Adsorption of Trimethylamine, Ammonia and Pyrrole on Amorphous Silica-alumina

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It is evident from many studies[1] that the catalytic property of silica-alumina closely depends upon the nature of the acidity of its surface; the adsorption of basic gases on the catalyst has therefore been carried out to clarify the nature of the acidity from the standpoint of surface structure. The basicity of the gaseous molecule depends upon the electronegativity of the nitrogen atom of the molecule, such as trimethylamine and ammonia; the nitrogen atom of trimethylamine is regarded as being more basic than that of ammonia, since the electron cloud of three carbon atoms of the molecule concentrates more densely around the nitrogen atom than around the hydrogen atoms of ammonia. Pyrrole is considered to be neutral, because the π electrons of the nitrogen of the compound are incorporated into the sextet and so cannot coordinate with an acid without disrupting the "aromatic sextet." Richardson and Benson[2] investigated the adsorption of trimethylamine on silica-alumina by means of a spring balance included in an adiabatic calorimeter. They presented the correlations of the acidity and the catalytic activity with the heat of the adsorption of trimethylamine. Their results, however, were ambiguous in establishing the correlation of the heat of adsorption with the coverage, a correlation which is important in determining the amount of acid point. Clark et al.[3] have obtained the heats of the adsorption of ammonia on various silica-alumina from the adsorption isotherms. It is impossible, however, to compare these results because of the differences in the preparation of these samples. The present paper will report the results of the study of the surface nature of silica-alumina by means of the adsorption of gases of different basicities, i. e., trimethylamine, ammonia and pyrrole on silica, alumina and silica-alumina.

Experimental

The amorphous silica which was used for the column packing of the gas chromatography was furnished by the Kotaki Co. and was 120-mesh. Silica-alumina containing 2% alumina (SA-2) was

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[1] A. G. Obald, T. H. Milliken, Jr., and G. A. Mills, "Advances in Catalysis," Vol. 3, Academic Press, New York (1951), p. 199.

[2] R. L. Richardson and S. W. Benson, *J. Phys. Chem.*, **61**, 405 (1959).

[3] A. Clark, V. C. F. Holm and D. M. Blackburn, *J. Catalysis*, **1**, 244 (1962).

prepared in the usual way by co-precipitation from solutions of sodium silicate and sodium aluminate.

Silica-alumina containing 13% alumina (SA-13) was furnished by the Davison Chemical Co. Silica-alumina containing 26% alumina (SA-26) was furnished by the Nikki Chemical Co. It was in tablet form. Trimethylamine and pyrrole were carefully purified by means of a vacuum distillation. Ammonia was distilled by pumping it after freezing.

The apparatus used for testing trimethylamine and ammonia was the same as that described elsewhere.4) The volume of the reaction vessel, including the McLeod gauge, was about 350 cc. An adsorption spring balance made of quartz was used for testing the pyrrole. The reaction vessel of this experiment was a modification of that used by Richardson an Benson.2) The diameter of the reaction vessel and its length were 30 mm. and 550 mm. respectively. Helix elongation was measured by a cathetometer, giving measurements within 0.05 mm., while the sensibility Y (mm.) of helix was expressed as $Y=0.220X+0.004$, where X denotes the gravity (mg.) of the sample. Prior to the adsorption measurement, the sample was degassed at a constant temperature of 200 and 500°C for about 20 hr. to remove physically adsorbed water or constitutional water from the sample. After the pressure had attained the order of 10^{-6} mmHg, the temperature was lowered to the reaction temperature. In the cases of trimethylamine and ammonia, the gas was admitted and the decrease in pressure was followed by the McLeod gauge until the equilibrium pressure was obtained. The temperature of the reaction vessel was raised or lowered at 20-degree intervals in the range from 100 to 140°C. In the case of pyrrole, the amount of gas still remaining on the surface after the evacuation was measured using the spring balance. That is, a certain amount of pyrrole was admitted into the reaction vessel and the mixture was kept for about one hour; then the vessel was evacuated under a constant temperature until the helix elongation indicated a constant value. The sample was changed anew for every series of adsorption studies on the sample evacuated at a certain temperature.

The BET areas were measured by means of nitrogen adsorption at −196°C. The loss of the water included in each such sample was measured by the spring balance. The titration of the acidity of silica-alumina was made in anhydrous benzene, using *p*-dimethylaminoazobenzene as an indicator in the same way as has been described by Tamele.5)

Results

The adsorption isotherms of trimethylamine on silica and alumina evacuated at 200 and 500°C are shown in Fig. 1. The adsorption on silica was reversible in all the regions investigated, and the Langmuir equation could be approximately adapted to the isotherms; however, it could not be adapted for the isotherms on alumina, though the adsorption occurred reversibly. Figures 2—6 show the adsorption isotherms of trimethylamine on SA-2, SA-13 and SA-26, and those of ammonia on SA-13 and SA-26, respectively. Every isotherm shows a steep rise in an initial region but then enters a region of slow rise. The dependence of the adsorption amount on the temperature in the region of steep rise was conspicuously small. The velocity of the desorption by the evacuation or by the elevation of the temperature in this region was very slow, as if the adsorption were irreversible. It was determined, however, that the adsorption of this region was reversible, because the amount of adsorption on a virgin sample was practically equal to that of the sample which had been preliminarily covered by a certain

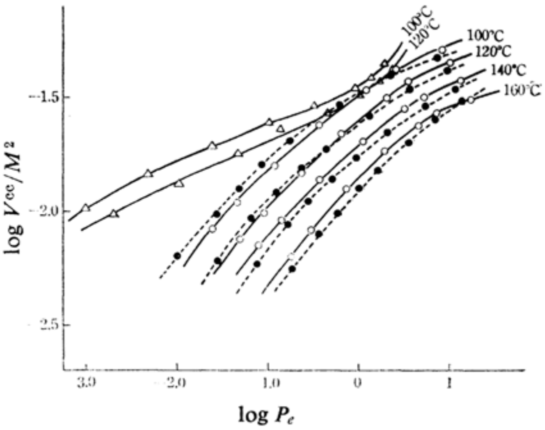

Fig. 1. Adsorption isotherms of trimethylamine on silica and alumina.

-△- Alumina evacuated at 200°C
-○- Silica evacuated at 200°C
--●- Silica evacuated at 500°C

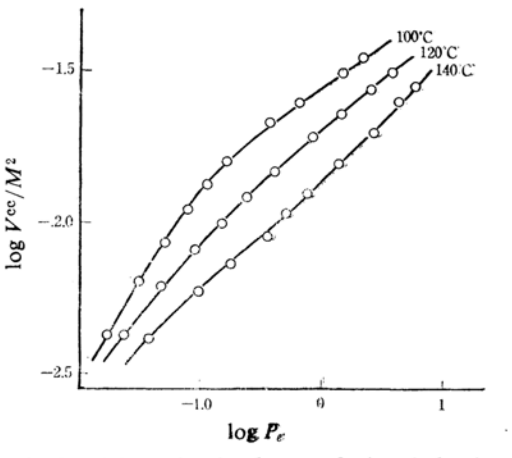

Fig. 2. Adsorption isotherms of trimethylamine on SA-2 evacuated at 200°C.

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4) T. Takeuchi and M. Sakaguchi, This Bulletin, **30**, 182 (1957).

5) M. W. Tamele, *Discussions Faraday Soc.*, **8**, 270 (1950).

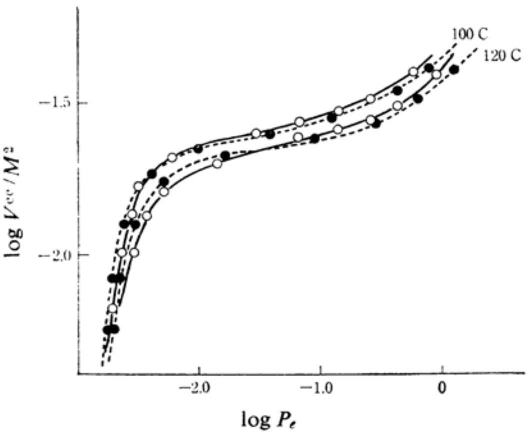

Fig. 3. Adsorption isotherms of trimethylamine on SA-13.
-○- Evacuated at 200°C
--●-- Evacuated at 500°C

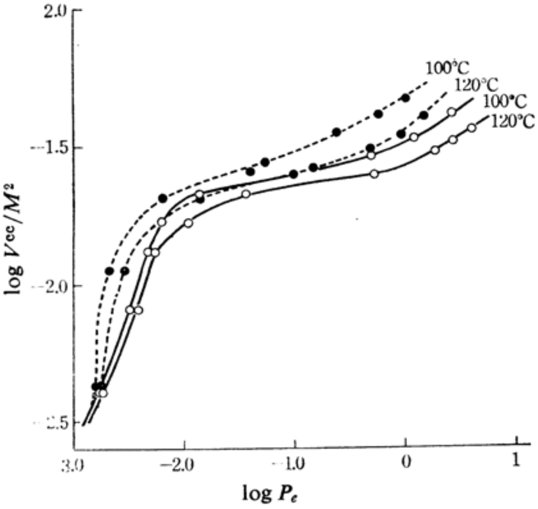

Fig. 4. Adsorption isotherms of trimethylamine on SA-26.
-○- Evacuated at 200°C
--●-- Evacuated at 500°C

amount of gas, if the samples were kept under the same conditions of temperature and equilibrium pressure.

The heats of the adsorption of trimethylamine on silica and alumina obtained from the isotherms by adapting the Clausius-Clapeyron equation are summarized in Fig. 7. The heat of adsorption on silica was not practically affected by the variation in the coverage and the temperature of evacuation. However, that on alumina decreased markedly with an increase in the coverage. The heats of the adsorption of trimethylamine and ammonia on silica-alumina are summarized in Figs. 8 and 9. The heats always increased markedly with an increase in the coverage, but then decreased gradually. The coverages which gave the maximum heat varied with the samples in the order of the alumina concentration. The shift is toward the greater coverage by the elevation of the evacuation temperature. Table I shows the amount of pyrrole remaining on silica-alumina after the evacuation had been made, the amount of acid point measured by the titration,* the amounts

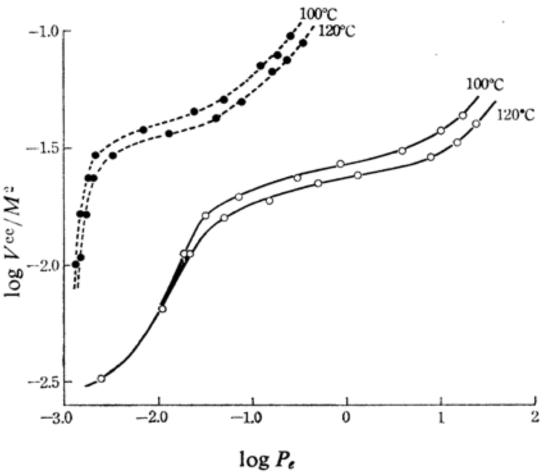

Fig. 5. Adsorption isotherms of ammonia on SA-13.
-○- Evacuated at 200°C
--●-- Evacuated at 500°C

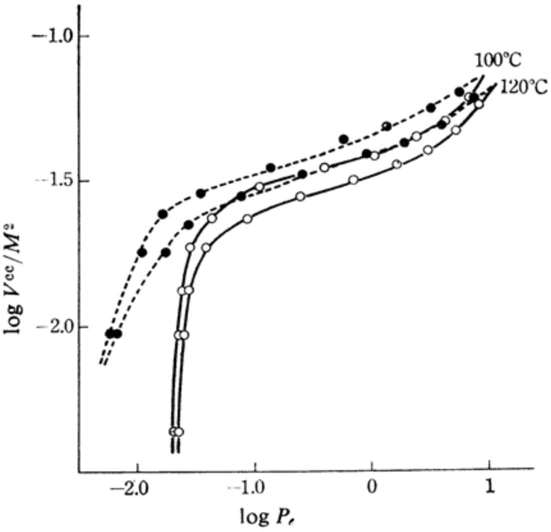

Fig. 6. Adsorption isotherms of ammonia on SA-26.
-○- Evacuated at 200°C
--●-- Evacuated at 500°C

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* The amount of the acid point of SA-26 could not be determined by the titration, because the decolorization of the surface by *n*-butylamine was not uniform.

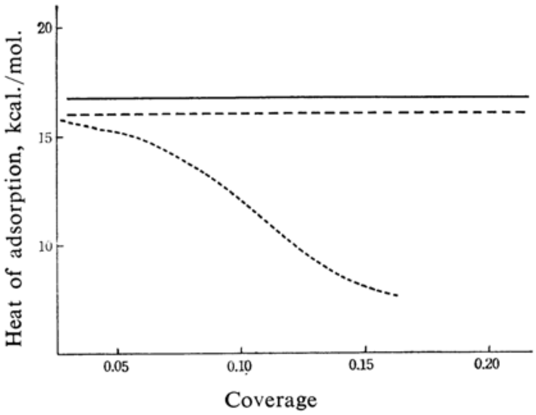

Fig. 7. The heats of adsorption of trimethylamine on silica and alumina.

—— Silica evacuated at 200°C
- - - Silica evacuated at 500°C
...... Alumina evacuated at 200°C

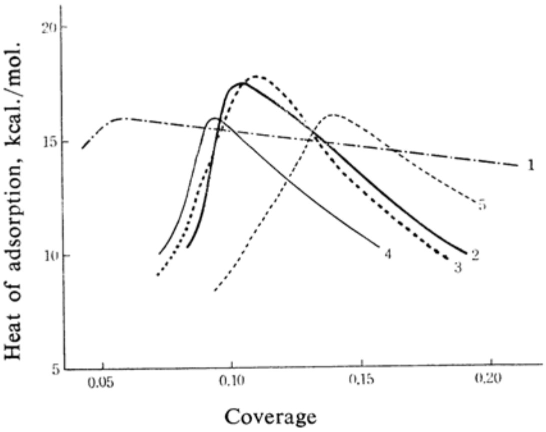

Fig. 8. The heats of adsorption of trimethylamine on silica-alumina.

1: SA-2 evacuated at 200°C
2: SA-13 evacuated at 200°C
3: SA-13 evacuated at 500°C
4: SA-26 evacuated at 200°C
5: SA-26 evacuated at 500°C

TABLE I. AMOUNTS OF THE ACID POINT MEASURED BY THE ADSORPTION OF GAS AND THE TITRATION

% of alumina	2	13		26	
Temp. evacuated, °C	200	200	500	200	500
BET area, m^2/g.	305	405	339	295	262
Amount adsorbed mol. 10^7					
Pyrrole		0.90	1.05		
Trimethylamine	0.63	0.91	1.05	1.10	1.43
Ammonia		1.41	2.14	1.30	1.75
n-Butylamine		0.94	1.15		

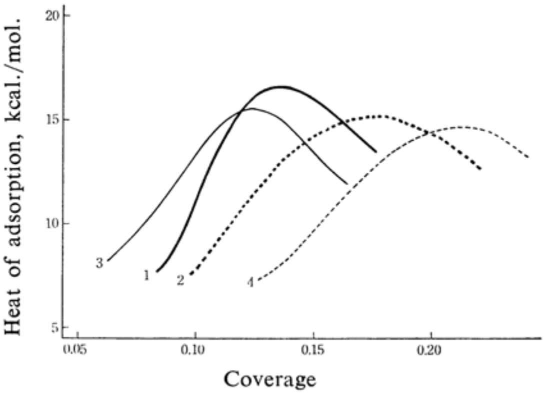

Fig. 9. The heats of adsorption of ammonia on silica-alumina.

1: SA-13 evacuated at 200°C
2: SA-13 evacuated at 500°C
3: SA-26 evacuated at 200°C
4: SA-26 evacuated at 500°C

of trimethylamine and ammonia adsorbed up to the steep rise of every isotherm, and the BET areas of the samples.

Discussion

The heat of adsorption at the region near zero coverage could not be obtained in this study because of the difficulty of accurately reading pressures of less than 10^{-4} mmHg. Richardson and Benson[2] have reported that the initial heats of the adsorption of trimethylamine on two kinds of silica-alumina were about 38 kcal. and 33 kcal. respectively, and that they decreased with an increase in the amount of gas adsorbed. Clark et al.[3] reported that the heat of adsorption of ammonia on silica-alumina of various compositions began at more than 40 kcal. These, and the reports published recently by other authors,[6,7] suggest that the peak of heat on silica-alumina in our study should succeed the decrease after the initial great heat. Therefore, we call the peak the "secondary peak."

Table I indicates that the amount of gas adsorbed at the secondary peak of the heat in each silica-alumina is approximately equal to the amount of acid point measured by the titration. Such coincidence suggests that the secondary peak of the heat is caused by the complete occupation of the basic gas to both Lewis and Brønsted acid points. Beebe[8] and Rhodin[9] had found that the heat of the

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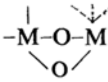
[6] V. Kevorkian and R. O. Steiner, *J. Phys. Chem.*, **67**, 545 (1963).

[7] P. Y. Hsieh, *J. Catalysis*, **2**, 211 (1963).

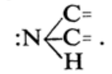
[8] R. A. Beebe and D. M. Young, *J. Phys. Chem.*, **58**, 93 (1954).

[9] T. N. Rhodin, *J. Am. Chem. Soc.*, **72**, 5691 (1950).

physical adsorption of gas is increased by the interaction of gas near the completion of the monolayer. In our results, however, the coverage which gave the secondary peak was far less than unity. Moreover, the distance between aluminum atoms seems too large for mutual interaction due to the van der Waals force if the acid points are assumed to exist uniformly on the surface. Danforth[10] had proposed that silica-alumina is formed by the interconnecting rings of six silica tetrahedra, whose silicon atoms on the outer side are replaced by aluminum atoms keeping the distance of 5 Å. Though such a structure might be suitable for silica-alumina, the silica-alumina of our experiment should be considered to be formed by the mixture of perfect and inperfect structures, comprising the structures of pure silica and alumina. In view of the above situation, it can be proposed that the acid points, both Brønsted and Lewis acid points, exist in clusters, and that such acidic domains will be covered preferentially by basic gas at the initial stage of the adsorption. If these domains are regarded as aggregations of acidic points with different strengths, the adsorption occurs probably in an order of strength indicating a gradual decrease of heat, and the secondary peak of the heat would depend upon the mutual attraction of molecules adsorbing closely to one another.

The coverage of the secondary peak of the heat on ammonia was greater than that of trimethylamine and approached toward unity by the elevation of the evacuation temperature. These facts would reveal that ammonia is adsorbed partly on non-acid points as well as on acid points, before the completion of the monolayer on the acidic domains. Ammonia seems to adsorb more readily than trimethylamine and pyrrole on silica-alumina in virtue of the formation of a hydrogen bridge between its hydrogen atom and the lone pair electron of the oxygen of the adsorbent. Zettlemoyer and Chessick[11] proposed, as had been assumed by Young,[12] that the elevation of the evacuation temperature causes water to be removed from silica-alumina and produces surface sites of the  $-\mathrm{M{-}O{-}M^*}-$, where M and M* indicate silicon and aluminum atoms respectively. The increase of the oxygen on the surface would increase the amount of adsorption due to the hydrogen bridge. If the adsorption of ammonia occurs when the electron is switched to the acid point, the polarization will be accelerated by the shift of the electron of hydrogen atoms toward the nitrogen atom, and the attractive force between ammonia molecules will be strengthened; as a result, the piled-up adsorption of ammonia may be considered to occur. It is considered impossible, in view of their structure, for the hydrogen atoms of trimethylamine and pyrrole to form the hydrogen bridge.

The heat of the adsorption of trimethylamine on pure silica was approximately constant over the wide region of coverage, and it was practically the same as that of the secondary peak in silica-alumina catalysts. This fact reveals that the adsorption of trimethylamine initiated at active points, such as holes, crevices or crystal defects, as had been discussed by de Boer,[13] and spread gradually from these points to form two-dimensional layers by the van der Waals force of the adsorbing molecules. The heat of the adsorption of trimethylamine on SA-2 was approximately constant, except for the initial region of small heat. This might be explained combining the conceptions of the surface nature of silica and silica-alumina which have been proposed above. Most of the surface of SA-2 would be similar to that of silica, and the basic gas would begin the adsorption from the acid point then on the surface of the silica type, behaving in the way which has been proposed above. The correlation between the heat of trimethylamine and the coverage on alumina would reveal that the adsorption is of the chemical type, and suggests that the surface is substantially different from that of silica.

The unexpected characteristics of pyrrole in the adsorption on silica-alumina may be explained as follows. Two out of the six π electrons in the ring of pyrrole are localized toward the nitrogen atom when it adsorbs on the acid point, and they fill one of four sp^3 orbitals forming a lone pair in a pyramidal configuration,  $:\mathrm{N}\begin{cases}\mathrm{C}=\\\mathrm{C}=\\\mathrm{H}\end{cases}$. Consequently, the nitrogen atom of pyrrole can behave like that of trimethylamine or ammonia on the surface.

Summary

The adsorptions of trimethylamine, pyrrole and ammonia on pure silica, alumina and three silica-aluminas with (2%, 13% and 26% of alumina) have been studied. Isosteric heats have been obtained from adsorption isotherms at 100 and 120°C. A conspicuous rise, followed

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[10] J. D. Danforth, "Advances in Catalysis," Vol. 9, Academic Press, New York (1957), p. 558.

[11] A. C. Zettlemoyer and J. J. Chessick, *J. Phys. Chem.*, **64**, 1131 (1960).

[12] G. J. Young, *J. Colloid Sci.*, **13**, 67 (1958).

[13] J. H. de Boer, "Advances in Catalysis," Vol. 8, Academic Press, New York (1956), p. 17.

by a gradual fall, was observed at an early stage of the heat curve obtained from the isotherm on silica-alumina, but not from those on silica and alumina. At the peak of the curve, the amount of the adsorption of trimethylamine agreed with that of pyrrole, both of which, again, agreed with the amount of the acid point as measured by the titration using *n*-butylamine. The amount of ammonia was twice as large as that of the acid point. The acid points of silica-alumina are assumed to exist in clusters on the surface. The rise of heat is due to the mutual interaction of the adsorbed molecules, the peak indicating the completion of the monolayer on such acid domains.

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