SYNTHESIS OF ORGANOAMINE-SILICA HYBRIDS USING CASHEW NUT SHELL LIQUID COMPONENTS AS TEMPLATES FOR THE CATALYSIS OF A MODEL HENRY REACTION

[1]SC Msigala and JEG [2]Mdoe*

[1]Department of Physical Sciences, Sokoine University of Agriculture, P. O. Box 3038, Morogoro, Tanzania
[2]Chemistry Department, University of Dar es Salaam, P. O. Box 35061, Dar es Salaam, Tanzania
*E-mail: mdoe@chem.udsm.ac.tz

ABSTRACT

Organoamine-silica hybrids were prepared by a co-condensation of tetraethoxysilane (TEOS) and different aminoalkoxysilanes, namely, 3-aminopropyltrimethoxysilane, N-(3(trimethoxysilyl)propyl)-ethylenediamine and 3[2(2-amino)ethylamino]propyl trimethoxysilane, at different ratios using cashew nut shell liquid (CNSL) components as templates. Of the major components of CNSL tested, only cardanol was found to be efficient as a template as it yielded 66% of the hybrid. The prepared materials were characterized by diffuse reflectance Fourier Transform Infrared (FTIR), Atomic Force Microscopy and acid titration. Results indicated that indeed the organoamine groups were attached onto the silica surface, with a maximum loading of 2.9 mmol organic group per g silica. The materials were found to be very active as catalysts in a model Henry reaction, with yields ranging from 81% to 98%. The catalytic efficiency was found to depend on the type of template, amount of loading, type of aminoalkoxysilanes incorporated onto the silica framework and the ratio of aminoalkoxysilane to TEOS.

Key words: Organoamine-silica hybrids, micelle templated silica, cashew nut shell liquid.

INTRODUCTION

The discovery of ordered mesoporous silicates, M41S (Beck *et al*. 1992) about two decades ago has renewed an interest in developing template-directed materials using various surfactants. As such, a number of surfactants ranging from both neutral to ionic have been used in the process. Major focus so far has been on the preparation of organic-silica hybrids by direct incorporation of organic groups through co-condensation or by grafting the organic groups onto the surface of pre-formed mesoporous silica using commercial neutral or cationic surfactants (Macquarrie *et al*. 1999, Huh *et al*. 2004, Yokoi *et al*. 2003, Wang *et al*. 2005). The co-condensation method, however, is often preferred to the grafting pathway because it minimizes processing steps and provides a more uniform distribution of the organic

functionalities (Walcarius *et al*. 2003). In addition, one-pot co-condensation synthesis often provides a higher loading of organic functionalities without blocking the framework mesopores (Macquarrie *et al*. 1997).

Organic-silica hybrids nanostructures (*i.e.* nanoparticles such as hollow spheres, rods, fibers or tubes) have so far found a number of applications in catalysis (Mdoe 2002), separation (Yoshitake *et al*. 2003) and sensor design (Lin *et al*. 2001). In catalysis, for instance Mdoe *et al*. (2003a) synthesized polyamine-silica hybrids that were used effectively as catalysts for epoxidation of enones. On the other hand, Macquarrie *et al*. (1997) found that γ-aminopropyl-silica were effective catalysts for the Knoevenagel condensation of a wide range of carbonyl compounds. Furthermore, Mdoe *et al*.

(2003b) prepared organoamine-silica hybrids on neutral commercial templates, materials that showed good to excellent activities and selectivity in model Michael addition reactions in a range of substrates. In a different study, Hilonga *et al.* (2009) managed to prepare polyamine-silica hybrids using cashew nut shell liquid (CNSL) as a template. The resultant hybrids had desirable properties similar to those prepared over commercial templates. The hybrids were successfully applied in the immobilization of invertase enzyme (Kinunda *et al.* 2011) as well as in supporting copper Schiff base catalyst (Hamad *et al.* 2011). The immobilized invertase showed higher activity than the ones prepared over commercial templates whereas the supported copper Schiff base catalysts were active and reusable in the epoxidation of higher alkenes at room temperature and in oxidation of maleic acid. With the exception of the study on the suitability of the materials to support copper Schiff base catalysts, the potential of the CNSL-templated organoamine-silica hybrids as base catalysts has never been described. In addition, the specific component(s) of the CNSL responsible for the templating process during the synthesis of the hybrids has never been established.

In this paper we report results on the synthesis of organoamine-silica hybrids using CNSL components as templates. Results on the catalytic activity of the materials are also reported.

EXPERIMENTAL
Materials and Reagents
Cashew nut shells were collected from Mtwara cashew nut processing factory, in Tanzania and taken to the Chemistry laboratory at the University of Dar-es-Salaam for further processing. Chemicals such as 3-[2(2-amino)ethylamino]propyltrimethoxysilane (assay 97%), 3-

aminopropyltrimethoxysilane (assay 97%), N-(3-(trimethoxysily)propyl)-ethylene diamine (assay 97%), nitroethane and other standard laboratory grade reagents were purchased from Aldrich, whereas tetraethoxysilane, (assay $\geq$ 98%) was purchased from Fluka Chemie. All chemicals were used as received.

Extraction of Cashew Nut Shell Liquid (CNSL)
The CNSL was extracted by soaking cashew nut shells in petroleum ether for three days. Dark brownish oil was obtained. The oil was concentrated using a rotavap machine (model Buchi R-205) at about 40°C of water bath.

Isolation and Decarboxylation of Anacardic Acid
Isolation of anacardic acid from natural CNSL was done using a procedure reported by Paramashivappa *et al.* (2001), with some modifications (Philip *et al.* 2007). Thereafter the isolated anarcadic acid was decarboxylated by heating it in a furnace at about 200°C for 4 h to achieve cardanol. The decarboxylation was proved by FTIR spectroscopy of cardanol.

Synthesis of Organoamine-Silica Hybrids
Cardanol and anacardic acid, being the major components of technical and solvent extracted CNSL, respectively, were screened as templates in the synthesis of organoamine-silica hybrids. The synthesis was done following a procedure reported by Hilonga *et al.* (2009). The organic group precursors, *i.e.*, 3-aminopropyltrimethoxysilane, N-(3-(trimethoxysily)propyl)-ethylene diamine or 3-[2(2-amino)ethylamino]propyltrimethoxysilane and TEOS were added at molar ratios of organic group to silica precursors of 1:4 or 1:9.

Some organoamine-silica hybrids were prepared through a co-templating route whereby a mixture of cardanol and *n*-dodecylamine were used as a template. In this case, 2.5 g of *n*-dodecylamine was mixed with 1.5 g of cardanol in an aqueous ethanol (ethanol 46 ml of absolute ethanol and 53 ml of distilled water) at room temperature. In some cases *n*-dodecylamine, which is an established commercial template (Macquarrie *et al*. 1999), was used alone for comparison purposes.

Characterization of the Organoamine-Silica Hybrids

The hybrids were characterised by a variety of standard techniques. The physical structure of the materials was studied by Atomic Force Microscopy (AFM) on a Version 3.0 Digital AFM instrument. On the other hand, Infrared (IR) spectra were measured on a Perkin-Elmer 2000 FTIR spectrometer fitted with a diffuse reflectance unit to establish the functional groups present on the surfaces of the materials. The samples were initially dried at 100°C prior to analysis and then run at room temperature as mixtures with KBr. Determination of the amount of surface bound species (*i.e.*, loading) was done by HCl acid titration. Typically, the amount of surface bound species is equivalent to the amount of HCl acid consumed.

Catalytic Activity Tests

A Henry reaction was used as a model base catalysed reaction to test the activity of the prepared materials. The reaction was carried out as follows; 15 ml (0.22 mol) nitroethane was mixed with 3 ml (0.03 mol) benzaldehyde in the presence of 0.5 g organoamine-silica hybrid and 0.5 ml *n*-dodecane as a gas chromatography (GC) internal standard. The mixture was refluxed and the progress of the reaction monitored by withdrawing 1 ml of the reaction mixture periodically, and running it in a GC.

RESULTS AND DISCUSSION

The Suitability of the Major Components of CNSL as Templates in the Synthesis of Organoamine-Silica Hybrids

According to Tyman *et al*. (1978), a typical solvent extracted CNSL contains 60 – 65% anarcadic acid, 15 - 20% cardol, 10% cardanol and traces of 2-methyl cardol. Upon heating to about 200°C anarcadic acid is readily decarboxylated to give cardanol. In this work anarcadic acid and cardanol were used as templates in the synthesis of organoamine-silica hybrids. It was observed that whereas cardanol gave 66.3% yield of the hybrid, anarcadic acid gave only 9.2% yield. The low yield observed in the case of anarcadic acid could be attributed to the possible reaction between the carboxylic groups in the anarcadic acid and amino groups in the aminoalkoxysilanes. As a results, self-catalysis of the co-condensation process was not possible hence leading to low yield. It has been established before that amines do catalyse the condensation of silica precursors in a sol-gel process (Jones 2001). Due to the low yield obtained when anarcadic acid was used as a template, most of the hybrids reported in this work were prepared using cardanol as a template.

Since the prepared materials were basic in nature, HCl acid titration technique was employed for determining the amino groups loading onto the silica. The results obtained are shown in Figure 1. It can be seen from this figure that the overall organic groups loading ranges from 0.5 to 2.9 mmol g^{-1}. It is also seen that at 1:9 aminoalkoxysilane to TEOS ratio the co-templated hybrids show the highest loadings at this ratio regardless of the type of the aminoalkoxysilane. At this ratio the organic group loading increases depending on the nature of the template. The trend of the loading in increasing order is cardanol-templated hybrid < dodecylamine-templated hybrid < co-templated hybrid. The same trend is observed in all classes of orgnoamine hybrids (i.e., monoamine-,

diamine- and triamine-based hybrids). However, when the ratio of aminoalkoxysilane to TEOS is increased from 1:9 to 1:4 the loading trend becomes: cardanol templated hybrid < co-templated hybrid < dodecyalamine-templated hybrid. As explained above, cardanol always produced materials with the lowest loadings regardless of the nature of the amino group as well as the aminoalkoxysilane to TEOS ratio. This observation may be due to the fact that the co-condensation process involving cardanol as a template is the one with the least amount of amino groups in the reaction mixture since the only source of the amino groups is the aminoalkoxysilane. The other systems have dodecyalamine as an additional source of amino groups apart from the aminoalkoxysilane. In that case it is least catalysed and consequently less amino group loadings. At higher ratios of aminoalkoxysilane to TEOS, cardanol still produces hybrids with least loadings. However, the co-templated materials showed consistently higher loadings relative to those produced from dodecylamine, an observation that needs further exploration.
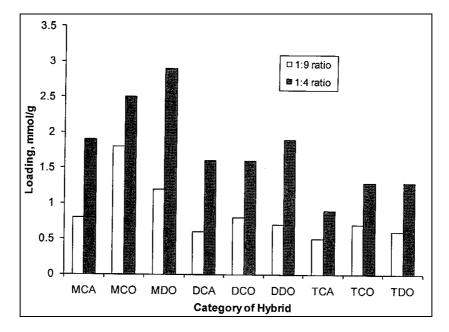

Figure 1: Organic group loadings for the prepared organoamine-silica hybrids at aminoalkoxysilane to TEOS ratios of 1:4 and 1:9 (**Note:** MCA = cardanol-templated monoamine hybrid, MCO = co-templated monoamine hybrid, MDO = dodecylamine-templated monoamine hybrid, DCA = cardanol-templated diamine hybrid, DCO = co-templated diamine hybrid, DDO = dodecylamine-templated diamine hybrid, TCA = cardanol-templated triamine hybrid, TCO = co-templated triamine hybrid, TDO = dodecylamine-templated triamine hybrid).

As seen from Figure 1 loadings at a ratio of 1:4 are higher than at 1:9, an observation that is also observed by Macquarrie *et al.* (1999) and Hilonga *et al.* (2009). At a 1:9 ratio most silanol functional groups are left unmodified owing to much higher amount of silica precursor relative to the amount of aminoalkoxysilane.

The type of aminoalkoxysilane incorporated into silica also had some effects on the loading. Triamine-based hybrids had the least loading, followed by diamine- and monoamine-based hybrids in that order. This observation is attributed to steric effects. A triamino group being the largest molecule of the three is most sterically hindered and therefore only a few molecules are anchored onto silica surface whereas for the monoamine, many molecules could be anchored owing to their small sizes.

The Identities of the Functional Groups on the Organoamine-silica Hybrids
Analysis of the resulting hybrids by diffuse reflectance FTIR showed that the expected organic functionalities were present in the frameworks of the hybrids as exemplified by Figure 2. This is evidenced by the N-H bending mode at about 1530 cm^{-1} as well as the aliphatic C-H stretching mode at 2950 cm^{-1}, as reported also elsewhere (Mdoe 2002). In addition to the vibrations attributable to the supported organic groups, vibrations associated with the silica framework were also present. These were observed at 1850 cm^{-1} and 1100 cm^{-1} due to the Si-O-Si bond. All spectra also showed a hydrogen bonded Si-OH stretching band at 3200 - 3650 cm^{-1}. The N-H stretching band appears in a similar region but is masked by the Si-OH band. Most spectra constituted a peak for adsorbed water molecules at around 1650 cm^{-1}.
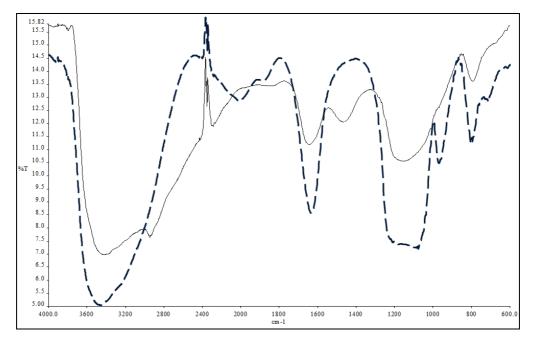

Figure 2   FTIR spectrum for a) a typical organoamine-silica hybrid, b) a similarly prepared unmodified silica.

Atomic Force Microscopy Data
A grain of a material is usually a complex entity composed of a porous solid, serving as the support for one or more catalytically active phase(s), in turn influencing catalytic activity. In this study, the grain sizes of the prepared hybrids were determined by AFM. A typical micrograph is given in Figure 3.

Generally, the primary particles of the materials were irregular in shape with average grain sizes ranging from 0.25 to 0.4 µm. It was also observed that the micrographs of hybrids prepared using cardanol had relatively smaller grain sizes than those prepared using *n*-dodecylamine or a co-template. The sizes were generally smaller than those of similar materials prepared using CNSL as a template (Hilonga

et al. 2009). In the later case, the grain size average for polyamine-silica hybrids prepared using technical CNSL was about 0.5 µm wide. The reason for this observation is not very apparent, though it could be attributable to synergistic effects of the phenolic components in the CNSL. This calls for further investigation.
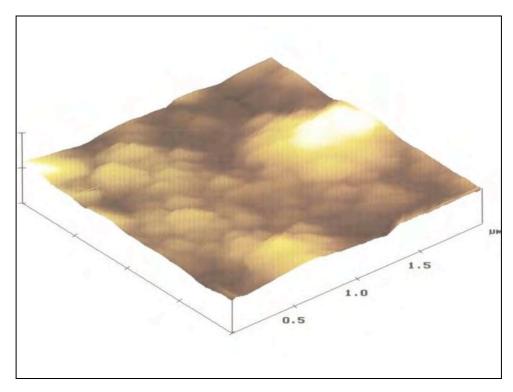

Figure 3:   A three dimensional AFM micrograph for a typical organoamine-silica hybrid.

Catalytic Activity of the Prepared Organoamine-silica Hybrids in a Model Reaction
The prepared materials were tested as base catalysts in a reaction between excess nitroethane and benzaldehyde, a Henry reaction. The progress of the reaction was monitored by GC using *n*-dodecane as an

internal standard and the results are given in Figures 4 – 8.

Figures 4 and 5 show results for conversion of benzaldehyde to product by monoamine- and diamine-based hybrids, respectively, that were prepared using different templates at an aminoalkoxysilane to TEOS ratio of 1:9. As seen in the figures the type of

template used in preparing the hybrids had some influence on the catalytic efficiency. Whereas cardanol-templated hybrids afforded an 80% conversion to product after 180 min., co-templated hybrids afforded about 99% after 140 min. On the other hand, the dodecylamine-templated hybrids gave about 98% product after 180 min. Thus, cardanol-templated hybrids ranked lowest in

the catalytic efficiency of all the three categories of the hybrids. It has been reported before that a template determines the arrangement of active groups and surface area of hybrids (Anderson *et al.* 1993), which in turn influence catalytic efficiency. This is consistent with the low organic group loading discussed before.
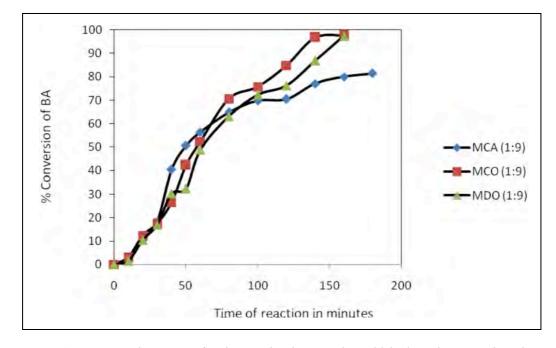

Figure 4   Conversion curves for the reaction between benzaldehyde and excess nitroethane using MDO (1:9), MCA (1:9) and MCO (1:9) hybrids as catalysts.
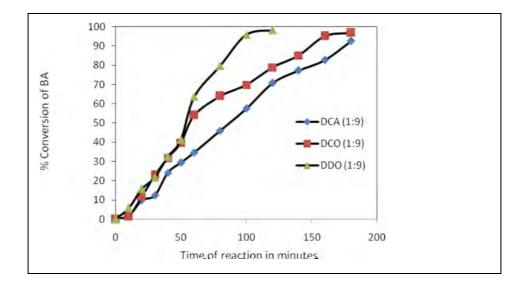
Figure 5   Conversion curves for the reaction between benzaldehyde and excess nitroethane using DCA (1:9), DDO (1:9) and DCO (1:9) as catalysts.

The ratio of aminoalkoxysilane to TEOS is another factor that influenced catalytic efficiency. A greater ratio leads to higher loading and hence higher catalytic activity. This is exemplified by Figures 6 and 7. Consequently the ratio of aminoalkoxysilane to TEOS of 1:4 led to a higher catalytic activity compared to 1:9 ratios, regardless of the type of template used. The results concur well with other similarly published results (Mdoe 2002 and Mdoe *et al.* 2003a).
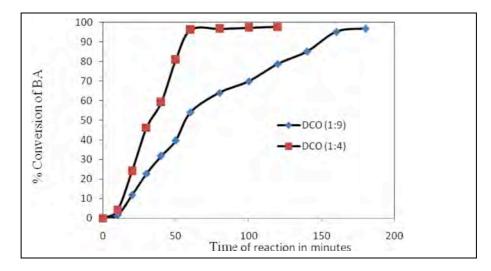

Figure 6   Conversion curves for the reaction between benzaldehyde and excess nitroethane using DCO (1:4) and DCO (1:9) hybrids as catalysts.
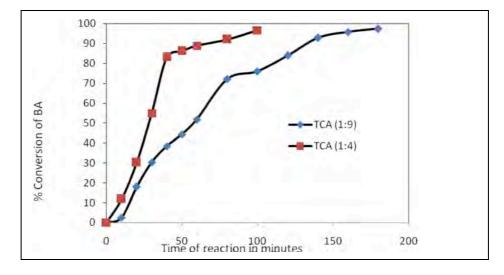
Figure 7: Conversion curves for the reaction between benzaldehyde and excess nitroethane using TCA (1:4) and TCA (1:9) hybrids as catalysts.

The presence of densely populated organic groups reduces the surface areas and pore volume of the materials (Krishna *et al.* 2007). Densely populated organoamine catalysts are typically accompanied by loss of catalytic efficiency. For higher loaded hybrids most active groups are embedded within the bulk structure and hence do not take part in catalysis. For instance, Mdoe *et al.* (2003b) observed that organoamine-silica hybrids with loading of 2.9 mmol per g gave 95% conversion of Michael product in 1.5 h whereas a 2.2 mmol per gram material afforded 94% in 1.2 h. However, this observation was not very apparent for the materials reported in this study. This is probably due to the fact that CNSL based surfactants produce hybrids with larger pore sizes (Hilonga *et al.* 2009) thus reducing diffusion limitations.

The type of aminoalkoxysilane incorporated onto silica surface also influenced the catalytic efficiency of the prepared materials. The triamine-based hybrids had the highest catalytic efficiency compared to diamine- and monoamine-based hybrids (Figure 8). A triamine molecule has three amino groups, thus has the greatest number of active sites per molecule. Hence, if all parameters are held constant, the trend of catalytic efficiency in the increasing order is monoamine-, diamine- and triamine-based hybrids. A different study by Mdoe (2002) also showed triamine-based hybrids to be more active than their diamine-based counterparts.
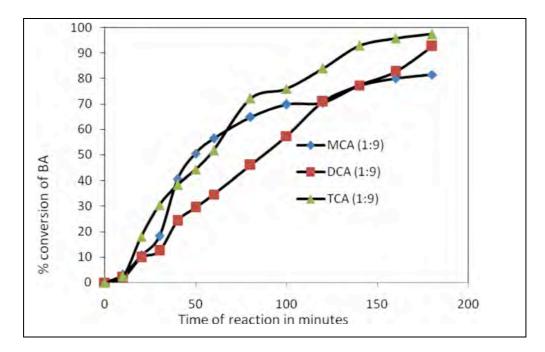
Figure 8   Conversion curves for the reaction between benzaldehyde and excess nitroethane using MCA (1:9), DCA (1:9) and TCA (1:9) hybrids as catalysts

CONCLUSION

In conclusion, organoamine-silica hybrids were successfully synthesized using CNSL components (i.e., cardanol and anarcadic acid) as structure directors. However, cardanol was found to be more effective as it gave 66% yield whereas anarcadic acid gave only 6%. The hybrids were effective as base catalysts in a model Henry reaction, with yields ranging from 81% to 98%. The catalytic activity was however dependent on the type of template used in preparing the hybrids, the organic group loading, and the type of amino group incorporated onto the silica framework.

REFERENCES

Anderson S, Anderson H and Sanders KMJ 1993 Expanded Roles for Template in Synthesis. *J. Acc. Chem. Res.* **26**: 469-475

Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CTW, Olson DH and Sheppard EW 1992 A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.* **114**: 10834-10843

Hamad F, Mubofu EB and Makame YMM 2011 Wet Oxidation of Maleic Acid by Copper (II) Schiff Base Catalysts Prepared Using Cashew Nut Shell Liquid Tempalates. *Catal. Sci. Technol.* **1**: 444-452

Hilonga A, Mdoe JEG, and Mkayula LL 2009 Synthesis of Mono-, Di- and Triamino-silica Composites Using Cashew nut Shell Liquid as a Template *Int. J. Biochemphys* **17**: 26-31

Huh S, Wiench JW, Yoo J-C, Pruski M, and Lin VSY 2003 Organic Functionalization and Morphology Control of Mesoporous Silicas via a Co-Condensation Synthesis Method *Chem. Mater.* **15**: 4247–4256

Jones SM 2001 Amine catalysed condensation of tetraethylorthosilicate *J. Non-crystalline solids* **291**: 206-210

Krishna K, Sharma and Asefa T 2007 Efficient Bifunctional Nanocatalysts by Simple Postgrafting of Spatially Isolated Catalytic Groups on Mesoporous Materials. *J. Angew. Chew. Int. Ed.* **46**: 2879-2882

Lin VS, Lai CY, Huang J, Song SA and Xu S 2001 Molecular recognition inside of multifunctionalized mesoporous silicas: toward selective fluorescence detection of dopamine and glucosamine. *J Am Chem Soc.* **123**: 11510-11511

Macquarrie DJ, Clark JH, Lambert A, Mdoe JEG, and Priest A 1997 Catalysis of the Knoevenagel Reaction by γ-Aminopropylsilica. *J. Reactive & Func. Polymer.* **35**: 153-158

Macquarrie, DJ, Dominic BJ, Mdoe JEG and Clark JH 1999 Organically modified Hexagonal Mesoporous Silicates. *New J. Chem.* **23**: 539-544

Mdoe JEG 2002 Preparation, Characterisation and Application of Polyaminesilica hybrids in the epoxidation of, α,β-Unsaturated olefins. *Bull. Chem. Soc. Ethiop.* **16:** 103-112

Mdoe JEG, Clark JH and Macquarrie DJ 2003b Catalysis of the Michael Reactions by N,N'-Dimethylaminopropyl Derivatised Micelle Templated Silica: Effect of Solvent And Catalyst Loading. *Bull. Chem. Soc. Ethiop.* **17**: 219-234

Mdoe JEG, Macquarrie DJ, Clark JH 2003a One-pot Preparation of Polyamine-silica Hybrids and Their Use in the Epoxidation of Cyclohex-2-ene-1-one. *J. Molecular Catal. A. Chem.* **198**: 241-247

Mubofu EB, Mdoe JEG and Kinunda G 2011 The activity of invertase immobilized on Cashew Nut Shell Liquid-templated large pore silica hybrids. *Catal. Sci. Technol.,* **1**: 1423-1431

Paramashivappan R, Kumar PP, Vithayathil JP and Rao SA 2001 Novel Method for Isolation of Major Phenolic Constituents from Cashew Nut Shell Liquid. *J. Agric. Food Chem.* **49**: 2548-2551

Philip JYN, Buchweishaija J, Mkayula LL and Ye L 2007 Preparation of molecularly imprinted polymers using anacardic acid monomers derived from Cashew Nut Shell Liquid. *J. Agric. Food Chem.* **55**: 8870–8876

Tyman JHP, Wilczynski D and Kashani MA 1978 Compositional studies on technical cashew nutshell liquid (CNSL) by chromatography and mass spectroscopy. *J. American Oil Chemists' Soc.* **55**: 663-668

Walcarius A and Delacote C 2003 Rate of Access to the Binding Sites in Organically Modified Silicates. 3. Effect of Structure and Density of Functional Groups in Mesoporous Solids Obtained by the Co-Condensation Route. *Chem. Mater.* **15**: 4181-4192.

Wang X, Tseng Y, Chan JCC and Cheng S 2005 Catalytic Applications of Aminopropylated Mesoporous Silica Prepared by a Template Free Route in Flavanones Synthesis. *J. Catal.* **233***: 266-275

Yokoi T, Yoshitake H and Tatsumi T 2004 Synthesis of amino-functionalized MCM-41 *via* direct co-condensation and post-synthesis grafting methods using mono-, di- and tri-amino-organoalkoxysilanes. *J. Mater. Chem.* **14**: 951-957

Yoshitake H, Yokoi T and Tatsumi T 2003 Adsorption Behavior of Arsenate at Transition Metal Cations Captured by Amino-Functionalized Mesoporous Silicas. *Chem. Mater.* **15**: 1713-1721