

Benghazi University
Faculty of science
Department of chemistry



**Surface acid-base properties of supported
molybdenum oxide catalysts**

A Thesis

**Submitted as partial fulfillment for the requirements of
the Master Degree of Science in Chemistry**

By

Hend Mohamed Al-hawari

Supervised

Dr. Khaled Edbey

***Associate Prof. of Physical
Chemistry***

Co-supervised

Dr. Abdelhadi Benhamid

***Assistant Prof. of Inorganic
Chemistry***

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بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

(یَرْفَعُ اللّٰهُ الَّذِیْنَ اٰمَنُوْا مِنْكُمْ وَالَّذِیْنَ

اٰتَوْا الْعِلْمَ

دَرَجَاتٍ وَاللّٰهُ یَمَّا تَعْمَلُوْنَ خَیْرًا)

صدق الله العظيم

سورة المجادلة رقم(10)

**Dedication To my
Parents, Husband,
and my kids**

Acknowledgement

A word of thank should be always given to God, the source of all knowledge, by this abundant grace this work has come productionreal.

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Abbreviations

AHM	Ammonium Hepta Molybdate
IEP	Iso Electrical Point
HDS	Hydrodesulfurization
SCR	Selective Catalytic Reduction
XRD	X-ray Powder Diffractometry
FTIR	Fourier Transform Infra red Spectroscopy
LRS	Laser Raman Spectroscopy
PWHM	Peak Width at Half Maximum
Ei	Initial Electrode Potential
ASTM	American Society for Testing and Materials
JCPDS	Joint Committee on Powder Diffraction Standards
USA	United States of America

Abstract

Alumina and silica supported molybdenum oxide catalysts at different loading in the range 3 – 20 wt % of molybdena were prepared by wet impregnation and calcinated at 823K for 3 h in air . An analogous series of catalysts were sulfated by impregnation with up to 6 wt % SO_4^{2-} from aqueous solutions of $(\text{NH}_4)_2\text{SO}_4$ and then calcined in a similar fashion. The supports (silica and alumina) were calcined at 823 K for 3 h in air. Unsupported molybedna catalysts were prepared by calcinations of ammonium hepta molybedate at 823 K for 3 h. Supports, un supported, supported and modified sulfated catalysts thus obtained were characterized by X–ray diffractometry, Ex–situ fourier transform transmission infrared Spectroscopy, Laser Raman Spectroscopy and the acidity was probed by potentiometric titration with n-butyl amine.

The results suggest that molybdenum oxide at low loading levels show high dispersion on alumina surfaces. Whereas, at high loading levels the formation of MoO_3 bulk phase on alumina increased. In the presence of molybdenum oxide loadings up to 20 wt % exist as a bulk phase in three-dimensional structures on the surface of silica are XRD and laser Raman detectable. The presence of sulfate ions improve of the three-dimensional molybdenum oxide rather than the two-

dimensional one on the surface of alumina, and silica supports. The surface acidity of alumina and silica increased with increasing the loading level of molybdena. The acidity of sulfated catalysts is higher than sulfated free catalysts.

الخواص الحمضية والقاعدية السطحية لحفازات

أكسيد الموليبدنوم المدعمة

من أهم المحفزات حيث استخدمت في الكيمياء البترولية والتخليقات العضوية لسنوات عديدة.

استخدام المحفزات الحامضية الصلبة يوفر مزايا عديدة مقارنة مع استخدام المحفزات الحامضية السائلة ومن هذه المميزات :

(1) لأوعية التفاعل والمفاعلات .
(2) الانتقائية . (3) المحفزات الحامضية الصلبة لا تسبب تآكل

(4) لمحفزات الغير متجانسه لها تطبيقات واسعة نها Hydrocarbon isomerasion

تحضير محفزات أكسيد الموليبدنوم حيث توضح

(dispersing) عامل النشط على المدعم للحصول على نشاطية عالية.

الخطوة الاولى يتم تبليل المدعم الصلب بمحلول مكون من أملاح المادة الاولي

الأخرى هي تجفيف التحميص (calcination) التنشيط. هذا النوع من التحضير يعتمد على

العوامل القياسية مثل طبيعة مستوى التحميل من العامل النشط، ودرجة الحرارة

تم تحضير أكسيد الموليبدنوم غير مدعم ج امونيوم الموليبدنوم السباعي

في جو ثابت من الهواء في درجة 823 3 ساعات . وقد تم اختيار درجة

حرارة التكليل (calcination) على أساس نتائج التحليل الحراري .

كسيد المدعم من قبل الألومينا والسليكا تم تحضيرها عن طريق تشريب

(impregnation) المساحيق المدعمة بمحلول مائي لملح امونيوم الموليبدنوم السباعي بنسب

وزنية من 3-20% تجفيف و 823 للأكاسيد

المدعمة المحورة بالكبريتات تم تحضيرها بنفس الطريقة.

الباحث العديد من وسائل التقنية الفيزيوكيميائية الحديثة المختلفة من

هذه التقنيات حيود الأشعة السينية (XRD) ومطياف امتصاص وتشتت الأشعة

(FTIREx- situ spectroscopy) . يزرر امان الطيف (Laser raman)

والحامضية للسطح بطريقة potentiometric titration with n- butyl amine

تتبع التغيرات السطحية الناجمة عن المعالجات المختلفة لهذه الحفازات ومنها وضحت

الدراسات الفيزيوكيميائية النتائج التالية:

1-أكسيد الموليبدنيوم الغير مدعم متحصل عليه من كلسنة ammonium heptamolybdate 823K 3 ساعات في جو مفرغ من الهواء والموليبدنيوم المدعم ومحفزات الكبريتات متحصل عليها من كلسنة عند 823K لمدة ساعتين.

2- XRD من الألومينا المدعمة توضح زيادة في particle size crystalline زيادة مستوى التحميل لأكسيد الموليبدنيوم و شوهد تأثير مشابه في حالة الألومينا المدعمة مع كبريتات (xMoAIS) يسلك زيادة حجم الجسيمات مع زيادة مستوى التحميل من أكسيد الموليبدنيوم.

3- XRD من السيليكا المدعمة توضح ارتفاع الانتشار عند التحميل المنخفض (3,5wt%) وعند اعلى تحميل نلاحظ زيادة في particle size crystalline مع زيادة التحميل و في المحفزات المدعمة مع الكبريتات (xMoSiS) نفس التأثير.

4- نتائج التحليل الطيفي FTIR (dispersion) أكسيد الموليبدنيوم المحور بالكبريتات (xMoAIS) هو أكبر من بل الألومينا (xMoAl).

5- نتائج التحليل الطيفي FTIR (dispersion) أكسيد الموليبدنيوم المحور بالكبريتات (xMoSiS) هو أكبر من قبل السيليكا (xMoSi).

6 - اظهرت ليزر رامان ارتباط عالي وتكوين كثافة عالية لأكسيد الموليبدنيوم المحور بالكبريتات (xMoAIS) اكسيد الموليبدنيوم المدعم من قبل الألومينا (xMoAl).

7 - اظهرت ليزر رامان عالية (sharp) تزيد مع زيادة التحميل م (xMoSiS, xMoSi) دليل لتكوين crystallineMoO₃.

8- potentiometric titration of n- butyl amin بتقدير ووصف حامضية لموليبدنيوم المدعمة ومحفزات الكبريتات ووضحت لنا النتائج التالية :

1- الحامضية للسطح تزداد مع زيادة مستوى التحميل MoO₃ .

2- مضية السطح AIMo على من حامضية SiMo الحامضية للا لومينا Ei= 12 mV بينما قوة سطح الحامضية للسيليكا Ei= -10 mV .

3- رينات تزيد من حامضية السطح وقوته.

Summary

Solid acids have been extensively used as catalysts carriers in petroleum chemistry and organic syntheses for many years. Use of solid acid catalysts provides the following several advantages compared with use of liquid acid catalysts:

- 1) High catalytic activity and selectivity are frequently observed.
- 2) Solid acid catalysts do not cause the corrosion of vessels or reactors.
- 3) Increasing applications are found in heterogeneous catalysis, for wide variety of applications such as hydrocarbon isomerisation.

Preparation of supported molybdenum oxide catalysts by impregnating supports exhibits dispersion of an active agent on a support to obtain product with high activity. The first step is wetting the solid support with a solution of precursor salts. The other steps are drying, washing, calcinations, and activation. Such preparation depends on the same parameters such as nature of support, the loading level of active phase, and temperature by the use of the same technique.

In support material, the interaction is strongly dependent on the precursor, the preparation method, thermal treatment (drying, calcination), metal content, and activation conditions. All these parameters have clear influence on the particle size of the catalyst. For unsupported molybdenum oxide obtained by thermal decomposition of ammonium hepta-molybdate at 823 K in a static atmosphere of air

for 3h. The calcination temperature was chosen on the basis of thermal analysis results.

Supported molybdenum catalysts on alumina and silica were obtained by calcination at 823 K for 2h.

Alumina and silica supported molybdenum oxide as well as their sulfated counter parts, using $(\text{NH}_4)_2\text{SO}_4$ were prepared by impregnation and calcinations at 823K for 3 h.

To accomplish such aim a number of techniques have been used to study the structure of the prepared catalysts via. (XRD), (Ex-FTIR), Laser Raman spectroscopy, and the acidity of the surface was measured by potentiometric titration with n-butyl amine.

General conclusions

1- Unsupported molybdenum oxide (MoO_3) were obtained by calcination of the ammonium hepta molybdate at 823K for 3 h in a

static atmosphere. The final catalysts of supported molybdena and sulfated catalysts were obtained by calcinations at 823 K for 2 h.

2- XRD results of alumina supported molybdenum oxide exhibits the crystallinity of catalysts and particle size increase with increasing the loading level of molybdenum oxide. The similar effect was observed in the case of sulfated alumina supported molybdenum oxide (xMoAlS).

3- XRD results of silica supported molybdenum oxide exhibits high dispersion at low loading level (3,5wt%) whereas at higher loading level the crystallinity and particle size increased with increasing loading level of molybdenum oxide. Sulfate catalysts of (xMoSi) show the similar effect.

4- FTIR spectroscopic results reveal that the dispersion capacity of molybdenum oxide from MoAlS is larger than the molybdenum oxide from MoAl.

5- FTIR spectra of MoSi and MoSiS catalysts show the dispersion capacity of molybdenum oxide from MoSiS is bigger than the molybdenum oxide from MoSi.

6- The results obtained from Laser Raman Spectroscopy of xMoAl catalysts indicate that the formation of molybdenum oxide of higher bond order in xMoAlS catalysts than in xMoAl catalysts.

7- The results obtained from Laser Raman Spectroscopy of xMoSi catalysts indicated the higher intensity absorption (sharp) increase with increasing of loading level of MO_3 (xMoSi and xMoSiS) indicate the formation of crystalline MO_3 .

8- Potentiometric titration of n-butyl amine probe molecule provide an extremely useful determination of surface acid characteristics of supported molybdena and sulfated catalysts and exhibited the following results:

a- The total surface acidity and strength of tested catalysts increased with an increase in loading levels of MoO_3 .

b- The surface acidity of alumina supported molybdena catalysts were higher than the surface acidity of silica supported molybdena catalysts. Because surface of alumina strong acid sites $E_i=12$ mV and surface of silica medium acid sites $E_i= -10$ mV.

c –Sulfation catalysts enhances the surface acidity and increases the strength of acidity.

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المدعمة المحورة بالكبريتات تم تحضيرها بنفس الطريقة.

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4- أظهرت نتائج التحليل الطيفي FTIR (dispersion) أكسيد الموليبيدينوم MoSiS هو أكبر من ذلك من أكسيد الموليبيدينوم من MoSi

5 - ليزر رامان النتائج أشارت MoAL تكوين أكسيد الموليبيدينوم xMoAIS اعلى مما كانت عليه في xMoAl .

6 - يزر رامان مع وجود اختلافات في كثافة امتصاص حيث ظهر زيادة في (sharp) مع زيادة التحميل م (xMoSiS,xMoSi) دليل لتكوين تشكيل crystallineMoO₃.

7- الحامضية للسطح تزداد مع زيادة مستوى التحميل ل MoO₃.

8- حامضية السطح AIMo اعلى من حامضية السطح SiMo..

9-المحفزات المدعمة مع الكبريتات تزيد من حامضية السطح وقوته.

10- potentiometric titration of n- butyl amine تفيدنا بتقدير ووصف حامضية السطح للموليبيدينوم المدعمة ومحفزات الكبريتات.

Chapter I

Introduction

1.1 Introduction

The concept of catalysis as a method of controlling the rate and direction of a chemical reaction has captured the imagination of scientists since Berzelius in 1835 coordinated a number of disparate observations on chemical transformation by attributing them to “catalytic force”. The term catalysis refers to the “decomposition of bodies” by this force. At about the same time Mitscherlich [1] introduced the term contact action for a similar group of phenomena. Ideas of what constitutes a catalyst and the mechanism of catalytic activity have since undergone continuous refinement by enormous industrial importance of catalyst as illustrated by a variety of catalytic processes characteristic of modern petroleum refineries and of the chemical industries. Most of these processes involve solid catalysts. In practice catalysis is primarily a technology that draws on many fields such as organic chemistry, surface chemistry, solid state and physical metallurgy. A basic concept is that a catalyzed reaction involves the transitory adsorption (always chemisorption)

of one or more of the reactants onto the surface of the catalyst, rearrangement of bonding and desorption of products.

Definition of catalyst : A catalyst is a substance that increases the rate of reaction toward equilibrium without being appreciably consumed in the process. Catalyst have strong impact on the selectivity of chemical reaction. This means that completely different products can be obtained from a given starting material by using different catalyst systems [2].

1.1.1 Heterogeneous catalysis

Catalysis is homogeneous when the catalyst is soluble in the reaction medium and heterogeneous when the catalyst is existing in a phase distinctly different from the phase of the reaction medium. In most instances of heterogeneous catalysis, the catalyst is a solid that is brought into contact with gas or liquid reactants to bring about a transformation. From this comes the expression "contact catalysis" frequently used to designate heterogeneous catalysis. Those transformations catalyzed by enzymes have a special classification independent of their homogeneous or heterogeneous nature.

Heterogeneous catalysis is especially important to modern industry. By 1962, for example, heterogeneous catalysts already accounted for 18 % of the manufactured products in the USA and that percentage has continued to increase. Thus in the manufacturing of ammonia, the most important inorganic chemical, 60 million tons of ammonia are produced annually from 23 million tons of hydrocarbons, 54 million tons of water and 50 million tons of nitrogen from the air through seven or eight successive unit processes, of which only one, the adsorption of CO_2 does not involve heterogeneous catalysis. Furthermore, over 80 % of the molecules in the millions of tons of crude oil processed annually throughout the world come into contact with a solid catalyst at one time or another in their trips through refineries. Finally, catalysts offer the most promising means of reducing the by product pollution resulting from modern life with catalytic mufflers, example, reducing the CO, hydrocarbons and nitrogen oxides in automotive exhausts by 80 %.

1.1.2 Catalysis impregnated supports

The preparation of catalysts by impregnating supports aligns all the unit operations toward dispersing an active agent on a support that may be inert or catalytically active. The first operation of wetting the solid support with a solution of precursor salt is made by particular character. The other operations, drying, washing, calcinations, activation, are ruled by the same laws, depend on the same parameters, and use the same equipment. The active agent never introduced into a porous support in its final form but it passes by the intermediary of a precursor, the choice of which holds great importance for the quality of the final deposit, its structure, its grain size, its distribution as a function of the diameter of the granule. Two types of impregnation can be considered depending on whether or not an interaction exists between the support and the precursors at the moment.

1.1.2.1 Impregnation with no interaction between support and catalysts

If the support does not have its own catalytic activity, its role is to suitably present the catalytic agents. It gives the finished catalyst form, its texture and its mechanical resistance. Here again, the choice of precursors is important, they must be sufficiently soluble in the impregnating solvent, which is usually water and they must provide the final preparation with the best catalyst possible.

1.1.2.1.1 Wetting a support with precursor solution

Two methods of contacting may be distinguished, depending on the volume of solution:

1- Wet impregnation

In this method an excess of solution is used. After a certain time, the solid is separated and the excess solvent is removed by drying. The composition of the batch solution will change and release of debris can form mud. This makes it difficult to completely use the solution. The heat of adsorption is released in a short time.

2- Incipient wetness impregnation

The volume of the solution of appropriate concentration is equal or slightly less than the pore volume of the support. Control of the operation must be precise and repeated applications of the solution may be necessary. The maximum loading is limited by the precursor in the solution. The concentration profile of the impregnated compound depends on the mass transfer condition within the pores during impregnation and drying. Advantages of impregnation method include it is simplicity, rapidity, capability for depositing the precursor at high metal loading [3].

1.1.2.1.2 Drying impregnated supports

Drying: The water and other liquids entrapped within the pores of gel structure are removed during this stage. Drying is performed at temperature of about 100 to 200 °C till constant weight [3].

1.1.2.1.3 Calcining impregnated supports

This may have several purposes. One is to eliminate extraneous material such as binders and die lubricants, as well as volatile and unstable anions and cations, which are not desired in final catalyst. Second, a

substantially elevated temperature is usually needed to increase the strength of the final pellet by causing incipient sintering. Excessive sintering will reduce the catalyst activity by reducing surface area.

Hence conversions to the oxide form. The catalyst should be heated under controlled conditions to a temperature at least as high as will be encountered in the plant reactor to remove water, the oxide or metal compound that is the active catalyst, may form with carrier or may dissolve in the carrier to form the solid solution [1].

1.1.3 Properties and characteristics of industrial catalysts

For catalyst design purposes it is first necessary to translate catalyst performance parameters into a physical picture of catalyst structure. Different performance parameters can give rise to different structural features and so a compromise is generally required. For example it is commonly found in industrial applications that initial catalyst activity may be sacrificed in favor of improved catalyst stability, since the activity is lowered one operating is prolonged.

life time for which the catalyst keeps a sufficient level activity or selectivity. First, we should therefore discuss some of the relationships between the catalyst performance parameters and physical structure.

Activity: The activity of catalyst refers to the rate at which it causes the reaction to proceed to chemical equilibrium [1]. The activity arises from maximizing both the dispersion and availability of active catalytic material [4].

Stability: By stability we refer to the loss in activity with time. This is due to one or several of four main causes; fouling of the active surface with in volatile reaction by products, sintering or crystal growth of the active material, poisoning of the active surface by feed impurities, and blockage of the support pore structure.

Sintering: Sintering of heterogeneous catalysts is often referred to as the loss of catalytic surface area due to growth of large particles from the smaller particles. Sintering is complex and may be influenced by many parameters such as sintering time, chemical environment, catalyst composition, structure and support morphology.

Sintering is the reason for loss of activity for many industrial catalyst systems[5].

Fouling: Fouling of the active surface by reaction by product is a real problem, which typically can be partially met by selective poisoning of the active ingredient. In a general sense the use of bimetallic supported catalysts would also commonly fall into this category, since selective poisoning implies a close control over the ratio of poison to active material. In this case a severe constraint is imposed upon catalyst design in that both active and moderating components should ideally be in a constant ratio throughout the catalyst support [4].

Poisoning: Poisoning of the catalyst by impurities introduced with the reactants can often be minimized by placing the active material deep within the catalyst support structure, and since most catalyst supports are also good absorbents, poisons frequently can be selectively removed by such absorption before reaching the active surface. An example would be the removal of traces of lead from a car exhaust by the surface of catalyst support. A catalyst design modification of this technique would be the deposition of a poison-resistant catalyst.

Finally, blockage of the support pore structure is critically dependent upon the pore size distribution of the support. Normally a correct balance of large and small pores is required; the former to aid reactant transport and the latter to provide the large surface necessary for the optimal dispersion of the active components. Whereas one might intuitively expect that small pores would block more readily, an important exception has only recently been recognized [4].

Selectivity: The selectivity of a catalyst is a measure of the extent to which the catalyst accelerates the reaction to form one or more of desired products, which are usually intermediates, instead of those formed by reaction to the overall state of lowest free energy. The selectivity usually varies with pressure, temperature, reactant composition and extent of conversion catalyst. For precision one should refer to the selectivity of catalyzed reaction under specified conditions. The selectivity is determined in the first instance by the functionality of the catalyst, but also in part by thermodynamic equilibrium considerations. Thus, a certain un desired product may be largely avoided if it is possible to operate under conditions in which the equilibrium concentration of the product is negligible.

Selectivity is defined as the percentage of the consumed reactant that forms the desired product[1].

1.2 The ideal catalyst and the optimum catalyst

In addition to the fundamental properties that come from the very definition of a catalyst, i.e., activity, selectivity and stability, industrial applications require that a catalyst be regenerable, reproducible, mechanically stable, original, economical and possess suitable morphological characteristics.

All of the above properties and characteristics are not independent; when one of them is changed for improvement, the others are also modified and they are not necessarily in the direction of an overall improvement. As a result, industrial catalysts are never ideal. Fortunately, however, the ideal is not altogether indispensable. Certain properties, such as activity and reproducibility are always necessary, but selectivity, for example has hardly any meaning in reactions like ammonia synthesis and the same holds true for thermal conductivity in an isothermal reactions. Stability is always of interest but becomes less important in processes that include continuous catalysis regeneration,

when it is regenerability must be optimized. Furthermore, originality can be of secondary importance for certain manufacturing situations such as those relevant to national defense.

The goal, therefore, is not an ideal catalyst but the optimum, which may be defined by economic feasibility studies concerning not only the catalyst but also the rest of the process. And when the catalytic process is established and the catalyst in question must compete as a replacement, the replacement catalyst's cost and method of manufacture predominate in arriving at the optimum formula.

Depending on the use and the economic competition, therefore, the optimization studies establish consecution among the properties and characteristics of a catalyst; and knowledge of this consecution helps to better the efforts of the research team responsible for developing the catalyst and its process.

1.3 Types of acid and base sites on metal oxide surface

This research mostly deals with oxide materials that have industrial application like catalytic cracking and isomerisation of hydrocarbons, alkylation of paraffins, aromatics, dehydration, and dehydrogenation [6-9].

Acidity and basicity depend on the nature of the oxide, the charge and radius of metal ions, the character of the metal–oxygen bonds as influenced by coordination numbers of the anions and cations and the filling of the metal d-orbitals [10]. In general terms, a solid acid may be understood as a solid on which the color of a basic indicator changes or as a solid on which a base is chemically adsorbed more strictly following both the Brønsted and Lewis definitions. A solid acid shows a tendency to donate a proton or accept an electron pair whereas a solid base tends to accept a proton or to donate an electron pair.

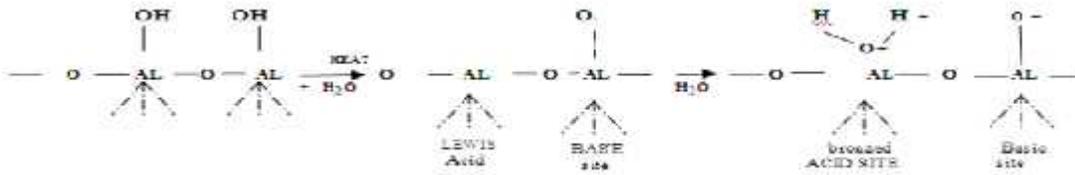
The acid strength of a solid is defined as the ability of the surface to convert an adsorbed neutral base into its conjugate acid. If the reaction proceeds by means of proton transfer from the surface to the adsorbate, the acid strength is expressed by the Hammett acidity function H_0 .

[11,12]. Also, the color of suitable indicators adsorbed on a surface will give a measure of its acid strength. The amine titration method gives the sum of the amounts of both Brønsted and Lewis acid since both electron pair acceptors and proton donors on the surface will react with either the electron pair($\overset{\cdot\cdot}{\text{N}}=$) of the indicator or with the amine (N:) to form a coordination bond.

Acid strength of the surface of acid sites of metal oxides was measured by adsorption of basic gas molecules. When gaseous bases are adsorbed on acid sites, a base adsorbed strong acid site is more stable than one adsorbed on weak acid site and is difficult to adsorb. The amount of a gaseous base which a solid can absorb chemically from the gaseous phase is a measure of the amount of acid on its surface.

Catalytic activity has been used as a measure of surface acidity and acid strength [13]. The activity for the dehydration of isopropyl alcohol or the iso-merization of butene in the presence of an excess of air is reported to be a good measure of acidity of some oxidation catalysts.

Mechanism of the generation of acidity on the surface of alumina



The Lewis acid site is visualized as an incompletely coordinated aluminum atom formed by dehydration and the weak Brønsted site as a Lewis site which has adsorbed moisture. Calcined alumina does not exhibit any basic property by the indicator method but does when it is exposed to moisture [14]. The effect of moisture may be interpreted as follows: The electronegativity of the Lewis site is weakened by adsorption of water, since an electron pair from the oxygen atom of the water molecule is donated to the Lewis site. Thus, the negative charge of oxygen at the basic site becomes higher when water is adsorbed on a Lewis site due to a weaker inductive effect of the aluminum atom.

1.4 Solid acid catalysts and catalysis

Solid acids have been extensively used as catalysts or catalyst carriers in petroleum chemistry and organic syntheses for many years. Use of solid acid catalysts provides the following several advantages compared with use of liquid acid catalysts:

- 1) High catalytic activity and selectivity are frequently observed.
- 2) Solid acid catalysts do not corrode reaction vessels or reactors.
- 3) Repeated use of solid acid catalysts is possible.
- 4) Separation of a solid acid catalyst from a reaction mixture is easy.
- 5) There is no problem for the disposal of used solid acid catalysts; though disposal of liquid catalysts requires much money for treatment to make it environmentally safe [15].

More recently, increasing applications for solid acids are being found in heterogeneous catalysis, for a wide variety of applications such as hydrocarbon isomerisation, cracking, hydrocracking, dehydration and alkylation. Generally used solid acids catalysts for these reactions include

zeolites [16], modified clays (acid treated and pillared clays) and metal oxide based systems.

The definition of solid super acid, according to Gillespie [17] is any solid acid having acidity stronger than that 100% sulphuric acid, i.e. $H_0 < -12$ [18,19], where H_0 is Hammett function. Recently various kinds of solid super acids have been developed, *via* metal oxides, mixed oxides, graphite, metal salts.

Metal oxides and mixed oxides containing small amounts of sulphate ion, zeolites, heteropoly acids and mixed oxides (WO_3/ZrO_2 , MoO_3/ZrO_2 , WO_3/SnO_2 , etc.). Among these different solid super acids, systems in the first group have a possibility of leaching or evaporating of halogen compounds, due to which these systems are proven to be environmentally undesirable as catalysts [20-22]. Recent studies revealed that sulfate modified metal oxides are promising catalysts for many industrially important reactions.

In sulfate treated metal oxides the super acidic sites are created only when the sulfate ions are doped on amorphous oxides followed by calcination to crystallisation. The sulfate ions can be introduced on the metal surface by using, different sulfating agents like H_2SO_4 , $(NH_4)_2SO_4$,

SO₂, SO₃ and H₂S. Among these H₂SO₄ and (NH₄)₂SO₄ are most commonly used for sulfation. Sulfated metal oxides are prepared by impregnating hydrous metal oxide with sulfating solution for a fixed time, followed either by evaporation of solution to dryness, or filtering off the excess solution. It was pointed out that existence of covalent S=O in sulfur complexes formed on the metal oxide surface is necessary for the generation of high acidity [23-25].

Yamaguchi *et al.*, suggest that strong surface acidity generation on sulfate modification can be attributed to the electron withdrawing effect of sulfate group, which lead to coordinatively unsaturated and electron deficient metal centres that behave as strong Lewis acid sites [26,27]. It was shown that in the sulfate modified metal oxides the sulfate groups are described as covalently bonded. Besides the inductive effect of the sulfate group, three other factors *via.* valency, electronegativity and co-ordination number of the metal cation of metal oxide are found to affect the acidic strength of sulfate promoted metal oxides [27].

1.5 Catalyst case studies

1.5.1 Pure alumina:

Alumina is the most widely used support because it is inexpensive, structurally stable and because it can be prepared with a wide variety of pore sizes and pore size distributions. Commercial materials are available with surface areas in the range of 100-600m²/g.

The most important aluminas for use as carriers are the transition aluminas. γ -Al₂O₃ is of great interest since it has a high area and is relatively stable over the temperature range of interest for most catalytic reactions [1]. Thus, it is the most widely used as a support in several chemical industries [28,29]. The important solid used in the pure state or mixed with other oxides in catalysis, glass manufactures, ceramic and refractors [30]. Many authors [31] have studied the combination of alkali metals with alumina, there are many reports refer to the increase in catalytic activity of transition metal oxides loaded onto an alumina support [32,33].

1.5.2 Pure Silica:

A solid acid catalyst such as silica is widely used in many kinds of chemical reaction [34]. Silica has been extensively used as a catalyst carrier and as an adsorbing agent due to its high surface area and thermal stability to heating over wide range of temperatures [35] and is known to have weak acid sites as $H_o + 3.3$.

Silica is produced by the reaction of an alkali meta silicate with an acid. This done by bubbling carbon dioxide through a dilute solution of sodium meta silicate (water glass) or by the addition of dilute acid to pH of about 7. Heating the gel to about 100 °C removes only the physically adsorbed water giving the material commonly referred to as silica gel. Heating to 500 °C decreases the surface hydroxide concentration to about 20-30 % of the present on the 200 °C heated material.

Silica is more resistant to acidic media than alumina but it is adversely affected by a strongly alkaline environment [1].

1.5.3 Molybdenum oxide:

Molybdena catalysts have been used for quite a long time. The term molybdena is used here to denote a composite catalyst consisting of

molybdenum oxide supported on an activated support, commonly alumina.

Supported molybdenum oxide catalysts have been extensively studied because of their numerous catalytic applications in the petroleum, chemical and pollution control industries[36,37].

These catalysts are prepared by deposition of catalytically active molybdenum oxide on the surface of an oxide support (Al_2O_3 , ZrO_2 , SiO_2 , MgO). Catalysts based on molybdenum oxide are widely used in the selective alkene oxidation reaction.

Mo-Mg-O catalysts exhibited very high alkene selectivity for the oxidative dehydrogenation of alkene[38,39].

Many investigations showed that molybdenum oxide could be readily supported over oxides like SnO_2 , Fe_2O_3 , TiO_2 , Al_2O_3 [40,41].

All these systems showed high activity for oxidation of methanol.

Molybdena supported silica catalysts are widely used in a number of reaction such as propene metathesis, propene oxidation. The activity increase when MoO_3 is supported on TiO_2 , Al_2O_3 , SiO_2 [42].

1.5.4 Alumina-supported molybdenum oxide catalysts

Transition metal oxides supported on oxide carriers are used mainly in the field of selective oxidation reactions [43]. Supported molybdenum oxide catalysts have been extensively studied because of their numerous catalytic applications in petroleum, chemical and pollution control industries.

These catalysts are usually prepared by deposition of catalytically active molybdenum oxide component on the surface of an oxide support (TiO_2 , Al_2O_3 , ZrO_2 , SiO_2 and MgO) [36]. The high flexibility of supported Mo-catalysts is related to the different molecular structures that molybdenum species can simultaneously possess when supported and to the ability of Mo atom to assume various oxidation states, depending on the pre-treatment and / or the reaction atmosphere. Earlier Al_2O_3 , TiO_2 , SiO_2 and MgO were used as supports for molybdenum oxide by various authors studied their various physico-chemical and catalytic properties [37,44-48]. It is a well-known catalysts based on multi component oxides exhibit a better performance rather than when component oxide were used separately [49]. Molybdenum supported on

oxides such as γ -alumina, silica and alumina-silica is widely used in such petroleum refining processes as Hydro treating or hydro cracking [50].

Supported molybdenum oxide catalysts have been studied for numerous reactions like partial oxidation of alcohols [50-54], alkanes [55,56] and the selective catalytic reduction (SCR) of nitric oxide [57,58].

Conventionally, hydrated ammonium hepta molybdate and impregnation are chosen as Mo-precursor and preparation method, respectively. Because of the acidic character of the aqueous molybdate solutions (pH value from 5 to 6) often used in the impregnations, the poly molybdate anions can bound to the support surface and can polymerize/de polymerize during calcinations[59-61] causing alteration of molybdenum aggregation.

Alumina is a very commonly used support for molybdenum. In recent years, alumina supported catalysts have attracted considerable attention due to their industrial and technological application. Many studies devoted for understanding the nature of interaction of molybdenum species with alumina support [62-64].

The molybdena has a very high dispersion in $\text{MoO}_3 / \text{Al}_2\text{O}_3$ catalysts. The molybdena forms monolayer on Al_2O_3 surface. During the impregnation and calcination steps, the molybdena is fixed on Al-OH groups forming Al-O-Mo bonds [44,65]. In the presence of low amounts of MoO_3 (4wt.%) the formation isolated, tetrahedrally coordinated $[\text{MoO}_4]$ species is preferred. High molybdena loadings or thermal treatment favours the formation of polymeric molybdate structures in which the Mo (VI) ion is octahedrally coordinated. Crystalline molybdena is usually observed when the molybdena amounts are more than 15Wt % and $\text{Al}_2(\text{MoO}_4)_3$ formation has been found at calcination temperatures at about 650 °C [66]. Much stronger molybdena-support interaction in the Al_2O_3 than in the SiO_2 system [67-72].

Molybdena-alumina catalysts are used industrially in both reduced (oxidic) and sulfide forms. These catalysts are active for various reactions, such as metathesis of propene[73,74], polymerization of ethane[75], hydrogenation of propane [76] and hydro-desulfurization (HDS) of thiophenic compounds [77-82].

1.5.5 Silica supported molybdenum oxide catalyst

Previous studies have shown that catalytic properties may depend on the molybdenum oxide structure as well as the choice of the support material [49,83-85]. For a detailed understanding of supported molybdenum oxide catalysts one strategy may be to separate the effects of molybdenum oxide structure from those of support material. Silica seems to be the material of choice considering its weak interaction with molybdenum oxide. The relatively inert of silica the detailed state of the deposited supported molybdenum oxide may still depend on variety of parameter such as silica material and its pre-treatment, the synthesis procedure. For highly dispersed molybdenum oxide supported on silica a hydrated and a dehydrated state have to be distinguished.

The hydrated state is present when the sample is exposed to moisture under ambient condition. If the sample is treated in dry synthetic air at elevated temperature (350°C), the molybdenum oxide is converted into a dehydrated state [86]. A recent study by Leyrer et al. [87] on MoO_3 on Al_2O_3 and on SiO_2 showed that spreading occurs on

alumina surfaces over macroscopic distances but spreading did not take place on silica.

Generally, it has been found that alumina-supported MoO_3 catalysts of a high dispersion can be obtained up to high loadings [88,89,61], but that the formation of MoO_3 crystallites occurs at significantly lower loadings in SiO_2 supported catalysts. The difference in interaction between the metal precursor (usually from ammonium hepta molybdate (AHM)), dissolved in water and the alumina and silica supports brings about the difference in dispersion. The interaction between the precursor and the support depends on the sign of the surface charge of the support and of the dissolved complexes of precursor. Accordingly, SiO_2 which have (iso electrical point (IEP) ~ 2) behaves like an acid support as compared to Al_2O_3 (IEP ~ 7). Iso electrical point (IEP) of solid can be defined as the pH value at which its zeta potential is zero. The reason that there is an IEP for the oxide surfaces is that the partial charge is determined by a competition between two reactions: one that makes the surface positive and one that makes it negative ($\text{MOH} + \text{H}^+ \rightarrow \text{MOH}_2^+$), ($\text{MOH} + \text{OH}^- \rightarrow \text{MO}^- + \text{H}_2\text{O}$). At low pH values the first reaction dominates and the surface is positive while at high pH the second

reaction prevails and the surface becomes negative [90]. At the pH of an AHM solution (~ 5.5), the interaction between the anionic hepta molybdate clusters and the positively charged Al_2O_3 - surface is better than between the clusters and the SiO_2 -surface, which is negatively charged. This leads to spreading of the molybdena phase over Al_2O_3 . Because of the lack of interaction between hepta molybdate and SiO_2 formation of MoO_3 - crystallites in $\text{MoO}_3/\text{SiO}_2$ catalyst occurs at low loading, as frequently reported [88,89,61].

During drying and calcination, these crystallites tend to further coalescence due to the high solubility of hexavalent molybdenum species in water, and volatility of $\text{MoO}_2(\text{OH})_2$. Consequently, the dispersion of silica –supported catalysts is not very stable and usually these catalysts exhibit bulk MoO_3 features in catalytic test reaction. A number of authors disclosed influence of water on dispersion of supported molybdenum oxide [85-87, 61]. It is generally accepted that water promotes the dispersion of molybdena on surface of Al_2O_3 . Various mechanisms for this process have been proposed [86].

1.6 Objects of investigation

Supported molybdenum oxide catalysts are widely used for Hydrodesulphurization, hydrodenitrogenation, hydrodemetallation and which, reportedly, may be of use in the hydrogenation of coal to crude oil. The molybdenum species in such systems may be oxide- or sulfide-like in nature. Considerable work has already been carried out on the characterization of molybdena species supported on a variety of materials. However, there is still considerable scope for the determination of the physicochemical properties, and of such parameters as activity, selectivity and regeneration of these systems, and on how these properties are affected by the preparative conditions, the nature of the support and its pore structure other parameters such as the loading level of the active component and the nature and concentration of promoters will be of importance. Also the local structures assumed by the molybdenum-oxygen surface species play a decisive role in determining the catalytic activity and selectivity of calcined catalysts. In order to accomplish these objectives the following steps are carried out:

1. Preparation of supported molybdena at various loading levels, using the two different supports (SiO_2 and Al_2O_3), the impregnation method, and subsequent drying at $120\text{ }^\circ\text{C}$ and calcination at $600\text{ }^\circ\text{C}$.
2. Characterization of surface structures assumed by the supported molybdena species by means ex-situ FTIR, Laser Raman Spectroscopy and XRD.

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Chapter II
Preparation and
physico-chemical
characterization of
catalysts

Preparation of catalysts

2.1. Materials.

2.1.1 Parent compound.

2.1.1.1 Ammonium hepta molybdate $(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$, high purity, Merck, was used as precursor for supported and unsupported MoO_x catalysts.

2.1.2 Support materials.

2.1.2.1 Alumina

High surface area ($100 \pm 10 \text{ m}^2/\text{g}$) aluminum oxide of Degussa AG (Frankfurt, Germany) was used as carrier for supported catalysts. The material bulk was shown by x-ray diffractometry to assume a crystalline structure largely similar to that of γ -modification (ASTM Card No. 10-425).

2.1.2.2 Silica

Silica ($200 \pm 10 \text{ m}^2/\text{g}$), the other catalyst support material, was also a Degussa product. It is commercially known as Aerosil-200. Also it is amorphous to x-ray diffractometry.

2.1.3 Unsupported molybdenum oxide.

Unsupported molybdenum oxide was obtained by calcinations of ammonium hepta molybdate (AHM) at 823 K in a static atmosphere of air for 3 h.

2.1.4 Supported molybdenum oxide.

Supported molybdenum oxide samples were prepared by wet impregnation method [1], using alumina and silica as support materials and aqueous solution of AHM as the impregnating solution.

The impregnation solution was prepared by dissolving a calculated amount of the precursors AHM of the required loads 3, 5, 10, 15 and 20 wt% MoO₃ 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 120 C° 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 823K for 3 h in air of the corresponding impregnated supports. The resulting catalysts were kept dry on CaCl₂, till further use. For convenience, the

various catalysts are denoted below by 3MoAl indicates the 3 wt%-MoO₃ loaded alumina supported molybdenum oxide catalyst, Where as 3MoSi indicates the 3 wt%-MoO₃ loaded silica supported molybdenum oxide catalyst.

Sulfated catalysts were obtained from alumina and silica supported MoO₃ 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 (NH₄)₂SO₄ 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 calcinations was approximately 6 wt % SO₄.

2.2 Physicochemical characterization of catalysts.

2.2.1 X-ray powder diffractometry (XRD)

XRD is a technique used for the identification of the bulk structure of macro-crystalline materials, which is used on measurement of structure-sensitive high energy X-ray radiation. It involves characterization of materials using data that are dependent on the atomic organization in crystal lattices containing planes of high atomic density. A monochromatic beam of high-energy X-ray photons will be scattered by these atomic arrays. Consequently, a diffracted X-ray line (or peak) will occur for each unique set of planes in the lattice [2].

The inter planner spacing d_{hkl} (Miller indices) in Å or nm, is related to the diffraction angle (2θ) by Bragg's equations [3]:

$$n\lambda = 2d \sin \theta \dots\dots\dots(1)$$

X-ray powder diffractograms were recorded, using Ni-filtered CuK - radiation ($\lambda = 1.54056 \text{ \AA}$); on a JSX - 60 PA Jeol X-ray spectrometer. The generator at 35 KV and 20 mA, and the diffractometer at 2θ diverging and receiving slits and at a scan rate of 20 mm/ min. The sample ground to a particle size less than 44 μ and packed into the wall of a sample holder, and then mounted in a horizontal position. Diffraction

patterns (I/I_0 vis. d-spacing (\AA) derived from the powder diffractograms were matched with relevant ASTM-standard patterns [4]. Crystallite sizing (D_{hkl}) was carried out using the line broadening technique in conjunction with Scherrer's formula [5]:

$$D_{hkl} = 0.9 \lambda / B_{hkl} \cdot \cos \theta \quad \dots\dots\dots(2)$$

Where, B_{hkl} is the width at half peak maximum in radians, λ is the incident wavelength ($\lambda = 1.54051 \text{\AA}$) and θ is the diffraction angle.

2.2.2 Fourier–transform infrared Spectroscopy (FTIR)

Infrared spectroscopy (IR) remains the most widely used, and usually most effective, spectroscopic method for characterization of the surface chemistry of heterogeneous catalysts [6]. It is an easy way to identify the presence of certain functional groups in molecule [7,8].

Fourier transform infrared (FTIR) spectroscopy is widely employed for characterization of the catalyst surface [9,6], it is still unclear whether the regularities obtained under conditions of spectral pretreatments and measurements (evacuation, temperature) can be used for interpreting and predicting the surface properties during adsorption of a precursor or in a catalytic reaction.

FTIR spectrometers offer two pronounced advantages over dispersive instruments: higher energy throughput and faster data acquisition or higher signal-to-noise ratio. Data processing is easy. These features are significant when examining very strongly absorbing and scattering solid and when following dynamic processes. Much IR transmission work, however, requires examination of only limited frequency ranges at medium resolution and computerized dispersive spectrometer.

Ex-situ FT-IR spectra of supports, unsupported and supported catalysts were taken at frequency range $4000 - 400 \text{ cm}^{-1}$. This was done at a resolution of 4 cm^{-1} using a model Genesis-II FT-IR Mattson Fourier-transform infrared spectrometer (USA) and an online PC with win first Lite (V 1.02) software for spectra acquisition and handling. The spectra were taken for thin ($> 20 \text{ mg / cm}$) lightly loaded ($> 1\text{-wt \%}$) wafer of KBr-supported test samples. About 1–2 mg of the catalyst as a fine powder was mixed well with spectroscopy pure KBr powder and was finally grinded in agate mortar.

2.2.3 Laser Raman spectroscopy

The application of Raman spectroscopy to the surface studies has been reviewed in [10-15]. As compared to other vibrational spectroscopy can widely be used for investigations of the surface species on oxides, on supported and bulk of metals on supported oxides and at the water solid interface. In IR spectroscopy a molecule absorbs photons with the same frequency as its vibrations. In contrast, Raman spectroscopy is based on the inelastic scattering of photons, which lose energy by exciting vibration in the sample.

In the Raman spectroscopic experiments, ca. 90 mg of the catalyst was pressed into pellets, of 5 mm diameter and 0.8 mm thickness. The catalyst as pellets were heated (5 k/min) in stream of O₂ (40 ml/min) at 770 k for 1 h to remove the contaminated carbonates and organic materials. The spectra were recorded at room temperatures. The Raman spectra was recorded over range characteristics to the structure of SO₄²⁻ and molybdenum oxide, the range at 1200-100 cm⁻¹ on a computer controlled Dilor OMARS89 spectrometer which was equipped with an optical multichannel analyser (OMA) Model IRY12 From Spectroscopy Instrument. The excitation line was at 488 nm from an Ar ion Laser. For a

given spectrum, the excitation power at the sample was constant. The Raman spectra were measured with up to 5 cm^{-1} spectral resolution with an absolute accuracy of $\pm 1 \text{ cm}^{-1}$.

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Chapter III

Result and discussion

Results and discussion.

3.1 X-ray powder diffraction

3.1.1 XRD of alumina supported molybdenum oxide

X-ray powder diffraction of alumina, molybdena and supported molybdena catalysts (xMoAl) at different loading levels are shown in (Fig. 1). The XRD patterns of alumina display a few weak broad peaks which are indicative of fine crystallites of the γ -Al₂O₃ phase (JCPDS 29–1486). The average crystallite size derived from the peak width at half maximum (PWHM) was ca. 10.3 ± 1 nm (Table 1). The pattern of pure molybdenum oxide (MoO₃) found to be highly crystalline and exhibited several sharp peaks (Fig. 1).

X-ray diffractograms of the calcined products of supported catalysts xMoAl at 823 K for 3 h at different loading levels samples are shown in (Fig.1). The XRD patterns of 3MoAl and 5MoAl catalysts display the XRD pattern of γ -alumina structure. This is mean that MoO₃ will have high dispersed on alumina till 5 wt% of MoO₃. The XRD pattern of 10MoAl display peaks characteristic to bulk MoO₃ was formed. These peaks become more intense as the molybdenum oxide content of catalyst increased (Fig.1). The molybdena has a very high dispersion in

MoO₃/ Al₂O₃ catalysts at low loading level (3, 5MoAl). In the presence of low amounts of MoO₃ (3 wt %) the formation isolated tetrahedrally coordinated [MoO₄] species is preferred. High molybdena loadings favor the formation of polymeric molybdate structures in which the Mo (VI) ion is octahedrally coordinated. Crystalline molybdena is usually observed when the molybdena amounts is higher than 15 wt% and Al₂(MoO₄)₃ formation [1-5]. The difference in the XRD patterns of the supported catalyst from that of pure support and molybdena is an indication of much strong molybdena-support interaction.

The data cited in Table 1 reveal that the particle size obtained from XRD data of alumina supported molybdenum oxide catalysts increases with increasing the molybdena content.

The XRD diffractogram of sulfated alumina supported molybdena catalysts (xMoAlS) are shown in (Fig. 2). The XRD patterns of xMoAlS display peaks at low loading levels (3MoAlS) characteristic to bulk MoO₃ formation. These peaks increase with increasing the MoO₃ loaded, which lead to the increases the bulk of MoO₃. The data obtained from XRD indicated that the presence of sulfate ion lead to formation of MoO₃

at low loading level (3MoAl). Also the particle size of these catalysts increases with increasing of molybdena content see Table 1.

Table 1. The results of particle size obtained from XRD data of alumina supported molybdenum oxide at different loading levels and sulfated catalysts.

Samples	Particles size (D = 1 nm)
Al	10.3
MoO ₃	38.4
3MoAl	16.1
5 MoAl	16.1
10 MoAl	20.2
15MoAl	23.4
20 MoAl	26.1
3MoAlS	14.1
5MoAlS	15.6
10MoAlS	17.3
15MoAlS	21.4
20MoAlS	23.3

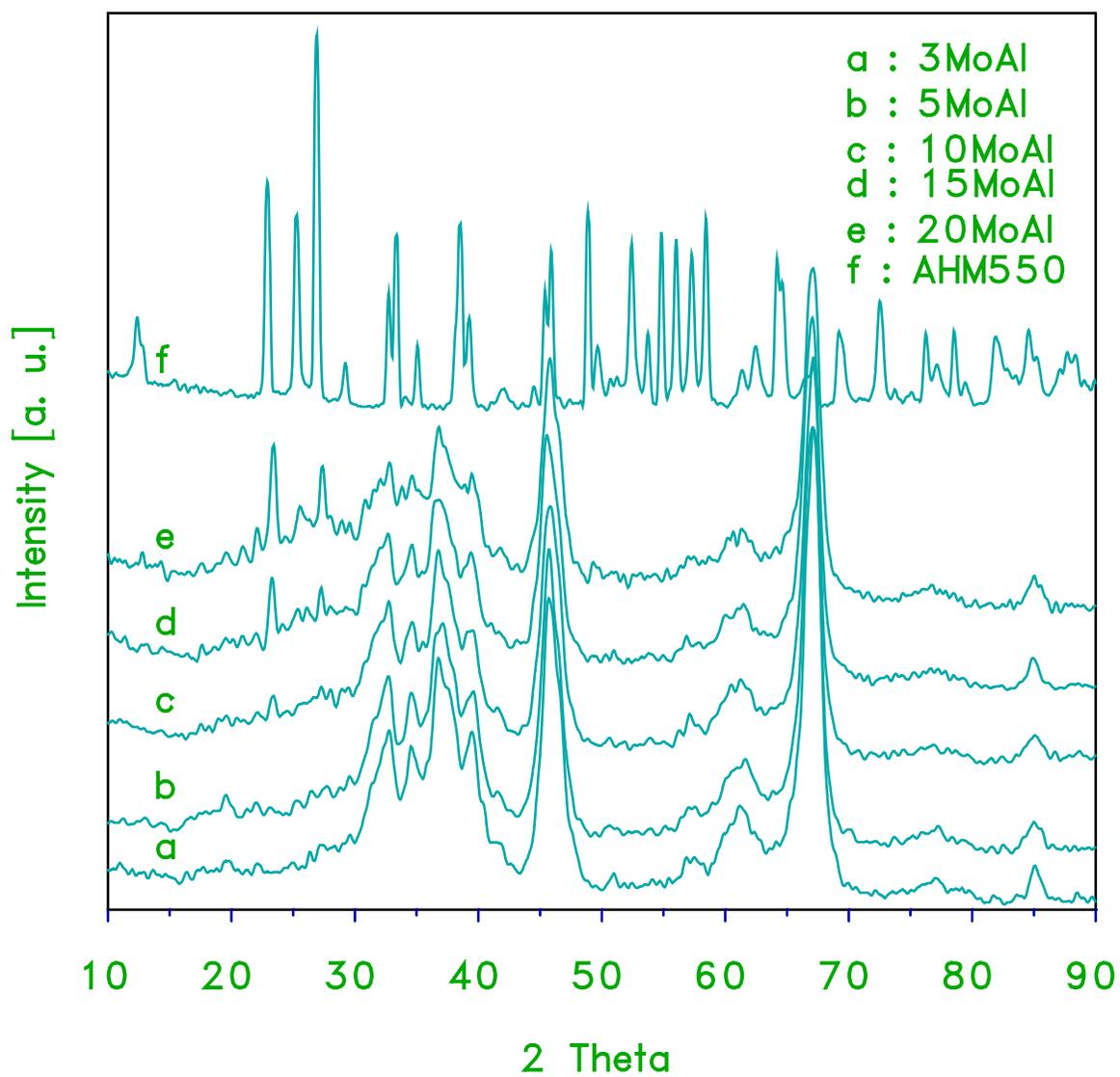


Fig. 1. X-ray powder diffractograms for xMoAl catalysts. Diffractograms of the support and unsupported MoO₃ are inset for comparison.

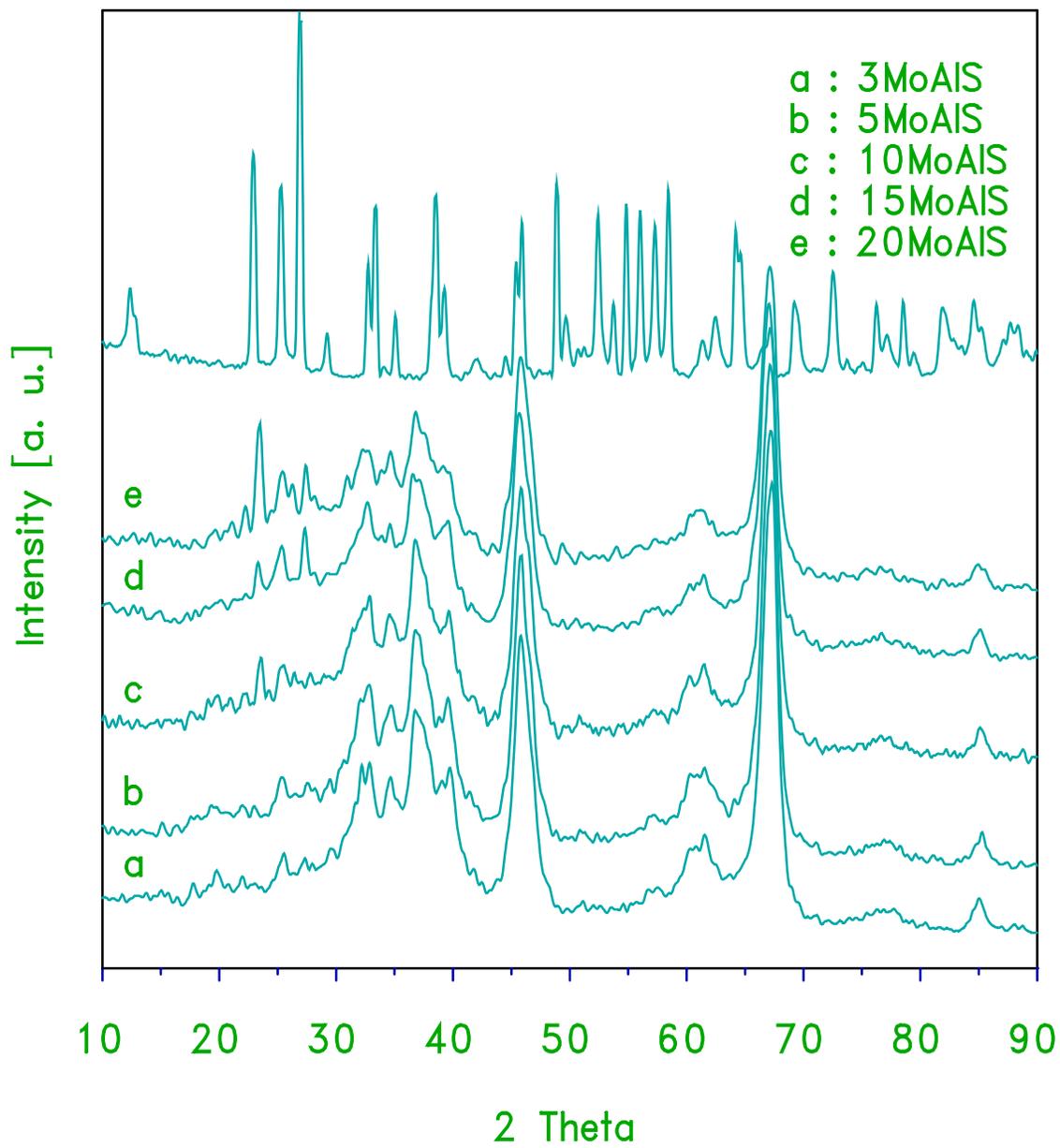


Fig. 2. X-ray powder diffractograms for xMoAIS catalysts.

Diffractograms of the support and unsupported MO_3 are inset for comparison.

3.1.2 XRD of silica supported molybdenum oxide

X-ray powder diffraction of pure silica and silica supported molybdenum oxide (xMoSi) at different loading levels are shown in (Fig. 3). The XRD patterns of silica display a broad peak due to non-crystalline silica (amorphous). The diffractograms of 3MoSi displays dominantly peak due to support (silica), and well-defined peaks that can be found in the diffractogram of MoO₃ (Fig. 3). It was observed that the MoO₃ species were highly dispersed on silica at 3 wt%, 5% loaded. This result indicates that molybdena species are not crystallized but highly dispersed or exist as amorphous phase without the possibility to know if the absence of any diffraction peak was due to absence of long-range order of MoO₃ or to low amount of MoO₃ to observe diffraction[6,7]. While at higher loading levels 10wt% start the formation of bulk MoO₃. The formation of bulk molybdena increases with increasing the loading levels. The patterns at highest loading levels 10, 15 and 20MoAl reveal the main presence of stable phase MoO₃ orthorhombic crystal structure appeared at higher loading[8]. The particle size of these samples increases with increasing the loading level of molybdenum oxide (Table2).

Table.2. The results of particle size obtained from XRD data of silica supported molybdenum oxide at different loading levels and sulfated catalysts

Samples	Particles size (D = 1 nm)
MoO ₃	38.4
10 MoSi	25.4
15MoSi	28.3
20 MoSi	33.4
10MoSiS	23.3
15MoSiS	25.8
20MoSiS	31.4

X-ray diffractograms of sulfated silica supported molybdena catalysts at different loading levels are shown in (Fig.4). The diffractogram pattern exhibited by 3- and 5MoSiS is similar to that presented above for 3- and 5MoSi (Fig. 3) in showing that high dispersion of MoO₃ at this loading levels. Also, at higher loading levels ≥ 10 wt% the crystalline MoO₃ was increased. The particle size of xMoSiS samples increases with increasing the loading levels up to 20 wt% see Table2.

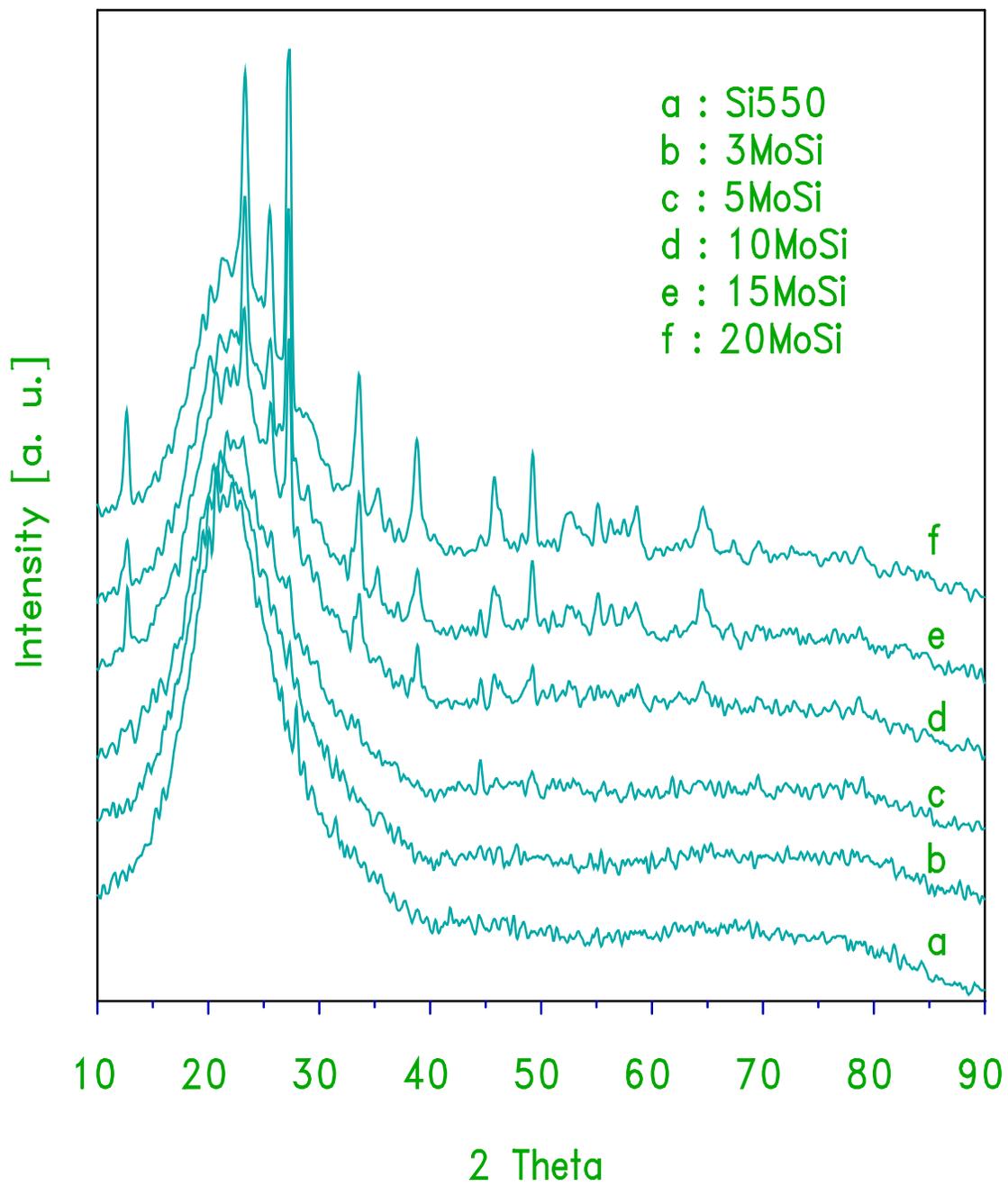


Fig. 3. X-ray powder diffractograms for xMoSi catalysts. Diffractograms of the support and unsupported MoO₃ are inset for comparison.

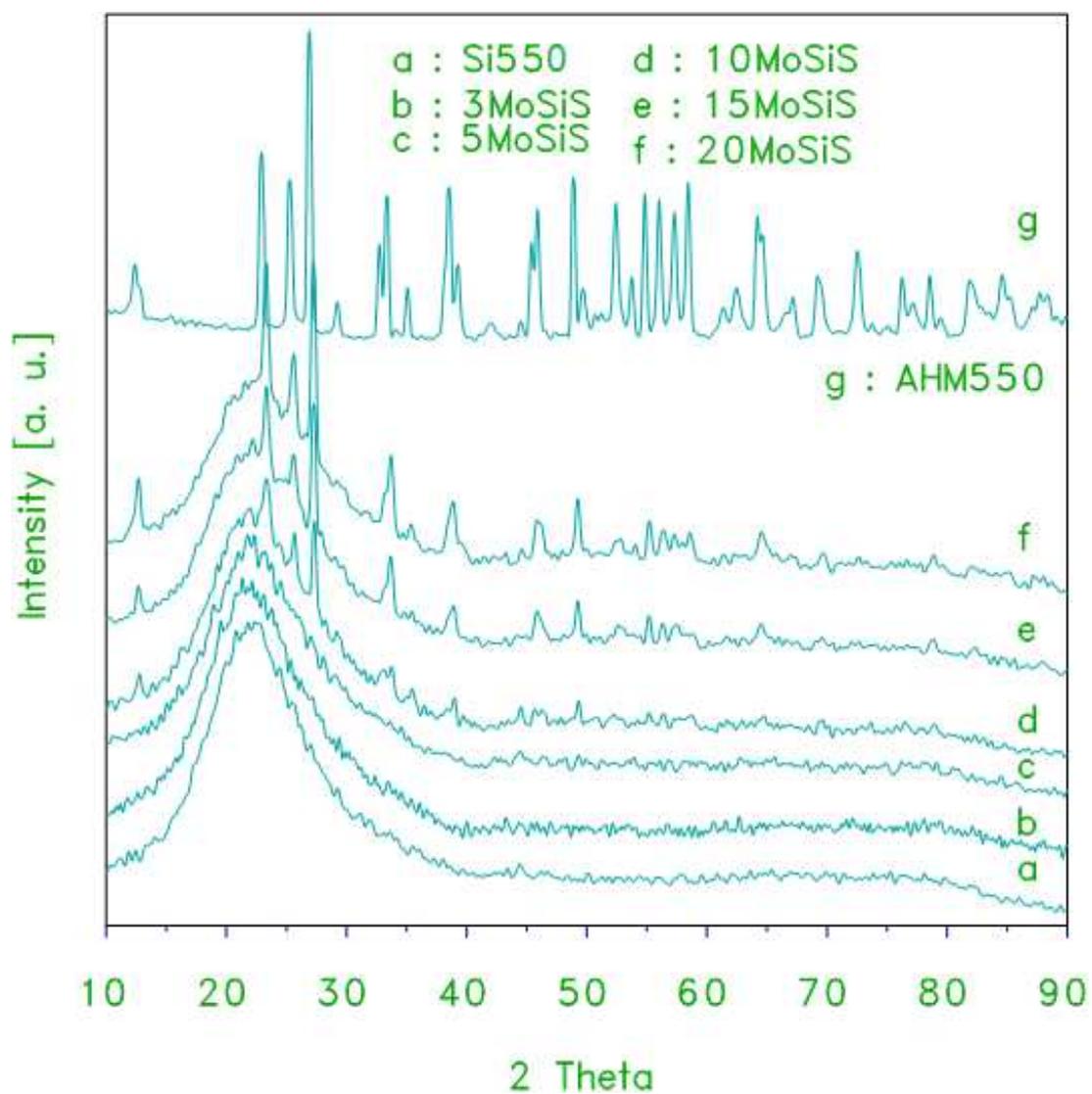


Fig.4. X-ray powder diffractograms for xMoSiS catalysts.

Diffractograms of support and unsupported MoO_3 are inset for comparison.

3.2 Ex-situ FTIR spectra of catalyst

3.2.1 Ex-situ FTIR spectra of alumina supported molybdenum oxide

Ex-situ FTIR spectroscopic analysis of the supported catalysts were performed to get deep information about the surface molybdenum oxide. (Fig.5). provides a comparison of the IR spectra obtained for the xMoAl samples, with those exhibited by alumina and molybdenum oxide. The spectrum of pure alumina displays two broad absorptions centered at 760 and 569 cm^{-1} in common. These frequencies may be attributed to the Al-O lattice vibrations of Al_2O_3 [9]. Support exhibited O-H stretching band at 3438 cm^{-1} indicating the presence of basic hydroxyls, and similar stretching band of supported catalyst exhibited in the range 3438 cm^{-1} . As the loading level of molybdenum oxide is increased, the two broad bands 828, 569 cm^{-1} decrease. The broad band of absorption indicated the formation of molybdenum oxide. As there was overlapping of Al-O bending vibration band in the range 828,760 and 569 cm^{-1} with Mo=O band in supported catalysts [1,5], association of Mo-O with Al-O was clearly indicated by the intensity and shift of bands in the lower region [10,11].

The IR spectra of sulfated, xMoAlS, catalyst samples (Fig.6), shows the similar spectra of xMoAl in(Fig. 5) the difference in spectra of xMoAlS loading level of sulfated xMoAlS increase become much strong absorptions at 828, 614 and 558 cm^{-1} resembling those shown for MoO_3 surface species in the spectra of alumina supported molybdenum oxide and intensity of three bands are more intense than the spectra of xMoAl catalysts. This indicates that the formation of molybdenum oxide of higher bond order in xMoAlS catalysts than in xMoAl.

Hence, the above IR spectral results are in a good agreement with the XRD results. By increasing the loading level of molybdenum oxide on alumina the crystallinity of MoO_3 increases dramatically. All the results discussed above clearly show the dispersion capacity of molybdenum oxide from MoAlS is larger compared with molybdenum oxide from MoAl.

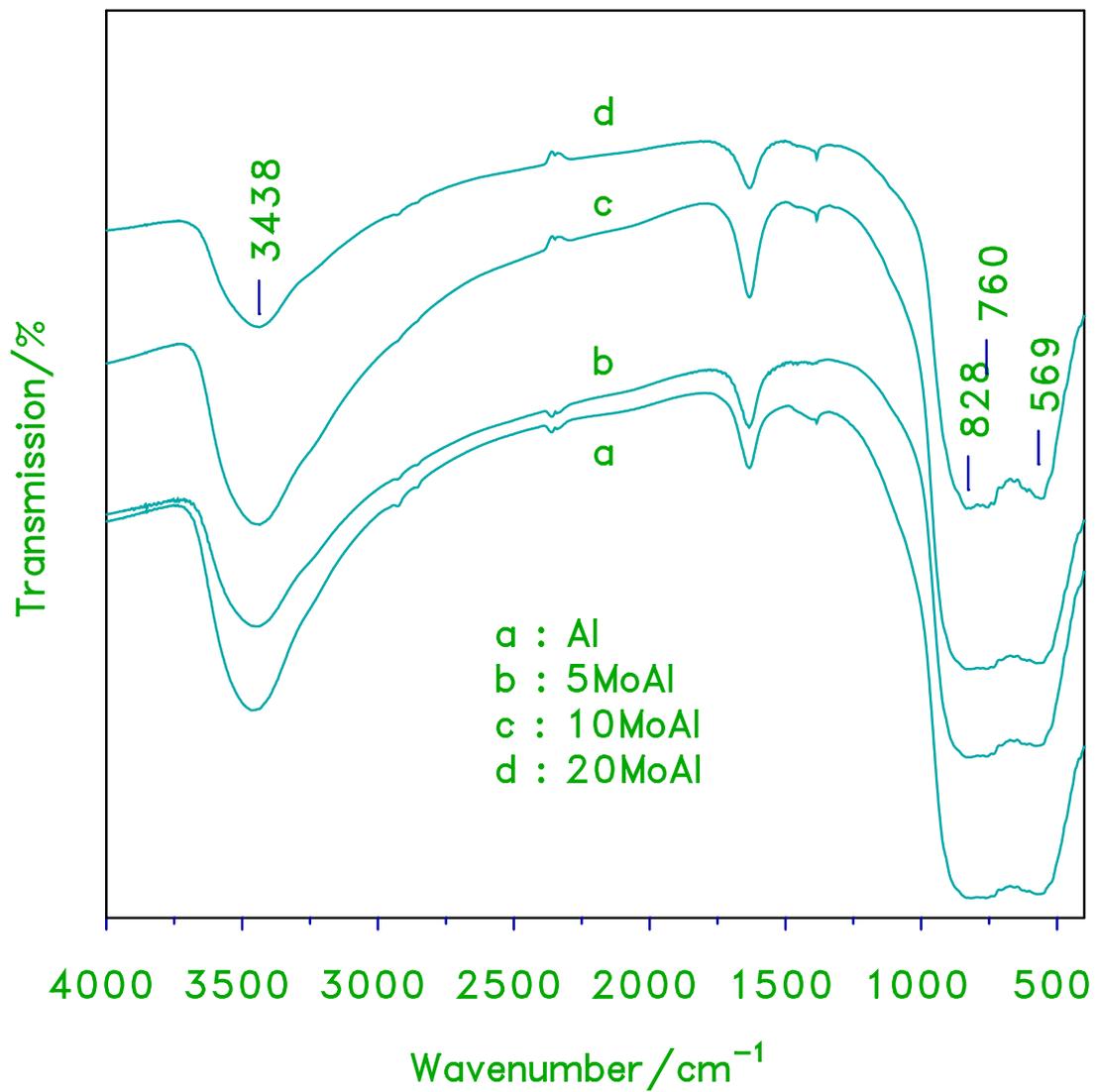


Fig.5. FT-IR transmission spectra obtained for molybdenum oxide, the indicated set of alumina supported molybdenum oxide.

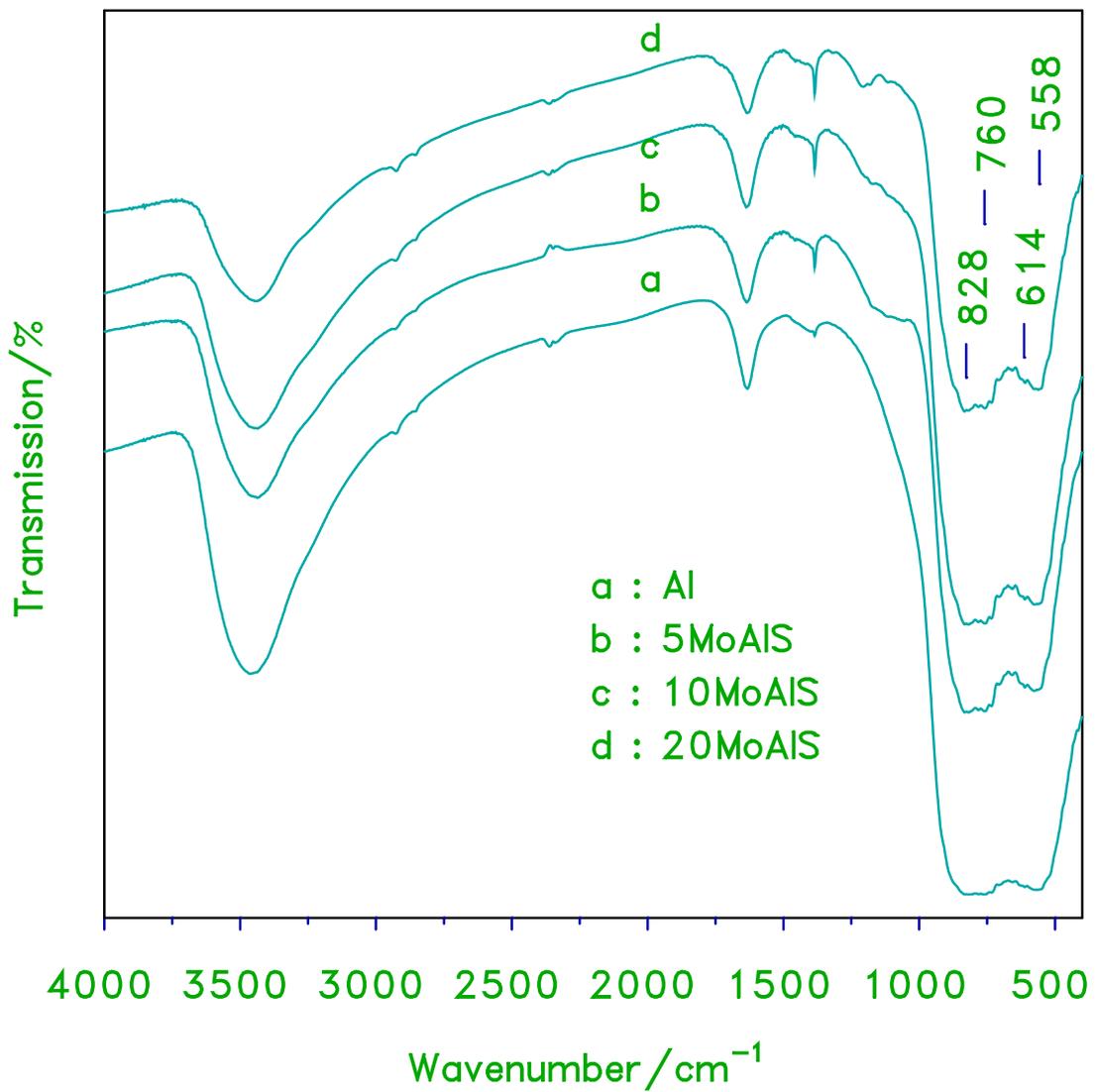


Fig.6 FT-IR transmission spectra the obtained for molybdenum oxide and the indicated set of sulfated xMoAIS.

3.2.2 *Ex-situ FTIR spectra of silica supported molybdenum oxide*

Ex-situ FTIR spectroscopic analysis of the supported catalysts was performed to get deep information about the surface molybdenum oxide. (Fig.7) provides a comparison of the IR spectra obtained for the xMoSi samples, with those exhibited by silica and molybdenum oxide. IR spectrum of pure silica display one broad absorption band centered at 1090 cm^{-1} , and two absorption bands centered at 795 and 499 cm^{-1} . These frequencies attributed to the Si-O lattice vibrations of SiO_2 . Water shows an intense characteristic broad absorption band centered at 3450 cm^{-1} assigned to O-H stretching in H-bonding [12]. IR spectrum display strong absorption at 499 cm^{-1} due to Mo-O lattice vibrations of molybdena phase [13]. As the loading level of molybdenum oxide is increased, the absorption gradually narrow with the emergence of much strong absorption resembling the shown for MoO_3 surface species in the spectra of silica supported molybdenum oxide (Fig.7). The intensities of these vibration bands increase with increasing the loading level of molybdenum oxide due to the increase in the formation of MoO_3 . There an overlapping of Si-O bending vibration band in the range 795 cm^{-1} with M=O band in supported catalysts.

The IR spectra of the sulfated, xMoSiS, catalyst samples (Fig. 8) is similar to the spectra of MoSi which shown in (Fig.7), with differences in an intensity absorption exhibits increase in absorption with increase of loading of xMoSiS in range 499 cm^{-1} indicates increase in formation of MoO_3 .

Hence, the above IR spectral results in a good agreement with the XRD results. It has been noted that by increasing the loading level of molybdenum oxide on silica the crystallinity of MoO_3 increases.

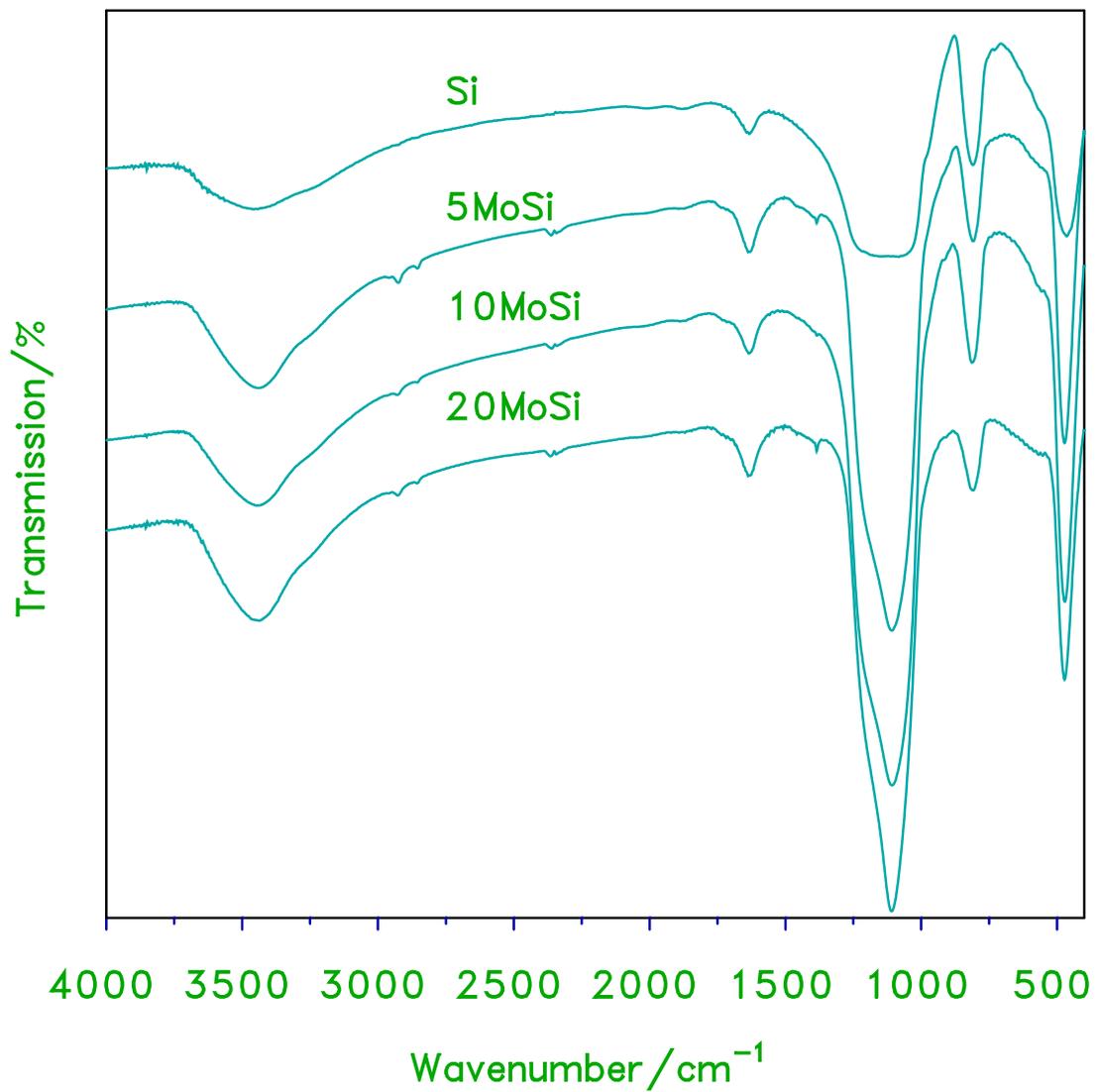


Fig.7. FT-IR transmission spectra obtained for molybdenum oxide, the indicated set of silica supported molybdenum oxide.

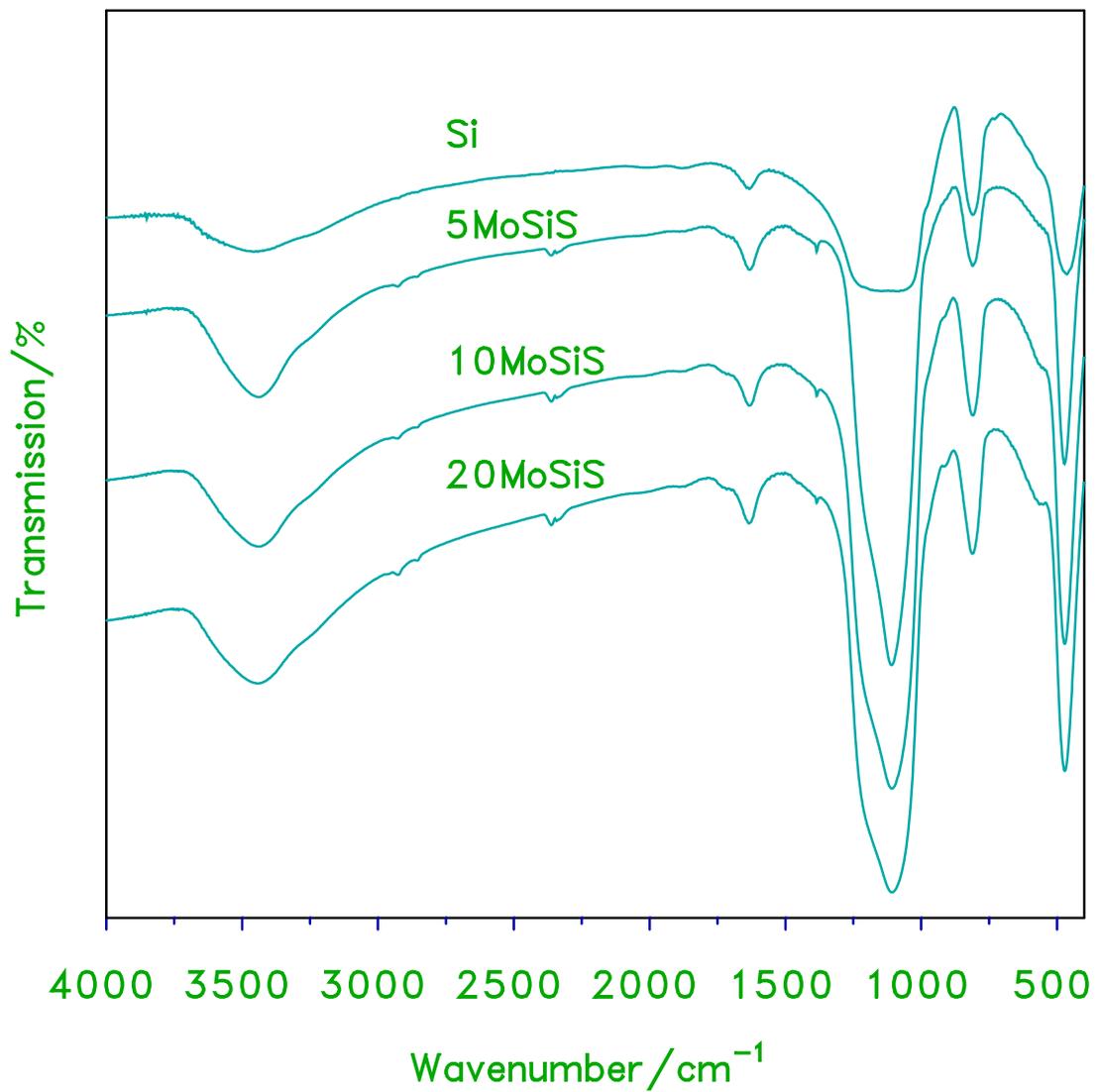


Fig.8. FT-IR transmission spectra the obtained for molybdenum oxide and the indicated set of sulfated xMoSiS.

3.3 Laser Raman spectra of catalysts

3.3.1 Laser Raman spectra of alumina supported molybdenum oxide catalysts

The result of the Laser Raman spectra obtained for the xMoAl samples at different loading levels presented in (fig. 9). All catalysts display bands at 956 cm^{-1} (Mo=O stretching) at low molybdenum loading (5MoAl) tetrahedrally coordinated species (MoO_4^{2-}) are present as small amount. With increasing the MoO_3 loading (10MoAl) formation of new bands appear at 222 and 356 cm^{-1} to 375 cm^{-1} (Mo=O bending) and 834 , 900 cm^{-1} (asymmetric Mo-O-Mo stretching) and shift to higher values of bands 956 and 997 cm^{-1} this shift can be attributed to a decrease in the bond strength of O-Mo-O groups that are joined to the support, because the high surface density of MoO_3 species present in this catalyst. At moderate loadings (between 5 and 20 wt% MoO_3), tetrahedrally coordinated MoO_x species are present at 5MoAl catalyst [14,15]. And increase in the amount of molybdenum oxide at 10MoAl catalyst the octahedrally coordinated species can be observed and more crystalline.

The Raman spectra of sulfated, xMoAlS, catalyst samples (Fig. 9) show the similar spectra of xMoAl but the difference in spectra of

xMoAlS loading level of sulfated xMoAlS increase become much strong absorptions at 853, 900 and 956 cm^{-1} resembling those shown for MoO_3 surface species in the spectra of alumina supported molybdenum oxide and intensity of three bands are more intense than the spectra of xMoAl catalysts. This indicates that the formation of molybdenum oxide of higher bond order in xMoAlS catalysts than in xMoAl

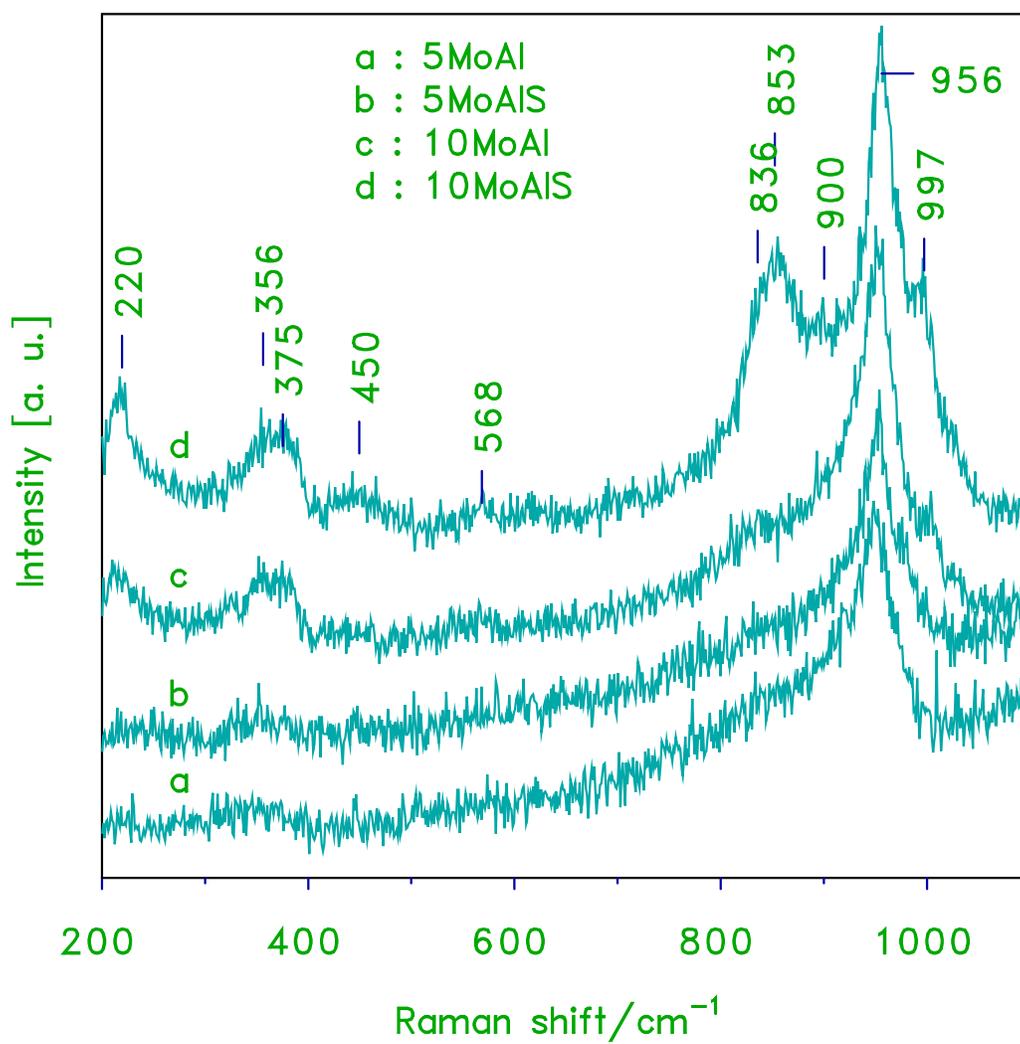


Fig.9. Laser Raman spectra of alumina supported molybdenum oxide

Catalysts with sulfated xMoAlS catalysts

3.3.2 Laser Raman spectra of silica supported molybdenum oxide

Catalysts

Laser Raman spectroscopic analysis of the supported catalysts was performed to get deep information about the surface of molybdenum oxide. (Fig.10) shows a comparison of the Laser Raman spectra obtained for the xMoSi samples, with those exhibited by silica and molybdenum oxide. At low loading for 5MoSi, the presence of MoO₃ on the surface of 5MoSi as a dispersed which exhibits two small vibrational bands at 816 and 992 cm⁻¹ of molybdena. The appeared bands indicate that they have small effect on the formation of molybdenum oxide [16]. By increasing MoO₃ loaded for 10 wt% become more intensive with increasing of density and new bands appears at 216 and 241 cm⁻¹. The new bands can be assigned to molybdenyl bending as isolated and the Mo = O stretching mod shifts from 281 to 289 cm⁻¹ and at 666 cm⁻¹ (the shift and the change of band shape of the molybdenyl vibration can be interpreted as an indication that the two bands belong to at least two different contribution of the present molybdenum oxide species) and the presence of two sharp bands indicates that the surface molybdenum oxide species [17,18,19]. At a higher loading levels the characteristic bands of crystalline MoO₃ are clearly observed.

The Raman spectra of the sulfated, $x\text{MoSiS}$, catalyst samples (Fig.10). similar to the spectra of MoSi with differences in an intensity absorption exhibits increase in absorption and more sharp with increase of loading of $x\text{MoSiS}$ in range 816 and 992 cm^{-1} indicates increase in formation of MoO_3 crystalline.

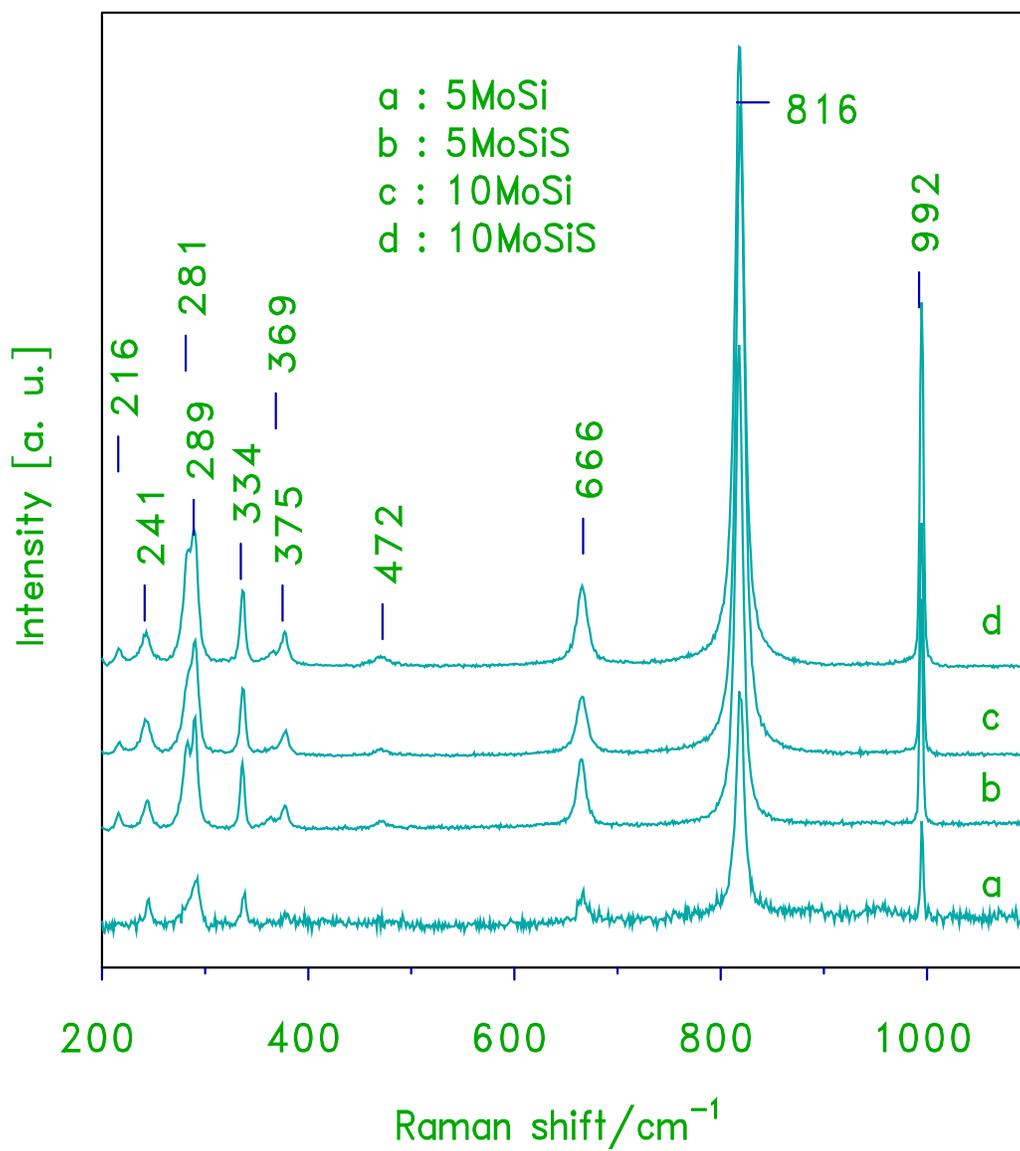


Fig.10. *Laser Raman spectra of silica supported molybdenum oxide*

Catalysts with sulfated xMoSiS catalysts

3.4 Conclusions

A series of alumina and silica supported molybdenum oxide were prepared using ammonium hepta molybdate at different loading levels (3 – 20 wt% of molybdenum oxide) by the impregnating method. Surface and bulk characterization of supported catalysts by X-ray diffractometry, FT-IR spectroscopy and Laser Raman spectroscopy leads to the following conclusion :

1- XRD results of alumina supported molybdenum oxide exhibits the crystallinity of catalysts and particle size increase with increasing the loading level of molybdenum oxide. The similar effect was observed in case of sulfated alumina supported molybdenum oxide (xMoAlS).

2- XRD results of silica supported molybdenum oxide exhibits high dispersion at low loading level (3,5wt%) whereas at higher loading levels the crystallinity and particle size increase with increasing loading level of molybdenum oxide. Sulfate catalysts of (xMoSi) show the similar effect.

3- FTIR spectroscopic results obtained indicate the dispersion capacity of molybdenum oxide from MoAlS is larger than of molybdenum oxide from MoAl.

4- FTIR spectra of MoSi and MoSiS catalysts show the dispersion capacity of molybdenum oxide from MoSiS is bigger than of molybdenum oxide from MoSi.

5- The results obtained from Laser Raman Spectroscopy of xMoAl catalysts indicated the formation of molybdenum oxide of higher bond order in xMoAlS catalysts than in xMoAl catalysts.

6- The results obtained from Laser Raman Spectroscopy of xMoSi catalysts indicated that the higher intensity absorption (sharp) increase with increasing of loading level of MO_3 (xMoSi and xMoSiS) indicate the formation of crystalline MO_3 .

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Chapter IV
Surface acidity of
the catalysts
measured by
potentiometric
titration of n-butyl
amine

Surface acidity of the catalysts measured by potentiometric titration of n-butyl amine

4.1 Prelude

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 (Bronsted) 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 measurements of the catalysts by means of a potentiometric titration with n-butyl amine 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).

Therefore, the aim of the present study is to characterize 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-butyl amine as a probe.

4.2 Experimental

The total acidity of the solid samples was measured by means of potentiometric titration [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 2h. then, the suspension was 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.

4.3 Results and Discussion

The surface acidity measurements of the prepared catalysts by means of potentiometric titration with n-butyl amine 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-butyl

amine 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] .

4. 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. For comparison, the surface acidity of pure silica catalysts represented 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 reveal 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 are listed in Table 1, which's reveals that increases in the acidity with 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	Ei (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

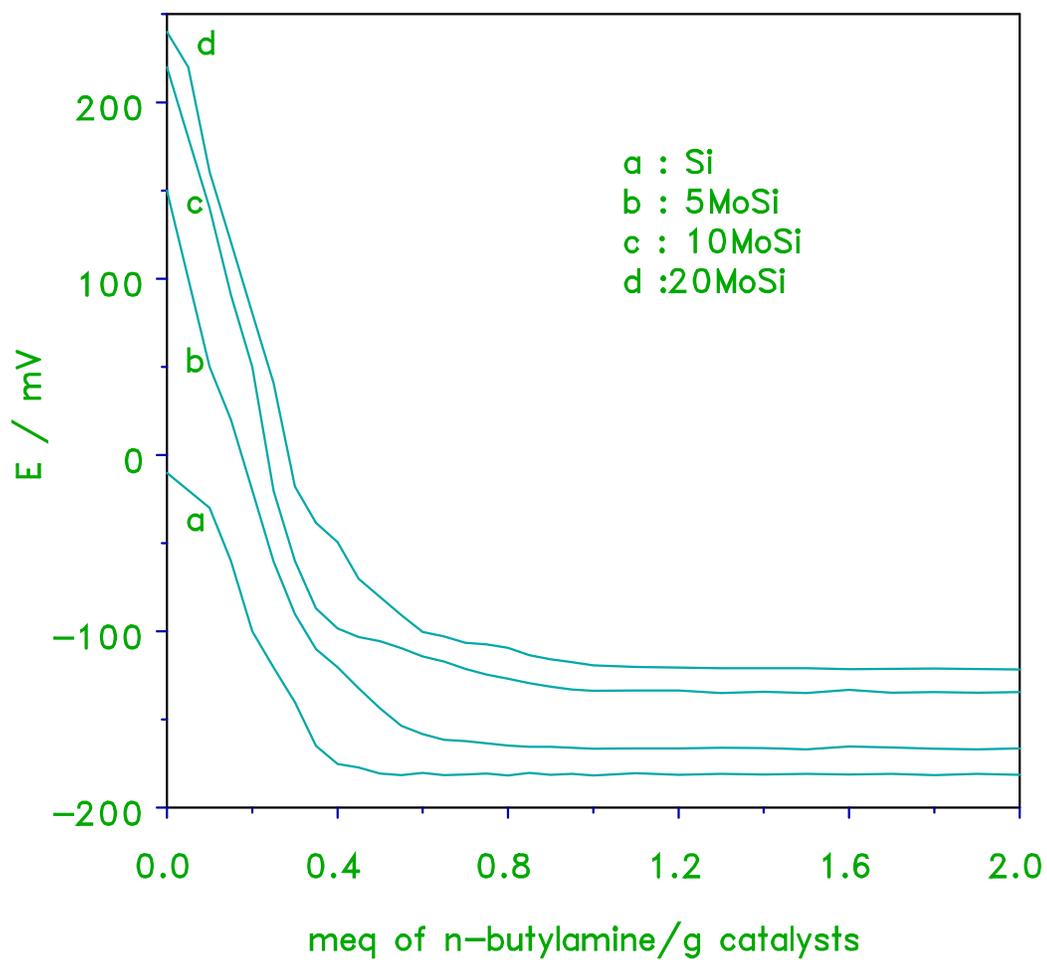


Fig. 1: Potentiometric titration curves of n-butyl amine in acetonitrile for the silica and silica supported molybdena catalysts (xMoSi).

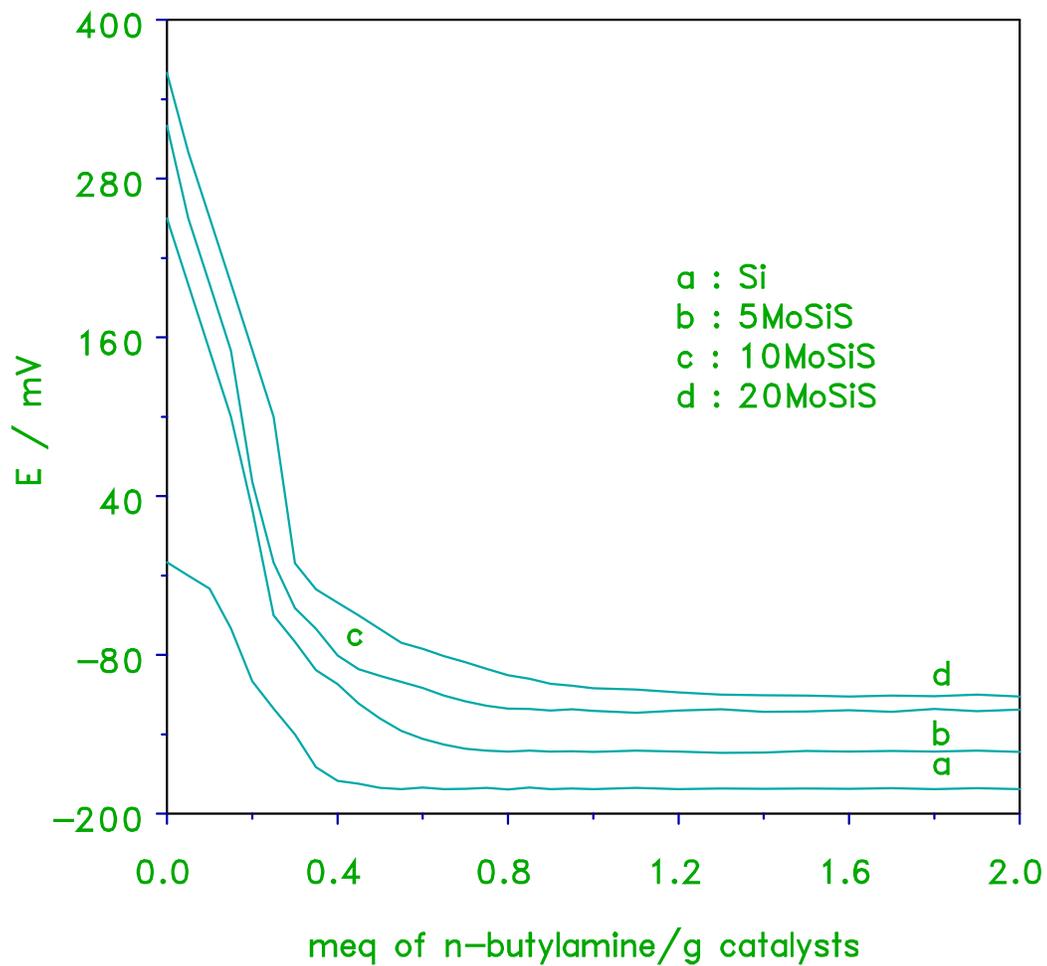


Fig. 2: Potentiometric titration curves of n-butyl amine in acetonitrile for the silica supported molybdena and sulfated catalysts (xMoSiS).

4. 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), where the amount of acidity and the total number of acid sites/g catalyst was evaluated, table 2. It seems that the free alumina display strong acid sites, $E_i=12\text{mV}$ Supported molybdena catalysts show increases of amount of acidity, number and strength of acid sites to reach 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 MoO_3 loaded on alumina up to 20 wt % MoO_3 .

Modification with sulfate was accompanied by a gradual increase of both number and strength of acid sites to reach maximum at 20MoAlS 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 shows very strong acid sites up to $E_i= 450 \text{ mV}$ for 20MoAlS.

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

Table 2.

The surface acidity of alumina supported molybdena and sulfated catalysts.

Samples	Ei (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

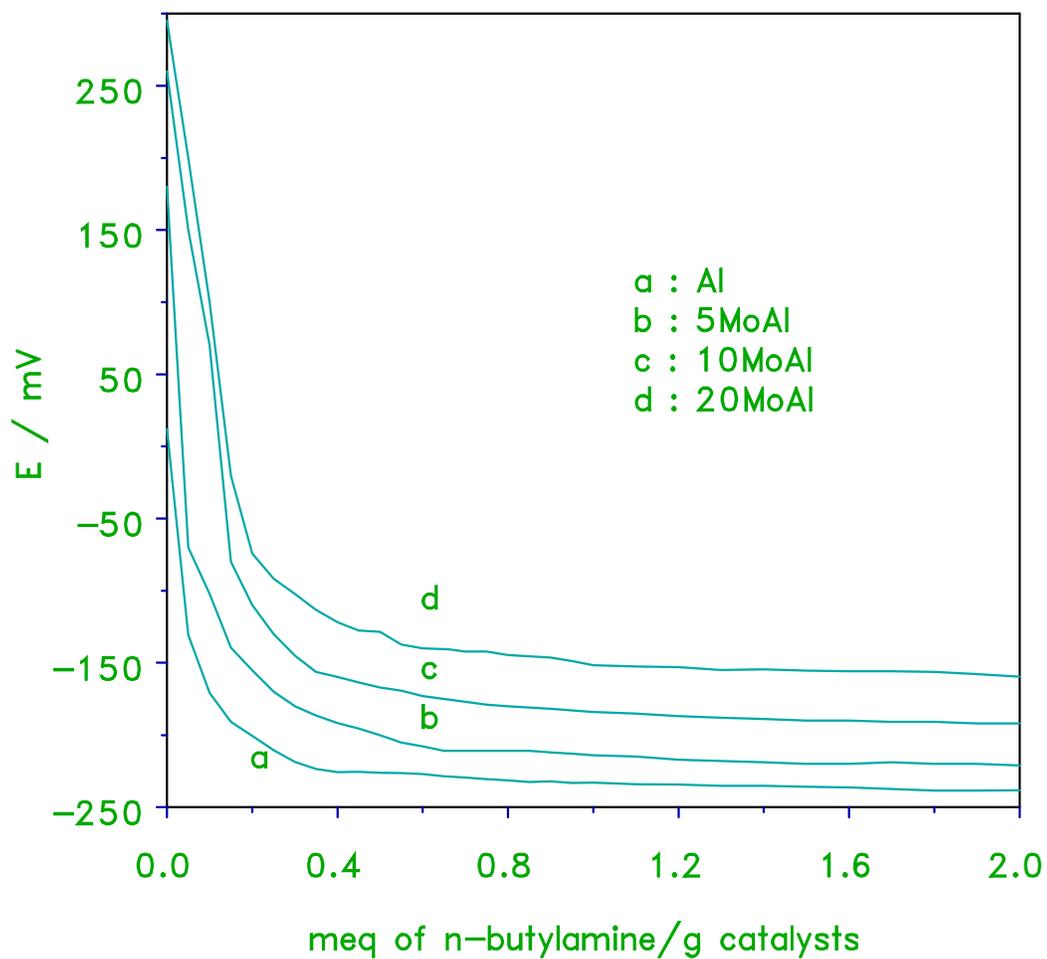


Fig. 3: Potentiometric titration curves of n-butyl amine in acetonitrile for the alumina and alumina supported molybdena catalysts (xMoAl).

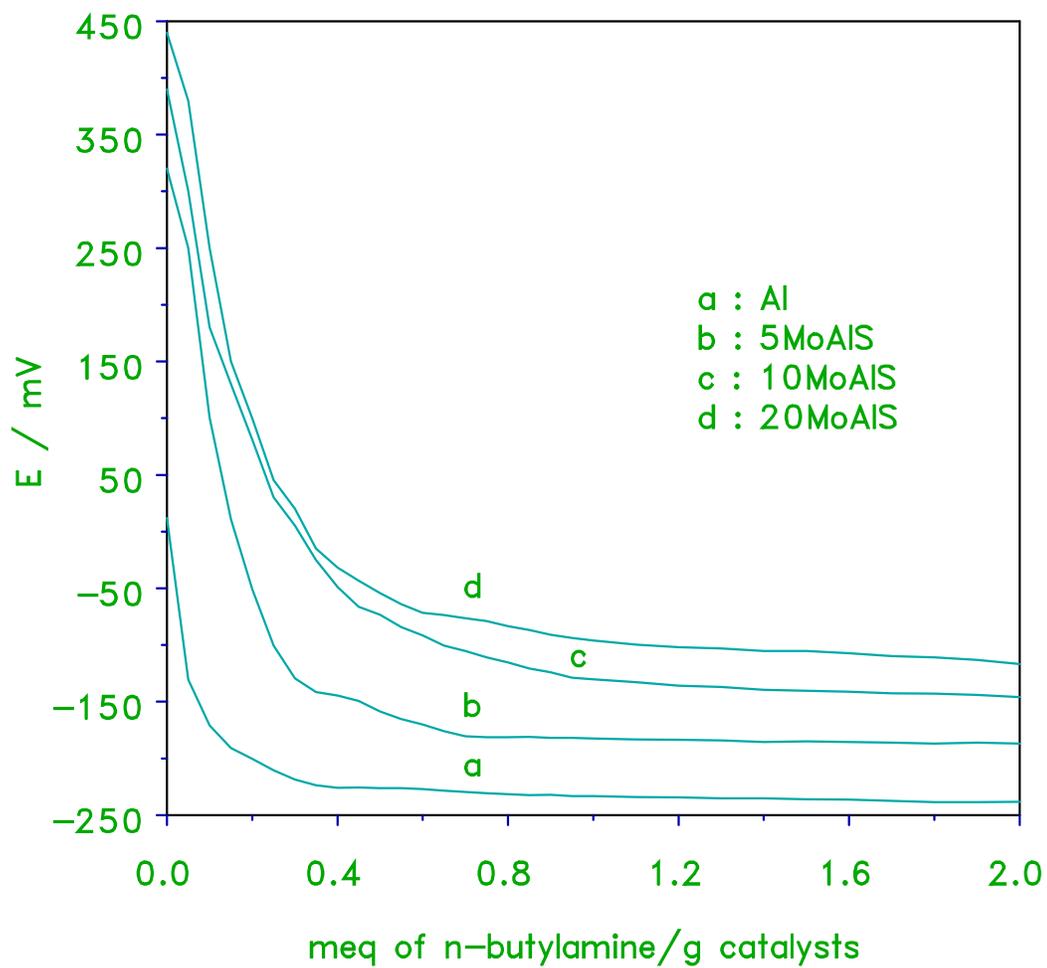


Fig. 4: Potentiometric titration curves of n-butyl amine in acetonitrile for the alumina supported molybdena and sulfated catalysts (xMoAIS).

4.4 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 the 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 are higher than surface acidity of silica supported molybdena catalysts. Sulfation enhances the surface acidity and increases the strength of acidity due to the inductive effect of S=O. Potentiometric titration of n-butyl amine probe molecule provide an extremely useful determination of surface acid characteristics of supported molybdena and sulfated catalysts.

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رسالة مقدمة لاستكمال متطلبات الحصول على درجة الماجستير

في الكيمياء الفيزيائية

بنغازي , ليبيا

2015