

Surface Acidity of the Supported Molybdenum oxide Catalysts Probed by Potentiometric Titration of *n*-butylamine

Abstract

A series of alumina and silica supported molybdenum oxide catalysts were prepared using ammonium *heptamolybdate* at different loading levels (5 – 20 wt% of molybdenum oxide) by the impregnating method. The total acidity of the solid catalysts was measured by means of potentiometric titration. The supported catalysts possess very strong acid sites (*may be contain both Brønsted and Lewis acid sites*). The total surface acidity was observed to increase dramatically with increasing of loading levels. However the surface acidity of alumina supported molybdena catalysts are found to be higher than surface acidity of silica supported molybdena catalysts. Sulfation modification remarkably enhances the surface acidity and increases the strength of acidity due to the inductive effect of S=O.

Kew words: Supported molybdenum oxide catalysts, Acidity, Potentiometric titration

1. Introduction

Solid acid catalysts have assumed a great importance due to their huge application potential in chemical industry, specifically in the oil refining industry [1-4]. Solid acids and bases are widely used to catalyze various reactions at the solid-gas or solid liquid interface. The increase in activity is believed to arise from increase in the surface acidity of the modified oxide [5]. In order to understand the mechanism of their catalytic action and to predict their activity and selectivity we need quantitative information about the number and strength of the acid or basic centers on their surface [6-8] and qualitative information on the nature of the acid sites, i. e. protonic (*Brønsted*) or a protonic (Lewis) sites. A suitable choice of probe molecule is extremely important in the development of the accurate methods of studying the acid and base properties of catalyst surfaces.

Different techniques have been used to study the surface acidity of solids. Particularly, the adsorption of water and basic probe molecules followed gravimetrically [9], volumetrically, micro calorimetrically [10,11] and with IR [12-22]. Raman and NMR [23], spectroscopes have been applied to investigate surface acidity. Contrarily, the desorption of such probe molecules followed by temperature-programmed techniques have also been applied [24].

Titration methods [25-28] and activity measurements in catalytic test reactions [29-31] have also been among the thoroughly applied methods. The application of these techniques has added greatly to our knowledge about the surface acidity of solid surfaces; however it has also revealed the complexity of predicting the acid strength and number of acid centers on solid surfaces.

The acidity measurement of the catalysts by a potentiometric titration with *n*-butylamine was used to estimate the total number of acid sites and their relative strength. As a criterion to interpret the obtained results, it was suggested that the initial electrode potential (E_i) indicates the maximum acid strength of the sites. The value of meq amine/g solid, where the plateau is reached, indicates the total number of acid sites [32-34]. On the other hand, the acid strength of these sites may be classified according to the following scale [32,34] $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ (weak sites) and $E_i < -100$ mV (very weak sites).

This paper presents a study on characterization of the nature of surface acidity (the amount of surface acidity and the strength of the surface acid sites) of alumina and silica supported molybdena catalysts and modified sulfated samples using *n*-butylamine as a probe molecule.

2. Material

2.1. Catalyst preparation

Ammonium heptamolybdate (AHM), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, high purity (Merck) was used as precursor for supported and unsupported MoO_x catalysts. Unsupported molybdenum oxide was obtained by calcinations of AHM at 823 K in a static atmosphere of air for 3 h.

Supported molybdenum oxide samples were prepared by wet impregnation method [35], using alumina of high surface area ($100 \pm 10 \text{ m}^2/\text{g}$) aluminum oxide (Degussa AG, Frankfurt, Germany) and silica ($200 \pm 10 \text{ m}^2/\text{g}$), was also a Degussa product and used as support materials and aqueous solution of AHM in the impregnating solution. The impregnation solution was prepared by dissolving a calculated amount of the precursors AHM of the required loads 5, 10, and 20 wt% MoO_3 in the final supported oxide materials in a suitable volume of distilled water (50 cc/g support).

The support powder particles were sprayed slowly onto the impregnation solution, while being continuously stirred. The free water was removed by evaporation at 390 K for 1 h. The

AHM impregnated support material thus yield was dried at 390 K for 24 h in an oven. Supported molybdenum oxide on alumina (xMoAl) and silica (xMoSi) were obtained by calcinations at 823 K for 3 h in air of the corresponding impregnated supports. The resulting catalysts were kept dry on CaCl_2 , till further use. For convenience, the various catalysts are denoted below by 5MoAl indicates the 5 wt%- MoO_3 loaded alumina supported molybdenum oxide catalyst, whereas 5MoSi indicates the 5 wt%- MoO_3 loaded silica supported molybdenum oxide catalyst.

Sulfated catalysts were obtained from alumina and silica supported MoO_3 catalysts (xMoAl and xMoSi) by impregnation with ammonium sulfate. The impregnation was carried out by immersing the dried supported catalysts (xMoAl or xMoSi) in an aqueous solution containing a desired amount of $(\text{NH}_4)_2\text{SO}_4$ and evaporating to dryness, followed by calcining similarly as in case of supported catalysts. The supported catalysts promoted with sulfate were designated as xMoAlS or xMoSiS. The amount of sulfate adsorbed on supported catalysts after impregnation and before calcination is approximately 6 wt% SO_4^{2-} .

2.2. Characterization

For characterizing the surface acidity of the solid catalysts, *n*-butylamine used as probe molecule [35,36]. About 50 mg of solid catalyst was suspended in 20ml acetonitrile (purity 99.9 %, Merck), and stirred for 2 h. The initial electrode potential (E_i , mV) was measured after stirring for 2 h. Then, the suspension as titrated with 0.1N *n*-butylamine in acetonitrile at 0.05 ml/min. The electrode potential variation was measured with an Orion 420 digital A model using a double junction electrode.

3. Results and Discussion

The surface acidity measurements of the prepared catalysts by means of potentiometric titration with *n*-butylamine in acetonitrile [37] were used to estimate the amount of acid sites and their relative acid strength according to the value of the initial electrode potential (E_i). *n*-butylamine is a strong base and can be adsorbed on acid sites of different strength and types, thus it titrates both Lewis and Brønsted sites [38] .

3.1. Silica supported molybdena and sulfated catalysts

The titration curves obtained for silica supported molybdena (xMoSi) catalysts at different loading levels presented in (Fig. 1). The computed amount of the acid sites (meq./g) and the number of the acid sites per gram (N/g) as well as the values of E_i are listed in Table 1. The results obtained for surface acidity measurements reveal that the surface of pure silica show medium acid sites. The results of surface acidity measurements clearly show that all the

samples of supported catalysts (xMoSi) have very strong acidity, with E_i values in the range of -10 to 240 mV. The loading of molybdena enhances the acid strength of the catalyst. Then, the surface acid strength of silica supported molybdena catalysts increases with increasing the loading level of the MoO_3 . The maximum acid strength is exhibited by the catalyst 20MoSi at higher loading level of molybdena catalyst.

The loading of xMoSi catalyst with sulfate ions causes a remarkable increase of surface acidity presented in (Fig. 2). Since the amount of acidity and the number of acid sites (N/g) for xMoSiS catalysts (Table 1) reveal that the acidity increased with the addition of sulfate ions. Also, the amount of acidity and number of acid sites of sulfated catalysts are higher than free sulfate catalysts (Table 1).

Table 1: The surface acidity of silica supported molybdena and sulfated catalysts.

Samples	E_i (mV)	Acidity amount (meq./g)	The number of acid sites (g x 10^{19})
Si	-10	0.2	1.2
5MoSi	150	0.60	3.6
10MoSi	220	0.81	4.8
20MoSi	240	0.93	5.6
5MoSiS	250	0.75	4.5
10MoSiS	320	1.05	6.3
20MoSiS	360	1.2	7.2

3.2. Alumina-supported molybdena and sulfated catalysts

The titration curves of alumina supported molybdena catalysts at different loading levels (xMoAl) presented in (Fig. 3), whereas the amount of acidity and the total number of acid sites/g catalyst were evaluated, Table 2.

It seems the free alumina display strong acid sites, $E_i=12\text{mV}$. Supported molybdena catalysts show increases of the amount of acidity, number and strength of acid sites to reach a maximum at 20 wt% of molybdena supported on alumina (20MoAl). This means that the

surface acidity of supported catalysts (xMoAl) increases with increasing the amount of MoO₃ loaded on alumina up to 20 wt% MoO₃.

Modification with sulfate was accompanied by a gradual increase of both number and strength of acid sites to reach a maximum at 20MoAlS, which presented in (Fig. 4). The sulfated samples show the highest acidity; which is attributed to the strong interactions between sulfates and xMoAl surfaces. Moreover, these samples clearly show very strong acid sites up to $E_i = 440$ mV for 20MoAlS.

This finding threw the light on the dependence of the number of acidities as well as the acid strength on the amount of molybdena and sulfate content.

Table 2: The surface acidity of alumina supported molybdena and sulfated catalysts.

Samples	E_i (mV)	Acidity amount (meq./g)	The number of acid sites (g x 10 ¹⁹)
Al	12	0.60	3.6
5MoAl	180	0.75	4.5
10MoAl	260	0.91	5.4
20MoAl	295	1.1	6.6
5MoAlS	320	0.9	5.4
10MoAlS	390	1.35	8.1
20MoAlS	440	1.45	8.7

4. Conclusions

Pure alumina surfaces exhibited strong acidic sites compared with pure silica surfaces which display medium acid sites. The supported catalysts possess very strong acid sites and contain both Brønsted and Lewis acid sites. The acid strength of acid sites is strongest for higher loading level of molybdena on silica and alumina catalysts. The total surface acidity increased with an increase of loading levels. The surface acidity of alumina supported molybdena catalysts is higher than surface acidity of silica supported molybdena catalysts. However, the sulfation found to be to enhances the surface acidity and increases the strength of acidity due to the inductive effect of S=O. Potentiometric titration of n-butylamine probe

molecule provide an extremely useful determination of surface acid characteristics of supported molybdena and sulfated catalysts.

5. References

- [1] J. R. Shon, *J. Indus. Eng. Chem.*, 10 (1) (2004) 1.
- [2] K. Tanabe, M. Misono, Y. Ono and H. Hattori, "New Solids Acids And Bases," Elsevier Science Publisher B-V, Amsterdam (1989) 300.
- [3] K. Arata, "Solid Superacids," *Advances in Catalysis*, 37 (1990) 165.
- [4] B. H. Davis, R. A. Keogh and R. Srinivasan, *Catal. Today*, 20 (20) (1994) 219.
- [5] A. Clearfield, G. P. D. Serrette and A. H. Khazi-Syed, *Catal. Today*, 20 (1994) 295.
- [6] B. S. Goldstein, in "Experimental Methods in Catalytic Research", *Academic Press*, New York (1968) 361.
- [7] K. Tanabe, "Solid Acids and Bases" Tokyo, Kodansha and New York-London, *Academic Press* (1970).
- [8] F. Forni, *Catal. Rev.*, 8 (1973) 65.
- [9] M. Deeb and W. K. Z. Hall, *Phys. Chem. Neue Folge*, 144 (1985) 85.
- [10] C. Martinez and N. Dumesic, *Adv. Catal.*, 38 (1992) 149.
- [11] V. Solinas and I. Ferno, *Catal. Today*, 41 (1998) 179.
- [12] T. Mishra and K. Parida, *J. Mater. Chem.*, 7 (1) (1997) 147.
- [13] C. Morterra and G. Cerrato, *Phys. Chem.*, 1 (1999) 2825.
- [14] M. M. Mortland, K. V. Raman, *Clays and Clay Miner.*, 16 (1968) 393.
- [15] D. R. Brown and C. N. Rhodes, *Catal. Letters*, 54 (1997) 35.
- [16] E. P. Parry, *J. Catal.*, 2 (1963) 371.
- [17] M. R. Basila, T. R. Kantner and K. H. Rhee, *J. Phys. Chem.*, 68 (11) (1964) 3197.
- [18] T. Morimoto, J. Irnai and M. Nagao, *J. Phys. Chem.*, 78 (7) (1974) 704.
- [19] H. Miyata, Y. Nakagawa, T. Ono and Y. Kubokawa, *J. Chem. Soc., Faraday Trans. I*, 79 (1983) 2343.
- [20] A. Coriva, V. Fornes, A. Mifsud and J. Perez-Pariente, *Clay Miner.*, 19 (1984) 673.
- [21] H. Miyata, T. Mukai, T. Ono and Y. Kubokawa, *J. Chem. Soc.*,

- 172 Faraday Trans. I, 84 (11) (1988) 4137.
- 173 [22] C. Blanco, J. Herrero, S. Merdioroz and J. A. Pajares, *Clay*
- 174 *Miner.*, 36(4) (1988) 364.
- 175 [23] A. L. Blumenfeld and J. J. Fripiat, *J. phys. Chem. B*, 101(1997) 6670.
- 176 [24] D. R. Brown and C. N. Rhodes, *Thermo chem. Acta*, 294 (1997) 33.
- 177 [25] M. Richter, B. Parlitz, R. Eckelt and R. Fricke, *Chem. Commun.*, 4 (1997) 383.
- 178 [26] O. Johnson, *J. Phys. Chem.*, 59 (1955) 827.
- 179 [27] H. A. Benesi, *J. Phys. Chem.*, 61 (1957) 970.
- 180 [28] T. Henmi and K. Wada, *Clay Miner.*, 10 (1974) 231.
- 181 [29] B. S. Kapoor, *Clay Miner.*, 9 (1972) 425.
- 182 [30] R. H. Loeppert, L. W. Zelazny and B. G. Volk, *Soil sci. Soc. Am. J.*,
- 183 41(1977) 1101.
- 184 [31] M. Guisnet, *Catalysis by acids and bases*, Ed.: B. Imlick,
- 185 Elsevier Amsterdam (1985).
- 186 [32] A. Gervasini and A. Auroux, *J. Catal.*, 131 (1990) 190.
- 187 [33] A. Coroma and H. Garcia, *Catal. Today*, 38 (1997) 257.
- 188 [34] P. Sharma, S. Vyas and A. Patel, *J. Mol. Catal.*, 214 (2004) 281.
- 189 [35] E. A. El-Sharkawy, A. S. Khder and A. I. Ahmed, *Micropor.*
- 190 *Mesopor. Mater.*, 102 (2007) 128.
- 191 [36] R. Cid and G. Pecci, *J. Appl. Catal. A*: 14 (1985) 15.
- 192 [37] K. N. Rao, K.M. Reddy, N. Lingaiah, I. Suryanarayana and P. S.
- 193 Saiprasad, *J. Appl. Catal. A*: 300 (2006) 139.
- 194 [38] D. O. Bennaradi, G. P Romanelli, J. C. Autino and L. R. Pizzio,
- 195 *J. Appl. Catal. A*: 324 (2007) 62.

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197 Figure captions

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199 Fig. 1

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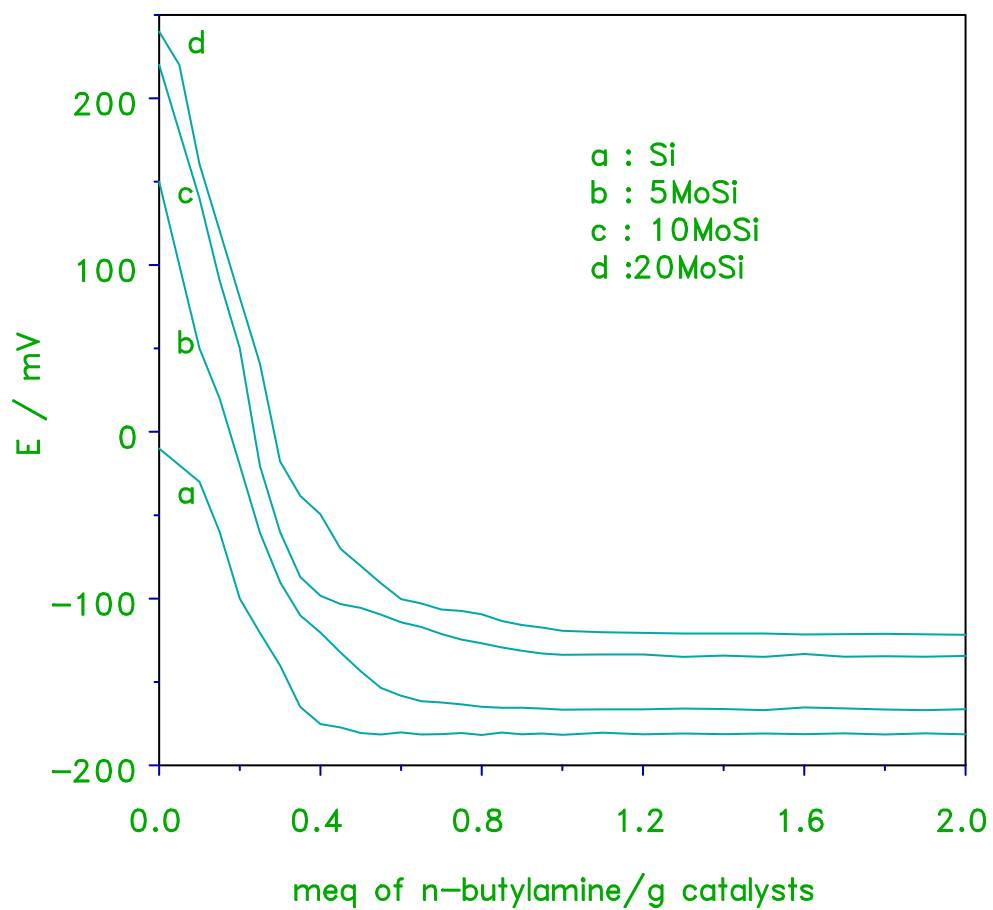


Fig. 1: Potentiometric titration curves of n-butylamine in acetonitrile for the silica and silica supported molybdena catalysts (xMoSi).

Fig. 2

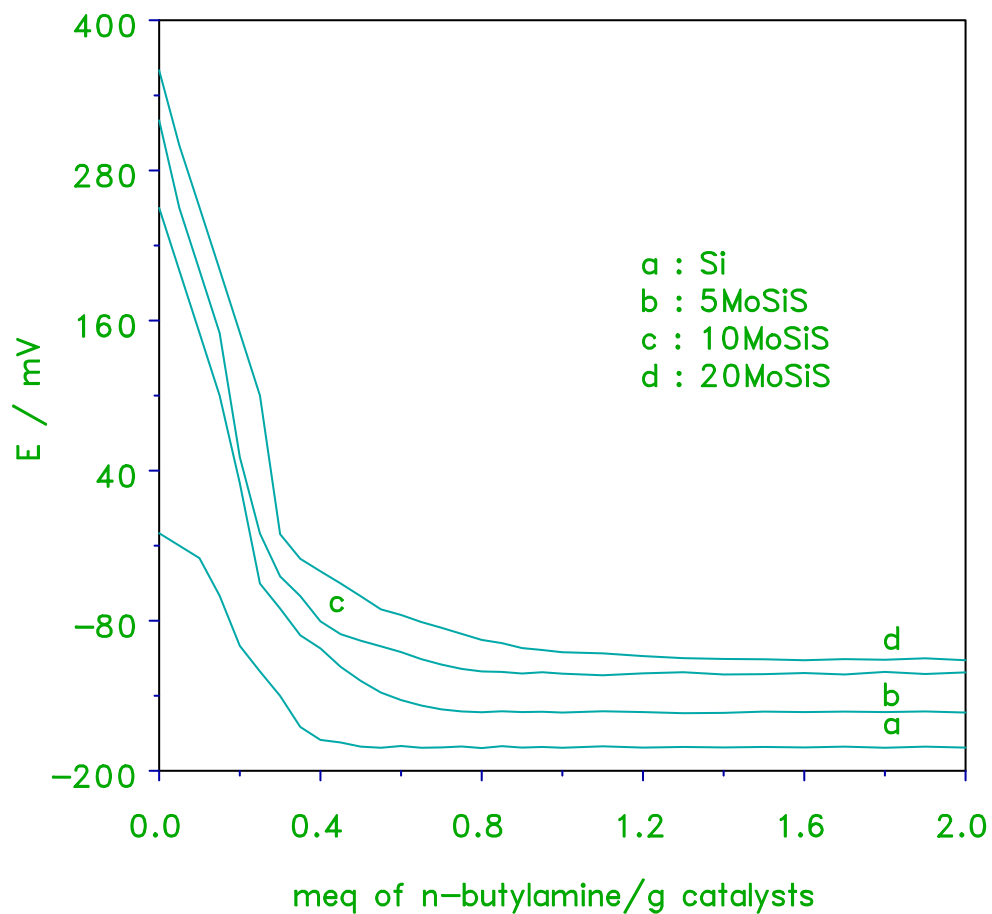


Fig. 2: Potentiometric titration curves of *n*-butylamine in acetonitrile for the silica supported molybdena and sulfated catalysts (xMoSiS).

Fig. 3

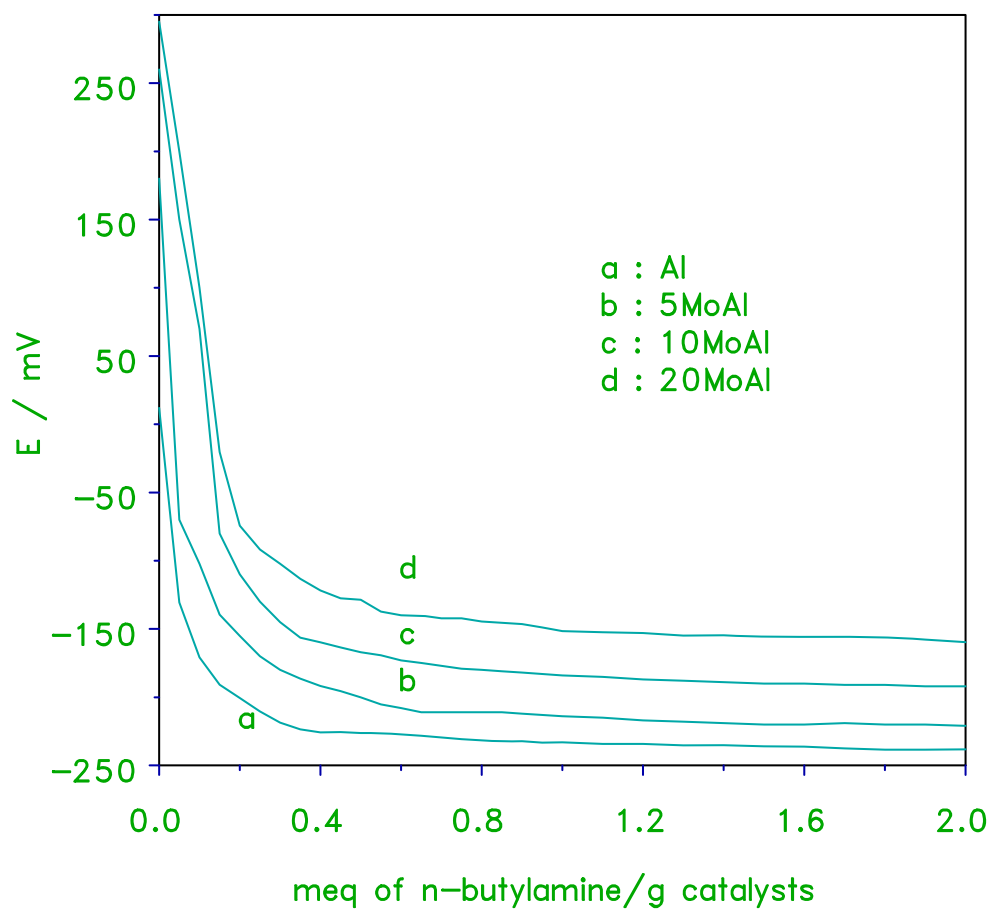


Fig. 3: Potentiometric titration curves of n-butylamine in acetonitrile for the alumina and alumina supported molybdena catalysts (xMoAl).

Fig. 4

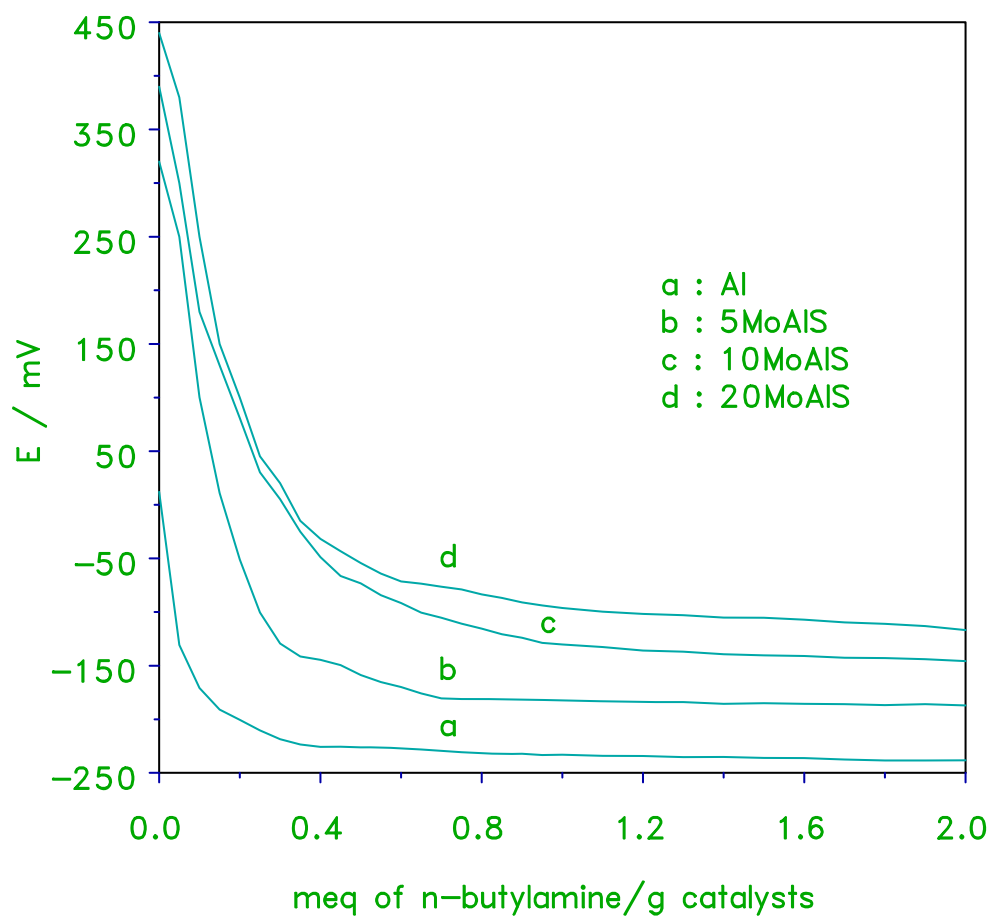


Fig. 4: Potentiometric titration curves of n-butylamine in acetonitrile for the alumina supported molybdena and sulfated catalysts (xMoAIS).