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Direct Measurement of the Interaction Energy between Solids and Gases. III. Comparison of the Calorimetric Titration Method with the Amine Titration Method for the Determination of Acid Strength Distribution of Silica–Alumina Surface

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The acid strength distribution of silica–alumina catalyst (alumina content 13 wt%) evacuated at 400 °C for 5 h was determined by the measurement of heat of adsorption of ammonia, and compared with that determined by amine titration by use of a series of Hammett indicators. The heats of adsorption of ammonia on silica–alumina poisoned with Hammett indicators were also measured in order to obtain the relation between the dissociation constant of the acid ($\mathrm{p}K_a$) and the heat of adsorption. When the dissociation constants of acid were equal to -5.6 and $+3.3$, the differential heats of adsorption of ammonia were observed to be 76.1 and 55.1 kJ/mol, respectively. The number of acid sites calculated from the heat *vs.* adsorbed amount curve was found to be about twice as large as that determined by amine titration. The discrepancy is discussed.

In previous papers, calorimetric titration with ammonia gas was reported for various solids (silica–alumina:alumina content 13 and 28 wt%, decationated zeolites and silica gel).[1,2] The adsorption energy distribution curve was derived for each sample from calorimetric data. The curve obtained shows a new aspect of the acid strength distribution of solid acid catalysts: the differential heat of adsorption of ammonia corresponds to the acid strength and the adsorbed amount of ammonia to the number of acid sites.

The acid strength is generally expressed by the Hammett acidity function, H_0, which is related to the dissociation constant of acid, $\mathrm{p}K_a$, as

$$H_0 = \mathrm{p}K_a + \log([\mathrm{B}]/[\mathrm{BH}^+]) \quad \text{(Brønsted acid)}$$

$$H_0 = \mathrm{p}K_a + \log([\mathrm{B}]/[\mathrm{BA}]) \quad \text{(Lewis acid)}$$

where [B] and [BH^+] are the concentrations of the base and its conjugated acid, respectively, and [BA] is the concentration of the coordination compound of Lewis acid A and Lewis base B. The number and the strength of acid sites can be determined by butylamine titration by use of indicators with known $\mathrm{p}K_a$ values.[3] However, the method is unsuitable for colored samples. Moreover, indicator molecules are so large that they can scarcely migrate into micro pores of porous materials such as silica–alumina. Though silica–alumina has been known to have stronger acid sites than $\mathrm{p}K_a = -8.2$, the color change of indicator corresponding to these regions can hardly be recognized with the naked eye.

Calorimetric method can overcome these disadvantages. However, the relationship between a differential heat of adsorption of basic gas and an acid strength or $\mathrm{p}K_a$ value has not been clarified as yet. The purpose of this study is to correlate the heat of adsorption of ammonia with the acid strength and to compare calorimetric titration with amine titriation.

Experimental

The solid acid catalyst used in this study was commercial FCC silica–alumina (alumina content 13 wt%, Catalysts & Chemicals Ind. Co., Ltd.). Each sample was pretreated at 400 °C under 10^{-5} Torr for 5 h before measurement. Butylamine titration was carried out before and after ammonia adsorption at different coverages in cyclohexane with use of a series of Hammett indicators: anthraquinone ($\mathrm{p}K_a = -8.2$), benzylideneacetophenone ($\mathrm{p}K_a = -5.6$), dicinnamylideneacetone ($\mathrm{p}K_a = -3.0$), *p*-anilinoazobenzene ($\mathrm{p}K_a = +1.5$), *p*-dimethylaminoazobenzene ($\mathrm{p}K_a = +3.3$).

The heat of adsorption of ammonia was measured with a twin conduction type calorimeter.[1,2,4] In most cases, calorimetric measurement and ammonia titration in solid-gas phase with use of the indicators were carried out simultaneously. Specific surface area was determined by the BET nitrogen method. Surface coverage of ammonia gas was calculated by assuming a cross sectional area of ammonia molecule to be 16 Å^2.

Results and Discussion

Figure 1 shows the relation between the preadsorbed amount of ammonia and the subsequently titrated amount with butylamine for each indicator. The end point of butylamine titration changed with the preadsorbed amount of ammonia for every indicator; as an example, when the indicator was benzylidene-

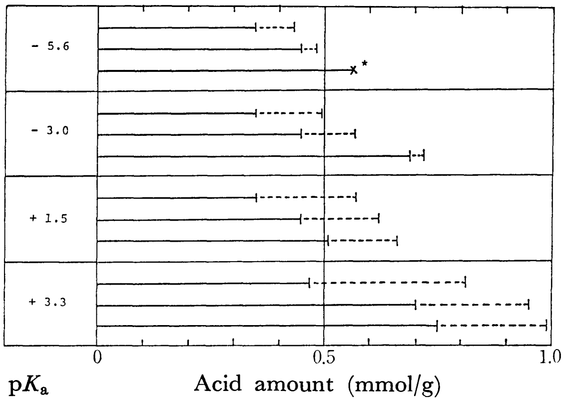

Fig. 1. Effect of ammonia poisoning on the acid amount titrated with butylamine.
Solid line: preadsorbed amount of ammonia.
Dashed line: titrated amount of butylamine after preadsorption of ammonia.
* Color change from the basic to the acidic was not observed.

Table 1. Calculated n value (on the basis of Fig. 1)

pK_a	−5.6	−3.0	+1.5	+3.3
n	2.0	2.8	2.0	2.6
		2.4	3.0	1.3
		(5.0)	1.8	1.6
Average		n=2.2		

Table 2. Acid amount determined by adsorbed amount of butylamine (1) and ammonia (2) (mmol/g)

pK_a	≦−5.6	≦−3.0	≦+1.5	≦+3.3
(1)	0.24	0.31	0.38	0.56
	0.24	0.33	0.39	0.57
			0.39	0.59
Average	0.24	0.32	0.38	0.57
(2)	0.52	0.68	0.83	1.21
	0.51	0.73	0.82	1.24
			0.84	1.27
Average	0.51	0.70	0.83	1.24

acetophenone(pK_a=−5.6) and the preadsorbed amount of ammonia 0.45 mmol/g, the titrated amount of butylamine was 0.03 mmol/g, while the end point was 0.43 mmol/g at 0.35 mmol/g of preadsorbed ammonia. If butylamine molecules were adsorbed on acid sites in the same manner as ammonia, the end point would be independent of the preadsorbed amount of ammonia. However, this is not the case. The number of acid sites can be considered constant after pretreatment at the same temperature under the same pressure for the same period. Hence, the following simple equation should hold for every indicator:

$$x + ny = k, \qquad (1)$$

where x is the preadsorbed amount of ammonia, y the titrated amount of butylamine, k the constant corresponding to the number of acid sites, and n the constant correlating the number of ammonia molecules with that of butylamine molecules adsorbed on silica–alumina surface. The values of n, calculated by means of Eq. 1 and on the basis of Fig. 1, are given in Table 1. Some scattering of values can be ascribed to the error of the titrated amount of butylamine. The average value, n=2.2, is considered to be reasonable as clarified in the following.

The numbers of acid sites calculated by use of conversion factor, n=2.2, are given in Table 2. They are constant within errors for a given pK_a value. Thus, if one ammonia molecule is adsorbed on one acid site, one butylamine molecule seems to occupy about two sites. The cross sectional area of ammonia molecule is 16 Å^2, and that of butylamine molecule 32 Å^2. Moreover, acid sites on silica–alumina surface seem to be localized due to localization of aluminum atom or ion.[5] The value of conversion factor, n=2.2, seems to depend mainly on the ratio of cross sectional areas, 32 Å^2/16 Å^2. Other factors such as the difference of basicity of amines may hardly affect the conversion factor.

In amine titration using Hammett indicators, butylamine in benzene or cyclohexane is generally used. In this study ammonia gas titration with a series of Hammett indicators was carried out, along with simultaneous calorimetric measurements for silica–alumina catalyst. Change from the basic to the acidic color was clearly observed as in amine titration in cyclohexane solution. The end points of gas titrations are shown in Table 3. These values are in good agreement with those in Table 2. The period required for adsorption equilibrium of ammonia was expected to be much shorter than that of butylamine in cyclohexane solution, since the diffusion rate of molecule in the gas phase is about ten thousand times as large as that in the liquid phase. The adsorption equilibrium seems to be attained within one or two hours, as estimated by simultaneous calorimetric measurement. Figure 2 shows the results of calorimetric measurement carried out simultaneously with gas titration. Each q-V (or q-θ) curve for the sample poisoned with indicator is similar in shape to that of the original sample. They are lower than the curve of the original sample by several kJ/mol in the low coverage range, coinciding with it in the higher coverage. The V values (adsorbed amount of am-

Table 3. Acid amount determined by ammonia gas titration by use of Hammett indicator and the corresponding q value

pK_a	≦−5.6	≦−3.0	≦+1.5	≦+3.3
V (mmol/g)	0.52	0.71	0.83	1.23
q (kJ/mol)	76.1	65.6	61.8	55.1

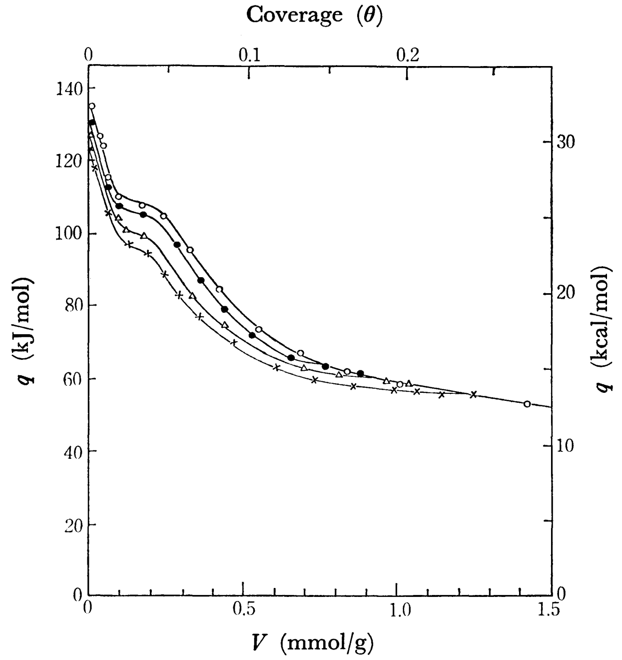

Fig. 2. Effect of poisoning with indicator on the differential heat of adsorption of ammonia. (pretreatment temperature; 400 °C)
○: Original sample, ●: poisoned with dicinnamylideneacetone (pK_a=−3.0), △: poisoned with p-anilinoazobenzene (pK_a=+1.5), ×: poisoned with p-dimethylaminoazobenzene (pK_a=+3.3).

monia) at points where two curves coincide are in good agreement with those given in Tables 2 and 3 for all indicators. Smaller q values of the sample poisoned with the indicator, in the low coverage, can be ascribed to the desorption of the indicator. If we assume that the mechanism of ammonia titration consists of the desorption of indicator and the subsequent adsorption of ammonia, the observed heat of adsorption can be expressed by the following equation:

$$Q = nq_{(\mathrm{ads})} + mq_{(\mathrm{des})}, \qquad (2)$$

where Q(kJ) is the observed heat, $q_{(\mathrm{ads})}$(kJ/mol) the heat of adsorption of ammonia, $q_{(\mathrm{des})}$(kJ/mol) the heat of desorption of indicator (negative value), n(mol) the adsorbed amount of ammonia, and m(mol) the desorbed amount of indicator. The q value in Fig. 2 derived from Eq. 2 is given by

$$q = Q/n = q_{(\mathrm{ads})} + (m/n)q_{(\mathrm{des})}. \qquad (3)$$

The factor m/n represents the number of indicator molecules replaced by one ammonia molecule. Decrease in the q value, accompanied by poisoning with indicator, reflects the term $(m/n)\times q_{(\mathrm{des})}$ in Eq. 3.

In order to determine $q_{(\mathrm{des})}$, the heat of adsorption of indicator from indicator–cyclohexane solution was measured by a twin conduction type calorimeter. The adsorbed amount of indicator was determined spectroscopically before and after measurement. The adsorbed amounts of indicators, the heats of adsorption of indicators and the corresponding adsorbed amount of ammonia are given in Table 4. For p-dimethylaminoazobenzene, the ratio of the ammonia molecules adsorbed to the desorbed molecules of indicator, m/n in Eq. 3, is 0.21 on the assumption that the adsorbed amount of indicator is equal to its desorbed amount. Since the integral heat of adsorption of indicator is presumably equal to the integral heat of desorption, $(m/n)\times q_{(\mathrm{des})}$ in Eq. 3 can be equated to −19.0 kJ/mol for p-dimethylaminoazobenzene and −15.7 kJ/mol for p-anilinoazobenzene. A decrease in the q value induced by poisoning with indicator is sufficiently explained in terms of these values.

TABLE 4. THE HEAT OF ADSORPTION OF INDICATOR FROM INDICATOR–CYCLOHEXANE SOLUTION (1), THE ADSORBED AMOUNT OF INDICATOR (2), AND THE CORRESPONDING ADSORBED AMOUNT OF AMMONIA (3)

Indicator	$\mathrm{p}K_a = +1.5$	$\mathrm{p}K_a = +3.3$
(1) (kJ/mol)	75.2	90.3
(2) (mmol/g)	0.17	0.26
(3) (mmol/g)	0.83	1.24

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