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Process Intensification of Catalysed Henry Reaction using Copper-Wool Catalyst in a Spinning Mesh Disc Reactor

Parimala Shivaprasad¹, Matthew David Jones², Darrell Alec Patterson¹, Emma Anna Carolina Emanuelsson^{1*}

^{1, 1*}*Department of Chemical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, UK, eaep20@bath.ac.uk*

²*Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK*

Abstract

The spinning mesh disc reactor (SMDR) is a novel process intensification technology which uses centrifugal force to drive reaction fluid over a mesh supported catalyst on a rotating disc. The potential of the SMDR for organic synthesis has been demonstrated for the first time for Henry reaction¹ using copper immobilised on woollen cloth mesh. A new protocol for copper immobilisation on wool has been developed producing a superior catalyst to the homogeneous copper triflate system: copper heterogenised on wool afforded a higher batch conversion (85%) (cf. 57% for the homogeneous case) in the same timeframe. In the SMDR, the reaction was more efficient than either homogeneous or heterogeneous batch reaction: with further optimisation the conversion increased from 77% to 93% as the spinning speed of the disc increased from 250 to 450 RPM at a flowrate of 3 ml s⁻¹. There was only a 3% reduction in conversion on re-use of copper wool over 3 cycles under similar experimental conditions indicating that this catalyst is robust. Pure wool was also found to have some catalytic activity for the Henry reaction, giving a maximum conversion of 85% at 450 RPM in the SMDR. However, it deactivated significantly with reuse and therefore cannot be considered a stable, robust catalyst. Overall, the results show that the copper immobilised wool in the SMDR can be used to improve the conversions for the Henry reaction and that there is therefore promise for the SMDR to be extended to other traditional solvent based reactions.

Keywords: Spinning mesh disc reactor, Copper immobilisation, Woollen cloth support, Henry reaction, Intensified solvent reaction system

1. Introduction

Process intensification can be synonymous with enhanced reaction efficiencies, lower chemical inventory, reduced operating costs and reduction in process waste generation [1]. The spinning disc reactor (SDR) is a process intensification technology where liquid is impinged at the centre of a rotating disc, producing a thin

film with a high shear stress on the surface of the disc due to the centrifugal force associated with the rotating disc [2]. This allows for short residence times, an increase in mass/heat transfer and high shear forces resulting in better mixing [3]. The SDR has been applied for fast and highly viscous reactions such as in the manufacturing of pharmaceuticals [4], production of polymers [5], precipitation processes [6], synthesis of nanoparticles [7] and biodiesel production [8].

The spinning mesh disc reactor (SMDR), an innovative reactor design, builds on the SDR concept but it also has a cloth with an immobilised catalyst resting on top of the disc surface. The cloth both protects the catalyst from hydrodynamic forces, and allows for an increase in mass transfer both on top and within the cloth, creating a zone of rapid mixing. The SMDR demonstrated a 18% increase in reaction conversion under the same experimental conditions as a conventional batch stirred tank reactor (BSTR) for the hydrolysis of tributyrin using immobilised lipase on wool as a catalyst [9]. 80% of the initial activity of the lipase cloth was retained for 15 cycles, further exemplifying the robustness of the reactor. Residence time distribution (RTD) studies show that the SMDR is a well-mixed reactor, in difference to SDR, which exhibits plug flow behaviour [10]. Scale-up of the SMDR was easily achieved by increasing the number of cloths resting on the disc, increasing the conversion with an increase in the catalyst loading [11]. Similar to the micro-reactor concept, SMDR can be scaled up by “numbering up” i.e. increasing the number of reactors or by increasing the number of discs on the rotation shaft. This is in contrast to traditional reactors where scale up requires re-design in terms of parameters such as Prandtl and Reynold's numbers, thus accelerating transfer of lab scale processes to industrial applications [2, 11, 12]. To demonstrate and investigate the versatility of the SMDR, the next step is to extend the application from aqueous enzyme catalysis to chemical synthesis in organic solvents using non-biological immobilized catalysts on cloths.

Key advantages with immobilizing catalysts is the potential to facilitate catalyst recovery and re-use. This has resulted in research towards finding the most appropriate support material and immobilisation methods for a wide range of catalysts. Materials including silica, zeolites and activated carbon have been widely used as catalyst supports [13]. Cloths are an alternative, less researched, promising material for catalyst immobilisation due to their superior mechanical properties, versatility, low pressure drop and increased mass transfer [14]. Research has shown that wool is an attractive support for enzyme immobilisation as it is

inexpensive, has a large surface area (ca. 200 m² g⁻¹) and is rich in surface functional groups (like tyrosine, glutamic and aspartic acid groups) [15-19]. However, limited literature is available on immobilisation of metals or simple complexes thereof on wool. One such report by Yuan et al [20] involves the use of palladium immobilised on wool for asymmetric hydrogenation of diacetone alcohol. The resulting metal cloth was found to be robust over several cycles and wool-Pd complex was naturally chiral resulting in the synthesis of optically pure products. Copper has also been immobilized on wool to improve its antibacterial properties [21, 22], but the protocol involves numerous time consuming and energy intensive reaction steps.

Copper has recently been shown to catalyse the nitroaldol condensation reaction (Henry reaction) using immobilised copper triflate on silica and zeolite supports (conversions ~ 70 to 90% and enantiomeric excess (ee)~ 40%) with current drawbacks such as long reaction times and reduced selectivity [23]. The Henry reaction is principally a reaction between a nitroalkane and an aldehyde in the presence of a base resulting in the formation of β -nitroalcohol, a building block for various pharmaceuticals like (S)-propranolol, Amprenavir, the HIV protease inhibitor to name a few [23]. It is an important reaction in organic chemistry as it produces a new carbon-carbon bond. Most of the conventional metal catalysts for the reaction like zinc (II), chromium (III), cobalt (II) and lanthanum (III) are either toxic, expensive or not biocompatible, which are imperative pre-requisites for drug manufacture in the pharmaceutical industries [24]. Copper is cheap, bio-compatible, and relatively harmless and thus has the potential to be the metal of choice for Henry reaction.

The aim of this paper is thus (i) to demonstrate the versatility of the SMDR, (ii) to develop a simple, effective and reusable immobilisation protocols for copper on wool and (iii) to enhance the selectivity, ee and the reaction rate for the Henry reaction. The copper wool will be fully characterised, and the reaction rates, selectivity and ee will be compared between batch reactions and the SMDR for both plain wool and copper wool. The effect of operating parameters in the SMDR such as spinning speed and flow rate will be investigated and optimised.

2. Materials and Methods

2.1 Materials

All chemicals and solvents were purchased from Sigma Aldrich and used as received unless mentioned otherwise. Wool (unbleached cloth of 1.5 mm thickness) was procured from Trellis (Otago, New Zealand). All solutions were prepared using deionised water (Reservoir-Elga).

2.2 Catalyst immobilisation on wool

A four step procedure was used to immobilise copper triflate on wool. Woollen cloth was cut into circular piece of diameter 12 cm, each weighing 12 g. The cloth was first treated with a solution containing hydrogen peroxide (30 %, 30 ml l⁻¹) and sodium silicate (2 g l⁻¹) in a pH 9 buffer (0.1 M sodium bicarbonate and sodium carbonate) for 70 min at 55 °C. The cloth was washed with deionised water thrice (5 minutes for every cycle) and air dried. The bleached cloth was then soaked for 2 hours at room temperature in a 2 % (w/v) solution of polyethyleneimine (PEI) (adjusted to pH 8 using hydrochloric acid) and washed with deionised water. Post surface modification with PEI, wool was soaked in a copper triflate solution in methanol (0.1 g l⁻¹) for 24 hours followed by immersing the cloth in a 0.5 % (w/v) glutaraldehyde solution in pH 6 buffer (0.1 M sodium hydrogen phosphate and sodium dihydrogen phosphate) for 10 minutes for crosslinking and rinsed with deionised water.

2.3 Material characterisation techniques

In order to analyse the effect of pre-treatment and the reaction on wool, Fourier transform infrared spectroscopic analysis (FTIR) was carried out using a Perkin-Elmer-100 FTIR spectrometer. The plain and copper wool samples were scanned from 4000 to 600 cm⁻¹ with 16 scans per wavelength. The background spectra without any sample was obtained before analysing the samples of interest. Solid state UV-Vis spectroscopy of plain wool and copper wool was carried using a Perkin-Elmer Lambda (650) UV-Vis spectrophotometer. Square pieces of wool were analysed without any further sample preparation. The light absorbance of the samples were determined by scanning the samples from 200 to 800 nm. Baseline was obtained using plain wool. The Thermal gravimetric (TG) analysis of plain and copper wool was carried out using Setaram TG-92 to determine the effect of temperature on the physical properties of the catalyst. The samples were heated to 700 °C at a heating rate of 5 °C min⁻¹ and the corresponding loss in wool weight was recorded. Scanning Electron Microscopy (SEM) images of plain wool and copper wool were obtained using a JEOL SEM6480LV. Wool fibres were stuck onto a double sided carbon adhesive tape, which was then

mounted on the sample holder. The plain wool and copper wool samples were coated with gold for improved imaging. Energy Dispersive X-Ray analysis (EDX) was carried out to determine the elemental composition of plain wool and copper wool using an Oxford INCA X-Act SDD X-ray detector coupled to the SEM6480LV. Sample preparation for EDX analysis was similar to that used for SEM without the gold coating. The copper loading on wool was determined using X-ray photoelectron spectroscopy (XPS) carried out by the Nexus facility at Newcastle University using an Axis Nova spectroscope and CasaXPS was used to analyse the spectrum. Square samples of 1cm² were prepared by sticking wool fibres of uniform lengths on a double sided adhesive tape.

2.4 Reaction conditions

2.4.1 Nitroaldol condensation reaction in batch

In a typical batch process, ethanol (10 ml) was added to the catalyst (0.15 g) and stirred. Benzaldehyde (1 mmol), nitromethane (10 mmol) and triethylamine (0.16 mmol) were added and reaction was carried out at 25 °C for 24 hours in triplicates in a reaction carousel.

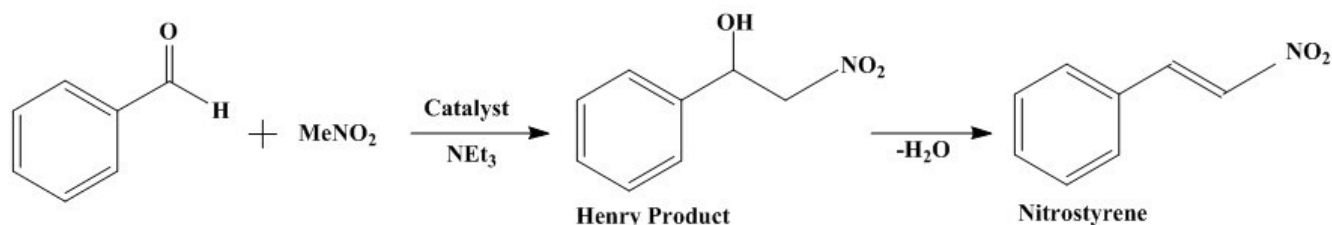


Figure 1: The Henry reaction between benzaldehyde and nitromethane. This also illustrates the potential side product, nitrostyrene.

Neat samples drawn out at 4, 6 and 24 hours were used for NMR spectroscopic and GC analysis to determine the conversion of the reaction. The enantiomeric excess was determined using HPLC.

2.4.2 Nitroaldol condensation reaction in SMDR

The SMDR primarily is a circulating batch reactor which is centrally fed overhead (Figure 2). The reactor consists of a rotor (Heidolph RZR 2021), with a variable speed, connected to a glass disc (12 cm diameter and 2 mm thick) with a metal rod. The disc is the critical component of the reactor as the cloth rests on top of the disc. The cloth was cut to the size of the disc and placed on the disc without any fastening. The disc is surrounded by a steel chamber shaped as a funnel. The liquid feed is pumped to the centre of the disc by a peristaltic pump (Watson-Marlow 503U) through a feed pipe. The position of the overhead feed pipe is such that the liquid feed impacts the centre of the cloth with minimum splashing to allow maximum wetting of the cloth. The centrifugal force enables the formation of uniform film of the feed on the surface of the cloth and ensures good contact between the reactants and the cloth. The steel funnel is used to contain and funnel down any liquid spun off the edge of the disc into the reactant vessel. In order to facilitate the reaction under an inert atmosphere, the entire set-up was sealed on all sides with perspex panels with gas inlet at the bottom and an outlet at the top. Before the reaction, the box housing the reactor was purged and filled with nitrogen gas under 0.3 bar pressure and 8 l min^{-1} gas flow rate. The entire box was filled with nitrogen in 15 minutes, after which the gas flowrate was reduced to 2 l min^{-1} to compensate for any gas leakage. The nitrogen atmosphere was ensured by monitoring depletion of oxygen levels using an oxygen probe.

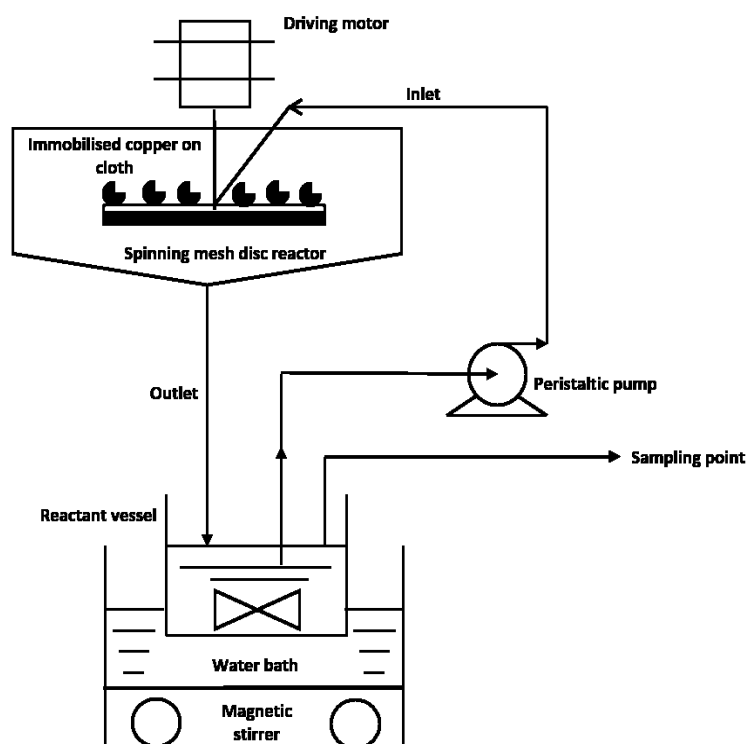


Figure 2: Schematic diagram of the spinning mesh disc reactor (SMDR) used in the present study

Benzaldehyde (1 mmol), nitromethane (10 mmol), triethylamine (0.16 μmol) and dodecane (0.5 mmol) were dissolved in 250 ml ethanol and the reaction was carried out at 25 $^{\circ}\text{C}$. The disc was connected to the driving motor and spun at the desired speed. The reaction was started by turning on the peristaltic pump and was carried out for 5 hours. 1.5 ml of samples were taken out every 5 minutes for the first 30 minutes and every hour thereafter and analysed using GC and the final sample was also analysed using NMR spectroscopy. The effect of spinning speed and shear stress on the reaction conversion was studied. The surface shear is directly proportional to the spinning speed and reaches a maximum at the disc edge. The following equation is used to calculate the surface shear [25]:

$$S = \left(\frac{3Qr\omega^4}{2\pi\nu^2} \right)^{1/3}$$

Where, S = surface shear (s^{-1}); Q = volumetric flow rate ($\text{m}^3 \text{s}^{-1}$); r = radial distance (m);

ω = angular velocity (rad s^{-1}); ν = kinematic viscosity ($\text{m}^2 \text{s}^{-1}$).

The average surface shear on the surface of the disc can be calculated using the equation of distribution on the surface as follows:

$$\bar{S} = \frac{1}{R} \int_0^R S dr = \frac{3}{4} \left(\frac{3QR\omega^4}{2\pi\nu^2} \right)^{1/3}$$

Where: R = the radius of the disc.

In the present study, the average surface shear was used to characterise the performance of the reactor.

2.4.3 Gas Chromatography (GC)

The conversion of the reaction and the formation of the product was monitored using a Varian CP-3800 gas chromatograph model. A CP-Sil-8 CB column (30 m \times 0.32 mm) with a film thickness of 0.25 μm was used. The injector and detector temperature were maintained at 220 $^{\circ}\text{C}$ and 250 $^{\circ}\text{C}$ respectively. The column oven was held at 40 $^{\circ}\text{C}$ for 3 minutes, heated to 200 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$ and held for 2 minutes thereafter. Dodecane (0.6 mmol) was used as the internal standard (IS).

2.4.4 Proton NMR Spectroscopy

Detection of product and conversion of the reaction was determined by analysis of the ^1H NMR spectra. Neat samples were used for all the analysis. 0.1 ml of the sample was dissolved in 0.6 ml of deuterated chloroform and the samples were run in a 300 MHz Bruker Spectrometer. Conversion using NMR spectroscopy was determined by the analysis of the ^1H integral of benzaldehyde at 9.94 ppm to the ^1H integral of $\text{PhCH(OH)CH}_2\text{NO}_2$ at 5.45 ppm, as previously detailed elsewhere [23].

2.4.5 High Performance Liquid Chromatography (HPLC)

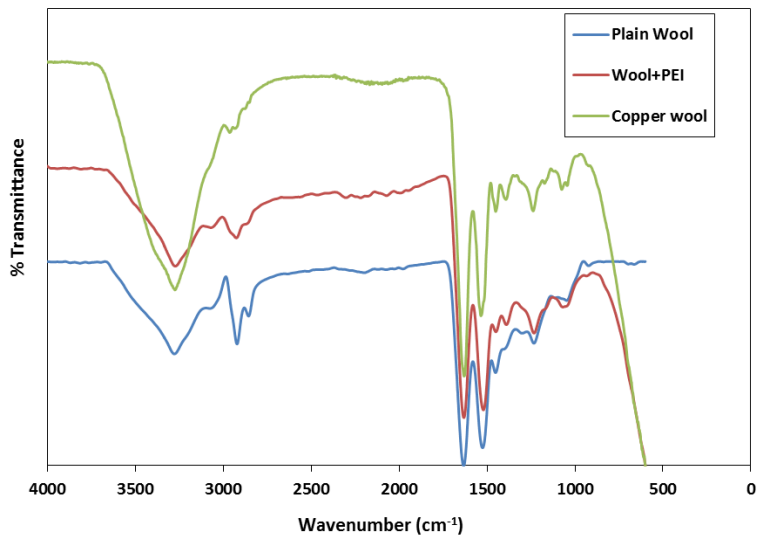
To determine the enantiomeric excess of the product, HPLC was carried out using Agilent technologies-1260 infinity with UV detector (254 nm). An Astec Chirobiotic V2 chiral column was used. The flow rate of IPA and hexane (1:9) was maintained at 0.5 ml/min. The enantiomeric excess (ee) was calculated using the following equation:

$$ee = \frac{(R - S)}{(R + S)}$$

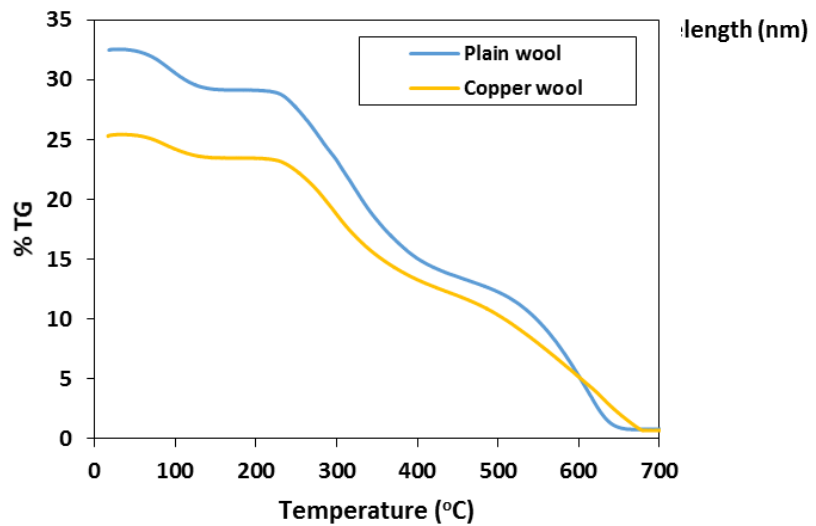
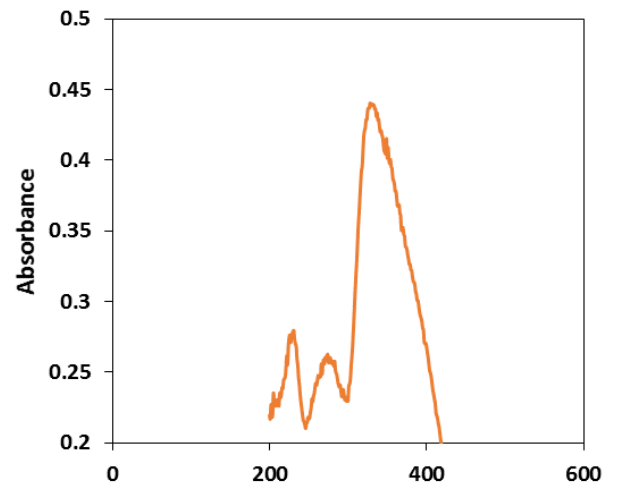
3. Results and Discussion

3.1 Spectroscopic analysis of wool

FTIR spectra analysis was used to determine the functional groups present in wool (Figure 3(a)). In plain wool, the broad peak at 3280 cm^{-1} can be attributed to N-H stretching bond and the sharp peaks at 1633 cm^{-1} , 1525 cm^{-1} and 1236 cm^{-1} is due the presence of S-H and N-H groups present in wool. Post PEI treatment, the new peak at 3070 cm^{-1} and 1392 cm^{-1} is due to the N-H stretching bond induced by PEI. Along with the reduced intensity of the peak at 2929 cm^{-1} , it can be inferred that PEI was successfully immobilised on wool [9]. In the FTIR spectra of copper wool, there is a reduction in the intensity of peaks at 1523 cm^{-1} , 1639 cm^{-1} and 1234 cm^{-1} indicating the interaction of the metal with the amide I (N-H stretching bond), amide II (C-N stretching bond) and amide III (N-H bending bond) indicating the formation of copper-keratin complex on wool [26]. The immobilisation of copper on wool was further confirmed by UV spectroscopy. Post copper immobilisation on wool, a broad peak observed at a wavelength of 336 nm (Figure 3(b)). Copper has a high affinity for nitrogen base groups and thus, we hypothesise that the Cu(II) ions are ligated to the nitrogen containing amino acid residues present in wool [27].



(a)



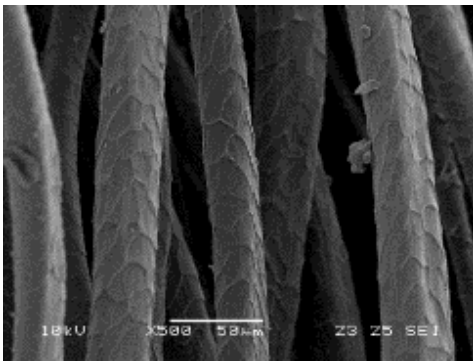
(c)

Figure 3: (a) FTIR spectrum of plain wool and copper wool, (b) Solid state UV spectrum of plain wool and copper wool and (c) TG analysis of plain wool and copper wool in air

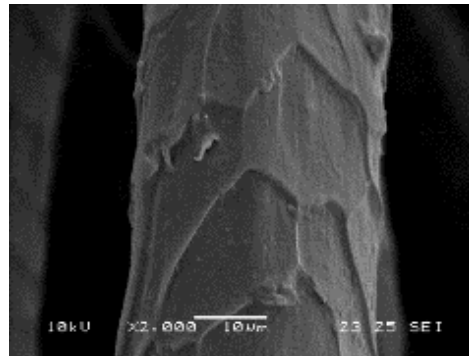
The thermal stability of plain and copper wool was carried out by TG analysis as shown in (Figure 3(c)). In the TG profile of plain wool, the initial weight loss up to 120 °C is due to the hydrogen bonded water within the wool fibres. The second step of weight loss occurs at over 200 °C due to the thermal decomposition of cysteine and terminal amino acid groups. From 430 °C to 600 °C, the weight loss is due to the oxidation of the carbonised residue. In the TG profile of copper wool, an increase in the weight loss in the third stage of decomposition compared to plain wool confirms the immobilisation of copper on wool [28].

SEM analysis of wool was carried out to understand the morphology of plain and copper wool. The morphology of plain wool fibres is characterised by tiled cuticle cells on the surface of the fibre with a fibre

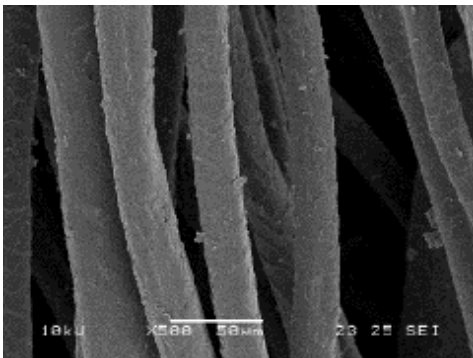
diameter of 2.6 μ m (Figure 4 (a-b)). Individual copper particles are not clearly visible in the SEM image of copper wool, however, the loss of definition of the scales on the fibre surface is indicative of a coating on top of them resulting in surface modification of wool (Figure 4 (c-d)).



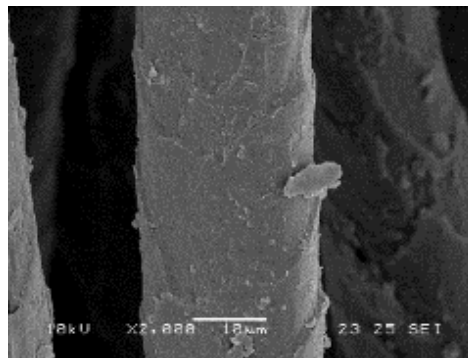
(a)



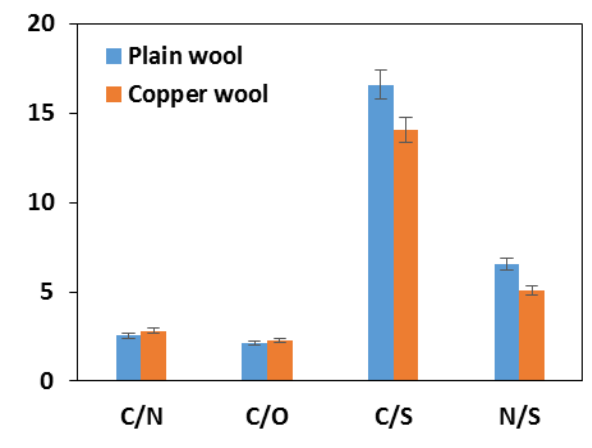
(b)



(c)



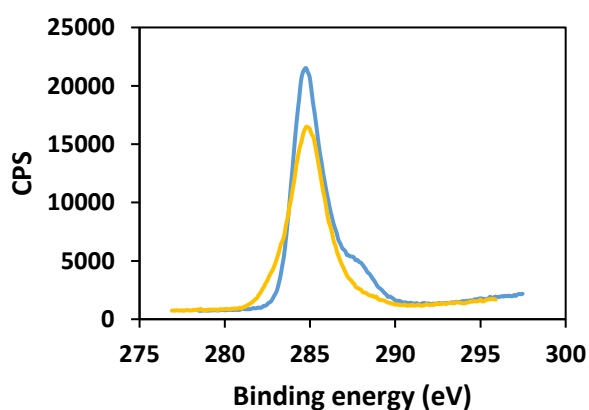
(d)



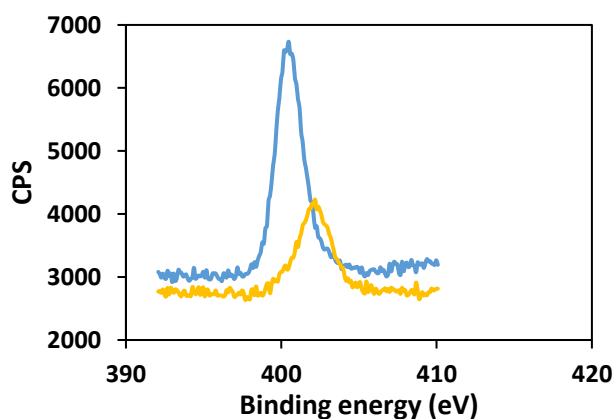
(e)

Figure 4: SEM images of: (a-b) Plain wool, (c-d) Copper wool and (e) Elemental ratios present in plain wool and copper wool analysed using EDX

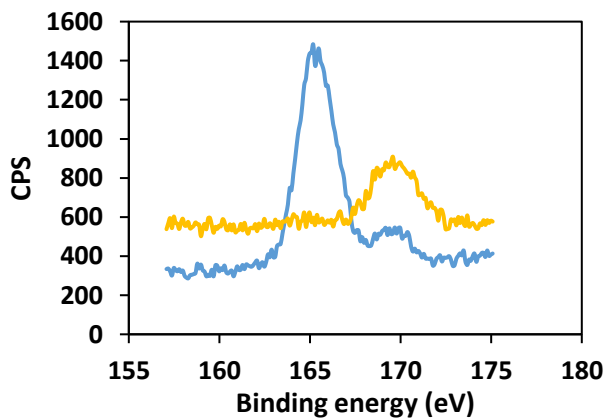
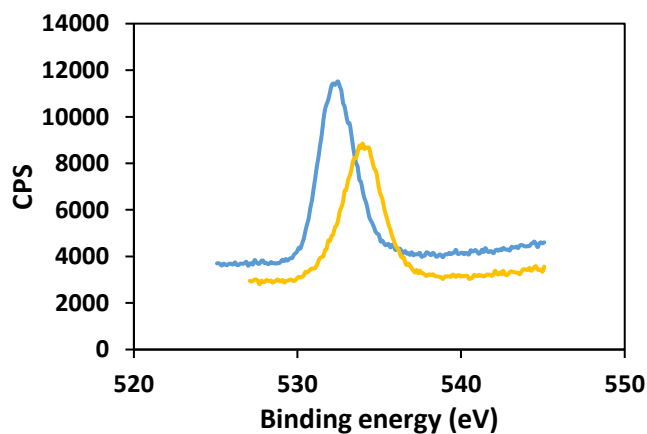
The results from EDX analysis of wool are expressed as elemental ratio as quantification of individual elements is associated with instrument inaccuracy (Figure 4(e)). A copper loading (determined via EDX) of 0.82% was obtained on the surface of wool. The change in C/N post copper immobilisation is almost negligible indicating that none of the surface lipids were lost from the wool cloth. Wool remains un-oxidised post copper immobilisation as C/O is almost constant [29]. A decrease in C/S and N/S post copper immobilisation may be ascribed to the presence of sulphur from copper triflate which further confirms copper immobilisation on wool. The survey spectrum obtained from the XPS analysis of plain wool indicated the presence of carbon (82.55 %), oxygen (10.05 %), nitrogen (5.7 %) and sulphur (1.71 %). Immobilisation of copper triflate on wool was confirmed by the presence of copper (0.67 %) and fluorine (5.3 %). From the elemental scans, there is a clear indication of a change in the binding energy of copper wool which indicates the interaction between the amino acid residues present in wool and copper triflate (Figure 5(a-d)). Also, the presence of Cu2p in copper wool further confirms copper immobilisation on wool (Figure 5(e)).



(a)

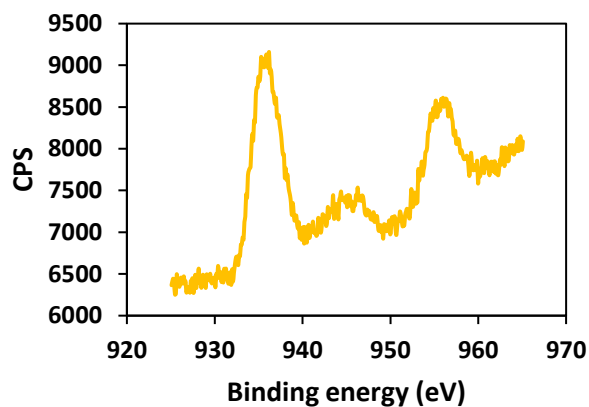


(b)



(c)

(d)



(e)

Figure 5: Elemental scans of plain wool and copper wool. (a) C1s, (b) N1s, (c) O1s, (d) S2p and (e) Cu2p

— Plain wool — Copper Wool

3.2 Copper cloth for nitroaldol condensation reaction

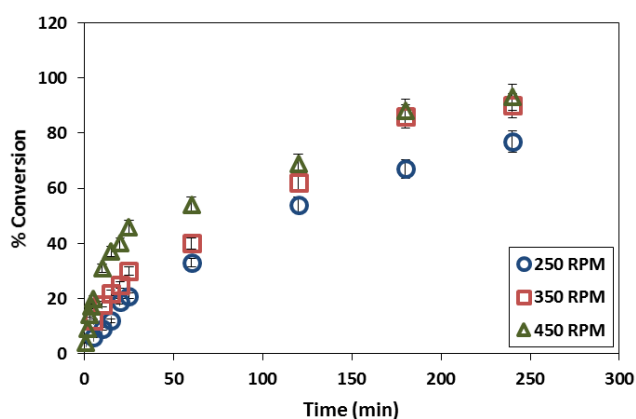
The reaction in batch was carried out using copper triflate immobilised on wool and free copper triflate and a reaction conversion of 85% and 57% was obtained respectively (Table 1). Catalyst immobilisation is usually associated with a reduction in reaction conversion compared to the free catalyst. The reactants in the bulk solutions have to overcome the diffusion resistance offered by a stagnant liquid film on the surface of the cloth to come in contact with the catalyst present on and within the cloth. However, in the present study, the increase in conversion may be due to the formation of copper-protein complex on wool which maybe a more efficient catalyst.

Table 1: Results of nitroaldol condensation reaction in batch using free and immobilised copper triflate

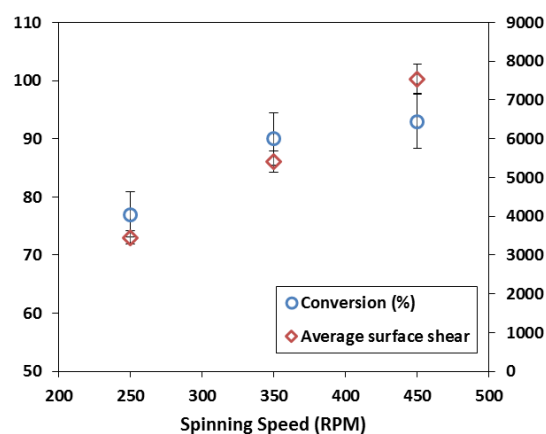
Catalyst	Time (h)	% Conversion
Free copper triflate (homogeneous, batch)	4	38
	6	42
	24	57
Copper cloth	4	41

(heterogeneous bath)	6	63
	24	85

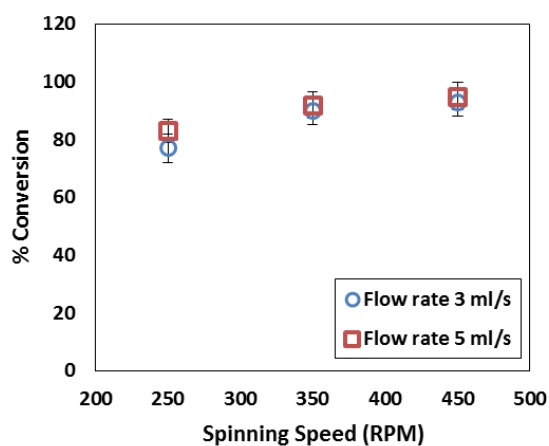
In the SMDR, the conversion of the reaction was found to be 90% accompanied by a reduction in the reaction time to 5 hours (Figure 6(a)). The conversion obtained in the present study is higher than that reported in literature for Henry reaction in batch [23]. A higher reaction conversion in the SMDR is due to the decrease in mass transfer resistance between the catalyst and the reactant in the thin film on and within the cloth owing to the rapid mixing associated with the spinning disc as opposed to the liquid flow in a batch system which is centrifugally forced over the immobilised catalyst. Another reason for this can be due to the increased residence time of the reactant on the immobilised catalyst on the cloth surface ensuring a constant presence of the reactant in reaction zone.



(a)



(b)



(c)

Figure 6: (a) Effect of spinning speed on reaction conversion and (b) Correlation between reaction conversion and average surface shear (Flow rate: 3 ml/s and spinning speed 350 RPM) and (c) Effect of feed flowrate on reaction conversion

The effect of spinning speed and feed flowrate on reaction conversion was studied. Average surface shear is proportional to the spinning speed of the disc and research has shown that this results in a higher degree of mixing on the surface of the disc, hence improving the overall reaction conversion [9, 10]. The reaction conversion increased from 77% to 93% as the spinning speed of the disc increased from 250 to 450 RPM at a flowrate of 3 ml s⁻¹ (Figure 6(b)). A higher flowrate of the reactant feed results in an increase in conversion as the frequency of contact between the immobilised catalyst and the reactant is much higher. There was a 4% increase in the reaction conversion on an average as the flowrate increased from 3ml s⁻¹ to 5 ml s⁻¹ (Figure 6(c)). Enantiomeric studies were carried out and the ee of the reaction catalysed by copper wool was found to be 64% (SMDR), compared to essentially a racemic mixture obtained by reaction catalysed by free copper triflate.

3.8 Catalytic activity of wool for nitroaldol condensation reaction

As a part of the continuing studies of the reaction, it was found that plain wool exhibited catalytic properties by itself. A conversion of 77% was observed with plain wool after 24 hours in batch compared to 85% conversion obtained with copper wool under similar experimental conditions (Table 2). Wool is made of natural amino acids to which its catalytic activity can be attributed. The aldol reaction has been shown to be catalysed by amino-acids, an example being proline [30] and other metal free systems are well known [31]. Post reaction, the wool acquired a yellowish-brown tint which may be due to the oxidation of tyrosine to quinone, as tyrosine is highly reactive and influences the property of wool [32]. In the SMDR, reaction conversion increased with increase in the spin speed of the disc (Figure 7). Also, this allows the liquid feed to flow through the cloth, increasing the contact with the functional groups present in wool. A maximum conversion of 85% was obtained at a spin speed of 450 RPM.

Table 2: Results of nitroaldol condensation reaction in batch catalysed by copper triflate and plain wool

Catalyst	Time (h)	% Conversion
Free copper triflate	4	38
(homogeneous batch)	6	42
	24	57
Plain wool	4	35
(heterogeneous batch)	6	50
	24	77

The re-usability of plain wool as a catalyst was tested by measuring the product formation using the same cloth for 2nd cycle, in the SMDR. The reaction conversion decreased by almost 40% on re-use of wool (Figure 8(a)). Comparatively, there was only 3% reduction in conversion on re-use of copper wool over 3 cycles under similar experimental conditions (Figure 8(b)), which further confirms the stability of the copper-wool complex formed. This demonstrates the robustness of the copper cloth for multiple cycles.

To study the effect of solvent on plain wool, fresh wool was treated with ethanol for 4 hours in the reactor under identical reaction conditions and the solvent treated wool was used for Henry's reaction. It was found that conversion was closer to that obtained by carrying out the reaction with used wool. The binding energy of wool when re-used increases, as the O1s scan indicates the possible oxidation of wool accompanied by a change in the fibre morphology (Figure 9 (a-b)). The carboxylic acid groups present in wool are active reaction sites and easily accessible to alcohols of lower molecular weight [32]. Esterification of carboxylic acid functionality can occur in the presence of ethanol, which could be the reason for decreased product formation of wool on 2nd run. Additionally, the reduction in conversion may also be due to the high surface shear on the disc surface which may cause leaching of proteins into the solution, thus reducing the amount of catalyst sites available for reaction.

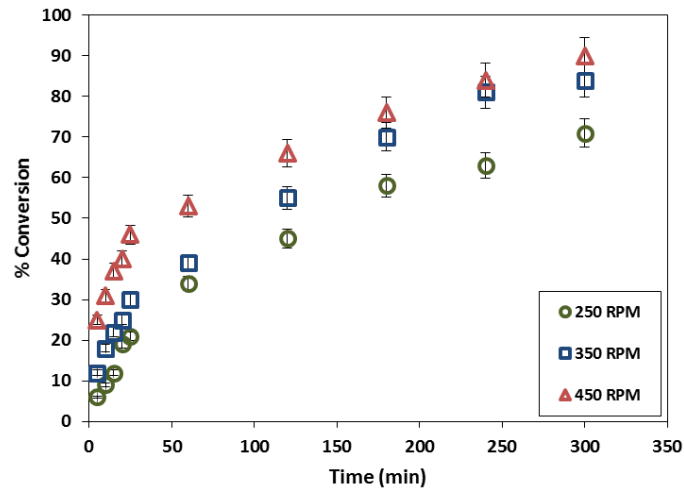


Figure 7: Effect of spinning speed on reaction conversion catalysed by wool. Flow rate: 3 ml/s

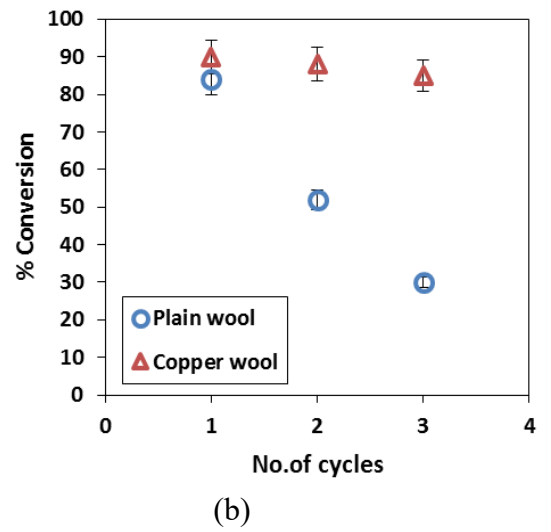
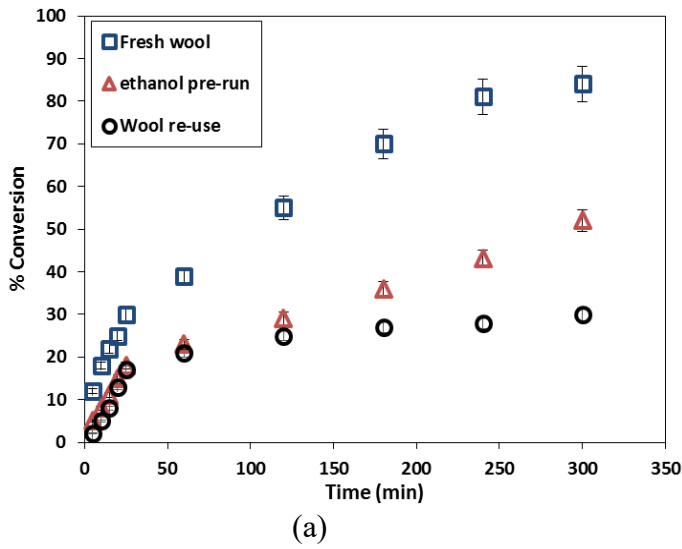
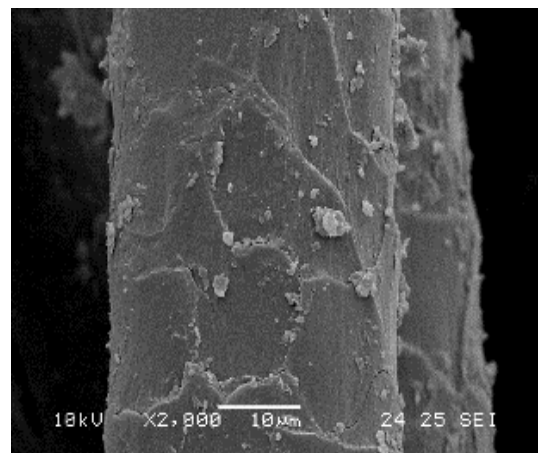
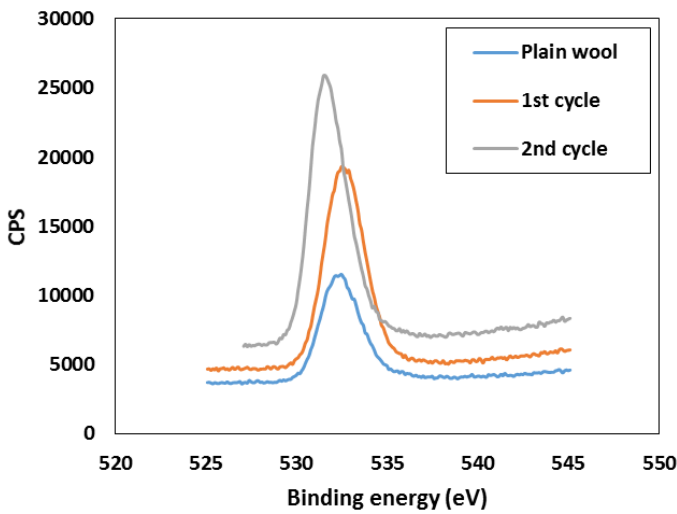


Figure 8: (a) Effect of wool re-use on reaction conversion and (b) Comparison of re-use of plain wool and copper wool over 3 cycles. (Flow rate: 3 ml/s, spinning speed: 350 RPM)



(a)

(b)

Figure 9: (a) O1s scan of used wool and (b) SEM image of used wool

4. Conclusion

In this study, copper triflate was successfully immobilised on wool using a simple protocol. The copper cloth and free copper triflate were used as a catalyst for Henry reaction in batch and a conversion of 85% and 57% were obtained respectively after 24 hours proving that the copper-protein complex was a better catalyst. The reaction was carried out in the SMDR with the copper cloth and a conversion of 90% was achieved after 5 hours at a spinning speed of 350 RPM, accompanied by an increase in 'ee' to 64%. The marked increase in the reaction conversion is due to the improved mass transfer on the surface of the disc. The reaction conversion increased by an average of 4% as the feed flow rate increased from 3 ml s⁻¹ to 5 ml s⁻¹. There was a steady increase in the conversion with an increase in the spinning speed from 250 RPM to 350 RPM accompanied by the increase in the average surface shear and better mixing on the disc surface. In addition to being a good catalyst support, wool also exhibited catalytic properties on par with conventional metal catalysts. A maximum conversion of 85% was obtained at a spinning speed of 450 RPM in the SMDR. However, there was a reduction in reaction conversion on reuse which may be due to the oxidation of wool or change in the fibre morphology. This shows that wool is a potential green catalyst for chemical processes if the catalyst deactivation can be controlled. Overall, the reactor was successfully used for the Henry reaction and can be used for other chemical processes which can benefit from improved reaction engineering. Work is on-going to investigate this process for other reactions and future work will aim to examine the economic and life cycle assessment of this technology.

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