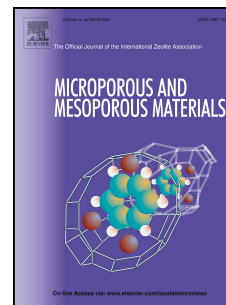


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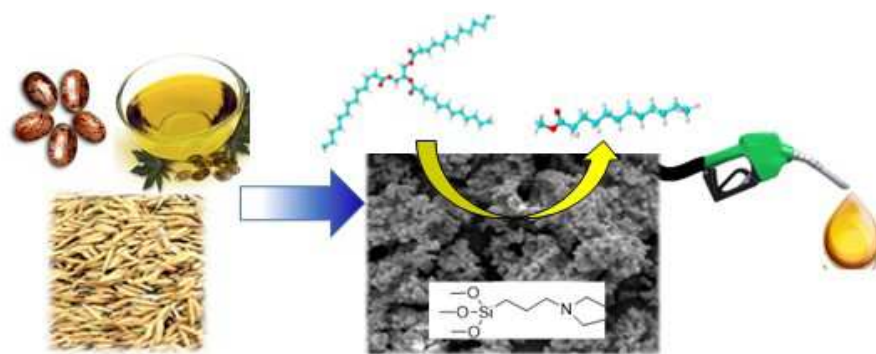
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Journal Pre-proof

Valorisation of rice husk silica waste: Organo-amine functionalized castor oil templated mesoporous silicas for biofuels synthesis.

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Abstract

Rice husk is a rich source of waste silica which has potential for application in the preparation of porous materials for use as catalyst supports or sorbents. Here we report on the synthesis of rice husk silica (RHS) and mesoporous templated rice husk silica (MT-RHS) using sodium silicate, obtained from rice husk ash, and castor oil as a pore directing agent. The resulting silicas were functionalized with 3-aminopropyltriethoxysilane (APTS) or 3-diethylaminopropyltrimethoxysilane (DEPA), and their catalytic activity evaluated in the transesterification of model C₄-C₁₂ triglycerides (TAG) to their corresponding fatty acid methyl esters, of relevance to biodiesel synthesis. Castor oil templating enhances the surface area of rice husk silica, and introduces uniform 4 nm mesopores, albeit as a disordered pore network. Post-

synthetic grafting of silica by APTS or DEPA resulted in base site loadings of 0.5 and 0.8 mmol g^{-1} respectively on RHS and MT-RHS. Turnover frequencies of amine-functionalized MT-RHS were 45-65% greater than those of their amine-functionalized RHS counterparts for tributyrin transesterification. Switching from a primary (APTS) to tertiary (DEPA) amine increased activity three-fold, delivering 80 % tributyrin conversion to methyl butyrate in 6 h. DEPA-MT-RHS was effective for the transesterification of C₈ and C₁₂ triglycerides, with methyl caproate and methyl laurate selectivities of 93 % and 71 % respectively in 24 h.

1. Introduction

Anthropogenic CO₂ emissions and associated climate change, resulting from continued use of fossil fuel energy feedstocks, continues to drive the development of carbon neutral renewable energy technologies. The bio-refinery concept is widely advanced as one such route to sustainable fuels and chemicals from non-fossil feedstocks, notably agricultural, forestry, or food waste,[1, 2] but requires cost-effective catalysts to improve the economics of bio-based products.[3] Biodiesel comprises fatty acid methyl esters (FAMEs), and when derived from waste oils [4] or inedible plants or algae, [5] is an important renewable (liquid) fuel that can contribute to greenhouse gas mitigation in the transport sector. However, commercial production of FAME proceeds by transesterification of triglyceride (TAG) components of such oils catalyzed by NaOMe or NaOH, and is inherently inefficient due to energy-intensive processing required to remove the soluble base catalyst and purify the fuel, and associated large quantities of contaminated water.[6] Sustainable biodiesel therefore requires both appropriately sourced bio-oil feedstocks, and the development of solid (heterogeneous) base catalysts enabling facile FAME separation and continuous processing. The cost of catalyst synthesis can be mitigated through using waste-derived materials as catalyst precursors.[7] Rice husk waste, a low value by-product of the rice milling process with poor nutritional value and high silica content, is a potential precursor for the synthesis of silica catalysts. Risk residue valorization is a priority for developing countries where it can mitigate health and environmental problems associated with current field burning disposal;[8],[9] uncontrolled burning of rice husk waste releases crystalline silica particles, which when airborne can cause health problems such as silicosis.[10]

Rice husk waste is a significant energy source for methane and hydrogen production,[11, 12]

from biomass power plants, however environmental concerns remain regarding the resulting ash disposal.[13] Ash produced by the controlled burning of rice husk waste contains amorphous silica, a potential precursor for the production of functional materials including silicon carbides, silicon nitrides and zeolites. Rice husk silicas are also employed in the industrial manufacturing of cement, cleaning agents, and reinforced rubber or polymer composites.[14] Rice husk valorization as a silica source for the preparation of porous materials including zeolites, [15] and mesoporous templated materials (e.g. SBA-15 and MCM-41),[16, 17] has attracted attention for adsorption [18, 19] and catalysis [20, 21] applications.

Mesoporous silicas are typically synthesized from expensive silicon alkoxides such as tetraethylorthosilicate (TEOS),[22] hence an alternative, low cost silica source is desirable. The conversion of rice husk ash to sodium silicate (a precursor to mesoporous silicas) is thus attractive from both an economical and environmental perspective. Several methods have been employed to produce silica from rice husk,[23] with organic functionalization commonly used for the production of adsorbents for water purification,[24-26] CO₂ sequestration,[27-29] or immobilization of metal nanoparticles.[30-32] Organo-functionalized (non-templated) variants have been explored for acetic acid esterification and phenol alkylation.[33, 34] The synthesis of mesoporous silicas from rice husk silica using synthetic templates such as Pluronic P-123 and cetyltrimethylammonium bromide yields materials with high surface areas and narrow pore size distributions.[35, 36] However, the use of bioderived templates is preferable to improve the sustainability of templated silica production.[37] Castor oil, a viscous pale yellow oil extracted from non-edible castor seeds, has been successfully used as a mesopore template during the sol-gel synthesis of silica from TEOS.[38] However, there are no reports of castor oil as a surfactant template for sodium silicate extracted from rice husk ash.

Here we report the synthesis and characterization of castor oil templated rice husk derived silica (RHS), its subsequent functionalization with primary and tertiary organo-amines, and catalytic application in the transesterification of C₄₋₁₂ TAGs as model reactants for biodiesel production. Castor oil templating of RHS increased the mesoporosity and activity of the resulting solid base catalysts, with tertiary amine functionalised RHS exhibiting a 5-fold rate enhancement over the primary amine analogue.

2. Experimental

i. Materials and chemicals

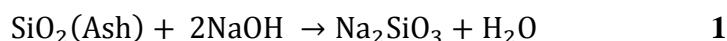
Rice husks were collected from a local rice mill at Toangoma, Kigamboni District, Dar es Salaam City, Tanzania. Toluene (>99.5 %), n-hexane (<97 %), sodium hydroxide, hydrochloric acid, diethyl-3-(trimethoxysilyl)propylamine (DEPA) (96 %), (3-aminopropyl)trimethoxysilane (APTS) (97 %), ethanol (>99.8 %), methanol (>99.9 %), tributyrin (>99 %), tricaprylin (>90 %), trilaurin (>99 %) and butanol (99.8 %) were purchased from Sigma Aldrich and used without further purification. Castor oil was extracted from castor seeds collected from Iringa and Dodoma Regions of Tanzania.

ii. Castor oil extraction:

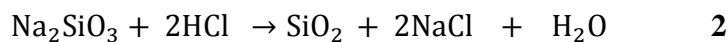
Castor oil extraction was performed according to our recently reported method.[38] Briefly, castor oil was obtained by Soxhlet extraction using 250 ml *n*-hexane as the extracting solvent. 10 g of crushed castor seeds were placed in a thimble in the centre of the extractor and *n*-hexane heated in a round bottom flask at 60 °C, and the *n*-hexane vapor condensed and passed through the thimble. The extract was collected in the round bottom flask for 6 h, with 2 mL of castor oil obtained per 10 g of crushed castor seeds after evaporation of residual hexane.

iii. Preparation of silica from rice husk ash:

Rice husk ash (RHA) was obtained by burning 20 g of rice husks in a high temperature muffle furnace (Model F46120CM) at 600 °C for 5 h. Rice husk silica was subsequently obtained as previously reported,[26] by dissolution of 10 g portions of RHA in 200 mL of 2 M NaOH solution, followed by heating to 100 °C for 1 hour, and cooling to room temperature. The mixture was filtered to obtain sodium silicate solution, and the residue discarded. Equation 1 shows the formation of sodium silicate from the reaction of rice husk ash and NaOH (used as limiting reagent to ensure its completion in the reaction). 4.6 g (23%) of RHA were obtained from each 20 g of rice husk.



Equation 2 shows the process of obtaining SiO₂ from sodium silicate solution, with 8.5 g (85%) of silica obtained for every 10 g of rice hush ash converted to sodium silicate.



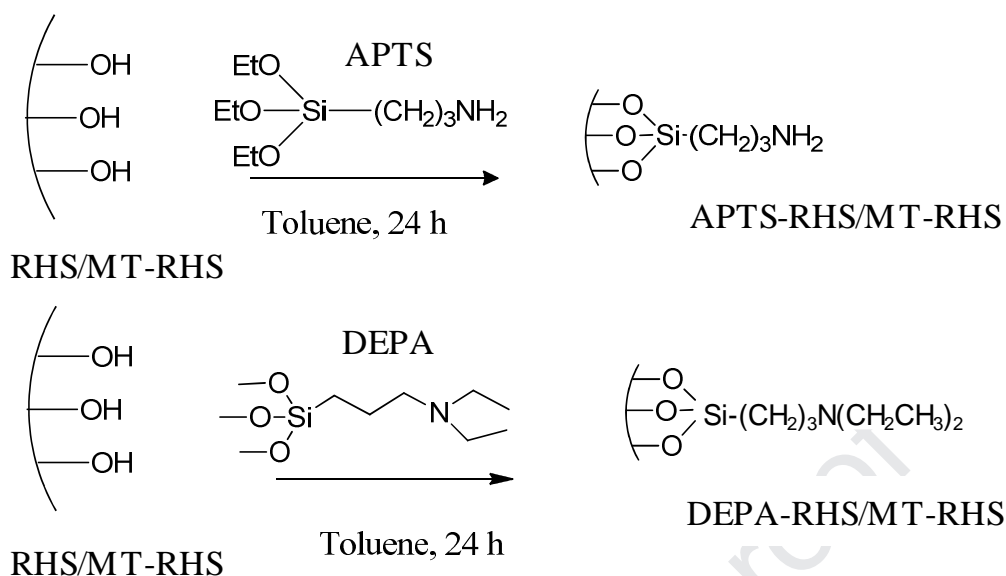
Silica was precipitated from sodium silicate performed by lowering the pH of the solution from 11.8 to 7.2 through the dropwise addition of 2 M HCl. The resulting precipitates were vacuum filtered and washed with excess distilled water to remove residual sodium chloride. The obtained rice husk silica (RHS) materials were then oven dried at 90 °C for 24 h.

iv. Synthesis of micelle templated silica with castor oil

Castor oil (2.5 g) was dissolved in a stirred mixture of 53 mL distilled water and 47 mL ethanol. The resulting mixture was stirred at 35 °C for 2 h prior to the addition of 23 mL of sodium silicate solution from RHA (corresponding to a ricinoleic acid:sodium silicate molar ratio of approximately 1:2), stirred for a subsequent 24 h, and then aged at 80 °C for an additional 24 h in the sealed vessel. Formation of a complex fatty acid/sodium salt vesicular system is expected to result from partial neutralization of ricinoleic acid from castor oil by the Na⁺ from sodium silicate as previously observed for oleic acid.[39] The organic castor oil template was subsequently removed by Soxhlet extraction using 200 mL ethanol as the refluxing solvent at 70 °C for 10 h. The solid materials obtained were then washed in ethanol and dried at 90 °C to give a white powder. The resulting solid materials were termed micelle templated-rice husk silica (MT-RHS).

v. Functionalization of RHS and MT-RHS

Silica functionalization was performed by post-synthetic derivatization. In a typical experiment, 2 g of either RHS or MT-RHS were oven dried at 100 °C for 1 h and then dispersed in 60 mL of dry toluene under stirring for 1 h, followed by the addition of 1 mL of APTS or DEPA. The resulting mixtures were refluxed at 130 °C for 24 h. In all cases, the resulting solid powders were filtration, washed with methanol, and dried overnight at 100 °C. The primary and tertiary amine functionalized silicas were termed APTS-RHS, APTS-MT-RHS, DEPA-RHS and DEPA-MT-RHS (**Scheme 1**).



Scheme 1: Functionalisation of rice husk silica (RHS) and micelle templated rice husk silica (MT-RHS) with primary or tertiary amines.

vi. Materials characterization

Powder X-ray diffraction patterns were measured on a Bruker AXS D8 Advance X-Ray diffractometer, equipped with nickel filtered Cu K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$). Nitrogen physisorption was performed using a Quantachrome Nova 4200 porosimeter. Pore size distributions were determined using the Barrett-Joyner-Halend (BJH) method, applied to the desorption branch of the isotherms, while surface areas were determined by the Brunauer-Emmett-Teller (BET) method for p/p_0 between 0.05-0.3. Samples were degassed at $120 \text{ }^{\circ}\text{C}$ for 3 h prior to analysis. Analysis of the surface morphology of the materials was performed using a Zeiss Ultra Plus Field Emission Gun Scanning Electron Microscopy (FEG SEM) at 10 kV. Samples were carbon coated using a Quorum coater (Model Q150TE) prior to SEM characterization. DRIFTS measurements were conducted in air using a Thermo Nicolet 6700 FTIR spectrometer; samples were prepared by compressing a well-mixed sample containing 25 mg of catalyst powder and 225 mg KBr into the sample holder. KBr was used for a background subtraction. Surface compositions were determined by XPS using a Kratos Axis HSi spectrometer equipped with a charge neutralizer and monochromated Al K_{α} source (1486.7 eV) at normal emission; binding energies were referenced to adventitious carbon at 284.8 eV. TGA

was performed using PerkinElmer Pyris 6 thermal analyzer under flowing N₂ (30 ml/min) between 40-800 °C (ramp rate 10 °C/min).

vii. Transesterification reactions

Initial transesterification tests were performed using tributyrin, a C₄ triglyceride (TAG). Reactions were conducted at 60 °C in a Radleys reaction station employing 10 mmol of tributyrin, 1 mmol of dihexylether (internal standard), 300 mmol of methanol and 50 mg of catalyst in a two-necked round bottom flask. Reactions were run for 24 h, with samples periodically withdrawn, filtered, and diluted in dichloromethane prior to analysis by gas chromatography.

Transesterification of longer chain TAGs were also performed at 90 °C in a 100 ml ACE™ pressure flask, employing 10 mmol of tributyrin, tricaprylin (C₈), or trilaurin (C₁₂), 1 mmol dihexyl ether, 45 ml of methanol and 37 wt% of butanol (to ensure dissolution of the longer chain TAGs) and 50 mg of catalyst. Reactions were run for 24 h with samples periodically withdrawn, filtered, and diluted in dichloromethane prior to analysis by gas chromatography.

Tributyrin conversion and corresponding methyl butyrate production were monitored using a Varian 450-GC equipped with a Phenomenex ZB-5HT Inferno 15 m × 0.32 mm × 0.10 μm, while analysis of C₈ and C₁₂ TAGs and corresponding FAMEs used a 1079 programmable, direct on-column injector and Phenomenex ZB-1 HT Inferno 15 m × 0.53 mm × 0.15 μm capillary column. All catalytic data points are the average of 3 injections. FAME selectivity was calculated from $([FAME]/[TAG \text{ conversion}]) \times 100$, with initial rates determined from the linear portion of the conversion profile during the first 60 min of the reaction. Recycle tests were performed for tributyrin transesterification, with the catalyst recovered by centrifugation after 24 h reaction, washed with methanol and dried before re-use. All recycle experiments were performed at 60 °C, using 50 mg catalyst and a 1:30 molar ratio of tributyrin to methanol.

3. Results and Discussion

i. Materials characterisation

Elemental analysis of the parent RHS (**Table S1**) confirms that it was free from transition metal contaminants and only contained trace residual sodium from the sodium silicate precursor, most likely as NaCl. Successful synthesis of RHS and MT-RHS was first verified by N₂ porosimetry

(**Figure 1** and **Table 1**). RHS exhibited a type II isotherm consistent with a non-porous or macroporous structure, whereas the castor oil templated MT-RHS exhibited a type IV isotherm with a hysteresis loop at $p/p_0 = 0.45-1.0$, indicating the formation of mesopores. BET surface areas increased from 146 to 224 m^2g^{-1} with castor oil templating, with corresponding BJH analysis revealing well-defined 4 nm mesopores for MT-RHS (**Figure 1 inset**), demonstrating that ricinoleic acid was an effective mesopore-directing template during silica sol-gel synthesis from sodium silicate, as previously reported for oleic acid.[39] No low angle reflections were observed by XRD for the templated materials indicating the absence of long-range pore order in MT-RHS, with only a broad peak at $2\theta = 22^\circ$ consistent with amorphous silica (**Figure S2**).

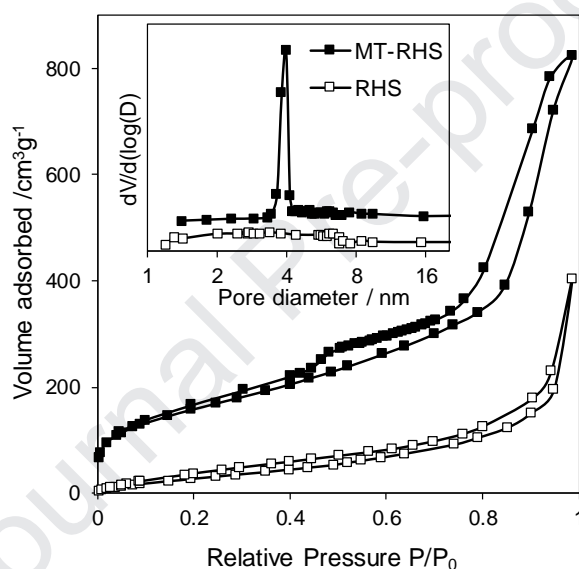


Figure 1: N_2 adsorption isotherms and pore size distribution for MT-RHS and RHS.

Table 1: Textural properties and functional group loading of rice husk silica materials.

Sample	BET surface area $/ \text{m}^2\text{g}^{-1}$	Pore Volume $/ \text{cm}^3\text{g}^{-1}$	Average BJH pore diameter $/ \text{nm}$	Amine loading ^a $/ \text{mmol.g}^{-1}$
RHS	146	0.22	-	-
APTS-RHS	116	0.21	-	0.54
DEPA-RHS	73	0.15	-	0.46
MT-RHS	224	1.24	4.0	-

APTS-MT-RHS	192	0.49	3.6	0.78
DEPA-MT-RHS	98	0.21	3.7	0.85

^aTGA analysis between 250-780 °C, assuming the complete decomposition and loss of $C_3H_6NH_2$ and $C_3H_6N(C_2H_5)_2$.

The surface morphologies of parent RHS and MT-RHS were examined by SEM (**Figure 2**). Both exhibited a coral sponge-like appearance similar to fumed silica[40] comprising fused agglomerates of spherical microstructures.

Amine functionalization decreased the surface areas and pore volumes of RHS and MT-RHS materials (**Table 1**, **Figure 3** and **Figure S1**), and mesopore diameters for MT-RHS, with the tertiary amine inducing a larger pore contraction than the primary amine, presumably reflecting the greater steric bulk of the former. The higher area MT-RHS support afforded higher APTS and DEPA loadings than their RHS counterparts (**Table 1** and **Figure S3**), reflecting the corresponding greater silanol density of the former (**Figure S4**). The similar APTS and DEPA loading observed for each support are consistent with a common coordination mode to surface silanols.

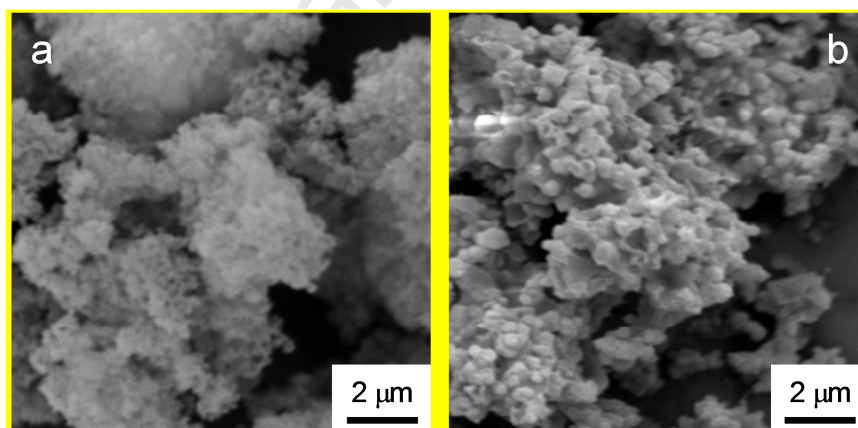


Figure 2: SEM micrographs for a) RHS and b) MT-RHS.

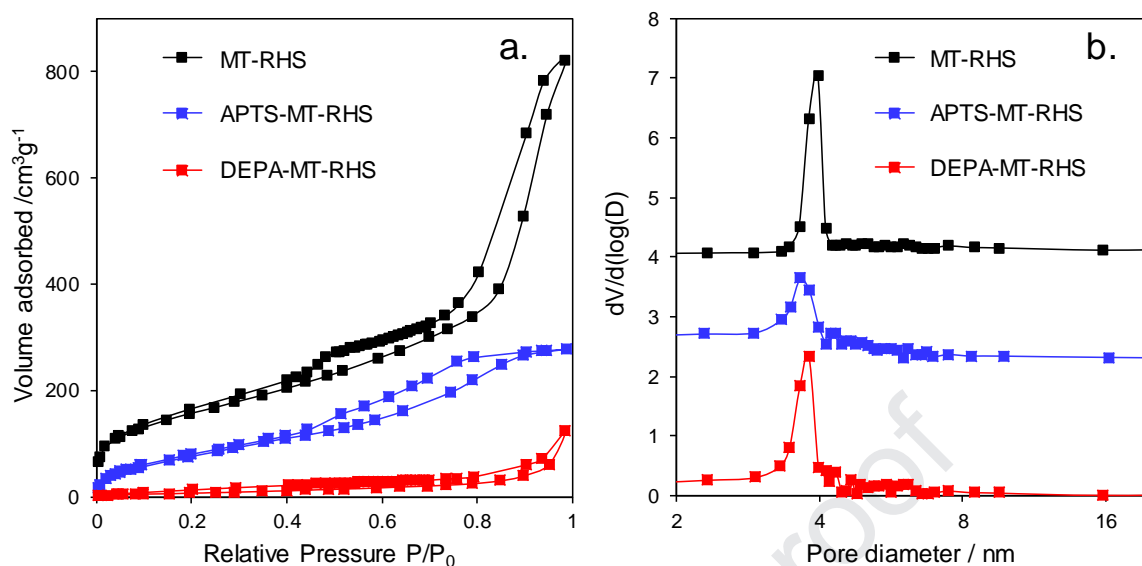


Figure 3: N_2 adsorption-desorption isotherms and corresponding pore size distributions for amine functionalized MT-RHS.

Surface analysis by XPS revealed a single nitrogen chemical environment for amine functionalized RHS and MT-RHS with a N 1s binding energy of 400 eV consistent with that expected for amine groups (**Figure 4**).[41]

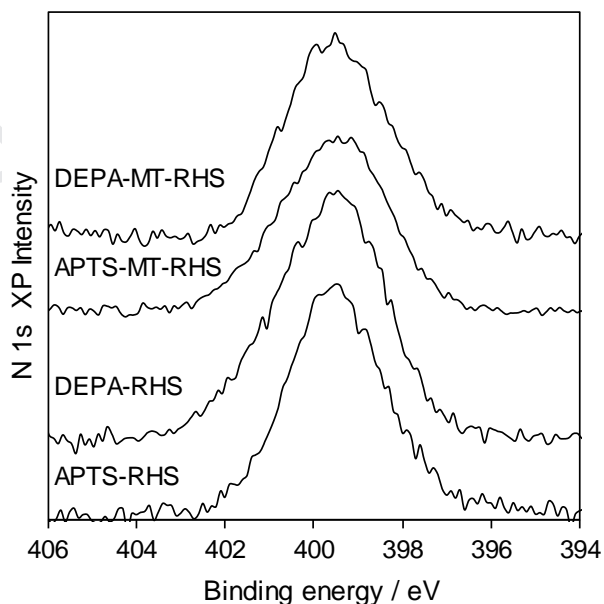


Figure 4: N 1s XPS spectra for RHS and MT-RHS functionalized with primary and tertiary amines

Surface chemistry of the parent and functionalized RHS and MT-RHS materials was analysed by DRIFTS (**Figure 5** and **Figures S4-5**). As-synthesized RHS and MT-RHS exhibited a strong peak at 1076 cm^{-1} due to siloxane (Si-O-Si) and silanol (Si-O-H) modes at 803 and 3569 cm^{-1} respectively. The intensity of the latter decreased upon functionalization, concomitant with the appearance of new bands at $3250\text{-}3400\text{ cm}^{-1}$ (assigned to ν_s and ν_{as} in NH_2) and 1626 cm^{-1} ($\delta\text{ N-H}$) for APTS, and 1250 cm^{-1} ($\nu\text{C-N stretch}$) for DEPA, consistent with amine grafting at silanol grafting at surface silanols. Amine functionalized silicas also exhibited bands at 2915 and 2859 cm^{-1} (νCH_2 of the propyl linker), with DEPA exhibiting additional bands at 2798 and 2967 cm^{-1} attributed to the CH_2 and CH_3 modes of the ethyl groups of the tertiary amine.

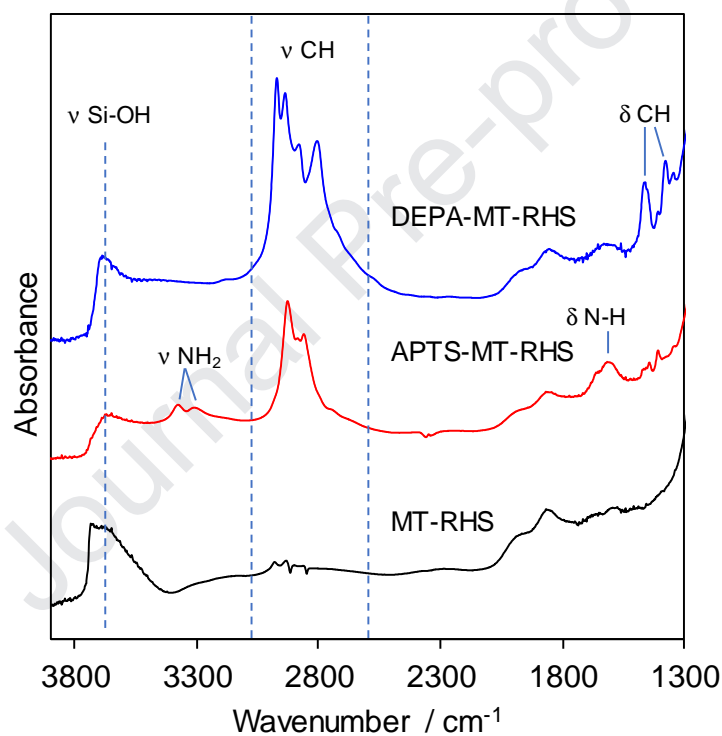


Figure 5: DRIFT spectra of primary (APTS-MT-RHS) and tertiary (DEPA-MT-RHS) amine functionalized micelle templated rice husk silica.

ii. Catalytic Activity:

Amine derivatized RHS and MT-RHS were first evaluated for the transesterification of tributyrin with methanol to evaluate the impact of mesoporosity and amine selection (**Table 2** and **Figure 6**). Control reactions revealed tributyrin conversions of 5 % and 11 % for the parent MT-RHS

and RHS. Turnover frequencies (TOFs) for tributyrin conversion, and the yield of methyl butyrate, were higher for the MT-RHS than RHS catalysts, and for the tertiary versus primary amine (correlating with their basicity). The higher activity of the MT-RHS is attributed to improved mass transport and amine accessibility, while the higher TOF of the tertiary amine is attributed to its fractionally stronger basicity.[42-45] The maximum TOF of 140 h^{-1} for the DEPA-MT-RHS catalyst compares favorably with recent reports for other solid bases including nano-MgO (84 h^{-1}),[46] MgO-ZrO₂ (100 h^{-1}), [47],[48] and a Mg₃Al hydrotalcite (60 h^{-1}),[49] but is less than observed for macroporous Mg-Al hydrotalcites (376 h^{-1}) for which mass transport is extremely efficient.[50] Recycle tests for DEPA-MT-RHS evidenced modest catalyst stability, with only a 10 % decrease in conversion following the first re-use (**Figure S6**), albeit dropping by 50 % after five re-uses.

Table 2: Reaction data for the amine functionalized RHS and MT-RHS for tributyrin transesterification.^d

Catalyst	Specific activity ^a / $\text{mmol h}^{-1} \text{ g}^{-1}$	TB Conversion ^b / %	MB Yield ^b / mmol	MB selectivity ^b / %	TOF ^{a,c} / h^{-1}
RHS	-	11	-	-	-
APTS-RHS	20	96	19	67	37
DEPA-RHS	41	98	22	75	89
MT-RHS	-	5	-	-	-
APTS-MT-RHS	42	97	23	80	54
DEPA-MT-RHS	125	99	24	81	147

^a1 h reaction; ^b24 h reaction; ^cNormalised to amine loading from TGA. ^dConditions: 10 mmol tributyrin, 1 mmol dihexylether (internal standard), 300 mmol of methanol and 50 mg of catalyst, temperature $60 \text{ }^{\circ} \text{C}$.

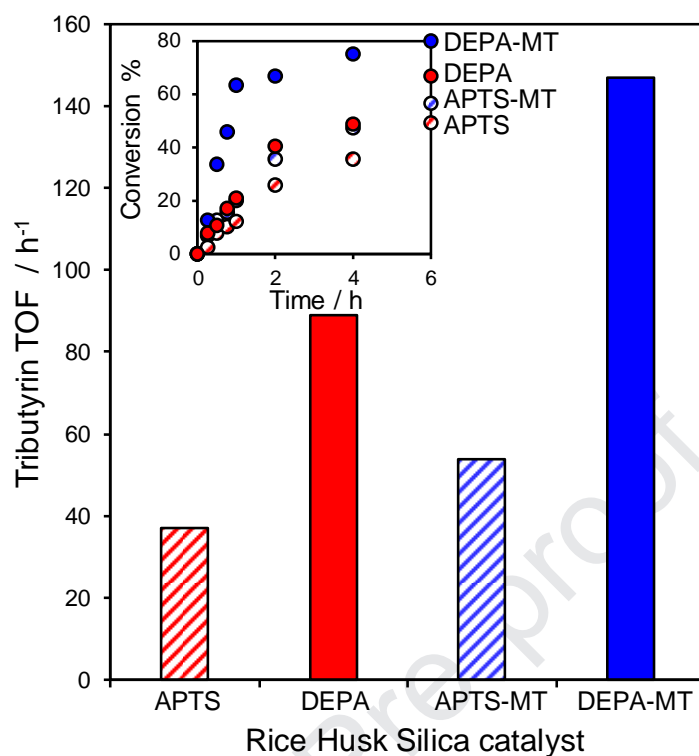


Figure 6: Turnover frequencies for tributyrin transesterification with methanol over amine functionalized RHS and MT-RHS. Inset shows corresponding tributyrin reaction profiles. Conditions: 10 mmol tributyrin, 1 mmol dihexylether (internal standard), 300 mmol of methanol and 50 mg of catalyst, temperature 60° C.

The versatility of DEPA-MT-RHS was further examined in the transesterification of C₈ and C₁₂ TAGs (**Figure 7**). Conversion and activity decreased with TAG chain length from C₄ > C₈ > C₁₂, attributed to slower diffusion and poorer active site accessibility of the bulkier oils, as previously observed for a macroporous Mg-Al hydrotalcite and Cs-doped MgO.[50, 51] The measured TOFs are superior to those obtained using nanoparticulate MgO, but lower than for Cs-doped MgO [51] or a macroporous Mg-Al hydrotalcite [50] which are stronger bases. FAME selectivities of 93 % and 71 % were obtained for methyl caproate and methyl laurate respectively after 24 h.

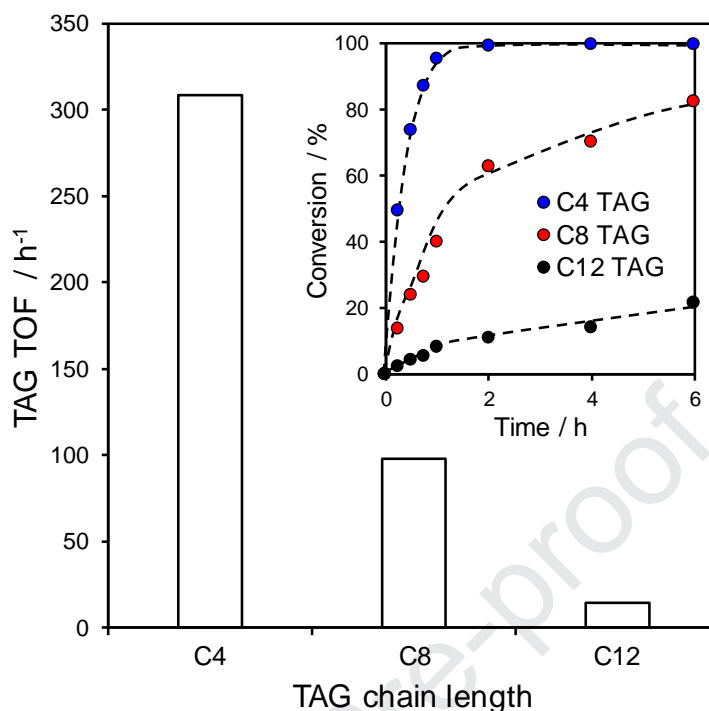


Figure 2: Turnover frequencies for C4, C8, and C12 transesterification with methanol over DEPA-MT-RHS. Inset shows corresponding reaction profiles. Conditions: 10 mmol of TAG, 1 mmol dihexylether (internal standard), 45 ml of methanol and 37 wt% of butanol (to solubilize longer chain TAGs) and 50 mg of catalyst, 90 °C in a 100 ml ACE™ pressure flask.

Rice-husk silica is a promising precursor for the synthesis of mesoporous solid base catalysts using castor oil (likely ricinoleic acid) as a renewable structure directing agent. Tertiary amine functionalised rice husk silicas exhibit excellent activity and modest stability for triglyceride transesterification, and future studies will explore the broader application of these materials in continuous flow processing of bio-oils.

Conclusions

Mesoporous micelle templated rice husk silica (MT-RHS) with well-defined 4 nm pores were successfully synthesized using sodium silicate obtained from rice husk ash and castor oil as a surfactant template. MT-RHS possessed a high surface area than its non-templated counterpart, indicating that castor oil acts as pore directing agent. Templated mesoporous silica comprised agglomerates of spherical microstructures, but lacked long range mesopore order. Amine

functionalization with primary (APTS) or tertiary (DEPA) amines afforded solid base catalysts active for the low temperature transesterification of C₄-C₁₂ triglycerides to their corresponding fatty acid methyl ester. Catalyst activity decreased from DEPA-MT-RHS>DEPA-RHS>APTS-MT-RHS>APTS-RHS, with DEPA-MT-RHS exhibiting a 65 % enhancement in activity relative to the RHS counterpart. DEPA-MT-RHS was recyclable, with only a 10 % loss in C₄ TAG conversion after the first re-use, and proved effective for the transesterification of longer chain C₈ and C₁₂ triglycerides to their corresponding FAMEs.

Acknowledgments

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#Dedicated to the memory of the late Professor Egid Beatus Mubofu, who was an inspiration to so many young Green Chemists. Greatly admired and missed - forever remembered.

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Valorisation of rice husk silica waste: Organo-amine functionalized castor oil templated mesoporous silicas for biofuels synthesis.

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Highlights

- Mesoporous silica synthesized from rice husk ash and a castor oil template.
- Templating increases surface area and introduces well-defined 4nm pores.
- Successful functionalisation with primary and tertiary amine demonstrated.
- Tertiary amine functionalised silicas most active in transesterification.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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