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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 14(1), 93-100
Issue Date	1966-04
Doc URL	http://hdl.handle.net/2115/24809
Type	bulletin (article)
File Information	14(1)_P93-100.pdf

MEASUREMENT OF ACIDITY AND BASICITY
OF SILICA-ALUMINA AND ACIDITY OF ZINC SULFIDE
BY CALORIMETRIC TITRATION

By

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(Received Feburary 9, 1966)

Abstract

Surtace acidities of silica-alumina and zinc sulfide and the basicity of silica-alumina were measured by a calorimetric titration, using n-butylamine or trichloroacetic acid as a titrating base or acid respectively. It was found that silica-alumina showed acidity of ca. 0.8 mmol/g and basicity of ca. 0.6 mmol/g. Zinc sulfide showed ca. 1.3 mmol/g acidity. The observed acidities of both silica-alumina and zinc sulfide were found greater than those measured by an indicator method, suggesting the existence of weak acid sites which could not be measured by the latter method. Heat of the reaction of silica-alumina with n-butylamine was obtained as 13.8 ± 0.4 kcal/mol.

Introduction

We have previously measured the surface acidity and basicity of many solids such as metal oxides, sulfates, sulfides etc. by titrating with n-butylamine or benzoic acid, using acid-base indicators[1]. In the present work, calorimetric titration method was employed for the determination of both acidity and basicity of solids and the observed values were compared with those measured by the method using indicators. The calorimetric determination of surface acidity was first conducted by TRAMBOUZE et al.[2] and developed recently by TOPCHIEVA et al.[3] In their works, ethylacetate and dioxane which react with Lewis acid alone were used as titrating bases, while we employed n-butylamine to measure the sum of Brönsted and Lewis acidity. Trichloroacetic acid was aslo employed in order to measure the basicity of silica-alumina which could not be measured by the indicator method as we have reported previously[1].

Experimental

Materials and Reagents

Silica-alumina was prepared by precipitation from sodium silicate solution

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and aluminum nitrate solution followed by heating the precipitate in air at 500°C[4]. The acidity was found to be 0.55 mmol/g by means of the indicator method with methyl red ($pKa = +4.8$) or dimethyl yellow ($pKa = +3.3$) and n-butylamine as a titrating reagent. Zine sulfide was a guaranteed reagent of Kanto Chemical Co. Its acidity by the indicator method was the same as that reported in our previous paper[1].

Benzene, trichloroacetic acid (both guaranteed reagents of Kanto Chemical Co.) and n-butylamine (guaranteed reagent of Tokyo Chemical Industry) were used without further purification. The concentration of trichloroacetic acid in benzene was determined by titrating with n-butylamine, using bromthymol blue as an indicator.

Measurement of Acidity and Basicity

100 ml of benzene and 3~5 g of solid materials were put into a 500 ml Dewar vessel equipped with a Beckmann thermometer, a glass stirrer and a microburette. For thermal insulation, the vessel was covered with a thick cork. The contents of the vessel were stirred and the slight rise in temperature due to the mechanical heat generation was read every two minutes as shown by crosses (line M) in Fig. 1. Then 0.5 ml or 1 ml of n-butylamine was added
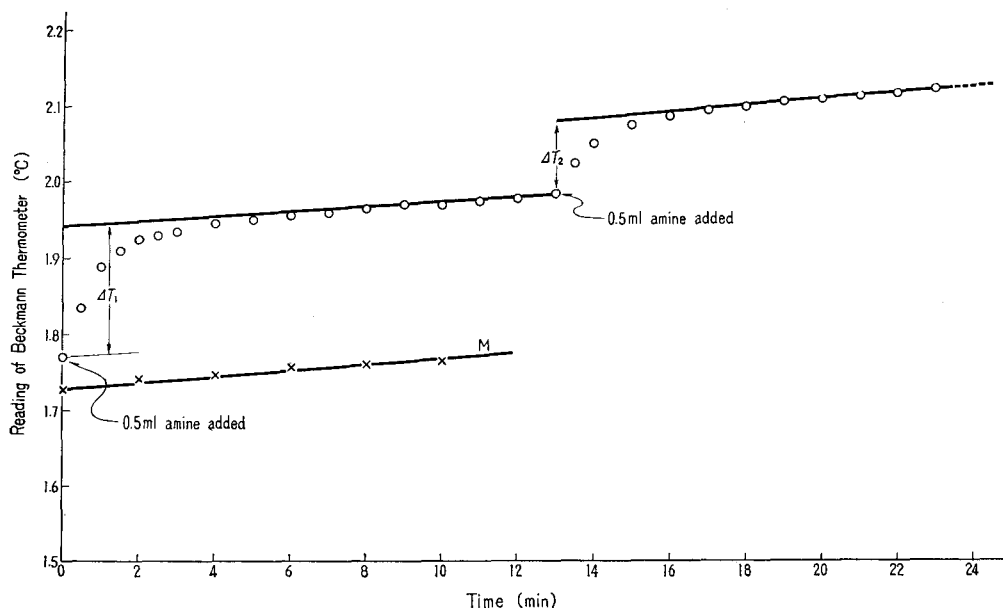

Fig. 1. Temperature rise due to the heat of reaction of silica-alumina (3.9 g) with 1.01 N n-butylamine (0.5 mℓ). Line M shows temperature rise where no amine is added.

from a microburette and the temperature rise due to the heat of the acid-base reaction was read every 30 or 60 seconds as shown by circles in Fig. 1. After the rate of temperature increase reduced to the constant value due to stirring, as indicated by a temperature-time relation parallel with line M, another 0.5 or 1 ml amine was added and the temperature rise was recorded similarly. This procedure was repeated until no further temperature increase due to the reaction could be brought about by further addition of amine. The temperature increase due to the heat of acid-base reaction is given by the differences ΔTi of parallel lines before and after each addition of amine.

The integrated increase in temperature, $\Delta Tn = \sum \Delta Ti$, was plotted against the titre volume of amine as shown in Figs. 3 and 4. At the end point of the titration, the curves become flat, indicating $\Delta Tn = \Delta Tn + 1$, The acidity is obtained from the total amount of amine which can be read at the end point.

The basicity was measured similarly by using trichloroacetic acid instead of n-butylamine as a titrating reagent. Since the heat of dissolution of trichloroacetic acid is not negligible (see a dotted line*) of Fig. 5), rather large correction for this effect and the mechanical one had to be made to obtain the plots of Fig. 6.

The Heat of Reaction of Silica-alumina with Amine

The heat of the reaction $(-\Delta H)$ was calculated from Eq. (1) using total temperature increase, ΔTt, sample weight W, acidity A and heat capacity Q.
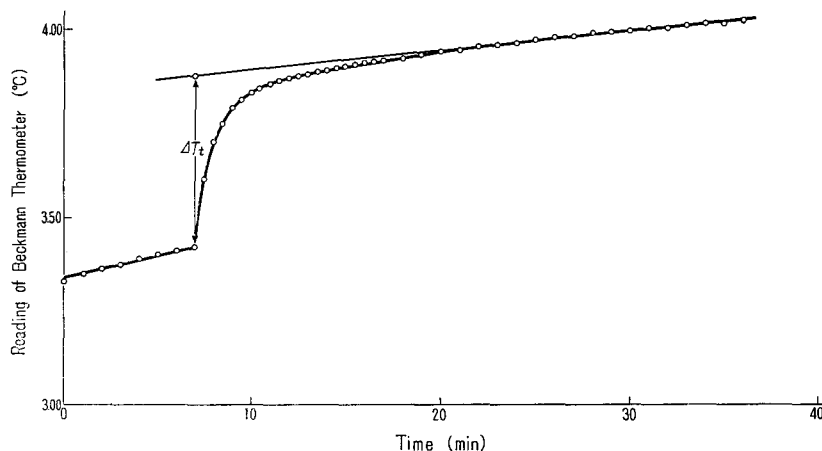

Fig. 2. Temperature rise due to the heat of reaction of silica-alumina (3.45 g) with 1.00 N n-butylamine (5 mℓ).

*) which also contains a small temperature increase due to mechanical heat.

$$-\Delta H = \frac{Q \times \Delta Tt}{A \times W}\,(\text{kcal/mol}) \tag{1}$$

ΔTt was obtained by reading the temperature increase brought about by the addition of excess amine for neutralizing solid acid as shown in Fig. 2. The heat capacity in the same system was calculated to be 49 $\pm$ 1 cal/deg using the equation.

$$Q = \frac{I \times V \times t}{4.18 \times \Delta Tq}\,, \tag{2}$$

where the value of the temperature increase ΔTq was 0.928°C when an electric power $(V=3.0V, I=190\,mA)$ was supplied for 5 min. to NICHROM wire as heater.

The heat of reaction of silica-alumina with n-butylamine was thus found to be 13.8 $\pm$ 0.4 kcal/mol.

Results and Discussion

Acidities of Silica-alumina and Zinc Sulfide

Amine titration curves for silica-alumina and zinc sulfide are shown in Figs. 3 and 4. The titres of 1.01 N n-bytylamine required for neutralizing 3.9 g of silica-alumina and 3.76 g of zinc sulfide are 3 and 5 ml, respectively. Thus, the acidity is calculated to be 0.78 mmol/g for silica-alumina and 1.3 mmol/g
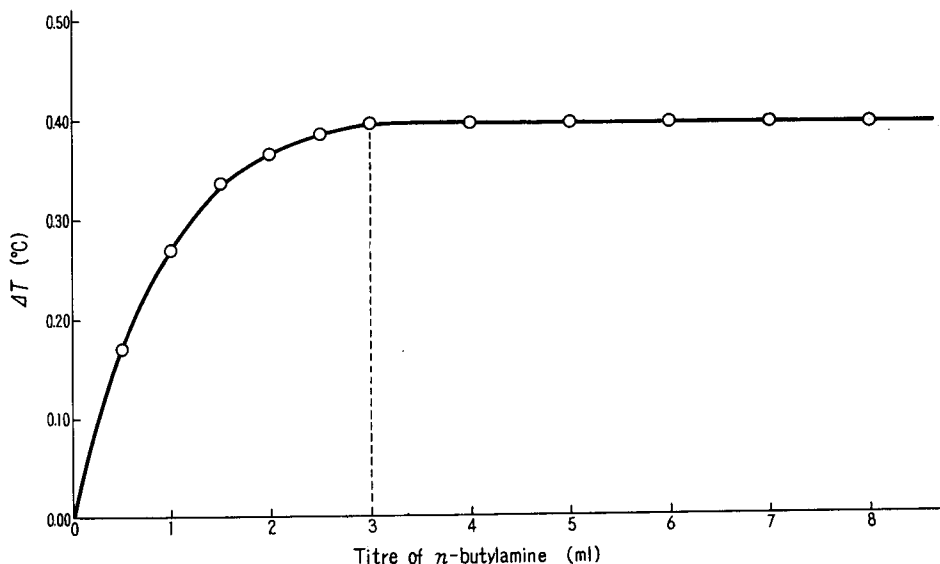
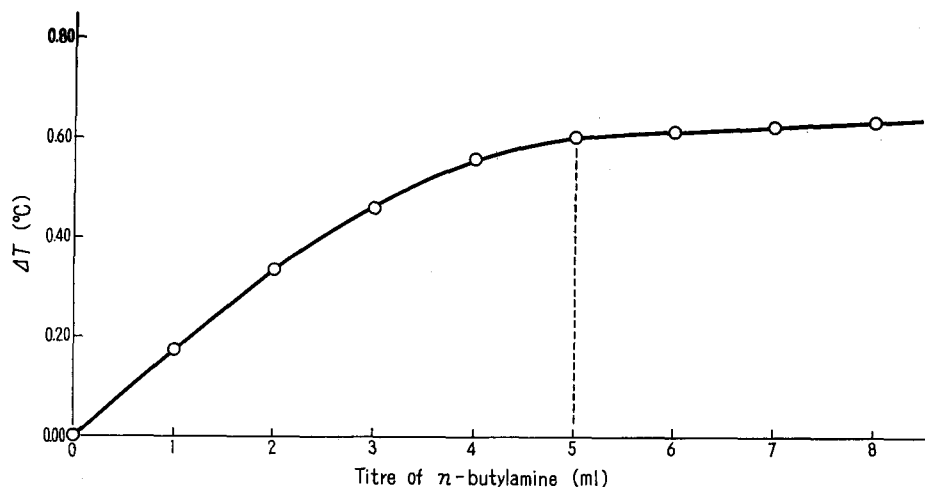**Fig. 3.** Titration curve. $SiO_2 \cdot Al_2O_3$; 3.9 g, n-butylamine; 1.01 N

Fig. 4. Titration curve. ZnS; 3.76 g, n-butylamine; 1.01 N.

for zinc sulfide. These values are higher than those measured by the indicator method, as illustrated in Table 1. This indicates that the acid sites exist whose acid strength is less than $pKa = +4.8$ for silica-alumina and $pKa = +6.8$ for

TABLE 1. Acidity of $SiO_2 \cdot Al_2O_3$ and ZnS.

Solid Acids	Calorimetric Titration Method mmol/g	Indicator Method (mmol/g)			
		NR*⁾	MR*⁾	PNA*⁾	DY*⁾
$SiO_2 \cdot Al_2O_3$	0.78	—	0.55	0.55	----
ZnS	1.3	0.773**⁾	0.36**⁾	0.092**⁾	0**⁾

*) NR; neutral red ($pKa = +6.8$), MR; methyl red ($pKa = +4.8$), PNA; phenylazo-α-naphthylamine ($pKa = +4.0$), dimethyl yellow ($pKa = +3.3$).

**) See ref. 1.

zinc sulfide and that they can be measured by the calorimetric titration method, using a comparatively strong base, n-butylamine.

It is also seen in Figs. 3 and 4 that the rate of temperature rise becomes gradually smaller as the total amount of amine titre is increased. This seems to indicate that there exists an energetic heterogeneity of acid sites, as pointed out by TOPCHIEVA *et al.*[3] The slow reaction of amine with acid sites having smaller acid strength and the slower diffusion of amine molecule into micro-pores of solid catalysts may result in the slower rate of temperature rise.
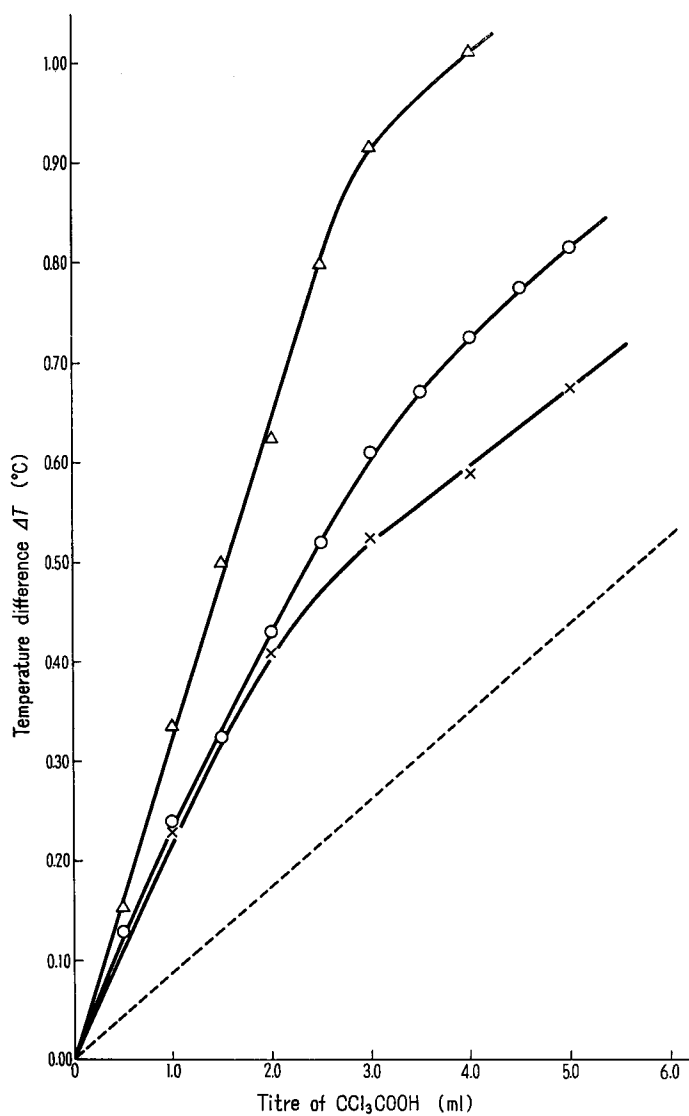
Kozo TANABE and Tsutomu YAMAGUCHI

Fig. 5. Titration curves. $SiO_2 \cdot Al_2O_3$: △; 4.08 g, ○; 4.15 g, ×; 4.22 g. Trichloroacetie acid; 0.810 N. Dotted line shows temperature rise due to the heat of dissolution plus mechanical heat.

Basicity of Silica-alumina

Titration curves for basicity measurement of silica-alumina are given in Fig. 6. Taking 3 ml as the amount of trichloroacetic acid required for neutralizing basic sites of silica-alumina, the basicity is calculated to be 0.58~0.60 mmol/g.[*] Since trichloroacetic acid is a fairly strong acid, comparatively weak basic sites must be also included in the observed basicity. Nevertheless,
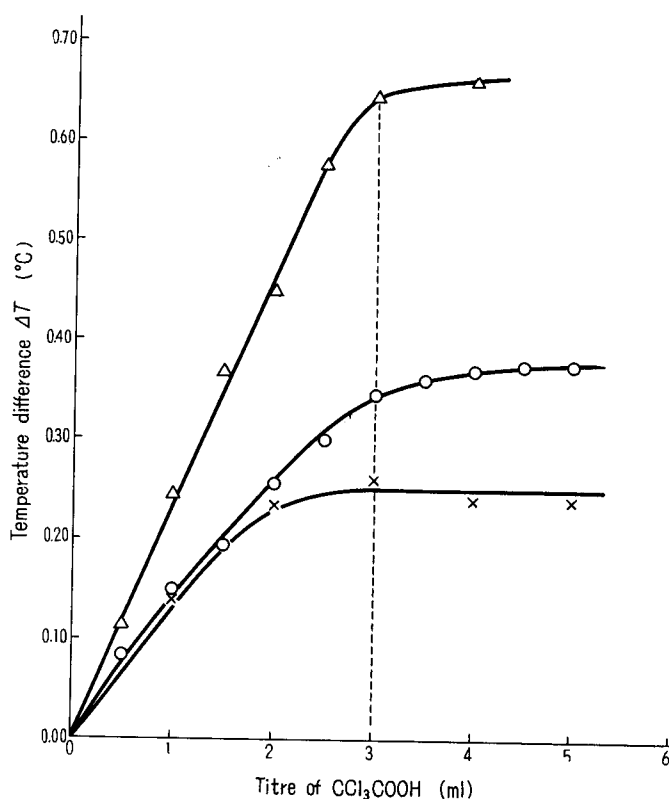

Fig. 6. Corrected titration curve for basicity determination.
$SiO_2 \cdot Al_2O_3$: △; 4.08 g, ○; 4.15 g, ×; 4.22 g.
$CHCl_3COOH$; 0.810 N.

the fact that basic sites as well as acid sites do exist on slica-alumina is of great importance in a view-point of acid-base bifunctional catalysis. It was already reported by BROUWER[5] that double-bond isomerization of olefins on

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[*] An attempt to measure basicity by titrating with benzoic acid using bromthymol blue as an indicator failed in the case of silica-alumina, since the adsorbed indicator did not show its basic color (see ref. 1).

Kozo TANABE and Tsutomu YAMAGUCHI

solid acids such as silica-alumina largely occurs by way of a concerted reaction, under the assumption of a bifunctional nature of acid and base. Recently, PINES[6] also proposed a concerted mechanism for the dehydration of alcohol catalyzed by alumina and SCHWAB[7] gave evidence for the existence of basic points on the catalyst, although a question remains as to his method of boron fluoride adsorption.[8]

Acknowledgment

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