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Highly dispersed palladium nanoparticles grafted onto nanocrystalline starch for the oxidation of alcohols using molecular oxygen as an oxidant

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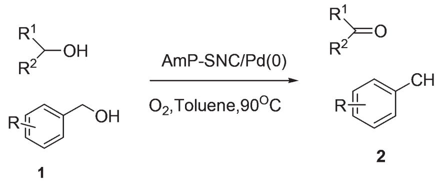
Highly dispersed Pd-nanoparticles grafted onto amino-functionalized nanocrystalline starch were found to be excellent heterogeneous catalysts for the aerobic oxidation of a variety of alcohols to their corresponding carbonyl compounds in excellent yields. The prepared catalyst was found to be selective for the oxidation of primary alcohols to aldehydes without giving over-oxidation products and was recycled several times without any leaching of the metal into the solution.

The development of nanobiocatalysis[1] and nanostructured hybrid materials[2] has attracted ever increasing attention because of their potential applications in various fields including catalysis. Recently, starch nanocrystals owing to their desirable characteristics such as inexpensive, abundant, biocompatible, biodegradable, and nontoxic have been receiving considerable interest.[3] In addition, these nanocrystals exhibit some unique properties, because of the nanometric size effect, compared to their conventional microcomposite counterparts. Starch nanocrystals, prepared by hydrolysis of native starch granules,[4] have been extensively used in drug delivery systems;[5] however, their use in the area of catalysis is rather limited. Selective oxidation of alcohols to their corresponding carbonyl compounds is a reaction of fundamental importance in industrial organic chemistry.[6] Conventionally the oxidation of alcohols is performed by using stoichiometric amounts of high-valent metal reagents, producing copious amounts of metallic wastes, and therefore is undesirable from both an environmental and an economic perspective.[7] Thus, increasing attention is being paid to the development of catalytic oxidation methods by using environmentally friendly oxidants such as O_2, H_2O_2 *etc.*[8] In this regard, several methods exist that use molecular oxygen for the oxidation of alcohols by using various homogeneous and heterogeneous Pd,[9] Ru,[10] Co,[11] bimetallic Au-Pd[12] and Cu[13] based catalysts. Owing to the limitations such as difficult recovery and recycling of homogeneous catalysts, the oxidation of alcohols using heterogeneous catalysts is desired as they offer the advantages of facile recovery and reusability of the expensive metal catalyst.[14] Recently, supported Pd nanoparticles have been widely used for the selective oxidation of alcohols by molecular oxygen.[15] Most of the supports used for the preparation of these catalysts are limited to the use of activated carbon, alumina, silica and organic polymers.[16]

However, increasing attention has recently been paid to the use of biopolymers for supporting catalytic metals as these materials not only provide remarkable affinities for catalytic metals, but also their structure can stimulate the reactivity and selectivity of the catalyst.[17] Among the different biopolymers known, starch materials have been chosen as promising materials for supporting the metal catalysts *via* chemical modifications.[18] In this context, recently Clark *et al.*[19] reported expanded corn starch as excellent support materials for Pd-catalysts for organic transformations. However to the best of our knowledge, no literature exists on the use of nanocrystalline starch materials as supports for developing heterogeneous Pd-catalysts. In the present paper, we report for the first time the synthesis of highly dispersed Pd(0) nanoparticles grafted onto chemically modified nanocrystalline starch, their characterization and we report on their use for the oxidation of alcohols using molecular oxygen as an oxidant (Scheme 1).



Scheme 1 [AmP-SNC/Pd(0)] catalyzed oxidation of alcohols.

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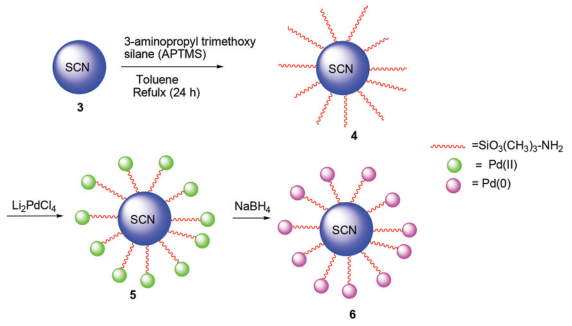
[b] Analytical Sciences Division, CSIR-Indian Institute of Petroleum, Mohkampur, Dehradun-248005, India

Synthesis and characterization of amino-functionalized nanocrystalline starch grafted Pd(0) nanoparticles {AmP-SNC/Pd(0)} 6

A schematic representation of the synthesis of amino-functionalized nanocrystalline starch grafted Pd nanoparticles **6** is shown in Scheme 2. Nanocrystalline starch was readily synthesized by the acid hydrolysis of native corn starch material by following a literature procedure.[4]

Starch nanocrystals possess a reactive surface covered with hydroxyl groups, which provides the possibility of modification *via* a chemical reaction strategy. Synthesized nanocrystals of starch were treated with 3-aminopropyltrimethoxysilane (APTMS) to obtain amino-functionalized starch nanocrystals ($SNC-NH_2$). The chemical modification of starch nanocrystals (SNC) was confirmed by FTIR analysis.

The presence of a large number of hydroxyl and amine groups in the starch nanocrystals explains the high affinity of the support for metal ions. The chemical nature and functionalities present on starch nanocrystals were revealed by FTIR.[20] The presence of bands at 3309 cm^{-1} in the $SNC-NH_2$ sample assigned to the N–H stretching vibrations and at 2931 and 2870 cm^{-1} corresponding to C–H vibrations confirmed the presence of aminopropyl functionalities on the starch nanocrystals. The crystalline nature of the material was confirmed by XRD[21] as shown in Fig. 1. The XRD pattern of nanocrystalline starch (SNC) **3** indicates that the developed catalytic material is of almost crystalline nature with very small fraction, which is revealed by very weak and broad diffraction peaks at around $2\theta = 16.84$ and $2\theta = 22.68$. The XRD pattern of aminopropyl modified nanocrystalline starch (AmP-SNC) grafted Pd(0) nanoparticles **6** indicates that the developed catalytic material is of almost amorphous nature, which is revealed by very weak peaks at $2\theta = 39$. This peak confirms the grafting of Pd(0) nanoparticles on the nanocrystalline starch support. Inductively coupled plasma (ICP-AES) analysis indicated 6.25 wt% of Pd on the nanocrystalline starch.



Scheme 2 Synthesis of [AmP-SNC/Pd(0)] **6**.

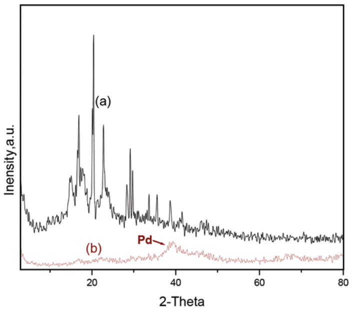


Fig. 1 XRD pattern of (a) nanostarch and (b) [AmP-SNC/Pd(0)] catalyst.

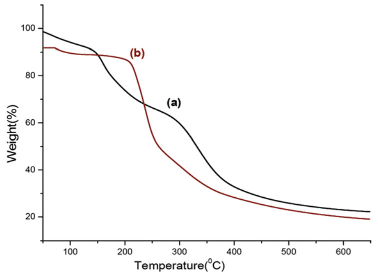


Fig. 2 TGA pattern of (a) nanostarch **4** and (b) [AmP-SNC/Pd(0)] **6**.

The thermal stability of the as-synthesized materials **4** and **6** was determined by TGA analysis[22] (Fig. 2). It can be seen that nanocrystals of starch **3** show 26.21% weight loss near 100–150 °C, evidently owing to evaporation of the water molecules which are held in the material. The second significant weight loss of about 70% is observed in the range of 300–350 °C, due to thermal decomposition of chemical functionalities present on the starch nanocrystals. Similarly, in material **6**, an initial weight loss is observed near 100 °C, because of the evaporation of water. The second significant weight loss of about 26.98% is observed at 200–250 °C, due to the decomposition of organic functionalized moieties. With the temperature enhanced continuously, the material was found to be decomposed gradually, and the weight loss became more and more obvious. The decomposition of the starch grafted palladium was complete when the temperature was raised to 370 °C with the formation of palladium oxide as a residue.

The transmission electron microscope (TEM) image shown in Fig. 3 clearly indicates that the Pd nanoparticles produced are well dispersed with a narrow size distribution in the range of 2–5 nm in the synthesized material **6**.

In order to ascertain the complete reduction and oxidation states of the palladium, the prepared [AmP-SNC/Pd(0)] catalyst was characterized by XPS analysis (Fig. 4). The XPS spectrum shows two peaks with binding energies of 335.7 and 341.1 eV,

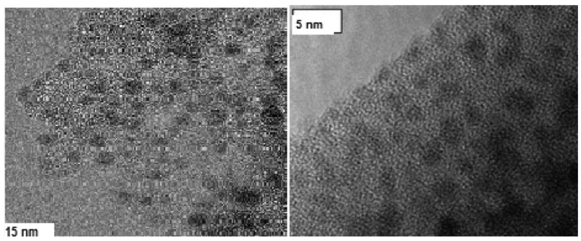


Fig. 3 TEM image of the [AmP-SNC/Pd(0)].

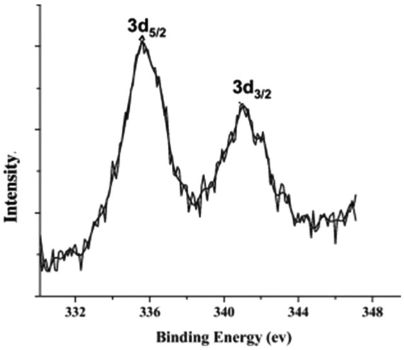


Fig. 4 XPS spectra of the [AmP-SNC/Pd(0)].

which are characteristic peaks of Pd $3d_{5/2}$ and Pd $3d_{3/2}$. These are the typical valence state peaks of Pd(0) and are comparable with the literature values.[23]

Catalytic activity of the nanostarch grafted Pd catalyst 6

The catalytic activity of the synthesized catalyst **6** was checked in the aerobic oxidation of alcohols under molecular oxygen. Benzhydrol was used as a model substrate to study the effects of the catalyst, the reaction temperature and the solvent. The results of these experiments are summarized in Table 1. Initially the reaction was tested in different solvents by using different organic solvents such as acetonitrile, DMF, toluene and *p*-xylene. Among the various solvents studied, aprotic polar solvents such as acetonitrile and DMF were found to be least effective and provided poor conversion of benzhydrol to benzophenone under an oxygen atmosphere (Table 1, entries 1 and 2). This is probably due to the coordination of the solvent molecules to the palladium metal, resulting in poisoning and deactivation of the catalyst. The reaction proceeded with moderate yield when water was used as a solvent (Table 1, entry 3). Aromatic solvents such as toluene and *p*-xylene were found to be the most promising solvents for this reaction (Table 1, entries 3 and 4). Based on these findings we have selected toluene as the reaction media for further studies. The reaction was found to be very slow at room temperature; however at 90 °C, the reaction was found to be faster and provided 94% isolated yield of the benzophenone in 1 h under an oxygen atmosphere. Similarly in the absence of a catalyst under an oxygen atmosphere, the reaction did not take place even in a prolonged reaction time of 12 h.

Table 1 Results of screening experiments[a]

Entry	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	CH_3CN	Reflux	8	10
2	DMF	90	8	5
3	H_2O	Reflux	3.5	65
4	*p*-Xylene	90	1.0	89
5	Toluene	90	1.0	94

[a] Reaction conditions: benzhydrol (10 mmol), **6** (0.2 g), and solvent (15 mL) under an oxygen atmosphere. [b] Isolated yields.

Next, the scope of the developed catalytic system was studied by performing the oxidation of a variety of primary and secondary alcohols under the described reaction conditions. The results are presented in Table 2. The catalytic system demonstrated an excellent reactivity and selectivity for the oxidation of benzyl alcohols to corresponding benzaldehydes without any evidence for the formation of overoxidation products, *i.e.* carboxylic acids. From the results for the benzylic substrates with different substituents (Table 2, entries 8–12), we found that electron-donating groups such as Me, OMe in the *para*-position enhanced the reaction more significantly than the electron-withdrawing groups. Similarly a variety of secondary alcohols including benzoins and 1,2-diols could be oxidized to the corresponding ketones in good to excellent yields under similar reaction conditions (Table 2, entries 1–7). The developed catalytic system could also be applied successfully for the oxidation of heterocyclic alcohols such as 2-thiophenemethanol (Table 2, entry 13). This is an advantage over several transition metal based catalysts, where the strong coordination of the heteroatom to the metal center is well known to deactivate the catalyst.

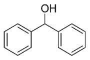
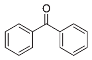
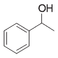
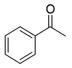
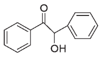
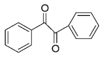
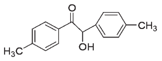
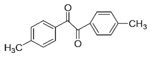
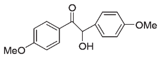
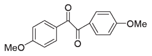
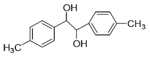
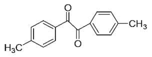
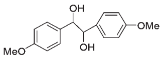
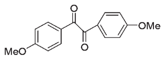
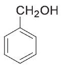
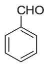
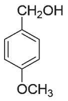
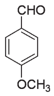
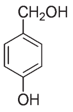
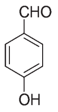
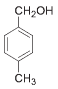
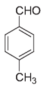
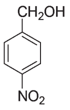
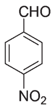
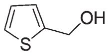
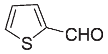
Next we tested the recycling of the catalyst for the oxidation of benzhydrol under the reaction conditions described above for the aerobic oxidation of alcohols. After the completion of the reaction, the catalyst could be easily recovered by centrifugation followed by washing with water and reused for subsequent runs. The recovered catalyst showed an efficient recycling ability without giving any change in the reaction time and the yield of the product (Fig. 5).

The hot filtration test was performed in the oxidation of **1a** to confirm that no leaching had occurred. The catalyst was refluxed in toluene for 3 h and then was separated by filtration of the hot reaction mixture. The solvent was then charged with the substrate and subjected to oxidation under an oxygen atmosphere for 12 h under identical reaction conditions. GC analysis of the catalyst-free reaction indicated that no oxidation of the substrate had occurred under these conditions. The absence of palladium in the filtrate solution was further confirmed by ICP-AES analysis, which indicated no detectable content of Pd in the filtrate. These results confirmed the heterogeneous nature of the developed catalytic system for the oxidation of alcohols.

Conclusions

In conclusion, we have demonstrated the synthesis of a highly dispersed Pd nanocatalyst grafted on nanocrystalline starch for the first time. The developed nanocatalyst was found to be a highly efficient heterogeneous catalyst for the oxidation of alcohols by using molecular oxygen as the terminal oxidant. Primary aliphatic and benzylic alcohols were oxidized to their corresponding carbonyl compounds in high to excellent yields. The catalyst was found to be highly stable and was recycled several times without any leaching of the metal into the solution.

Table 2 Pd-catalyzed oxidation of alcohols[a]

Entry	Alcohol	Product	Time (h)	Yield[b] (%)	TOF (h^{-1})
1			1.5	97	64.5
2			1.0	95	95.0
3			0.5	98	196
4			0.5	98	196
5			0.5	96	192
6			2.5	94	37.6
7			3.5	92	26.3
8			1.0	95	95.0
9			1.25	96	76.8
10			2.0	89	44.5
11			1.0	92	92.0
12			3.5	86	24.6
13			3.0	88	29.3

[a] Reaction conditions: substrate (10 mmol), **6** (1 mol%), and toluene (15 mL) at 90 °C under an oxygen atmosphere. [b] Isolated yields.

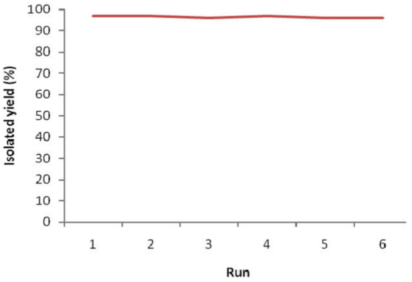


Fig. 5 Recycling experiments.

Experimental section

The nanostarch and the final catalyst powder were each mixed with potassium bromide (KBr) powder to form pellets in order to record the FTIR spectra. Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) of these samples were performed using a thermal analyzer TA-SDT Q-600. All samples were analyzed in the temperature range of 30–650 °C at a heating rate of 10 °C min^{-1} under nitrogen flow. Loading of palladium was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, PS-3000UV, Leeman Labs). 10 mg of each sample was dissolved in 1 mL of concentrated HNO_3, heated and diluted to 10 mL. The resulting solutions were filtered and subjected to an analysis for Pd content by ICP-AES analysis. Further, a nanostructural feature of the prepared catalyst was examined using a transmission electron microscope (TEM, JEOL 3010) at an accelerating voltage of 300 kV.

Synthesis of nanocrystalline starch (SNC) 3

Nanocrystalline starch was prepared by acid hydrolysis of native starch material by following the literature procedure given by Angellier *et al.*[4a] In a typical procedure, starch powder (36 g) was mixed with a sulfuric acid (250 mL; 2.87 mol L^{-1})

solution. The suspension was placed at 45 °C to hydrolyze for 7 days under stirring; the resulting suspension was centrifuged and washed successively with deionized water until neutrality. An ultrasonic treatment was then employed to ensure better dispersion of starch nanocrystals.

Chemical modification of 3 by (3-aminopropyl)trimethoxysilane (AmP-SNC) 4

Chemical modification of corn starch nanocrystals was carried out using 3-aminopropyltrimethoxysilane as a grafting agent. In a typical experiment, starch nanocrystals (1 g) were mixed with toluene (20 mL) and 3-aminopropyltriethoxysilane (20 mmol, 4.5 g). The resulting mixture was then refluxed for 24 h with continuous stirring under a nitrogen atmosphere. The modified starch nanocrystals were recovered by filtration and subjected to Soxhlet extraction in CH_2Cl_2 for 24 h. The resulting nanostarch material was dried under vacuum for 6 h. The yield was 1.8 g.

Preparation of Pd(0)/AmP-SNC 6

The chemically modified **4** (1.0 g) was suspended in a pH-adjusted deionized water solution by using 0.1 N LiOH (pH 8; 25 mL) and was allowed to stir at room temperature for 15 min. Li_2PdCl_4 was prepared by mixing LiCl (0.13904 g, 3.28 mmol) and $PdCl_2$ (0.29082 mg, 1.64 mmol) in water (30 mL), and the suspension was allowed to stir at 80 °C until a homogeneous solution was obtained. The resulting dark red solution was cooled and filtered, pH-adjusted (pH 8), and then added to a dispersion of AmP-SNC in water, and the resulting suspension was left to stir overnight. The suspension was then centrifuged, and the separated brown solid was washed with water (5 times). The brown solid was then re-suspended in water (30 mL), followed by slow addition of $NaBH_4$ (0.6204 mg, 16.4 mmol) suspended in water (15 mL), and the mixture was allowed to stir for 2 h. The resulting suspension was then centrifuged to separate the desired solid material which was thoroughly washed with ethanol and dried under vacuum for 5 h.

General procedure for the oxidation

A mixture of benzhydrol (10 mmol) and **6** (0.2 g, 1 mol% Pd; loading 0.6 mmol g^{-1}) in toluene (15 mL) was heated at 90 °C under stirring by using an oxygen balloon. The progress of the reaction was monitored by thin layer chromatography on silica gel. On completion, the reaction mixture was cooled to room temperature and centrifuged to separate the catalyst. The solvent was removed under reduced pressure and the product was obtained by passing it through a column of silica gel and eluting with EtOAc–hexane (1 : 9). The catalyst was dried at 50 °C for 1 h and can be reused for recycling experiments.

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Notes and references

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