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# Heterogeneous catalysis on chitosan-based materials: a review

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## Abstract

Chitosan is an optically active biopolymer that is characterized by a strong affinity for transition metals. The polymer can be used as a support for the preparation of heterogeneous catalysts in the form of colloids, flakes, gel beads, fibers (including hollow fibers), or immobilized on inorganic supports (alumina, silica, or other metal oxides). The conformation of the polymer (together with its flexibility) is an important advantage for this kind of application. The ease with which it can be modified physically and chemically opens up avenues for manufacturing a wide range of catalysts for applications in the fields of hydrogenation, oxidation, and fine chemical synthesis reactions. This review summarizes the main advances published over the last 15 years, outlining the procedures for preparing these materials, describing how they are tested in a series of reactions and discussing the main controlling parameters that should be taken into account in order to optimize their catalytic activity.

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**Keywords:** Chitosan; Heterogeneous catalysis; Polymer conditioning; Hydrogenation; Reduction; Oxidation; Metal crystals; Diffusion properties

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## 1. Introduction

Chitosan is a very abundant biopolymer obtained by the alkaline deacetylation of chitin (a polymer made up of acetylglucosamine units). Chitin is present in the exoskeletons of crustaceans, the cuticles of insects and the cell walls of most fungi. Chitosan is actually a heteropolymer containing both glucosamine units and acetylglucosamine units [1] (Fig. 1). The presence of amine groups explains its unique properties among biopolymers: (a) its cationic behavior in acidic solutions, and (b) its affinity for metal ions. Metal ion sorption can occur through chelation mechanisms for metal cations in near neutral solutions or through electrostatic attraction and ion exchange for metal anions in acidic solutions [2].

While most studies focusing on the interactions of chitosan with metal ions were carried out to recover strategic metals or remove hazardous metals from dilute solutions, increasing attention has recently been paid to the manufacturing of elaborate materials based on metal-chitosan reactions. For example, several studies have expressed an interest in combining the effects of metal ions and chitosan for treating plant disease [3], manufacturing batteries [4–6], as well as manufacturing optical and electronic devices [7,8]. However, a growing number of papers have been published since the 1980s' in the field of chitosan for supported catalysis (or heterogeneous catalysis) (Fig. 2). There are many reasons for this recent interest in using chitosan for supporting catalytic metals: high sorption capacities, stability of metal anions (such as Pt and Pd) on chitosan, and physical

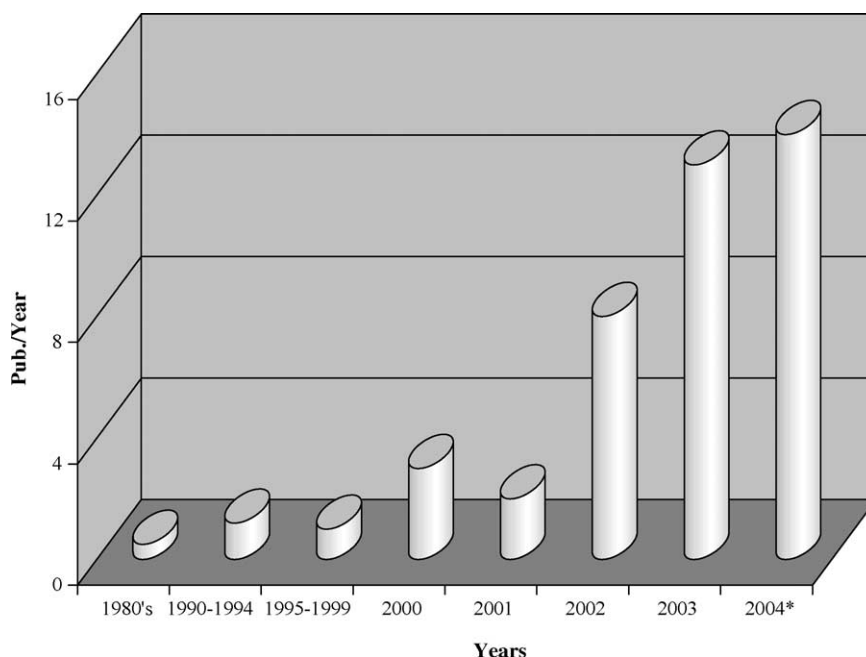


Fig. 1. Publication frequency on chitosan-supported catalysis from 1980s (\*: first 9 months of year 2004).

(and chemical) versatility of the biopolymer. The polymer can be conditioned in different forms: flakes, gel beads, membranes, fibers, hollow fibers, sponge, or supported on inert materials (silica gel, alumina, etc.) [2]. While homogeneous catalysis offers interesting properties (low influence of diffusion mechanisms on reaction performance, for example) [9], it may be necessary to include an additional separation process at the end of the reaction to recover the catalytic metal, especially in the case of precious and strategic metals. This separation process may represent a very difficult challenge in some cases. For this reason many developments have focused on the immobilization of catalytic metals on inert materials [10], or functionalized solids [11]. Most of the supports used for the preparation of heterogeneous catalysts are activated carbon [12–16], alumina [17–20], or silica gel [21,22]. However, increasing attention has recently been paid to the use of polymers for supporting catalytic metals [23–29]. Not only do these materials provide interesting affinities for catalytic metals, but their structure can also induce specific properties such as enhanced stereo-selectivity (chirality) [30]. The conformation of polymeric chains contributes to the orientation of reactions [31,32]; this can be related to their ability to

selectively bind enantiomers [33,34]. Traditionally, important studies have been performed using synthetic polymers; however, for the last 10 years an important effort has been devoted to the use of biopolymers [35]. For example, many studies of biopolymer-supported catalysis have focused on the use of starch derivatives [36], gelatin [37], alginate or alginic acid [38], cellulose derivatives [39,40], or chitin and chitosan materials [41–45]. Indeed, biopolymers very often present interesting enantio-selective properties [46,47] due to their conformation and stereochemistry, which provide specific chiral properties.

Though chitosan itself (without metal immobilization) has been used as a catalyst for some reactions involved in the synthesis of fine chemicals [48,49],

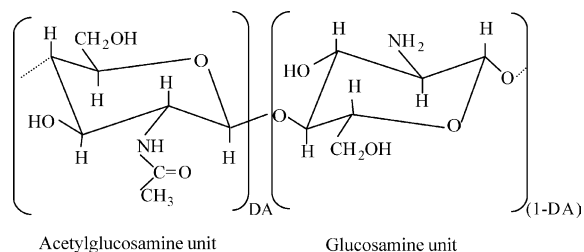


Fig. 2. Chitosan structure.

most of the publications dealing with chitosan use in supported catalysis focus on metal-supported catalysis. The present review reports (a) the main characteristics of chitosan with regard to heterogeneous catalysis (i.e. properties of chitosan relative to metal sorption, conditioning of the biopolymer), (b) some examples of chitosan use for the preparation of heterogeneous catalysts, and (c) the main controlling parameters for optimal use of these materials (in order to point out the necessary criteria to manufacture these new materials).

## 2. Characteristics of chitosan for the preparation of supported catalysts

### 2.1. Polymer properties

Chitosan is a deacetylated derivative of chitin. Actually, the hetero-polymer is constituted of glucosamine and acetylglucosamine units (Fig. 1). Their relative proportion fixes the degree of acetylation (DA) that controls many properties of the polymer: its acid–base properties and its solubility [50]. Indeed, the intrinsic  $pK_a$  of chitosan depends on the degree of deacetylation, the ionic strength and the charge neutralization of amine groups; in practice it lies within 6.3–6.7 for fully neutralized amine functions when the degree of acetylation does not exceed 50% [50]. The protonation of amine groups causes the polymer to dissolve in acidic solutions. Another consequence of amine group protonation is a decrease in the sorption of metal cations in acidic solutions due to the competition of protons and metal cations for interaction with amine groups. Another important characteristic of chitosan is the molecular weight influencing the polymer's solubility and viscosity in solution. The rheological properties of chitosan such as chain stiffness, length of repeating units, and chain coiling may be of great effect when using catalysis supported on colloids (coupling for example catalytic reactions with ultrafiltration separation process) since it affects the availability and the accessibility to active sites. The viscosity of chitosan also greatly influences chitosan conditioning processes. An additional advantage of chitosan is the high hydrophilic character of the polymer due to the large number of hydroxyl groups present on its backbone.

Among the other parameters that have a great impact on metal sorption are polymer porosity and material crystallinity. Depending on the origin of the polymer and its treatment during the extraction from raw material (squid pen, shrimp shell), the residual crystallinity may vary considerably. Crystallinity controls polymer hydration, which in turn determines the accessibility to internal sites [51–54]. This parameter strongly influences the kinetics of hydration and sorption [55–57]. The dissolving of the polymer breaks the hydrogen bond between polymer chains. The reduced polymer crystallinity can be maintained through freeze-drying of the chitosan solution, while an air-drying or oven-drying procedure partially reestablishes polymer crystallinity. The conditioning of the polymer (preparing for example chitosan gels) can strongly reduce the influence of this important parameter. The low porosity of chitosan flakes is also an important limiting parameter: the contact time required to reach equilibrium usually lengthens with increasing size of chitosan flakes. The resistance to intraparticle diffusion controls overall kinetics for the sorption of metal ions, especially for large-size polynuclear species. Decreasing the size of sorbent particles improves the sorption properties of the biopolymer; especially when chitosan is cross-linked. Indeed, this chemical treatment involves supplementary linkages that limit the transfer of solute molecules. However, especially small particle sizes are not compatible with large-scale applications: for example, in fixed-bed columns, small particles induce head loss and column blocking. This limiting effect can be compensated with the physical modification of the polymer: gel bead conditioning, in addition to the decrease of polymer crystallinity, allows expansion of the porous structure network, which in turn enhances the transport of metal ions. Basically, any process that could decrease the size of active layers (i.e. supporting chitosan as a thin layer on inert material, preparing thin membranes, etc.) can be helpful for improving sorption performances. This criterion is also very important for the catalytic activity of chitosan-supported catalysts: diffusion restrictions will decrease the efficiency of the material for catalysis by decreasing the accessibility of substrate molecules to active internal sites and the diffusion of reaction products out of the catalyst.

## 2.2. Metal ion sorption

The interactions of chitosan with metal ions have been abundantly described [2,58]. Three mechanisms are usually cited for the interpretation of metal sorption on chitosan material: (a) metal chelation, (b) electrostatic attraction (or ion exchange), and (c) formation of ion pairs. Though ion pair formation may be of interest for the uptake of some alkaline or alkaline-earth metal cations (for example: uptake of the ion pair formed by interaction of strontium with carbonate anions [59]), the most interesting mechanisms involved in the preparation of catalysts are chelation and electrostatic attraction.

The presence of a large number of amine groups on the biopolymer explains the uptake of metal cations on the free electronic doublet of nitrogen at near neutral pH. The sorption of these metal cations is controlled by the pH: the competition of protons drastically reduces the sorption of metal cations below pH 4–4.5 [60]. Chitosan's affinity for metal ions is also strongly influenced by the environmental conditions of amine functions. Hence, the cross-linking of chitosan with glutaraldehyde (formation of imine functions) decreases the availability of amine functions for the chelation of metal cations and with a high cross-linking ratio the uptake capacity drastically decreases [60,61]. In the case of metal cations such as Cu(II), very high sorption capacities have been obtained [62–64]: it is frequent to reach sorption capacities as high as  $200 \text{ mg Cu g}^{-1}$  (i.e.  $3 \text{ mmol Cu g}^{-1}$ ). The presence of chelating agents in the solution may strongly influence sorption performance [65], as well as sorption mechanisms [66]. Indeed the complexation of metal cations with soluble ligands changes the speciation of metal cations and in some cases form metal anions that can only be sorbed in acidic solutions on protonated amine groups. This can be of great interest when special chemical forms of metal are required (especially metal complexes that can affect the reactivity of the catalytic metal). The interpretation of molecular interactions is very controversial. In the case of copper for example, several types of interaction mechanisms are cited involving one amine group per mole of copper bound (pendant mechanism) or two amine groups (bridging model). This may be of great influence on the availability of metal ions and their reactivity for catalytic

applications. For more details on the interactions of metal ions with chitosan the reader is directed to the reviews published by Varma et al. [58] and Guibal [2].

In the case of metal anions such as anionic complexes of platinum, palladium or gold with chloride ions [67–73], or chromate [74–76], molybdate [77–79], vanadate [80] the sorption mechanism involves their electrostatic attraction to protonated amine groups. The optimum pH range for metal sorption and stability on the polymer is pH 2–4. This optimum pH range may be explained by two reasons: (a) the speciation of metal anions (formation of adsorbable species: predominance of polynuclear forms for molybdate, vanadate for example; or chloro-anionic complexes); (b) the protonation of amine groups (for electronic balance) and the competition of anions (brought by the acid: excessive acidity strongly limits the uptake performance). The solubility of chitosan in acidic solutions (with the exception of sulfuric acid) usually requires a cross-linking of the polymer to prevent its dissolving. Glutaraldehyde is frequently used for the stabilization of the polymer: the Schiff base reaction between amine groups and aldehyde groups increases the stability of the biopolymer [61,81]. This is especially important in the case of platinum, palladium or gold sorption since these metal ions require the formation of chloro-anionic species for optimum sorption and in this case it is not possible to use sulfuric acid for pH control. Kramareva et al. discuss the formation of Pd–chitosan complexes (coordination of palladium with two amine groups on chitosan) [82]. In the case of molybdate and vanadate, sulfuric acid can be used for pH control and the cross-linking of the polymer is not a prerequisite. In this case also, sorption capacities can reach several hundred milligrams metal per gram of sorbent:  $1\text{--}2 \text{ mmol metal g}^{-1}$  (for Pt and Pd) and up to  $7\text{--}10 \text{ mmol metal g}^{-1}$  (for Mo and V, due to the sorption of polynuclear species: heptamolybdate, decavanadate). In the case of the sorption of metal anions the environment of amine groups is not so important as it is in the case of metal cations sorption involving direct chelation of metal cations through the free electron doublet of nitrogen. Here, the mechanism involves only the electronic positive charge on protonated amine group, which is less drastically affected by the reaction of amine groups with aldehyde functions. In the case of precious

and strategic metals the stability of the metal on the polymer is a critical parameter. In most cases highly acidic solutions are required to desorb the metals from the loaded material, and at near neutral pH the metals are very stable (the amount of metal loss does not exceed a few percent of metal loaded on the material).

Chitosan has proved itself capable of metal reduction, depending on (a) the treatment of chitosan (cross-linking with glutaraldehyde may result in the presence of free aldehyde functions not involved in linkages with amine groups of the biopolymer, which may cause partial reduction of the metals), and (b) the intrinsic properties of metal ions (especially their normal oxido-reduction potential). The effect of the polymer on metal reduction may also be enhanced by light exposure [7,8,83,84]. This stability of the oxidation state of the metal loaded on chitosan may be of great importance for its catalytic activity.

### 3. Polymer conditioning for the preparation of catalytic material

The limiting parameters for the immobilization of metal ions on chitosan have been briefly listed and

an efficient strategy for decreasing their impact may consist of changing the conditioning of the polymer. This change in the conditioning of the polymer may affect the application process, depending on the structure of the final product (dissolved state, fiber, flakes, beads, hollow fiber, supported on inorganic membrane, etc.). Fig. 3 shows some of these chitosan conditionings.

#### 3.1. Flakes

Most of the studies focusing on chitosan have been performed on chitosan flakes, since they are easier to manage than gelled materials (wet material for which it is more difficult to evaluate the actual amount of active material, i.e. gel beads, wet fibers) [45]. To prevent chitosan from dissolving it is usually necessary to reinforce polymer stability by a cross-linking treatment [85], except in the case where both metal sorption (and metal reduction, when required) and catalytic reaction can be operated at neutral or slightly alkaline pH. The main limiting parameter with flaked material will be the size of chitosan particles due to diffusion restrictions. The size of sorbent/catalyst particles should not exceed

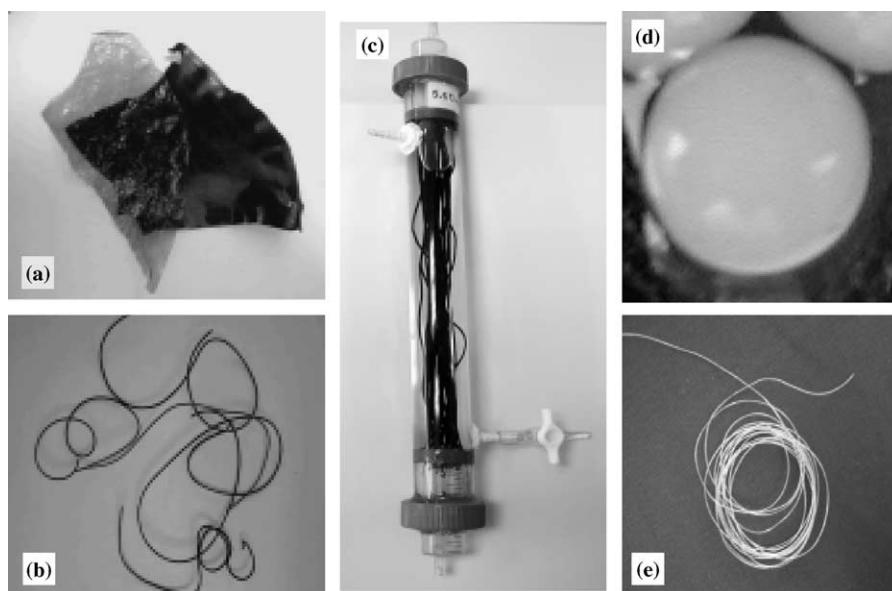


Fig. 3. Examples of chitosan conditioning: (a) chitosan membranes loaded with palladium (before and after metal reduction: clear and dark membranes, respectively); (b) chitosan hollow fibers, loaded with palladium and chemically reduced; (c) module of catalytic chitosan hollow fibers; (d) chitosan gel bead; (e) chitosan fiber.



100–150  $\mu\text{m}$  to avoid significant diminutions in kinetic rates. In most cases, the uptake of metal ions is performed in water, although a few studies use organic solvents (such as ethanol) [86].

The versatility of chitosan is not limited to the physical modification of the polymer. Hence, the presence of hydroxyl groups and amine functions offers a very high chemical reactivity to the polymer [87,88]. New functional groups can be grafted onto the polymer to increase its reactivity [1,87] and improve sorption selectivity [71,89]. For example, in the case of the synthesis of catalysts, as well as glutaraldehyde cross-linking (required for metal uptake in acidic solutions), several chemical modifications have been proposed including the synthesis of Schiff base derivatives of chitosan [90–92]. These chemical modifications can be used to improve metal uptake or to modify the selectivity of the catalytic reaction (the chirality being modified by the presence of substituted groups). These modifications can be also used for the design of chitosan derivatives under different conditionings (gel beads, etc.). For example Zhu et al. prepared a derivative of chitosan that is soluble in organic solvents (hydroxypropyl chitosan) which is subsequently modified by grafting (dimethylamino)ethyl groups for the immobilization of  $\text{Rh}_6$  cluster complex ( $\text{Rh}_6(\text{CO})_{16}$ ) [93].

### 3.2. Gel beads

Gel beads have been used for the preparation of catalyst particles [82,94,95]. Several strategies can be followed to prepare this kind of material. The preparation of the chitosan gel beads can be operated independently of the preparation of the catalyst. The polymer is dissolved in acetic acid and the viscous solution of chitosan is pumped through a thin nozzle into an alkaline coagulation bath. The alkaline coagulation bath can be substituted with ionotropic gelation media, consisting of tripolyphosphate ions or metal ions [96,97].

The resulting beads can be used in one of two common strategies for the uptake of metal ions by (a) the adsorption process, and (b) the co-precipitation process. The adsorption process may require cross-linking treatment to prevent polymer dissolving in the case the metal is adsorbed in acidic aqueous media; in the case of alcoholic media the cross-linked treatment is not necessary. The cross-linking treatment may

consist of formation of new linkages between polymer chains, or the reaction of amine groups with other compounds (aldehyde functions, for example) to decrease their protonation, and therefore polymer dissolving. A chitosan–metal complex can be produced in hydrochloric acid solution, followed by the distribution of the solution into a neutralization batch forming spherical globules, this is the co-precipitation method. The globules are then filtered and dried at room temperature for 48 h [82,94,95]. Kucherov et al. [94] describe a variant of this procedure: they dissolve the metal–chitosan complex into hexane in the presence of SPAN<sup>®</sup> 60 at high agitation speed (3000 rpm) to improve the formation of water-in-oil emulsion. After slightly reducing the agitation speed, a cross-linking agent is added drop-wise for the stabilization of the emulsified particles. The choice between the different strategies is controlled by the chemistry of metals to be bound on the material: their ability to coagulate chitosan, their stability in weakly acidic solutions, and their solubility at the required pH are some of the parameters that can orientate the selection of the manufacture procedure.

The catalyst particles can be used as produced or reduced in case of the oxidation state of the metal is not appropriate for the specific reaction. For example, the catalytic metal (Pd, Pt, etc.) used in hydrogenation processes should be in the zero-oxidation degree. Several reducing agents can be used for their reduction (see below, Section 4).

Gel bead conditioning can also help preventing the dispersion of catalyst nanoparticles; the polymer serves as a porous scaffold: accessible by substrates and porous to the products of the reaction, but sufficiently packed to retain catalyst particles. The nanoparticles are mixed with polymer solution before performing the coagulation or the polymerization of this inclusion matrix. This process has been used with synthetic polymers for the immobilization of metals such as Zn and Fe (in the form of nanoparticles) for the reduction of inorganic and organic contaminants [98]. This process could be also developed with chitosan to form the inclusion matrix.

### 3.3. Fibers & hollow fibers

In the case of the preparation of fibers and hollow fibers, a two-step procedure is also used: (a) dissolving



the polymer in acetic acid solution followed by (b) extrusion of the viscous solution through a thin nozzle and coagulation of the solution with a suitable neutralization or coagulation agent [99,100]. The viscous solution can be directly extruded in the solution or be extruded in air, the extruded fiber falling into the coagulating agent. The height of fall controls the diameter of the fiber [101–103]. In the case of solid fibers, the coagulated fiber can be rinsed and dried to increase the strength of the fiber. In the case of hollow fibers the manufacturing procedure consists in co-extruding the viscous solution of chitosan and a core liquid [104]. The core liquid is pumped concentrically to the chitosan solution using a double-spinneret (Fig. 4). The extruded hollow fiber falls down into an alkaline coagulating bath: the distance between the spinneret and the surface of coagulation bath is 30 cm. Another process has been cited for the preparation of chitosan hollow fibers, consisting in coagulating chitosan fibers in an ionotropic gelation medium followed by forced extrusion of the non-coagulated core (at the center of the fiber) [102,103].

Therefore, the metal ions can be sorbed before being reduced (if necessary, depending on the oxidation state

required for the target catalytic reaction). When the cross-linking treatment is required prior to metal sorption, for precious metals such as Pd, Pt and Au, for example, the conventional cross-linking procedure with glutaraldehyde cannot be used since this treatment induces a brittleness of the fiber, which is not compatible with fiber handling. A treatment of the fiber with a sulfate solution ( $1 \text{ g L}^{-1}$ ) at neutral pH allows the chemical stabilization of the fiber, which prevents it degrading during precious metal sorption procedures. The treatment of chitosan hollow fibers with glutaraldehyde has been cited [104]; however, the concentration of glutaraldehyde in the cross-linking solution was very low (about 0.4% w/w), far below the amount of cross-linking agent required for an efficient stabilization of the biopolymer for metal immobilization in drastic conditions (pH 2). The drying of the fiber may also result in brittleness that can be controlled by placing the fiber in aqueous glycerol solution to plastify the fiber.

### 3.4. Membranes

There is abundant literature concerning the preparation of flat membranes [99,105–111]. Most of the techniques cited for the preparation of chitosan membranes consist in dissolving chitosan in acetic acid followed by casting the solution on a surface (such as a Petri dish) to allow solvent evaporation, before coagulating the dried membrane with an alkaline solution. However, this treatment results in limited diffusion properties [112].

Zheng and Ruckenstein [113] describe a procedure for the preparation of membranes with tailored pore size using a porogen: silica (the porogen) is added with chitosan to acetic acid solution. The mixed suspension is spread on a plate, and the solvent is evaporated. After drying, the thin membrane is neutralized in concentrated NaOH, which simultaneously serves to dissolve silica in the frame of the membrane resulting in highly porous material.

### 3.5. Supported on inorganic supports

In many applications, the poor diffusion properties of chitosan or its weak mechanical properties (especially for thin membranes) require the chitosan to be deposited in thin layers on the surface of porous

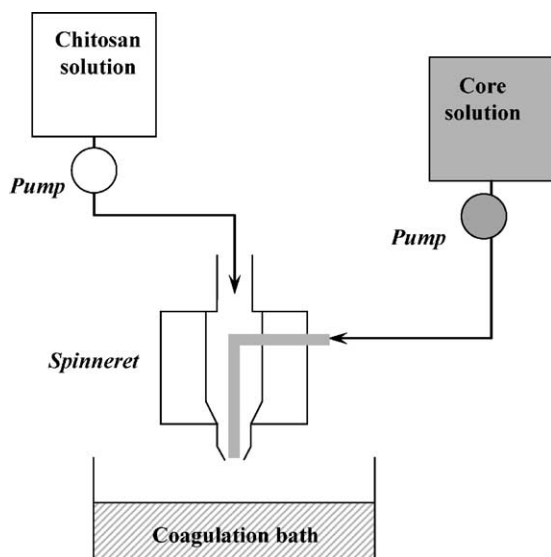


Fig. 4. Spinneret system for the extrusion of hollow fibers (derived from [104]). Chitosan hollow fibers, Z. Modrzejewska, W. Eckstein; Copyright © (2004, John Wiley & Sons), 'Reprinted with permission of John Wiley & Sons, Inc.'

materials to improve the specific surface area and mechanical properties, and to optimize efficacy and accessibility to the chitosan's internal amino groups. This is especially important when catalytic metals are deposited on chitosan: if the restrictions of the material to diffusion limit the accessibility to internal sites, inaccessible metal immobilized on the biopolymer remains inactive.

Silica beads and glass beads have been used to immobilize chitosan for the preparation of advanced sorbents [114–116]. This process consists in mixing wet beads with a chitosan solution (2% w/w in acetic acid). The impregnation procedure is followed by neutralization at pH 8 to solidify and fix the coating layer. The final treatment consists in cross linking chitosan with glutaraldehyde [116]. This treatment can be applied with porous supports (such as alumina and silica beads), while with non-porous materials (to which chitosan cannot be attached) it is necessary to activate the support, first by attaching reactive functions to their surface (such as 3-aminopropyltriethoxysilane, an amino derivative bearing silane functions) before reacting with a cross-linking agent (glutaraldehyde, L-cysteine derivative) [114,115]. The cross-linking treatment is frequently used when the sorption of the catalytic metal (in the second step of catalyst preparation) is to be operated at acidic pH in aqueous solutions. Yin et al. propose another procedure for the preparation of chitosan–palladium catalyst supported on silica: the first step consists in the impregnation of silica particles followed by the precipitation of chitosan at alkaline pH, while the sorption step is performed in solvent (ethanol for example) under reflux [86,117,118].

Chitosan can also be immobilized on amorphous silica particles after the metal–chitosan complex has formed [94]. For example in the case of copper–chitosan complex, the solution is mixed with silica gel in the first step followed by the neutralization of the suspension. The complex coagulates in situ and the organic–mineral composite is repeatedly washed until it reaches neutral pH before being dried at room temperature. Alternatively, the silica support can be mixed with chitosan solution before the mixture is put in contact with glutaraldehyde (for cross-linking) [94]. The slurry is therefore repeatedly washed and filtered off. The functionalized sorbent can be used for

the sorption of catalytic metal, in aqueous media or solvent media (alcohol, for example).

An alternative procedure for the deposition of chitosan on the surface of silica or alumina material consists in putting the mineral material into a chitosan solution (in acetic acid) then precipitating the polymer (either alone or as a mixture with polyelectrolytes, such as polyacrylic, polymethacrylic or poly(ethyleneimine)) using a solvent (acetone for example) [117]. Huang et al. [119] use a similar procedure for the preparation of nanosized palladium catalysts.

Steenkamp et al. [120,121] propose several procedures for the preparation of alumina/chitosan composite membranes. After describing the preparation of tubular supports (based on the mixing of ammonium polymethacrylate with  $\alpha$ - $\text{Al}_2\text{O}_3$  powder, centrifugal casting and sintering), they describe the coating process they use for depositing porous chitosan membranes. A chitosan solution is prepared by dissolving chitosan in acetic acid in the presence of silica gel 60. Then, the ceramic tube is filled with this suspension and most of this solution is evacuated leaving only a very thin chitosan layer at the surface of the support. The operation is repeated several times and the solvent is finally evaporated. Dried membrane is immersed in NaOH solution at 80 °C to generate the porous supported coating membrane: dissolving of silica gel particles combined with heat treatment allows pore formation and strengthening of the mechanical properties of the coating layer. To prevent the shrinkage of the layer, glycerol solution can be used to impregnate the layer before the drying step [120]. Several alternative processes have been proposed including the cross-linking of the polymer using epichlorohydrin in alkaline conditions.

### 3.6. Dissolved state/colloid/nanoparticles

Actually, the processes using this kind of chitosan conditioning can be considered to be intermediary between homogeneous and heterogeneous catalysis [82]. Since chitosan is soluble in acidic solution, it is possible to prepare soluble complexing macromolecules, which can be used to bind metal ions in solution. Therefore an ultrafiltration membrane can physically retain the metal ions bound onto the biopolymer, given that the membrane cut-off is below the hydrodynamic size of the dissolved

macromolecule. This process has been used to recover metal ions from dilute solutions: this is the base of the polymer enhanced ultrafiltration process (PEUF) [122–124]. Loaded polymer can be washed off to remove the excess of free metal and to give a metal–chitosan complex that could be used for catalytic applications. The system would consist of the reaction of the substrate with the metal–chitosan complex followed by the membrane separation of substrate/products from the metal-loaded catalytic macromolecule. Though the process has not been well documented in the literature, it sounds very promising since it allows optimum access of the substrate to catalytic sites, with limited impact due to diffusion limitations. This forms the basis of colloidal-supported catalysis, which has been described for other systems by Ford [26]. This dissolved-state conditioning is obviously limited to applications where the oxidation state of the metal should not be changed or when this change of oxidation state is not followed by the insolubilization or the precipitation of the metal-loaded macromolecule.

Nanoparticles are retaining increasing attention, due to (a) high surface of exchange (large surface area/mass ratios), (b) high surface energy, and (c) many surface defects causing high catalytic activity. However, these nanoparticles are frequently unstable, and tend to aggregate or precipitate, which causes a reduction in their catalytic activity. To prevent coagulation and precipitation, it is possible to use protective colloid or polymer coating during the formation of nanosized metal catalysts. Ishizuki et al. [125] describe a procedure for the preparation of precious metal particles protected with chitosan. The metal ion solution is mixed with a chitosan solution; the mixture is heated under reflux. After the solution boils, the reducing agent is added drop-wise to the mixture. The solution is rapidly cooled when the color of the solution changes. The particles can be recovered by centrifugation.

#### 4. Processes for metal immobilization and activation

As pointed out in previous sections, specially designed sorbents can be used for the sorption of metal ions using the specific chelating or

ion-exchange properties of chitosan. This sorption can be operated in aqueous media or in solvent (alcohol/water mixtures). This is the so-called adsorption process. Metal sorption properties have been described above and the reader can consult for more details reviews recently published on this topic for optimum conditions [2,58]. Generally the optimum conditions for the sorption of metal cations (by chelation) correspond to a pH range around neutral (i.e. pH 5–8), while optimum sorption of metal anions by electrostatic attraction occurs at acidic pH (in the range pH 2–4). It is interesting to observe that in the synthesis of chitosan-based catalysts using ethanol/water solvent, the pH of the solution is not considered to be a crucial parameter: the salt is directly added to ethanol and mixed with chitosan dissolved in acetic acid. No reference to pH is cited in these cases.

The other mechanism cited for the preparation of chitosan-based catalysts is the co-precipitation process. In this case the chitosan solution is mixed with the metal solution; the resulting solution is precipitated in an alkaline solution in order to coagulate the chitosan. This is close to an entrapment process (the inclusion process already cited). It is possible to use chitosan's properties to form membranes, gel beads or fibers which can be used to entrap catalytic particles or nano-particles in the polymeric network by a drying or coagulating process.

The comparison of impregnation and precipitation methods is well documented [82,95,126]. Isaeva et al. [126] observe that the hydrogenation activities of catalytic systems prepared by the co-precipitation method are low compared to those prepared by the impregnation method; they explain this weak activity of co-precipitated materials to their low metal contents: Pd is partially leached from chitosan during the precipitation in the alkali solution. On the other hand the catalysts produced by the impregnation method give comparable performance to those of conventional heterogeneous materials, at least for sample prepared by impregnation in water. They observe that in the case of Pd immobilization in alcohol the catalysts are almost inactive when using dry chitosan fibers and micro beads, regardless of the metal content, while a preliminary swelling step dramatically increases the catalytic activity of the same materials.

The kind of metal to be used depends on the target reaction; some examples are given in Section 5.

However, in the case of reduction reactions (hydrogenation reaction for example), the immobilized metal on chitosan surfaces or in chitosan matrices should be submitted to a reduction treatment. The choice of chemical agent for the reduction of immobilized metals depends on the metals, the immobilization process and the conditioning of the polymer. Ishizuki et al. [125] tested the addition of hydrazine monohydrate, formaldehyde (in alkaline solution), and pentaerythritol to the chitosan–metal ion solution for the preparation of chitosan-protected metal particles. While formaldehyde only reduces  $\text{HAuCl}_4$ , the other reducing agents are able to reduce  $\text{H}_2\text{PtCl}_6$ ,  $\text{PdCl}_2$ , and  $\text{RhCl}_3$ . This can be clearly correlated to the reducing strength of these chemical agents. In the case of hydrazine-based reduction Ishizuki et al. [125] observe that the size of the crystallite (which is indicative of the potential catalytic activity) is controlled by the amount of chitosan added to metal solution: increasing the relative ratio chitosan/metal reduces the size of catalytic crystallites up to a critical ratio above which the size of crystallites does not change. At the same time, the dispersion stability of the catalytic metals sharply increases when the concentration of chitosan reaches a critical value almost the same whatever the metal (among Au, Pt, Pd and Rh). However, size differences show chitin is more effective with Au than other selected metals. They prepare bi-metallic catalysts and observe that the proportion of respective metals strongly affects the dispersion stability and the size of catalytic crystallites. The particle composition remains independent of chitosan concentration (i.e. feed concentration in the mixture). In the preparation of composites of chitosan/polyacrylic acid and chitosan/poly-methacrylic acid (supported on silica particles) for the immobilization of Pd, Jin et al. [117] and Yin et al. [86] conduct metal uptake and reduction process directly in ethanol solution at boiling temperature (with reflux condenser). They observe that 20% of immobilized Pd is not reduced to a zero-valent oxidation state. Yuan et al. [127] use a similar procedure for the preparation of a chitin–platinum complex to be supported on silica. An alternative process is cited by Huang et al. [119] for the reduction of palladium–chitosan complex immobilized on silica

particles: the hydrogenation reaction takes place in alcohol solution with hydrogen bubbling.

Vincent and Guibal [85] tested several reducing treatments for the reduction of palladium on chitosan flakes. Several reagents have been tested: sodium borohydride, sodium formate, in situ hydrogen production. The best catalytic performances are obtained with in situ hydrogen production (reaction of sulfuric acid with zinc powder), while the worst reduction is obtained with sodium formate; this can be correlated to the relative strength of these reducing agents.

While the processes described above consists in the immobilization of the catalytic metal on chitosan-based support, Zhu et al. [128] propose another process based on the immobilization of the catalytic metal in the reactive media by in situ formation of a metal cluster complex. They prepare several 2-(dimethylamino)ethyl derivatives of chitin for the immobilization of rhodium salt ( $\text{Rh}_6(\text{CO})_{16}$ ). The Rh cluster complexes can be used for the reduction of benzaldehyde and nitrobenzene using CO and water as the hydrogen source. This reduction is based on the principle of water–gas shift reaction (WGS). The reduction reaction is operated by mixing the substrate (either benzaldehyde or nitrobenzene) with chitin derivative and rhodium salt in toluene and water. The reaction is initiated by introduction of CO at 80 °C. Zhu et al. suggest that under WGS conditions  $\text{Rh}_6(\text{CO})_{16}$  transformed to  $\text{Rh}_6(\text{CO})_{15}\text{H}^-$  by a nucleophilic attack of  $\text{OH}^-$ ; the anionic rhodium salt therefore binds to ammonium cation of the polymer through ionic bonding. 2-(dimethylamino)ethyl derivatives of chitin are prepared by (a) the alkali chitin method, involving reaction of chitin in alkaline media with 2-(dimethylamino)ethyl chloride (DMAE-Cl) with tetrapolyammonium bromide as the activator (and further precipitation in acetone/ethanol media); (b) the organic solvent method, consisting in the reaction of DMAE-Cl after chitin has been reacted in dimethylsulfoxide solvent with sodium hydride (the final product is precipitated in acetone/ethanol media); (c) the homogeneous method. The homogeneous method consists in dissolving chitin in LiCl and dimethylacetamide under agitation and heating (50 °C) overnight. The mixture is then lowered to 0 °C. The clear viscous solution is then reacted with NaH for 6 h at 75 °C. DMAE-Cl is then added under

agitation for 18 h. The final product is obtained by precipitation in acetone. Zhu et al. [128] prepared supports with the different methods and with different substitution degrees and they found that both the degree of substitution and the preparation method strongly control the conversion yield. They conclude that the most efficient chitin derivative is obtained with the homogeneous method: heterogeneous preparations result in partial deacetylation and non-uniform structures of the catalyst.

## 5. Examples of reactions catalyzed with chitosan-supported materials

Most of the research focusing on the use of chitosan in supported catalysis deals with oxidation and reductive hydrogenation reactions; however, a few papers have been devoted to fine chemical synthesis, and other more specific reactions (ring opening polymerization, carbonylation, etc.). Some examples are listed below.

### 5.1. Oxidation reactions

Chiessi et al. [64] prepare branched-chain derivatives of chitosan, which are soluble in water, for the binding of Cu(II). Chiessi and Pispisa [44] use some of these chitosan derivatives for binding Cu(II) and Fe(III) for the air oxidation of adrenaline (epinephrine, or 3,4-dihydroxy- $\alpha$ -(methylamino-methyl)benzyl alcohol) and DOPA (3-(3,4-dihydroxyphenyl)alanine) at pH 8.5. The identification of the reaction pathway is complex and the products of the reaction depend on the oxidation power of the central metal ion. Oxidation of adrenaline occurs by intramolecular electron transfer within a binary adduct (substrate and molecular oxygen) in the case of iron-supported chitosan, while with copper-supported catalyst a ternary intermediate is involved (substrate, copper ion and oxygen), in which Cu(II) acts as an electron mediator. More recently Paradossi et al. [129] prepared chitosan hydrogels using fully oxidized  $\beta$ -cyclodextrin for the uptake of copper and the application of this material for the oxidation of adrenaline.

Recently, Finashina et al. [91] oxidized adrenaline and DOPA by molecular oxygen using CoSalen

(a Co(II) complex of bis(salicylideneethylene diamine)) immobilized on chitosan and chitosan modified by 4-pyridinecarboxaldehyde. Chitosan is dissolved in acetic acid under heating and stirring, and 4-pyridinecarboxaldehyde dissolved in methanol is added drop-wise to the viscous solution. After 90 min of reaction the pH is adjusted to 6. The gel is washed off several times with water as well as methanol and finally air-dried at room temperature. Chitosan (or chitosan derivative) is added to a saturated solution of CoSalen in water for the immobilization of metal complex on the polymer support. Alternatively, the polymer dissolved in HCl is mixed with CoSalen to prepare a homogeneous catalyst. This mixture can also be used for the preparation of the precipitated form of this catalyst: the mixture is dropped into a NaOH neutralization bath to form dark-brown globules. The homogeneous preparation is also used for coating silica gel (pre-conditioned by alkaline treatment): the 'alkaline' silica gel is dipped into a CoSalen–chitosan solution. Alternatively, the 'alkaline' silica gel can be dipped into chitosan solution, prior to immobilization of CoSalen complex. After washing and drying, catalytic experiments are performed by contact of the catalyst with catechol-amine substrates (adrenaline, DOPA) under dioxygen flow. The catalytic performance is strongly controlled by the conditioning of the catalyst. The size of chitosan particles greatly influences catalytic performance, indicating that diffusion restrictions play an important role in the kinetic performance. This may explain the better efficiency reached using silica as the support for chitosan. Depositing a thin layer of chitosan derivative–CoSalen on macroporous silica increases catalytic activities. CoSalen was also used by Hu et al. [130] for the preparation of an oxidation catalyst supported on *N*-(4-pyridylmethylidene)-chitosan. The rate of oxidation of DOPA obeys a Michaelis–Menten type equation that confirms the formation of a catalyst–substrate complex.

Chang et al. [131] use non-noble metals (nickel and manganese) bound to nitrobenzaldehyde immobilized on chitosan for the oxidation of hydrocarbons with molecular oxygen under mild conditions. Chitosan is mixed with *o*- or *m*-nitrobenzaldehyde in benzene overnight under reflux, while the substrate is reacted with epichlorohydrin and NaOH dissolved in dichloroethane. The mixture is stirred for 10 h at



40 °C. The dried product obtained is mixed with nickel chloride (or manganese acetate) in anhydrous ethanol under reflux for 10 h. The reactivity of the catalysts depends on the structure of the precursor (*ortho*- or *meta*-precursor, *o*- or *m*-nitrobenzaldehyde) and the substrate. With *o*-nitrobenzaldehyde–chitosan–Ni (*o*-NC–Ni) no activity is detected for ethylbenzene, contrary to *n*- and *i*-propylbenzene. In the case of *o*-NC–Mn and *m*-NC–Ni, comparable catalytic activities are obtained regardless of the substrate, while none of these substrates is oxidized with *m*-NC–Mn. The most significant differences between the various substrates have been observed in the orientation of the reaction: with ethylbenzene and *n*-propylbenzene, the products of the reaction are the corresponding  $\alpha$ -alcohols and  $\alpha$ -ketones; while with isopropylbenzene the oxidation products are 2-benzyl-isopropanol and isopropylbenzene peroxide. This confirms that chitosan has potential for controlled catalytic regioselectivity. They discuss the catalytic mechanism and suggest that the substrate is first oxidized by molecular oxygen to  $\alpha$ -alcohol and then transformed to  $\alpha$ -ketones in the presence of catalyst.

Kucherov's group [94,95] recently published a series of papers on the use of heterogenized catalysts obtained by immobilization of copper on chitosan (and other polymers) for the oxidation of *o*- and *p*-dihydroxybenzene (in aqueous medium) into quinones. Several copper catalysts were prepared:

- (i) homogeneous catalyst (copper chloride mixed with chitosan solution obtained by polymer dissolving in acetic acid);
- (ii) copper co-precipitated with chitosan (the homogeneous catalyst is precipitated in NaOH);
- (iii) copper adsorbed on chitosan gel beads with copper–chitosan complex immobilized on silica gel (impregnation of porous support with the homogeneous catalyst, followed by precipitation in NaOH),
- (iv) copper immobilized chitosan supported on silica gel (silica gel dipped into chitosan solution followed by (a) cross-linking with glutaraldehyde, and in a subsequent step by (b) copper adsorption),
- (v) copper–chitosan complex modified by cross-linking (water-in-oil emulsion of copper complex

with hexane and an emulsifying agent (SPAN 60), followed by glutaraldehyde cross-linking).

These materials were tested for the oxidation of *ortho*- and *para*-dihydroxybenzene with air into *ortho*- and *para*-benzoquinone, respectively. The authors observe that when using homogeneous systems, the complexation of copper with hydroquinone limits the formation of quinone products. This contrasts with the results obtained with a heterogenized catalyst, whose catalytic properties are substantially higher. It appears that intermediate quinhydrone formed at the initial stage of the reaction yields a stable molecular complex with amino-groups of heterogenized Cu–chitosan. With raw chitosan particles the efficiency of the process is better with the precipitated material compared to the 'adsorption-type' catalyst. In the case of the catalyst prepared by adsorption, there is an accumulation of copper at the surface of the sorbent that is responsible of the great efficiency of the process at the initial stage of the reaction, while in the second stage of the process the efficiency substantially decreases. They explain this behavior by the formation of a stable molecular complex between amine groups of chitosan and the products of the reaction (final product and intermediate quinhydrone). With 'precipitation-type' catalyst the distribution of active sites is more dispersed and more homogeneous; this allows maintaining the activity for a longer reaction time. The catalytic activity of the Cu–chitosan catalyst immobilized on silica is significantly higher than that of bulk catalyst, especially with macroporous silica. Indeed, the comparison of catalysts prepared with macroporous and microporous silica shows that the specific surface is not the key parameter: despite greater specific surface area ( $1010 \text{ m}^2 \text{ g}^{-1}$ ) MCM-41 silica with very small channels (4 nm) is less efficient than macroporous silica (with lower specific surface area of  $210 \text{ m}^2 \text{ g}^{-1}$ ). The blocking of the pores by chitosan prevents the diffusion of metal ions, substrate and products. Using thin films of Cu–chitosan (with low copper content) supported on the macroporous support significantly increases the efficiency of the process. Compared on the basis of copper content in the different catalytic systems the catalytic activity can be increased by up to 2 orders of magnitude. Kucherov et al. [132] compare the activity of different

Cu-polymer catalysts supported on silica using chitosan in comparison to synthetic polymers (i.e. composite of poly(ethyleneimine) (PEI)/polyacrylic acid (PPA)) for the oxidation of *ortho*-, *para*-dihydroxybenzenes and DOPA. They observe that chitosan is much more efficient, due to better film-forming properties. The formation of a thin and continuous layer at the surface of inorganic material provides a more effective use of active Cu sites. They also show that these silica-supported Cu-complexes have a higher catalytic activity than bulk Cu-polymer complexes. Bulk metal-polymer complexes (including Cu-chitosan Cu-PEI/PAA, and Cu-diimine impregnated polystyrene, Cu-polyarylate and Cu-polymethylmethacrylate) are compared showing that for the most efficient systems (i.e. Cu-chitosan and Cu-PPA) the symmetry of isolated copper sites approximates a coordinatively unsaturated square-planar structure: the coordination of copper ions plays a central role in the catalytic efficiency of the metal. They also underline the possible contribution of hydrophilicity to the reaction pattern.

Kramareva et al. [82] consider the possibility of using Pd-immobilized on chitosan-based materials for oxidation reactions. They prepare a series of Pd-based catalysts using the adsorption-type and the co-precipitation type procedures previously described (with palladium chloride instead of copper chloride). They investigate the structure of the products using FTIR and EXAFS analysis and conclude that in the 'adsorption-type' product, the adsorbed Pd bearing two Cl (in a hydrated form) is linked to two amine groups; after catalyst reduction, chloride atoms disappear and Pd metal bands appear with formation of dimmers. The structure is different in the case of the 'co-precipitation-type' catalyst: Pd is linked to two amine groups and two OH groups of different chitosan monomer units (1 Pd with four different glucosamine units). The Pd-N bonds are stronger than those involved in the formation of Pd-N complex with the adsorption method: complexing with chelate ligands instead of monodentate ligands. After metal reduction, different structures may exist on the basis of the formation of trimers (triangular structure or long open chain). They use these materials for preliminary catalytic tests for the oxidation of terminal olefins. They observe that in neutral media, the catalyst formed by the coprecipitation procedure causes olefin

isomerization and poor oxidation activity; while the catalyst prepared by the adsorption process shows greater efficiency for the oxidation of olefins using  $\text{H}_2\text{O}_2$  in acidic media for copper re-oxidation [82,133].

Guibal et al. [134] also investigate the use of chitosan as a support for copper for hydroquinone oxidation. The oxidizing agent has to be carefully selected: dioxygen provides very selective oxidation but low production rates compared to hydrogen peroxide. With this drastic oxidizing agent ( $\text{H}_2\text{O}_2$ ) the kinetics of the oxidation reaction are strongly increased but at the expense of a loss in selectivity, resulting in the synthesis of secondary products. This decrease in selectivity is controlled by the amount of catalyst and concentration of hydrogen peroxide. The optimization of the process depends on these parameters that appear to be dependent. Short contact times of the catalyst with the substrate limit the synthesis of by-products. For these reasons the use of a hollow chitosan fiber loaded with copper and with dioxygen as the oxidizing agent seems to be very promising. The solution could be pumped through the lumen of the fiber with dioxygen present outside of the fiber: the controlled diffusion of dioxygen through the fiber and its reaction at the surface of catalytic metal will provide controlled oxidizing conditions that are expected to be appropriate for selective oxidation of *p*-benzoquinone. The use of dioxygen and short contact times is expected to prevent the formation of secondary products.

A recent work by Guo et al. [135] has shown that chitosan can be used for the immobilization of iron tetraphenylporphyrin in order to prepare a catalyst for air oxidation of cyclohexane. A solution of chloro-tetraphenylporphinato-iron(III) (dissolved in benzene) is added to a chitosan solution (in acetic acid), after the pH of chitosan solution is controlled to neutrality using sodium carbonate. The catalyst is added to cyclohexane and the oxidation is operated with dioxygen in absence of reductants and solvents. The amine groups of chitosan coordinate axially with the iron atoms of chloro-tetraphenylporphinato-iron(III) to form chitosan-supported iron porphyrin, which has better catalytic power than the corresponding unsupported iron porphyrin, and significantly greater efficiency than the soluble cobalt catalyst used in industry. Cyclohexane is transformed to cyclohexanol and cyclohexanone; the selectivity of the reaction



changes with time. Catalytic efficiency is maintained at the same level for at least 12 cycles. This work clearly demonstrates the interest of chitosan for the immobilization of metalloporphyrin; this technique can be also used for the immobilization of phthalocyanines that are powerful oxidizing agents [136,137]. This seems to be a promising research area.

## 5.2. Hydrogenation reactions

Ishizuki et al. [125] observed that chitosan can be used to protect precious metal particles, and used these colloid-supported materials for the decomposition of hydrogen peroxide and the hydrogenation of methylvinylketone. The experimental procedure for catalyst preparation has already been described (see above). For hydrogen peroxide decomposition, the reaction is performed using a composite Au–Pt catalyst in sulfuric acidic solution (2 M) at 40 °C. In the case of the hydrogenation of methylvinylketone the reaction is performed using a composite Au–Pd catalyst at 60 °C, the solution being saturated with hydrogen. Each of these reactions obeys first-order kinetics relative to the substrate and the catalyst.

A series of chitosan–synthetic polymer composites have been prepared by Jin et al. [117] for the immobilization of Pd. A mixed chitosan solution (dissolved in acetic acid) and dilute polyacrylic acid (PAA), or polymethacrylic acid (PMA) is added dropwise to silica particles. After homogenization, acetone is added to the slurry to precipitate the chitosan material. The metal is impregnated by contact with palladium chloride solution in ethanol under agitation with reflux. The dark-brown solid is used after drying for hydrogenation of nitrobenzene (into aniline) or acrylic acid (into propionic acid) in methanol with the aid of hydrogen. The relative proportions of chitosan and synthetic polymer were varied: the best composition for maximum catalytic efficiency is found for a similar amount of biopolymer and synthetic polymer. PAA- and PMA–chitosan composites give similar trends with a slightly better efficiency when using PAA–chitosan material. Under selected experimental conditions, acrylic acid is more efficiently hydrogenated than nitrobenzene: the reaction time for complete conversion is 2–3 times greater for nitrobenzene than for acrylic acid. It is also interesting to note that

the reaction does not produce by-products: the catalysts are not only very efficient but also selective.

Silica-supported chitosan–palladium catalysts have been used for the hydrogenation of nitrobenzene, hexene-1, acrylic acid, chloronitrobenzene and phenol to aniline, hexane, propionic acid, chloroaniline and cyclohexanone, respectively [138–140]. For the preparation of supported-catalyst, chitosan is dissolved in acetic acid solution and then silica is added to the solution at 40 °C. Sodium hydroxide is added drop-wise to the slurry in order to cause chitosan precipitation (controlling the pH to 13). Palladium chloride is mixed in ethanol medium with a fixed amount of chitosan–silica support under reflux. Palladium reduction occurs simultaneously with metal uptake (as shown by the dark grey color of the solid). Wang et al. [138] immobilize palladium on chitin using methanol as the solvent. Unfortunately, they did not fully characterize the chitin (especially the deacetylation degree). They observe that Pd–chitin is not only a very active but also a very selective catalyst for the hydrogenation of nitrobenzene, hexene-1 and acrylic acid. The catalytic activity of Pd–chitin is lower than that of Pd immobilized on chitosan–silica composite, regardless of the substrate and the pH of the solution. The hydrogenation reaction takes place over a wide range of pH (between pH 2 and 11) but with a greater activity in alkaline solutions. The comparison of Pd immobilized on chitin and chitosan flakes (immobilization performed in solvent) shows the greater reactivity of the chitin-based material. In the hydrogenation of phenol to cyclohexanone using Pd immobilized on silica–chitosan material they observe that the reaction is selective (no formation of by-products) and that the conversion yield increases with increasing polymer/Pd ratio at the optimum temperature of 70 °C [139]. In the case of the hydrogenation of nitrobenzenes on a Pd/chitosan/silica catalyst, An et al. [140] also obtain a very selective transformation of chloronitrobenzenes in their respective chloroaniline solutions using hydrogen gas. The maximum catalytic activity in the initial stage of the reaction is obtained with a polymer/Pd molar ratio of 50. Changing the solvent of the reaction affects the initial rate and also the time required for complete conversion of the substrate: methanol, ethanol and cyclohexane give comparable catalytic performance, better than those obtained in

toluene and THF solvents. The temperature should be in the range 30–45 °C to increase hydrogenation rate and to lower the reaction time.

In the asymmetric hydrogenation of ketones (acetophenone, propiophenone, 3-methyl-2-butanone and 4-methyl-2-pentanone), to corresponding alcohols ((*R*)-(+)-1-phenyl-1-ethanol, (*R*)-(+)-1-phenyl-1-propanol, (*R*)-(+)-3-methyl-2-butanol, (*R*)-(+)-4-methyl-2-pentanol) Yin et al. use similar catalysts under hydrogen [86]. In the case of aromatic ketones (acetophenone and propiophenone), both the conversion yield and the optical yield are drastically controlled by the N:Pd molar ratio: the yield of the reaction increases with increasing N:Pd while the optical yield reaches a maximum in the range of N:Pd 2.3–3.1 for acetophenone and continuously lowers with decreasing N:Pd ratio in the case of propiophenone. For acetophenone the optical yield can reach as high as 99%, indicating the catalyst to be enantioselective. This selectivity is significantly better than that obtained with propiophenone: the catalyst is very sensitive to metal content and to small modifications to the structure of the substrate. In the case of aliphatic ketones, the conversion yield is close to 100%. The optical yield is very high for (*R*)-(+)-3-methyl-2-butanone (increasing with decreasing the ratio N:Pd) and significantly greater than that obtained with (*R*)-(+)-4-methyl-2-pentanone. They conclude that the optical yield is very sensitive to (a) the N:Pd ratio in the complex, and (b) small changes in the ketone structure.

Zhou et al. [141] use magnesium oxide for supporting chitosan–Rh complex to perform asymmetric hydrogenation of diketones. Chitosan is dissolved in acetic acid and the pH progressively increased to 7, magnesium oxide (in powder) is added to the solution and the pH is raised to deposit chitosan on the surface of the mineral oxide. Rhodium chloride dissolved in ethanol is mixed with MgO–chitosan under reflux with nitrogen atmosphere for 12 h. The asymmetric hydrogenation is performed on 2,3-butanedione and 2,4-pentanedione by contact of the diketone with the catalyst in a solvent with hydrogen gas. Increasing the amount of Rh immobilized on the support increases the yield of the reaction, but the highest stereoselectivity is reached with a Rh content of 0.1 mmol Rh g<sup>−1</sup> support: 2,3-butanedione is preferentially transformed

to (2*S*,3*S*)-(+)-2,3-butanediol and 2,4-pentanedione is transformed to (2*S*,4*S*)-(+)-pentanediol. Changing the solvent affects not only the conversion yield but also the optical yield: ethanol appears the most appropriate solvent for this reaction. Increasing the temperature to 60 °C increases substrate conversion to 100%, but at the expense of a decrease in reaction stereoselectivity (from 87 and 81 to 26 and 36% for butanedione and pentanedione, respectively); the temperature for maximum optical yield is around 28 °C. Re-used several times, the catalyst maintains equivalent performance in terms of both conversion yield and stereoselectivity.

Another example of asymmetric hydrogenation is given by Yuan et al. [127] using a similar procedure for the immobilization of platinum on silica–chitin composite. This catalyst is used for the hydrogenation of  $\alpha$ -phenylethanol in HCl/ethanol solvent with hydrogen gas. They show that the conversion of substrate increases with the amount of Pt immobilized (mmol Pt g<sup>−1</sup>). The substrate is only converted to 1-cyclohexylethanol: the catalyst is selective for this asymmetric hydrogenation, regardless of platinum content. On the other hand, when the amount of Pt on the catalyst increases (and exceeds 0.1 mmol g<sup>−1</sup>) the enantiomer excess for *R*-(+)-1-cyclohexylethanol drastically decreases. At low Pd loading, all metal active centers are chiral catalytic centers for the reaction, while increasing the metal content causes some of these active centers to become achiral. When changing the temperature of the reaction between 20 and 70 °C, it appears that the maximum conversion occurs at a temperature of 40 °C with no change in the selectivity of the reaction. However, when the temperature exceeds 30 °C, the excess of *R* enantiomer drops dramatically and the product of the reaction becomes an optically inactive racemate at temperature higher than 50 °C. The solvent used strongly influences both the conversion yield and the excess of *R* enantiomer. The best solvent is ethanol, but when using methanol and 1,4-dioxane the enantiomer excess (for *R*) is close to that obtained with ethanol, at the expense of a decrease in conversion yield; cyclohexane shows poor conversion and weak *R* enantiomer excess and 1,2-dichloroethanol gives an optically inactive racemate. The conversion yield is controlled by the addition of HCl: a clear optimum is found with the addition of 0.02 mmol of HCl for given experimental conditions (in 5 mL of ethanol, 1 mmol

of substrate, Pt: 0.01 mmol). The stereoselectivity of the reaction is not affected by the reaction time, while the conversion increases with reaction time until 24 h above which the conversion tends to level off. The catalyst is re-used six times without significant changes in the conversion and stereoselectivity. This catalyst is characterized by its high activity and stereoselectivity.

The reduction of benzaldehyde and nitrobenzene is described by Zhu et al. [93] using a derivative of chitosan already described for the immobilization of Rh carbonyl cluster ( $\text{Rh}_6(\text{CO})_{16}$ ) and carbon monoxide (at high pressure, i.e. 10 atm). Instead of molecular hydrogen, water is used as the hydrogen supply for this water–gas shift reaction. Benzaldehyde is transformed to benzyl alcohol with a maximum yield obtained at 80 °C, and has its conversion rate increasing with the amount of catalyst. The solvent has a large impact on the conversion: 2-ethoxyethanol is much more efficient than toluene. Under optimum conditions (2-ethoxyethanol,  $T$ : 80 °C), benzaldehyde conversion exceeds 96%. Nitrobenzene is converted to aniline with yield of 70% in 2-ethoxyethanol solvent (which is more appropriate than toluene).

Huang et al. [119] prepare nanosized palladium catalysts protected by chitosan and silica; these catalysts are tested for the hydrogenation of nitrobenzene in ethanol under 1 atm hydrogen pressure. When preparing, first chitosan is dissolved in acetic acid solution, then silica is added to the solution. The mixture is dipped into acetone to give a chitosan shell and silica core. After drying, the powder is dipped into a  $\text{PdCl}_2$  solution (pH 1–2). After refluxing the mixture, the catalyst is dried and washed with ethanol. The reduction of palladium is performed in ethanol with hydrogen. The size of catalytic clusters strongly depends on the polymer/metal ratio: the size of catalytic clusters increases when decreasing the polymer/metal ratio. However, the catalytic activity (measured by hydrogen uptake rate) is not proportional to the size of clusters. The optimum catalytic activity is found for a silica/chitosan ratio around 7–8:1. Actually this optimum ratio corresponds to the formation of a monolayer at the surface of silica gel particles (a chitosan shell thickness close to 50 nm, which corresponds more or less the double of the gyration radius of a polymer coil). The composite material is modeled in relation with catalytic activity

and three different locations of Pd adsorption were identified [119]:

- (a) the external layer of the polymer;
- (b) the polymer network; and,
- (c) the innermost surface of the polymer layer at the interface with the silica (Fig. 5).

The external layer is directly in contact with the solution, the reaction is thus instantaneous but the aggregation of particles may induce significant loss of catalytic activity. Within the polymer network the reaction rate can be controlled by diffusion properties, while the innermost surface of the polymer layer is much less active due to very limited penetration in the polymer layers.

Adlim et al. [142] use several procedures derived from Ishizuki et al. [125] and Yin et al. [86] for manufacturing Pd- and Pt-based catalysts in the form of colloids and  $\text{TiO}_2$ -supported materials, respectively. For the preparation of colloids,  $\text{PdCl}_2$  is dissolved in HCl; after acid solvent evaporation, the red residue is dissolved in acetic acid to prepare the ‘mother’ metal solution. For platinum, freshly prepared solution ( $\text{K}_2\text{PtCl}_4$  being dissolved in HCl) can be directly used. Chitosan is dissolved in acetic acid and diluted with an equal volume of methanol, and the resulting solution is added to various volumes of mother metal solution (either Pd or Pt acid solution) to obtain different polymer/metal molar ratios. The resulting colloids can be reduced using three different

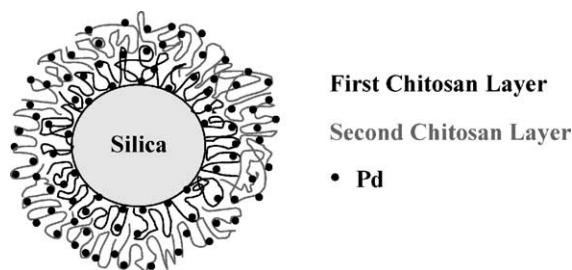


Fig. 5. Diffusion restrictions for chitosan-supported on silica particles—distribution of Pd at the outer surface of the composite silica–chitosan material; in the polymer layers and at the inorganic surface (derived from [119]). Synthesis and properties of nanosized palladium catalysts protected by chitosan/silica; A. Huang, Y. Liu, L. Chen, J. Hua; Copyright © (2002, John Wiley & Sons), ‘Reprinted with permission of John Wiley & Sons, Inc.’

procedures: (a) methanol reduction (refluxing the alcoholic solution in an oil bath), (b) sodium borohydride reduction (reaction of chitosan–metal colloids with  $\text{NaBH}_4$  in alcoholic medium in a closed vessel purged of oxygen), and (c) hydrazine reduction (contact of chitosan–metal colloids in alcoholic medium with  $\text{N}_2\text{H}_4$ ). The progress of the reaction is followed by UV–VIS analysis. For the preparation of catalysts immobilized on  $\text{TiO}_2$ , first the chitosan is dissolved in acetic acid and then dissolved with methanol,  $\text{TiO}_2$  suspended in a mixture of acetic acid and methanol is subsequently dropped into the chitosan solution. After impregnation,  $\text{NaOH}$  is added to precipitate chitosan on the inorganic support. The dried chitosan/ $\text{TiO}_2$  material is suspended in a methanol/water (v/v) mixture under agitation. The suspension is added under stirring to metal solution (prepared by dissolving salt in ethanol) for 24 h at room temperature. The metal is reduced by the procedures described for the preparation of colloid catalysts. Pd reduction is more difficult (requiring higher concentrations of reducing agents) and slower than that of Pt: these results correlate to the relative reduction potential of Pt and Pd in acidic solutions. The finest and best dispersed particles of chitosan–Pd or chitosan–Pt are obtained with a methanol or borohydride reduction procedure, while reduction with hydrazine results in the formation of large aggregates. Under optimum reducing conditions the size of Pd or Pt particles does not exceed 2.2 nm (with narrow size distribution). In most cases, the size of catalytic particles is not influenced by the metal/polymer ratio; however, in the case of a Pd catalyst reduced with methanol, the size of the particles increases when the metal/polymer ratio is reduced. When immobilized on  $\text{TiO}_2$  the size of catalytic particles is significantly increased to 7–10 nm. These catalysts are used for the hydrogenation of octene and cyclooctene in methanol using hydrogen gas. In the case of cyclooctene, the only product of the reaction, regardless of the metal immobilized on the chitosan-colloids, is cyclooctane. It is more complex in the case of octene hydrogenation: the reaction is selective when using platinum with production of octane, while with Pd, in addition to octane, two isomers are produced (2-octene and 3-octene). Generally the catalytic activity of platinum for octene hydrogenation decreases with decreasing metal/chitosan ratio

and the ranking of reduction procedures is as follows: methanol  $\gg$  borohydride  $>$  hydrazine. Compared to data found in the literature, the chitosan-supported catalysts are relatively more reactive than those obtained with inorganic and synthetic polymer supports. For a Pd-catalyst, the efficiency of the system is lower than for a system with Pt: this efficiency decreases with lower polymer/metal ratio (with simultaneous production of octene isomers). The higher efficiency of Pt (versus Pd) is confirmed by the determination of initial rate constants (calculated in the initial stage of the reaction assuming zero order kinetics): the initial rates are 3–8 times greater for Pt than Pd when methanol is used for metal reduction.

A series of papers has recently been published by Vincent et al. on the use of palladium supported on chitosan for the reduction of chromate [85], and the hydrogenation of phenolic compounds (including chlorophenol [143]; nitrophenol [144–146] and nitroaniline [147]). Chitosan flakes cross-linked with glutaraldehyde are mixed with palladium chloride at pH 2. Palladium reduction is operated with sodium formate, sodium borohydride or hydrogen (produced in situ by reaction of sulfuric acid with zinc powder). The best results were obtained with in situ generation of hydrogen. XPS analysis has shown that only 60% of total palladium (at the surface of catalyst particles) are actually reduced to Pd(0). The size of metal crystals has been determined by TEM analysis: though some aggregates have been observed, most of Pd crystals have a diameter in the range of 4–5 nm. Initial experiments have been performed using chromate reduction to optimize the synthesis of the catalyst [85]. An optimized catalyst (using hydrogen-type reduction) was therefore used for the reductive hydrogenation of chlorophenol [143]. The hydrogenation process uses sodium formate as the hydrogen donor. Optimum degradation of chlorophenol is achieved at pH 3. Several parameters have been investigated for optimizing catalytic reaction: catalyst dosage, hydrogen donor concentration, chlorophenol concentration and temperature. Dehalogenation leads to the formation of phenol and with selected experimental conditions to the production of cyclohexanol or cyclohexanone: actually, the reaction is a combination of dehalogenation and dearomatization mechanisms that has been previously cited for

the hydrogenation reaction of phenol derivatives on Pd-supported catalysts [148]. It seems that the dearomatization occurs simultaneously with dehalogenation since under selected experimental conditions phenol cannot be directly dearomatized in cyclohexanol or cyclohexanone. This contrasts with the results obtained by Tang et al. [139] who achieved a good conversion of phenol to cyclohexanone with a Pd catalyst immobilized on a silica–chitosan composite (using the alkaline neutralization procedure of silica and chitosan solution mixture followed by Pd uptake in alcoholic medium). In a more recent work they show that hydrogenation efficiency for different substrates can be ranked in the following order: phenol > *m*-cresol > *p*-cresol >> *o*-cresol, to cyclohexanone, 3-, 4- and 2-methylcyclohexanone, respectively [149]. Optimum conversion is reached at a temperature around 70 °C, using cyclohexane solvent with a N:Pd molar ratio of 8 [149]. Increasing the catalyst dosage increases the degradation rate but at the expense of a decrease in the efficiency of the metal catalyst (TOF, turnover frequency) [143]. The final concentration of the substrate appears to be more controlled by the concentration of hydrogen donor than by the amount of catalyst. A 50-fold excess of hydrogen donor (compared to chlorophenol) is required to achieve the complete degradation of the substrate (efficiency greater than 98%). Increasing the temperature increases chlorophenol dehalogenation and the activation energy is found to be close to 20–25 kJ mol<sup>-1</sup>. In the case of nitrophenol hydrogenation, acidic pH also proves more favorable than neutral pH: pH should be controlled in the range 4–5 [144]. Nitrophenol is first converted into aminophenol before being transformed into different products depending on experimental conditions such as oxidative or reductive experimental conditions, or the type of nitrophenol. The reaction proceeds by hydrogen transfer: both the substrate and the hydrogen donor adsorb on the surface of the catalyst crystals, and the degradation of formate into carbon dioxide and hydrogen induces the reduction of nitrophenol. In most cases, the degradation rate obeys the first-order equation, except when the hydrogen donor is not in large excess. Table 1 reports the corresponding equations that can be used for fitting experimental data. The excess of hydrogen donor required for complete degradation of nitrophenol is lower

Table 1

Summary of kinetic equations used for the modeling of degradation kinetics [18,144]

Model	Equation	Modeling
Pseudo-first order	$\frac{dC(t)}{dt} = -k_0 C(t)$	$\ln \left[ \frac{C(t)}{C_0} \right] = -k_0 t$
Kinetic variable	$\frac{dC(t)}{dt} = \frac{-k_1 C(t)}{1 + k_2 C(t)}$	$t = \frac{1}{k_1} \left[ \ln \left[ \frac{C_0}{C(t)} \right] + k_2 (C_0 - C(t)) \right]$

$k_0$  (min<sup>-1</sup>),  $k_1$  (min<sup>-1</sup>),  $k_2$  (L mg<sup>-1</sup>): kinetic coefficients;  $C_{eq}$  (mg L<sup>-1</sup>): residual equilibrium concentration (case of reversible kinetic model).

(i.e. 10-fold excess) than for chlorophenol. However, increasing the temperature diminishes the excess of hydrogen donor [146] (Fig. 6). The activation energy for nitrophenol hydrogenation is found in the range 17–26 kJ mol<sup>-1</sup>, depending on catalyst dosage (Fig. 7). The free energy of activation is around 90–100 kJ mol<sup>-1</sup> [146]. The entropy of the reaction also varies with catalyst dosage between –224 and –254 J mol<sup>-1</sup> K<sup>-1</sup>, while the enthalpy of the reaction is in the range 15–24 kJ mol<sup>-1</sup>. Changing the velocity of agitation hardly influences the kinetics of the degradation; this indicates that the predominant step in the kinetic control of the reaction is not the resistance to external film diffusion [144]. The study of the effect of catalyst particle size, catalyst dosage (Fig. 8) and catalyst loading (metal content) leads to

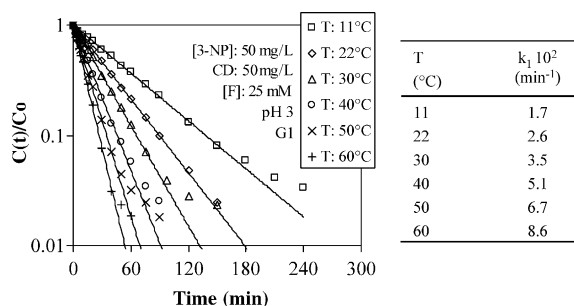


Fig. 6. Influence of temperature on the hydrogenation of 3-nitrophenol using sodium formate as the hydrogen donor and chitosan-supported Pd catalyst (derived from [146]). Reprinted from Journal of Environmental Management, 71, E. Guibal and T. Vincent, Chitosan-supported palladium catalyst. IV. Influence of temperature on nitrophenol degradation, p. 97–106, Copyright (2004), with permission from Elsevier.



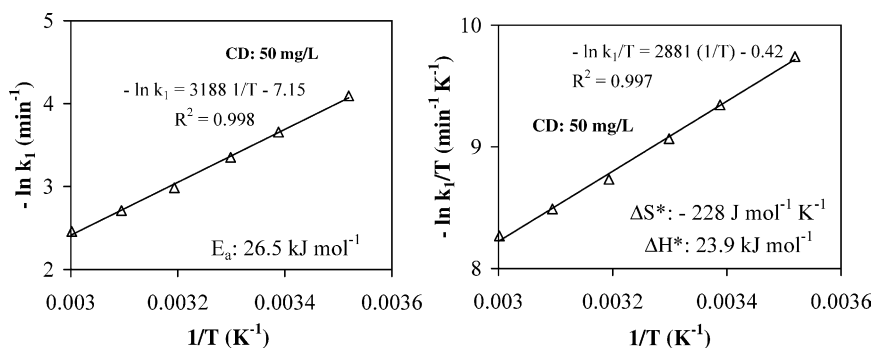


Fig. 7. Thermodynamic data obtained from Fig. 6 (derived from [146]). Reprinted from Journal of Environmental Management, 71, E. Guibal and T. Vincent, Chitosan-supported palladium catalyst. IV. Influence of temperature on nitrophenol degradation, p. 97–106, Copyright (2004), with permission from Elsevier.

the conclusion that internal catalytic sites play a limited role in the conversion process and that the reaction should be limited to the external surface of the catalyst. Similar conclusions are reached in the case of nitroaniline hydrogenation [147] (Figs. 9 and 10). The optimum use of the catalyst will be achieved using microparticles or depositing the supporting polymer as a thin layer at the surface of inert and porous material. An alternative process may consist in using catalytic chitosan hollow fibers. The concept is based on the preparation of hollow fibers treated with sulfate (to prevent the polymer dissolving in acidic solutions) and with palladium chloride (to adsorb catalytic metal) prior to hydrogen reduction. The solution to be treated is pumped into the lumen of the fiber while the outside of the fiber is in contact with hydrogen donor solution (sodium formate) or

hydrogen gas in the outlet compartment. The process has been tested for the degradation of nitrophenol [145]. In the case of sodium formate the hydrogen donor solution is recirculated and the pH maintained at 4 with formic acid (Fig. 11). This new conditioning process increases catalytic activity compared with the flaked material, up to five times greater under selected experimental conditions. Moreover, the use of this conditioning process enables better control of experimental conditions (pH, control of sodium formate and substrate concentrations), and reduces the effect of some parameters, such as the size of catalyst particles. Using hydrogen gas reduces the production of secondary contaminated flows, such as those occurring by transfer of nitrophenol through the membrane into the sodium formate solution at the outer surface of the fiber. Experimental conditions are expected to be easier to control using this

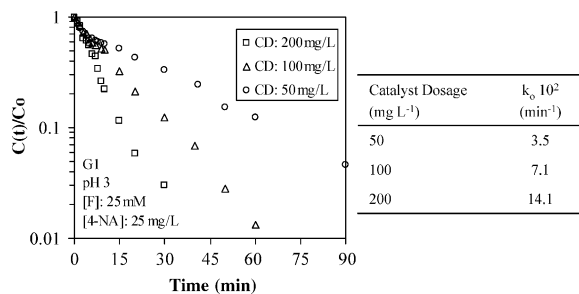


Fig. 8. Influence of catalyst dosage on the hydrogenation of 4-nitroaniline using sodium formate as the hydrogen donor and chitosan-supported Pd catalyst (derived from [147]). Chitosan-supported palladium catalyst. VI. Nitroaniline degradation, T. Vincent, F. Peirano, E. Guibal; Copyright © (2004, John Wiley & Sons), 'Reprinted with permission of John Wiley & Sons, Inc.

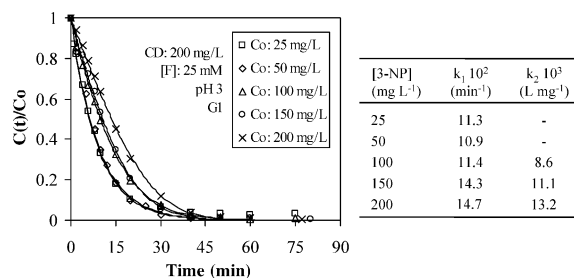


Fig. 9. Influence of substrate concentration on the hydrogenation of 3-nitrophenol using sodium formate as the hydrogen donor and chitosan-supported Pd catalyst (derived from [144]). Reprinted with permission from [144]. Copyright (2003) American Chemical Society.

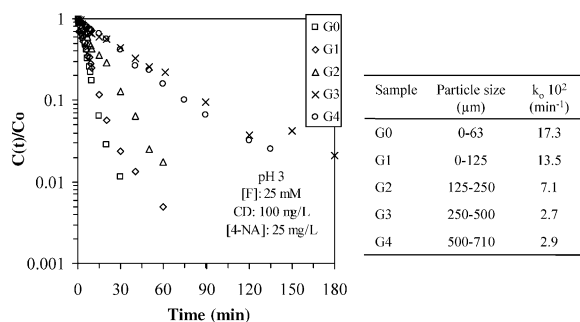


Fig. 10. Influence of the size of catalyst particles on the hydrogenation of 4-nitroaniline using sodium formate as the hydrogen donor and chitosan-supported Pd catalyst (derived from [147]). Chitosan supported palladium catalyst. VI. Nitroaniline degradation; T. Vincent, F. Peirano, E. Guibal; Copyright © (2004, John Wiley & Sons), 'Reprinted with permission of John Wiley & Sons, Inc.'

hydrogen donor. Moreover, using hydrogen gas avoids introducing an additional contaminant (unreacted sodium formate) into the treated solution. Both the sodium formate and the hydrogen gas

systems are characterized under a wide range of experimental conditions, taking into account parameters such as nitrophenol concentration, formate concentration or hydrogen pressure, and residence time. A key parameter appears to be the residence time. However, optimization of the process requires that the concentration of the hydrogen donor be taken into account, since increasing its concentration (or pressure) reduces the minimum residence time needed to reach a fixed level of nitrophenol conversion. Comparing the catalytic activity for each system leads to the conclusion that the sodium formate system is more efficient for nitrophenol degradation. However, taking into account the other advantages of the hydrogen gas system, the question remains open. It would be interesting to check the efficiency of a system involving a very short residence time but with significant recycling of the solution. An increase in system efficiency is expected.

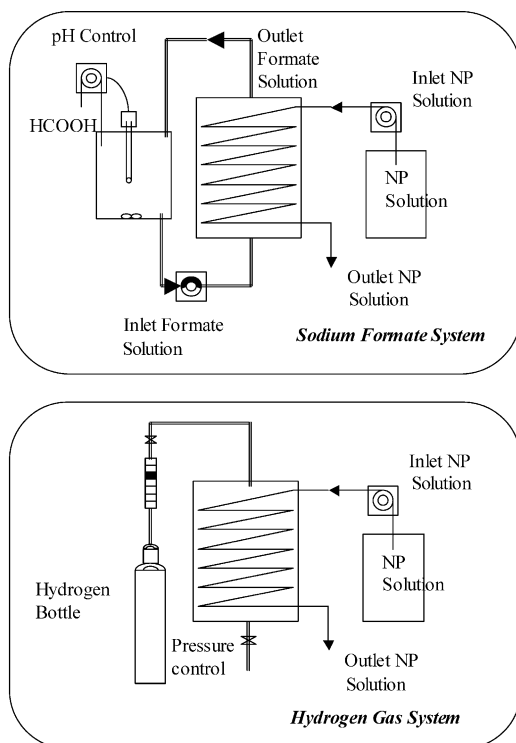
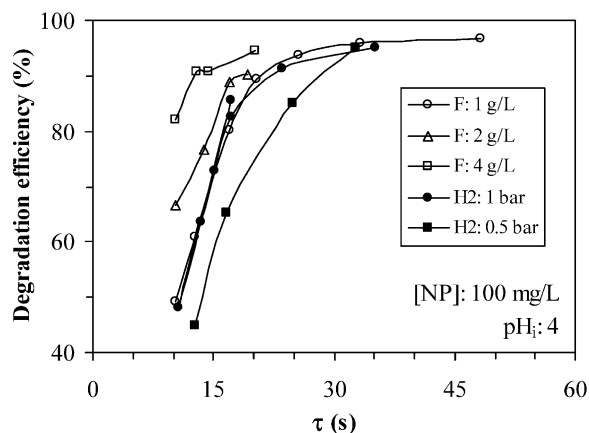


Fig. 11. Experimental apparatus used for the hydrogenation of 3-nitrophenol using either sodium formate or hydrogen gas as the hydrogen donor—effect of mean residence time on the degradation efficiency of the substrate (derived from [144]). Reprinted with permission from [144]. Copyright (2003) American Chemical Society.



Though most hydrogenation reactions using chitosan as a support have been performed with platinum group metals, non-noble metals (Ni, Cu, Cr and Zn) have also been used for the hydrogenation of aromatic nitro compounds (conversion of nitrobenzene to aniline) [150]. The catalytic reaction strongly depends on metal type, temperature, solvent, and hydrogen pressure. Binary metal catalysts give higher efficiencies than single-metal catalysts: highest conversion yields are obtained with Cu/Zn and Cu/Cr systems immobilized on chitosan/silica composite materials. For example, yields as high as 96–100% have been recorded for Cr/Cu and Cu/Zn binary catalyst while yields do not exceed 9% with single-metal catalysts. Conversion yield sharply increases when the reaction temperature is raised to 120–125 °C. Several solvent systems have been tested with the following yields sequence: ethanol (close to 100%)  $\gg$  methanol (close to 80%)  $\gg$  water (close to 40%)  $\gg$  THF and 1,4-dioxane (close to 1%). In the case of Cu/Zn catalyst (same molar content), the proportion of chitosan versus Cu (or Zn) was varied; and the optimum yield is obtained with a molar chitosan/metal ratio close to 12–13. The catalyst (silica/chitosan/Cu–Zn) gives comparably high conversion yields with other aromatic nitro compounds: 2-nitroanisole, 1-chloro-4-nitrobenzene, 2-nitroaniline and 2-nitrotoluene [150].

### 5.3. Allylic substitution reactions (Trost–Tsuji reaction)

Quignard et al. [45] describe the preparation of a palladium catalyst supported on chitosan for the allylic substitution of (*E*)-cinnamyl ethyl carbonate by morpholine. This reaction is an example of important carbon–carbon and carbon–heteroatom bond formation reactions. For the preparation of this catalytic system, the authors take advantage of the high surface hydrophilic character of chitosan for heterogenizing biphasic water/organic catalytic systems by the supported aqueous phase methodology. Palladium acetate is mixed with trisulfonated triphenylphosphine (TPPTS) in degassed water at 40 °C for 30 min to improve metal stability (formation of palladium–phosphine complex). The reduction of Pd(II) to Pd(0) is instantaneous (formation of Pd(TPPTS)<sub>3</sub> and simultaneous oxidation of TPPTS present in excess). The mixture is poured on chitosan

(pre-evacuated at room temperature,  $10^{-2}$  Torr). The slurry is stirred for 30 min at 40 °C and evacuated at low pressure overnight at room temperature. The reaction is carried out by contact of (*E*)-cinnamyl ethyl carbonate with morpholine in benzonitrile solvent (in a Schlenk tube) in the presence of the catalyst. A small given amount of water is added; allowing 30 min to reach equilibrium at room temperature. The reaction is initiated by raising the temperature to 50 °C. Quignard et al. [45] observe that the conversion yield strongly increases with additional water added to the solvent (i.e. benzonitrile). Compared to the performance obtained with silica-supported material under similar experimental conditions chitosan-supported catalyst appears less efficient, due to the residual crystallinity of the material and the low specific surface, which decreases diffusion properties, as well as accessibility to reactive sites. They improve the efficiency of the reaction by adding cetyltrimethylammonium bromide (CTAB, a cationic surfactant) to the reactive medium. This addition of CTAB increases the lipophilic character of the outer surface, improves the dispersion of the catalyst in benzonitrile and favors the accessibility of water to the amorphous part of the solid particles (and concomitantly to active catalytic sites). They observe that regardless of the experimental conditions the amount of Pd leached from the support does not exceed 1% in the presence of CTAB.

In a recent paper, Buisson and Quignard [35] use the same procedure for the preparation and testing of catalysts based on biopolymers: cellulose, polygalacturonic acid (PGA) and chitosan. They test several organic solvents: higher catalytic activities are reached with acetonitrile (which is miscible to water and has a higher dielectric constant). The differences observed between the various supports correlate to their specific surface area and their degree of crystallinity: hence, PGA, which is characterized by lower crystallinity and substantially higher specific surface area, proves more efficient. The catalytic activity is improved by using an ionic surfactant (CTAB and sodium dodecylsulfate, SDS), at the expense of an increase in Pd leaching: SDS seems to be more efficient than CTAB in improving the catalytic efficiency of chitosan-supported material.

#### 5.4. Suzuki and Heck reactions

A recent paper by Hardy et al. [151] tests the use of chitosan as a support for the immobilization of Pd salt to promote the Suzuki and Heck reactions. These coupling reactions are frequently used for the preparation of intermediary products in the synthesis of fine chemicals. Chitosan is modified by grafting 2-pyridinecarboxaldehyde in ethanol medium (under reflux). The solid is reacted with palladium acetate in acetone. After washing under reflux with ethanol, toluene and acetonitrile, the catalyst is dried. The Suzuki reaction is performed by mixing a fixed amount of catalyst into *o*-xylene; the slurry is therefore mixed with bromobenzene, benzeneboronic acid, potassium carbonate and *n*-dodecane, at appropriate temperature. The conversion yield depends on the substrate/Pd ratio: it should be equal or below 1200. Reflux temperature (i.e. 143 °C) shows more potential than lower temperatures for increasing the production of biphenyls. The recycling of the catalyst is improved when it is washed off with methanol, removing organic compounds that may block access to active sites. Similar experiments with several substrates show that electron donating substituents are more efficiently converted, while nitro-containing substrates caused problems, such as catalyst decomposition and formation of black solids. They observe that the kinetics of the reaction is comparable to that obtained with homogeneous catalysis (using butylamine, 2-pyridinecarboxaldehyde and palladium acetate), and they conclude that diffusion does not represent a critical parameter for heterogenized catalyst. They also show that 2-bromopyridine and bromopyrone can be converted with conversion yields higher than 74% into 2-phenylpyridine and 4-phenylpyrone, respectively, opening the route for the production of pharmaceutical products.

They carry out the reaction of iodobenzene with butyl acrylate, and the reaction of styrene with bromobenzene as tests for the Heck reaction to produce butyl cinnamate and stilbene, respectively, with a similar conversion yield (around 87%). They observe that the catalytic performance is similar to that obtained with silica-supported catalytic system.

#### 5.5. Polymerization

Inaki et al. [152,153] use chitosan and a glycol derivative of chitosan for the immobilization of copper and use the complex for the polymerization of vinyl monomers in carbon tetrachloride. They identify an initiation mechanism that involves the reduction of Cu(II) to Cu(I) in situ, followed by the transfer of a free radical to carbon tetrachloride to form trichloromethyl radical, which initiates the polymerization of acrylonitrile and methyl methacrylate. Different behaviors were observed for glucosamine and chitosan with varying pH. At high pH (i.e. pH 11) they observe high catalytic activity which they correlate to a redox reaction of the reducing endgroup of glucosamine with the Cu(II) complex. Though the presence of reducing ends is shown to be favorable, this is not sufficient to explain the high catalytic activity of the chitosan material: the comparison of the catalytic activity of copper in the presence of glucosamine, acetylglucosamine or glucose shows (in solvent system) that glucosamine is much more reactive than the other materials bearing reducing ends. At slightly acidic pH (pH 4–6.5), the complex is formed between 2 units of glucosamine and Cu(II) by coordination with one amino group and one adjacent hydroxyl group on each monomer; and the initiation of the polymerization is not observed. Increasing the pH increased the catalytic conversion, at alkaline pH the complex between Cu and glucosamine units involved one amino group and one adjacent oxygen atom on each glucosamine units. In this case they suggest that the primary free radical was assumed to be formed by a reaction of the copper(II) complex with a free amine unit or by a redox reaction accompanying ligand substitution to give an amino free radical. With the polymer, the coordination of copper involves three amine groups at slightly acidic pH (pH 5) and the polymerization reaction is not initiated. The complex changes in structure with increasing pH (between 7 and 9) as a chelate is formed between Cu(II) and two amino groups and two hydroxyl groups; the conversion reached a maximum in this pH range. Indeed, under these conditions chitosan exists in the form of a neutral polymer, which forms the most compact conformation, causing the closest proximity between the units. In the presence of NaCl, Inaki et al. [152] obtained an increase in

the polymerization of methyl methacrylate; they correlate this improvement in reaction yield to a change in the conformation of the polymer due to salt effect. Changing the molar ratio between amino groups and copper leads to considerable changes in polymerization; maximum catalytic activity is obtained when amino groups are in large excess (i.e. 10:1). Uncoordinated glucosamine units on the polymer chains appear to be necessary for efficient polymerization. Inaki et al. [153] obtain similar trends with a 6-glycol derivative of chitosan. The influence of the addition of neutral salts and the effect of temperature on the polymerization rate and yield confirm the strong influence of chitosan conformation on the performance of polymerization.

More recently, Huai-min and Xian-su [154] have shown that a complex of chitosan with cobalt can be used for the selective polymerization of vinyl acetate. A chitosan film is soaked in a  $\text{CoCl}_2$  aqueous solution before being dehydrated in ethanol and finally dried at 60 °C under vacuum. The polymerization of vinyl acetate (and other vinyl monomers such as methyl methacrylate, styrene, acrylamide and methyl acrylate) is performed at pH 7 and room temperature in presence of sodium sulfite. The kinetics is characterized by a first induction period, whose duration depends on the type of vinyl monomer, followed by a dynamic step. The induction period varies from 27 s for vinyl acetate to 2 min with methyl methacrylate and up to 4 h for styrene, acrylamide and methyl acrylate. The type of vinyl monomer also controls the yield of the reaction: 53% with vinyl acetate, 20% for methyl methacrylate and below 5% for other substrates. These results demonstrate the relative selectivity of this catalyst for the polymerization of vinyl acetate. Testing the reaction in presence of *p*-benzenediol, Huai-min and Xian-su [154] observe that this addition stopped the reaction as it occurs when the mechanism involve free radical polymerization mechanism. The observation of the FT-IR spectra of the products (similar to those obtained with the suggested reaction) confirms this mechanism.

Zeng et al. [155] use rare-earth catalysts (Y, La, Pr, Nd and Er) supported on chitosan for the ring-opening polymerization of propylene oxide. They prepare the catalyst by contact of metal oxide (dissolved in HCl solution) with a chitosan solution (dissolved in

acetic acid). The pH is finally controlled to 6.7 using dilute ammonia solution. The metal–chitosan complex is precipitated by adding an acetone–ethanol mixture; the solid is filtered and dried. The metal–chitosan complex is dispersed in toluene and air is flushed out by nitrogen gas under heating and reflux. Triisobutyl aluminum (Al) is added at 60 °C (under reflux) for 2 h before reacting the mixture with dried acetylacetone (acac) at room temperature for 1 h. These chitosan-supported catalysts are used to polymerize propylene oxide at 70 °C (manufacturing of polypropylene oxide, PPO). The type of rare-earth element immobilized on chitosan weakly affects the polymerization performance (conversion yield: 170 kg PPO  $\text{mol}^{-1}$  rare earth; high molecular weight: close to 10<sup>6</sup> g  $\text{mol}^{-1}$ ) and yttrium, being cheaper, is often preferred for the preparation of this catalyst. The best catalytic performance (molecular weight and conversion yield) is obtained with Al/Y and acac/Al that have ratios around 70 and 0.5, respectively. Increasing the reaction temperature causes the catalytic activity and molecular weight of the resulting polymer to increase. Zeng et al. [155] observe that the chitosan-supported materials have a higher stereoselectivity (based on the percentage of isotactic PPO) than conventional systems. The molecular weight of PPO sharply increases with reaction time and tends to level off above 8 h. The catalytic activity is approximately 16 times higher than that obtained with conventional catalytic systems. The optimum content of Y in the catalyst is in the range 0.5–0.6 mmol Y g<sup>-1</sup> chitosan, above which the embedment of yttrium atoms results in lower efficiency of the catalytic metal. The polymerization reaction rate is first order with respect to catalyst and monomer concentration. The polymerization rate constant at 60 °C is 1.39 L  $\text{mol}^{-1} \text{min}^{-1}$  (i.e. about 10 times greater than conventional material). The apparent activation energy of the optimized system is close to 37 kJ  $\text{mol}^{-1}$ .

### 5.6. Cyclopropanation of olefins

Cyclopropane derivatives are very important in organic chemistry owing to the frequent existence of this kind of structure in biologically active molecules. Metal complexes bearing chiral ligands can transfer carbene from diazo-compounds to alkenes. The primary reason limiting their industrial

scale application is the difficulty of recovering these chiral ligands at the end of the reaction. Heterogeneous catalysis using chiral supports may be a solution to this problem. Wang et al. [92] prepare a series of six derivatives of salicylaldehyde they subsequently react with chitosan to prepare Schiff base derivatives of chitosan. They use these derivatives for the uptake of a copper salt ( $\text{Cu}(\text{OAc})_2$ ) in ethanol medium. The chitosan-supported Cu catalyst is used for the cyclopropanation of olefins (styrene,  $\alpha$ -methylstyrene, 1-heptene, 1-octene, 1-nonene, 2,5-dimethyl-2,4-hexadiene) using ethyl (or butyl) diazoacetate in 1,2-dichloroethane solvent. They observe that increasing the amount of copper does not significantly change the conversion yield, but decreases the enantioselectivity of the transformation: this may be explained by a fraction of copper that absorbs at the surface of the support and does not really coordinate. The optimum copper composition is considered to be 4.4% (w/w). The conversion yield remains almost constant over five recyclings of the catalyst, while the enantioselectivity of the reaction progressively decreases. When using ethyl diazoacetate and styrene as substrates, neither the electron-withdrawing ability nor the bulky substituents on the salicylaldehyde derivative have much effect on conversion yield and enantioselectivity for the preparation of *cis* and *trans* isomers. In the case of butyl diazoacetate, there is a significant increase in reaction enantioselectivity, but a strong decrease in conversion yield. Comparing the catalytic performances of the catalysts prepared from different salicylaldehyde derivatives shows that the steric effect is more significant than the electronic effect in improving the enantioselectivity of the reaction. Butyl substituents on salicylaldehyde moieties behave favorably for the enantioselectivity of the reaction (especially in the case of butyl diazoacetate substrate). With this catalyst the cyclopropanation generally achieves a higher conversion yield and better enantioselectivity with heptene, octane and nonene compared to styrene, methylstyrene and 2,5-dimethyl-2,4-hexadiene. Other copper salts can be used, as described by Sun et al. [156], with similar experimental procedures.

### 5.7. Asymmetric dihydroxylation of olefins

Huang et al. [157] immobilize osmium tetroxide on a chitosan–silica composite for the vicinal hydroxylation of olefins. Silica is dispersed in chitosan solution (dissolved in acetic acid), polymer is coated on the mineral surface by reprecipitation at pH 13. Osmium tetroxide is dissolved in *tert*-butyl alcohol (completed with a few drops of *t*-butanoic acid); the mixture of metal alcoholic solution with chitosan-coated silica is stirred under reflux and nitrogen atmosphere for 24 h. The catalytic reaction is performed in *tert*-butyl alcohol/water (v/v) in the presence of potassium hexacyanoferrate ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) as the cooxidant and potassium carbonate. The catalyst is used for the dihydroxylation of styrene,  $\alpha$ -methylstyrene, 1-heptene, 1 octene and 1-decene to prepare (*R*)-(–)-1-phenyl-1,2-ethanediol, (*R*)-(–)-2-phenyl-1,2-propanediol, (*S*)-(–)-1,2-heptanediol, (*S*)-(–)-1,2-octanediol, (*R*)-(–)-1,2-decanediol, respectively. The conversion yield ranges between 50 and 90%: the highest yield (ca. 89%) and the highest optical yield (ca. 81%) is attained with 1-heptene. The conversion yield of styrene continuously increases with metal content in the catalyst, while the maximum optical yield is reached with Os content around  $0.067 \text{ mmol Os g}^{-1}$ . The catalyst is re-used for six cycles; the catalytic activity and optical yield (stereoselectivity) decrease only slightly when the catalyst is recycled.

Xue et al. [158] use a cobalt catalyst immobilized on chitosan–silica composite support for the asymmetric hydration of 1-octene to prepare (*S*)-(+)-2-octanol. The catalyst is prepared by the uptake of cobalt chloride on chitosan–silica material in alcoholic media. The chitosan–silica support is prepared by the precipitation of silica impregnated chitosan (dissolved in acetic acid) in NaOH solution. The reaction is operated in a water/solvent mixture with hydrogen gas. The optimum conversion yield as well as the optical yield is obtained with a 10:1 silica/chitosan molar ratio. Varying the amount of cobalt immobilized on the support leads to substantial differences in both the conversion yield and the optical yield: optimum performance is obtained for a cobalt content of  $0.5 \text{ mmol Co g}^{-1}$  support. Both the conversion efficiency and the optical yields reach a maximum

when the substrate/Co molar ratio approaches 50. The performance of the system is strongly controlled by reaction time: below 10 h, very poor conversion of the substrate is observed. The conversion and optical yields simultaneously increase until 30 h contact time (98% for both conversion yield and optical yield); eventually the conversion reaches 100% but at the expense of a loss of optical yield (which decreases to 49%). The catalyst was re-used for five cycles without significant change in the efficiency of the process or its selectivity. Under optimum experimental conditions (chitosan/silica ratio; Co/support ratio; catalysts dosage; reaction time) it is possible to achieve a complete and selective conversion of 1-octene to (*S*)-(+)-2-octanol.

Köckritz et al. [159] also investigated the hydroxylation of olefins using osmium salt immobilized on chitin. Osmium tetroxide was mixed with chitin in acetonitrile solvent (with different metal/polymer molar ratio). Impregnated particles were finally filtered and solvent was evaporated. This catalyst proved efficient for the hydrogenation of  $\alpha$ -methylstyrene in the presence of *N*-methyl morpholine *N*-oxide in a weakly acidic medium (i.e. pH 5). The more active and selective catalysts are those with a higher loading of osmium tetroxide; unfortunately, the enantiomeric excess does not exceed 3–4% ee, regardless of metal content and the recycling of the catalyst proves unsuccessful. They also tested chitosan as a support (instead of chitin); in this case the catalytic activity is remarkably low compared to chitin material. They comment that the low activity of chitosan-supported catalyst may be explained by the higher binding constant of amine groups in chitosan compared to chitin. However, they suggest taking advantage of this strong interaction of the metal with chitosan for the recovery of osmium tetroxide at the end of the catalytic reaction, when the catalytic metal is used under homogeneous conditions. Chitosan proves much more efficient than chitin for the sorption of osmium tetroxide in solvent media (dichloromethane): this method of scavenging osmium contaminations provides an interesting alternative to the heterogeneous dihydroxylation reaction.

### 5.8. Carbonylation reactions

Zhang and Xia [118] use a Pd-catalyst supported on chitosan deposited on silica particles for the carbonylation of 6-methoxy-2-vinylnaphtalene. The chitosan–silica composite is prepared by impregnation and precipitation, the support is finally mixed with an alcoholic solution of palladium chloride (previously reacted for 24 h with ethanol to form a red–brown solution). The substrate is mainly converted into methyl ester of Naproxen (a non-steroidal anti-inflammatory drug), and its linear isomer (methyl 3-(6'-methoxy-2'-naphthyl) propanoate); additionally, in some cases the later can be partially transformed by etherification with methanol. The reaction is performed in dioxane with alcohol and carbon monoxide (at the optimum pressure of 4 MPa) at the temperature of 100 °C. The nature of the alcohol is not a critical parameter: methanol, ethanol, *n*- and *i*-propanol hardly change the overall efficiency of the reaction. Using methanol improves the regioselectivity of the reaction, while *i*-propanol decreases the selectivity. The hydroesterification of the substrate is favored in the presence of an acid promoter (HCl, rather than *p*-toluenesulfonic acid) and in the presence of triphenylphosphine (PPh<sub>3</sub>). In the absence of PPh<sub>3</sub> the conversion yield strongly decreases due to the formation of inactive bulk particles: triphenylphosphine contributes to the stabilization of molecular Pd species (optimum ratio: PPh<sub>3</sub>/Pd: 3). The efficiency of the reaction is increased when a second metal (Co, Fe, Cr, Mn, Cu, Ni) is added in the reaction medium, especially when the metal is added in the form of a chloride salt (chloride ions contribute to the stabilization of the catalytic metal). The highest conversion yield and the best selectivity are obtained using NiCl<sub>2</sub> as the second metal. TEM analysis of catalyst particles indicates that Pd crystallites are between 5 and 15 nm in size. The efficiency of the process was tested under selected optimum conditions for the conversion of styrene and derivatives for comparison with the conversion of 6-methoxy-2-vinylnaphtalene. The conversion yield and selectivity of the reaction are of the same order for styrene, but significantly lower for styrene derivatives.



It is interesting to observe that the conversion yield for the reference reaction is comparable for the chitosan-supported catalyst to the homogeneous reaction ( $\text{PdCl}_2/\text{NiCl}_2$ ) and to synthetic polymer-supported catalyst (polyvinylpyrrolidone) while the selectivity of the reaction is significantly increased when using chitosan-supported material. The recycling of the catalyst (for several catalytic cycles) can be enhanced using *p*-benzoquinone as a co-catalyst (for Pd stabilization).

Chitosan was also used by Kolesnichenko et al. [160] for the carbonylation of methylacetate. Though the reaction was carried out in a homogeneous mode, it is interesting to show how chitosan can contribute to improve reaction stability and economics of the process. Kolesnichenko and co-workers used a homogeneous catalyst based on  $\text{RhCl}_3$  in the presence of polymeric nitrogen- and oxygen-containing supports for the conversion of methyl acetate into acetic anhydride. The reaction is operated in the presence of a  $\text{CO}_2$  atmosphere (mixed with  $\text{H}_2$ ) and iodine salts ( $\text{MeI}$  and  $\text{LiI}$ ). Several nitrogen-containing polymers including natural materials (chitin, chitosan and polyglucin) and synthetic materials (styrene derivatives and pyridylmaleimide) are tested. In the absence of polymer (i.e. with only rhodium salt) the reaction is slow and in the case of polyglucin an induction period is observed, while this lag phase does not appear when chitosan is added to the reaction media. The addition of iodide salt (in the form of  $\text{LiI}$ ) strongly increases the reaction rate and avoids the induction phase: (a)  $\text{LiI}$  increases the rate of inactive  $\text{Rh}^{\text{III}}$  transformation into active  $\text{Rh}^{\text{I}}$ ; (b)  $\text{LiI}$  changes the reaction route (accelerating the liberation of  $\text{MeI}$ , oxidative addition reaction). This last step in the process avoids the formation of  $\text{HI}$  or  $\text{I}_2$  which is known to enhance the formation of inactive  $\text{Rh}(\text{CO})_2\text{I}_4^-$  instead of catalytically active  $\text{Rh}(\text{CO})_2\text{I}_2^-$ . The presence of chitosan stabilizes the catalytically active species. The major drawback of  $\text{LiI}$  salt is related to its cost. Kolesnichenko et al. [160] show that the presence of chitosan allows other cheaper salts, such as  $\text{AcOLi}$  or  $\text{Li}_2\text{CO}_3$ , to be used as reaction promoter with negligible impact on reaction kinetics, contrary to the results obtained with  $\text{RhCl}_3$  alone (without polymer). They explain the positive effect of chitosan by its capability of

alkylating  $\text{MeI}$  on the nitrogen atom; therefore, the coordination of the alkylated macroligand with the catalytically active  $\text{Rh}(\text{CO})_2\text{I}_2^-$  favors the oxidation of  $\text{MeI}$  to the  $\text{Rh}$  atom. The weakness of the process is related to the loss of  $\text{Rh}$  other reaction cycles; Kolesnichenko et al. [160] suggest using a distillation process for recycling the catalyst and co-catalysts ( $\text{LiI}$  and chitosan) and they obtain constant initial reaction rate for at least four catalytic cycles. The carbonylation of benzyl alcohol to phenylacetic acid in the presence of  $\text{RhCl}_3$  and  $\text{HI}$  was also studied by Kolesnichenko et al. [161]. The reaction is enhanced using benzyl chloride as a coreactant and  $\text{KI}$  as a promoter. These reagents increase conversion yield and contribute to reduce the temperature required for this reaction. The use of chitosan as a promoter also proves interesting for the stabilization of benzyl iodide (produced during the catalytic cycle) and makes it possible to increase the selectivity of the process even at elevated temperatures. Indeed, without chitosan, the reaction produces high-boiling products and toluene, in the presence of chitosan the production of phenylacetic acid is significantly increased while the production of secondary products does not exceed 10%, even at elevated temperature (150–180 °C).

### 5.9. Monoglyceride synthesis

Valentin et al. [48] and Molvinger et al. [49] describe the addition of a fatty acid (lauric acid) on glycidol to prepare monoglyceride ( $\alpha$ -monolaurin) using chitosan with an expanded structure. The expansion of the chitosan structure is achieved by supercritical  $\text{CO}_2$  drying from chitosan solution (in acetic acid) as gel beads [49] or after being immobilized on hybrid chitosan–silica particles [48]. Hybrid material is obtained by reacting an acidic chitosan solution with TEOS (tetraethoxysilane), silica condensation is catalyzed by addition of sodium fluoride, before drying the solid material by supercritical  $\text{CO}_2$ . The catalytic reaction is performed by contact of identical amounts of lauric acid and glycidol in toluene solvent in the presence of chitosan material at 70 °C. The yield of the reaction and its selectivity strongly depend on the manufacturing of the chitosan–silica hybrid material. It is important to prevent glycidol polymerization.

## 6. Critical parameters for the preparation of chitosan-supported catalysts

### 6.1. Porosity, diffusion and site accessibility

Duff et al. [162] point out the importance of site accessibility on catalytic performance. They correlate the activity of platinum-colloid catalysts (for hydrogenation reactions in methanol) stabilized by polyvinylpyrrolidone (free and immobilized on oxide supports, before and after calcination) to the accessibility of catalytic sites. On platinum colloids, the polymer layer limits accessibility to surface sites, but it is extremely well solvated in methanol. A solvent-rich surface layer forms that improves the diffusion of reactant molecules to the metal surface. When the catalyst is immobilized, a lower catalytic activity is obtained due to restricted access to surface sites. After calcination, the oxidation of PVP results in holes that enhance accessibility to Pt surface.

The influence of intraparticle diffusion has been investigated using Pd-catalysts supported on chitosan flakes of different diameters for the hydrogenation of nitrophenol and nitroaniline [144,147]. These experiments show that the reaction is located on the external layers of catalyst particles: the strong decrease of kinetic rates with increasing the size of catalysts confirms a contribution of the resistance to intraparticle diffusion in the control of reaction kinetics. External diffusion effects are more limited on the control of kinetics. This justifies immobilizing chitosan as a conditioning layer on inert materials with high specific surface area (ceramics, alumina, silica, activated carbon). This would combine the specific reactivity of chitosan (in relation with polymer conformation) with the porosity and high surface areas of inorganic materials.

In the immobilization of Pd nano-particles on silica functionalized by chitosan, Huang et al. [119] model the catalyst as a mineral core coated with a first polymer layer on which other polymer chains can be adsorbed; Pd can be (a) immobilized on silica surface (internal sites), (b) scattered in the polymer networks, and (c) adsorbed on the outer surface (Fig. 5). Depending on the amount of chitosan (compared to silica) the number of layers immobilized on silica surface will increase, which can cause diffusion limitations. Lower accessibility to internal metal

sites can reduce the kinetic rate and even the reactivity of metal crystals. Optimum catalytic efficiency is found for monolayer coverage of the silica surface, corresponding to a thickness of 40–50 nm (double the gyration radius of the polymer).

It is important to optimize the selection of the inorganic support prior to chitosan immobilization to prevent pore blockage due to the polymer deposit. Hence, Kuchеров et al. [94] compare the catalytic activity of different Cu-catalysts prepared by Cu immobilization on silica–chitosan composites with different silica materials (meso- and micro-porous silica). The blockage of nanopores by chitosan in the microporous silica strongly limits catalytic performance (metal immobilization, accessibility to active sites and diffusion kinetics), while with macroporous silica the catalytic efficiency of immobilized metals is strongly increased. They also compare the catalytic performance for materials prepared by the so-called adsorption and co-precipitation processes. While the adsorption process shows higher initial activity (in the early stage phase of the process) than the material elaborated with the co-precipitation process, after a longer contact time both processes give similar kinetics (in the second stage of the reaction). This is explained by the higher distribution of Cu at the external surface for the adsorption method (strong initial activity), but the formation of intermediary products (quinhydrone, for example) stable with amine groups of chitosan limits the reactivity of the material, while this mechanism is minimized when the catalytic metal is more dispersed in the core of the globules in the case of co-precipitation method [94].

### 6.2. Size of metal crystallites

There are a number of studies that highlight the correlation between catalytic activity and size of metal catalyst particles on colloids [125,142,163], nanoparticles [142,164], immobilized on mineral supports [165–168], and organic supports [119]. The size of metal particles is usually determined physically by TEM (transmission electron microscopy, Fig. 12) or HRTEM (High resolution TEM), measuring the cross-sectional average particle size. However, this technique has a high error potential since only very small areas can be examined at any one time. Heterogeneities in the products are not detected and



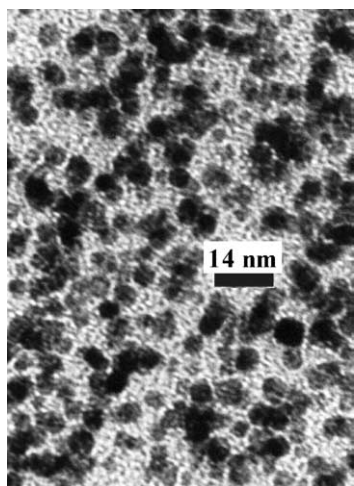


Fig. 12. Transmission electron micrograph of Pd-catalyst immobilized on chitosan particles. Reprinted from [147]: chitosan supported palladium catalyst. VI. Nitroaniline degradation; T. Vincent, F. Peirano, E. Guibal; Copyright © (2004, John Wiley & Sons), 'Reprinted with permission of John Wiley & Sons, Inc.'

taken into account in the determination of particle size [169]. The average grain size (crystal diameter) can also be obtained using the Scherrer equation from broadening of the peaks in a wide angle X-ray scattering (WAXS) measurement of the material [170]

$$d = \frac{k\lambda}{\beta(\theta) \cos \theta}$$

where  $\lambda$  is the X-ray wavelength (nm),  $\beta(\theta)$  the full width at half maximum (rad) of the identification peak,  $\theta$  is the diffraction angle and  $k$  a constant typical of the equipment.

Stevens et al. [169] point out the drawback of WAXS for the characterization of very small crystals, which lead to poorly resolved peaks. This makes it difficult to extract a precise value for the full peak at half maximum (FWHM) used in the Scherrer equation. They suggest using small-angle X-ray scattering (SAXS) for a more reliable determination of crystal size lower than 3 nm.

The effect of crystal size and metal dispersion on catalytic efficiency is due to an increase in the external metal surface area available for reaction. In most cases, decreasing the size of metal sites enhances catalytic activity for colloid-supported materials

[163], and for inorganic supports [165,171]. High surface area usually favors the reactivity of immobilized metal. However, the size of catalytic particles also controls the selectivity of the reaction due to different adsorption geometry of the substrate on particles of different sizes [165], or to different electron-deficient properties of the immobilized metal (also due to low surface coordination numbers) [168,172]. In some cases an optimum in the size of catalytic sites is found [166]. Sonochemical treatment can be used to control the size of metal sites and in turn control the enantioselectivity of the catalytic reaction [173].

The size of metal particles is controlled by the respective amounts of chitosan and metal for colloid-supported catalysts [125]. Increasing the relative amount of chitosan diminishes the size of metal crystals and increases the stability of the catalyst particles. In the case of bi-metallic catalysts (Au–Pt) the size of catalyst particles decreases and their stability increases when the molar fraction of Pt increases. The hydrogenation rate decreases with decreasing fraction of Pt (or Pd). This correlation between chitosan amount and catalytic efficiency is not systematic; in the case of gold–chitosan nanocomposites tested for the elimination of hydroxyl radicals (antioxidant effect) Esumi et al. [164] found optimum concentrations of chitosan to maximize the rate constant and diameter of gold nanoparticles. These critical concentrations are slightly different and they conclude that it is not possible in this case to correlate catalytic activity to the size of catalyst particles. In the case of polyvinylpyrrolidone-protected Pd nanoparticles, Hirai et al. [25] show that the size of metal nanoparticles depends on both the molecular weight of the polymer and the polymer/metal ratio. The impact of the molecular weight of the chitosan has not been frequently investigated in the many studies dedicated to chitosan-supported heterogeneous catalysis, but this parameter seems very important. The authors also show that size of Pd nanoparticles cannot be correlated to the catalytic activity but they conclude that the hydrogenation activity depends on specific surface area of Pd nanoparticles much more strongly than the thickness of adsorbed layer of polyvinylpyrrolidone [164]. Adlim et al. [142] prepare Pd and Pt catalysts supported on chitosan colloids, and they give

the best experimental conditions for metal reduction with regard to the size of metal particles: sodium borohydride and methanol appear more interesting than hydrazine for preparing 2–3 nm diameter range Pd and Pt particles, respectively. In this case, increasing the relative amount of chitosan hardly influences the size of catalytic particles but may contribute to greater aggregation of these particles. For Pd nanoparticles immobilized on chitosan/silica material, hydrogen uptake (measured as an indicator of hydrogenation potential of the catalyst) shows an optimum for chitosan layer thickness on the surface of silica close to double the gyration radius of chitosan, which in turn depends on the molecular weight of the polymer [119]. The thickness of this layer also depends on the chitosan/silica ratio [142]. The catalytic activity is uncorrelated to the size of nanoparticles (which decreases with increasing silica/chitosan ratio). Adlim et al. [142] point out the influence of diffusion properties and accessibility to catalytic sites. The addition of a co-catalyst may contribute to preventing metal aggregation and improving catalytic activity [118].

### 6.3. Metal content and oxidation state

Inaki et al. [152,153] point out the optimum molar ratio between Cu and amine groups of chitosan derivatives for the polymerization of vinyl monomers: they conclude that the maximum conversion of the substrate requires an excess of the ligand, possibly due to the influence of reducing ends on the polymer, which contribute to the initiation of the polymerization. The content of catalytic metal (reported as the metal/polymer ratio of support, mmol g<sup>-1</sup> or mmol mol<sup>-1</sup>) not only controls the efficiency of the process, but also the stereoselectivity of the transformation [86,127,141]. At low metal content Yuan et al. [127] observe low global efficiency but complete selectivity for the asymmetric hydrogenation of  $\alpha$ -phenylethanol; while increasing the amount of catalytic metal improves the efficiency of the process with a simultaneous decrease in stereoselectivity. They interpret these results by the coexistence of two catalytic sites of high metal content: the first being chiral and the other achiral. This interpretation would benefit from an in-depth study of catalyst particle size. Another interpretation of this loss of stereoselectivity (or at least a complementary

explanation) could be related to an increase in the size of metal sites due to an aggregation effect. Adlim et al. [142] show that both turnover frequency (mol product mol metal<sup>-1</sup> h<sup>-1</sup>) and selectivity increase with greater metal/polymer ratios.

The oxidation state of the metal on chitosan is a key parameter in the efficiency of the catalytic metal. For example, some of the processes used for the synthesis of these catalysts involve a metal reduction step. The catalytic activity is therefore correlated to the actual oxidation state of the metal on the material. X-ray photoelectron spectroscopy (XPS) is the usual analysis for the determination of oxidation state of metal immobilized on catalytic metals. This technique is also used for the identification of the chemical groups involved in the immobilization of the metals. The change in the binding energy (BE, eV) of the atom in reactive chemical groups (N in amine groups, for example) is helpful for confirming the contribution of the relevant groups. A careful analysis of the data is required for some metals since the electron beam impact may contribute to an analytical artifact leading to a misinterpretation of BE. Despite the generalized use of XPS for the characterization of chitosan-supported catalysts [82,86,95,118,130,131,149,156], only a few papers show full XPS spectra or/and clear interpretation and quantification of the part of metal that has been reduced [117,144]. Vincent and Guibal [144] indicate that for Pd-immobilized on chitosan flakes by adsorption and reduced with in situ generated hydrogen Pd(0) was only 50–60% of total metal amount at the surface of the catalyst. The comparison of reduction procedures and more generally the evaluation of catalytic activities require perfect determination of the exact quantity of active metal. The diffusion properties of chitosan (poor porosity) controls metal sorption, but may also control the reduction process and therefore the number of active sites.

### 6.4. Molecular structure of metal–chitosan assemblies

The activity of a catalyst is not only due to metal content but also to its configuration and the environment of the metal. Electron spin resonance (ESR), EXAFS and Mössbauer spectroscopy are useful tools for the identification of the structure of metal–chitosan complexes [44,129]. The flexibility of

chitosan chains is an important advantage for metal uptake but it makes the metal loaded on the chitosan stereoselective, which is responsible for chiral reactions (asymmetric hydrogenation for example) [86,127,141]. In the study of vinyl polymerization, Inaki et al. [152,153] clearly show the impact of polymer conformation on reaction rate: the flexibility controlled by the pH (neutralization of cationic charges of amino groups), the presence of neutral salts, and temperature strongly interfere with the geometry of the metal–polymer complex and its reactivity.

The environment of the metal and more specifically the spatial arrangement of ligands around the metal have a certain effect on the reaction mechanism [131]. Chitosan modified with nitrobenzaldehyde serves as a support for Mn and Ni for the catalytic oxidation of hydrocarbons: *ortho*- or *meta*-position on nitrobenzaldehyde ligand controls the reactivity and the selectivity of the reaction. Similarly the cyclopropanation of olefins is enhanced by copper immobilized on Schiff base derivatives of chitosan [92]. The substituents on the salicylaldehyde moiety of the catalysts significantly affect the enantioselectivity of the reaction. They conclude that the steric effect is more important than the electronic effect. Sun et al. [156] compare the cyclopropanation of olefins with several copper-based derivatives of chitosan; they observe that Schiff base derivatives of chitosan have much greater activity and higher selectivity than copper immobilized on raw chitosan.

The derivation of chitosan with pyridylmethylene enables Hu et al. [130] to sorb CoSalen. They use this material for the oxidation reaction and observe that the polymer supported complex is more efficient than the corresponding monomeric complex. This enhancement of catalytic activity is explained by a site isolation effect caused by the polymer chain. Hence, CoSalen (a four-coordinated Co(II) complex) does not bind oxygen strongly and easily forms inactive dimmers. However, it can bind oxygen in the presence of a suitable monodentate Lewis base (the peroxo bridged species of CoSalen,  $(\text{CoSalen})_2\text{O}_2$ ), which is unable to directly catalyze oxidation. The site isolation effect brought by pyridylmethylidene chitosan prevents the formation of dimmers and peroxo-bridged dimmers, improving the formation of an active species of superoxo cobalt complex  $(\text{Co(III)O}_2^-)$ .

Paradossi et al. [129] utilize the stiffness of the gel formed by the reaction of oxidized  $\beta$ -cyclodextrin to prepare a Cu-catalyst. The host cavities in the chitosan-based network might be modulated according to the geometry of the guest molecule and/or multivalent ions to be trapped in the hydrogel. This may contribute to higher catalytic selectivity.

An important work was performed by the Kucherov and Kramareva group on the characterization of the interactions between chitosan and metals such as copper [94,95,132], and palladium [82]. They correlate these properties with their catalytic activity. They show that the matrix of heterogenized chitosan is able to stabilize and retain copper ions in a highly unsaturated, coordinative state (water molecules penetrating in the catalyst do not coordinate with copper as additional ligands), which allows the uptake of molecular oxygen and the re-oxidation of copper sites (reduced in the course of the oxidation reaction). Low copper content is required for optimum use of the metal; in this case, all copper ions are detectable by ESR and the symmetry of copper ions in chitosan is close to square-planar coordination. It is important to avoid excessive loading of the polymer to prevent magnetic interaction between closely arranged Cu(II) ions. Comparing the performance of Cu-based materials obtained by immobilization of the metal on different polymeric supports shows that the hydrophilicity of the support may contribute to the activity; however, the most important parameter seems to be the structural parameter (high degree of coordinative unsaturation). After immobilization on silica, the catalytic activity is significantly increased [132]. In the case of Pd–chitosan complexes, the structure of the material depends on the preparation procedure: for the adsorption process the coordination sphere is near to that of a  $\text{Pd}(\text{NH}_2\text{-Chit})_2\text{Cl}_2$  complex while for the co-precipitation process the metal forms a chelate complex (palladium coordinated to amino and hydroxyl groups of chitosan). After chemical reduction (with sodium borohydride) the aggregation of Pd remains very low, but the structure formed from the chelate complex obtained from co-precipitation has a higher degree of aggregation: possibly  $\text{Pd}_3$  triangular structures as opposed to  $\text{Pd}_2$  dimers in the case of the adsorption complex.

Huai-min and Xian-su [154] also investigated the structure of the chitosan–Co complex they use for

the polymerization of vinyl acetate. Using XPS and FT-IR analyses they show that the metal is bound to both nitrogen and oxygen atoms in the polymer chain and that the coordination polymer possesses the same shake-up peaks as  $\text{CoCl}_2$ ; they conclude that the complex is high spin and that the coordination number of  $\text{Co(II)}$  centers is four, in agreement with electrical conductivity measurements. The structure of the complex (high spin) is favorable for the free radical polymerization mechanism.

As pointed out above, Köckritz et al. [159] have shown that the catalytic activity of osmium tetroxide immobilized on chitin is much higher than that obtained by metal immobilization on chitosan. They explain this weaker activity on chitosan-supported catalyst to a higher binding of the metal on free amine groups that decreases the availability of metal for catalyzing the hydroxylation of olefins. This is further evidence of the impact of metal–chitosan interactions mechanism (and strength) on the catalytic activity of the heterogeneous material.

## 7. Main limitations to the spreading of heterogeneous catalysis supported on chitosan

Section 1 pointed out the mechanisms involved in the sorption of metal ions and the limiting parameters for their uptake efficiency, in relation with polymer properties. The accessibility to internal sites, the poor porosity of the raw material, and the limitations due to diffusion properties are important limiting factors. These limiting factors are also important for the catalytic activity of supported catalysts based on chitosan (this is described in Section 6). Several solutions exist for improving diffusion properties; they are described in Section 3 focusing on polymer conditioning. Appropriate conditioning improves the accessibility to internal reactive sites (gel beads) or decreases the diffusion dimension (reducing the size of polymer layers: membranes, hollow fibers, polymer deposition on suitable carrier). These modifications can offer technical solutions to minimize the effect of these limiting factors but they contribute to increase the cost of supported materials. This may be one of the reasons that could explain that despite an increasing number of research papers, chitosan-supported materials have not been applied on the industrial

scale. Some additional reasons may explain the difficulty in transferring the process to industrial applications: (a) stability of the polymer; (b) variability in the polymer characteristics; (c) production levels.

### 7.1. Polymer stability

Being a biopolymer, chitosan is biodegradable. This may be a serious drawback for long-term applications. The stability of the polymer against biodegradation is of great concern for application involving water-soluble forms of chitosan (for colloid-supported catalysis on chitosan). The degradation of chitosan resulting from bacterial/fungal contamination, but also from acidic hydrolysis may lead to a significant decrease of polymer weight, which in turn limits the retention of the polymer (using for example ultrafiltration membrane). It is possible to reinforce the stability of the polymer to biodegradation; and cross-linking treatment has been shown to significantly improve polymer stability.

Another important criterion to be taken into account concerns thermal effects on polymer stability. Compared to conventional resins, chitosan is less stable [174]. The polymer begins to lose water at 81 °C; the first exothermic effect appears at 311 °C. In the first stages of the degradation (low temperature below 400 °C), FTIR analysis of pyrolysis products shows unsaturated materials, while at high temperature degradation of the glycopyranosic ring is achieved. The lower thermal stability of chitosan may be of great interest at the end of catalyst life cycle since it will decrease the energy required to destroy the polymer. Moreover, the products of the degradation are more environmentally friendly than those produced during thermal degradation of conventional synthetic polymers [175]. The substitution of new functional groups on chitosan may affect thermal stability. Actually, several studies have shown conflicting conclusions depending on the kind of grafted groups: in the case of mercaptan derivative, it was found that the chemical modification slightly increased the stability of glycopyranosic ring [174], while in the case of chitosan Schiff bases the grafting of aromatic aldehyde derivatives slightly decreased thermal stability [176]. In the case of metal-loaded chitosan, Sreenivasan [177] concludes that thermal

behavior depends on the nature of the metal. He observed that the structural alterations induced by the chelation process should alter the thermal stability of the complexes but the decomposition temperature was only very slightly increased compared to raw chitosan. Chelation is known to change the conformation of the chitosan polymer. Disturbance of the natural ordering of the polymer might be expected to lead to thermal instability, while additional bridging through metal ions might be expected to lead to enhancement of thermal stability. He attributed the small increase in the decomposition temperature of the complexes to the combined effect of these antagonistic effects.

Mechanical stability is another concern in the evaluation of catalyst applicability. Though chitosan in powder and flakes is relatively mechanically stable, conditioning in the form of chitosan gel beads, for example, significantly changes mechanical stability. The beads are deformable in their raw form with interesting elastic properties. The cross-linking treatment with glutaraldehyde leads to the formation of relatively strong beads (personal observation) but the beads lose their elasticity and deformability (due to supplementary linkages between polymer chains); under high pressure constraints the beads break and small granules are formed. This is a serious drawback for applications on a large scale. Another possibility for reinforcing mechanical stability consists in drying the beads. However, as pointed out above, the drying step must be performed under strict control to avoid losing diffusion properties (drying in the presence of saccharose for example).

### 7.2. Standardization of production parameters

There is also a need for a better standardization of production process to be able to prepare reproducible chitosan batches. As pointed out above, metal uptake properties are strongly controlled by the characteristics of the chitosan. Changes in the specifications of the polymer may significantly change sorption performance, which in turn may impact the preparation of catalysts, and would require adaptation of the design process, which is not favorable to a widespread chitosan-based technology.

## 8. Conclusions

Chitosan has been shown to be a very promising support for the immobilization of catalytic metals. The strong affinity of this biopolymer for metal ions, as well as its high sorption capacities for catalytic metals such as copper, platinum, palladium can explain these interesting perspectives. Another important parameter to explain its potential for catalytic applications is related to its versatility. The biopolymer can be easily modified (a) chemically to improve its sorption properties and stability in acidic solutions; and (b) physically to improve diffusion properties and make optimum use of catalytic metals (the low porosity of the material requires using thin layers of the polymer). These properties may explain the increasing number of papers recently dedicated to the use of chitosan as a support for catalytic chemical reactions in fields as different as oxidation processes, reductive hydrogenation reactions and the synthesis of fine chemicals. Promising perspectives are identified in application processes using special conditioning of chitosan materials (deposited on ceramics, hollow fibers and colloids) though complementary research seems necessary before the processes can be transferred to industry. Some important parameters for the optimization of catalytic activity have been identified: size of catalytic supports (and their diffusion properties: porosity, accessibility to internal sites, etc.), size of metal particles, environment of metal (links with ligands, spatial conformation, etc.), metal content and oxidation state of the metal. A better knowledge of the impact of these parameters helps in designing new chitosan-based catalysts: thickness of polymer layer on inorganic support (amount of biopolymer/external surface area of inorganic support), molar metal/polymer ratio, metal immobilization process (adsorption, precipitation, deposition, etc.), polymer modification (grafting of functional groups that controls the environment of catalytic metals).

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