Screening of the Catalytic Activity of Pd^0 and Pd^{2+}- Supported on Chitosan Beads and Cryogels

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Abstract

Here, we report the results of screening of the catalytic activity of Pd-containing chitosan beads and cryogels in the cross-coupling reaction, hydrogenation of alkenes, nitro-, and carbonyl compounds and the hydrodechlorination of chlorophenols. Pd^0-containing chitosan beads and cryogels show moderate catalytic activity in the reduction of alkenes and nitroaromatics. The conversion of nitroaromatics decreases for substrates with electron-withdrawing substituents, while the conversion of alkenes increases with the activation of carbon-carbon double bonds. For several substrates, a significant difference in kinetics and conversion degrees was observed for Pd nanoparticles supported on chitosan beads and cryogels. It was found that conversion in the hydrodechlorination reaction depends on substrate structure, being higher for substrates containing substituents with a positive mesomeric effect. Pd^{2+}-chitosan catalysts showed high catalytic activity in cross-coupling (Heck reaction) offering the following advantages over known catalytic systems: lower reaction temperature, the selective functionalisation of C-I bonds, and the possibility to perform reactions with iodobenzene without base addition.

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1. Introduction

Chitosan production is constantly being extended, in particular due to the development of aquaculture, an increase in the level of processing of chitin-containing bioresources, and, as a result, the generation of substantial amounts of wastes at large manufacturing facilities. A number of methods to produce functionalised chitosan derivatives have already been implemented at the industrial scale, proving economic soundness and the high demand for such materials on the market. Aside from biomedical applications, functional materials based on chitosan and its derivatives are specifically in demand for water treatment technologies, environmental remediation, and "green" catalysis, where the nontoxicity and biodegradability of the polymers are important. The development of new chitosan-containing functional materials is based not only on achievements in the synthesis of new chitosan derivatives, but is also determined by the availability of the simple methods for the fabrication of beads, microspheres, films, threads, tubes and other forms for versatile applications.

Recently, we have suggested a method for the granulation of chitosan and its derivatives through the extrusion of cross-linked gels, which can be used for the fabrication of metal catalysts [1]. High interest in the utilisation of chitosan as a catalyst support is determined by several factors. First of all, the high sorption capacity of chitosan toward ions of noble and transition metals [2] enables one to control metal loading and fabricate metal nanoparticles "*in situ*" via the reduction of pre-adsorbed metal ions. Such an approach yields more stable composite catalysts compared to those obtained via the impregnation-reduction method [3] due to the strong interactions between the surface of the metal nanoparticles and functional groups of the polymeric support. Besides, chitosan, as a polybase, can facilitate reactions catalysed by organic or inorganic bases, thus making chemical transformations under milder conditions without additional reagents possible.

Another important issue for composite catalysts is the morphology and surface area of the polymeric support. The use of soft templates – hydrogels and cryogels of various functional polymers – for the synthesis of metal nanoparticles has attracted more attention in the last decade due to the expected or proven higher catalytic activity of such composite catalysts [4]. Although some examples of non-medical applications of chitosan cryogels are known [5], the potential of this type of materials in catalysis has not yet been explored.

Here, we report the results of screening the catalytic activity of Pd-containing chitosan beads and cryogels in the cross-coupling reaction, the hydrogenation of alkenes, nitro-, and carbonyl compounds and the hydrodechlorination of chlorophenols.

2. Materials and methods

2.1. Materials

Chitosan with a degree of deacetylation of 0.8, molecular weight of 500 kDa and ash content of 0.15% (HMW-chitosan) was purchased from JSC "Bioprogress" (Russia). The chitosan degree of acetylation was estimated using the method of ^1H NMR spectroscopy, and the molecular weight by viscometry [6]. Low molecular weight chitosan (LMW-chitosan) was purchased from Aldrich (CAS # 448869) and used as received. Glutaric aldehyde in the form of 25% aqueous solution, sodium boron hydride (98%), and all organic substrates were purchased from Alfa Aesar and used without purification.

2.2. Fabrication of Pd-catalysts supported on chitosan beads and cryogel

Chitosan beads were obtained as follows: 2 g (0.012 mol) of HMW-chitosan was dissolved in 40 mL of 0.3 M solution of HCl containing 0.48 mL (0.012 mol) of 25% solution of glutaric aldehyde. The gel was extruded from a polyvinyl chloride (PVC) tube (internal diameter 2.5 mm) with simultaneous cutting and dried at 70°C for 1 h. The beads were of a cylindrical shape with a diameter of 1 mm.

Chitosan cryogel was obtained as follows: 0.36 ml of glutaric aldehyde solution (25%) was added under intensive stirring into the 3% chitosan solution in HCl (pH was pre-adjusted to 4.5), which was pre-cooled to -1°C using an ice/NaCl bath. The mixture was immediately placed into plastic tubes with an inner diameter of 4 mm and kept in a freezer at -20°C for 7 days. The cryogel was immersed in 1% HAc solution to remove all soluble material, neutralised with 0.1 M NaOH solution and thoroughly washed with distilled water. Chitosan cryogels were cut into cylinders with a length of 4-5 mm.

To obtain Pd-containing catalysts, 100 mg of dry beads or cryogel was added to 20 mL of 0.001 M HCl solution containing a pre-determined concentration of PdCl$_2$ and kept at 25°C for 18 h under constant stirring. The Pd concentration was calculated to obtain chitosan beads and cryogels containing 4% and 0.1% of palladium, respectively, assuming a 100% recovery of metal ions from solution. The solids after sorption were filtered, washed with water until neutral pH, immersed in 0.5% of NaBH$_4$, and kept for 1 h under constant stirring to reduce Pd^{2+} to Pd^0. The composite catalysts were washed with water and dried at room temperature until a constant weight. The palladium oxidation state after reduction – 80% of Pd^0 and 20% of Pd^{2+} – was confirmed using the method of X-ray photoelectron spectroscopy, as described in [1]. The palladium content was controlled using the method of atomic absorption spectrometry after the decomposition of beads and cryogels with aqua regia (Solaar M6, Thermo Scientific, USA).

The morphology of chitosan beads in the cross-section was investigated by scanning electron microscopy (SEM) using Carl Zeiss Crossbeam 1540 and Ultra 55+ electron microscopes. The morphology of chitosan cryogel was investigated by the Cryo SEM method using the Quorum PP3010T Cryo-SEM Preparation System. Small pieces of cryogel samples were plunged into nitrogen cooled to almost freezing (-210°C; slushy nitrogen) using a Prepdek™ workstation. Then, frozen samples were transferred through a vacuum to the cryo preparation chamber mounted on FEI Versa 3D SEM. Samples were fractured with a cooled blade and then transferred directly to the cold stage (-170°C) in the SEM chamber. To reveal the features of the structure, the sublimation procedure was done. SEM imaging was performed in a high vacuum mode.

2.3. Catalytic activity of Pd-chitosan beads in hydrogenation reactions

The catalytic activity of the Pd^0-chitosan beads in the hydrogenation of alkenes, nitro-, and carbonyl compounds was estimated as follows: 0.1 g of the substrate was added to 6 ml of ethanol or methanol containing 0.050 g of the Pd^0-chitosan catalyst. The hydrodechlorination of chlorophenols was performed as follows: 0.12 g of the substrate was added to 6 ml of the water containing 0.050 g of the Pd^0-chitosan catalyst and 0.1 g NaOH. Hydrogenation was performed at a constant hydrogen flow of 50 ml/min during 5 h at 25°C under constant stirring. The reaction media after separation from the catalyst were analysed by gas chromatography employing a gas chromatography/mass spectrometry system Trace GC Ultra DSQ II with a quartz capillary column Thermo TR-ms (Thermo Scientific, USA). The analysis of products of unsaturated carboxylic acid hydrogenation was performed with 1H-NMR spectroscopy employing a Bruker AVANCE-500 spectrometer (Bruker, Germany).

2.4. Catalytic activity of Pd-chitosan beads in cross-coupling reaction

The catalytic activity of the Pd^{2+}-chitosan beads in cross-coupling reactions was estimated as follows: 1 mmol of the substrate, 1.5 mmol of butyl acrylate and 2 mmol of tributylamine or another base (triethylamine, NaOH, K_2CO_3) was dissolved in 3 ml of N,N-dimethylformamide; after that, 0.03 g of Pd^{2+}-chitosan beads was added and the mixture was heated to 140°C and maintained there for 6h. After separation from the catalyst, the reaction media were analysed by gas chromatography employing the gas chromatography/mass spectrometry system Trace GC Ultra DSQ II.

3. Results and discussion

3.1 Catalytic activity of Pd⁰-chitosan in the hydrogenation of alkenes and nitroaromatics

Both Pd⁰-containing chitosan beads and cryogels show moderate catalytic activity in the reduction of alkenes and nitroaromatics with molecular hydrogen under standard conditions (1 atm, 25°C) – Schemes 1 and 2, Tables 1 and 2. As follows from the degree of conversion, only active functional groups are reduced under these conditions – the carbon-carbon double bond and the nitro group of the aromatic substrate. In the case of nitroaromatics, conversion decreases for substrates with electron-withdrawing substituents (Table 1). The conversion of alkenes increases with activation of the carbon-carbon double bond (Table 2).
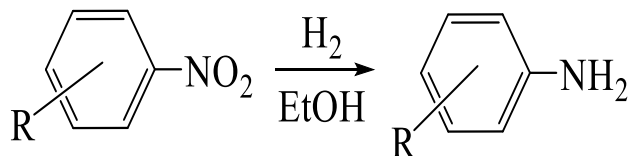
Scheme 1. Reduction of nitroaromatics with molecular hydrogen using a Pd⁰-chitosan catalyst
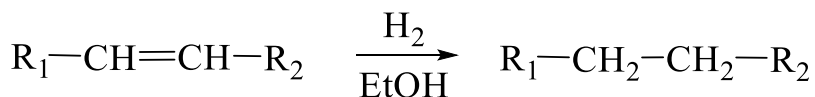
Scheme 2. Reduction of alkenes with molecular hydrogen using a Pd⁰-chitosan catalyst

Attempts at carbonyl group reduction were only successful in the case of acetylacetone and 4-cyanoacetophenone. The conversion of 4-hydroxy-2-pentanone and 1-(4-cyanophenyl)ethanol was 6 and 10%, respectively, which is comparable with the conversion obtained using a commercial Pd(10%)/C catalyst – 8% and 38%, respectively.

Table 2 shows a significant difference in the kinetics and conversion of alkenes by catalytic reduction with Pd nanoparticles supported on chitosan beads and cryogels. One of the possible reasons for the slow kinetics of 4-nitrophenol reduction was the low accessibility of palladium nanoparticles due to the shrinkage of chitosan beads in an alkaline media [1]. Figure 1 shows differences in the morphology of chitosan beads and the cryogel. We previously showed [1] that palladium in chitosan beads cross-linked with glutaraldehyde is concentrated in the surface layer with a thickness of 8-10 mm. The highly porous structure of the cryogel ensures the more homogeneous distribution

and accessibility of the palladium nanoparticles in the bulk of the cryogel (weak Pd signal was observed in all cryogel spots with SEM-EDX) and facilitates the diffusion of the substrate to the metal catalyst surface. Thus, a much higher conversion on Pd^0-chitosan cryogels compared to Pd^0-chitosan beads can be reached during shorter periods of time, even at a ten-fold lower palladium content, as observed for acrylonitrile conversion. It should be mentioned that the conversion of acrylonitrile dropped drastically when the ethanol was replaced by methanol as the solvent. Significantly better kinetics of maleic acid hydrogenation was also observed for palladium supported on a chitosan cryogel. However, there were no examples when the hydrogenation reaction proceeds on Pd^0-chitosan cryogel but not on Pd^0-chitosan beads.

Table 1. Conversion of nitroaromatics in hydrogenation reaction with molecular hydrogen catalysed by Pd^0-chitosan beads (4% of Pd)
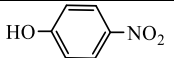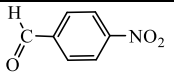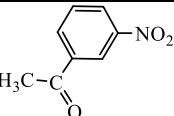
Substrate		Solvent	Conversion, %
HO—◯—NO$_2$	4-nitrophenol	water, ethanol	100
(4-nitrobenzaldehyde structure)	4-nitrobenzaldehyde	ethanol	20
(3-nitroacetophenon structure)	3-nitroacetophenon	ethanol	8

Table 2. Conversion of alkene derivatives in hydrogenation reaction with molecular hydrogen catalysed by Pd^0-chitosan beads and cryogels (R$_1$ and R$_2$ according to Scheme 2)

R$_1$	R$_2$	Substrate	Type of support	Pd cont. %	Solvent	Time h	Conversion, %
CH$_3$(CH$_2$)$_9$–	H–	1-dodecen	bead	4	ethanol	5	8
CH$_3$C(O)(CH$_2$)$_2$–	H–	5-hexen-2-one	bead	4	ethanol	5	16
PhC(O)–	trans Ph–	aceto-phenone	bead	4	ethanol	5	20
N≡C–	H–	acrylo-nitrile	bead	4	ethanol	5	29
			cryogel	0.1	ethanol	1	76
			cryogel	0.1	methanol	1	3
HOOC–	cis HOOC–	maleic acid	bead	4	water	5	100
			bead	0.1	water	1	6
			cryogel	0.1	water	1	55
HOOC–	trans HOOC–	fumaric acid	bead	4	water	5	66
NO$_2$–	trans Ph–	trans-β-nitrostyrene	bead	4	ethanol	5	0

Thus, despite the moderate activity of Pd^0-chitosan catalysts, they can be applied for the selective reduction of nitro groups and carbon-carbon double bonds of activated alkene.

3.2 Catalytic activity of Pd^0-chitosan in hydrodechlorination of chlorophenols

Catalytic hydrodechlorination is a common process to eliminate the hazard of chloroaromatic compounds released into the environment due to their application as antiseptic agents, agrochemicals etc. [7,8]. Pd^0-catalysts supported on chitosan beads show moderate activity in the hydrodechlorination of chloroaromatic derivatives in water under mild conditions (Scheme 3, Table 3).
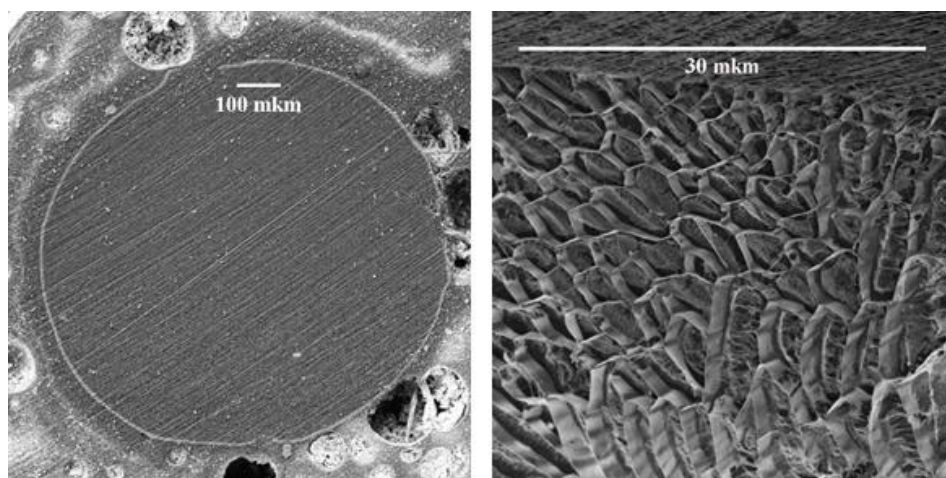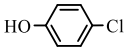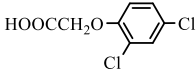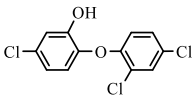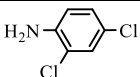

Figure 1. SEM images for Pd^0-chitosan bead fixed in the epoxy resin (left, SEM) and cryogel (right, cryo-SEM)
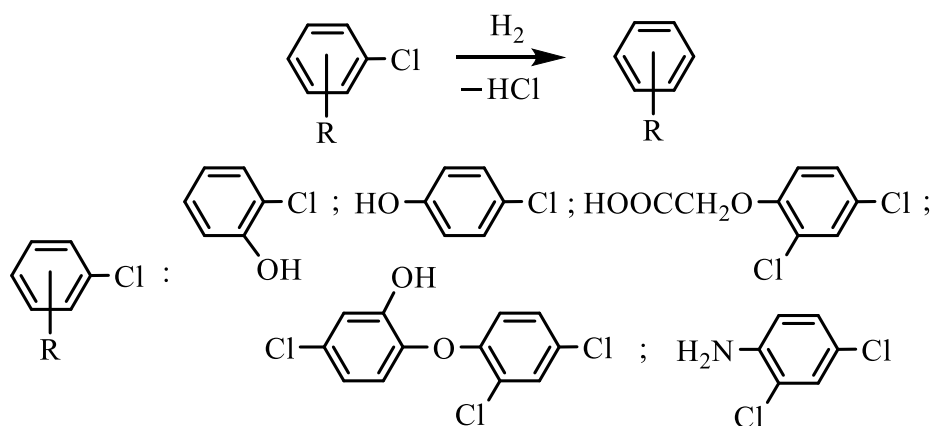
Scheme 3. Hydrodechlorination of chloroaromatic derivatives with molecular hydrogen using Pd^0-chitosan catalysts

Table 3. Conversion of chlorophenols via hydrodechlorination with molecular hydrogen using Pd^0-chitosan beads (4% of Pd) as a catalyst and water/NaOH as a solvent

Substrate		Conversion, %
	2-chlorophenol	11
	4-chlorophenol	15/55 (10 h)
	2,4-dichlorophenoxyacetic acid	12
	triclosan	30
	2,4-dichloroaniline	20

As follows from data in Table 3, conversion in the hydrodechlorination reaction depends on the substrate structure. The conversion is higher for substrates with substituents with a positive mesomeric effect. The maximal conversion (30%) was found for triclosan, while only 7% of triclosan can be converted in a reaction with molecular hydrogen without a catalyst [8]. The low accessibility of palladium nanoparticles as a substrate due to bead shrinkage in an alkaline medium can be one reason for the moderate reaction rates, when the Pd^0 catalyst is supported on chitosan beads. However, the possibility of the complete dechlorination of chlorophenols under mild conditions opens up prospects for the further development and application of this type of catalyst for the neutralisation and utilisation of hazardous chloroaromatics.

3.3 Catalytic activity of Pd^0-chitosan in cross-coupling reaction

Pd^{2+}-chitosan beads can be used as a heterogeneous catalyst in the cross-coupling reaction between aryl iodides and compounds with activated alkene (Heck reaction) (Scheme 4) with high catalytic activity (Table 4).
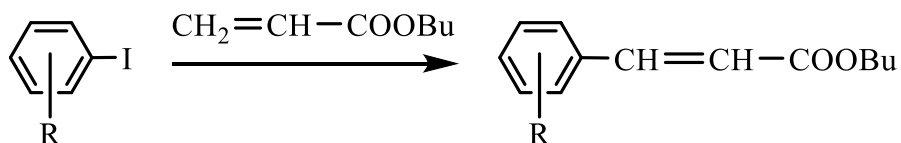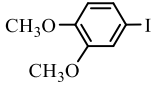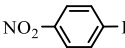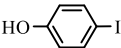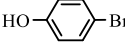

Scheme 4. Heck reaction using Pd^{2+}-chitosan catalysts

Although the Heck reaction typically proceeds in the presence of a base (Bu$_3$N), in the case of iodobenzene, high conversion can be reached using only Pd^{2+}-chitosan beads as a catalyst. Substituted iodobenzenes react with butyl acrylate only in the presence of organic bases; however, Pd^{2+}-chitosan catalysts allow the usage of the more commercially available base - Et$_3$N - and provide high conversion for certain substrates at a lower temperature - 100°C (Table 4). However, this reaction does not proceed in

water or with the addition of inorganic bases. It is worth mentioning that the selectivity of interactions is restricted to iodobenzene derivatives, since 4-bromophenol does not participate in the Heck reaction in the presence of Pd^{2+}-chitosan catalysts.

Table 4. Conversion of butyl acrylate in Heck reaction with iodobenzene derivatives using Pd^{2+}-chitosan beads (4% of Pd) as a catalyst and N,N-dimethylformamide as a solvent (140°C, 6 hours)

Substrate		Base	Conversion, %
[structure] —I	iodobenzene	Bu_3N	67
		without base	71
CH_3O [structure] —I, CH_3O	1-iodo-3,4-dimethoxybenzene	Bu_3N	34
		Et_3N (at 100°C)	1
		without base	1
NO_2 [structure] —I	1-iodo-4-nitrobenzene	Bu_3N	29
		Et_3N (at 100°C)	31
		without base	4
HO [structure] —I	4-iodophenol	Bu_3N	32
		NaOH (H_2O as a solvent)	5
		Et_3N (at 100°C)	65
		K_2CO_3	0
HO [structure] —Br	4-bromophenol	Bu_3N	0

When another activated alkene is used instead of butyl acrylate (Scheme 5), the reaction proceeds with lower conversion. Conversion in reaction with acrylic acid, acrylonitrile and 2-vinylpyridine was 2%, 19%, and 23%, respectively.

$$HO-\langle\rangle-I \xrightarrow{CH_2=CH-R} HO-\langle\rangle-CH=CH-R$$

$$R: -COOH ; -CN ; \langle\text{pyridine}\rangle$$
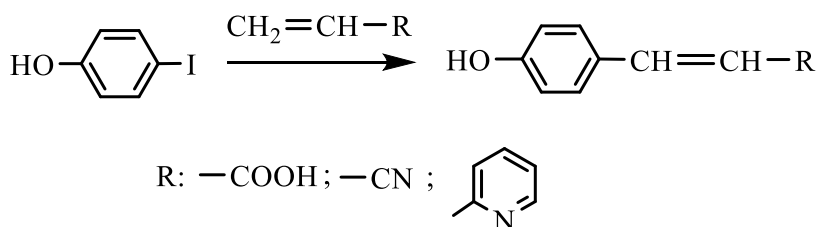
Scheme 5. Heck reaction of 4-iodophenol using the Pd^{2+}-chitosan catalyst

Taking into account the known mechanism of Heck reaction, involving the release of Pd(II) ions from the catalyst surface and their subsequent reduction, one can assume that aside from providing support for metal ions, amino carbohydrates can also play the roles of reducing agents and bases. Thus, variation in chitosan functionalities can be used to tune the properties of Pd-chitosan composite catalysts to perform Heck reactions under mild conditions without the addition of a base. In contrast to data in the literature [9,10], Pd^{2+}-chitosan catalysts offer the following advantages: lower reaction temperature, selective functionalisation of C-I bonds, the possibility to avoid phosphines and specific ligands.

4. Conclusions

Composite catalysts containing Pd^0 and Pd^{2+} have been fabricated via the adsorption or adsorption/reduction of Pd^{2+} ions on chitosan beads and cryogels. The morphology of the materials was investigated by SEM and cryo-SEM techniques, which revealed the highly porous structure of chitosan cryogels with palladium distributed in the bulk of the material, while in the case of beads, it was concentrated in the thin layer at the bead surface. The activity of Pd-chitosan catalysts has been investigated in cross-coupling reactions, the hydrogenation of alkenes, nitro-, and carbonyl compounds and the hydrodechlorination of chlorophenols. Pd^0-containing chitosan beads and cryogels show moderate catalytic activity in the reduction of alkenes and nitroaromatics and the hydrodechlorination of chloroaromatics with molecular hydrogen. Conversion significantly depends on the substrate structure; also, high differences in reaction kinetics were observed for Pd^0 supported on beads and cryogels. The results show that Pd^0-chitosan catalysts can be applied for the selective reduction of nitro groups and carbon-carbon double bonds of activated alkene and the decomposition of hazardous chloro-organic compounds. The very high catalytic activity of Pd^{2+}-chitosan catalysts in cross-coupling (Heck reaction) allows their application for the selective functionalisation of C-I bonds at lower temperatures and the possibility to perform reactions without phosphines or specific ligands.

5. Acknowledgements

6. References

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