CHARACTERISATION ACID BASE PROPERTIES AND CATALYTIC ACTIVITY OF MAGNESIA- ALUMINA MIXED OXIDES

Final Report

Submitted to

The University Grants Commission

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Preface

The acidic and basic properties of catalysts are very important for the development of scientific criteria in catalyst application. Simple oxides usually offer poor catalytic activity and selectivity when compared to multi component systems. In most case metal-oxides are to be modified chemically or physically so as to get desired catalytic activity for a particular reaction. The availability of suitable supports for metal catalyts is of fundamental importance in heterogenous catalysis. Due to its good structural and mechanical properties and its low cost г-alumina is one of the most used supports especially in hydrotreating catalysis.

Some of the important reactions, that require metal oxides as catalysts are oxidation, oxidative dehydrogenation, dehydrodimerization and several acid base catalysed reactions.

Good correlation has been found between acid base properties and catalytic activity. No effort has so far been made to correlate the acid base properties and catalytic activity of magnesia- alumina mixed oxides The present project gives emphasis on characterisation, acid-base properties and catalytic activity of alumina and magnesia mixed oxides.

Jalaja J.Malayan

Aknowledgement

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Introduction

The acidic and basic properties of catalysts are very important for the development of scientific criteria in catalyst application. Solid acids and bases are characterized by amount, strength and nature of acid-base centers. In heterogeneous catalysis many close correlations between the catalytic activity including its selectivity and acid–base properties have been indicated (Merguro,K et al,1980),

According to Fuller (Fuller M.J etal,1975) the correlation between catalytic activity and acid base properties of metal oxides can be explained by the strength of acid base interactions between reacting molecule and catalyst surface. The generation of new acid sites on mixing two oxides was proposed by Thomas and co workers (Thomas C.I etal, 1949). They seems that generation of new sites is associated with the charge inbalance at locally formed M_1-O-M_2 bonding where M_1 is the host metal ion and M_2 is the doped or mixed metal ion.

Some of the important reactions require metal oxides as catalysts are oxidation, oxidative dehydrogenation, dehydrodimerization and several acid base catalysed reactions.

Acid base properties of metal oxides

The acid sites and base sites coexist in adjacent positions on the surface of acid catalyst, participating together in most of the reactions. Quantitative information on the base strength distribution of solid base surfaces are essential for the studies of solid base catalysis. The acid base properties of solid bases such as MgO and CaO are determined from the adsorption power of phenol vapour (Naccashe C etal, 1966).

Malinowski and Sczepanska (1963) measured the amount of Bronsted acidity by potentiometric titration of solid acid in anhydrous picoline with 0.1 N solution of sodium methoxide. Leftin and Hall (1962) reported that the amount of Lewis acid site can be determined from the amount of triphenyl carbonium ion formed when the solid acid abstract a hydride ion from triphenyl methane. (Leftin,H.P et al,1962).

The number of Bronsted sites on a solid surface may be derived from the number of free protons in aqueous solution arising from the exchange of protons or hydrogen atom (Basila,M.R. et al, 1955).

Catalytic activity of alumina in a range of reactions such as isomerisation of hydrocarbons and polymerisation of olefins have all been attributed to the acidic properties of the surface (Peri J.B ,1967). Mizuno, et al carried out olefin polymerization over silica–alumina and found that strong Lewis acid sites are active in this reaction.(Mizuno,K et al, 1976). Binary metal oxides such as SiO_2 - Al_2O_3 , SiO_2 - MgO , SiO_2 - ZrO_2 and Al_2O_3 - B_2O_3 have been used as solid base catalysts , since their surface acidities are well known (Tanabe,K 1971).

-Al_2O_3 , $SiO_2 - MgO$, $SiO_2 - ZrO_2$ and Al_2O_3 - B_2O_3 have been used as solid base catalysts , since their surface acidities are well known (Tanabe,K 1971).

Acid base strength of solid metal oxygen compounds such as metal oxides, sulphates, hydroxides and carbonates were measured on a common H_0 scale. The strongest H_0 value of acid sites was found to be approximately equal to the strongest H_0 value of basic sites. The equally strongest H_0 value was termed $H_{0,max}$. Hence solid of high $H_{0,max}$ value posses strong basic sites and a solid of low $H_{0,max}$ value should have strong acid sites and weak basic sites (Yamanaka T etal,1976).

When ammonia chemisorbed on surface possessing acid properties, ammonia can interact with the acid protons, electron acceptor sites and hydrogen from weakly or neutral hydroxyls and thus can detect most of the different types of acid sites (Kijenski T etal, 1989). An ammonia molecule can retained on the surface of oxides in different modes,

a) Hydrogen bonding, it is weakest mode of interaction.
b) Transfer of proton from surface hydroxyl to adsorbate.
c) Co ordination to an electron deficient metal atom.

Thus a fairly reliable interpretation of the TPD pattern of NH_3 from solid acids can be attributed to ammonia chemisorbed on weak, medium and strong sites respectively (Kung M.C etal, 1985).

Correlation between catalytic and acid base properties of metal oxides

Simple oxides usually offer poor catalytic activity and selectivity when compared to multi component systems. T. Yamanaka and K. Tanabe determined the basicity of a series of oxides and found that basicity at base strength ($H_0 \geq 1.5$) has the order $ZnO > TiO_2 > BaO >$ activated $Al_2O_3 > ZrO_2 > MgSO_4 > MoO_3$ (Yamanaka. T etal, 1975). Catalyst deactivation studies by aldol condensation was carried out on alumina magnesia mixed oxides (Diez V.K etal, 2003).

The availability of suitable supports for metal catalysis is of fundamental importance in heterogenous catalysis. Due to its good structural and mechanical properties and its low cost r-alumina is one of the most used supports especially in hydrotreating catalysis (Topsee H etal, 1996). The chemical interaction between alumina and supported phases may contribute to the catalyst stability against sintering process. Amorphous silica with its high purity and high surface area is also used as support (Vyatiz R etal, 1993). However it generally leads to lower activity catalysts and since it interacts less with the active species , allows detailed studies of catalyst characterization (Breysse M etal, 1991).

Most of the acid-base catalysts used in various chemical transformations are based on inorganic oxides . In most case metal oxides are to be modified chemically or physically so as to get desired catalytic activity for a particular reaction. Metal oxides, because of their ability to take part in the exchange of electrons, protons or oxide ions are used as catalysts in both redox and acid-base catalysis (J.Haber, 1992). In metal oxides coordinative unsaturation is principally responsible for the ability towards adsorption and catalysis of various reactions. The exposed cations and anions of the metal oxide surface form acidic and basic

sites as well as acid-base pairs. Besides this the variable valency of the cations results in the ability of oxides to undergo oxidations and reductions.

The effect of metal oxides on the thermal decomposition of Barium nitrate was reported (Babu,I,M et al,2003). Perovskite type mixed oxides were good in esterification, oxidation and reduction reactions (Sugunan,S et al, 1997). Mixed oxides of cerium and aluminium were found to be effective catalysts for oxidation-reduction reactions.(Sugunan,S et al,1995). Solid acid catalysis is one of the most important areas of research and assumes great relevance as an economic alternative to the many homogeneously catalysed industrially important reactions.

Oppenauer oxidation named after Rupert Victor Oppenauer is a gentle method (Oppenauer,1937) for oxidizing alcohols to ketones. The three common catalysts in the Oppenauer oxidation are aluminium t-butoxide, isopropoxide and phenoxide. In the modified Oppenauer oxidation by Schinz and Lauehesuer (Schinz etal , 1949) benzopheone was found to be satisfactory oxidizing agent. Since it cannot undergo condensation in the presence of a strongly basic catalyst.

According to Oppenauer a solvent is necessary for the oxidation of alcohols. Toluene is employed occasionally. Time and temperature can be varied over a wide range depending upon the alcohol to be oxidized although the choice of solvent and hydrogen acceptor naturally controls the maximum temperature that can be reached. This method has several disadvantages such as need for tedious purification and unreusability of the catalyst. Heterogenous

Esterification is usually carried out using a homogenous hydrogen ion catalyst. This method has a disadvantage of isolation of products. Recently solid superacid catalysts have been employed for esterification (Sugunan S etal, 1997)

Kuno etal (1991) have shown that liquid phase oxidation of primary and secondary alcohols proceeds effectively using benzophenone as the hydrogen acceptor. Heterogeneous catalysis has several advantages in the isolation of products and require a high reaction temperature .

GC/MS Analysis

Gas chromatography-mass spectroscopy (GC/MS) is one of the so called hyphenated analytical techniques. It is actually two techniques that. are combined to form a single method of analyzing mixtures of chemicals. Gas chromatography separated the components of mixture and mass spectroscopy characterizes each of the components individually. They are used extensively in the medical, pharmacological, environmental, and law enforcement fields. To effectively use GC/MS evidence , one must understand the process. First, the GC process will be considered, and then the MS instrument will be presented. After a background in GC and MS is obtained, the reader learn how to analyze the evidence produced by these instruments (Frederic Douglas p 1-9).

Experimental

Mixed oxides of different composition (3% MgO-Al$_2$O$_3$), 9% MgO/ Al2O3, 15% MgO/ Al$_2$O$_3$ and 20% MgO/Al$_2$O$_3$) were prepared by co-precipitation from their nitrate solution.

Co-Precipitation Method

Aqueous ammonia (5%) solution was added to an aqueous solution containing required amount of magnesium nitrate and aluminium nitrate until the precipitation (Arai T etal, 1989) was complete. The precipitate was washed with distilled water, filtered and dried overnight at 110°C , then powdered and sieved to prepare sample of 100-200 mesh.

These samples were calcinated at 500°C for 4hrs in a muffle furnace. Reference samples of pure MgO and Al$_2$O$_3$ were prepared by hydroxide method (Snell F.D etal , 1973).

Table 1

Experimental conditions used in the preparation of Alumina Magnesia mixed oxides

Sample designation	mmol of MgO/g of Al_2O_3
3% MgO/Al_2O_3	.795
9% MgO/Al_2O_3	2.387
15% MgO/Al_2O_3	3.975
20% MgO/Al_2O_3	5.299

Preparation of 3% MgO/Al_2O_3

Molecular weight of aluminium nitrate nona hydrate = 375.13

Molecular weight of Magnesium nitrate hexa hydrate = 256.41

Weight of Mg $(NO_3)_2$. 6 H_2O = 1.964 g

Weight of Al $(NO_3)_2$. $9H_2O$ = 73.36 g

1.964 g Mg $(NO_3)_2$.$6H_2O$ =0.3126 MgO.

73.36 g Al$(NO_3)_2$. 9 H_2O =10 g Al_2O_3

Weight % of MgO $= \dfrac{.3126 \times 100}{10+0.3126}$

=3.03 %.

Weight of MgO/ g of Al_2O_3 = 0.03126

Number of m mol of MgO = $\dfrac{0.03126 \times 1000}{40.40}$

= 0.795

Mixed oxides were characterized using FTIR. FTIR spectra (Appendix I) were measured by KBr disc method; over range 4000-400cm^{-1} using Shimadzu DR 5001 instrument.

XRD patterns were recorded in a Rigaku D-maxCx-ray diffractometer using Nickel filtered Cu-Kα radiation (Appendix II).

Surface area of the samples were achieved in a Micromeritics Gemini surface area analyzer by the low temperature N_2 adsorption method (Appendix III). The values in m^2 g^{-1} were as follows, activation temperature is given in brackets : MgO (500^{0}C) 72.74, 3% MgO/Al_2O_3 (500^{0}C) 231.29, 9% MgO/Al_2O_3(500^{0}C) 200.53, 15% MgO/Al_2O_3 (500^{0}C) 241.89, 20% MgO/Al_2O_3 (500^{0}C) 234.21, Al_2O_3 (500^{0}C) 193.91.

Acid base strength measurement using Hammett Indicator

Acidity and basicity of oxides were determined by titration method using Hammett Indicators, the pk_a values are given in parenthesis, crystal violet(0.8), dimethyl yellow (3.3),methyl red (4.8), neutral red (6.8), bromothymol blue (7.2) and 4-nitro aniline(18.4). Of these only dimethyl yellow, methyl red, neutral red and bromothymol blue responded to acidity/basicity of these oxides (Yamanaka

.T etal, 1975). A .1% solution of indicator in purified benzene (Vogel A.I, 1973) was used. The basicity was determined by titration with trichloroacetic acid and acidity with n-butyl amine. The end point of the titration was taken when the colour change was observed on the white solid (Tanabe K,1971).

The $H_{0,max}$ values of these oxides were det6ermined from the acid-base strength distribution curves (Fig:I). The acid base strength distribution curves intersect at a point on the abscissa where acidity=basicity=0.

Acid strength measurement using Temperature Programmed Desorption of Ammonia

The strength of acid sites of mixed oxide was determined by TPD of ammonia. The catalysts were pretreated in the TPD apparatus under a dynamic vaccum at 10°C /min up to 350°C for 4 hrs. The samples were then cooled and exposed to ammonia at a high pressure for 30 minutes. After this the catalysts were outgassed for 30 minutes at 100°C to remove physisorbed ammonia.
Finally the samples were cooled to 25°C and TPD of ammonia was carried under dynamic vaccum (Di Cosimo J.I etal 1998). The desorbed ammonia is passed into H_2SO_4 and titrated againt NaOH.
Desorption (°C)

100-200   weak acid sites
200-400   medium acid sites
400-600   strong acid sites

Studies on Catalytic activity of mixed oxides

Esterification

The esterification reaction was carried out in a 50ml round bottomed flask equipped with a reflux condenser in which the catalyst (0.5 g), acetic acid (2 mmol), n-butanol (32 mmol) and n-decane (.05 mmol) used as internal standard were placed. The reaction temperature was maintained at 98° C and stirred using magnetic stirrer for 5hrs. The product was analysed by means of GCMS by comparison of mass spectrum with that of the standard sample,

Reagents used for acidity/basicity measurement

Purification of acetic acid

LR Grade reagent obtained from Merck was purified by adding some acetic anhydride to react with the water present. It was then heated for 1 hr just below boiling in the presence of 2g CrO_3 per 100 ml and then fractionally distilled. The fraction at 116°C –118°C was collected (Perrin D.D, 1983)

Purification of n-butanol

LR Grade reagent obtained from Merck was further purified by drying with anhydrous K_2CO_3 and fractionally distilled. The fraction boiling at 116.5 °C was collected (A.I Vogel, 1973, p-886).

Oxidation of Cyclohexanol to Cyclohexanone

In a round bottomed flask (100cc) equipped with a reflex condenser were placed catalyst (0.5g) , 10cm^3 of a toluene solution of cyclohexanol (0.25 mmol) benzophenone (14.6 m mol) and n-decane (.05 mmol) as an internal standard (Sugunan S etal 1995). The contents were heated and stirred using a magnetic stirrer under gentle reflex for 2hrs at 110°c.

Reagents used for activity measurement

Cyclohexanol

Cyclohexanol obtained from Merck was refluxed with freshly ignited CaO and then fractionally distilled. The fraction boiling at 161.1°c was collected (A.I Vogel, 1973, p-185.

Toluene

SQ grade toluene obtained from Qualigens Fine chemicals was shaken twice with cold concentrated H_2SO_4 (100 ml of acid for 1 liter of toluene), then with water, aqueous 5% $NaHCO_3$ and again with water. Then it was dried with $CaSO_4$, distilled and fraction distilling at 110°c was collected (ibid, p-487)

n-Decane

LR grade reagent purified by shaking with conc. H_2SO_4 . It was washed with H_2O and aq. $NaHCO_3$. Finally it was washed with more water, then it was dried with $MgSO_4$, refluxed with sodium and distilled . The fraction distilling at 174° C was collected (ibid , p-190)

Benzophenone was supplied by Sisco Laboratoratories Pvt .Ltd.

The product analysis was carried out using GC/MS.

Results and Discussion

The oxide surface generally terminate with surface hydroxyl groups which are quite polar and give strong IR bands in the region 4000-3000 cm^{-1}. The IR band in the 1400-1300 cm^{-1} region in the supported oxides is assigned to Mg-O stretching vibrations. The IR band in the regio 1100-1000 cm^{-1} in the mixed oxides is assigned to Al-O stretching vibrations. The generation of new sites on mixing two oxides is associated with the charge inbalance at the locally formed M_1-O-M_2 bonding, where M_1 is the host metal ion and M_2 is the mixed metal ion (Thomas C.I etal, 1949) . From the increase in stretching frequencies we could assume that as the weight % increases MgO species are highly dispersed (Al-O-Mg) on the Al_2O_3 surface. IR spectral data are attatched in APPENDIX I

In the X- ray diffraction pattern (Appendix II) different `d` values are shown for pure mixed oxides. Difference in the `d` values indicates the formation of mixed oxides. The signal intensity of Al_2O_3 decreases due to incorporation of MgO.

Acidity measured with an indicator shows the number of acidic sites whose acid strength $H_0 \le pk_a$ of the indicator and the basicity shows the number of basic sites whose base strength $H_0 \ge pk_a$ of the indicator. Acidity and basicity of MgO/AL_2O_3 are given in Table II. Magnesia treated alumina shows a basic character intermediate between MgO and Al_2O_3. Pure MgO exhibits the highest strength basic sites which consists predominantly of O^{2-} anions. Magnesia

alumina mixed oxides possess three different types of basic sites , isolated O^{2-} ions, O^{2-} on metal oxygen pairs and OH groups (Dicosimo J.I etal , 1998).

From $H_{0,max}$ values we could confirm that magnesia alumina mixed oxides are less basic than MgO and more basic than Al_2O_3. $H_{0,max}$ can be
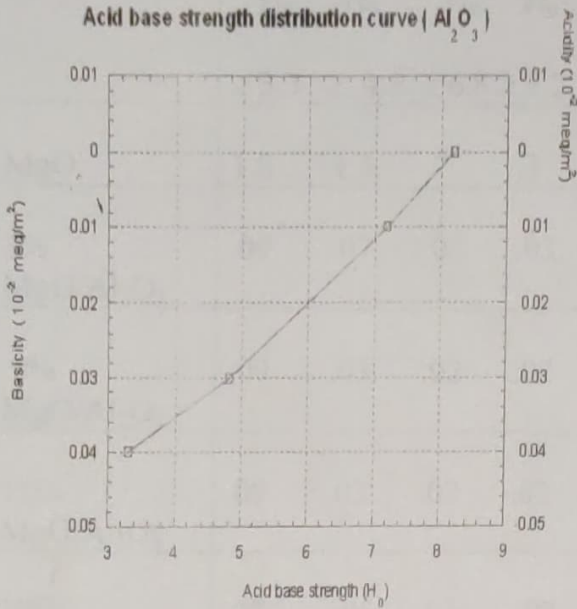

Fig. I

regarded as a practical parameter to represent acid base properties of solids which is sensitive to surface structure. It is known that a solid with a large positive $H_{0,max}$ has strong basic sites and that with a large negative value has weak basic sites (Yamanaka.T etal,1976)

Table II

Catalysts	Basicity (10^{-2} meq/m^2)				Acidity (10^{-2} meq/m^2)				
	H_0	H_0	H_0	H_0	H_0	H_0	H_0	H_0	$H_{0,max}$
	≥ 3.3	≥ 4.8	≥ 6.8	≥ 7.2	≤ 3.3	≤ 4.8	≤ 6.8	≤ 7.2	
MgO	1.8	1.5	.7	.3	0	0	0	0	10.2
3% MgO/Al$_2$O$_3$	.09	.07	.03	.03	0	0	0	0	9.1
9% MgO/Al$_2$O$_3$	.09	.03	.02	.02	0	0	0	0	8.5
15% MgO/Al$_2$O$_3$	.09	.03	.02	.02	0	0	0	0	8.3
20% MgO/Al$_2$O$_3$	.08	.05	.03	.03	0	0	0	0	9.5
' Al$_2$O$_3$	.04	.03	.01	.01	0	0	0	0	8.2

In the esterification reaction the product formed according to the following reaction

$$CH_3COOH + C_4H_9OH \rightarrow CH_3COOC_4H_9 \text{ (n-butyl acetate)}$$
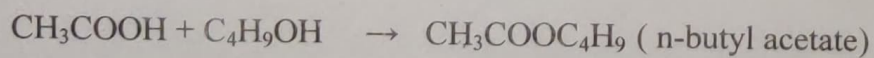
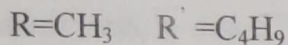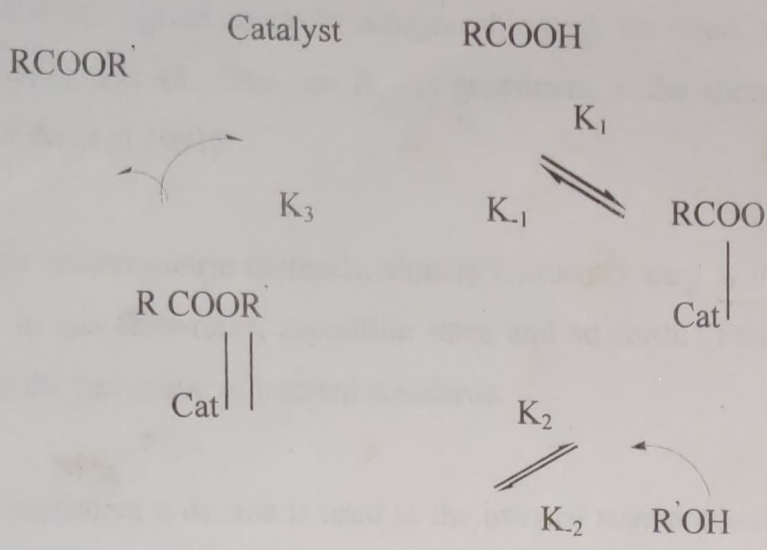The results obtained from GCMS are shown in Table III

Table III

| Samples	Formation of n-butyl acetate % conversion
Al_2O_3	75
3% MgO /Al_2O_3	68
9% MgO /Al_2O_3	55
15% MgO /Al_2O_3	53
20% MgO /Al_2O_3	39
MgO	37

The GCMS data of n-butyl acetate and the samples are attached in Appendix IV.

A mechanism has been proposed for the esterification reaction. The rate determining step is the step subsequent to the adsorption of carboxylic acid and alcohol on the catalyst.(Peter Sykes ,1982)

$$\text{RCOOR'} \xrightarrow[K_3]{\text{Catalyst}} \text{RCOOH} \rightleftharpoons[K_{-1}]{K_1} \text{RCOO}$$

Catalyst   RCOOH

RCOOR'

K_1

K_3 K_{-1} RCOO

R'COOR'   Cat

Cat K_2

                          K_{-2} R'OH

$R = CH_3$ $R' = C_4H_9$

The H^+ ions on the surface layer of catalyst will catalyse the reaction. In the mass spectrum X-axis represents the m/z ratios. The Y-axis represents signal intensity for each of the fragments detected during the scan. From the mass spectral data, peaks at m/e 43, 56 and 61 are obtained which are characteristic of n-butyl acetate.

In esters four ions can result from bond cleavage next to $C = O$.

$$[\text{RCOOR'}]^{.+} \longrightarrow R^+ + [\text{RCOO}]^+$$

$$[\text{RCOOR'}]^{.+} \longrightarrow R\text{-}CO^+ + [OR']^+$$
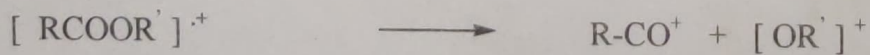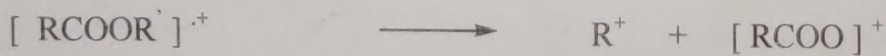
The ion $R-C=O^+$ gives an easily recognizable peak for esters .the base peak for an ester is at m/z 43. The ion R^+ is prominent in the short chain esters (Silverstein R.M et al 1991)

In atomic spectrometric methods, signals frequently vary with time due to fluctuations in gas flow-rates, aspiration rates and so forth. Precision can be improved by the technique of internal standards.

In our experiment n-decane is used as the internal standard and gives a peak at m/e 57. Since the largest peak in the mass spectrum corresponds to the most abundant peak at m/z 57, it is taken as the base peak. Its intensity is arbitrarily given the value of 100 and all other values are represented as percentages of base peak.

The catalytic activity depends on the acid-base properties of catalysts. A qualitative measure of acid site strength was obtained by trmperature programmed desorption of ammonia. The results are shown in Table IV.

Table IV

Ammonia adsorbed mmol / g

Sample	Weak acid sites	Medium acid sites	Strong acid sites	Total acid strength mmol/g
Al_2O_3	0.28	0.40 ✓	0.33	1.01
3% MgO /Al_2O_3	0.25 ✓	0.23	0.19	0.67
9% MgO /Al_2O_3	0.20 ✓	0.14	0.19	0.53
15% MgO /Al_2O_3	0.12	0.23	0.12	0.47
20% MgO /Al_2O_3	0.16	0.14	0.16	0.46
MgO	0.34	0.05	0.04	0.43

Result a dis'ca

A fairly reliable interpretation of the TPD pattern of ammonia from solid acids can be attributed to ammonia chemisorbed on weak, medium and strong sites respectively. It was found that Mg-Al mixed oxides and pure oxides contain both Bronsted OH groups and Lewis acid sites. The acid site density increases with increasing alumina content .Because of the presence of isolated O^{2-} basic centers pure MgO exhibited poor acidity .(Di Cosimo et al 1998) and low activity. The number of Bronsted sites on a solid surface may be derived from the number of free protons in aqueous solution arising from the exchange of proton or hydrogen atom.
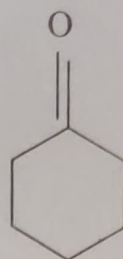
Catalytic activity of the following samples (MgO , 3% MgO/ Al_2O_3, 9% MgO/Al_2O_3 20% MgO/Al_2O_3 and Al_2O_3) towards Oppenauer oxidation of cyclohexanol to cyclohexanone in presence of benzophenone. and toluene.
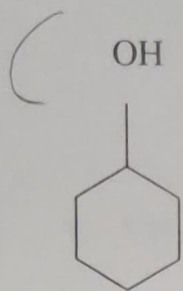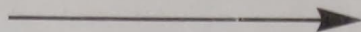
| Cyclohexanol | Benzophenone,Toluene | Cyclohexanone |

Benzophenone - $C_6H_5COC_6H_5$

Toluene   - $C_6H_5CH_3$

When a ketone in the presence of a base is used as the oxidizing agent, the reaction is known as Oppenauer oxidation .this reaction is the reverse of Meerwein Pondorf Verley type reduction of ketones. The catalytic activity of the oxides can be rationalized in terms of the mechanism proposed by Shibagaki etal (Shibagaki K etal, 1988) for oxidation using ZrO_2 as the catalyst.

drawing

It has already been established from primary kinetic isotope effect studies that K_3 is the rate determining step . The mechanism involve hydride transfer from alcohol to carbonyl carbon of the ketone. The ketone (benzophenone) has high ability for oxidizing the alcohol to ketone and to resist aldol condansation. Lewis basicity of the catalyst surface favours the hydride transfer.

25
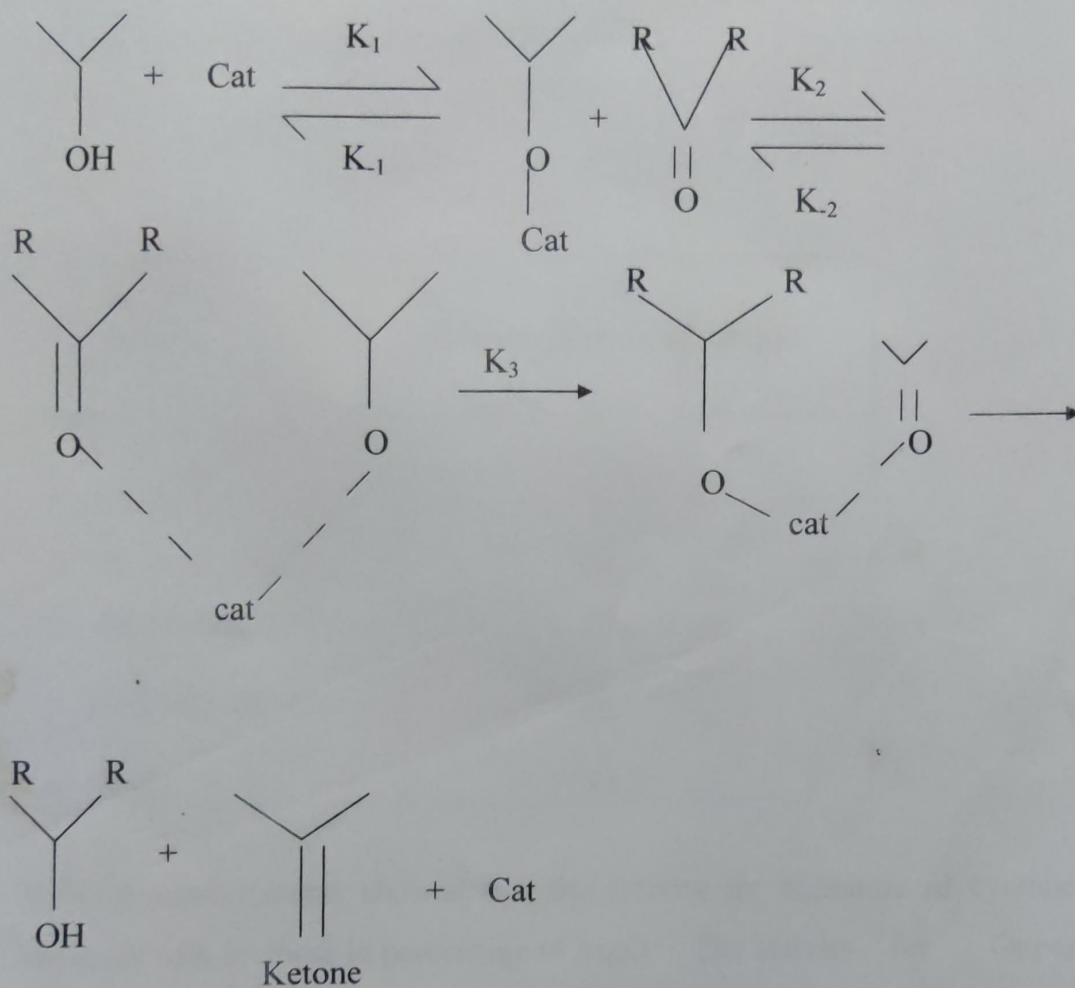
Reduction of benzophenone is the slowest process because of the lower electron density at the carbonyl carbon of the benzophenone.
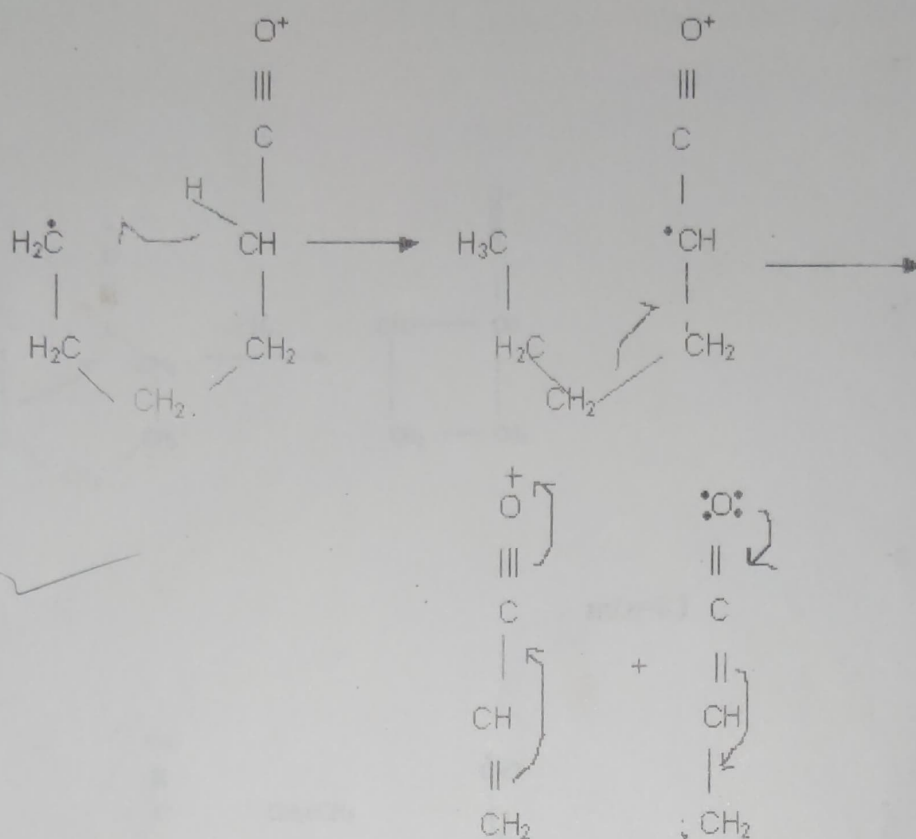
Dehydration of catalytic surface resuls in the formation of Lewis acid and basic sites. Two or more oxides ions occupy immediately adjoining surface sites and a potential electron doner site is created. At lower activation temperature,

unsolvated hydroxyl ions are responsible for the electron transfer (Flockhart B. etal,1969)   The results obtained from GC/MS are shown in Table V. The mass spectral data are attached in Appendix V
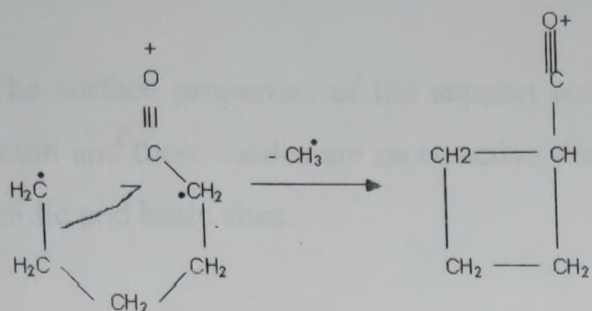
Table V

Sample	% Conversion /g of sample
I Al_2O_3	14
Ii 3% MgO / Al_2O_3	22
iii 9% MgO/Al_2O_3	28
v 20% MgO/Al_2O_3	38
vi MgO	93

Activity measurements showed that the activity for oxidation of cyclohexanol increases with increase in percentage of MgO.   The activity   for   Oppenauer oxidation of cyclohexanol increases in the fallowing order. MgO $>$ 20% MgO/Al_2O_3 $>$ 9% MgO/ Al_2O_3 $>$ 3% MgO/ Al_2O_3 $>$ Al_2O_3 . The mass spectral data has shown the peaks at m/z values 55,83 and 42 which are characteristic of cyclohexanone (Silver Stein R,M etal 1991 p-24)

$$
\begin{array}{ccc}
O^+ & & O^+ \\
||| & & ||| \\
C & & C \\
\end{array}
$$

H₂Ċ ⟶ CH ⟶ H₃C   •CH ⟶

H₂C   CH₂   H₂C   CH₂

CH₂   CH₂

(reaction scheme)

$$\overset{+}{O} \quad \quad :O:$$

C $\quad$ + $\quad$ C

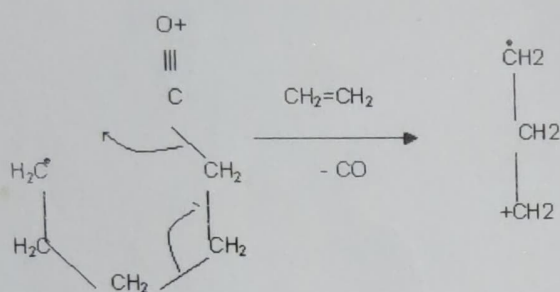CH $\quad\quad$ CH

CH₂ $\quad\quad$ CH₂

M/Z=55

As in the case of aliphatic ketones, the primary cleavage of cyclic ketones is adjacent to the C=O group, but the ion thus formed must undergo further cleavage to produce a fragment. The base peak in the spectrum of cyclohexanone is at m/z 55.   Here occurs a hydrogen shift to convert a primary radical to a conjugated secondary radical followed by formation of resonance stabilized ion having m/z 55 The other distinctive peaks are at m/z 83 and 42 in the spectrum of cyclohexanone

$$
\begin{array}{c}
\overset{+}{O} \\
\parallel \\
C \\
H_2\overset{\bullet}{C} \diagup \quad \diagdown \overset{\bullet}{C}H_2 \\
H_2C \qquad\qquad CH_2 \\
\diagdown CH_2 \diagup
\end{array}
\quad \xrightarrow{-\ \overset{\bullet}{C}H_3} \quad
\begin{array}{c}
\overset{O+}{\underset{\displaystyle\parallel\parallel}{C}} \\
\;| \\
CH2 \!\!-\!\!-\!\! CH \\
| \qquad\quad | \\
CH_2 \!-\! CH_2
\end{array}
$$

m/z=83

$$
\begin{array}{c}
\overset{O+}{\underset{\displaystyle\parallel\parallel}{C}} \\
\diagup\;\diagdown \\
H_2\overset{\bullet}{C} \qquad CH_2 \\
| \qquad\qquad | \\
H_2C \diagdown \quad \diagup CH_2 \\
CH_2
\end{array}
\quad
\begin{array}{c}
CH_2{=}CH_2 \\
\xrightarrow{\hspace{1.5cm}} \\
-\ CO
\end{array}
\quad
\begin{array}{c}
\overset{\bullet}{C}H2 \\
| \\
CH2 \\
| \\
+\overset{\bullet}{C}H2
\end{array}
$$

m/z=42

On pure MgO strong basic sites consists predominantly of O^{2-} anions. Lewis atidity predominates on Al_2O_3 surface. Incorporation of MgO in to the lattice of Al_2O_3 introduces moderate acidity neutralizing the strong acid sites of alumina. The basicity of the oxides increases in the following order MgO $>$MgO/$Al_2O_3>Al_2O_3$. Hence we have found that as the weight percentage of MgO increases catalytic activity towards Oppenauer oxidation is also increased.

The acidity of the oxides is found to decrease , as the weight percentage of alumina is increased.   Here the catalytic acivity parallel the acid base properties of the oxides.

The surface properties of the support considerably improve upon magnesia addition and these oxides are more active than Al_2O_3 due to proper combination of acidic and basic sites.

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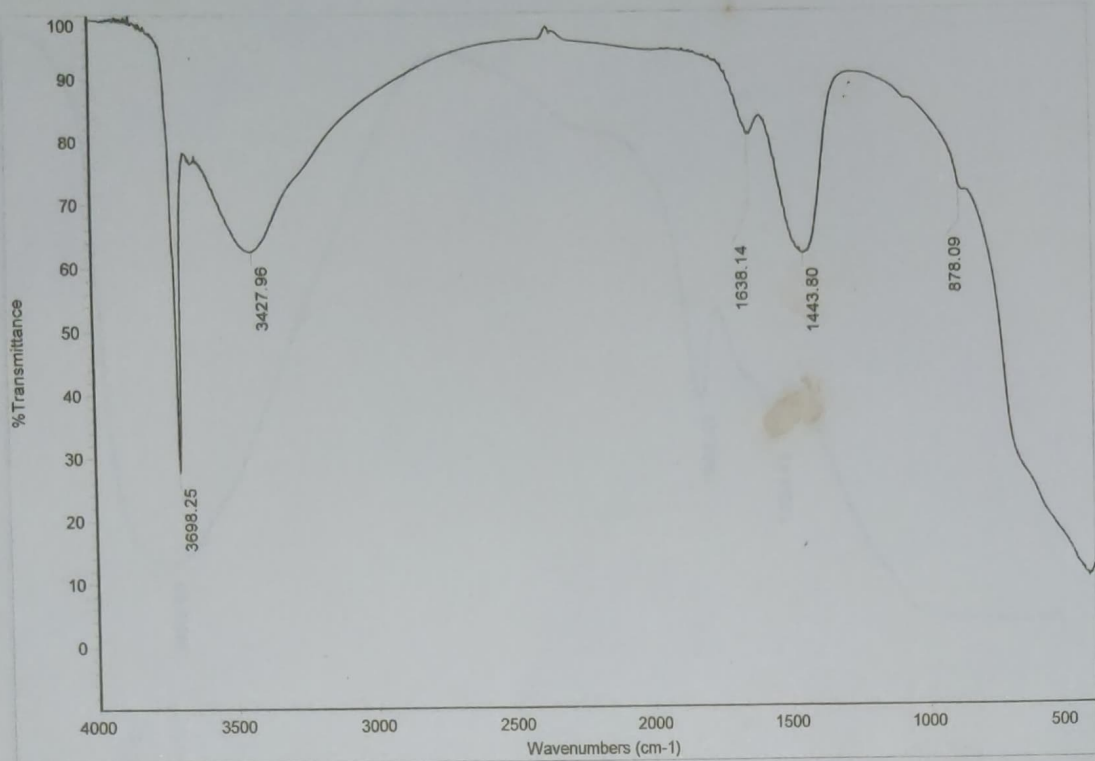40. Yamanaka T and Tanabe K, 1976 , *J. Phys, Chem*, **79**, 2409.

APPENDIX I
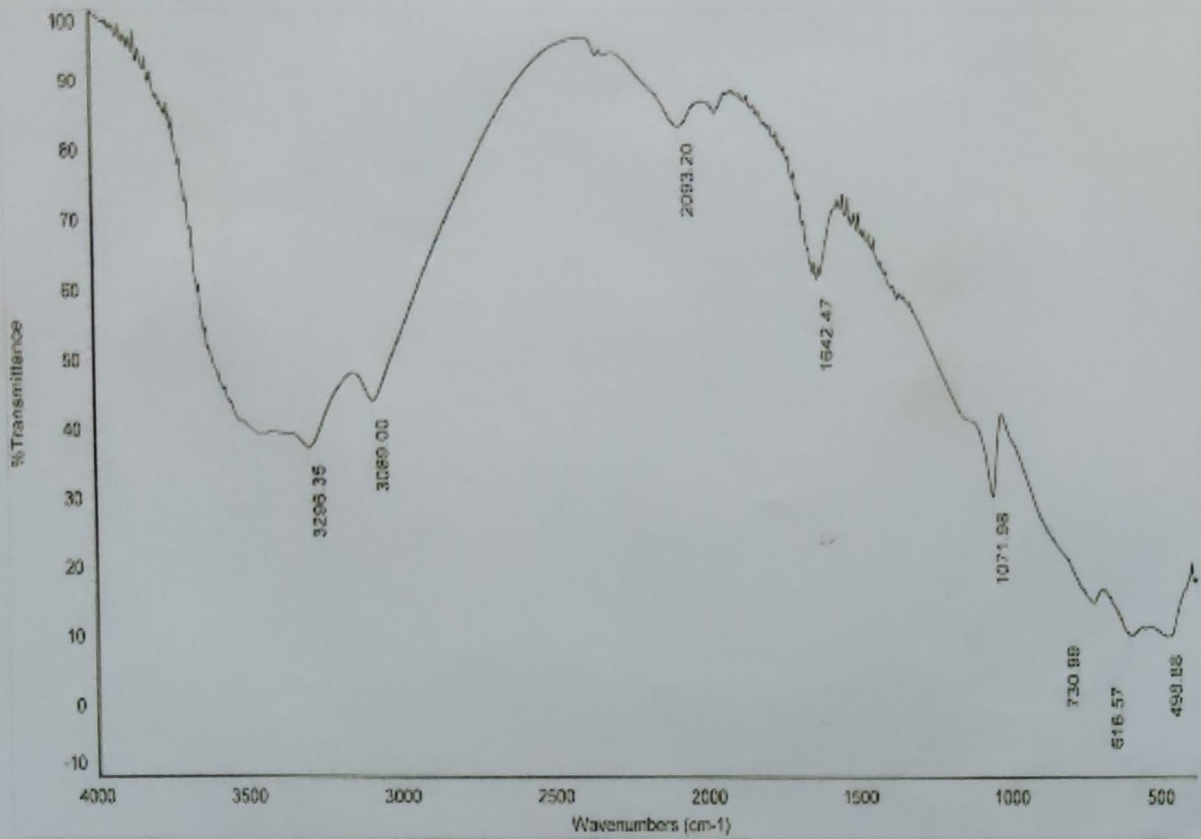
Date: Tue Jan 09 10:46 11 2007 (GMT-08:00) SAIFFT070103A_01 (SIII)
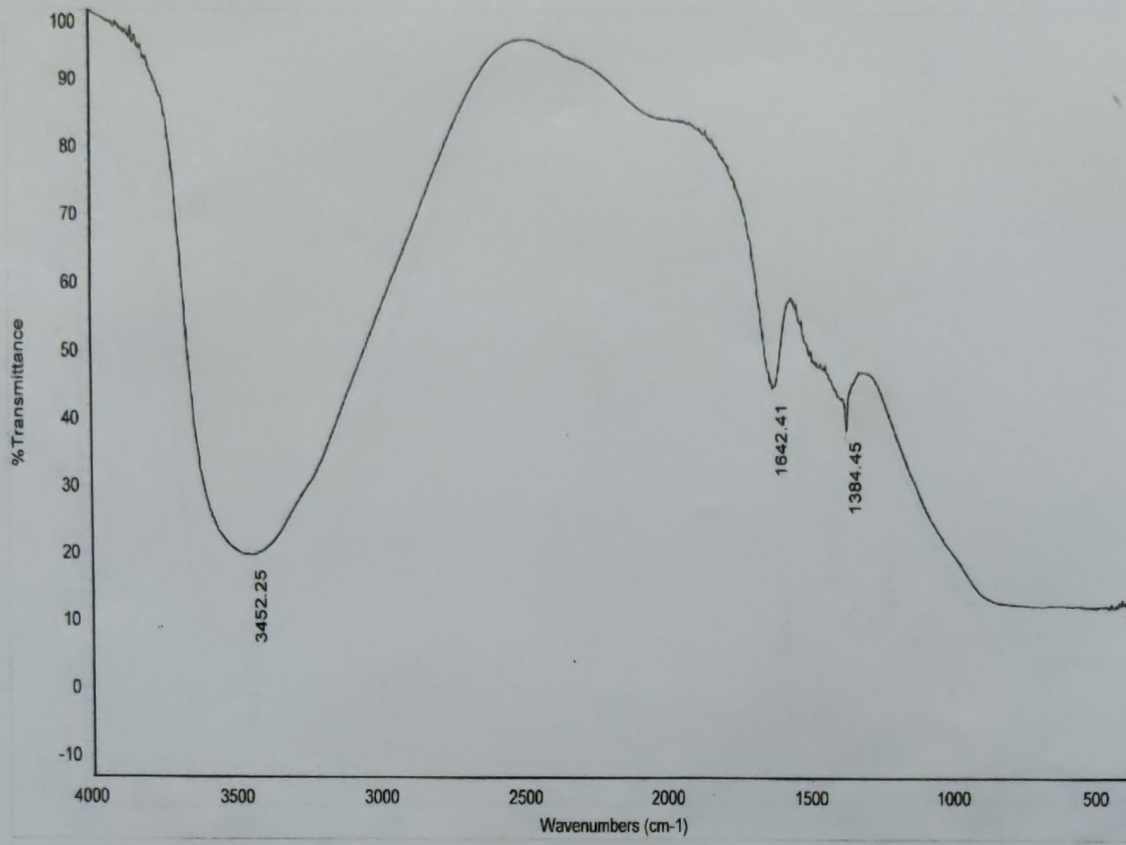
Scans: 32

Resolution: 4.000

Al$_2$O$_3$

Date: Wed Mar 07 16:05:45 2007 (GMT-08:(SAIFFT070224A-01 (Sample-6) KBr

Scans: 32

Resolution: 4.000

MgO

Date: Tue Jan 09 11:25:34 2007 (GMT-08:00)   SAIFFT070103A_03 (SII)

Scans: 32

Resolution: 4.000

9 % MgO/Al$_2$O$_3$
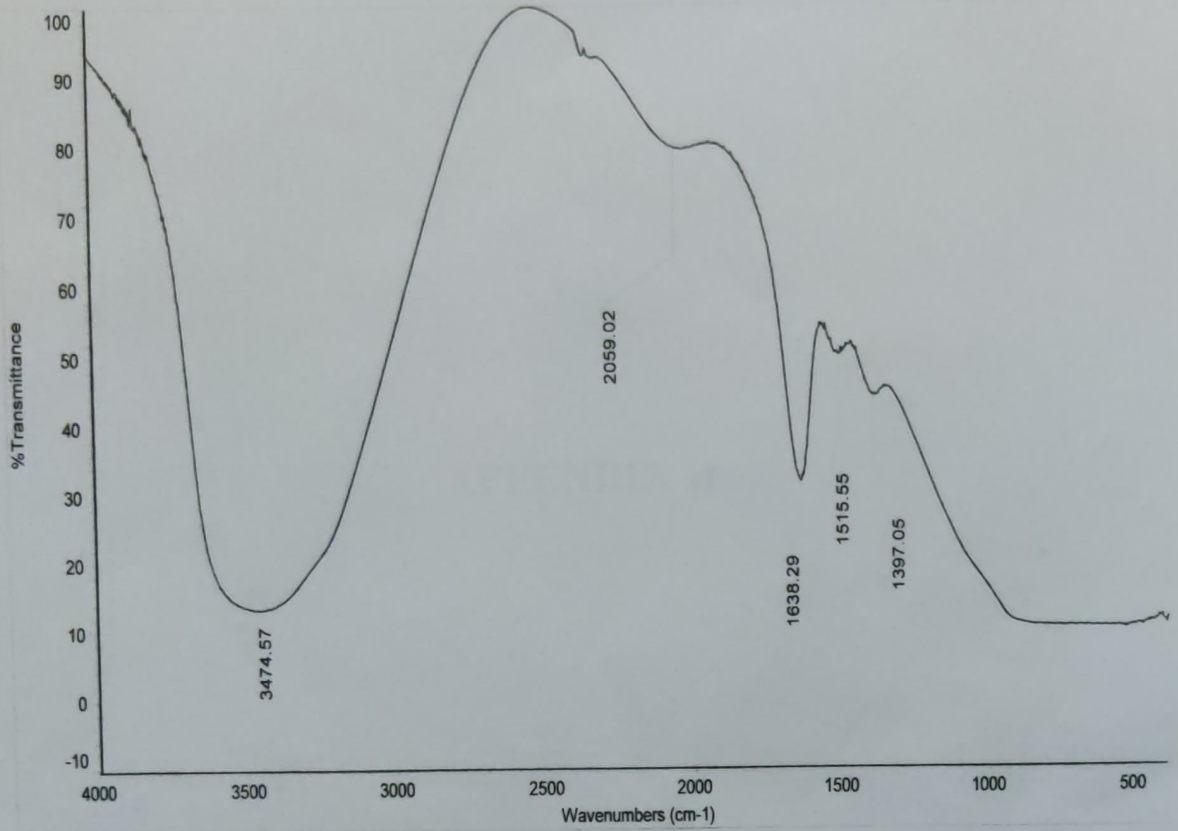
20% MgO/Al$_2$O$_3$

APPENDIX II

XRD

Al2O3
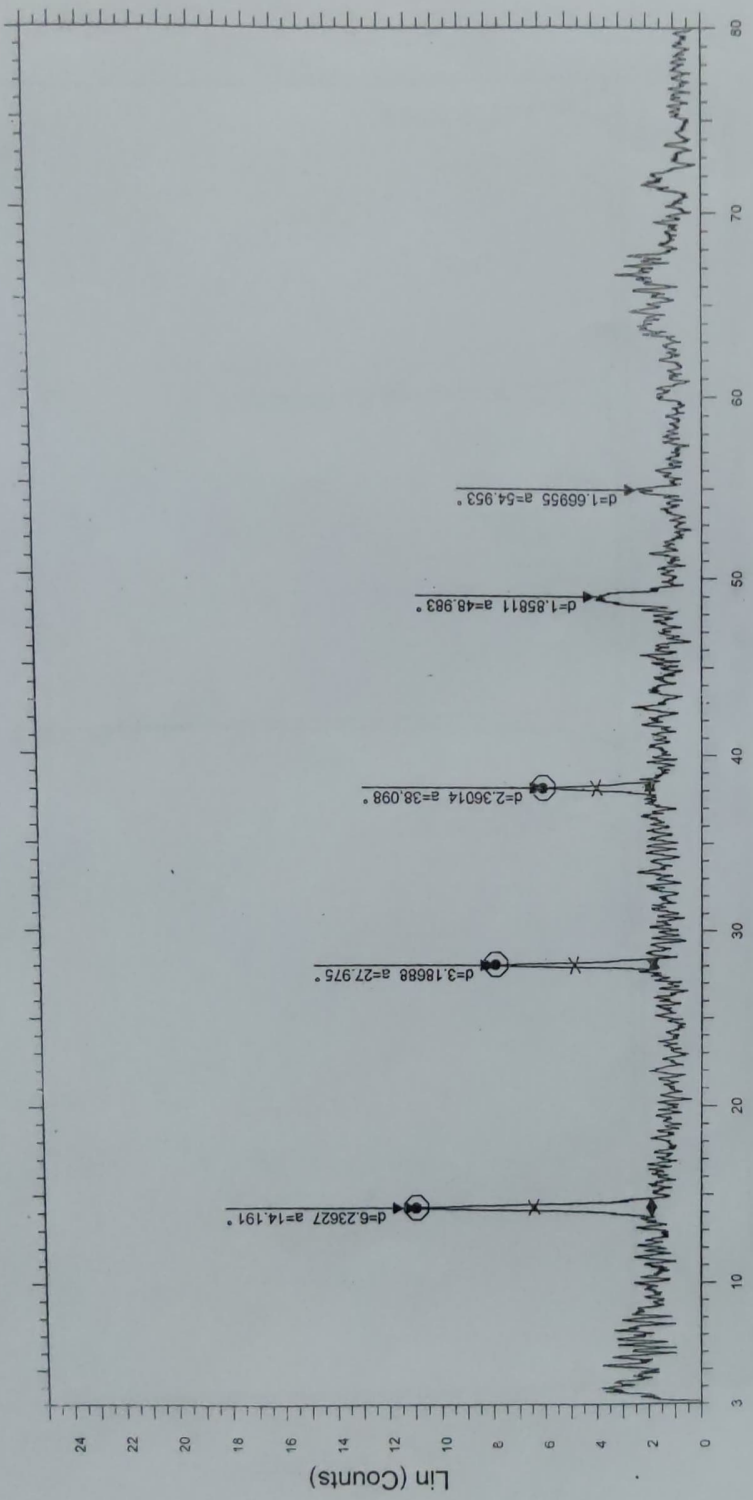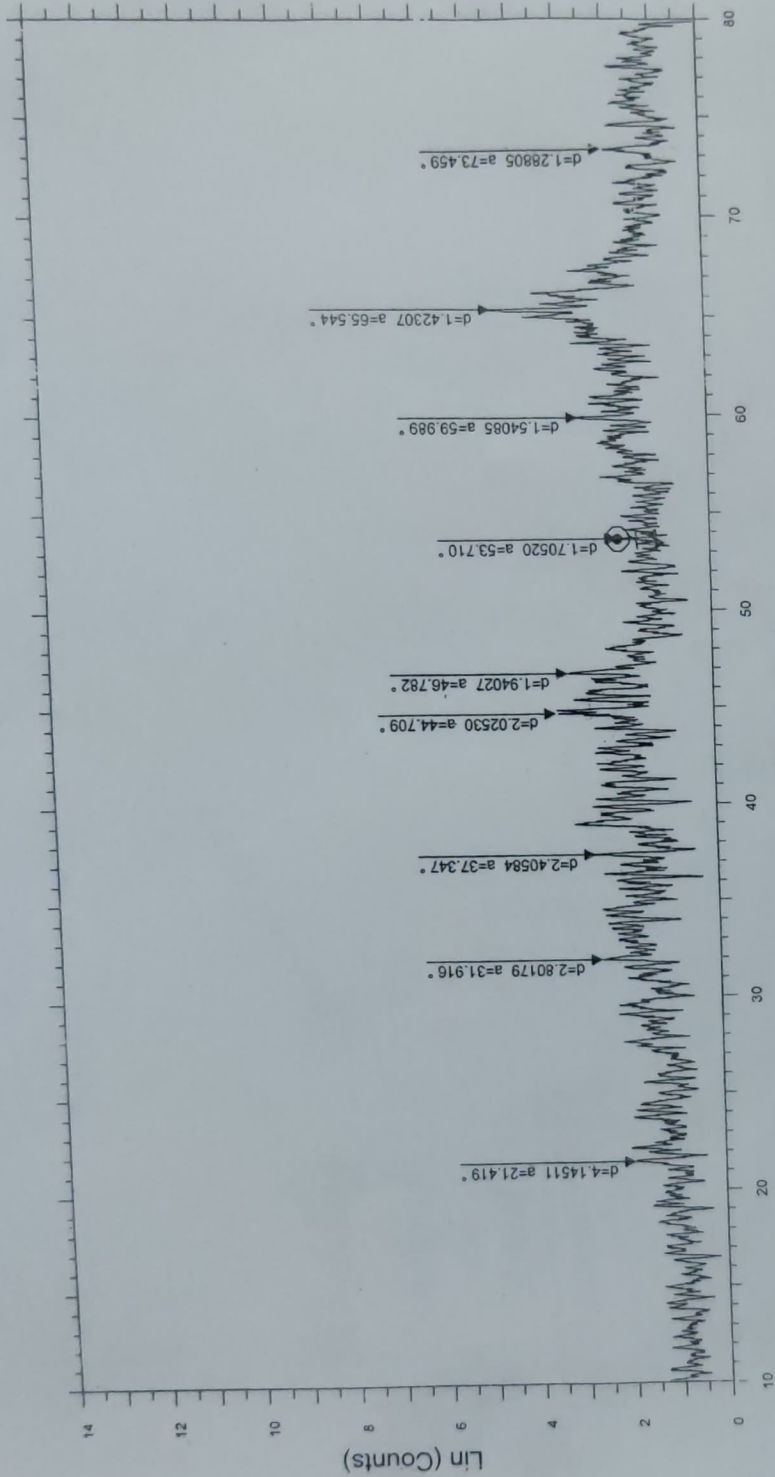

2-Theta - Scale

S III Al2O3 - File: SAIFXR070103A-01(SIII).raw - Type: 2Th/Th locked - Start: 3.000 ° - End: 80.000 ° - Step: 0.010 ° - Step time: 0.2 s - Temp.: 25 °C (Room) - Time Started: 1168491
1) S III Al2O3 - Left Angle: 13.660 ° - Right Angle: 14.730 ° - FWHM: 0.352 ° - Net Area: 18.23 Cps x deg.
2) S III Al2O3 - Left Angle: 27.690 ° - Right Angle: 28.370 ° - FWHM: 0.266 ° - Net Area: 8.829 Cps x deg.
3) S III Al2O3 - Left Angle: 37.770 ° - Right Angle: 38.560 ° - FWHM: 0.294 ° - Net Area: 6.362 Cps x deg.
Operations: Smooth 0.150 | Background 1.000,1.000 | Import

MgO
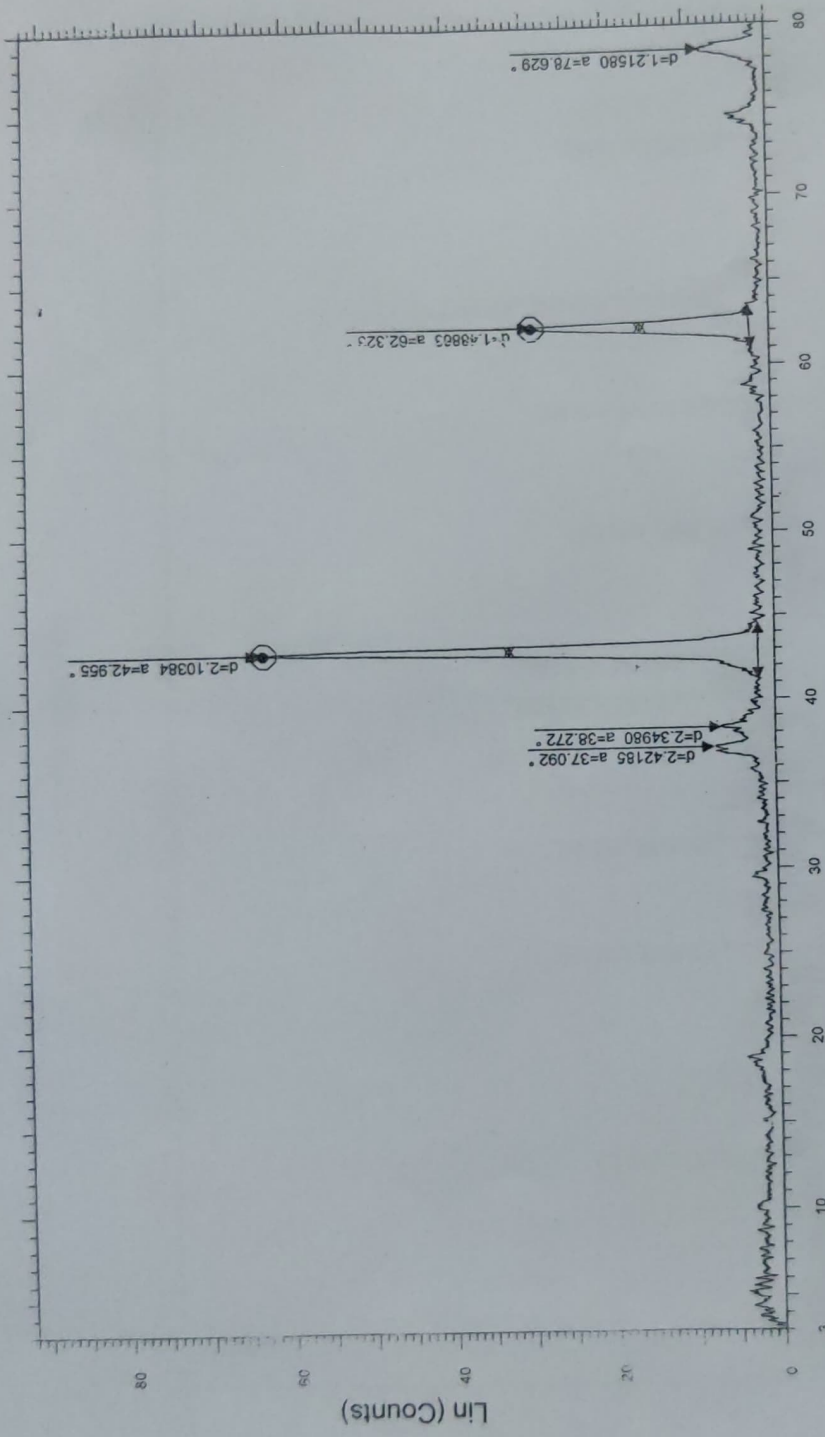
2-Theta - Scale

Sample IV - File: SAIFXR070224A-01(Sample IV).raw - Type: 2Th/Th locked - Start: 3.000 ° - End: 80.000 ° - Step: 0.010 ° - Step time: 0.2 s - Temp: 25 °C (Room) - Time Star
① Sample IV - Left Angle: 41.170 ° - Right Angle: 44.510 ° - FWHM: 0.577 ° - Raw Area: 249.9 Cps x deg.
② Sample IV - Left Angle: 60.960 ° - Right Angle: 63.530 ° - FWHM: 0.642 ° - Raw Area: 128.9 Cps x deg.
Operations: Smooth 0.150 | Background 0.000,1.000 | Import

XRD

20% MgO/Al$_2$O$_3$

Lin (Counts)

2-Theta - Scale

d=4.14511 a=21.419°
d=2.80179 a=31.916°
d=2.40584 a=37.347°
d=2.02530 a=44.709°
d=1.94027 a=46.782°
d=1.70520 a=53.710°
d=1.54085 a=59.989°
d=1.42307 a=65.544°
d=1.28805 a=73.459°

S II - File: SAIFXR070103A-02(SII).raw - Type: 2Th/Th locked - Start: 3.000 ° - End: 80.000 ° - Step: 0.010 ° - Step time: 0.2 s - Temp.: 25 °C (Room) - Time Started: 1168493440 s - 2
S II - Left Angle: 6.120 ° - Right Angle: 6.590 ° - FWHM: 0.219 ° - Net Area: 2.672 Cps x deg.
1) S II - Left Angle: 53.790 ° - Right Angle: 53.790 ° - FWHM: 0.101 ° - Net Area: 0.434 Cps x deg.
2) S II - Left Angle: 53.600 ° -
Operations: Smooth 0.150 | Background 1.000,1.000 | Import

APPENDIX III

Al_2O_3

Sample: S.
Operator: RESHMI
Submitter: COCHIN UNIVERSITY,KOCHIN
File: C:\WIN3000\DATA\000-347.SMP

Started: 1/17/2002 4:59:08AM
Completed: 1/17/2002 6:00:45AM
Report Time: 1/18/2002 12:38:52AM
Warm Free Space: 10.9519 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2266 g
Cold Free Space: 33.0690 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Summary Report

Surface Area

Single point surface area at P/Po = 0.306241499: 249.5840 m²/g

BET Surface Area: 259.5431 m²/g

3% MgO/Al_2O_3

Sample:
Operator: RESHMI
Submitter: COCHIN UNIVERSITY,KOCHIN
File: C:\WIN3000\DATA\000-344.SMP

Started: 1/15/2002 11:13:32PM
Completed: 1/16/2002 11:51:08PM
Report Time: 1/18/2002 12:36:05AM
Warm Free Space: 10.9302 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2826 g
Cold Free Space: 32.3977 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Summary Report

Surface Area

Single point surface area at P/Po = 0.295701977: 225.7807 m²/g

BET Surface Area: 231.2955 m²/g

Sample: $9\%\ MgO/Al_2O_3$
Operator: RESHMI
Submitter: COCHIN UNIVERSITY, KOCHIN
File: C:\WIN3000\DATA\000-345.SMP

Started: 1/16/2002 12:44:44AM
Completed: 1/16/2002 2:04:05AM
Report Time: 1/18/2002 12:37:56AM
Warm Free Space: 11.0944 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2756 g
Cold Free Space: 32.8191 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Summary Report

Surface Area

Single point surface area at P/Po = 0.297874525: 195.2734 m²/g

BET Surface Area: 200.5365 m²/g

Sample: $15\%\ MgO/Al_2O_3$
Operator: RESHMI
Submitter: COCHIN UNIVERSITY, KOCHIN
File: C:\WIN3000\DATA\000-348.SMP

Started: 1/17/2002 4:59:08AM
Completed: 1/17/2002 6:00:45AM
Report Time: 1/18/2002 12:39:19AM
Warm Free Space: 10.9001 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2416 g
Cold Free Space: 33.0400 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Summary Report

Surface Area

Single point surface area at P/Po = 0.296568804: 235.6193 m²/g

BET Surface Area: 241.8979 m²/g

Sample: 20% MgO/Al_2O_3
Operator: RESHMI
Submitter: COCHIN UNIVERSITY,KOCHIN
File: C:\WIN3000\DATA\000-346.SMP

Started: 1/16/2002 12:44:44AM
Completed: 1/16/2002 2:04:05AM
Report Time: 1/18/2002 12:38:18AM
Warm Free Space: 11.0246 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.2904 g
Cold Free Space: 32.8133 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Summary Report

Surface Area

Single point surface area at P/Po = 0.296885682: 229.2346 m²/g

BET Surface Area: 234.5756 m²/g

Sample: MgO
Operator: RESHMI
Submitter: COCHIN UNIVERSITY,KOCHIN
File: C:\WIN3000\DATA\000-343.SMP

Started: 1/15/2002 11:13:32PM
Completed: 1/16/2002 11:51:08PM
Report Time: 1/18/2002 12:35:36AM
Warm Free Space: 11.5330 cm³ Measured
Equilibration Interval: 5 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: -195.800 °C
Sample Mass: 0.3008 g
Cold Free Space: 34.6444 cm³ Measured
Low Pressure Dose: None
Automatic Degas: No

Summary Report

Surface Area

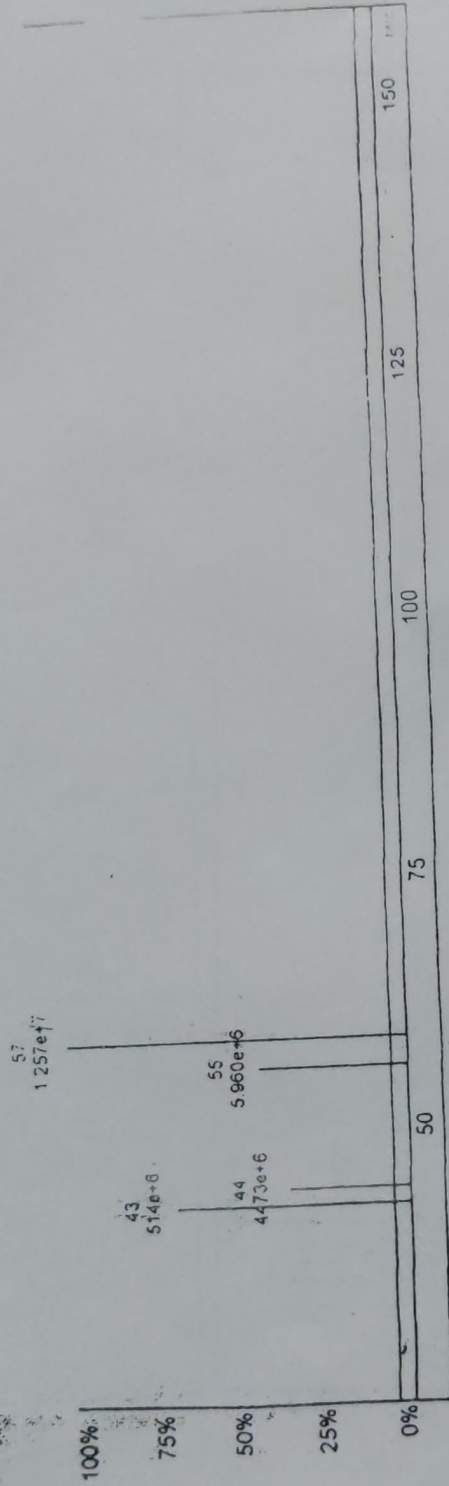Single point surface area at P/Po = 0.300612482: 71.4335 m²/g

BET Surface Area: 72.7473 m²/g

APPENDIX IV

Original n-butylacetate

ORIGINAL n-butylacetate
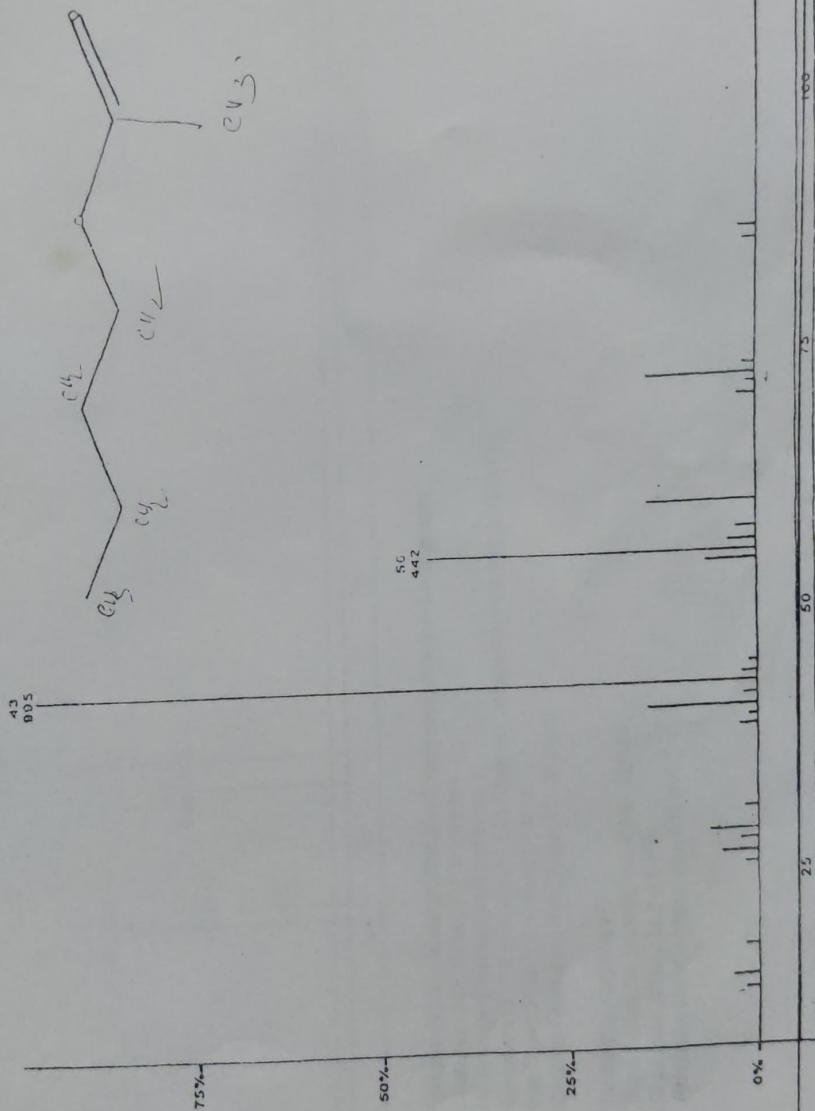
Sample - A Pure Al_2O_3

Spectrum from ... atsaifgc060420a-02(sample4) repeat 4-21-2006.xms
Scan. No.: 299. Time : 7.178 minutes
No averaging. Background corrected
Comment : 7.178 min. Scan : 299 Channel : Merged Ion: NA RIC 5.784e+7(
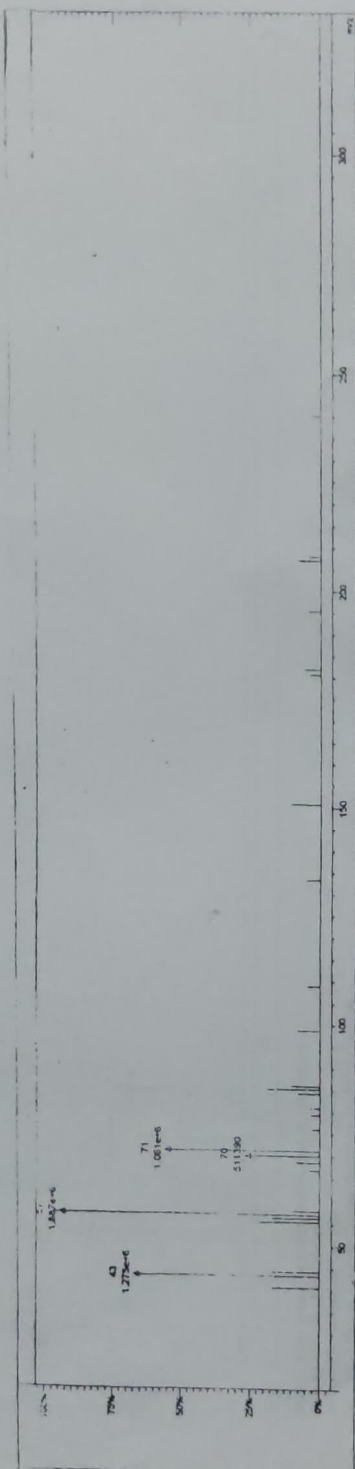Pair Count 20 MW:0 Formula: None
CAS No: None Acquired range: 40 - 500 m/z

Method Description : EI
Scan 1 Channel Description. 40.0 - 600.0>
Scan Information: cp = 1.0 PSI
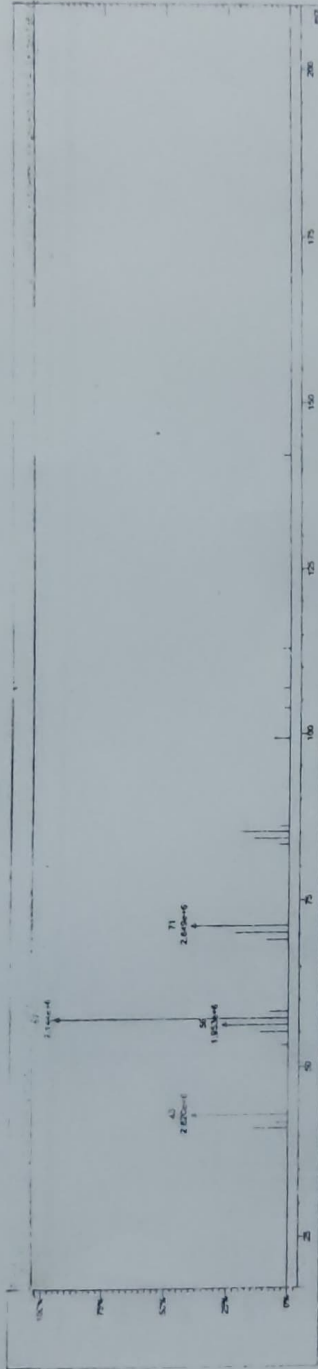Precursor Mass Range : 40 - 500 m/z

Mass labels: 43 514e+8, 44 4.73e+6, 55 5.960e+6, 57 1.257e+7

Sample - B 3% MgO/Al$_2$O$_3$

Spectrum from _.cllegetsatigc070713a-03(sample 4) 7-16-2007.xms
Scan No: 91, Time: 3.628 minutes
No averaging. Background corrected.
Comment: 3.628 min. Scan: 91 Channel: Merged Ion NA RIC: 1.607e+7 (B
Par Count: 28 MW: 0 Formula: None
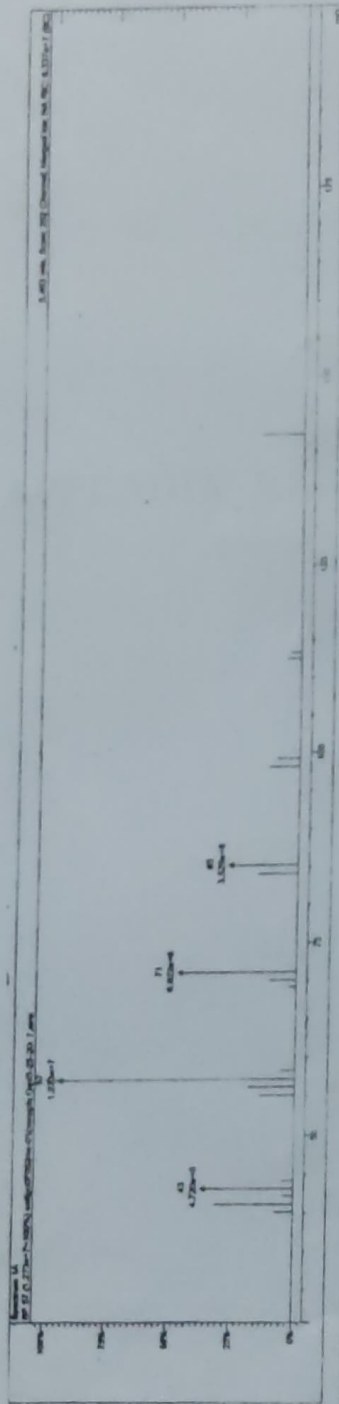CAS No: None Acquired Range: 40 - 600 m/z

Method Description: EI
Scan 1 Channel Description: 40.0 - 600.0 >
Scan Information: cp = 0.1 PSI
Precursor Mass Range: 40 - 600 m/z

Sample - C 9% MgO/Al_2O_3

Spectrum from ..ethoxylcall.gx07(07)13s-02(sample 3) 7-16-2007.xms
Scan No: 90, Time: 3.598 minutes
No averaging. Background corrected.
Comment: 3.598 min. Scan: 90 Channel: Merged Ion: NA RIC: 2.12e+7 (B
Pair Count: 34   MW: 0   Formula: None
CAS No: None Acquired Range: 40 - 600 m/z

Method Description: B
  Scan 1 Channel Description: 40.0 - 600.0 >
  Scan Information: cp = 0.2 PSI
  Precursor Mass Range: 40 - 600 m/z

Sample - D 15% MgO/Al$_2$O$_3$

Sample - E   20% MgO/Al$_2$O$_3$

Spectrum from __collegetusrtgd070713a-01(sample 2) 7-16-2007.sms
Scan No. 91,   Time: 3.609 minutes
No averaging. Background corrected
Comment: 3.609 min. Scan: 91 Channel: Merged Ion: NA RIC: 3.435e+7 (8
Per Count: 20   MW: 0   Formula: None
CAS No: None Acquired Range: 40 - 600 m/z

Method Description: B
Scan 1 Channel Description: 40.0 - 600.0 >
Scan Information: cp = 0.3 PSI
Precursor Mass Range: 40 - 600 m/z

Sample - F   Pure MgO