

# WET OXIDATION OF MALEIC ACID BY A PUMICE SUPPORTED COPPER (II) SHIFF BASE CATALYST

JEG Mdoe<sup>1\*</sup> RAJ Minja<sup>2</sup> and L Daniel<sup>2</sup>

<sup>1</sup>Chemistry Department, University of Dar es Salaam, P. O. Box 35061, Dar es Salaam, Tanzania

<sup>2</sup>Department of Chemical and Mining Engineering, University of Dar es Salaam, P. O. Box 35131, Dar es Salaam, Tanzania

\*Corresponding author: james\_mdое@yahoo.co.uk

---

## ABSTRACT

*Pumice supported Cu (II) Schiff base catalysts were prepared by surface chemical modification followed by complexation with Cu (II) acetate. The resulting materials were characterised by Diffuse Reflectance Fourier Transform Spectroscopy (DRIFTS) to confirm the modification. The materials were tested in a wet oxidation of maleic acid using air or hydrogen peroxide as an oxidant. Results indicate that up to 80% degradation of maleic acid could be achieved in the presence of the catalyst using hydrogen peroxide as an oxidant. The degradation was found to depend on the type of oxidant, temperature and whether the parent pumice was acid pre-treated or not prior to the preparation of the catalyst.*

---

**Keywords:** Supported Cu (II) Schiff base, maleic acid degradation, pumice

## INTRODUCTION

Water pollution is a serious problem in the global context. It has been suggested that it is the leading cause of deaths and diseases worldwide and that it accounts for the deaths of more than 14,000 people daily (West 2006). Tanzania is not an exception. It is reported that among the potential sources of ground and surface water pollutants in Tanzania include discharges from industrial processes, domestic wastewaters and agricultural activities (Sheya and Nyamsika 1996). One among the pollutants found in the discharged wastewater, especially from textile, pharmaceuticals, paper and pulp industries are phenols and other aromatic compounds such as toluene. Of the available technologies for degrading toxic wastes, the most common is biodegradation whereby microorganisms play an important role in degrading the organic wastes. However, this process is limited when pollutants are toxic to the microorganisms. In addition, the residence time for biodegradation reaction is long, sometimes taking several days. One of the alternative technologies for oxidizing

toxic organic wastes that are currently under serious investigation is the catalytic wet oxidation (CWO) process. This process involves contacting an oxidizing agent, an organic pollutant and a catalyst in aqueous medium. The process is reported to have higher pollutant conversion levels, low energy consumption and it is environmentally friendly (Masende 2004). However, one of the challenging issues on the application of this process is the high cost of the catalyst. It is envisaged however, that if the catalyst is obtainable at low cost, the process can go a long way in solving environmental problems caused by discharge of organic wastes.

Tanzania is endowed with abundant amount of pumice soils that are found in areas such as Mbeya, Arusha and Moshi. Pumice is naturally porous and hence possesses high particle surface area which can be utilized as reaction sites. Due to its abundant availability as well as good physicochemical properties, it is potentially a good catalyst support. Indeed it has been used before as a

support for palladium catalysts in the hydrogenation of 1,3-cyclooctadiene and phenyl acetylene (Duca *et al.* 1996). Similarly, Ni/pumice catalyst has been developed and used on a laboratory scale to study reactivity in carbon monoxide hydrogenation (Brito *et al.* 2004). Furthermore, pumice modified with hexadecyltrimethyl ammonium bromide and benzyldimethyl tetradecylammonium chloride has been used for sorption of phenol and 4-chlorophenol from solutions (Akbal 2005). On the other hand, pumice supported copper catalysts are also reported to have been used in degradation of cyanide from aqueous solutions (Kitis *et al.* 2005). In the later case it was observed that the specific surface area as well as the surface chemistry of particular pumice does affect both the rate as well as the extent of cyanide destruction.

As far as CWO process is concerned, a number of researches have been conducted to find active and stable catalysts for the process (. For instance, Valkaj *et al.* (2007) investigated different types of Cu/ZSM-5 catalysts for catalytic wet peroxide oxidation of phenol. In a different study, copper supported onto micelle templated silica was investigated in the catalytic wet peroxide oxidation of maleic acid in aqueous phase (Daniel and Katima 2009). Recently, a novel heterogeneous copper(II) Schiff base catalyst was successfully prepared using a Cashew Nut Shell Liquid (CNSL) templating agent (Hamad *et al.* 2011). The catalyst was tested on the oxidation of maleic acid at room temperature using H<sub>2</sub>O<sub>2</sub> as an oxidant. The catalysts showed very good catalytic efficiency, with a yield of up to 90% and a turn over number of about 1000 in ten minutes (Hamad *et al.* 2011).

Despite a number of active catalytic systems that have been developed so far for the CWO process, most of them are developed by impregnation method and hence are

hampered by leaching of the active component (Wu *et al.* 2001), or they are developed from expensive materials and hence are not viable economically. This study has explored the possibility of utilizing low cost pumice soils in producing heterogeneous copper catalysts that are developed through covalent attachment of the active component. The catalysts were tested in wet oxidation of maleic acid, which is one of the oxidation intermediates of phenol.

## EXPERIMENTAL

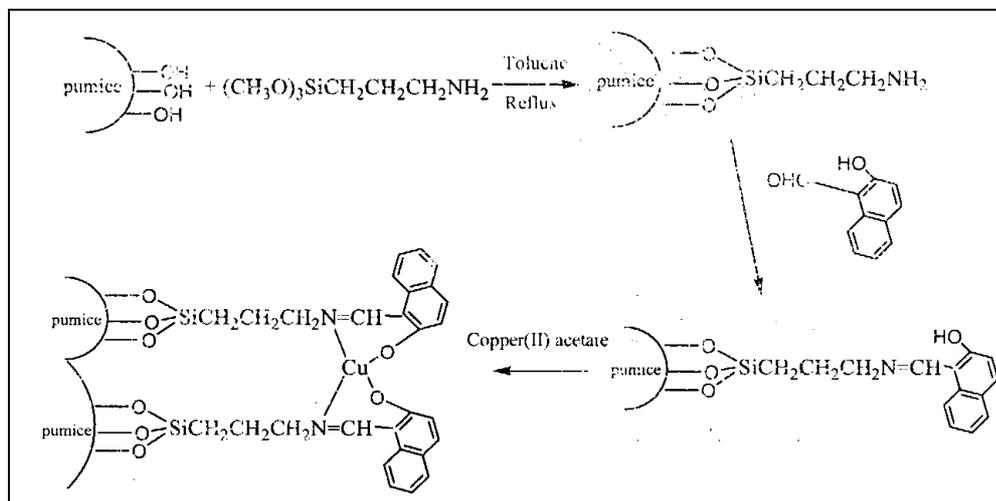
### Preparation of the Pumice Samples

The pumice soil samples were collected from Mbeya (MB) and Moshi (MS) regions located in the southern and northern parts of Tanzania, respectively. After collection the samples were cleaned using deionised water to remove soluble impurities, then dried and ground to a fine powder. The samples were then tested for their thermal stability through calcinations at various temperatures. Before using the pumice samples as catalyst support, acid leaching was carried out. The procedure involved treatment with 10 ml of 3.0 M HCl for every gram of pumice for 10 h at 70 °C. This was repeated with fresh acid at least three times to ensure maximum leaching of exchangeable cations. After thorough washing with deionized water, the samples were dried in air at 110 °C, cooled and stored for further use.

### Preparation of the Pumice Supported Copper Catalysts

The anchoring of a copper Schiff base onto pumice involved a number of steps. First, a pre-treated pumice sample was modified by attaching 3-aminopropyltrimethoxysilane onto its surface (Macquarrie *et al.* 1997). This was followed by reacting the modified pumice with 2-hydroxy-1-naphthaldehyde to produce a Schiff base ligand (Figure 1). Then a solution of copper acetate of predetermined concentration was added and the mixture refluxed in toluene for 3 h. The

resulting material was then dried in air at 110 °C.



**Figure 1:** Preparation of supported copper catalyst by a covalent bonding method

#### **Characterization of the Catalyst Support and Pumice Supported Copper Catalyst**

A number of techniques were applied to characterize the catalyst support as well as the supported copper catalyst. The porosity properties of the materials were studied by nitrogen physisorption. This was performed at Brown University, USA using an Autosorb-1 system from Quantachrome Corp. Prior to the analysis the samples were outgassed at 300°C. Nitrogen gas was used as an adsorbate at 77.4 K whereas 8571 Alumina, supplied by U.S. Department of Commerce, National Institute of Standards and Technology (NIST), was used as a reference material. Scanning electron microscopy (SEM) images were also performed at Brown University, USA using Hitachi SEM S2400 instrument at electron gun energy of 8 keV. On the other hand, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analyses of the materials were done at the Department of Physics, University of Dar es Salaam, Tanzania by using a Perkin-Elmer 2000 Fourier Transform Infrared (FTIR). The samples were initially dried at 100 °C prior

to analysis and then run at room temperature as mixtures with KBr. X-ray Fluorescence (XRF) analysis was also conducted at Brown University, USA to determine the chemical composition of the pumice samples.

#### **Experimental Set-up for Catalytic Tests**

The catalytic tests were performed at the Department of Chemical and Mining Engineering, University of Dar es Salaam, Tanzania for maleic acid oxidation in a batch stirred reactor at a temperature range from 30 to 100 °C at atmospheric pressure. The procedure involved adding 0.07 g of maleic acid into the reactor and making the solution to 350 ml using distilled water. Thereafter 3 g of the copper catalyst and 7 ml of 30% hydrogen peroxide were introduced. The stirrer speed was set between 80 and 150 rpm.

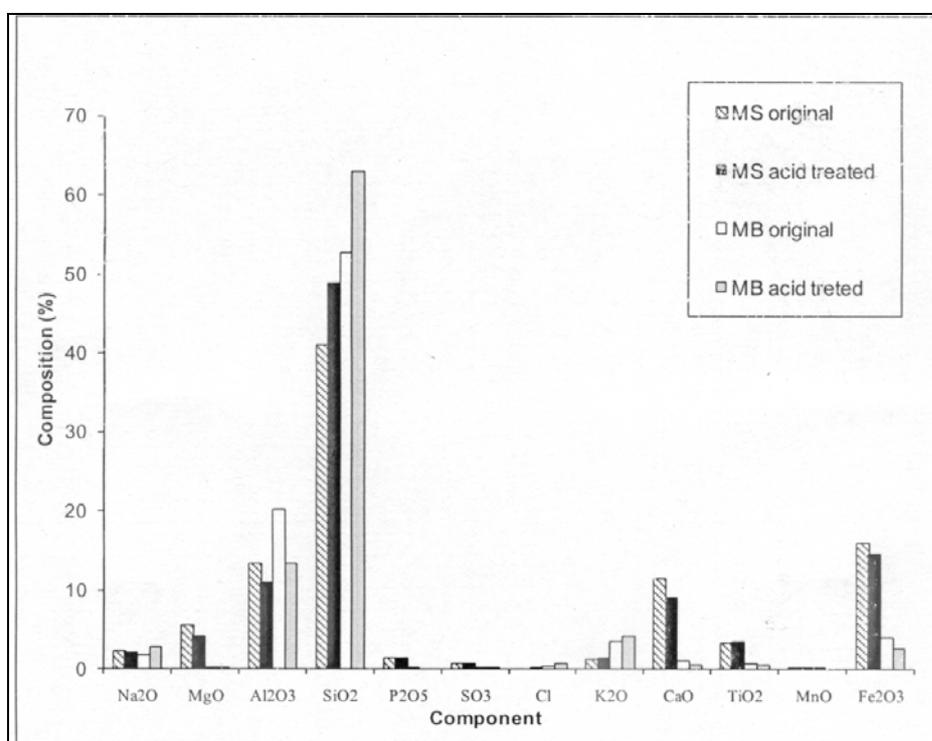
The samples from the reactor were drawn at a fixed interval of 10 minutes, and their compositions were determined using an HPLC set (Merck-Hitachi) which consists of a HPLC pump (L-6200A Intelligent Pump),

sampler (AS-2000A Autosampler), column heater (Merck T-6300), detector (L-4250 UV-VIS Detector) and an integrator (D-2500 Chromato-Integrator). The separation of the components was achieved by a 300 x 8 ID mm Shodex, Rspak KC-811 column packed with ion-exchange resin gels of

sulphonated rigid styrene-divinylbenzene co-polymer. Elution was performed at a flow rate of 1 ml/min at a temperature of 40 °C. Determination of residual maleic acid concentration was done by DAXLITE software on a PC by calculating the area under the chromatogram peaks.

## RESULTS AND DISCUSSION

### Physicochemical Properties of the Pumice Samples



**Figure 2:** Composition of pumice samples as determined by XRD

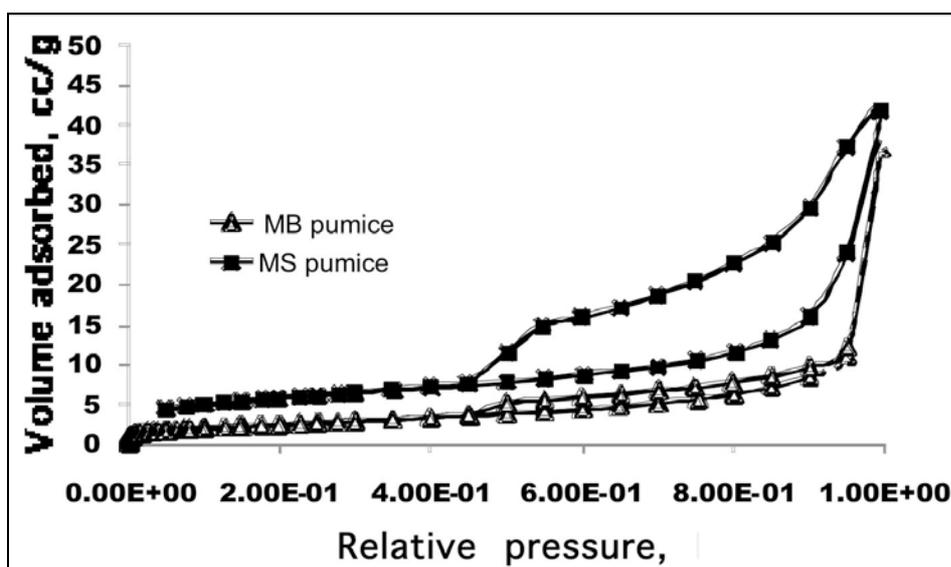
The two samples that were collected from Mbeya and Moshi were characterized by XRF, nitrogen physisorption and SEM analysis in order to establish their physicochemical properties. Figure 2 gives the composition of the two samples as analysed by the XRF. As seen from the figure the most abundant component in both samples is SiO<sub>2</sub> (42 - 55%). Other components include

Al<sub>2</sub>O<sub>3</sub> (13 - 20%), CaO (2 - 14%), Fe<sub>2</sub>O<sub>3</sub> (4 - 15%), Na<sub>2</sub>O (2%), K<sub>2</sub>O (1 - 4%), MgO (6%), TiO<sub>2</sub> (1 - 4%) and other minor components. It is also noted that the Moshi sample is richer in Fe<sub>2</sub>O<sub>3</sub> than the sample from Mbeya. Treating the samples with the acid removes the components by about 2 - 10%. As expected, the treatment does not remove SiO<sub>2</sub> because it is located at the

centre of the crystal structure (Brito *et al.* 2004). Since the other components are removed by this process while SiO<sub>2</sub> is not removed, the resulting product contains higher percent of SiO<sub>2</sub> than the untreated sample.

The porosity properties of the pumice samples were determined by analysis of nitrogen adsorption isotherms using the BET method. The shapes of the isotherms obtained for the two materials are type IV (Rouquerol & Sing 1999), with characteristic hysteresis loops (Figure 3). This is typical for mesoporous materials

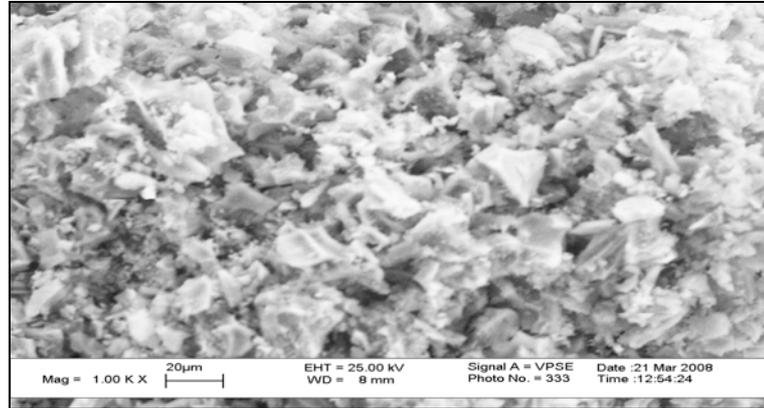
(Rouquerol & Sing 1999). The adsorption shows an initial gradual increase of nitrogen uptake at low relative pressure (< 0.1) attributed to formation of nitrogen monolayer on the adsorbent surfaces. This is followed by a plateau and then a sharp rise of nitrogen uptake starting from about P/P<sub>0</sub> = 0.85. The sharp rise can be associated with the formation of multilayers of the adsorbate, causing capillary condensation in the pores. Comparisons of nitrogen uptake for the two materials reveal that the sample from Moshi has a higher capacity than the sample from Mbeya.



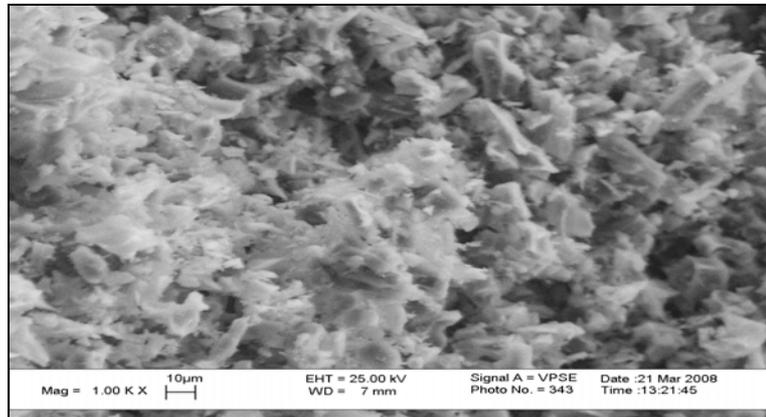
**Figure 3:** Adsorption-Desorption isotherms of the pumice samples from Mbeya (MB) and Moshi (MS).

Figures 4 and 5 give the scanning electron micrographs of the original pumice and 500 °C calcined samples from Mbeya and Moshi, respectively. As seen in Figure 4 the sample from Mbeya contains loosely packed primary particles of mixed shapes which do not change upon calcinations to 500 °C. On the other hand, the micrographs of original

pumice and 500 °C calcined samples from Moshi (Figure 5) show particles that have irregular shapes and are packed together into big blocks. The particles disintegrate upon heating to 500 °C. In both cases, however, the particle sizes are in the micron-sized range.

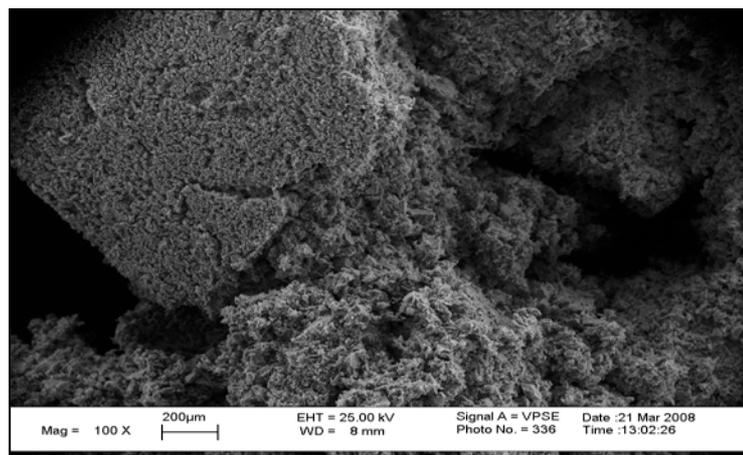


**a**

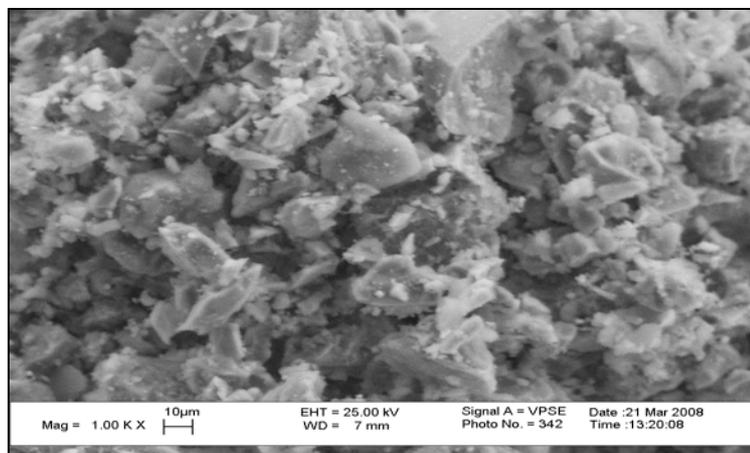


**b**

**Figure 4:** Micrographs of pumice samples from Mbeya (a) original, (b) calcined at 500 °C.



**a**



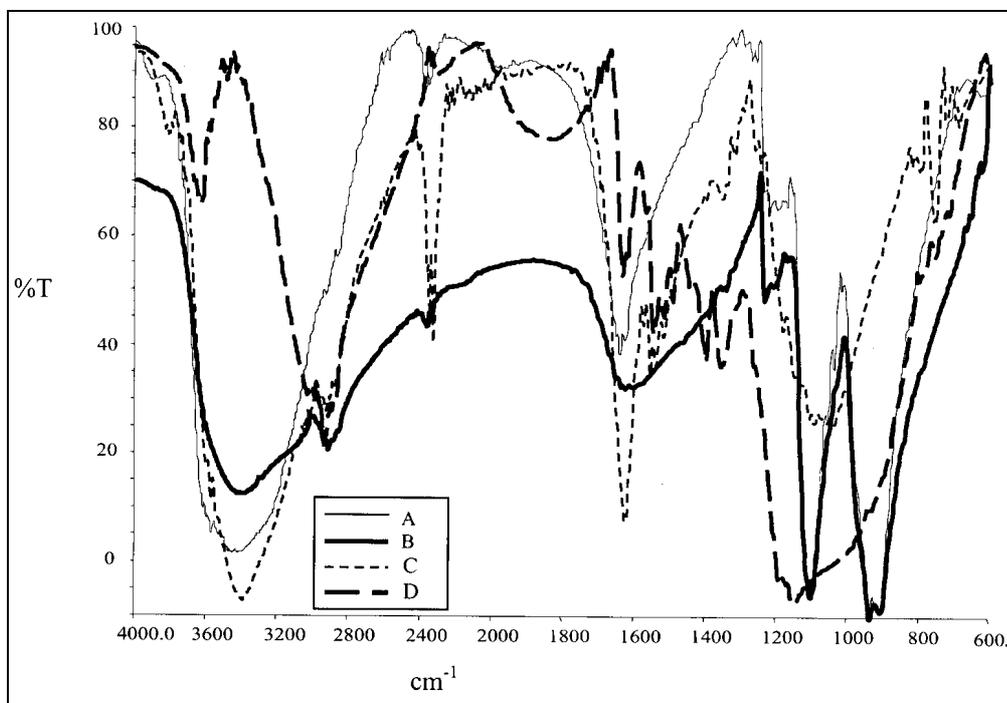
**b**

**Figure 5:** Micrographs of pumice samples from Moshi (a) original (b) calcined at 500 °C

The development of the pumice-supported catalyst was monitored stepwise using DRIFTS technique. Figure 6 gives the spectra of the material at various stages of development. It is evident from the spectra that the aminopropyl groups were successfully introduced onto the pumice surface due to the N-H bending mode at  $1630\text{ cm}^{-1}$ , the C-H stretching vibration frequency at  $2950\text{ cm}^{-1}$ , and the C-H bending mode at  $1300\text{ cm}^{-1}$ . These vibration bands were absent in the spectrum of unmodified pumice. Upon reacting the aminopropyl-functionalised pumice with 2-hydroxy-1-naphthaldehyde the resulting material gave a Schiff base whose spectrum showed a band at  $1640\text{ cm}^{-1}$  attributed to N=C stretching vibration. Other new bands were observed at  $1550\text{ cm}^{-1}$  and  $1560\text{ cm}^{-1}$  corresponding to the aromatic ring breathing mode. Upon complexation of copper with the supported Schiff base, the N=C stretching vibration shifted to a lower

frequency. The presence of the azomethine vibration band in the spectrum of the supported Schiff base and its shift to lower frequencies in the spectra of the supported copper Schiff base catalysts confirms the coordination of the azomethine nitrogen with copper (Figure 6).

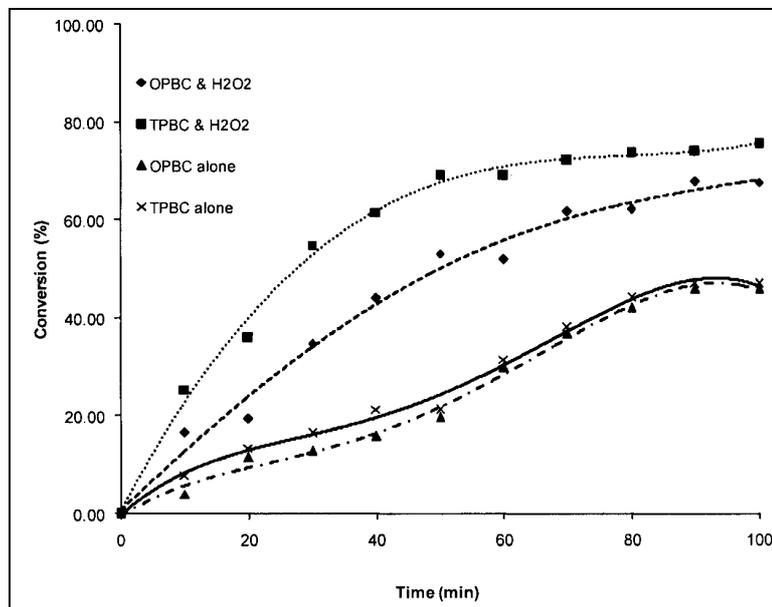
The pumice supported copper (II) Schiff base was tested in the catalytic wet oxidation of maleic acid. The study was conducted at different temperatures using air or hydrogen peroxide as an oxidant. The catalysts were prepared using original or acid pretreated pumice samples collected from Mbeya and Moshi. Preliminary results indicated that the performance of the catalysts prepared from the samples collected from the two different areas were nearly identical. In that case the reported results were obtained using the pumice sample collected from Moshi.



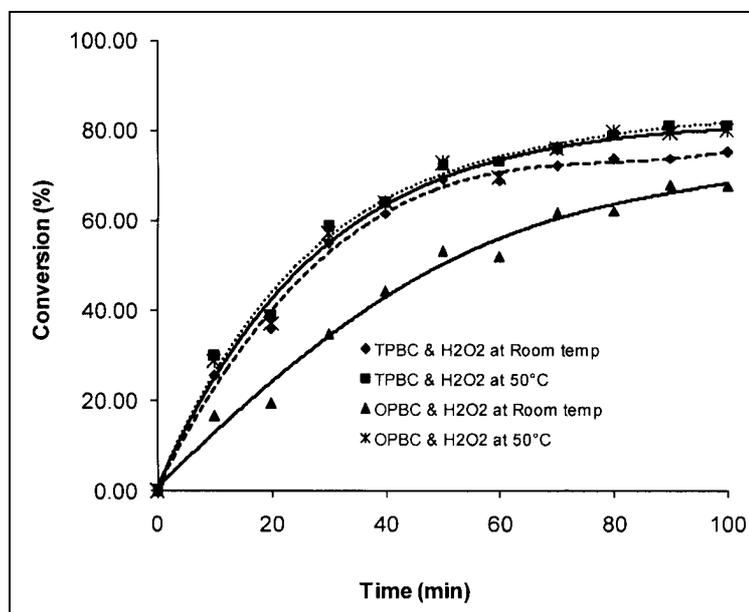
**Figure 6** Spectra of the material at different stages of preparation (A= original pumice, B = aminopropylsilyl-functionalized pumice, C = pumice supported Schiff base, D = pumice supported copper (II) Schiff base catalyst).

Figure 7 shows the extent to which maleic acid is catalytically degraded to carbon dioxide and water at room temperature, using air or hydrogen peroxide as oxidants. As seen from the figure it can be seen that spontaneous degradation of maleic acid at room temperature was very low, not exceeding 13% in 100 minutes. The degradation tendency increased when pumice supported copper (II) Schiff bases were used as catalysts. However, the extent of the oxidation was variable depending on the type of oxidant used, and whether the catalyst was prepared using acid pretreated or non acid pretreated pumice. Further, results indicate that the acid pretreated pumice-based catalyst is more active than the non acid pretreated-based catalyst in the test reaction. In addition, hydrogen peroxide

causes a higher and faster oxidation of maleic acid than air, especially when an acid pretreated pumice-based catalyst was used. It can further be seen that whereas peroxide wet oxidation of the maleic acid using the acid pretreated pumice-based catalyst achieves about 80% degradation in 60 minutes, air oxidation achieves only about 45% degradation in 80 minutes. When the temperature was increased to 50 °C, degradation of maleic acid also increased (Figure 8). The effect of temperature was the same in both non acid pretreated pumice-based catalyst and the acid pretreated one. This means that pumice could be utilized without acid treatment where temperature can be raised but in cases where room ambient temperatures are employed, acid treated pumice would be beneficial.



**Figure 7:** Effect of acid treatment and H<sub>2</sub>O<sub>2</sub> on conversion of maleic acid at room temperature. (NB: OPBC = original pumice-based catalyst, TPBC = acid treated pumice-based catalyst)



**Figure 8:** The effect of temperature on conversion of maleic acid

Generally, the performance of the developed catalysts was comparable to that of Pt/graphite catalyst which was found to degrade maleic acid between 10 - 90% (Sheldon 1996). However, the later degradation was conducted at 120 to 157 °C whereas in this case it was between room temperature and 50 °C.

### CONCLUSION

Pumice samples collected from Mbeya and Moshi areas in Tanzania were studied for their potential as supports for copper (II) Schiff bases. XRF studies of the pumice parent materials indicated that they were composed of SiO<sub>2</sub> (42 -55%), Al<sub>2</sub>O<sub>3</sub> (13 - 20%), CaO (2 -14%), Fe<sub>2</sub>O<sub>3</sub> (4 - 15%) and other minor components. The materials had micron-sized loosely packed primary particles of irregular shapes. The parent materials were used to prepare supported Cu (II) Schiff base catalyst by a stepwise surface chemical modification. Prior to the modification some samples were acid pretreated to remove physisorbed materials. The success of the modification process was confirmed by a diffuse reflectance infrared Fourier transform spectroscopy. The materials were tested as catalysts in wet oxidation of maleic acid using air or hydrogen peroxide as oxidants. Results indicate that the materials could catalyse up to 80% degradation of the maleic acid at temperatures ranging from room temperature to 50 °C using hydrogen peroxide as an oxidant. Under the experimental conditions, increase of temperature showed only a slight increase in the degradation. When air was used as an oxidant the degradation was up to 45% only. Acid pre-treatment of the pumice before the preparation of the catalyst also affected the performance of the catalyst. The acid pretreated pumice-based catalysts showed a higher activity than the non acid pretreated ones especially at ambient temperature.

### ACKNOWLEDGEMENTS

The authors would like to thank Sida/SAREC-core support and the University of Dar es Salaam for financial support. We are also thankful to Brown University for assisting in the analysis of our samples.

### REFERENCES

- Akbal F 2005 Sorption of phenol and 4-chlorophenol onto pumice treated with cationic surfactant. *J. Environ. Manage.* **74**: 239-244.
- Brito A, Garcí'a FC, Ivarez A, Arvelo R, Fierro JLG and Dí'az C 2004 High surface area support/catalyst derived from natural pumice. Study of pretreatment variables. *Ind. Eng. Chem.* **43**: 1659-1664
- Daniel L and Katima JHY 2009 Factors influencing catalytic wet peroxide oxidation of maleic acid in aqueous phase over copper/micelle templated silica-3-aminopropyltrimethoxysilane catalyst. *Water Sci. Tech.* **60**: 2621-2627
- Duca D, Frusteri F, Parmaliana A and Deganello G 1996 Selective hydrogenation of acetylene in ethylene feedstocks on Pd catalysts. *Appl. Catal.* **146**: 269-284
- Hamad FB, Mubofu EB and Makame YMM 2011 Wet oxidation of maleic acid by copper(II) Schiff base catalysts prepared using cashew nut shell liquid templates. *Catal. Sci. Technol.* **1**: 444-452
- Kitis M, Karakaya E, Yigit NO, Civelekoglu G and Akcil A 2005 Heterogeneous catalytic degradation of cyanide using copper-impregnated pumice and hydrogen peroxide. *Water Res.* **39**: 1652-1662
- Macquarrie DJ, Clark JH, Lambert A, Mdoe JEG and Priest A 1997 The use of aminopropylsilica as a base catalyst in the Knoevenagel reaction. *React. Funct. Polymers* **35**: 153-158.
- Masende ZPG 2004 *Catalytic wet oxidation of organic wastes using platinum*

- catalysts*. PhD Thesis, Technische Universiteit Eindhoven.
- Rouquerol F and Sing K 1999 Adsorption by Powders and Porous Solids: Principles Methodology and Applications. Academic Press, London.
- Sheldon RA 1996 Synthesis of oxiranes. In: Cornils B and Herrmann WA (ed) *Applied homogeneous catalysis by organometallic compounds* VCH, Weinheim etc. pp 411-423.
- Sheya MS and Nyamusika SSM 1996 Environmentally sound technologies: some policy perspectives. In: Mwandosya MJ, Luhanga ML and Mugurusi EK (ed) *Environmental protection and sustainable development*, CEET, Dar es salaam.
- Valkaj KM, Katovic A and Zrncevi\_ S 2007 Investigation of the catalytic wet peroxide oxidation of phenol over different types of Cu/ZSM-5 catalyst. *J Hazard Mater.* **144**: 663-667
- West L 2006 World Water Day: A Billion People Worldwide Lack Safe Drinking Water. <http://environment.about.com/od/environmentalevents/a/waterdayqa.htm>.
- Wu Q, Hu X, Yue PL, Zhao XS, Lu GQ., 2001 Copper MCM-41 as catalyst for the wet oxidation of phenol. *Appl. Catal. B: Environmental* **32**: 151-156