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EFFECTS OF PREPARATION ON THE PROPERTIES OF NIOBIA-ALUMINA BINARY OXIDES

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Niobia/Alumina (Nb_2O_5/Al_2O_3) mixed oxides and SiO_2-supported Nb_2O_5/Al_2O_3 binary oxides were prepared over a wide composition range. The mixed oxides were prepared by co-precipitation and the supported oxides were synthesized by incipient wetness impregnation. All of the binary oxides were calcined (500° C) in oxygen and had a further high temperature (1000° C) ramp in flowing helium, to determine if the materials were stable. All oxides were found to be amorphous after calcination, while the mixed oxides formed crystallites after the high temperature ramp. By using Hammett indicators and titrating with n-butylamine, the binary oxides all showed high acid strength and acidity. The catalytic activities of these materials were investigated by the 1-butene isomerization reaction. The mixed oxides generally exhibited the strongest and largest number of acid sites and the least amount of stability, while the supported oxides showed the greatest catalytic activity for 1-butene isomerization and the greatest amount of surface stability. Crysallization of the mixed oxides played a large role in the properties of these samples. (cont)

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The supported niobia/alumina surface oxides were prepared using both a sequential impregnation and coimpregnation technique with no variation in the chemical and physical properties. Changing the surface composition of the supported binary oxides had a small effect on the properties of these materials. No correlation could be found in this set of mixed and supported oxides between the activity in isomerization and the total acidity of the material, indicating a combination of Brönsted and Lewis acid sites on the surface.

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ABSTRACT

Niobia/alumina (Nb_2O_5/Al_2O_3) mixed oxides and SiO_2-supported Nb_2O_5/Al_2O_3 binary oxides were prepared over a wide composition range. The mixed oxides were prepared by coprecipitation and the supported oxides were synthesized by incipient wetness impregnation. All of the binary oxides were calcined (500° C) in oxygen and had a further high temperature (1000° C) ramp in flowing helium, to determine if the materials were stable.

All oxides were found to be amorphous after calcination, while the mixed oxides formed crystallites after the high temperature ramp. By using Hammett indicators and titrating with n-butylamine, the binary oxides all showed high acid strength and acidity. The catalytic activities of these materials were investigated by the 1-butene isomerization reaction. The mixed oxides generally exhibited the strongest and largest number of acid sites and the least amount of stability, while the supported oxides showed the greatest catalytic activity for 1-butene isomerization and the greatest amount of surface stability. Crystallization of the mixed oxides played a large role in the properties of these samples.

The supported niobia/alumina surface oxides were prepared using both a sequential impregnation and coimpregnation technique with no variation in the chemical and physical properties. Changing the surface composition of the supported binary oxides had a small effect on the properties of these materials. No correlation could be found in this set of mixed and supported oxides between the activity in isomerization and the total acidity of the material, indicating a combination of Brönsted and Lewis acid sites on the surface.

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1. INTRODUCTION

1.1 General

Binary oxide catalysts, materials containing two different oxides, are widely used and are of great importance for a number of industrial processes such as catalytic cracking, oxidation, and dehydration.[1,2,3] Understanding the acidic properties of these metal oxides is an important step towards effectively utilizing these materials in catalytic and adsorptive processes. There is great interest in the physical and chemical properties of mixed and supported metal oxides because of the ability to change the acidic properties of these materials by simply choosing different metal oxide components and also different concentrations of these constituents.[1] Thus, binary oxides are very interesting from a fundamental and industrial point of view for the ability to possibly tailor a catalyst from two oxides, and produce a material that has properties very different from the separate components. This a noble goal; however, at present it is generally understood that materials prepared from arbitrary combinations of metal oxides may have complex structures.[4] This has slowed progress in the understanding of the acidic properties of these materials, and how to relate them to the structure of the catalysts.[5] It is also not always known what structure is desired, and coupled with the problems in preparation of these oxides, one can easily see the importance of research in this area. It is the goal of this research to study the effects of preparation on the physical and chemical properties of binary oxides, specifically mixed and supported-niobia and alumina. A study of the properties of these materials will lead to a greater fundamental understanding of the acidic nature of these oxides, and the different oxide-oxide interactions that occur in both the supported and mixed oxide systems.

There are two basic types of binary oxides which are currently used industrially.[1] The first is a homogeneous chemical mixture of the two oxides, known as a mixed oxide. These binary oxides (e.g. SiO_2/Al_2O_3) are well known for their great acidic properties and are used primarily as acid catalysts or as bifunctional supports.[2] The materials used in many previous studies have been prepared over a wide composition range by a standard coprecipitation procedure.[1,2] These mixed oxides display unique acidic properties, but they have complex structures that are not completely understood.[6] The second type of material is a supported-binary oxide, in which two different oxides are supported on the same substrate such as silica. Little information is available from the literature for supported-binary oxides; however, there is an abundant supply of information on supported-single oxides.[7,8] There are many different substrates, such as TiO_2, Al_2O_3, or SiO_2, that are available for supporting the oxides.[9,10,11] These supported oxides can have properties very different from those of the pure oxide because of the interactions with the support. For example, V_2O_5 supported as a monolayer on TiO_2 is a superior catalyst for the selective oxidation of o-xylene to phthalic anhydride than unsupported bulk V_2O_5.[9,12] Similar types of support interactions, either strong or weak, have been investigated in numerous other studies and will be discussed later. The problem with these supported systems is the difficulty associated with forming a stable oxide layer on the support. This problem is further complicated when there are two oxides to be supported on the same substrate. An understanding of the oxide-oxide interactions should help in the explanation of the physical properties of the binary oxides studied in this research.

1.2 Objective and Scope of Work

The objectives of this research were to prepare a series of binary oxides of niobia/alumina and to investigate the effects of preparation on the properties of these oxides. This study was conducted on a series of chemically mixed and supported-binary oxides of niobia and alumina. With the mixed oxides, the effect of composition and thermal treatment were investigated to understand how the structure and properties were affected. The effects of preparation, composition, and thermal treatment on the properties of the surface phase oxide series were all investigated to gain a better understanding on the stability of these materials and the oxide-oxide interactions which occur on the surface.

Niobia and alumina were chosen for this research based on previous results of work done on both mixed and surface phase oxides containing similar constituents. For mixed oxides, it is well known that SiO_2/Al_2O_3 is very acidic as shown by its industrial use as an acid catalyst.[1,2,3] Recent results from our group showed that Nb_2O_5/SiO_2 is also a very acidic material as indicated by titrations with n-butylamine and isomerization reactions with 1-butene.[13] It follows that Nb_2O_5/Al_2O_3 should also possess acidic properties as this work will show to be the case. A cursory study on this system was recently done by our group that indicated some interesting properties requiring further investigation. Choosing the components for the supported-binary oxides followed a similar reasoning to that of the mixed oxides and will be discussed below.

It is known that SiO_2/Al_2O_3, with SiO_2 being the major component, is a classic acid catalyst.[3] Silica-supported alumina below monolayer coverages has also been documented as having acidic properties.[14,15] It is also known from Chen's work that Nb_2O_5/SiO_2, with SiO_2 being the major component, is also an acidic material.[13] And recent work from our group indicates that silica-supported niobia below monolayer coverages also has strong evidence for acidity.[16] Furthermore, it appears as though the surface phase oxide of niobia supported on silica is also stable.[17] This is a desirable property since the material will resist sintering upon heating, and hopefully retain its catalytic and acidic properties. Therefore, in an extension of this work that also parallels that of the mixed oxides, the silica was used as a support for a binary mixture of niobia and alumina of varying composition. Both the mixed and supported-binary oxides of niobia and alumina were found to exhibit important acidic and catalytic properties that are of fundamental interest and industrial importance in terms of acid catalysts. This study has laid important groundwork by showing the effects of preparation on the properties of niobia/alumina binary oxides. The next section will further explain some points that were briefly mentioned here.

2. BACKGROUND

2.1 General

It is well known that SiO_2/Al_2O_3 mixed oxides are catalysts with very strong acidic properties.[3] Not until very recently were the acidic properties of Nb_2O_5 and its applications as an acid catalyst known.[18] Recent work from our group has shown mixed oxides of Nb_2O_5/SiO_2 to exhibit properties of an acid catalyst.[13] This has spurned research into the area of Nb_2O_5/Al_2O_3 mixed oxides as well as supported-Nb_2O_5/Al_2O_3 binary oxides. Before one can study the properties and the effects that preparation may have on these properties, there is a need to understand some fundamental background information:

- The current level of understanding on the acidity of mixed and surface phase oxides.
- The theories of acidity in binary oxides.
- The characterization of oxides as model catalysts by the use of reactions such as 1-butene isomerization.

The following sections will give a review of the current literature on these points and go into detail as to how they relate to this research.

2.2 Acidic Binary Oxides

2.2.1 Mixed Oxides

In the field of catalysis, mixed oxides are important because of their strong acidic properties. These oxides cover a large array of forms and structures and can be used either as catalysts or catalyst supports. Research on mixed oxides using different starting materials, preparation steps, and composition of components, has shown these catalysts capable of being crystalline, amorphous, or heterogeneous materials.[1,14] Currently, the role of structure as it relates to the properties of catalysts is not well understood.

There are a number of ways to synthesize mixed oxides, as reviewed by Courty.[19] The preparation technique used in this study involved the coprecipitation of oxides. This coprecipitation method has been used by Tanabe to study mixed oxides of TiO_2/SiO_2, TiO_2/Al_2O_3, and SiO_2/Al_2O_3.[20,21,2] These materials were found to be quite acidic with their acidity changing as a function of oxide composition and calcination temperature. The acidity of these materials were found to be even stronger than some industrial catalysts.[20,21,2] Work by Tanabe has shown evidence for the effective use of niobia as both an acidic material and catalyst or catalyst support.[18] It has also been shown that when niobia is combined with another oxide, strong acidic and catalytic properties may develop.[13,22] For example, Nb_2O_5/TiO_2 shows a high catalytic activity for the reduction of NO with NH_3.[22] Ko and Chen showed that an XRD amorphous mixed oxide of Nb_2O_5/SiO_2 was very acidic and that its acidity also changed with the oxide composition.[13] All of these materials have been shown to be very active toward reactions catalyzed by acid sites. This current study focused mainly on how the physical properties of the niobia/alumina mixed oxides were dependent on different types of preparation (i.e. varying composition and thermal treatment). Structural changes accompanying the heat treatment on this system were also briefly investigated by our group.[23] The role of these structures is currently not well understood.

2.2.2 Surface Phase Oxides

Surface phase oxides are materials made by depositing one oxide on the surface of another oxide, as Murrell and Yates did for titania-silica.[24] In this type of arrangement, an oxide substrate is coated with another oxide in the form of a thin layer. This layer can be a partial monolayer to several monolayers in thickness, depending on preparation. An understanding of the properties of these surface oxides has become important since these oxides are used extensively as catalytic cracking, oxidation, and dehydration catalysts. Although the majority of hydrotreating (e.g. hydrocracking) catalysts are supported on alumina , there is a growing interest for the use of silica-supported catalysts, because these could be less prone to coke formation presumably since the silica carrier has a lower acidity; coke formation being a major catalyst deactivator in such processes.[7]

It has recently been discovered that supporting one oxide on another oxide possibly generates interactions that may lead to the development of commercially important catalysts. An example of this is that V_2O_5 supported on TiO_2 (anatase) selectively oxidizes o-xylene to phthalic anhydride much more readily than unsupported V_2O_5.[9,12] Forming a surface monolayer of these supported species was found to be responsible for the catalytic behavior.[9]

It has also recently been found by a number of researchers that surface oxides are acidic at coverages below a monolayer.[4,5,14,15,16,24] Both Dumesic and Bourne found that Al_2O_3 supported on SiO_2 below monolayer coverages was acidic from pyridine adsorption studies.[14,15] They concluded that both Lewis and Brönsted acid sites were present on the surface with the Lewis sites being the stronger of the two. Murrell and Yates discovered that a 1 wt.% coverage of TiO_2 on SiO_2 was also acidic.[24] Studies done by Burke indicated that both monolayer and partial monolayer coverages of Nb_2O_5 supported on SiO_2 are acidic.[16] What is interesting in Burke's study is the fact that the partial surface coverage of the supported Nb_2O_5 has a higher acid strength and acidity than the full monolayer coverage.[16]

It has been shown in previous studies that the silica substrate is well suited for supporting oxides.[4,5] Since silica alone has little to no acidity, changes in acidity can be easily observed and attributed to an added component. In Connell and Dumesic's study, they were interested in materials in the regime of dilute binary oxides; i.e. materials that contain two components with the major component controlling the structure. Since their materials were prepared by impregnation, the minor oxide component was expected to be located near the surface.[4] One may assume that similar acid sites generated from the addition of a second oxide might also occur on the surface of true binary oxides, which would in general have a different bulk structure from the individual component.

The current research takes a very similar approach to the work of Connell and Dumesic. However, instead of only looking at how one oxide interacts on the surface, this study looked at how a supported binary oxide interacts with the silica substrate and with each other. The assumptions made before should still hold in this system; that is, the major component, silica, controls the structure, and the minor oxides, niobia and alumina, are located near the surface. Although adding a second oxide to the silica support may seem a trivial matter, it complicates things enormously. Now one must worry about a number of things: whether the niobia and alumina are strongly interacting together with weak interactions to the silica surface; whether the niobia and alumina are weakly interacting together with strong interactions to the silica surface; or whether the situation is somewhere in between these two extremes and moderate interactions are shared among all the oxides. If the supported binary oxides strongly interact with each other, then one might expect to find acid sites and properties similar to those of the binary mixed oxides. If the supported binary oxides show strong independent interactions with the substrate, then one could expect the acid sites to be similar to each of the oxides supported independently on silica, and the existence of a linear relationship among the properties. Moderate interactions among all the oxides will then obviously be somewhere in between these two cases. To our knowledge there has been no study done on supported niobia/alumina binary oxides of various preparations and composition. Therefore, it is the goal of this research to investigate the effect that different preparations have on the properties of both mixed and supported niobia/alumina binary oxides.

2.3 Acid Strength and Acidity

Solid acids have been extensively used and studied as catalysts or catalyst carriers in the petroleum industry and organic syntheses for the past 50 years. Currently, acid catalyzed reactions are by far the most commercially important and include a wide range of reactions such as catalytic cracking, polymerization, alkylation, and isomerization.[25,26] The use of solid acid catalysts provides the following advantages compared with the use of liquid acid catalysts:[1]

- High catalytic activity and selectivity are frequently observed;
- Corrosion in reactor vessels is minimal;
- Repeated use of the catalyst is possible;
- Ease of separation of solid acid catalyst from reaction mixture;
- Disposal of spent catalyst offers no environmental problems.

The importance of solid acids as catalysts has caused an extensive study of the acidic properties on catalyst surfaces, the structure of acid sites, and their catalytic action. For example, Rodenas et al. studied the surface and catalytic properties of TiO_2/Al_2O_3 and proposed hypotheses as to the structure of the acid sites.[21] Even more recently has it been found that niobia is a strong solid acid with a very high activity and selectivity in ethylene hydration.[27] The study undertaken here has also focused mainly on the acidic and catalytic properties of the materials and the nature of the surface acid sites.

A solid acid may be understood in simple terms as a solid which changes the color of a basic indicator, or as a solid on which a base is chemically adsorbed. More specifically there are two types of acid sites found on solid acids. Brönsted acid sites have tendencies to donate protons, while Lewis acid sites accept electron pairs. The distinction between the two sites is important because the catalytic and acidic properties of these acid sites can be very different. The next sections will go into more detail as to how the solid surface can be characterized in terms of acid strength and acidity.

2.3.1 Acid Strength

Walling defined the acid strength of a solid surface as the ability of the surface to convert an adsorbed neutral base to its conjugate acid.[28] If the reaction proceeds by means of proton transfer from the surface to the adsorbate, then the acid site is of Brönsted nature and the acid strength is expressed by the Hammett acidity function H_o:[1]

$$H_o = -\log\frac{a_{H^+} f_B}{f_{BH^+}} \qquad (2.1)$$

or

$$H_o = pKa + \log\frac{[B]}{[BH^+]} \qquad (2.2)$$

where a_{H^+} is the proton activity, [B] and [BH$^+$] are the concentrations of the neutral base(basic indicator) and its conjugate acid respectively, and f_B and f_{BH^+} are the corresponding activity coefficients. Similarly, if the reaction proceeds by means of an electron pair transfer from the adsorbate to the surface, the acid site is of Lewis nature and the acid strength is expressed by H_o as:[1]

$$H_o = -\log\frac{a_A f_B}{f_{AB}} \qquad (2.3)$$

or

$$H_o = pKa + \log\frac{[B]}{[AB]} \qquad (2.4)$$

where a_A is the activity of the Lewis acid, [B] and [AB] are the concentrations of the neutral base (basic indicator) and its conjugate acid respectively, and f_B and f_{AB} are the corresponding activity coefficients.

The above equations indicate that at the equivalence point (where [B]/[BH$^+$] or [B]/[AB] = 1), H_o = pKa. Titrating a sample oxide with a range of indicators, each possessing a different pKa value, allows one to obtain an acid strength in terms of H_o. Thus, the color of suitable indicators, those readily distinguishable from one another such as red and yellow while in their acidic and basic forms respectively, adsorbed on a surface will give a measure of its acid strength. If the color is that of the acidic form of the indicator, then the value of the H_o function of the surface is equal to or lower than the pKa of the conjugate acid of the indicator. Lower values of H_0 correspond to greater acid strengths; hence, the lower the pKa, the greater is the acid strength of the solid.[1,2,3]

2.3.2 Acidity

The amount of acid on a solid is usually expressed as the number or millimoles of acid sites per unit weight or surface area of the solid, and is obtained by measuring the amount of a base which reacts with the solid acid.[1,29] This quantity has been loosely referred to as acidity. In this research, the technique used to study the acidic properties of the surfaces was that used by Benesi.[1,2,3] The determination of strength and amount of solid acid were made by using Hammett indicators and n-butylamine titration. The usefulness of this method is easily seen because it enables a determination of the amount of acid at various acid strengths by the amine titration. However, this method measures the total amount of both Brönsted and Lewis acids. This is indeed a downfall, because it is often necessary to distinguish between Brönsted and Lewis acid sites in order to fully characterize a solid acid and its catalytic properties.

2.3.3 Theories of Acidity in Binary Oxides

Most binary oxides are known to have surface acidities that are greater than the sum of the single component oxides which make up the chemical mixture. This generation effect in acidity can easily be explained in terms of Pauling's electrostatic valence rule.[30] This rule states that the local charge imbalances that result from the mixing of the oxides, is the reason that acidity develops in the mixture. Publications by Tanabe, Seiyama, and Kung have proposed predictive models for the formation of acid sites and acid types in mixed oxides which are extensions of Pauling's rule.[1,31,32] Connell and Dumesic have also recently proposed predictive models for acid site and acid type generation of surface phase oxides that are based on Pauling's electrostatic bonding rules as well.[5] These models will be separately discussed for clarity.

2.3.3.1 Tanabe's Model

Tanabe et al. developed a model which predicts what kinds of binary oxides will form acid sites and whether they will be of the Brönsted or Lewis type.[1] The acidity generation is caused by an excess of positive or negative charge in a model binary oxide structure. Excessive positive charge will produce Lewis acids through the creation of electron pair acceptor sites. Excessive negative charge will generate Brönsted acids through the association of protons with oxygens to neutralize the electronic charges. Tanabe's model structure has the following constraints:

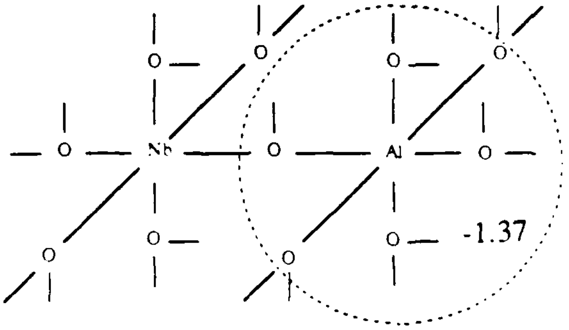
- The coordination numbers (and valences) of both the major metal ion and minor metal ion components are maintained even when mixed.
- The coordination number (and valence) for the oxygen ion of the major metal ion component is retained for all the oxygen ions in the binary oxide.

Even with the above restrictions, Tanabe's hypothesis correctly predicted acidity generation in 90% of the chemically mixed oxides studied.

An example of the application of this theory is demonstrated for the Nb_2O_5/Al_2O_3 mixed oxides. In pure niobia, the coordination numbers for oxygen and niobium are 2.4 and 6 respectively. In alumina, the coordination numbers for oxygen and aluminum are 3.5 and 5.25 respectively.[5] The charge distribution from each metal ion to the surrounding oxygens is assumed to be even and is thus equal to the total charge of the metal ion divided by its coordination number. Figures 2-1 (a) and 2-1 (b) show the cases when Nb_2O_5 is the major oxide, and when Al_2O_3 is the major oxide respectively. In the Nb_2O_5 - rich environment, the three positive charges of aluminum are distributed to the 5.25 bonds, while the two negative charges of the oxygen atom are distributed to 2.4 bonds. Therefore, the charge difference at one bond is given by $(+3 / 5.25) + (-2 / 2.4) = -0.26$, and accounting for all bonds gives $(-0.26) \times 5.25 = -1.37$ in excess. This excess of negative charge should result in Brönsted acidity, because protons are considered to associate with the oxygens in order to maintain charge neutrality. In the

Figure 2-1: TANABE'S ACIDITY MODEL FOR Nb_2O_5/Al_2O_3

A) Nb_2O_5 is the Major Oxide:



+1.37

(proton donor)

Bronsted Acid

Coordination Numbers

O: 2.4

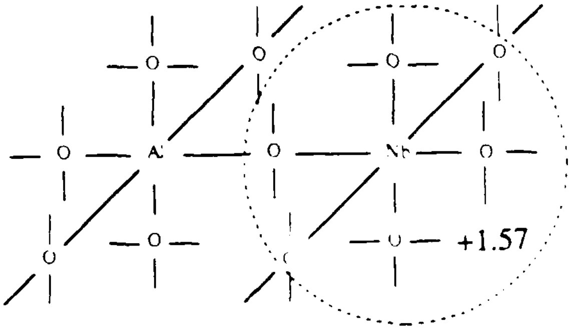
Nb: 6

Al: 5.25

Charge Difference Between Al - O: (+3 / 5.25) + (-2 / 2.4) = -0.26

Total Charge Difference Per Unit: (-0.26) x 5.25 = -1.37

B) Al_2O_3 is the Major Oxide:



-1.57

(electron acceptor)

Lewis Acid

Coordination Number:

O: 3.5

Nb: 6

Al: 5.25

Charge Difference Between Nb - O: (+5 / 6) + (-2 / 3.5) = +0.26

Total Charge Difference Per Unit: (+0.26) x 6 = +1.57

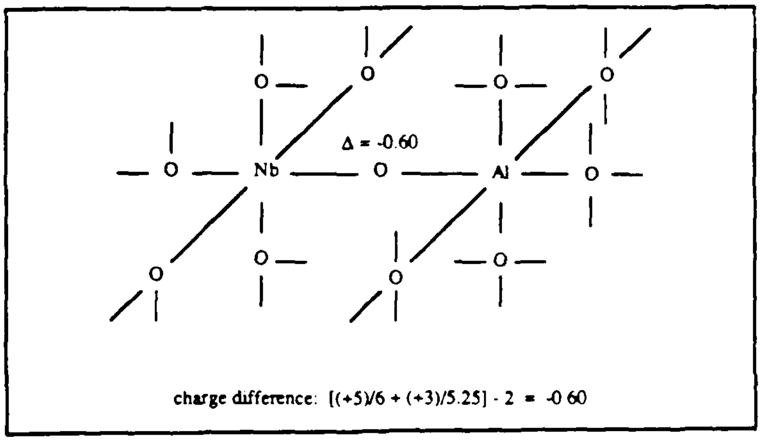
Al_2O_3 - rich environment, the five positive charges of the niobium atom are distributed to 6 bonds, while the two negative charges of the oxygen atom are distributed to 3.5 bonds. Therefore, the charge difference for each bond is $(+5 / 6) + (-2 / 3.5) = +0.26$, and accounting for all 6 bonds gives $(+0.26) \times 6 = +1.57$ in excess. In this case, the large excess of positive charge should result in Lewis acidity. As will be shown later, this Nb_2O_5/Al_2O_3 mixed oxide did indeed exhibit a very high acidity and acid strength.

2.3.3.2 Seiyama's Model

Seiyama has presented a slightly different model for the generation of acidity in binary mixed oxides.[31] He assumed that acid sites form at the boundaries where two oxides come into contact. The assumptions he made are listed below:

- The coordination numbers (and valences) of each metal ion are maintained as that of the pure oxide.
- The coordination number (and valence) of each oxygen atom depends on the type of metal ion that oxygen is associated with. If the oxygen is associated with a single metal ion, it retains the coordination number found in that metal oxide. If oxygen is shared between different metal ions, then its coordination number is 2 (it must be on a phase boundary). See Figure 2-2.

Figure 2-2: SEIYAMA'S MODEL FOR ACIDITY GENERATION



The Nb_2O_5/Al_2O_3 mixed oxide will contain an excessive negative charge of -0.60. The +5 / 6 charge of Nb and +3 / 5.25 charge of Al are distributed to the boundary oxygen which has 2 negative charges; therefore, the charge difference around the oxygen becomes -0.60, and Brönsted acidity is expected. This theory is limited to the cases where phase boundaries comprise a large percentage of the binary oxide, while Tanabe's model can be applied to all amorphous binary oxides.

2.3.3.3 Kung's Model

Kung has recently developed a predictive model for the acidity in dilute binary oxides by examining the effects of substituting a cation A into the matrix of an oxide BO_Z.[32] The first effect deals with the substitutional A cation, and results from a different electrostatic potential for the A cation in the BO_Z oxide matrix from that found for A in its pure oxide, AO_Y. When a substituted cation experiences a more negative potential than is found in its own lattice, the cation will become more electron deficient in its own matrix. Hence, it will be more likely to accept electrons and act as a Lewis acid. When there is a relatively positive potential surrounding the substituting ion, Kung predicts no local acidity.

The second effect deals with the differences in formal oxidation states between the substituting and the major oxide component cations. This difference in cation oxidation states creates charge imbalances in the mixed oxide matrix and in order to achieve neutrality defects are created which can result in acidity. The substituting cation is assumed to have the same coordination number as the major component. When the oxidation state of A is less than that of B ($Y<Z$), a net negative charge results, and in order to balance this excess charge, a proton may be adsorbed onto an oxygen to form a Brönsted acid. When the oxidation state of A is greater than that of B ($Y>Z$) a positive charge results which can be balanced by a cation vacancy, thus a Lewis acid site may be formed because cation vacancies are electron deficient.

When Kung's model is applied to the Nb_2O_5/Al_2O_3 system, Brönsted acidity is predicted in the matrix when niobia is the major oxide and Lewis acidity is possible at the alumina sites; however, Lewis acidity is predicted in the matrix when alumina is the major oxide (see Table 2-1). These predictions match almost identically with those of

Tanabe's except that Lewis acidity is possible as well as Brönsted acidity when niobia is the major component. Kung's model also does equally well as Tanabe's at predicting acidity in other oxide systems. This is really no surprise since both are based on Pauling's electrostatic valence rule. One downfall of Kung's model is that it is only applicable in the limit of dilute solution when substituting ions are far apart for the approximation of electrostatic potentials.

Table 2-1: KUNG'S ACIDITY MODEL FOR Nb_2O_5/Al_2O_3

			Type of Acid Site	
Matrix Oxide BO_Z	**Substituting Oxide AO_Y**	**CASE**	**At Substituting Ion**	**In Matrix**
$NbO_{2.5}$	$AlO_{1.5}$	$Y<Z$	Lewis	Brönsted
$AlO_{1.5}$	$NbO_{2.5}$	$Y>Z$	None	Lewis

All three of the models mentioned above have their limitations. These models do not directly apply to surface properties; however, they do predict acidity from the bulk structures. Also, the assumptions made in the models in defining the structure are greatly simplified. There may be strains in the oxide lattices when a metal cation substitution takes place that may not allow configurations defined by Kung and Tanabe. These models work well, although they are simple, to offer a fundamental understanding of acidity, one which is based on the electrostatic potentials within the oxides.

2.3.3.4 Connell and Dumesic's Model

Connell and Dumesic's model is used to predict Lewis acid sites in the limit of dilute binary oxides where the major component controls the oxide structure and the dopant surface concentration controls the number of acid sites.[5] They used silica as the major oxide component and a variety of dopant cations for their study on Lewis acid generation. This model as well as all of the previous ones mentioned was based on Pauling's electrostatic valence rule. This model is subject to the following constraints:

- The local structure for the major component (oxide) is not dramatically altered by the addition of a minor component (oxide). The coordination numbers (and valences) of the major component metal ions and all oxygen ions are retained from those of the pure major component.
- The valence of the substituting metal ion is retained from that of the pure oxide.
- The doping cation can not easily form a solid solution or a crystalline mixed oxide, and also the doping cation must be bonded to the host oxide sufficiently strongly so that it does not sinter into particles of its own oxide.
- The host oxide must be acidic or at least not strongly basic.

For example, oxygen has a coordination number of two in silica. The charge transfer along each cation to anion bond according to Pauling's rule is 2/2 or 1. Therefore, for a +2 cation on the silica surface, two bonds are required for charge neutrality. For a +5 cation, the number of bonds increases to five. Thus, if the coordination number predicted by these simple rules is smaller than 4 for a typical cation with a +3, +4, or +5 charge, the *probability* that the cation may be coordinatively unsaturated is larger and it functions as a Lewis acid site.[5] This model does not predict Lewis acid strengths, but merely predicts the existence of Lewis acids. Also, it merely states that the probability of forming acid sites becomes greater as the predicted coordination number decreases. This model only involves valence and coordination numbers of the metal cations on the silica surface, in accord with Pauling's electrostatic bond strength rules. Despite the simplicity of this model, it successfully predicted that all seven singly supported oxides studied by their group would generate Lewis acidity.[14] A prediction for Brönsted acidity has been developed that is explained by a special bonding configuration.[14] It was also discovered in Dumesic's study that alumina deposited as a partial monolayer on silica had both Brönsted and Lewis acid sites.[14,15]

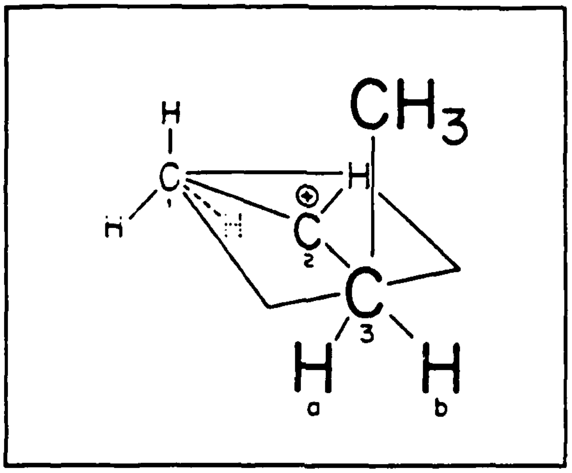
2.4 1-Butene Isomerization

It has been known for quite some time that acid catalysts easily isomerize olefins.[33] It has also been suggested that Brönsted acids are much more active than Lewis acids for skeletal transformations of hydrocarbons.[3] In particular, the acid catalyzed isomerization of 1-butene has been thoroughly investigated over a wide range of catalysts: SiO_2/Al_2O_3[33], Nb_2O_5/SiO_2[13], TiO_2/Al_2O_3[21], and many other binary oxides. Because this reaction has been so extensively studied, it makes a suitable test reaction to investigate the activity and selectivity of solid acids and to compare the results with the literature.

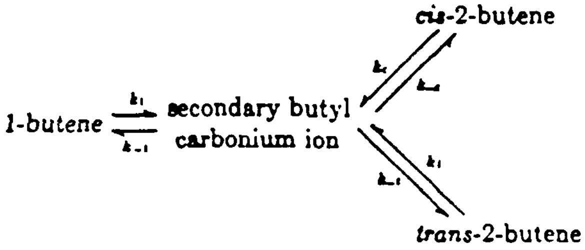
The stereoselective catalytic isomerization of 1-butene has been studied over a wide variety of catalysts.[34] Kinetic and mechanistic studies of n-butene isomerization have also been studied by a number of researchers.[35,36,37,38] Hall has recently proposed a model to explain the observed selectivities and the temperature dependence of the cis/trans ratio.[39] A 2-butyl carbonium ion common intermediate was used to explain the results.

It is established from many studies that 1-butene isomerizes via a highly reactive carbonium ion. The ion can be formed by a number of methods, but the simplest is by abstraction of a proton from a Brönsted acid site to the 1-butene molecule. A model of this classical ion is seen in Figure 2-3.[38]

Figure 2-3: CLASSICAL 2-BUTYL CARBONIUM ION INTERMEDIATE[38]



A schematic of the reaction is listed in Equation 2.5.[38]



(2.5)

From Figure 2-3, one first notices that the two hydrogens on the C_3 atom are labelled as a) and b) because they are geometrically different.[38] Should the H_a atom be lost, the methyl group would tend to fall into a cis-configuration, whereas, if H_b were lost, trans-2-butene would result as the product. Since the two C_3 - H bonds are energetically similar, one would expect them to be broken with equal probabilities at all temperatures.[38] This would result in cis/trans-2-butene ratios of about 1, which is what this study also found for all calcined (500° C) catalysts. Hall has recently developed a model for discussing why a cis/trans ratio different from unity would result from a common intermediate.[39] The main result from his research was that the intermediate is a carbonium ion with some kind of special interaction with the surface which would create a larger energy barrier for the formation of trans-2-butene or cis-2-butene and thus create a larger or smaller cis/trans ratio respectively.

It is generally agreed that Brönsted acid sites are responsible for a share of the activity of acid catalysts, and that such a tool is valuable for studying acid catalyst properties.[3] There has also been research in trying to derive correlations between acidity and activity of 1-butene isomerization; however, most of these studies used n-butylamine titration which detects both Brönsted and Lewis acids with no differentiation between them. Thus, it is difficult to decide what acid sites actually catalyze this reaction. Results on studies of SiO_2/Al_2O_3, Nb_2O_5/SiO_2, and TiO_2/SiO_2 in catalyzing 1-butene isomerization show that the selectivities (cis/trans-2-butene) are all around 1 indicating the mechanism proceeds via a carbonium ion intermediate.[38,13,20] Results from this study also indicate cis/trans ratios of around 1 for both Nb_2O_5/Al_2O_3 and supported-Nb_2O_5/Al_2O_3 oxides.

2.5 Summary

A review of the current literature indicates that no work has been done on either the mixed oxide system of Nb_2O_5/Al_2O_3 or the supported-Nb_2O_5/Al_2O_3 binary oxide system. In fact, little work has been done with respect to supporting two oxides on a substrate, while the literature has an abundant supply of research done on singly supported oxides. These mixed and supported-mixed oxides need to be explored in order to characterize them with respect to their acidic and catalytic properties. Different types of preparation will also need to be explored to understand if this has any effect on the properties of the oxides.

In addition to researching these materials because studies have not been done on this combination of oxides, it is important to understand what type of oxide-oxide interactions occur in these oxides. The thermal stability of these oxides is also unclear.

For example, will the surface phase oxides sinter into crystallites (indicating strong interactions among each other), or will they remain dispersed on the surface (indicating strong substrate interaction) and resist sintering with a strong surface stability? These questions will need to be addressed as will the stability of the mixed oxides upon a thermal driving force. It is unclear whether any of the mixed oxides or supported-mixed oxides will form compounds or remain completely amorphous to heat treatments. Understanding how different preparation methods affect the acidic and catalytic properties of the supported oxides, should lead to a better understanding in the oxide-oxide interactions that occur in these materials. Varying the composition of the niobia/alumina oxides will change the major oxide component and give some more insight to these materials. The study of the effects of preparation and the resulting structures on the acidic and catalytic properties of niobia-alumina binary oxides is the objective of this research.

3. EXPERIMENTAL

3.1 General

Samples of niobia-alumina binary oxides were prepared either as mixed oxides (Nb_2O_5/Al_2O_3) or as surface phase oxides (SiO_2-supported Nb_2O_5/Al_2O_3) with varying molar compositions. Each of these samples was studied with several techniques for an extensive characterization. Characterization procedures were identical for both sets of binary oxides. The following sections will provide the necessary experimental procedures for each technique.

3.2 Preparation of Binary Oxides

The following section shows the preparation of mixed oxides of Nb_2O_5/Al_2O_3 and SiO_2-supported Nb_2O_5/Al_2O_3. The supported-binary oxides were prepared to have the same surface atomic compositions as the mixed oxides for ease of comparison. The different preparation techniques for both types of binary oxides are separately discussed for clarity.

3.2.1 Nb_2O_5/Al_2O_3 Mixed Oxide Preparation

There were several steps necessary in the preparation of the niobia/alumina mixed oxides. A standard co-precipitation method was used and is outlined in Table 3-1. In a typical run, 25 g of niobium(V) ethoxide (Alfa Products) was added to 2000 ml of methanol (99.9% Fisher Scientific Company) under constant mechanical stirring which resulted in a yellowish tint to the solution. Aluminum nitrate (Alfa Products) was then added to the stirred mixture with no color change. Various niobium/aluminum molar

Table 3-1: EXPERIMENTAL PROCEDURE FOR MIXED OXIDE SYNTHESIS

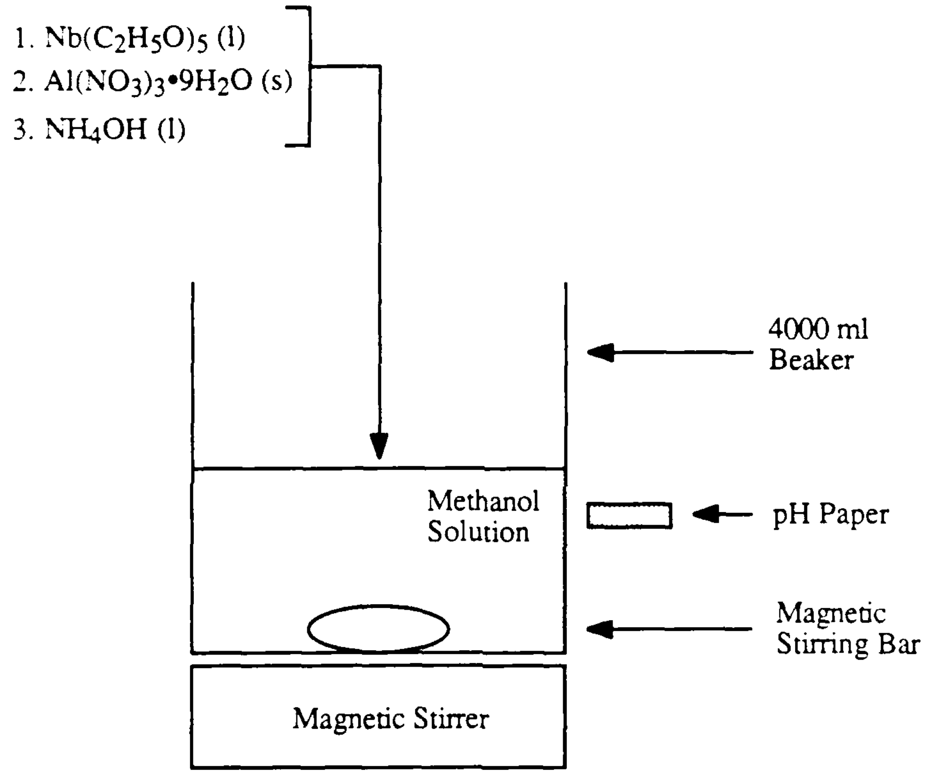
PROCESS	STEPS AND CONDITIONS OF PROCEDURE
AGITATION	1. Add methanol (2000 ml) 2. Add niobium (V) ethoxide (niobia precursor) 3. Measure out varying amount of aluminum nitrate (alumina precursor) depending on composition 4. Equilibrate for 1 hour
REACTION	1. Constant mechanical stirring 2. Add NH_4OH *dropwise until solution* pH is 7 3. Let sit overnight and settle
FILTERING	1. Use mechanical pump to aid in filtering process 2. Use filter paper with smaller particle retention if solution goes through paper
WASHING	1. Wash 4-5 times using deionized water 2. Agitate filter cake until a homogeneous solution with no clumps results
DRYING	1. Heat overnight in vacuum oven at 383 K
CALCINING	1. Heat in N_2 (300 cc/min) at 673 K for 2 hours 2. Heat in O_2 (300 cc/min) at 773 K for 2 hours

compositions could then be achieved by controlling how much aluminum nitrate was added. In this research, three atomic compositions were made: Nb_2O_5/Al_2O_3 mixed oxides with the Nb/Al molar percent compositions of 75/25, 50/50, and 25/75 %. Stoichiometric calculations for all the mixed oxides can be found in Appendix A. After the aluminum nitrate was added, the liquid mixture was allowed to equilibrate for about 1 hour in order to insure a homogeneous solution. Then, NH_4OH (28 wt.% NH_3, Fisher Scientific Company) was added dropwise until the resulting solution reached a pH of about 7 (see Figure 3-1). A cloudy solution began to form at around a pH of 4, which then gave rise to a milky white precipitate at a pH equal to 5. NH_4OH was then added until there was no further increase in precipitation and the solution was no longer acidic. The following describes the general reaction scheme.

$$Nb(C_2H_5O)_5(l) + Al(NO_3)_3\bullet 9H_2O(s) \xrightarrow{\substack{CH_3OH(l)\\ NH_4OH(l)}} \text{Hydroxide(ppt)} + \text{byproducts} \quad (3.1)$$

The resulting white precipitate was allowed to settle out from the methanol solution overnight in order to make the separation easier. The clear methanol solution above the precipitate was then decanted off. A number of cycles (4-5) of washing with deionized water and filtering (mechanical pump aided in filtration) on filter paper (No. 1 Qualitative, Whatman Limited) were repeated to insure that all the hydroxide precipitate was free from any ions that may contaminate the oxide (see Figure 3-2). The resulting filter cake was then dried in a vacuum air oven at 383 K overnight. This material was ground to a fine powder (> 100 mesh) and then subjected to the standard calcination procedure. This procedure consisted of heating the powder in N_2 (300 cc/min) at 673 K for 2 hours to get rid of any impurities present, and then calcined in O_2 (300 cc/min) at 773 K for 2 hours to fully oxidize the sample (see Figure 3-3). The resulting mixed oxide was cooled to room temperature, with no hold at 773 K, under a reduced O_2 flow (50 cc/min), and then

Figure 3-1: SCEMATIC OF MIXED OXIDE CO-PRECIPITATION METHOD



STEPS	PROCEDURE
1,2	Feed Desired Amounts of Oxide Precursors
3	Add Until pH of Solution is 7

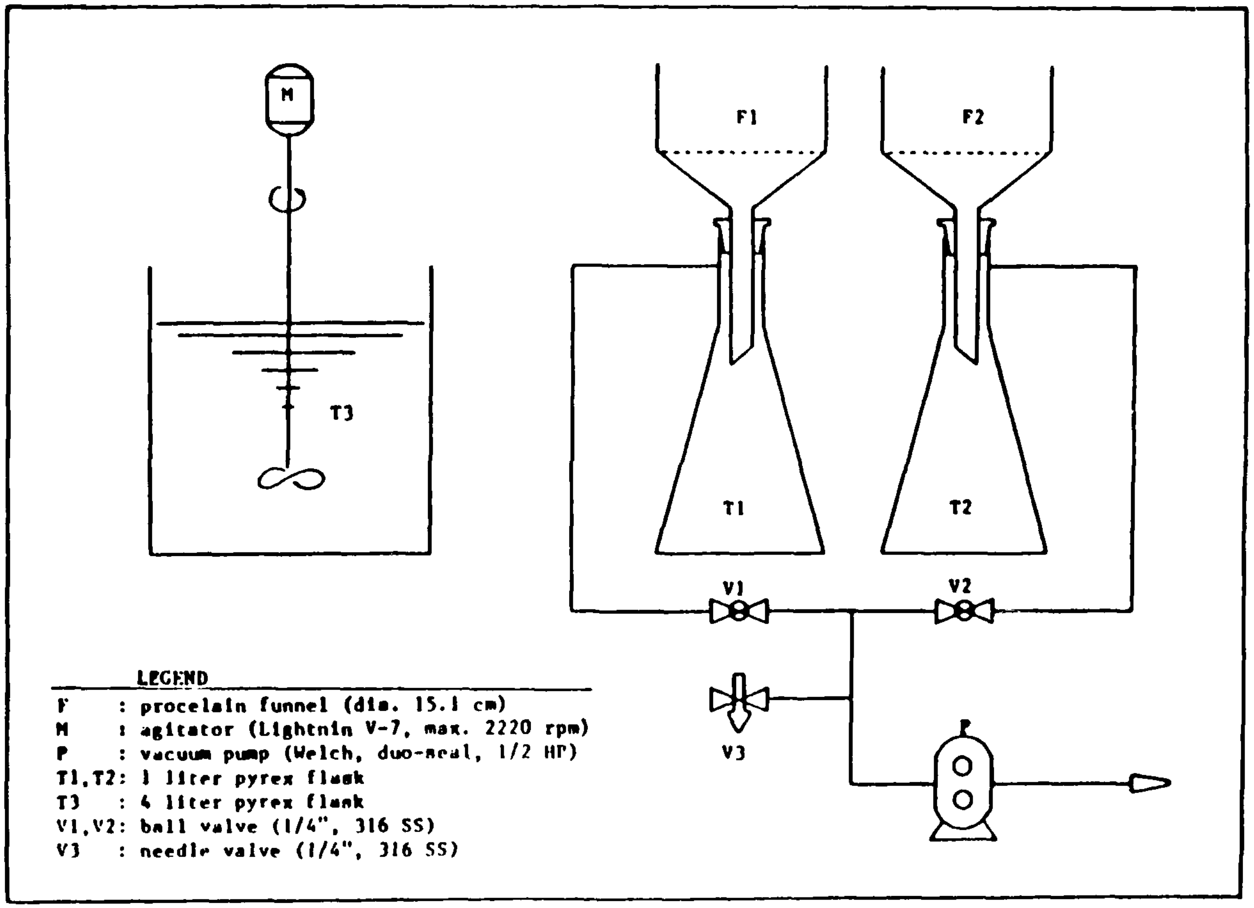


Figure 3-2 SCHEMATIC OF FILTRATION AND WASHING SYSTEM[13]

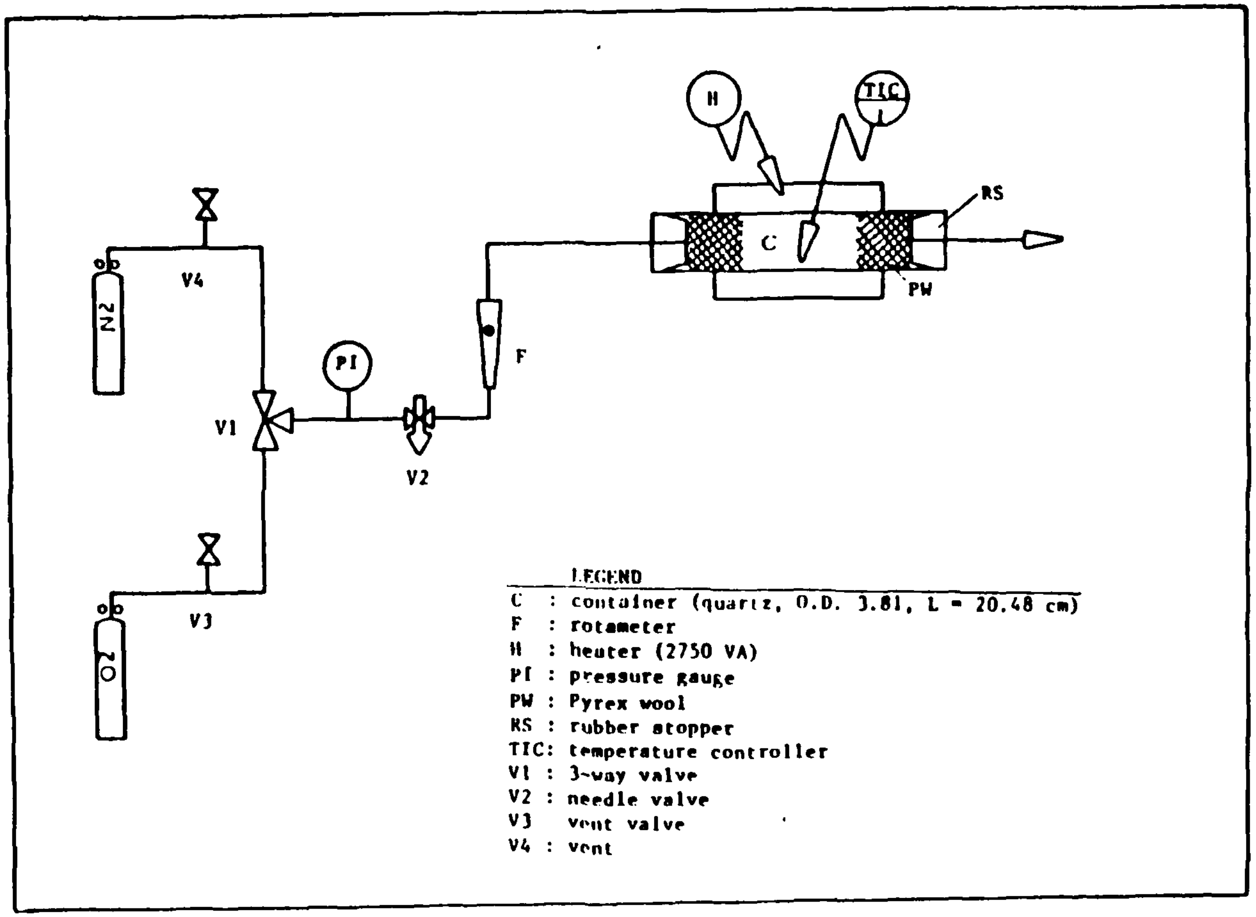


Figure 3-3 SCHEMATIC OF CALCINATION APPARATUS[13]

placed in vials and stored in a dessicator for future experiments. The notations of the three prepared mixed oxides are: NA(75/25), NA(50/50) and NA(25/75). The numbers in parentheses correspond to the percent molar compositions of the niobium and aluminum atoms.

3.2.2 Surface Oxide Preparation

The supported catalysts used in this study were all prepared on the basis of calculations that would allow the support, silica gel catalyst (Grade 952, Davison Specialty Chemical Company), to have a one monolayer coverage of binary oxide on the surface (S.A. of silica gel ~ 300 m^2/g). These catalysts had surface loadings with molar compositions equivalent to those of the mixed oxides. Calculations for determining these loadings were based on one molecule of $NbO_{2.5}$ occupying an area of 16×10^{-20} m^2 and one molecule of $AlO_{1.5}$ occupying an area of 20×10^{-20} m^2. More specific calculations for determining different niobium/aluminum atom compositions are located in Appendix B. When only one oxide (i.e. niobia) was impregnated onto the silica surface, the loading was the same as if the second oxide (i.e. alumina) were present in order to make a one monolayer surface coverage. Therefore, the supported single oxides only partially covered the surface. The following sections will describe the catalysts prepared and the nomenclature that will be used to describe them throughout the rest of this thesis.

3.2.2.1 SiO_2-supported Nb_2O_5 or Al_2O_3

These single oxide supported samples were prepared by incipient wetness impregnation using 1.8 ml of solution per gram of SiO_2 as the incipient wetness point. The preparation method is shown in Table 3-2. The niobia and alumina precursors used for the impregnation were niobium(V) ethoxide (Alfa Products) and aluminum-s-butoxide (95 %, Alfa Products) respectively. These precursors were measured and dissolved in enough n-hexane (99 %, Fisher Scientific Company) to reach incipient wetness with the

Table 3-2: EXPERIMENTAL PROCEDURE FOR SURFACE OXIDE SYNTHESIS

PROCESS	STEPS AND CONDITIONS OF PROCEDURE
MIXING	1. Measure out niobia and/or alumina precursors 2. Place n-hexane in niobia or alumina precursors or both to dissolve material 3. Mix solution to insure good dispersion
IMPREGNATION	1. Carefully add solution to silica support dropwise to avoid clumping of mixture 2. Stir vigorously after each addition of solution (especially near incipient wetness point)
DRYING	1. Heat overnight in vacuum oven at 383 K
CALCINING	1. Heat in N_2 (300 cc/min) at 673 K for 2 hours 2. Heat in O_2 (300 cc/min) at 773 K for 2 hours 3. Repeat above steps for a sequential impregnation

amount of support used. The Nb or Al solution was then added dropwise to the silica support and distributed homogeneously throughout the mixture by using a mortar and pestle (see Figure 3-4). The samples were then dried in a vacuum air oven at 383 K overnight. These supported oxides were then calcined following the standard procedure: heating in N_2 (300 cc/min) at 673 K for 2 hours, and then calcined in O_2 (300 cc/min) at 773 K for 2 hours. These samples were then cooled to room temperature in O_2 and placed in vials and stored for future use. Different Nb_2O_5 or Al_2O_3 loadings on the silica gel could easily be made by weighing out appropriate amounts of precursor for the support. In this study two different loadings for both oxides were prepared: SiO_2-supported Nb_2O_5 with notations of Nb/Al(3/1) Pre and Nb/Al(1/1) Pre, and SiO_2-supported Al_2O_3 with names of Al/Nb(1/3) Pre and Al/Nb(1/1) Pre. The reference of Pre indicates that the second oxide has not been deposited onto the substrate and that this material will be later used in the sequential impregnation. Also, the numbers located in parentheses indicate the niobium/aluminum or aluminum/niobium molar ratio.

3.2.2.2 Sequential Impregnation, SiO_2-supported Nb_2O_5/Al_2O_3

These supported-binary oxide catalysts were also prepared by incipient wetness impregnation. The niobia and alumina precursors were the same as those used in the supported-single oxide catalysts. In this preparation, these samples were sequentially impregnated with niobia first and then alumina or vice versa to see if the preparation sequence had any effect on the physical properties of these oxides. For brevity I will only look at impregnating the Nb/Al(3/1) Pre sample with Al_2O_3, although the steps are identical for impregnating the Al/Nb(1/3) Pre sample with Nb_2O_5. Calculations for the loadings used in these next steps can be found in Appendix B. An amount of Nb/Al(3/1) Pre was weighed. Enough aluminum-s-butoxide was then weighed which would give the appropriate surface molar percent composition (i.e. Nb/Al(75/25)). The alumina precursor was then dissolved in n-hexane and added dropwise (very carefully) to the

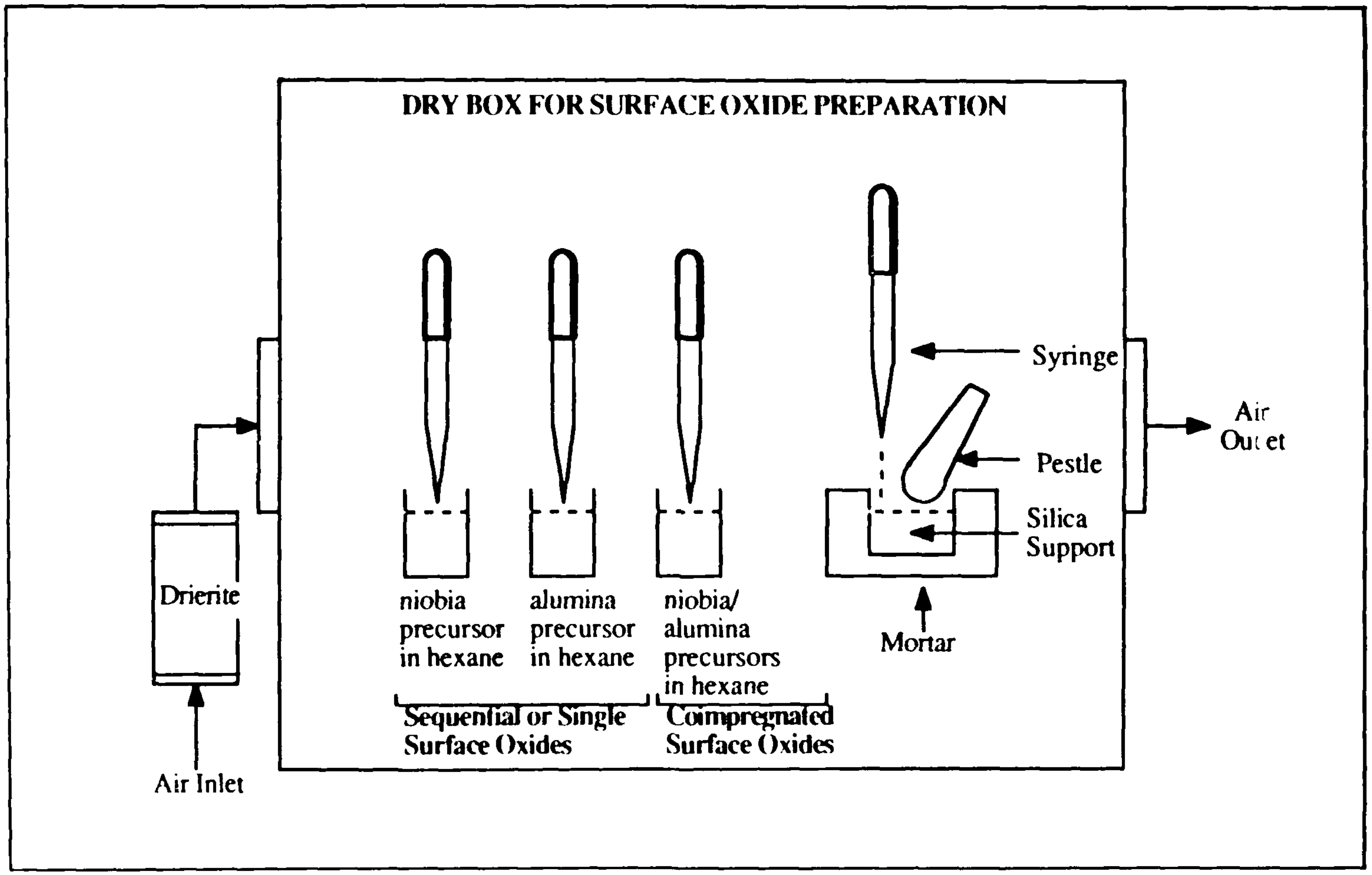


Figure 3-4: SCHEMATIC OF SURFACE OXIDE INCIPIENT WETNESS IMPREGNATION METHOD

supported-Nb_2O_5 until the incipient wetness point was reached. The solution was distributed homogeneously throughout the mixture by mortar and pestle. The sample was then dried in a vacuum air oven at 383 K overnight. This sequentially impregnated supported binary oxide (Nb/Al(3/1) Seq) along with the other sequentially impregnated catalyst (Al/Nb(1/3) Seq) were then calcined according to the standard procedure. The resulting surface oxides were stored in glass vials until needed.

3.2.2.3 Coimpregnation, SiO_2-supported Nb_2O_5/Al_2O_3

The following coimpregnated, supported-binary oxides were also prepared by incipient wetness impregnation using 1.8 ml of solution per gram of SiO_2 as the incipient wetness point. In this preparation, the samples were coimpregnated onto the support with the same precursors as used in preparing the other surface oxides. Again for brevity I will only describe one of the samples prepared, but the steps were identical for the preparation of the other two catalysts. An amount of niobia precursor and alumina precursor are separately weighed giving a surface molar composition of Nb/Al(3/1). These precursors are dissolved together in hexane, with enough hexane then added to insure that the incipient wetness point will be reached upon impregnation. Vigorous mixing of this solution insured that the precursors were well dispersed in solution to give a homogeneous mixture. This solution was then added dropwise to an appropriate amount of support and distributed uniformly throughout the sample by use of a mortar and pestle. The samples were then dried, as before, in a vacuum air oven at 383 K overnight. This coimpregnated-surface oxide was then calcined following the standard procedure. These samples were cooled to room temperature in O_2 and stored in vials until needed. Three different coimpregnated-surface oxides were prepared: 1. Coimpregnated, supported Nb_2O_5/Al_2O_3(75/25) (Nb/Al(3/1) Co), 2. Coimpregnated, supported Nb_2O_5/Al_2O_3(50/50) (Nb/Al(1/1) Co), 3. Coimpregnated, supported Nb_2O_5/Al_2O_3(25/75) (Nb/Al(1/3) Co). The notations in parentheses describe the coimpregnated catalysts and will be used throughout the rest of the thesis. Also, a summary of all oxides and their compositions and notations can be found in Table 3-3.

3.3 Characterization of Binary Oxides

3.3.1 B.E.T. Surface Area

The total surface areas of all mixed and surface oxides were determined with a commercial Quantasorb Unit (Quantachrome Corporation).[40] The system included two thermal conductivity detectors in one cell, one was located upstream as a reference and one was downstream from the sample. The difference in the thermal conductivity of the gas streams was detected, and this signal was integrated with respect to time to give the amount adsorbed or desorbed from the oxide sample. The desorption signals were the signals integrated because they gave Gaussian distributions. The adsorption signals were usually accompanied by non-Gaussian distributions (tailing curves) which were difficult to integrate. A calibrated volume of gas was injected into the system to determine the integrated counts to that given amount of gas. Mixtures of both 10 % N_2 balance He (Grade 5, Airco) and 30 % N_2 balance He (Grade 5, Airco) were used in the experiments. The single point-BET method was used, and the calculations for the surface areas can be found in the Quantasorb manual with the computer program for the calculation located in Appendix C.[40] Most of the oxides tested had high surface areas, so 100 to 200 milligrams of sample were used along with 10 cc as the calibration gas volume.

3.3.2 Differential Thermal Analysis (DTA)

Differential thermal analysis was used to study the heat effects of crystallite formation of the binary oxides when heated in He. The DTA experiments were performed on a Perkin-Elmer DTA Model 1700 High Temperature Differential Thermal

Table 3-3: NOMENCLATURE USED TO DESCRIBE SURFACE PHASE AND MIXED OXIDES

Supported Surface Phase Oxide or Mixed Oxide	Referred Name
Mixed Oxide Nb_2O_5/Al_2O_3 (Nb/Al(75/25))	NA(75/25)
Mixed Oxide Nb_2O_5/Al_2O_3 (Nb/Al(50/50))	NA(50/50)
Mixed Oxide Nb_2O_5/Al_2O_3 (Nb/Al(25/75))	NA(25/75)
Silica-Supported Nb_2O_5 (Nb/Al(3/1) with no Al)	Nb/Al(3/1) Pre
Silica-Supported Nb_2O_5 (Nb/Al(1/1) with no Al)	Nb/Al(1/1) Pre
Silica-Supported Al_2O_3 (Al/Nb(1/3) with no Nb)	Al/Nb(1/3) Pre
Silica-Supported Al_2O_3 (Al/Nb(1/1) with no Nb)	Al/Nb(1/1) Pre
Sequential Impregnation, Supported Nb_2O_5/Al_2O_3 (Nb/Al(3/1))	Nb/Al(3/1) Seq
Sequential Impregnation, Supported Al_2O_3/Nb_2O_5 (Al/Nb(1/3))	Al/Nb(1/3) Seq
Coimpregnation, Supported Nb_2O_5/Al_2O_3 (Nb/Al(3/1))	Nb/Al(3/1) Co
Coimpregnation, Supported Nb_2O_5/Al_2O_3 (Nb/Al(1/1))	Nb/Al(1/1) Co
Coimpregnation, Supported Nb_2O_5/Al_2O_3 (Nb/Al(1/3))	Nb/Al(1/3) Co

Analyzer. Approximately 30 milligrams of sample were analyzed in an inert atmosphere of helium flowing at 50 cc/min. The samples were then heated with a temperature ramping program from 25 to 1000° C at 10° C/min.

3.3.3 X-Ray Diffraction (XRD)

X-ray diffraction was used to observe the crystalline phases present in the prepared oxides both after calcination and after heat treating the samples in 50 cc/min of He with a heating ramp from 25 to 1000° C at 10° C/min with no hold. The XRD experiments were performed on a Rigaku diffractometer in the Department of Metallurgical Engineering and Materials Science. A molybdenum source was used with a copper filter. XRD slides were prepared by suspending an oxide in a colloidion solution (2/3 amyl acetate and 1/3 colloidion) on one side of a microscope slide. This mixture was spread over the slide to allow an even dispersion of powder particles, and then allowed to sit for approximately one day so the colloidion solution could evaporate. Scanning angles (2Θ) ranged from 5 to 35 degrees, and were scanned at 2 degrees/min. Two series of experiments were performed for each oxide. First, XRD scans were taken of calcined samples to determine if any crystallization occurred in the calcination step. Then, samples that had been previously calcined were heated under the same heating program and conditions of a DTA run (25 to 1000° C at 10° C/min with no hold, 50 cc/min He flow). These heat treated samples were then examined by XRD to determine whether crystallization had occurred with the heat treatment.

3.3.4 Acid Strength and Acidity

3.3.4.1 Acid Strength

The acid sites on various oxide surfaces may differ in amount and strength. Some oxides may have a large number of acid sites with a low acid strength, while others may have only a few acid sites which have a high acid strength.[2] The Benesi titration method with Hammett indicators was used to measure the number and strength of acid sites over the oxides in this study.[41] Table 3-4 shows these indicators and their pKa values along with the equivalent acidity in terms of percent H_2SO_4. The method of determining acid strength was made by placing approximately 40 milligrams of sample into a ground test tube, adding 1-2 ml of benzene and then 3 drops of indicator (0.1 wt. % in benzene), and then shaking briefly. Adsorption proceeded very rapidly, if it occurred at all, with a striking change in color between the basic and acidic forms of the indicator.[1] It should also be noted that the lower the pKa value of the indicator, the greater the acid strength of the solid.

3.3.4.2 Acidity

The amount (or acidity) of a solid acid was measured by amine titration *immediately after a determination of acid strength* by the Benesi method.[3] The method consisted of titrating a solid acid suspended in benzene with 0.05 N n-butylamine, using a range of various indicators. The indicator changes color into its acidic form when adsorbed onto a solid acid. Therefore, the titres of n-butylamine required to restore the color of its basic form give a measure of the number of acid sites on the surface.

Since the indicator which had been adsorbed on the acid sites must be replaced by the titrating base, *the basic strength of the amine must be higher than the indicator*. The use of the various indicators with different pKa values, as noted before, allows a determination of acidity at various acid strengths by amine titration. The amine titration method gave the sum of the amounts of both Brönsted and Lewis acid sites, since both electron pair acceptors and proton donors on the surface would react with either the electron pair ($-\dot{N}=$) of the indicator or that of the amine($\equiv$N:) to form a coordination bond.[2]

Table 3-4: INDICATORS USED FOR ACID STRENGTH MEASUREMENTS

	Color			
INDICATORS	**BASE**	**ACID**	**pKa**	**wt.% H_2SO_4**
Methyl Red	yellow	red	+4.8	5×10^{-5}
Dimethyl Yellow	yellow	red	+3.3	3×10^{-4}
4(Phenylazo)-Diphenylamine	yellow	purple	+1.5	2×10^{-2}
Dicinnamalacetone	yellow	red	-3.0	48
Benzalacetophenone	colorless	yellow	-5.6	71
Anthraquinone	colorless	yellow	-8.2	90

Great precautions were taken to prevent effects from titration time, powder size, volume of added indicator, and moisture on the measured acid amounts. All samples used were ≥ 100 mesh particles. The same amount of indicator was added to each sample, and the titration times for the oxides all spanned a period of 1 to 2 days. The greatest precaution taken was against moisture. Trace amounts of water can poison the strongest acid sites, as water has the properties of both a base and an acid. All titrations were done in a dry glove box (see Figure 3-5) that had a recirculation pump attached with drierite, and a gas line that allowed the box to be purged with N_2. All indicators were mixed with benzene (99.9%, Aldrich) which had been further dried with molecular sieves and stored in a dessicator which was also located in the glove box. The oxide samples were weighed out in vials and heated, with caps and stirring bars, in a vacuum oven at 383 K for one hour to free the surface of any physisorbed water. The ground vials were then spread with vacuum grease to prevent any evaporation that occurred with the added benzene. Also, all titrations were carried out using a digital pipette (4710, Eppendorf) which facilitated the use of small volumes of base, 10 - 100 μl, to be added to the samples, which were stirred with micromagnetic bars to insure equilibrium between the solution and surface was established. Endpoints of the mixed oxides were difficult to determine because they would slowly change the color of the indicator unlike the surface oxides which had rapid color changes. Therefore, endpoints for the mixed oxides were determined visibly when roughly half of the solid was the color of the basic form of the adsorbed indicator and the other half of the solid was the color of the acidic form of the adsorbed indicator.

3.3.5 1-Butene (1-C_4H_8) Isomerization

The catalytic activities of Nb_2O_5/Al_2O_3 mixed oxides and SiO_2-supported Nb_2O_5/Al_2O_3 were studied with the isomerization of 1-butene in a continuous flow micro-reactor shown schematically in Figure 3-6. This system had a feedback control

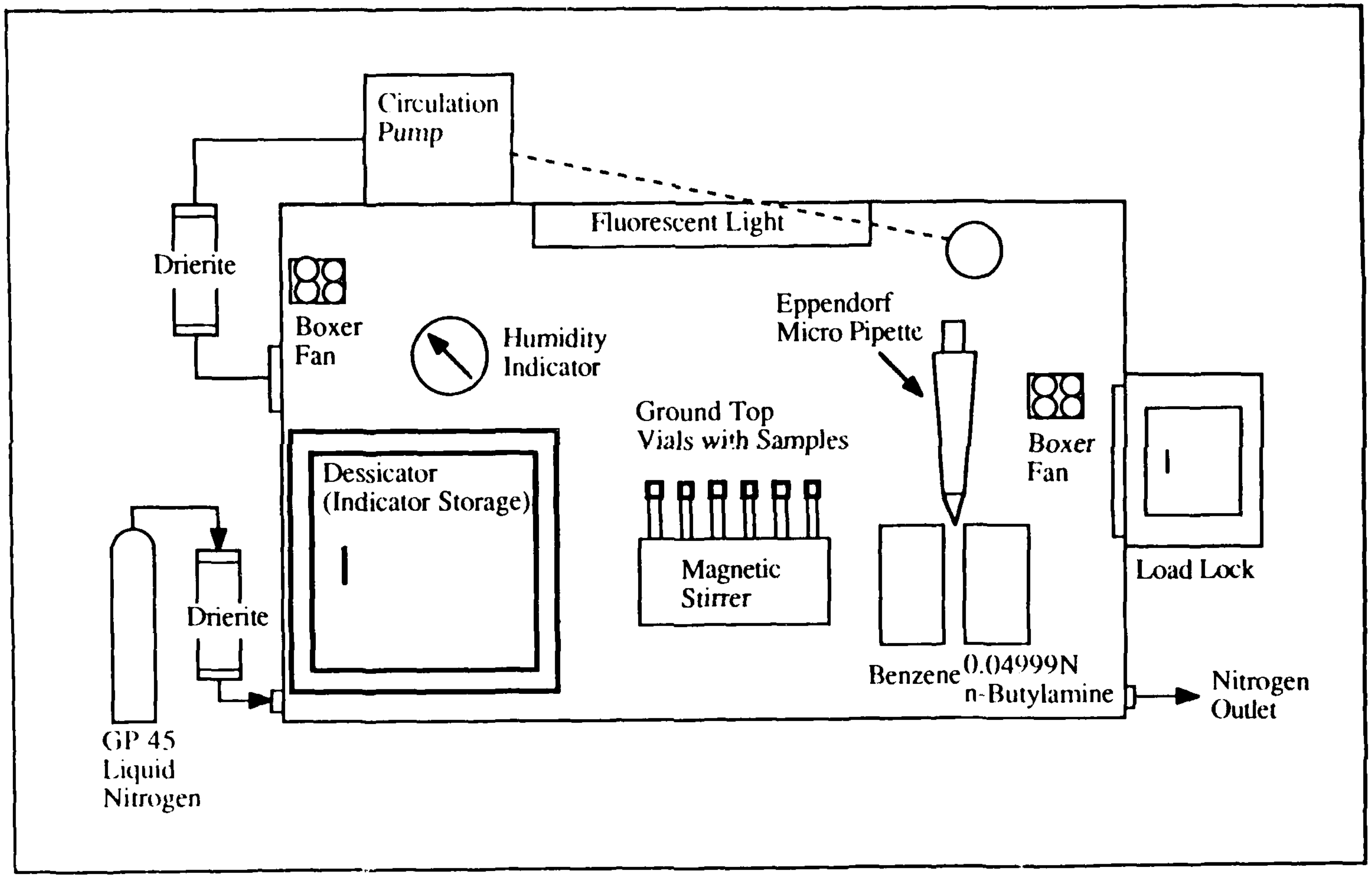


Figure 3-5: SCHEMATIC OF DRY BOX FOR N-BUTYLAMINE TITRATIONS

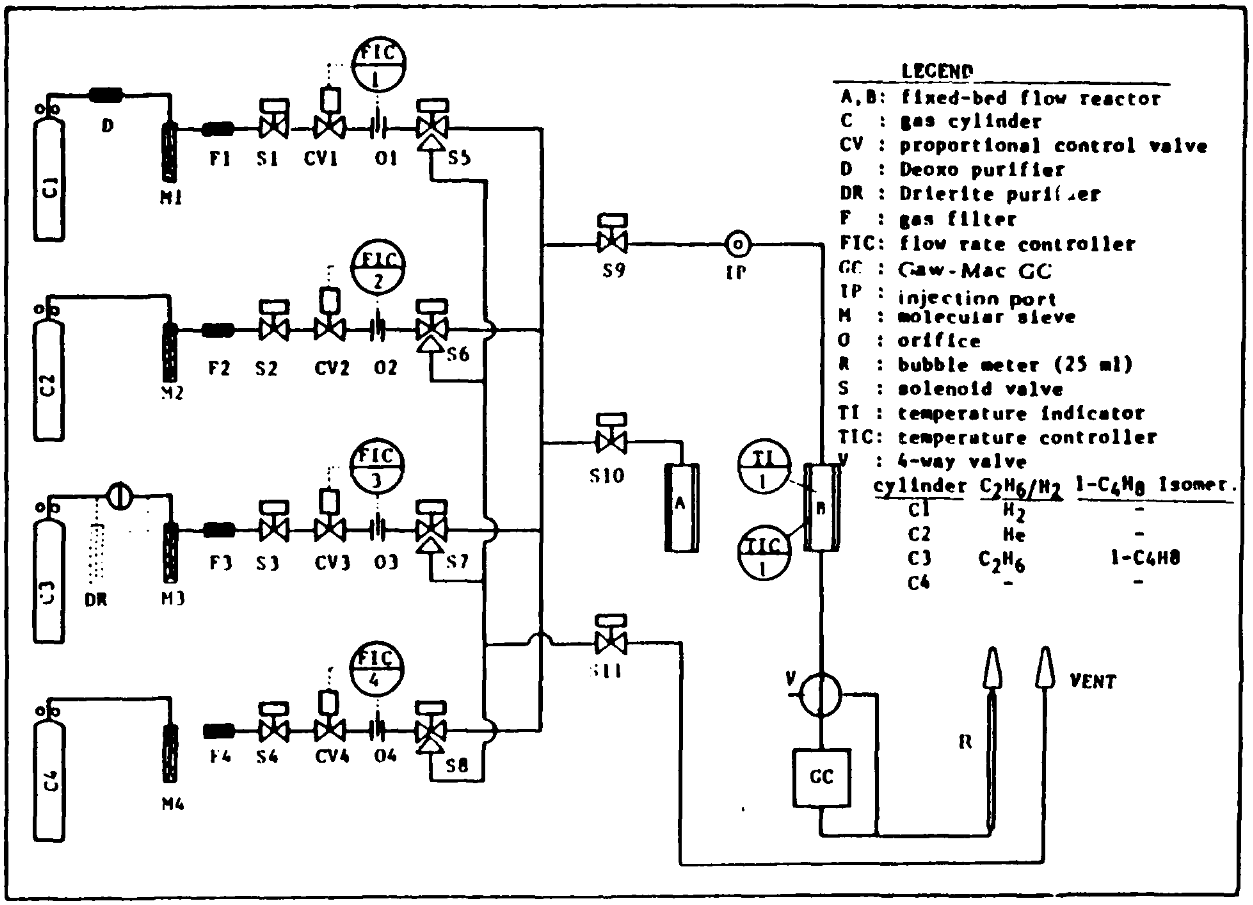


Figure 3-6 SCHEMATIC OF $1-C_4H_8$ ISOMERIZATION REACTION SYSTEM[13]

system for the gas flow rates, a reactor with a temperature controller, and gas analysis system, all attached to a control panel.

3.3.5.1 Gas Handling System

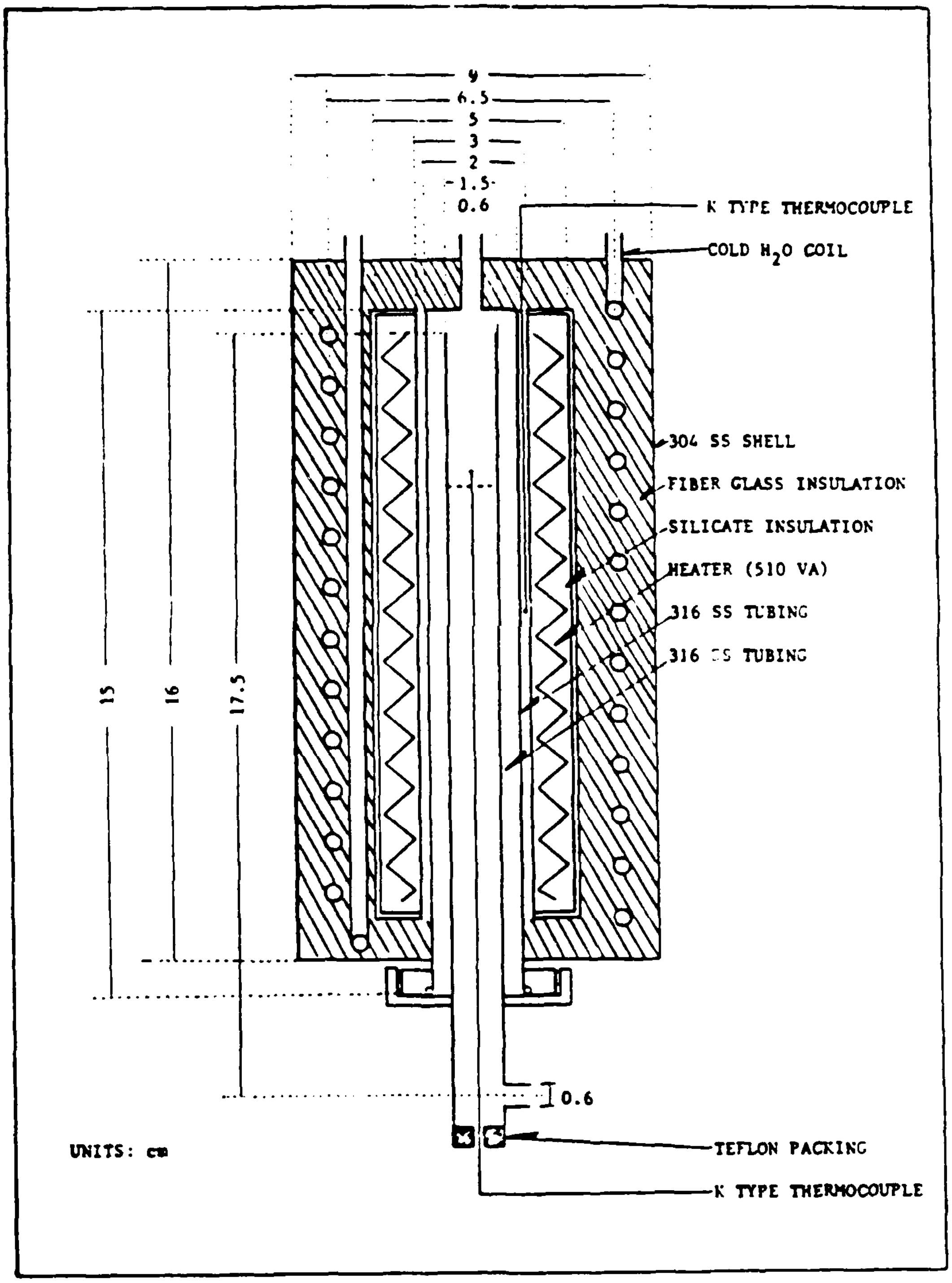
The gas handling system consisted of molecular sieve purifiers (Linde 4A), filters (Swagelok), on/off solenoid valves (General Valve Co.), proportional control valves (Brooks Instrument Co.), orifices and pressure transducers, and three-way valves (General Valve Co.) for both of the feed lines. The 1-C_4H_8 gas flowed directly to the reactor, while the He gas passed through the molecular sieve trap before entering the reactor as a carrier gas. Helium (Grade 5, Airco) was used as a carrier gas for the research grade 1-C_4H_8 (99.8%, Matheson). The two gases were well mixed before entering the reaction chamber.

3.3.5.2 Reactor

The micro-reactor consisted of a 1.5 cm O.D. vertical tube (316 stainless steel) equipped with a fritted disk to support the catalyst bed. The reactor was heated by a tubular ceramic heating element. The temperature of the furnace was sensed by a K-type thermocouple and controlled by a PID programmable temperature controller (Series CN-2010, Omega Engineering Co.). The bed was located in the middle of the furnace and had a height of 1 cm. The reactor temperature was also measured by a K-type thermocouple located in the center of the catalyst bed and was displayed with a digital temperature indicator (400B, Omega Engineering Co.).

The gaseous reactants were fed through the top of the reactor and reacted over the catalyst sample. The product gas was diverted through a 4-way valve to a vent or a gas chromatograph (GC) for analysis. A detailed drawing of the micro-reactor is shown in Figure 3-7.

Figure 3-7 SCHEMATIC OF FIXED BED MICRO-REACTOR[13]



3.3.5.3 Product Analysis System

The outlet gas from the reactor was connected to a programmable GC (Series 550P, Gow Mac) where the gaseous products were analyzed using a stainless steel 2m x 1/8" column containing 0.19 wt.% picric acid on 80/100 mesh Carbopack C packing (Supelco, Inc.). A manual valve was used to inject samples. A 40° C isothermal program was used for all experiments. The output signal of the GC was analyzed with an HP 3390A integrator. The operating conditions for both GC and integrator are included in Appendix D. Some of the mixed oxides after a 1000° C ramp gave results which were difficult to integrate because of the low surface areas and distorted (non-Gaussian) peaks. These results were handled by a special integrator program which can also be found in Appendix D.

3.3.5.4 Experimental Procedure

A 100 to 200 milligram sample was used in all experiments. The conversion was maintained as low as possible to eliminate the effects of heat and mass transfer. Reactions were carried out at 423 K and 1 atmosphere in the micro-reactor. Gas products from the reaction were taken every 12 minutes using a manual sampling valve and analyzed by the gas chromatograph. Helium was used as the carrier gas and a total flowrate of 100 SCCM (Standard Cubic Centimeters per Minute) was maintained. The flow of 1-butene was kept at 5 SCCM.

In order to maintain consistency, the same pretreatment conditions were used on all oxide samples. All samples were treated at 298 K under He gas at 50 SCCM for 2-3 hours (overnight preferably) until no background 1-butene was detected. Then the samples were pretreated at 473 K for 1 hour under He gas at 50 SCCM. The reactor was then cooled to 423 K and conditioned for 2 hours with the reaction mixture or until the activity of the catalyst was steady.

Under the conditions listed, no iso-butene was detected in the product stream. Therefore, since cis- and trans-2-butene were the only two products of interest, the reaction rate was calculated as follows and recorded at different times.

$$X_{C_4} = \left(1 - \frac{S_{C_4}A_{C_4}}{\sum_{i=1}^{n} S_i A_i}\right) \times 100$$

$$r_{C_4} = \left(\frac{X_{C_4}}{100}\right) x \left(C_4 \frac{cc}{min}\right) x \left(\frac{1}{22400\ cc/mol}\right) x \left(\frac{1}{W(g)}\right) x \left(\frac{60\ min}{hr}\right) x \left(\frac{1}{S.A.(m^2/g)}\right)$$

where C_4: 1-butene
X_{C4}: Mole % conversion of 1-C_4H_8
S: RRM values (see Appendix D)
A: GC Area (counts)
i: Component of 1-C_4H_8, cis- and trans-2-butene
n: total number of C_4H_8 isomers
r_{C4}: Reaction rate of 1-C_4H_8 (mol/hr-m^2)
W: Weight of catalyst (g)
S.A.: Surface area of catalyst (m^2/g)

The flowrates were all calculated at standard conditions (STP). The selectivity (cis-/trans-2-butene) were calculated as the ratio of the two products analyzed by the GC. A basic program is included in Appendix E for calculations of the activities and selectivities.

4. RESULTS

4.1 General

The main focus of this research was to investigate the effects of preparation on the properties of niobia/alumina binary oxides. These binary oxides ranged from mixed to surface phase oxides in which different methods of preparing the surface oxide, sequential or coimpregnated, were investigated. Thermal pretreatments were also studied on all binary oxides to see how their properties were affected. The physical and chemical properties necessary in understanding the behavior of the oxide-oxide interactions range from surface area determination to catalytic activity. The BET surface area and different techniques used to determine crystallinity of the binary oxides will be investigated in this section. Also, acid strength and acidity of the samples were studied using Hammett indicators and n-butylamine titration; and the steady-state reaction activity and selectivity of the oxides were measured using 1-butene isomerization. The combination of all these techniques was investigated to give a better understanding of the role of oxide-oxide interactions.

4.2 Mixed Oxides

The mixed oxides investigated in this section are NA(75/25), NA(50/50), and NA(25/75). All samples were calcined following the standard procedure, and in order to determine the effects of thermal pretreatment, they were ramped to 1000° C (10° C/min) in He (50 SCCM) then cooled, with no hold at 1000° C. The crystallinity, acidity, and activity of the mixed oxides were investigated as a function of niobia content and heat treatment. The DTA and XRD scans found in this study were identical with results found earlier by our group.[23] Also, the activity data found in this work followed the same general trend in composition as those results which were investigated earlier.[42]

4.2.1 Physical Characterization

4.2.1.1 BET Surface Area

A standard 1-point BET method was used to measure the total surface area of all oxides prepared. The results are shown in Table 4-1 and Figure 4-1 for the samples both after calcination and after high temperature heat treatment. The surface area of the Nb_2O_5/Al_2O_3 mixed oxides decreased with increasing niobia content. A striking change in surface area was seen when the oxides were heat treated. The most notable of these changes was the total collapse in surface area of the NA(50/50) catalyst.

4.2.1.2 DTA Study

The DTA spectra for the mixed oxides are presented in Figure 4-2. Conditions were the same on all runs. Significant heat effects were shown to occur with all three mixed oxides. It will be seen later that these correspond to phase transformations of the mixed oxides.

4.2.1.3 XRD Study

The XRD diffraction patterns of the mixed oxides after calcination in O_2 are shown in Figure 4-3. The patterns were amorphous as suggested by the absence of diffraction peaks. The diffraction pattern for the mixed oxides after the heat treatment (1000° C) are shown in Figure 4-4. All mixed oxides crystallized as evidenced by the sharp peaks and were indexed by our group in a previous study. It was found that all of the mixed oxides formed compounds of aluminum niobate ($AlNbO_4$), while NA(75/25)

Table 4-1: BET SURFACE AREA MEASUREMENTS FOR Nb_2O_5/Al_2O_3 MIXED OXIDES

(I.) Mixed Oxides after O_2 Calcination (500° C):

Sample	Area(m^2/g-oxide)
NA(75/25)	5.0
NA(50/50)	209.3
NA(25/75)	257.0

(II.) Mixed Oxides after 1000° C Ramp in He:

Sample	Area(m^2/g-oxide)
NA(75/25)	4.4
NA(50/50)	0.8
NA(25/75)	80.7

Figure 4-1 BET SURFACE AREA MEASUREMENTS FOR Nb_2O_5/Al_2O_3

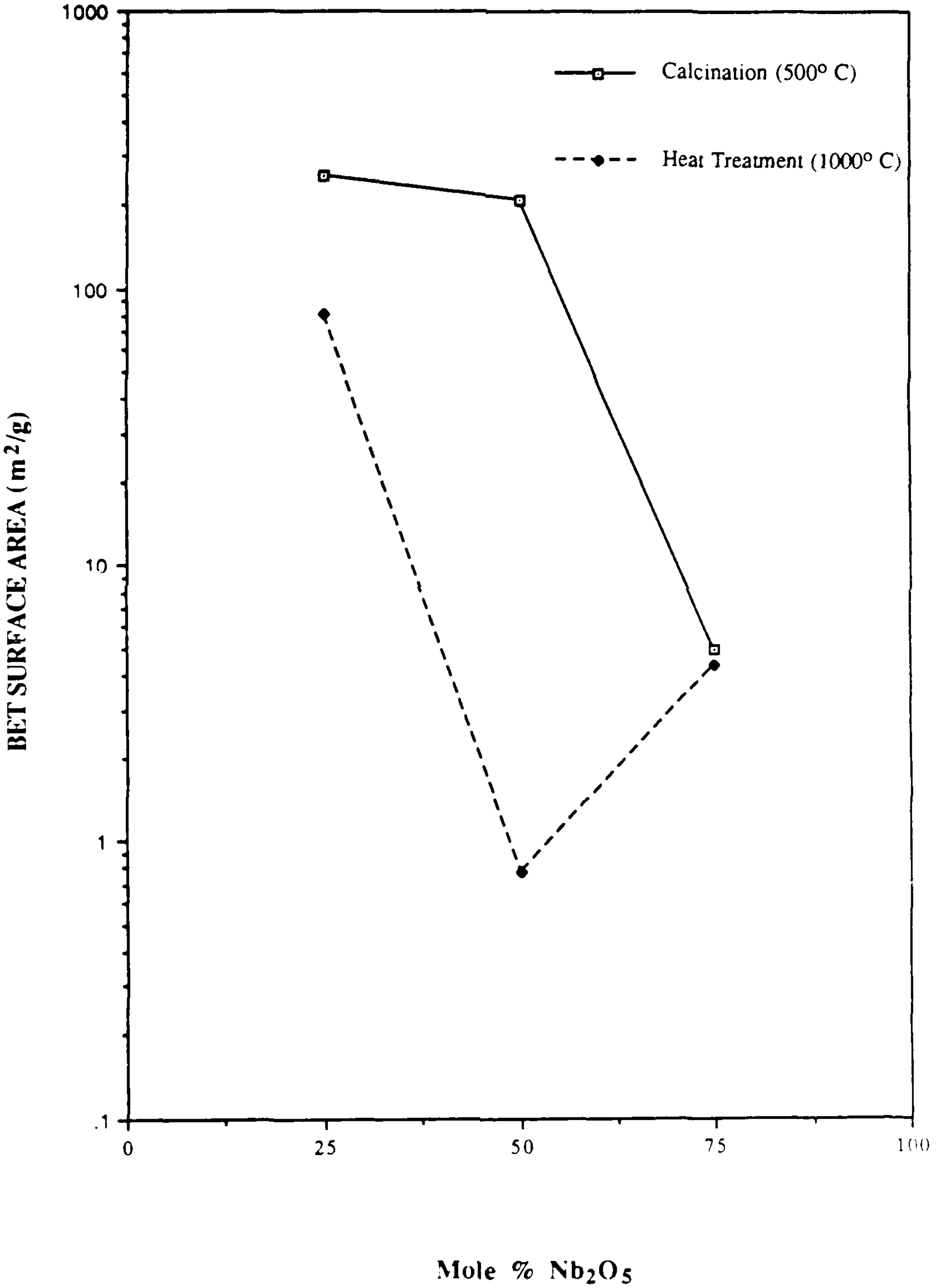


Figure 4-2 DTA SCANS OF Nb_2O_5/Al_2O_3 MIXED OXIDES

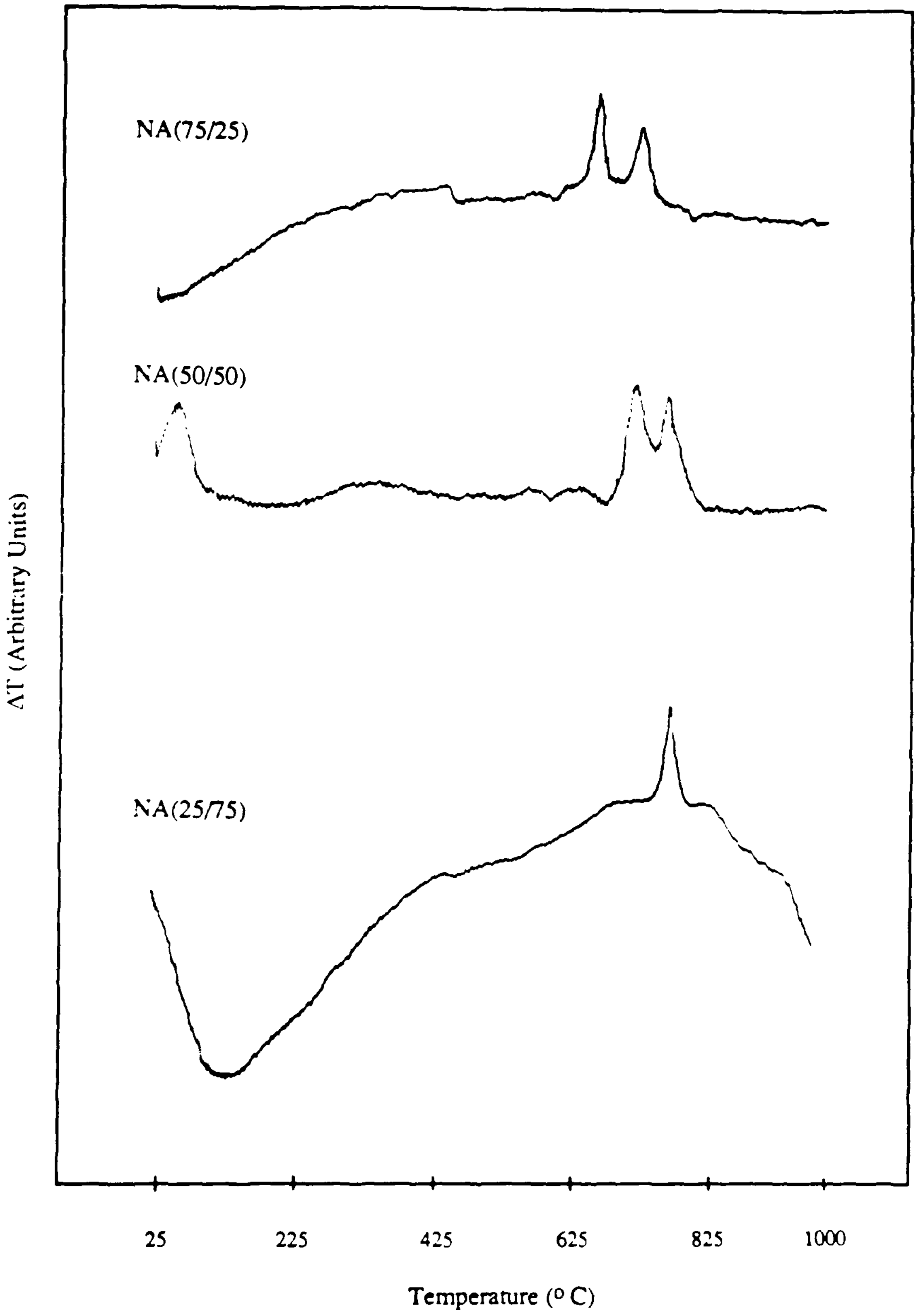


Figure 4-3 XRD SCANS OF CALCINED (500° C) Nb_2O_5/Al_2O_3 MIXED OXIDES

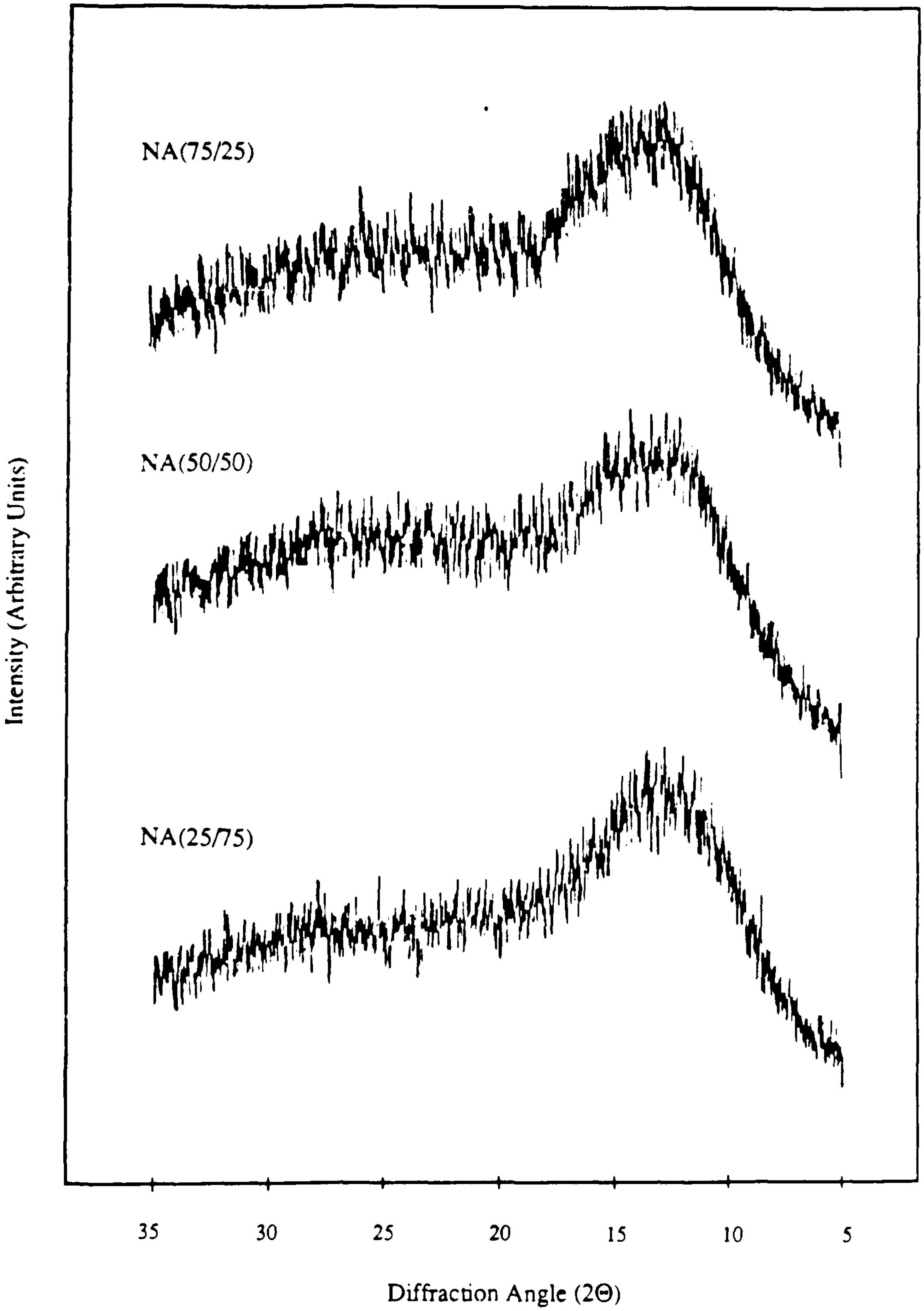
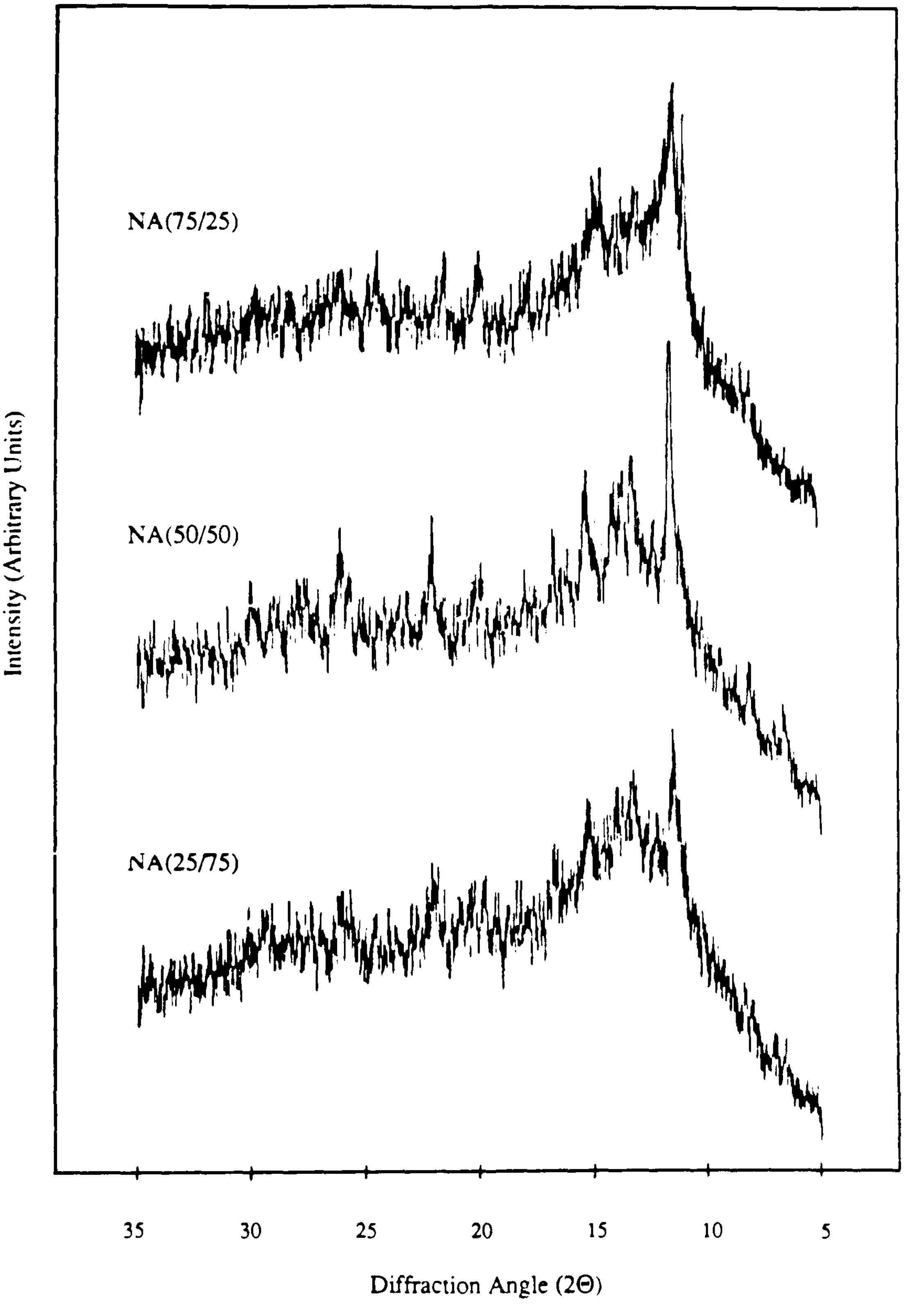


Figure 4-4 XRD SCANS OF HEAT TREATED (1000° C) Nb_2O_5/Al_2O_3 MIXED OXIDES



also formed M-niobia.[23] This showed that these oxides were not stable upon the given heat treatment.

4.2.2 Surface Acidity Determination

4.2.2.1 Acid Strength

The acid strengths of the three mixed oxides are shown in Table 4-2 as a function of the pKa values of Hammett indicators. In this table, a "-" sign shows that the indicator stayed in its basic form, meaning that the acid strength of the surface is less than the corresponding pKa value. The "+" sign means that the indicator is in its acid form, or that the surface has an acid strength greater than or equal to the corresponding pKa value. The "+/-" sign indicates that it was very hard to tell if the sample was acidic, but upon addition of the smallest amount of base available (3 μl), turned the indicator to its basic color. This table shows that all mixed oxides prepared after calcination in O_2 had acid sites which tested positive at a pKa of -8.2, equal to the strongest acid strengths that have been studied by Shibata, et al.[43] These mixed oxides all had higher acid strengths than any of the single oxides comprising them.[1,13] After heat-treatment, the only mixed oxide that had any acid strength (pKa = -5.6) was NA(25/75). The other two oxides barely turned the first three indicators to acid forms, and upon addition of 3 μl of amine were transformed to their bright basic forms.

4.2.2.2 Acidity

The mixed oxides were pretreated in air under vacuum at 383 K for 1 hour and then transferred immediately to the dry glove box while still warm to eliminate any physisorbed water on the sample surface. Figure 4-5 shows the acidity between different acid strengths for the Nb_2O_5/Al_2O_3 mixed oxide system in a bar chart. These values are also listed in Table 4-3. For ease of comparisons later, one needs to choose a consistent

Table 4-2: ACID STRENGTH OF Nb_2O_5/Al_2O_3 MIXED OXIDES

(I.) Nb_2O_5/Al_2O_3 Samples after Calcination (500° C):

	pKa					
Sample	+4.8	+3.3	+1.5	-3.0	-5.6	-8.2
NA(75/25)	+	+	+	+	+	+/-
NA(50/50)	+	+	+	+	+	+
NA(25/75)	+	+	+	+	+	+

(II.) Nb_2O_5/Al_2O_3 Samples after Heat Treatment (1000° C):

	pKa					
Sample	+4.8	+3.3	+1.5	-3.0	-5.6	-8.2
NA(75/25)	+/-	+/-	+/-	-	-	-
NA(50/50)	+/-	+/-	+/-	-	-	-
NA(25/75)	+	+	+	+	+	-

+: turned indicator to acid form

-: turned indicator to basic form

+/-: barely turned indicator to acid form, if at all

Figure 4-5 ACIDITY OF Nb_2O_5/Al_2O_3 MIXED OXIDES BETWEEN DIFFERENT ACID STRENGTHS AFTER CALCINATION (500° C)

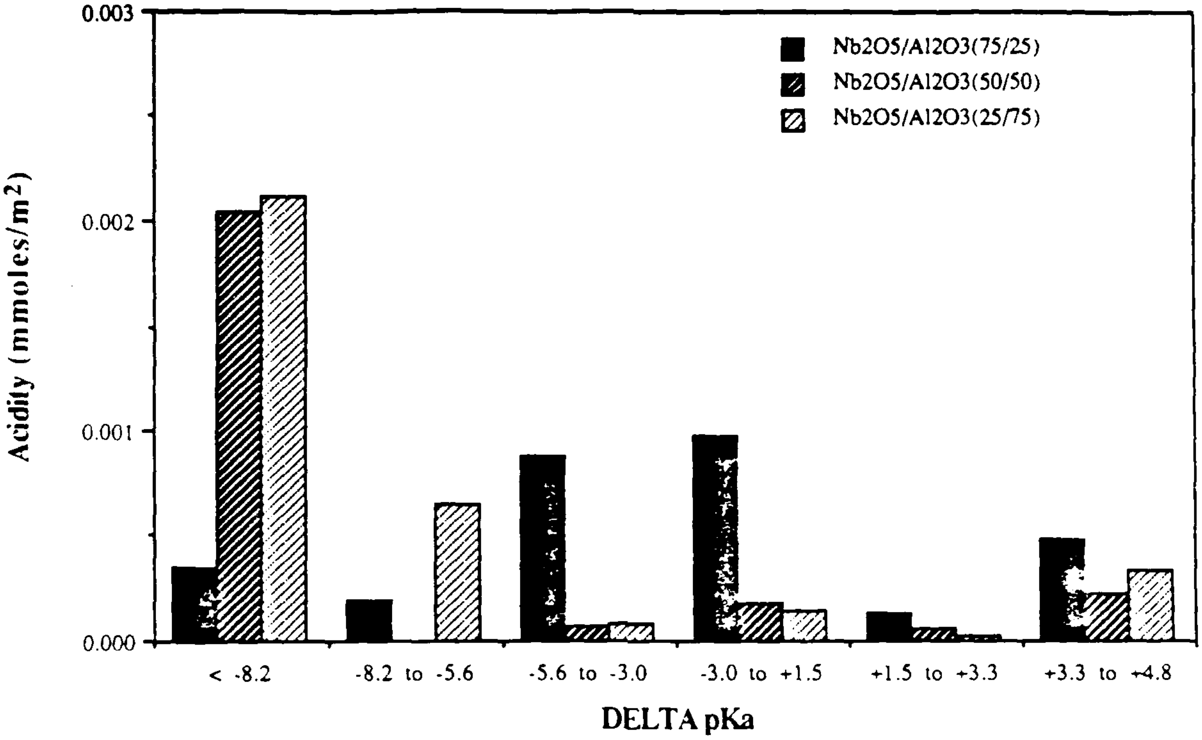


Figure 4-6 ACIDITY OF Nb_2O_5/Al_2O_3 MIXED OXIDES BETWEEN DIFFERENT ACID STRENGTHS AFTER HEAT TREATMENT (1000° C)

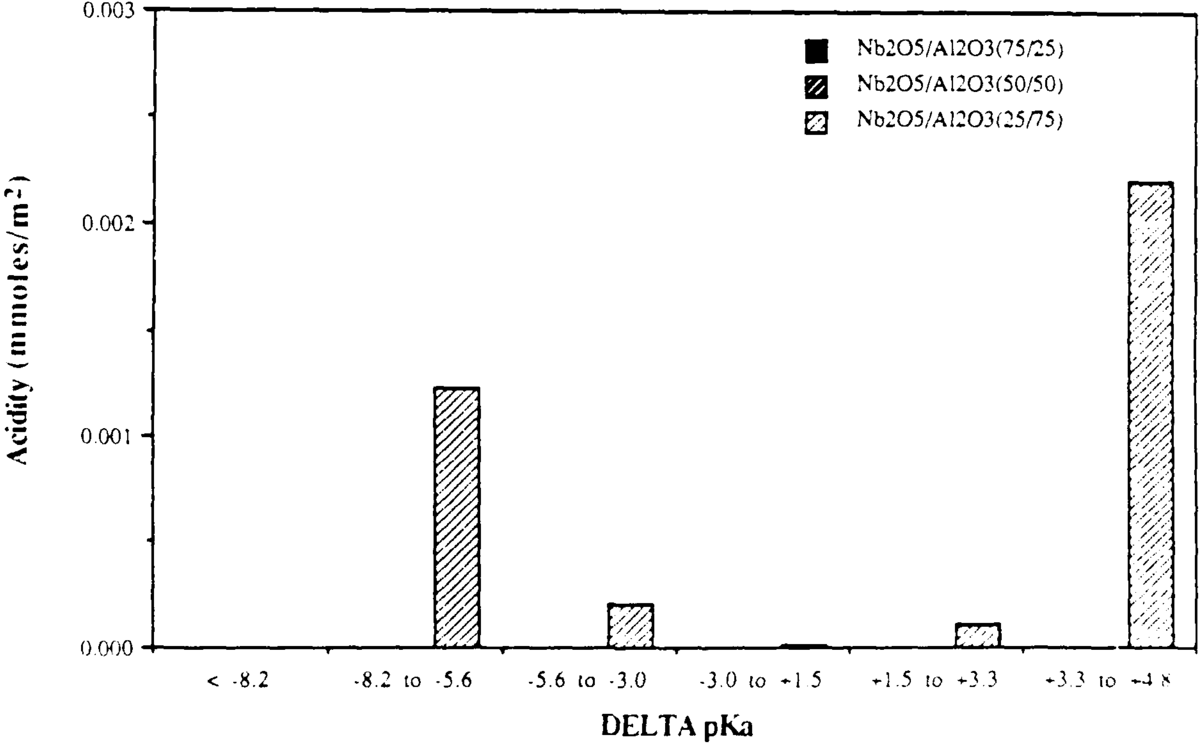


Table 4-3: ACIDITY OF Nb_2O_5/Al_2O_3 MIXED OXIDES BETWEEN DIFFERENT ACID STRENGTHS

(I.) Mixed Oxides after Calcination (500° C):

Sample	Delta pKa=	Acidity (mmoles/m^2) x 10^4 +4.8 to +3.3	+3.3 to +1.5	+1.5 to -3.0	-3.0 to -5.6	-5.6 to -8.2	<-8.2
NA(75/25)		4.8	1.3	9.8	8.8	1.9	3.5
NA(50/50)		2.3	0.6	1.8	0.8	0.0	20.5
NA(25/75)		3.4	0.2	1.4	0.9	6.5	21.2

(II.) Mixed Oxides after Heat Treatment (1000° C):

Sample	Delta pKa=	Acidity (mmoles/m^2) x 10^4 +4.8 to +3.3	+3.3 to +1.5	+1.5 to -3.0	-3.0 to -5.6	-5.6 to -8.2	<-8.2
NA(75/25)		0.0	0.0	0.0	0.0	0.0	0.0
NA(50/50)		0.0	0.0	0.0	0.0	0.0	0.0
NA(25/75)		22.0	1.1	0.2	2.1	12.2	0.0

basis. The basis used in this presentation is the acidity per unit surface area; however, it should be noted that one could have easily chosen the acidity per unit weight, but this would have given slightly different results because of the large surface area variations.

Figure 4-6 shows the acidity of the mixed oxides as a function of delta pKa after the heat treatment (1000° C) in He. Again, these values are listed in Table 4-3. It is obvious that NA(25/75) is the only mixed oxide that is still acidic. The other two binary oxides had undergone phase changes that within the limits of the experiment showed no acidity or acid strength. These figures indicate that most of the acid sites after calcination were of high acid strength ($pKa < -8.2$), but after heat treatment the acid sites were mostly of a much lower acid strength ($pKa > +3.3$).

4.2.3 1-C_4H_8 Isomerization

4.2.3.1 Time on Stream (TOS) and Activities

In this research, all mixed oxides were pretreated under 50 SCCM He for 1 hr at 473 K. This temperature was then lowered to 423 K to conduct the 1-butene isomerization reactions. Again, for comparison a consistent basis is needed and in this research, the basis is activity per unit area. The catalytic activities and TOS for the mixed oxide samples are shown in Figure 4-7 and Figure 4-8 after calcination and after heat treatment respectively. The activities of the single oxides of Nb_2O_5 and Al_2O_3 are low compared to their corresponding mixed oxides.[13] All the samples studied after calcination achieved a steady state activity after being reacted for about 100 min. The initial (3 min after reaction) and steady state activities did not vary by more than a factor of 2 indicating that the deactivation of the sample was not severe. The NA(75/25) mixed oxide after heat treatment, however, showed significant deactivation as the initial and steady-state activities varied by an order of magnitude. The steady state activities are

Figure 4-7 Nb_2O_5/Al_2O_3 MIXED OXIDE ACTIVITY VS. TOS AFTER CALCINATION (500° C)

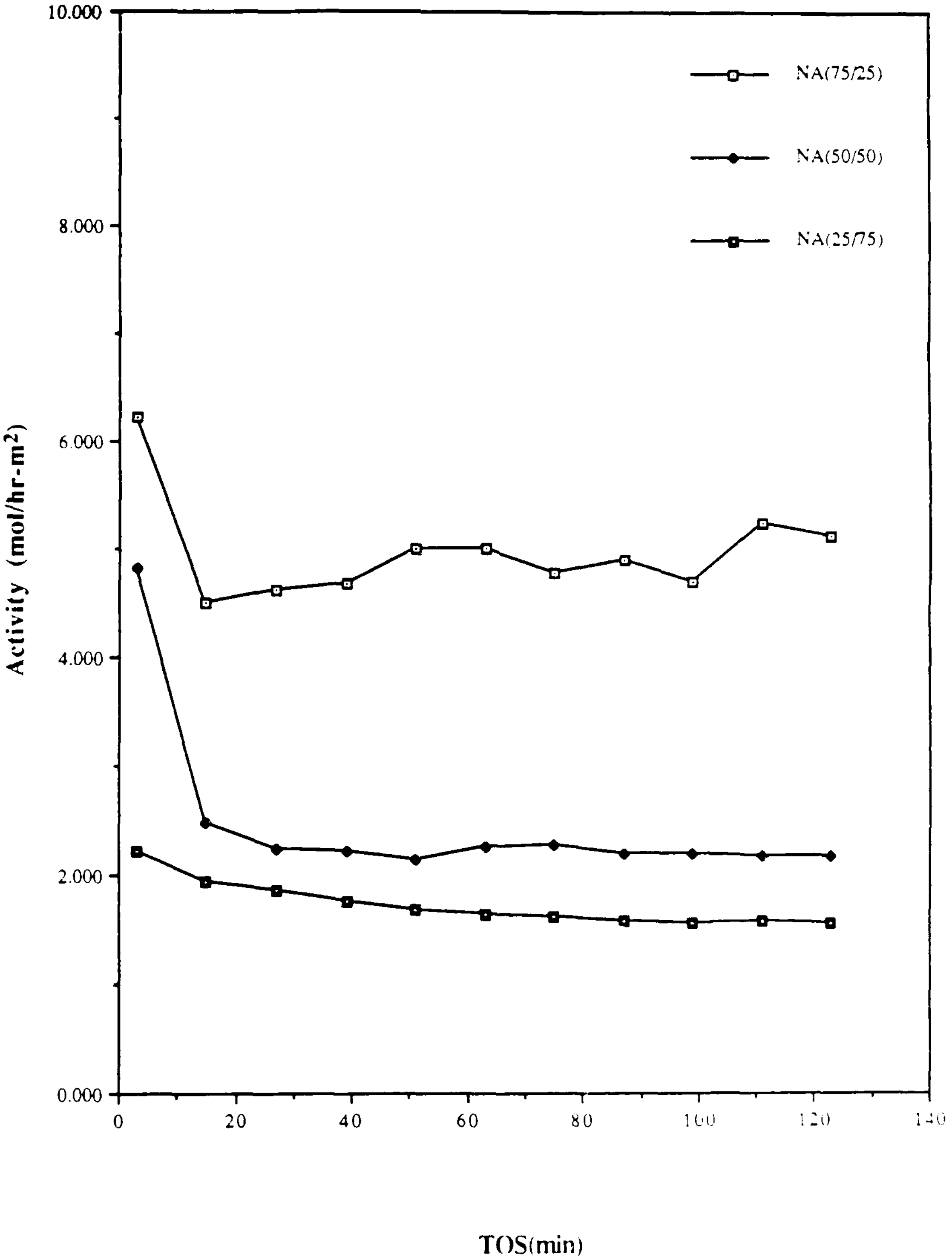
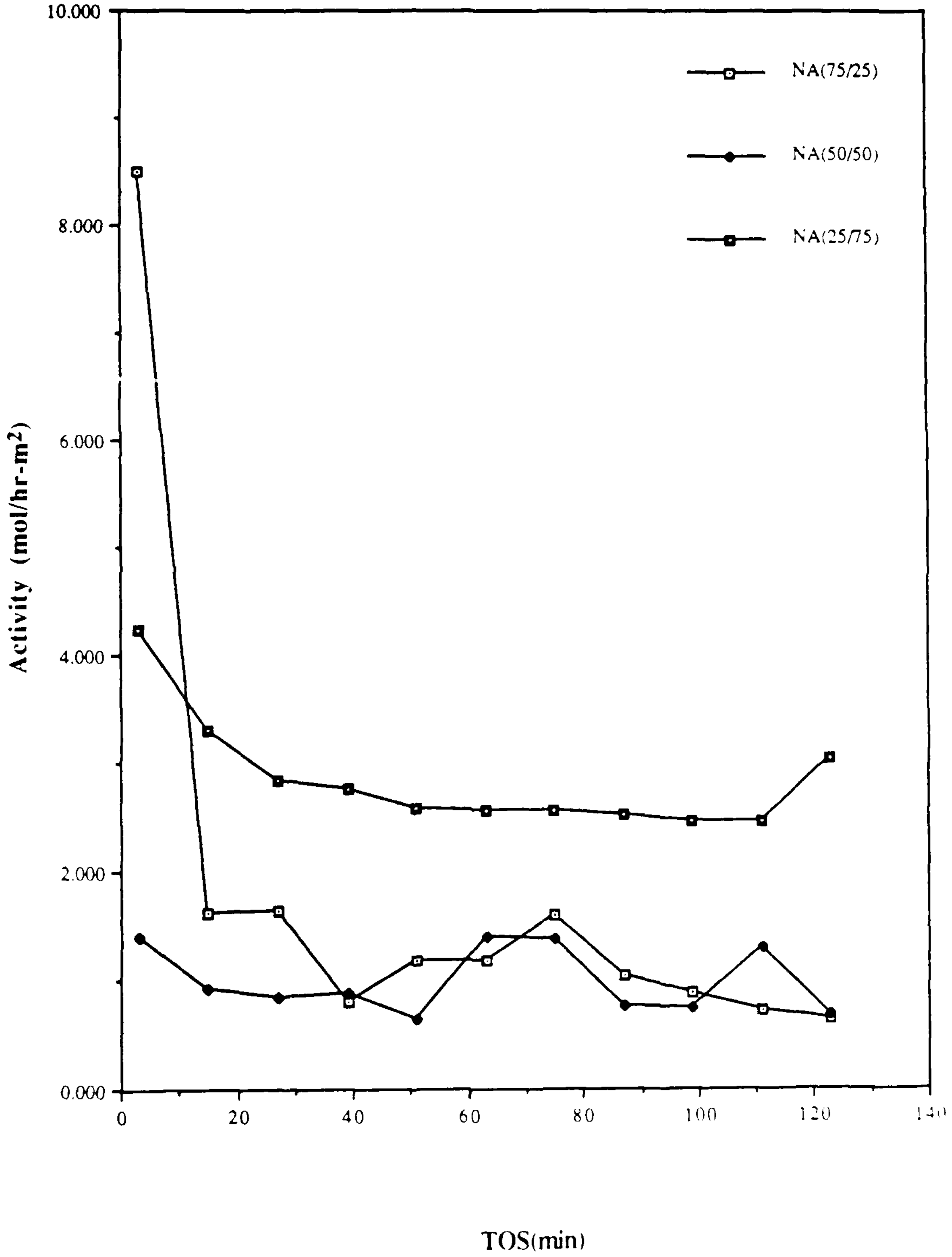


Figure 4-8 Nb_2O_5/Al_2O_3 MIXED OXIDE ACTIVITY VS. TOS AFTER HEAT TREATMENT (1000° C)



tabulated as a function of both composition and thermal treatment in Table 4-4 and are graphed in Figure 4-9.

4.2.3.2 Selectivity

The selectivities, defined as the ratio of cis-2-butene to trans-2-butene, of the mixed oxides are shown as a function of composition and thermal pretreatment in Figure 4-10. It is quite apparent from the figure that the selectivity for NA(75/25) is much different from the other two oxides after calcination, indicating that this sample may have a different reaction mechanism. Also, after heat treatment (1000° C) one can easily see that the NA(75/25) and NA(25/75) samples have comparable selectivities to those after calcination, while the NA(50/50) selectivity decreased by an order of magnitude, possibly indicating a restructured surface and different reaction mechanism.

4.3 Preparation Effect on SiO_2-Supported Nb_2O_5/Al_2O_3 Surface Oxides

The supported surface oxides studied in this section are Nb/Al(3/1) Pre, Al/Nb(1/3) Pre, Nb/Al(3/1) Seq, Al/Nb(1/3) Seq, and Nb/Al(3/1) Co. These were studied to see if the different preparations (separate, sequential, or coimpregnated) changed the properties of the supported binary oxides. Also studied in this next section are Nb/Al(1/1) Pre, Al/Nb(1/1) Pre, and Nb/Al(1/1) Co, to see if the coimpregnated properties could be attributed to each separate supported oxide. All samples were calcined and heat treated (1000° C) following the standard procedures.

4.3.1 Physical Characterization

Table 4-4: STEADY STATE ACTIVITY AND SELECTIVITY OF Nb_2O_5/Al_2O_3 MIXED OXIDES

(I.) Mixed Oxides after Calcination (500° C):

Sample	Activity (mol/hr-m^2)x10^3	Selectivity (cis/trans)
NA(75/25)	5.1	0.30
NA(50/50)	1.9	1.66
NA(25/75)	1.5	1.79

(II.) Mixed Oxides after Heat Treatment (1000° C):

Sample	Activity (mol/hr-m^2)x10^3	Selectivity (cis/trans)
NA(75/25)	0.7	0.65
NA(50/50)	0.7	0.20
NA(25/75)	2.6	1.81

Figure 4-9 STEADY STATE ACTIVITY OF Nb_2O_5/Al_2O_3 MIXED OXIDES

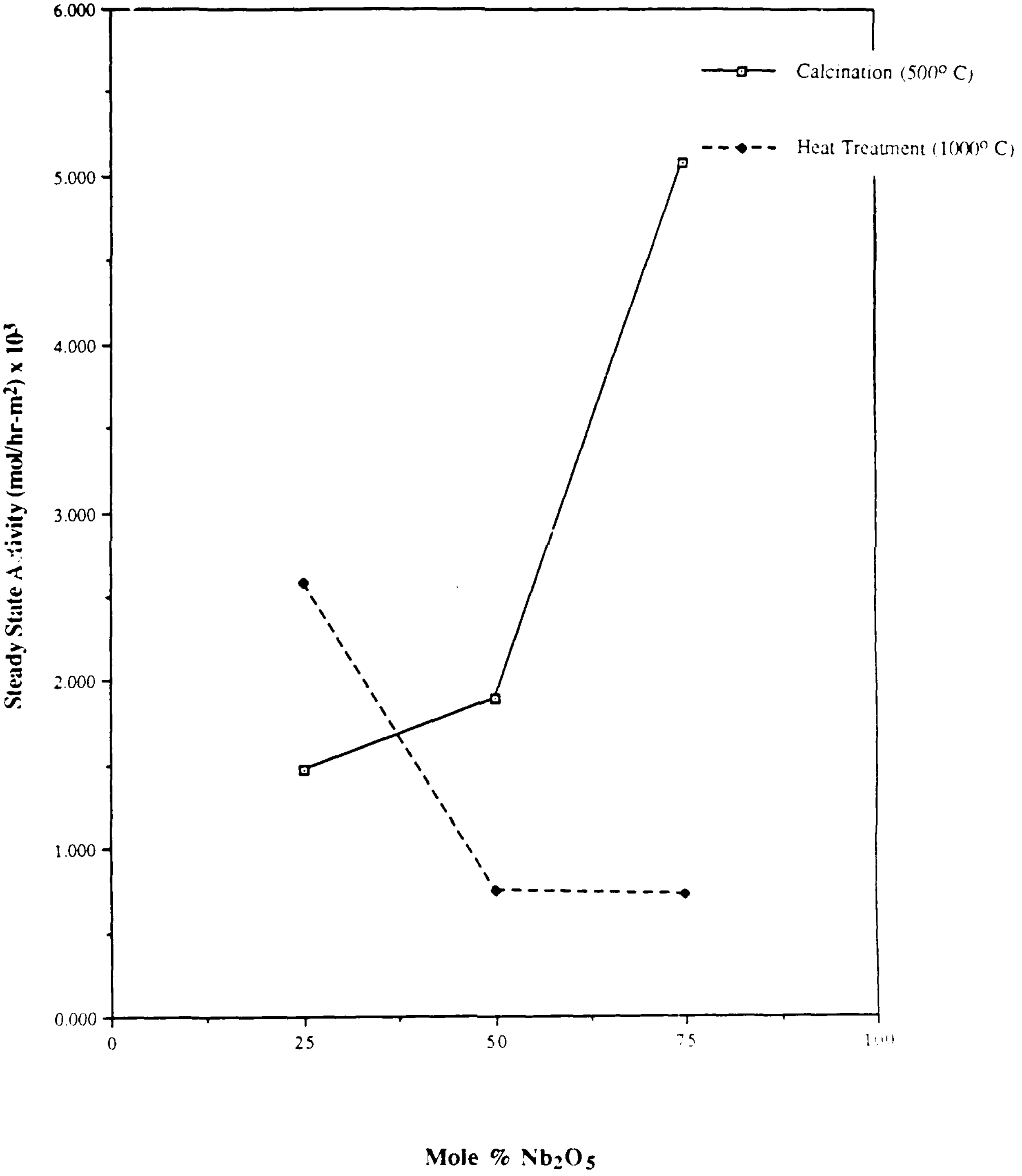
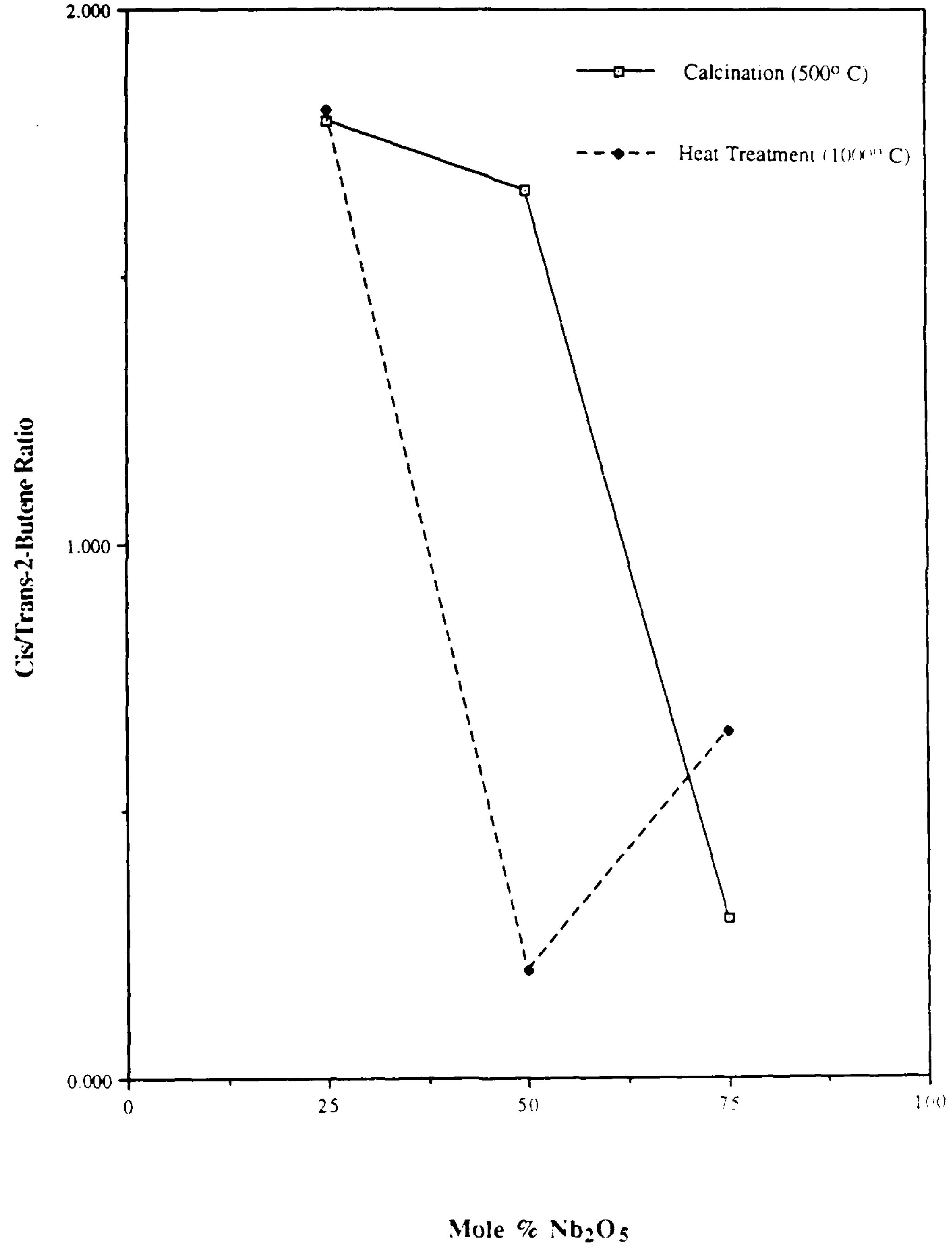


Figure 4-10 SELECTIVITY OF Nb_2O_5/Al_2O_3 MIXED OXIDES



4.3.1.1 BET Surface Area

A standard 1-point BET method was used to measure the total surface areas of all the surface oxides prepared. The results of the surface areas both after calcination and heat treatment are shown in Table 4-5. All the supported oxides lost surface area when heated, but significant changes were not observed as with the mixed oxides. The supported alumina samples had the largest areas of all oxides studied. Also, the coimpregnated surface oxide with the greater alumina content had the larger surface area.

4.3.1.2 DTA Study

The DTA spectra of the surface oxides are shown in Figure 4-11 and Figure 4-12. Conditions were held constant for all runs and are described in Section 2.3.2. It is seen that no significant heat effects occurred on any of the supported binary oxides. The fluctuations that occurred on the graphs are background noise from the experimental apparatus.

4.3.1.3 XRD Study

X-ray diffraction patterns of the supported-surface oxides after calcination in O_2 are shown in Figures 4-13 to 4-14. The patterns were entirely amorphous as shown by the absence of diffraction peaks. The diffraction patterns after heat treatment (1000° C) are shown in Figures 4-15 to 4-16. One can easily see that these patterns are also amorphous, thus showing the stability of the supported surface oxides. Silica was not examined in either the DTA or XRD studies because it is well recognized to undergo no crystallization under these heat treatment conditions.

Table 4-5: BET SURFACE AREA MEASUREMENTS FOR SiO_2-SUPPORTED Nb_2O_5/Al_2O_3

	After Calcination (500° C)		After H.T. (1000° C)	
Supported Samples	Area (m^2/g)	Area (m^2/g SiO_2)	Area (m^2/g)	Area (m^2/g SiO_2)
Nb/Al(3/1) Pre	264.7	343.0	183.0	237.2
Nb/Al(1/1) Pre	320.0	378.9	251.0	297.2
Al/Nb(1/3) Pre	358.3	371.7	301.3	312.6
Al/Nb(1/1) Pre	364.0	389.7	340.0	364.0
Nb/Al(3/1) Seq	276.3	368.4	185.4	247.2
Al/Nb(1/3) Seq	325.0	432.2	199.5	265.3
Nb/Al(3/1) Co	324.1	431.1	143.2	190.5
Nb/Al(1/1) Co	346.5	434.7	195.1	244.8
Silica Gel (SiO_2)	315.0	315.0	314.0	314.0

Figure 4-11 DTA SCANS OF SUPPORTED SURFACE OXIDES NB/AL(3/1)

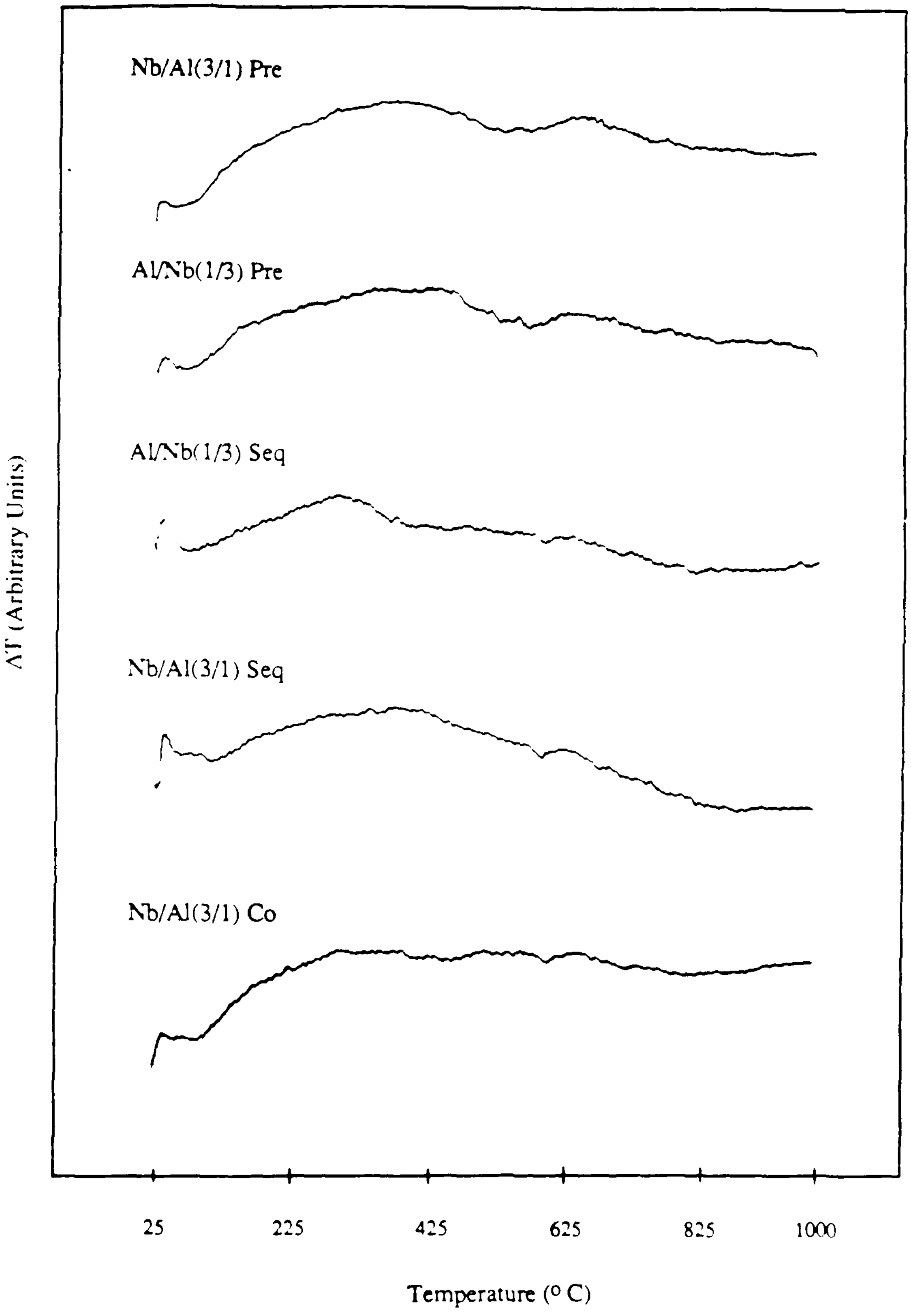


Figure 4-12 DTA SCANS OF SUPPORTED SURFACE OXIDES NB/AL(1/1)

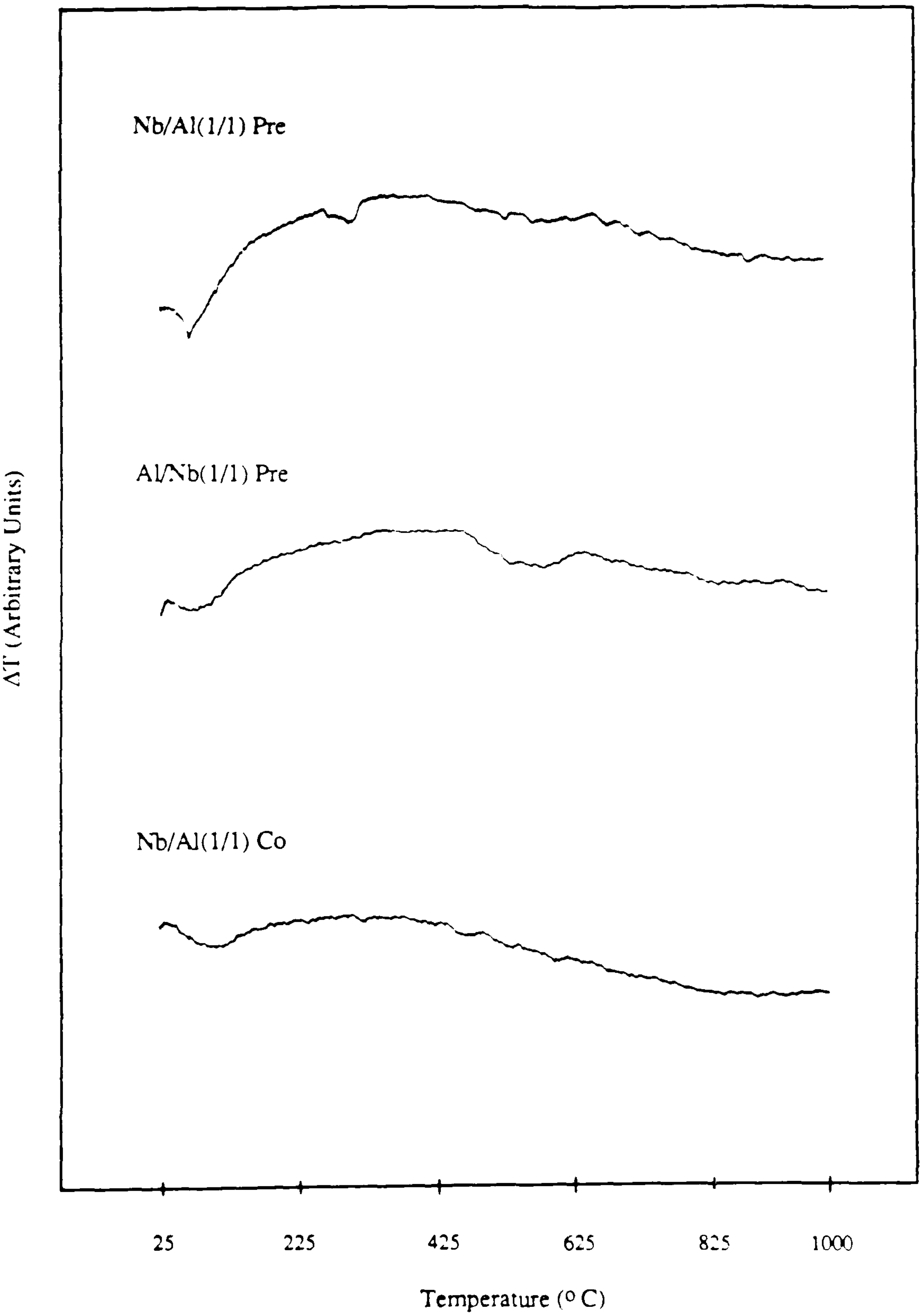


Figure 4-13 XRD SCANS OF CALCINED (500° C) SURFACE OXIDES NB/AL(3/1)

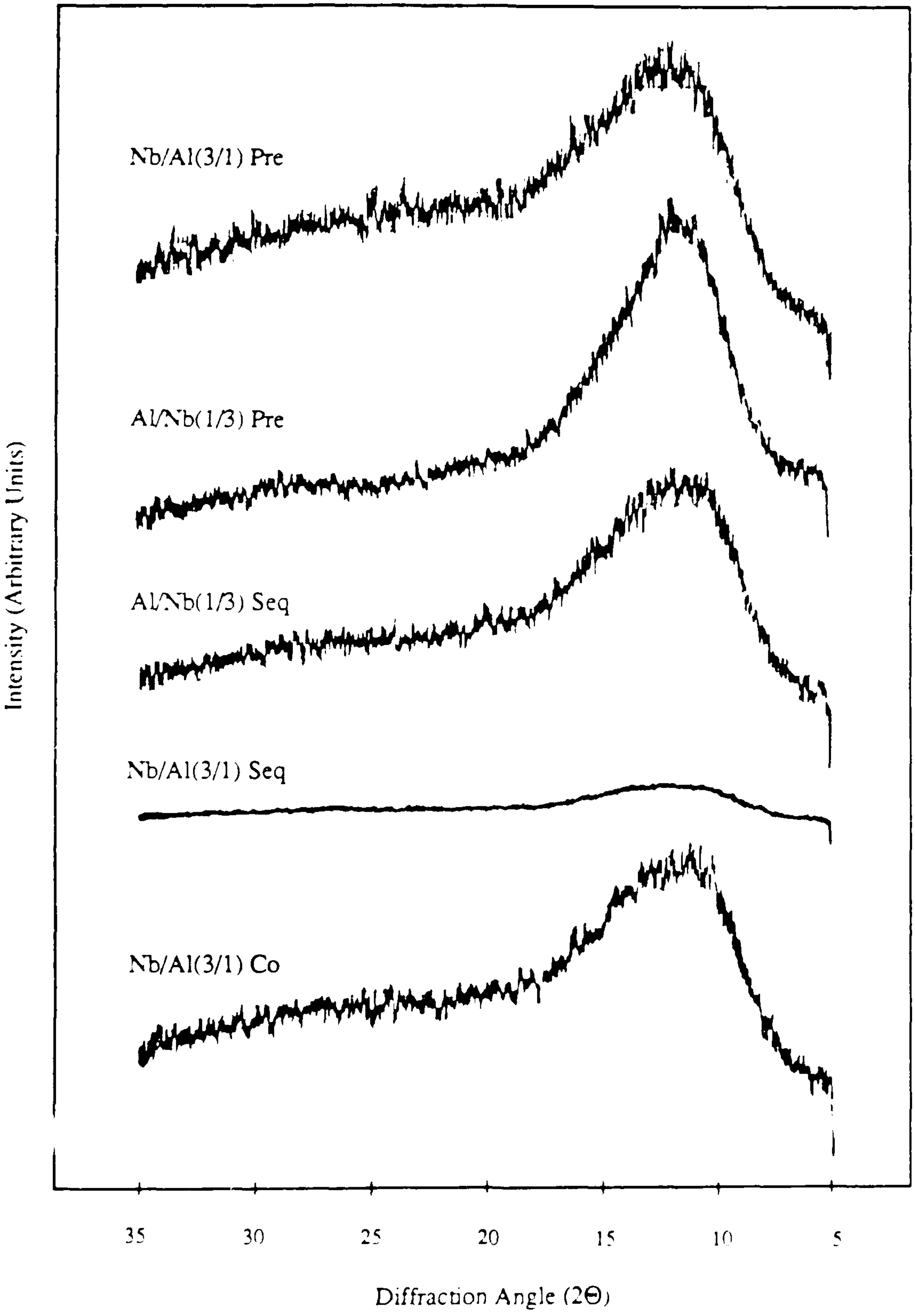


Figure 4-14 XRD SCANS OF CALCINED (500° C) SURFACE OXIDES
NB/AL(1/1)

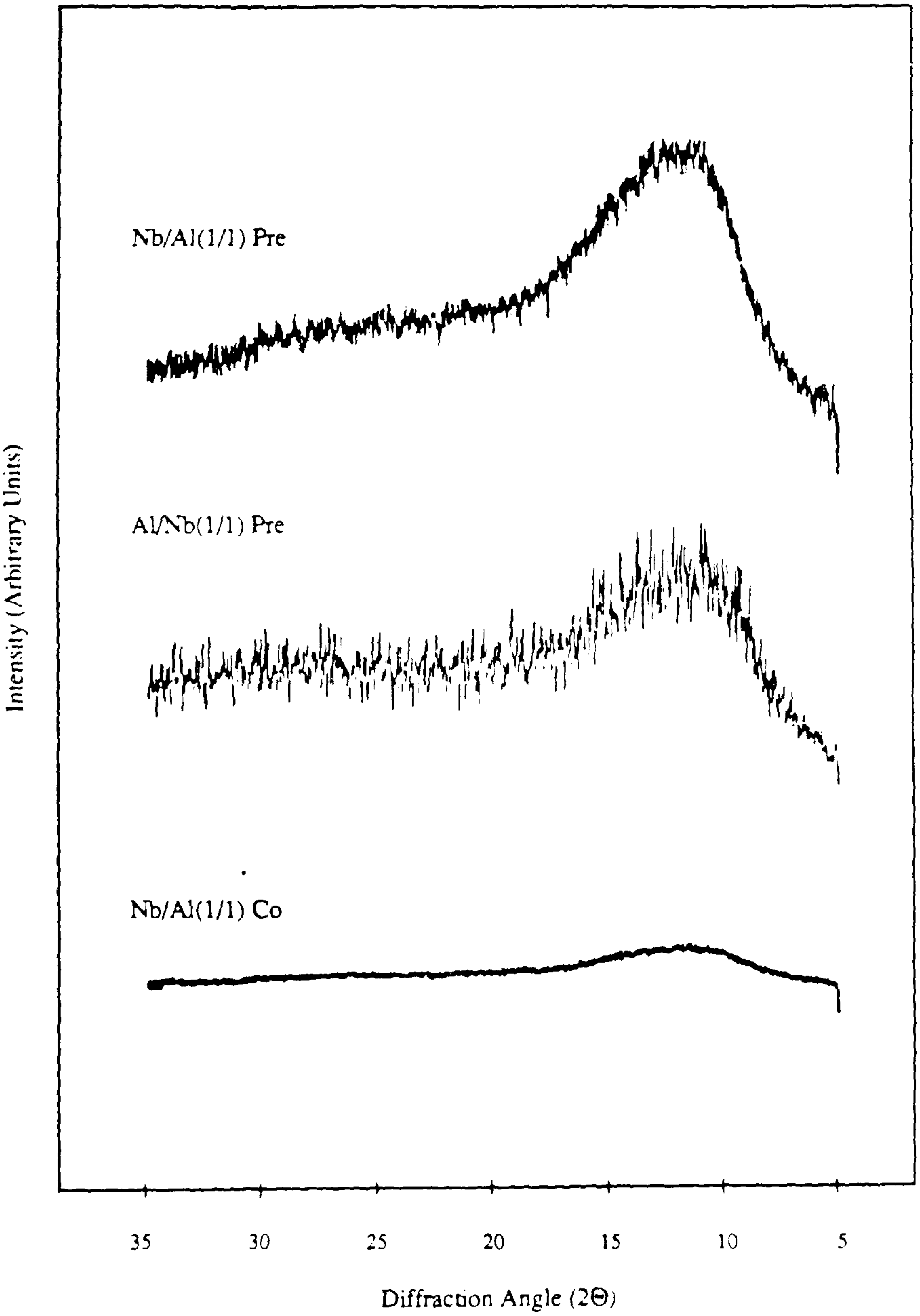


Figure 4-15 XRD SCANS OF HEAT TREATED (1000° C) SURFACE OXIDES NB/AL(3/1)

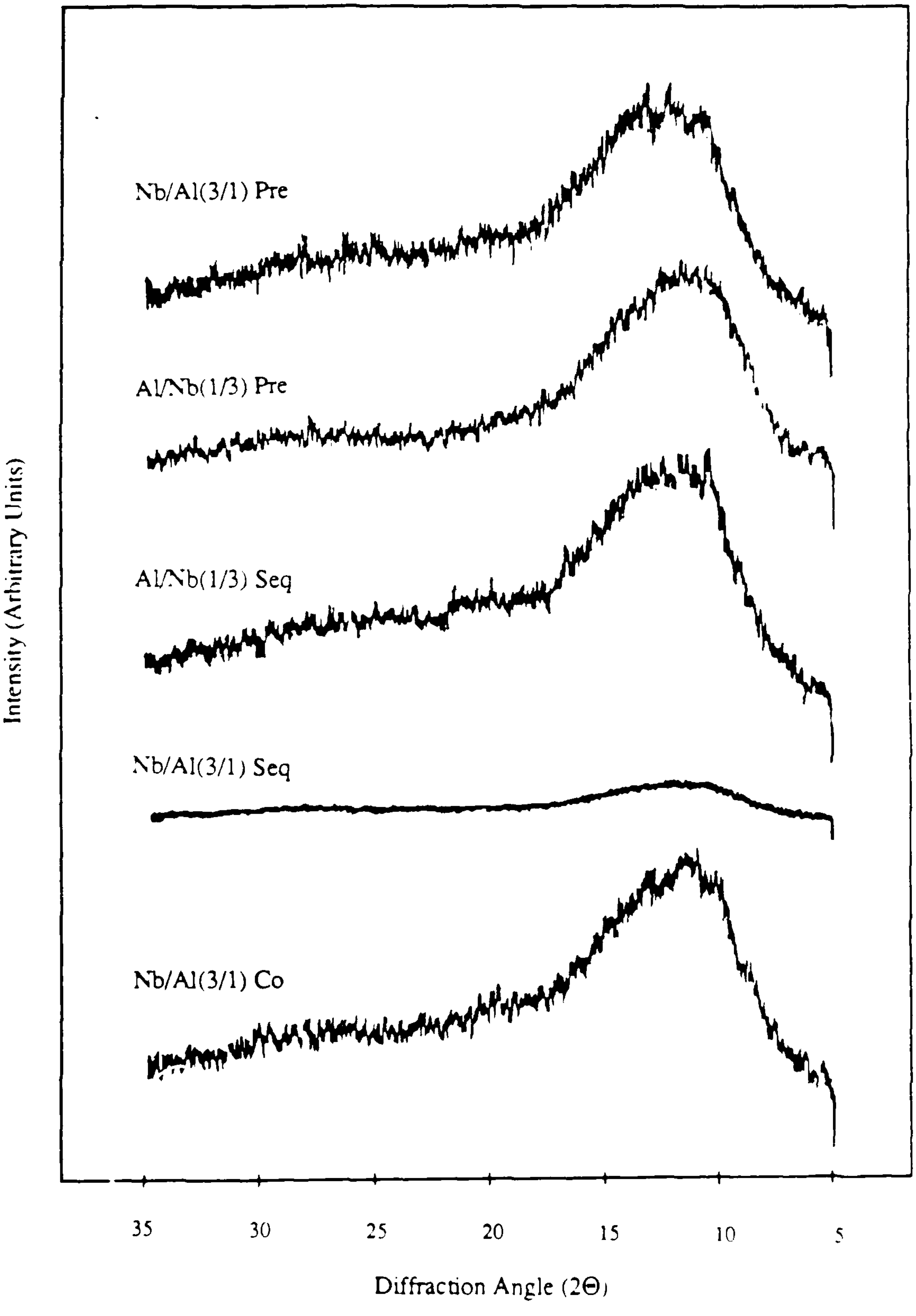
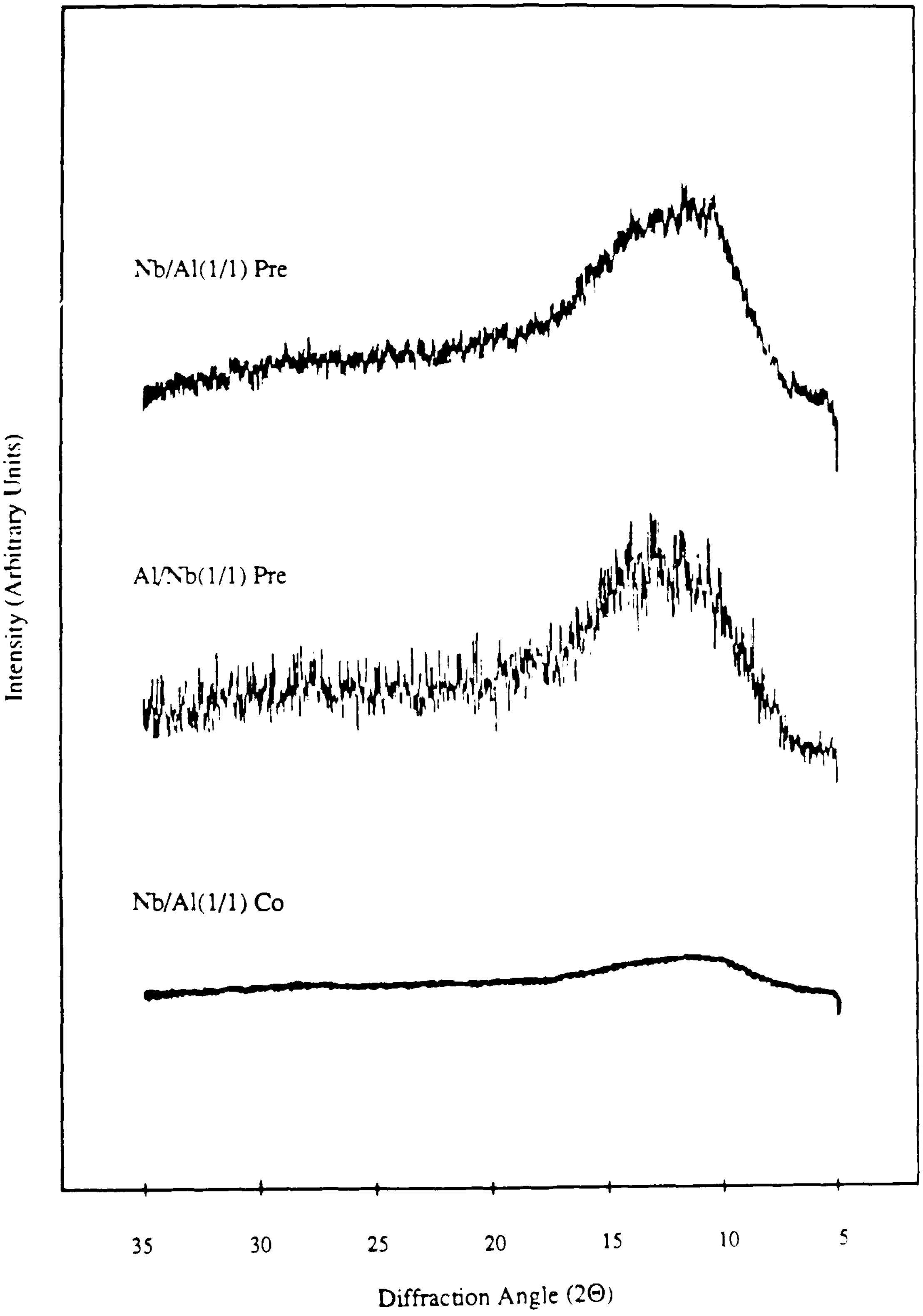


Figure 4-16 XRD SCANS OF HEAT TREATED (1000° C) SURFACE OXIDES NB/AL(1/1)



4.3.2 Surface Acidity Determination

4.3.2.1 Acid Strength

The acid strengths of the surface oxides are listed in Table 4-6 as a function of pKa. The sign convention is the same as before. This table shows that the supported surface oxides all have surprisingly strong acid sites. These acid sites are as strong as the strongest mixed oxides previously studied by other researchers.[2,43] It is obvious from the table that pure silica gel has weak acid sites, thus confirming what previous researchers had found for this supporting oxide.[4,11] After the heat treatment it is noticed that the supported alumina catalysts had stronger acid sites than after calcination, and that the supported niobia samples had slightly weaker acid sites than after calcination.

4.3.2.2 Acidity

The supported surface oxides were pretreated in air under vacuum at 383 K for 1 hr to remove any physisorbed water on the surface. Table 4-7 is a collection of acidity data for the supported oxides between different acid strengths. Figures 4-17 and 4-18 show the acidity between different acid strengths of the silica-supported niobia or alumina under different loadings after calcination and after heat treatment respectively. It is interesting to note here that as the loading of the oxide on the support increases so does its acidity per unit area at the highest acid strength, while the acidities at the other acid strengths remain almost identical. Figures 4-19 and 4-20 indicate how Nb/Al(1/1) Co compares to the separate supported oxides comprising it, both after calcination and after heat treatment respectively. The acidity charts of Nb/Al(1/1) Co and Nb/Al(1/1) Pre look similar. The acidity is nearly identical throughout the entire range of delta pKa values. Only at one extreme is there a significant difference where Nb/Al(1/1) Co has half as many of the weaker acid sites ($+3.3 < pKa < +4.8$) as the Nb/Al(1/1) Pre surface oxide. Figures 4-21 and 4-22 show how Nb/Al(3/1) Co compares to the separate supported

Table 4-6: ACID STRENGTH OF SUPPORTED SURFACE OXIDES

(I.) Surface Oxides after Calcination (500° C):

	pKa					
Sample	+4.8	+3.3	+1.5	-3.0	-5.6	-8.2
Nb/Al(3/1) Pre	+	+	+	+	+	+
Nb/Al(1/1) Pre	+	+	+	+	+	+
Al/Nb(1/3) Pre	+	+	+	+	+	-
Al/Nb(1/1) Pre	+	+	+	+	+	+/-
Nb/Al(3/1) Seq	+	+	+	+	+	+
Al/Nb(1/3) Seq	+	+	+	+	+	+
Nb/Al(3/1) Co	+	+	+	+	+	+
Nb/Al(1/1) Co	+	+	+	+	+	+
Silica Gel	+	+	-	-	-	-

(II.) Surface Oxides after Heat Treatment (1000° C):

	pKa					
Sample	+4.8	+3.3	+1.5	-3.0	-5.6	-8.2
Nb/Al(3/1) Pre	+	+	+	+	+	+
Nb/Al(1/1) Pre	+	+	+	+	+	+/-
Al/Nb(1/3) Pre	+	+	+	+	+	+
Al/Nb(1/1) Pre	+	+	+	+	+	+
Nb/Al(3/1) Seq	+	+	+	+	+	+
Al/Nb(1/3) Seq	+	+	+	+	+	+
Nb/Al(3/1) Co	+	+	+	+	+	+
Nb/Al(1/1) Co	+	+	+	+	+	+
Silica Gel	+	+	-	-	-	-

+: Turned Indicator to Acid Form

-: Turned Indicator to Basic Form

+/-: Barely Turned Indicator to Acid Form, if at all

Table 4-7: ACIDITY OF SUPPORTED SURFACE OXIDES BETWEEN DIFFERENT ACID STRENGTHS

(I.) Surface Oxides after Calcination (500° C):

Sample	Delta pKa=	Acidity (mmoles/m^2) x 10^4 +4.8 to +3.3	+3.3 to +1.5	+1.5 to -3.0	-3.0 to -5.6	-5.6 to -8.2	<-8.2
Nb/Al(3/1) Pre		10.3	1.3	0.4	2.6	6.1	6.1
Nb/Al(1/1) Pre		10.2	1.0	1.7	4.2	6.5	2.4
Al/Nb(1/3) Pre		3.8	2.3	0.1	1.1	3.1	0.0
Al/Nb(1/1) Pre		5.9	3.7	0.1	1.7	3.1	0.7
Nb/Al(3/1) Seq		9.2	1.8	0.3	2.2	4.8	7.3
Al/Nb(1/3) Seq		8.8	4.3	0.2	3.7	2.6	7.1
Nb/Al(3/1) Co		8.5	3.0	0.4	0.7	7.0	5.4
Nb/Al(1/1) Co		4.3	3.3	0.3	2.5	7.4	3.3
Silica Gel		7.5	2.3	0.0	0.0	0.0	0.0

(II.) Surface Oxides after Heat Treatment (1000° C):

Sample	Delta pKa=	Acidity (mmoles/m^2) x 10^4 +4.8 to +3.3	+3.3 to +1.5	+1.5 to -3.0	-3.0 to -5.6	-5.6 to -8.2	<-8.2
Nb/Al(3/1) Pre		16.8	2.6	0.9	2.0	11.0	4.9
Nb/Al(1/1) Pre		16.1	3.1	1.8	3.6	10.3	0.2
Al/Nb(1/3) Pre		8.6	1.8	1.0	0.1	5.4	1.0
Al/Nb(1/1) Pre		11.9	1.8	0.3	2.9	4.4	0.9
Nb/Al(3/1) Seq		14.8	2.4	1.1	1.0	10.5	8.4
Al/Nb(1/3) Seq		7.1	3.9	0.6	1.1	7.5	9.1
Nb/Al(3/1) Co		12.3	6.4	0.6	2.1	11.5	4.5
Nb/Al(1/1) Co		10.6	0.4	0.0	2.2	12.2	1.4
Silica Gel		7.0	2.8	0.0	0.0	0.0	0.0

Figure 4-17 ACIDITY OF SUPPORTED NIOBIA OR ALUMINA BETWEEN DIFFERENT ACID STRENGTHS AFTER CALCINATION

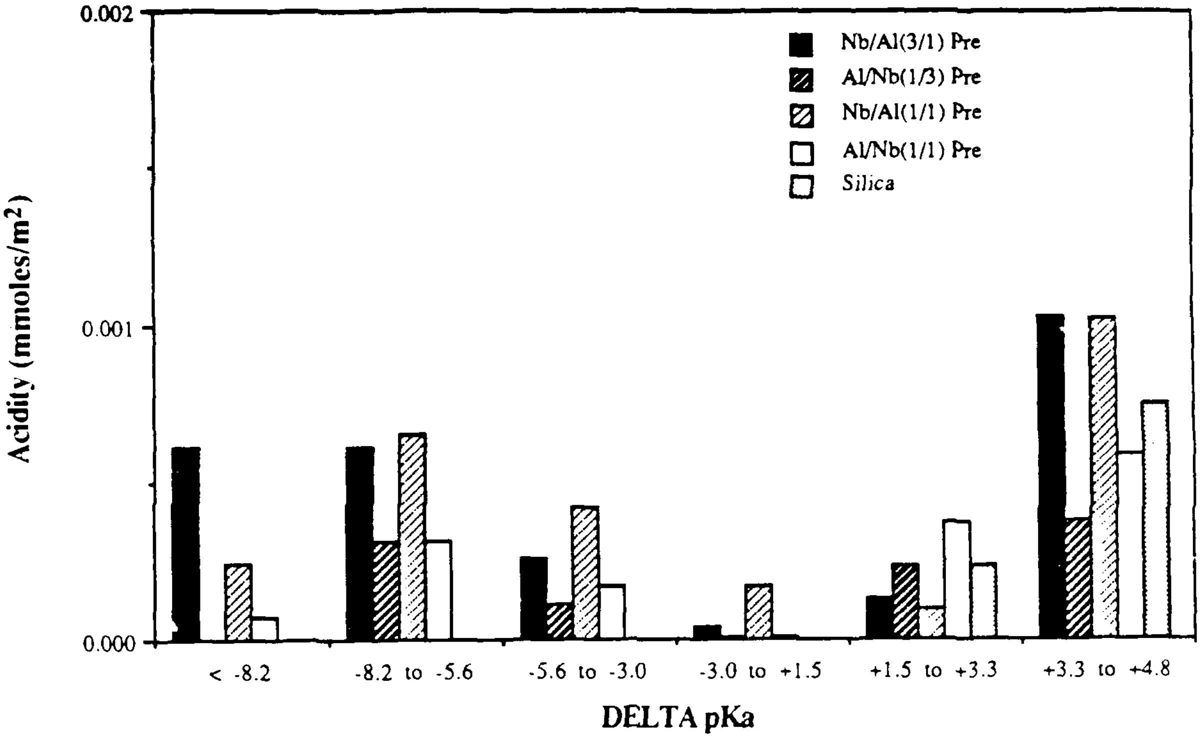


Figure 4-18 ACIDITY OF SUPPORTED NIOBIA OR ALUMINA BETWEEN DIFFERENT ACID STRENGTHS AFTER HEAT TREATMENT

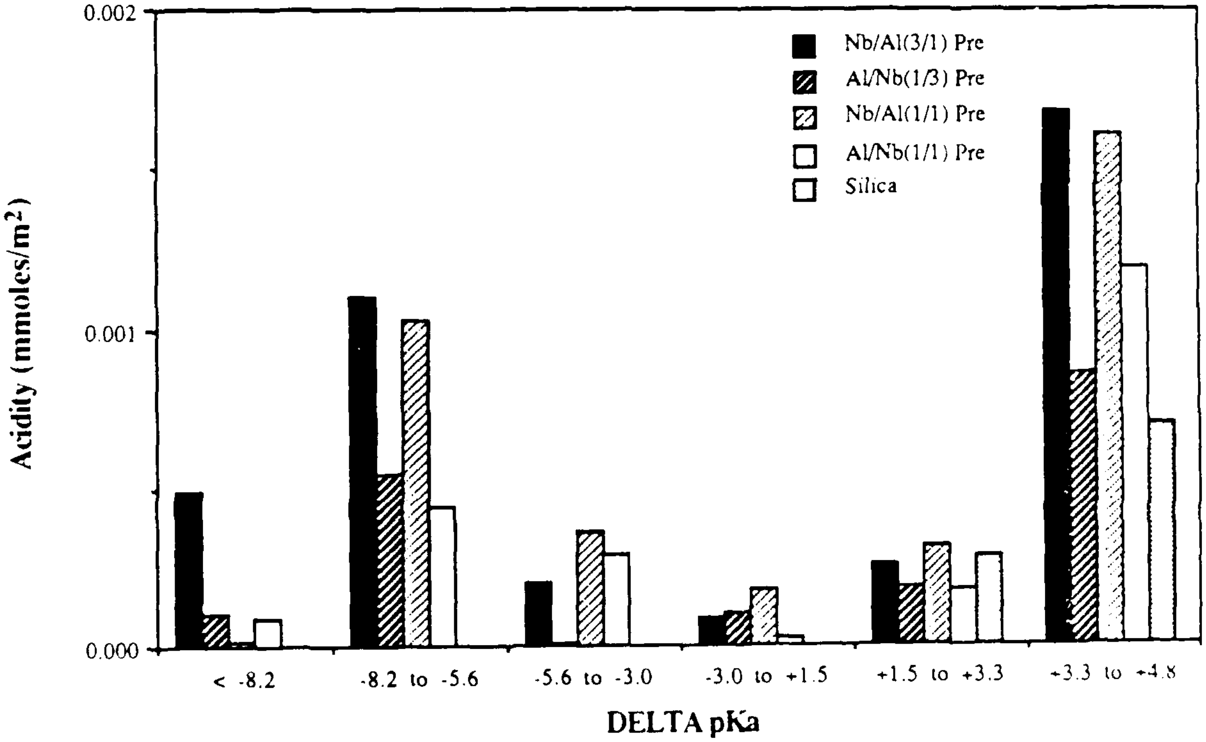


Figure 4-19 ACIDITY OF NB/AL(1/1) BETWEEN DIFFERENT ACID STRENGTHS AFTER CALCINATION (500° C)

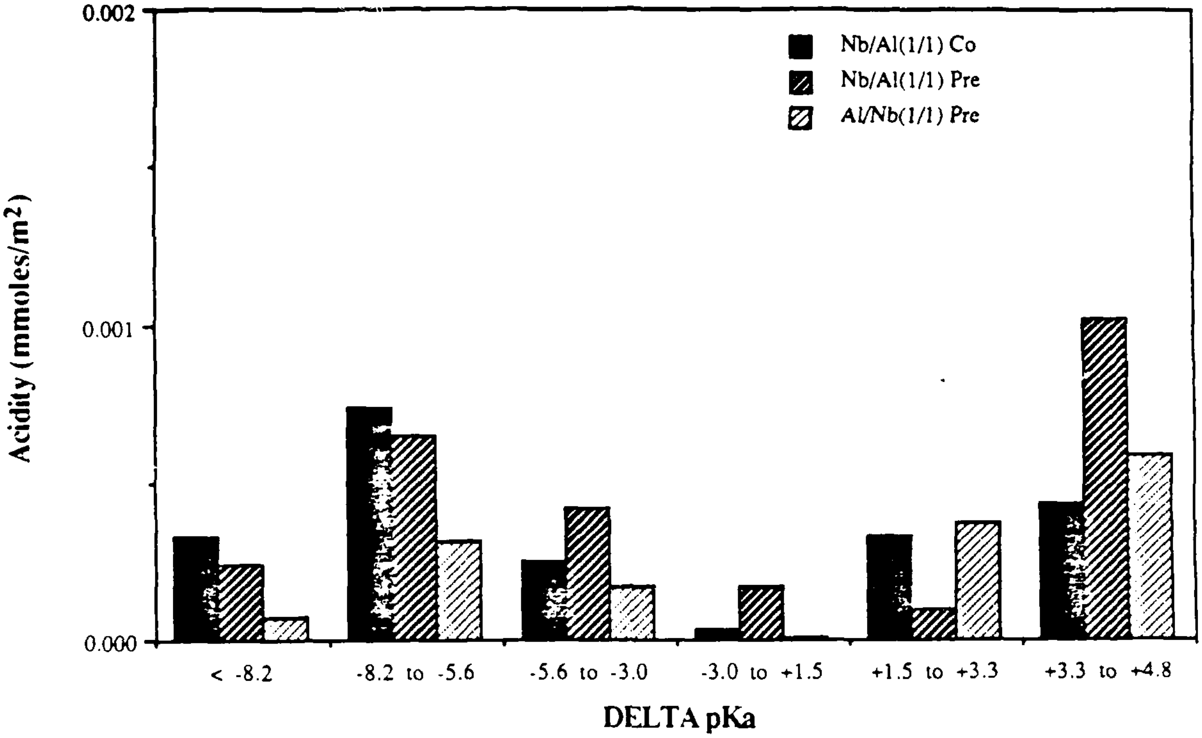


Figure 4-20 ACIDITY OF NB/AL(1/1) BETWEEN DIFFERENT ACID STRENGTHS AFTER HEAT TREATMENT (1000° C)

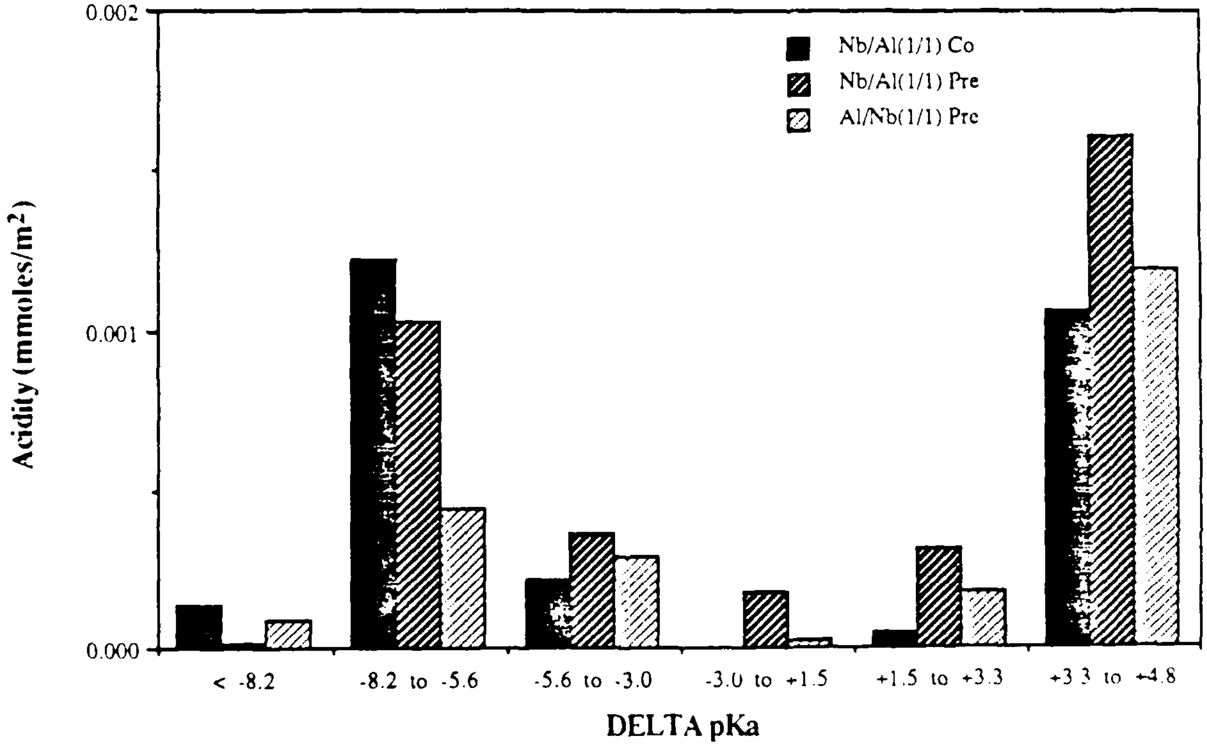


Figure 4-21 ACIDITY OF NB/AL(3/1) BETWEEN DIFFERENT ACID STRENGTHS AFTER CALCINATION (500° C)

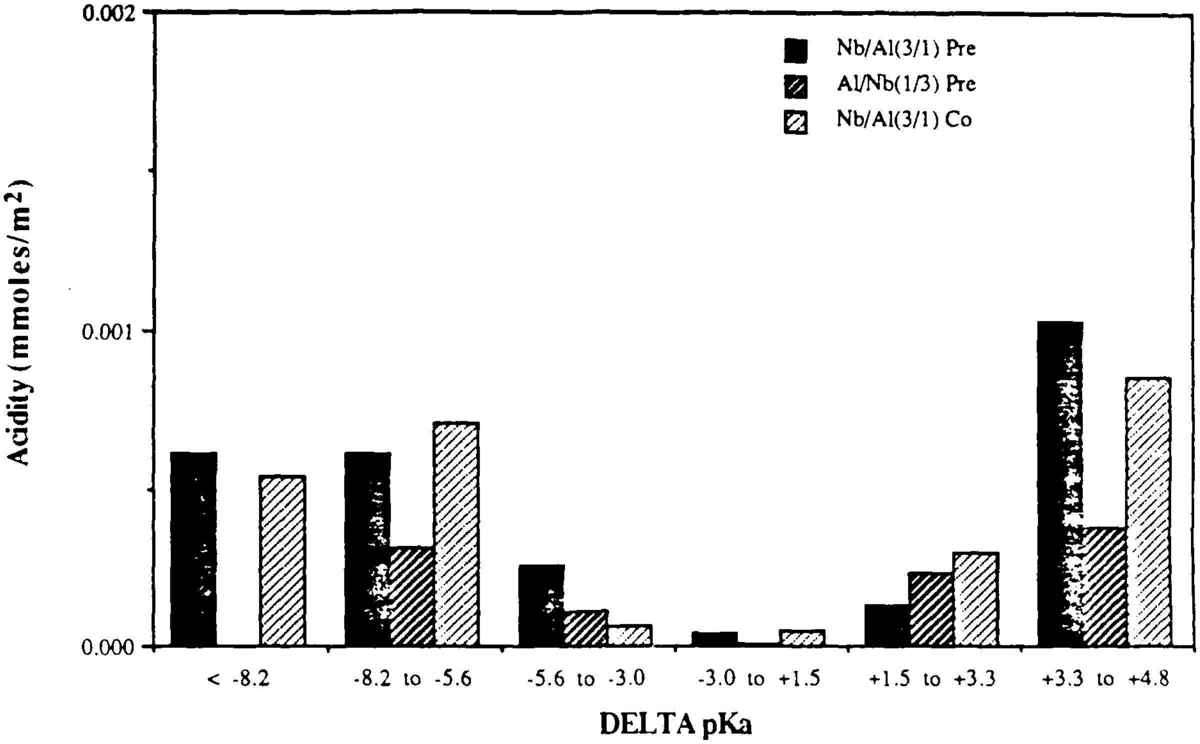
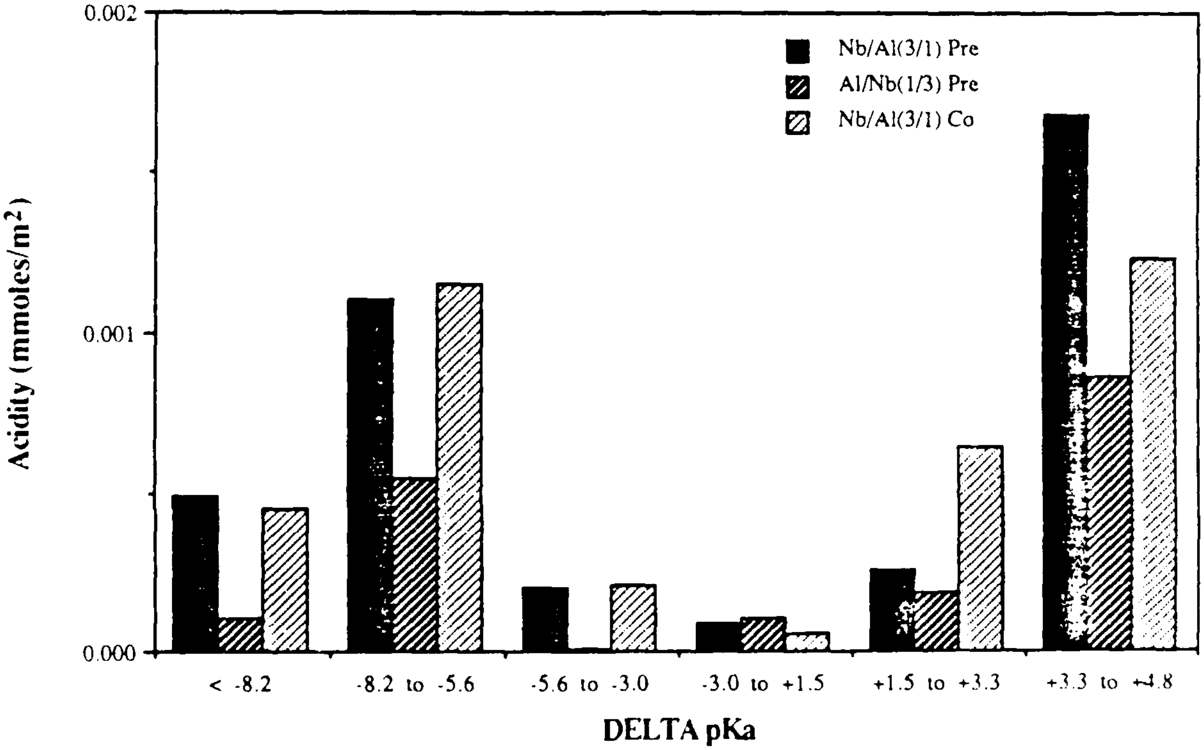


Figure 4-22 ACIDITY OF NB/AL(3/1) BETWEEN DIFFERENT ACID STRENGTHS AFTER HEAT TREATMENT (1000° C)



oxides comprising it after calcination and heat treatment respectively. The acidity charts of Nb/Al(3/1) Co and Nb/Al(3/1) Pre look very similar. Throughout the entire range, the acidity at the different delta pKa values is nearly identical. This behavior is similar to that observed with the Nb/Al(1/1) surface oxide system. Figures 4-23 and 4-24 show acidity as a function of delta pKa for the different methods of preparing Nb/Al(3/1) (2 sequentials and 1 coimpregnation) after calcination and after heat treatment respectively. All graphs look very similar indicating that the preparation technique had no influence on the acidity of the supported oxide.

After heat treatment the supported niobia oxides had decreases in the strongest acid sites and a corresponding increase in the weakest and moderately strong acid sites. The supported alumina oxides had increases in both the strong, moderately strong, and weak acid sites after the heat treatment. The coimpregnated surface oxides had increases of acidity across the entire delta pKa range except for the strongest acid sites (pKa < -8.2) where they decreased slightly upon heat treating.

4.3.3 1-C_4H_8 Isomerization

4.3.3.1 TOS and Activities

All supported surface oxides were pretreated for 1 hr at 473 K under He (50 SCCM). The temperature was reduced to 423 K to conduct the 1-butene isomerization reactions. The catalytic activities and selectivities of the samples are listed in Table 4-8 for both thermal treatments. The most obvious relation from the table is that silica is inactive to the reaction. The Al/Nb(1/1) Pre surface oxide after calcination has a very high activity, in fact, it was the largest out of all mixed and supported oxides studied after calcination. The activities for the supported-Nb/Al(3/1) oxides were all comparable, while the activity of the Nb/Al(1/1) Co oxide, compared to the Nb/Al(3/1) oxides, was about 20 % higher

Figure 4-23 ACIDITY OF NB/AL(3/1) (SEQ AND CO) BETWEEN DIFFERENT ACID STRENGTHS AFTER CALCINATION (500° C)

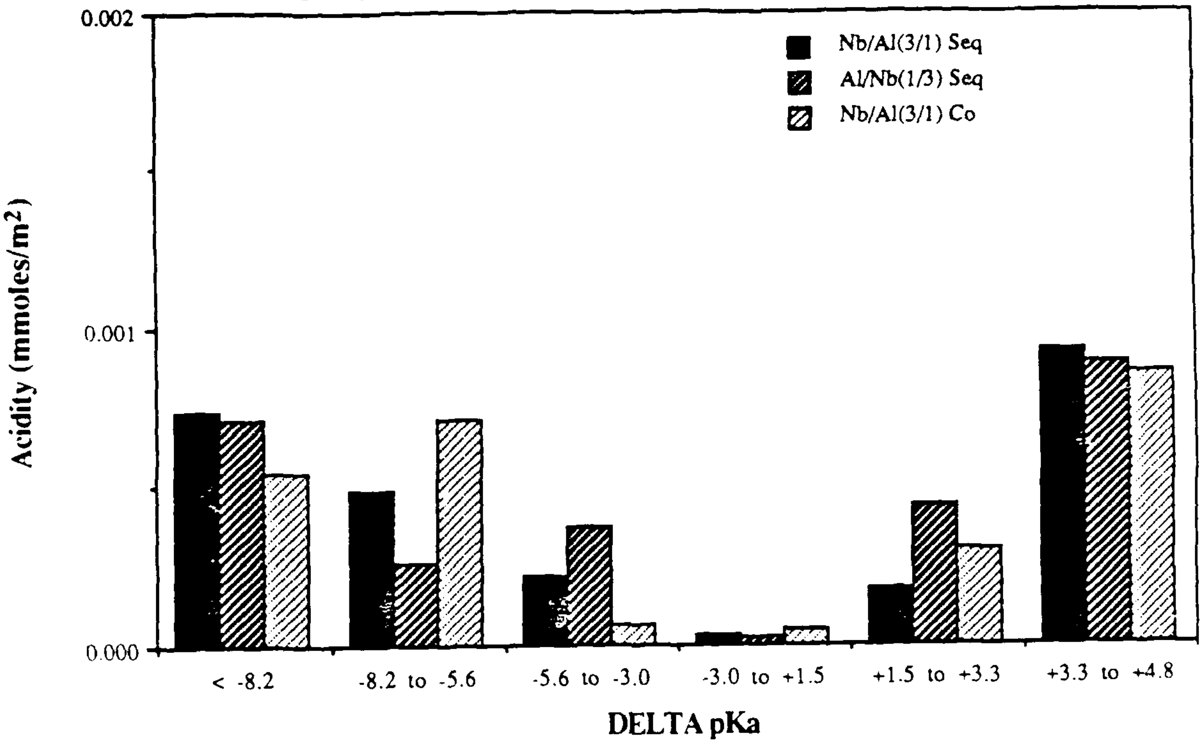


Figure 4-24 ACIDITY OF NB/AL(3/1) (SEQ AND CO) BETWEEN DIFFERENT ACID STRENGTHS AFTER HEAT TREATMENT (1000° C)

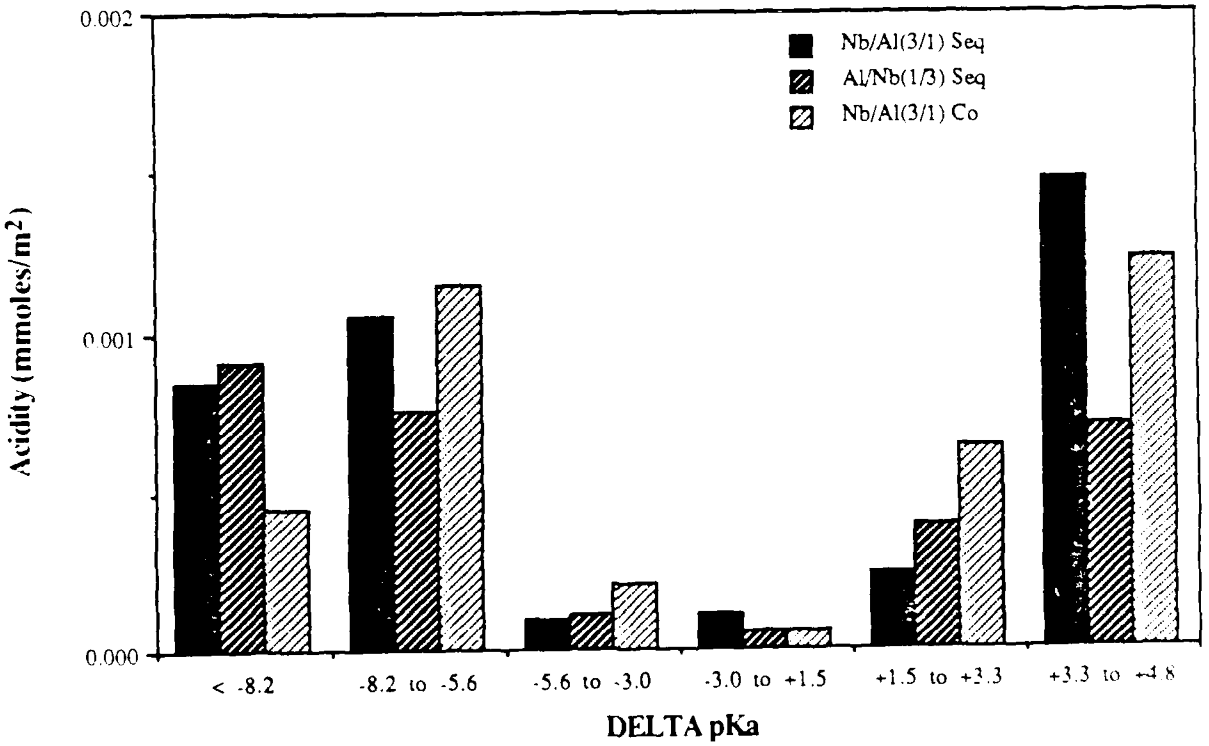


Table 4-8: STEADY-STATE ACTIVITY AND SELECTIVITY OF SUPPORTED SURFACE OXIDES

(I.) Surface Oxides after Calcination (500° C):

Sample	Activity (mol/hr-m^2)x10^3	Selectivity (cis/trans)
Nb/Al(3/1) Pre	1.5	1.44
Nb/Al(1/1) Pre	1.1	1.40
Al/Nb(1/3) Pre	3.6	1.17
Al/Nb(1/1) Pre	17.4	0.88
Nb/Al(3/1) Seq	4.8	1.27
Al/Nb(1/3) Seq	5.5	1.18
Nb/Al(3/1) Co	5.9	1.09
Nb/Al(1/1) Co	6.8	1.04
Silica Gel	0.02	0.00

(II.) Surface Oxides after Heat Treatment (1000° C):

Sample	Activity (mol/hr-m^2)x10^3	Selectivity (cis/trans)
Nb/Al(3/1) Pre	2.3	0.10
Nb/Al(1/1) Pre	3.8	0.13
Al/Nb(1/3) Pre	19.0	1.36
Al/Nb(1/1) Pre	22.8	1.03
Nb/Al(3/1) Seq	8.8	0.31
Al/Nb(1/3) Seq	8.1	0.44
Nb/Al(3/1) Co	5.6	0.60
Nb/Al(1/1) Co	6.8	1.43
Silica Gel	0.02	0.00

After heat treatment (1000° C), the activity of the supported alumina and niobia oxides went up significantly. The sequentially impregnated oxides also had activities that increased by approximately 70 % upon the heat treatment. The activity of the coimpregnated surface oxides (Nb/Al(3/1) Co and Nb/Al(1/1) Co) after heat treatment remained the same.

4.3.3.2 *Selectivities*

The selectivities of the surface oxide samples for the isomerization reaction are listed in Table 4-8. All oxide samples had selectivities around 1 after calcination. After heat treatment (1000° C), the supported alumina and Nb/Al(1/1) Co still had selectivities around 1. But, the selectivity of the supported niobia went down dramatically by an order of magnitude to 0.1. The supported-Nb/Al(3/1) oxides (niobia rich oxides) also had dramatic decreases in selectivities to around 0.5.

4.4 Composition Effect on Coimpregnated Nb_2O_5/Al_2O_3 Surface Oxides

The supported surface oxides studied in this section are Nb/Al(3/1) Co, Nb/Al(1/1) Co, and Nb/Al(1/3) Co. These three oxides were studied to see how changes in the composition of the surface were reflected in their chemical properties. Each of the samples was calcined and heat treated according to the same procedures as before.

4.4.1 Physical Characterization

4.4.1.1 BET Surface Area

A standard 1-point BET method was used to measure the total surface areas of the three coimpregnated surface oxides. Table 4-9 shows the results of the surface areas both after calcination and after heat treatment. It is interesting to note that the supported oxide

Table 4-9: BET SURFACE AREA MEASUREMENTS FOR COIMPREGNATED SiO_2-SUPPORTED Nb_2O_5/Al_2O_3

	After Calcination (500° C)		After H.T. (1000° C)	
Supported Samples	**Area (m^2/g)**	**Area (m^2/g SiO_2)**	**Area (m^2/g)**	**Area (m^2/g SiO_2)**
Nb/Al(3/1) Co	324.1	431.1	143.2	190.5
Nb/Al(1/1) Co	346.5	434.7	195.1	244.8
Nb/Al(1/3) Co	362.1	430.1	208.6	247.8

with the larger alumina content also has the larger total surface area. Again, all the oxides lost surface area when heated, but no significant changes were seen as with the mixed oxides.

4.4.1.2 DTA Study

The DTA spectra of the supported surface oxides are shown in Figure 4-25. Conditions were the same for all reactions and can be found elsewhere. It is easily seen that there were no significant heat effects for any of the supported binary oxides. Any fluctuations that occurred are background noise from the apparatus.

4.4.1.3 XRD Study

X-ray diffraction patterns of the coimpregnated surface oxides after calcination are shown in Figure 4-26. The samples are entirely amorphous because of the absence of any observable diffraction peaks. The diffraction patterns after heat treatment (1000° C) are shown in Figure 4-27. Again, it is easily seen that the supported surface oxides are amorphous to XRD, thus showing the stability of these surface oxides.

4.4.2 Surface Acidity Measurement

4.4.2.1 Acid Strength

The acid strengths of the coimpregnated surface oxides are listed in Table 4-10 as a function of pKa and thermal treatment. All samples studied had very strong acid sites ($pKa < -8.2$) that are as strong as any mixed oxides previously studied. Even after heat treatment (1000° C) these strong acid sites remain.

Figure 4-25 DTA SCANS OF COIMPREGNATED SURFACE OXIDES

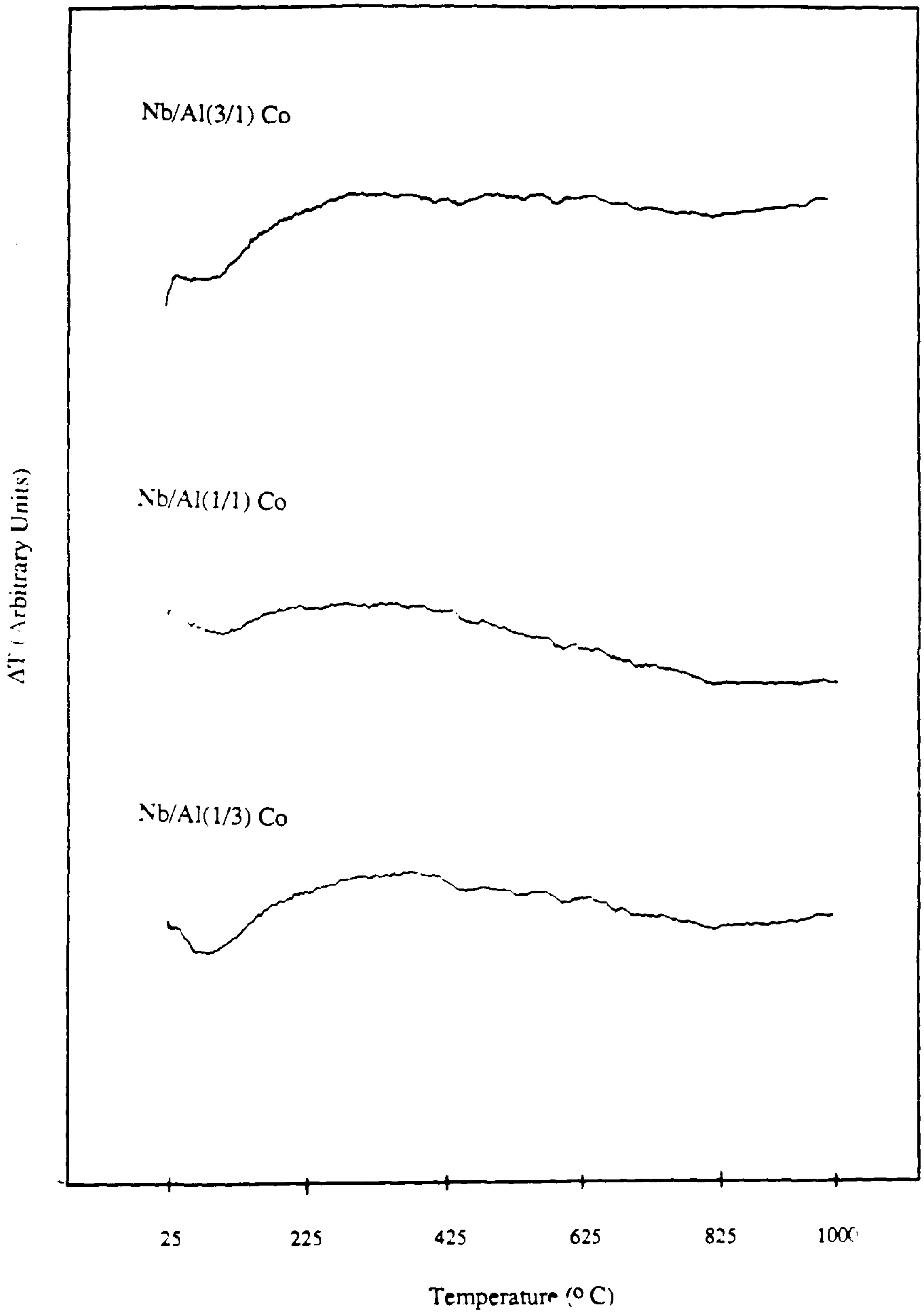


Figure 4-26 XRD SCANS OF COIMPREGNATED SURFACE OXIDES AFTER CALCINATION (500° C)

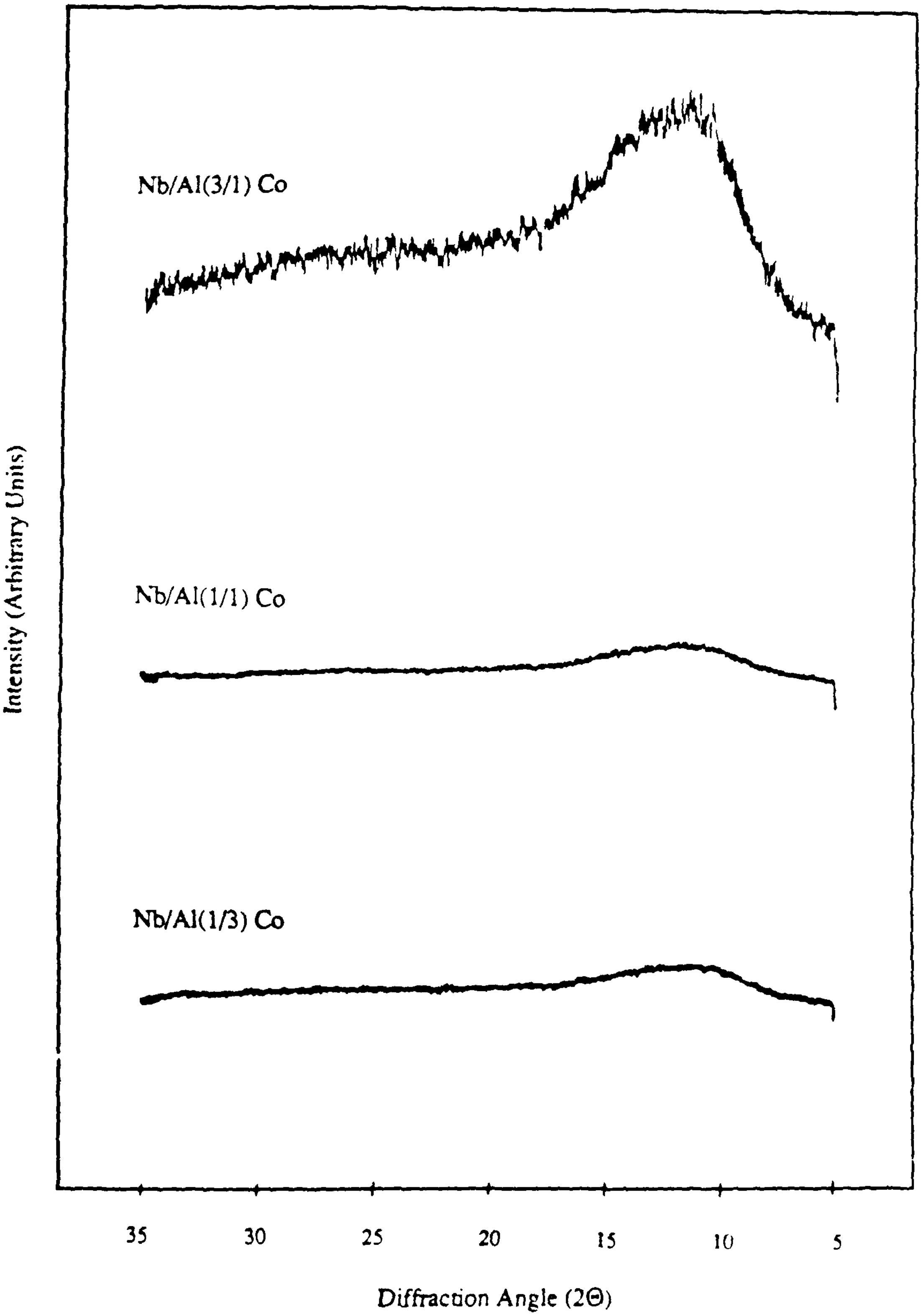


Figure 4-27 XRD SCANS OF COIMPREGNATED SURFACE OXIDES AFTER HEAT TREATMENT (1000° C)

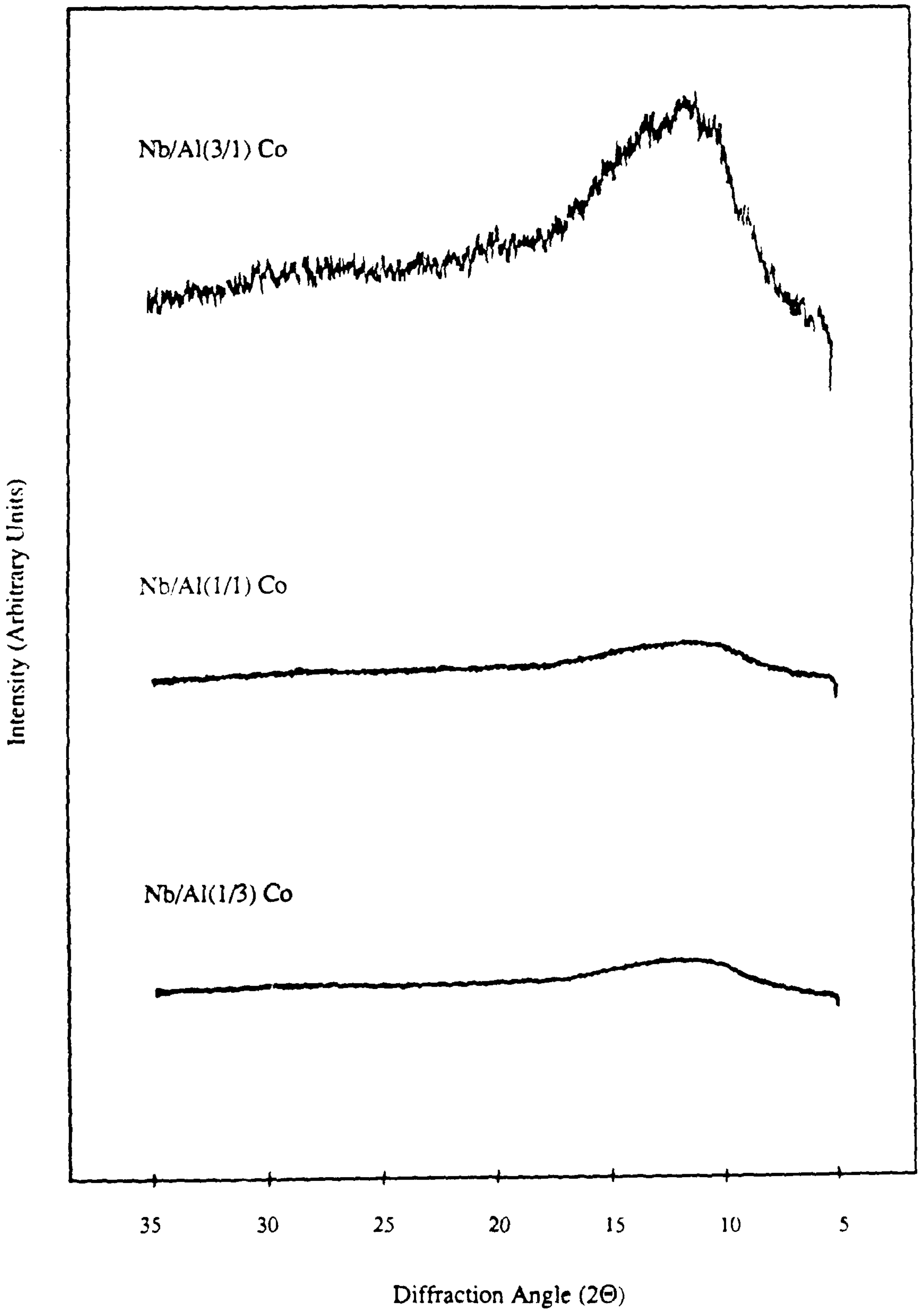


Table 4-10: ACID STRENGTH OF COIMPREGNATED SURFACE OXIDES

(I.) Surface Oxides after Calcination (500° C):

	pKa					
Sample	+4.8	+3.3	+1.5	-3.0	-5.6	-8.2
Nb/Al(3/1) Co	+	+	+	+	+	+
Nb/Al(1/1) Co	+	+	+	+	+	+
Nb/Al(1/3) Co	+	+	+	+	+	+

(II.) Surface Oxides after Heat Treatment (1000° C):

	pKa					
Sample	+4.8	+3.3	+1.5	-3.0	-5.6	-8.2
Nb/Al(3/1) Co	+	+	+	+	+	+
Nb/Al(1/1) Co	+	+	+	+	+	+
Nb/Al(1/3) Co	+	+	+	+	+	+

+: Turned Indicator to Acid Form

-: Turned Indicator to Basic Form

+/-: Barely Turned Indicator to Acid Form, if at all

4.4.2.2 Acidity

The coimpregnated surface oxides were pretreated in air under vacuum at 383 K for about 1 hr to remove any physisorbed water on the sample surface. Table 4-11 is a collection of acidity data for the coimpregnated surface oxides between different acid strengths. Figure 4-28 shows a chart of the acidity between different acid strengths of the coimpregnated supported oxides after calcination. Figure 4-29 is a plot of acidity vs. delta pKa also, but contains the oxides after they had been heat treated (1000° C). It is interesting to notice how after calcination the Nb/Al(1/3) Co oxide had the lowest acidity of all three samples, but after heat treatment had the greatest acidity of the oxides. Over the entire delta pKa range it nearly doubled its acidity (even at the strongest acid sites) which is very similar to the way that the supported alumina samples behaved after the heat treatment. The other two surface oxides, Nb/Al(3/1) Co and Nb/Al(1/1) Co, also had total acidities that increased by 40 % and 20 % respectively from the calcination to the heat treatment step.

4.4.3 1-C_4H_8 Isomerization

4.4.3.1 TOS and Activities

All coimpregnated surface oxides had pretreatments similar to those of the other samples previously mentioned and can be found in Section 2.3.5. The temperature for all reactions was kept at 423 K. The steady-state activities and selectivities of the catalysts are listed in Table 4-12 for both thermal treatments. The Nb/Al(3/1) Co and Nb/Al(1/1) Co samples have approximately the same activities both after calcination and after heat treatment. The Nb/Al(1/3) Co catalyst, however, nearly doubles its activity after the heat treatment. This behavior is similar to that of the supported alumina catalysts.

Table 4-11: ACIDITY OF COIMPREGNATED SURFACE OXIDES BETWEEN DIFFERENT ACID STRENGTHS

(I.) Surface Oxides after Calcination (500° C):

Sample	Delta pKa=	Acidity (mmoles/m^2) x 10^4 +4.8 to +3.3	+3.3 to +1.5	+1.5 to -3.0	-3.0 to -5.6	-5.6 to -8.2	<-8.2
Nb/Al(3/1) Co		8.5	3.0	0.4	0.7	7.0	5.4
Nb/Al(1/1) Co		4.3	3.3	0.3	2.5	7.4	3.3
Nb/Al(1/3) Co		5.8	3.2	0.1	2.4	4.9	3.5

(II.) Surface Oxides after Heat Treatment (1000° C):

Sample	Delta pKa=	Acidity (mmoles/m^2) x 10^4 +4.8 to +3.3	+3.3 to +1.5	+1.5 to -3.0	-3.0 to -5.6	-5.6 to -8.2	<-8.2
Nb/Al(3/1) Co		12.3	6.4	0.6	2.1	11.5	4.5
Nb/Al(1/1) Co		10.6	0.4	0.0	2.2	12.2	1.4
Nb/Al(1/3) Co		10.6	4.0	2.1	3.7	11.1	6.6

Figure 4-28 ACIDITY OF COIMPREGNATED SURFACE OXIDES BETWEEN DIFFERENT ACID STRENGTHS AFTER CALCINATION (500° C)

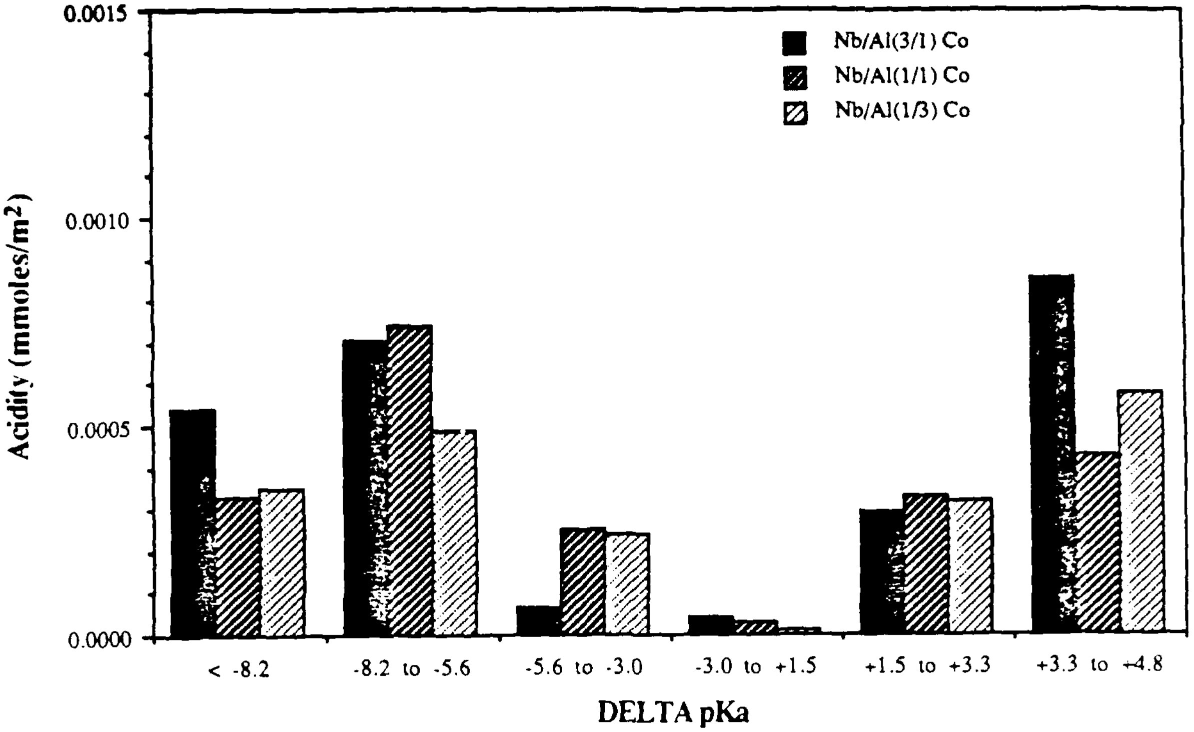


Figure 4-29 ACIDITY OF COIMPREGNATED SURFACE OXIDES BETWEEN DIFFERENT ACID STRENGTHS AFTER HEAT TREATMENT

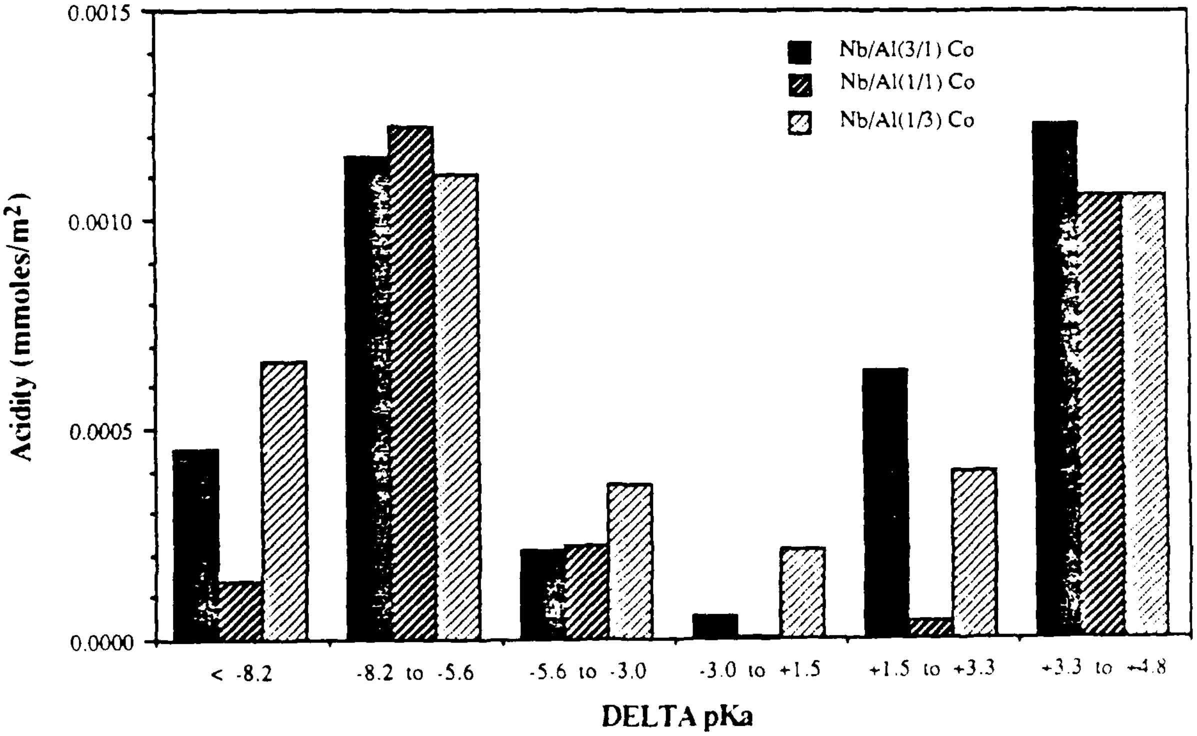


Table 4-12: STEADY STATE ACTIVITY AND SELECTIVITY OF COIMPREGNATED SURFACE OXIDES

(I.) Surface Oxides after Calcination (500° C):

Sample	Activity (mol/hr-m^2)x10^3	Selectivity (cis/trans)
Nb/Al(3/1) Co	5.9	1.09
Nb/Al(1/1) Co	6.8	1.04
Nb/Al(1/3) Co	8.5	0.96

(II.) Surface Oxides after Heat Treatment (1000° C):

Sample	Activity (mol/hr-m^2)x10^3	Selectivity (cis/trans)
Nb/Al(3/1) Co	5.6	0.60
Nb/Al(1/1) Co	6.8	1.43
Nb/Al(1/3) Co	16.2	1.31

4.4.3.2 Selectivites

The selectivities of the coimpregnated samples are listed in Table 4-12. All three catalysts had selectivities of 1 after calcination. The selectivity of the niobia rich sample went down approximately by a factor of two, while the selectivites of the other two alumina rich samples went up by about 40 % which is similar to the behavior of the supported niobia and alumina samples respectively.

5. DISCUSSION

5.1 General

In this study, a series of Nb_2O_5/Al_2O_3 binary oxides were successfully prepared and analyzed. All of the mixed oxides were found to exhibit extremely strong acidic properties as well as catalytic activities. The supported surface oxides also exhibited surprisingly strong acid sites. These samples were also found to catalyze the 1-butene isomerization reaction. These binary oxides were also subjected to different preparations and compositions as well as heat treatments with some interesting results. The following sections will discuss these results and try to provide some understanding into the role of the oxide-oxide interactions in these materials.

5.2 Mixed Oxide / Surface Oxide Comparison

In an effort to understand the type or role of oxide-oxide interactions, one must look at how the properties of the mixed and supported-binary oxides are similar or different. In comparing these binary oxides the first result that was noticed was the ease of crystallization from the niobia/alumina mixed oxides. Previous results from our group in XRD studies have shown that these oxides form compounds of $AlNbO_4$ (aluminum niobate) and crystalline forms of niobia (M-niobia) when subjected to a 1000° C ramp heat treatment in flowing He.[23] These XRD results are listed in Table 5-1. Contrasting these results is the surprising stability of the surface phase oxides. These are also listed in Table 5-1 along with the mixed oxides. The lack of diffraction peaks in all of the surface oxide spectra suggested that the deposited phases were all well dispersed as crystallites smaller than 3 nm in diameter (detection limit for Mo radiation due to line

Table 5-1: XRD RESULTS Nb_2O_5/Al_2O_3 BINARY OXIDES[23]

(I.) Nb_2O_5/Al_2O_3 Mixed Oxides

Sample	Calcination (500º C)	Heat Treatment (1000º C)
NA(75/25)	Amorphous	$AlNbO_4$ and M-niobia
NA(50/50)	Amorphous	$AlNbO_4$
NA(25/75)	Amorphous	$AlNbO_4$

(II.) Supported-Nb_2O_5/Al_2O_3 Surface Oxides

Sample	Calcination (500º C)	Heat Treatment (1000º C)
Nb/Al(3/1) Co	Amorphous	Amorphous
Nb/Al(1/1) Co	Amorphous	Amorphous
Nb/Al(1/3) Co	Amorphous	Amorphous

broadening) or amorphous. This result was somewhat surprising because of the ease of crystallization in the mixed oxides and also by the fact that multilayers of niobia were found to possess crystalline phases of niobia (TT-niobia).[16,17] The silica substrate seems to stabilize both the niobia and alumina independently, thus indicating strong interactions of the oxides with the support.

The acidity plots among the mixed and supported-surface phase binary oxides are very interesting. The graphs are located in Figures 5-1 to 5-6 and also indicate the effects of the thermal treatments. In Figures 5-1 and 5-2, the comparison of NA(75/25) to Nb/Al(3/1) Co can be seen. It is noticed immediately that these graphs are not very similar. Instead, the Nb/Al(3/1) Co surface oxide looks very similar to the graphs of the Nb/Al(3/1) Pre surface oxide, the main constituent making up the coimpregnated oxide. This implies that the supported-surface oxide has little to no surface interaction among the niobia and alumina oxides. The mixed oxide seems to have a uniform acid site distribution, while the surface oxides have primarily just very strong or weak acid sites with little to no moderate sites. Upon the 1000° C heat treatment, the mixed oxide appeared to lose all of its acidity. This could possibly be a surface area effect problem, because of the limitations of the titration system. But this still would have only affected the weaker acid sites, since it clearly had no strong acid sites ($pKa < -3.0$); see Table 4-2 for acid strength distributions. Thus crystallization has a large effect on the properties of the mixed oxide system. With the same heat treatment, the surface oxides seemed to increase their acidity in both the very strong and weak acid sites, with little to no acidity in the moderate acid site region. This same effect was seen in the other figures as well.

In Figures 5-3 and 5-4, NA(50/50) is compared to Nb/Al(1/1) Co. Again, there is a remarkable difference between the two graphs. The biggest difference noticed was the large number of very strong acid sites on the mixed oxide. There are at least 5 times as many very strong sites ($pKa < -8.2$) on the mixed oxide as there are on the surface oxide. Again, the Nb/Al(1/1) Co surface oxide looks very similar to the Nb/Al(1/1) Pre,

Figure 5-1 ACIDITY MEASUREMENTS OF NB/AL(3/1) BINARY OXIDES AFTER CALCINATION (500° C)

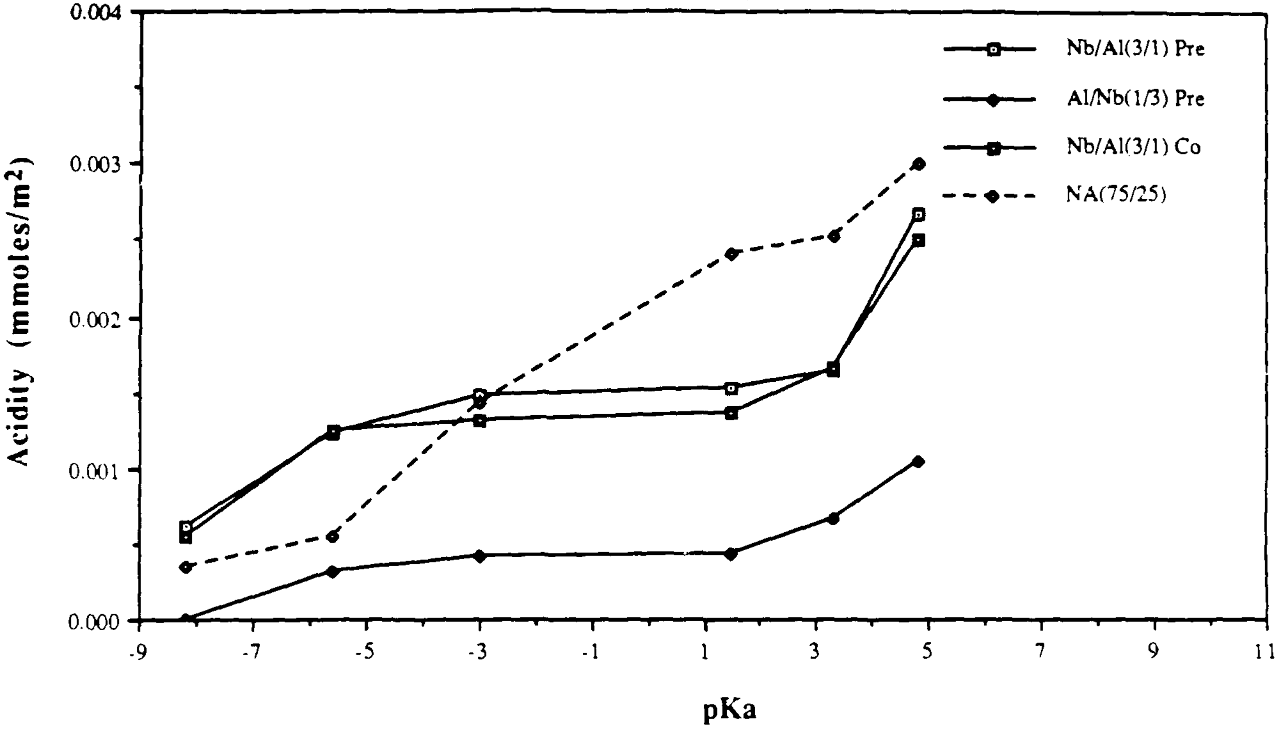


Figure 5-2 ACIDITY MEASUREMENTS OF NB/AL(3/1) BINARY OXIDES AFTER HEAT TREATMENT (1000° C)

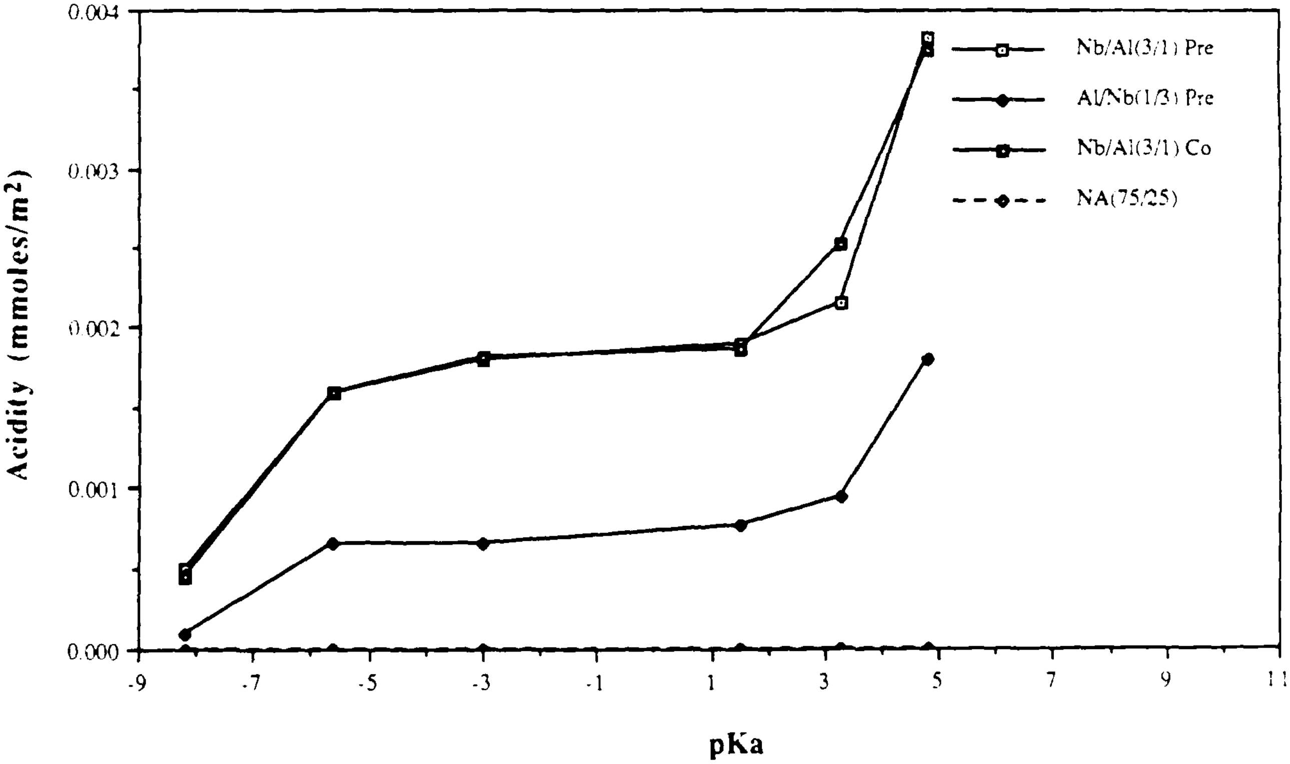


Figure 5-3 ACIDITY MEASUREMENTS OF NB/AL(1/1) BINARY OXIDES AFTER CALCINATION (500° C)

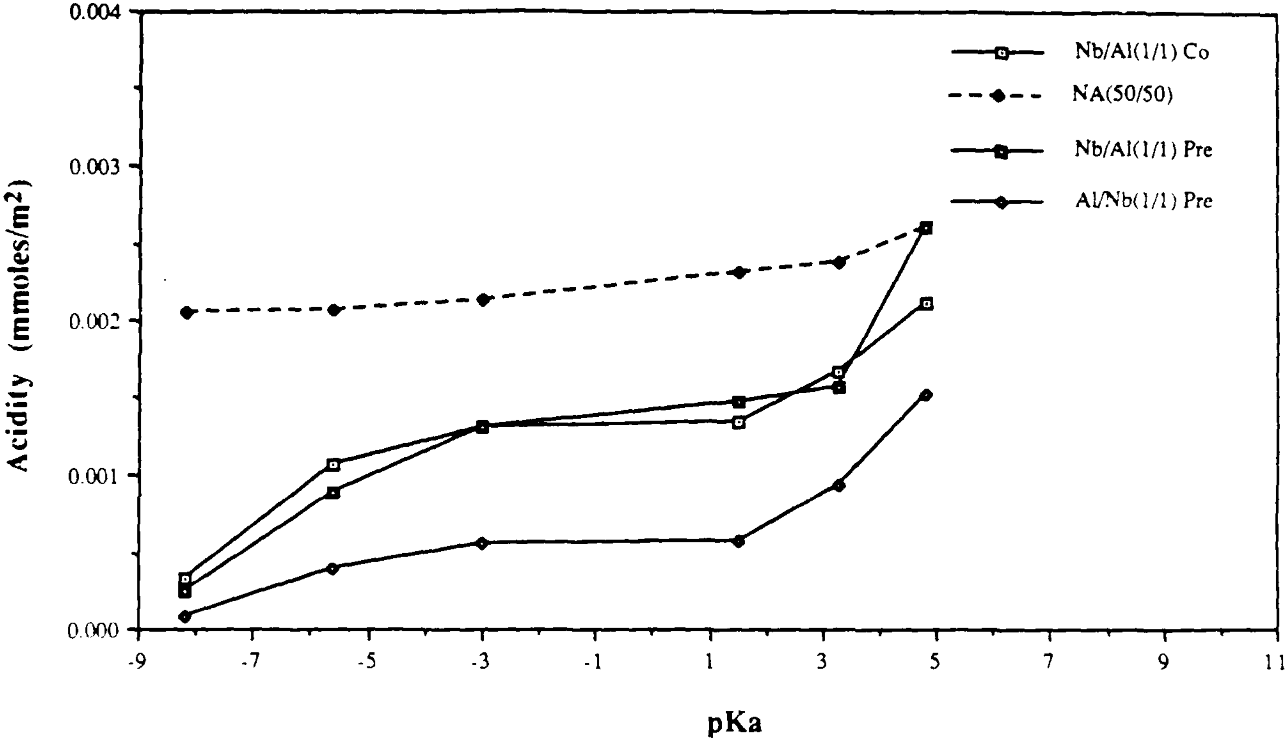
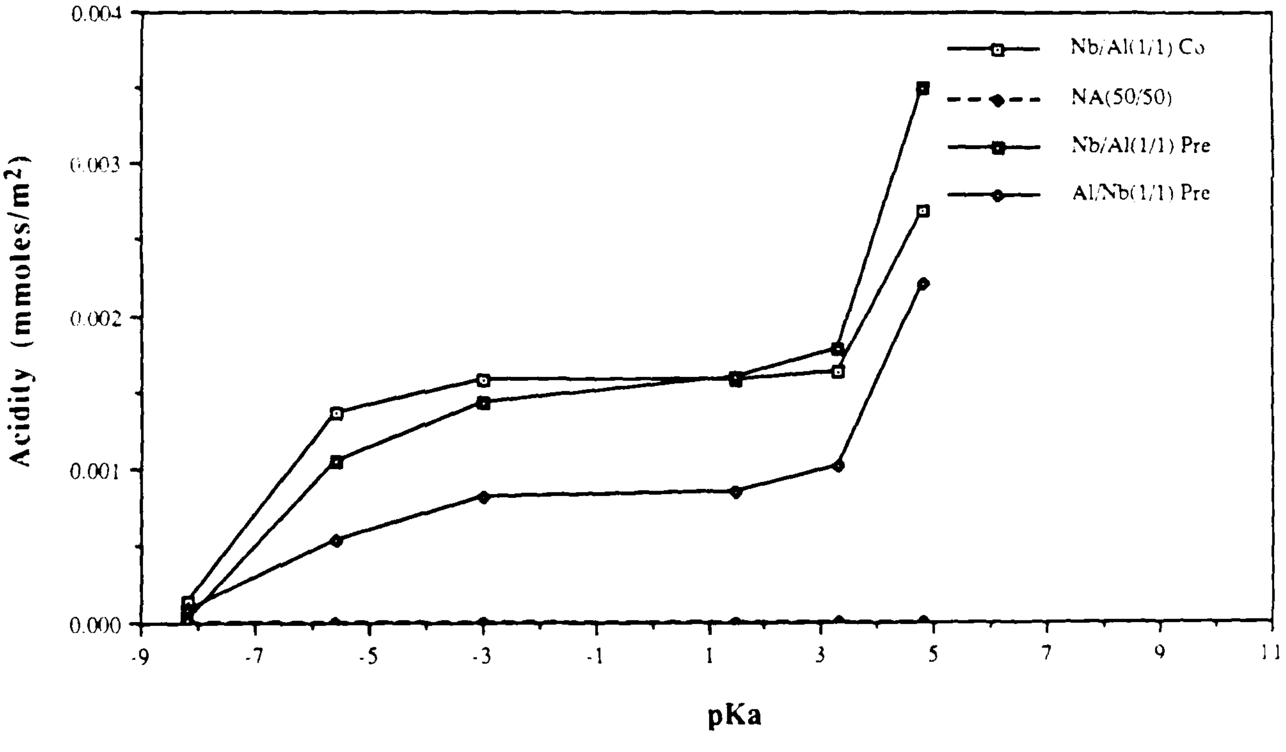


Figure 5-4 ACIDITY MEASUREMENTS OF NB/AL(1/1) BINARY OXIDES AFTER HEAT TREATMENT (1000° C)



both after calcination and after heat treatment. This similarity, plus the fact that the mixed oxide has many stronger acid sites, possibly due to niobia-alumina interactions, indicates that the surface oxide species are strongly interacting with the silica substrate with little to no interaction among themselves. Again, with the 1000° C heat treatment, the mixed oxide lost all of its acidity. This again, could be a surface area effect problem, since $AlNbO_4$ was formed during the heating stage and significantly lowered its surface area by two orders of magnitude. But as with NA(75/25), this sample, NA(50/50), clearly had no strong acid sites (pKa < -3.0). Thus, the acidity of these compounds is clearly a function of the crystallinity involved. The surface oxides seemed to increase the number of strong and weak acid sites, similar to those of the Nb/Al(3/1) surface oxides.

In Figures 5-5 and 5-6, NA(25/75) is compared to Nb/Al(1/3) Co. The major distinction between these graphs again is the large number of strong acid sites on the mixed oxide. There are about 5 times as many very strong acid sites (pKa < -8.2) on the mixed oxide as there are on the supported surface oxide. Correlating these strong acid sites with niobia-alumina interactions, again indicates that the surface oxide species are interacting with the substrate with little to no niobia-alumina interactions on the surface. Upon heating to 1000° C, NA(25/75) lost all its very strong acid sites, presumably because of the formation of $AlNbO_4$. The Nb/Al(1/3) Co surface oxide exhibited more very strong acid sites upon heating than the mixed oxide as seen in Figure 5-6. Besides the stronger acid sites associated with the surface oxide, the two graphs look very similar. It is difficult to assess what is actually occurring on the surface, but since the supported alumina samples show the same behavior as Nb/Al(1/3) Co (an alumina rich species), it is possible that there may be some surface rearrangements occurring with the alumina or formation of alumina crystallites on the surface which are too small to be picked up by XRD.

The activities and activation energies of the binary oxides with respect to 1-butene isomerization are listed in Table 5-2.[42] Figure 5-7 shows the coimpregnated surface

Figure 5-5 ACIDITY MEASUREMENTS OF NB/AL(1/3) BINARY OXIDES AFTER CALCINATION (500° C)

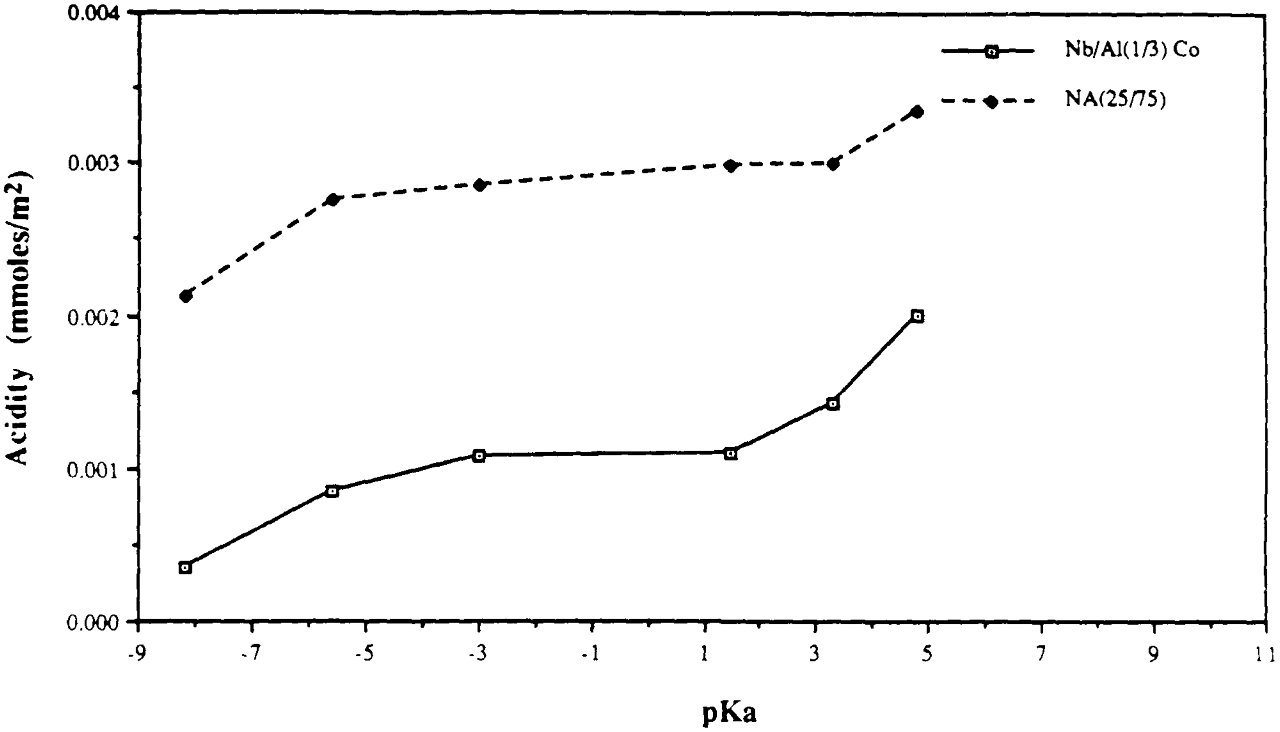


Figure 5-6 ACIDITY MEASUREMENTS OF NB/AL(1/3) BINARY OXIDES AFTER HEAT TREATMENT (1000° C)

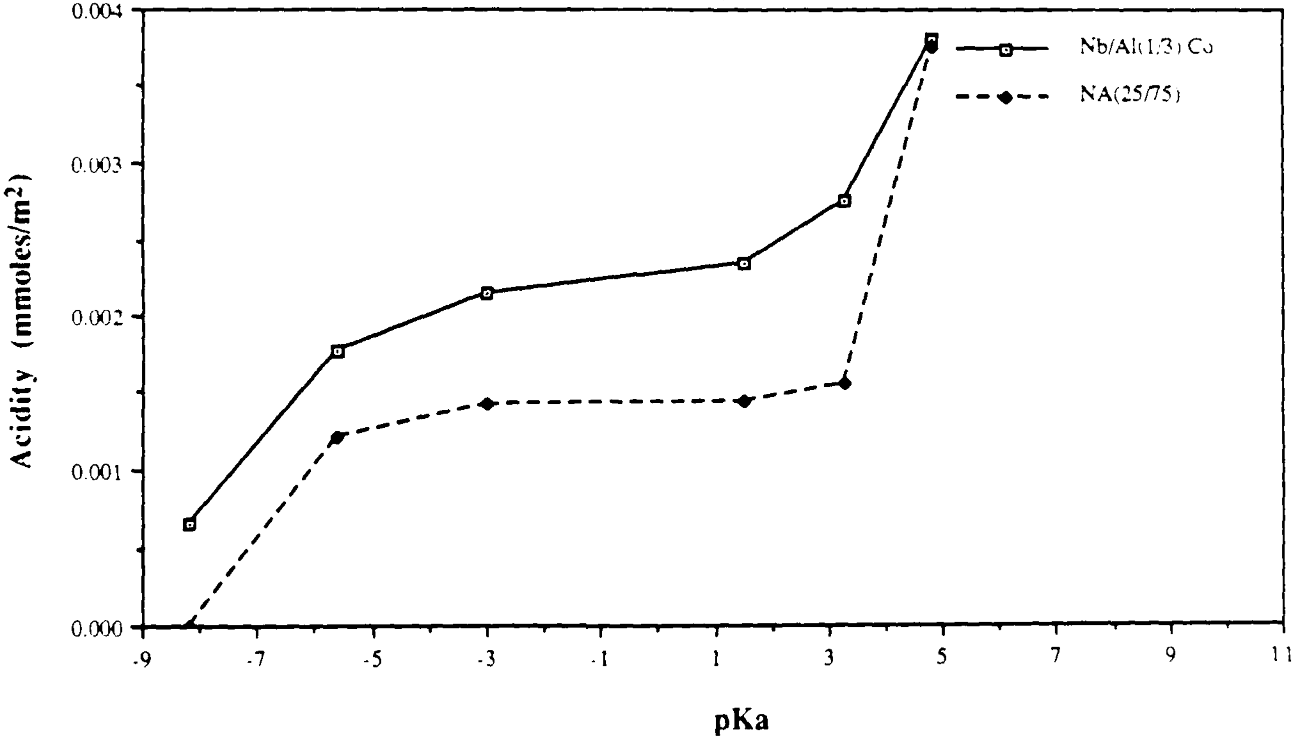


Table 5-2: STEADY-STATE 1-BUTENE ISOMERIZATION ACTIVITIES AND ACTIVATION ENERGIES OF Nb_2O_5/Al_2O_3 BINARY OXIDES

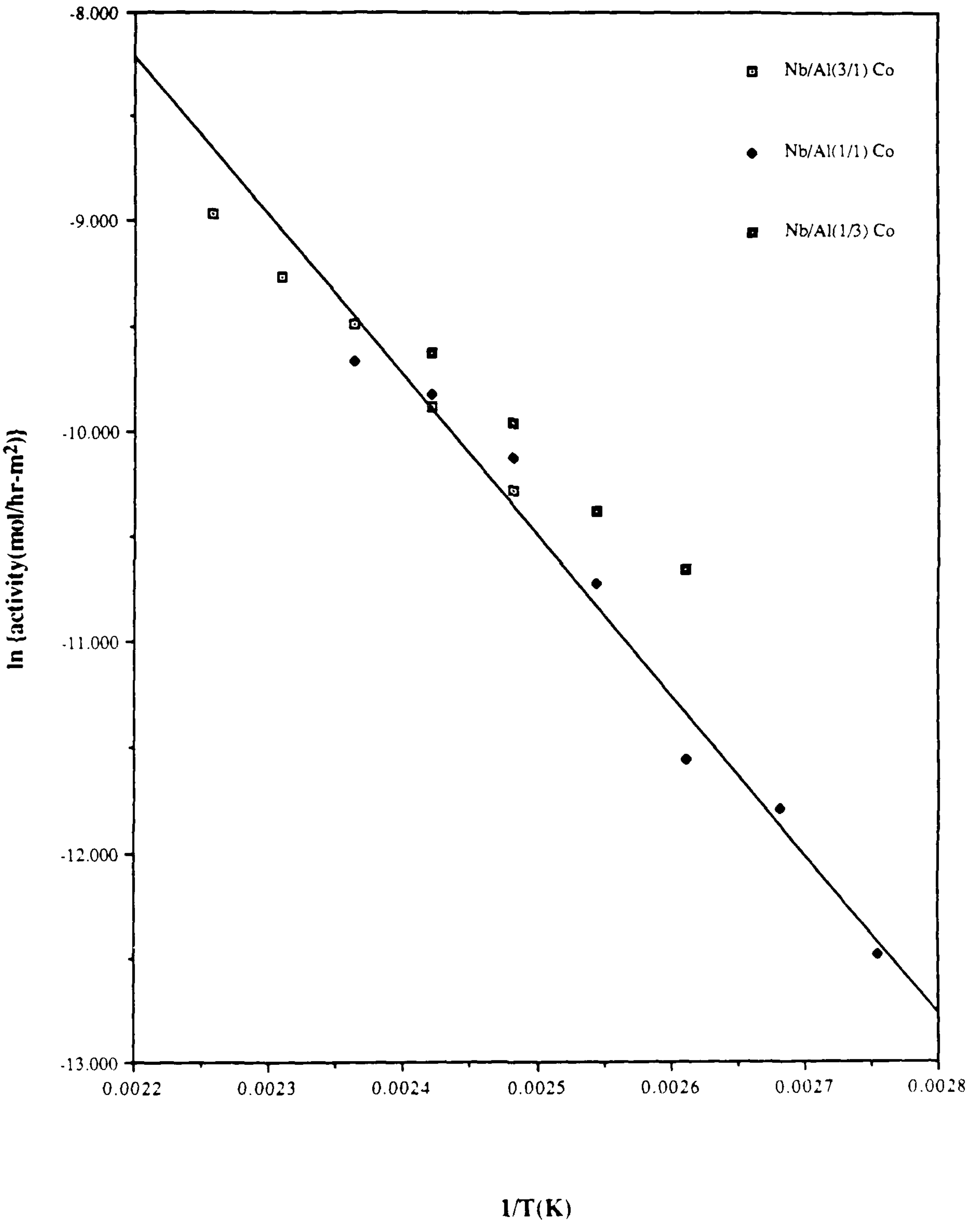
(I.) Binary Oxides after Calcination (500° C):

Sample	Activity (mol/hr-m2)x10^3	Activation Energy (kcal/gmole)[42]
NA(75/25)	5.08	18.1
NA(50/50)	1.90	22.9
NA(25/75)	1.47	19.4
Nb/Al(3/1) Co	5.86	11.5
Nb/Al(1/1) Co	6.82	15.1
Nb/Al(1/3) Co	8.48	11.0

(II.) Binary Oxides after Heat Treatment (1000° C):

Sample	Activity (mol/hr-m2)x10^3
NA(75/25)	0.73
NA(50/50)	0.75
NA(25/75)	2.58
Nb/Al(3/1) Co	5.63
Nb/Al(1/1) Co	7.70
Nb/Al(1/3) Co	16.20

Figure 5-7 ACTIVITY OF SURFACE OXIDES AS A FUNCTION OF REACTION TEMPERATURE AFTER CALCINATION (500° C)



oxide activity as a function of reaction temperature after the samples had been calcined. The surface oxides all show an increase in activity with increasing alumina content; however, the reverse is true with the mixed oxides of niobia/alumina. One explanation of this fact could be that the isomerization reaction is not catalyzed by acid sites as strong as those found on the niobia/alumina mixed oxides or there is a considerable coking effect that may be hindering the reaction.[44] The activation energies for the reaction were all found to be approximately 1.5 times higher for the mixed oxides than for the supported oxides, with a notable increase in activation energy for the Nb/Al(1/1) binary oxides. This could also help explain the higher catalytic activities for the surface phase oxides than the mixed oxides.

The selectivities (cis/trans-2-butene ratio) for all the calcined (500^o C) surface oxides were around 1 for different reaction temperatures, see Figure 5-8. This indicated that the reaction proceeded by a 2-butyl carbonium ion intermediate.[39] Also, for the calcined mixed oxides, the cis/trans ratios were about 1 for different reaction temperatures, see Figure 5-9. Tanabe found for different compositions of TiO_2/SiO_2 the cis/trans ratio to be be around 1.5 and concluded that the 2-butyl carbonium ion was the reaction intermediate.[20] Chen also found for certain niobia rich compounds of Nb_2O_5/SiO_2 that the ratio of cis/trans-2-butene was about 0.6, which is almost identical to the results in this study with niobia being the major component of Nb_2O_5/Al_2O_3.[13] Thus, it appears that the mechanism on the mixed oxides of niobia/alumina is also based on the carbonium ion intermediate.

5.3 *Effect of Preparation on Supported Surface Oxides*

The effect of different preparation methods was investigated for the supported surface oxide system of Nb/Al(3/1). Three different preparation techniques, two sequential and one coimpregnated method, were employed. The values of acidity are

Figure 5-8 SELECTIVITIES OF SUPPORTED NIOBIA/ALUMINA SURFACE OXIDES AFTER CALCINATION (500° C)

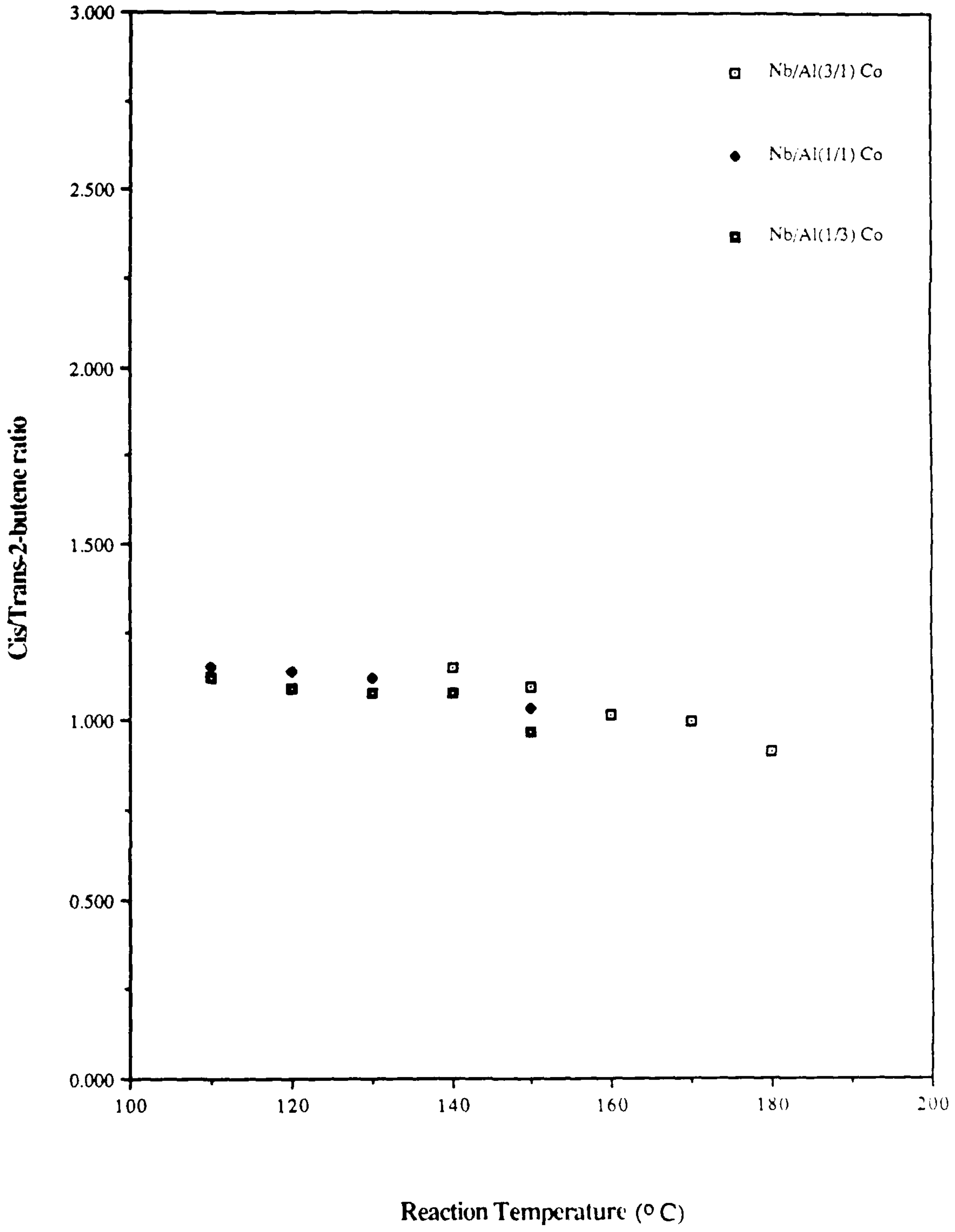
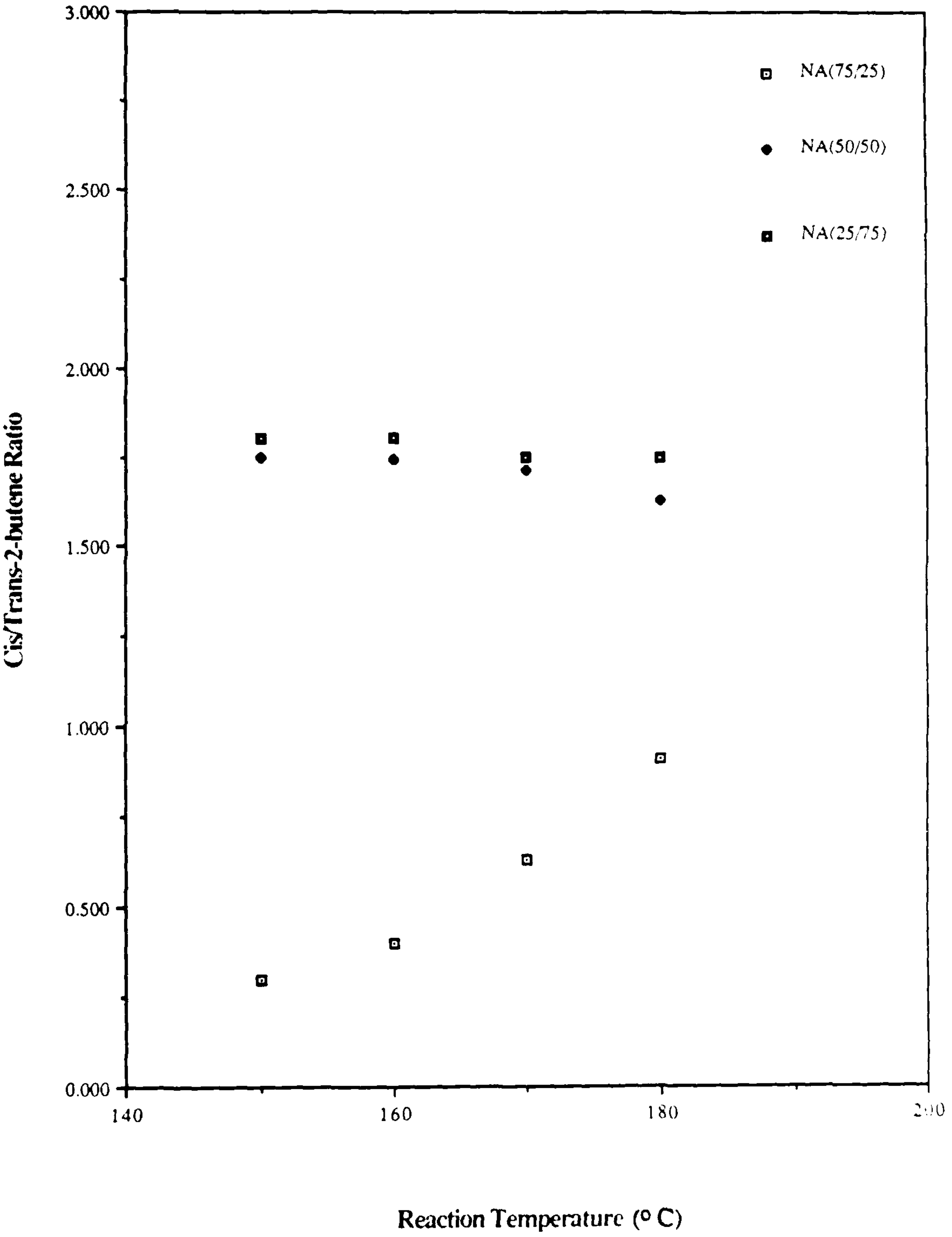


Figure 5-9 SELECTIVITIES OF NIOBIA/ALUMINA MIXED OXIDES AFTER CALCINATION (500° C)



graphed as a function of pKa in Figures 5-10 and 5-11. It is clearly seen that there is no difference in the acidic properties of these surface phase oxides. This again gives evidence that the oxide species are separately interacting with the silica substrate since the method of depositing the oxides on the surface has no influence on the acidic characteristics of the materials.

Various surface coverage amounts of supported niobia and supported alumina were investigated and are listed in Table 5-3. This is further shown graphically in Figures 5-12 and 5-13. All values listed are reported on an acidity per weight of surface species basis. It is easily seen from this figure that the acidity is greatest for the surface species present in the lesser amount. This seems to indicate that acidity depends upon the amount of surface species present. For the calcined (500° C) supported oxide species studied here, the acidity corresponds to ratios of about 1 acid site per surface oxide species, which is identical to what other studies have found for supported surface species at very low loadings.[4,24] When these samples were heat treated to 1000° C, both of the supported alumina surface oxides increased in acidity while the supported niobia oxides had acidities that decreased, as shown in Figure 5-13. The Al/Nb(1/3) Pre surface oxide had a large increase in acid strength and acidity as well as activity that is difficult to interpret other than suggesting a possible surface or structural rearrangement that may have occurred in the sample. The reduced acidities of the supported-niobia samples could possibly be a sign that crystallites of niobia are forming on the surface that are too small to be detected by X-ray diffraction.

5.4 Effect of Composition on Supported Surface Oxides

The effect of different compositions was investigated for the coimpregnated supported binary oxides and is shown in Figures 5-14 and 5-15. As was seen with the different preparation techniques, the three different surface compositions do not show any

Figure 5-10 PREPARATION EFFECT ON NB/AL(3/1) SURFACE OXIDES AFTER CALCINATION (500° C)

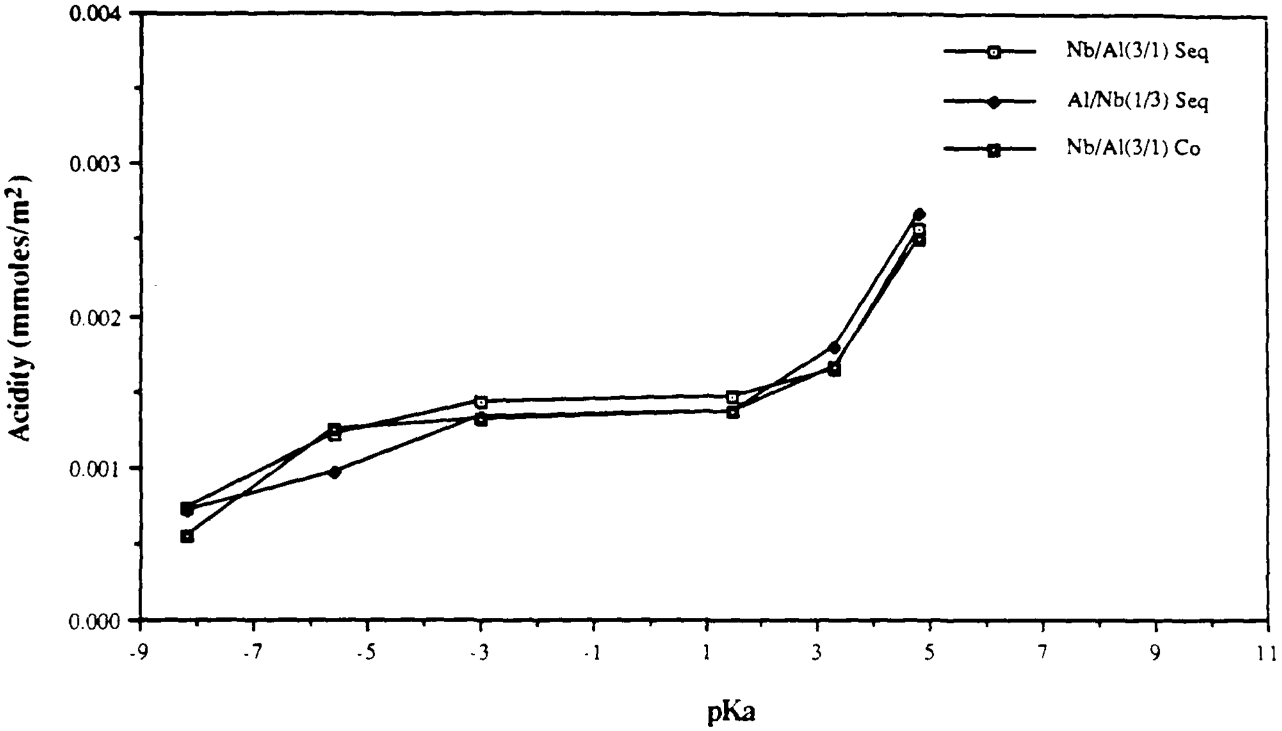


Figure 5-11 PREPARATION EFFECT ON NB/AL(3/1) SURFACE OXIDES AFTER HEAT TREATMENT (1000° C)

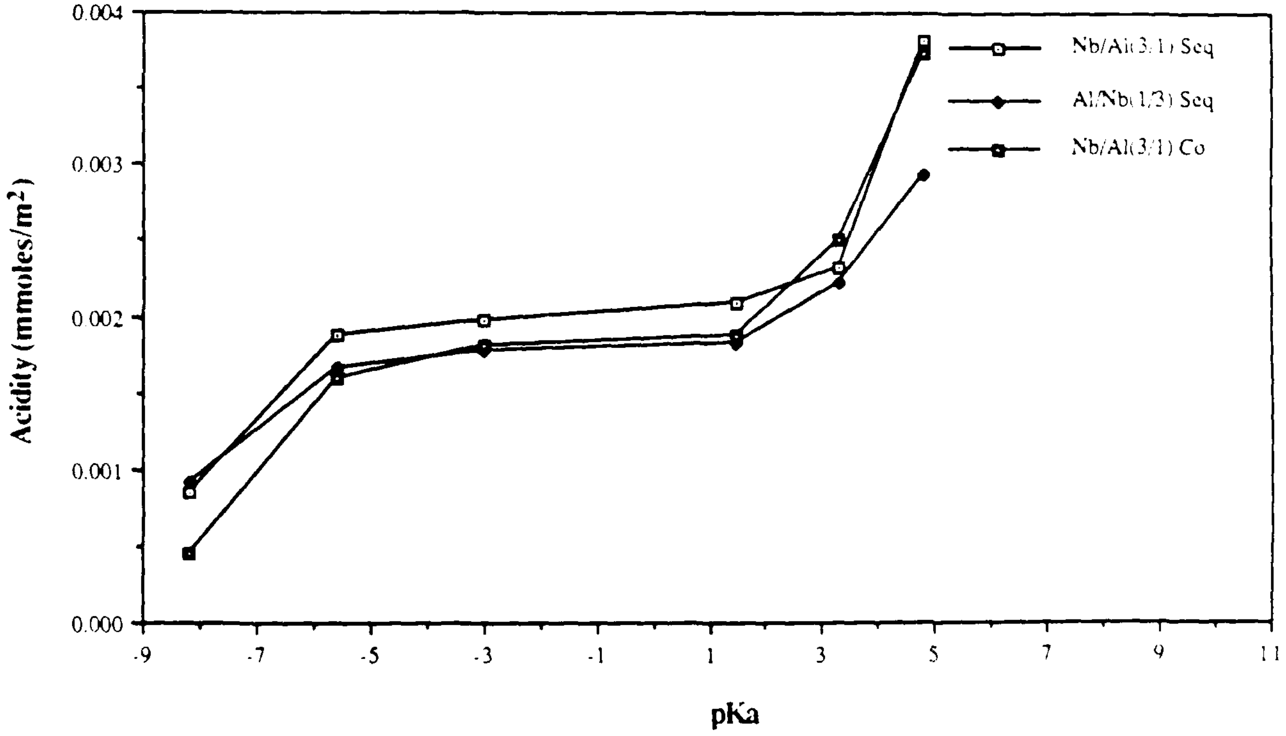


Table 5-3: ACID PROPERTIES OF SUPPORTED NIOBIA OR ALUMINA

(I.) Surface Oxides after Calcination (500° C):

Sample	pKa= +4.8	+3.3	+1.5	-3.0	-5.6	-8.2
	Acidity (mmoles/g niobia or alumina)					
Nb/Al(3/1) Pre	3.53	2.17	2.00	1.95	1.61	0.81
Nb/Al(1/1) Pre	5.34	3.23	3.03	2.69	1.83	0.50
Al/Nb(1/3) Pre	10.21	6.50	4.26	4.10	3.08	0.00
Al/Nb(1/1) Pre	8.41	5.16	3.13	3.06	2.13	0.41

(II.) Surface Oxides after Heat Treatment (1000° C):

Sample	pKa= +4.8	+3.3	+1.5	-3.0	-5.6	-8.2
	Acidity (mmoles/g niobia or alumina)					
Nb/Al(3/1) Pre	3.35	1.88	1.65	1.58	1.40	0.43
Nb/Al(1/1) Pre	5.67	3.07	2.58	2.28	1.70	0.03
Al/Nb(1/3) Pre	16.27	8.54	6.88	5.95	5.85	0.93
Al/Nb(1/1) Pre	11.34	5.25	4.35	4.21	2.72	0.45

Figure 5-12 ACIDIC PROPERTIES OF SUPPORTED NIOBIA OR ALUMINA AFTER CALCINATION (500° C)

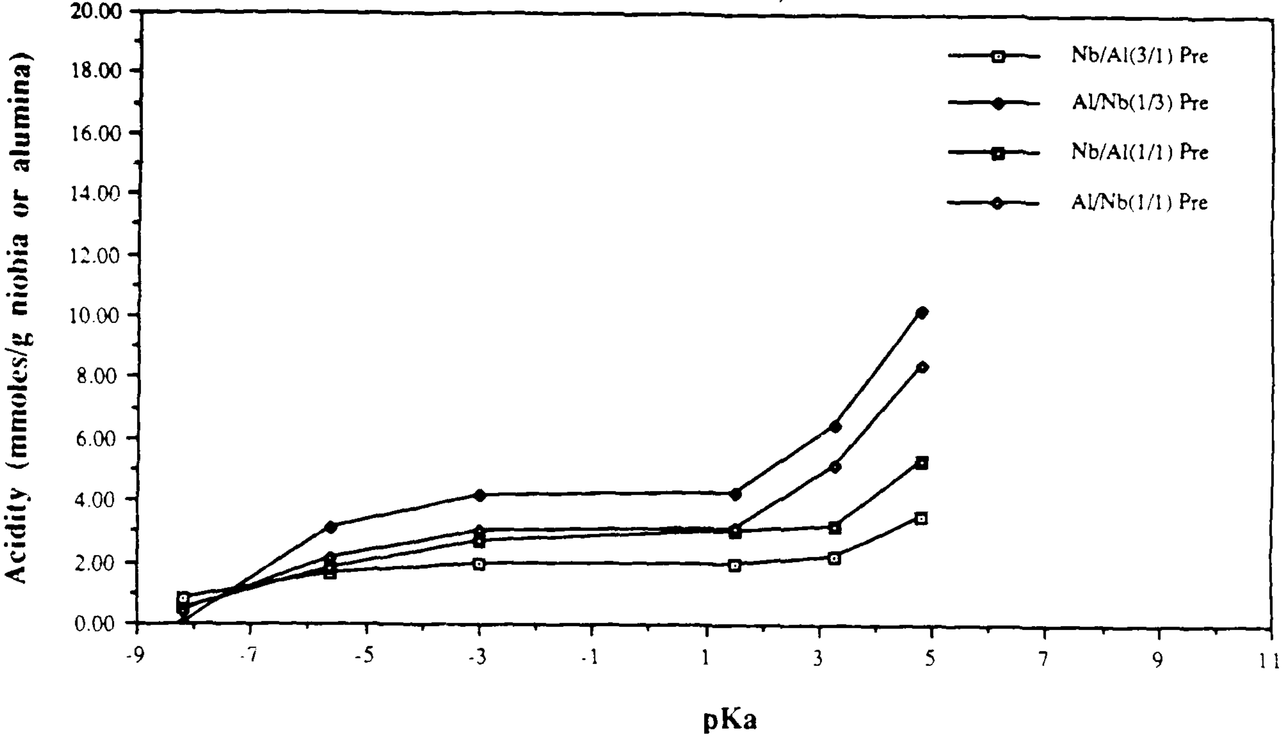


Figure 5-13 ACIDIC PROPERTIES OF SUPPORTED NIOBIA OR ALUMINA AFTER HEAT TREATMENT (1000° C)

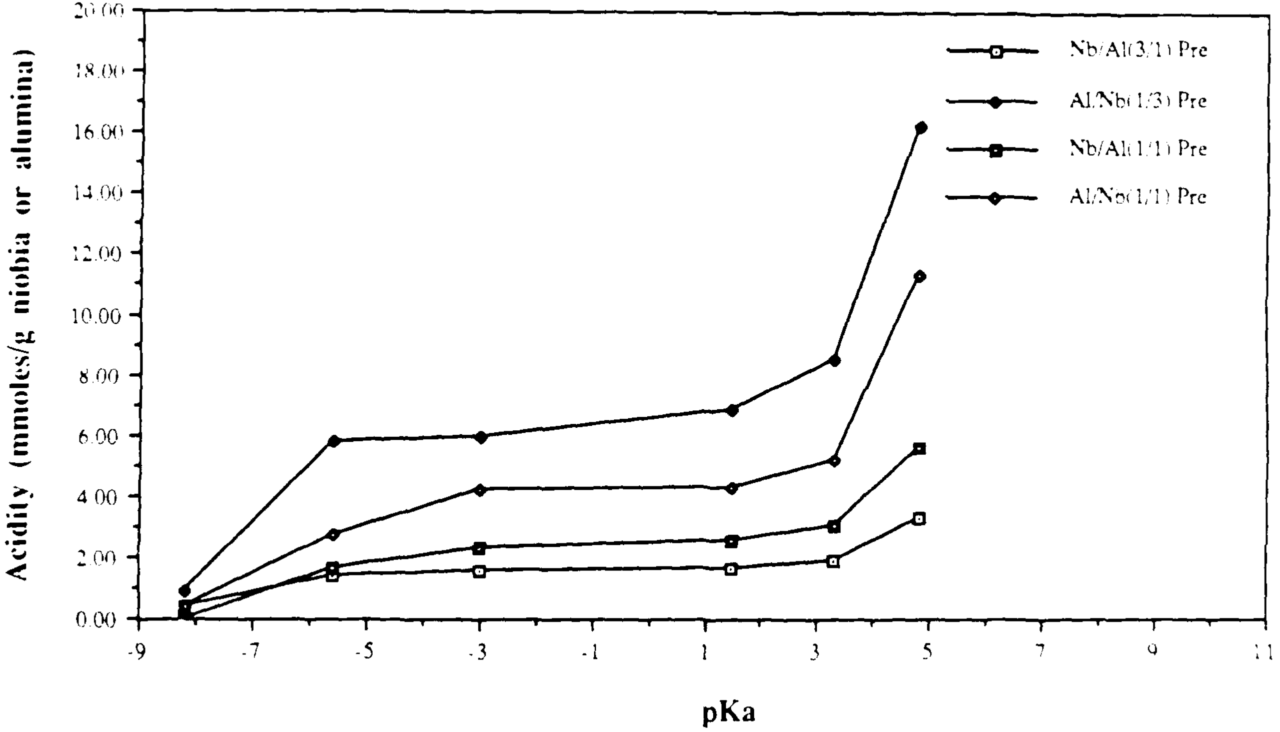


Figure 5-14 COMPOSITION EFFECT ON SUPPORTED NB/AL BINARY OXIDES AFTER CALCINATION (500° C)

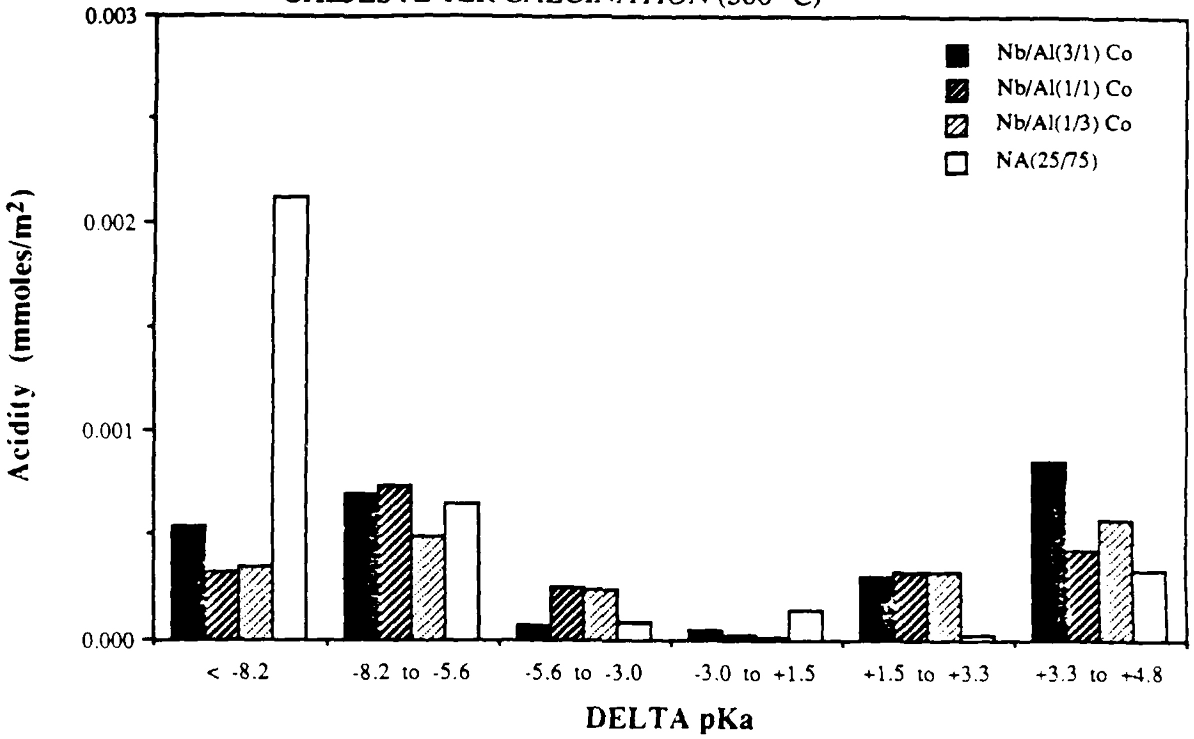
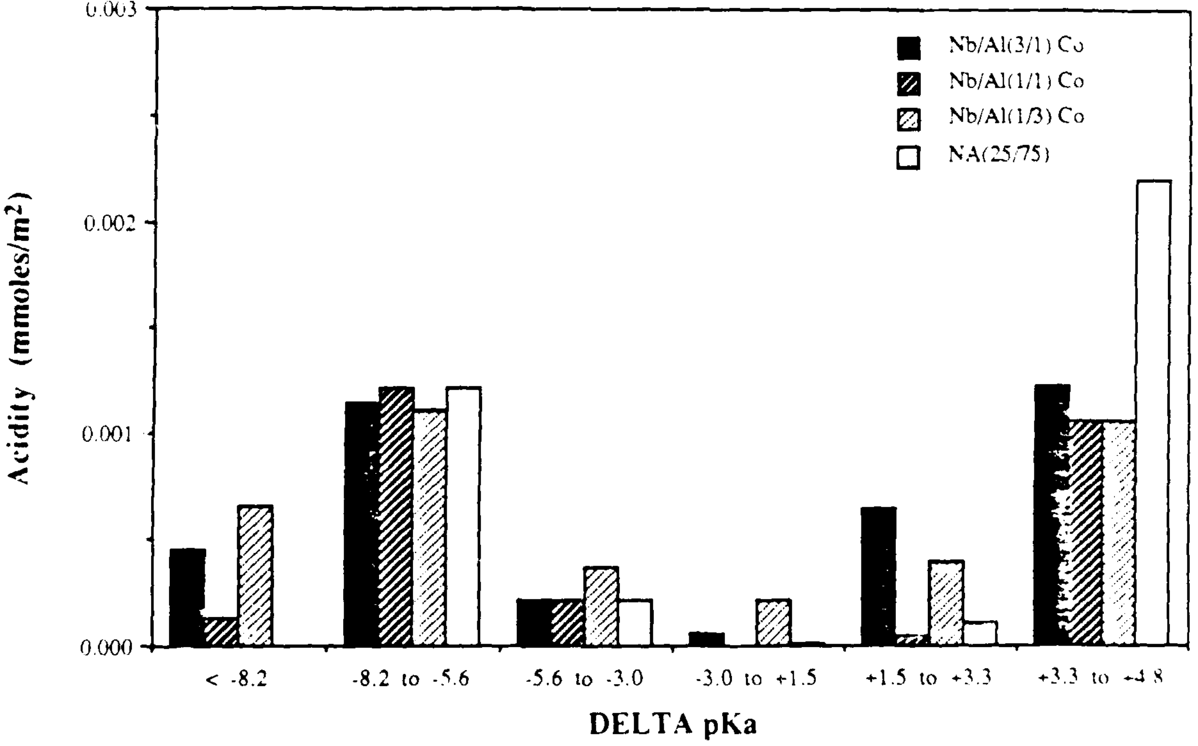


Figure 5-15 COMPOSITION EFFECT ON SUPPORTED NB/AL BINARY OXIDES AFTER HEAT TREATMENT (1000° C)



large differences after calcination that are not within experimental uncertainty. Even after the 1000° C heat treatment there seem to be no real outstanding differences. It is not until one looks closely at the two figures and notices that after calcination the Nb/Al(1/3) Co seems to be on the low side of acidity at every acid strength, and that upon heat treating it seems to be on the high side of acidity at almost every acid strength. This behavior seems to be attributed to alumina since this is the only alumina rich sample in the series, and that this same type of increase was seen on the silica-supported alumina samples as indicated in Figures 4-17 and 4-18.

Included in Figures 5-14 and 5-15 is the NA(25/75) mixed oxide sample. This mixed oxide had primarily very strong acid sites after calcination (500° C), while the surface oxides all seemed to have a wide variety of acid sites. After heat treatment (1000° C) there seems to be a bimodal distribution that is beginning to develop. This is most prevalent in the mixed oxide; however, one can also see it forming among the supported oxides as well. We were unable to determine what types of acid sites (Brönsted or Lewis) these are which are developing, since the n-butylamine titration using Hammett indicators measures the sum of both Brönsted and Lewis acid sites with no distinction between the two.

5.5 Summary

The results of this study indicate that both mixed and supported-surface phase binary oxides of niobia and alumina can be prepared which exhibit strong acidic properties and catalytic activities. The mixed oxides generally exhibited the strongest and largest number number of acid sites and the least amount of stability, while the supported surface oxides showed the greatest catalytic activity for 1-butene isomerization and the greatest amount of surface stability. Crystallization of the mixed oxides played a large role in the properties of these samples. The stabilization of the supported-surface phase oxides gave them desirable properties as compared to the mixed oxides which were shown to sinter quite easily. Thus, this work demonstrated that the effects of preparation can greatly influence the properties of niobia/alumina binary oxides. This study of both the mixed and supported-binary oxides also gave some understanding of the type of interaction that occurs on these oxides.

6. SUMMARY AND RECOMMENDATIONS

6.1 Summary

This study was conducted on a series of chemically mixed and supported-binary oxides of niobia and alumina. More specifically, this research focused on the effects of preparation on the properties of these binary oxides. By studying these two different sets of oxides and using them as acid catalysts, we observed the following results:

Mixed Oxides:

- Homogeneous Nb_2O_5/Al_2O_3 mixed oxides can be prepared over a wide composition range.
- These binary oxides exhibit catalytic behavior and extremely high acid strength and acidity, and are amorphous to calcination (500° C).
- These mixed oxides crystallize to M-niobia and form $AlNbO_4$ compounds upon heat treatment (1000° C).
- The acidic and catalytic properties are functions of both composition and crystallization.

Supported Surface Oxides:

- Stable SiO_2-supported Nb_2O_5/Al_2O_3 surface oxides can be prepared over a large composition range.
- These surface oxides exhibit high acid strength and acidity and have large catalytic activities toward 1-butene isomerization.
- Different preparations, sequential or coimpregnation, have no effect on the physical properties of the surface phase oxides.
- The supported oxides show strong interactions with the substrate with little to no oxide-oxide interaction on the surface.
- Partial monolayer coverages of niobia or alumina over silica affect acidic properties with about 1 acid site generated per surface oxide species added.

6.2 Recommendations

The results in this study have provided some necessary and fundamental groundwork in the field of mixed and supported-binary oxides of niobia and alumina. There are a number of questions that remain to be addressed in this field and I have listed a few recommendations that may help answer some of them. The recommendations for future work are as follows:

- Use Fourier Transform Infrared spectroscopy (FTIR) to identify the various hydroxl groups on the surface of these oxides, and also combine this work with the use of pyridine adsorption studies to help further characterize the distribution of acid sites.

- Use new preparation techniques such as Supercritical Liquid Extraction (SLE) with sol-gels to prepare new high surface area mixed oxides.

- Use Laser Raman Spectroscopy (LRS) to determine if small crystallites of niobia, alumina, or some compound between these oxides are forming on the silica substrate that is beyond the detection limits of X-ray diffraction.

- Use more severe heat treatments to try and induce crystallization of the surface phase oxides and characterize the compounds that crystallize out of these oxides.

The problems which this study addressed are numerous and we have only begun to scratch the surface on the full story of these binary oxides. This investigation provides a fundamental and important step in understanding the effects of preparation on the properties and oxide-oxide interactions in niobia/alumina binary oxides. This study also provides some basic observations which will hopefully spurn further research into this commercially important field.

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APPENDIX A

Mixed Oxides: Stoichiometric Calculations and Loadings (Experimental Values):

MW of$Al(NO_3)_3 \cdot 9H_2O$ = 375.15 g/mole — MW of Al_2O_3 = 101.96 g/mole

MW of $Nb(OC_2H_5)_5$ = 318.22 g/mole — MW of Nb_2O_5 = 265.81 g/mole

1. NA(75/25):

(19.6947 g $Al(NO_3)_3{*}9H_2O$)/(375.15 g/mol) = 0.0525 mol Al

(50.000 g $Nb(OC_2H_5)_5$)/(318.22 g/mol) = 0.1571 mol Nb

(1 mol Al_2/2 mol Al)x(0.0525 mol Al) = (0.0262 mol Al_2)x(101.96 g/mol) = 2.676 g Al_2O_3

(1 mol Nb_2/2 mol Nb)x(0.1571 mol Nb) = (0.0786 mol Nb_2)x(265.81 g/mol) = 20.8826 g Nb_2O_5

wt. % Al_2O_3 = 2.676/(2.676 + 20.8826) x 100 = 11.36 %

wt. % Nb_2O_5 = 20.8826/(2.676 + 20.8826) x 100 = 88.64 %

2. NA(50/50):

(29.4893 g $Al(NO_3)_3{*}9H_2O$)/(375.15 g/mol) = 0.0786 mol Al

(25.000 g $Nb(OC_2H_5)_5$)/(318.22 g/mol) = 0.0786 mol Nb

(1 mol Al_2/2 mol Al)x(0.0786 mol Al) = (0.0393 mol Al_2)x(101.96 g/mol) = 4.007 g Al_2O_3

(1 mol Nb_2/2 mol Nb)x(0.0786 mol Nb) = (0.0393 mol Nb_2)x(265.81 g/mol) = 10.4410 g Nb_2O_5

wt. % Al_2O_3 = 4.007/(4.007 + 10.4410) x 100 = 27.74 %

wt. % Nb_2O_5 = 10.4410/(4.007 + 10.4410) x 100 = 72.26 %

3.NA(25/75):

(88.600 g $Al(NO_3)_3{*}9H_2O$)/(375.15 g/mol) = 0.2362 mol Al

(25.000 g $Nb(OC_2H_5)_5$)/(318.22 g/mol) = 0.0786 mol Nb

(1 mol Al_2/2 mol Al)x(0.2362 mol Al) = (0.1181 mol Al_2)x(101.96 g/mol) = 12.041 g Al_2O_3

(1 mol Nb_2/2 mol Nb)x(0.0786 mol Nb) = (0.0393 mol Nb_2)x(265.81 g/mol) = 10.4410 g Nb_2O_5

wt. % Al_2O_3 = 12.041/(12.041 + 10.4410) x 100 = 53.56 %

wt. % Nb_2O_5 = 10.4410/(12.041 + 10.4410) x 100 = 46.44 %

APPENDIX B

Surface Oxide: Stoichiometric Calculations and Loadings (Experimental Values):

MW of $Al(OC_4H_9)_3$ = 246.33 g/mole   MW of Al_2O_3 = 101.96 g/mole

MW of $Nb(OC_2H_5)_5$ = 318.22 g/mole   MW of Nb_2O_5 = 265.81 g/mole

Surface Area of $NbO_{2.5}$ = 16 x 10^{-20} m^2/unit $NbO_{2.5}$

Surface Area of $AlO_{1.5}$ = 20 x 10^{-20} m^2/unit $AlO_{1.5}$

SAMPLE CALCULATIONS FOR COIMPREGNATED SAMPLES:

1. Nb/Al(3/1) Co:

Basically a 3/1 mixture: $[3x(16x10^{-20}) + 1x(20x10^{-20})]\ m^2 = 68x10^{-20}\ m^2$/unit Nb_3Al

(300 m^2/g SiO_2)/($68x10^{-20}$ m^2/unit Nb_3Al) = $4.41x10^{20}$ unit $Nb_3Al/gSiO_2$

($4.41x10^{20}$ unit $Al/gSiO_2$)/($6.02x10^{23}$ unit Al/mole Al) = $7.33x10^{-4}$ mole $Al/gSiO_2$

($4.41x10^{20}$ unit $Nb_3/gSiO_2$)(3 unit Nb/1 unit Nb_3)/($6.02x10^{23}$ unit Nb/mole Nb) = $2.20x10^{-3}$ mole$Nb/gSiO_2$

($7.33x10^{-4}$ mole $Al/gSiO_2$)(246.33 g/mole $Al(OC_4H_9)_3$) = 0.181 g $Al(OC_4H_9)_3/gSiO_2$

($2.20x10^{-3}$ mole $Nb/gSiO_2$)(318.22 g/mole $Nb(OC_2H_5)_5$) = 0.700 g $Nb(OC_2H_5)_5/gSiO_2$

AMOUNT OF NIOBIA PRECURSOR: 0.700 g $Nb(OC_2H_5)_5$/g SiO_2

AMOUNT OF ALUMINA PRECURSOR: 0.181 g $Al(OC_4H_9)_3$/g SiO_2

% Surface Area Coverages for Nb(3/1) Co:

Nb % Coverage = 3x16/(3x16 + 1x20) = 0.706 or 70.6 %

Al % Coverage = 1x20/(3x16 + 1x20) = 0.294 or 29.4 %

2. Nb/Al(1/1) Co:

(# molecules Al/g SiO_2)($20x10^{-20}$ m^2/unit Al) + (# molecules Nb/g SiO_2)($16x10^{-20}$ m^2/unit Nb) = $300m^2/gSiO_2$

(# molecules $AlO_{1.5}$/g SiO_2) = (# molecules $NbO_{2.5}$/g SiO_2)

(# molecules $AlO_{1.5}$/g SiO_2)($20\text{x}10^{-20}$ m^2/unit Al + $16\text{x}10^{-20}$ m^2/unit Nb) = 300 m^2/g SiO_2

(# molecules $AlO_{1.5}$/g SiO_2)($36\text{x}10^{-20}$ m^2/unit Al) = 300 m^2/g SiO_2

(# molecules $AlO_{1.5}$/g SiO_2) = $8.33\text{x}10^{20}$ molecules/g SiO_2

($8.33\text{x}10^{20}$ molecules/g SiO_2)/($6.02\text{x}10^{23}$ molecules/mole Nb) = $1.38\text{x}10^{-3}$ moles Nb/g SiO_2

($8.33\text{x}10^{20}$ molecules/g SiO_2)/($6.02\text{x}10^{23}$ molecules/mole Al) = $1.38\text{x}10^{-3}$ moles Al/g SiO_2

($1.38\text{x}10^{-3}$ moles Nb/g SiO_2)(318.22 g/mole $Nb(OC_2H_5)_5$) = 0.440 g $Nb(OC_2H_5)_5$/g SiO_2

($1.38\text{x}10^{-3}$ moles Al/g SiO_2)(246.33 g/mole $Al(OC_4H_9)_3$) = 0.341 g $Al(OC_4H_9)_3$/g SiO_2

AMOUNT OF NIOBIA PRECURSOR: 0.440 g $Nb(OC_2H_5)_5$/g SiO_2

AMOUNT OF ALUMINA PRECURSOR: 0.341 g $Al(OC_4H_9)_3$/g SiO_2

% Surface Area Coverages for Nb/Al(1/1) Co:

($8.33\text{x}10^{20}$ molecules Al/g SiO_2)($20\text{x}10^{-20}$ m^2/molecule Al) = 166.67 m^2 Al/g SiO_2

($8.33\text{x}10^{20}$ molecules Nb/g SiO_2)($16\text{x}10^{-20}$ m^2/molecule Nb) = 133.33 m^2 Nb/g SiO_2

Al % Coverage = 166.67/(133.33 + 166.67) = 0.556 or 55.6 %

Nb % Coverage = 133.33/(133.33 + 166.67) = 0.444 or 44.4 %

3. Nb/Al(1/3) Co:

Basically a 1/3 mixture: [1x($16\text{x}10^{-20}$) + 3x($20\text{x}10^{-20}$)]m^2 = $76\text{x}10^{-20}$ m^2/unit $NbAl_3$

(300 m^2/g SiO_2)/($76\text{x}10^{-20}$ m^2/unit $NbAl_3$) = $3.947\text{x}10^{20}$ unit $NbAl_3$/g SiO_2

(3unitsAl/1unitAl_3)($3.947\text{x}10^{20}$unitAl_3/gSiO_2)/($6.02\text{x}10^{23}$unitAl/moleAl) = $1.967\text{x}10^{-3}$moleAl/gSiO_2

($3.947\text{x}10^{20}$ unit Nb/g SiO_2)/($6.02\text{x}10^{23}$ unit Nb/mole Nb) = $6.556\text{x}10^{-4}$ mole Nb/g SiO_2

($1.967\text{x}10^{-3}$ mole Al/g SiO_2)(246.33 g/mole $Al(OC_4H_9)_3$) = 0.4845 g Al/g SiO_2

($6.556\text{x}10^{-4}$ mole Nb/g SiO_2)(318.22 g/mole $Nb(OC_2H_5)_5$) = 0.2086 g Nb/g SiO_2

AMOUNT OF ALUMINA PRECURSOR: 0.4845 g $Al(OC_4H_9)_3$/g SiO_2

AMOUNT OF NIOBIA PRECURSOR: 0.2086 g $Nb(OC_2H_5)_5$/g SiO_2

% Surface Area Coverages for Nb/Al(1/3) Co:

Al % Coverage = 3x20/(1x16 + 3x20) = 0.7895 or 78.95%

Nb % Coverage = 1x16/(1x16 + 3x20) = 0.2105 or 21.05%

SAMPLE CALCULATIONS FOR SEQUENTIAL IMPREGNATIONS (EXPERIMENTAL VALUES):

4. Nb/Al(3/1) Seq:

weight of $Nb(OC_2H_5)_5$ = 7.086 g **(Experimental Value)**

# of moles of Nb = (7.086 g/318.22 g/mole) = 0.0223 moles Nb

(1 Nb_2/2 Nb)(0.0223 moles Nb) = 0.01113 moles Nb_2 units

(0.01113 moles Nb_2O_5)(265.82 g/mole) = 2.9596 g Nb_2O_5

7.086g $Nb(OC_2H_5)_5$/10.00g SiO_2 => 2.9596 g Nb_2O_5/10.00 g SiO_2 = **0.29596g Nb_2O_5/1g SiO_2**

weight % SiO_2 = 1.0/(1.0 + 0.29596) x 100 = 77.16 %

weight % Nb_2O_5 = 0.29596/(1.0 + 0.29596) x 100 = 22.84 %

LOADING OF ALUMINA ON Nb/Al(3/1) Seq:

From Previous Calculation:

Loading: 0.181 g $Al(OC_4H_9)_3$/g SiO_2

For Calcined Sample:

Loading: (0.181g$Al(OC_4H_9)_3$/gSiO_2)(1.0gSiO_2/(1.0 + 0.29596)g tot. wght.) = 0.1397gAl/gTotal

LOADING: 0.1397 g $Al(OC_4H_9)_3$/g Sample(total weight)

5. Nb/Al(1/1) Seq:

weight of $Nb(OC_2H_5)_5$ = 6.626 g **(Experimental Value)**

# of mole of Nb = (6.626g/318.22g/mole) = 0.0208 moles Nb

(1 Nb_2/2 Nb)(0.0208 moles Nb) = 0.0104 moles Nb_2 units

(0.0104 moles Nb_2O_5 units)(265.82 g/mole) = 2.765g Nb_2O_5

6.626g $Nb(OC_2H_5)_5$ /15.0133gSiO_2 => 2.765g Nb_2O_5/15.0133gSiO_2 = **0.1841g Nb_2O_5/1g SiO_2**

weight % SiO_2 = 1.0/(1.0 + 0.184) = 84.45 %

weight % Nb_2O_5 = 0.184/(1.0 + 0.184) = 15.55 %

LOADING OF ALUMINA ON Nb/Al(1/1) Seq:

From Previous Calculation:

Loading: 0.341 g $Al(OC_4H_9)_3$/g SiO_2

For Calcined Sample:

Loading: (0.341 g $Al(OC_4H_9)_3$/g SiO_2)(1.0 g SiO_2/(1.0 + 0.184) g tot. wght.) = 0.2879 g Al/g Total

LOADING: 0.2879 g $Al(OC_4H_9)_3$/g Sample(total weight)

SAMPLE CALCULATIONS FOR SILICA-SUPPORTED NIOBIA OR ALUMINA SAMPLES (EXPERIMENTAL VALUES):

6. Nb/Al(3/1) Pre:

AMOUNT OF NIOBIA PRECURSOR: 0.700g $Nb(OC_2H_5)_5$/gSiO_2

10.0004 g SiO_2

(7.086 g $Nb(OC_2H_5)_5$)/(1 mole/318.22 g) = 0.0223 moles $Nb(OC_2H_5)_5$

7.086 g $Nb(OC_2H_5)_5$/10.0004 g SiO_2 => 2.9596 g Nb_2O_5/10.0004g SiO_2 = 0.2960 g Nb_2O_5/g SiO_2

weight % SiO_2 = 1.0/(1.0 + 0.296) x 100 = 77.16 %

weight % Nb_2O_5 = 0.296/(1.0 + 0.296) x 100 = 22.84 %

7. Nb/Al(1/1) Pre:

AMOUNT OF NIOBIA PRECURSOR: 0.440 g $Nb(OC_2H_5)_5$/g SiO_2

15.0133 g SiO_2

(6.626 g $Nb(OC_2H_5)_5$)/(1 mole/318.22 g) = 0.0208 moles $Nb(OC_2H_5)_5$

6.626 g $Nb(OC_2H_5)_5$/15.0133 g SiO_2 => 2.7646 g Nb_2O_5/15.0133 g SiO_2 = 0.1841 g Nb_2O_5/g SiO_2

weight % SiO_2 = 1.0/(1.0 + 0.184) x 100 = 84.45 %

weight % Nb_2O_5 = 0.184/(1.0 + 0.184) x 100 = 15.55 %

8. Al/Nb(1/3) Pre:

AMOUNT OF ALUMINA PRECURSOR: 0.181g $Al(OC_4H_9)_3$/g SiO_2

11.3271 g SiO_2

(2.0502 g $Al(OC_4H_9)_3$)/(1 mole/246.33 g) = 0.00832 moles $Al(OC_4H_9)_3$

2.0502g $Al(OC_4H_9)_3$/11.3271 g SiO_2 => 0.4242g Al_2O_3/11.3271 g SiO_2 = 0.03745 g Al_2O_3/g SiO_2

weight % SiO_2 = 1.0/(1.0 + 0.03745) x 100 = 96.39 %

weight % Al_2O_3 = 0.03745/(1.0 + 0.03745) x 100 = 3.61 %

9. Al/Nb(1/1) Pre:

AMOUNT OF ALUMINA PRECURSOR: 0.341g $Al(OC_4H_9)_3$/g SiO_2

8.2205 g SiO_2

(2.8032 g $Al(OC_4H_9)_3$)/(1 mole/246.33 g) = 0.01138 moles $Al(OC_4H_9)_3$

2.8032g $Al(OC_4H_9)_3$/8.2205 g SiO_2 => 0.58014g Al_2O_3/8.2205 g SiO_2 = 0.07057 g Al_2O_3/g SiO_2

weight % SiO_2 = 1.0/(1.0 + 0.07057) x 100 = 93.41 %

weight % Al_2O_3 = 0.07057/(1.0 + 0.07057) x 100 = 6.59 %

APPENDIX C

Single Point B.E.T. Surface Area Calculation Program:

```
5   REM " BET.BAS BASIC PROGRAM FOR 1 POINT BET SURFACE CALCULATION "
20  N = 6.023 * 10^23
30  R = 82.1
40  ACS = 16.2 * 10^-20
50  INPUT " CALIBRATION GAS VOLUME (CC): ", VC
55  INPUT " MIXED OXIDE ID ------------: ", ID$
60  INPUT " AMBIENT PRESSURE (mm Hg) --: ", PA
70  INPUT " AMBIENT TEMPERATURE (C) ---: ", TK
80  INPUT " CATALSYT WEIGHT(gm) -------: ", WT
81 INPUT "The number of runs to be calculated: ",RUNS
82 DIM S(RUNS), ST(RUNS), A(RUNS), AC(RUNS)
83 INPUT "the percent of nitrogen : ",PER
90  T = TK + 273.2
100 PO = PA + 15
110 PN2 = PA * PER/100
120 FOR I = 1 TO RUNS
130 PRINT " AREA OF DESORPTION (COUNTS)  run("; I; "): ";
135 INPUT  A(I)
140 PRINT " AREA OF CALIBRATION (COUNTS) run("; I; "): ";
145 INPUT AC(I)
150 ST(I) = (1-PN2/PO) * (A(I)/AC(I)) * VC * (N * ACS * (PA/760) / (R * T))
160 S(I)  = ST(I) / WT
170 NEXT I
175 PRINT " MIXED OXIDE ID : "; ID$
180 PRINT " PRESSURE(mmHg)  TEMPERATURE(C)    CATALYST WEIGHT(gm)"
190 PRINT USING "     ###.##        "; PA;
192 PRINT USING "      ###.#        "; TK;
194 PRINT USING "      #.####       "; WT
195 PRINT
199 GOTO 240
200 PRINT " RUN #     DESORPTION(COUNTS)  CALIBRATION(COUNTS)    M^2      (M^2/G)"
210 FOR J = 1 TO RUNS
220 PRINT USING "    ##     "; J;
222 PRINT USING "             #####      "; A(J);
224 PRINT USING "             #####      "; AC(J);
226 PRINT USING " ###.##  "; ST(J);
226 PRINT USING " ###.##  "; S(J)
230 NEXT J
231 PRINT "average surface area is:"
232 PRINT USING " ###.## "; AVG
233 GOTO 290
239 SUM=0
240 FOR K = 1 TO RUNS
250 SUM = S(K)+SUM
260 NEXT K
270 AVG = SUM/RUNS
280 GOTO 200
290 SYSTEM
```

APPENDIX D

Operating Conditions for GC and Integrator:

(I.) Relative Thermal Response Data and Retention Time[45] :

COMPOUND	RELATIVE RESPONSE/MOLE	RETENTION TIME (min)
1-Butene	81	6.01 ± 0.05
cis-2-Butene	85	9.01 ± 0.08
trans-2-Butene	87	10.29 ± 0.09

(II.) GC Operating Conditions:

He Gas Flow Rates:	
Channel A	: 25.5 ml/min
Channel B	: 80.5 ml/min
Detector Current	: 130 mA
Attenuation	: 1
Detector	: TC
Injector Temperature	: 313 K
Detector Temperature	: 313 K
Oven Temperature	: 313 K
On Line Sampling Time	: 10 sec

(III.) Integrator Settings:

Model: HP 3390A

Analysis Programs:

Normal Detection Program

```
RUN PRMTRS
ZERO   =  10
ATT 2↑ =  0
CHT SP =  1.0
PK WD  =  0.20
THRSH  = -1
AR REJ =  0

RPRT OPTNS
  2. RF UNC PKS=       0.0000E+00
  3. MUL FACTOR=       1.0000E+00
  4. PK HEIGHT MODE        NO
  5. EXTEND RT             NO
  6. RPRT UNC PKS          NO

TIME TBL
   4.00 PK WD  =  0.80
   4.00 ZERO   =  10
   4.00 ATT 2↑ =  3
   6.90 ZERO   =  10
   6.80 ATT 2↑ =  0
  11.00 STOP

CALIB TBL
EMPTY
```

Sensitive Detection Program

```
RUN PRMTRS
ZERO   =  10
ATT 2↑ =  0
CHT SP =  1.0
PK WD  =  0.20
THRSH  = -1
AR REJ =  0

RPRT OPTNS
  2. RF UNC PKS=       0.0000E+00
  3. MUL FACTOR=       1.0000E+00
  4. PK HEIGHT MODE        NO
  5. EXTEND RT             NO
  6  RPRT UNC PKS          NO

TIME TBL
   4.00 PK WD  =  0.80
   4.00 ZERO   =  10
   4.00 ATT 2↑ =  3
   6.80 ZERO   =  10
   6.80 ATT 2↑ = -3
   6.90 THRSH  = -6
   6.80 PK WD  =  0.64
  11.00 STOP

CALIB TBL
EMPTY
```

APPENDIX E

Basic Computer Program for 1-C_4H_8:

```
10  REM "C4H8.BAS" BASIC PROGRAM FOR 1-C4H8 ISOMERIZATION
20  REM INPUT:   CATWT   =  CATALYST WEIGHT (GM)
30  REM          TR      =  REACTION TEMPERATURE(C)
40  REM          CATID   =  CATALYST ID
50  REM          HEFLOW  =  He FLOW RATE (SCCM)
60  REM          C4FLOW  =  1-C4H8 FLOW RATE (SCCM)
70  REM          TIME(I)=  REACTION TIME (MIN) AT POINT I
80  REM OUTPUT: "C4H8.DAT" TIME(I), CONVERSION(I), REACTION RATE(I)
90  REM          MOL% (I), CIS/TRANS RATIO(I)
100 REM OTHERS:  A1(I)   =  AREA OF 1-C4H8 AT POINT I
110 REM          A2(I)   =  AREA OF ISO-C4H8 AT POINT I
120 REM          A3(I)   =  AREA OF CIS-C4H8 AT POINT I
130 REM          A4(I)   =  AREA OF TRANS-C4H8 AT POINT I
140 REM          WTi(I)  =  WEIGHT FRACTION OF i
150 REM          Xi(I)   =  MOLE PERCENT OF i
160 REM          RATIO(I)= CIS/TRANS RATIO AT POINT I
170 REM          I       =  POINTS OF DATA IN REACTION
180 DIM TIME(20), A1(20), A2(20), A3(20), A4(20), WT1(20), WT2(20)
190 DIM WT3(20), WT4(20), X1(20), X2(20), X3(20), X4(20)
200 DIM RATIO(20), CONVR(20), RATE(20), NH3(20), RATEM(20)
210 INPUT " DATE          : ",TODAT$
220 INPUT " CATALYST ID: ",CATID$
230 INPUT " CATALYST WEIGHT(GM)      : ",CATWT
235 INPUT " SURFACE AREA (m**2/g)   : ",SA
240 INPUT " REACTION TEMP(C)         : ",TR
250 INPUT " He FLOW RATE(SCCM)       : ",HEFLOW
260 INPUT " 1-C4H8 FLOW RATE(SCCM) : ",C4FLOW
280 INPUT " WOULD YOU LIKE TO LOAD BATCH DATA (Y/N) ";CH1$
290 IF CH1$ = "n" OR CH1$ = "N" THEN 410
295 INPUT "FILENAME--",AME$
300 OPEN AME$ FOR INPUT AS #1
305 M=4
310 NUM = 1
320 WHILE M > 0
330 INPUT #1, TIME(NUM)
340 INPUT #1, NH3(NUM)
350 INPUT #1, A1(NUM)
355 A2(NUM) = 0
360 INPUT #1, A3(NUM)
370 INPUT #1, A4(NUM)
380 PRINT TIME(NUM); NH3(NUM); A1(NUM) ; A2(NUM); A3(NUM); A4(NUM)
385 NUM = NUM + 1
390 IF EOF(1) THEN M = 0
395 WEND
400 CLOSE #1
402 N = NUM - 1
405 GOTO 525
407 INPUT " DATA POINTS              : ",N
410 FOR I= 1 TO N
420 PRINT
430 PRINT " TIME ON STREAM(MIN)    AT POINT(";I;") = ";
440 INPUT   TIME(I)
450 PRINT " AREA OF 1-C4H8         AT POINT(";I;") = ";
460 INPUT   A1(I)
470 A2(I) = 0
480 PRINT " AREA OF CIS-C4H8       AT POINT(";I;") = ";
490 INPUT A3(I)
500 PRINT " AREA OF TRANS-C4H8     AT POINT(";I;") = ";
510 INPUT A4(I)
520 NEXT I
525 INPUT "OUTPUT FILENAME-- ",AME0$
```

```
[illegible]
540 PRINT #2,"==============================================================="
550 PRINT #2,
560 PRINT #2,"DATE                 : ";T(1-4
565 PRINT #2,"CATALYST NAME      : ";CAT1$
570 PRINT #2,"CATALYST WEIGHT(GM)    :";CATWT
572 PRINT #2,"SURFACE AREA M**2/GM  :";SA
575 PRINT #2,"REACTION TEMP(C)       :";TR
580 PRINT #2,'He FLOW RATE(SCCM)     :";HEFLOW
590 PRINT #2," 1-C4H8 FLOW RATE(SCCM):';C4FLOW
600 PRINT #2,
610 PRINT #2,"        TOS              1-C4 RATE                 MOL%      CIS TRANS

620 PRINT #2,"POINT (MIN) CONVR  MOL/HR/GM MOL/HR/M2 100 CIS-C4 TRANS-C4 RATIO"
630 PRINT #2,"----- ----- -----  --------- ------------ ====== ======== ====="
640 FOR I= 1 TO N
650 WT1(I) = A1(I)/(A1(I)+1.0123*A2(I)+1.0494*A3(I)+1.0741*A4(I))
660 WT2(I) = 1.012*A2(I)/(A1(I)+1.012*A2(I)+1.049*A3(I)+1.074*A4(I))
670 WT3(I) = 1.049*A3(I)/(A1(I)+1.012*A2(I)+1.049*A3(I)+1.074*A4(I))
680 WT4(I) = 1.074*A4(I)/(A1(I)+1.012*A2(I)+1.049*A3(I)+1.074*A4(I))
690 X1(I) = WT1(I)*100
700 X2(I) = WT2(I)*100
710 X3(I) = WT3(I)*100
720 X4(I) = WT4(I)*100
730 RATIO(I) = WT3(I)/WT4(I)
740 CONVR(I) = (WT2(I)+WT3(I)+WT4(I))/(WT1(I)+WT2(I)+WT3(I)+WT4(I))
750 RATE(I) = C4FLOW*60*CONVR(I)/(22400*CATWT)
752 RATEM(I) = RATE(I)*100/SA
755 PRINT #2, USING" ##   ";I;
760 PRINT #2, USING"###.#   ";TIME(I);
770 PRINT #2, USING"#.####";CONVR(I);
780 PRINT #2, USING" ##.###### ";RATE(I);
790 PRINT #2, USING" ##.##.### ";RATEM(I);
800 PRINT #2, USING"   ##.## ";X3(I);
810 PRINT #2, USING"  ##.##";X4(I);
820 PRINT #2, USING"  ##.## ";RATIO(I)
830 NEXT I
840 PRINT #2,
850 PRINT #2,"-----------------------------------------------------------"
860 PRINT #2,"         TOS    NH3                     AREA (COUNTS)"
870 PRINT #2,"POINT (MIN)   (ML)     1-C4     ISO-C4   CIS-C   TRANS-C4 "
880 PRINT #2,"----- -----   ----   ========  ======    =====   ======== "
890 FOR I = 1 TO N
895 PRINT #2, USING" ##    ";I;
900 PRINT #2, USING"###.#    ";TIME(I);
910 PRINT #2, USING" #.## ";NH3(I);
915 PRINT #2, USING"#######   ";A1(I);A2(I);A3(I);A4(I)
920 NEXT I
930 PRINT #2,"=========================================================== "
940 PRINT #2,
950 CLOSE #2
960 INPUT " WOULD YOU LIKE TO MAKE A PLOT FILE (Y/N) ";CH2$
970 IF CH2$ = "n" OR CH2$ = "N" THEN 995
975 INPUT "FILENAME-- ",AME$
976 OPEN AME$ FOR OUTPUT AS #2
980 FOR I= 1 TO N
982 PRINT #2, USING" ###.#  ";TIME(I);
984 PRINT #2, USING" ##.######   ";RATE(I);
985 PRINT #2, USING" ##.######   ";RATEM(I)
990 NEXT I
992 CLOSE #2
995 SYSTEM
```