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Direct Measurement of the Interaction Energy between Solids and Gases. VI. Calorimetric Studies on Acidic Properties of Solid Super Acids Prepared from Silica–Alumina

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Solid super acids were prepared by the reaction of gaseous antimony pentafluoride with silica–alumina and heats of adsorption of ammonia on their surfaces were measured. Solid super acids gave about 170 kJ/mol of an initial differential heat of adsorption and their adsorption energies were mainly distributed in the vicinity of 137 kJ/mol, while the initial differential heat of adsorption on original silica–alumina was about 150 kJ/mol and its adsorption energy was chiefly distributed in the vicinity of 117 kJ/mol. Therefore, it was shown that solid super acid had stronger, more homogeneous and much more acid sites than original silica–alumina.

An acid of which the strength is higher than that of 100 wt% H_2SO_4 ($H_0 = -10.6$) is called "super acid," which seems to play an important role in catalyst chemistry.[1–3] The representative liquid super acids are $SbF_5 \cdot FSO_3H$ and $SbF_5 \cdot HF$, whose acid strengths were measured to be $H_0 < -18$ and $H_0 = -15.1$ respectively,[1–3] and others were also investigated by Gillespie *et al.*[4,5] Since liquid super acids are very difficult to deal with as catalysts in the practical reaction system, the synthesis of solid super acids has been required because of easy separation of products from a reaction system and of other advantages. Tanabe and Hattori[6,9] succeeded in the synthesis of several solid super acids such as SbF_5–TiO_2–SiO_2 and SbF_5–SiO_2–Al_2O_3 whose acid strengths are $-13.16 \geqq H_0 > -13.75$ and $-13.75 \geqq H_0 > -14.52$ respectively and which are catalytically active for the reaction of butane and isobutane at room temperature.

In this study, solid super acids (SbSA(I)—(V)) were prepared by the reaction of gaseous antimony pentafluoride with silica–alumina and heats of adsorption of ammonia on their surfaces were measured so as to clarify their surface acidic properties.

Experimental

Silica–alumina cracking catalyst (alumina 13 wt%, SA-13) supplied by Catalysts and Chemicals Ind. Co., Ltd., was evacuated at 500 °C under 10^{-3} Pa for 5 h before treatment with antimony pentafluoride. Antimony pentafluoride (SbF_5) supplied by PCR Research Chem., Inc. was used after distillation.

Solid super acids were prepared by contacting pretreated SA-13 with vapor of SbF_5 in a reaction tube made of pyrex glass for 10 minutes at room temperature, subsequently evacuating for about 20 minutes at 50 °C and repeating the above procedure twice (SbSA(I)), four times (SbSA(II)), eight times (SbSA(III)), thirteen times (SbSA(IV)) or twenty times (SbSA(V)). All of the samples were stored in the desiccator before use.

Gas adsorption calorimetries and infrared measurements were carried out as described in previous papers.[7,8] The content of antimony was determined as follows. A solid super acid was immersed into 1 mol dm^{-3} hydrochloric acid in order to extract completely surface antimony; extracted antimony was analysed by atomic absorption method.

Results

Antimony contents of each sample shown in Table 1 increased with an increase in the number of the treatment. Figure 1 shows differential heat of adsorption of ammonia on SbSA samples, which are extremely higher than that on orginal silica–alumina. Moreover, adsorbed amount of ammonia in the region of high differential heats of adsorption was much greater than that for SA-13. These results indicate the appearance of higher strong acid sites on silica–alumina surface by the treatment with SbF_5 vapor. The initial heat of readsorption of ammonia on SA-13 which was NH_3-preadsorbed and evacuated overnight at 25 °C was about 75 kJ/mol and equal to that on each of SbSA samples which were similarly pretreated. The adsorbed amount of ammonia increased linearly with an increase in antimony content as shown in Fig. 2, where A shows the adsorbed amount above

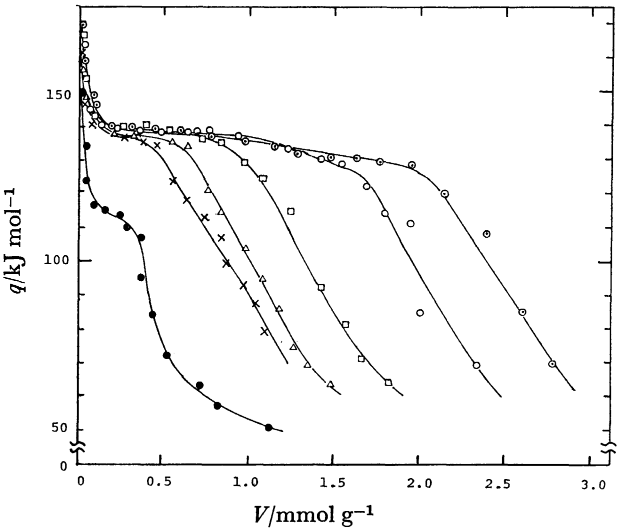

Fig. 1. Differential heats of adsorption of ammonia on solid super acids evacuated at 25 °C and SA-13 evacuated at 500 °C.
×: SbSA(I), △: SbSA(II), □: SbSA(III), ○: SbSA(IV), ⊙: SbSA(V), ●: SA-13.

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TABLE 1. ANTIMONY CONTENT OF SOLID SUPER ACID

Sample	SbSA(I)	SbSA(II)	SbSA(III)	SbSA(IV)	SbSA(V)
Number of the treatment run	2	4	8	13	20
$\frac{\text{Sb Content}}{\text{mmol g}^{-1}}$	0.69	0.94	1.31	1.72	2.22

75 kJ/mol, B that above 130 kJ/mol and C that between 75 and 130 kJ/mol. Therefore, antimony atoms may be involved in the generation of acid sites on SbSA.

In Fig. 3, ammonia gas adsorption energy distributions on SbSA samples are shown. Fairly sharp maxima were observed for each of SbSA samples at the same heat of adsorption, 137 kJ/mol, and the number of acid sites at this region increased with antimony content. This suggests that the acid sites generated by the treatment with SbF_5 may be homogeneously distributed.

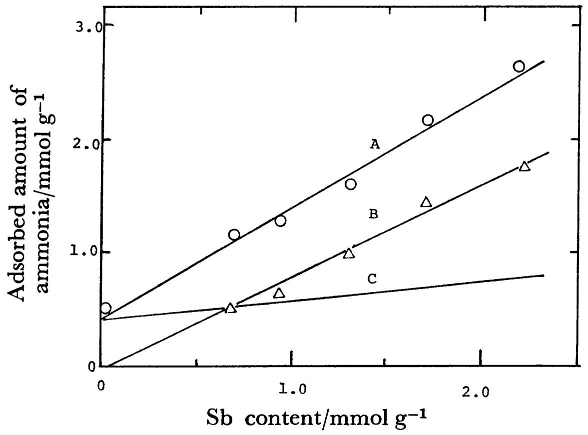


Fig. 2. Relation between Sb content and adsorbed amount of ammonia.
A: Adsorbed amount of ammonia above 75 kJ/mol, B: adsorbed amount of ammonia above 130 kJ/mol, C: adsorbed amount of ammonia between 75 and 130 kJ/mol.

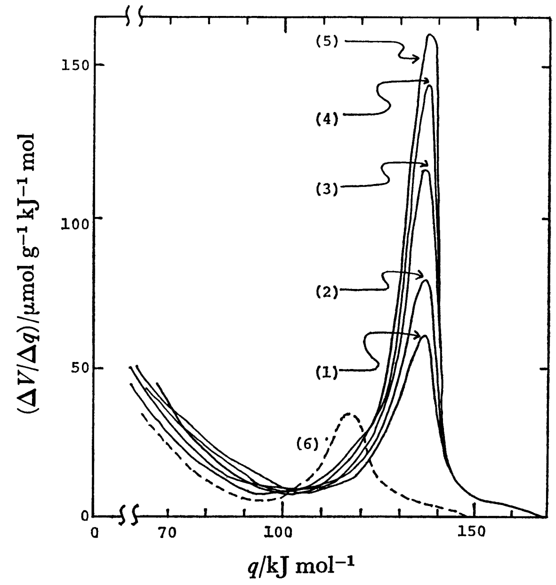
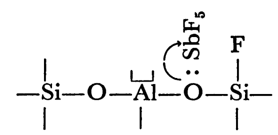


Fig. 3. Ammonia gas adsorption energy distributions for solid super acdis and SA-13.
(1): SbSA(I), (2): SbSA(II), (3): SbSA(III), (4): SbSA(IV), (5): SbSA(V), (6): SA-13.

Discussion

Tanabe *et al.*[9] proposed the following surface model of solid super acid (SbF_5–SiO_2–Al_2O_3).



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{\sqcup}{\underset{|}{\mathrm{Al}}}-\overset{\mathrm{SbF_5}}{\overset{:}{\mathrm{O}}}-\overset{\mathrm{F}}{\underset{|}{\mathrm{Si}}}-$$

The acid strength of Lewis sites on surface aluminum ions becomes higher by an inductive effect of SbF_5 coordinated on neighboring oxygen ion. Lewis acid amount of SA-13 dehydrated at 500 °C *in vacuo* was determined to be about 180 μmol/g (from adsorbed amount of ammonia) based on the assumption described in previous paper[8] that only Lewis acid sites are present above 115 kJ/mol of differential heat of adsorption of ammonia in the case of silica–alumina (SA-13). If the surface model of SbSA is explained only by Tanabe's proposal, the adsorbed amount of ammonia above 130 kJ/mol should be about 180 μmol/g. The observed value shown in Fig. 2 implies that an another model of the acid generation would also be possible.

Infrared spectra of pyridine adsorbed on some solid super acids are shown in Fig. 4. The measurements were carried out at 25 °C after contacting SbSA samples evacuated at 50 °C with pyridine vapor for 10 min

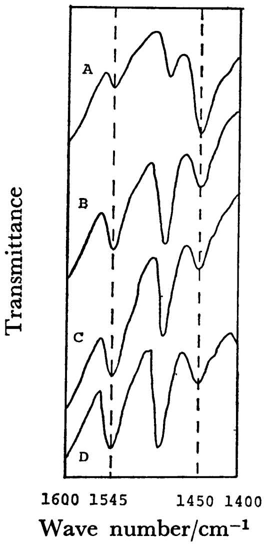


Fig. 4. Infrared spectra of adsorbed pyridine on solid super acids and SA-13.
A: SA-13, B: SbSA(II), C: SbSA(III), D: SbSA(IV).

Table 2. Ratio of the number of Brönsted acid sites to that of Lewis ones

Sample	SA-13	SbSA(II)	SbSA(III)	SbSA(IV)
B-site / L-site	4	9	11	16

and subsequent evacuation at 100 °C. All SbSA samples gave absorption peaks both at 1545 cm^{-1} and 1450 cm^{-1}, which indicates the presence of Brönsted and Lewis acid sites. The ratio of the number of Brönsted acid sites to that of Lewis ones was determined by their absorption intensity on the basis of the assumption that the ratio of the absorption coefficient of the 1450 cm^{-1} band to that of the 1545 cm^{-1} band, $\varepsilon_{1450}/\varepsilon_{1545}$, is 8.8,[10] and is shown in Table 2. The results show that the fraction of Brönsted sites on SbSA sample was greater than that on SA-13 and increased with antimony content. Hydrogen atoms are mostly present as surface hydroxyl groups on the original silica–alumina and may be involved in the generation of Brönsted acid sites by the interaction with SbF_5 molecules. The amount of residual hydroxyl groups of SA-13 after evacuation at 500 °C was gravimetrically determined to be 1.4 mmol/g by successive ignition loss *in vacuo* from 500 °C to 1200 °C by use of a Cahn electromagnetic microbalance. The transformation of surface hydroxyl groups into acid sites would be enhanced by an increase in the number of the treatment times with SbF_5 vapor, which was suggested by the finding that the site distribution at 137 kJ/mol became large with the treatment times. The maximum at 117 kJ/mol for original SA-13 disappeared by the treatment with SbF_5, accompanied by an appearance of the maximum at 137 kJ/mol. This suggests that the nature of inherent acid sites on SA-13 changed with the treatment with SbF_5.

The highest acid strength of SbF_5–SiO_2–Al_2O_3 prepared by Tanabe *et al.* was reported to be $-13.75 \geqq H_0 > -14.52$[6,9], while SbSA samples in this study gave about 170 kJ/mol of an initial differential heat of adsorption and their adsorption energies were mainly distributed in the vicinity of 137 kJ/mol. The differential heat value, $q = 137$ kJ/mol, seems to correspond to the acid strength, $H_0 \fallingdotseq -14$, on the basis of the relation between q and pK_a value described in a previous paper,[11] which is similar to the value measured by Tanabe *et al.* The finding that SbF_5–SiO_2–Al_2O_3 exhibited high activity for the reaction of butane at 20 °C[6,9] might be attributed to the presence of a great number of acid sites with high differential heat of adsorption of ammonia above 130 kJ/mol.

It was concluded that solid super acid (SbSA samples) had stronger, more homogeneous and much more acid sites than original SA-13 and that most of acid sites on the former are Brönsted sites.

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