

Basic Molecules as Probes for the Study of Mo-Alumina Catalysts

Basic molecules like ammonia and pyridine have been extensively used to poison coordinatively unsaturated sites on the surface of oxides (1). Cowley and Massoth have recently used pyridine as a probe to study the active site concentration in sulfided Mo-alumina for the hydrodesulfurization of benzothiophene (2). The catalytic activity was found to decrease linearly with the amount of adsorbed pyridine indicating that basic molecules adsorb on active desulfurization sites. In view of the importance of surface acid sites in the reactions occurring on sulfided Mo-alumina, studies were carried out to characterize semiquantitatively the energetics of the acid site-basic molecule interactions. For this purpose, the thermodynamics of adsorption of ammonia, in the submonolayer region, on alumina and Mo-alumina, in the calcined form and after sulfidation, has been studied using the methods of statistical thermodynamics. The following characteristics of the acidic sites have been quantitatively estimated; (i) their specific concentration, N (cm^{-2}); (ii) the distribution of the isosteric heats of adsorption of ammonia, q_{st} ; and (iii) the differential surface entropy of ammonia, \bar{S}_T , at various coverages.

The alumina support was a commercial sample (Ketjen, CK 300) onto which 750 ppm of Na was introduced by impregnation with an aqueous solution of NaOH. To prepare Mo-alumina, an aqueous solution of ammonium paramolybdate (BDH) containing enough molybdenum to give 12% MoO_3 by wt in the final catalyst was impregnated on the above alumina. The material was then dried at 333 K in air for 12 hr and then calcined at 848 K in air for 2 hr. Ammonia of high purity was supplied by

Air Products Ltd., Allentown, Pa., USA.

Sulfidation was carried out at atmospheric pressure as follows: the temperature of the sample (3 ml) was raised to 523 K in pure dry hydrogen (75 ml min^{-1}). At this temperature, the feed consisting of 2% CS_2 in benzene (9 ml hr^{-1}) was introduced. The temperature was then raised to 623 K and the sulfidation continued for 5 hr. The sample was then cooled in an atmosphere of hydrogen.

For NH_3 adsorption experiments, about 0.2–0.4 g of the sample was taken in a glass vessel which was then attached to a conventional high vacuum volumetric adsorption system. The samples were first evacuated for 5 hr at 773 K. Adsorption of NH_3 was then carried out at various temperatures in the range 513–573 K.

Some adsorption isotherms of NH_3 on alumina and Mo-alumina in both the calcined and sulfided forms are shown in Fig. 1. The Langmuir equation was found to fit the data satisfactorily, the value of R , the linear regression coefficient, in all cases being above 0.99. As may be seen from Fig. 1, there was a reduction in the amount of NH_3 adsorbed on sulfidation on all the samples indicating that some acid sites are eliminated on sulfidation.

To characterize the energetics of the acid site-base molecule interaction further, the isosteric heat of adsorption, q_{st} , was calculated at various coverages in the range $5\text{--}15 \times 10^{13}$ of N , the number of NH_3 molecules adsorbed per cm^2 , using the integrated form of the clausius-clapeyron equation. The variation of q_{st} with N for alumina and Mo-alumina is shown in Fig. 2. Our values for alumina are in good agreement with those of Clark *et al.* (3), especially at low cover-

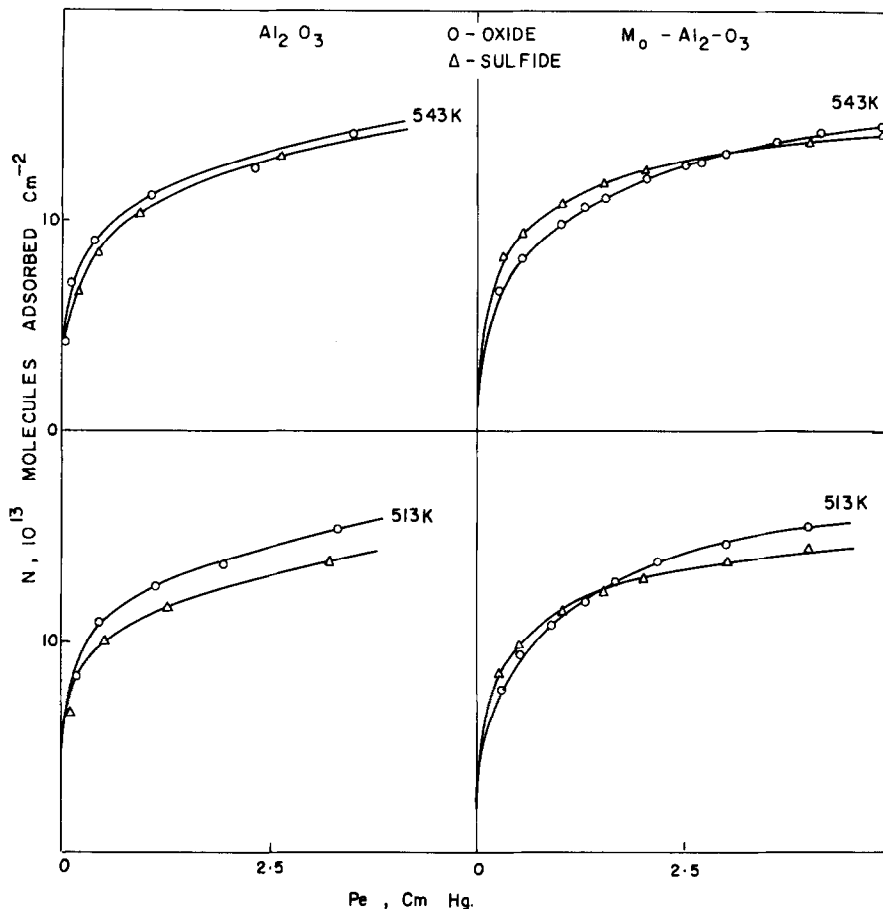
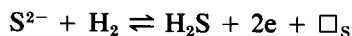


FIG. 1. Adsorption isotherms of ammonia on alumina and Mo-alumina.

ages. For example, at a value of $N = 7 \times 10^{13} \text{ cm}^{-2}$ Clark *et al.* obtained a value of q_{st} of $22 \text{ kcal mole}^{-1}$ to be compared to 21 kcal in our case. On sulfidation, even though the amount of NH_3 adsorbed goes down (Fig. 1), the strength of the acid sites increases significantly (Fig. 2). The increase in the strength of the strong acid sites of alumina ($q_{st} > 10 \text{ kcal}$) on sulfidation indicates that the coordinative unsaturation of surface Al^{3+} ions is further increased by the loss of additional hydroxyl groups leading to an increase of the net positive charge at Al^{3+} and hence an increase in its acid strength.

On deposition of molybdenum oxide, there is a marked reduction in both the number (Fig. 1) and strength (Fig. 2) of the acid sites. Moreover, the variation of q_{st}

with coverage was also less marked than in the case of alumina. On sulfidation, even though there is a reduction in the total amount of NH_3 adsorbed, there is a remarkable increase in the strength of the acid sites across the whole spectrum (Fig. 2). This increase cannot be attributed solely to the exposure of the alumina surface on crystallization of the MoS_2 species since the acid sites on sulfided Mo-alumina are found to be stronger than those of even sulfided alumina. Hence, new acidic sites involving most probably anionic vacancies on the MoS_2 species are created on reduction-cum-sulfidation of calcined Mo-alumina as indicated below:



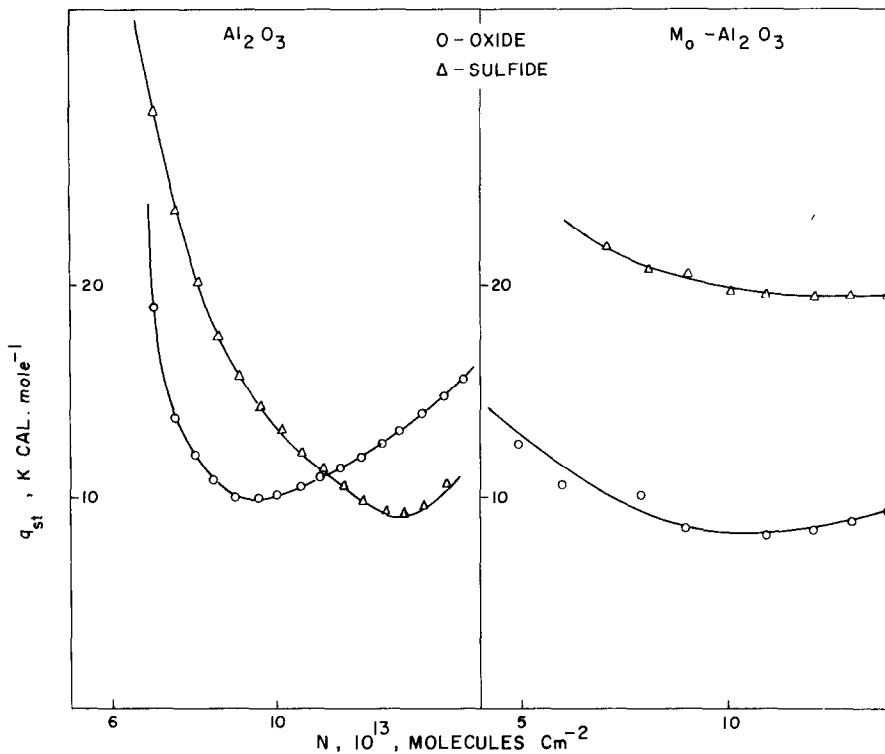


FIG. 2. Variation of q_{st} , the isosteric heat of adsorption, with coverage.

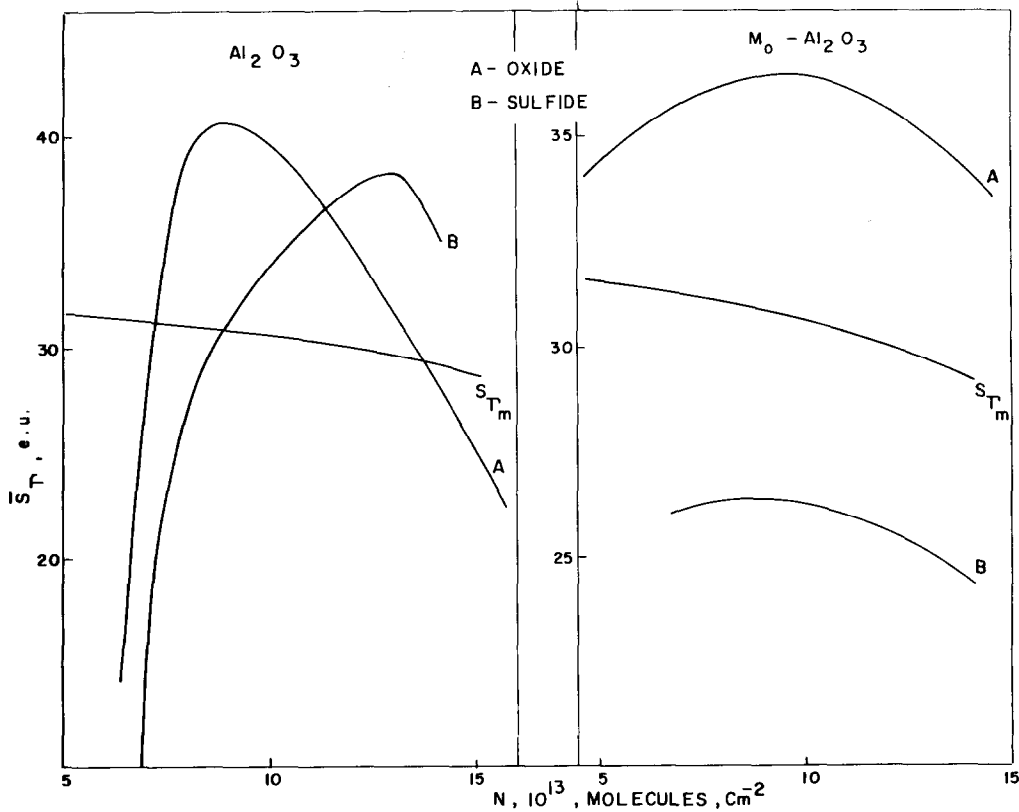


FIG. 3. Variation of \bar{S}_T , the differential molar entropy of adsorbed ammonia with coverage at 543 K. Values of \bar{S}_{Tm} , the differential entropy of adsorbed ammonia, considered as a two-dimensional gas, are also shown.

where \square_s is an anionic vacancy. As in the case of the calcined sample, q_{st} values on sulfided Mo–alumina also did not change much with coverage (Fig. 2).

In order to evaluate the mobility of adsorbed NH_3 molecules, their differential molar entropies, \bar{S}_r , were calculated by the procedure of Clark *et al.* (3). Figure 3 illustrates the variation of \bar{S}_r at 543 K with coverage on alumina and Mo–alumina, respectively, in both the calcined and sulfided states. The entropy of gaseous NH_3 at 543 K is 51.75 eu (4). Figure 3 also illustrates the variation with coverage of $\bar{S}_{r,m}$, the differential molar entropies of NH_3 treated as a perfect two-dimensional adsorbed gas at 543 K. These values were calculated on the assumption (5) that the only loss accompanying adsorption is one translational degree of freedom in the direction perpendicular to the surface. It is seen that NH_3 molecules adsorbed on sulfided Mo–alumina, in contrast to those on calcined Mo–alumina, are not mobile and are localized at fixed adsorption sites. More details of the energetics and entropy of NH_3 molecules adsorbed on sulfided Mo–alumina and Co–Mo–alumina are given elsewhere (6).

In summary, it may be concluded that sulfided Mo–alumina contains acid sites whose strength, as evaluated from the heat of adsorption and surface mobility of adsorbed base molecules, is higher than that of even the alumina support.

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