

KERALA STATE COUNCIL FOR SCIENCE, TECHNOLOGY AND ENVIRONMENT
STUDENT PROJECT REPORT (FINAL), 2016-17

1. Project Title :

Surface Characterization and Catalytic Activity of ZnO-Al₂O₃ Mixed Oxides

2. File No: 4/SPS 59/2016/KSCSTE, dated 23-9-2016

3. Name & Address of the student: Akhila Binny

II M.Sc Chemistry,

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Associate Professor,

Department of Chemistry

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& Co-Investigator with mobile No.

NA

5. Broad Area of Research:

Physical Chemistry

6. Specific Area: Preparation, Characterisation and Catalytic Activity of
ZnO-Al₂O₃ Mixed Oxides

7. Date of Start: 21-10-2016

8. Total cost of Project: Rs-16315/-

9 Approved Objectives of the proposal:

Solid acids and bases are characterized by amount, strength and nature of acid –base centers. Mixed oxides have larger surface area and good catalyst for different reactions. The incorporation of ZnO into Al₂O₃ may alter the acid-base properties. Surface hydroxyls on metal oxides are shown to differ in chemical properties and differences in acidity between hydroxyl groups on several oxide surfaces have been reported. Oppenauer oxidation is essentially a reversal of MPV reduction.

10. Methodology (500 words):

Metal oxides play a very important role in many areas of chemistry, physics and materials science. A mixed oxide is an oxide that contains more than one chemical element or cations of a single element in several states of oxidation. The Oppenauer oxidation over samaria alumina mixed oxides were reported [1]. In 1937 Oppenauer showed that unsolvated steroid alcohols could be oxidised to the corresponding ketone in excellent yields through the use of aluminium t-butoxide in the presence of a large amount of acetone, that compound functioning as the hydrogen acceptor and the large excess serving to shift the equilibrium in the desired direction [2]. In view of the reversible nature of the reaction, many statements as to the mechanism of the Meerwein Ponndorf-Verley reduction [3] are equally applicable to the Oppenauer oxidation. Activation of the alcoholic hydrogen atom by aluminium resulting in hydrogen bonding has also been proposed by Woodward et al [4].

ZnO-Al₂O₃ mixed oxides of different composition were prepared by co-precipitation method [5] from their nitrate solutions (10% ZnO-Al₂O₃ ,20% ZnO-Al₂O₃ , 40% ZnO-Al₂O₃ ,60% ZnO-Al₂O₃, 80 % ZnO-Al₂O₃).Pure oxides were prepared by hydroxide method from their nitrate solutions [6]. All the samples were activated at 500⁰C for 2hrs before the reaction was carried out.

Surface Characterization

The mixed oxide formation may be monitored by powder X-ray diffraction pattern combining those of the pure phases. As the reaction proceeds a new set of reflections corresponding to the product Al₂ZnO₄ emerges and grows in intensity at the expense of reflections from Al₂O₃ and ZnO. On completion of the reaction the powdered diffraction pattern will be that of pure Al₂ZnO₄. The XRD peaks clearly show the crystalline nature of mixed oxides. The XRD data of pure oxides and mixed oxides are given in APPENDIX A (Fig I).The SEM micrographs were used to observe surface morphology of oxide particles. Micrographs show polycrystalline and uniformly distributed particles of oxide system. The SEM micrographs of ZnO,Al₂O₃ and ZnO/Al₂O₃are given below (Fig II).

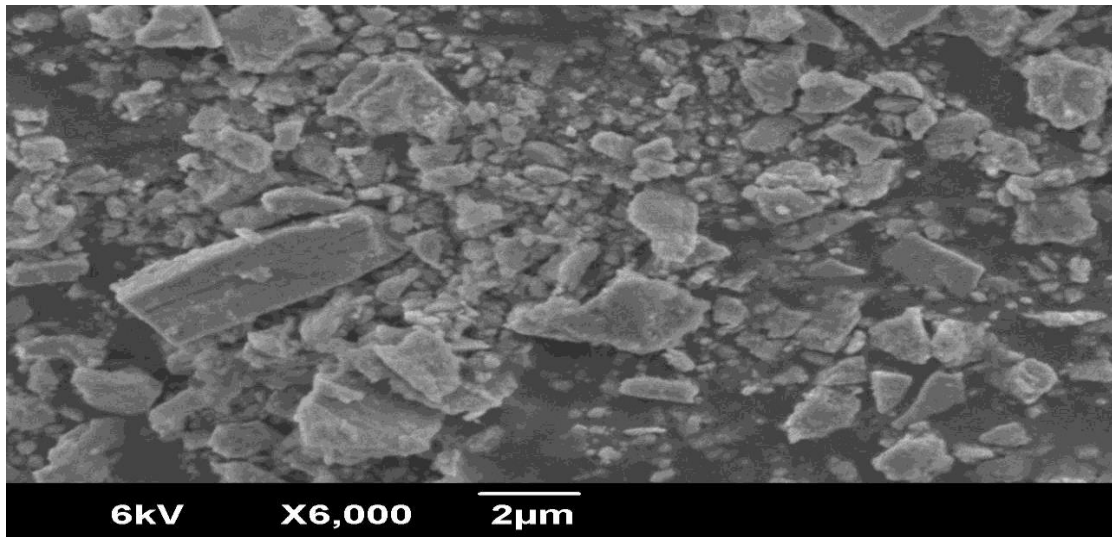
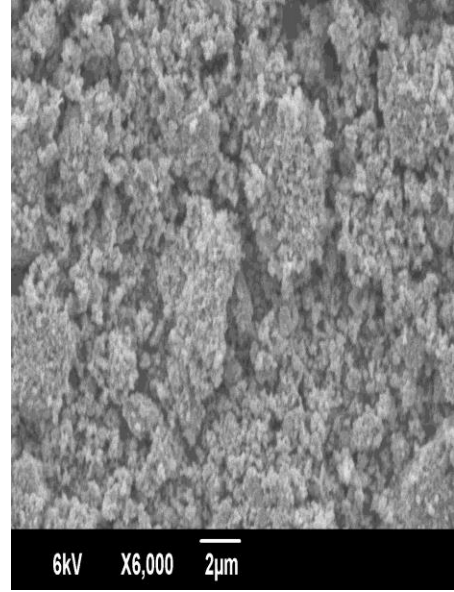


Fig. II

The IR spectra of product Cyclohexanone and pure Cyclohexanone are given (Fig. III)

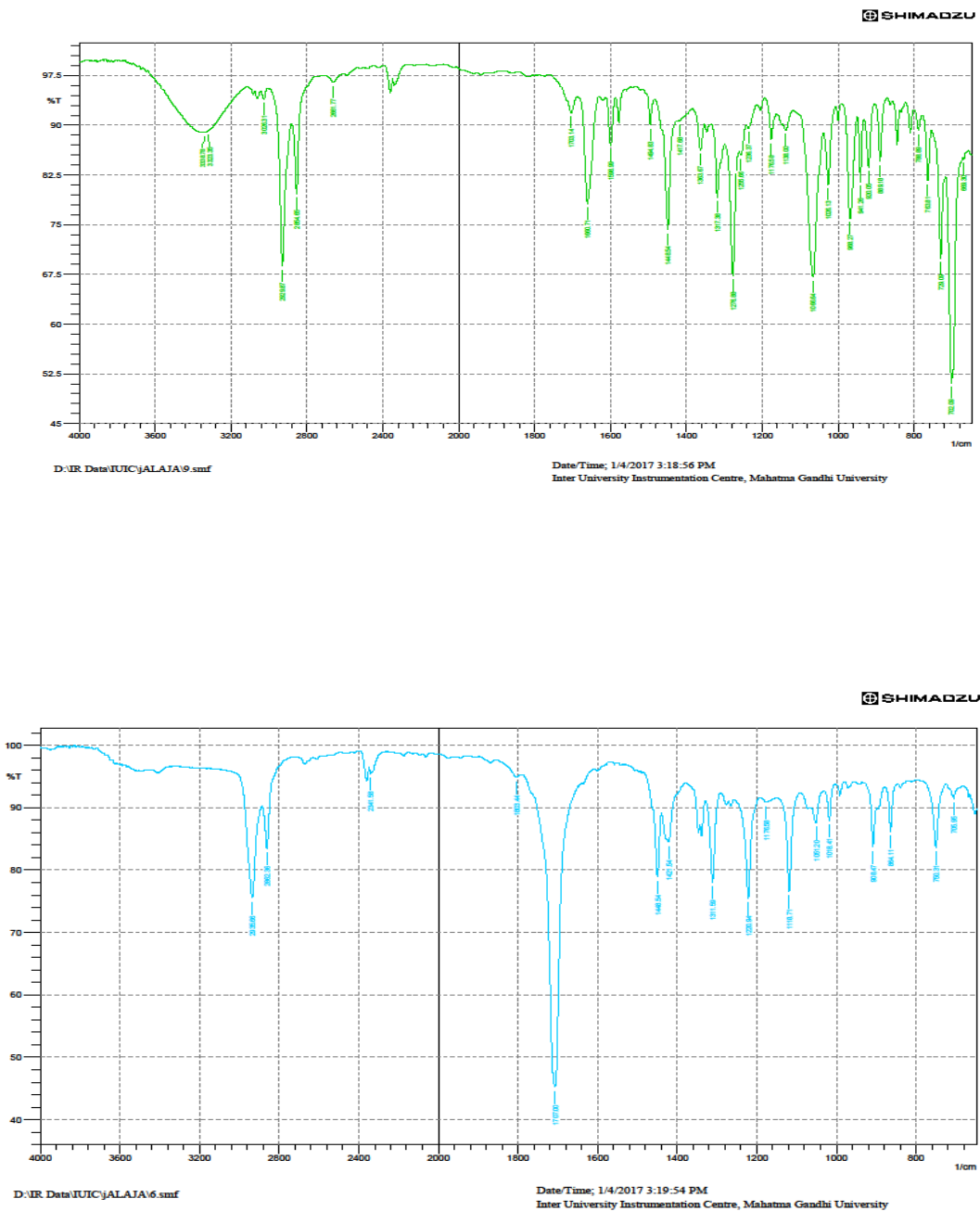


Fig. III

Catalytic activity measurement

Oxidation of alcohol (Oppenauer Oxidation)

In a round bottomed flask (50 cm³) equipped with a reflux condenser were placed catalyst (.5g) (100-200 mesh) , 10 cm³ of the toluene solution of the cyclohexanol (.25 mmol) , benzophenone (14.6mmol) and n- decane (.20 mmol) as an internal standard. The contents were heated under gentle reflux for 2 hours at 100⁰C.The reaction product was analyzed by means of TLC, GCMS and IR.

11. Salient Research Achievements:

a) New observations:

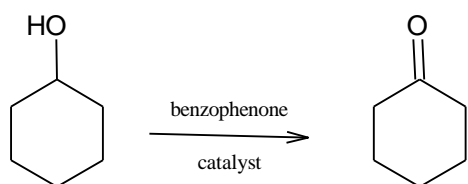
From the XRD pattern it is seen that Al₂ZnO₄ formation is completed at 60% ZnO-Al₂O₃ which contained reflections from both oxides and there after remains the same. The particle size of the pure and mixed oxides are of nano dimensions. Experiments on planar substrates under ZnO excess have confirmed that SSR in the Al₂O₃-ZnO system leads to a ZnAl₂O₄ layer formation in the presence of 3D voids [7]. The oxide surface generally terminated with surface hydroxyl groups which gives strong IR bands in the region 4000-3000 cm⁻¹ . The IR bands in 1600-1800cm⁻¹ are assigned to OH bending and metal oxide stretching vibrations.

From the relative abundance in GCMS, even though the product % is less, the ZnO--Al₂O₃ mixed oxides can be used in any base-catalysed reaction. The IR spectra of product mixture also showed the presence of cyclohexanone (1710cm⁻¹). Among the oxides studied 20% ZnO – Al₂O₃ , 40% ZnO- Al₂O₃ , and 60% ZnO – Al₂O₃ showed the catalytic activity for oxidation of cyclohexanol to cyclohexanone. Other oxide systems do not respond to Oppenauer oxidation. The main fragments are at m/z values 55, 98, 42, 83&70.In the case of ketones there is a strong molecular ion peak at m/z 55. Oppenauer oxidation of secondary alcohols proceeds efficiently using benzophenone as the hydrogen acceptor [8]. It has the high ability for oxidizing the alcohol and to resist aldol condensation [9].The catalytic activity of these oxides can be rationalized in terms of the mechanism proposed by Shibagaki etal [10]. It has already been established from primary kinetic isotope effect that k₃ is the rate determining step [10]. The mechanism involves hydride transfer from alcohol to the carbonyl carbon of the ketone. Lewis basicity of the catalyst surface favors the hydride transfer.

Here the reduction of benzophenone is slow because of the lowest electron density at the carbonyl carbon of the benzophenone. Here the catalytic activity decreases in the order 60%

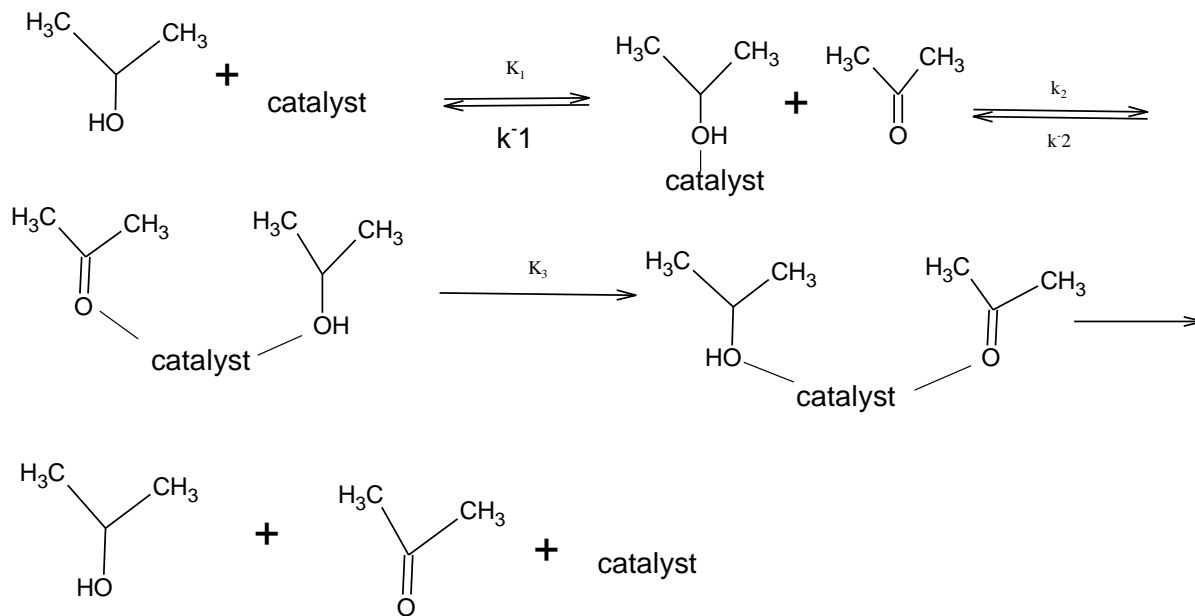
ZnO-Al₂O₃ > 40% ZnO-Al₂O₃ > 20% ZnO-Al₂O₃. Other oxide systems do not respond to Oppenauer Oxidation. The retention time of cyclohexanone is about 3.11-3.78. The GCMS data of cyclohexanone product obtained using different mixed oxide composition as catalyst is given in APPENDIX B (Fig.IV)

It was reported that the surface oxygen responsible for strong basic features could originate from the ZnO (11) structure only and would be more pronounced in materials of higher crystallinity. 60% ZnO-Al₂O₃ showed higher crystallinity and show good response towards the base catalysed Oppenauer oxidation.

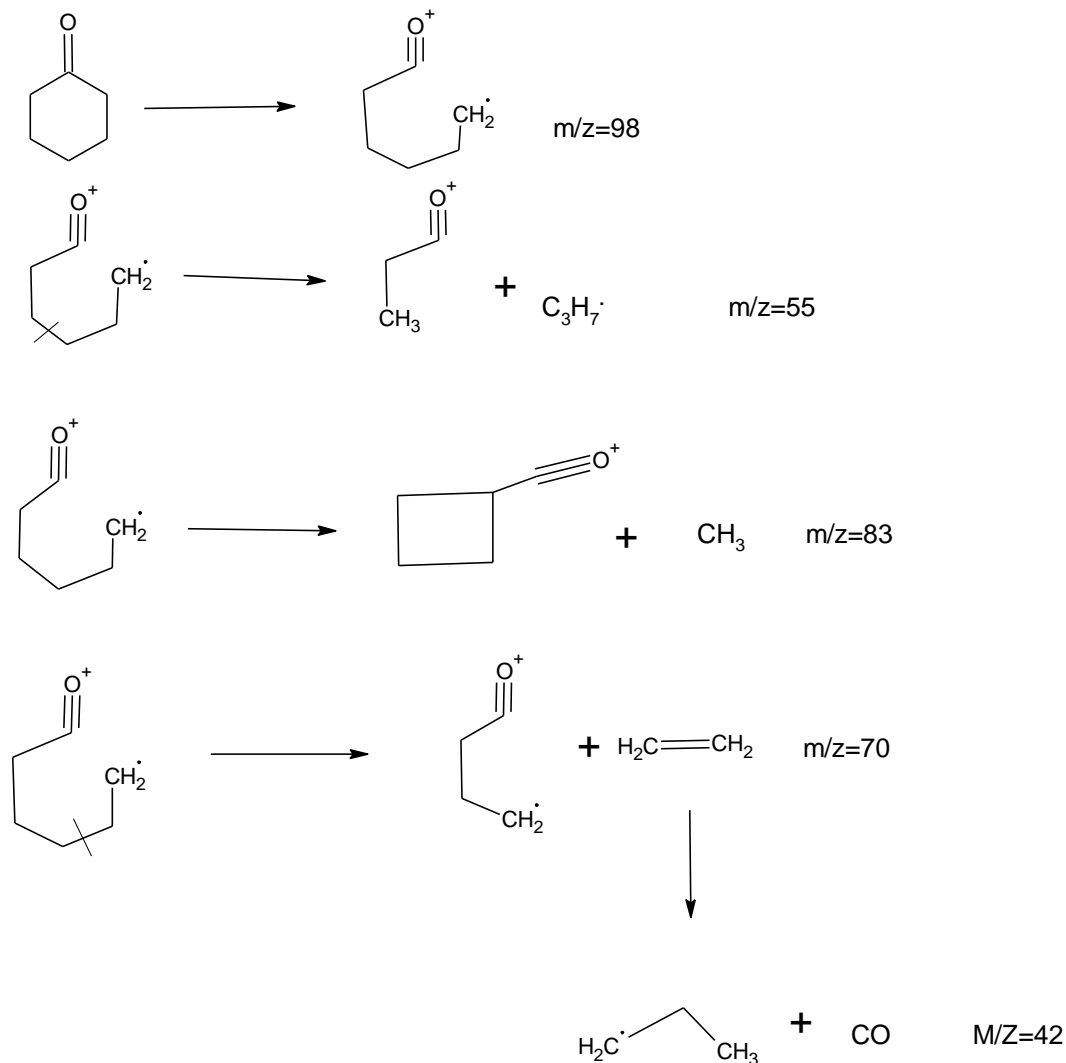


No by product was observed during the reaction.

Mechanism



In cyclohexanone the following fragmentation may occur.



The main fragments are at m/z values 55, 98, 42, 83&70.

b) Innovations/Technologies developed:

The supported catalytic activity was growing with decreasing acidity, but the ratio of the acidic to basic sites and the homogeneity were found as the main criteria for determining the activity. Here the catalytic activity may be due to proper combination of acidic and basic sites. Dehydration of the catalyst surface results in the formation of two kinds of defects at the domain boundaries. At one of these two or more immediately adjoining vacancies in the surface layer results in an abnormally exposed metal cation. The resultant localized positive charge makes this site an electron acceptor and gives the oxidizing character. At the second type of active site two

or more oxide ions occupy immediately adjoining surface sites and a potential electron donor site is created.

c) Application Potential

Zinc oxide is a wide band gap (3.4 eV) semiconductor which has broad range of potential uses in optical and electrical applications such as in solar energy conversion, thin film transistors, photo catalysis, gas sensors, cosmetics, photo luminescent and sensor materials. The substitution of Zn^{2+} ions with group III ions generates extra electrons and improve zinc optical, electrical, thermal and magnetic properties. Synthetic mixed oxides are components of many ceramics with remarkable properties and important advanced technological applications.

d) Any other:

One Paper entitled ‘Surface Characterization and Catalytic Activity of Zinc Alumina Mixed Oxides’ based on the work has been accepted for publication in the *Baselius Researcher*, ISSN No.0975-8658, Vol.No XVIII, No.1, January-June 2017(pp 100-107 proof separately attached) . All M.Sc Students were benefited from the project work and it helped them to become potent researchers.

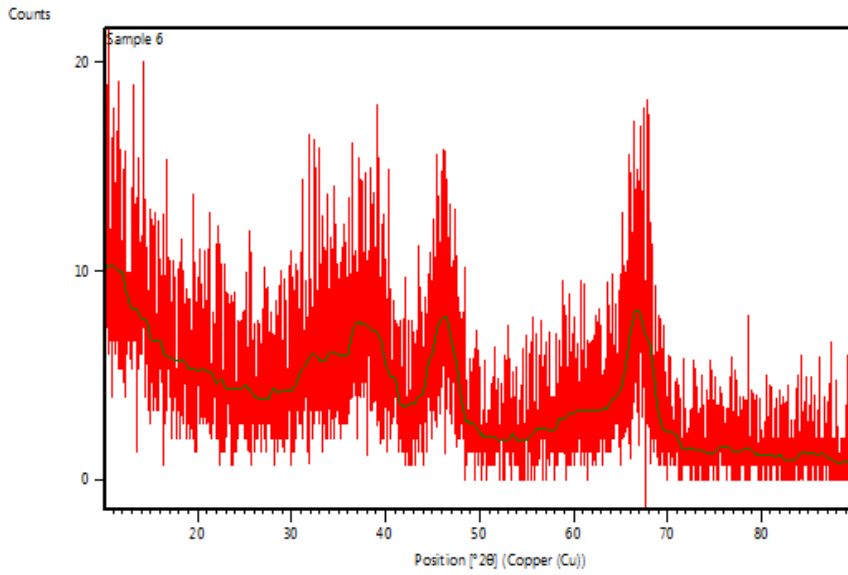
12.References

1. S.Sugunan and J.M Jalaja, Electron Donating Properties and Catalytic Activity of Samarium oxide and its mixed oxides with alumina, *React.Kinet.Catal.Lett*, 1995,55, No.2, pp 399-406.
2. Oppenauer, *Recl.Trav.Chim.Pays-Bas*, 1937, 56, pp137-144.
3. A.I Wilds, *Org.React*. 1944, 2, p 137.
4. Woodward, Wendler and Brutschy, *J.Am.Chem.Soc*, 1945, 67, p 1425.
5. T.Arai, K.Maruya, K.Domen and T.Onishi, *Bull.Chem.Soc.Jap*, 1989, 62, p 349.
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7. H.J Fan, M.Knez, R.Scholz, D.Hesse, K.Nielsch, M.Zacharias and U.Gosele, *NanoLetters*, 2007, 7, p 993.
8. H.Kuno, K.Takahashi, M.Shibagaki and H.Matsushita *Bull.Chem.Soc.Japan*, 1990.63, p 1943.
9. H.Kuno, K.Takahashi, M.Shibagaki and H.Matsushita *Bull.Chem.Soc.Japan*, 1991.64, p312.

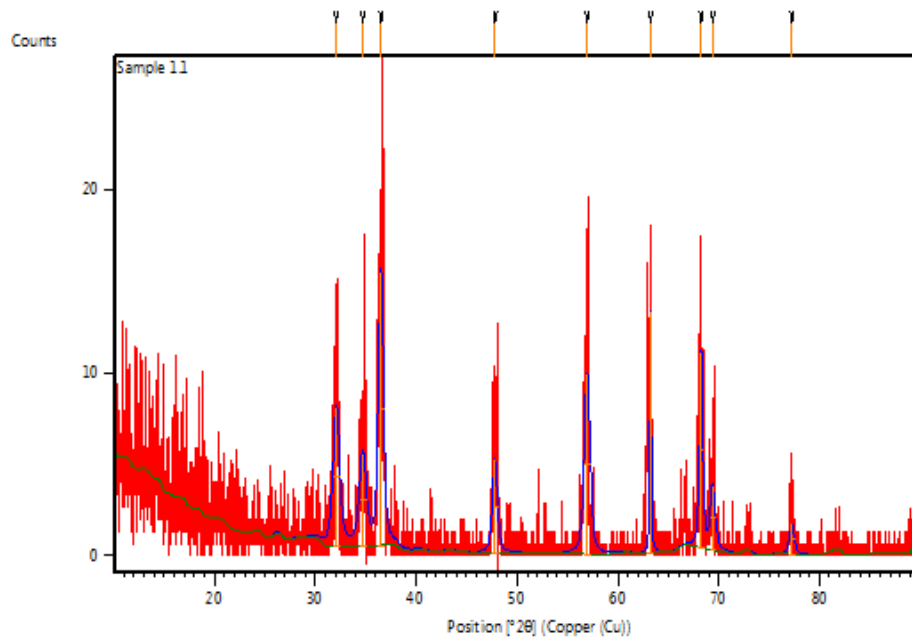
10. M.Shibagaki, K.Takahashi and H.Matsushita, *Bull.Chem.Soc.Japan*, 1988,61, p 328.
11. Adrien Mekki Berrada, Didier Grondin, Simona Bennici and Aline Auroux, Design of amphoteric mixed oxides of Zinc and group III elements, migration effects on basic features, *Online Journal*, 2012.

APPENDIX A & APPENDIX B
(XRD & GCMS)

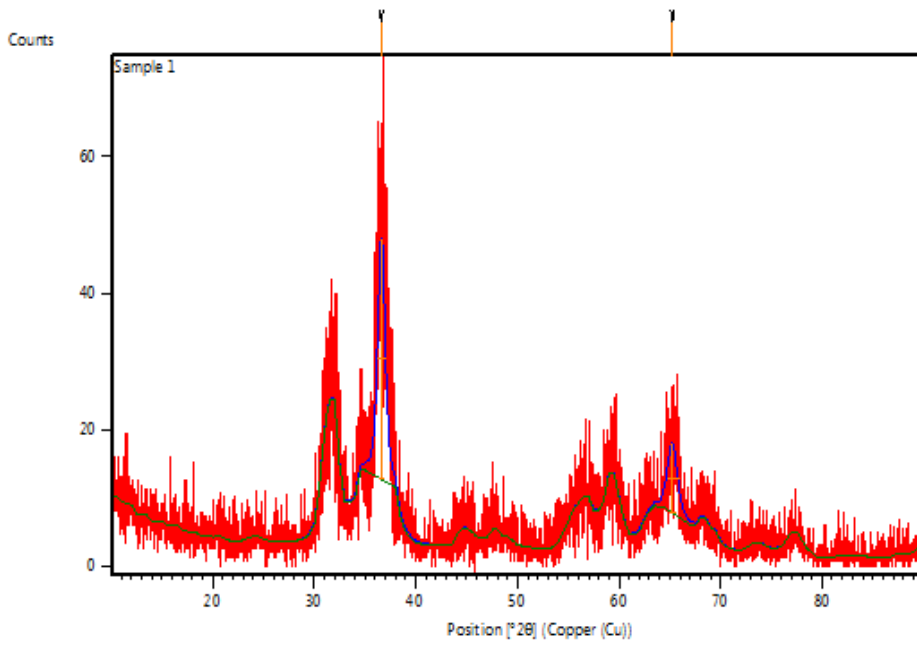
APPENDIX A XRD of Al₂O₃ (Fig I a)



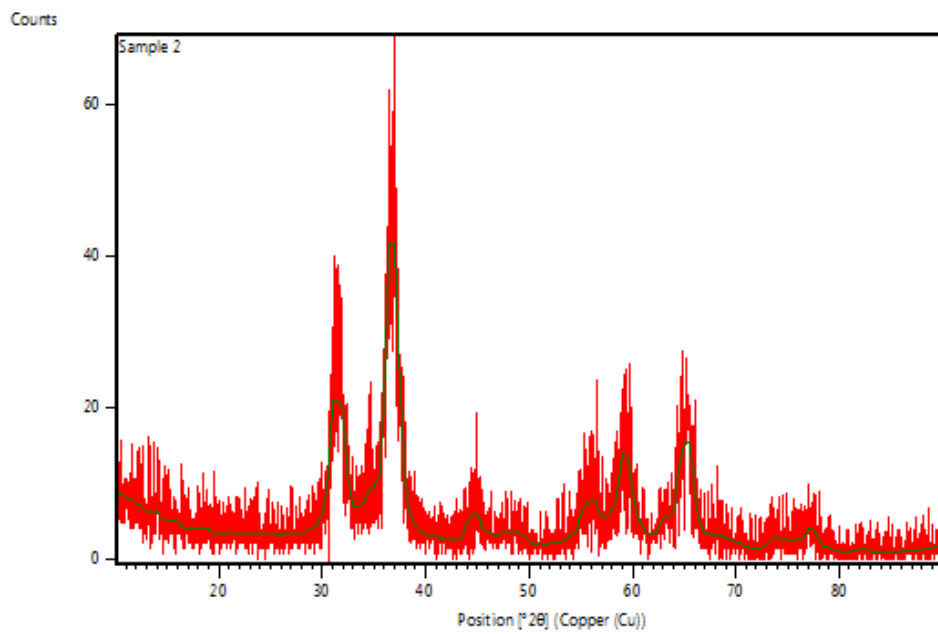
XRD of ZnO(FigIb)



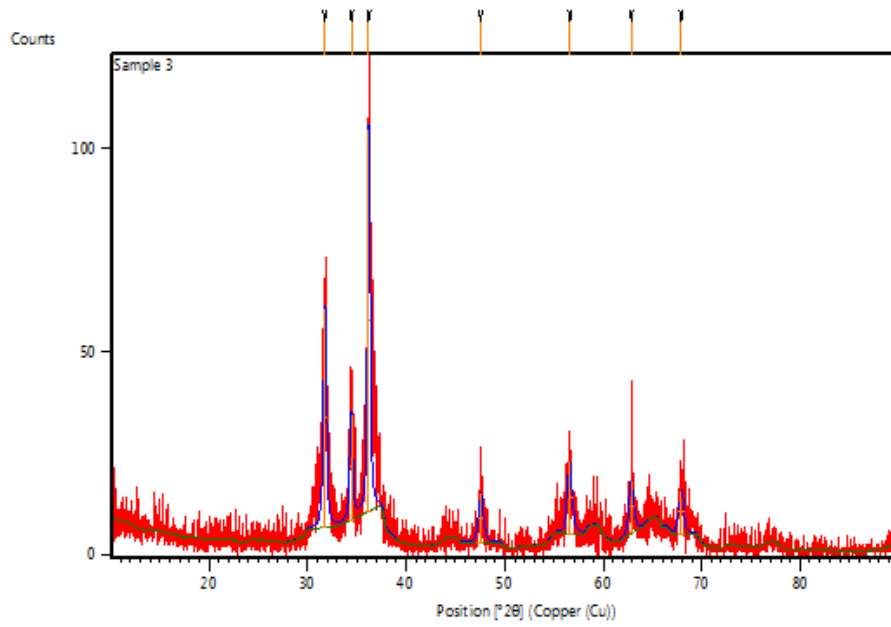
XRD of 10% ZnO-Al₂O₃ mixed oxide (Fig 1c)



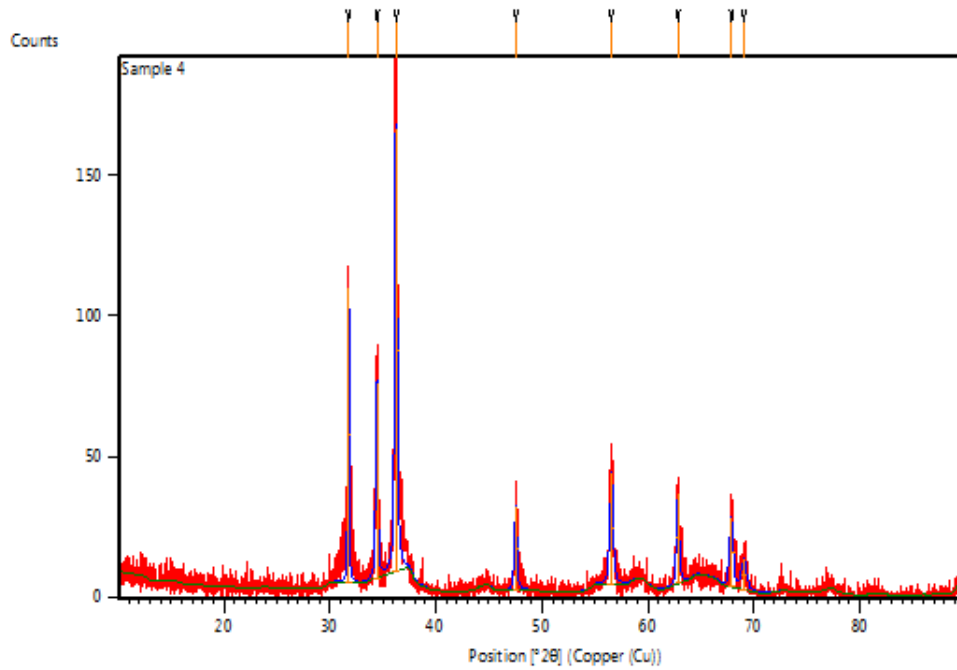
XRD of 20% ZnO-Al₂O₃ mixed oxide (Fig 1d)



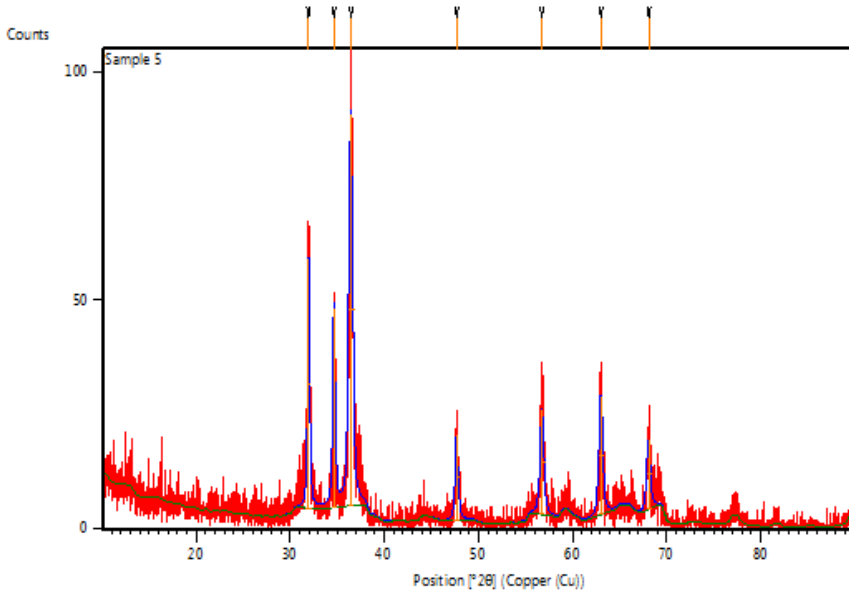
XRD of 40% ZnO-Al₂O₃ mixed oxide (Fig Ie)



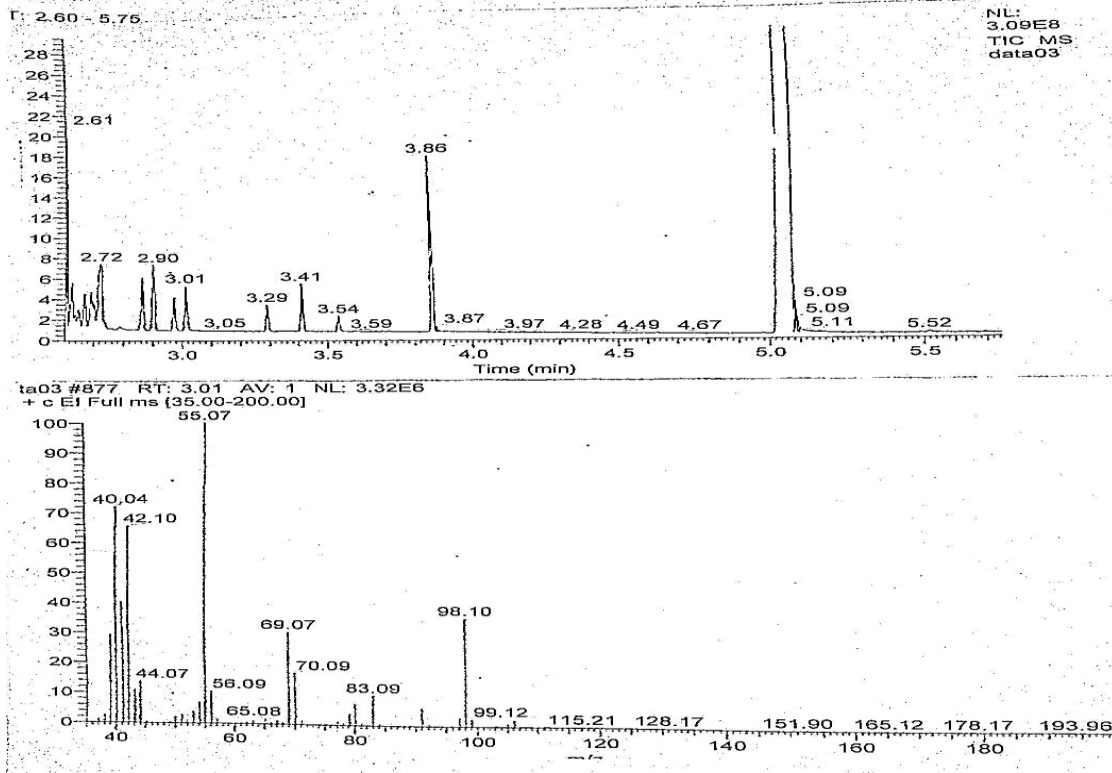
XRD of 60% ZnO-Al₂O₃ mixed oxide (Fig If)

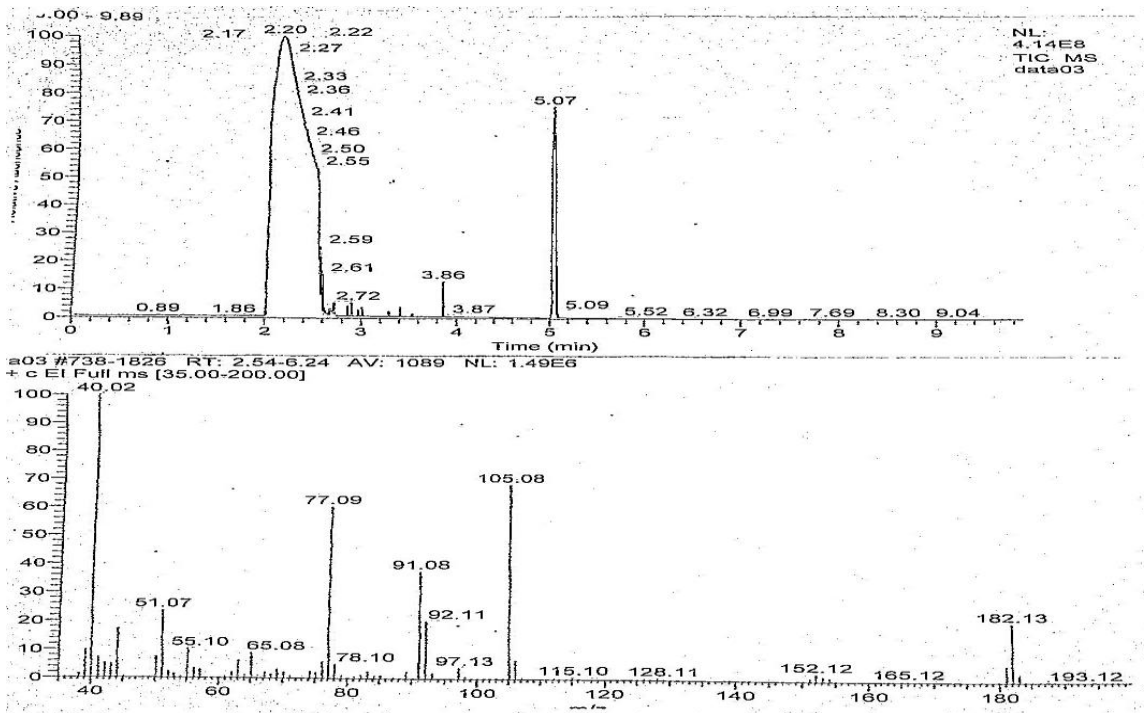


XRD of 80% ZnO-Al₂O₃ mixed oxide(Fig Ig)

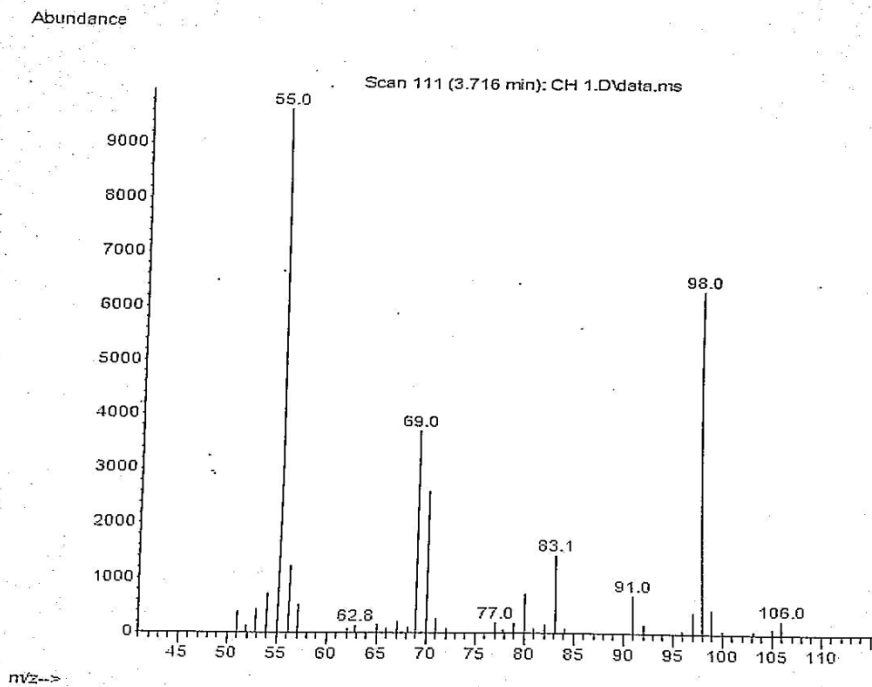


Appendix-B GC-MS spectra of 60% ZnO-Al₂O₃ (Fig IVa)

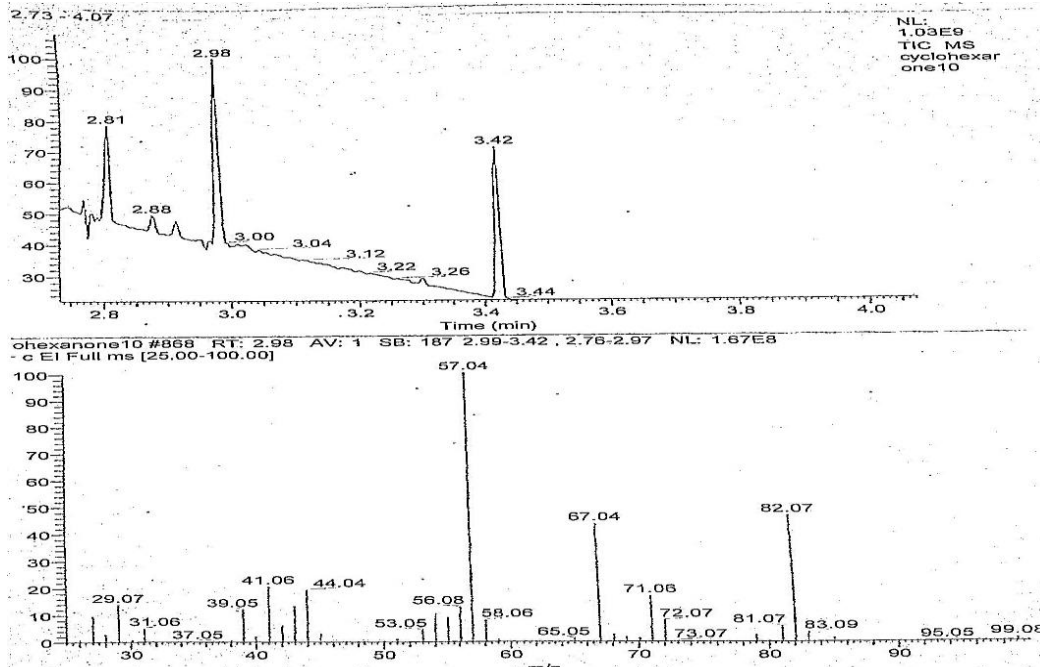




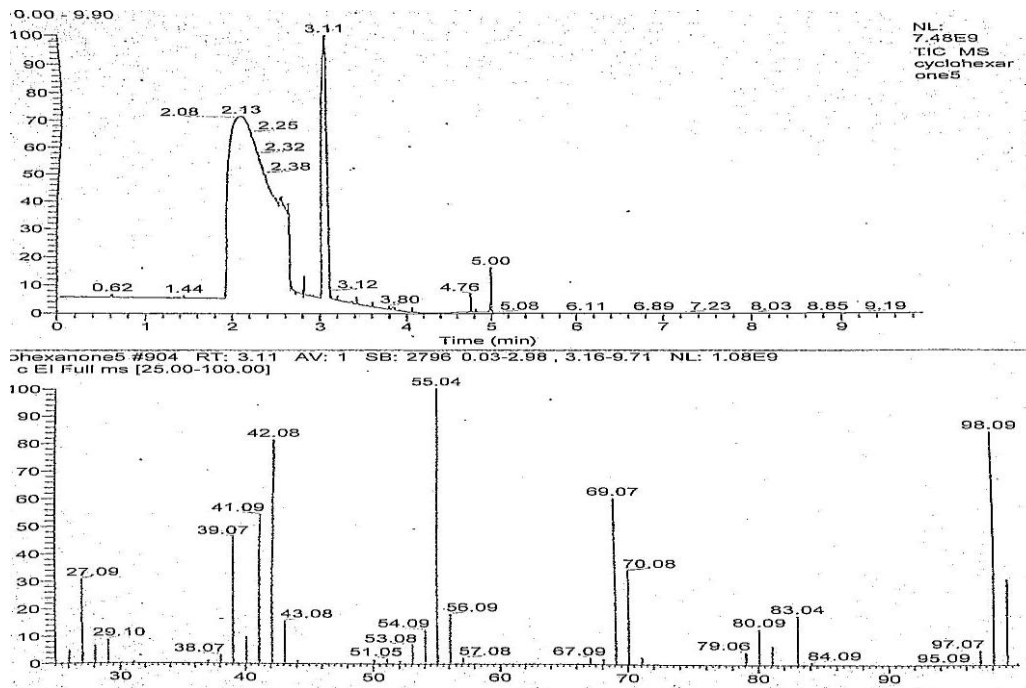
GC-MS spectra of 20% ZnO-Al₂O₃ (Fig IVb)



GC-MS spectra of 40% ZnO-Al₂O₃ (Fig IV c)



GC-MS spectra of Al₂O₃(Fig IVd)



GC-MS spectra of Cyclohexanone (Fig IV e)



Kerala State Council for Science, Technology and Environment

23-09-2016

Dr. Anilkumar C
Principal Scientist & Head
Science Education Division

4/SPS 59/2016/KSCSTE

Dear Dr. Jalaja J Malayan,

Sub:- Financial assistance from KSCSTE for student project reg.
Ref:- Your application dated 3.07.2016 received under Student Project scheme

This is to invite your attention to the reference cited and to inform that the project proposal titled '**Surface characterisation and catalytic activity of ZnO-Al₂O₃ mixed oxides**' submitted by Dr. Jalaja J Malayan as PI and Akhila Binny as student investigator(s) has been approved. An amount of **₹13000/-** is sanctioned by the Council. The budget estimate of the project will be as detailed below.

SL.NO.	ITEMS	AMOUNT(₹)
1.	Consumables	5000
2.	Travel	-
3.	Research Literature & Documentation	-
4.	Others (Sample analysis)	8000
	Total	13000

The PI has to submit the signed 'Terms and Conditions' and the date of start of the project may be intimated to the Council. On completion of the project you should submit one hard copy and a soft copy of the final report (in pdf to spkscste@gmail.com), audited Statement of Expenditure and Utilization Certificate counter signed by the Head of the Institution for releasing the grant. The format for final report, SE & UC can be downloaded from www.kscste.kerala.gov.in.

Thanking you,

Yours sincerely,

Anilkumar C

To,

Dr. Jalaja J Malayan, Associate Professor, Department of Chemistry, Baselius College,
Kottayam 686001

Copy to:

The Principal, Baselius College, Kottayam 686001
Akhila Binny, Student(s), Department of Chemistry, Baselius College, Kottayam 686001

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