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Chapter

Leveraging Dendrimer Macromolecules for the Encapsulation and Stabilisation of Nano-Sized Ruthenium Catalysts: Evaluation of Catalytic Reaction Kinetics in the Reduction of Pollutants Organic Dyes, Oxidation of Alcohols and Alkenes as Well as Hydrogenation Reactions

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Abstract

Encapsulation of nano-sized metal catalysts within the dendrimers macromolecules' frameworks has been well documented thus far. Dendrimers are described as symmetric, monodispersed macromolecules resembling a tree-like branched structure and have been utilised as both a template and stabilising agent for the fabrication of metal (noble and non-noble) nano-catalysts. For this purpose, different types of dendrimers can be employed. The use of dendrimers for metal catalysts stabilisation or encapsulation offers several advantages in catalysis. For example, the dendrimer template allows the synthesis of catalytically active monodispersed nanoparticles and the dendrimers template itself does not passivate the metal active atoms during the catalytic process. Additionally, dendrimers have the potential to act as a "vehicle" that can be leveraged for the fabrication of heterogeneous catalysts. For example, surface groups of the dendrimers can be functionalised to chemically link the dendrimer-encapsulated nanoparticles (DENs) with solid supports such as silica. A significant number of studies on the synthesis and catalytic evaluation of dendrimer-metal nanocomposite materials (e.g. Ruthenium-based) onvarious reactions can be found in the literature. This chapter, however, will particularly focus on the recent developments on the synthesis, characterisation and catalytic applications of dendrimer-derived (colloidal and supported) Ruthenium catalysts.

1. Introduction

With the rapid increase in environmental problems such as pollution and climate change, the search for chemical processes that offer solutions to mitigate these challenges has also intensively received a lot of attention from researchers around the globe in the past decades. More recently, the revised Transformation Agenda by the United Nation has firmly advocated for the attainment of Sustainable Development Goals (SDG) by year 2030 [1]. As a result, more efforts have been projected into the development of sustainable material science and nanotechnology. For example, it has become more imperative to innovate materials and technology that can be utilized in the nanoscale range. Additionally, the materials and technologies must be environmentally friendly, recyclable, cost-effective and sustainable. The synthesis of nano-sized metal and non-metal catalysts using "green" processes, among other chemical processes, is one of the examples of the ongoing efforts by scientists towards the attainment of SDG. This is because nanocatalysts derived from metal nanoparticles have been found to possess different and unique chemical and physical characteristics as compared to those observed in their bulk counterpart catalysts [2]. Some of these characteristics include higher surface area, robustness, and better stability as compared to other conventional nanocatalysts [3–5]. Due to the high surface area of metal nanoparticles, a significant portion of their active atoms are available for catalysis. This in turn, results in the superior performance of nanoparticle catalysts due to enhanced contact between the reactants and the catalysts during the reaction process. It is also widely believed that as the size of the metal NPs decreases, the surface area increase (and vice-versa) and that the catalytic rate is directly proportional to the number of catalytic active sites exposed [6].

Because metal nanoparticle catalysts are well dispersed in solution, particularly unsupported colloidal nanoparticles, it has always been tempting to often classify them as "homogeneous" catalysts. However, these metal NPs have been perceived to be insoluble in many organic solvents use for common yet important reactions. On assumption that colloidal NPs do not dissolve in organic solvents that are often used during chemical reactions, they are rendered to act as "heterogeneous green' catalysts [7]. As such, it is believed that these colloidal NPs can be recovered easily after the reaction using suitable various techniques. However, the recovery and separation of colloidal nanoparticles from the final reaction products have been found to be a complex process and hence very little progress has been made on the advancement of recycling these catalysts to this end [8–10].

Some attempts to establish whether nanoparticle catalysed reactions follow a homogeneous or heterogeneous mechanisms have been made by few researchers. For example, in a study published by Nemanashi and Meijboom entitled; "cat in a bag recycling of dendrimer encapsulated Au nanoparticles by use of dialysis membrane bag in the reduction of 4-nitrophenol reduction: proof of heterogeneous catalysis", a heterogeneous type of mechanism was suggested [11]. In their study, dendrimer encapsulated Au nanoparticles Au-DENs with an average particle size ranging between 2.1 and 3.1 nm were trapped into a permeable dialysis membrane bag which only allows for the diffusion (in and out) of small reactants molecules. The entrapped Au-DENs were dipped into a reaction flask containing aqueous solutions

of 4-Nitrophenol and an excess reducing agent (NaBH₄) while keeping the system under stirring. The reactants molecules diffused inside the dialysis bag containing the catalyst and made contact with the surface of the Au-DENs catalyst for the product formation. The product (4-aminophenol) formation was monitored by analysing a reaction solution sampled over time using UV-vis spectrometry. Post-reaction characterisation of the catalyst by techniques such as Transmission Electron Microscope (TEM) revealed that the DEN catalysts retained their original particle sizes and showed no leaching even after three reaction cycles. It was concluded that the catalytic reduction of 4-NP occurs on the NPs' surface as opposed to induced by leaching of metal NPs atoms into solution. However, some researchers have suggested in their review articles that both heterogeneous and homogeneous type of mechanisms for various metal nanoparticles catalysed reactions [12, 13]. Narayan et al. have recently reviewed the synthesis and utilisation of metal nanoparticles (NPs) as "green" catalysts [7]. The issue of whether metal nanoparticles catalysis follows a homogeneous or heterogeneous reaction mechanism remain an ongoing debate in catalysis research.

2. Synthesis of metal nanoparticles

Generally, two main approaches are employed for the synthesis of nanoparticles—top-to-bottom method and the bottom-up [14]. The main distinct difference between these two methods is the starting precursor for the formation of nanoparticles. For instance, the top-to- bottom approach entails the process in which the bulk material is used as a starting material and the particle size is reduced to nano-sized particles via different physical, chemical chapter, or mechanical processes [15]. On the other hand, the bottom-up approach involves making use of molecules, small particles or atoms as starting materials for the assembling of nanoparticles via processes such as the liquid state synthesis method (chemical reduction) [16]. This particular chapter will solely focus on the latter approach for the synthesis of nanoparticle with more emphasis on the synthesis of dendrimer stabilised Ruthenium nanoparticle catalysts. The synthesis of dendrimer-based Ruthenium nanocatalysts (Ru-DENs) will be discussed in detail in the succeeding sections of this chapter.

Based on the afore-mentioned main two approaches that are used for the preparation of metal nanoparticles, different methods (physical and chemical processes) can be explored for their synthesis depending on the targeted final physical and chemical properties (size, morphology, application, etc) of the nanoparticles to be produced. For instance, a physical process such as flame spray pyrolysis (FSP) can be employed if the target is to produce nanoparticles on a large scale [17]. Alternatively, the synthesis of monodispersed nanoparticles with a well-defined spherical shape can be achieved by employing a chemical process proposed by J. Turkevich. For example, Kimling et al. reported the synthesis of spherical, monodispersed Au nanoparticles using the Turkevich method [18]. This was simply achieved by reduction of citrate at 100°C, and subsequent mixing with gold hydrochlorate solution. To synthesise nanoparticles of different sizes using this method, the concentration of citrate solution (capping agent) can manipulated.

Equally so, a variety of stabilising or capping agents can be employed depending on the method chosen for the synthesis of metal nanoparticles. The use of a suitable stabiliser during the synthesis of metal nanoparticles is vital, particularly those aimed to be utilised in catalysis. This stabilisation is primarily vital to circumvent unwanted phenomena to occur on the catalyst, particularly during the catalytic processes

usually carried out under harsh conditions. For example, phenomena such as sinter-ing, migration-coalescence, and agglomeration may lead to catalyst deactivation dur-ing the catalysis process. Therefore, various organic ligands such as ionic liquids (ILs) [2, 19–22], simple amines, phosphines, and thiols [12, 23, 24], cyclodextrins [25–29], caliraxenes [30–32], polymers [7, 12, 33–35], surfactants [36, 37], and dendrimers [38–43]. Of these metal nanoparticles' stabilising agents, dendrimers have been found to be versatile and potentially offer a considerable number of advantages, particularly in catalysis [40, 43]. This chapter gives a comprehensive discussion on the utilisation of dendrimers macromolecules as stabilising and encapsulating agents for ruthenium metal nanoparticles as well as their applications in various reactions such as reduc-tion of pollutants dyes, oxidation of methanol, hydrogenations of biomass-derived molecules and other organic compounds.

Dendrimers macromolecules are classified as hyperbranched polymers, with a well-defined, monodispersed, tree-like three-dimensional structure. These versatile macromolecules possess three main structural components; (a) interior core, (b) inte-rior branching units, and (c) the periphery, attached to the outermost branching unit (see **Figure 1**). The synthesis of dendrimers is carried out using either the convergent or the divergent methods. The divergent approach entails an iteration sequence of reaction steps in which iteration from the core unit lead to higher dendrimer genera-tion. On the contrary, the divergent method involves a process of synthesising the dendrimer from periphery units towards the core units via a two-stage process. Vögtle et al. reported the first synthetic procedure for the construction of well- defined dendrimers in 1978 via divergent approach and referred to the used procedure as "cascade synthesis" [45]. Few years later, Tomalia et al. reported the modified Vögtle's procedure for the synthesis of independent, divergent, and macromolecular "true dendrimers", poly(amidoamine) (PAMAM) dendrimers [46]. Newkome et al. also reported the synthesis of what they termed "arborols" (a synonym for dendrimers) during the same year as Tomalia and co-workers [47]. The first example for the conver-gent synthesis of dendrimers was reported by Hawker and Fréchet in 1990 [48].

Since their (dendrimers) discovery, these materials have found a wide range of applications in nanoscience. For instance, they have extensively been used in areas such as in drug delivery [49], sensors [50], electronic devices [51], wastewater treat-ment [52] and catalysis [53], to name just a few. However, this chapter will solely focus on the latter applications, in which dendrimers are utilised for the stabilisation and
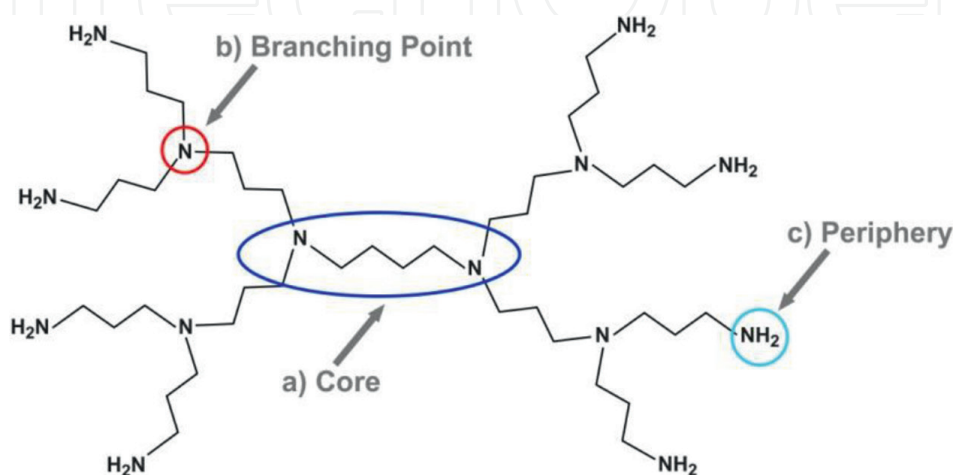

Figure 1.
A typical schematic illustration of the structural components of poly(propylene imine) (PPI) dendrimer molecule [44].

encapsulation during the synthesis of catalytically active homogeneous and heterogeneous metal nanoparticles, particularly ruthenium based.

3. Dendrimers for encapsulation of metal nanocatalysts

Green chemistry advocates for the use of set of principles that seek to promote elimination or minimising the use or generation of hazardous chemicals during the design, manufacture, and application of chemical products. Catalysis is one of the outlined important principles (of the 12) of green chemistry. The evolution of nanomaterials (such as metal nanoparticles) in the past decades offers a great platform for the attainment of sustainable, green catalysis practises. Many essential products (such as medicine, polymers, fibres, fuels, paints, lubricants) used by humans in the modern time are produced through catalytic processes. Therefore, catalysis plays a pivotal role in chemical transformation in chemical industries. For example, it has been reported that 90% of manufactured chemicals involves at least one catalytic process [54]. Because nanocatalysts possess high surface energy, which renders them thermodynamically unstable, possibilities of deactivation due to migration and coalescence during catalytic processes are always high, especially for processes carried out at elevated temperatures.

As a strategy for the fabrication of more stable, sustainable and catalytically active "green" metal nanocatalysts, many researchers have explored the encapsulation of metal nanocatalysts within different materials (encapsulating agents) using various methods. These encapsulating agents include materials such as inorganic oxides nanoshells (SiO_2, TiO_2, CeO_2), nanoporous materials (mesoporous materials, zeolites, metal-organic frameworks, covalent organic frameworks), and organic capsules (dendrimers, porous organic cages) [55]. In most cases, the synergetic effect is established between the metal nanoparticles and the encapsulating material and has been observed to greatly enhance the catalyst's activity and selectivity. More importantly, such catalysts are more stable and can easily be recyclable without losing their activity, making them almost ideal "green" catalysts. This chapter will focus on the encapsulation of ruthenium nanocatalysts within dendrimer frameworks (Ru-DENs), their characterisation, and catalytic applications.

4. Synthesis and characterisation of dendrimer-encapsulated ruthenium as well as their applications in catalysis

A simple two-step process involving complexation of the aqueous dendrimer solution and metal ions, followed by the reduction of the dendrimer-metal ions composite precursors is generally carried out for the synthesis of DENs. The dendrimer-metal ion composite, a precursor for DENs, is prepared by addition of the desired amount of metal ions (such as Pt^{2+}, Pd^{2+}, Au^{3+}, Ag^+, Cu^{2+}, Ni^{2+}, Ru^{3+}) to the dendrimer solution [43]. This process is usually carried out in aqueous media, however, in some cases, organic solvents have been used [56]. Different generations of PAMAM dendrimers having complexing (−NH) and non-complexing (−OH) peripheral groups have been used for this purpose. It is noteworthy to mention that other types of dendrimers have also been used successfully for the synthesis of DENs [57]. Metal ions partition into the interior tertiary amine groups of the dendrimer for a complete complexation of the dendrimer-metal ions composite. The extent of this complexation process

can be monitored using simple characterisation techniques such as UV-vis, EPR, MALDI-MS, and XPS [58]. For example, during the complexation of PAMAM dendrimers with Cu^{2+} ions for the preparation of Cu-DENs, a strong ligand-to-ligand charge transfer (LMCT) band at λ 300 nm and a 605 nm shift of the d-d optical transition is observed [59]. Subsequent addition of an excess reducing agent (such as $NaBH_4$ or H_2) to the dendrimer-metal ion composite result in the formation of mono-dispersed small nanoparticles trapped within the dendrimer cavities/framework. **Figure 2** gives an example of a schematic illustration for the synthesis of dendrimer encapsulated mono- and bimetallic Ru nanoparticles. Various synthetic methods for the preparation of bimetallic DENs are detailed elsewhere [42, 60].

In cases where dendrimers used for the complexation of metal ions possess primary groups, such as amine-terminated dendrimers, the reduction process may lead to the formation of nanoparticles that are not entirely encapsulated within the dendrimer frameworks. The coordination of metal ions to the primary amine groups in such instance can be avoided by carrying out the synthesis under acidic conditions. This is because, the commonly used dendrimers, PAMAM, are polyprotic bases possessing surface primary amine groups that are more basic than interior tertiary amine groups. As such, acidic conditions have been shown to effectively drive the coordination of metal ions to the tertiary amines while avoiding coordination with surface primary amine groups on the periphery [61].

There are several advantages outlined for the use of dendrimers as hosts materials for metal nanoparticles intended for utilisation in catalysis in various reactions: (i) because dendrimers themselves are of a uniform structure and composition, the yielded encapsulated nanoparticles are of well-defined shape [62], (ii) since the nanoparticles are encapsulated within the dendrimer frameworks, agglomeration, which may lead to deactivation during catalysis is greatly circumvented [63], (iii) the nanoparticles trapped within the dendrimer framework are confined primarily by steric effects and a significant portion of their active atoms is unpassivated and available to take part in catalytic reactions [10], (iv) dendrimer branches can be used as selective gates to allow access of substrates molecules to the catalytically active
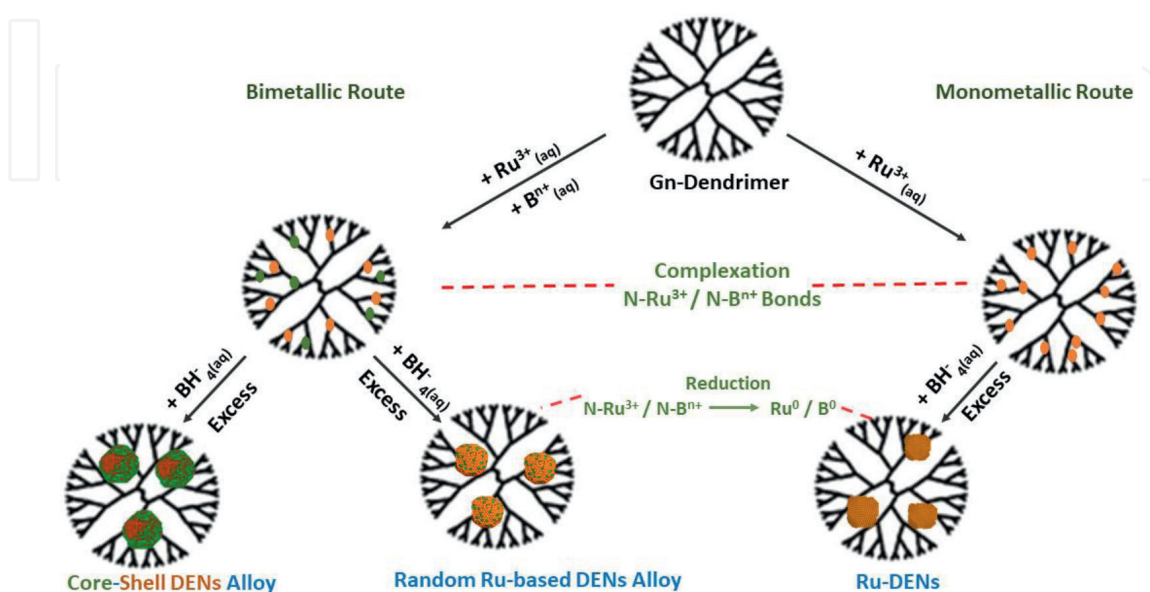
Figure 2.
Schematic illustration for the synthesis of monometallic and bimetallic Ru-DENs.

encapsulated metal nanoparticles [64], and (v) the primary groups on the periphery of the dendrimers can be tailored to control the solubility of the hybrid nanocomposite and used as a "vehicle" for linking nanoparticles to the surfaces and other polymers for "heterogenization" of colloidal nanoparticles [65, 66].

With the advancement of technologies in recent years, these as-synthesised DENs catalysts have been characterised using more sophisticated techniques [67]. This characterisation is carried out to determine physical and chemical properties such as the actual size, surface structure, valency, chemical composition, electron band gap, light emission, absorption, and scattering and diffraction properties. The most commonly used characterisation techniques for this purpose include nuclear magnetic resonance spectroscopy (NMR), infra-red spectroscopy (IR), ultra-violet and visible spectroscopy (UV-vis), transition electron microscopy (TEM), scanning tunnelling microscopy (STM), scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (RDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), extended X-ray adsorption fine structure spectroscopy (EXAFS), X-ray absorption near-edge spectroscopy (XANES), atomic force microscopy (AFM).

Crooks and co-workers pioneered the synthesis of DENs. The first example of the synthesis of DENs was reported for Cu-DENs by the same research group of Crook [59]. Fourth-generation hydroxyl-terminated PAMAM dendrimers (G4-PAMAM-OH) was used as a templating agent for this purpose. UV-vis spectroscopy was used to monitor the coordination of Cu^{2+} ions with the tertiary amine groups of dendrimers. For example, the weak, broad absorption band responsible for aqueous Cu^{2+} ions at λ 810 nm significantly shifted to 605 nm and the emergence of a new strong band at 300 nm in the case of G4-PAMAM/Cu^{2+} composite solution. Titration experiments conducted for the coordination of Cu^{2+} ions to the tertiary amine groups of the dendrimers led to the conclusion that each Cu^{2+} ion is more likely to coordinate with two tertiary amine groups of the G4-PAMAM-OH dendrimers. Subsequent reduction of the G4-PAMAM/Cu^{2+} composite solution by excess $NaBH_4$ resulted in the formation of Cu-DENs having an average particle diameter of less than 1.8 nm as determined by TEM. The formation of these Cu-DENs was also evidenced by the disappearance of the initial bands of the G4-PAMAM/Cu^{2+} composite solution. Additionally, a change in solution colour from blue to golden brown colour was observed as an indication for the formation of Cu-DENs.

Since then, there has been a plethora of publications covering the use of dendrimers for the encapsulation of other noble and non-noble metals such as Pt, Au, Ag, Pd, Rh, and Ru [41, 67]. However, this chapter will exclusively put more focus on the synthesis of Ru-DENs (colloidal) and Ru-DENs derived supported Ru catalysts as well as their applications in various reactions such as hydrogenation of alkenes or carbonyl compounds, and oxidation of alcohols. Additionally, the bimetallic alloys of Ru-based DEN catalysts prepared will also be fully explored. Ruthenium based catalysts (supported or unsupported) were rarely used in the past to catalyse hydrogenation reactions involved in the petrochemical industry and chemical synthesis. Instead, optimum activities and selectivities of the desired products for these reactions were achieved by utilisation of other catalysts such as platinum, palladium, rhodium, or nickel. However, ruthenium catalysts have been found to exhibit superior activity in such reactions in the past few decades [68–70]. For example, a review article entitled "heterogeneous Ru catalysts as the emerging potential superior catalysts in the selective hydrogenation of bio-derived levulinic acid to γ-valerolactone: effect of particle size, solvent, and support on activity, stability, and selectivity" has been recently published by Maumela et al. [71].

The first example for the synthesis of dendrimer-encapsulated Ru nanoparticles was reported by Lafaye et al. [72]. Aqueous solutions of hydroxyl-terminated fourth generation PAMAM dendrimers and $RuCl_3$ were used for the preparation of the dendrimer/ metal ion composite using a metal ion to dendrimer molar ratio of 40:1. The coordination of the Ru^{3+} ions to the dendrimer amine groups was monitored by UV-vis spectroscopy in this case. Absorption peaks at 286 and 400 nm were both attributed to the complexation of the Ru^{3+} ion and the tertiary amine groups within the PAMAM dendrimer template. However, when this complexation is allowed to occur for a lengthy period of time (3 days) under inert conditions, the shift in the initial peaks was observed. For example, the absorption peak initially at 286 nm shifted to 280 nm, while that at 400 nm shifted to 407 nm. These peaks were still assigned to the Ru-amine complexation that formed within the dendrimer structure. The reduction of the composite solution was carried out by bubbling H_2 for 1 h at room temperature, yielding nanoparticles with a narrow size distribution and an average diameter of 1.2 nm (see **Figure 3a**). These as-synthesised Ru-DENs were subsequently immobilised onto Al_2O_3 support *via* wet impregnation method, followed by the removal of the dendrimer template by thermal treatment at 300°C. The thermal treatment, however, resulted in an increase in particle size by almost 50%, with average size being measured to be 2.0 nm (see **Figure 3b**),
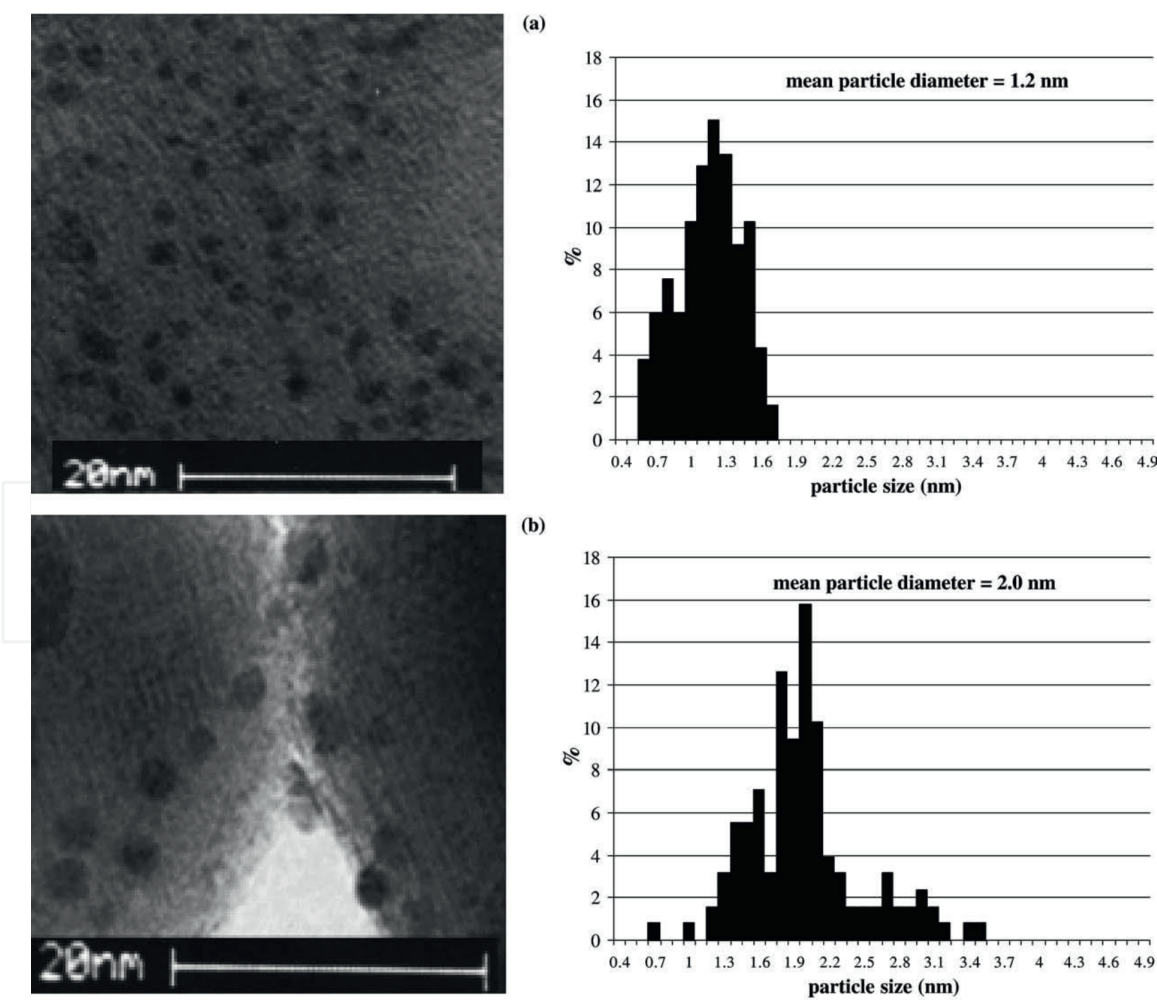

Figure 3.
HRTEM images and metal particle size distribution of (a) the Ru-G$_4$OH PAMAM dendrimer nanocomposite precursor, (b) a 1%wt Ru/Al$_2$O$_3$ catalyst prepared from the Ru-G$_4$OH PAMAM dendrimer nanocomposite precursor and reduced for 2 h at 300°C [72].

though still well-dispersed on the alumina support surface. The increased in particle sizes was attributed to sintering which may have occurred during the dendrimer removal process. No catalytic applications experiments were reported for these catalysts.

The same research group investigated the effect of support material on the sintering by immobilisation of dendrimer-derived Ru nanoparticles onto three different support materials (low-surface-area γ-alumina, high-surface-area γ-alumina, and SiO_2) few years later [73]. In this case, the ability of dendrimers to allow for the synthesis of particles with varying sizes was tested by using different generations (G 4–5) of hydroxyl-terminated PAMAM dendrimers as well as dendrimer-to-metal molar ratios were used to prepare the Ru-DEN precursors. For instance, for generation 4 dendrimers, a dendrimer-to-metal molar ratio of 1:20 and 1:40 were used, while for generation 5, dendrimer to metal ion molar ratios of 1:60 and 1:100 were used. The average particle sizes determined by high resolution TEM were measured to be 0.9 nm and 1.2 nm for 1:20 and 1:40 molar ratios, respectively. For generation 5, particle sizes for 1:60 and 1:100 molar ratios were determined to both have average sizes of 1.4 nm. These average particle sizes were found to be 10–20% greater than the expected calculated theoretical average sizes. As in the previous case, the immobilisation of these DEN precursors onto different support materials resulted in an increase of particle sizes by 75%, attributed to sintering. However, this sintering was found not to be induced by the type of support materials used.

4.1 Synthesis, characterisation and catalytic applications of unsupported colloidal mono- and bimetallic Ru-DENs

4.1.1 Monometallic Ru-DENs/DSNs for reduction of 4-Nitrophenol

4-Nitrophenol (4-NP) and its derivatives are considered among some of the major pollutants, hazardous waste [74]. The United State Environmental Protection Agency (US EPA) has labelled these pollutants as priority toxic pollutants [1]. 4-NP and its derivatives are generally generated from agricultural sectors and manufacturing industries. For example, it is a waste product from companies that manufacture explosives, dyes, and other chemical products [75]. This has rendered these organic compounds to be the most common non-biodegradable and toxic persistent pollutants in industrial, agricultural wastewater and aquatic environment [76]. Moreover, 4-NP is produced in large quantities worldwide and is considered the most toxic as compared to other mono-nitrophenols [1]. The presence of nitrogen group on this compound makes it more stable, as a consequence, chemical and biological degradation of wastewater polluted with 4-NP is challenging. Therefore, the development of sustainable and environmentally friendly methods to remove these compounds from wastewater is of great importance.

More recently, Ru-DEN catalysts have been found to exhibit excellent activity in the conversion of 4-NP to 4-aminophenol (4-AMP) and other organic pollutants in the presence of excess reducing agents such as $NaBH_4$ or H_2 [38]. 4-AMP, on the other hand, is a commercially valuable intermediate for the synthesis of anti-pyretic and analgesic drugs [77]. The reduction of 4-NP is analysed by monitoring the change in the absorbance peak at around λ 400 nm (maximum absorption peak for 4-NP) and the emergence of a new absorption peak around λ 310 nm, which is attributed to the formation of the 4-AMP product. This reaction is accompanied by the formation of isosbestic points on the UV-vis spectra, signalling that there is no side product (except 4-AMP) formed.

One of the earliest example of Ru-DENs catalysed reduction of 4-NP to 4-AMP can be traced back to the work published by Antonels and Meijboom [78]. Generation

4–6 of commercial hydroxyl-terminated PAMAM dendrimers were employed for the synthesis of Ru-DENs with varying particle sizes. Characterisation techniques such as IR, UV-vis, and TEM were used for the synthesis process as well as determining the resulting Ru-DENs morphology and sizes. Notably, the increase in dendrimer generation resulted in an increase in average particle sizes. For instance, the nanoparticles, with almost-spherical shape, prepared using generation 4, 5, and 6 PAMAM dendrimers were determined to have average particle sizes of 1.2 ± 0.07 nm, 1.4 ± 0.12 nm, and 2.2 ± 0.26 nm, respectively. It should be noted, however, that different metals to dendrimer molar ratios were used for different dendrimer generation. **Figure 4** shows TEM images and particle size distribution reported in Ref. [78].

The catalytic investigation of these Ru-DENs catalysts was performed in the selective reduction of 4-NP to produce 4-AMP. This reaction was set up under first-order
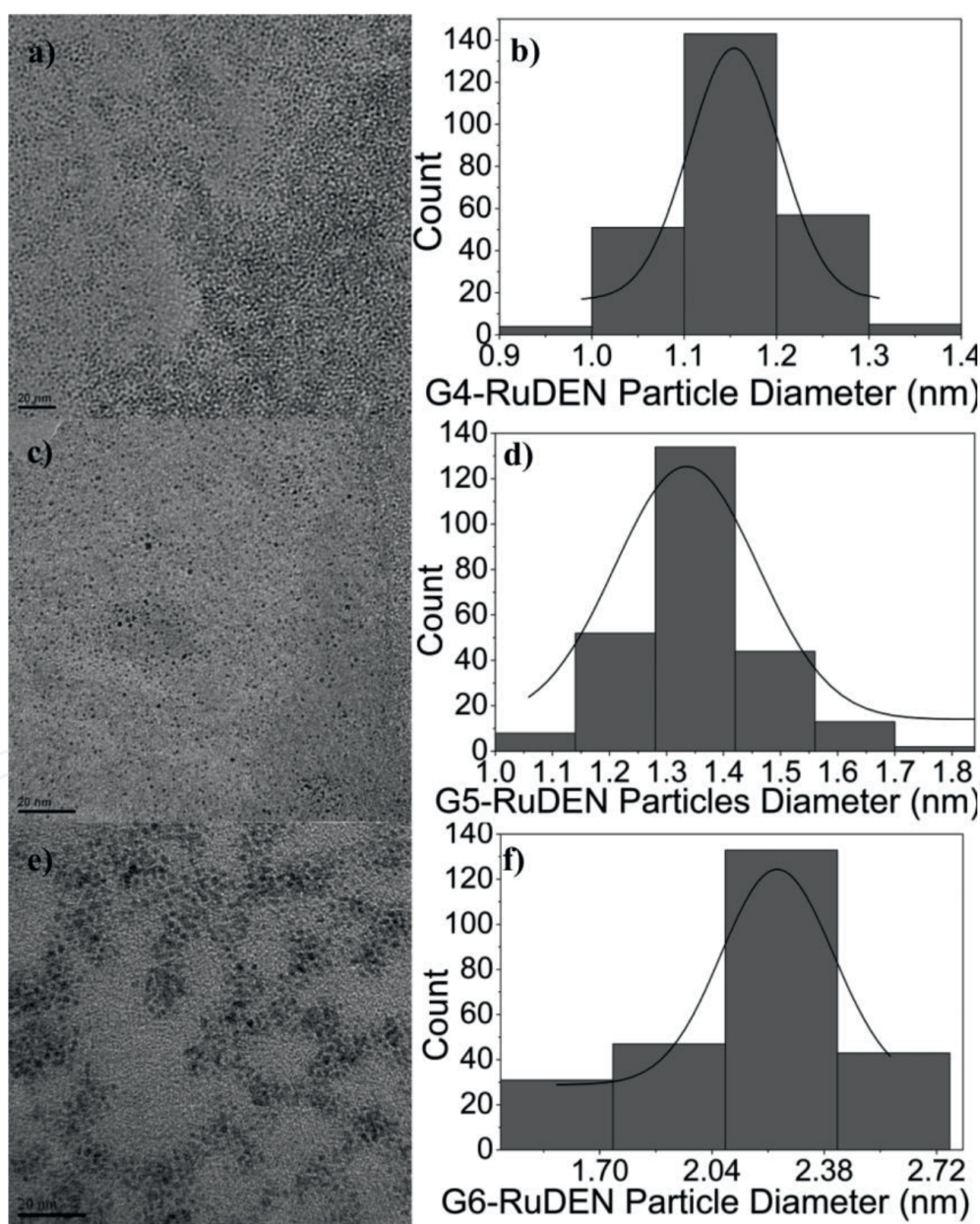

Figure 4.
(a) HRTEM image of G4-RuDEN, (b) histogram for the particle distribution for G4-RuDEN, (c) HRTEM image of G5-RuDEN and (d) histogram for the particle distribution for G5-RuDEN, (e) HRTEM image of G6-RuDEN, and (f) histogram for the particle distribution for G6-RuDEN [78].

conditions, by ensuring that the reducing agent, $NaBH_4$, is always in large excess relative to the 4-NP substrate. The calculated apparent rate constants (k_{app}) for the generation 4, 5, and 6 dendrimer catalysts were determined to be 3.96×10^{-4} s^{-1}, 6.40×10^{-4} s^{-1}, and 2.90×10^{-4} s^{-1}, respectively. The kinetic analysis was done based on the assumption that the reaction occur on the nanoparticle surface and hence follow the Langmuir-Hinshelwood mechanism. For this purpose, two sets of kinetic data were collected. One set of k_{app} data was collected by varying the concentration of 4-NP while keeping BH_4^- concentration and temperature constant. The second set of k_{app} data was collected by varying the BH_4^- concentration while the 4-NP concentration and temperature were kept constant. It was observed that the apparent rate constant appear to increase with the increase in BH_4^- concentration. On the contrary, the k_{app} was found to decrease as the concentration of 4-NP is increased. The observed decrease in the apparent rate constant as 4-NP is increased was attributed to the fact that as the more 4-NP is injected into the reaction system, the catalyst's surface becomes more saturated as less active atoms are available for the BH_4^- to react with the catalyst. This suggests that there is a competition for adsorption between the substrate and the reactant with the nanoparticle surface.

Another example of Ru-DENs catalysed reduction of 4-NP was reported by Murugan and Pakrudheen [79]. Their study entails the initial synthesis of the generation 2 amphiphilic poly(propylene imine) (PPI) dendrimer template. The characterisation of the synthesised dendrimer template was done using various techniques such as FT-IR, NMR, and MALD-TOF. The as-synthesised dendrimer was further utilised for the stabilisation and encapsulation of Ru nanoparticles (Ru-DENs), which were characterised using UV-vis, FT-IR, TEM, and XRD. For example, characterisation by TEM revealed that the formed Ru-DENs had an average particle size of 0.8 ± 0.3 nm. The formation of these ultra small-sized Ru-DENs was attributed to the smaller hydrodynamic diameter of PPI dendrimers as compared to that of PAMAM counterparts. Therefore, the interaction between the metal ions and the tertiary amine of the PPI dendrimers is believed to be stronger, allowing for the formation of smaller nanoparticles. The catalytic properties of the prepared Ru-DENs were evaluated in the reduction of 4-NP to yield 4-AMP. As with other related studies, the pseudo-first-order reaction kinetics conditions were applied in this case too. The observed reaction rate constant of 15.95×10^{-4} s^{-1}. The increase in the concentrations of BH_4^- and the catalyst while keeping other parameters constant was found to result in an increase in the reaction rate constant. For instance, an increase in the borohydride concentration from 20 mM to 60 mM resulted in the increase of the rate constant from 4.66×10^{-4} s^{-1} to 8.92×10^{-4} s^{-1}. Similarly, an increase in the rate constant from 7.93 to 15.95 was observed as the concentration of the catalyst is varied from 0.02 mM to 0.08 mM.

4.1.2 Bimetallic of Ru-based DENs/DSNs catalysts for reduction of 4-Nitrophenol and hydrogenation reactions

A synthesis of a series of Ru-Ni bimetallic DEN catalysts via intradendrimer redox displacement was reported by Marvin et al. [80]. In their study, nickel was chosen as an appropriate metal partner for a displacement method to prepare Ru and RuNi bimetallic DEN catalysts. Generally, the displacement synthetic method was carried out by the initial formation of Ni DENs (1:30 of dendrimer: metal ion molar ratio) using commercially obtain generation 4 hydroxyl-terminated PAMAM dendrimer. The synthesis of Ru or bimetallic RuNi DENs can be obtained by addition of equimolar of Ru^{3+} or any molar ratio smaller than that initially used for Ni^{2+} for the formation

of Ni DENs, respectively. For instance, a variety of bimetallic RuNi DEN catalysts were prepared via displacement using molar excess ratios ranging between 5 and 20 for Ru^{3+} and Ni^{2+}. The resulting bimetallic DEN catalysts were labelled as Ru_5Ni_{30}, $Ru_{10}Ni_{30}$, $Ru_{15}Ni_{30}$, and $Ru_{20}Ni_{30}$-DENs. The catalytic activity of these DEN catalysts was evaluated in the reduction of 4-NP. All RuNi bimetallic DEN catalysts were found to display a superior activity as compared to either monometallic Ru- or Ni-DEN catalysts. Among all bimetallic DEN catalysts, the highest average rate constant ($2.2\ s^{-1}$) was observed for the $Ru_{10}Ni_{30}$ DEN catalyst. On the contrary, the nickel dominated bimetallic catalyst (Ru_5Ni_{30}) showed the smallest average catalytic rate ($0.95\ s^{-1}$).

Wang and Peng reported the synthesis of new class of fourth-generation poly(propylene imine) dendrimer functionalised with 32 triolefinic 15-membered microcycles on the surface (G5-M). The synthesised G4-M dendrimer was characterised using NMR, IR, and elemental analysis (EA). The prepared G4-M dendrimer was utilised for the fabrication and stabilisation of bimetallic RuRh nanoparticles (RuRh-DSNs) via co-complexation method [81]. Stabilisation was achieved by ensuring that metal ions of Ru and Rh are coordinated with both the surface groups and the tertiary of the PPI dendrimer prior to the reduction of the dendrimer-metal ions composite with excess $NaBH_4$. In this study, dendrimer stabilised bimetallic RuRh nanoparticles with various molar ratios (G4-M (Ru_xRh_y)) were prepared and characterised using high-resolution TEM and EDS techniques to determine the particle sizes and morphology. The average nanoparticles diameter for the G4-M (Ru_7Rh_3), G4-M (Ru_5Rh_5), G4-M (Ru_3Rh_7) bimetallic catalysts were determined to be 6.1 ± 1.4 nm, 4.5 ± 1.5 nm, 7.7 ± 2.1 nm, respectively. The morphology of these nanoparticles was observed to be nearly uniform and almost spherical with a Gaussian-like size distribution.

The catalytic activity of the RuRh bimetallic nanoparticles was investigated in the hydrogenation of nitrile-butadiene rubber (NBR). The hydrogenation capability of these catalysts was measured in terms of the degree of hydrogenation (HD). All bimetallic RuRh DSNs were found to give larger HD as compared to the corresponding monometallic Ru or Rh DSNs, despite the latter having smaller average particle sizes. The G4-M (Ru_3Rh_7 catalyst was found to exhibit higher catalytic hydrogenation activity than the other evaluated two bimetallic ones. The recycling study performed using the G4-M (Ru_3Rh_7 catalyst showed that only a slight loss of catalytic activity was observed even after 3 reaction cycles. Higher catalytic activities displayed by the bimetallic catalysts were attributed to the electronic effect. Some other catalytic reactions involving monometallic and bimetallic colloidal Ru-based DEN catalysts have been summarised in **Table 1**.

4.2 Synthesis, characterisation and catalytic applications of supported mono- and bimetallic Ru-DENs

These coming sections will focus on the synthesis and characterisation of supported monometallic Ru-DEN and bimetallic Ru-based DEN catalysts as well as their catalytic applications in the hydrogenation reactions involving aromatic compounds (such as phenols), methanol and biomass-derived molecules (such as levulinic acid).

4.2.1 Monometallic supported Ru-DENs/DSNs catalysts for hydrogenation reactions

More recently, an interesting study on the synthesis of new two types of second-generation dendrimers using the divergent approach has been reported by Keshtiara et al. [91]. The first-generation dendrimer (a precursor for second-generation) was

Catalyst	Substrate	Time (h)	Conversion (%)	Current density/ mA•⁻cm²	TOF (h⁻¹)	Ref
Ru_{40}-DENs	LA	5	>99		5025	[82]
Ru_{40}@Meso-TiO₂	LA	5	92		3878	[82]
Ru_{40}@Meso-SiO₂	LA	5	94		5314	[82]
G4-RuSil60	Citral	4	84		—	[83]
G5-RuSil60	Citral	4	22		—	[83]
G6-RuSil60	Citral	4	12		—	[83]
0.15 wt% G4-RuSil100	Toulene	—	73.5		—	[84]
Ru-DENs	PMHS	2	44		—	[85]
Ru7Rh3-DENs	PMHS	2	71		—	[85]
Ru5Rh5-DENs	PMHS	2	79		—	[85]
G4OH-Pt₂₀Ru₂₀/C[a]	Methanol	—	—	17.8 ± 2.4	—	[86]
G4OH-Pt₂₀Ru₂₀/C[b]	Methanol	—	—	13.6 ± 4.6	—	[86]
20% Pt-Ru PAMAM/ CNF	Methanol	—	—	0.25	—	[87]
PPI-dendr-PEG-Ru-90	Benzene	2	99		—	[88]
PPI-dendr-PEG-Ru-20	Benzene	2	>85		—	[88]
PPI-dendr-PEG-Ru-90	Phenol	2	>80		—	[88]
PPI-dendr-PEG-Ru-20	Phenol	2	>70		—	[88]
Ru_{np}-nSTDP	Cyclooctene	4	93		13.84	[89]
Ru_{np}-nSTDP	Cyclohexene	4	90		13.39	[89]
Ru_{np}-nSTDP	Benzyl alcohol	4	90		17.85	[89]
Dendrimer-Derived PtRu/SiO₂	3,4-epoxy-1-butene	—	—		1162[c]	[90]

PMHS = poly(methylhydro)siloxane.[a]Catalyst activated at 500°C.
[b]Catalyst activated at 400°C.
[c]min⁻¹.

Table 1.
Summary of dendrimer stabilised/encapsulated Ru-based catalysed reactions.

prepared from hexakis(bromomethyl)benzene (hex) core and vanillin branches. The second step for the synthesis of two types of second-generation dendrimers involves the reaction of the first-generation dendrimer precursor with *ortho*-aminopyridine (py) and *para*-aminobenzoic acid (bza) to produce second-generation dendrimers, hexpyD and hexbzaD, respectively. The produced dendrimers were characterised using techniques such as attenuated total reflectance-infrared (ATR-IR), field-emission scanning electron microscopy (FE-SEM), NMR, and TEM, among others. These dendrimers were subsequently reacted with Ru^{3+} ions (in DMF solvent) to form hexanuclear Ru (III) chloride complexes. The formed complexes were each immobilised on a silica support in 2-methoxyethanol solvent and allowed to mix for 24 h. An excess of $NaBH_4$ was then added to these complexes-silica mixtures, resulting in the formation of dendrimer encapsulated/stabilised Ru nanoparticles immobilised on silica support (S-D/RuNPs).

TEM analysis of the S-D/TEM catalysts revealed that the Ru nanoparticles synthesised from hexpyD and hexbzaD have average sizes ranging from 0.2–4 nm to 0.6–20 nm, respectively. Small sized-Ru nanoparticles obtained for S-D/RuNPs composite material was attributed to the steric hindrance that exists on the periphery of the hexpyD dendrimer template. **Figure 5** shows TEM images (captured on different scales) for silica supported Ru nanoparticles synthesised using hexpyD dendriemer. These TEM results correlated well with the XRD analysis. For example, the broad peaks observed around $2\theta = 21.8°$ on the XRD patterns for S-D/RuNPs synthesised from hexpyD and hexbzaD (**Figure 6a** and **b**) were attributed to the presence of amorphous silica. While the peaks observed at $2\theta = 21.8°$ (**Figure 5a** and **b**) were assigned to the existence of RuO that may have formed because of the surface oxidation of metallic Ru NPs. On the other hand, isotherms collected from BET N_2 adsorption-desorption analysis showed characteristics of mesoporous materials (type IV isotherms) and possess relatively high BET surface area and narrow pore size distribution (see **Figure 7a** and **b**). The specific surface area of 165 and 303 m^2/g was measured for S-D/RuNPs derived from hexpyD and hexbzaD, respectively.

The catalytic evaluation of these S-D/RuNPs catalysts was performed in the hydrogenation of citral to 3,7-dimethyloctanol. Significant conversion rates (about 40%) were observed for both catalyst only 30 min of the reaction at the optimum reaction conditions applied and as such, turnover frequencies (TOFs) for these catalysts were calculated based on the first 30 min of the reaction. The S-D/RuNPs prepared using
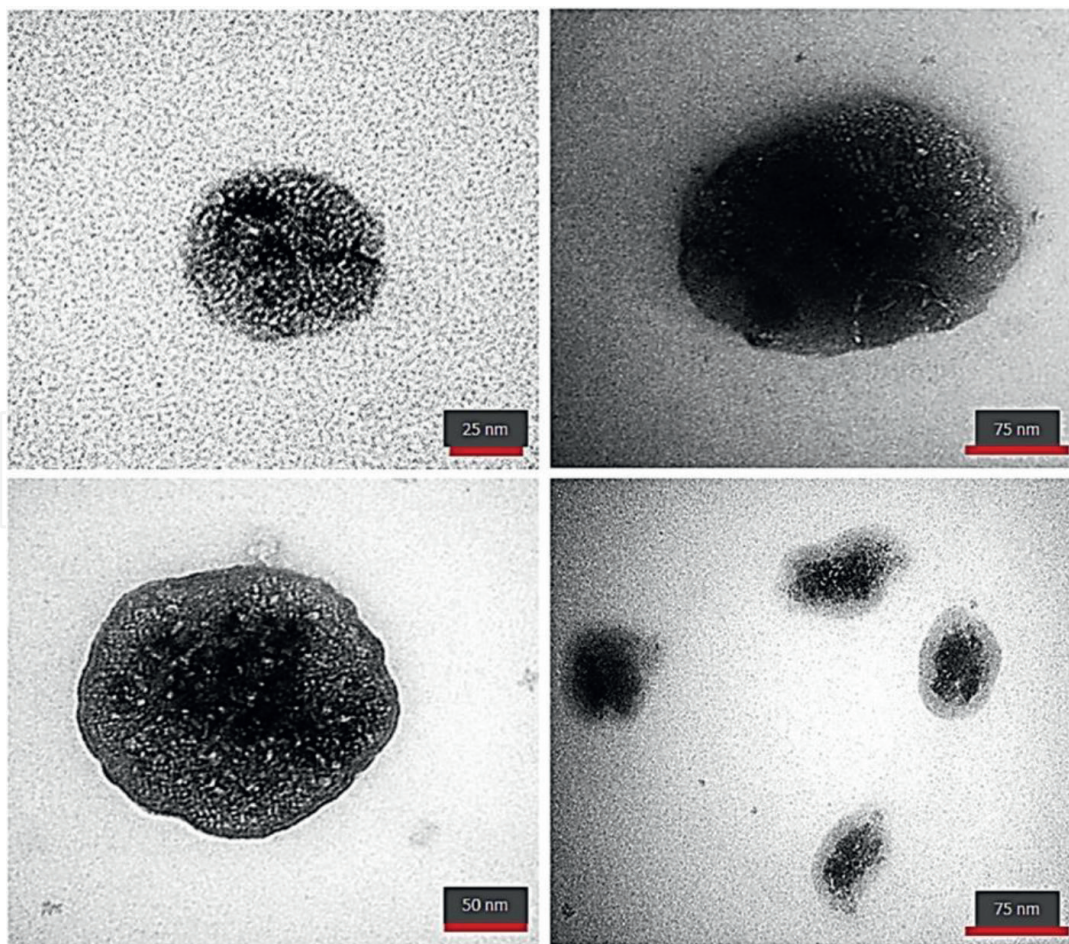

Figure 5.
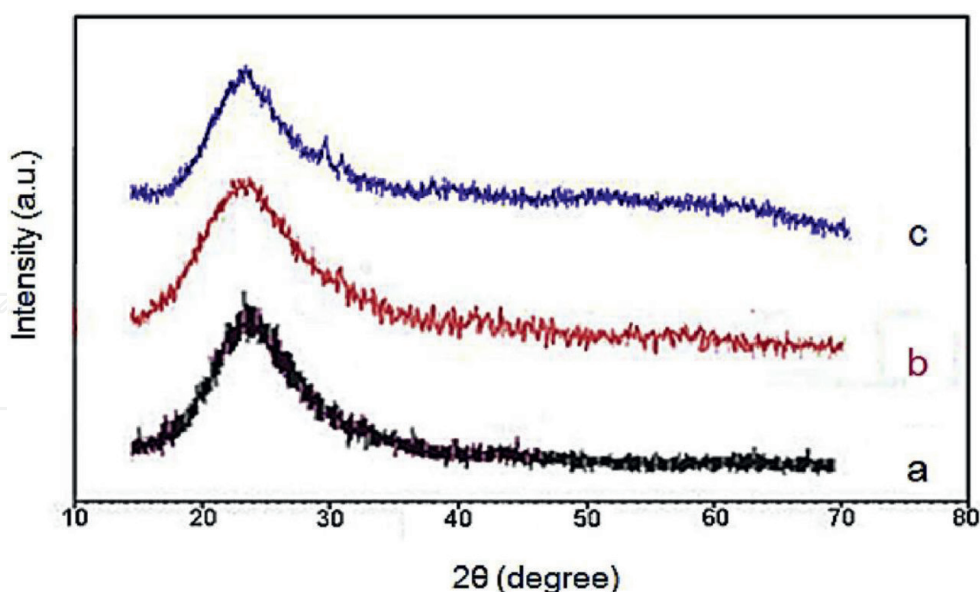*TEM images of S-D/RuNPs prepared from hexpyD [91].*

Figure 6.
XRD patterns of amorphous silica (a), and S-D/RuNPs prepared from hexpyD (b) and hexbzaD (c) [91].
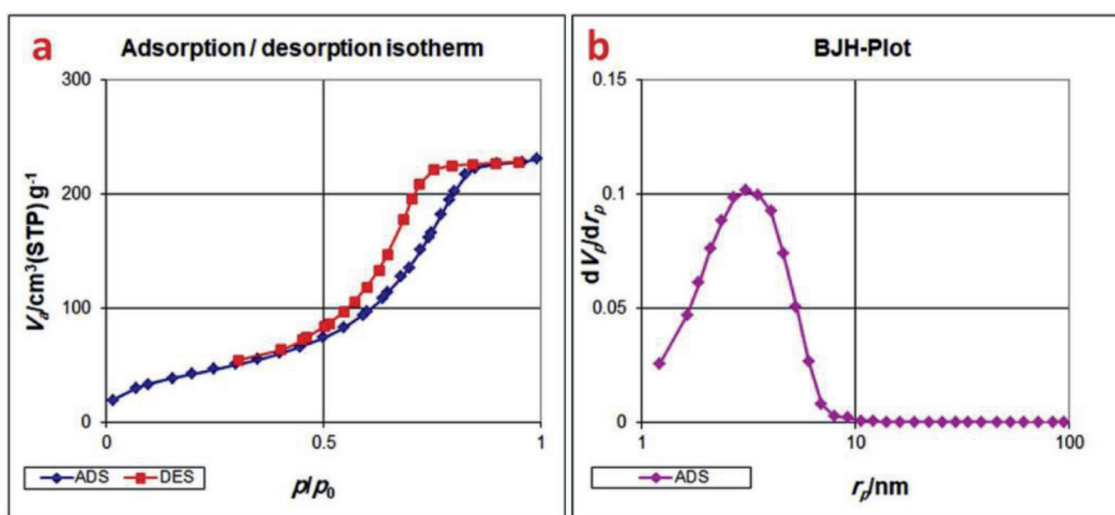

Figure 7.
Nitrogen adsorption-desorption isotherms (77 K) (a) and pore size distribution (b) of S-D/RuNPs prepared from hexpyD [91].

the hexbzaD dendrimer was found to exhibit greater TOF as compared to the one prepared using the hexpyD dendrimer. This was attributed to less sterically hindered surfaces of the hexbzaD dendrimer as well as the large particles for RuNPs prepared from hexbzaD, which provide a large number of adsorption sites.

The hydrogenation of alkyl-substituted phenols to the corresponding alkyl substituted cyclohexanols over organo-silica supported dendrimer-stabilised Ru nanocatalysts catalyst has also been reported by Karakhanov et al. [92]. In this case, two types of silica support materials were fabricated through the modification of the dendrimer template. Ideally, the PPI dendrimers were modified with (3-glyidoxy-propyl)trimethoxysilane using ethanol as a solvent. After this, the acid-catalysed hydrolysis and polymerisation of $Si(OEt)_4$ occur for the formation of ordered porous dendrimer-silica materials (dendr-G3-SiO_2). Alternatively, mesoporous dendrimer-silica materials were prepared by the addition of aqueous Pluronic P123 polymer to

the previously modified dendrimer-silica materials (dend-G3-*meso*-SiO$_2$). The PPI dendrimers were playing the templating role for the pore formation for both cases. These materials were thoroughly characterised using IR, XPS, NMR, and TEM to confirm the coordination of the dendrimer with the silica support.

The synthesis of Ru nanoparticles immobilised onto these dendrimer-modified silica supports was carried out by using the wetness impregnation method, which involved the addition of an aqueous solution of Ru^{3+} ions to either of the dendr-G3-SiO$_2$ or dendr-G2-*meso*-SiO$_2$ support networks. This resulted in the coordination of Ru ions with the amino groups of the dendrimer frameworks. The reduction of Ru^{3+} ions was carried out using NaBH$_4$ in water-ethanol medium, at room temperature, resulting in the formation of dendr-G3-SiO$_2$-Ru and dendr-G2-*meso*-SiO$_2$-Ru catalysts. The average Ru nanoparticles in the dendr-G3-SiO$_2$-Ru and G2-*meso*-SiO$_2$-Ru catalysts, as determined byTEM analysis were found to be 0.97 ± 0.09 nm and 1.28 ± 0.09 nm, respectively. These catalysts were evaluated in the hydrogenation of alkyl substituted phenols. The dendr-G2-*meso*-SiO$_2$-Ru catalyst was found to generally exhibit superior activity as compared to the dendr-G3-SiO$_2$-Ru catalyst. For instance, the hydrogenation of meta-substituted phenol turnover frequency for the hydrogenation of meta-substituted phenol was calculated to be 6090 h^{-1} for the dendr-G2-*meso*-SiO$_2$-Ru catalysts as compared to 1841 h^{-1} obtained for the dendr-G3-SiO$_2$-Ru catalyst under similar reaction conditions. Both catalysts, however, displayed appreciable stability as could be re-used several times without any significant loss in their initial activities.

The same research group of Karakhanov also reported the hydrogenation of a sustainable, biomass-derived molecule, levulinic acid (LA) and its esters to γ-valerolactone (GVL) catalysed by similar type of catalysts (G3-dendr-SiO$_2$-Ru G2-dendr-*meso*-SiO$_2$) as those used for the hydrogenation of phenols [93]. The reaction rate and the yield for GVL were found to be influenced by several factors such as temperature, H$_2$ pressure, solvent, and support nature. For example, the mesoporous silica supported dendrimer stabilised Ru catalyst gave quantitative GVL yields (above 95%) within 2 h when the reaction temperature is set at 120°C. However, when the reaction temperature is decreased from 120 to 80°C, it took 6 h to obtain a quantitative yields of GVL. Similarly, when excess amount of water solvent is used (LA:H$_2$O = 1:2) the conversion of LA was found to also increase. The promoting effect of water on the hydrogenation of LA has also been reported by other authors [71]. Just like in the case of catalytic hydrogenation of phenols (using similar catalysts) reported by this group, the G2-dendr-*meso*-SiO$_2$ catalyst was found to display superior activity compared to its counterpart, G3-dendr-SiO$_2$-Ru catalyst under similar reaction conditions. This enhanced activity observed for the G2-dendr-*meso*-SiO$_2$ catalyst was attributed to the carrier structure of the catalyst.

4.2.2 Bimetallic supported Ru-DENs/DSNs catalysts for hydrogenation and oxidation reactions

Bimetallic Ru-containing DEN catalysts have also been reported to exhibit superior catalytic activity, particularly in reactions such as oxidation of methanol. Of these Ru-based bimetallic DEN catalysts, supported Pt-Ru dendrimer encapsulated/stabilised nanoparticles appear to have been well investigated, especially in the oxidation of methanol. For example, Calderón et al. reported the electro-oxidation of methanol catalysed by carbon-nanofibers (CNF) supported dendrimer stabilised Pt-Ru nanoparticles [94]. Different generations (G0–3) of PAMAM dendrimers were used for the stabilisation of the synthesised supported Pt-Ru bimetallic nanoparticles

in this case. The dendrimer generation was found to have an effect on the resulting bimetallic nanoparticles. For instance, TEM analysis revealed that nanoparticles synthesised using generation zero had low dispersion on the CNF support. Moreover, the average particle size was found to decrease with an increase in dendrimer generation. For example, the average nanoparticle size of 3.7 ± 0.1 nm was obtained for generation-zero dendrimer, while generation three nanoparticles had an average size of 1.9 ± 0.4 nm prior to heat treatment. The heat treatment applied to clean the surface of the nanoparticles (and possibly remove the organic dendrimer template) also generally resulted in an increase in average particle sizes irrespective of the dendrimer generation.

Preliminary catalytic activity of both sets of catalysts (non-heat treated and heat-treated) in the electrochemical oxidation of methanol was evaluated in the supporting electrolyte. The non-heat treated catalysts, particularly those prepared in generation 0, 2, and 3 dendrimers, showed high capacitive currents for the hydrogen adsorption-desorption process. The decrease in capacitive currents was observed for all heat-treated catalysts, indicating a possible removal of the dendrimer template during heat treatment process of the catalysts. The catalytic activities for electrochemical oxidation of methanol for all catalysts were done using voltamperometric studies. All heat-treated catalysts were found to have higher activities (high current densities) for methanol oxidation. This was attributed to the high content of Ru oxides on the surface of these heat treated catalysts, which is believed to enhance the oxidation of methanol.

Bimetallic PdRu nanoparticles prepared based on the stabilisation using third-generation PPI dendrimers crosslinked by hexamethylene diisocynate (HMDI) support have also been utilised for the catalytic hydrogenation of aromatic compounds such as benzene and its derivatives under two-phase condition [95]. The synthesised bimetallic PdRu nanoparticles were determined to have a small average size of 0.8 ± 0.1 nm by TEM Although the bimetallic PdRu catalyst showed an increased hydrogenation rate for benzene substrate (due to synergistic effect of Pd and Ru) as compared to its monometallic Ru catalyst counterpart, its (bimetallic) activity drastically dropped in the case of substituted aromatic compounds. This was attributed to the steric hindrance that exist in the third-generation dendrimer structure. **Table 1** contains a summary of the reported catalytic system involving supported monometallic and bimetallic dendrimer-derived Ru catalysts.

5. Effect of optimization/modification of dendrimer macromolecules on the size of the NPs

Cognizant of all the discussion on the leveraging of dendrimers for stabilisation and encapsulation of metal nanoparticles outlined in this chapter, it is imperative to highlight that the optimization of the dendrimer macromolecule structure has also been found to have an effect on the size of the formed NPs. The dendrimer macromolecules condition can be can be optimised in few ways. For instance, peripheral groups of the dendrimer can be functionalized or protonated. For example, dendrimer-metal composite synthesised using amine- or carboxylic acid-terminated dendrimers usually favours the complexation of the metal ions on both the periphery groups and the tertiary amines. Reduction of such dendrimer-metal ions composite will yield the mixture of both inter- and intradendrimer nanoparticles. The interdendrimer nanoparticles (DSNs) are usually bigger than

the intradendrimer nanoparticles (DENs). This is because DSNs are stabilised by primary groups and are therefore prone to agglomeration as opposed to the DENs. In order to avoid the formation of a mixture of both DSNs and DENs, the peripheral groups can be functionalized or protonated (pH adjustment) [42]. For example, the pH of the aqueous dendrimer solution can be adjusted to be in the range between pH 2 and 5 to protonate the primary amine groups, leaving tertiary available for complexation with metal ions. Subsequent reduction will favour the formation of small-sized, monodispersed, and nearly spherical DENs. Alternatively, the surface groups can be functionalized to quaternary ammonium terminated groups to circumvent complexation of metal ions with primary groups, which in turn promote the formation of DENs.

6. Conclusions

Dendrimers can be leveraged for the synthesis of stable and catalytically active Ru (and nanoparticles (and other noble metals). Different nanoparticle sizes of the Ru-DEN catalysts can be tailored by manipulation of the dendrimers-to-metal ions molar ratios. The size of the dendrimer and the encapsulated nanocatalyst can have an effect on the catalytic performance. Although the synthesis of these Ru-DENs (and other metal DENs) may look straightforward in theory, it is actually tedious and has to be carried out cautiously to avoid errors as very low concentrations are used, particularly for academic research purposes. Dendrimer-derived Ru catalysts have been proven to be excellent catalysts in the hydrogenation and oxidation reactions involving several substrates such as phenols, citral, and methanol. The use of emerging technologies such as liquid handling robotics can also assist in minimising these potential human errors. Although there is a plethora of research publications for the synthesis of DEN catalysts emerging from academic researchers around the globe, it must poignantly be hinted that commercial dendrimers are excessively commercially expensive for emerging researchers to afford, particularly from developing countries as those found in the African continent. Therefore, research on the use of low-cost, "in-house" synthesised dendrimers for nanocatalysts encapsulation must be promoted to enhance participation from emerging young researchers coming from poor countries or institutions. Additionally, although the use of these types of catalysts (DENs) have shown great potential to catalyse various reactions, their use in the manufacturing industries is still lacking.

Dendrimer-derived bimetallic Ru-based catalyst proved to have superior activity compared to monometallic Ru catalysts, particularly in reactions such as methanol oxidation and hydrogenation of aromatic compounds. However, the synthesis of Ru-DENs catalysts using sustainable and environmentally friendly reagents is yet to be exploited. For example, the use of environmentally friendly precursors and solvents for the synthesis of metal catalysts is still to be fully exploited. More importantly, synthetic methods that make use of sustainable and environmentally friendly templating agents such as biopolymers (such as chitosan) for the encapsulation of nanocatalysts must be developed.

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