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Selective Hydration of Nitriles to Amides Over Titania Supported Palladium Exchanged Vanadium Incorporated Molybdophosphoric Acid Catalysts

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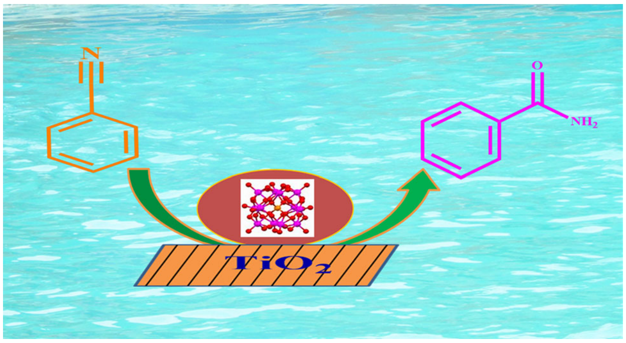
Abstract Titania supported palladium exchanged vanadium incorporated molybdophosphoric acid ($PdMPAV_1$) catalysts were prepared and characterized by FT-IR, X-ray diffraction and Laser Raman spectroscopy. The characterization results confirmed the presence of vanadium and palladium into the primary and secondary structure of Keggin ion of heteropoly molybdate respectively. The $PdMPAV_1$ was dispersed on support with intact Keggin ion structure. These catalysts were studied for selective hydration of nitriles to amides. The $PdMPAV_1$was highly active compared to the molybdophosphoric acid containing either vanadium or palladium. The catalyst with 20 % $PdMPAV_1$ dispersed on TiO_2 showed highest activity compare to other catalysts. A variety of nitriles were tested over this catalyst and found that the catalyst was active to yield corresponding amides. Different reaction parameters were studied and optimum conditions were established. The $PdMPAV_1/TiO_2$ catalyst exhibited consistent activity during reuse.

Graphical Abstract



Keywords Nitrile · Amide · Hydration · Palladium · Molybdophosporic acid

1 Introduction

Development of reusable heterogeneous catalysts in water is an important system in terms of environment and industrial point of view. Hydration of nitriles using reusable catalysts is one such example. Hydration of nitriles to the corresponding amides is an important and useful reaction in pharmaceutical industry [1, 2]. Amides are one of the most important functional groups in nature as amide linkages are the key chemical connections of proteins. These are versatile building blocks in synthetic organic chemistry, and exhibit a wide range of industrial applications [3–5]. For example, hydration of acrylonitrile produces annually more than 2×10^5 tons of acrylamide and is the most important technology [6]. Amides are typically prepared from the combination of carboxylic acids and its derivatives such as halides, anhydrides or esters with

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amines. However, these methods are not desired as they have several drawbacks such as use of toxic, corrosive and expensive materials. These approaches are associated with problems like highly exothermic reactions, low tolerance to sensitive functional groups, complex reaction conditions and wasteful procedures [7–9]. The traditional homogeneous catalytic systems for synthesis of amides require organic solvents and strong acid/base catalysts. These strong acid/base catalysts led to over-hydrolysis of amides into undesirable carboxylic acids and results in the formation of large amount of salts after neutralization [10–16]. In addition, many functional groups, for example, carbon–carbon double bonds, do not tolerate such forcing conditions, which results in decreased selectivity for amides. Various metal complexes and organometallic compounds such as Ru [17, 18], Rh [19, 20], Ag [21], Ni [22], Pd [23, 24] have been reported as effective homogeneous catalysts in organic and/or aqueous medium for synthesis of amides. The main problem associated with these systems is the separation of catalyst from product. All these difficulties can be overcome by the use of heterogeneous catalysts [25]. Hydration of nitriles with heterogeneous catalyst has emerged as an alternative efficient synthetic route that avoids the formation of undesirable side products and use of corrosive acidic or basic media. Different heterogeneous catalysts such as Ag nano particles supported on silica, hydroxyapatite [26], and Pd nano particles [27], KF/Al_2O_3, Na/HAP, MnO_2/SiO_2, bulk and supported NiO catalysts [28] has been reported. Most of these catalysts suffer from low activity and reusability.

Heteropoly acids (HPAs) are well known acid and oxidation catalysts. These are having wide range of applications, especially in fine chemical synthesis. However their applications are limited in bulk form as they are soluble in polar solvents, possess low surface area and less thermal stability. In order to overcome these difficulties HPAs could be modified at molecular level. Heteropoly acids, especially the Keggin-type, can be modified by converting them into salts, incorporation of various other transition metal ions like V into the Keggin frame work or by supporting them on various solid supports [29–31].

In continuation of our quest for development of modified Keggin type heteropoly acid catalysts for various organic transformations [32], in the present work titania supported vanadium incorporated palladium exchanged molybdophosporic acid is reported as a heterogeneous catalysts for the selective hydration of nitriles. Molybdophosporic acid, a known oxidation catalyst among HPAs, is modified to increase its oxidizing ability further by incorporation of vanadium and exchanging its protons with palladium. The catalysts characteristics were derived from different spectroscopy techniques and correlated with observed nitrile hydration activity.

2 Experimental

2.1 Catalyst Preparation

Vanadium incorporated molybdophosphoric acid catalysts (MPAV) were prepared according to the reported procedure [33]. In the synthesis of $MPAV_1$ (one vanadium replacing one Mo) hot aqueous solutions of disodium hydrogen phosphate and sodium metavanadate were mixed in the required proportions. The mixture was cooled and acidified with concentrated sulphuric acid. To this mixture calculated amount of an aqueous solution of sodium molybdate dihydrate was added. Concentrated sulphuric acid was subsequently added slowly with stirring. During this addition the colour changed from dark red to light red. The MPAV formed was extracted with diethyl ether since the heteropoly acid was present in the middle layer as a heteropoly etherate. The ether was removed on a rota vapour. The orange solid obtained was dissolved in water and concentrated until the crystals appeared. Preparation of catalysts with two and three V atoms was also followed similar to that of $MPAV_1$ except by taking the required amount of sodium metavanadate and sodium molybdate.

In the preparation of palladium exchanged $MPAV_1$ catalyst, the required quantity of $MPAV_1$ was dissolved in minimum amount of water and to this required quantity of aqueous solution of palladium nitrate was added slowly with constant stirring. The excess water was removed on hot plate and the catalyst masses were dried in an air oven at 120 °C for 12 h. Finally the catalysts were calcined at 300 °C for 2 h. This $PdMPAV_1$ was supported on TiO_2 by impregnation method. The required quantity of $PdMPAV_1$ was dissolved in minimum amount of water and this solution was added to TiO_2 dropwise with constant stirring. The excess water was removed using hot plate and the catalyst masses were dried in an air oven at 120 °C for 12 h. The final catalysts were obtained after calcination at 300 °C for 2 h. These catalysts were denoted as 5–25 % $PdMPAV_1/TiO_2$.

2.2 Characterization of Catalysts

The FT-IR spectrum was recorded on a Bio-rod Excalibur series spectrometer using the KBr disc method.

X-ray powder diffraction patterns were recorded on of Rigaku Miniflex diffractometer using CuKα radiation (1.5406 Å) at 40 kV and 30 mA and secondary graphite monochromatic. The measurements were obtained in steps of 0.045° with account time of 0.5 S and in the 2θ range of 10–80°.

Confocal Micro-Raman spectra recorded at room temperature in the range of 200–1200 cm^{-1} using Horiba

Jobin–Yvon Lab Ram HR spectrometer with a 17 mW internal He–Ne (Helium–Neon) laser source of excitation wavelength of 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were usually loosely spread onto a glass slide below the confocal microscope for Raman measurements.

2.3 General Reaction Procedure

In a typical reaction procedure 1 mmol benzonitrile and 3 ml of H_2O was taken in a sealed tube. About 80 mg of catalyst was added to this reaction mixture and stirred at 140 °C on a oil bath for stipulated reaction time. The progress of the reaction was monitored by using thin layer chromatography. The products were identified by GC–MS (SHIMADZU-2010) analysis by separating the products on a DB-5 column.

3 Results and Discussion

3.1 Characterization

FT-IR spectra of the palladium exchanged vanadium incorporated molybdophosphoric acid catalysts are presented in Fig. 1. The spectra of MPA supported on titania (without vanadium) was also presented for sake of comparison. The catalysts mainly exhibited bands at 1063, 963 and 863 cm^{-1} that were assigned to stretching vibrations of P–O_a (O_a = oxygen atoms bound to three Mo atoms and to P) Mo–O_t (O_t = terminal oxygen), Mo–O_b–Mo (O_b = -corner sharing bridging oxygen) respectively [33]. The TiO_2 support absorbs the IR signal below 800 cm^{-1} that prevents collection of weak Keggin vibrations in this region. In the case of $PdMPAV_1/TiO_2$ catalysts Mo–O band shifted toward lower wave number compared to parent MPA due to reduced structure symmetry [34]. The shift in wave number suggests the incorporation of V into primary structure of heteropoly molybdate [35].

XRD patterns of titania supported $PdMPAV_1$ catalysts are presented in Fig. 2. For the sake of comparison titania and $MPAV_1/TiO_2$ diffraction patterns are also shown in the insert of the figure. In the spectra the crystalline anatase phases of TiO_2 patterns were predominant. Only small diffraction lines at 2θ values of 10° and 25° indicate the presence Keggin ion structure of PdMPAV [36]. These results supports that the active component PdMPAV was well dispersed on titania.

Figure 3 shows the Raman spectra of $PdMPAV_1/TiO_2$ catalysts. The characteristic bands of titania are dominant in the spectra. Only small band at 1003 cm^{-1} related to M = O_t vibration of Keggin ion of MPAV was observed. The predominant bands at 392, 510 and 632 cm^{-1} originated from anatase phase of TiO_2 were seen for all the samples. The absence of a band around 1034 cm^{-1} indicates that there was no free V_2O_5 on the surface of MPA [37]. FT-IR and Raman results suggest that V is incorporated into the primary structure of MPA Keggin ion.

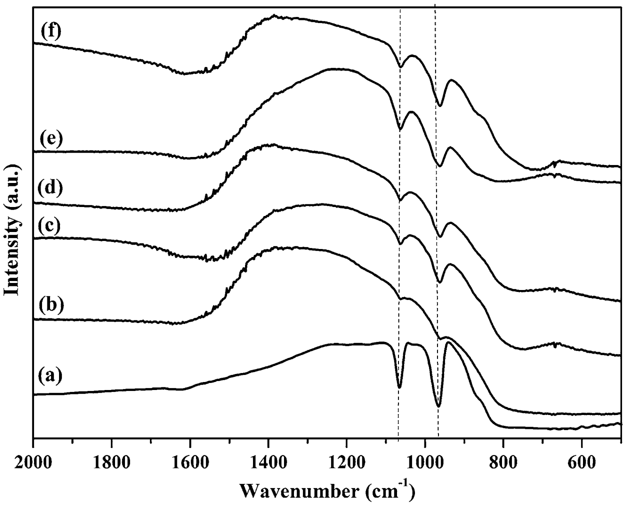


Fig. 1 FT-IR spectra of palladium exchanged vanadium incorporated molybdophosphoric acid supported on titania catalysts. *a* MPA/TiO_2, *b* $5PdMPAV_1/TiO_2$, *c* $10PdMPAV_1/TiO_2$, *d* $15PdMPAV_1/TiO_2$, *e* $20PdMPAV_1/TiO_2$, *f* $25PdMPAV_1/TiO_2$

3.2 Catalysts Activity for Hydration of Nitrile to Amide

The catalytic activity of bulk MPA, PdMPA, $MPAV_1$ and $PdMPAV_1$ were tested for the hydration of benzonitrile under aqueous conditions without any organic solvent as shown in Scheme 1. Benzonitrile was taken as a model substrate for the hydration of nitriles. Initially the reaction was carried using bulk MPA as catalyst and observed 15 % of amide formation. When the protons of MPA exchanged with Pd (PdMPA), the yield of amide formation increased up to 57 %. The reaction was also carried with $MPAV_1$ catalyst and it gave about 44 % yield of amide. The conversion of benzonitrile and yield of the amide substantially increased up to 92 % when the protons of MPA exchanged with palladium and also one of the Mo atom replaced with vanadium ($PdMPAV_1$). Most of these bulk heteropoly acids were homogeneous under present reaction conditions. These bulk PdMPAV catalysts are supported on titania to make them as heterogeneous catalysts. Titania was chosen as a support because it preserves the Keggin unit even at higher temperature than its unsupported form. Another important aspect of the titania support is that it has capability of releasing oxygen from surface due to mobility of lattice oxygen and to form oxygen vacancies at relatively mild conditions [30]. The catalysts with different content of

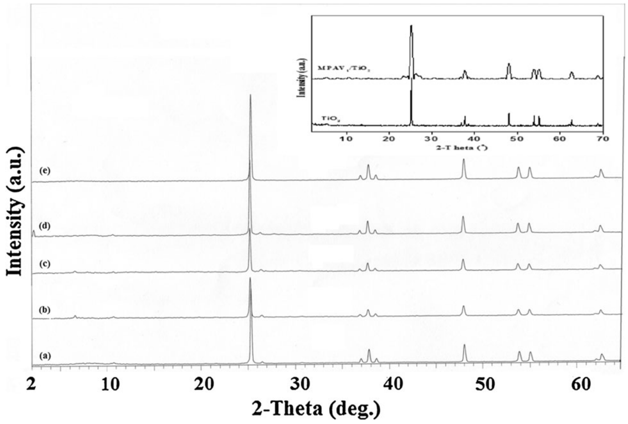


Fig. 2 XRD patterns of palladium exchanged vanadium incorporated molybdophosporic acid supported on titania catalysts. *a* 5PdMPAV$_1$/TiO$_2$, *b* 10PdMPAV$_1$/TiO$_2$, *c* 15PdMPAV$_1$/TiO$_2$, *d* 20PdMPAV$_1$/TiO$_2$, *e* 25PdMPAV$_1$/TiO$_2$

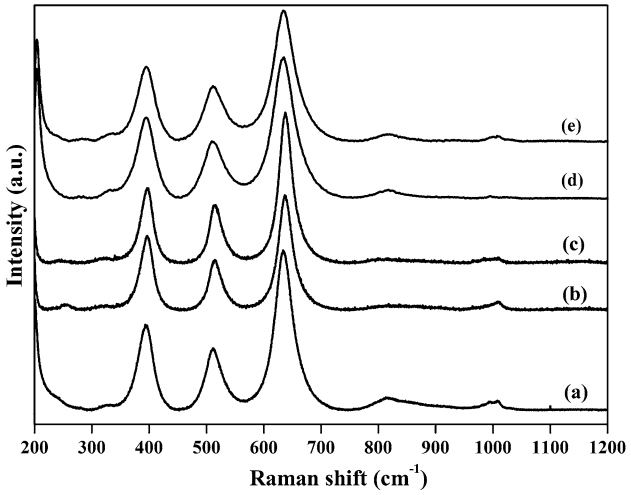


Fig. 3 Raman Spectra of palladium exchanged vanadium incorporated molybdophosporic acid supported on titania catalysts. *a* 5PdMPAV$_1$/TiO$_2$, *b* 10PdMPAV$_1$/TiO$_2$, *c* 15PdMPAV$_1$/TiO$_2$, *d* 20PdMPAV$_1$/TiO$_2$, *e* 25PdMPAV$_1$/TiO$_2$

PdMPAV$_1$ supported on titania were prepared and evaluated for hydration of nitrile to amides and the results are shown in Table 1. The PdMPAV1/TiO$_2$ catalysts activity increased with increase in the content of PdMPAV$_1$ from 5 to 20 %. At low content of PdMPAV$_1$ on TiO$_2$ the yield of the product was only 20.5 %. The catalyst with 20 % PdMPAV$_1$ on TiO$_2$ showed about 97 % yield of amide. When the PdMPAV$_1$ content increased to 25 %, the yield of the benzamide was decreased and at the same time benzoic acid was formed as a side product. The formation of benzoic acid might be due to over hydrolysis of benzamide. Hydration of nitriles was achieved using Pd (II) complexes. It is reported that Pd in its oxidation form is active for the hydration of nitriles [38]. Ru (II) or Cu (II) complexes are also showed activity for the nitrile hydration [16, 39]. In the present catalysts Pd is exchanged with protons of heteopoly molybdtae and it presents as Pd (II). The presence of Pd and V in the catalysts was responsible for high hydration activity. The catalyst without Pd and V (MPA/TiO$_2$) showed very low activity.

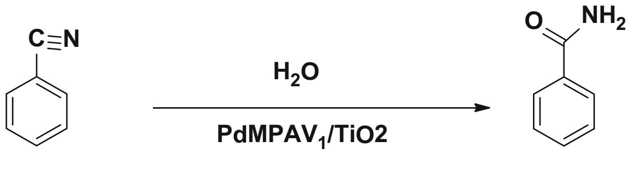
A number of structurally diverse aromatic and aliphatic nitriles were screened for studying the generality as well as the efficiency of the present catalyst and the results are shown in Table 2. The 20 % PdMPAV$_1$/TiO$_2$ catalyst was highly active for the synthesis of substituted amides with high yield to the corresponding products. Aromatic nitriles are more reactive compare to aliphatic nitriles. Nitriles bearing both electron-donating and electron-withdrawing functionalities were also found to undergo in a facile manner with excellent yields.

The plausible reaction mechanism over the catalyst is schematically shown in Scheme 2. In this reaction pathway water and nitrile group coordinates on the catalyst surface. In the first step nitrile group is activated by palladium sites and in the second step activated complex undergoes nucleophilic attack by an adjacent hydroxyl ion. In the third step tautomerism of the coordinated imines led to form the amide, which is readily removed from the catalyst surface.

The time on stream analysis for the hydration of nitrile to amide over 20 % PdMPAV$_1$/TiO$_2$ catalyst was studied and the results are shown in Table 3. This study was undertaken to know about the formation of amide with time. Initially at the start of the reaction formation of amide was less and as the reaction progresses the formation of amide is gradually increased up to 6 h. Further increase in the time the yield of amide was decreased and consequently formation of acid was observed.

3.2.1 Effect of Reaction Temperature on Hydration of Nitrile

In order to optimize the reaction parameters for the hydration of amides, the most active 20 % PdMPAV$_1$/TiO$_2$ catalyst was selected as system catalyst. Hydration of benzonitrile was carried to establish the reaction parameters. The influence of reaction temperature on the hydration of nitriles over 20 % PdMPAV$_1$/TiO$_2$ catalyst was



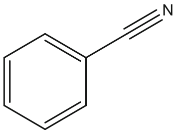
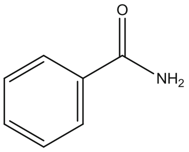
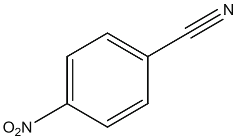
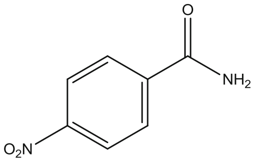
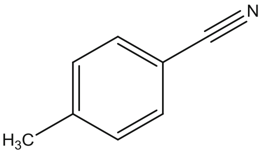
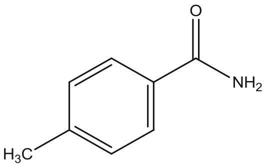
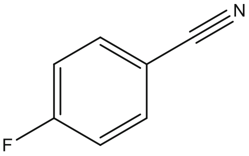
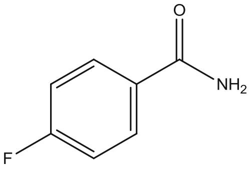
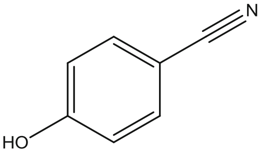
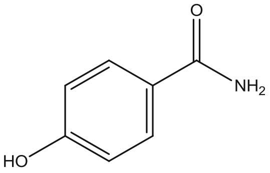
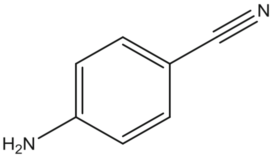
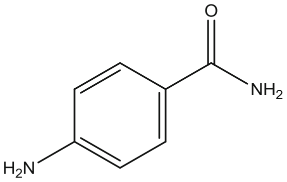
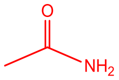
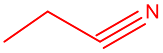
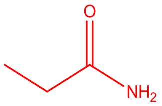
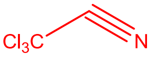
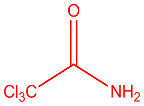
Scheme 1 Hydration of benzonitrile to benzamide

Table 1 Effect of $PdMPAV_1$ content on titania for selective hydration of nitriles

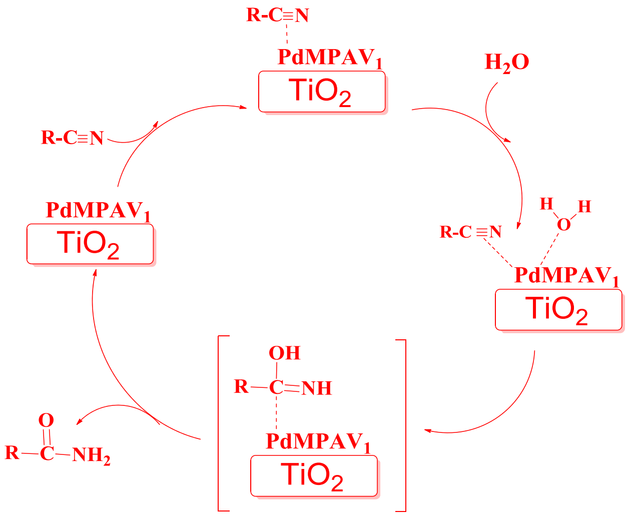
Catalyst	Nitrile conversion (%)	Amide yield (%)	Acid yield (%)
$20MPA/TiO_2$	8	8	–
$5PdMPAV_1/TiO_2$	20.5	20.5	–
$10PdMPAV_1/TiO_2$	40	38	–
$15PdMPAV_1/TiO_2$	70	68	2
$20PdMPAV_1/TiO_2$	100	97	3
$25PdMPAV_1/TiO_2$	98	88	10

Reaction conditions Benzonitrile: 1 mmol, *Water* 3 ml, *Catalyst* 80 mg, *Temperature* 140 °C, *Reaction time* 6 h

Table 2 Synthesis of substituted amides over $PdMPAV_1/TiO_2$ catalyst

Nitrile	Amide	Amide yield (%)	Acid yield (%)
		97	3
		95	5
		93	7
		96	4
		92	8
		94	6
		54	54
		48	46
		52	52

Reaction conditions Nitrile: 1 mmol, *Water* 3 ml, *Reaction temperature* 140 °C, *Reaction time* 6 h



Scheme 2 Plausible reaction mechanism for the hydration of nitriles over $PdMPAV_1/TiO_2$ catalyst

Table 3 Effect of time on hydration of nitriles

Time (h)	Amide yield (%)	Acid yield (%)
1	17	–
2	32	–
3	51	–
4	63	–
5	84	2
6	97	3
7	92	8

Reaction conditions Nitrile: 1 mmol, *Water* 3 ml, *Catalyst* 80 mg, *Reaction temperature* 140 °C

evaluated by varying the reaction temperature from 80 to 160 °C and the results are shown in Table 4. The conversion was increased with increase in reaction temperature. When the reaction was carried at low temperature the formation of amide was very less. However, when the reaction temperature increased to 140 °C the conversion was nearly 100 % and the yield of the amide was 97 %. Further increase in reaction temperature to 160 °C, the yield of amide was decreased and subsequent formation of acid was observed.

3.2.2 *Effect of Catalyst Weight on Hydration of Nitrile*

The effect of catalyst weight on the hydration of nitriles was also studied and the results are shown in Table 5. The amount of catalyst varied from 0.04 to 0.1 g. At lower amount of catalyst, conversion and yield of the product was very low. The optimum activity was observed when the catalyst amount used was 0.08 g. Further increase in the catalyst content the selectivity to desired product was decreased. This was mainly due to over hydrolysis leading to the formation of benzoic acid. The hydration reaction required reasonable amount of active catalytic sites to yield maximum amount of product.

3.2.3 *Reusability of the Catalyst*

The main aspect of heterogeneous catalysts is their reusability. Therefore, the recycling potential of $PdMPAV_1/TiO_2$ catalyst was studied for this reaction. After completion of the reaction catalyst was separated by filtration and washed with ethyl acetate followed by drying at 120 °C. The results obtained by recycling the catalyst are shown in

Table 4 Effect of reaction temperature on hydration of nitrile

Temperature (°C)	Nitrile conversion (%)	Amide yield (%)	Acid yield (%)
80	20	20	–
100	53	51	2
120	70	68	2
140	100	97	3
160	100	85	15

Reaction conditions Benzonitrile: 1 mmol, *Water*: 3 ml, *Catalyst* 80 mg, *Reaction time* 6 h

Table 5 Effect of catalyst weight on hydration of nitrile

Catalyst weight	Nitrile conversion (%)	Amide yield (%)	Acid yield (%)
40	42	42	–
60	85	83	2
80	100	97	3
100	100	89	11

Reaction conditions Benzonitrile: 1 mmol, *Water* 3 ml, *Reaction temperature*: 140 °C, *Reaction time* 6 h

Table 6 Recycling results of 20 % $PdMPAV_1/TiO_2$ catalyst

No. of recycles	Nitrile conversion (%)	Amide yield (%)	Acid yield (%)
Fresh	100	97.0	3.0
1	98.2	95.2	3.0
2	96.4	94.8	1.6
3	95.8	94.5	1.3

Reaction conditions Nitrile: 1 mmol, *Water* 3 ml, *Catalyst* 80 mg, *Reaction temperature* 140 °C

Table 6. The amide yield after three cycles was almost same and these results suggest that the catalyst is reusable with consistent activity. The fresh and reused catalyst was characterized by ICP-AES in order to know the leaching of any Pd in the catalyst. The ICP-AES analysis results indicate that there was no considerable change in the Pd content in both fresh (2.14 %) and reused catalyst (2.08 %). This result confirms that there was no leaching of Pd and suggests the heterogeneous nature of the catalyst.

4 Conclusions

Titania supported palladium exchanged molybdovanadophosphoric acid catalysts were prepared with intact Keggin structure. $PdMPAV_1/TiO_2$ was an efficient catalyst for selective hydration of nitrile to amides under mild reaction conditions. The activity of the catalyst depends on V and Pd present in Keggin heteropoly molybdate. This catalyst is active for the selective hydration of nitriles containing various electron donating and electron withdrawing groups to the corresponding amides in high yields. The hydration of nitriles activity also depended on reaction temperature and amount of catalyst. The catalyst is easy to recover and reusable without any loss in activity. In the present catalyst Pd is exchanged with the protons of $MPAV_1$ and exists as Pd (II) and the redox properties of V might be helping in achieving the high activity towards the hydration of nitriles to amides.

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