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Highly Dispersible and Magnetically Recyclable Poly(1-Vinyl Imidazole) Brush coated Magnetic Nanoparticle: an Effective Support for Immobilization of Palladium Nanoparticles

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Abstract

A heterogeneous recoverable catalyst was prepared via complexation of palladium onto the surface of magnetic nanoparticles coated by poly(1-vinyl imidazole) brush. The stable, active and reusable catalyst was proven to be highly active in aerobic oxidation of primary and secondary alcohols with excellent yields. Only 0.1 mol% of catalyst was used to oxidize 1 mmol of primary and secondary alcohols. The catalyst was readily recovered and reused up to 10 times under the described reaction condition without significant loss of activity.

Keywords: Magnetic catalyst, Palladium catalyst, Oxidation

Introduction

Selective oxidation of alcohols to corresponding aldehydes or ketones is one of the necessary and common transformations in organic synthesis from the academic and industrial point of view due to its applications as a valuable intermediate for pharmaceuticals, dyes, fragrances and flame retardants.¹⁻⁴ As a result, there are a large number of available methods however many of the most commonly used methods generate an intolerably high amount of toxic waste which violates green chemistry regulations.⁵⁻⁷

With the economic and environmental concerns, the use of molecular oxygen as an inexpensive, readily available and clean oxidant has received considerable attention as a desirable green process for selective oxidation of alcohols.^{8,10} In this regard, several transition metals such as, cobalt,¹¹ copper,¹² gold,¹³ iron,¹⁴ osmium,¹⁵ ruthenium,¹⁶ vanadium¹⁷ and palladium¹⁸ have been used as homogeneous catalysts in oxidation reactions based on molecular oxygen. Among them, Pd based catalysts are the most promising choice due to high efficiency and selectivity in the alcohol oxidation reaction.¹⁹ However, these methods have encountered many problems and challenges including recyclability and reusability issues, the high pressure of O₂ especially in flammable organic solvents, usage of costly or toxic additives, difficult catalyst separation and the use of a high amount of catalyst.

To overcome the separation problem of homogenous catalysts, the concept of heterogenizing of homogeneous catalyst has emerged to combine advantages of both a homogeneous and heterogeneous catalyst.²⁰⁻²⁴ In order to achieve this, active species (transition metals) are immobilized onto the solid supports to form a heterogeneous catalyst. Various support materials have been used for immobilization of Pd such as Al₂O₃,²⁵ mesoporous silica,²⁶ cellulose,²⁷ nanocrystalline starch,²⁸ graphene,²⁹ hydroxylapatite,³⁰ and carbon.³¹ However, these supported

catalysts suffer from major drawbacks, including high metal leaching, low metal loading, low activity, tedious work-up procedure, difficulties in synthetic process and recovery.

A novel approach to solve the mentioned problems of traditional Pd supported catalysts is immobilization of Pd on polymeric supports.³² Several types of polymers have been used as support for immobilization of Pd.³³⁻³⁷ Although, these Pd supported polymeric systems are efficient but relatively low stability at high temperature, high leaching and low catalytic activity limit their applications. Accordingly, with the aim of increased ease of recovery, increased loading and stability of the catalyst, non-toxic magnetic nanoparticles as an environmentally-friendly material could be a desirable choice to immobilize polymeric support.³⁸

In this study, we report the synthesis and application of poly(vinyl imidazole)/Pd coated magnetic nanoparticles as an efficient catalyst. In this catalytic system, magnetic nanoparticles are coated by a polymeric support which bears palladium nanoparticles. Strong complexation could dramatically enhance catalytic activity for selective oxidation of alcohols in water medium. In addition, easy separation and recovery of the catalyst due to magnetic properties present an interesting alternative to other synthetic oxidation methods.

Experimental

Reagents and analysis

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonia (30%) and methyl acrylate were obtained from Merck, 1-Vinylimidazole, tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) were obtained from Aldrich. 1-Vinylimidazole was distilled before use and 2'-Azobisisobutyronitrile (AIBN, Kanto, 97%) was recrystallized in ethanol.

Thin layer chromatography (TLC) was employed with silica gel 60 F254 plates and visualized by UV light. FT-IR spectra of the samples were taken using an ABB Bomen MB-100 FT-IR spectrometer. The samples were powdered and mixed with KBr to make pellets. Thermogravimetric analysis (TGA) was acquired under a nitrogen atmosphere with a TGA Q 50 Thermogravimetric analyzer. Transmission electron microscopy (TEM) images were taken with a Philips CM30 electron microscope. The morphology of the catalyst was observed using a MIRA3 TESCAN scanning electron microscope (SEM).

Synthesis of amine functionalized magnetic nanoparticles (MNPs)

6.80 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.50 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were added to 300 mL deionized water in a 250 mL round bottom flask under nitrogen atmosphere at room temperature; 70 mL ammonia solution was then added dropwise into the mixture while it was vigorously stirred. When the color of solution changed to black, the magnetite particles were separated with external magnetic force and then washed several times with deionized water. 3 g of Fe_3O_4 was suspended in 500 mL of 4/1 ethanol/water mixture by ultrasonication and pH was adjusted to 10 by adding ammonia solution. Afterwards, 20 mL of tetraethoxysilane (TEOS) was added dropwise to the magnetic solution (during 3 h) and the mixture was stirred using a mechanical stirrer under nitrogen atmosphere at 50 °C. The stirring was continued for another 3 h. Then, the silica coated magnetic nanoparticles ($\text{Fe}_3\text{O}_4 @ \text{SiO}_2$) were magnetically separated and washed three times with deionized water and ethanol. The final dark brown product was dried under vacuum at 50 °C for 24 h.

3 g of dry silica coated magnetic nanoparticles were suspended in 100 mL of 4/1 ethanol/water mixture and the mixture was sonicated for 30 min and a solution of 6 mL of 3-

aminopropyltriethoxysilane (APTES) added and heated at desired temperature (80 °C) for 24 h. After completion of the reaction, the solution was allowed to cool to room temperature. Finally, Fe₃O₄@SiO₂@APTES (noted as MNPs) were separated by an external magnet and washed three times with dry methanol and dried under vacuum for 24 h.

Synthesis of poly(1-vinylimidazole-co-methyl acrylate)

2 g of 1-vinylimidazole and 0.5 g of methyl acrylate were dissolved in 5 mL methanol in a 50 mL round bottom flask. The content of the flask was deoxygenated under argon for 20 min and AIBN was added to initiate polymerization. The flask was equipped with a condenser and placed in an oil bath at 75 °C for 18 h. After completion of the reaction, solvent was evaporated and the solid product was washed five times with water (5×30 mL) and the final copolymer was dried in vacuum at 50 °C.

Synthesis of the catalyst (MNP@PVim@Pd)

MNP (0.3 g) and poly(1-vinylimidazole-co-methyl acrylate) (1.0 g) were loaded into a 25 mL round bottom flask and 10 mL ethanol was added to the mixture. The mixture was sonicated for 20 min and then deoxygenated under argon for another 20 min. The flask was equipped with a condenser and placed in an oil bath at 80 °C for 24 h. The desired solid product (MNP@PVim) was magnetically separated and washed four times with methanol (4× 20 mL) and dried under vacuum at 50 °C.

To increase the solubility of PdCl₂ in water, PdCl₂ (0.044 g) and an excess amount of KCl (0.075 g) were dissolved in 10 mL deionized water in a 25 mL round bottom flask. The mixture was stirred at room temperature for 1 h until an orange solution was formed. MNP@PVim (0.5 g)

was then added into the solution and the mixture was stirred at room temperature for 24 h. Subsequently, 0.094 g of NaBH₄ was added to the mixture to reduce Pd (II) to Pd (0). The reaction product (MNP@PVim@Pd) was magnetically separated, washed five times with methanol (5×30 mL) and dried under vacuum at 50 °C.

General procedure for selective oxidation of alcohols catalyzed by MNP@PVim@Pd

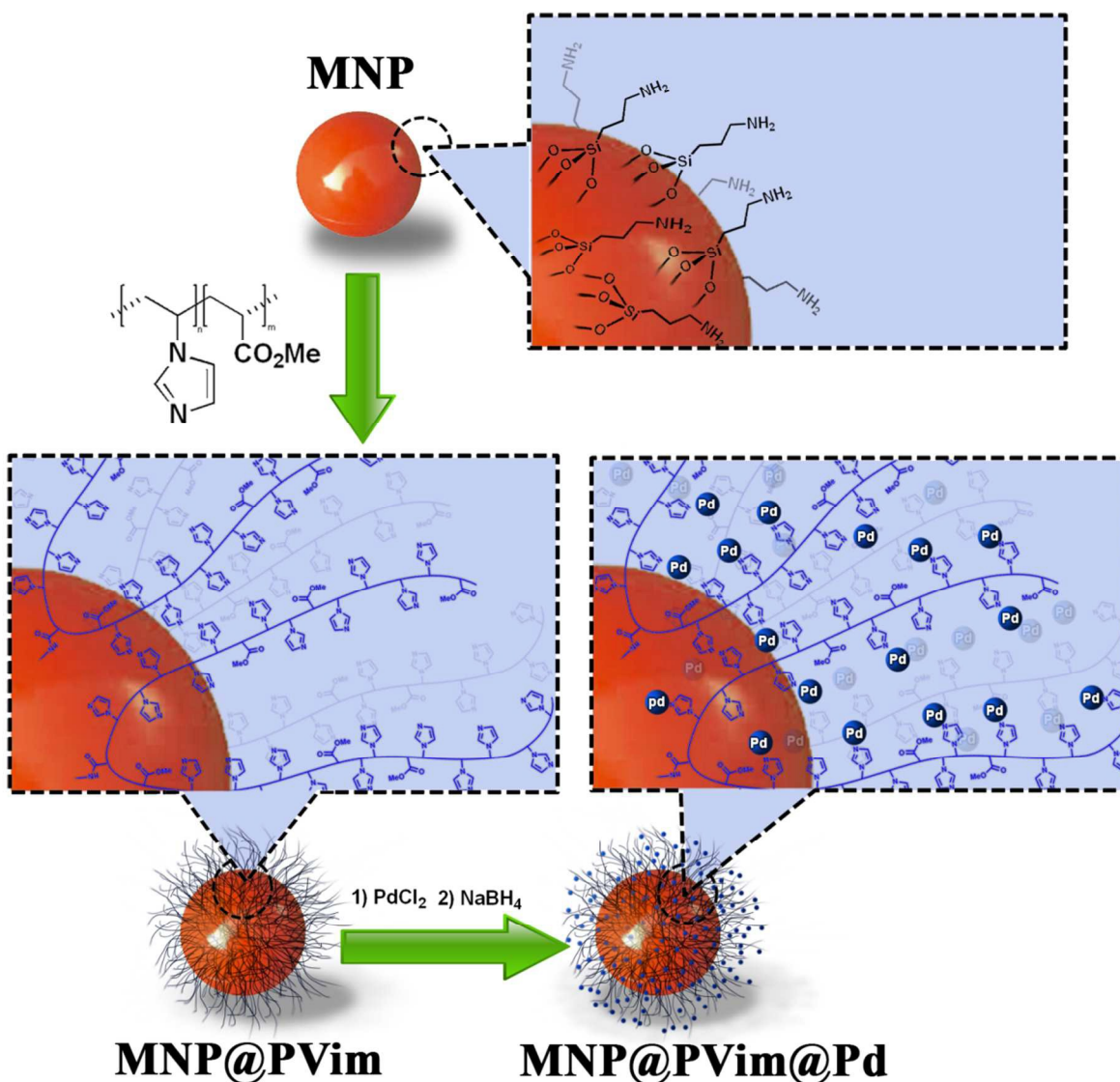
The activity of the supported Pd catalyst was investigated for selective oxidation of alcohols using atmosphere pressure as a source of oxygen (aerobic oxidation). 1 mmol of alcohol, 1 mmol of potassium carbonate and 2 mL water were loaded into a 25 mL round bottom flask, and the flask was equipped with a condenser. 5 mg of MNP@PVim@Pd was then added to the mixture which was vigorously stirred for an appropriate time under reflux condition at 100 °C in an oil bath. After completion of the reaction (monitored by TLC), the reaction was terminated and the catalyst was magnetically separated. Following this, the catalyst was washed three times with methanol (5×30 mL) and dried for another run. The organic product was extracted by hot ethyl acetate and analyzed by gas chromatography (GC).

Result and Discussion

Co-precipitation of iron (II) and iron (III) in alkali solution was used to synthesis Fe₃O₄ nanoparticles with excellent magnetism which permits the catalyst to be recovered easily. Surface modification of Fe₃O₄ with SiO₂ was performed with TEOS in order to enhance its chemical stability in the next synthesis steps. Coating of the MNP surface with APTES is essential for covalent attachment of copolymer onto MNP surface. Magnetic nanoparticles coated poly (1-vinyl imidazole-co-methyl acrylate) was prepared *via* co-polymer grafting to the

surface of functionalized MNPs. This approach would be useful in high temperature applications due to the presence of polymer chains which could prevent aggregation of MNPs. Palladium ions were loaded by complexation of palladium chloride and co-polymer chains on the surface of MNPs, which is depicted in Scheme 1. Afterward, NaBH_4 was applied to reduce Pd (II) and resulted in the desired magnetic poly (1-vinyl imidazole-co-methyl acrylate)-immobilized Pd nanoparticles.

Such an approach for synthesis of heterogeneous catalyst increases the loading level of palladium ions, due to the polymer coating, as relative to a conventional heterogeneous catalyst. As a result, a low percentage amount of catalyst is required in comparison with the substrate which makes it an effective protocol for industrial applications. Moreover, polymer coating prevents agglomeration of Pd nanoparticles on the surface of MNPs.



Scheme 1 Synthesis and structure of MNP@PVim@Pd.

At this step, FT-IR was utilized to characterize the catalyst structure. Fig. 1, shows the FT-IR spectra of Fe₃O₄ (a), Fe₃O₄@SiO₂ (b), MNP (c), poly(1-vinyl imidazole-co-methyl acrylate) (d) and MNP@PVim (e). The FT-IR spectrum of Fe₃O₄ reveals a stretching mode vibration of Fe-O at 640 cm⁻¹ and Fe₃O₄@SiO₂ shows an additional peak at 1100 cm⁻¹ which verifies the presence of Si-O in the structure (Fig. 1a, 1b). Coating of APTES onto the surface of Fe₃O₄ is confirmed by the stretching mode vibration of C-O at 1011 cm⁻¹ and C-N at 1364 cm⁻¹ in Fig. 1b.

Furthermore, N-H bending modes at 1622 cm^{-1} and aliphatic C-H bands at 2859 cm^{-1} and 2922 cm^{-1} clearly confirm coating of APTES onto the surface of Fe_3O_4 . The FT-IR spectrum of copolymer (Fig. 1c) displays characteristic peaks of imidazole rings at 1497 cm^{-1} and 1650 cm^{-1} which are attributed to C=C and C=N, respectively. Moreover, a weak peak at 2930 cm^{-1} is representative of aliphatic C-H band which clearly indicates the presence of the imidazole ring. In addition, a new band at 1729 cm^{-1} is attributed to C=O vibration mode which affirmed the presence of methyl acrylate. After polymer coating onto the surface of MNP, all specific peaks of MNP and polymer are easily observed (Fig. 1d). Moreover, a peak at 1690 cm^{-1} verifies the formation of amides in the catalyst structure. These results confirmed that MNPs were properly coated by co-polymer.

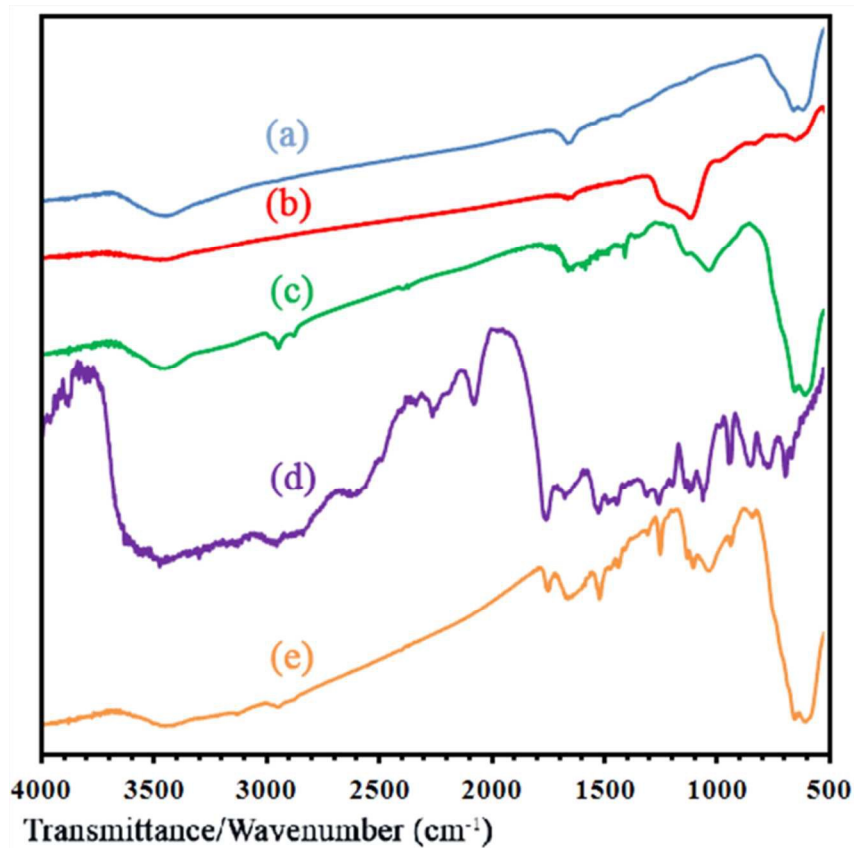


Fig. 1 FT-IR spectrum of Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@SiO_2$ (b), MNP (c), poly(vinyl imidazole-co-methyl acrylate) (d), MNP@PVim (e).

The thermal stability and organic content of MNP@PVim was evaluated by thermal gravimetric analysis (Fig. 2). From the weight loss in the TGA curve of MNP (Fig. 2Ia), the loading amount of APTES is 0.51 mmol g^{-1} . Based on the TGA curve of MNP@PVim (Fig. 2Ib), the content of co-polymer on the surface of MNP is about 20 wt%. In the DTG curve of the MNP@PVim three main peaks were seen. Loss of adsorbed water molecules can be seen below $100 \text{ }^\circ\text{C}$. Two other peaks at $280 \text{ }^\circ\text{C}$ and $390 \text{ }^\circ\text{C}$ are attributed to methyl acrylate and imidazole parts in the polymer structure, respectively. These results proved that the catalyst is thermally stable and could be used under harsh reaction condition at high temperature (under $500 \text{ }^\circ\text{C}$).

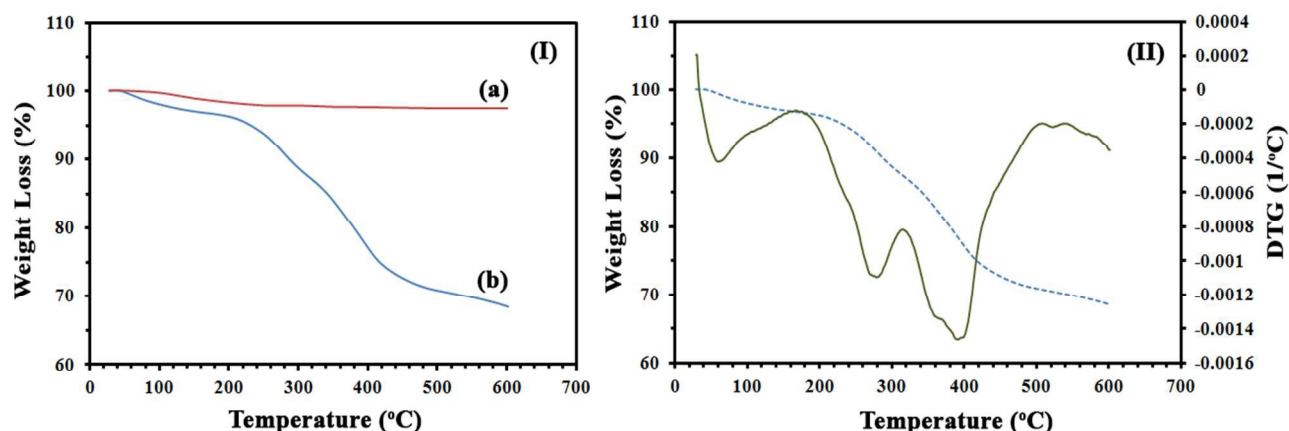


Fig. 2 (I) TGA curve of MNP (a) and MNP@PVim (b); (II) DTG curve for MNP@PVim.

The X-ray diffraction pattern of MNP@PVim@Pd is shown in Fig. 3, with characteristic peaks and relative intensity, which completely matches with the standard Fe_3O_4 (red lines) (JCPDC file No. 19-0629). These results confirmed that the modifications did not produce a phase change in the Fe_3O_4 particles. The XRD pattern of Pd nanoparticle cannot be seen in Fig. 3 due to the amount of Pd nanoparticles is less than MNPs.

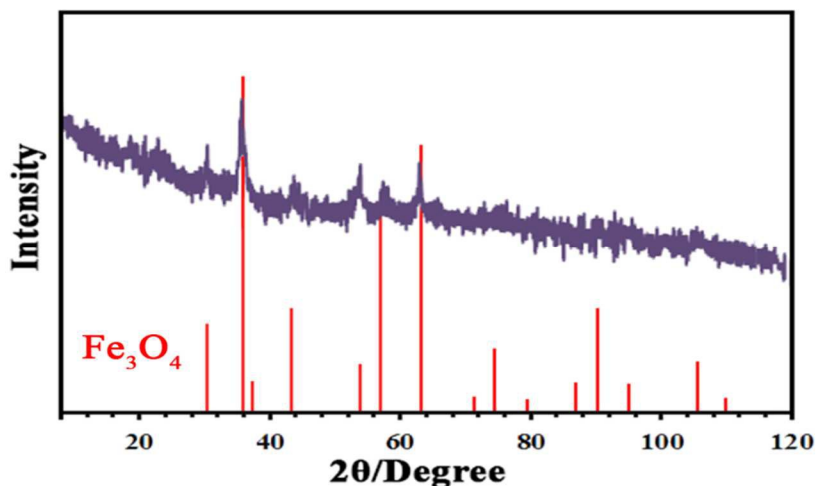


Fig. 3 The XRD pattern of MNP@PVim@Pd

Vibrating sample (VSM) has been employed to measure the magnetic properties of the catalyst. The VSM curves of MNP@PVim@Pd and Fe_3O_4 are depicted in Fig. 4 which show small coercivities and indicate the superparamagnetic nature of both materials. The saturation magnetization of MNP@PVim@Pd is smaller than bare MNP due to polymer coating of MNPs. However, the magnetization of the catalyst is high enough to ease the recovery process.

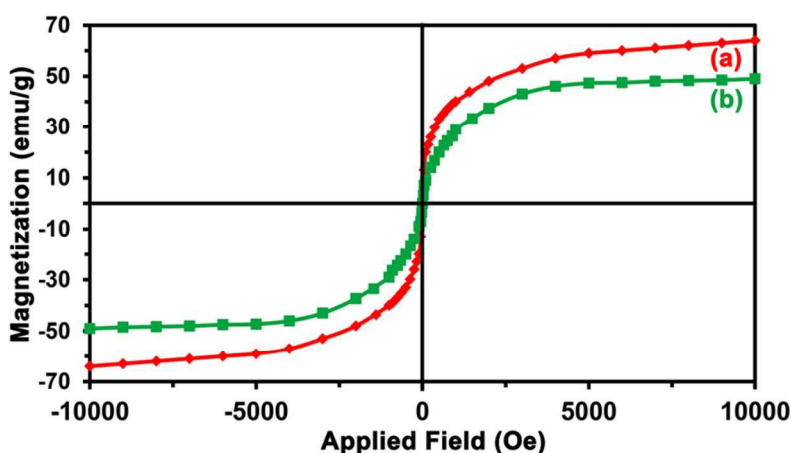


Fig. 4 Magnetization curves of MNP (a) and MNP@PVim@Pd (b).

The surface morphology of MNP@PVim@Pd was investigated using SEM which is illustrated in Fig. 5a. The SEM image of the catalyst shows the presence of well dispersed polymer coated magnetic nanoparticles. Energy-dispersive X-ray spectroscopy (EDS) analysis of the catalyst directly confirmed the presence of Pd in the catalyst structure (Fig. 5b).

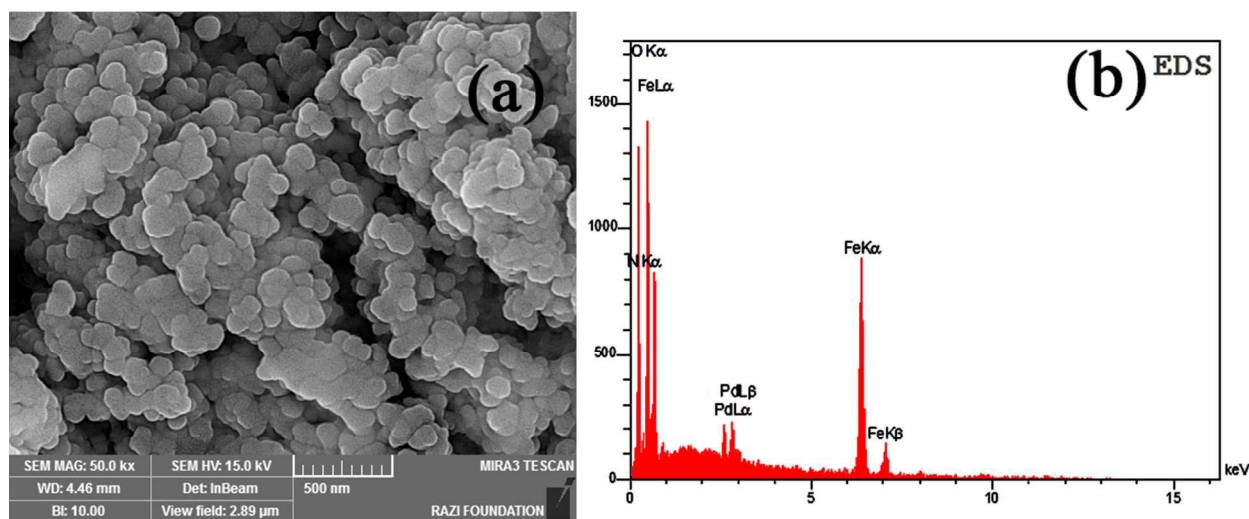


Fig. 5 SEM image of MNP@PVim@Pd (a); EDS analysis of MNP@PVim@Pd (b).

The TEM image of magnetic nanoparticles is represented in supporting information (Fig. 1s). The TEM image of MNP@PVim@Pd is shown in Fig. 6. The TEM image of the catalyst shows that palladium nanoparticles with the average size of 3 nm are dispersed in the polymeric matrix.

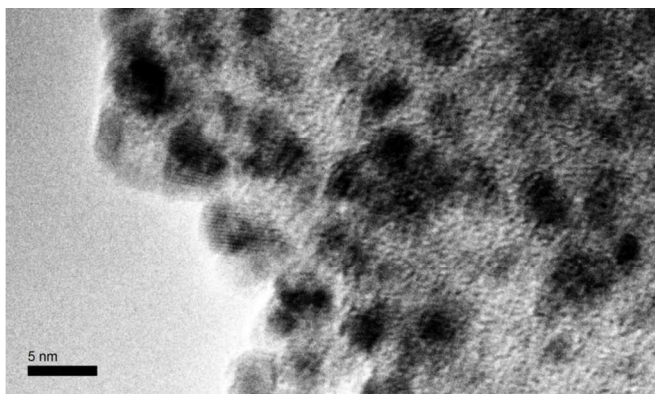


Fig. 6 TEM image of MNP@PVim@Pd

Gel permeation chromatography (GPC) curve of the copolymer is shown in the Fig. 7. As seen in the GPC curve of the copolymer, a single peak is observed, which suggests the monodispersity of M_w and the absence of neither homopolymer nor monomers. Based on the GPC curve, M_w and PDI of the copolymer are 7500 g/mol and 2.4, respectively.

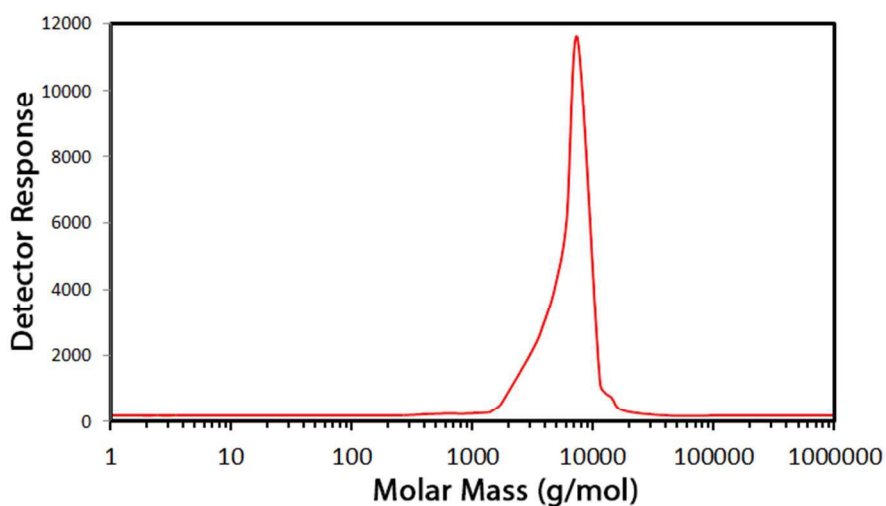


Fig.7 GPC curve of copolymer.

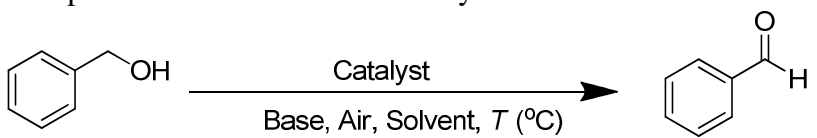
Atomic absorption spectroscopy (AAS) is a suitable method to determine the loading amount of transition metals. It was found that the loading amount of Pd in the catalyst is 0.31 mmol g⁻¹.

These results established the high capability of imidazole groups to coordinate Pd ions in the structure of the catalyst.

The catalytic performance of MNP@PVim@Pd was investigated in the oxidation of alcohols. In order to obtain the best catalytic activity, several optimizations, such as catalyst loading, solvent, temperature, time and different bases were examined to obtain the best reaction condition for oxidation of alcohols. Oxidation reaction of alcohols can be conducted in a broad range of organic solvents. However, production of high amount of toxic waste restricts its utilization in practical scale. Hence, water as a universal solvent with low cost and intrinsically green could stand out in the role of chosen solvent. Therefore, we focused our attention to optimize catalyst loading, base, temperature and time in water medium (Table 1). As seen in Table 1, no significant amount of product was observed when no catalyst has been used even at higher temperature (Entries 1, 2). The result of entry 3 shows that MNP@PVim has no catalytic activity in the absence of palladium, however the use of 0.6 mol% of MNP@PVim@Pd gave 84% yield at 70 °C. It was found that reduction in the amount of catalyst and temperature could reduce the yield of products (Entries 4 to 8). As seen in the Table 1, increasing the temperature to 100 °C improved the oxidation yield up to 99% (Entry 9). With the goal of using a lower amount of catalyst, applying 0.1 mol% of MNP@PVim@Pd at 100 °C was designated for further optimization of the model reaction (Entry 10). Several other bases were also tested which gave lower yields (Entries 11 to 16). In solvent free condition, no substantial product was obtained (Entry17). This could be related to difficulties in mixing of substrates under the solvent free condition. In order to accentuate the expediency of water as a solvent, some other organic solvents were also tested and the results are shown in entries 18 to 22. To investigate the capability of the catalyst in large scale application, very small amount of the catalyst was used to

oxidize benzyl alcohol. 10 mmol of reactants were utilized while only 0.1 mol% of catalyst was consumed to give 92% yield in longer reaction time (30 h) (Entry 23).

Table 1 Control experiment for oxidation of benzyl alcohol.^a



Entry	Catalyst	Solvent	Cat. Loading (mol%)	T (°C)	Time (h)	Base	Yield ^b (%)
1	-	H ₂ O	-	70	24	K ₂ CO ₃	<1 ^c
2	-	H ₂ O	-	100	24	K ₂ CO ₃	<3 ^c
3	MNP@PVim	H ₂ O	10 mg	100	24	K ₂ CO ₃	20
4	MNP@PVim@Pd	H ₂ O	0.6	70	24	K ₂ CO ₃	84
5	MNP@PVim@Pd	H ₂ O	0.3	70	24	K ₂ CO ₃	81
6	MNP@PVim@Pd	H ₂ O	0.1	70	24	K ₂ CO ₃	76
7	MNP@PVim@Pd	H ₂ O	0.09	70	24	K ₂ CO ₃	54
8	MNP@PVim@Pd	H ₂ O	0.03	70	24	K ₂ CO ₃	43
9	MNP@PVim@Pd	H ₂ O	0.1	100	24	K ₂ CO ₃	99
10	MNP@PVim@Pd	H ₂ O	0.1	100	18	K ₂ CO ₃	99
11	MNP@PVim@Pd	H ₂ O	0.1	100	18	Na ₂ CO ₃	99
12	MNP@PVim@Pd	H ₂ O	0.1	100	18	Cs ₂ CO ₃	75
13	MNP@PVim@Pd	H ₂ O	0.1	100	18	CH ₃ ONa	80
14	MNP@PVim@Pd	H ₂ O	0.1	100	18	NaOH	65
15	MNP@PVim@Pd	H ₂ O	0.1	100	18	Et ₃ N	27
16	MNP@PVim@Pd	H ₂ O	0.1	100	18	^t BuOK	73
17	MNP@PVim@Pd	neat	0.1	100	18	K ₂ CO ₃	40
18	MNP@PVim@Pd	CH ₃ CN	0.1	100	18	K ₂ CO ₃	62
19	MNP@PVim@Pd	DMF	0.1	100	18	K ₂ CO ₃	65
20	MNP@PVim@Pd	Toluene	0.1	100	18	K ₂ CO ₃	53
21	MNP@PVim@Pd	THF	0.1	100	18	K ₂ CO ₃	24
22	MNP@PVim@Pd	^t BuOH	0.1	100	18	K ₂ CO ₃	52
23	MNP@PVim@Pd ^d	H ₂ O	0.1	100	30	K ₂ CO ₃	92

^a Reaction condition: Benzyl alcohol (1 mmol), base (1 mmol), solvent (2 mL).

^b GC yield.

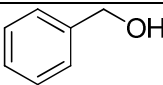
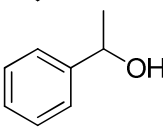
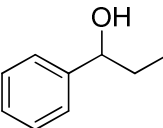
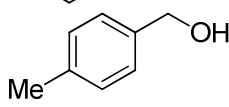
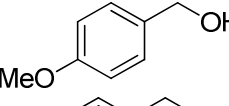
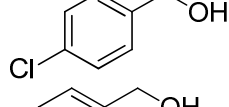
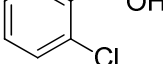
^c Mainly recovery of the starting materials.

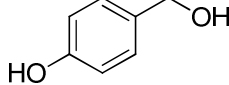
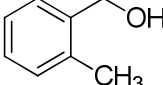
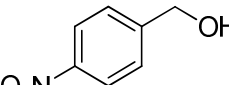
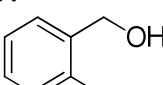
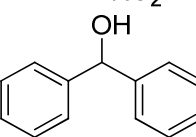
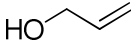
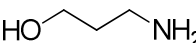
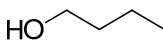
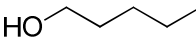
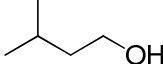
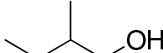
^d 10 mmol scale of reactant.

The scope of the selective oxidation reaction of alcohols catalyzed by MNP@PVim@Pd with respect to the various primary and secondary alcohols was also explored (under the optimized

reaction condition). It was revealed that the catalyst is highly selective since no benzoic acid was produced. Wide diversity of benzyl alcohol substrates including electron withdrawing and electron donating groups were readily oxidized under optimized reaction condition to corresponding benzaldehydes with excellent to good yields. Electron withdrawing groups like Cl and NO₂ substitutes required longer reaction time with lower yields in comparison with electron donating groups (Entries 4 to 11). Furthermore, oxidations of three kinds of secondary alcohols under the same reaction condition were also examined and satisfactory conversion was achieved (Entries 2, 3 and 12). Some primary aliphatic alcohols were also tested (Entries 13-18). These kinds of alcohols showed lower yields in compare with aromatic ones. These results reveal the efficiency of MNP@PVim@Pd for the selective oxidation of alcohols.

Table 2 Oxidation of alcohols catalyzed by MNP@PVim@Pd.^a

Entry	Substrates	Time (h)	Yield (%) ^b
1		18	99
2		17	89
3		17	87
4		19	90
5		19	92
6		20	85
7		20	84

8		17	83
9		21	80
10		22.5	77
11		22.5	75
12		21	90
13		22	78
14		22	73
15		22	74
16		22	74
17		22	74
18		22	74

^a Reaction condition: Alcohol (1 mmol), K₂CO₃ (1mmol), MNP@PVim@Pd (0.1 mol%), H₂O (2 mL), 100 °C.

^b Yields were determined by GC.

An important aspect of heterogeneous catalyst in large scale application is the recyclability and reusability of the exerted catalyst. To explore this potential, oxidation of benzyl alcohol in the optimized reaction condition was carried out. After completion of the reaction, the catalyst was easily separated and was used for the next run. As seen in Fig. 8, the catalyst was reused for 10 runs without significant loss of activity.

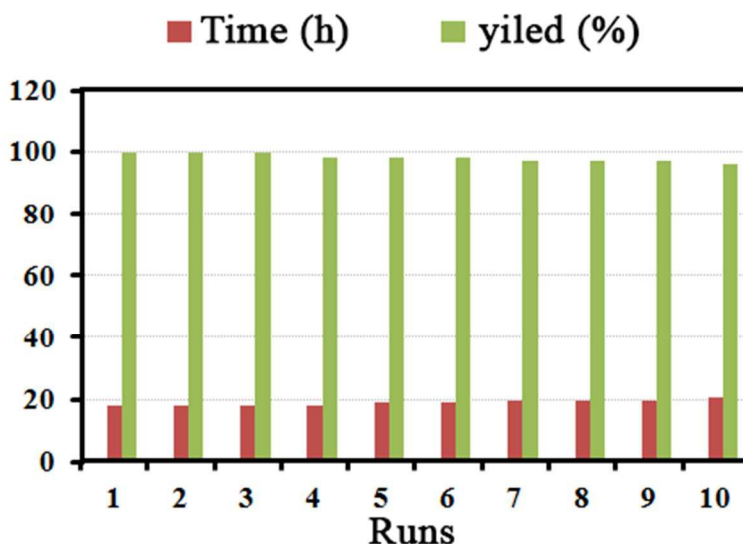


Fig. 8 Recycling experiment.

To verify whether the observed catalytic activity is derived from leached metal species or solid support, the typical metal leaching test was performed. To demonstrate the heterogeneity of the catalyst, the oxidation of benzyl alcohol under optimized reaction condition was conducted. After 6 h, the reaction was stopped and the catalyst was completely separated with external magnetic force. The reaction mixture allowed stirring for 18 h without catalyst and no more benzaldehyde was obtained (Fig. 9). After separation of catalyst, the reaction mixture was analyzed by induction coupled plasma (ICP-AES) and no palladium specie was detected. These results corroborate the exact heterogeneity of MNP@PVim@Pd. Moreover, no remarkable change in the catalyst structure was seen in FT-IR spectrum and TEM image of the recycled catalyst (See supporting information Fig S3 and Fig S4) which truly establishes the stability of the catalyst even after 10 subsequent runs.

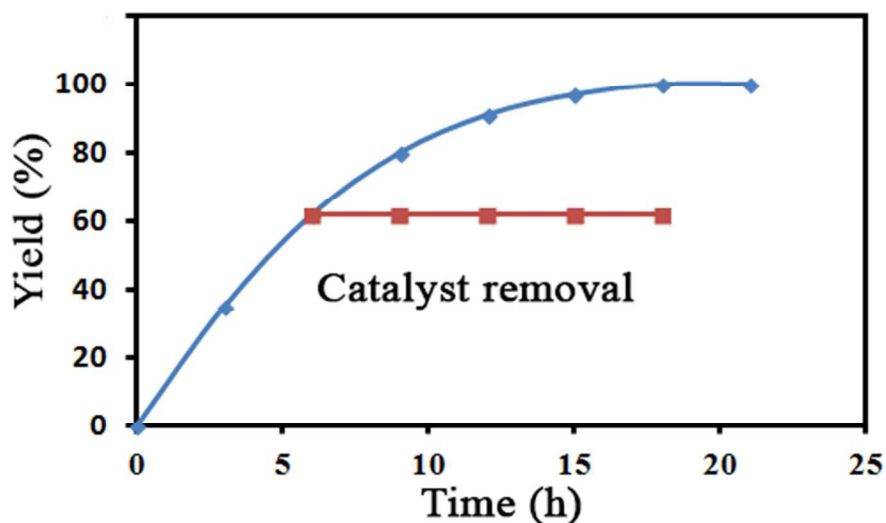


Fig. 9 Leaching experiment. Blue line: reaction in the presence of catalyst and Red line: reaction after removal of catalyst.

Conclusion

In summary, we have developed a novel and green method to oxidize primary and secondary alcohols to corresponding aldehydes or ketones *via* magnetically reusable palladium catalyst. The resulting catalyst demonstrated high activity and selectivity in the oxidation of alcohols with an ideal green process under atmospheric pressure in water medium. The catalyst was recovered easily by an external magnet and reused in subsequent runs (10 runs) without significant loss of activity. The operational simplicity, purity and high yields of products, absence of organic solvents, use of atmospheric pressure of molecular oxygen as an oxidant and the high recyclability of the catalyst (up to 10 runs) validate the potential of this catalyst for large scale applications.

Supporting information

Supporting information may be found in the online version of this article.

Acknowledgments

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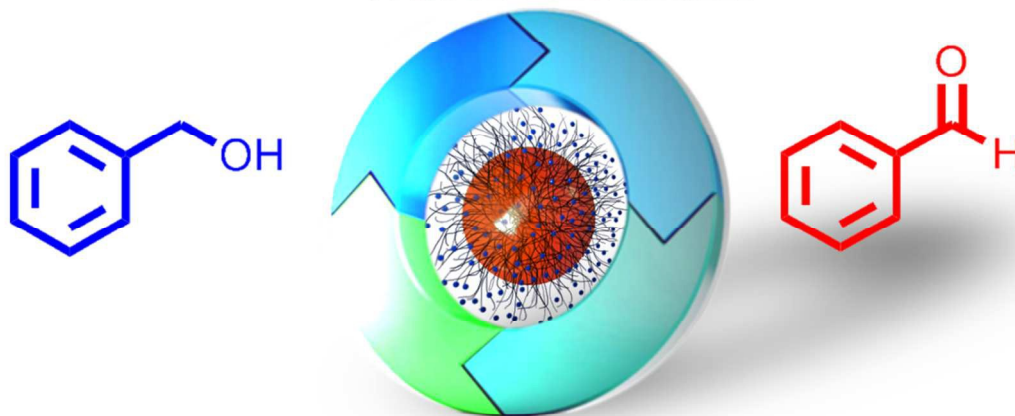
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Graphical Abstract

Highly Dispersible and Magnetically Recyclable Poly(1-Vinyl Imidazole) Brush coated Magnetic Nanoparticle: an Effective Support for Immobilization of Palladium Nanoparticles

**0.1 mol% Catalyst
Water Medium**



**10 Times Reuse
Magnetically Recyclable**

A heterogeneous recoverable catalyst was prepared via complexation of palladium onto the surface of magnetic nanoparticles coated by poly(1-vinyl imidazole) brush. The stable, active and reusable catalyst was proven to be highly active in aerobic oxidation of primary and secondary alcohols with excellent yields. Only 0.1 mol% of catalyst was used to oxidize 1 mmol of primary and secondary alcohols.