J. Surface Sci. Technol., Vol 22, No. 1-2, pp. 25-33, 2006

Measurement of Brönsted Acidity of Silica-Alumina Solid Catalyst by Base Exchange Method

M. A. RAHMAN, M. A. K. AZAD, S. AHSAN, S. ISLAM, M. A. MOTIN and M. ASADULLAH*

Department of Applied Chemistry and Chemical Technology, University of Rajshahi, Rajshahi 6205, Bangladesh.

Abstract — Silica-Alumina catalysts having three different Si/Al ratios were prepared. Surface acidity of these catalyst samples was measured by the base exchange method using aqueous ammonium acetate, CH_3COONH_4 solution and the results were compared with those measured by the base exchange method using KOH and NH_4OH as adsorbates from aqueous solution. The amount of K^+ and NH_4^+ adsorbed was determined titrimetrically and spectrophotometrically, respectively for measuring the concentration of K^+ and NH_4^+ in the solution before and after adsorption. It was found that the surface acidity was more pronounced when ammonium acetate solution was used as an adsorbate. With the use of NH_4OH and KOH as bases considerable dealumination takes place with a consequent decrease of surface acidity of the catalyst samples. In all cases, the surface acidity increased with decrease of sample size. It is seen that surface acidity measured with NH_4OH becomes closer to that measured with KOH at the same(?) Si/Al ratio, but contrary to this, surface acidity measured with NH_4OH becomes closer to that measured with CH_3COONH_4 at high Si/Al ratio. This phenomenon is attributed to dealumination of silica-alumina catalyst samples by the strong base.

Keywords : *Surface acidity, silica-alumina catalysts, Brönsted acidity, base exchange.*

INTRODUCTION

The concept of surface acidity of highly divided solid particles was derived originally to explain the action of acid surface in catalytic reaction. Acid sites on the catalyst

---

*Author for correspondence. Tel : 880-721-750041 Ext : 4106, Fax : 880-721-750064
E-mail : asad@ru.ac.bd; asadullah8666@yahoo.com

surface are believed to be the centres for the reactions to take place. Acid catalysis is important in petroleum processing. Unit processes like catalytic cracking [1], hydrocracking [2], isomerization [3], aromatization [4], fine chemical preparation [5], etc. are most important where large tonnage use of solid acids are found.

Finely divided catalyst particles may contain both Lewis and Brönsted acid sites. Both nature and strength of acid sites play an important role in determining catalytic activity of many solid catalysts. A direct relationship between catalytic activity and surface acidity of cracking catalysts has been established [1]. Therefore, measurement of surface acidity of solid catalysts is of immense importance from technological point of view because it not only helps characterize a catalyst sample but also provides a method of screening of a catalyst sample for yield in a process. Consequently, a varied number of methods are available for the measurement of surface acidity of solid catalysts, of which, the aqueous method [6-10], the amine titration method [11-14], Infra Red (IR) pyridine adsorption method [15-17], Fourier Transform Infra Red (FTIR) and Temperature Programmed Desorption (TPD) of ammonia method [17-19] and microcalorimetric method [17, 20-27] are in common use. Cracking catalyst generally exhibits both Brönsted and Lewis acid sites. Above methods either determines total acidity or any of the aforesaid two types of acid sites. The amine titration method determines total surface acidity, both Brönsted and Lewis acid sites and this method was employed for characterizing silica-alumina catalyst samples prepared in this laboratory [14]. On the other hand, of the aqueous methods, base exchange method and method of titration of aqueous slurry with a standard base, measure Brönsted acid sites only [10].

In the present work, the surface acidity of silica-alumina catalyst samples prepared in this laboratory has been measured by the base exchange method using ammonium acetate as a base and the results were compared with those measured using NH_4OH and KOH as bases.

EXPERIMENTAL

Materials : Sodium metasilicate powder, aluminum chloride hexahydrate (99%), sodium hydroxide 97.5%, hydrochoric acid (36.5%), potasium iodide (99.5%), mercuric chloride (99%), ammonia solution (25%), ammonium acetate (96%), ammonium chloride (99.5%), pH meter (Corning, Model 215), oven (Gallenkamp Regd., Model OV-445), Muffle furnace (Type MV2 22OV 2-6KW CV3612/1973), spectrophotometer (Ogawa Seiki, Model-ANA-75) were used for this investigation.

Methods : *Preparation of silica-alumina catalyst* — Silica-alumina catalyst samples of different Si/Al ratios were prepared by coprecipitating aluminum hydroxide, freshly prepared from aluminum chloride hexahydrate and ammonia, with sodium metasilicate solutions in deionized water. The pH of the solution(?) was brought to 3 by adding concentrated hydrochloric acid. The resulting suspension was stirred and kept standing for 12 hours. Then it was filtered, washed with deionized water, dried in an oven at 110°C and ground in a mortar using a pestle. The catalyst powders so obtained were sieved through 25–200 mesh standard sieves and activated at 450°C in a furnace for 3 hours in an atmosphere of nitrogen gas [27].

Construction of Calibration Curve for the Spectrophotometric Method

The amount of ammonium ion adsorbed by the catalyst samples was determined by measuring the concentration of ammonium salt by a spectrophotometer before and after adsorption. For spectrophotometric measurement Nessler Reagent was added to the solution of ammonium salt to develope colour. For the estimation of ammonium ions using Nessler Reagent, very dilute solution was needed. Therefore, 2.00×10^{-4} M solutions of ammonium acetate or ammonium chloride for calibration and ammonium hydroxide for measurement of surface acidity were prepared.

For the calibration experiment, 5, 10, 15 and 20 ml of ammonium acetate solution were taken in separate 50 ml volumetric flasks and 1 ml Nessler reagent was added to each flask. The contents were made up to the mark and allowed to stand for 10 minutes. An equal volume of blank solution was prepared following the same procedure but excluding only ammonium acetate. The zero absorbance or 100% transmittance mark of the spectrophotometer was adjusted first by using the blank solution. The wavelength selected was 420 nm and the absorbances of the standard solutions were noted. The standard calibration curve was obtained by plotting absorbance against concentration of ammonium acetate solution. These experiments were repeated using ammonium chloride solution. Calibration curve was prepared by plotting the absorbance against the strength of standard solutions. The use of ammonium acetate and ammonium chloride solutions yielded the same straight line showing the validity of ammonium acetate as a primary standard (Fig. 1).

Estimation of Surface Acidity of Silica-Alumina Catalyst using Ammonium Acetate and Ammonium Hydroxide

Catalyst samples of 100–200 mesh were activated first for half an hour at 450°C in N_2 atmosphere and then cooled in a desiccator for half an hour. 0.1 g each of the samples was placed in three separate screw-cap vial and 10 ml of 0.01 (M) ammonium acetate solution were added in each vial and the vials were shaken for about 1 minute. For blank 10 ml of ammonium acetate solution was taken in another vial without catalyst. These vials were kept for 24 hours to reach equilibrium between ammonium acetate solution and catalyst sample, during this time they were agitated intermittently

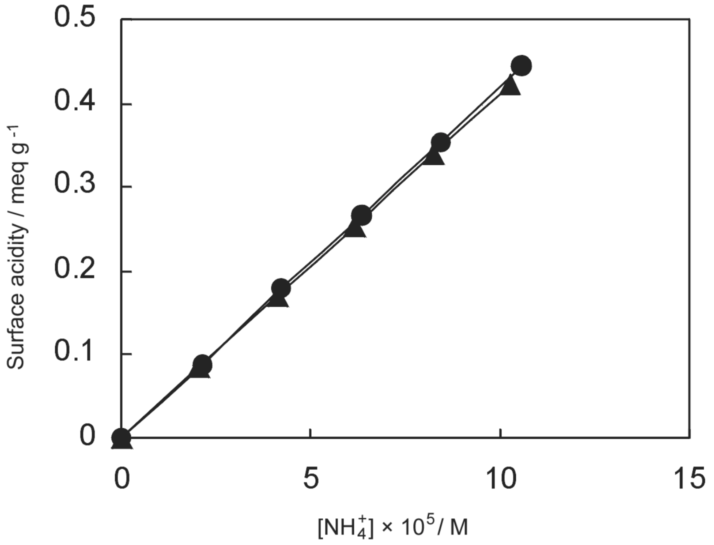

Fig. 1. Calibration curve for NH_4^+ estimation.

three times. The solutions from each vial with catalyst were decanted in three separate 50 ml volumetric flask and were shaken for a while. 1 ml of ammonium acetate solution from each flask and from the blank was then pipetted out in four separate 50 ml volumetric flasks and diluted by adding deionized water upto the mark from which 15 ml of each solution was taken in other four separate 50 ml volumetric flasks. 1 ml Nessler reagent was then added to each flask and made upto the mark and the contents were well shaken and allowed to stand for 10 minutes. They gave three test solutions and a blank. To adjust zero absorbance of the spectrophotometer 1 ml of Nessler reagent was taken in another 50 ml volumetric flask and was diluted upto the mark with de-ionized water. 10 ml of each test solution and the blank was taken in the spectrophotometer cell and the absorbance was measured and noted. Concentration of ammonium ion was read off from the standard calibration curve. From the concentration difference between the blank and the test solution the ammonium ion consumed per gram of catalyst was computed to give the surface acidity of the catalyst in meq/g. Similar experiments were carried out using ammonium hydroxide.

Estimation of Surface Acidity of Silica-Alumina Catalyst using Potassium Hydroxide as a Base

5 g of Alumina-Silica catalyst were weighed to the nearest 0.01 gram and added to 200 ml of 0.1M potassium hydroxide solution (standardized). The mixture

was agitated for 0.5 min., and at the end of 1 min. a 10ml sample was withdrawn with a pipette. Agitation was continued for the first half of the second minute and the catalyst was allowed to settle again before the second 10ml sample was withdrawn. Samples were withdrawn at the end of 1, 2, 3, 4, 5, 6, 10, 15 and 30 min., a 0.5 min. settling period was allowed before each sample was withdrawn. Each sample was dropped in one of a series of funnels fitted with filter paper. Five ml of each filtered sample were removed from the test tube, in which it was collected and titrated with standardized 0.1M hydrochloric acid using phenolphthalein as an indicator. It was decided to use the value obtained after 30 min., which, in virtually all cases, was very close to the final equilibrium value as indicated by the close agreement between the 15 and 30 min. values.

RESULTS AND DISCUSSION

Silica alumina catalysts were prepared having silica-alumina ratio of 90 : 10, 80 : 20, 70 : 30 and 50 : 50. Surface acidity of these catalyst samples was measured by base exchange method using CH_3COONH_4 as an adsorbate. Surface acidity of the same catalyst samples was also measured using NH_4OH and KOH as bases and the results were compared with those using CH_3COONH_4.

We have first investigated the effect of Si/Al ratio on the surface acidity and the variations of surface acidity with Si/Al ratio as measured using CH_3COONH_4, NH_4OH and KOH are shown in Fig. 2. The effect of sample size on the surface acidity has also been investigated and these results are shown graphically in Fig. 3 (a–d), respectively for catalyst samples having Si/Al ratio of 50 : 50, 70 : 30, 80 : 20 and 90 : 10. From Fig. 2 it is seen that surface acidity decreases with the decrease of aluminum content of silica-alumina catalyst sample and from Fig. 3 (a–d) it is seen that surface acidity increases with the decrease of sample size of the catalyst samples. These general trends of results are quite in agreement with the previously reported results [9, 10] but some interesting facts are revealed on examining the results in Fig. 2 and 3 (a-d). These are as follows : From Fig. 2 it is seen that surface acidity is invariably greater when measured with CH_3COONH_4 than that of when measured with KOH. But interestingly, when measured with NH_4OH surface acidity of catalyst sample having Si/Al ratio surface acidity of 50:50 tends to approach a value obtained when measured with KOH; to the contrary, of catalyst sample when measured with NH_4OH having Si/Al ratio of 90 : 10 tends to equal to that measured with CH_3COONH_4.

It is noticed further that in all cases surface acidity decreases with the decrease of aluminum content of the catalyst samples but the surface acidity measured with KOH, though lower, for all Si/Al ratios, it tends to approach values obtained when

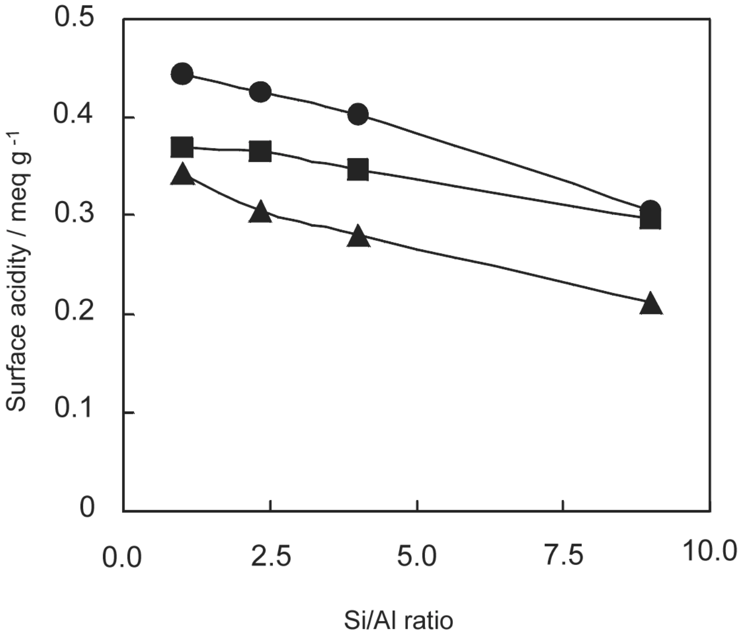

Fig. 2. Effect of Si/Al ratio on surface acidity. • CH_3COONH_4, ■ NH_4OH and ▲ KOH.

measured with CH_3COONH_4 al low Si/Al ratio. A plausible explanation of this phenomenon may be attributed to dealumination of silica-alumina catalyst by the bases; KOH is a strong base and it dealuminates silica-alumina catalyst appreciably resulting in lower surface acidity of the catalyst samples than that when measured with CH_3COONH_4. NH_4OH is a weak base and it dealuminates silica-alumina catalyst appreciably only when aluminum content of the catalyst samples are high. This explanation is corroborated by the fact that, unlike CH_3COONH_4, during base exchange with NH_4OH and KOH turbidity of the supernatant was observed which was more pronounced with KOH as a base.

Similar patterns of results were obtained during measurement of variation of surface acidity with sample size of the catalyst sample with 50 : 50 Si/Al ratio. Fig. 3 (a) values of surface acidity measured with NH_4OH tend to be closer to that measured with KOH but to the contrary, as the Si/Al ratio increases (decrease in the aluminum content) value of surface acidity measured with NH_4OH increasingly trend to be closer to that of measure with CH_3COONH_4 [Fig. 3 (b-d)] but at low aluminum, contents of silica alumina catalysts the values of surface acidity measured with three bases at higher sample sizes became very small and close to one another.

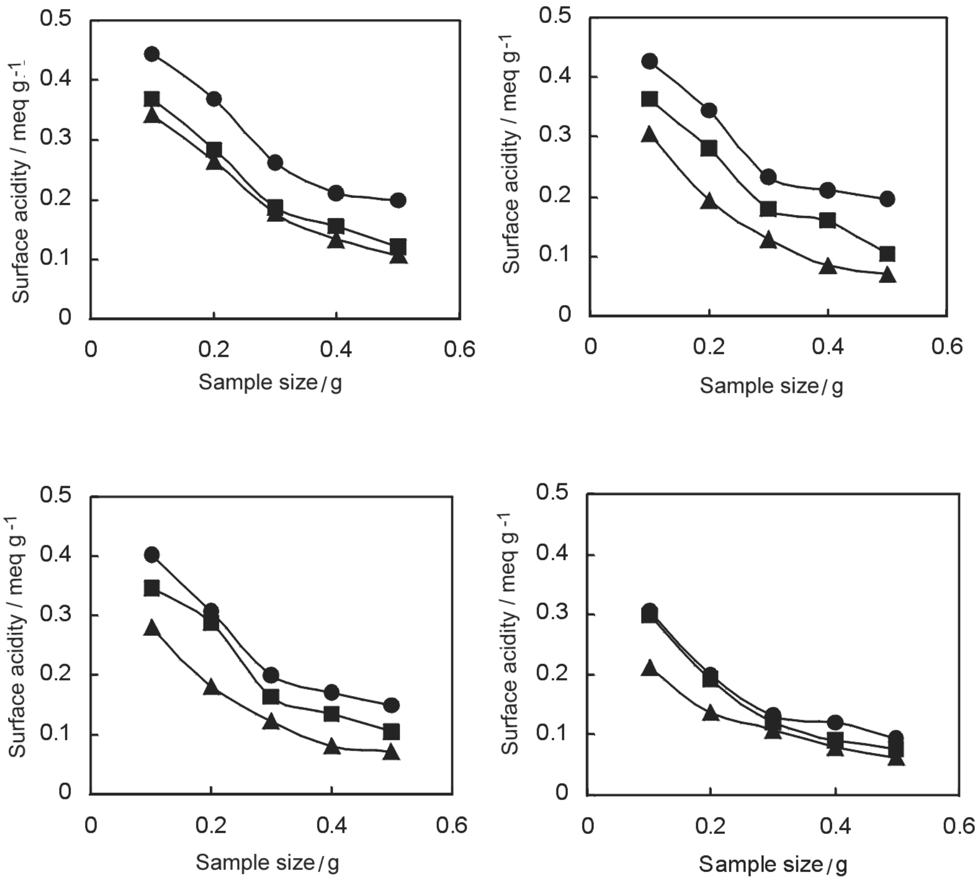

Fig. 3. Effect of sample size on surface acidity. Si:Al; (a) 50:50, (b) 70:30,(c) 80:20 and (d) 90:10. • CH_3COONH_4, ■ NH_4OH and ▲ KOH.

Since the surface acidity of a given silica-alumina catalyst sample appear to depend on the nature of bases and considerable dealumination takes place with strong a base the results of surface acidity measurement with the base exchange method should be viewed with caution. But the dependence of surface acidity on the strength of bases has one advantage that the evaluation of equilibrium constant of the base exchange reaction may lead one to calculate the relative strength of the acid sites in the catalyst samples.

CONCLUSION

Surface acidity of silica-alumina catalyst measured by the base exchange method depends on the Si/Al ratio; as the aluminum content of the catalyst increases surface acidity increases. This is also observed that surface acidity of silica-alumina catalyst increases with decrease of sample size. This is further observed that use of strong base in the base exchange method incurs considerable dealumination of the silica-alumina catalyst. Therefore, care should be taken in selecting a base for measuring the surface acidity of the silica-alumina catalyst by the base exchanged method. A salt of weak acid and weak base like CH_3COONH_4 is suitable for measuring surface acidity of silica-alumina catalyst.

REFERENCES

1. M. R. Guisnet, Acc. Chem. Res., 23, 392 (1990).
2. A. Corma, A. Martinez-soria and J. B. Monton, J. Catal., 153, 25 (1995).
3. C. P. Nicolaides, App. Catal. A: General, 185, 211 (1999).
4. C. P. Nicolaides, N. P. Sincadu and M. S. Scurrell, Catalysis Today, 71, 429 (2002).
5. M. J. Climent, A. Corma, S. Iborra, M. C. Navarro, and J. Primo, J. Catal., 161, 783 (1996).
6. C. L. Thomas, Ind. Eng. Chem., 41, 2564 (1949).
7. C. F. Holm, G. C. Bailey and Alfred Clark, J. Phys. Chem., 63. 129 (1959).
8. H. A. Bensi and B.H.C. Winquist, Adv. Catal., 27, 98 (1987).
9. A. K. Bandhapadhyay, S. K. Roy and G. S. Murty, Indian J. Chem., 28A, 222 (1989).
10. M. A. Rahman, M. R. Zaman and M. A. K. Azad, Bang. J. Sci. Ind. Res., 33, 479 (1998).
11. M. W. Tamele, Discuss. Faraday Soc., 8, 270 (1950).
12. H. A. Bensi, J. Phys. Chem., 61, 970 (1957).
13. K. K. Unger, U. R. Kettlemann and W. K. Kries, J. Chem. Tech. Biotechnol., 61, 970 (1981).
14. M. A. Rahman, M. R. Zaman and K. Biswas, Bang. J. Sci. Res., 32, 226 (1997).
15. E. P. Parry, J. Catal., 2, 371 (1963).
16. G. Connell and J. A. Dumesic, J. Catal., 105, 285 (1987).
17. N. Cardona-Martinez and J. A. Dumesic, J. Catal., 125, 427 (1990).
18. S. G. Hegde, R. Kumar, R. N. Bhatt and P. Rtuasamy, Zeolites, 9, 233 (1989).

19. J. Dakta, B. Gil, A. Kubacka, Zeolites, 18, 245 (1997).

20. M. Sasidharan, S. G. Hegde and R. Kumar, Microporous and Mesoporous, 24, 59 (1998).

21. P. C. Gravelle, Catal. Rev., 16, 37 (1977).

22. K. Tsutsumi, Hong Qui Koh, S. Hagiwara and H. Takahashi, Bull. Chem. Soc. Japan, 48, 3546 (1975).

23. A. Auoroux, U. Boils, P. Wiezchowski, P. C. Gravelle and J. C. Vedine, J. Chem. Soc. Faraday Trans. 1, 75, 2544 (1979).

24. G. Coudurier, A. Auoroux, J. C. Vedine, R. D. Fulee, L. Abrams and R. D. Shannon, J. Catal., 108, 1 (1987).

25. H. Thamm, H. G. Zerschkewitz and H. Stah, Zeolites, 8, 151 (1988).

26. D. Chen, S. Sharma, N. Cardona-Martinez, Z. A. Dumesic, V. A. Bell, G. D. Hodge and R. Mondon, J. Catal., 136, 392 (1992).

27. M. A. Rahman, M. A. K. Azad and M. S. R. Sarkar, J. Surface Sci. Technol, 14, 70 (1998).