Oxidation Catalysts for Stain Bleaching

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Abstract

This thesis focuses on the evaluation of precious metal nanoparticles in the application of oxygen activation for stain bleaching.

The first section looks at tea stains in solution, demonstrating that colloidal metal nanoparticles can be used to discolour fruit tea solutions as an initial proof of concept. This section goes on to develop model compound oxidations to run alongside the bleaching of stained cloth samples and to give empirical data for the kinetics of stain bleaching using the catalysts prepared in this study. Catechol and gallic acid have been chosen for this purpose, as they represent the aromatic hydroxylated compounds that are found in teas and represent their chromophoric constituents. Supported metal catalysts Au, Pd, Pt, AuPt, AuPd and PdPt on titania were chosen due to the higher activity of these catalysts found compared to the unsupported catalysts as a result of tests with stained cloth samples.

Sections two and three look into the use of supported and unsupported monometallic and bimetallic precious metal catalysts for stain bleaching on stained cloth samples, specifically tea stained cotton cloth samples denoted E-167. These catalysts, namely Pd, Au, Pt, AuPd, PdPt and AuPt are tested alongside the mediators TEMPO, TAED and Violuric acid for their activity. The results of the tests are compared with the problem of staining of the cloths by the catalysts themselves highlighted and attempts at decoupling this staining phenomenon discussed. It is clear that this issue would require complete abatement before commercial use could be considered for these catalysts. The latter half of the final section briefly examines the use of unsupported catalysts for dye transfer inhibition, where staining of a cloth sample isn't of concern and so promising results are presented.

Acknowledgements

I would like to thank all of those who helped me through my time working on this project, namely; Professors Stuart Taylor and Graham Hutchings, Gemma Brett, Peter Miedziak, Robert Armstrong and from Henkel Antje Gebert and Nadine Bluhm.

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1. Introduction

1.1. Catalysis

Though not in name, the process of catalysis was observed first by an Elizabeth Fulhame, who described that water is utilised in some oxidation processes and then regenerated after the reaction[1]. Following her work the term was coined and now given a definition which states that a catalyst increases the rate of a reaction without being consumed itself during the reaction[2]. In figure 1.1 the energy level diagram for a catalytic reaction and an uncatalyzed reaction is displayed. It shows that the thermodynamics of a reaction are not altered by a catalyst, only the kinetics through lowering the transition state energies associated with the reaction[3]. By offering lower energy transition states the reaction pathway will change but the beginning and end states will stay the same, therefore there will be no change in the free energy of the reaction. The catalysed reaction will have a lower energy barrier than the uncatalysed reaction and therefore be a more energetically favourable process.

In a catalytic process there are number of steps which are carried out. First the reactants will diffuse to the catalyst surface, penetrating the boundary layer of the catalyst. From here the particle will diffuse into the pore sites of the catalyst to find a suitable surface. The reactants will then adsorb to the surface where the reaction can take place, often the rate determining step if we are not working at higher temperatures. The particles will then desorb and diffuse away from the catalyst surface towards the boundary layer of the particle, before diffusing entirely. The overall rate of the catalytic reaction can therefore depend on the ease of these diffusion steps, as well as the kinetics of the adsorption and desorption steps. It is therefore quite clear that the mass transfer of particles can become instrumental in the overall reaction rate for a catalytic process and must be considered as well as the kinetic reaction properties.

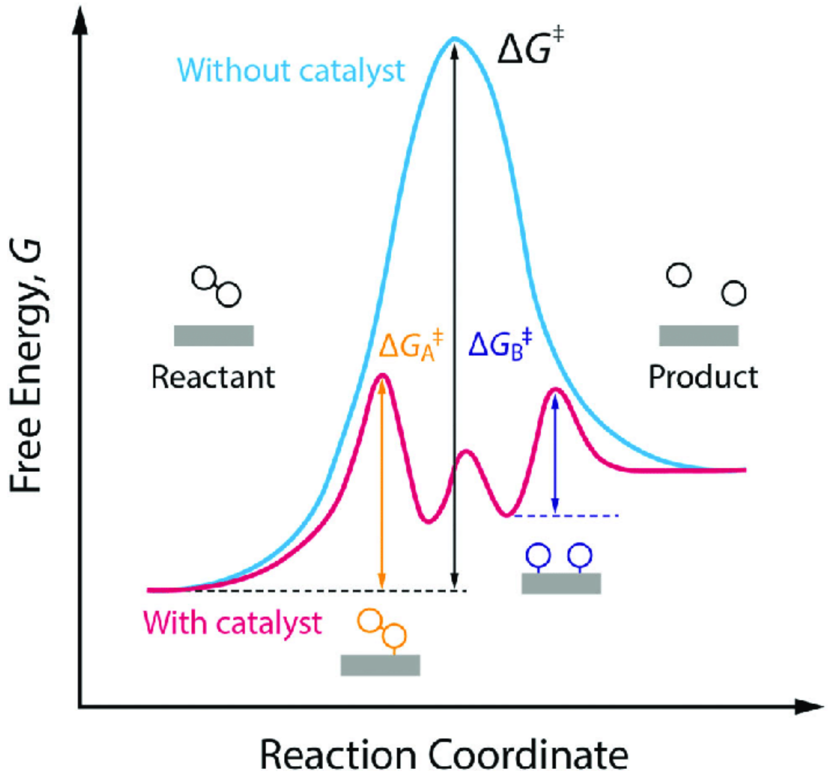

Figure 1.1: Energy profile of a reaction proceeding catalytically and without[4].

Catalysis can be further subdivided into three separate categories, homogeneous, heterogeneous and biocatalysis. Homogeneous catalysis refers to a reaction in which the catalyst is in the same phase as the reactant, generally both will be in the liquid phase. A well-known industrial example of such is that of the Wacker process, where ethylene is oxidised to acetaldehyde by a Pd (II) catalyst[5]. The scheme for this reaction can be seen in figure 1.2**.** Oxygen is consumed, with Pd (II) being regenerated by the complimentary Cu cycling between the +1 and +2 oxidation states. Through the use of homogeneous catalysts great specificity and activity can be achieved, even in mild conditions, though a problem arises when we need to then separate the products from the reactants and the catalyst. This problem is overcome through the heralding of the heterogeneous catalyst, in which the catalyst is in a different phase than the reactants and products, saving the need for separation post-reaction. Perhaps the most famous example of catalysis is of the Haber-Bosch process, utilising promoted iron catalysts in the artificial fixation of nitrogen to ammonia for use in fertiliser[6]. It has been postulated that the dramatic population explosion of the human species would not have been possible without its introduction to the fertisiler industry[7]. Biocatalysis involves the use of living systems (or their enzymes) to speed up useful reactions, and its use dates back 6000 years to the Sumerians in the form of brewing, where yeast is still used to ferment a starch source in water to form alcoholic beverages.

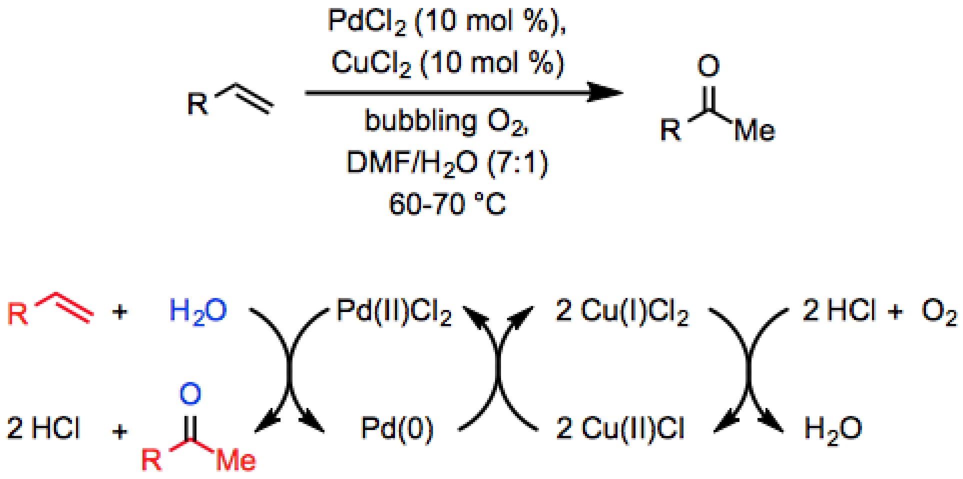

Figure 1.2: Schematic of the Wacker process.

There are three main reaction mechanisms for a system to react with a heterogeneous catalyst[9] and these are shown in figure 1.3. These are the Langmuir-Hinshelwood mechanism, where the reactant species will adsorb to the surface before the reaction takes place, the Eley-Rideal mechanism, where an adsorbed species reacts with a further species that is this in the gas phase, and the Mars-van Krevelen mechanism, where a reactant which has adsorbed to the surface will react with oxygen in the lattice of the adsorbing species. This oxygen is then regenerated from gaseous oxygen.

Although it is considered that a catalyst is not to be consumed in the reaction by definition, it is often observed that a catalyst will lose its abilities over time due to a number of factors[10]. These can include chemical changes in the catalyst as a result of temperature[11], pressure and pH changes, as well as deactivation due to poor desorption of products[12], poisoning by contaminant metals[13] or introduction of competitive inhibitors[14]. Typically sintering due to reaction conditions or following high heat treatments is a common cause for catalyst deactivation and lead a reduction in the number of catalytically active site to the agglomeration of particles on a support surface.

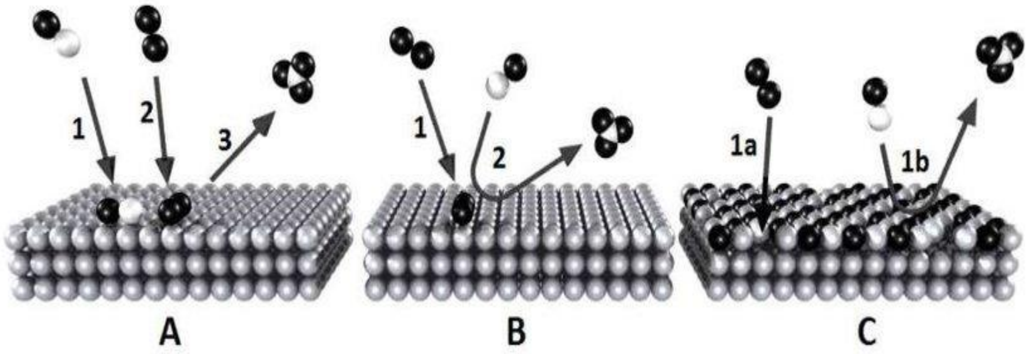

Figure 1.3: Graphical explanation of A) Langmuir-Hinshelwood mechanism, B) Eley-Rideal mechanism and C) Mars-van Krevelen mechanism[8].

1.2. Nanoparticles

Nanoparticles are defined as structures in which at least one of the dimensions is between 1-100 nm[15]. Their properties are expressed between that of the bulk and atomic scales, with their large surface to volume ratios offering interesting perspectives for chemists in their utilisation for metal catalysts, through the divergence of their physicochemical properties from bulk phase metals[16]. This is shown in figure 1.4, where the band structure of a nanocrystal is augmented in comparison to that of the bulk. Here the density of states in the band structure is decreased leading to a band gap energy between that of bulk material and a single molecule. A particular advantage metal nanoparticles have over bulk metal in terms of the activity is the exposure and greater comparative proportion of high energy surface sites; kinks, steps, single corner, that are believed to be intrinsic in their high activity[17].

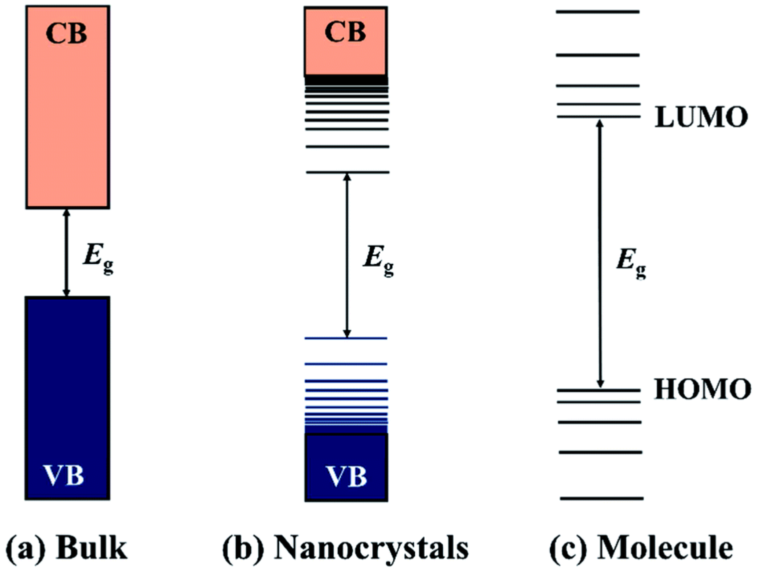

Figure 1.4: An example of the differences in energy states for different types of semiconducting materials: (a) bulk semiconductors, (b) nanocrystal semiconductor, (c) molecular semiconductor[18].

Nanoparticles can be prepared physically or chemically[19], depending on whether one would prefer to destroy or create, with physical methods making use of grinding procedures to obliterate bulk metals to successively smaller particles, eventually reaching the nanoscale, or chemical, an example of which is the reduction of metal precursors in solution form small clusters of atoms. Chemical routes offer a greater degree of control of the resultant particle geometry and size, which can be augmented depending on the synthetic procedure[15,20–23]. An example of different nanoparticles that find use in medicine are shown in figure 1.5, which is indicative of the wide range of synthetic procedure that are involved in producing such a variety of final products.

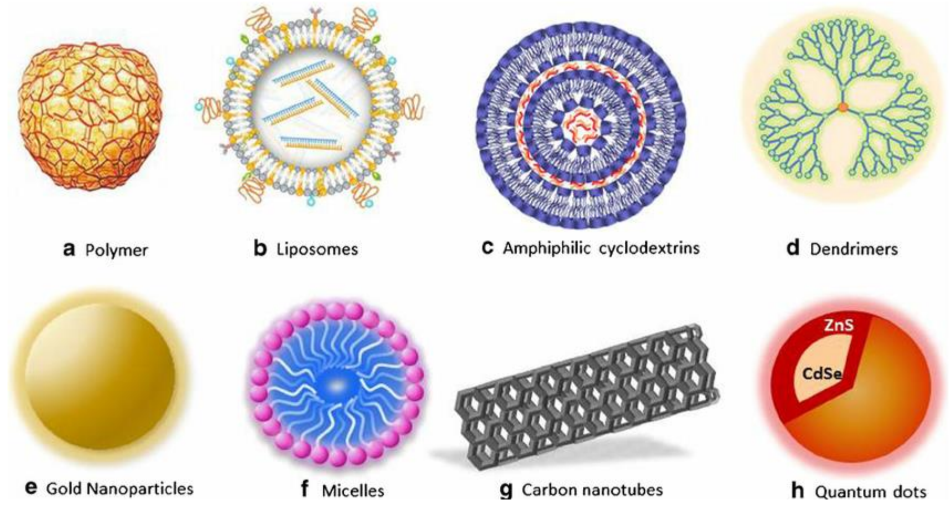

Figure 1.5: A variety of nanoparticles that have uses in medicine[24].

There are numerous methods for preparing nanoparticular catalysts, with research directed towards the design of synthesis that favours control over the size and shape of the catalysts, and those which can be reproduced and easily scaled up to industrial quantity[25]. These preparation methods include chemical vapour deposition (CVD)[26], electrochemical deposition[23], impregnation[27], deposition precipitation[28] and colloidal techniques[29] among others. Colloidal methods in particular allow for the precise control of the shape and size of the of the particles, which is particularly useful considering a large portion of nanoparticle production techniques return catalysts with a broad particle size dispersion[21]. About 90% of chemical manufacturing processes utilise catalysts[30] consisting of particles with such variation in their particle sizes[31,32], not ideal considering the number of reactions performed industrially that are influenced by the nature of the nanoparticulate surfaces in which their substrates interact. CO oxidation is an example of this[33], where low coordinate Au clusters are the active site when gold nanoparticles are used for the catalytic reaction.

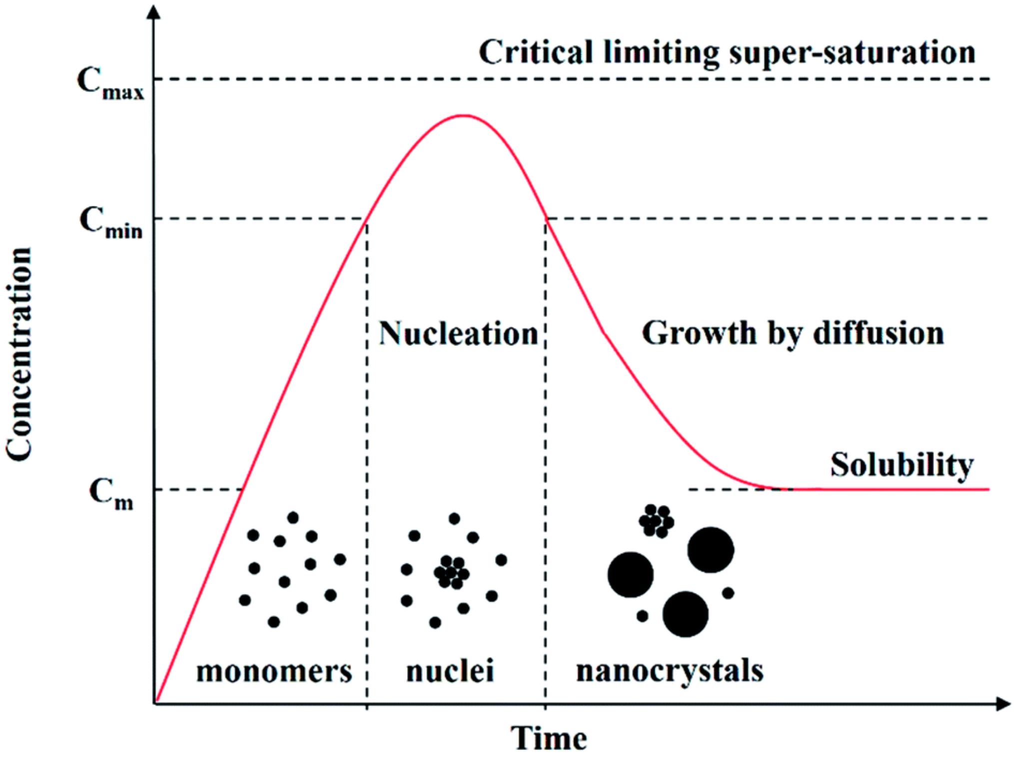

Figure 1.6: LaMer diagram depicting formation of nanoparticles as a function of time according to the concentration of monomers[18].

There are three main methods of colloid preparation, all of which follow the LaMer model for nanoparticle growth[34] which is graphically described in figure 1.6. The first stage in this process for a seedless growth represents the nucleation of precursor atoms to form monomers. Concentration of these monomers builds until a super-saturation point is reached, at which point burst nucleation occurs involving the spontaneous coagulation of monomers to form clusters. This can happen simultaneously along with formation of new monomers, depending on the diffusion rate of monomers towards each other in comparison to the rate of new monomer formation, these rates influencing the final number and sizes of nanoparticles[35]. As the rate of diffusion continues to improve with the rate of new monomer formation, nanocrystals begin to form, with the final shape of these crystals highly dependent on the conditions and reagents used in the procedure[21].

The first preparation method to be discussed is that of the chemical reduction method, whereby a metal precursor, generally in the form of an ionic salt, is reduced (through use of sodium, alcohols, citric acid, hydrides etc.). This methodology was first reported by Faraday in 1857[36], who used phosphorous to reduce $HAuCl_4$[36]. The modern procedure utilises a strong reducing agent ($NaBH_4$) with the addition of a stabilising agent (ligands, surfactants, polymers) to aid in the stability of the final metal nanoparticle. The size and shape of these nanoparticles can be influenced by the choice of precursor, reducing agent, stabilising agent, relative concentrations, temperatures and reactions times, giving a great deal of control over the desired product quality[37]. Composition can also be altered through introduction of an additional metal precursor allowing for the tuning of the more electronic properties of the catalysts. The malleability of the preparation method of these catalysts make them great tools in organic reaction mechanisms, such as for in oxidation reactions[38] and hydrogenations[39].

Electrochemical synthesis of colloids involves six steps[40]. First the bulk anode is dissolved oxidatively, with the following cationic metal ions migrating to the cathode. These ions are reduced forming metal atoms of zero valency. Growth of the metal particles can then proceed via the LaMer model as discussed previously, with the addition of stabilisation agents to protect the size of these particles followed by the precipitation of fully formed nanoparticles. The benefit of this procedures comes from the ability to operate without the worry for contamination from via the byproducts of chemical reducing agents, and the facile isolation of the desired products. In utilisation of electrochemical synthesis of colloids, the size control aspects come from the current density applied, as well as migration period of the cations and reaction temperature and time.

Colloids may also be formed through the thermolysis of metal salts, which in the current methodologies involves the hot injection of metal salts into an organic phase of coordinating solvents, though the size variation tends to be greater than that of colloids prepared by other methods[41]. In order to isolate the smaller particles, hydrophilic solvent is slowly added to the dispersion. The larger particles will precipitate first and so will leave behind particles with a more congruent particle size distribution once separate.

As mentioned previously the size and shape of the final nanoparticle, in the case of metal precursor reduction can be influenced by the nature of the precursor, the reducing agent, the solvent, the temperature and time of the reaction, but also by the nature of the stabilising agents that can cap the growth of the particles on addition[22], as well as protect the final particles from agglomeration. These stabilising agents can come in the form of polymers, ligands, dendrimers or micelles[37]. These additives surround the formed nanoparticles and stabilise the structures through electrostatic and steric means, or a combination of both[42].

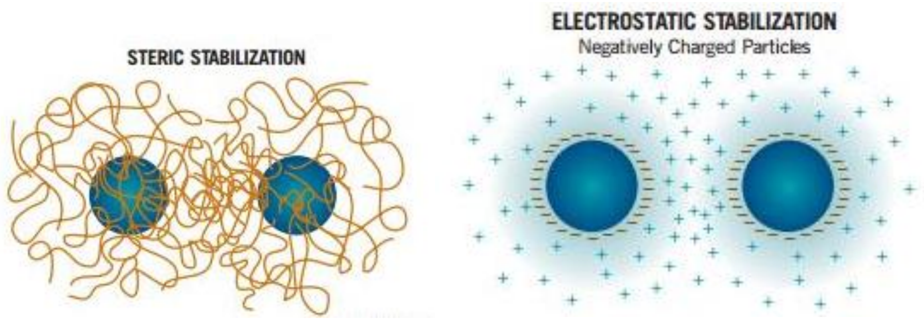

Figure 1.7: Graphical description of steric and electrostatic stabilisation of nanoparticles[43].

The two methods of stabilization of colloidal nanoparticles are depicture in figure 1.7. For electrostatic stabilisation the nanoparticles become encapsulated by an electrical double layer, formed from association of ions from the starting materials with the nanoparticles. This electrical double layer generates a Coulombic repulsion effect between nanoparticles on any attempt at agglomeration. Steric stabilisation is achieved through the adsorption of polymers, surfactants, dendrimers or other large molecules to the surface of the nanoparticles. These large polymeric groups prevent the metals from interacting with one another and coalescing.

1.3. Supported Nanoparticles as Catalysts

Following the generation of nanoparticles, it is quite often necessary to load them onto a support surface in order to promote stability[15], or to influence their activity through metal support interactions[44], where it is observed that the properties of atoms at the metal-support interface vary to those of the bulk. It has even been shown that supporting of these particles allow for the stabilisation of colloidal nanoparticles created in the absence of polymer stabilisers[45]. Often metal oxides are chosen due to their acid/base properties and the mobility of lattice oxygen in cases, where generated O vacancies at metal-support interfaces are important for the activation of elemental oxygen[46,47]. It was noted by Haruta et al that the support places such a role in the activity and final selectivity of the loaded gold in CO oxidation[48], meaning the choice of support is imperative when formulating a support nanoparticle for a catalytic system. The following are examples of nanoparticle preparations that involve such loading of the nanoparticles onto such supports.

Standard impregnation (imp) involves the mixing of a metal precursor with its support to form a slurry which is then dried and calcined. Such procedures can give particles sizes in the range of 4-25 nm, with this size distribution difficult to control[49]. The dispersion of the metal will depend on the pore volume of support in relation to the volume of metal added, with excess of metal precursor solution referring to the practice of wet impregnation[50].

Modified Impregnation (mod-imp) is a preparation method, based on the impregnation discussed above but with an excess of HCl added to the reaction mixture [27]. Here an excess of anionic Cl ligands help stabilise the formation of Au-Pd nanoparticles between 2-5 nm. A calcination step in a reducing atmosphere helps to remove excess Cl^- that would impede activity through poisoning of active sites. In comparison to the same catalysts prepared by impregnation and sol immobilisation, catalysts prepared by modified impregnation were found to be 4 times more active for direct hydrogen peroxide synthesis from H_2 and O_2, as well as more active for the solvent free oxidation of benzyl alcohol[27].

Deposition Precipitation (DP) was developed to provide high loadings of metal onto the support surface[49]. It does so by adjusting the reaction pH in relation to the isoelectric point (IEP) of the support to grant the best affinity of precursor to support. By controlling the pH the level of metal loading and particle sizes can be augmented in accordance with what is desired. The resulting solid is washed, filtered and dried and may be calcined before use.

The method for sol immobilisation begins with that of the colloid preparation discussed previously, but adds a step of immobilisation of the colloidal nanoparticles onto a solid support[51]. The support is added to the colloidal solution which will have its pH adjusted through addition of acid/base to help in the attraction of the precursor to the support. The resulting solid is filtered, washed and dried and can be used with or without a calcination step as any excess chlorine is removed through washing of the filtrate. This procedure is limited in the variety of supports available to it, as the deposition of the nanoparticles and therein their affinity for the support is dependent on the iso-electric point (IEP) of the support[52].

Co-Precipitation involves the addition of both the metal precursor and support material (preferably nitrates) to a solution and their subsequent precipitation at alkaline pH[52]. The resulting precipitate is filtered washed and dried and generally heat-treated before use. In order to obtain well dispersed particles on the support, it is important to concentrate the metal precursor solution and to add a neutralising agent to reduce the solubility of metal-hydroxy species.

With the continuous need for milder conditions within industrial catalytic reactions, where pressures, temperatures and byproducts are often less than desirable in a word perpetually seeking a greener existence, the heralding of the metal nanoparticle offers a new realm of possibilities[53]. From early work by Haruta that nanoparticles of gold could be used for the low temperature oxidation of CO[54], precious metal nanoparticles are being used for the oxidation of alkylaromatics[55], activation of the C-H bond[56], oxidation of alcohols[57,58] and the production of hydrogen peroxide[59], for example. The use of nanogold is advantageous as a stable, non-toxic heterogeneous catalyst that is able to produce eco-friendly oxidant species[60] on reaction with O_2 avoiding the use of harmful stoichiometric reagents such as active DMSO in Swern oxidation[61]. Through the use of catalytic nanoparticles, the oxidant species may be generated in situ and abate the need for such reagents.

Benzaldehyde, which is used in the pharmaceutical and food additive industries, is traditionally synthesised from the chlorination of toluene followed by saponification[62]. A rather unfriendly process considering the use of halogens and acidic solvents, heterogeneous catalysts are proving a much more environmentally friendly method of producing benzaldehyde, instead through the oxidation of benzyl alcohol[51,55]. Enache *et al* looked at the use of gold palladium bimetallic nanoparticles for the selective oxidation of benzyl alcohol and found that the activity was dependent also on the ratio of the two metals used, with the highest activity being found for a metal ratio of 1:1 by weight. The data is shown in table 1.1. Palladium was responsible for the higher activity, but induced a lower selectivity for the desired product, while gold rich catalysts lead to a higher selectivity of benzaldehyde being achieved. These results indicate that for bimetallic catalysts it is important to consider the interactions that these metals will have together, and how a careful examination of the properties of each for a given process can lead to the design of an optimal catalyst.

	Catalyst									
	5% Au/TiO_2		**4% Au–1% Pd/TiO_2**		**2.5% Au–2.5% Pd/TiO_2**		**1% Au–4% Pd/TiO_2**		**5% Pd/TiO_2**	
Time on line (h)	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0
Conversion (%)	0.1	0.2	1.0	1.9	1.9	3.4	1.0	2.3	1.2	2.5
Selectivity (%)										
Benzaldehyde	100	95.0	94.0	91.3	82.8	85.6	80.6	79.1	65.6	69.8
Benzoic acid	–	2.3	1.3	1.8	3.1	1.2	1.8	1.1	0.7	1.2
Toluene	–	2.6	2.5	3.5	5.6	7.0	7.7	13.8	21.7	20.5
Benzyl benzoate	–	–	2.2	3.2	8.5	6.2	5.0	3.9	4.4	5.7

Table 1.1: Effect of the Au:Pd ratio on the oxidation of benzyl alcohol at 100 °C. Reaction conditions: 100 °C, 0.1 g catalyst, 40 ml benzyl alcohol, PO_2 10 bar.[55]

Catalytic oxidation of glycerol with O_2 has also been reported over supported nanoparticulate catalysts, where its valorisation is desired due to increased availability as a by-product in the development of green processes for bio-fuels. In this state it is unsuitable for use in fine chemical production and so selective oxidation to desired products can give new life to it as a feedstock in chemical synthesis. It was shown that gold nanoparticles could react with glycerol in the presence of base to form lower carbon number products[58,63]. Through these experiments it was shown that the selectivity to certain products, as for benzyl alcohol oxidation, could be controlled through use of different metals, as well as by the preparation method used to generate the nanoparticles and the nature and the amount of the base used.

Molecular oxygen is a safe, abundant and powerful oxidant, and would be incredibly useful to oxidation reactions if it weren’t for the high kinetic barriers to its use in chemical reactions. This inactivity stems from the ground state electronic configuration of triplet oxygen, containing unpaired electrons with parallel spins, rendering it unable to interact with molecules which would commonly be found in the singlet ground state with paired electrons. Through activation, triplet oxygen can be converted to the singlet state which overcomes this spin restriction, generating a variety of species ready for utilisation in chemical reaction. Traditionally the reduction of O_2 has been carried out by organometallic complexes[64] though now precious metal nanoparticles are becoming of interest for their ability to catalytically activate oxygen to generate useful species[59,65–67]. These particles are synthesised by the sol immobilisation method have a mean particle size of 2-4 nm, granting a high surface area/volume ratio and therefore higher catalytic activity.

In a theoretical study of CO oxidation, the interaction of molecular oxygen with a gold atomic cluster was examined[68]. It was found that oxygen can easily either dissociate or react directly with adsorbed CO and that once dissociated, adsorbed oxygen is bonded strongly to low coordinate Au clusters in comparison to the bond strength of O to an Au(111) surface. This highlights the importance of using consistently small nanoparticles in comparison to catalyst preparation methods that would return particles of greater size or of greater size range, in consideration of the goal of these catalysts. With respect to adsorbed O_2, the adsorption energy and the reaction barrier were found to be lower for these clusters than for adsorbed oxygen on Au(111) and stepped Au(211) surfaces. The rational for the more facile dissociation comes from the energetic benefits offered by the geometry of the Au clusters in comparison to the surfaces. Corma et al further investigated this through DFT calculations to discern that the activation of molecule oxygen is invariably sensitive to the geometry of the surface atoms[69] and so a procedure to guarantee consistency of particle morphology and size in paramount in the study of oxygen activation. It was also found that once supported the most active sites for dissociation were found to be at the metal-support interface, and not the particle surface itself.

1.4. A Brief History of Bleach

Bleaching refers to, in the particular case of within the washing process, the removal of coloured staining of textiles, either outright or through changing of the colour to a lighter colour[70]. These staining molecules come in the form of anthrocynanin dyes, which are present in coloured fruits; chlorophyll which is found in grass and green leafy vegetables; carotenoids which make up the colour in carrots, tomatoes and peppers; curcumin dyes present in curry and mustard; anthocyanins and humic acids found in red wine, coffee, tea and cocoa products as well as tannins which aid in the constitution of the colour of fruit and tea. These molecules contain chromophores, which is the moiety which is responsible for the compounds colour. In general it is highly conjugated sections of the molecule which give the molecule its colour, and give rise to hydrophobicity in tandem. It is desired to cleave this conjugation through oxidative cleavage of the bonds or through hydroxylation by an oxidant species, also known as the bleaching reagent, which would lead to degradation of conjugation and the eventual loss of a chromophore through continued oxidation reactions of the molecule[71].

Starting with the ancient Egyptians and the Fullones of ancient Rome, the washing of clothes had its humble beginnings in a purely mechanical method, whereby they would be treated through beating, rubbing and being tread upon[70]. It was known that rainwater was more effective for washing, as well as hot water being more efficient than cold. The Egyptians found soda ash (sodium carbonate) to be useful additive in the washing process, known now to be a proficient water softener. This was combined with sodium silicate in 1878 by Henkel's Bleich-soda[72], a product which could make better use of the water softening effects demonstrated by sodium carbonate to greatly precipitate calcium and magnesium ions, which could lead to the discolouration of fabrics. Paired with soap, it could diminish the build-up of insoluble soap residues, which are inactive in the washing process. Despite the literal translation of Bleich-soda being bleaching soda, it contained no bleach. The first laundry detergent to contain bleach however was also released by Henkel in 1907 and sold under the brand Persil and remains a household name is Europe. The name comes from the ingredients sodium **per**borate and sodium **sil**icate, with these being combined with soap and sodium carbonate for the commercial product.

Persil was the first to be described as a self-activating detergent, as the release of hydrogen peroxide from sodium perborate in solution would initiate the bleaching effect and reduce the need for mechanical action in the washing process. It is known as an oxygen based bleaching agent, to distinguish itself from the chlorine based bleaching agents, which although are more powerful compounds, are too reactive to be used in detergents[73]. Although effective, the exact manner by which hydrogen peroxide can lead to the destruction of chromophores and removal of stains is something that still is being researched, with the formation of radicals, singlet oxygen and products of hydrogen peroxide decomposition being considered of importance[74–77].

The sodium perborate addition allowed for excellent bleaching activity to be observed with the detergents at washing temperatures near the boiling point of water (at 95°C)[78]. Due to energy concerns there is an increasing trend towards washing at lower temperatures, especially in Europe where modern fibres require lower temperatures[79]. European convention tends to favour washing at 40°C, whereas even lower temperatures can be popular internationally. Hydrogen peroxide, being thermodynamically unstable, dissociates to water and oxygen at high temperature according to the equation (1), where S refers to an oxidisable substrate.

$$2H_2O_2 \rightarrow 2H_2O + \ O_2(^3\sum_{g}^{-}) \qquad (1)$$

$$H_2O_2 + S \ \rightarrow H_2O + S - oxidized \quad (2)$$

The ground state oxygen generated is not useful for bleaching processes, and so a more desired reaction would be that of (2), where the active oxygen of hydrogen peroxide is available for substrate oxidation. The amount of evolved oxygen represents the active oxygen content of a bleaching compound, which for hydrogen peroxide is 47%[73]. The term active oxygen refers to the variety of peroxo compounds generated by hydrogen peroxide decomposition, of which one of the oxygen atoms is useful for the bleaching of a substrate. These decomposites are represented in Figure 1.8, expressing an activation process which is still not entirely well described[8]. These oxo-species are an ensemble representing the active oxygen contained within hydrogen peroxide, with their relative abundance in solution being dependent on the reaction conditions. Some of these are considered too short lived to be of great importance in a direct bleaching process, such as singlet oxygen[75,76], though all are interrelated through a further set of reactions. In the absence of substrate they decay in accordance with equation (2) towards disproportionation.

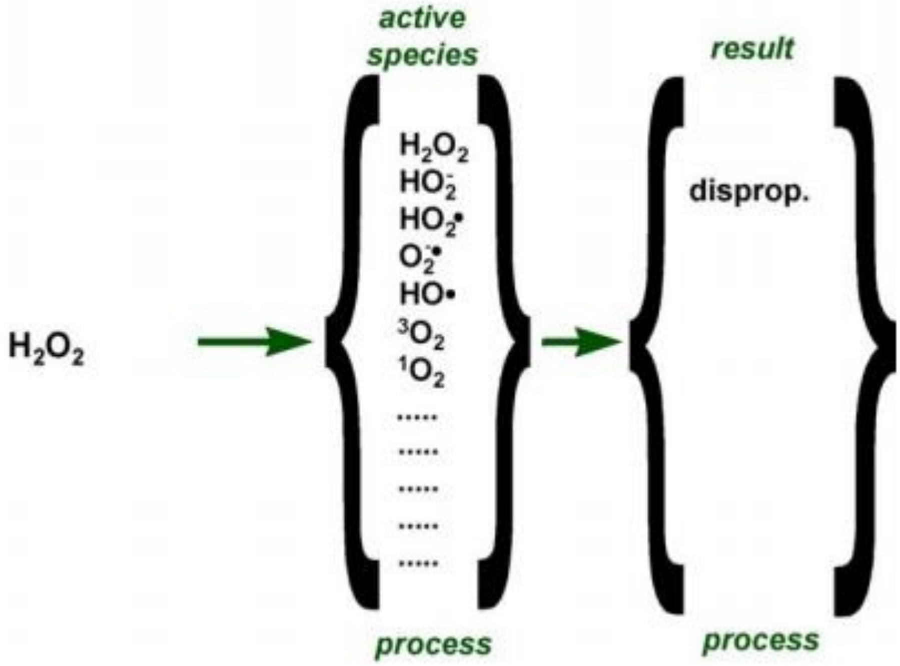

Figure 1.8: Model for the disproportionation of hydrogen peroxide in the absence of catalyst and substrate[8].

At lower temperatures (~60 °C) the bleaching power of hydrogen peroxide is insufficient for purpose, due to its kinetic stability in ambient conditions, and so research is being carried out to allow for its activation through more kinetic methods. This problem has been somewhat circumvented through the use of activators such as tetraacetylethylenediamine (TAED), which is the main activator found in European detergents, while sodium nonanoyloxybenzenesulfonate (NOBS) dominates in North America[80]. Bleaching activators consist of two elements, a peroxy acid precursor and a leaving group[70]. The peroxy acid precursor is important in that it is responsible for the bleaching prowess of the resultant peroxy acid, while the leaving group is paramount to the solubility of the activator. In the design and development of a activator, strategies were developed by Grime and Clauss which stated that: the perhydrolysis rate would be increase by using more facile leaving groups, the reactivity of the peroxy acid would be increased by increasing the oxidation potential, the efficiency of surface bleaching should be increased over solution bleaching by improving the surface activity of the formed peroxy acid and to improve the bleaching of hydrophobic stains over hydrophilic through careful consideration of the hydrophilic/lipophilic balance (HLB) of the peroxy acid species[81]. This balance determines which stains the peroxy acid will bleach more efficiently.

In alkaline solutions containing hydrogen peroxide, the perhydroxyl anion, the predominant form at increasing pH[82], attacks TriAED and DAED, releasing about two molar equivalents of peroxyethanoic acid as seen in Figure 1.9 below. Theoretically four moles of peroxyethanoic acid could be achieved from each mole of TAED utilised, however this is not the case in practice where a maximum of two moles of the acid are generated due to increase in the pK_a of the leaving group. Furthermore two equivalents of the peroxy acid is generally not achieved due to a saponification competing reaction with hydroxide anions.

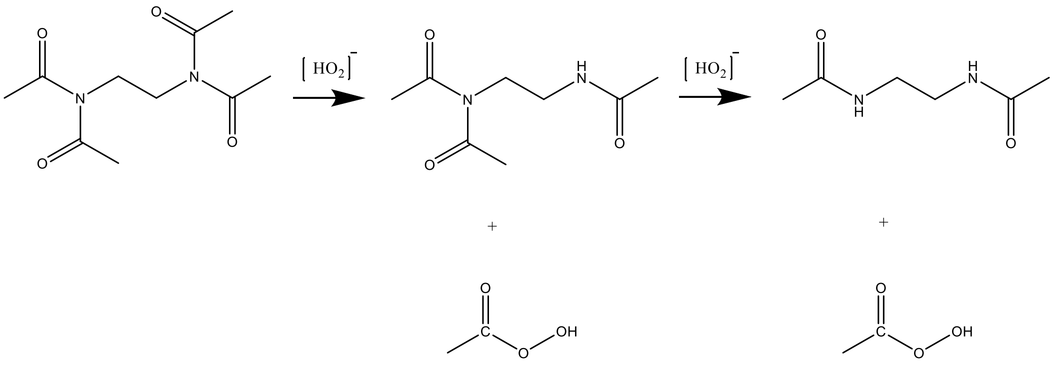

Figure 1.9: Perhydrolysis of TAED to yield active peroxyethanoic acid[73].

NOBS is a long chain activator, which was designed to allow for facile approach to hydrophobic stains on the fabric surface[83], with Tide being the first commercial detergent to include it. On attack by the perhydroxyl anion, NOBS forms peroxynonanoic acid, releasing an inert salt. Once peroxynonanoic acid has formed, it may react with another molecule of NOBS, generating a controlled dinonanoyl peroxide (Figure 1.10) which can be active on different stains to peroxynonanoic acid. The production of dinonanoyl peroxide may be modulated by controlling the persalt to NOBS ratio of the detergent and the pH of washing. Other activators such as sodium lauroyloxybenzene sulfonate (LOBS), which is a more hydrophobic homologue of NOBS and DOBA which uses 4-hydroxy benzoic acid as the leaving group[81] and both are most commonly used in japan. LOBS was the first activator to be included in liquid detergents and expressed a higher anti-microbial effect than TAED at lower concentrations, which is also the case with DOBA.

The demand for lower wash temperatures and shortened wash cycles are pressuring for the development of bleach activators with greater activity, especially as TAED has been in use since 1973, and NOBS being first used in 1988, it has been a long since improvement in the commercial state of the art. A number of nitrile species are being looked at which release peroxyimidic acids for the low temperature activation of bleach. Unfortunately many of these have been found to be linked to dye and fabric damage and so have not been added to commercial products. A new bleach activator, N-[4-(triethylammoniomethyl)benzoyl]caprolactam chloride (TBCC) has been developed and has been shown to be more effective at bleaching than TAED in the same conditions, with no apparent damage to cloth fibres or dye[84]. It is believed that the bleaching efficacy of these species are directly related to their ability to decompose hydrogen peroxide, with TBCC offering the greatest level of hydrogen peroxide decomposition.

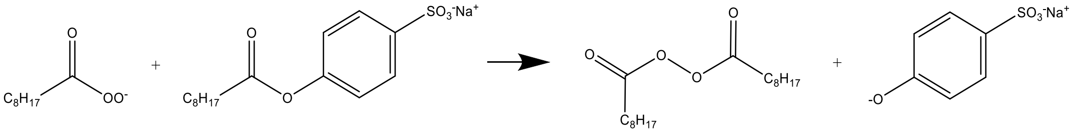

Figure 1.10: Formation of dinonanoyl peroxide[73].

TAED and NOBS represent the standard of bleaching activators in commercial products and are effective at increasing the activity of hydrogen peroxide at T = 40°C, but at even lower temperatures bleaching results are unsatisfactory[77], as well as the fact that the use of activators is still a stoichiometric process requiring a large volume of reagent to be added to the detergent recipe, so current research is focusing as well on developing compounds that will activate hydrogen peroxide for bleaching purposes at these temperatures, and with greater efficiency[85–92].

1.5. Catalytic Bleach

The first commercial catalytic hydrogen peroxide activator was introduced by Unilever in 1994[93]. It was added first in the form of the Persil Power brand, and then also added to the detergent formula for Radion and Surf powder concentrate. This so called ‘Accelerator’ consists of a binuclear manganese complex coordinated by 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN). It was first reported within an examination of several of these manganese complexes derived from TMACN or related ligands[92], the most affective catalyst being the complex shown figure 1.11.

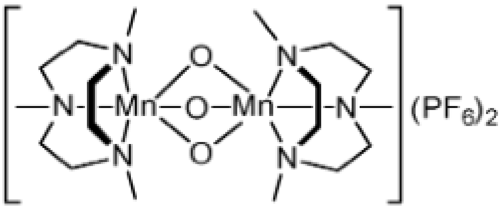

Figure 1.11: Dimanganese complex for hydrogen peroxide activation[92].

It was found that the triazacyclononane moiety was important for high catalytic activity and is considered to be related to the additional stability these ligands provide over manganese salts in bleaching processes. It was also found that there was a pH dependence on the bleaching activity for some of the complexes, and in the case of the complex above higher pH relayed higher activity, indicating the possible importance of the perhydroxyl anion in the bleaching mechanism as some research has indicated[75,76]. In order to probe the mechanism of these complexes, catechol was chosen to model tea stains, due to the quantity of polyphenolic chromophores within tea[94]. A 16 line EPR signal indicated the dinuclear centre is in the state Mn(III)-Mn(IV), with this signal being more stable in the compound above at higher pH, indicating the importance of the stability of this state in the mechanism[92]. This species arises from a one electron transfer from the anionic substrate to the Mn(IV)-Mn(IV) core in alkaline conditions, generating a radical species on the specific substrate[95]. Further probes to elucidate the active oxidant for these complexes detected the presence of a Mn(V)=O species stabilised by coordination of polyphenoxy groups[96].

Following the release of this product, reports were published that found that dye and fabric damage occurred after minimal washing, with a report from Henkel finding that damage was occuring after just 12 washes when using the Dutch brand of Persil Power, Omo Power[93]. A report commissioned by Proctor and Gamble found that the dye damage was dye dependent[97]. The catalyst with hydrogen peroxide was tested against TAED and hydrogen peroxide, with fabric damage being qualified by tensile strength and the relative loss of the average degree of polymerisation, while dye damage was examined by reflectance spectroscopy. It was found that the manganese catalyst additive lead to much greater fibre damage after ten washing cycles than through use of TAED as activator, with blue, brown and black dyes inducing a greater level of fibre damage on the cloth. Furthermore the catalyst was found to be very effective at destroying the chromophore of the blue dye in comparison with the others. This unacceptable level of fabric damage lead to a reformulation of Persil Power to New Generation Persil, which did not contain any manganese catalyst[98]. Persil Power was officially withdrawn from the market in 1995[99]. Although not useful for the bleaching of textiles, related complexes such as Mn oxalate dihidrate are used in dishwashing detergent formulae.

Not to be discouraged by this set-back, the scientific community continued to look for alternative metal bleach catalysts that would not cause such damage. Some examples of these include iron(III)-tetraamido macrocyclic ligands[88], phthalocyanine metal complexes containing various metals[90], manganese porphyrins[89] and phythalocyanin zinc complexes containing Schiff base complexes[91]. The important features of these complexes from a comparison include the dinuclear complex centres, the large bidentate ligands which contribute in not just the definite structure but also make these complex affective charge reservoirs. They may be used to stabilise the oxidation states that will be experienced during the activation process or be used to fill antibonding orbitals on substrates and aid in oxidation itself. With the new millennium new Mn-terpyridine complexes were devised and were shown to have better bleaching ability for fabric at 25°C and 40°C than through the use of TAED, and expressing similar dye damage to that exhibited by TAED[100]. This class of catalyst owes its prowess to the electron-donating hydroxy and amine groups located in the 4-position of the pyridine moieties and is highly dependent on this substitution pattern. These catalysts were also demonstrated to be stable in the alkaline conditions that would be present in the detergent recipe, as well as in the presence of hydrogen peroxide with the highest activity being achieved at pH 10.

Of concern is the notion that the metal contained within catalytic complexes could end up being released and deposit onto the fabric itself, leading to damage and colouration. This has led to a branch of metal-free organocatalysis developing within the world of catalytic bleach. These are known as metal-free oxygen transfer agents, which can work with traditional activators to allow for the efficient bleaching at lower temperatures[71]. Examples of these are dioxiranes, oxaziridines and oxaziridinium salts**.** Cyclic sulfonimines offer the most potential in terms of detergent applications, with their high reactivity deriving itself from the electron withdrawing effect of the sulfonyl group (CITE). Examples of these catalyst are shown in figure 1.12 as CSI 1 and CSI 2 respectively, which can grant a high bleaching effect at the cost of dye damage in combination with TAED, with highest activity observed beyween pH 9-11.

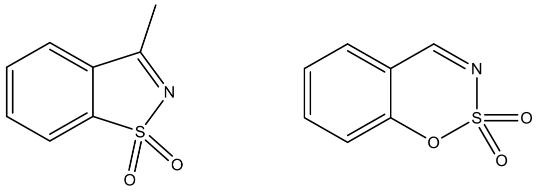

Figure 1.12: Organic catalysts CSI 1 and CSI 2.

In order for a catalyst to be considered for addition to laundry detergent, it must adhere to certain criteria[73]. The bleach catalyst much be; active in the low temperature aqueous alkaline washing conditions, compatible with the entire recipe of detergent, stable, catalytically decompose hydrogen peroxide, selectively remove stains and not damage dye and fabrics through its process, cost effective, not produce any environmentally harmful by-products and cause no damage to the washing machine hardware. Meeting these criteria represents a challenge to the use of organometallic complexes, due to the low stability of organic ligands in the presence of water and the selective activity to stains only, and so industry has yet to produce a worthy catalyst.

1.6. Aims of the project

This project first aims to show that precious monometallic and bimetallic nanoparticles, supported or unsupported, may be used to bleach homogeneous stains in solution. Following this a model compound will be chosen to allow examination of the finer chemistry at play with respect to the process, using supported metal catalysts for the facile comparison to literature. A number of organic compounds have been chosen which represent staining components of tea. These compounds are gallic acid, catechol and resorcinol with the reasons for their use discussed within this work. This will provide the chemical basis and understanding for the proceeding chapters.

The following chapters have been divided between examining monometallic and bimetallic catalysts respectively, for their use in bleaching stained cloth samples, in a reaction scheme modelling a washing machine. The first chapter looking at monometallic colloids prepared using PVA and PVP, as well as supported metal catalysts and a comparison of these catalysts using different additives, which will be referred to as mediators, with their use intended to compliment the bleaching. The mediators will be representing the current commercial state of the art, as well as prospective reagents for use in bleaching detergents.

Whilst carrying out these reactions on the cloths a staining phenomenon was observed, being caused by the catalyst and so a chunk of the final result chapter is devoted to obtaining an understanding of the reasons for the staining and discussing methods of abatement. This is imperative if these catalysts are ever to be considered commercially viable.

Finally, these catalysts will be tested for their efficacy in Dye Transfer Inhibition (DTI), which involves the destruction of staining chromophores in solution generated by dyed fabric during the washing cycle. It is expected that colloidal catalysts will be effective for this procedure, due to the literature proven ability of these catalyst to oxidise conjugated molecules, stripping them of colour.

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2. Experimental

2.1. Materials

All reagents were used as received.

Water (HPLC grade, Fischer)

Palladium chloride (Sigma Aldrich)

Hydrogen tetrachloroaurate trihydrate (Sigma Aldrich)

Platinum Chloride (Johnson Matthey)

Titanium Dioxide (TiO_2, Degussa)

Sodium borohydride (98%, Sigma Aldrich)

Polyvinyl alcohol (80% hydrolysed, Sigma Aldrich)

Sulfuric acid (Fisher)

Hydrochloric acid (Fisher)

Potassium hydrogen phthalate (99.95%, Sigma Aldrich)

Sodium bicarbonate (99.7%, Sigma Aldrich)

Sodium hydrogen carbonate (99.7%, Sigma Aldrich)

Sodium hydroxide (pellets, >98%, Sigma Aldrich)

Trizma base (99.9%, Sigma Aldrich)

Catechin (97%, Sigma Aldrich)

Catechol (99%, Sigma Aldrich)

Resorcinol (99%, Sigma Aldrich)

Gallic acid (98%, Sigma Aldrich)

Stained cloth samples (Henkel)

Blank cloth samples (Henkel)

Phosphoric acid (85 wt. % aqueous solution, Sigma Aldrich)

2.2. Synthesis of chemicals

2.2.1. Colloid

A solution of metal precursor (0.01 g of metal in 400 mL of water) was stabilised with polyvinvyl alcohol (PVA) or polyvinylpyrrolidone (PVP) (weight ratio of metal to stabiliser 1:0.65) and subsequently reduced with $NaBH_4$ (molar ratio of metal to borohydride 1:5 for Au, Pd, 1:10 for Pt). The colloid was left to stir for 30 min before use.

2.2.2. Au colloid (monometallic example)

A solution of Au (0.01g of Au in 400 mL of water; $HAuCl_4$ precursor) was stabilised with PVA (0.65 mL of a 1 wt % solution) and subsequently reduced with $NaBH_4$ (3.62 mL of a 0.1 M solution). The colloid was left to stir for 30 min before use. The synthesis was repeated for Pd and Pt colloids ($PdCl_2$ and H_2PtCl_6 precursors).

2.2.3. 1% AuPd colloid (bimetallic example)

AuPd colloid was synthesised with a 1:1 weight ratio. A solution of Au and Pd (0.005 g of each metal in 400 mL of water; $HAuCl_4$ and $PdCl_2$ precursors) was stabilised with PVA (0.65 mL of a 1 wt % solution) and subsequently reduced with $NaBH_4$ (3.62 mL of a 0.1 M solution). The colloid was left to stir for 30 min before use. The synthesis was repeated for AuPt and PdPt colloids.

2.2.4. 1% Pt/TiO_2 prepared by sol immobilisation

A solution of Pt (0.01g of Pt in 400 mL of water; H_2PtCl_6 precursor) was stabilised with PVA (0.65 mL of a 1 wt % solution) and subsequently reduced with $NaBH_4$ (7.24 mL of a 0.1 M solution). The colloid was left to stir for 30 min before titania was added (Degussa P-25, 0.99g) and acidified (H_2SO_4). The solution was stirred for 1 hour before being filtered, washed and dried at 110 °C for 16 hours. Synthesis was repeated for Pd/TiO, Au/TiO, AuPd/TiO_2, PdPt/TiO and AuPt/TiO_2.

2.2.5. Impregnation catalysts

Metallic catalysts were prepared supported on titania by wet impregnation method. In the case of 1% Au-Pd catalyst, 0.005 g of each metal was dissolved in 4 ml of water. TiO_2 (Degussa P-25, 0.99g) was added and the solution stirred at 80 °C until a thick paste was formed. The paste was dried at 110 °C for 16 hours and then calcined at 400 °C under static air for 3 hours at 10 °C/min.

2.2.7. pH 5 buffer

NaOH (250 ml; 0.1 M) was added slowly to potassium hydrogen phthalate (250 ml; 0.1 M). Brought to 1 L with deionised water.

2.2.8. pH 7 buffer

HCl (500 ml: 0.1 M) was added slowly to Trizma (500 ml: 0.1 M).

2.2.9. pH 10 buffer

$NaHCO_3$ (500 ml: 0.1 M) was added to Na_2CO_3 (500 ml: 0.1 M)

2.2.10. Tetraacetylethylenediamine (TAED) solution

The concentration of TAED used was 0.179 g/L.

2.2.11. Violuric acid solution

Viouric acid was prepared in a stock solution of 0.025 M.

2.2.10. (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) solution

TEMPO was prepared in a stock solution of 0.025 M.

2.3. Catalyst testing

2.3.1. Cloth testing in HEL autoclave reactors

A piece of E-167 tea stained cloth was cut into 1 inch squares and placed in a 75 ml autoclave reactor charged with catalyst (8.2 mg solid; 20 ml colloid), mediator (2 ml) and reaction volume brought to 50 ml with buffer. Reactions were run at 60 °C for 30 mins under 10 bar of O_2, and stirring speed set to 1000 rpm. The cloths were removed, washed with water (100 ml) and allowed to dry.

2.3.2. Cloth testing on hotplate

A piece of E-167 cloth was cut into 1 inch squares and placed in a 100 ml round bottom flask charged with catalyst (8.2 mg), mediator and reaction volume brought to 50 ml with buffer. Reactions were run at 60 °C for 1 hour in air or under 3 bar of O_2. Cloths were then removed and washed with water (100 ml).

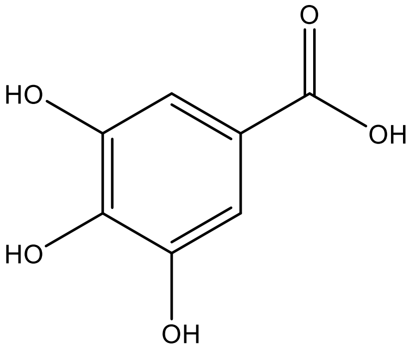
2.4. Model Compound Oxidation

2.4.1. Catechin Oxidation

Catechin (10 ml; 0.003 M) and sol immobilised catalyst (100:1 substrate:metal ratio) were added to a colaver reactor. The reaction was carried out at 60 °C for 4.5 hours at 3 bar oxygen. 0.5 ml samples were taken for analysis at 30, 90, 150, 210 and 270 minutes.

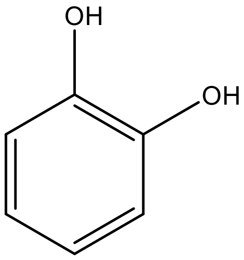
2.4.2. Gallic Acid Oxidation

Gallic acid (10 ml; 0.003 M) and sol immobilised catalyst (100:1 substrate:metal ratio) were added to a colaver reactor. The reaction was carried out at 60 °C for 4.5 hours at 3 bar oxygen. 0.5 ml samples were taken for analysis at 30, 90, 150, 210 and 270 minutes.



2.4.3. Catechol Oxidation

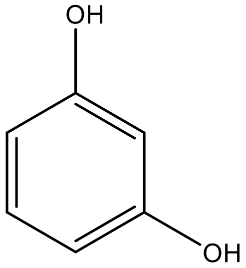
Catechol (10 ml; 0.003 M) and sol immobilised catalyst (100:1 substrate:metal ratio) were added to a colaver reactor. The reaction was carried out at 60 °C for 4.5 hours at 3 bar



oxygen. 0.5 ml amples were taken for analysis at 30, 90, 150, 210 and 270 minutes.

2.4.4. Resorcinol Oxidation

Resorcinol (10 ml; 0.003 M) and sol immobilised catalyst (100:1 substrate:metal ratio) were added to a colaver reactor. The reaction was carried out at 60 °C for 4.5 hours at 3 bar oxygen. 0.5 ml samples were taken for analysis at 30, 90, 150, 210 and 270 minutes.



2.5. Experimental Analysis and Catalyst Characterisation

2.5.1. UV-Spectroscopy

UV-Vis spectroscopy is useful in the analysis of chromophores which absorb radiation in the UV-Visible region of the electromagnetic spectrum i.e. between 200 – 900 nm[1]. This technique involves the irradiation of pi or non-bonding electrons to an excited state, generally a transition from the HOMO to the LUMO orbital, as illustrated in figure 2.1. The wavelength required to cause an excitation is dependent on the qualities of the system being examined, meaning a change in the transition energy can relate to a chemical change in the system. This excitation is seen as an absorbance on the spectrum, which by the Beer-Lambert law is directly related to the concentration of the chromophore examined.

$$A = \varepsilon . c . l$$

Where A is the absorbance, c is the concentration of the of the analyte in M, l is the path length and ε is the extinction coefficient for the analyte. Through this formula the concentration of a UV active analyte can be observed over time.

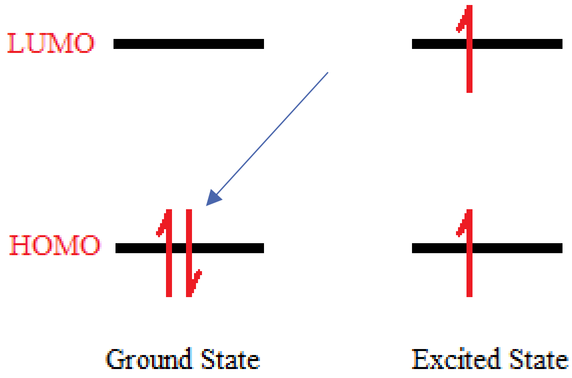


Figure 2.1: Illustrating the electron transition giving rise to UV radiation.

2.5.1.1. UV-Spectroscopy Experimental

UV-Vis spectra were obtained using a Cary UV 4000 Spectrophotometer. Samples were deposited into quartz cuvettes of 1 cm path length and collected across a wavelength range of 200-800 nm.

2.5.2. HPLC

High Performance Liquid Chromotography (HPLC) allows for the separation and identification of liquid phase molecules by passing them through a column containing a stationary phase of chromatographic packing material[1]. A sample is injected into the column which is carried via an eluent mobile phase, with components of the sample being separated on the basis of different component characteristics, such as molecule size or polarity.

Depending on the sample being eluted the mobile phase can be augmented to allow for better separation. This can be done by preparing a gradient mobile phase in which the concentration of each of the component solvents changes throughout the column. This is in contrast to an isocratic mobile phase of just a single solvent.

The sample as it passes through the stationary phase will have components of differing affinity to the microporous particles within the column. All of the component molecules will compete for binding sites on the particles as it passes through the column and towards the detector. This will lead to each compound eluting at different rates, granting separation of the sample solution. The sample is then passed through to two detectors, a Refractive Index Detector (RID) which measures changes in the composition of the eluting sample, allowing it to detect molecules which are not UV active. The second detector is a UV-Vis detector, which is more sensitive and can be used to analyse molecules which are UV active.

2.5.2.1. HPLC Experimental

Analysis was carried out using an Agilent 1200 series with RI and UV-Vis detectors. Reactants and products were separated using a MetaCarb 67H column. The mobile phase was an aqueous solution of phosphoric acid (0.01 M) with a flow rate of 0.8 ml/min. External calibrations were performed for each compound and potential product being tested, using concentrations of 0.15 M, 0.6 M, 0.03 M and 0.0075 M, monitoring the signal intensity at each compound’s respective retention time.

2.5.3. Gas Chromatography Mass Spectrometry (GC-MS)

GC-MS combines the separation procedure of Gas Chromatography with the identification processes of Mass Spectrometry. It will produce a spectrum of sample retention times, with a mass spectrum at each peak. A sample will first be injected and vaporised in the injector port, which will be heated, and then carried through the stationary phase of the column by the carrier gas mobile phase (generally helium). The stationary phase consists of the column through which the sample components will be separated in accordance with their affinity to the column. The column temperature must be controlled as changes in the temperature will lead to variation in the sample elution times and is related to the boiling point of the sample. At the end of the column the sample will be ionized and pass through a detector. The detector used will depend on the sample to be analysed, as what can be detected will depend on the detector selectivity.

A Flame Ionization Detector (FID) is an example of a selective detector, while a Thermal Conductivity Detector (TCD) is an example of a universal detector. In an FID the effluent is mixed with hydrogen and air and exposed to a flame. The organic composites in the sample will produce ions on combustion, proportional to the concentration of the organic species in the sample, which can conduct. Below the flame a voltage is applied with an electrode located above the flame, with the current arising from the pyrolysis of the composites measured. A TCD is universal in that it can be used for completely unknown samples, as it responds all compounds, instead of just organic as for in the case of an FID.

Mass-spectrometry allows for the identification of compounds based on characteristic fragmentation patterns[1]. First a molecule is ionized, which can be achieved through a variety of methods, commonly Electron Impact (EI) or Electrospray ionization (ESI). In EI ionization the sample is vaporised, with the gas phase molecules bombarded by electrons that are formed from a heated filament producing a bias voltage negative compared to the source. A sample molecule will be ionized on contact with this electron beam, giving rise to a molecular ion. ESI involves creating an electrospray formed through the application of a high voltage on the liquid sample. This spray is then aimed into the mass spectrometry where the droplets will evaporate to a gaseous phase. The voltages applied will eject ions from the molecules. The molecule following ionization will then fragment, with these molecular fragments entering an analyser where they can be separated based on their m/z ratio (mass to charge). A simple example of an analyser is the Time-of-Flight (TOF) mass spectrometer. These measure the travel time of ions over a distance with a specific kinetic energy. A detector will then record the relative abundance of each fragment, with spectrum of the relative intensities of each signal against the m/z ratio allowing for the production of spectra with distinct characteristic fragmentation patterns, granting for elucidation of the chemical composition of the sample.

2.5.6. Scanning Electron Microscopy (SEM) and X-Ray Energy Dispersive Spectroscopy (EDX)

SEM can be used to determine the size and shape of nanoparticles, with respect to its resolution limits, as well as in the case of this work to qualify the deposition of particles.

In principle it involves the interaction of a beam of electrons with a desired specimen[4]. Electrons are ejected from the gun, passing through an array of lenses and on reaching the sample will produce a variety of observable phenom as seen in the figure below, such as secondary electrons, X-rays and back scattered electrons, all of which probe to different depths of penetration and produce signals that can be observed by detectors to produce an image of the sample. High energy electrons interacting with the sample will eject electrons from an atomic orbital. A higher energy electron must fill this vacancy and so an X-ray photon with energy equal to this energy transition is ejected from the orbital[5]. These photons are detectable by an EDX, which transmits the energy level to a signal, and represents the signal as a wavelength, which will be characteristic to the atomic element that has been interacted with. Through this EDX is capable of both qualitative and quantitative analysis.

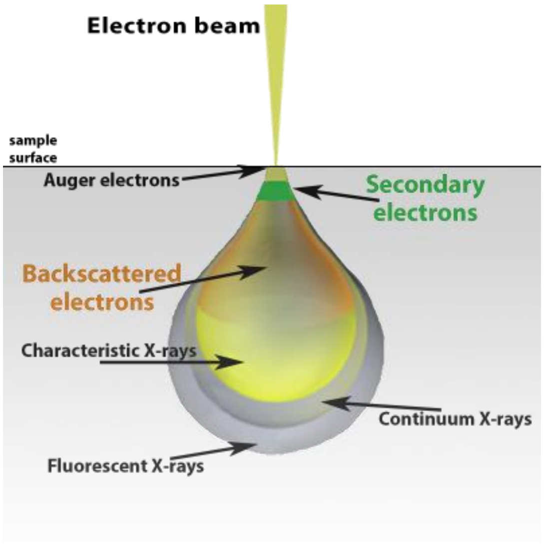


Figure 2.2: Results of an electron beam interacting with the surface. Note the depth of vision each interaction has[6].

2.5.6.1 SEM and EDX Experimental

SEM images were obtained using a Carl Zeiss EVO 40 chamber operating with an EHT at 10 kV. Images were collected using in lens and secondary electron detectors. An Oxford EDX analyser was used to collect EDX data and images.

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3. Determination of Catalyst Activity

3.1. Introduction

Through activation of molecular oxygen, triplet oxygen can be converted to the singlet state and generates species that can be used in oxidation reactions. Traditionally the reduction of O_2 has been carried out by organometallic complexes[1] though now precious metal nanoparticles are becoming of interest for their ability to catalytically activate oxygen to generate useful species[2,3], in particular for benzyl alcohol oxidation[4,5] and glycerol oxidation[6,7]. It is not necessary in terms of bleaching to remove entirely or mineralise a staining compound, merely removing the colour is sufficient. This approach is adopted herein with bleaching referring to a degradation of a chromophore. These precious metal catalysts have been tested and have proven their merit for the destruction of alcohols and conjugated systems, and so in this chapter their measure for the destruction of the chromophores of staining compounds will be examined.

Initially, the catalysts will undergo proof of concept experimentation with tea in solution and gauge their effectiveness for removing the colour of the samples. Tea was chosen for continuity of later work, which will look at tea stained cloth samples and how these catalysts can be used in the bleaching of these samples. Following this, model compounds are chosen to give a measure of catalyst activity to compliment the stained cloth reactions, with future scope to understand the chemical processes at work and how to design an optimised catalyst for catalytic bleaching. From this an understanding of the oxygen activation products can be obtained and allow for optimisation of the reaction pathway through modification of reaction conditions. The compounds derive from breaking up a catechin molecule into its constituent moieties for facile experimentation, as depicted in figure 3.1, whilst gallic acid was chosen as it functions as a building block for hydrolysable tannins, modelling the properties of these polyphenols (highly coloured). The mineralisation of which is covered in high temperature systems, as it is an undesirable compound found in the waste water of an assortment of industy[8].

Resorcinol, although it has its uses in the manufacture of specialty chemicals and adhesives, released into the environment can cause toxicological effects in humans and animals[9]. It has been shown that resorcinol exhibits antithyroid activity in humans, with it inhibiting the production of thyroid hormones, with these effects occurring at exposure levels between 34 – 122 mg/kg/day[10]. Catechol is also found in the industrial effluents of fine chemical and lubrication production[11] and due to its toxicity to aquatic life its abatement is also considered desirable.

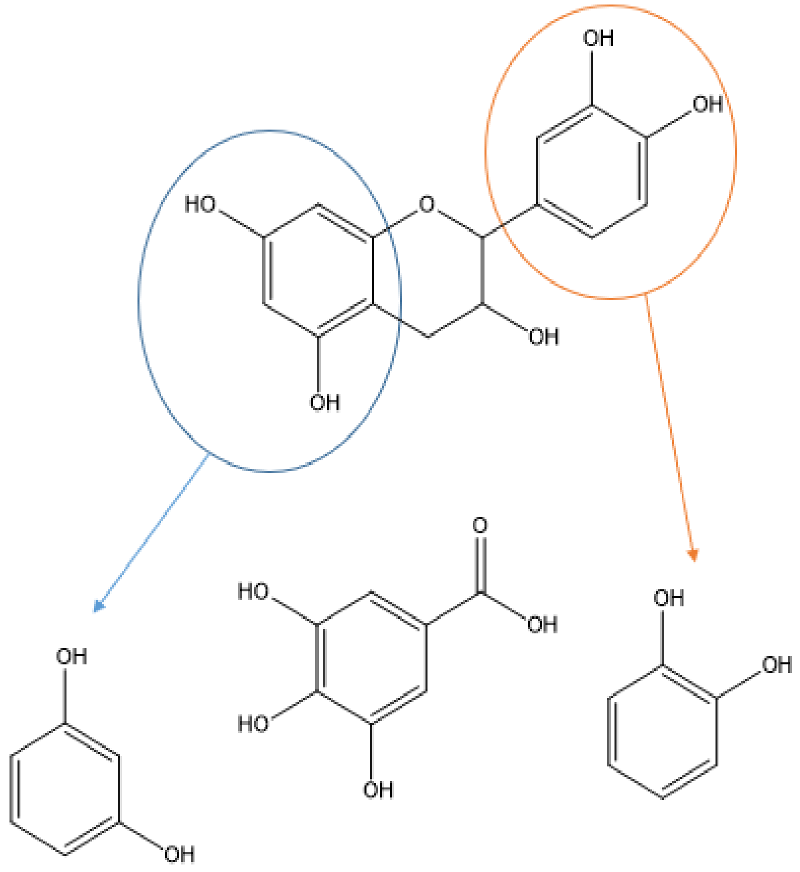


Figure 3.1: Derivation of the model compounds resorcinol and catechol, and structure of gallic acid between them.

In a theoretical study of CO oxidation, the interaction of molecular oxygen with a gold atomic cluster was examined[12]. This work highlights the requirement of small nanoparticles in comparison to catalyst preparation methods that would return particles of greater size or of greater size range. Considering this, preparation methods which guarantee a narrow size distribution of consistently small nanoparticles have been chosen and will be tested for their activity of the model compounds discussed in this chapter. Such activity will be compared against traditional impregnation catalysts, which although can return nanoparticles of the desired size, will also return a broad range of particle sizes accompanying them[13].

3.2. Experiments with fruit tea

Unsupported precious metal catalysts were tested using fruit tea, to show how these catalysts can be used to discolour the solutions. Twinnings fruit teabag brewed in 200 ml of water for 1 hour. 10 ml of tea, 5 ml colloid (0.125 mg metal) and brought up to 30 ml with water. Sampling was carried out at 0, 60, 120 and 180 minutes and analysed using UV-Vis. A figure of the first set of experiments is shown below, with fruit tea tested using a 1% 1:1 AuPd colloid shown against a control batch.

It can be seen from figure 3.2 the addition of colloid to the fruit tea solution does lead to a difference in the colour of the solution over the 3 hours in comparison with the control batch C, and this discolouration is greater in the reaction run at 60 °C than in the case of the reaction run at 30 °C. The colour of the fruit tea does not change in the case of batch C. This indicates that the colloids used are causing a reaction to occur that is leading to a discolouration of the fruit tea solution and that the rate of this reaction is increased upon increasing temperature. The monometallic constituent colloids were tested for their activity and the samples collected. with the figure below showing the samples obtained from these experiments at the same sampling times as the previous set of experiments. The palladium catalyst leads to the most dramatic effect in terms of the discolouration of the fruit tea sample, with an almost complete change from pink to yellow within the first hour.

Gold causes little change in the colour of the solution, although it is known more for its selectivity in oxidation reactions rather than its activity[14].

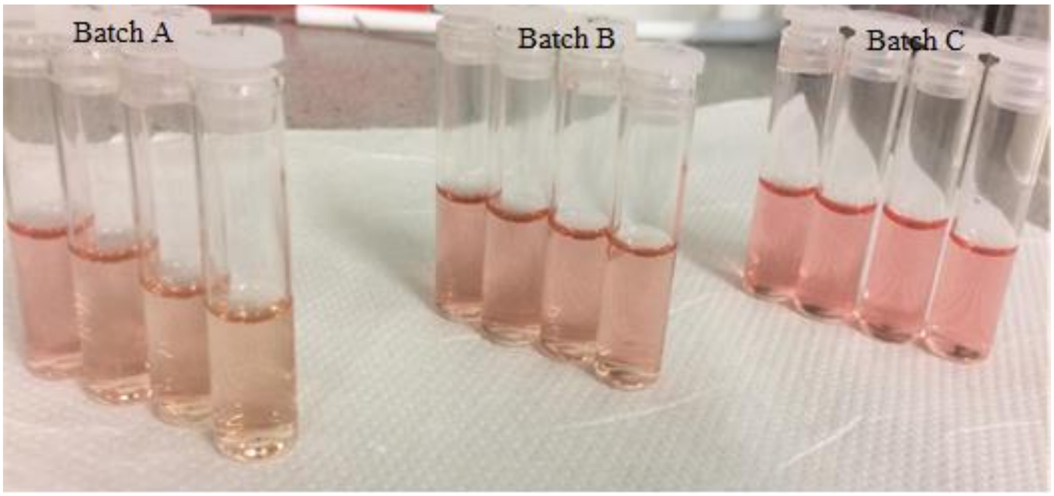


Figure 3.2: Samples taken at 0, 60, 120 and 180 minutes of the fruit tea oxidation reactions. Conditions: (A) 10 ml fruit tea, 5 ml AuPd colloid and 15 ml water at 60 °C, (B) 10 ml fruit tea, 5 ml AuPd colloid and 15 ml water at 30 °C and (C) 10 ml fruit tea and 20 ml water at 60 °C.

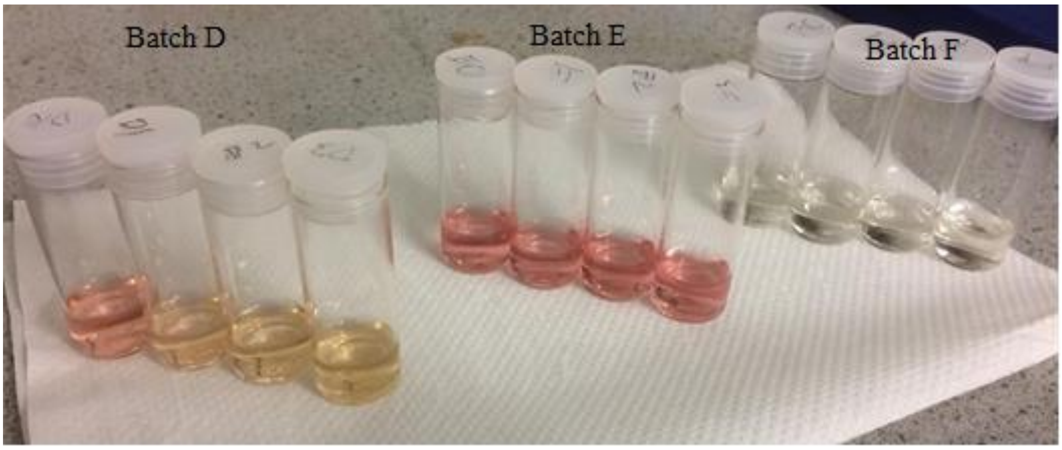


Figure 3.3: Samples taken at 0, 60, 120 and 180 minutes of the fruit tea oxidation reactions. Conditions: (D) 10 ml fruit tea, 5 ml Pd colloid and 15 ml water at 60 °C, (E) 10 ml fruit tea, 5 ml Au colloid and 15 ml water at 30 °C and (F) 5 ml AuPd colloid and 25 ml water at 60 °C.

From batch F it is clear that the discolouration is coming from a chemical change from chromophores within the fruit tea solution, and not just as a result of adding the colloidal solution, which is highly coloured itself. The catalysts are interacting with these chromophores (evident from the lack of change in batch C) and causing a chemical change which is causing a discolouration in the samples. The nature in which these catalysts are interacting with the chromophores needs to be explored.

3.3. Gallic Acid Oxidation

As described at the beginning of this chapter gallic acid was one of the model compounds chosen for the replication of the chemistry that would be taking place on a stained cloths surface. Gallic acid solution was placed in a reaction vessel, purged with oxygen and reacted, with periodic samples being taken and analysed with HPLC. The conversions over the reaction time are presented graphically, with the initial reactions being shown in figure 3.4. Supported catalysts were chosen due to the higher correlation associated in later chapters between cloth bleaching and use of supported catalysts compared with unsupported catalysts.

This figure represents the results of gallic acid oxidation over 4.5 hours in the presence of monometallic precious metal sol immobilised catalysts. Supported metal catalysts were chosen Titania was also tested as part of the control group, with and without additional oxygen. There is little or no conversion of the substrate without any catalyst added, while titania does show to have some effect by itself. The gold catalyst performs only marginally better than the controls, reaction was 14% conversion after the 4.5 hours. Supported palladium and platinum catalysts offer the highest conversion over the reaction time, with palladium reaching full conversion by the 3.5 hours, whilst platinum following not far behind. Gold containing catalyst performing poorly is unexpected for this reaction considering its affinity for the activation of oxygen[15–17]. If gold alone is inactive it could be utilised in a bimetallic catalyst to make use of the synergistic effects of the addition of a companion metal[18,19].

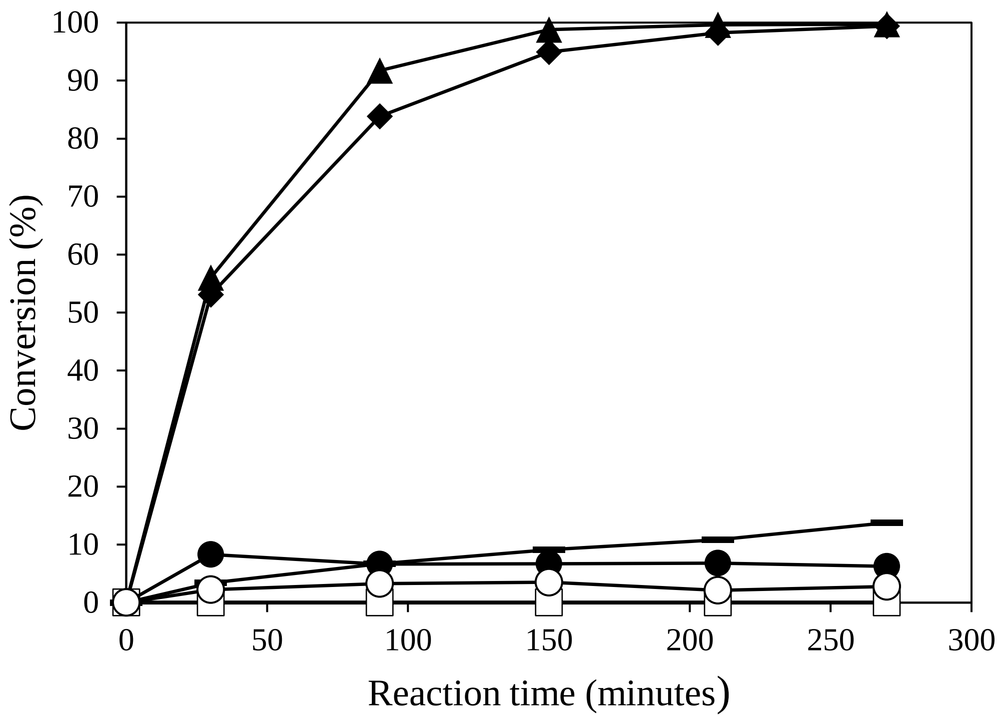


Figure 3.4: 10 ml Gallic acid (0.003 M) oxidised using 100:1 substrate:metal molar ratio of catalyst at 60 °C and 3 bar oxygen. Stirred at 1000 rpm for 270 mins Conditions: Pt/TiO_2 (♦), Pd/TiO_2 (▲), Au/TiO_2 (−), TiO_2 (●), TiO_2 in air (○), no catalyst (■) and no catalyst in air (□).

The following experiments involve the testing of bimetallic 1% AuPd/TiO_2 and 1% AuPt/TiO_2 catalysts and gauging their affinity for gallic acid oxidation. These catalysts have all been prepared by the same sol immbolisation technique using PVA as stabiliser. The results of these experiments are shown in figure 3.5. From figure 3.5 it can be deduced that by using gold a catalyst design recognising synergistic benefits of the combination of metals must be adhered to. The effects of synthesis with palladium metal are clearly offering a catalyst with more than twice the initial rate of the AuPt catalyst, which lags towards the rate of titania alone towards the start of the reaction. AuPt catalyst reaches complete conversion before the 3 hours mark. AuPd has been extensively used as a non-selective catalyst for alcohol oxidation[4,13,20,21], though it appears that the synergistic effects offered by platinum are of more imperative consideration with regard to the process at hand.

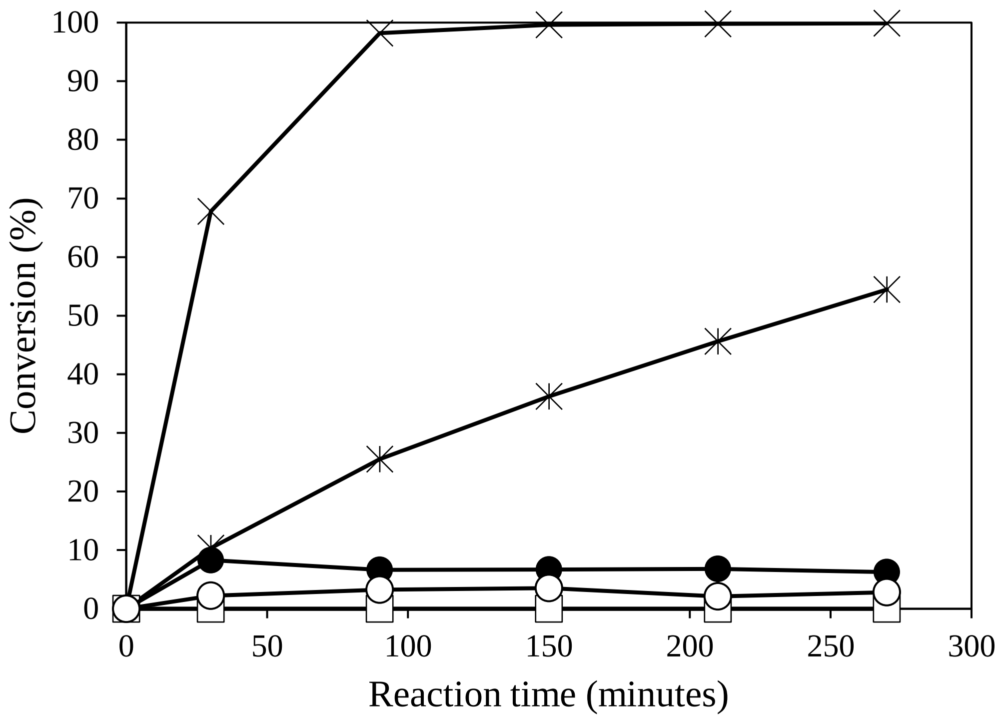


Figure 3.5: 10 ml Gallic acid (0.003 M) oxidised using 100:1 substrate:metal molar ratio of catalyst at 60 °C and 3 bar oxygen. Stirred at 1000 rpm for 270 mins. Conditions: AuPt/TiO$_2$ (⋇), AuPd/TiO$_2$ (×), TiO$_2$ (●), TiO$_2$ in air (○), no catalyst (■) and no catalyst in air (□).

With the high conversions observed for gallic acid with 3 bar of oxygen present, it was decided to then tests the different catalysts for their abilities in atmospheric conditions. In this case bimetallic PdPt would also be prepared and tested against the complete collection of sol immobilised catalysts. The results of these experiments are shown in figure 3.6. PdPt supported on titania reached maximum conversion within the first 90 minutes of the reaction, with none of the other catalysts approaching its rate during this phase of the reaction. Following this experiment the ratio of metal to substrate was decreased to 500:1 in the case of PdPt catalyst and still reached conversions of nearly 70% over the course of the reaction, highlighting the efficacy of this catalyst. Palladium and platinum on titania respectively follow the same trend as observed for the reactions supplied with 3 bar oxygen, with palladium performing marginally better, reaching 52% conversion over the course of the reaction compared to platinum’s 45%. Palladiums initial rate was comparable to that of the AuPd catalyst. Suggesting that palladium is the more active component in this case, rather than a synergistic effect being at play promoting the golds reactivity. With respect to control experiments titania reaches 5% conversion over the course of the reaction, higher than that of gold supported on titania, which did not exhibit any reactivity. Added to this the results show that rather than platinum promoting the activity of gold, it is possible the gold is inhibiting the reactivity of platinum, due to lower conversions presented for AuPt catalyst compared to Pt catalyst. It is possible that gold contains no active sites for the reaction that is being carried out to cause the destruction of gallic acid, and therefore addition of gold atoms to a cluster of palladium or platinum could be diluting active sites and inhibiting them. The synergistic components[22] of a AuPd/AuPt bimetallic catalyst should not be considered for this type of reaction.

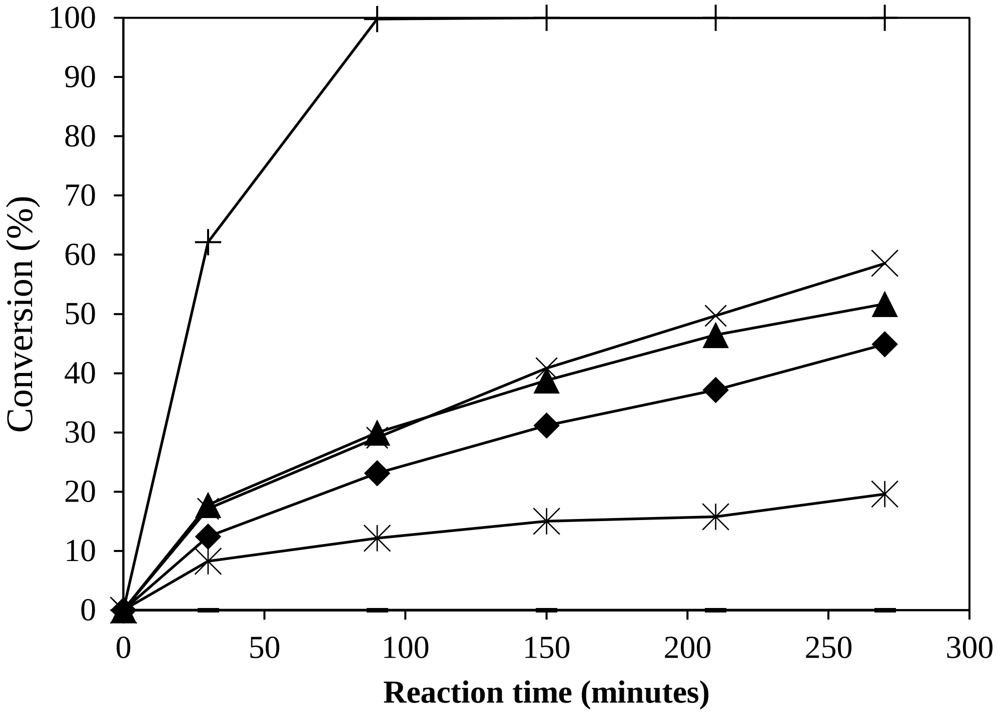


Figure 3.6: 10 ml Gallic acid (0.003 M) oxidised using 100:1 substrate:metal molar ratio of catalyst at 60 °C in air. Stirred at 1000 rpm for 270 mins. Conditions: PdPt/TiO$_2$ (+) AuPd/TiO$_2$ (×), Pd/TiO$_2$ (▲), Pt/TiO$_2$ (♦), AuPt/TiO2 (⋇), Au/TiO$_2$ (−).

Due to its median activity, platinum catalyst was chosen for variation of temperature studies to determine the dependency of temperature on the reaction kinetics. Figure 3.7 shows the results of these experiments. It can be seen that the initial rate is very comparable at the four temperatures examined. This is suggestive of a mass transfer limitation effect at the catalyst surface[23]. It is possible that here the products can not efficiently desorb from the catalyst to make way for incoming substrate molecules. As the reaction proceeds the trends follow a more expected fashion, with higher temperatures favouring higher turnovers. The results do indicate that beyond 50 °C the reaction is not dependent on temperature to increase the rate. It is likely diffusion controlled at this point.

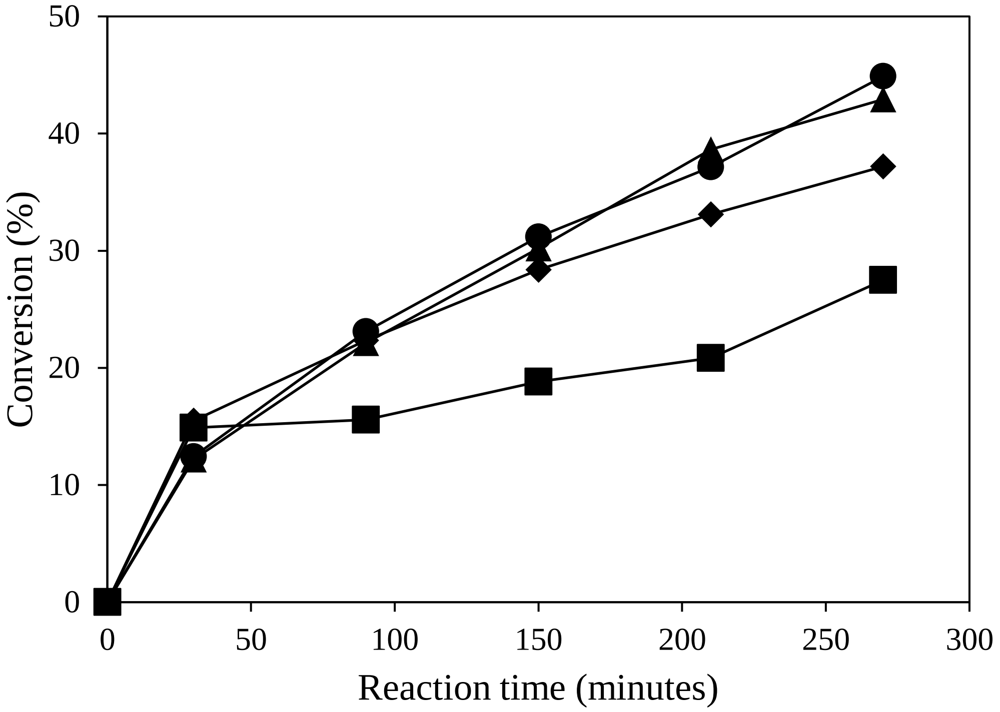


Figure 3.7: 10 ml Gallic acid (0.003 M) oxidised using 100:1 substrate:metal molar ratio of Pt/TiO$_2$ at T = 30 °C (■), T = 40 °C (♦), T = 50 °C (▲) and T = 60 °C (●). Stirred at 1000 rpm for 270 mins in air.

To determine if the reaction was mass transfer limited by the first sampling point and if the reaction was overall diffusion controlled. Figure 3.8 shows the conversions over time for reactions carried out using varying amounts of catalyst. As before and across all masses of catalyst tested the same high initial rate can be, followed by a lower rate as substrate is consumed and the reaction approaches a steady state. The proximity of 2 and 4 mg results and 8 and 10 mg could be due to error in measuring the low mass of catalyst used, regardless a consistent trend is observed in the addition of more catalyst adding a degree of reactivity. To better monitor this degree additional plots at the initial and final sampling times are observed in figure 3.9 and figure 3.10 respectively.

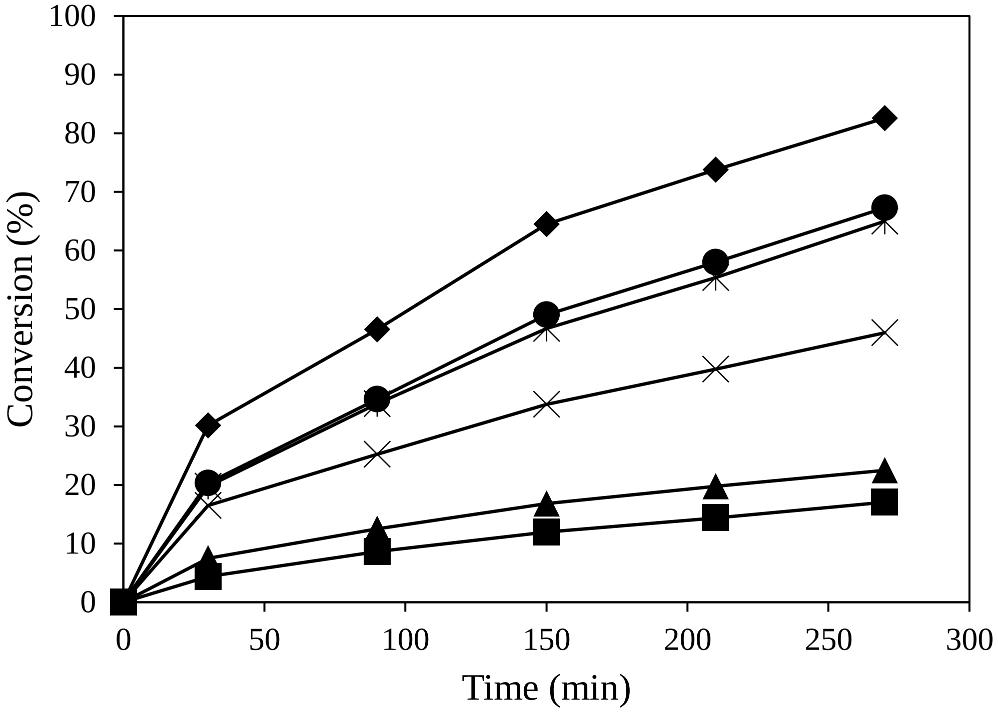
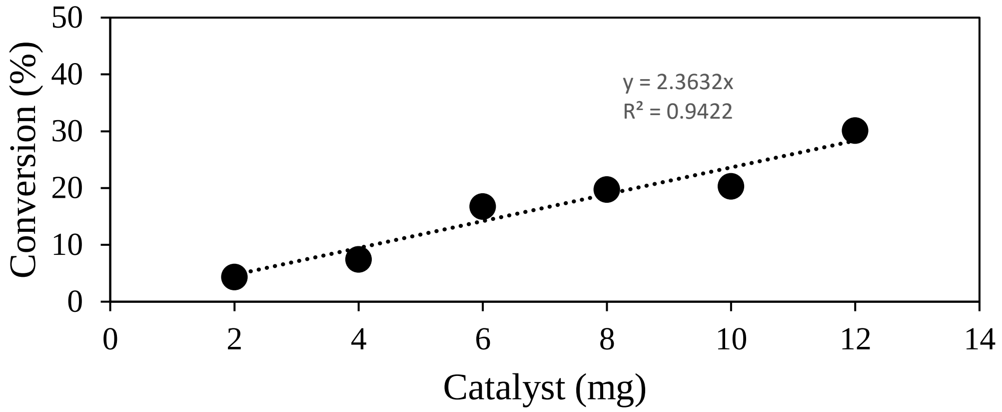


Figure 3.8: 10 ml Gallic acid (0.003 M) oxidised using varying amount of Pt/TiO_2: 2 mg (■), 4 mg (▲), 6 mg (×), 8 mg (⋇), 10 mg (●), 12 mg (♦). Stirred at 1000 rpm for 270 mins in air.

Figure 3.9 exhibits that for a two-fold increase in catalyst mass used, there is a doubling in the reaction rate at the initial sampling point. This indicates that here the reaction is operating in the kinetic regime at this time and not experiencing mass transfer difficulties of products and reactants. This was of concern due to the results of the temperature tests as well as the relatively high substrate to metal ratio of 100:1. The same results are viewable at the final reaction sampling time, confirming the kinetic control of the reaction scheme.



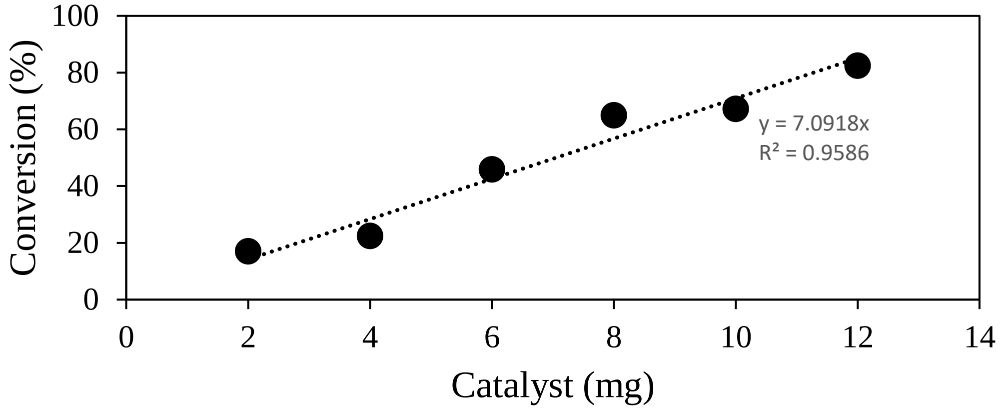


Figure 3.9 and 3.10: Conversion of 10 ml gallic acid (0.003 M) vs mass of Pt/TiO_2 graphs at 30 and 270 mins respectively at each amount of catalyst used.

3.4. Catechol oxidation

Catechol was chosen as the second model compound to test the ability of these catalysts for destroying conjugated systems and determine mechanisms. The results of experiments with this compound are shown in this section.

Figure 3.11 shows the results of catechol oxidation with 1% Pd, Pt and Au supported on titania. As with the previous molecule gallic acid, the Au catalyst is not as effective in the oxidation for catechol. Palladium and platinum are much more active. It is possible than these trends give a hint to the reaction mechanism at work here. It is possible that the access to certain oxidation states is favouring the optimal reaction pathway. Platinum and palladium favour the (IV) and (II) oxidation states[24] whereas gold will commonly be found in the (I) and (III) oxidation states[25]. XPS analysis would need to be used to qualify the oxidation states of the metal during the reaction scheme and discern if this is the reason for the difference in the reactivity of the metals. With regard to the blank reactions, catechol concentration did not change over the course of the sampling time. Following experiments with 3 bar oxygen the catalyst was tested in air. The results of these experiments are shown in figure 3.12.

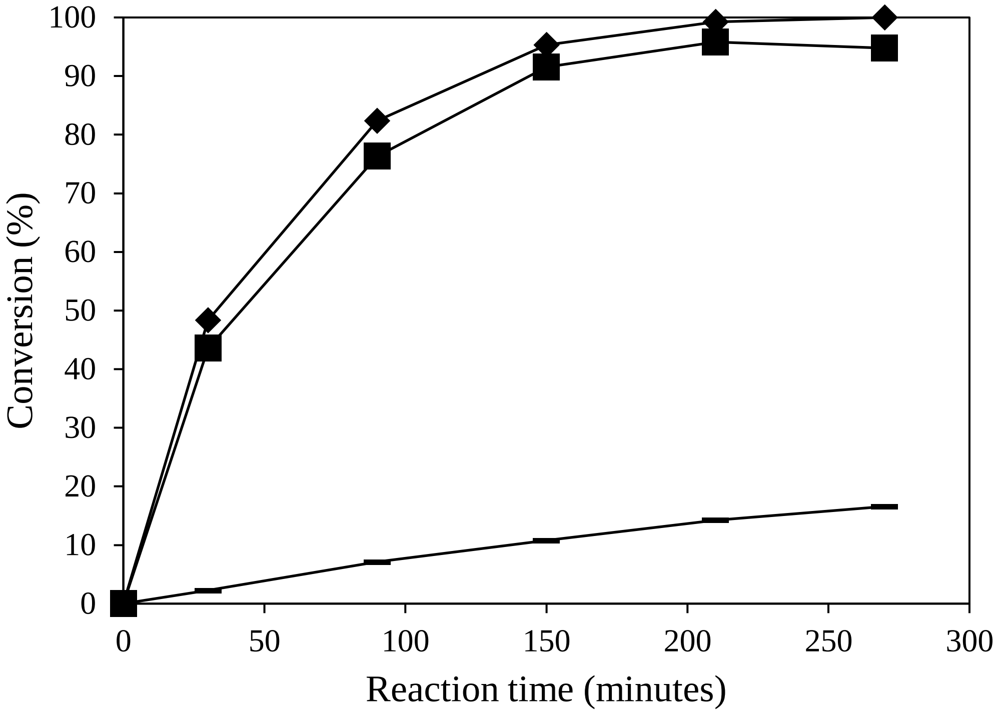


Figure 3.11: 10 ml Catechol (0.003 M) oxidised using 100:1 substrate:metal molar ratio of catalyst: Pd/TiO₂ (■), Pt/TiO₂ (♦), Au/TiO₂ (−). Stirred at 1000 rpm in air for 270 mins.

In this case the palladium catalyst is the most effective at the initial sampling point of 30 mins, although the platinum catalyst becomes more effective as the reaction proceeds. As catechol was active with these catalysts and resorcinol was not, it implies that having an ortho position hydroxy group is important for the reaction, implying that the catalyst may be helping form the o-quinone which then polymerises[26,27].

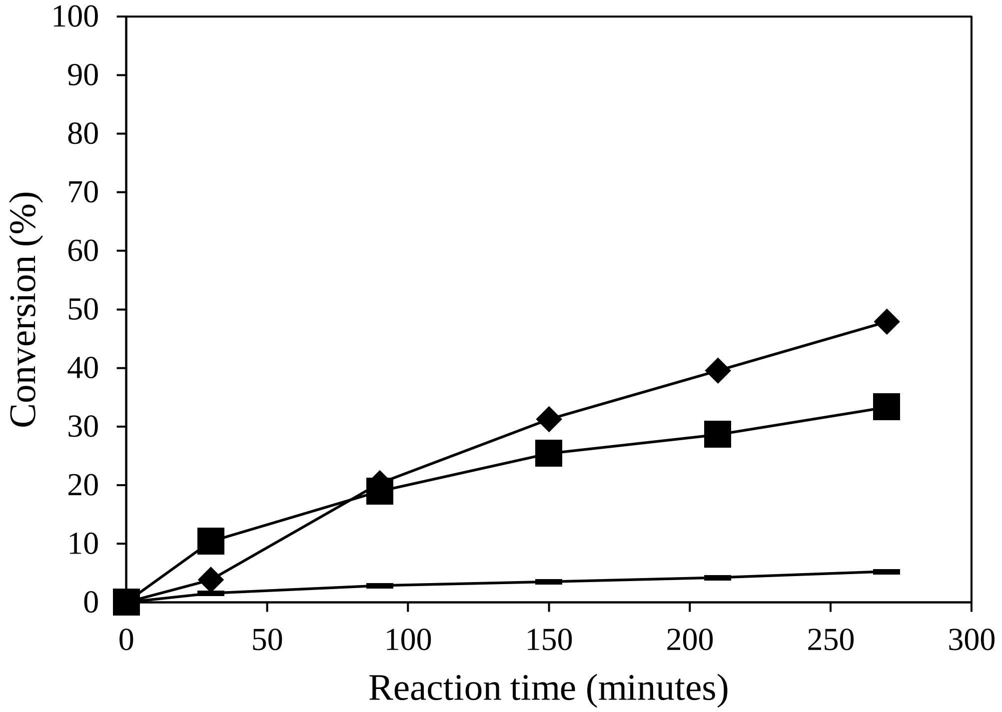


Figure 3.12: 10 ml catechol (0.003 M) oxidised using 100:1 substrate:metal molar ratio of catalyst: Pd/TiO_2 (■), Pt/TiO_2 (♦), Au/TiO_2 (−). Stirred at 1000 rpm in air for 270 mins.

The following graphs represent the experiments carried out to determine if catechol is exhibiting mass transfer limitation. The same trend is visible as was seen for gallic acid in that increase of the catalyst mass used leads to a scaled increase in the reactivity. Slight variations from the trend would be down to experimental errors.

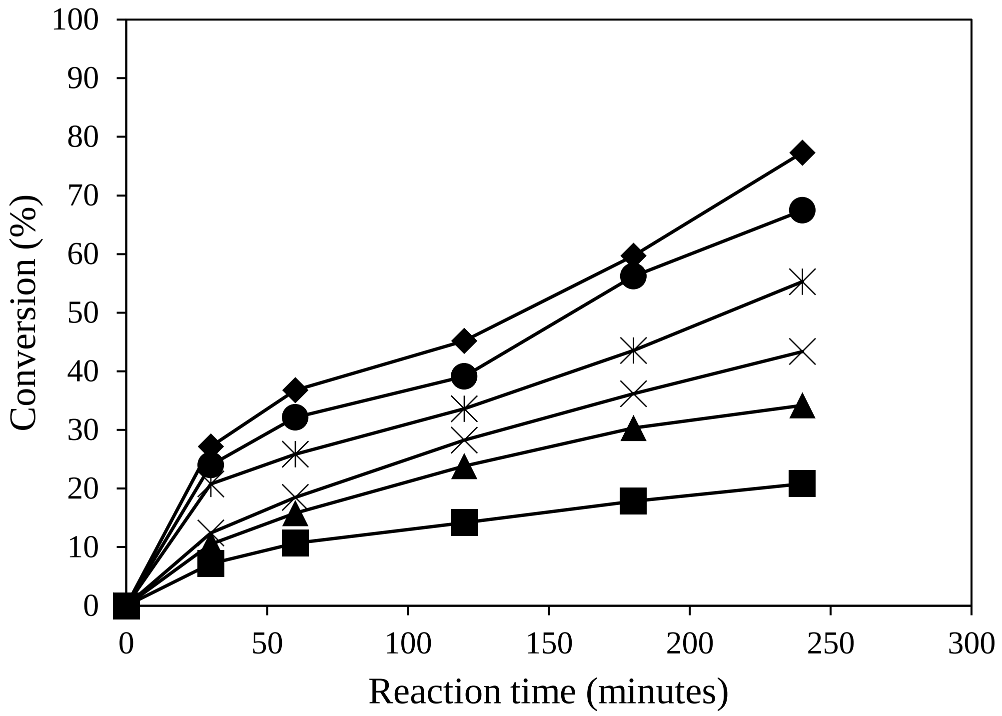


Figure 3.13: 10 ml catechol (0.003 M) oxidised using varying amount of Pt/TiO$_2$ catalyst: 2 mg (■), 4 mg (▲), 6 mg (×), 8 mg (x̶), 10 mg (●), 12 mg (♦). Stirred at 1000 rpm in air for 240 mins.

Graphs highlighting the conversion against the mass at the first and last sampling points are shown below and indicate that there are no mass transfer limitations observed for this reaction scheme. A doubling of the catalyst mass does indeed relate to a doubling in the catalyst reactivity for the substrate. This would be a concern if the reaction pathway would be to involve the production of polymeric compound, as this would likely inhibit the reaction through the steric blocking of the active sites. It is concluded that the reaction is operating in the kinetic regime.

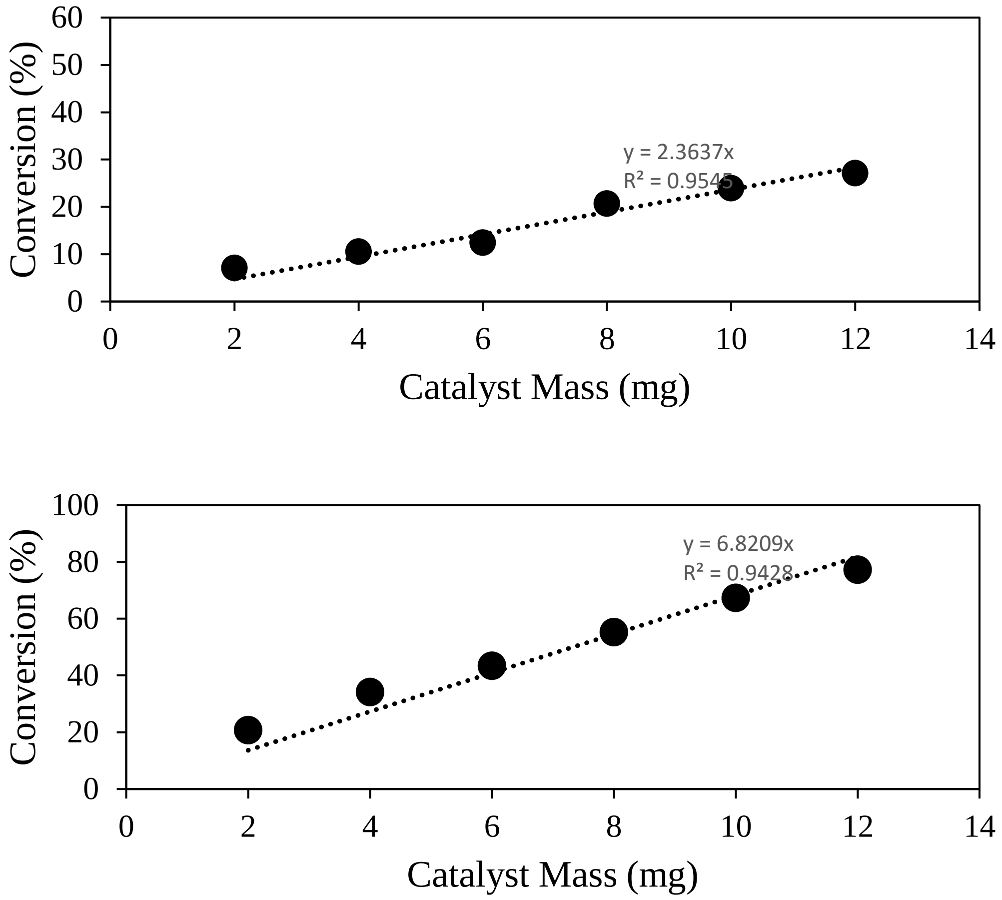


Figure 3.14 and 3.15: Conversion of 10 ml catefchol (0.003 M) vs Pt/TiO_2 mass graphs at 30 and 240 mins respectively at each amount of catalyst used. Stirred at 1000 rpm in air for 240 mins.

3.3. Comparison of catalyst preparation methods for catechol oxidation

Due to the differentiation in final particle characteristics due to the preparation method chosen for the catalyst, the sol catalysts tested and used in this work have been compared with catalysts from other preparation methods. In particular catalysts prepared by a conventional impregnation method and a modified impregnation method have been chosen. The modified impregnation method provides catalyst with a similar narrow size distribution to the sol immobilised catalyst, but avoids the use of cumbersome capping agents for stability of the particles[13]. The results in figure 3.16 do indicate that the narrow particle size distribution is of benefit for this reaction with sol immobilisation and modified impregnation catalysts having higher conversions than the impregnation catalyst. Sol immobilisation catalysts had the highest activity overall, reaching 75% over the 4 hour sampling time, almost twice as much as that of the modified impregnation catalyst at 38%.

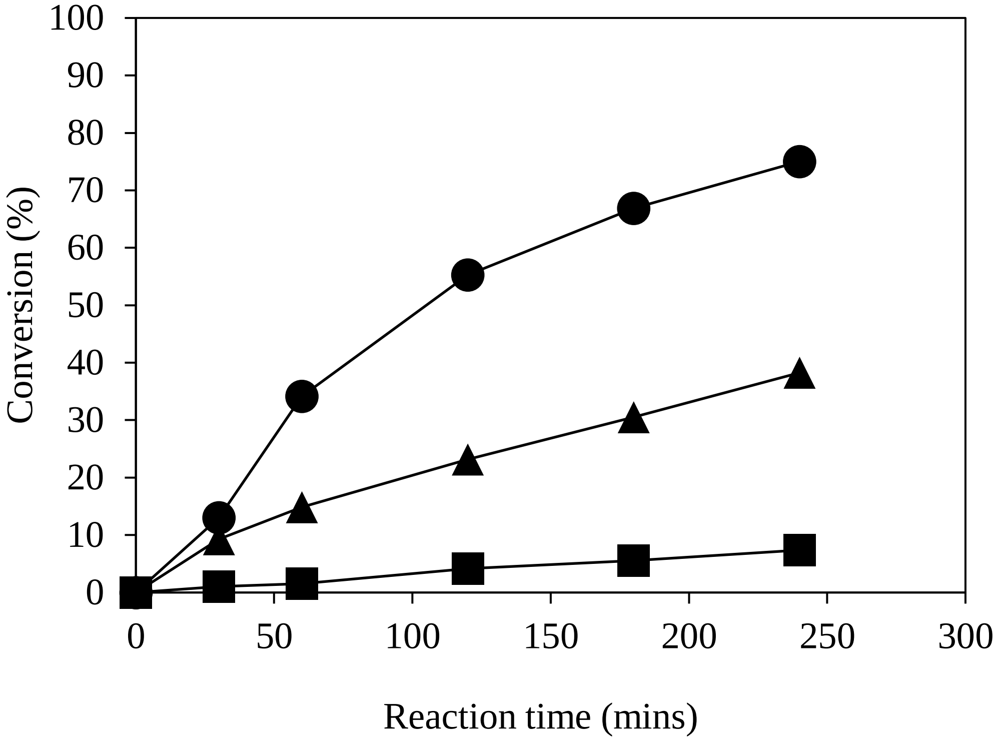


Figure 3.16: 10 ml catechol (0.003 M) oxidised using three AuPd/TiO_2 catalysts of different preparation method: Impregnation (■), modified impregnation (▲), sol immobilisation (●). Stirred at 1000 rpm for 240 mins in 3 bar O_2.

The catalysts were also tested in air for the reactivity for catechol and these results are shown in figure 3.17. Here a similar trend is observed in impregnation catalysts performed worse, with sol immobilised and impregnated catalysts performing better. Of interest in these results is the comparison between the sol immobilised catalyst and the modified impregnated catalyst. Although the modified impregnation catalyst has a higher initial rate, the sol immobilised catalyst begins to catch up and over a time period of longer than the sampling time will overtake the modified impregnation catalyst in reactivity. This suggests a different reaction pathway for the two catalysts, where the modified impregnation catalyst could be generating a species in the absence of additional oxygen that could be inhibiting reactivity. The reasoning for this could be the difference in elemental composition in individual reactive nanoalloys that will be carrying out these reactions. In the case of the modified impregnation catalyst, the excess anion method will be leading to clusters of AuPd that have a more random elemental composition in terms of their metallic ratio than the other catalysts will have[13]. Another potential rationale could be that the stabiliser is being removed over time, exposing more of the metal surface for reaction.

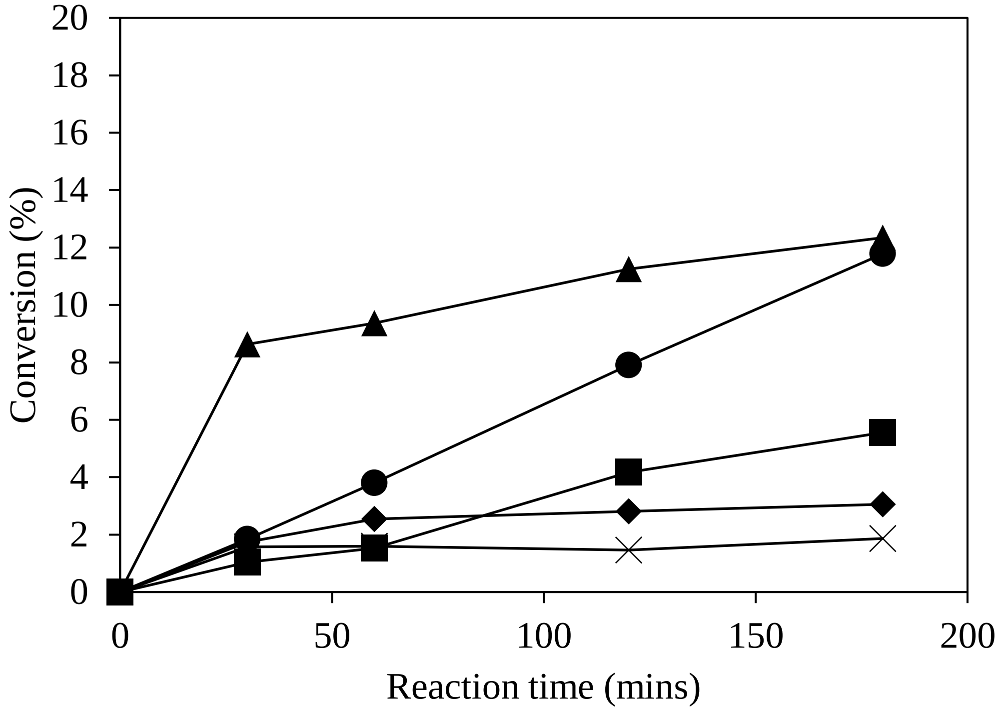


Figure 3.17: 10 ml catechol (0.003 M) oxidised using AuPd/TiO_2 catalyst prepared by three different methods: impregnation (■), modified impregnation (▲), titania (×), sol immobilisation (●), catechol alone (♦). Stirred at 1000 rpm for 180 mins in air.

The higher reactivity of the modified impregnated catalyst compared to the conventional impregnated catalyst could be due to the morphologies and atomic orientations post reduction step[13]. Both catalysts show the formation of core-shell clusters with Au rich cores and Pd rich shells, again indicating the higher activity of palladium while Au serving only for its synergy and to increase the open surface area of palladium. These particles prepared by Sankar et al. had mean values of particle size of 2.9 nm and 4.7 nm respectively, which suggests the particle size is the main difference owing to the higher activity of the two catalysts. Comparing the modified impregnation catalyst to the sol immobilised catalyst, the mean particle size was found to be slightly smaller, being 2.1 nm for sol immobilised nanoparticles[28]. This work suggests that the nanoparticles prepared by sol immobilisation would be found in a random alloy assortment, potentially explaining the difference in activity between it and the modified impregnation catalyst, due to the similar particle sizes.

3.5. Conclusions

The reactions involving solutions of tea proved that the catalysts can be used to cause discoloration, suggesting that the precious metal catalysts can be used to augment the chemical structure of the chromophore of staining compounds. The staining compounds within tea were then reacted specifically through the oxidation of the model compounds, giving definitive statistics for the activity of these catalysts for aromatic chromophores.

All of the catalysts were shown to be capable of reaction with gallic acid and catechol, with and without oxygen added to the reaction vessel. Palladium and platinum were shown to both be more effective than gold catalysts, and the reasons for why this may be, have been discussed. Gold in particular seemed to demonstrate impeding effects for the reactions, indicating a different mechanism from the other catalysts. Resorcinol did not react with the catalysts, due to the reduced activity afford to an OH on the meta position in comparison to an OH in the ortho and para positions[29].

The oxidations of gallic acid and catechol did not exhibit mass transfer limitations which were expected due to the results of temperature trials. These reactions are operating in the kinetic regime with the quantities of catalysts that have been used. The next step would be to properly characterise the reaction products of oxidation for both model compounds. This was being carried out alongside catalyst testing however, there was difficulty in separating the reaction products from each other and so full characterisation was not possible. It is believed that some of the major products are a result of a polymerisation reaction taking place in the case of catechol, due to the formation of an intermediate unstable quinone species[30].

The sol immolised catalysts were compared against a standard impregnated catalyst and a modified impregnation catalyst to compare activity. Both the sol immobilised and the modified impregnation catalyst showed greater activity, likely a result of the more consistent particle size compared to the impregnation catalyst. The difference between the sol and the modified impregnation catalyst could be down to the atomic orientations of each metal in the nanoparticle crystal lattice.

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4. Catalytic Washing using Monometallic Catalysts

In addition to the experiments which investigated how the catalyst prepared in this study interact specifically with model stain compounds, it was also important to establish how these catalysts function under more applicative conditions. It is not always the case that experiment will reflect the reality of a situation, so systematic testing of the supported and unsupported monometallic precious metal catalysts on stained cloth samples was examined. Specifically, cloths denoted to E167 tea stained cloths were used, to represent the work being done on the aromatic structures under examination in the previous chapter. These cloths will be tested in water, with additional O_2 pressures applied to aid the production of radical species, as reported in previous work[1–3]. Of course modern washing machine systems operate at atmospheric pressure without an additional gas feed[4], though it is the aim of this work to understand how the catalysts prepared work and to produce a catalyst which can be used in ambient conditions to generate reactive oxygen species in situ and deliver them to the stain for bleaching. It is desired to start with conditions to best help in reactive species generation, and then work back from there towards an ambient condition.

Experiments will be carried out in Cardiff University, with the analysis of the cloths taking place in Henkel for determination of the Y-value; a unitless measure of the brightness of a substrate. The Y-value can be thought of as a percentile, with the Y-value of a plain white cloth being 83.1. Understanding this, higher brightness values are favoured and numbers close to this value can be considered bleached. Tests are run in triplicates with the average result of each run reported in the data below. Error analysis carried out for an experiment batch (a batch constituting a graph in this thesis) reveals that the average variation from the mean brightness value for a cloth is 1.15, with the standard deviation being 1.56. An example of the cloths following experimentation is shown in the figure 4.1. The image shows a sample of cloths tested using different pH buffers, with mediator, the use of which will be discussed in each respective section in this chapter in addition to the specific catalyst being examined.

The motive for using the specific catalysts in this section has been discussed previously in this work. Colloidal catalysts will be prepared first and tested with the cloths as it is believed that due to the short lived nature of the reactive species, it is more optimal to have an unsupported catalyst that should be able to work in closer proximity to the substrate and unencumbered by a support. In this chapter, the choice of metal, choice of ligand and whether unsupported catalysts offer any benefits over colloids immobilised on a support material, will be discussed.

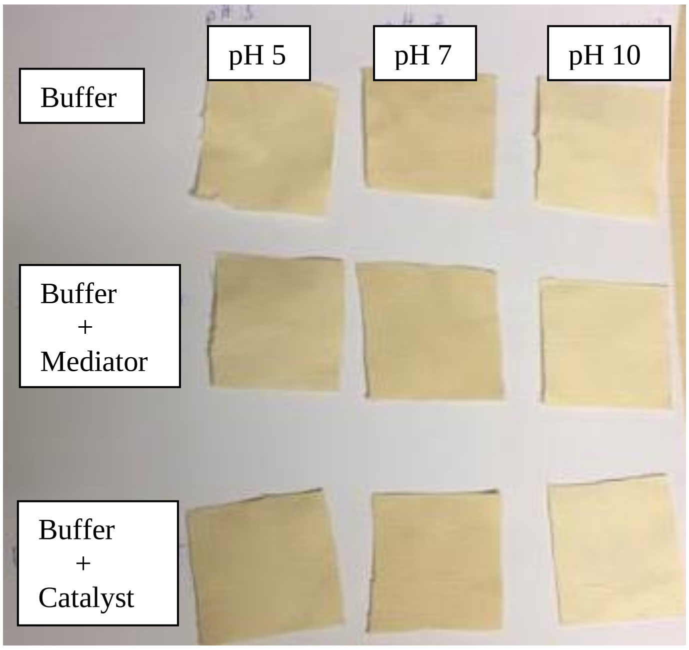

Figure 4.1: Image of cloths following testing in autoclave reactors.

4.1. Monometallic colloids on E167 tea stained cloths

These tests were undertaken in autoclave reactors using monometallic Au, Pd and Pt colloids. The colloids were prepared using the standard method discussed in chapter two and used immediately. The graphs in this chapter represent the average brightness value (Y-value) of each repeat experiment and are plotted according to the conditions of the experiment. For comparison the brightness value of an untested stained cloth and a white cloth is 44.3 and 83.1, respectively.

Figure 4.2 shows the Y-values of cloths tested over a range of temperatures to determine the optimal testing conditions. The Platinum colloid was used with and without mediator. In general, the addition of TAED leads to an increase in brightness value compared to the colloid alone, except in the case of the tests carried out at 30 °C. This is likely due to TAED's lower bleaching ability below 40 °C[5]. It is evident that higher temperatures result in increased bleaching and so, 60 °C will be used as the standard heating temperature for future experiments. The control in this case represents the brightness value of E167 untreated cloth.

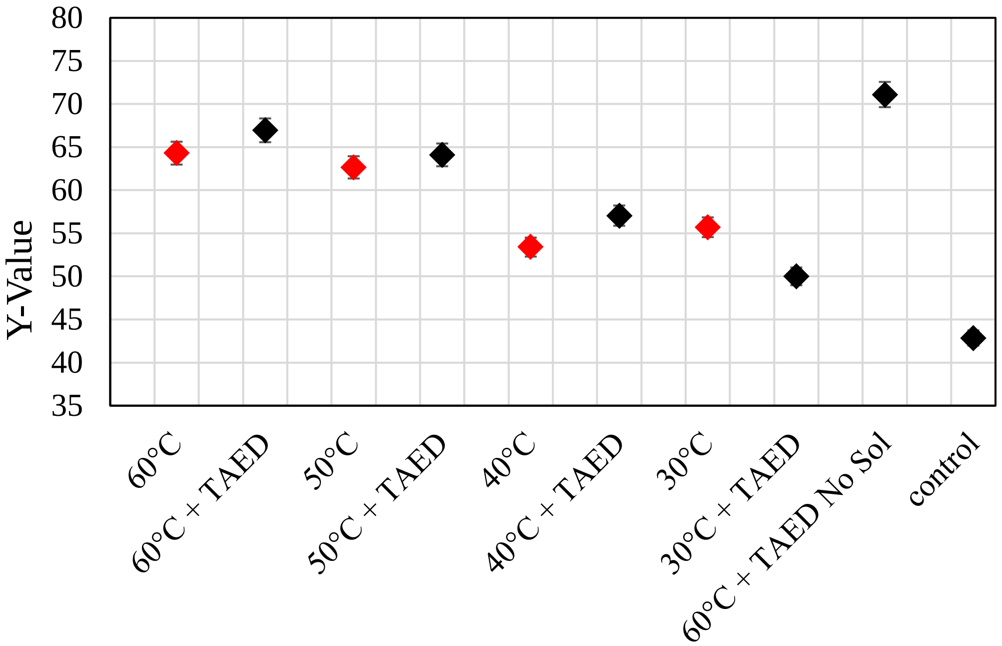

Figure 4.2: Brightness values for E-167 cloths tested for 30 minutes at different temperatures under 10 bar O_2, with Pt colloid with (♦) and without (♦) TAED. Reaction volume (50 ml) contained 2 ml mediator, 20 ml colloid and remainder water.

4.1.1. Tests using TEMPO as mediator

TEMPO is used as mediator as it is a stable radical, employed in organic chemistry for oxidation reactions[6]. Use of TEMPO, as well as the other mediators, is intended to facilitate transfer of the active species to the stain surface and carry out oxidation. In its use in organic mechanisms it also functions catalytically[7] and so stoichiometric quantities are not required for these experiments.

Figure 4.3 represents the brightness values of E167 tea stained cloths tested using 1% palladium colloid as catalyst. Each box in the graph represents a grouping of different conditions, the first of which represents experiments undertaken using pH buffer alone. This provides a benchmark to compare the catalytic experiments against use of just buffer. Modern detergents are buffered to pH 10.5 as the high pH values assist in the saponification of greasy residues, converting ester moieties into alcohols[8] which can be further oxidised and broken down. At pH 5 there is a decrease in brightness value upon addition of the colloid when compared to the corresponding control experiments; from 62.7 with only the buffer, to 61.2 with the buffer and 53.1 with the colloid. There is a slight increase in the brightness value to 55.1 upon addition of the mediator to the colloid. At pH 7 we see the same trend of decreases and ultimate increase in the brightness values, from 57 to 55.9 to 46.2 and 52.4 going across the graph in accordance with the conditions. At pH 10 there is a greater decrease in brightness value when the catalyst is added, and again there is an increase in the brightness value of the cloth when catalyst is utilised with the mediator. It can be inferred that the palladium colloid is causing a decrease in the brightness value by staining the cloth by the colloid itself, and that addition of the mediator leads to a reduction in this staining effect. This does not manage to overcome the staining of the cloth by the colloid, therefore the cloths tested by these experiments do not reach the levels of brightness exhibited by the control groups of the buffer or buffer and mediator, or the blank white cloth.

Figure 4.4 shows brightness values for stained cloths tested using a gold colloid with TEMPO. At pH 5 there is a steady decrease in brightness value going across the set of conditions and then a drop off when the colloid is used in the presence of the mediator, going from 59 for cloths tested with colloid and buffer to 39.9, which is lower than the untested cloth of 44.3. At pH 7 there is a decrease in brightness value that is more comparable to that of the cloths tested with Pd and TEMPO, in which the decrease in brightness value is more gradual without a large drop off when colloid is used with mediator. Contrastingly, there is not an improvement in the brightness value on using the colloid and mediator together as there was with the palladium colloid. Here the brightness value drops as for pH 5, going from 54 for buffer and colloid to 48.7 when used with mediator, albeit less drastically than for pH 5. For cloths tested using pH 10 buffer, again there is a decrease in brightness value on addition of the colloid. The results from Figure 4.4. evidence that there is staining of the cloth when the colloid is added across all pH values, however when mediator is used with the colloid there is a slight increase of 0.90.

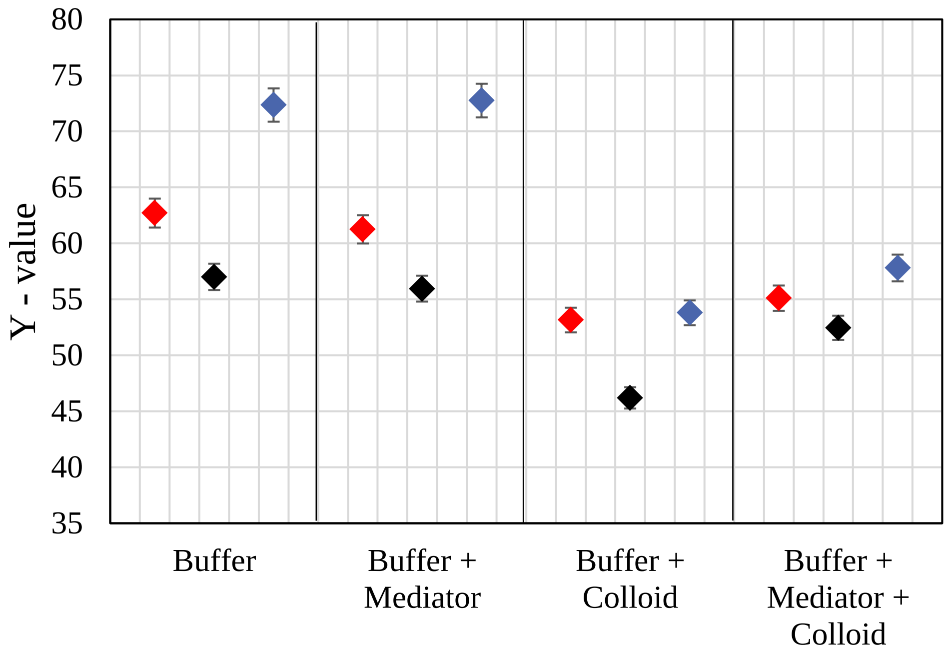

Figure 4.3: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pd colloid as catalyst and TEMPO as mediator. Reaction volume (50 ml) contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

The difference across the three pH values highlights the importance of selecting the appropriate pH buffer for each experiment. The reactive species which may be produced by these catalysts tend to be short lived[9] and their lifetimes can be extended depending on their environment (such as for the case of hydroxyl radical species[10]). It is possible that the lower brightness value seen when TEMPO is utilised with catalyst and pH 5 buffer is linked to the decay of TEMPO in acidic media[11]. The species generated by the catalyst may be in situ reacting further with TEMPO decomposition products and leading to the production of staining species.

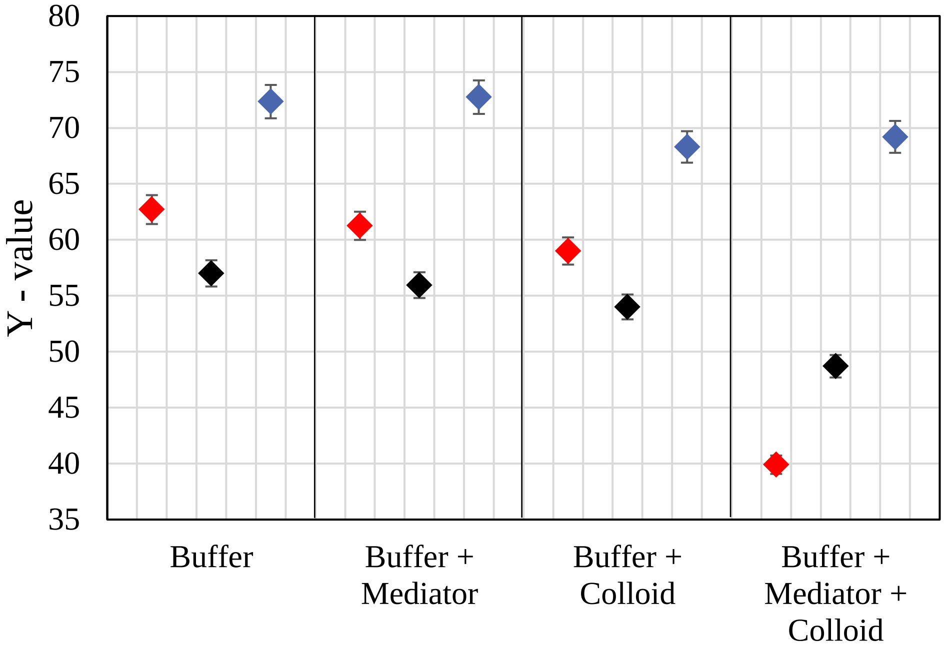

Figure 4.4: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Au colloid as catalyst and TEMPO as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

E167 cloths were then tested with platinum colloid, the brightness values of these tests are shown in figure 4.5. At pH 5 there is not much change in the brightness value when colloid is added compared to the controls, with cloth brightness value at 62.7 for the buffer alone to 61.3 and 61 for the mediator and colloidal tests respectively. There is however a decrease in the brightness values at this pH when both are used together, where the cloth brightness value drops to 55.8. At pH 7 there is little deviation in cloth brightness value in all conditions, with the mediator and colloid cloth returning a similar brightness value to the buffer control 56.7 vs 57. Cloths tested at pH 10 express a similar trend to that of the cloths tested with gold colloid, where there is a drop in the brightness values on addition of the colloid, and there is little difference in brightness value between colloid alone and mediator and colloid cloths (68.3 to 68), conversely showing a decrease rather than an increase in cloth brightness values.

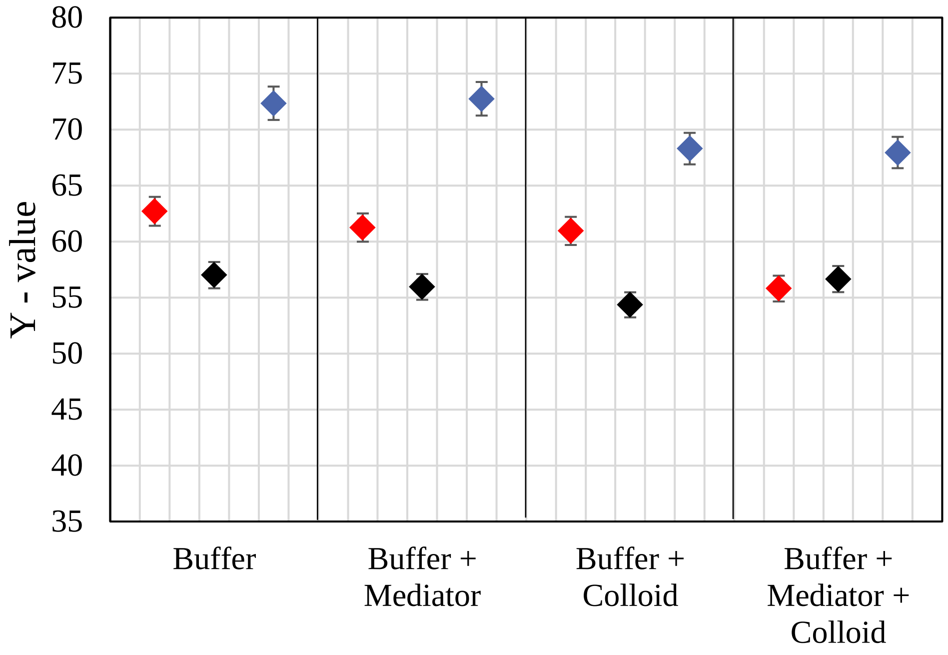

Figure 4.5: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt colloid as catalyst and TEMPO as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

Figure 4.6 presents an overlay of the results from each of the colloids for facile comparison with respect to the chosen mediator of TEMPO. Comparing the use of the metals in experiments with just the buffer there is a similar trend across all pH values, in that palladium colloids lead to the cloths exhibiting the lowest brightness values, with gold and platinum returning cloths of similar brightness values. Platinum colloid at pH 5 gave a comparable brightness value to the control of buffer and mediator, 60.95 compared to 61.25, and this was the only pH at which platinum performed better than the gold catalyst. When mediator is used with the colloid it has a positive effect on the palladium catalyst, but its addition can negatively impact the platinum and gold catalysts. At pH 5 it leads to a reduction in brightness value for both gold and platinum, though at pH 7 it only reduces the brightness value of the gold colloid compared to the experiments without the mediator (48.7 to 54). At this pH both platinum and palladium improve the brightness values of the cloths. It is difficult at present to draw conclusions as to whether the pH of the reaction is influencing the affinity of the colloid for the cloths, or if it is due to the pH affecting the bleaching abilities of the catalysts. Further tests would need to be done to decouple the staining effects of the colloids from the bleaching effects to give a clearer picture of the reaction details.

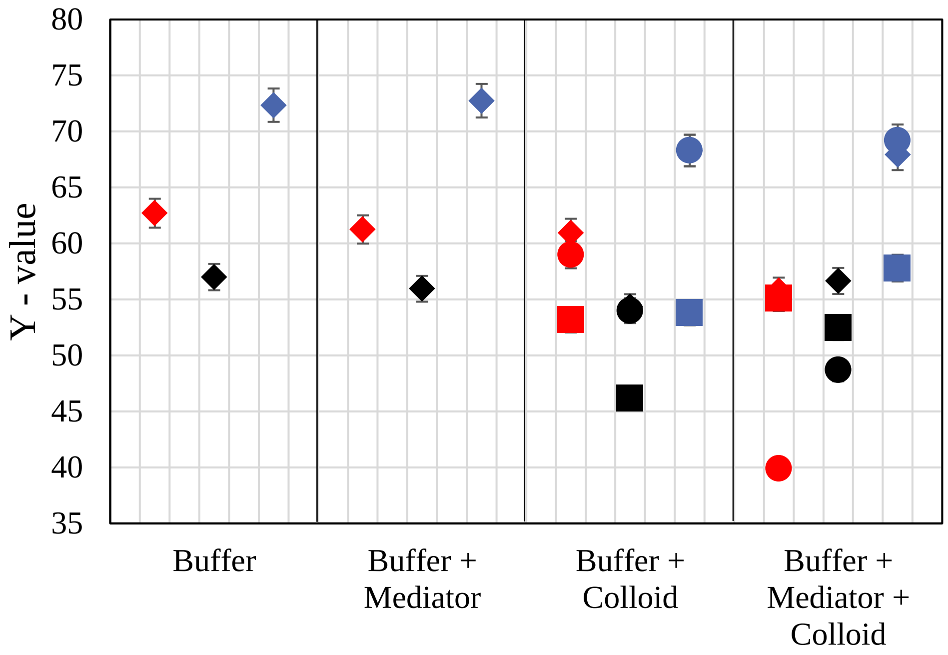

Figure 4.6: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with colloids as catalyst and violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦). Metals are denoted as: Pt (♦), Pd (■) and Au (●).

4.1.2. Tests using violuric acid as mediator

Violuric acid is a redox mediator[12] and may facilitate the transfer of electrons to the cloth and target the stain for oxidation reactions, and as with TEMPO is expected to help extend the lifetime of the short lived radical species generated by the catalysts and help in the diffusion of reactive oxygen species to the stain surface itself on the cloth surface.

Figure 4.7 shows the results of the E167 cloths tested with palladium colloid and the mediator. At all pH levels we see the same decrease in brightness value when comparing the mediator experiments to those of the colloids. This decrease is most dramatic in the case of cloths tested at pH 10, where the brightness value decreases from 72.9 to 53.8. This further demonstrates the staining effect observed previously for palladium catalysts when TEMPO was used as mediator. When mediator and colloid are used together there is an increase in the brightness value when compared to the use of colloid alone, with the brightness values of the cloths increasing from 53.1 to 57.5, 46.2 to 56 and 53.8 to 64.9 for pH 5, 7 and 10 respectively. The biggest increases in brightness values are for those cloths tested at pH 7 and 10. Comparing the controls for this set of experiments it can be seen that the brightness values of cloths tested at pH 5 and 7 are lower when mediator is used compared to the buffer alone. Violuric acid in solution is intensely coloured and at these pH values must be causing a staining effect to the cloths, but not for experiments tested at pH 10.

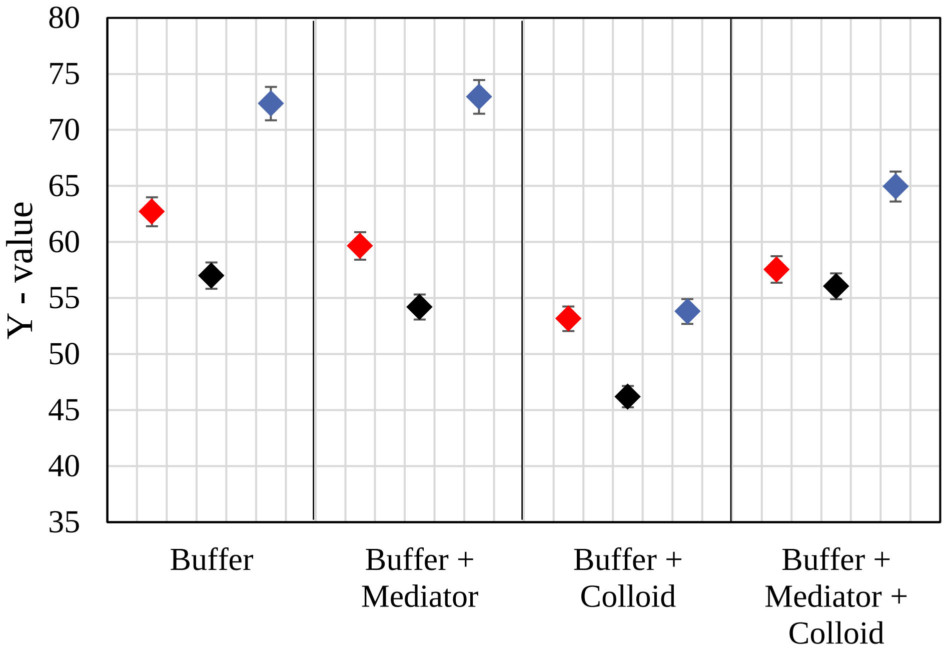

Figure 4.7: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pd colloid as catalyst and violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

Following palladium, gold colloid was tested with the current mediator under examination for its utility with this metal. Figure 4.8 expresses how the trends for experiments carried out at each pH compare agreeably, with the brightness value of the cloth decrease on addition of the colloid, and again on addition of colloid with the mediator, which is in directly contrary to tests carried out using palladium colloid. In this batch of experiments the brightness values decrease from 59 to 54.1 at pH 5, 54 to 49.9 for pH 7 and 68.3 to 62.5 for tests carried out at pH 10, on comparing the last two boxes.

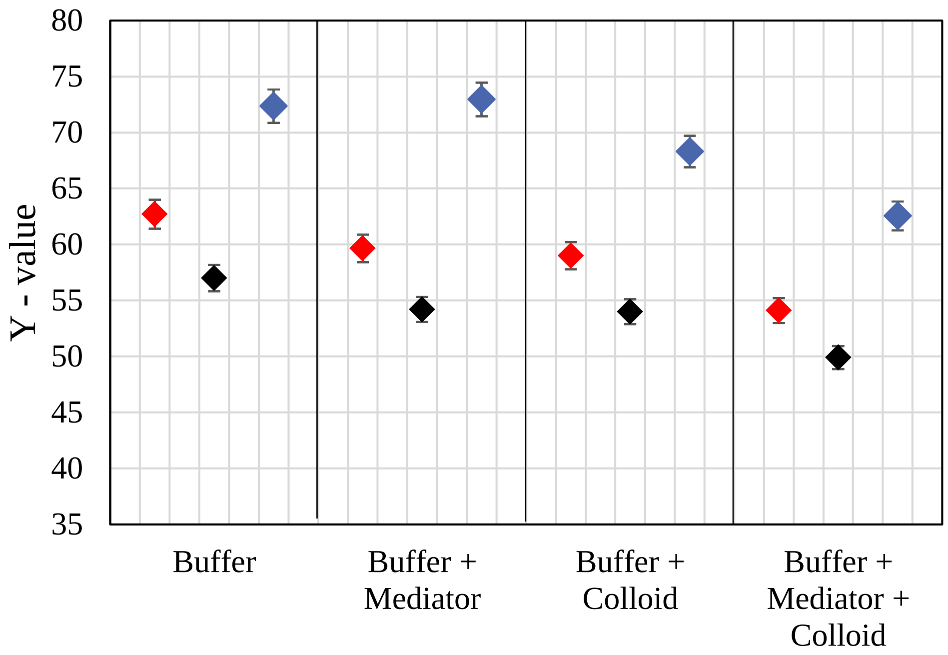

Figure 4.8: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Au colloid as catalyst and violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

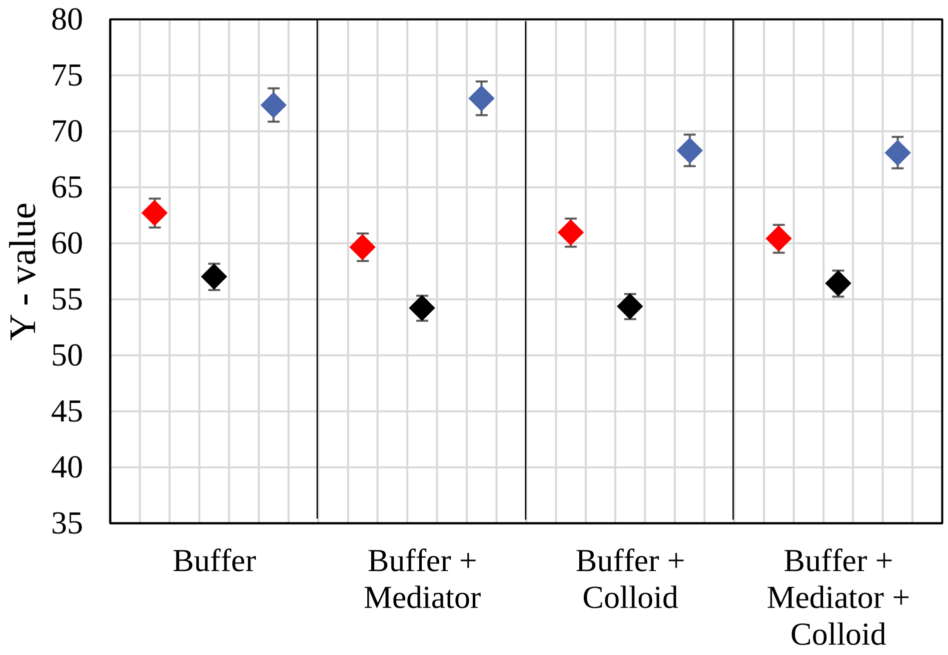

Figure 4.9: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt colloid as catalyst and violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

Figure 4.9 exhibits the final set of experiments carried out using violuric acid in this section, showing the brightness values of cloths tested using platinum colloid. In general, there is little change in the cloths observed between the different experimental conditions. In the case of pH 5 and 7 the differences in cloth brightness values are all within error, while at pH 10 there is a decrease in the brightness value on addition of colloid, and a comparable brightness value of cloth when colloid and mediator are used together, with brightness values of 68.3 and 68.1.

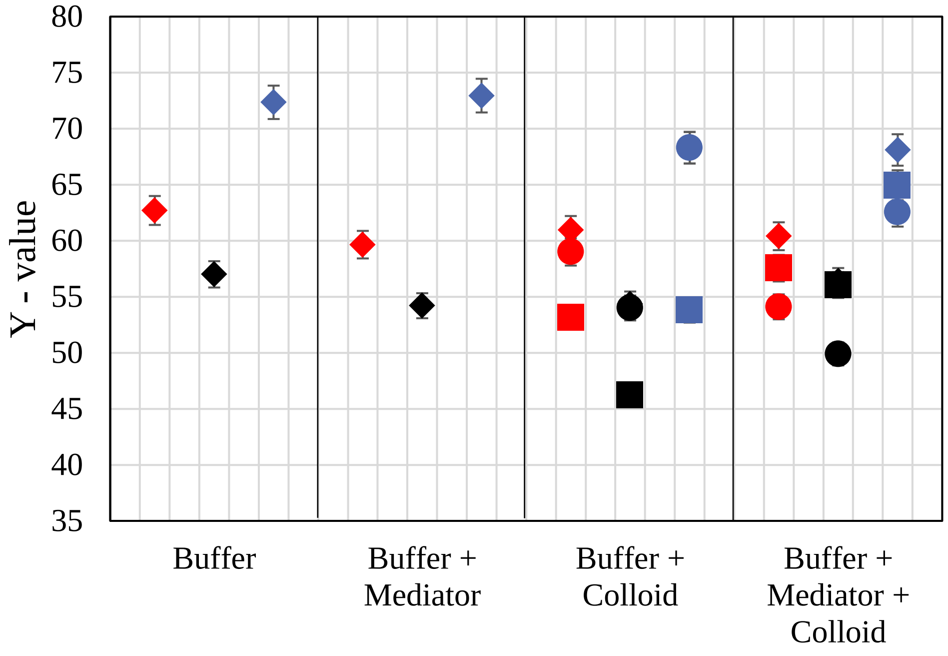

Figure 4.10: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with colloids as catalyst and violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦). Metals are denoted as: Pt (♦), Pd (■) and Au (●).

Figure 4.10 is a chart representing a comparison of all of the metals tested using violuric acid as the mediator. For cloths tested using buffer and catalyst, those tested using palladium returned the lowest brightness values of the three tested, with gold and platinum returning cloths of comparable brightness value. On addition of mediator, cloths tested using palladium improved their brightness values compared to those tested using palladium alone, while when the cloths were tested in the presence of the gold colloid a reduction in brightness values was observed. Overall addition of mediator made no change to cloths tested with platinum. On addition of mediator gold experiments became the worst performing, returning cloths with the lowest brightness values according to each pH, while platinum retained its effects.

4.1.3. Tests using TAED as mediator

TAED is used in modern detergents to generate peracids in solution[13], which have greater bleaching ability at lower temperatures than traditional hydrogen peroxide. The goal is to be able to produce a species in solution that can activate TAED and generate the bleaching peracids.

Figure 4.11 shows the first set of experiments carried out using TAED as mediator, in the presence of a palladium colloid. At pH 5 the brightness value decreases on addition of the colloid, from 62.7 and 62 in the cases of buffer and buffer and mediator, to 53. The brightness value of the cloth increases to 55.4 when the TAED is used with the colloid. Reaction conducted at pH 7 follow a similar trend, however it can initially be seen that there is a large decrease in brightness value of cloths on addition of mediator to the buffer (from 57 to 49.7). Once again the brightness value is reduced when colloid is used in the presence of the buffer, becoming 46.2, almost as low as untested cloth at 44.3. When the mediator and colloid are combined there is a slight increase in the brightness value, to above that of the control of buffer and mediator (51.5), though this difference falls within error, if compared to the control alone, but is still an improvement on cloths tested with colloid. Cloths tested at pH 10 show at decrease on addition of TAED, from 72.3 to 67 comparing buffer alone to mediator, with a large decrease in brightness values when palladium is used as catalyst compared to the mediator experiment. As with the experiments conducted at other pH values the brightness of the cloths increase when mediator is used in tandem with catalyst, increasing from 53.8 to 59.4.

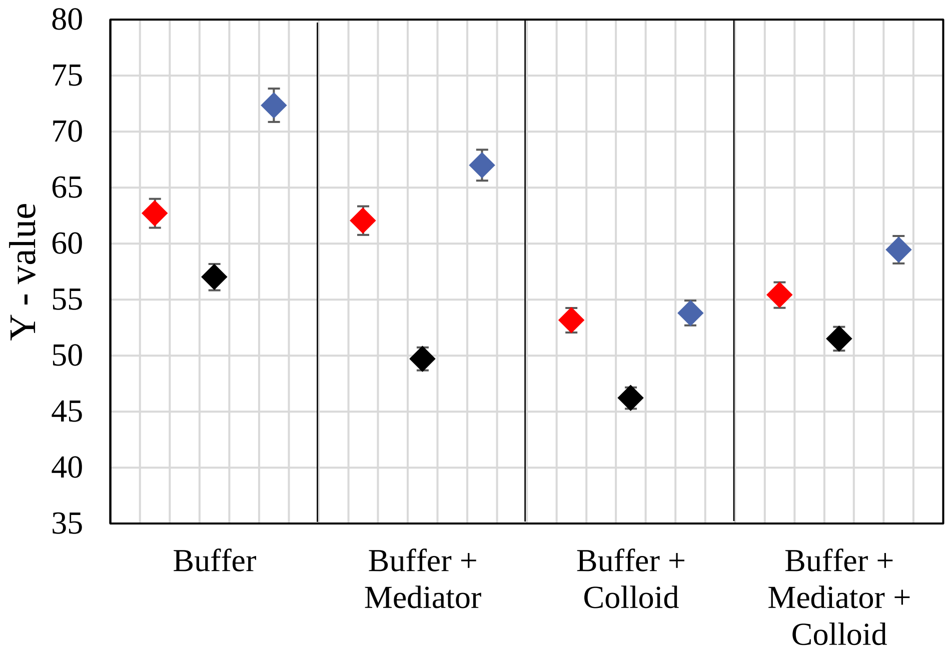

Figure 4.11: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pd colloid as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

In figure 4.12 the results of cloths tested with gold colloid are shown. At pH 5 there is a decrease in the brightness value of the cloths when colloid is used, going from 62.7 when buffer is used alone to 59, and again there is a lower brightness value to be observed with mediator is added with colloid, where the brightness value of these cloths becomes 54.4. At pH 10, following the decrease in brightness observed on addition of mediator to experiments, there is an increase when compared to experiments where colloid is used, with brightness values increase from 49.7 to 54 and 53.65. At pH 10 there is little difference between tests using mediator and tests using colloid, but there is an observable decrease in Y-value when colloid and mediator are used together, dropping to 63.1 from 68.3 in the case of colloid without mediator.

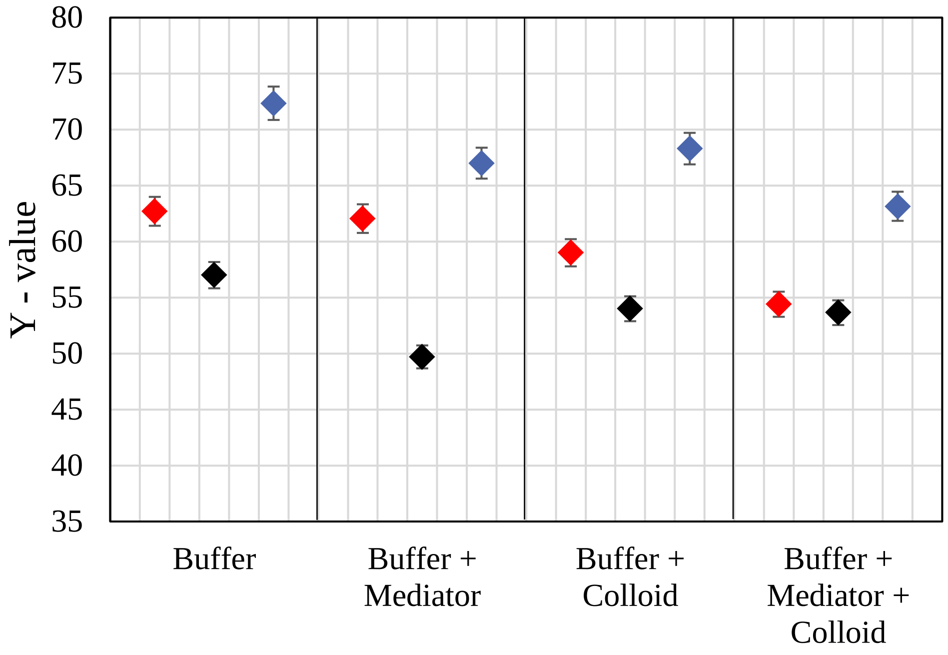

Figure 4.12: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Au colloid as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

Platinum colloid was tested using this mediator and the brightness values of these tested cloths are shown in figure 4.13. There is little difference to be observed across this set of experiments when comparing the different conditions and the different pH buffers used, with the most interesting result being within the experiments run at pH 7. There is an increase in brightness value expressed, from 54.35 to 57.35, when comparing colloid to colloid and mediator used together. As with the other mediators, we see that platinum colloid does not appear to be staining the cloth as much as the other metal colloids are, with the brightness values of the cloths being tested not tending to decrease on their addition.

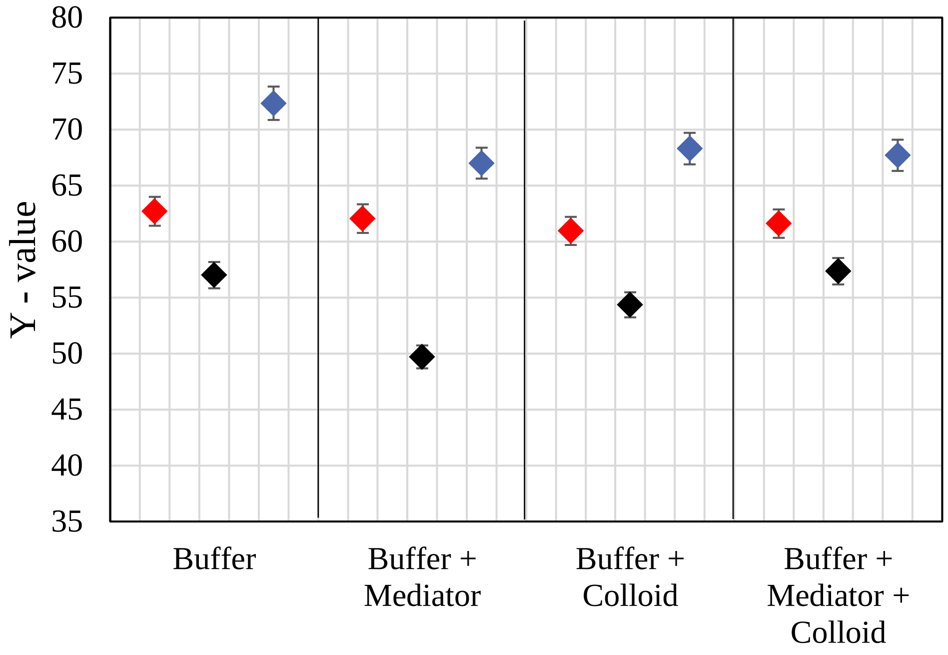

Figure 4.13: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt colloid as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

Figure 4.14 shows a comparison of all metals tested using TAED as mediator. With respect to the use of TAED, there is little difference in the brightness values of the cloths overall when comparing the buffer and mediator cloths to buffer and colloid cloths. On addition of mediator to the colloid the palladium tested cloths once again show an improvement compared with the colloid alone, with platinum tested cloths only exhibiting an improvement over the colloid at pH 7 (54.35 to 57.35). Tests utilising gold catalysts saw a reduction in brightness value on the addition of mediator at pH 5 (59 to 54.4) and pH 10 (68.3 to 63.15) but no change at pH 7.

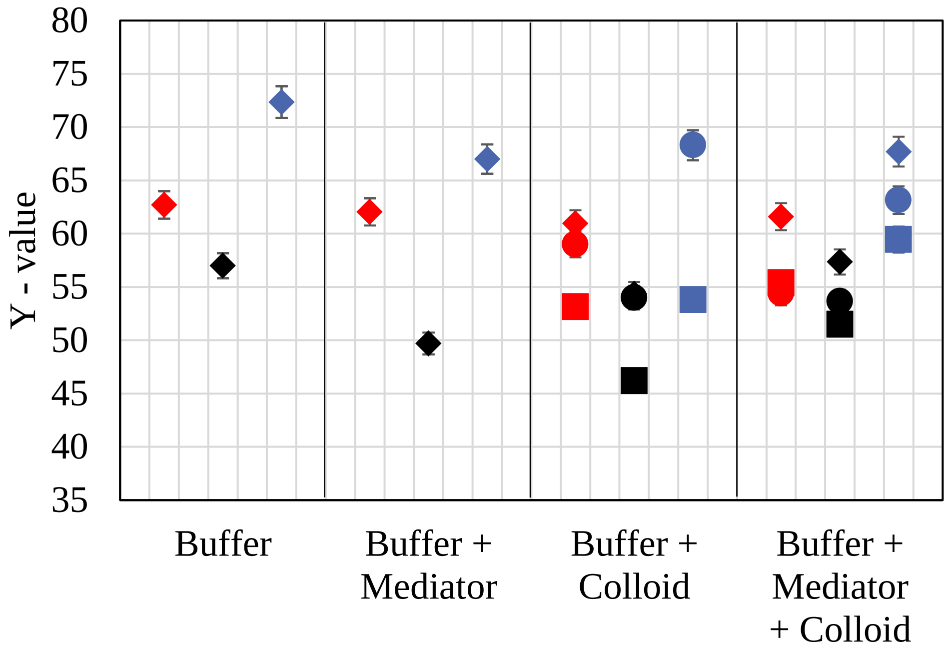

Figure 4.14: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with colloids as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦). Metals are denoted as: Pt (♦), Pd (■) and Au (●).

4.1.4. Comparison of mediators for each metal

The three figures in this section represent a comparison of each mediator, to see how they vary when considered for each catalyst that was used. Looking at the brightness values of cloths tested using buffer and mediator in figure 4.15, it can be seen that at pH 5 there is little difference in brightness values of the cloths between the selection of mediator. This changes at pH 7 and 10 however, where although cloths tested with TEMPO and violuric acid return similar brightness values, the cloths tested with TAED return the lowest brightness values (about 5 units of brightness lower than TEMPO and violuric acid tested cloths). TAED is used commercially to help generate bleaching species[13] so it is interesting to find that at certain pH levels it appears to lead to staining itself. This is possibly due to partial oxidation to TAED not being fully converted into active peracid species without the addition of a oxidising species. At pH 5 the combination of colloid and TEMPO causes a large degree of staining to the cloth (Y-value 39.9), reducing the brightness value to below that of untested cloth (44.3). For the other mediators at this pH there is no so much staining observed when the catalyst and mediator are used together. At pH 7 there is a reversal in the bleaching/staining abilities of the system. Under these conditions it is violuric acid and TEMPO which are causing a greater degree of staining when used in tandem with the gold colloid. The staining from the use of TEMPO does however appear to be less, with its cloth brightness value now being 48.7 compared with 39.9 at pH 5, and at pH 10 is returning cloths with the least amount of observable staining.

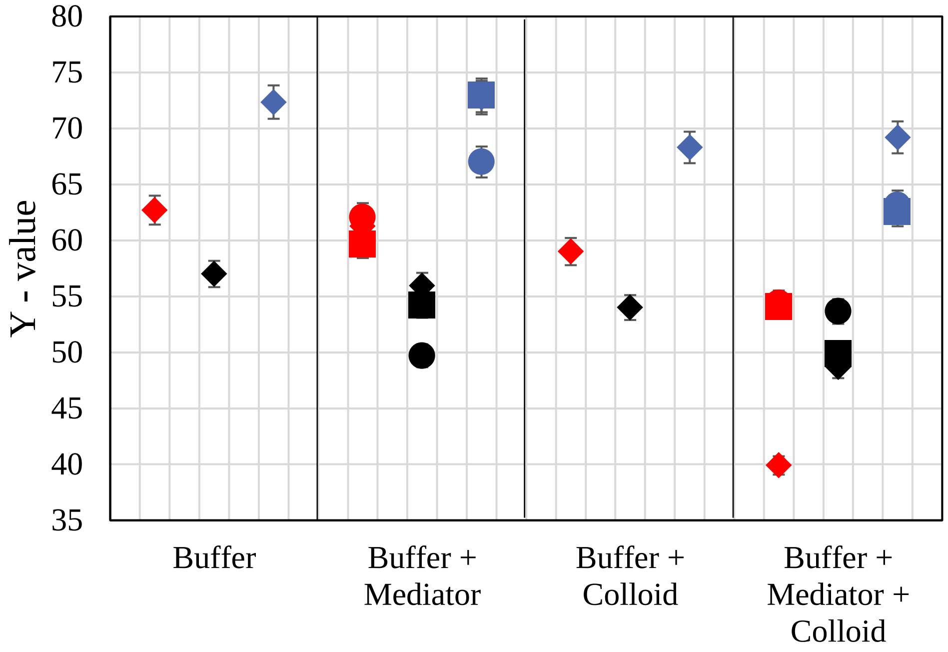

Figure 4.15: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Au colloid and TAED, violuric acid and TEMPO as mediators. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦). Metals are denoted as: TEMPO (♦), violuric acid (■) and TAED (●).

Figure 4.16 shows a comparison of the mediators when palladium catalyst was used. Here across all pH when catalyst and mediator is used in tandem, violuric acid and TAED grant cloths of the same brightness values, while cloths tested using TEMPO were observed to have the highest brightness values, with the disparity in brightness value increasing as higher pH is utilised, indicating a dependence of TEMPO on pH[11].

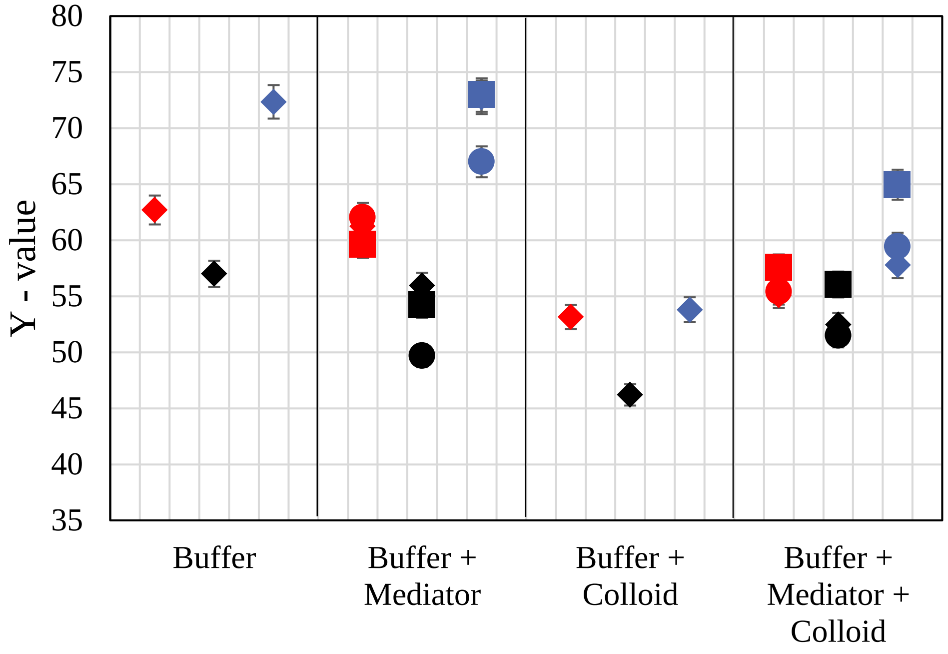

Figure 4.16: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pd colloid and TAED, violuric acid and TEMPO as mediators. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦). Metals are denoted as: TEMPO (♦), violuric acid (■) and TAED (●).

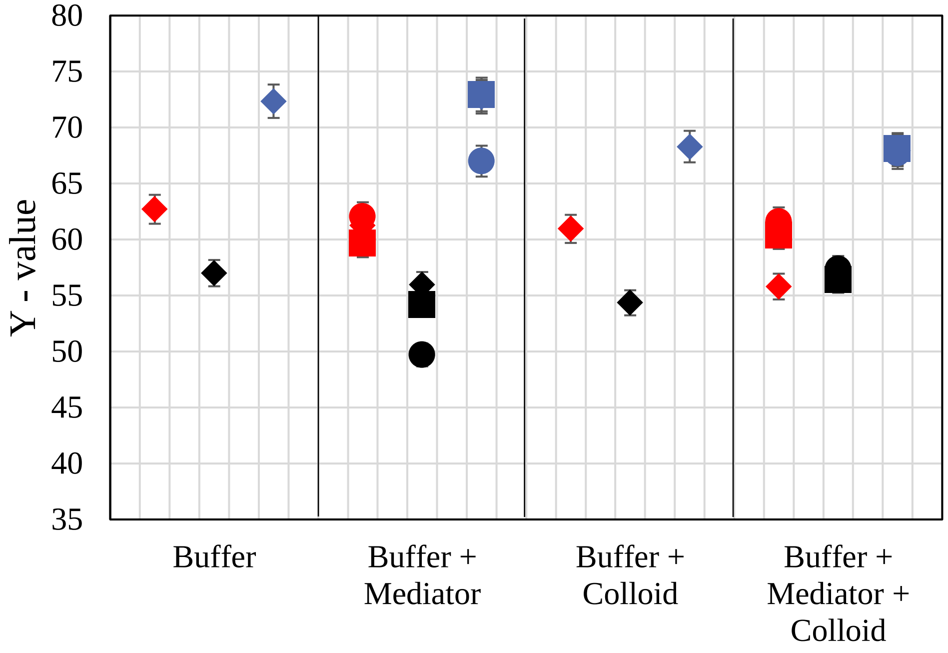

Figure 4.17: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt colloid and TAED, violuric acid and TEMPO as mediators. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦). Metals are denoted as: TEMPO (♦), violuric acid (■) and TAED (●).

In the case of tests using platinum colloids and the mediators, it can be seen in figure 4.17 that at pH 7 and 10 there is no significant difference between using any of violuric acid, TEMPO or TAED. At pH 5 there is a lower brightness value comparably for cloths tested using TEMPO.

4.2. Tests using Pt (PVP) as colloid

To investigate the effects of using different stabilising agents, corresponding Au, Pd and Pt colloids were prepared using the same methodology, but using PVP as the stabilising agent in place of PVA. PVA was initially considered as the colloidal stabiliser as the alcohol functionality in the polymer may increase the affinity of the colloid to the stain. Given the aforementioned results, it's possible that this is why the PVA stabilised colloids lead to the staining of the cloth. The alcoholic tail of the PVA could be attracted to the hydroxyl moieties of the cellulose repeat units that constitute the cotton[14]. For this reason, Pt colloids stabilised by PVP were tested using the same methodology. In figure 4.18 in the case of cloths tested in water, violuric acid facilitates some stain removal, with the brightness value increasing from 48 when tested with water alone to 55.6. The colloid itself does not lead to an increase in brightness value when tested with water. When buffered to pH 5, some additional stain removal is observed as being carried out by violuric acid, with brightness value increasing from 57.4 to 61 when mediator is added, with cloths tested with the catalyst at this pH only seeing an improvement in the brightness value when the violuric acid is used. At pH 7 there is no change to be seen across the series of tested cloths. Conversely at pH 10, violuric acid causes a reduction in brightness value of the cloth compared to pH buffer alone, with brightness value decreasing from 66.7 to 60. The cloth tested using just catalyst experienced less staining compared to that of violuric acid and buffer.

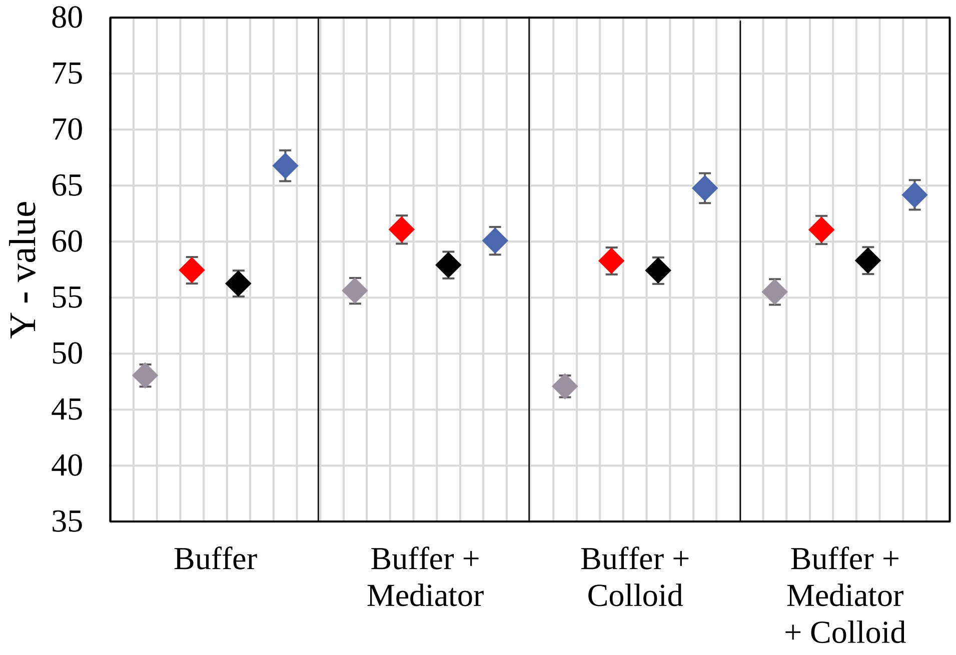

Figure 4.188: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt (PVP) colloid as catalyst and Violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for water (♦), pH 5 (♦), pH 7 (♦) and pH 10 (♦)

Figure 4.19 expresses the results for TAED tests. In this case, there is not much change to be observed in cloth brightness, across any of the testing conditions. Of note is the case of pH 5, where the highest brightness value is that of the catalyst and mediator, higher than the control (61.3 compared with 57.4 for the buffer alone). At pH 10 the catalyst and mediator (66.8) tested cloth expresses a brightness value which is comparable to that of the buffer control (66.7). For other pH values, there is not to be seen an improvement in the washing of the cloths when mediator is added to the reaction mixture, inclusive of catalyst. Cloths tested with water and TAED shows an improvement in brightness value over water alone, TAED offers an improvement in washing over water alone, though this is not replicated in any of the pH buffers.

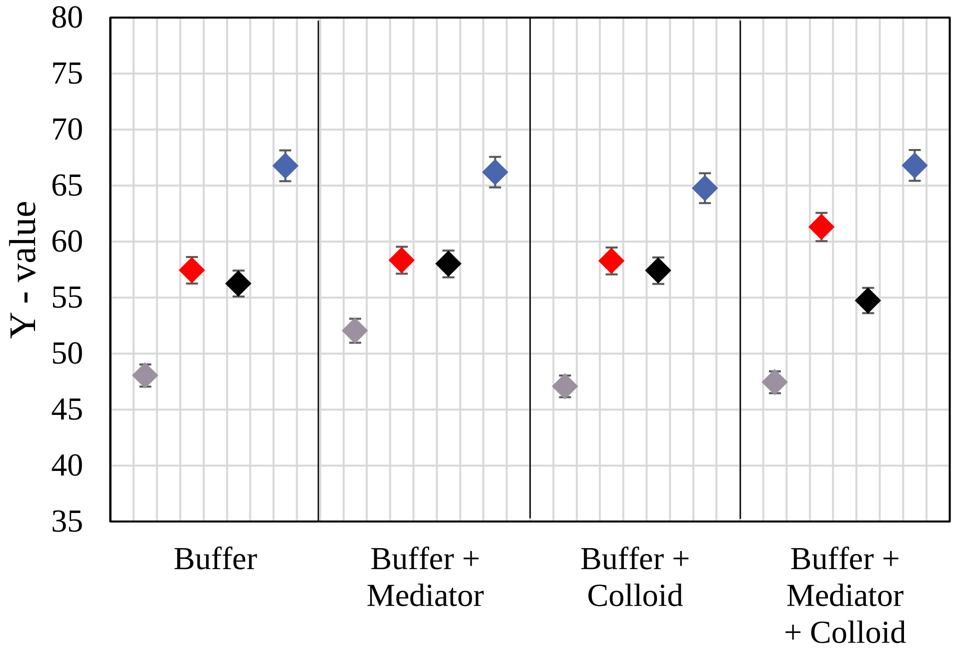

Figure 4.19: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt (PVP) colloid as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for water (♦), pH 5 (♦), pH 7 (♦) and pH 10 (♦).

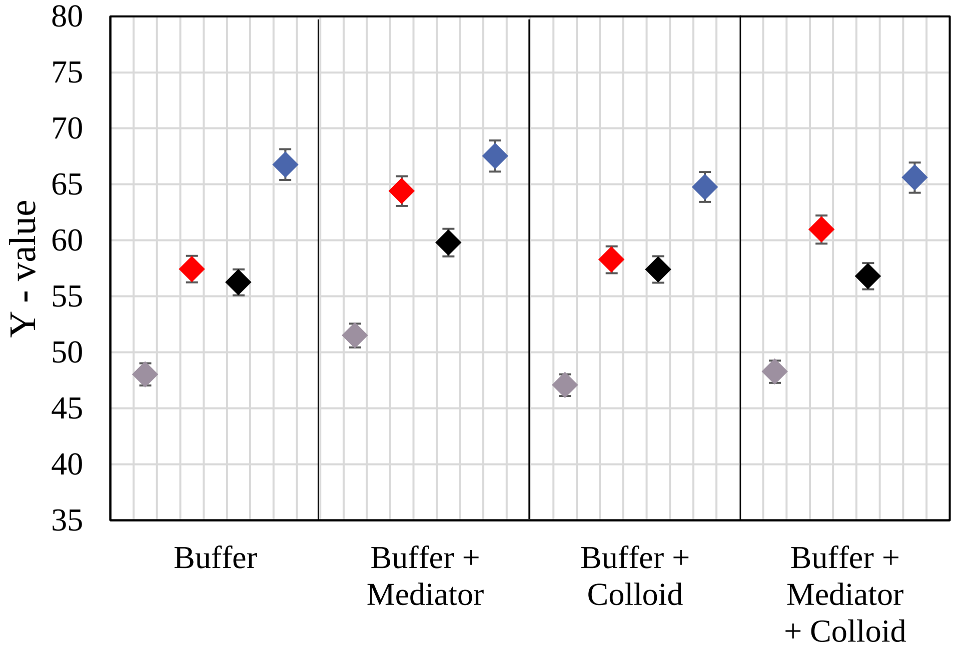

Figure 4.20: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt (PVP) colloid as catalyst and TEMPO as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for water (♦), pH 5 (♦), pH 7 (♦) and pH 10 (♦).

The brightness values for cloths tested using TEMPO are shown in figure 4.20. Here again, there is not much change across the series to be seen, showing little observable staining of the cloth by the catalyst. Across all pH levels the mediator control offered the highest brightness values. It does not appear that mediator offers any improvement on catalyst alone in these tests.

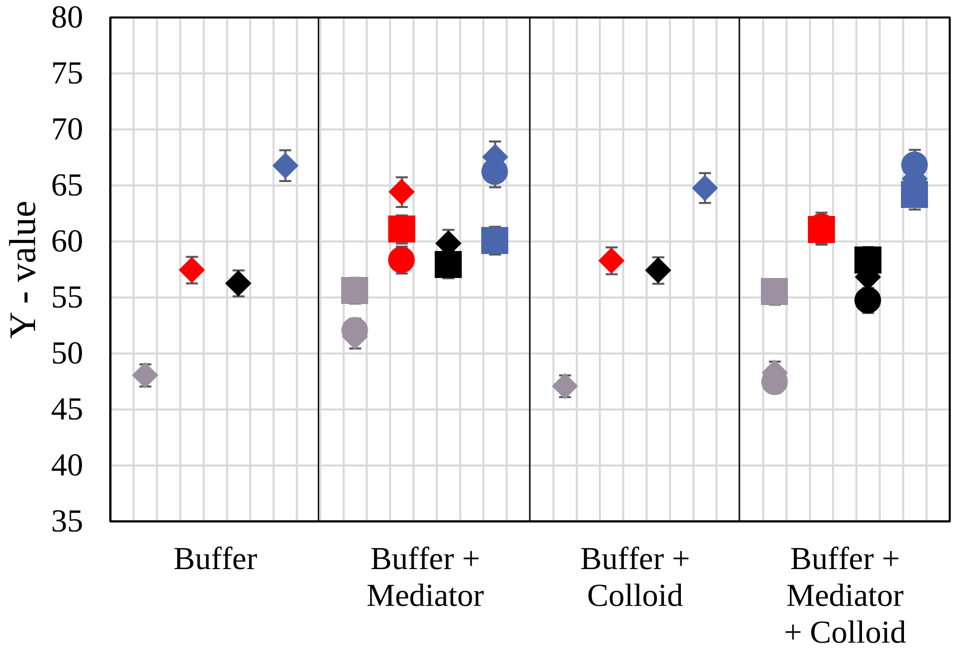

Figure 4.21: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt (PVP) catalyst and TAED, violuric acid and TEMPO as mediators. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for water (♦), pH 5 (♦), pH 7 (♦) and pH 10 (♦). Metals are denoted as: TEMPO (♦), violuric acid (■) and TAED (●).

Figure 4.21 shows an overlay of cloths tested using Pt (PVP) with the different mediators. There is no significant difference to be observed in choice of mediator overall. When catalyst and violuric acid is used in water, this cloth expresses a higher brightness value than the control experiments of pH 5 buffer alone, indicating a more favourable interaction of violuric acid in water than the buffers used. TAED and TEMPO performed comparably when used with catalyst.

A comparison of platinum sols prepared using PVA and PVP can be seen in figure 4.22 (PVA experiments carried out previously). There is not much difference in the brightness values of the cloths tested using the PVP prepared catalysts. These catalysts did not lead to much staining so it may be that tests using a Pd colloid might show a more visible difference between using the different stabilisers.

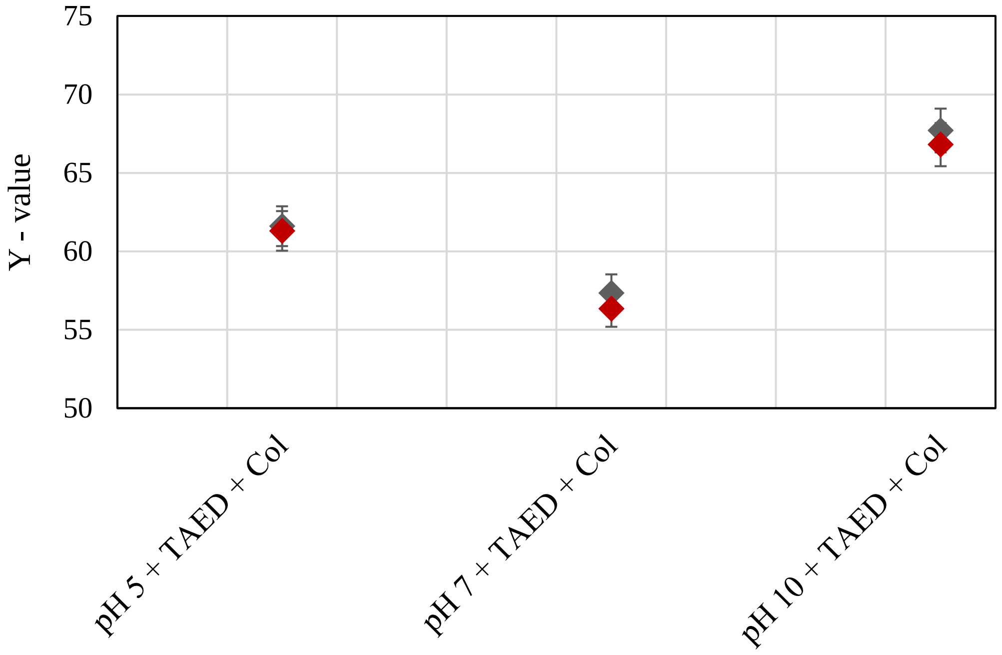

Figure 4.22: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with Pt (PVP ♦) and Pt (PVA ♦) colloids as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, 28 ml buffer.

4.3. Tests with supported monometallic catalysts

It is thought that by using colloidal catalysts, diffusion of reactive oxygen species generated by the catalysts will have less impeded diffusion, as the catalysts will already be more proximal to the stain than the solid catalysts. Tests with supported metal catalysts were carried out to validate this idea.

4.3.1. Autoclave experiments

To determine if the support has a role to play in the reaction, experiments were also carried out with just titania. The results of this are shown in figure 4.23 and 4.24, showing results with and without TAED as mediator, respectively. In the presence of water and pH 7 buffer, to be seen is the increase in cloth brightness on addition of titania, and a further increase in brightness value of cloth with the catalyst. This is not the case at pH 5, where the support performed better than the catalyst. For cloths tested in pH 10 buffer we see no observable difference between the cloths.

In figure 4.24, cloths tested in water and at pH 10 show no difference on addition of mediator along the condition series. pH 7 shows a similar increase in brightness value as without mediator, whereas at pH 5 there is the same subsequent decrease in cloth brightness value from using support alone to using supported catalyst.

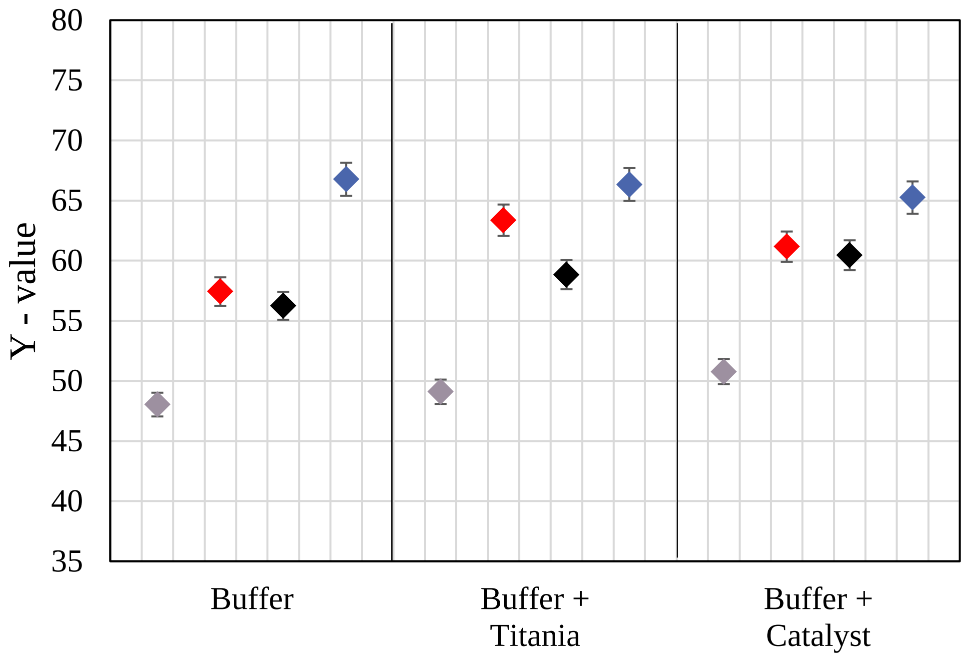

Figure 4.23: Comparison of E-167 cloths tested using supported platinum, and the titania alone. Conditions: 30 minutes at 60 °C and 10 bar O_2, 8.2 mg catalyst, 2 ml mediator, remainder buffer: water (◆), pH 5 (◆), pH 7 (◆) and pH 10 (◆)

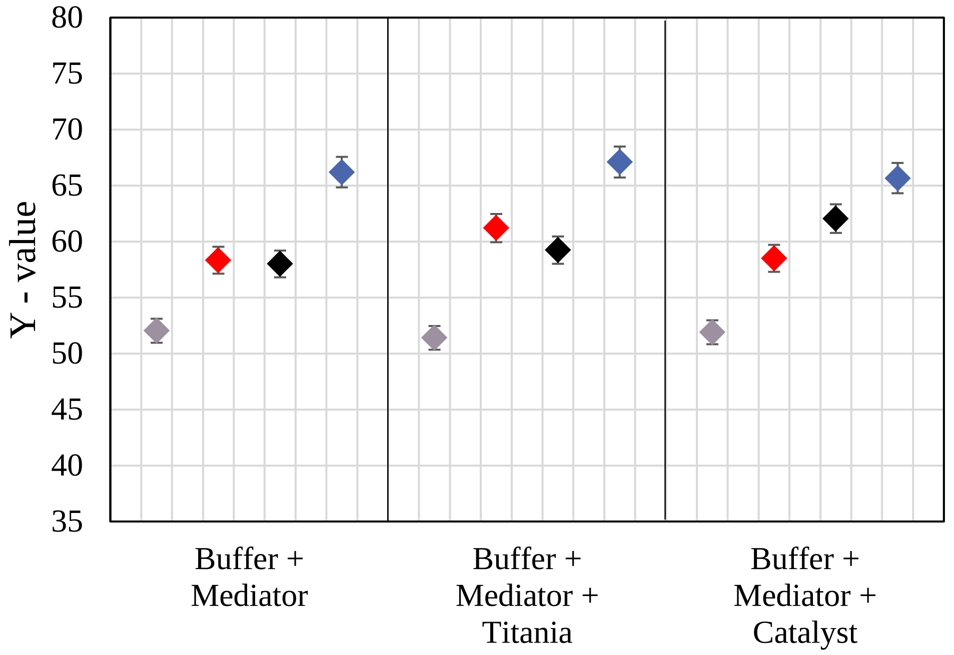

Figure 4.24: Comparing the E-167 cloths tested with supported catalyst and support alone, with addition of mediator. Conditions: 30 minutes at 60 °C and 10 bar O_2, 8.2 mg catalyst, 2 ml mediator, remainder buffer: Water (♦), pH 5 (♦), pH 7 (♦) and pH 10 (♦)

4.4. Conclusions

Previously we showed that all cloth samples express a degree of staining of the cloth samples by the colloids themselves. These were tested with monometallic Au, Pd and Pt catalysts using the three mediators; TAED, TEMPO and violuric acid. Gold and Platinum colloids show greater bleaching efficacy than the Palladium samples. This indicates either less staining of the cloths by the colloids or greater catalytic efficiency. Palladium containing catalysts led to the greatest degree of staining of the cloths. In general it is clear that any staining of the cloths by the metals themselves must be overcome if true bleaching and any bleaching is to be truly quantified by experiments that examine a sample's brightness value.

Higher reaction temperatures are favoured and so it was decided to begin at 60 °C with intention to work towards lower washing temperatures, to follow the global trend that calls for lower average washing temperatures due to environmental and economic concerns[15].

There was little difference to be found in the use of the three activators when paired with a Au, Pt or Pd colloid, though TAED was shown to exhibit staining of the cloth. This was also observed when violuric acid was utilized as the mediator, which at certain pH values led to discolouration of the cloth.

The test of the Pt (PVP) colloid proved inconclusive as results were comparable to that observed in the presence of a corresponding Pt (PVA) colloid. The test should be repeated using a more staining catalyst (Pd) where a bigger difference may be observed.

Among the cloths tested using solid catalysts some have returned brightness values better than the controls, confirming that supported catalysts are more effective at this time than the sols. Interestingly depending on the pH used, TiO_2 could lead to higher brightness values of cloth that the catalyst.

Looking at the trends for the solid catalysts, it does appear that the platinum supported on titania at pH 7 is more effective than the colloidal catalyst at the same pH value and under the same reaction conditions. This is contradictory to the understanding that colloidal nanoparticles could be more useful for this type of process than supported catalyst. The answer could lie in the benefits provided by the support in terms of catalyst stability and electronic state through metal support interactions (MSI)[16].

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5. Catalytic Washing using Bimetallic Catalysts

Examined in the previous chapter is the ability of monometallic colloidal and supported catalysts for the production of bleaching species. The potential for these catalysts proved to be limited and so the design of a more optimised catalyst is explored in this chapter. Colloidal catalysts are of interest due to their ability to be tuned with regard to their shape and size[1], and particularly of interest to this chapter is the ability to form bimetallic or even trimetallic species to tune the electronic properties of the catalyst[2–4]. The structure of the final catalyst may also be controlled, as well as the metallic arrangement (core-shell, alloy), which will also give rise to varying electronic properties of the catalyst.

It has been shown experimentally that Au nanoparticles have been used in the activation of molecular oxygen in catalytic applications, and theoretical elucidation of active sites are underway[5,6]. These studies indicated that low coordinated metal atoms are preferred sites for activation, and so an optimised catalyst will have as many of these sites as can be constructed. Careful manipulation of the final catalyst is desired to achieve this goal, and so tuning with a bimetallic synthethic process could be the ideal solution. Through a systematic testing regime examining the respective combinations of three metal types for bimetallic catalyst composition, the optimal preparation variables can be studied to establish the relationship between these variables and the catalytic activity. The three catalysts in question, AuPd, PdPt and AuPt will be prepared and testing using the same conditions affording the monometallic catalysts for ease of comparison.

Of concern to this work as understood from the previous chapter is the staining effect of the catalysts prepared herein on the cloths, and the manner in which this effect can be decoupled from the potential bleaching of these cloths. This will be examined briefly in this chapter, with a scope to further improvements considered in future considerations. It is imperative that the current staining procedure should be qualified and understood in order to progress the work and allow for true bleaching being carried out by the catalysts to be quantified.

Alongside an examination of the staining processes of the catalysts, which will utilise blank cloths, another feature of these catalysts will be examined which will also make use of blank unstained cloths. Dye Transfer Inhibition (DTI) is of interest to the detergent community in order to prevent colours running between clothes in a washing cycle through the preferential destruction of chromophores in solution with respect to dyes on clothes. It is believed that the colloidal catalysts will also be more effective in this activity due to their being in the same phase as dissolved dyes. The experiments will involve the analysis of a blank cloth following reaction with a catalyst and a dye donor cloth. The brightness value of the blank cloth following the experiment will be compared against a blank cloth that has been reacted with a donor cloth without any catalyst present, and so the difference will represent the efficacy.

5.1. Tests with unsupported catalysts

5.1.1. Tests using TEMPO as mediator

TEMPO is used as mediator as it is a stable radical that is employed in organic chemistry for oxidation reactions[7]. Use of TEMPO, as well as the other mediators, is intended to facilitate transfer of the active species to the stain surface and carry out oxidation. Figure 5.1 shows the results of the AuPd colloid after 30 minutes of washing, using TEMPO as mediator, at varied pH. For comparative purposes, untreated cloth has a Y – value of 44 and cloth tested in water at same conditions has a Y – value of 48. At pH 5 we see a decrease in brightness value as we add our sol catalyst, the same is observed at pH 7, and more dramatically at pH 10. The reason for this is the staining of the cloths by the colloid itself, as previously seen in the monometallic sol experiment. Addition of TEMPO does not offer any improvement to the bleaching of the cloths.

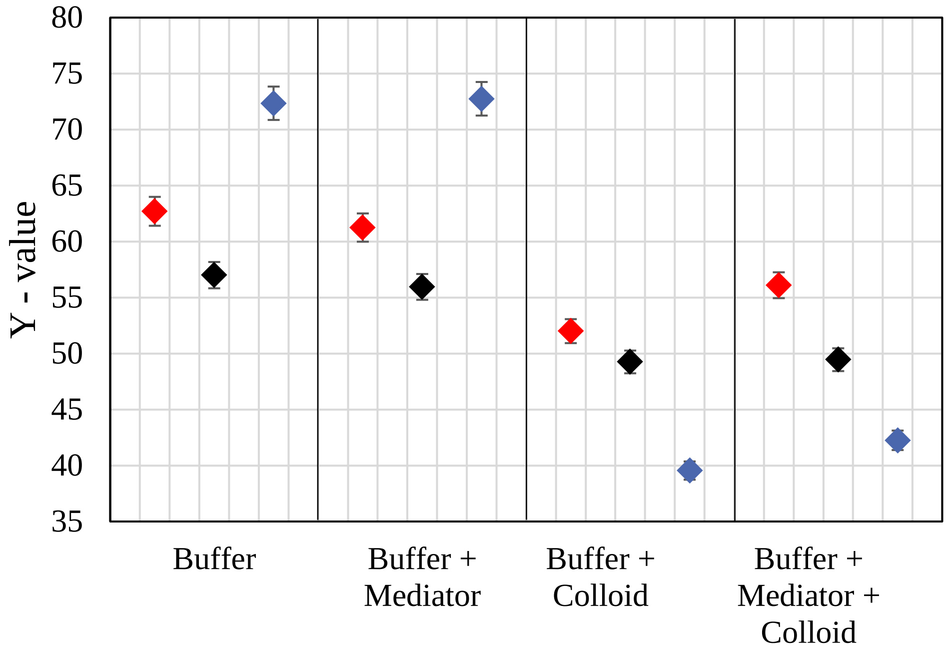

Figure 5.1: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with AuPd colloid as catalyst and TEMPO as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH (♦), pH 7 (♦) and pH 10 (♦).

Figure 5.2 shows the results of the cloths tested with AuPt colloid. We can see that at pH 5 there in a decrease in brightness value on addition of catalyst, whereas at pH 7 there is little change. At pH 10, again this decrease in the brightness value once sol is added is observed, but a slight increase when mediator is added (brightness value going from 63.75 to 66.3). The control cloths show higher brightness values than of those cloths tested with sol catalysts.

Figure 5.3 shows the TEMPO results for cloths tested using PdPt colloid. In general, we see a decrease in brightness value as we had colloid. At pH 5 there is an increase in the brightness value when mediator is added to the reaction mixture, but this brightness value is on par with the controls. At pH 7 little difference can be seen across the series, whereas at pH 10 a large decrease in the brightness value of the cloth is observed once colloid is added. This could be attributed to the pH 10 buffer causing a good amount of washing itself, whereas addition of colloid to the reaction mixture could be sticking to and staining the cloth.

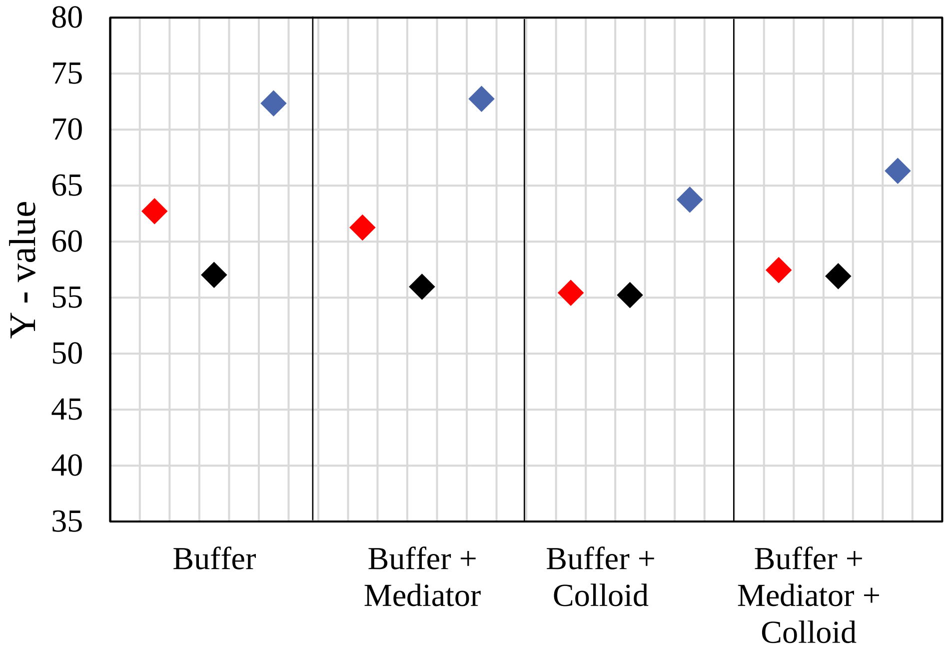

Figure 5.2: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with AuPt colloid as catalyst and TEMPO as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

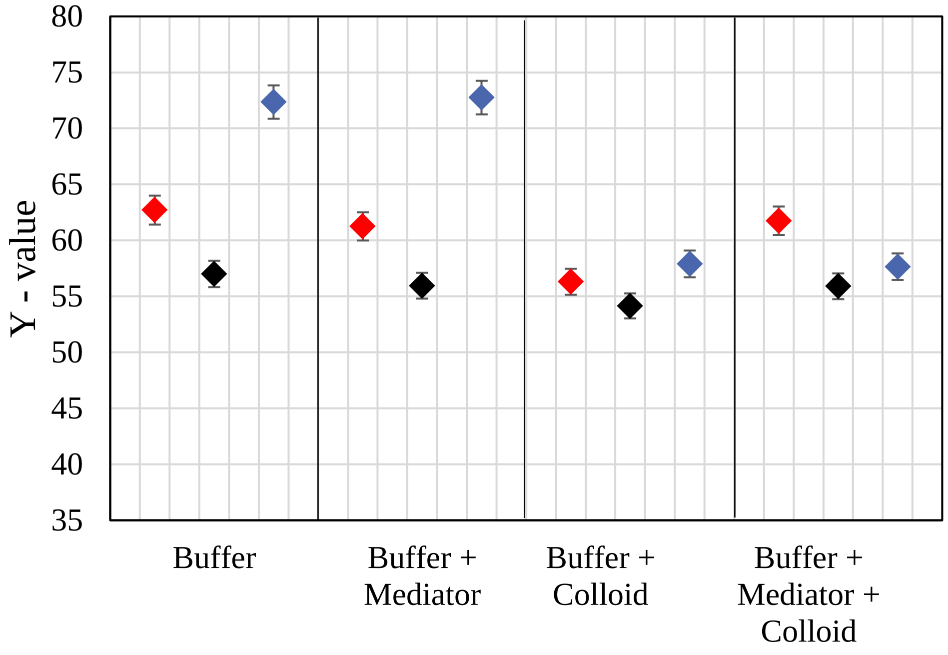

Figure 5.3: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with PdPt colloid as catalyst and TEMPO as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

In figure 5.4 the 3 graphs have been compared to show how TEMPO can have different effects on the cloth testing depending on the catalyst used. For AuPd tested cloths there is no change, we still see no improvement in the Y – values of the cloths on addition of TEMPO. For PdPt tested cloths there is no improvement except in the case of pH 5. Across all pH TEMPO seems to offer some improvement for the cloths tested using AuPt colloid, showing results that are comparable to the controls. The palladium containing catalysts show a large amount of staining of the cloths which can't be overcome through use of TEMPO, as shown in the previous chapter Platinum containing catalysts perform better, with AuPd performing the worst, showing massive deviation from control cloth brightness values.

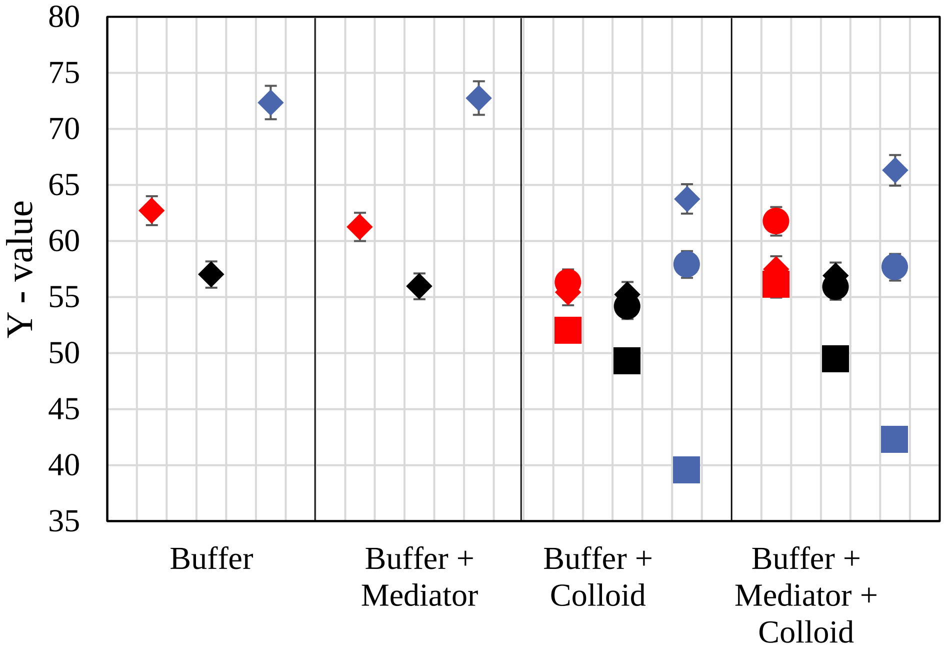

Figure .5.4: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with PdPt (●), AuPd (■) and AuPt (♦) colloids as catalyst and TEMPO as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, filled to 50 ml with buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦)

5.1.2. Tests using Violuric acid as mediator

Violuric acid is a redox mediator[8] and may facilitate the transfer of electrons to the cloth and target the stain for oxidation reactions. In Figure 5.5 the results of the cloths tested using AuPd colloid with violuric acid are shown. At pH 5 there is no improvement on controls on addition of catalyst. At pH 7 there is a similar trend to be observed. For cloths tested at pH 10 there is a significant decrease in the brightness value of the cloths on addition of the catalyst, but an improvement when mediator is added to the reaction mixture compared to the cloths tested using catalyst alone, although these cloths were not as bright as those cloths tested using just buffer and mediator.

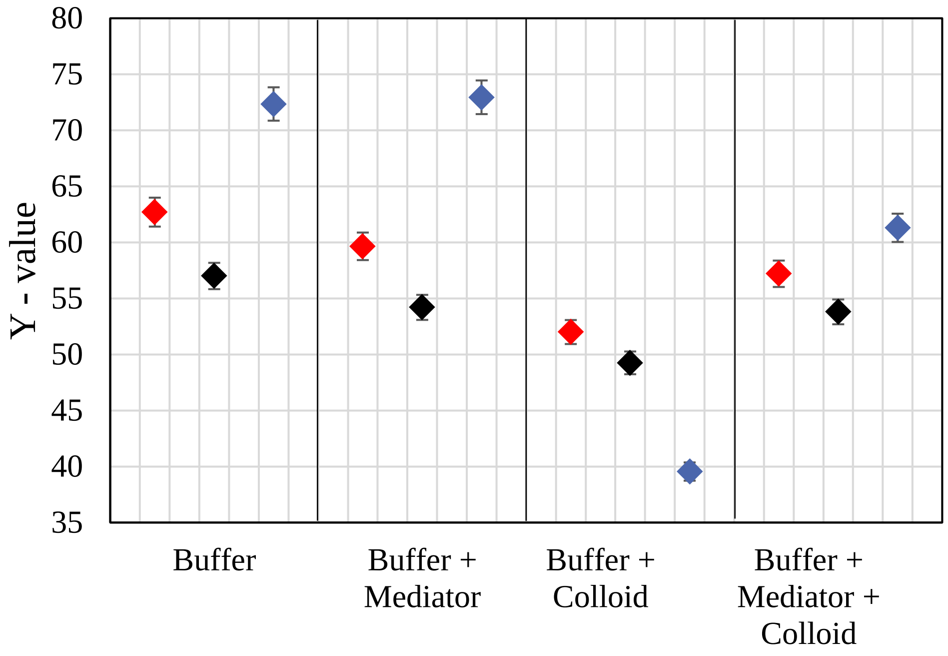

Figure 5.5: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with AuPd colloid as catalyst and Violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

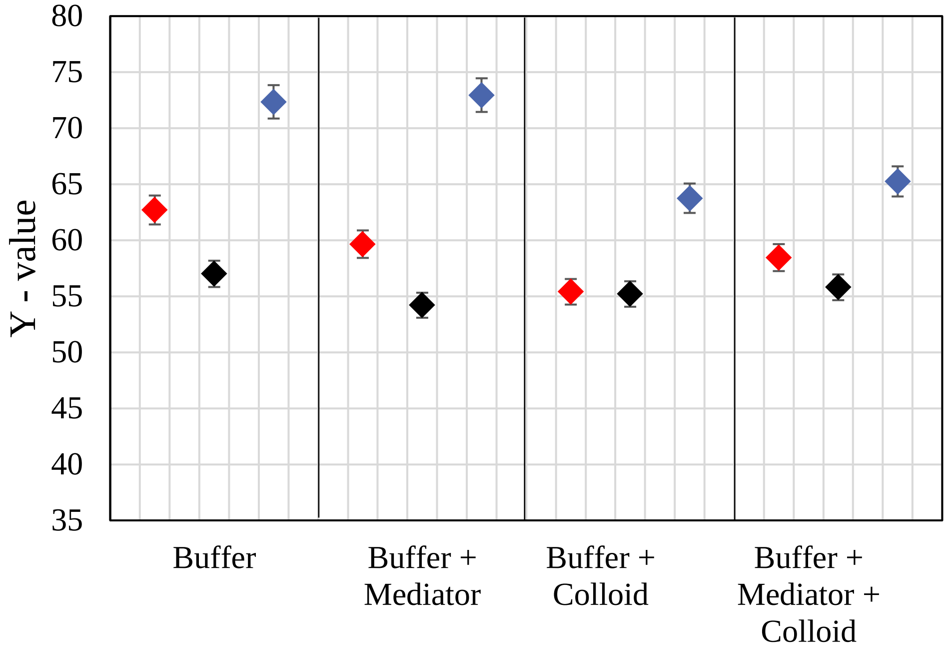

Figure 5.6: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with AuPt colloid as catalyst and Violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

Figure 5.6 shows the results of cloths testing using AuPt catalyst with violuric acid. In general, there is the same trend as observed for the cloths tested using AuPd catalyst. On addition of catalyst there is a decrease in brightness value across all pH values, although this is not as dramatic as it was for the previous catalyst, and the subsequent slight increase in brightness value following addition of mediator is observable for AuPt tested cloths as it was for AuPd.

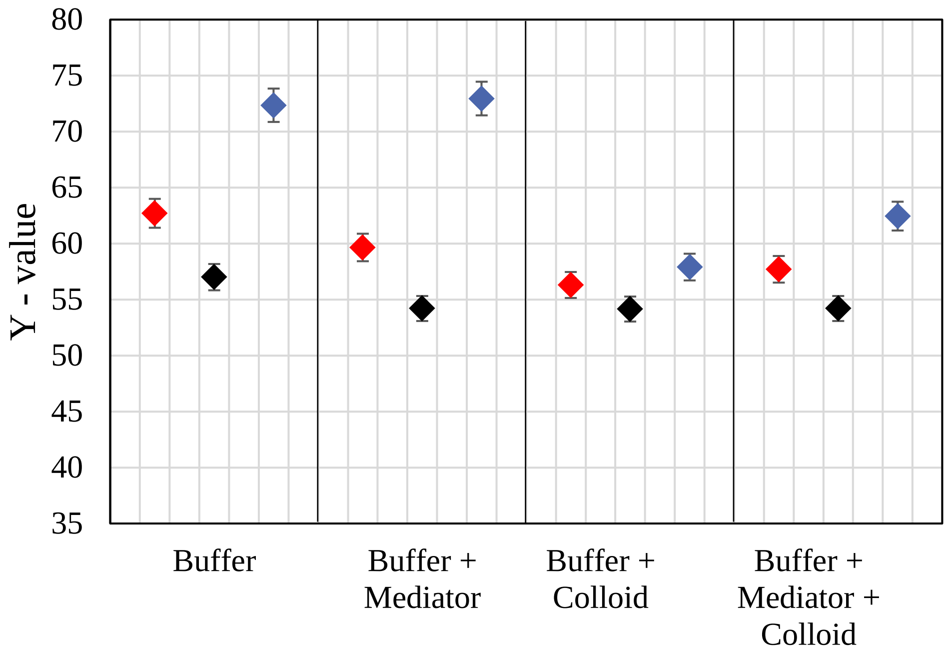

Figure 5.7: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with PdPt colloid as catalyst and Violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

In figure 5.7 the results for cloths testing using PdPt catalyst are shown. At pH 5 and pH 7 there is the same trend of decrease in brightness value of cloth on addition of catalyst, though not much change is witnessed as the conditions are changed. For experiments run at pH 10 there is a large decrease in Y – value once colloid is used. Once more there is a slight improvement on addition of violuric acid to colloid at pH 10.

Figure 5.8 overlays the results of the different catalysts using violuric acid as the mediator. For the 3 bimetallic catalysts tested there is not much change observed between them when mediator is added. As per the cloths tested using TEMPO, experiments undertaken using palladium containing catalysts led to a greater decrease in brightness value of the cloths compared to the controls, though addition of mediator helped to rectify this in part. Platinum containing catalysts performed better with AuPt performing the best of the three, with AuPd performing worst, leading to the greatest staining of cloth.

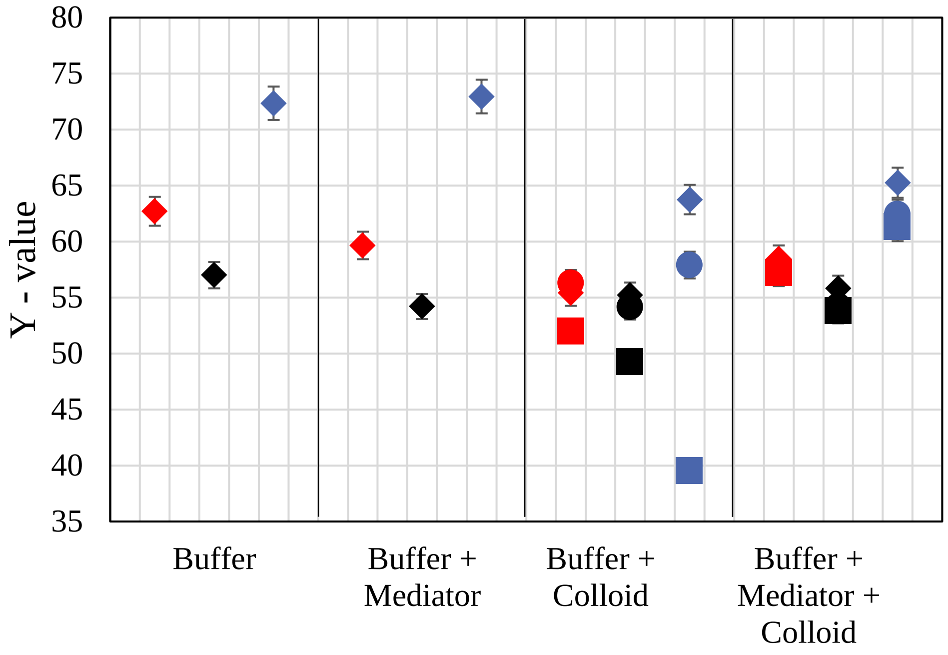

Figure 5.8: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with PdPt (●), AuPd (■) and AuPt (♦) colloids as catalyst and violuric acid as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, filled to 50 ml with buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦)

5.1.3. Tests using TAED as mediator

TAED is used in modern detergents to generate peracids in solution[9], which have greater bleaching ability at lower temperatures than traditional hydrogen peroxide. The goal is to be able to produce a species in solution that can activate TAED and generate the bleaching peracids. Figure 5.9 shows the results of cloths tested using AuPd catalyst with TAED as the mediator. At pH 5 and 7, there is a trend of decreasing cloth brightness value on addition of catalyst, which is lessoned in the case of pH 7 due to possible partial oxidation of the cloth by TAED in the case of TAED and buffer. There is an increase in brightness value in the case of pH 5 when TAED is added to the catalyst mixture. At pH 10 there is a large decrease in brightness value on addition of sol, as witnessed for violuric and TEMPO tested cloths, and the same improvement on addition of the mediator.

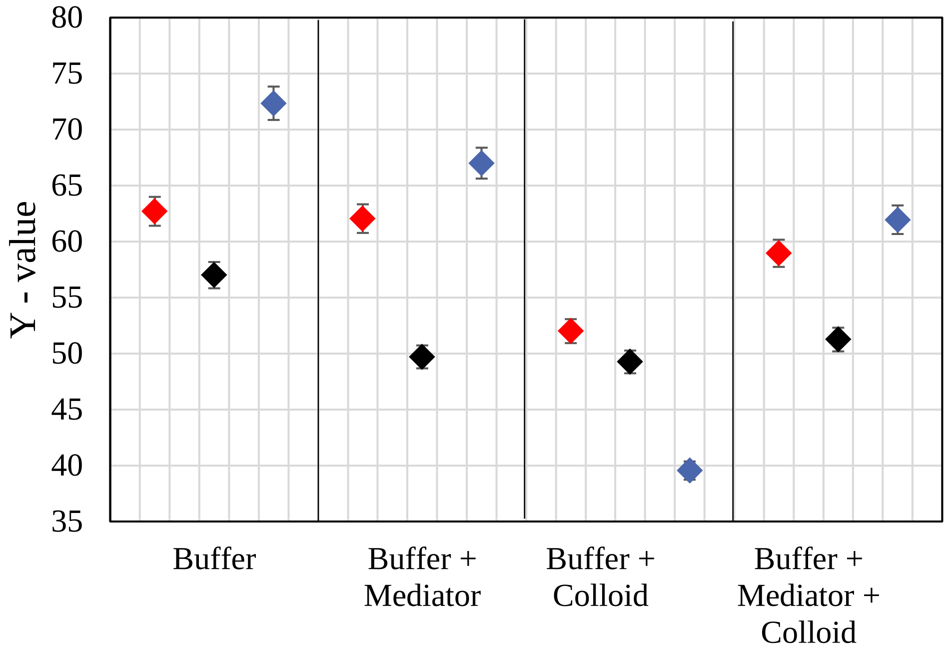

Figure 5.9: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with AuPd colloid as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

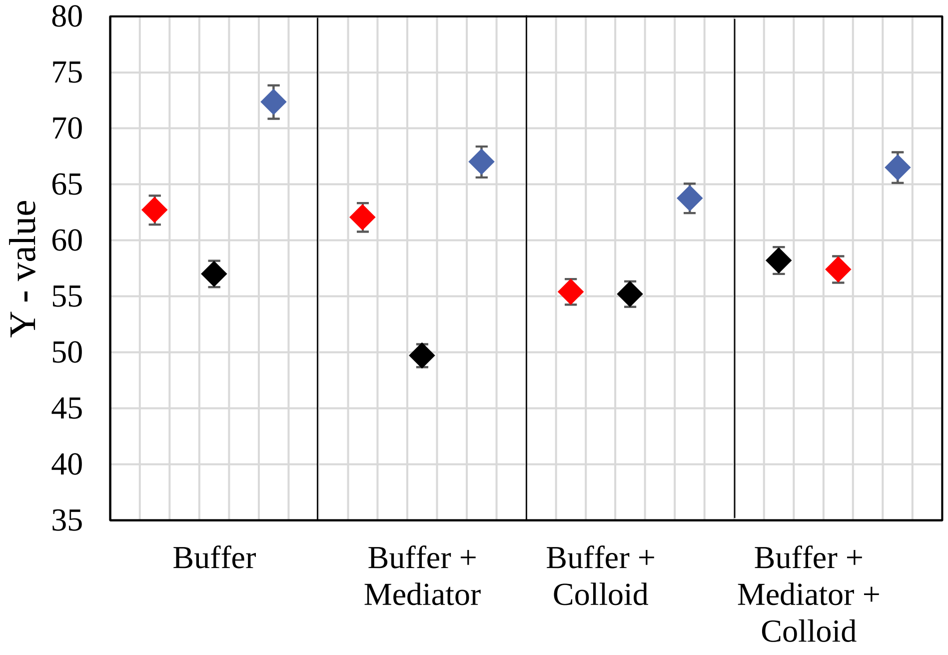

Figure 5.10: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with AuPt colloid as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

In figure 5.10 there is little difference to be observed across the series for the results of cloths tested using AuPt as the catalyst. There is the same decrease in brightness values on addition of TAED and catalyst, and some redemption of the system when TAED and AuPt are used together, compared with just use of the catalyst alone.

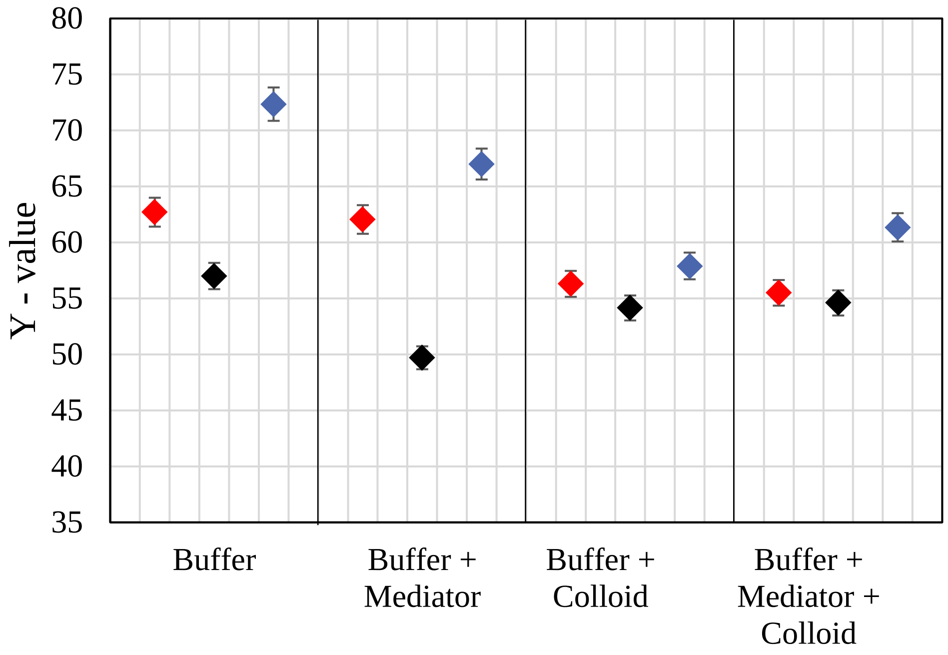

Figure 5.11: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with PdPt colloid as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, remainder buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦).

Figure 5.11 shows the results when PdPt colloid is used. pH 5 shows the same steady decrease of brightness value of the cloths on addition of colloid. At pH 7 the catalyst performs better than the TAED control, as was true for AuPt colloid. At pH 10 there is a decrease in brightness value for TAED compared to buffer alone, and the decrease in brightness on addition of colloid. Addition of mediator to sol again shows an improvement on sol alone, showing favourable interactions between the sol and catalyst for washing of the cloth.

Below in figure 5.12 there is an overlay of the previous results for TAED to allow comparison of the different bimetallic catalysts. It can again be seen that the mediator performed best when paired with AuPt, leading to cloths of higher brightness value than the other sols. Overall there is a decrease in brightness value on addition of TAED to buffer, possibly due to this partial oxidation phenomenon of the cloth stain. PdPt offers middling results whereas again, AuPd generally leads to producing cloths of the lowest brightness values following reaction.

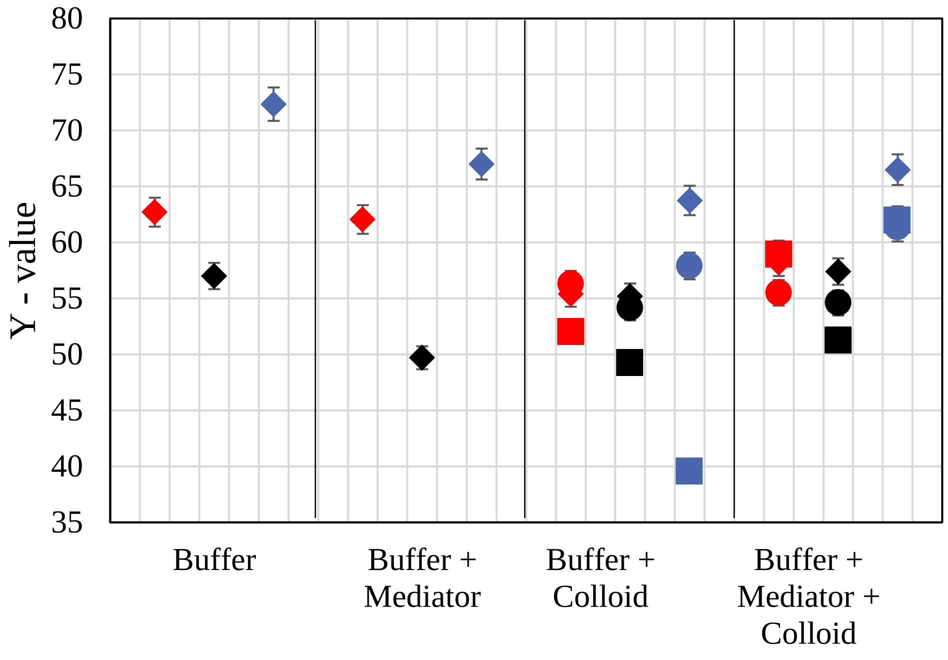

Figure 5.12: Brightness values for E-167 cloths tested for 30 minutes at 60 °C under 10 bar O_2, with PdPt (●), AuPd (■) and AuPt (♦) colloids as catalyst and TAED as mediator. Reaction volume contained 20 ml sol, 2 ml mediator, filled to 50 ml with buffer. Shows comparison of results for pH 5 (♦), pH 7 (♦) and pH 10 (♦)

5.2. Tests with supported catalysts

5.2.1. Autoclave experiments

From the results obtained it is clear that the colloidal catalysts are staining the cloths themselves, and to circumvent this issue, supported catalysts prepared by sol immobilisation were prepared and tested in autoclave reactors. It is believed that use of support should provide stability[10] and reduce mobility, potentially leading to a reduction in staining. In Figure 5.13 initial results of solid catalysts are presented. These tests were to examine the reaction dependence on oxygen pressure, as well as control experiments. It can be seen that in the majority of cases higher oxygen pressure is favourable, and that catalyst may offer some improvement on controls, but this is not the case for every test (catalyst led to a lower brightness value in the case of pH 10). Washing powder (20 mg) had similar results to that of the controls and the catalysts at pH 10, with addition of catalyst to the washing powder offering no benefit.

Figure 5.14 shows the results of cloths tested using AuPt immobilised on titania. These tests were carried out using the various pH buffers used for previous experiments. For cloths tested at pH 5 and pH 7, we see no real change under the different conditions and reaction compositions, including no difference between using 8.2 mg (standard) and 50 mg of catalyst, indicating a mass transfer limitation with respect to the reaction. The cloth that expresses the highest bleaching is that of pH 10 with catalyst and mediator, returning a brightness value higher than the control cloths. This coincides with the standard pH of washing detergent of about 10.5[11].

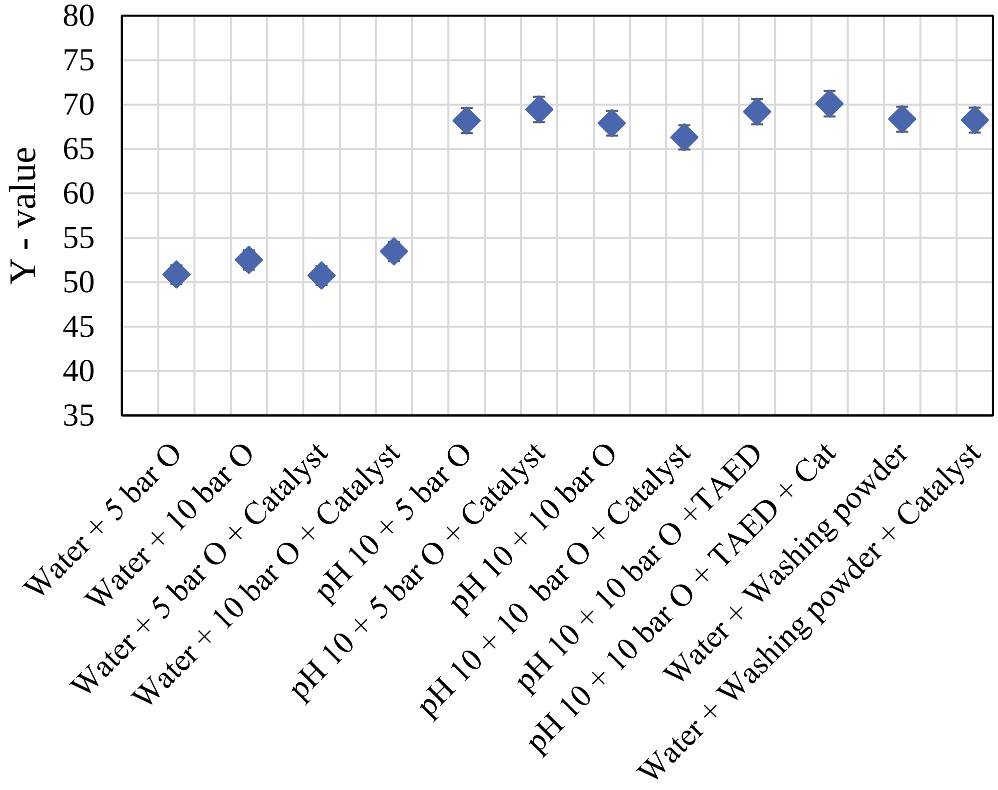

Figure 5.13: Initial solid catalyst testing on E-167 cloths. Carried out at 5 or 10 bar oxygen pressure, 30 minutes at 60 °C, 8.2mg catalyst, 2 ml mediator, 20 mg of washing powder, filled with buffer up to 50 ml, at pH 10.

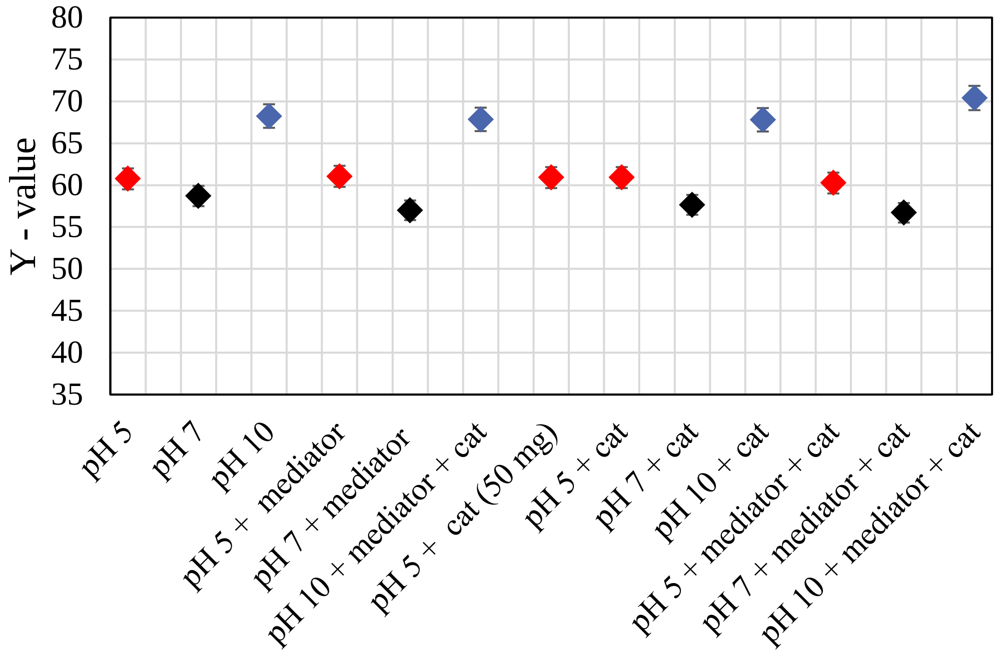

Figure 5.14: Systematic testing of supported AuPt catalyst on E-167 cloths. Conditions: 30 minutes at 60 °C and 10 bar O_2, 8.2 mg catalyst, 2 ml TAED, remainder buffer. pH 5 (◆), pH 7 (◆) and pH 10 (◆).

5.2.2 Open Flask Experiments

Tests in open round bottom flasks were begun to see if positive results could be obtained making use of ambient oxygen. In figure 5.15 it can be seen that the use of supported catalysts leads to a darkening of the cloth brightness value. This is apparent visibly at the end of the reaction, whereby catalyst settles on the cloth and stains it due to lack of stirring power of stirrer bars used. To combat this a more powerful overhead stirring fixture needs to be used to prevent catalyst settling on the cloth, leading to adsorption of catalyst onto the cloth surface. This form of staining if more apparent in cloths tested at pH 10 than in water. Water tested cloths show results comparable to that of the control, with supported platinum catalyst leading to less staining than AuPd catalyst, characteristic of the staining observed by palladium containing catalysts shown previously for unsupported colloidal catalysts. The second test involving Pt/TiO_2 allowed 30 minutes for the catalyst to stir in the vessel to achieve complete suspension of the catalyst in solution.

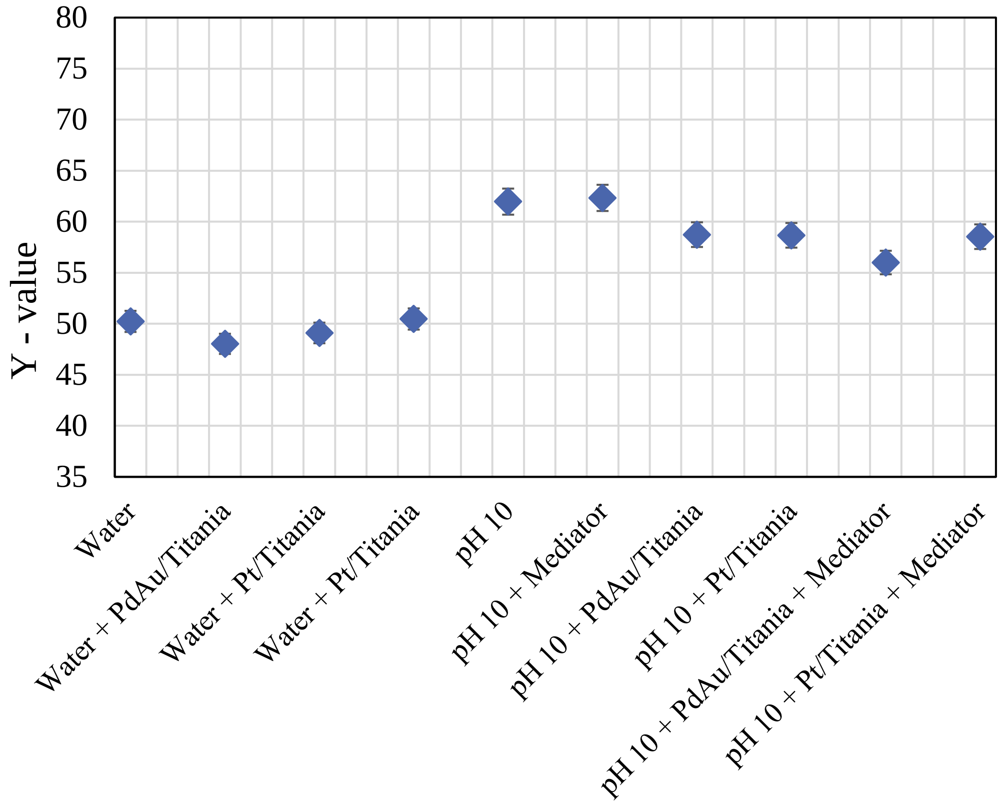

Figure 5.15: Showing results of open flask experiments for E-167 cloths. Conditions: 60 °C for 60 minutes, 2 ml mediator, 8.2mg of catalyst, remainder buffer up to 50 ml.

5.3 Decoupling bleaching from staining

It became clear during the running of the stained cloth experiments that there was a need to decouple any potential bleaching of the cloths from staining of them by the unsupported catalysts or by leached metal from the supported metal catalysts in order to truly quantify the bleaching efficacy of these catalysts. MP-AES analysis of the reaction solution was carried out before and after to examine the concentration of metal remaining following experiments, giving an indication of how much metal was sticking to the cloth. These tests were inconclusive and so futher experiments utilising SEM were carried out. To begin, blank cotton cloths were tested with the colloidal catalysts used for the cloth bleaching experiments. For reference, the brightness value of an untested coton cloth is 83, and from these experiments we can see that all cloths expressed staining following experiment, with palladium leading to a marginally greater degree of staining.

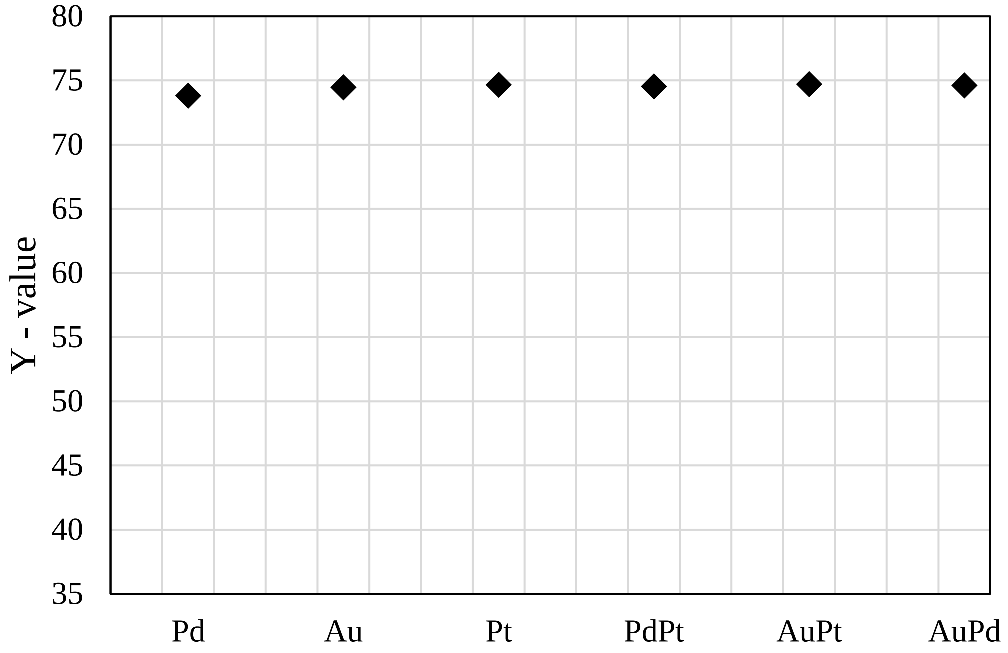

Figure 5.166: Brightness values for blank cloths tested at 60 °C for 30 mins at 10 bar O2, using 20 ml of colloid and 30 ml of water.

It can be seen that in figure 5.16 there is not much difference between the brightness values of the cloths using different colloids, although palladium does lead to a slightly lower brightness value than use of the other colloids. This is in contrast to what was seen for the E-167 tea stained cloths, which demonstrate that use of palladium containing colloids leads to a much greater decrease in brightness value compared with other metals.

Acknowledging the negative impact of having a catalyst that is attracted to and staining the cloth sample, it is also considered advantageous to have a catalyst that would also preferentially bind to the stain sample and not to unstained cloth. It was decided to run tests simultaneously, to understand the mechanism of staining of the cloths by the metal colloids as well as to gauge the catalyst preference for the stain. It is believed that preference for binding sites could be modified by augmentation of the capping agent of the catalyst. To carry out these experiments polka dot patterend cloths were prepared using tea, an example of which is shown below in figure 5.17.The first cloth represents untested cloth, the second showing cloth that has been tested with water alone, and the third tested in the presence of AuPd colloid. In this image it can clearly be seen that the catalyst is causing the tea stain to turn a darker shade, though does not seem to be having as much of an effect on the blank cloth surroundings.

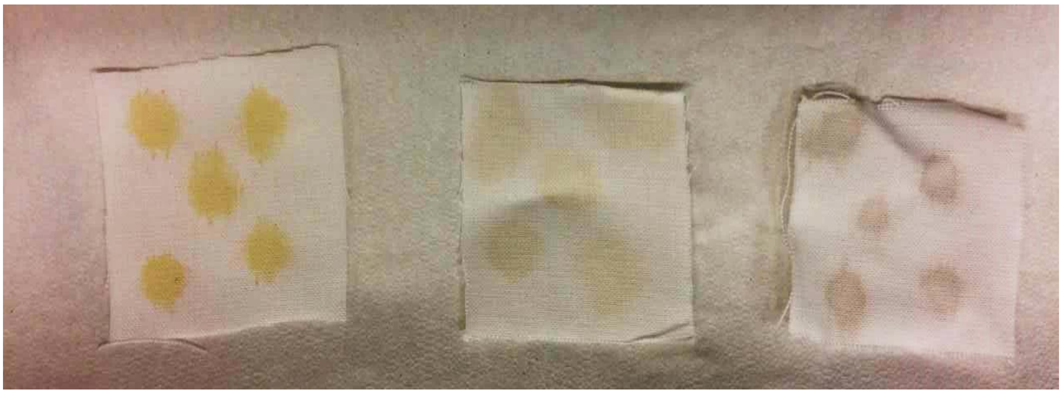

Figure 5.17: Polka dot patterend cloths stained with tea. Cloth 1: untested cloth, cloth 2: cloth tested with water only, cloth 3: cloth tested with water and AuPd colloid.

SEM analysis of these cloths showed no observable difference, with EDX failing to pick up any signal relating to depostede metals in the cloths. This indicates that the colour change is due to a chemical change rather than a darkening due to metal deposition. SEM images of each of the three cloths are shown below. The images are shown in the same respective order as figure 5.16.

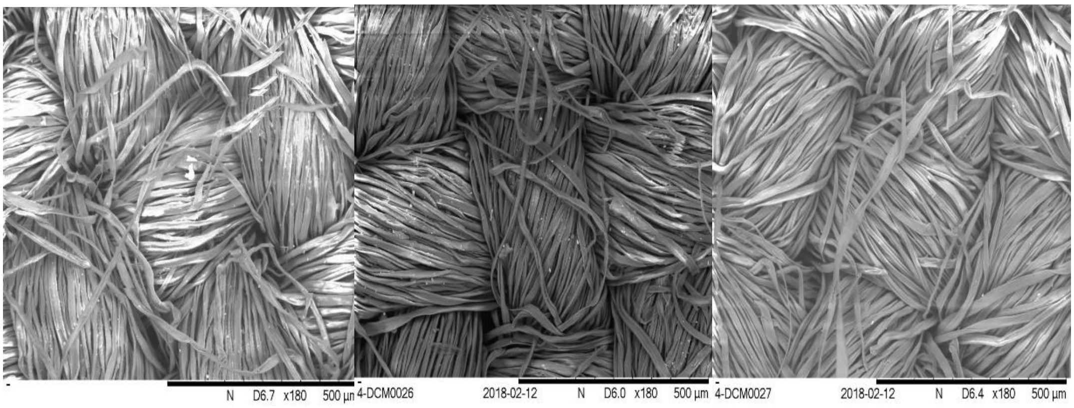

Figure 5.17: SEM images of polka dot patterened cloths. Cloth 1: untested cloth, cloth 2: cloth tested with water only, cloth 3: cloth tested with water and AuPd colloid.

Following tests with colloidal catalyst, supported AuPd/TiO_2 were also used with polka dot cloths, as well as with regular E167 tea stained cloths and untested blank cotton cloths, to see if the solid catalysts were depositing preferentially to any of these specific cloths. Images of E167 cloths tested with supported catalysts are shown in figure 5.18. In this image supported catalyst can be seen to be deposited within the fibres of the cloth sample. The same phenomenon is shown for blank cloths in figure 5.19.

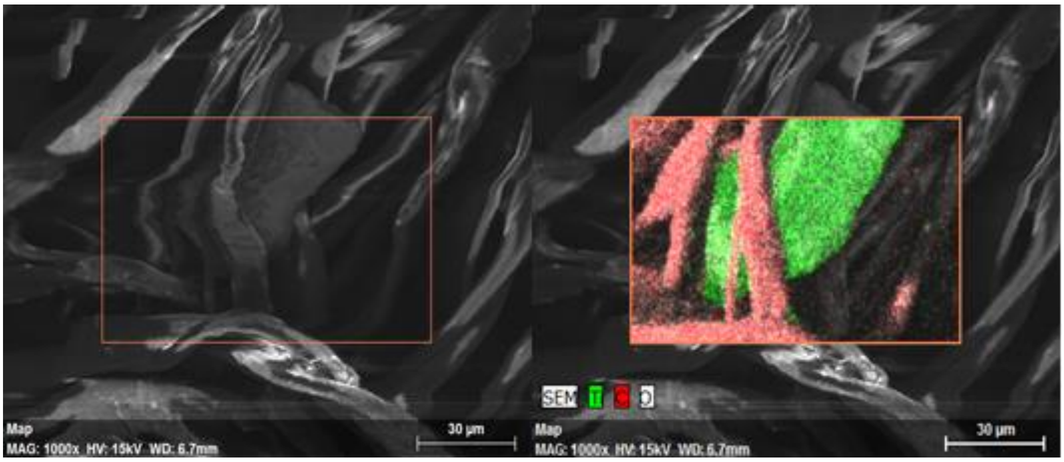

Figure 5.18: SEM images of E167 cloths showing embedding of supported catalysts.

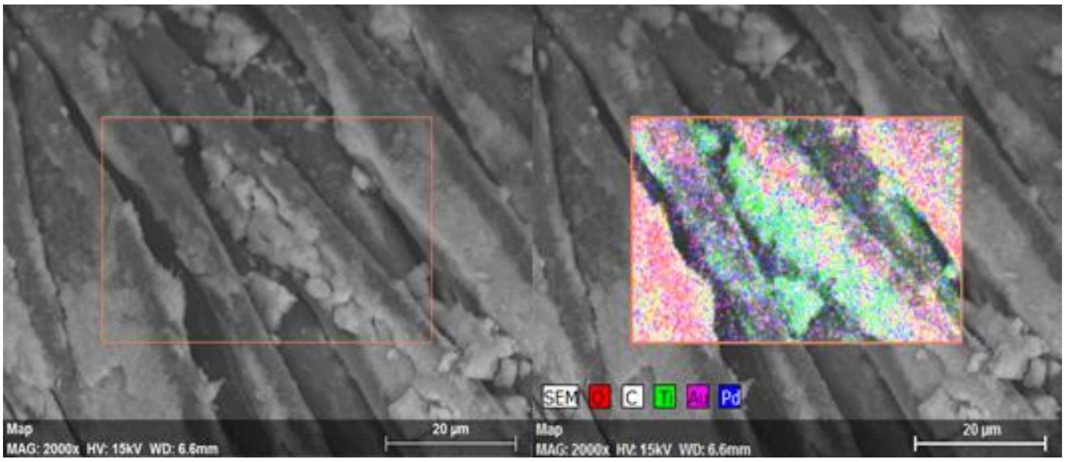

Figure 5.19: SEM images of blank cotton cloths showing embedding of catalyst.

These results indicate the through whatever mechanism is causing the catalyst to deposit into the cloth sample, it is occurring indiscrimenately in the case of pure cloth samples, E167 tea stained cloth and blank cotton cloth. The experiments were carried out on the polka dot patterened cloth to determine if on these cloths the catalyst would preferentially deposit to a stained site over a blank cotton site, as was observed to be the case optically for colloidal catalysts. The SEM images for polkda dot stained cloths are shown in figure 5.20.

Here again is seen the indiscriminate depositing of the supported metal catalysts onto the cloth samples. These results contrast those obtained from the experiments utilising colloidal catalysts, where optic observation indicated that the colloids were interacting preferentially with the stained sections of the cloths. Further work would need to be carried out to qualify this observation.

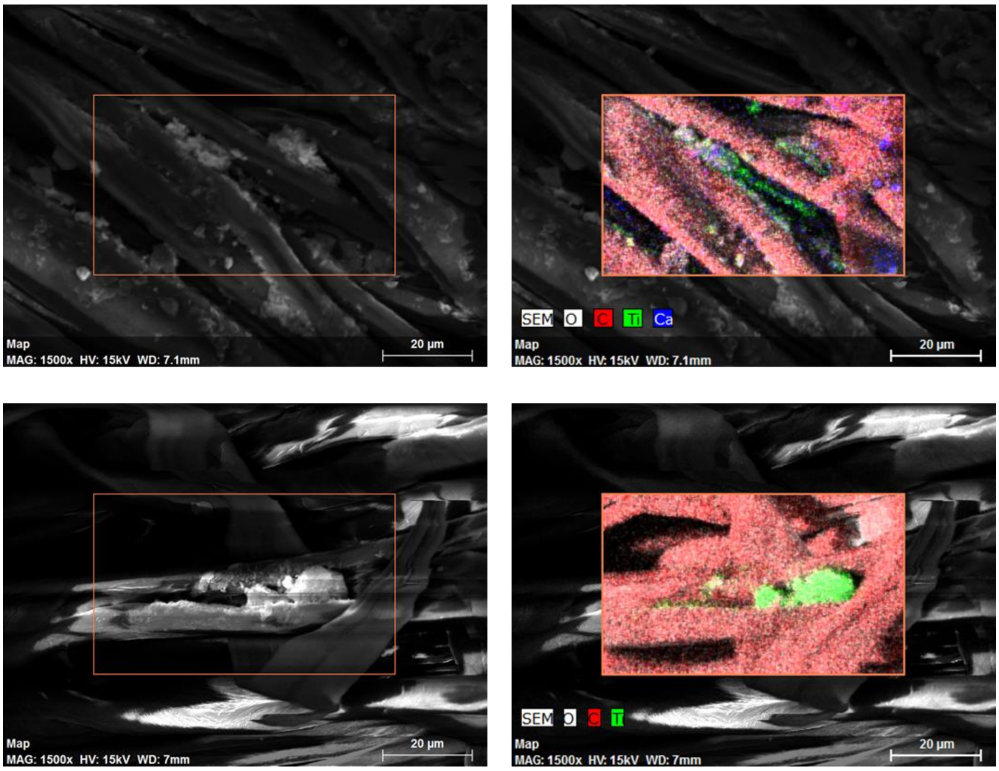

Figure 5.20: SEM images for polka dot patterened cloths. Top images correspond to images taken on the tea stain, while bottom images correspond to images taken off the stained sections on the cloth sample.

5.4. Dye Transfer Inhibition (DTI) Studies

Alongside tests to determine the use of these catalysts for bleaching stained cloth samples, and noting that these catalysts have been shown to have great oxidising potential for substrates in solution and shown in this work to be useful in the discolouration of homogeneous stains, their effectiveness at preventing the transference of stains will be examined. In domestic laundry bleaching, the prevention of in situ staining of clothes is known as dye transfer inhibition, with a commercial example being Colour Catcher. During standard washing procedures in the drum. colours from clothing can run and lead to the colouration of other materials. DTI prevents this and preserves the colour of the otherwise tainted garment. It would be advantageous if these catalysts could not only lead to the bleaching of stains, but also lead to the destruction of chromophores in solution that have bled from clothes, and prevent the dying of undyed material.

To examine the potential in this field dye bleeder experiments were carried out. A direct red donor cloth used as the bleeder sample and added to a reaction mixture containing blank cloth. Catalyst would be used in attempt to prevent the discolouration of this cloth through destruction of chromophores in solution. Brightness values of cloths tested in this maner can be seen and compared in figure 5.21. In this set of data colloidal catalysts are compared against supported metal catalysts with bimetallic AuPt acting as the active metal component. It can be seen that titania performed better than the controls (~70 to 68) when not used with TAED. It is possible that titania could be absorbing the dye directly, leading to less available pigment to discolour the blank cloth. In both cases, with TAED and without, the colloidal catalyst performed more favourably than the supported metal catalyst. The supported metal catalyst appears to be having no effect and is instead contributing to further staining of the cloths in comparison to the control cloths.

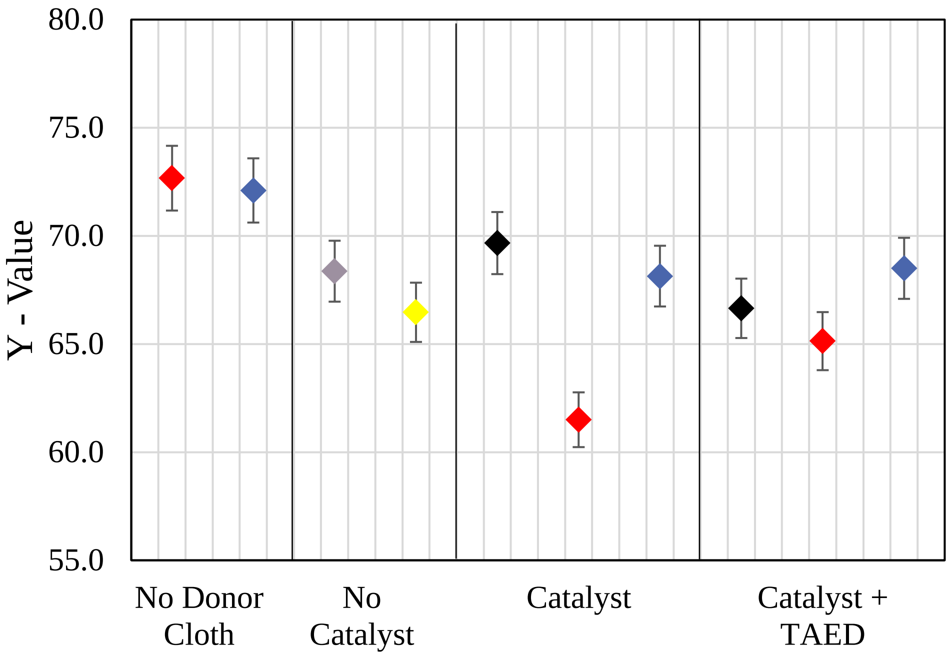

Figure 5.21: Brightness values for blank cloths tested for 30 minutes at 60 °C under 10 bar O_2, with direct red donor cloth. Catalysts used were AuPt (♦) and AuPt/TiO_2 (♦) and titania (♦).Water (♦) and TAED (♦) were controls. Reaction volume contained 20 ml sol, 2 ml mediator, filled to 50 ml with water.

Given the colloidal AuPt was shown to be more effective, the other bimetallic catalysts were utilised in the same process for comparison. The results of these experiments are shown in figure 5.22. It can be seen that there is little variation in cloth brightness value dependent on the choice of catalyst used, and that still none of the catalysts achieve the brightness value of a washed cloth with catalyst and no donor cloth. Also of note is that TAED appears to offer no benefit over use of catalyst alone, yet seems to lead to staining of the cloth in its solo use, compared to the use of water alone (66 compared to 68 brightness value).

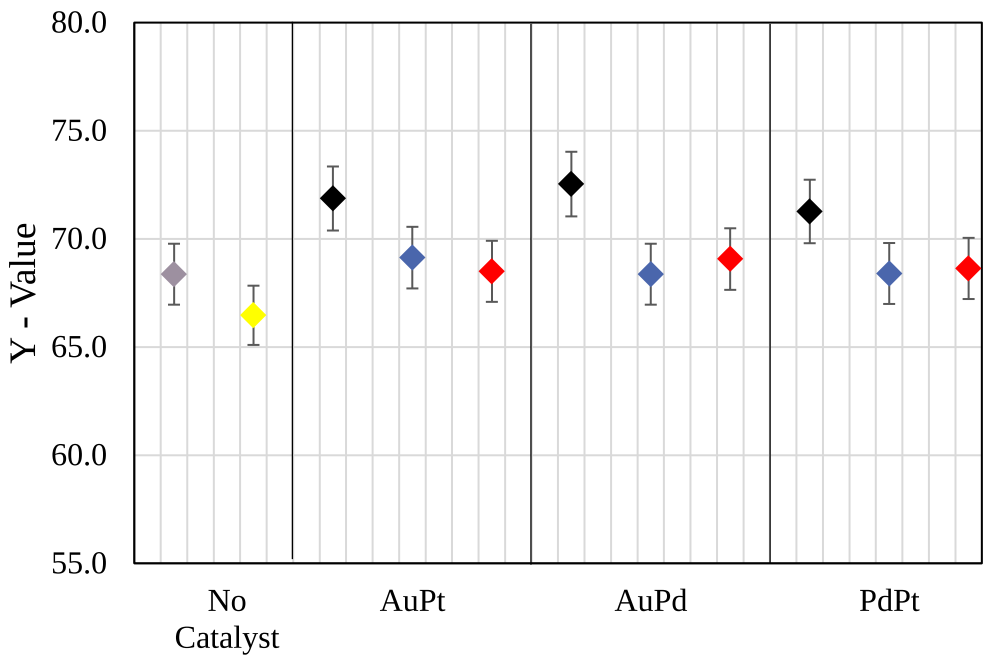

Figure 5.22: Brightness values for blank cloths tested for 30 minutes at 60 °C under 10 bar O_2, with direct red donor cloth. Catalysts used were AuPt, AuPd and PdPt. Water (♦) and TAED (♦) were controls. Tests were performed without donor cloth (♦), with catalyst alone (♦), and with catalyst and TAED (♦). Reaction volume contained 20 ml sol, 2 ml mediator, filled to 50 ml with water.

5.5. Conclusions

In the case of bimetallic catalysts there is still present the staining effect of the cloths by the catalysts, as we have seen with the monometallic variants. Palladium containing catalysts led to the greatest amount of cloth staining, which was also true for monometallic palladium catalyst, whereas platinum containing catalysts led to the least, owing to results that are comparable to those of the controls.

Violuric acid and TEMPO were able to overcome the staining expressed by cloths tested using AuPd at pH 10, but beyond this we could see little difference in the results between choosing different mediators. Work will need to be done to improve the complete activation of TAED, which appears to be a problem due to occasional staining of the cloths by TAED alone.

Tests carried out in open flask suggest the catalysts will need to be further optimised to be used outside of an excessive oxygen environment. Catalyst design will be important with the synergistic effects of different metal combinations for the activation of oxygen a primary point of consideration. These catalysts will be tested using the model compound reactions to elucidate reaction mechanisms and expand the current knowledge of metal nanoparticles for organic oxidation[2,12].

SEM analysis of the cloths failed to conclusively quantify the level of staining occurring during catalyst testing on the cloths. Until the staining effect is abated or a method of cloth whitening is obtained that can ignore this staining effect it will be difficult to ascertain a true measure of catalyst efficacy for stain bleaching. Further work into model compound oxidation will be paramount in helping to obtain the same information and will be also more useful in terms of catalyst design.

With regard to DTI studies, the colloidal catalysts do offer promise in comparison to the supported metal catalysts. It is quite possible that these catalysts offer an advantage due to the presence of a quasi-homogeneous phase with the liquid stain. If not for use in bleaching stained cloth samples, it would at least be prudent to consider their use in a DTI capacity.

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6. Conclusions and Future work

6.1. Chapter 3

The reactions involving solutions of tea proved that the catalysts can be used to cause discoloration, suggesting that the precious metal catalysts can be used to augment the chemical structure of the chromophore of staining compounds. All of the catalysts were shown to be capable of reaction with gallic acid and catechol, with and without oxygen added to the reaction vessel. Palladium and platinum were shown to both be more effective than gold catalysts, and the reasons for why this may be, have been discussed. Resorcinol did not react with the catalysts. Both the sol immobilised and the modified impregnation catalyst showed greater activity. The difference between the sol and the modified impregnation catalyst could be a result of the atomic orientations of each metal in the nanoparticle crystal lattice.

Future work surrounding this chapter would focus on the determination of the of the reaction products of catechol oxidation primarily, to see how the aromatic ring is mineralised. The results will be compared to literature evaluations of products to determine a reaction mechanism and will provide identification of the oxygen activation products which are generated by these catalysts. This will provide the information required to prepare an ideal catalyst for the activation of oxygen which will then be utilised to bleach the stained cloth samples.

6.2. Chapter 4

Previously we showed that all cloth samples express a degree of staining of the cloth samples by the colloids themselves. These were tested with monometallic Au, Pd and Pt catalysts using the three mediators; TAED, TEMPO and violuric acid. Gold and Platinum colloids show greater bleaching efficacy than the Palladium samples. This indicates either less staining of the cloths by the colloids or greater catalytic efficiency. Palladium containing catalysts led to the greatest degree of staining of the cloths. In general it is clear that any staining of the cloths by the metals themselves must be overcome if true bleaching and any bleaching is to be truly quantified by experiments that examine a samples brightness value. Among the cloths tested using solid catalysts some have returned brightness values better than the controls, confirming that supported catalysts are more effective at this time than the sols. Interestingly depending on the pH used, TiO_2 could lead to higher brightness values of cloth that the catalyst.

Ongoing work with this topic would depend initially on catalyst design from results of model compound studies. Alongside this however, work could be carried out on decoupling the bleaching effects of the catalysts from the staining effects. The would include using stabiliser free nanoparticles, as well as stabilisers that would have a lesser affinity for the cloth moieties and only be attracted to the stain, abating any staining of the cloths by the catalysts. Work would focus on using TAED as a mediator for the reactions, with catalyst design focused on activation of oxygen which would then activate TAED at low temperatures.

6.3. Chapter 5

In the case of bimetallic catalysts there is still present the staining effect of the cloths by the catalysts, as we have seen with the monometallic variants. Palladium containing catalysts led to the greatest amount of cloth staining, which was also true for monometallic palladium catalyst, whereas platinum containing catalysts led to the least, owing to results that are comparable to those of the controls. Tests carried out in open flask suggest the the catalysts will need to be further optimised to be used outside of an excessive oxygen environment. Catalyst design will be an important with the synergistic effects of different metal combinations for the activation of oxygen a primary point of consideration. SEM analysis of the cloths failed to conclusively quantify the level of staining occurring during catalyst testing on the cloths. With regard to DTI studies, the colloidal catalyst do offer promise in comparison to the supported metal catalysts. It is quite possible that these catalysts offer an advantage due to there presence in a quasi-homogeneous phase with the liquid stain. If not for use in bleaching stained cloth samples, it would at least be prudent to consider their use in a DTI capacity.

As with the previous chapter, the future would require a better understanding of model compound oxidation, as well as further understanding of the mechanism of staining of the cloth samples by the catalysts themselves. The DTI studies were promising, showing that these catalysts may not be as effective for bleaching stained cloth samples as they currently are, but can be favourably developed for preventing the transference of dyes and stains between fabrics in a wash cycle. As per the cloth tests, the catalyst design would depend on having a representative model system to best understand the chemistry of the system.