

# Immobilization of Imidazolium Hydrogen Sulphate on Silica as Efficient Ionic Liquid for Catalytic Acetylation of Glycerol

<sup>1</sup>Salihu Abdullahi Kiyawa, <sup>2</sup>Sama'ila Mu'azu Batagarawa, <sup>3</sup>Amina Salihi Bayero and <sup>3</sup>Yahaya Aliyu Danmaraya

<sup>1</sup>Department of Chemistry, Kabale University, P. O. Box 317, Kabale, Southwest Uganda.

<sup>2</sup>Department of Pure and Industrial Chemistry, Umaru Musa Yar'adua University, Katsina, Nigeria

<sup>3</sup>Department of Chemistry, Yusuf Maitama Sule University, Kano, Nigeria

## Abstract

Imidazole was immobilized onto silica via (3-chloropropyl) triethoxysilane. Characterization of the catalyst by TEM showed some orderly arrangement of pores similar to that of MCM-41 structure with an average diameter of 2.80 nm. Similarly, characterizations using CHN, FTIR and EDS analysis indicated successful immobilization of the imidazole on the silica matrix. This was later modified with H<sub>2</sub>SO<sub>4</sub> to form RHA-IMIHSO<sub>4</sub> ionic liquid. The catalytic activity of the catalyst was tested in the acetylation of glycerol to achieve a conversion of 75 %. The products obtained were 1,3-dioxane and 1,3-dioxolane.

**Keywords** - Rice husk, imidazole, acetylation, glycerol, dioxane

## I. INTRODUCTION

Many established work have been published on RH silica as a catalyst support (Adam and Ahmed, 2007, Adam et al., 2009, Adam and Fook, Tzong, 2004). The silica in RH has a very fine particle size, with high purity and moreover, the molecular units are dispersed naturally and uniformly. Furthermore, the preparation of silica materials has a benefit of producing quality silica powder and hence will reduce pollution problems (Chang, et al., 2001).

Ionic liquids (ILs) are liquids of which the boiling points are below 100 °C, typically comprising of large organic cations together with an organic or inorganic anion (Wasserscheid and Welton, 2002, Dupont et al, 2002). Especially, the class of imidazolium cation based ILs has proven to be highly attractive and resourceful (Plechkova and Seddon, 2008). Frequently encountered favorable characteristics of imidazolium cation based ILs are for example: high thermal stability, exists in liquid form over a wide temperature range, air and moisture stability, very low vapor pressure, wide electrochemical window, high conductivity and ionic mobility, easy recycling, and serve as a good solvent for a wide variety of organic and inorganic chemical compounds (Dupont et al., 2002, Plechkova and

Seddon, 2008). Besides, imidazolium ILs are “designable” as structural modifications in both the cation (especially the 1 and 3 positions of the imidazolium ring) and anion permit the tuning of properties like, e.g., miscibility with water and organic solvents, melting point and viscosity (Seddon et al., 2000).

Silica supported ILs have found applications as, for instance, a heterogeneous catalyst (Riisager et al., 2006), chromatographic material (Zhou, 2006), electronics (Wasiucionek and Breiter, 2000) and “template” for the formation of advanced nanostructures (Zhou et al, 2004). These silica-IL hybrids combine the advantages of ILs with those of solid silica materials and the ILs can be covalently attached or physisorbed. The physisorbed silica-IL hybrids can be prepared by either deposition of ILs on the silica surface or via the sol-gel technique. Imidazolium ILs have a great potential as templates for the preparation of nanoporous inorganic materials like, e.g., silica and titanium oxide, by the sol-gel process (Taubert, 2005). Imidazolium ionic liquid have also introduced the formation of highly organized nanostructures, large specific surface areas, high porosities and controllable pore sizes with a narrow size distribution (Taubert, 2005, Wang et al., 2007).

Glycerol is a by-product of biodiesel production and there is an alarming increase of glycerol in the market. Currently 350,000 tons per annum (tpa) is being produce in the USA and 600,000 tpa in Europe which is projected to increase due to replacement of 5.75 % of petroleum fuels with biofuel (Umbarkar et al., 2009). Synthesis of value added molecule from glycerol is an attractive alternative as a means of using this abundant raw material. One of the application of glycerol is in the acetalization reaction with aldehydes and ketones to yield isomeric five and six membered cyclic acetals 1,3-dioxin-5-ols as fine chemical intermediates. The acetalization reaction is also important for the protection of carbonyl groups during the manipulation of multifunctional organic molecules. Furthermore the reaction has direct application as fragrances, in cosmetic, food and beverage additives,

pharmaceuticals, in detergents, in lacquer industries and as ignition accelerators antiknocks additives in combustion engines and in port wine production. The research work reported a novel catalyst for the synthesis of the five and six-membered acetals.

## II. EXPERIMENTAL

All chemicals used were of analar grade, and used as purchased without further purification. All glass wares were thoroughly washed with water and rinsed with distilled water before use.

## III. PREPARATION OF CATALYST

The extraction of silica was performed as described by Farouk and Muazu (2013). The catalyst was prepared according to the procedure described below. About 3.0 g of extracted silica powder was added to 1 L of 1.0 M NaOH in a plastic container and stirred for 1 h at room temperature. The sodium silicate formed was filtered to remove undissolved particles. 6.0 mL (24.0 mmol) solution of Chloropropyl tiethoxy silane (CPTES) was then added to the solution of sodium silicate. The solution was titrated slowly with 3.0 M nitric acid to pH 3. The gel obtained was aged for 2 days in a covered plastic container and later separated from mother liquor by centrifuge. The sample was dried at 110 °C for 24 h and ground to powder, it was labeled as RHACCl. 2.0 g of the RHACCl was added to a solution of dry toluene (30ml) followed by addition of imidazole 1.5 g (22.0 mmol) and then triethylamine (3.07 mL, 22.0 mmol). The reaction mixture was refluxed at 110 °C in an oil bath for 48 h. The solid phase was filtered and washed with dichloromethane followed by absolute ethanol. The solid sample was then dried at 100 °C for 24 h and ground to powder. It was later mixed with 5 mL of

0.2M H<sub>2</sub>SO<sub>4</sub> and stirred for 24 h. The resulting solid was washed with water and dried at 100 °C for 24h. This was labelled as RHA-IMIHSO<sub>4</sub>.

### A. Catalyst Characterizations

The prepared catalyst was characterized by FT-IR spectroscopy (Perkin–Elmer System 2000) using KBR as reference material. The topography of the catalyst was obtained by transmission electron microscopy (TEM, model (Philips CM12) analysis. The morphology of the sample was determined by Scanning Electron Microscope (SEM), model Leica Cambridge S360.

### B. Catalytic Activity

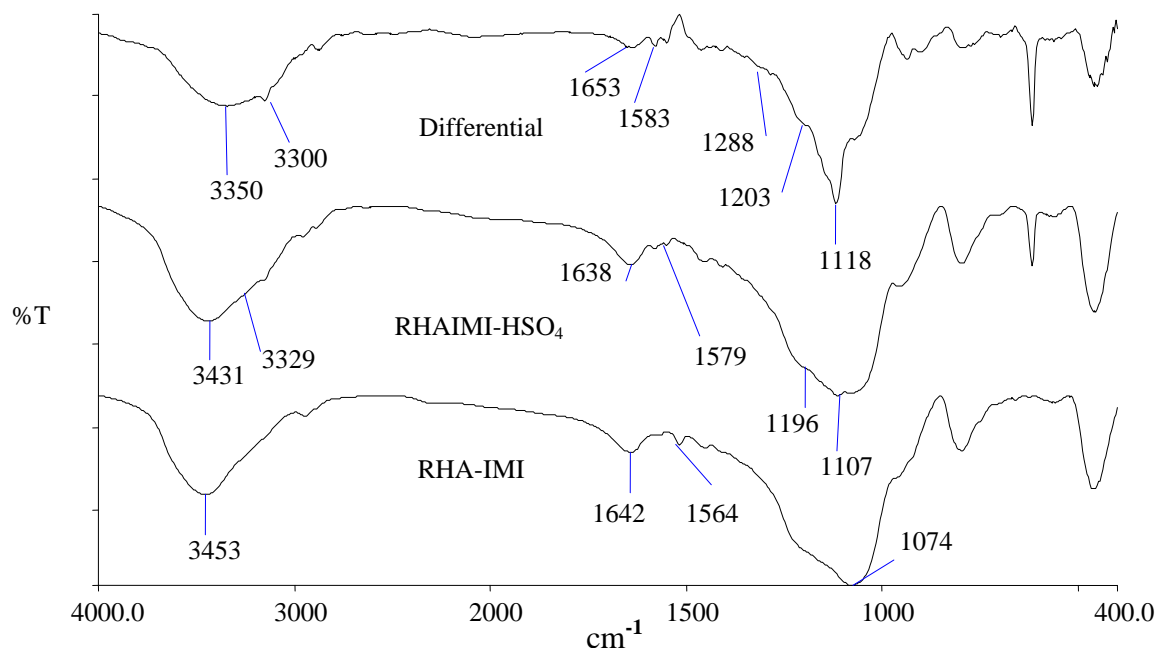
Acetylation reaction of glycerol with benzaldehyde was carried out in a 50 mL two-necked round-bottomed flask equipped with a reflux condenser. A sample of 0.1 g of RHA-IMI (activated overnight at 110 °C to minimize the moisture content) was transferred into the round bottom flask containing a magnetic stirrer, a mixture of glycerol (0.11 mol) and 15 g of toluene as solvent. After achieving the required reaction temperature at 120 °C, 8 mL of benzaldehyde was introduced into the flask. The reaction mixture was refluxed for 10 h. The effect of temperature, mass of catalyst, and reactants mole ratio were studied. An aliquot of the reaction mixture (0.5 mL) was analyzed by GC (Perkin Elmer, Clarus 500) equipped with a capillary column of Elite-wax (30 m x 0.32 mm)

## IV. RESULTS AND DISCUSSION

### A. Characterization of the catalyst

#### B. FT-IR analysis

Figure.1: FTIR spectra of RHA-IMI, RHA-IMIHSO<sub>4</sub> and the differential



The FTIR of RHA had been described by Ahmed and Adam, (2007). The Si-O-Si vibration appeared at  $1101\text{ cm}^{-1}$ , could be associated with the condensed silica network in RHA silica. This vibration was observed to have shifted to  $1078\text{ cm}^{-1}$  in RHACCl and  $1085\text{ cm}^{-1}$  in RHA-IMI. This reflected the chemical transformation that took place adjacent to the Si-O-Si framework by the initial immobilization of CPTES and later by imidazole. The broad band around  $3446\text{ cm}^{-1}$  is usually assigned to the O-H vibration of Si-OH and HO-H. The presence of imidazole ring was evident by the appearance of imine, C=N stretching at  $1646\text{ cm}^{-1}$  and the stretching of C-N at  $1568\text{ cm}^{-1}$  were very clear in the differential spectrum. Bands at  $1229\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  in the differential correspond to the Si-C bond. The appearance of vibrations due to C-N and C=N groups indicated a successful incorporation of the imidazole molecule into the RHACCl, forming a new compound RHA-IMI.

Figure 1 shows that the FTIR spectra of RHA-IMI, RHA-IMIHSO<sub>4</sub> and the differential

### C. SEM/EDS analysis

Figure 2 shows the TEM image of the catalyst. The presence of pores generally indicated the amorphous nature of the catalyst. EDS analysis showed the presence of nitrogen in RHA-IMI which we can conclude that the imidazole was immobilized on silica. From the amount of Cl present in the EDS of RHACCl (3.07 %) and RHA-IMI (1.19 %), the percentage loading of imidazole on the silica was calculated to be 61.27 % (Adam et al., 2010).

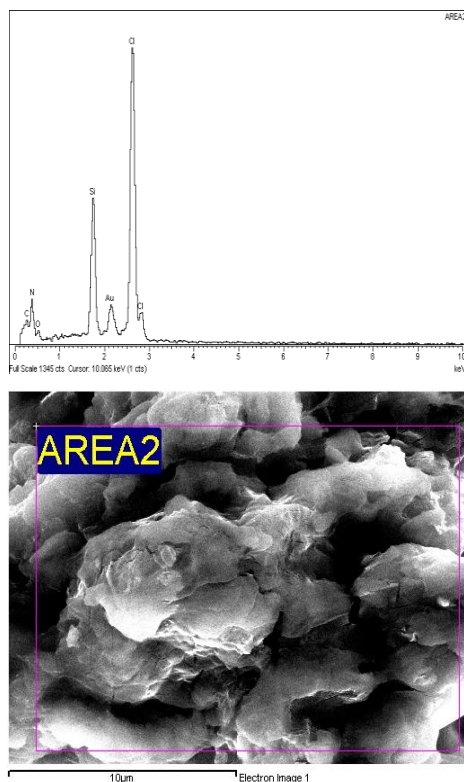


Fig. 2 SEM and EDS result of RHA-IMI

### D. TEM analysis

TEM micrograph of RHA-IMI is shown in Figures 3. It consists of well organized mesopores packed in hexagonal symmetry similar to MCM-41 structure with an average diameter of 2.80 nm.

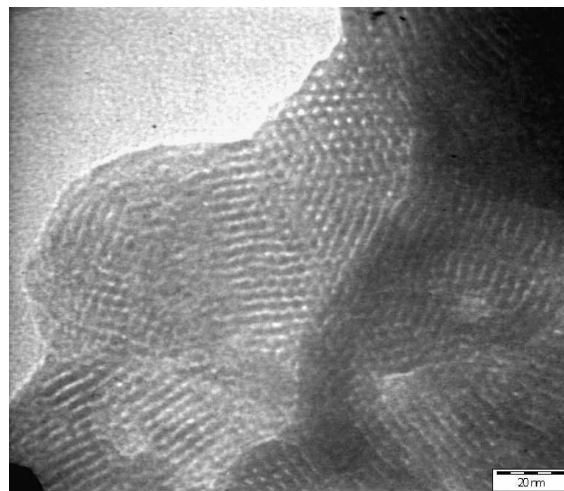


Fig. 3: TEM picture of RHA-IMI showing the Honey comb-like structures, similar to MCM-41

### F. catalytic reactions

The reaction of glycerol with benzaldehyde was carried out at various time intervals using different amounts of the catalyst and under different solvent conditions. The main products obtained from the reaction were 1,3-dioxane and 1,3-dioxolane as shown in Figure 4. The identification of these compounds was done by the GC-MS analysis. The optimized reaction conditions were determined using time of reaction, mass of catalyst used, amount of solvent involved and mole ratio of reactants.

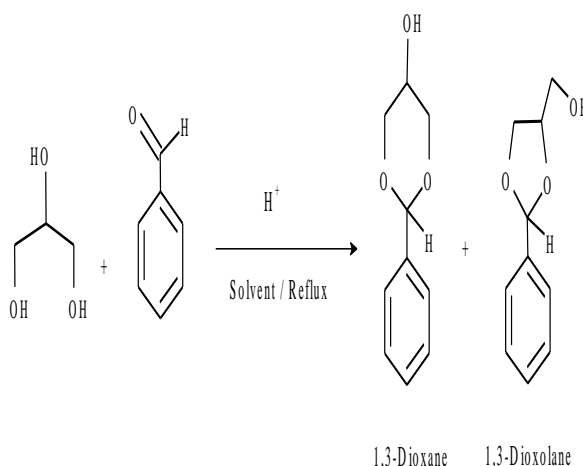
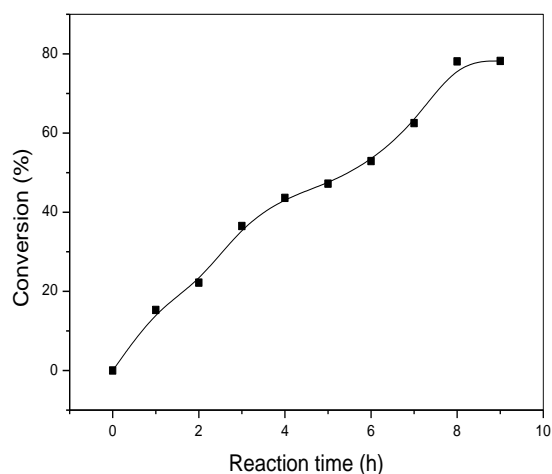


Fig 4: The acetalization of glycerol with benzaldehyde over an acid catalyst

### E. effect of reaction time

The initial conversion of benzaldehyde during the first hour was 16 % and increased to a maximum of 78 % in 8h. Thereafter, there was no significant change in the conversion.



**Fig. 5** Effect of time on the conversion of benzaldehyde in the acetalization of glycerol with benzaldehyde over RHA-IMIHSO<sub>4</sub>. The reaction conditions: mass of catalyst 0.15 g, mole ratio of Benz: Gly 1:2, and reaction temperature, 120 °C

### G. Effect of reaction temperature

The effect of temperature on the acetylation of glycerol was studied by varying the temperature from 100 to 120 °C at interval of 10 °C using the classical one-factor-at-a-time (OFAT) over a constant mass of 100mg RHA-IMIHSO<sub>4</sub> while other parameters were kept constant (benzaldehyde = 0.1 mol; glycerol = 0.11mol; toluene = 15mL and reaction time of 10 h).

The result showed that the conversion of benzaldehyde increases with an increase in temperature as shown in Table 1. At 90 °C the conversion was 63 % which increased to 71 % when the reaction temperature was raised to 100 °C. The optimum conversion of 84 % was achieved at 120 °C. Temperature above 120 could not be studied since it exceeded the boiling point of one of the reactants.

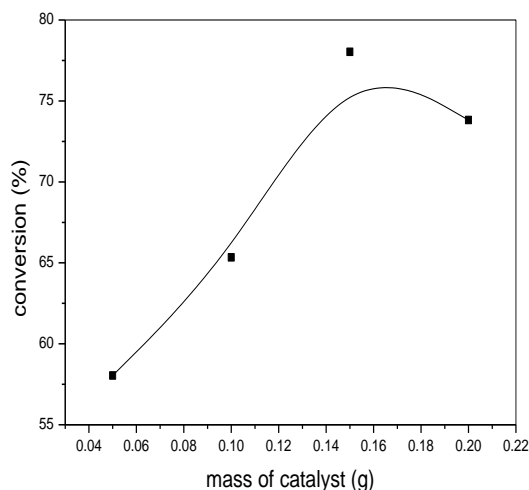
**Table 1.0: Effect of temperature on the conversion of glycerol**

S/N	Temperature (°C)	Conversion (%)
1	90	63
2	100	71
3	110	76
4	120	84

### H. effect of mass of catalyst

The effect of mass of catalyst on the acetalization of glycerol was studied by varying the weight between 50 and 200 mg, keeping the reaction temperature constant (120 °C), and the results is presented in Fig. 4. The conversion of benzaldehyde was found to increase from 57 % to 77 % when the mass of catalyst increased from 50 to 200 (mg). Further increase in mass of catalyst above 150 mg did not result in any increase of conversion. Instead, a slide decrease in the conversion was observed, which

could probably be due to the blocking of the active sites. Besides that, the decrease in the conversion could also arise due to the poisoning of the nitrogen sites responsible for the catalysis by water molecules via hydrogen bonding (Adam et al., 2010).



**Fig. 6:** Effect of catalyst mass on the conversion of glycerol

## V. CONCLUSION

In this paper, a heterogenous catalyst was prepared from functionalized RHA, CPTES and imidazole using a simple and eco friendly procedure. The spectroscopic data obtained showed that the imidazole molecule has been successfully anchored on the silica. The RHA-IMIHSO<sub>4</sub> showed good catalytic activity towards the acetalization of glycerol with 84% conversion of benzaldehyde to new products. The catalyst was easy to prepare and handle, thus it also promotes green chemistry.

## REFERENCES

- [1] Adam, F. Ahmed A. E. (2007). Indium incorporated silica from rice husk and its catalytic activity. *Micropor. Mesopor. Mater.*, 103, 284-295.
- [2] Adam, F. Premalatha R. and Iqbal A. (2009). The complete conversion of cyclohexane into cyclohexanol and cyclohexanone by a simple silica-chromium heterogeneous catalyst. *Appl. Catal. A Gen.*, 357, 93-99
- [3] Adam, F. and Fook. C.L (2009). Chromium modified silica from rice husk as an oxidative catalyst. *J. Porous Mat.*, 16, 291-298.
- [4] Chang, F.W. Tsay, M.T. and Liang. S.P. (2001). Hydrogenation of CO<sub>2</sub> over nickel catalysts supported on rice husk ash prepared by ion exchange. *Appl. Catal. A* 209, 217-227
- [5] Dupont, J. de Souza, R.F. and Suarez P.A.Z (2002). Ionic liquid (molten salt) phase organometallic catalysis. *Chem Rev* 102:3667
- [6] Plechkova, N.V. Seddon, K.R. (2008). Application of ionic liquid in chemical industries. *Chem Soc Rev* 37-123.
- [7] Riisager, A. Fehrmann, R. Haumann, M. and Wasserscheid P. (2006) Morphological Control of Room Temperature ionic liquid Templated Mesoporous Silica Nanoparticles for Controlled Release of Antibacteria agents. *Top Catal* 40-91.
- [8] Seddon, K.R. Stark, A. and Torres M. (2000). Influence of chloride, water and organic solvents on the physical properties of ionic liquids. *Pure Appl Chem* 72-2275.

- [9] Taubert A. (2005). Cubes and Hollow Rods from Ionic Liquid Emulsions. *Acta Chim Slov* 52, 168-170.
- [10] Tzong, H. L.(2004). Preparation and characterization of nano-structured silica from rice husk. *Material Science and Engineering: A* 364, 313-323.
- [11] Umbarkar, S.B., Kotbagi, T.V. Biradar, A.V., Pasricha, R., Chanale, J., Dongare, M.K., Madame, A.S., Lancelot, C., and Payen, E. (2009). Acetalization of glycerol using mesoporous MoO<sub>3</sub>/SiO<sub>2</sub> solid acid catalyst. *J. Mol. Catal. A* 310, 150-158.
- [12] Wang, T., Kaper, H., Antonietti, M. and Smarsly, B (2007). Templating Behaviour of a long chain ionic liquid in the hydrothermal synthesis of mesoporous silica. *Langmuir* 23, 1489-1495.
- [13] Wasserscheid, P. and Welton T. (2002). *Ionic liquids in synthesis*. VCH-Wiley, WEINHEIM
- [14] Zhou H. (2006). A metal-organic framework with entatic metal centres exhibiting high gas adsorption affinity. *Chem Eng Comm* 1963-1660.