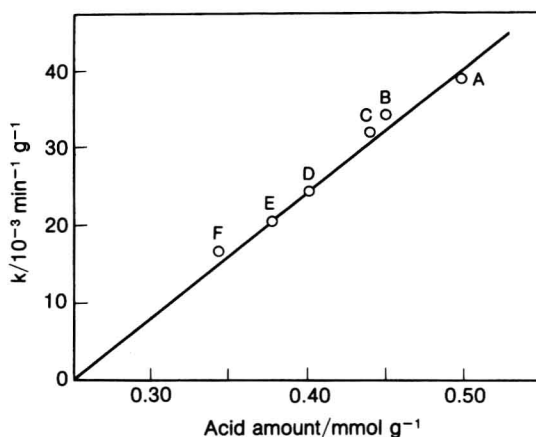


Fig. 2.2 First order rate constant of depolymerization of paraldehyde over various mixed catalysts vs. acid amount at $H_0 \leq -3$ of the catalysts.
 A; $\text{SiO}_2\text{-MoO}_3$, B; $\text{Al}_2\text{O}_3\text{-MoO}_3$, C; $\text{SiO}_2\text{-WO}_3$,
 D; $\text{Al}_2\text{O}_3\text{-WO}_3$, E; $\text{SiO}_2\text{-V}_2\text{O}_5$, F; $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$
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distribution on a solid surface by utilizing the chemisorption isotherms of a series of Hammett indicators on a solid suspended in a nonpolar solvent such as benzene or cyclohexane.¹⁰ The fraction of acid sites covered by the indicator was expressed by a Langmuir type equation, which includes both acid strength and the indicator concentration. The chemisorption isotherms of Hammett indicators can be converted to a cumulative distribution curve of acid strength. By this method, they measured the acid strength distribution of $\text{SiO}_2\text{-Al}_2\text{O}_3$ over a wide range of acid strength ($-15 \leq H_0 \leq -3$).¹⁰ Rys and Steinegger set up a model to relate the sorption of Hammett indicators onto proton-carrying solids with the protonation of these indicators in acid solutions.¹¹ From the relationship, the acid strength of Amberlyst-15 dispersed in water was found to correspond to an acid strength of 35 wt% aqueous sulfuric acid.

B. Gaseous Base Adsorption Method

When gaseous bases are adsorbed on acid sites, a base adsorbed on a strong acid site is more stable than one adsorbed on a weak acid site, and is more difficult to desorb. As elevated temperatures stimulate evacuation of the adsorbed bases from acid sites, those at weaker sites will be evacuated preferentially. Thus, the proportion of adsorbed base evacuated at various temperatures can give a measure of acid strength.

The amount of a gaseous base which a solid acid can adsorb chemically from the gaseous phase is a measure of the amount of acid on its surface. After a solid sample is put in a quartz spring balance and evacuated, the vapor of an organic base may be introduced for adsorption. When prolonged subsequent evacuation produces no further decrease in sample weight, then the base which is retained upon the sample is understood to be chemically adsorbed.¹²

Recently, temperature programmed desorption (TPD) of basic molecules such as ammonia, pyridine, *n*-butylamine, etc. is frequently used to characterize the acid