

Review

## Chitosan as a Natural Polymer for Heterogeneous Catalysts Support: A Short Review on Its Applications

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**Abstract:** Chitosan, a bio-based polymer which has similar characteristics to those of cellulose, exhibits cationic behavior in acidic solutions and strong affinity for metals ions. Thus, it has received increased attention for the preparation of heterogeneous catalysts. Recent studies demonstrated that chitosan-based catalysts had high sorption capacities, chelating activities, stability and versatility, which could be potentially applied as green reactants in various scientific and engineering applications. This study intends to review the recent development of chitosan-based catalysts, particularly in the aspects of the main mechanisms for preparing the materials and their applications in environmental green chemistry. Studies on the preparation of catalyst nanoparticles/nanospheres supported on chitosan were also reviewed.

**Keywords:** chitosan; green chemistry; catalyst; polymer

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### 1. Introduction

Chitosan, a natural polysaccharide-based biopolymer, has attracted considerable attention in various scientific and engineering applications [1]. For instances, chitosan was extensively investigated in metal extraction [2–4], chemical synthesis reaction [5,6] and electrolyte-based fuel cells studies [7,8]. Chitosan was explored to be a mild and direct solid catalyst in organic synthesis without any post-modification [6,9,10]. However, most of the research efforts have been reported to prepare functional derivatives of chitosan

by chemical modifications to serve the desired useful purpose [11]. The benefits of using chitosan in different applications include the following: (1) it is low-cost and eco-friendly; (2) it has the desirable property of hydrophilicity; (3) it allows chemical or physical modifications to customize its property; (4) it is chemically stable (e.g., high thermal stability up to 280 °C), nontoxic and biodegradable; (5) it contains metal anchoring functional groups [1,7,12–16].

As recent developments for greener, cleaner and more sustainable chemistry are being driven by a shift from petrochemical-based feedstocks to biological materials [17], chitosan is of particular interest for application in catalysis. Chitosan exhibits great potential in chemical applications and is commonly used as a catalyst supporters to promote the efficiency of chemical reactions [5,18]. The presence of readily functionalizable hydroxyl and amino groups on the chitosan and its insolubility in organic solvents make it very attractive in the application [19,20]. Besides, chitosan can be easily modified chemically or physically to become a versatile supporting material [21].

Among all types of catalysis systems, recent advances in catalysts for chemical synthesis have switched from homogeneous systems to heterogeneous ones. Heterogeneous catalysis systems provide the advantages of easy catalyst removal, recovery and recycling [13,22]. Moreover, the use of chitosan as novel supporting materials for heterogeneous catalysis is on the rise, mainly due to its high affinity to metal ions [13,14,23]. The unique properties of chitosan also enhanced its applicability for further functionalization and immobilization of metal complexes through covalent attachment [20].

Recent efforts in chitosan researche have been made to explore new applications in the area of catalysis. Chitosan-metal catalysts have been investigated in the chemical reactions of hydrogenation [5,24,25] and adsorption [26]. In addition, chitosan was employed to immobilize photocatalysts for easy recovery as well as enhancement of photodegradation [27,28]. This review intends to provide an overview of current applications of chitosan as heterogeneous catalysts supports. A variety of appropriately functionalized catalysts using chitosan as supports are discussed. Table 1 summarizes various chitosan-metal catalysis systems that are currently reviewed in this study.

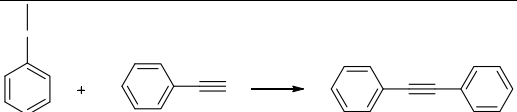
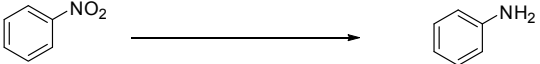
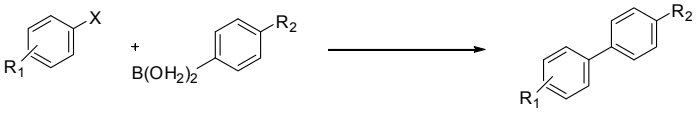
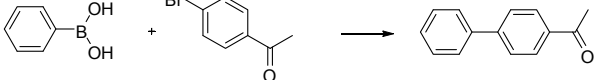
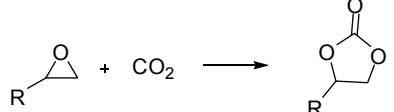
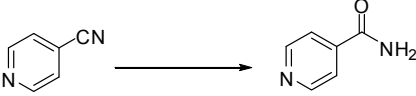
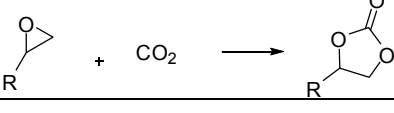
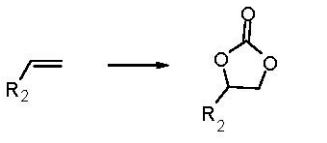
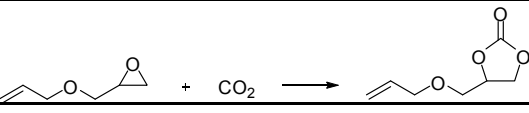
## **2. Preparation and Applications of Chitosan-Based Heterogeneous Catalysts**

### *2.1. Chemical Activation and Conversion*

#### *2.1.1. Metal Catalysts*

Recent research interest in using chitosan as catalytic metal supports has been due mainly to its high sorption capacity, stability of metal anions and physical and chemical versatility [14]. Preparation of chitosan-metal-based catalysts commonly involves co-precipitation by mixing chitosan into a metal solution in an alkaline solution, in order to coagulate the chitosan into nanoparticles or other forms. Metal nanoparticles that are formed strongly bound to chitosan encourage further investigation of its catalytic performance. Gold and silver nanoparticles are of special interest because of their unusual properties compared to bulk metals [29]. Transition metal ions such as palladium and ruthenium are also available for the development of hybrid catalyst complexes, as they are constantly applied to the synthesis of organic compounds.

**Table 1.** Summary of currently reviewed chitosan-metal catalysis systems.

Catalyst	Synthesis Reagents <sup>a</sup>	Reaction Scheme	Yield	Selectivity	Reference
Chitosan/Au	HAuCl <sub>4</sub>		70%	≥99%	[30]
Chitosan-Fe <sub>3</sub> O <sub>4</sub> -Pd	FeCl <sub>3</sub> ·6H <sub>2</sub> O, FeCl <sub>2</sub> ·4H <sub>2</sub> O, PdCl <sub>2</sub> , ethanol, NaBH <sub>4</sub>		>97%	99%	[5]
Chitosan/Pd(0)	Pd(OAc) <sub>2</sub> , dimethylsulfoxide, hydrazine hydrate, diglycidyl ether polyethylene glycol		98% <sup>b</sup>	-	[28]
Chitosan/Pd(II)	Pd(OAc) <sub>2</sub> , hexamethylene diisocyanate (HDI)		98%	-	[31]
Chitosan/quaternary ammonium salt	3-Chloro-2-hydroxypropyl trimethylammonium chloride, isopropanol		>73%	>99%	[19]
Chitosan/Ru	RuCl <sub>3</sub>		>99%	High	[11]
Functionalized chitosan	1-ethyl-3-methyl imidazolium halides		96%	>99%	[14]
Magnetic dual catalyst	FeCl <sub>3</sub> ·6H <sub>2</sub> O, FeCl <sub>2</sub> ·4H <sub>2</sub> O, Cobalt(II) acetylacetonate, quaternary triphenylphosphonium bromide		85%	79.6%	[18]
Quaternized chitosan	1-methyl-2-pyrrolidinone, NaI, CH <sub>3</sub> I		90%	>99%	[32]

<sup>a</sup> Main reagents exclude chitosan itself; <sup>b</sup> maximum yield.

## Palladium Catalysts

Palladium (Pd) is a well acknowledged transition metal catalyst for carbon-carbon bond formation (e.g., Heck or Suzuki reactions) [22,33], hydrogenation and acetalization [5] in the area of organic chemistry. The Pd catalysis usually allows selective reactions with high turnover numbers and turnover frequencies [34]. In addition, the amine groups on the chitosan-based catalyst are known to enhance the activity of Pd [35]. However, direct use of Pd as a catalyst is limited in homogeneous reaction systems due to the difficulties in separating and recycling the catalyst from the system [33]. Therefore, development of heterogeneous Pd catalysis systems is generally preferred.

Yi *et al.* [33] prepared a chitosan-supported Pd(0) catalytic system for Suzuki cross-coupling reactions. Preparation of the catalyst started with adsorption of Pd(II) onto the chitosan beads followed by adding hydrazine hydrate (in methanol) to convert Pd(II) to Pd(0). The as-prepared catalyst was cross-linked with either glutaraldehyde or diglycidyl ether polyethylene glycol to enhance its chemical and physical stability in reactions. Its catalysis test results revealed good catalytic activity for iodo- and bromoarenes under microwave activation. Microwave energy was useful to enhance the organic reactions and has been increasingly encouraged [31,36]. The addition of tetrabutylammonium bromide (TBAB) in the system also significantly enhanced the product yields by increasing the solubility of aryl halide for Suzuki cross-coupling in water. The as-prepared catalyst also showed high reusability after five cycles of uses due to its high stability and moderate leaching of Pd. The authors also confirmed that the randomly distributed  $\beta$ -(1,4)-linked-glucosamine and *N*-acetylglucosamine on chitosan made it suitable for water-compatible solid support of Pd in the Suzuki cross-coupling reaction.

To increase the affinity of Pd onto chitosan, Martina *et al.* [37] incorporated ultrasound to assist the cross-link of Pd(II) ions onto chitosan by interacting with hexamethylene diisocyanate. The sonication from ultrasound helped the removal of air bubbles in the bulk of chitosan derivatives and the breakdown of aggregated nanospheres [38]. Satisfactory yields of biaryl product were obtained under both microwave and ultrasound irradiations in the catalysis reaction with 4-bromoacetophenone and phenylboronic acid. However, a decrease of catalytic activity was observed after the third reuse. A similar approach was also developed by Schüßler *et al.* [39]. His research group proposed the use of hexamethylenediisocyanate to cross-link chitosan and load Pd. The as-prepared catalysts were then employed for the hydrogenation of substrates of cyclohex-2-enone, benzalacetophenone, 1,2-diphenylacetylene, and *N*-benzylidenaniline at mild conditions using a microwave reactor. Catalysis test results showed that the solvent used in reactions had nearly no influence on the selectivity of the reaction but it showed a great dependence on the conversion. The catalyst could be reused for up to ten times for hydrogenation of cyclohex-2-enone without showing a dramatic loss in immobilized metal content.

As magnetic material supported catalysts have revealed its insoluble and paramagnetic nature to enable easy and efficient separation from reaction mixture with an external magnetic field [5,30,35,40], a novel magnetic chitosan-based catalyst was proposed by Zhou *et al.* [5]. They used chitosan magnetite nanoparticles (chitosan-Fe<sub>3</sub>O<sub>4</sub>) to form Pd-based magnetic catalysts for fast hydrogenation of various aromatic nitro and acetalization of acrylonitrile under mild conditions. The catalyst was prepared by mixing the chitosan-Fe<sub>3</sub>O<sub>4</sub> nanoparticles with PdCl<sub>2</sub> in ethanol and then reduced by adding NaBH<sub>4</sub>. While using methanol or NaBH<sub>4</sub> as reducing agents, it was expected to control the Pd particles onto chitosan within the nanoparticle range of 1–2 nm [24]. Catalysis results confirmed high activity of the

as-prepared catalysts for the hydrogenation and acetalization reaction with almost complete conversion and 100% selectivity. Moreover, the catalyst could be recovered and recycled several times without significant loss in its activity, mainly due to the efficient stabilization of the active Pd species in the amine groups on the chitosan.

### Gold Catalyst

Elaboration of gold compounds in the field of nano-chemistry showed efficient catalysis activities for carbon-carbon bond formation and other organic synthesis [41,42]. However, the catalytic activity of gold could be considerably influenced by its dimension and interaction with supporting materials [42]. Previous studies also reported the possibility of a prepared gold nano-catalyst undergoing undesired agglomeration and precipitation before and after reactions [43]. Thus, the design of an active and selective gold-based catalyst is intended to invent an appropriate support in terms of its gold affinity, stabilization ability and large surface area [42,44].

Primo *et al.* [42] proposed the use of chitosan to increase dispersion of gold, as chitosan is a naturally available polymer and can act as macromolecular ligands for chelating gold nanoparticles. Presence of spatially isolated amino groups on chitosan also prompted the capture of gold nanoparticles in the polymers. Preparation of the catalyst started by dissolving chitosan in an acid solution, followed by a gelification in basic solution to increase its surface area and porosity, and then immersed in  $\text{HAuCl}_4$  solution. Scanning electronic microscopy results showed isolated chitosan fibrils with a diameter of 8–10 nm. The resulting catalyst was then utilized for Sonogashira cross coupling (70% yield with  $\geq 99\%$  selectivity) and homocoupling reactions under mild conditions. The catalyst could be used three times without major loss of catalytic activities over turn-over numbers of 18 and 26 for Sonogashira and homocoupling, respectively, as the material still retained its initial porosity.

A green approach to the synthesis of gold nanoparticle-chitosan catalyst by exposing chitosan in a gold salt solution ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  or  $\text{AgNO}_3$ ) under thermal treatment was attempted by Wei *et al.* [29]. The formation of gold NPs-chitosan involved two steps: the adsorption of gold ions onto chitosan and the subsequent reduction of gold species by chitosan. In this approach,  $\text{AuCl}_4$  ions could be simultaneously reduced to zero-valent gold nanoparticles by chitosan itself without any additional reductant in the thermal reduction. Transmission electron microscopy (TEM) images confirmed the formation of metal nanoparticles in the chitosan matrix, and shortening the reaction time contributed to formation of smaller gold particles. Formation of smaller particles increased the surface roughness of the catalyst, thus promoting the chemisorption and reduction reaction of the 4-nitrophenol to 4-aminophenol, although the catalyst was only effective for the first cycle.

Given the fact that chitosan not only functioned as a supporting matrix for catalyst preparation, it also served as a reductant and stabilizer for the formation and dispersions of gold nanoparticles, Qiu *et al.* [30] reported a synthesis approach to prepare magnetic gold nanoparticle-chitosan- $\text{Fe}_3\text{O}_4$  catalysts without employing any toxic reductants or capping agents. Their results verified that the  $\text{Fe}_3\text{O}_4$  nanospheres were strongly embedded into the chitosan by sharing the lone electron pairs between the nitrogen atom in amine on chitosan and Fe(II) or Fe(III) on the surface of  $\text{Fe}_3\text{O}_4$ . This as-prepared catalyst exhibited good catalytic performance for reduction of nitro compounds with more convenient magnetic recyclability after uses.

## Ruthenium Catalyst

Ruthenium (Ru) catalyst was well used for the aqueous hydration of nitriles to amides [45] and hydrogenation of esters [46] in the organic chemical industries. A molecular Ru catalyst was also developed for the water oxidation in a photosystem to generate renewable energy [47].

With the inspiration of using chitosan to extract Ru nanoparticles from aqueous solutions, Baig *et al.* [13] proposed the direct use of unmodified chitosan as a heterogeneous support for catalytic applications, thus eliminating the involvement of tedious synthesis procedures while immobilizing the Ru metal onto a magnetic support and enhanced its reusability. The immobilization of Ru over chitosan was done by suspending chitosan in an aqueous mixture of ruthenium chloride overnight at pH 9. The as-prepared catalyst had high yields and excellent selectivities on the hydration of nitriles and could be recovered and reused without affecting the reactivity. Babin *et al.* [48] also reported the use of a pivaloyl functionalized chitosan catalyst [Ru(*p*-cymene)Cl<sub>2</sub>] for the asymmetric transfer hydrogenation of ketones with up to 80% of reaction yield.

### 2.1.2. Nonmetal Catalysts

#### Quaternized Chitosan

In the age of increased concerns in global warming and climate change, CO<sub>2</sub> mitigation and fixation have received a lot of attention from both economic and environmental points of view. In particular, conversion of CO<sub>2</sub> into carbonates was of remarkable interest for reducing carbon emissions as well as reusing it as alternative resources (e.g., solvents) [32,49]. Quaternary ammonium salts, such as Bu<sub>4</sub>NBr, Et<sub>4</sub>NBr, are currently in use for industrial preparation of cyclic carbonates [50], and therefore have attracted much scientific attention in the development of heterogeneous catalysts for these applications. Recent studies also revealed the use semi-clathrate hydrates in the presence of quaternary ammonia salts of TBAB for CO<sub>2</sub> capture up to 95% [51,52].

A quaternary ammonium salt-functionalized chitosan catalyst was reported to be an efficient and recyclable catalyst for synthesis of propylene carbonate from propylene oxide and carbon dioxide in 100% yield and high selectivity without any organic solvent [18]. NaOH, isopropanol, 3-chloro-2-hydroxypropyl trimethylammonium chloride were used to prepare the quaternary ammonium salts by covalently bonding on chitosan, after magnetization. The results showed that the catalysts' performance strongly depended on the leaving ability and nucleophilicity of the anions on the chitosan-supported catalysts [49]. The as-prepared catalyst could be recovered and reused for at least five times without loss of its catalytic activity.

After Xie *et al.* demonstrated an efficient, reversible fixing system for CO<sub>2</sub> using chitosan/ionic liquid [53], a novel approach applying quaternized chitosan as a catalyst for the cycloaddition of epoxides from reacting allyl glycidyl ether (AGE) and CO<sub>2</sub> was attempted [54]. Rather than covalently tethering a quaternized species into the chitosan's backbone, they first reported the use of quaternized chitosan from quaternization on the primary amine group inherently on the chitosan itself to form a cationic biopolymer. Furthermore, the hydroxyl groups on the chitosan would enhance the catalysis on their own. The chitosan was synthesized with NaOH, NaI and CH<sub>3</sub>I in a 1-methyl-2-pyrrolidinone solution. The quaternized chitosan showed high catalytic efficiency for most of the tested monosubstituted terminal epoxides, while AGE revealed the highest conversion and yields for the production of the

corresponding cyclic carbonates with high selectivity. This approach provided a simple and easy route for synthesizing cyclic carbonates with high product yields and easy catalyst recycling. Their later study utilized microwaves to prepare quaternized chitosan catalysts for the cycloaddition of CO<sub>2</sub> and epoxides [55]. The as-prepared catalyst exhibited higher catalytic activity for the solvent-free cycloaddition of CO<sub>2</sub> and AGE, as compared to a conventional quaternized chitosan catalyst (non-microwave irradiated).

### Other Novel Catalysts

Sun *et al.* [16] developed an efficient, cheap and recyclable chitosan-based catalyst complex for cycloaddition reactions of CO<sub>2</sub> with various epoxides. In the system, chitosan was functionalized by 1-ethyl-3-methyl imidazolium halides (with Cl or Br ions) without the addition of solvents and metal co-catalysts. The as-prepared catalyst was tested for the reaction of propylene oxide and CO<sub>2</sub> to produce propylene carbonates. The results exhibited high product yields and showed easy recyclability of the as-prepared catalyst up to five times. A possible catalytic cycle for the hydrogen bond assisted ring-opening of epoxide and activation of CO<sub>2</sub> induced by the nucleophilic tertiary nitrogen of the chitosan was also proposed.

Direct synthesis of cyclic carbonates from olefins and CO<sub>2</sub> was achieved by Kumar *et al.* [20] using a dual catalysis system with magnetic chitosan. Preparation of the catalyst used cobalt(II) acetylacetonate complex (Co(acac)<sub>2</sub>) and quaternary triphenylphosphonium bromide (P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup>) to immobilize the substances onto magnetic chitosan. This method avoided the initial synthesis of epoxide that involved use of toxic or costly reagents. The magnetic heterogeneous catalyst has led to facile and efficient recovery of the catalyst from the reaction mixture [45].

### 2.2. Photocatalysts

In addition to its application in organic synthesis, chitosan has been studied extensively to act as a high-capacity adsorbent, for the efficient removal of various contaminants from wastewater, such as anionic and cationic dyes as well as heavy metal ions. In a comparative review study for the adsorption and removal of pollutants using different materials, chitosan was demonstrated to be a more effective adsorbent than even activated carbon [56]. Heterogeneous photocatalysts, such as titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO), have also been proven to effectively degrade many aromatic compounds to safer end products such as CO<sub>2</sub> and water [57,58]. Chitosan was also used to immobilize photocatalysts of zinc tetraamino phthalocyanine and Ag nanoparticles for ease recovery after photocatalysis [27]. Considering the abovementioned advantages of chitosan and photocatalysts, Zainel *et al.* [57] first explored the combination of using TiO<sub>2</sub> together with chitosan for the synergistic treatment of dye-containing wastewater under visible light illumination. The as-prepared catalyst was coated onto glass plates for a convenience mean of wastewater treatment. Recent studies also exhibited multifunctional performance of chitosan and TiO<sub>2</sub> or ZnO in heterogeneous photocatalysis applications, including increased adsorption capacity and enhanced photocatalytic activity [59–61].

Right after Zainel *et al.* successfully implemented the use of immobilized chitosan/TiO<sub>2</sub> catalysts for dye treatment, Nawi *et al.* [60] proposed a simple bilayer system consisting of TiO<sub>2</sub> and chitosan onto a glass plate for the removal of phenol. The authors also showed that the addition of epoxidized natural rubber (ENR<sub>50</sub>) and phenol-formaldehyde resin in the coating formula improved the deposition

properties of TiO<sub>2</sub> powder. The porous structure on as-prepared TiO<sub>2</sub> layers allowed better diffusion of the target pollutants as well as increased light penetration for photocatalytic reaction. Their later study utilized a similar system for the decolorization of reactive red 4 dye (RR4) solution [62]. A faster decolorization rate of RR4 by TiO<sub>2</sub>/chitosan/glass was observed and the rate was highly dependent on the TiO<sub>2</sub> loading and the initial pH of the solution.

A hybrid photocatalyst combining chitosan and ZnO was also proposed [63]. The catalyst was prepared by chemical precipitation method and revealed high photocatalytic activity for degradation of methylene blue dye under UV irradiation. Zhu *et al.* [64] managed to synthesize TiO<sub>2</sub>/ZnO/chitosan nanocomposite thin films by entrapping zinc ions and nanosized TiO<sub>2</sub> in chitosan thin films using solution casting approach. High-resolution TEM results revealed that the TiO<sub>2</sub>/ZnO were well-dispersed and uniform nanocomposite with diameter of 5–15 nm in the chitosan films. The catalyst also demonstrated high photocatalytic activity for decolorization of methyl orange.

### 3. Conclusions

This review provides an overview of recent advances on the applications of chitosan-based catalysts in both chemical synthesis and environmental remediation areas. It is evident that chitosan could be used as an efficient, reversible, recyclable and environmentally friendly catalyst support in various applications. The unique characteristics of high metal sorption capacity and hydrophilicity of chitosan could be of great use for further investment in heterogeneous catalysis systems.

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### Conflicts of Interest

The authors declare no conflict of interest.

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