BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 51 (2), 633—634 (1978)

Heat of Adsorption of Ammonia on Silica-Alumina at Low Surface Coverage

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(Received August 23, 1977)

Synopsis. Heats of adsorption of ammonia on silica-alumina at very low surface coverage were measured in details. The effects of ammonia adsorption on the glass wall and on the greese were corrected. The initial heat value agreed fairly well with the heat of neutralization of $NH_3(G)$ and $HCl(G)$. The diffusion of the gas had little effect on the value of heat of adsorption.

The integral heat of adsorption ($\Delta Q/\Delta n_S$) can be obtained by the measurement of heat effect (ΔQ) accompanying adsorption of a small dose (Δn_S) of gas. In order to obtain the differential heat of adsorption ($q=\partial Q/\partial n_S$), a calorimeter is required which is capable of measuring small amount of adsorbed gas and heats evoloved as accurately as possible.

In this study, the heat of adsorption of ammonia on silica-alumina was measured, particularly at very low surface coverage and also the influence of the diffusion of the gas on heat effects was examined.

Experimental

Heats of adsorption were determined in a twin conduction type calorimeter (Tokyo Riko Co., Ltd.) fitted with the apparatus which is schematically drawn in Fig. 1. The heat of adsorption was measured at 25 °C. The amount adsorbed was calculated from pressure change before and after adsorption measured by a MKS capacitance manometer (below≈10 Torr) and a mercury manometer (above≈10 Torr).

Silica-alumina (Al_2O_3, 13 wt%) was supplied by Shokubai Kasei Co., Ltd. and used as granules of 28—60 mesh. The surface area of silica-alumina measured by nitrogen adsorption was 557 m^2/g. About 0.5 g of silica-alumina was placed in a sample cell and pretreated at 400 °C under 10^{-5} Torr for 5 h.

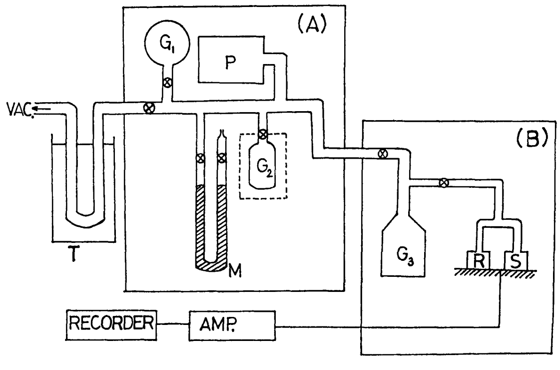

Fig. 1. Schematic diagram of vacuum system [A] and micro calorimeter [B].
T: Liquid nitrogen trap, M: mercury manometer,
P: capacitance manometer, G_1, G_2: gas storage bulb,
G_3: adsorbate reservoir, R: reference cell,
S: sample cell.
Temperatures of [A] and [B] were maintained at 25±0.1 °C and at 25±0.01 °C, respectively.

The twin conduction type calorimeter contained a reference cell constructed as similarly as the sample cell which eliminates the effects of external thermal disturbance and other effects such as the slight temperature difference between admitted gas and the calorimeter or heat of adiabatic compression. In this apparatus, when herium gas was admitted to the evacuated cell up to 2 Torr, no deflection of base line was detected in 50 μV full scale.

Results and Discussion

The adsorption of ammonia at extremely low coverage must be quite important with regard to the surface acidic nature of silica-alumina. However, detailed studies in this field have been lacking. In Fig. 2, the differential heat curve in the coverage lower than 0.007 is shown. The plots of a—d shown by open circles are the results obtained when about 0.41, 0.81, 2.62, and 4.8 μmol/g of ammonia were admitted several times in each case. In these experiments, no residual gas the pressure of which was higher than 10^{-4} Torr was detected. As can be seen from Fig. 2, discontinuous differential heat curves were obtained along with the difference of the amount of admitted gas. These discontinuity probably resulted from the adsorption of ammonia on the glass wall and on the greese system of gas holder G_3 in Fig. 1, which caused errors of the caluculation of amounts of ammonia adsorbed on the sample. Therefore, the effect of ammonia adsorption on the glass wall and on the greese was corrected by a conventional way.[1)] The corrected results of differential heat are shown by closed circles in Fig. 2. The initial heat value was observed to be 41 kcal/mol. This value agrees fairly well to the heat of neutralization of NH_3

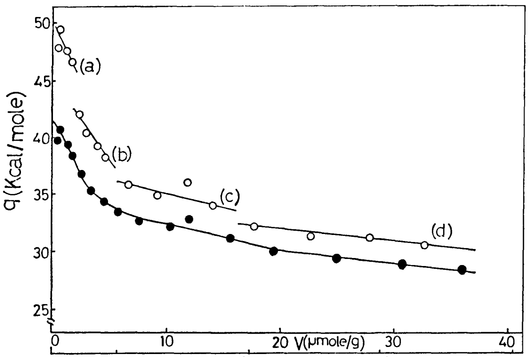

Fig. 2. Heats of adsorption of ammonia on silica-alumina at 25 °C.
○: Observed heat values, ●: corrected values.

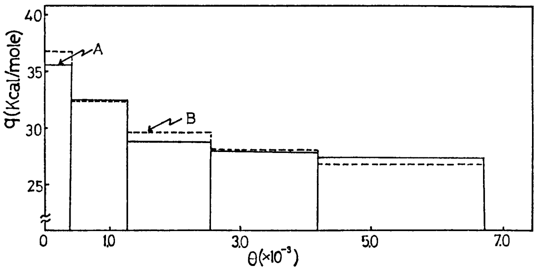

Fig. 3. Heats of adsorption of ammonia on silica–alumina at 25 °C. Stepped curve A, results obtained in case of admission of large doses of ammonia. Stepped curve B, integrated values of differential heats (small doses) in Fig. 2.

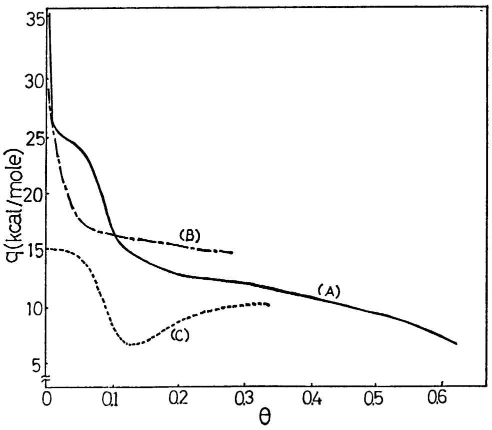

Fig. 4. Heats of adsorption of ammonia on silica–alumina. Curve A, present work (at 25 °C), Curve B, F. S. Stone *et al*, (at 30 °C), Curve C, P. Y. Hsieh (at 0 °C).

(G) and HCl (G). Moreover, differential heat curve decreased progressively and no anomalous behavior was observed.

In Fig. 3, a stepped curve A which shows the heats evolved during adsorptions of larger doses is compared with a stepped curve B which was obtained by integration of the values of differential heats in Fig. 2 (closed circles) in order to examine the influence of diffusion of ammonia in the sample layer. The fact that both curves are well coincident suggests that the diffusion of gas has little effect on the value of heat of adsorption.²⁾ The use of small dose is, therefore, favorable for adsorption studies on heterogeneous adsorbents and make it possible to measure heats of adsorption approaching true differential ones ($\partial Q/\partial n_S$).

The differential heat curve up to 0.6 of θ is shown in Fig. 4 together with the results of Hsieh³⁾ and Stone.⁴⁾ Their results, especially that of Hsieh, are very different from ours. The discrepancy may be ascribed to the difference of sensitivity of calorimeters used and also to the fact that they measured the heat by admission of larger dose of ammonia as well as to the difference of sample preparation methods. Our results indicate that there exist very strong chemisorption sites up to 0.02 of θ and almost homogeneous chemisorption sites between 0.02 and 0.06.

Work is in progress to examine the availability of micro calorimetric measurement in the field of acidic character of solid catalysts and will be published.

This work was partly supported by a Grant-in-Aid for Science Research from the Ministry of Education.

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