

Catalytic Efficiency of Palladium (II) Supported on Castor Oil Based Micelle Templated Silica for Peroxide Promoted Catalytic Wet Oxidation of Phenols

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Authors' contributions

This work was carried out in collaboration between both authors. Author MA performed the laboratory work, statistical analysis and wrote the first draft of the manuscript. Author EBM designed the research, arranged for financial support and wrote the catalyst preparation protocol. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2017/36966

Editor(s):

(1) Richard Sawadogo, Postdoc, Group Cell death & Natural Compounds Laboratoire de Biologie Moléculaire et Cellulaire du Cancer Hôpital Kirchberg, Luxembourg.

Reviewers:

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Complete Peer review History: <http://www.sciencedomain.org/review-history/21637>

Original Research Article

Received 25th September 2017
Accepted 24th October 2017
Published 30th October 2017

ABSTRACT

This work reports on the catalytic efficiency of the micelle templated silica based supported palladium catalysts. The supports were prepared by one-pot co-condensation of organoaminesilanes and tetraethoxysilane with 1:4 and 1:9 loading ratios in presence of castor oil template. The supports and supported catalysts were characterized by acid titration, Atomic Absorption Spectroscopy, Diffuse Reflectance Infrared Fourier Transform Spectroscopy and porosimeter. The loading of amino groups for the prepared materials ranged from 2.08 to 4.105 mmol g⁻¹ while the loading of palladium ranged from 1.05 to 1.73% w/w. The presence of absorption bands at around 3600-3100 cm⁻¹ reveals that the organoaminesilyl groups are successfully incorporated in each silica matrix prepared. The pore size distribution of these

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materials ranges from 2 to 20 nm with an average pore diameter of about 8 nm. The surface area of 3-aminopropyl functionalized micelle templated silica prepared by castor oil template is $428 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $1.1024 \text{ cm}^3 \text{ g}^{-1}$. The catalytic efficiencies range from 34.09 to 58.33% depending on the type of template used, organosilane to tetraethoxysilane ratio and, temperature at which the reaction was carried. The present investigation concludes that the catalysts are active on the oxidation of a mixture of phenols at 27°C and 70°C using hydrogen peroxide oxidant.

Keywords: Castor oil; micelle templated silica; phenol; wastewater.

1. INTRODUCTION

1.1 Wastewater Management

Phenolic compounds (Fig. 1) are hazardous wastes that are water soluble and usually contained in the wastewater of many industries, such as petroleum refineries, petrochemical plants, phenolic resin plants, pharmaceutical plants and brewery industries [1].

The phenol's toxicity in aquatic environment affects the nervous and circulation systems of aquatic animals even in low concentrations. These compounds cause death of fish and other aquatic species and thus changing the ecological equilibrium [2]. Many technologies have been investigated for removing and degradation of phenolic compounds in wastewater. They included, adsorption [3], biodegradation [4,5], extraction by liquid membrane [6], and oxidation [7-8]. Among them, oxidation technology has shown the potential to completely destroy phenol in wastewater [7-9]. In the oxidation process, phenol oxidizes to hydroquinone then into benzoquinone and catechol. Subsequent oxidation of these products, after opening of the aromatic ring, leads to the formation of aliphatic carboxylic acids such as maleic acid and fumaric acid [9].

When phenol is degraded to aliphatic carboxylic acids, the wastewater becomes more biodegradable [10] and less toxic [11]. The oxidation of phenol by several oxidizing agents such as ozone, ultraviolet light and hydrogen

peroxide has been extensively studied [12,13]. Thermal oxidation process and/or biological process can also be used in the removal of phenolic compounds from wastewater. However, these processes have some drawbacks, such as the difficulty of biological material recovery and the need for a large treatment area, the high energy cost of processing and the restrictions concerning the concentration of the pollutants to be treated [13]. Therefore, in this study the catalytic efficiency of the micelle templated silica (MTS) based palladium supported catalysts is reported. Palladium supported catalysts have been synthesized using castor oil and dodecylamine as templates. A study on the suitability of the supported palladium catalysts on the oxidation of a mixture of phenol, resorcinol and o-cresol as a model for brewery effluents has been performed.

1.2 Castor Oil as a Templating Agent

Castor oil is nonvolatile fatty oil extracted from castor oil beans. The oil contains a mixture of glycerides of fatty acids, the predominant acid being ricinoleic acid, $\text{C}_{17}\text{H}_{32}(\text{OH})\text{COOH}$ which comprises 74.1–90.4 % of the fatty acids. Other constituents include linoleic acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$ (4.1–10.32 %), oleic acid, $\text{C}_{18}\text{H}_{34}\text{O}_2$ (2.2–7.55%), palmitic acid, $\text{C}_{16}\text{H}_{32}\text{O}_2$ (0.8–2.59%), stearic acid, $\text{C}_{18}\text{H}_{36}\text{O}_2$ (0.7–2.81%) [14-16]. Castor oil is a renewable resource, and bio-degradable. The presence of hydroxyl group and double bonds (Fig. 2) makes it suitable for many chemical reactions and modifications. Although castor oil is a unique naturally-occurring compound, a

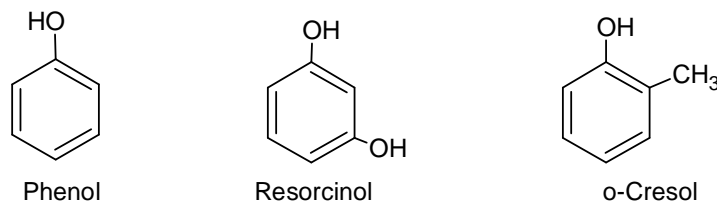


Fig. 1. Chemical structure of phenol, resorcinol and o-cresol

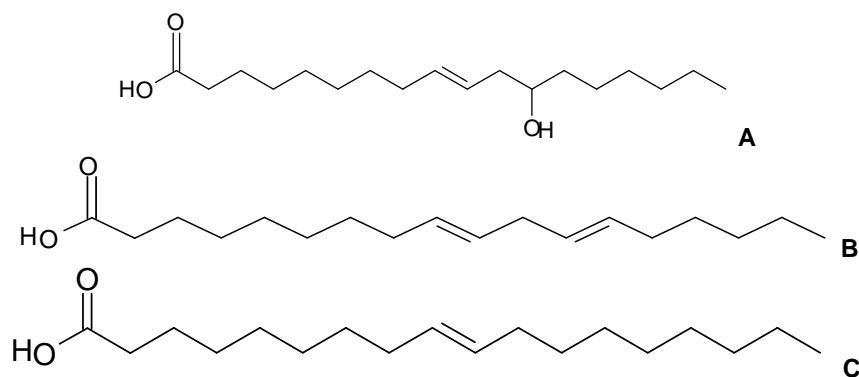


Fig. 2. Major chemical composition of castor oil [A= ricinoleic, B= Linoleic and C= Oleic acids]

limitation on its use is due to the slight reduction of its hydroxyl value and acid value upon storage. Both values may change by about 10% if stored for about 90 days [17]. The reduction of these values is due to the reaction between hydroxyl and carboxyl groups in the oil molecule to form estolides [17].

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Palladium (II) chloride (Lancaster), Tetraethyl orthosilicate 98%, 3-Aminopropyltriethoxysilane 97%, Dodecylamine 98%, 2-quinolinecarboxaldehyde 96%, Phenol 99%, Resorcinol 99%, o-Cresol 99% from Aldrich; Hydrochloric acid 35-38 % (LOBA CHEMIE PVT. LTD MUMBAI), Sodium hydroxide pellets 98% (Rochelle Chemicals), Toluene, methanol (HPLC grade), Ethanol 98%, Hydrogen peroxide 35%, n-hexane and Water for HPLC from Techno Net Scientific Chemical were used. All chemicals were used without further modification. Castor oil beans were collected from Kisarawe district, Coastal region Tanzania.

2.2 Extraction of Castor Oil

The castor oil was extracted by soaking ground castor nuts in n-hexane for 24 hours followed by concentration of oil using a rotavapour machine (model Buchi R-205) at 40°C.

2.3 Preparation of Aminopropyl Functionalized MTS (MTS-AMP)

The synthesis was done as described elsewhere [18] whereby to a well stirred solution of castor oil (2.5 g) in aqueous ethanol (52 ml of absolute

ethanol and 53 ml of distilled water), tetraethyl orthosilicate (38 g TEOS) and 3-aminopropyltriethoxysilane (9 g, AMPS) were added separately but simultaneously and rapidly while stirring at room temperature (27°C) and pressure. The pH of the solution was measured and found to be about 10.6. The mixture was initially clear, but increasingly became cloudy within the first five minutes and after 20 minutes it was completely white paste material. The white paste material formed was left for 12 hours for aging then was washed with excess ethanol and filtered under reduced pressure. The resulting powder was subjected to Soxhlet extraction using ethanol as a solvent for 8 hours so as to remove the template from the material. The final white powder was dried overnight at 90°C in an oven and stored for further modification.

2.4 Preparation of Schiff Base Support (MTS-AMP-Q)

The prepared aminopropyl functionalized MTS (1 in scheme 1) was reacted with quinoline-2-carboxaldehyde so as to obtain MTS supported Schiff base (2 in scheme 1). In a typical experiment, 10 g of dried MTS-AMP was thoroughly stirred with 150 ml absolute ethanol and thereafter a 0.3 g of 2-quinolinecarboxaldehyde ligand was slowly added. The mixture was refluxed and vigorously stirred for 6 hours. Then, the Schiff base modified silica (2) was filtered under reduced pressure; washed with excess ethanol and, dried overnight in an oven at 90°C. The product obtained was stored in a desiccator for characterization and further modification.

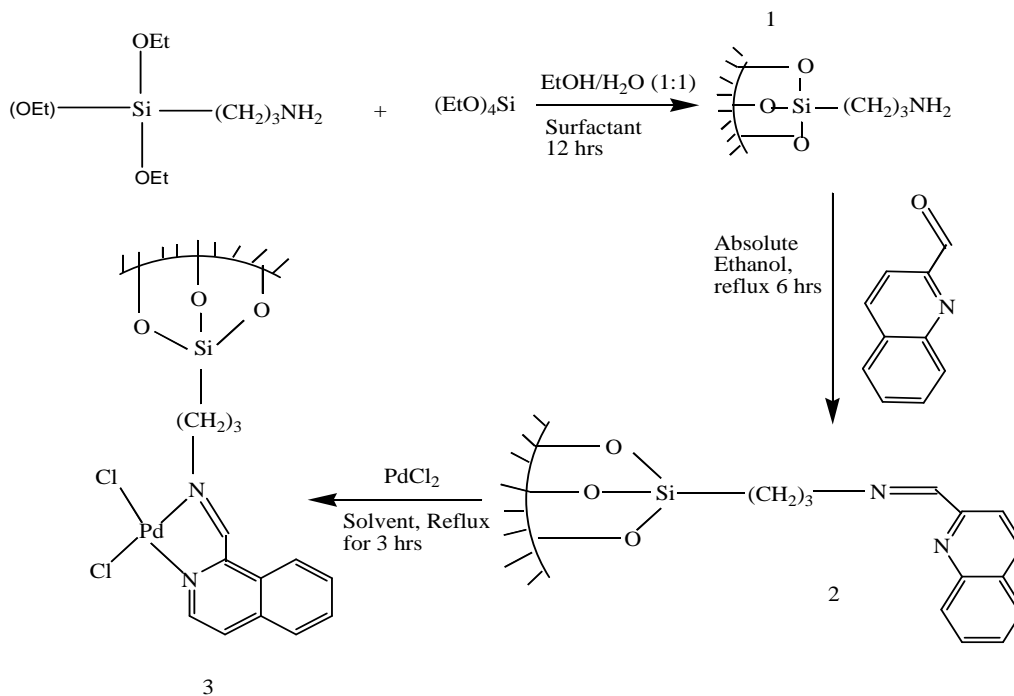
2.5 Preparation of Palladium Supported MTS Catalyst (MTS-AMP-Q-Pd)

The MTS supported palladium catalyst was achieved by reacting the modified Schiff base support MTS-AMP-Q, with a solution of palladium (II) chloride in toluene. The palladium (II) chloride solution was obtained by dissolving the salt in 10 ml of toluene. 5 g of the modified Schiff base support was treated with 0.354 g palladium (II) chloride solution in toluene. After refluxing for 5 hrs, the supported catalyst was filtered, washed with absolute ethanol and dried in air at room temperature. The supported palladium catalyst was then subjected for soxhelt extraction in acetone for 3 hrs in order to remove

any surface physisorbed palladium salt followed by drying in air at room temperature for 24 hours, thereafter it was stored for further analysis. The powder obtained was yellowish brown colored. Several catalysts were prepared as summarized in the Table 1.

2.6 Characterization of the Catalyst Support and Palladium Supported Catalyst

The properties of supports and the supported catalysts were determined by various methods. Atomic absorption spectrophotometer (AAS) was used to determine the amount of palladium supported. The amino groups were estimated by



Scheme 1. Stepwise catalyst preparation

Table 1. Catalysts prepared and their conditions applied in preparation

S/N	Catalyst code and identity	Condition(s) at which the catalyst was prepared
1	Catalyst 1 (1:9 DDA)	Mass of PdCl_2 used in preparation was 0.8 g in 10 g of the support.
2	Catalyst 2 (1:4 DDA)	Physisorbed Pd in the supports was removed by reflux method using ethanol as solvent
3	Catalyst 3 (1:9 DDA)	Mass of PdCl_2 used in preparation was 0.354 g in 10 g of the support.
4	Catalyst 4 (1:4 DDA)	
5	Catalyst 5 (1:9 CO)	
6	Catalyst 6 (1:4 CO)	Soxhelt extraction of any surface physisorbed palladium salt in acetone for three hours.

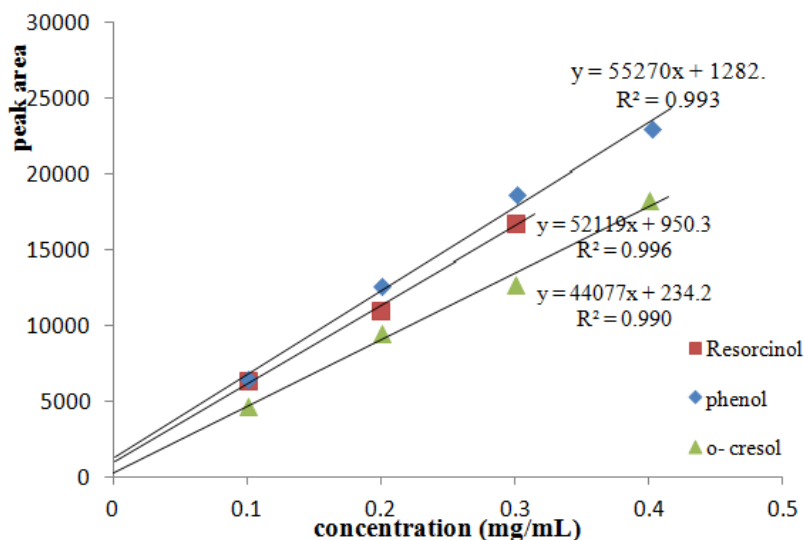


Fig. 3. Calibration curves for phenol, resorcinol and o-Cresol

acid titration approach; Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) was used in the qualitative determination of surface anchored functional groups. Nitrogen sorption experiments were used to determine the surface area, pore size, pore size distribution and porosity of the synthesized materials. The pore size distribution and surface area were determined by Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) model respectively. The adsorption-desorption isotherms were used to evaluate whether the synthesized samples were mesoporous materials.

2.7 Catalytic Activity Test

The activity of the MTS supported palladium catalysts were tested on the oxidation of phenol, resorcinol and o-cresol as model of brewery wastewater. Phenol, resorcinol and o-cresol stock solutions were prepared by dissolving the 2 g of pure substance into 500 mL titration flask to make a 0.4 mg/ml solution. A subsequent dilution was made so as to obtain a 0.3 mg/ml, 0.2 mg/ml and 0.1 mg/ml solution of each of the phenols in the present work. A mixture of phenol, resorcinol and o-cresol at each concentration prepared was made. Before sample analysis, High Performance Liquid Chromatography (HPLC) was calibrated using the prepared concentrations of the phenol, o-Cresol and resorcinol standards separately so as to identify their specific retention time. The calibration curves (Fig. 3) of each

prepared concentration of the standards were obtained.

Oxidation of the mixture of phenols in simulated wastewater was carried out using a 500 ml flat bottomed flask. The initial mixture contained 0.5 g MTS supported palladium catalyst, 250 ml simulated wastewater and 150 ml of 30% hydrogen peroxide (excess) constantly stirred, at room temperature. Small liquid samples were periodically drawn from the reaction mixture, at an interval of time (about 2 min), filtered using a 0.45 μm filter paper. The samples were analyzed using the HPLC low pressure system (Shimadzu 20AD) using a C18 reverse phase column (phenomenex luna 5 μm , 250 x 4.6 mm) at a flow rate of 1 ml/minute. The oven temperature was set at 30°C and the mobile phase was a 50:50 volume mixture of methanol and water. The final concentration of phenols was calculated from its respective peak area at the specified time.

3. RESULTS

3.1 Determination of NH_2 Loading by HCl Acid Titration and Palladium Content

The amino groups loading onto silica surface is determined by acid titration approach. The result shows that the amino groups for MTS materials is between 2.080 and 4.105 mMol of organoamine per gram of castor oil templated silica. When the commercially available dodecylamine (DDA) is used as the templating

material, the amino group loading is between 2.040 and 3.989 mMol g⁻¹. The analysis of palladium metal content in the catalysts ranges from 1.05 to 1.73% weight/weight. Table 2 presents a summary of metal contents and the amino groups of all catalysts prepared in the current work.

3.2 Functional Group Determination by DRIFT

Infrared spectra of materials that were prepared using castor oil as the templating agent at an organoaminesilane to TEOS ratio of 1:4 (Fig. 4) indicates vibrations attributable to the presence of the supported organic groups. These organic groups include N-H band at 3600 (broad) cm⁻¹ and C-H band at 2700-2950 cm⁻¹. These bands are associated with the aliphatic chains of the amine group. Also bands at 1600 -1550 cm⁻¹ and 700 -900 cm⁻¹ that are attributable to N-H vibrations are obtained. In addition to the vibrations attributable to the supported organic groups, vibrations associated with the silica lattice structure are also present. These are observed at 1000 to 1200 cm⁻¹ due to symmetrical and unsymmetrical stretching vibrations of the Si-O-Si linkage. A strongly observable feature in almost all the infrared spectra is the hydrogen-bonded SiOH stretching band at about 3650–3100 cm⁻¹. The N-H stretching band appears in a similar region but is obscured by the SiOH band. The peaks of interest could be identified thus confirming the presence of the amine groups on the silica surface. A C=N vibration in Fig. 4(b) and (c) is observable at 1580 cm⁻¹. However, infrared analysis indicated that the complexation of

palladium by the ligand had occurred, with the prominent C=N (stretch) of the imine being shifted to lower frequency (Fig. 4C) by 50 cm⁻¹. This shift of frequency is an indication of strong metal-ligand interaction [19,20]. Other infrared vibrations observable are due to amine C-N and aromatic C=C at 1350 -1300 and 1650 - 1470 cm⁻¹ respectively.

3.3 Nitrogen Physisorption Study

Nitrogen adsorption-desorption isotherms of the MTS-AMP (CO) material is shown in Fig. 5. The Nitrogen isotherms of these samples are of the type IV according to International Union of Pure and Applied Chemistry (IUPAC) classification [21]. They are typical for mesoporous solids which at low relative pressure (less than 0.1) showed a gradual increase in the amount of adsorbate with relative pressure. Above 0.1 relative pressures, the isotherm form a plateau followed by another sharp rise of nitrogen uptake starting from about 0.65 relative pressures. At higher pressures (P/Po = 1) the amount adsorbed raised steeply.

3.4 Catalytic Activity

The prepared catalysts were tested for their activity in the wet oxidation of simulated wastewater made by a mixture of phenol, o-cresol and resorcinol as one of the phenolic compounds that pollute the environment from brewery wastewater discharge using hydrogen peroxide oxidant at 27°C and 70°C. Fig. 6 indicates high conversion rates of phenolics to products when a 1:4 CO catalyst is employed than for uncatalyzed reaction. Phenol degraded much higher than resorcinol and o-cresol.

Table 2. Amino groups loading and palladium metal content on the MTS materials

S/No	MTS material	Amino group loading (in mMol/g)	% Pd
1	1:4 MTS –AMP (CO)	4.105	NA
2	1:4 MTS – AMP (DDA)	3.989	NA
3	1:9 MTS – AMP (CO)	3.684	NA
4	1:9 MTS - AMP (DDA)	3.416	NA
5	1:4 MTS – AMP-Q (DDA)	2.160	NA
6	1:4 MTS – AMP- Q (CO)	2.200	NA
7	1:9 MTS – AMP – Q (DDA)	2.040	NA
8	1:9 MTS – AMP – Q (CO)	2.080	NA
9	Catalyst 1 (1:9 DDA)*	NA	1.51
10	Catalyst 2 (1:4 DDA)*	NA	1.67
11	Catalyst 3 (1:9 DDA)	NA	1.05
12	Catalyst 4 (1:4 DDA)	NA	1.59
13	Catalyst 5 (1:9 CO)	NA	1.34
14	Catalyst 6 (1:4 CO)	NA	1.73

*Indicates the physisorbed palladium in the supports was removed by refluxing method

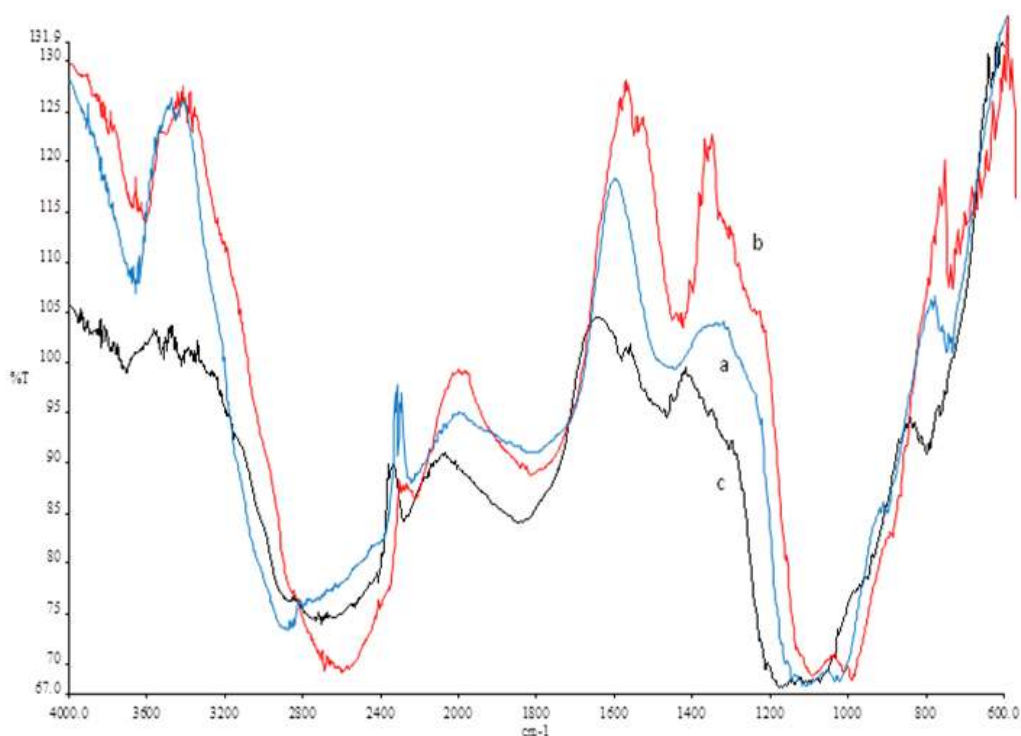


Fig. 4. DRIFT Spectra of (a) 1:4 MTS-AMP (CO) (b) MTS-AMP-Q (CO) and (c) Catalyst 1 (CO)

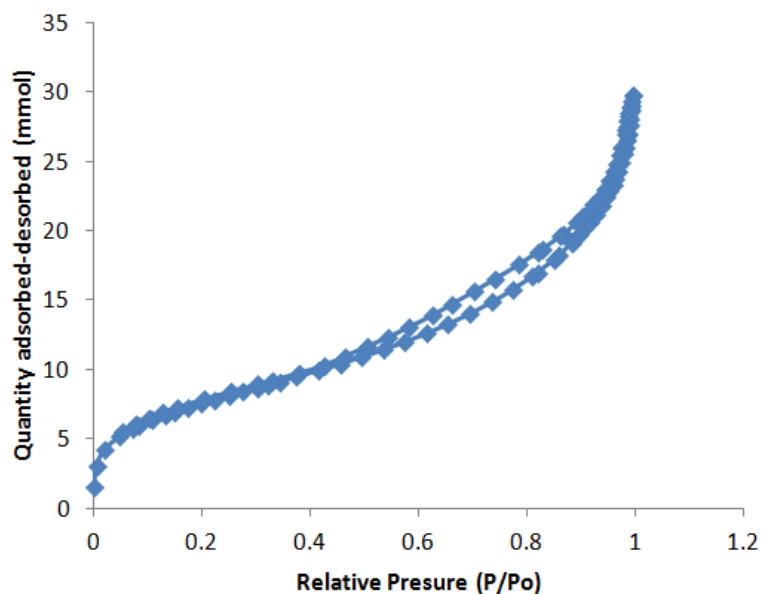


Fig. 5. Nitrogen adsorption-desorption isotherms for MTS-AMP (CO)

Fig. 7 indicates the reaction profiles of phenolics when a 1:4 CO catalyst is used over the 1:4 DDA catalysts at 27°C. The result indicates good conversion of phenol for both catalysts.

Resorcinol and o-Cresol are almost all converted to products at the same rates but higher for 1:4 CO catalysts than a 1:4 DDA catalyst.

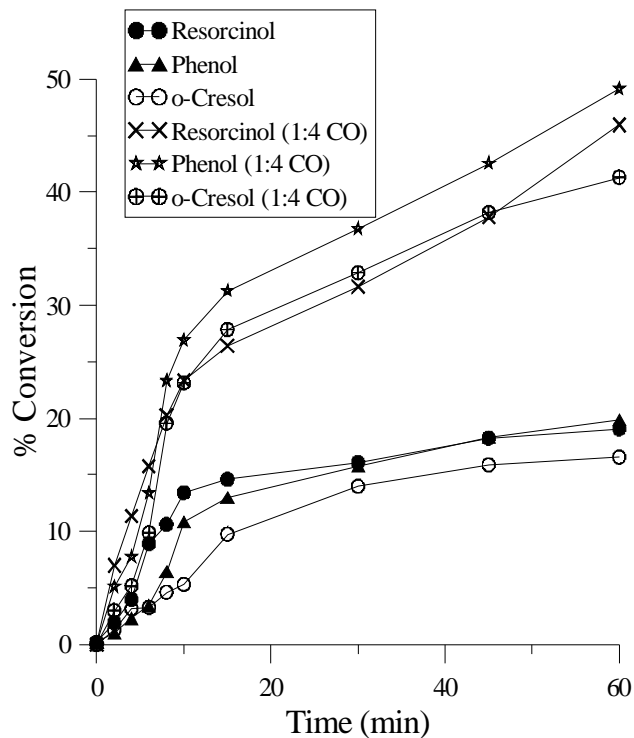


Fig. 6. The reaction profile for uncatalyzed and the catalyzed wet oxidation at 27°C

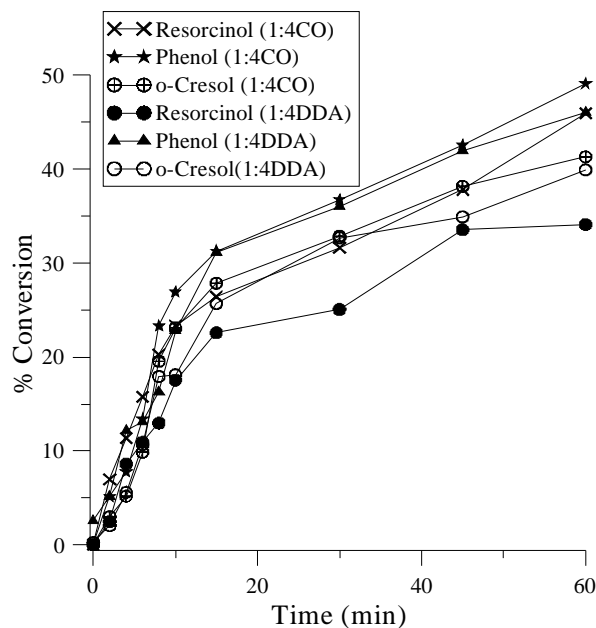


Fig. 7. The reaction profile of 1:4 Catalyst (DDA) and 1:4 Catalyst (CO) at 27°C

Fig. 8 indicates the reaction profiles of phenolics when the catalytic efficiency of 1:4 CO catalysts is compared at 27°C and 70°C. The catalytic efficiency decreases in the order resorcinol > phenol > o-cresol (at 70°C) > phenol > o-cresol > resorcinol at 27°C.

The reaction profile of a 1:4 catalyst (CO) and 1:9 catalyst (CO) at 27°C is presented by Fig. 9. Resorcinol is well converted to products for the reaction that employed a 1:4 CO catalyst than

phenol and o-cresol. However, high conversion rate is obtained when a 1:4 CO catalyst is used than 1:9 CO catalyst.

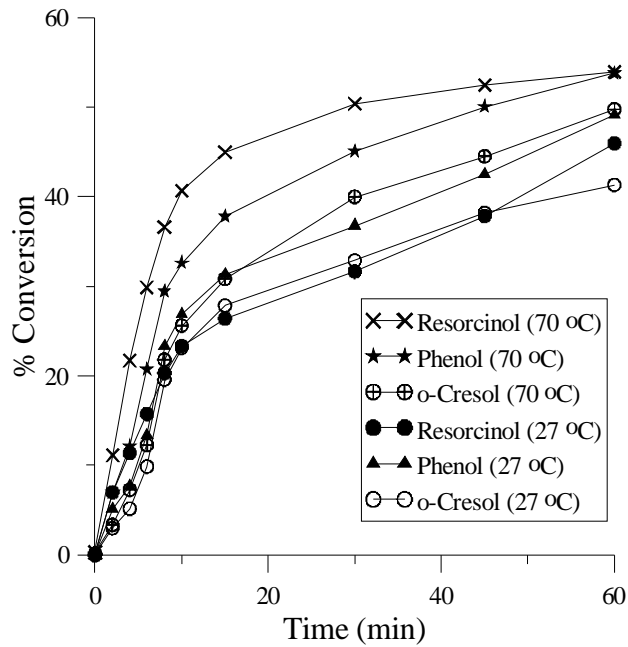


Fig. 8. The reaction profile of a 1:4 Catalyst (CO) at 27°C and at 70°C

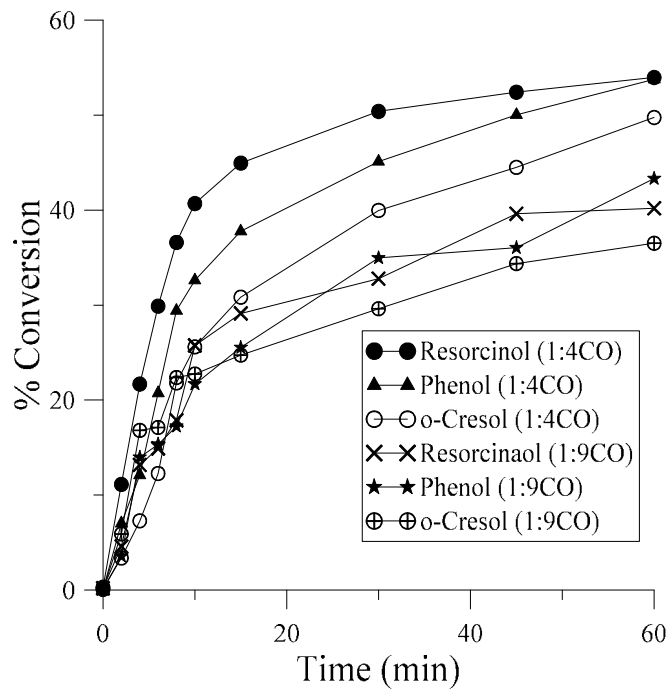


Fig. 9. The reaction profile of a 1:4 Catalyst (CO) and 1:9 Catalyst (CO) at 27°C

4. DISCUSSION

4.1 The Loading of the Functional Groups and Palladium Content

The loading of amino groups for unmodified MTS-AMP materials is higher in castor oil based MTS than in DDA materials. The possible reason for these observations could be the differences in the pore sizes of these materials. Thus material with large pore sizes facilitates easy accessibility of the amino groups by the acid [22]. The loading decreases in 2-quinolinecarboxaldehyde functionalized MTS-AMP as compared to MTS-AMP (Table 2). This decrease in amino loading is possibly due to the decrease in pore size when the MTS-AMP is functionalized with 2-quinoline carboxaldehyde ligand and thus other basic sites are not reachable during titration [22]. Moreover, the decrease in amino group loading might be caused by the decrease in basicity in MTS-AMP-Q as compared to that in MTS-AMP regardless of the increase in number of nitrogen which participate in imine bond formation by using its lone pair of electrons.

Amino group loadings at a ratio of 1:4 are higher than at 1:9 and this observations have been reported by other researchers [23]. When sol-gel approach is used, the amino loading can be high ca. 4 mMol/g for monoamine silica supports [24]. At 1:9 ratio, most silanol functional groups are left unmodified owing to a higher amount of silica precursor relative to amount of organoaminesilane [22]. Generally, the amount of organoaminesilyl groups incorporated onto silica is affected by the type of template used and the ratio of organoaminesilane to TEOS.

The variations of the palladium metal content in the prepared catalysts are due to the type of the template used, the method used in removing the physisorbed palladium as well as the organosilane to TEOS ratio. For example, catalyst 4 and 6 (Table 2) are both prepared at the same ratio of organoaminesilane to TEOS, catalyst 6 prepared using castor oil template has relatively higher palladium content than catalyst 4 made by using dodecylamine template. Similarly, catalyst 2 (1:4 DDA)* has higher palladium (1.67 %) content than catalyst 4 (1:4 DDA) though the same template was used in the preparation. In the former catalyst, the physisorbed palladium is removed by refluxing approach while in the later catalyst, soxhlet extraction approach is used. This implies that refluxing technique is not an

effective method in removing physisorbed traces of palladium in the supports.

4.2 Catalyst Activities

The results indicate low reaction rate for uncatalyzed reactions compared to reactions that a catalyst is employed (Fig. 6). This indicates the necessity of catalyzing the reaction. Based on individual compound comparison, the percentage conversion for resorcinol, phenol and o-Cresol is lower when a reaction is catalyzed by a 1:4 catalyst (DDA) than when a 1:4 catalyst (CO) is used (Fig. 7). This implies that the catalysts prepared by using castor oil surfactant are better than that prepared by dodecylamine under the same reaction conditions. Moreover, a reaction catalysed by the 1:4 catalysts (CO) gives better results than when the same reaction is catalysed by the 1:9 catalyst (CO) under the same reaction conditions (Fig. 9). The reason could be due to the accessibility of pore sites. The 1:4 catalyst (CO) posses larger pores than 1:9 catalyst (CO) and hence the active sites are more accessible than in the 1:9 catalyst (CO).

The catalytic efficiency of the prepared materials is also found to be influenced by the type of template used in the preparation of the catalyst. The template determines the arrangement of the active sites and the surface area of the silica supports which in turn influence the catalytic efficiency. Castor oil as a template, allowed relatively higher amount of organoaminesilane to be incorporated onto the silica surface compared to dodecylamine. A greater ratio leads to low loading and hence low catalytic activity. Consequently the ratio of 1:4 lead to a higher catalytic activity compared to 1:9 ratios regardless of the type of template used.

The temperature at which the reaction is carried out also affects the catalytic efficiency. When 1:4 catalysts (CO) is used at 27°C for 60 minutes, the percentage conversion for resorcinol, phenol and o-cresol increased upon varying the temperature to 70°C of the reaction. A slight increase in percentage conversion of the reactants to products is possibly caused by the decrease in Boltzman parameter of the reaction. A comparison of phenol degradation using MTS supported palladium catalysts and other oxidizing agents catalysts shows that these catalysts are good. For instance, it has been reported that only 20 to 60 % phenol degradation takes place within one hour using ozone and UV process [25]. Others have reported that 98% phenol

degradation could be achieved after 24 hrs upon addition of horseradish peroxidase enzyme (1 U cm^{-3}) and H_2O_2 (1 mMol dm^{-3}) to a solution of 94 mg dm^{-3} phenol [4]. The results of this study shows that 60 minutes of reaction is sufficient to achieve about 50 % of phenolic degradation at room temperature. The overall rate of phenols conversion into products is in the order of resorcinol > phenol > o-cresol. This trend is attributed mainly by substituent groups to the benzene ring. The hydroxyl group donates electrons to the benzene ring by mesomeric effect while methyl group donates by positive inductive effect. But the mesomeric effect outweigh the inductive effect, thus why resorcinol indeed is more degraded than the phenol and o-cresol.

Other studies has shown better phenol conversion. For example Pestunova et al. [26] obtained about 100% phenol removal in 0.5 hr at 90°C . Britto et al. [27] reported 100% phenol removal for the reaction performed at $38 \text{ }^\circ\text{C}$, in 6 hrs. Similarly, Feng et al. [28] reported 100% phenol removal in 35 minutes at room temperature. However, these researchers used a single reactant (phenol) to test their catalytic efficiency.

5. CONCLUSION

Castor oil as template gave relatively higher yield of 3-aminopropyl functionalized MTS support compared to dodecylamine. The supports made by employing castor oil gave relatively higher amino groups loading and consequently higher palladium content. Castor oil is therefore an effective and suitable template than dodecylamine for the synthesis of mesoporous silica supports. The supported palladium catalysts are effective as catalysts in the oxidation of phenolics in presence of hydrogen peroxide oxidant especially when the temperature at which the reaction takes place is greater than room temperature. Furthermore, the catalytic efficiency of the supported palladium catalysts depends on the type of template used in materials preparation, amino and metal loading, reaction temperature, reaction time and the ratio of organoaminesilane to TEOS.

ACKNOWLEDGEMENT

Special thanks are due to Belgium embassy in Tanzania (via BTC) for the financial support without which this work would not be possible.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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