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NOTES

Relationship between the Number and Strength of the Acid Sites on Solid Surfaces Using Ammonia Adsorption

The amount of acid or acidity, as a function of the acid strength, is an interesting feature of solid catalysts. This relationship can be obtained by an amine titration method using color indicators (*1*, *2*). This method, however, is limited to white or light colored catalysts.

By means of either a gravimetric or volumetric technique, the amount of a base adsorbed from the gas phase can be obtained as a function of its partial pressure. A relationship between the partial pressure of the base and the acid strength distribution of the adsorbent would be a useful tool, especially for studying the acid strength distribution of colored catalysts.

We were then led to try to establish this relationship employing a gravimetric technique for measuring the amount of base adsorbed from the gas phase as a function of the partial pressure, and the titration method of color indicators using *n*-butylamine to obtain the acidity as a function of the pK_a of the indicators.

A McBain microbalance was employed under continuous flow conditions at atmospheric pressure (P = 630 Torr). Acid amount or acidity is equivalent to the weight of base adsorbed and is a function of the base partial pressure (p), which was adjusted by mixing the base (ammonia or *n*-butylamine) with nitrogen. Ammonia was fed from a cylinder (Matheson 99.99% purity), and *n*-butylamine (BDH) from a jacketed drechsel bottle. The adsorption isotherms were obtained at temperatures ranging from room temperature up to 400°C, using partial pressures between 40 and 630 Torr for ammonia, and between 40 and 160 Torr for *n*-butylamine. All samples (0.1 g) were pretreated under a stream of nitrogen at 400°C for 2 hr.

The titration method was carried out as follows: 0.1-g portions of the sample were placed in small vials and also pretreated at 400°C for 2 hr. Subsequently they were placed in a desiccator bell allowing them to cool to room temperature. Benzene (3 ml) was then added to each vial, followed by addition of three drops of a benzene solution of one of the different indicators. The indicators employed (Eastman) ranged from $pK_a = +5$ (*p*-ethoxychrysoidin) to $pK_a = -2.4$ (*p*-nitrodiphenylamine). The vials were then closed with caps featuring injection septa, and placed in an ultrasonic vibrator, allowing the indicators to change to their acidic forms overnight. Afterward a 0.1 mol dm^{-3} solution of *n*-butylamine in benzene, introduced into the vials with a syringe microburette, was employed to titrate. The amount of *n*-butylamine required for changing back to the basic color was ascertained for each indicator, employing two or three samples.

The catalysts were prepared using solutions of ammonium molybdate and aluminium nitrate (Merck) to impregnate γ-alumina (Filtrol) and silica gel (Merck). After impregnation, the catalysts were dried at 110°C and calcined at 500°C. The following catalysts (all white powders) were employed for the acidity measurement by both of the methods described above (BET surface areas in parentheses):

Al_2O_3 (280 m^2/g)
12%MoO_3/Al_2O_3 (210 m^2/g)
25%Al_2O_3–SiO_2 (250 m^2/g)
12%MoO_3/25%Al_2O_3–SiO_2 (140 m^2/g)

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A comparison of the amounts of *n*-butylamine adsorbed from the gas phase at room temperature with the titers of *n*-butylamine was made for Al_2O_3 and 12% MoO_3/Al_2O_3 as adsorbents. Within the range of partial pressure and pK_a employed, remarkably higher amounts were observed for the gas phase method as compared to the values found by the titration method. For example, values for Al_2O_3 varied between 1.5 and 1.1 mmol/g for the former and between 0.30 and 0.05 mmol/g for the latter.

The use of ammonia in the gas phase method, instead of *n*-butylamine, produced even higher adsorption amounts. For example, values found at room temperature for Al_2O_3 varied between 2.8 and 1.3 mmol/g.

The higher adsorption amounts found at room temperature in the gravimetric technique may be due to physisorption of the gaseous molecules. With the titration method this effect is reduced probably because of coadsorption of the solvent (benzene).

In addition, the differences observed may also be the result of the smaller molecules being able to reach more surface area than larger ones, i.e., ammonia > *n*-butylamine > indicators.

In order to obtain similar results for both gravimetric and titration methods, a higher temperature may be used in the gravimetric method. For each of the catalysts, an examination of the adsorption isotherms between 50 and 400°C indicates that the adsorbed amounts of ammonia at 200°C are similar to the titers of *n*-butylamine. Placing both the pK_a of the indicators and the inverse of the molar fraction of ammonia ($1/x = P/p$) properly in the abscissa, both the titers of *n*-butylamine and the amounts of ammonia adsorbed obtained at 200°C coincide reasonably for all the catalysts tested, as can be observed in Fig. 1. The relation between both scales can be approximated to:

$$pK_a = (11 - 1/x)/2.$$

Accordingly, by finding the adsorption isotherm of ammonia at 200°C, the acid strength distribution may be found, within the range of pK_a studied, using the relationship presented above.

The slope of the acid strength distribution curve is an interesting characteristic indicating whether the acid sites are predominantly weak or strong. A flattened curve (near zero slope) indicates that all sites titrated have strength similar to that of the stronger sites titrated (i.e., near to the smaller pK_a employed). The proportion of weak sites progressively increases as the negative slope of the curve increases. The two cases may be designated as homogeneous and heterogeneous surfaces, respectively, the former having all sites with approximately the same strength equal or near that of the stronger sites, and the latter having a wider range of strengths among all sites.

Comparing values obtained for alumina and silica–alumina, it is noticed that silica–alumina has a higher acidity than alumina in the whole range of acid strength studied. According to the shape of the curves obtained, silica–alumina has a more homogeneous surface than alumina. Similar behavior has been noted elsewhere (*2*).

The results obtained indicate also that the incorporation of molybdenum produces an increase in acidity in both alumina and silica–alumina. Similar results have been reported by Ratnasamy *et al.* (*3*) and by Petrakis and Kiviat (*4*). This is probably due to the high oxidation states brought about in the mixed oxides by the incorporation of molybdenum. Pure MoO_3, Mo(VI), is a very acidic solid (*3*) and the oxidation state of molybdenum in the mixed oxides is held to be near to that found in pure MoO_3 (*4*).

The incorporation of molybdenum leads to a flatter curve in the case of alumina whereas for silica-alumina it leads to a more pronounced slope (Fig. 1). These results indicate completely opposite effects, i.e., homogenization and heterogenization, re-

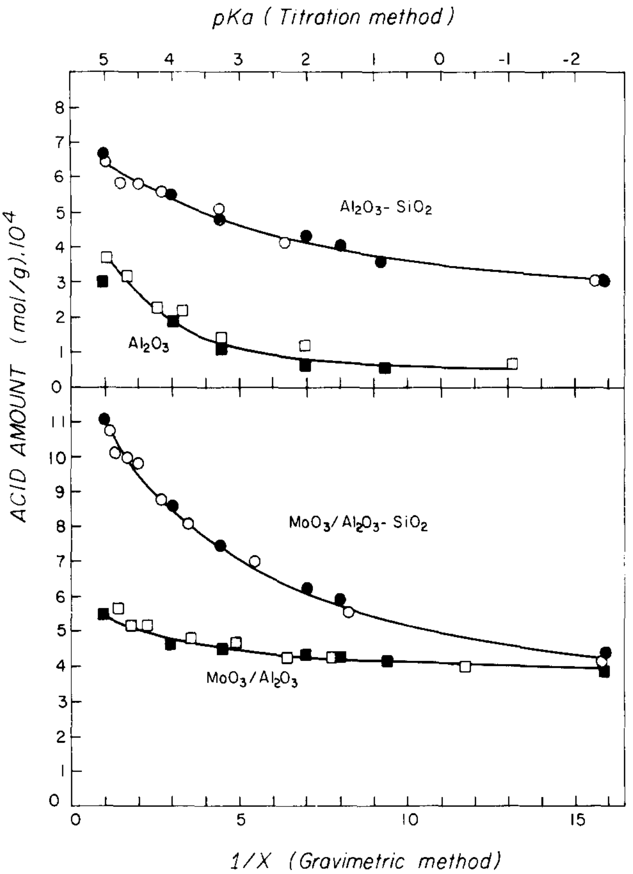

FIG. 1. Amounts of n-butylamine and ammonia employed by the titration method (filled symbols) and the gravimetric method (open symbols), respectively.

spectively. On alumina, the homogenization effect observed is probably a result of a solid reaction consisting of the formation of $Al_2(MoO_4)_3$. This reaction implies a crystalline rearrangement in the bulk accompanied by sintering (*5*); however, considering the high surface area of the support, the product of the solid reaction is probably in the form of a layer. A monolayer structure has been proposed in the literature (*6*) and is regarded as being comprised of an arrangement of molybdenum cations as found in MoO_3 (i.e., molybdenum occupying octahedral sites). The formation of an $Al_2(MoO_4)_3$ monolayer, in which molybdenum cations occupy tetrahedral sites, has been considered as well (*5*). In any case, the homogenization of the surface may also be explained by the formation of strong sites (*4*) intimately related to molybdenum cations. The strong sites are in a layer which entirely covers the alumina surface, therefore eliminating its previous more heterogeneous acid strength distribution.

From previous work (*7*), it can be concluded that silica interacts with molybdenum oxide to a lesser extent than does alumina. Accordingly, molybdenum oxide may interact with silica–alumina to form $Al_2(MoO_4)_3$ plus bare silica, producing a disconnection between alumina and silica. The possibility of formation of surface Mo–Al–Si complex oxidic phases cannot be discarded either. Therefore, a larger number of possible phases are feasible in MoO_3/Al_2O_3-SiO_2, which may be the reason for the heterogenization effect cited above.

The decreases in surface area observed when incorporating molybdenum can be attributed to sintering produced by the interaction of molybdenum oxide with the support during calcination (*5*), or to pore plugging resulting from the formation of crystals inside small pores. The relatively low melting point of MoO_3 (795°C) makes possible the partial melting of finely dispersed MoO_3 during calcination, probably leading to wetting of the surface and favoring the transport of molten molybdenum oxide to form larger crystals.

The proposed relationship between number and strength of acid sites is at present being tested using other adsorbents.

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