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Non-cross-linked Amphiphilic Copolymer Coated Palladium Nanoparticles: A Highly Efficient and Reusable Catalyst for Aerobic Oxidation of Alcohols

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This work intends to prepare the non-cross-linked coated palladium nanoparticles. The amphiphilic palladium composite, poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-*co*-(N-isopropylacrylamide)₁₂-Pd, p(ADA-INA)-Pd, was prepared by self-organization of inorganic materials and copolymer, poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-*co*-(N-isopropylacrylamide)₁₂. Anionic inorganic materials self-assembled with non-cross-linked cationic *co*-polymers were converted into self-organized metal-nanoparticles with polymeric matrixes. The physicochemical properties of the synthesized nanocomposite were characterized by Fourier transform infrared (FT-IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The compound p(ADA-INA)-Pd showed the most active catalytic capability in the oxidation of alcohols with high selectivity. The catalytic oxidation of benzyl alcohol, 4-MeO-benzyl alcohol, and 4-Cl-benzyl alcohol with molecular oxygen in acetonitrile and water were investigated. The catalyst could be easily recovered and reused without the change of catalyst structure and significant loss of catalytic activity after each use.

Keywords: Amphiphilic, Copolymer, Nanocomposite, Palladium, Heterogeneous, Oxidation

INTRODUCTION

Hybrid organic-inorganic materials due to the potential of synergistic effects that could arise by combining these supplementary components giving rise to promising new material properties are the focus of considerable research interest [1]. One of the most effective approaches towards the synthesis of functional inorganic and organic nanomaterials, for example nanoparticles, hollow spheres, membranes or mesoporous bulk materials is using self-organized surfactant solutions as reaction templates or media [2,3]. The outline behind these templating approaches is to turn the brittle structure of a dynamic, self-organized molecular assembly into a supramolecular material with high chemical and mechanical stability [4]. In the same way, self-assembly of amphiphilic copolymers and nanoparticles suggests an influential method to the

formation of multifunctional nanoparticles for different applications [5]. Unlike the bulk properties, the physicochemical response of NPs alone and upon assembly can be tuned depending upon the structure, shape, and morphology of the NP composites [6]. Also, the chemical and physical properties of copolymer-nanoparticle structures can be tuned by the morphologies of copolymer aggregates and the distributions of particles, which rely on the concentrations of copolymers and particles, the size and shape of particles, the selectivity of particles, *etc.* [7]. These materials because of their unique electronic, magnetic, and optical properties and potential applications, such as catalysis, semiconductor, and photonic and biomimetic materials that, strongly depend on the size and organization of the nanoparticles have attracted much attention [8]. Agglomeration of NPs and subsequent changes to their properties can be caused by several ways [9,10]. One way of realizing robust, colloiddally stable NPs with a narrow size distribution is covering them with an amphiphilic polymer

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[11].

There are different methods for modifying of metal nanoparticles with polymers, such as (a) in situ synthesis of nanoparticle using polymer as a template, (b) 'grafting to' polymer', and (c) 'grafting from polymer' [12]. In this paper, we used the first method for preparation of coated palladium nanoparticles. In this approach, a supramolecular assembly of an appropriate polymer is used to encapsulate a solution of tetrachloro-metal anion that is then to be reduced to form a nanoparticle within the confines of the polymer assembly [13]. C. Geidel *et al.* have reported similar examples. They reported the synthesis of a series of amphiphilic copolymers with variable positive and negative charge densities based on the same polymer backbone. In this way, they could obtain colloiddally stable, positively, and negatively charged NPs with a surface charge [14]. Also, Robert J. Hickey and co-worker reported how to control the self-assembly of magnetic nanoparticles and a prototypical amphiphilic block copolymer composed of poly(acrylic acid) and polystyrene (PAA-b-PS) [15].

Alcohol oxidation is one of the pivotal functional group transformations in organic chemistry [16]. Generally, oxidation is performed using stoichiometric amount of transition metal oxidants or sulfoxides that produces a large number of defective products, being intolerable in today's environmentally conscious world. Thus, the development of an environmentally friendly catalytic system for the oxidation of alcohol with molecular oxygen at atmospheric pressure in the green solvent is favorite and urgent work [17]. Recently, the aerobic oxidation of alcohol using heterogeneous noble metal nanocatalyst has gained a significant amount of interest since it avoids the use of toxic materials and oxidizing reagents and at the same time, no by-product other than water is produced. Of all the noble metal nanocatalysts such as Ag [18], Au [19], Pd [20], Pt [21], and Rh [22], Pd containing nanocatalysts have been promising because of not prone to leaching as due to the over oxidation. Yasuhiro Uozumi and co-worker designed an amphiphilic polymer resin-dispersion of nanoparticles of Pd for catalysis in water. Similarly, Kazuhiro Nakabayashi *et al.* also reported cross-linked core-shell nanoparticles based on amphiphilic block copolymers by RAFT polymerization and Pd-catalyzed Suzuki coupling reaction [23]. In addition, the amphiphilic polystyrene-poly(ethylene

glycol) (PS-PEG) resin-dispersion of nanoparticles of Pd exhibited high catalytic performance in the hydrodechlorination of chloroarenes under aqueous conditions. The amphiphilic resin supported Pd, and Pt nanoparticles could catalyze the oxidation of non-activated aliphatic and alicyclic alcohols, in water under normal pressure of oxygen gas to aldehydes, ketones, and carboxylic acids. α -Alkylation of ketones with primary alcohols as the alkylating agents was achieved by Viologen polymer-supported nano palladium catalyst [24].

In this study, we prepared solid-phase metal-nanoparticles *via* self-organization of inorganic materials and non-cross-linked polymers. Anionic inorganic materials are self-assembled with non-cross-linked cationic polymers to give insoluble supramolecular complexes. They were converted into insoluble self-organized metal-nanoparticles composed of the polymer matrices. The metal-nanoparticles are stabilized by matrix polymers to prevent leaching, aggregation, and deactivation; as a result, they can become active and recyclable solid-phase catalysts. The self-assembly behavior of amphiphilic block copolymer/nanoparticle mixture was experimentally reported by many research groups [25]. In this letter, we would like to inform the development of an environmentally benign solid-phase polymeric catalyst of nano palladium particles, p(ADA-INA)-Pd, and its application to the oxidation of alcohols. This novel catalyst showed outstanding stability and reusability in water and organic solvents, such as CH₃CN.

EXPERIMENTAL

Materials and Equipment

The monomer N-[3-(dimethylamino)propyl]acrylamide (Merck, Germany), C₁₂H₂₅Br (Merck, Germany), N-isopropylacrylamide (NIA) (Merck, Germany), azobisisobutyronitrile (AIBN) (Merck, Germany) were used in polymer preparation. PdCl₂ (Merck) was used as a metal ion source. Sodium borohydride (NaBH₄, 98%, Merck) was used in the reduction of metal ions to prepare metal nanoparticles. All the chemicals were used as received without further purification. FT-IR spectra were recorded in KBr disks with a Bruker FT-IR spectrophotometer. The exact amount of the palladium in the catalyst was determined by Varian Spectra AA 220 spectrophotometer.

Morphology of catalyst was investigated with scanning electron microscopy (SEM) *via* MIRA3 FEG SEM (Tescan, Czech Republic) and an accelerating voltage of 10 keV. Transmission electron microscopy (TEM, CM120 (Philips)) was used to find out the size of metal nanoparticles inside the nanocomposites. To image the palladium nanoparticles, TEM analysis was performed on a JEM-2100 (JEOL). The reaction products of oxidation were determined and analyzed using an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenylmethyl siloxane 30 m × 320 μm × 0.25 μm).

Preparation of IL monomer [3-(acryloylamino)propyl]dodecyldimethylammonium bromide (1). The IL monomer was prepared as follows: To the suspension of N-[3-(dimethylamino)propyl]acrylamide (1.0 ml, 6.07 mmol), Na₂CO₃ (0.161 g, 1.52 mmol) in MeOH and CH₃CN (12 ml each) was added bromododecane (2.92 ml, 12.1 mmol), and it was stirred at 60 °C for 48 h. On completion, the liquid was removed by distillation, and the solid was washed [26]. After drying under vacuum, [3-(acryloylamino)propyl]dodecyldimethylammonium bromide (1) was obtained. Yield: 92%. M. p.: 57-70 °C; FT-IR (KBr, cm⁻¹): 1645 (m), 1667 (vs), 2927-2972 (w), 3267 (m); ¹H NMR (250 MHz, CDCl₃): δ (ppm) = 0.76 (t, 3H), 1.41-1.70 (m, 18H), 1.74 (m, 2H), 1.98 (m, 2H), 3.13 (s, 6 H), 3.52 (m, 2H), 3.76 (m, 2H), 5.47 (d, 1H), 6.09-6.16 (d, 1H), 6.28-6.39 (dd, 1H), 8.24 (br s, 1H); ¹³C NMR (150 MHz, CDCl₃): δ (ppm) = 14.0, 22.5, 22.6, 26.0, 26.2, 29.2, 29.2, 29.4, 29.4, 29.4, 29.4, 31.7, 38.8, 51.1, 51.1, 62.3, 64.4, 126.1, 131.1, 166.5.

Preparation of IL copolymer poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-co-(N-isopropylacrylamide)₁₂} (2). The IL copolymer was prepared according to the literature procedure [26]. In detail, the obtained IL monomer, [3-(acryloylamino)propyl]dodecyldimethylammonium bromide, (1.46 g, 3.60 mmol) and N-isopropylacrylamide (4.89 g; 43.2 mmol) in t-BuOH (70 ml) were degassed by ultrasonication for 20 min under an argon atmosphere. After addition of azobisisobutyronitrile (AIBN) (23.7 mg; 0.144 mmol) and again degassing for 20 min, the mixture was refluxed at 75 °C for 48 h under an argon atmosphere. The residue was purified by sedimentation from CH₂Cl₂ and Et₂O to give (2) in 86% yield. FT-IR (KBr, cm⁻¹): 1618 (s),

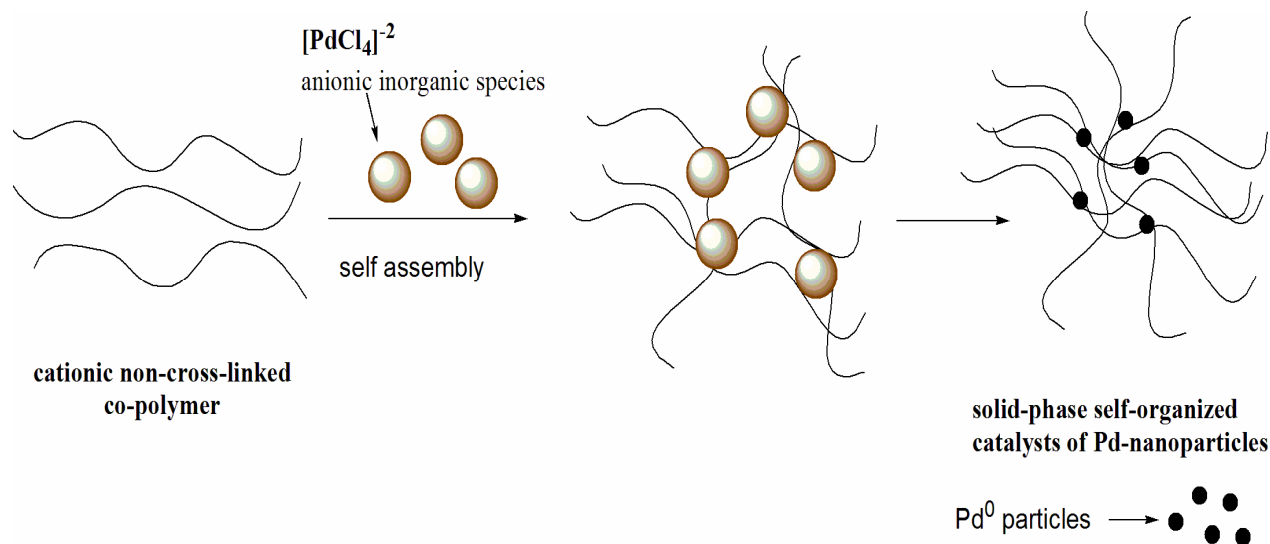
1664 (vs), 2850 (w), 2927 (w), 3065 (w), 3267 (m). ¹H NMR (250 MHz, CDCl₃): δ (ppm) = 0.79 (t, 3H), 1.80-2.71 (m, 133H), 3.16-4.60 (m, 24H), 6.47 (br s, 13H); ¹³C NMR (150 MHz, CDCl₃): δ (ppm) = 14.0, 22.4, 26.2, 28.0, 28.6, 29.0, 29.3, 29.4, 31.7, 32.7, 34.0, 41.2, 50.7, 62.6, 64.7, 164.8.

Preparation of the poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-co-(N-isopropylacrylamide)₁₂}-Pd, **p(ADA-INA)-Pd, nanocomposite (3).** For *in situ* fabrication of metal nanoparticles within poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-co-(N-isopropylacrylamide)₁₂}, first palladium ions were loaded into polymer network by dispersing 0.4 g of the dried (2) in 50 ml, 500 ppm ethanol solution of palladium chloride for 24 h at room temperature under continuous stirring. [PdCl₄]²⁻ ions loaded polymers were washed with ethanol to remove unbounded metal ions. Then, to reduce metal ions within polymer network, it was treated with 50 ml NaBH₄ (0.1 M). Finally, the prepared Pd composites were filtered, washed with deionized water and used for characterization. The amounts of metal nanoparticles entrapped in polymer matrices were calculated by AA spectroscopy after dissolution of metal nanoparticles embedded within the polymer by treating it with aqueous solution of 5 M HCl.

General Procedure for the Oxidation of Alcohols Catalyzed by p(ADA-INA)-Pd

A mixture of p(ADA-INA)-Pd (2 mg, 0.40 μmol) in CH₃CN as solvent (5.0 ml) was placed into a two-neck flask equipped with a magnetic stirrer bar. The flask was evacuated and refilled with pure oxygen (balloon filled). Then, the substrate (1.00 mmol) and isobutyraldehyde (5 mmol) were added into the solution with a syringe. The mixture was heated to reach the set temperature under O₂ atmosphere. The resulting mixture was vigorously stirred at 60 °C under O₂ atmosphere for 7 h. The oxidation products were identified by comparing the retention times with those of the authentic sample.

To test the reusability of the p(ADA-INA)-Pd composite, after every usage, the catalyst was separated from reaction mixture by filtration, washed with DI and reused under the same reaction conditions.



Scheme 1. Schematic illustration outlining the preparation and structure of the nanocatalyst p(ADA-INA)-Pd

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis of p(ADA-INA)-Pd is outlined in Scheme 1. The IL monomer [3-(acryloylamino)propyl] dodecyldimethylammonium bromide was first prepared and characterized by ^1H NMR. The IL copolymer poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-co-(N isopropylacrylamide) $_{12}$ } was synthesized by the free radical copolymerization of the IL monomer and N-isopropylacrylamide using AIBN as an initiator. Finally, the catalyst palladium composite was obtained by the reaction of poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-co-(N-isopropylacrylamide) $_{12}$ } with the $[\text{PdCl}_4]^{2-}$ solution and fully characterized by FT-IR, SEM, TEM and AA spectroscopy.

The FT-IR spectra of 2 and p(ADA-INA)-Pd are illustrated in Fig. 1. All the observed bands are in accordance with those reported in the literature [27-29]. The N-H stretching bands of the monomer (2) amide groups were observed at 3060 cm^{-1} (Fig. 1a). The C-H stretching of the alkyl group appeared at 2926 cm^{-1} and 2857 cm^{-1} , and the band at 1667 cm^{-1} related to the C=O of the amide group. Similarly, the band for N-H bending appeared at 1545 cm^{-1} , and the band at 1464 cm^{-1} clearly shows the existence of an ammonium ion [30]. After loading the palladium ions and reduction to Pd^0 nanoparticles, the small

shifts in FT-IR spectra of p(ADA-INA)-Pd is related to interactions between Pd and polymer matrix, as shown in Fig. 1b.

The amount of metal ion within the polymer matrix was determined using AA spectroscopy after HCl treatment; palladium was 0.02 mmol g^{-1} of the polymer. SEM images of p(ADA-INA)-Pd, demonstrated its homogeneous and highly porous nature (Fig. 2). The catalyst possesses many pores with diameters more than 50 nm. The porosity suggests a high surface-to-volume ratio and many reactive sites for the catalyst, which are highly beneficial for catalysis. These facts mean that the surface area and the reactive sites of an amphiphilic compound of p(ADA-INA)-Pd are extensive. Therefore, the substrates and reagents could infiltrate into the p(ADA-INA)-Pd effectively [31]. The existence of macropores should be one reason why $0.40\text{ }\mu\text{m}$ of p(ADA-INA)-Pd could work efficiently as a biphasic catalyst in spite of its insolubility in solvent.

Furthermore, the existence of metal nanoparticles was further evidenced by TEM images shown in Fig. 3. As can be seen, metal nanoparticles with spherical shape, about 30 nm, are distributed within p(ADA-INA) polymer matrices. The absence of aggregates in TEM image reveals that the copolymer hydrogel networks prepared in this study are suitable matrices for the in situ preparation and stabilization of Pd nanoparticles. The prevention against the aggregation of Pd nanoparticles was achieved due to cross-linked

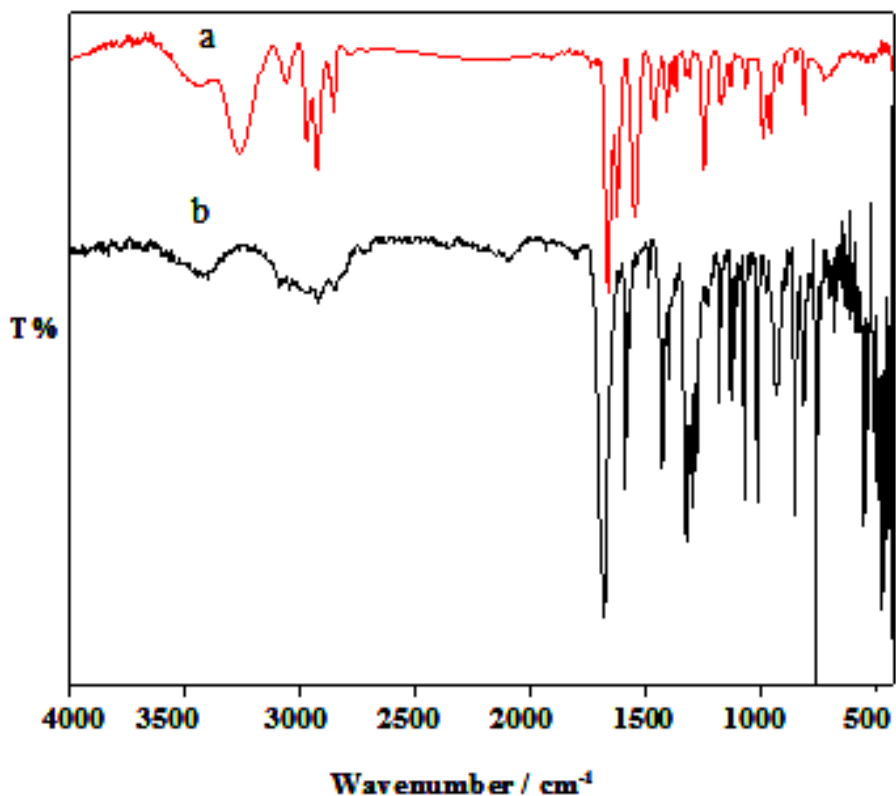


Fig. 1. FT-IR spectra of A) poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-co-(N-isopropylacrylamide)₁₂ (2), B) p(ADA-INA)-Pd.

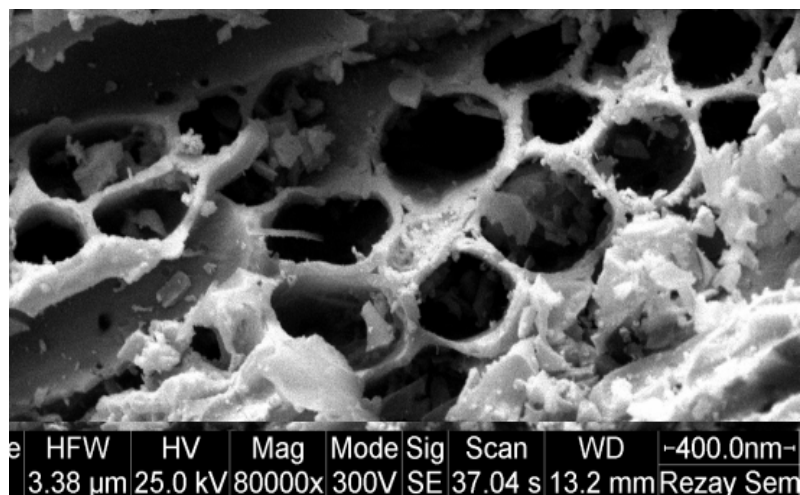


Fig. 2. SEM image of p(ADA-INA)-Pd which shows clearly its homogeneous and extended porosity.

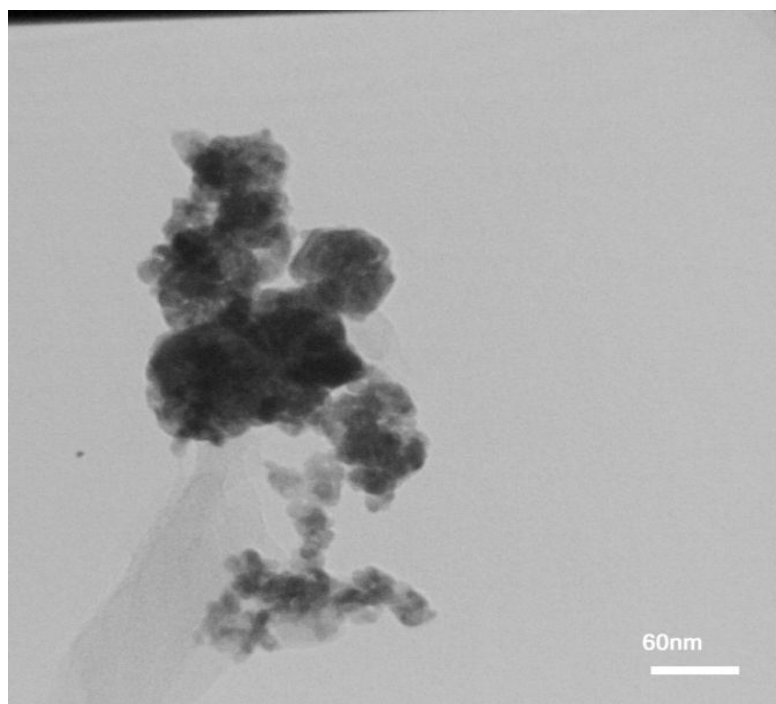
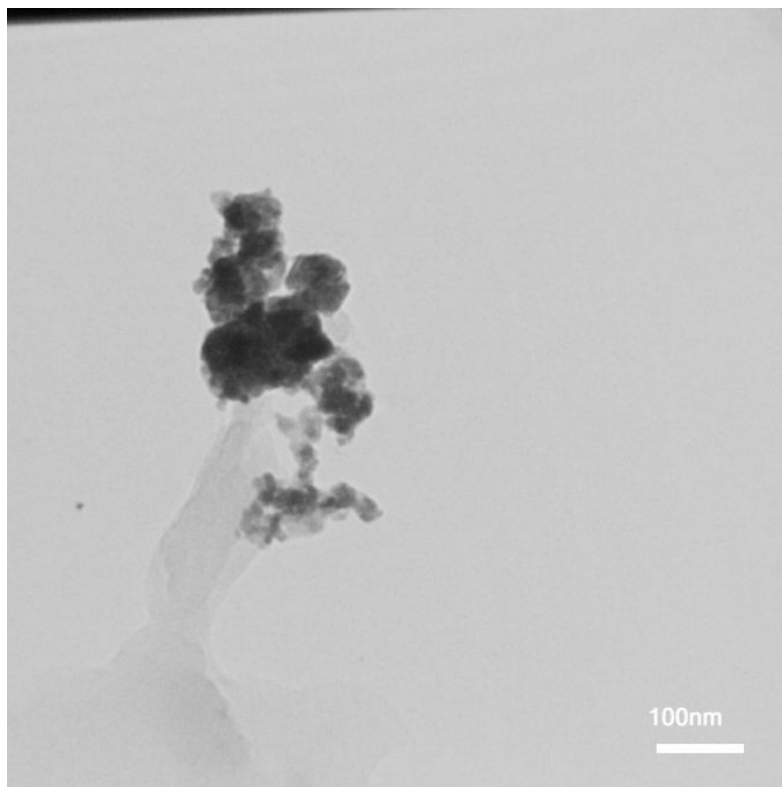


Fig. 3. TEM images of p(ADA-INA)-Pd nanocomposites.

polymeric network of hydrogel. In addition, the polymer sheets are visible in Fig. 3.

Oxidation of Alcohols by p(ADA-INA)-Pd and O₂ as Oxidant

The selective oxidation of alcohols, especially employing oxygen as a terminal oxidant, has been believed one of the most important reactions in organic synthesis [18]. With p(ADA-INA)-Pd catalyst in hand, we evaluated its catalytic activity for the aerobic oxidation of alcohols. Initially, benzyl alcohol was selected as a model substrate, and the oxidation reaction was carried out in acetonitrile at 60 °C with 0.40 μmol of p(ADA-INA)-Pd as catalyst, O₂ as oxidant and isobutyraldehyde (IBA) as co-catalyst. The blank experiment without catalyst exhibited low conversion (<7% at 60 °C after 7 h). However, in the presence of the catalyst, the conversion was increased. In addition, the conversion in the blank experiment without IBA was negligible. Thus, the presence a catalyst and IBA are necessary for achieving the oxidation. The oxidation of benzyl alcohol did not take place in the absence of co-catalyst. Encouraged by these results, we then directed our attention toward the oxidation of other primary benzyl alcohols with substituents such as 4-MeO and 4-Cl groups (Table 1, entries 2 and 3). The results showed that the electronic variation of the aromatic substituent affects its activity, which may be rationalized by invoking a radical mechanism, as shown in Scheme 2.

In continuation of our studies, catalyst activity was studied in H₂O, and the results are summarized in Table 1. While the presence of electron-donating -OMe group at the *para*- position of benzyl alcohol, increased the conversion of alcohols (Table 1, entry 2), withdrawing group Cl (Table 1, entry 3) decreased the conversion [32]. This trend is in accord with Hammett plot results and suggesting the formation of a transition state with a carbocationic character on the benzylic carbon during the discharge of hydrogen in the rate-determining step is involved in the oxidation pathway over the present catalysts [33]. Similar results have been reported in literature [18,20,34].

In comparison, the catalyst activity in CH₃CN was higher than H₂O and aldehyde as sole product observed in CH₃CN. Aldehyde and carboxylic acid were formed in H₂O medium. The high activity of the catalyst in CH₃CN may be

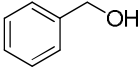
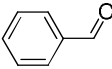
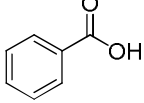
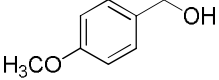
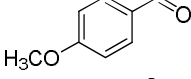
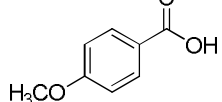
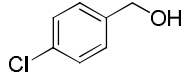
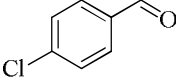
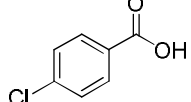
attributed to its hydrophobic properties. In fact, due to the nature properties of catalyst it can interact with hydrophobic CH₃CN and CH₃CN as an organic solvent can diffuse to polymer matrix easily. In addition, due to the solubility of a substrate, a co-catalyst in CH₃CN, the effective interaction between substrate and catalyst occurs, which results an increase in the conversion of the substrate [35]. The amphipathic character would allow this polymer matrix to interact efficiently with organic anions such as phenylmethanolate, phenoxides, carboxylates, *etc.*, by both electrostatic and/or hydrophobic interactions. In fact, organic polar solvents, such as CH₃CN, could affect access of the substrate to the active site by increasing the solubility and diffusion of reactants [36]. The miscibility/high solubility between p(ADA-INA)-Pd, substrate and solvent plays an essential role for oxidation efficiency. The excellent mismatch of polymer in terms of ionic nature, structural skeleton, and miscibility did overcome the limitation of mass transfer, favoring the catalytic activity [37]. Organic polar solvents could affect access of the substrate to the active site by increasing the solubility and diffusion of reactants in ionic liquids [38].

A hypothesis of the possible mechanisms of catalytic oxidation of alcohols by p(ADA-INA)-Pd are presented in Schemes 2 and 3. In acetonitrile, Pd⁰ reacts with O₂ to produce [(μ²-O₂)Pd] a peroxide, Scheme 2. The following hydrolysis affords the intermediate [RCO-Pd-OOH]. In the next steps, Pd⁰ and RCO-OOH are formed and benzyl alcohol is oxidized by RCO-OOH (2-methylpropaneperoxoic acid) to benzaldehyde. This pathway has been approved under different reaction conditions [39].

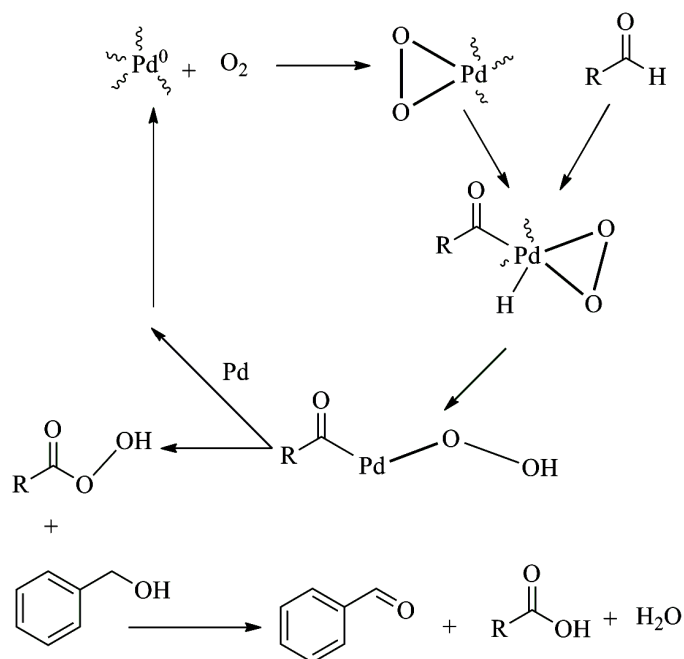
In H₂O, however, the oxidation reaction follows a different mechanism (Scheme 3). The deprotonation of alcohol is promoted by K₂CO₃ to form an alkoxide on the Pd surfaces. Pd catalyzes the β-hydride elimination to produce the corresponding aldehyde along with the formation of O₂ and H₂O.

The recyclability of p(ADA-INA)-Pd was investigated in several runs of the oxidation reaction of benzyl alcohol. At the end of the reaction, the catalyst was separated and its activity in the next runs was investigated. The activity of p(ADA-INA)-Pd was preserved even after 5 runs and the yield of the reaction did not change significantly. Atomic adsorption spectroscopy of the reaction mixture after

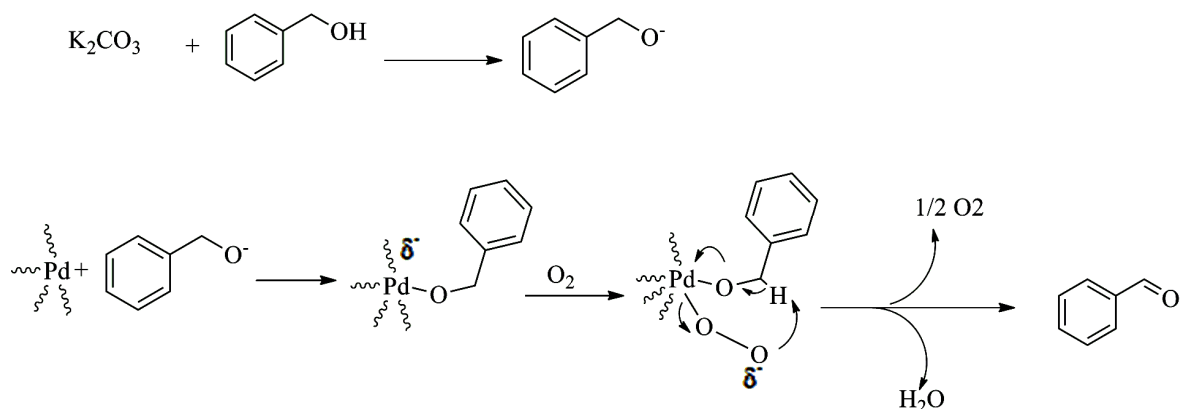
Table 1. Catalytic Activity of ADA-INA-Pd on the Oxidation of Benzyl Alcohol^a

| Entry | Substrate | Solvent | Conversion (%) ^b | Product | Selectivity (%) |
|-------|--|-------------------------------------|-----------------------------|---|-----------------|
| 1 |  | CH ₃ CN/H ₂ O | 72/44 |   | 100/92 0/8 |
| 2 |  | CH ₃ CN/H ₂ O | 80/68 |   | 100/95 0/5 |
| 3 |  | CH ₃ CN/H ₂ O | 63/21 |   | 100/87 0/13 |

^aCatalyst (0.002 g, 0.4 μmol), substrate (1.0 mmol), solvent (5 ml), co-catalyst. IBA 5 mmol or K₂CO₃ 1.1 mmol, temperature 60 °C, Time = 7 h under O₂ atmosphere. ^bConversions are based on the starting substrate.



Scheme 2. Proposed mechanism for the oxidation of benzylalcohol in CH₃CN in the presence of p(ADA-INA)-Pd and IBA.



Scheme 3. Plausible pathways for the oxidation of alcohols in the presence of p(ADA-INA)-Pd and K_2CO_3 in H_2O .

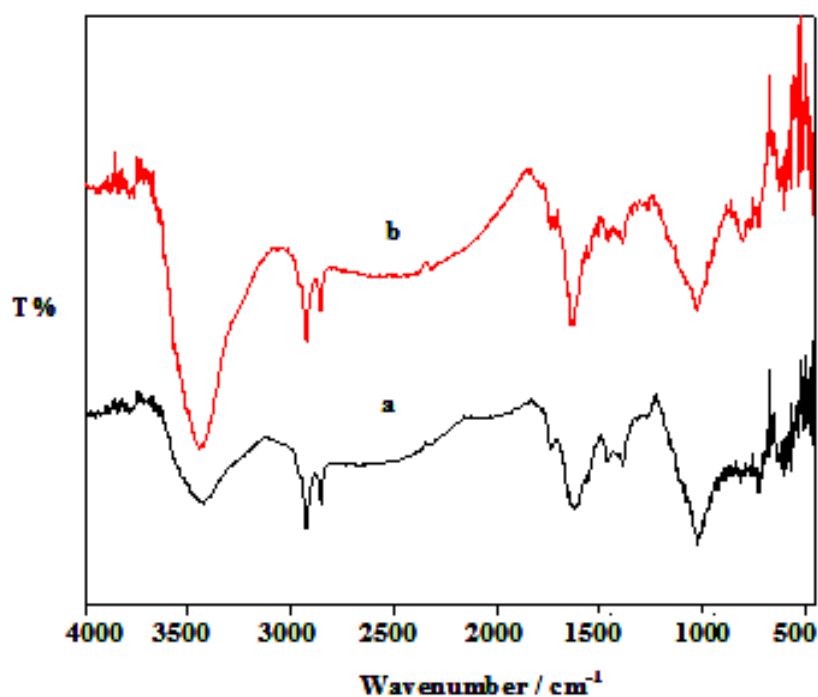


Fig. 4. FT-IR spectra of A) recycled catalyst in H_2O medium, B) recycled catalyst in the CH_3CN medium.

catalyst separation also confirmed that no free palladium ions are present in the solution. The FT-IR studies proved the stability of the supported catalyst. In these experiments, the catalyst was separated from the reaction mixture after each experiment, washed, dried, and characterized by FT-IR spectroscopy. The FT-IR spectrum for the recovered composites (Fig. 4) was well consistent with that of the

fresh one, demonstrating a durable catalyst structure accounting for the steadily catalytic reuse.

CONCLUSIONS

In summary, we have developed a new amphiphilic nanocatalyst, p(ADA-INA)-Pd, prepared by self-assembly

process of the non-cross-linked amphiphilic polymeric ligand with inorganic species. Using only 0.40 μmol of the catalyst with organic and H_2O solvents, the oxidation of alcohols with O_2 gave the desired products in excellent yield. Furthermore, the catalyst was easily prepared and purified. The catalyst is a macroporous complex showing a great potential to be used as an amphiphilic catalyst to other reactions, including the oxidation of alcohols. This catalyst can be conveniently recovered and steadily reused without any change in the structure of the catalyst and any significant loss of catalytic activity. The unique amphiphilic structure of the catalyst is revealed to be responsible for the catalyst's excellent performance in the oxidation of alcohols with O_2 by accelerating the mass transfer in organic as well as H_2O media.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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