Journal of Molecular Catalysis A: Chemical 356 (2012) 61–69

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Introduction of *N*-sulfonic acid poly(4-vinylpyridinum) chloride as an efficient and reusable catalyst for the chemoselective 1,1-diacetate protection and deprotection of aldehydes

Farhad Shirini*, Omid Goli Jolodar

Department of Chemistry, Faculty of Sciences, University of Guilan, Rasht, zip code 41335, Post Box 1914, Islamic Republic of Iran

ARTICLE INFO

Article history:
Received 9 October 2011
Received in revised form
29 December 2011
Accepted 1 January 2012
Available online 9 January 2012

Keywords:
Solid acids
N-sulfonic poly(4-vinylpyridinium) chloride
Poly(4-vinylpyridine)
1,1-Diacetates
Solvent-free reaction conditions

ABSTRACT

N-sulfonic acid poly(4-vinylpyridinium) chloride is easily prepared by the reaction of poly(4-vinylpyridine) with neat chlorosulfonic acid. This reagent can be used as an efficient catalyst for the preparation of 1,1-diacetates at room temperature and neat condition. Deprotection of the resulting 1,1-diacetates can also be achieved using the same catalyst in methanol. This new method consistently has the advantages of excellent yields and short reaction times. Further, the catalyst can be reused and recovered for several times.

1. Introduction

Solid acids have many advantages over liquid acids in organic catalysis. They do less harm to environment and have no corrosion or disposal of effluent problems. They are reusable and easy to be separated from liquid products. As economically and ecologically benign catalysts, their research and application have attracted much attention in chemistry and industry [1–6]. There are more than 100 industrial processes using over 103 solid acids at the end of last century [7]. The replacement of traditional homogeneous catalysts with solid acids becoming an inevitable trend.

However use of solid acid catalysts suffer from some disadvantages. Supported catalysts are in trouble with 'leaching' that leads to loss of activity [8]. Although zeolites have higher activity and their application is accompanied with the formation of undesired by-products due to the higher temperature needed for the reaction. On the other hand, ion exchange resins are limited in application because they are thermally unstable above 120 °C in the acid form [9]. Consequently, introduction of new solid acid catalysts that addresses these drawbacks is desirable.

In several industrially important processes a large amount of sulfuric acid is required because the water by-products lows their action down by diluting the acid. At the end of these processes, a large amount of "spent acid" is obtained which, in batch reactions, is usually neutralized and disposed of, while, in continuous processes, it has to be recycled by complex techniques. Moreover, sulfuric acid is corrosive and dangerous to transport and handle [10,11]. The above mentioned disadvantages for the application of concentrated sulfuric acid led to a substantial effort to develop viable alternatives, inter idea using some different types of new solid acids replacing sulfuric acid [12,13].

1,1-Diacetates have been used as suitable protecting groups for aldehydes because of their remarkable stability to neutral and basic conditions [14]. In addition, they can be converted into other useful functional groups by reaction with appropriate nucleophiles [15] and used as carbonyl surrogates for asymmetric synthesis [16]. 1,1-Diacetates, on the other hand, are ambident substrates containing two types of reactive carbon centers, the carbon atom of the protected aldehyde function and the carbonyl group in the ester moieties [17]. The relative acid stability of 1,1-diacetates is another interesting feature of such compounds in the field of *protection–deprotection* chemistry [18]. Usually, diacetates are prepared from the reaction of aldehydes and acetic anhydride under the catalysis of a variety of protic acids such as sulfuric, phosphoric, methanesulfonic and perchloric acids [19–21], solid acidic materials like Nafion-H [22], and Lewis acids such as iodine [23], trimethylchlorosilane and sodium iodide [24], zinc chloride [25], $FeCl_3$ [18,26], $FeSO_4$ [27], phosphorus trichloride

* Corresponding author. Tel.: +98 131 3233262; fax: +98 131 3233262.
E-mail address: shirini@guilan.ac.ir (F. Shirini).

1381-1169/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2012.01.002

[28], indium trichloride [29], $InBr_3$ [30], $Zr(HSO_4)_4$ [31], VSO_4 [32], cyanuric chloride [33], $Sc(OTf)_3$ [34], $Cu(OTf)_2$ [35], $Bi(OTf)_3$ [36], LiOTf [37] and $In(OTf)_3$ [38]. The use of montmorillonite clay [39], expansive graphite [40], zeolites [41], *N*-bromosuccinimide [42], ceric ammonium nitrate [43], NH_2SO_3H [44], WCl_6 [45], $AlPW_{12}O_{40}$ [46], $H_6P_2W_{18}O_{62}{\cdot}24H_2O$ [47], zirconium sulfophenyl phosphonate [48], $ZrCl_4$ [49], $LiBF_4$ [50], LiBr [51], $Zn(BF_4)_2$ [52], $Cu(BF4)_2{\cdot}xH2O$ [53], $Bi(NO_3)_3{\cdot}5H_2O$ [54], $LiClO_4$ [55] and (ZrO_2/SO_4^{2-}) [56] as catalysts has also been reported. Although, some of these methods have been used for the protection of aldehydes to the corresponding 1,1-diacetates with good to high yields, the majority of them suffer at least from one of disadvantages such as: prolonged reaction times, reaction under oxidizing conditions, using strong acids, low yields, harsh reaction conditions, difficulty in the preparation and moisture sensitivity of the catalysts, and high cost and high toxicity of the reagents. In addition, a few of the above mentioned catalysts are claimed to give protection as well as deprotection. Therefore, there is a scope to develop an alternative method for the protection of aldehydes as 1,1-diacetates and their deprotection.

2. Experimental

2.1. Materials

All chemicals were purchased from Merck or Fluka Chemical Companies. All yields refer to the isolated products. Products were characterized by their physical constants and comparison with authentic samples. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

2.2. Instrumentation

IR spectra were run on a Perkin–Elmer bio-spectrometer. The reaction conversions were measured by GC on a Shimadzu model GC-16A instrument. The ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) were run on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Microanalyses were performed on a Perkin–Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. X-ray diffraction (XRD) measurements were performed at room temperature on a Philips PW1830 generator X-ray powder diffractometer, using Ni filter and Cu-Kα radiation (λ = 1.542 Å). The scanning was over a range of 2θ = 10–70°. TGA and SEM analyses were performed on Polymer Laboratories TGA-PL thermal analysis instrument (heating rate of 10 °C/min) and on a Quanta 200 microscope (the samples were coated with gold powder on 682 Gatan Inc.), respectively. All measurements were conducted under nitrogen.

2.3. Catalyst preparation

Chlorosulfonic acid (1.5 mL, 22 mmol, as a >97% standard solution) was added to a suspension of powdered poly(4-vinylpyridine) (5.0 g) [poly(4-vinylpyridine) cross-linked with 2% DVB ~ 60 mesh, MW: 60,000; Fluka Chemica] in 10 mL dry CH_2Cl_2 over a period of 5 min. The mixture was stirred at room temperature for 6 h then dichloromethane was removed under reduced pressure. The solid powder was dried under vacuum at 65 °C for 48 h to afford NSPVPC (6.53 g) as a pale yellow powder.

2.4. Catalyst characterization

2.4.1. IR analysis

Fig. 1 presents the FTIR spectra of PVP and NSPVPC. As shown in this figure, presence of an extra sulfonic acid group on the pyridine nitrogen in the NSPVPC increased the number of vibrational modes and brought completely different FTIR spectrum [57–60]. In the case of NSPVPC, the broad band between 3250 and 3750 cm^{-1} that centered at 3419.56 cm^{-1} can be attributed to the —OH stretching of the $—SO_3H$ group. NSPVPC exhibited other characteristic absorption bands at 1234.36, 1168.78, 1027.99 and 856.34 cm^{-1}, which are assigned to the asymmetric and symmetric SO_2 stretching, S—OH bending and symmetric S—N stretching vibrations, respectively [61–63]. On the other hand, in the IR spectra of NSPVPC, the bands at 1554.52 and 1450.37 cm^{-1} are disappeared and a band at 1639.38 cm^{-1}, related to the sulfonated pyridine ion, is appeared. This observation may be ascribed to "some changes in aromatic ring" as a consequence of the sulfonated pyridine ion formation by the sulfonation reaction.

2.4.2. Powder X-ray diffraction

X-ray diffraction studies were performed for PVP and NSPVPC and the obtained diffractograms are displayed in Fig. 2. (It should be noted that PVP and NSPVPC were dried at 100 °C before analysis.) As shown in this figure, incorporation of $ClSO_3H$ leads to some changes in the diffractogram of PVP. In the diffractogram of PVP two broad reflexes centered at 2θ around 21° and 41.5° appeared. After modification of PVP by $ClSO_3H$ the position of the first peak (2θ around 23°) is changed and its intensity is reduced, and the broad peak at 2θ around 41° disappeared. These observations imply that the crystalline size of PVP is decreased after reaction with $ClSO_3H$.

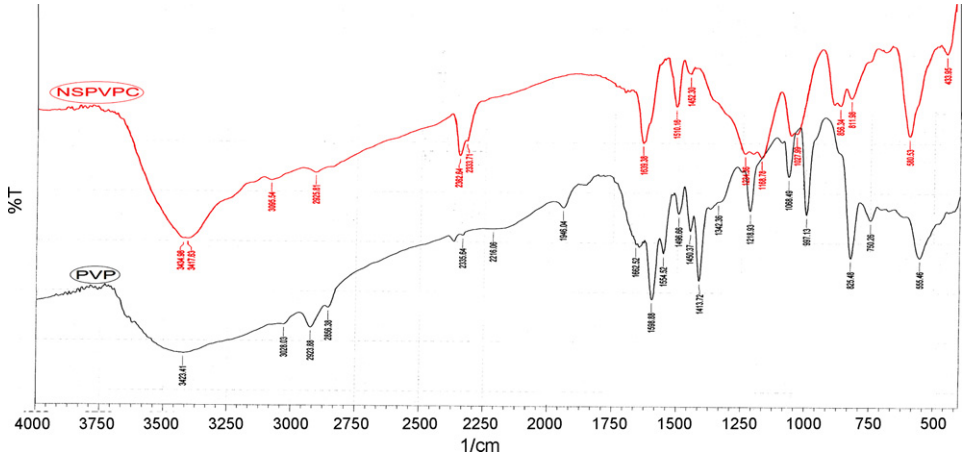


Fig. 1. FTIR spectra of PVP (down) and NSPVPC (up).

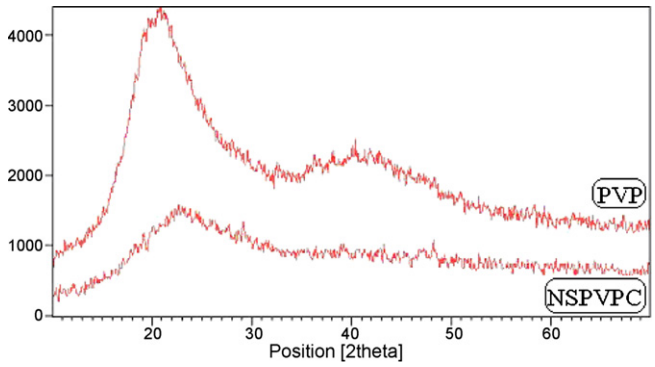


Fig. 2. XRD patterns of PVP (up) and NSPVPC (down).

2.4.3. Thermal analysis

Fig. 3 provides the TGA and DTGA (differential thermogravimetry) curves of poly(4-vinylpyridine) and catalyst under nitrogen. The TGA curve of PVP displayed a weight loss below 100 °C which is corresponding to the loss of the physically adsorbed water and bonded H_2O within the gallery of PVP. The polymer underwent complete degradation in the range of 325–413 °C. NSPVPC was degraded mainly by a four-stage process. The first weight loss which is observed in the range of 30–100 °C (T_{max} = 78.6), attributed to the loss of moisture contents. The second weight loss, started from 320 °C (320–340 °C, T_{max} = 325.6 °C) can be a result of the thermal decomposition of the pendant sulfonic groups. This is involved with a total overall weight loss of 77.8% of the catalyst. The sulfonated PVP moiety undergoes intermolecular bonding interactions in the solid state, leading to the formation of a rigid network structure which requires higher temperature for decomposition. This is confirmed by the third (490–510 °C, T_{max} = 500.0 °C) and fourth (590–680 °C, T_{max} = 610.0 °C) decomposition stages. The DTGA-TGA data show that the NSPVPC catalyst is stable to 285 °C.

2.4.4. SEM analysis

The SEM micrographs of PVP and NSPVPC showed that with chemical modification the primary structure of PVP was changed (Fig. 4). As seen in SEM images, the aggregation of particles was retarded by loaded $ClSO_3H$ groups. Both size reductions and retardation of aggregation resulted in increase in the surface area of the catalyst. This increased the catalytic activity of the catalyst in reaction. In the third SEM image with magnifying 30,000 the pendant sulfonic groups were observed on the sulfonated PVP polymer.

2.4.5. Acidity of the catalyst

The acid strength of NSPVPC was determined by the Hammett indicator method [64]. Using this method the catalyst was pretreated by being evacuated at 398 K for 2 h, then cooled to room temperature and allowed to contact with the vapor of the Hammett indicator. Anthraquinone (H_0 = −8.2), *p*-nitrotoluene (H_0 = −11.35) and 4-chloronitrobenzene (H_0 = −12.70) were used as indicators and benzene was used as the solvent (Table 1).

Acid contents of NSPVPC were determined by acid–base titration. In this method, a standard solution of NaOH was added to a

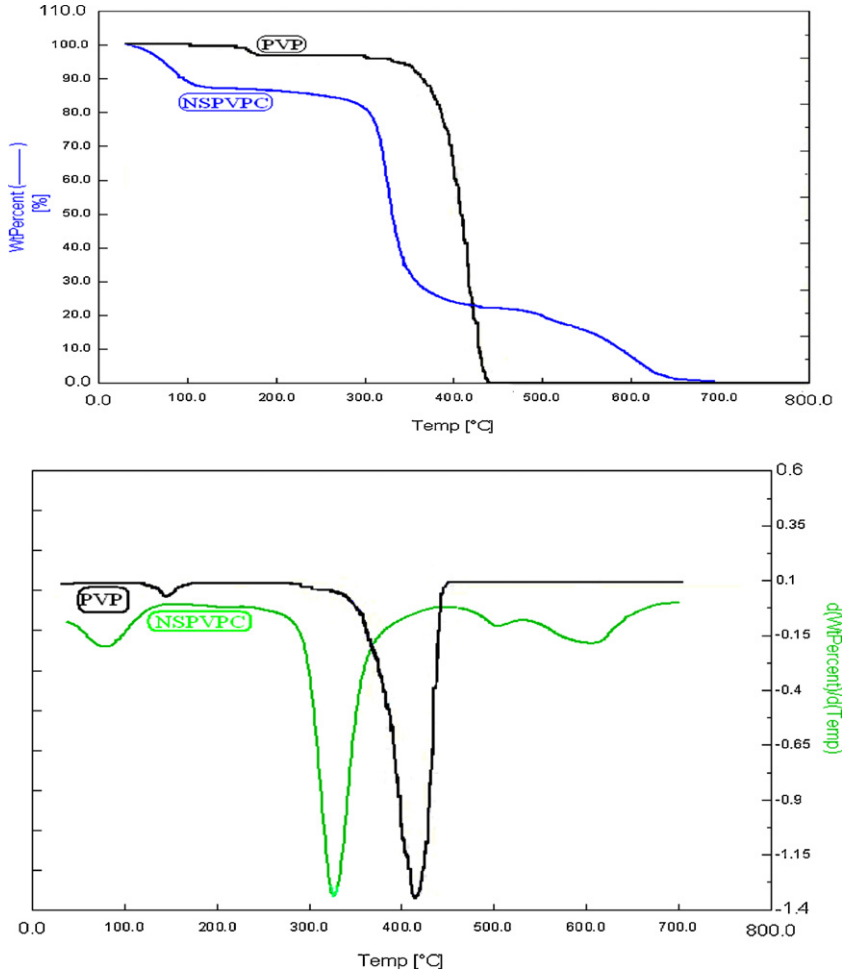


Fig. 3. TGA curves (up) for PVP and NSPVPC and DTA curves (down) for PVP and NSPVPC.

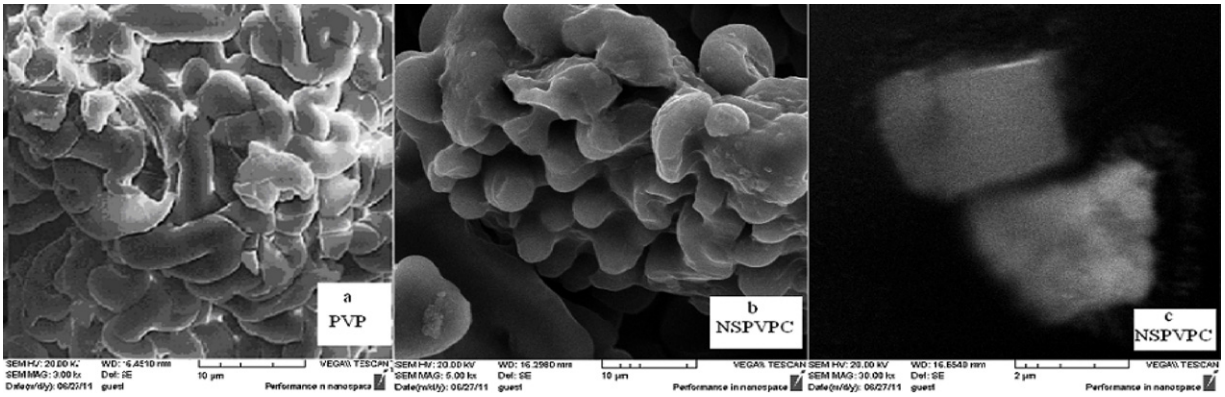


Fig. 4. SEM images of PVP (a) and NSPVPC (b and c).

suspension of the catalyst in H_2O–EtOH (1:1). Then the mixture was stirred for 2 h, and a 0.01% solution of phenolphthalein in EtOH was added to the suspension as an indicator. The solution was titrated with a standard HCl solution. The acid loading of NSPVPC was found to be in the range of 1.9 and 2.1 mmol g^{-1} by several parallel experiments.

2.5. General procedure for the preparation of 1,1-diacetates

A mixture of the substrate (1 mmol), acetic anhydride (2–6 mmol) and NSPVPC (10 mg) was stirred at room temperature for the time mentioned on Table 1. After completion of the reaction (monitored by TLC), ethyl acetate (3 × 5 mL) was added to the reaction mixture and the catalyst was recovered by filtration and washed with ethyl acetate (5 mL) and acetone (5 mL) and dried. The organic layer was successively washed with a saturated solution of $NaHCO_3$ (10 mL), brine (2 × 10 mL) and water (2 × 10 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel or recrystallization from cyclohexane gave the desired product in good to high yields. The spectral (IR, ^1H and ^{13}C NMR) data of new compounds are presented below:

A: Table 2, *entry 9*: white solid, m.p. 65–67 °C; IR (KBr): ν = 3650, 3500, 3010, 2910, 1760, 1610, 1590, 1490, 1430, 1370, 1245, 1200, 1160, 1060, 1010, 970, 940, 917, 790, 760, 700, 670, 600 cm^{-1}. ^1H NMR (300 MHz, DMSO-d6): δ 2.13 (s, 6H, 2× $COCH_3$), 3.38 (s, 3H, CH_3), 7.02 (d, 1H, J = 7.9 Hz, ArH), 7.50 (d, 1H, J = 7.9 Hz, ArH), 7.60–7.66 (m, 2H, J = 8.3, J = 7.7 Hz, ArH), 8.04 (s, 1H, $CH(OAc)_2$) ppm; ^{13}C NMR (75 MHz, DMSO-d6): δ 167.55, 147.74, 135.42, 133.82, 127.94, 125.12, 123.53, 87.83, 21.93, 21.00 ppm.

B: Table 2, *entry 22:* white solid, m.p. 96–98 °C; IR (KBr): ν = 3002, 2920, 1752, 1430, 1362, 1340, 1240, 1200, 1158, 1106, 1060, 1000, 942, 910, 808, 710, 680, 650, 600, 530, 510 cm^{-1}. ^1H NMR (300 MHz, DMSO-d6): δ 2.10 (s, 12H, 4× $COCH_3$), 7.52 (d, 1H, J = 7.8 Hz, ArH), 8.00 (d, 1H, J = 7.9 Hz, ArH), 8.17 (s, 1H, $CH(OAc)_2$), 8.43 (dd, 2H, J = 7.6, J = 8.2 Hz, ArH) ppm; ^{13}C NMR (75 MHz, DMSO-d6): δ 167.00, 141.19, 129.62, 128.82, 126.32, 102.33, 22.55 ppm.

C: Table 2, *entry 23:* white solid, m.p. 164–166 °C; IR (KBr): ν = 3020, 2910, 1758, 1430, 1378, 1338, 1200, 1118, 1060, 1008, 960, 940, 910, 852, 818, 604, 580, 540 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 6H, 2× $COCH_3$), 7.29 (d, 1H, J = 5.7 Hz, ArH), 7.41 (d, 1H, J = 5.1 Hz, ArH), 8.26 (s, 1H, $CH(OAc)_2$) ppm; ^{13}C NMR (75 MHz, DMSO): δ 167.00, 141.19, 129.82, 104.33, 21.55 ppm.

2.6. General procedure for deprotection of 1,1-diacetates

A mixture of the substrate (1 mmol) and NSPVPC (10 mg) in methanol (2 mL) was stirred at room temperature for the specified time in Table 2. After completion of the reaction (monitored by TLC), solvent was evaporated, the reaction mixture was triturated with Et_2O (20 mL) and filtered to separate the catalyst. The filtrate was washed successively with 10% aq. $NaHCO_3$ (3 × 10 mL) and water (10 mL) to remove excess of Ac_2O and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resultant product was passed through a short column of silica gel (*n*-hexane–EtOAc, 9:1) to afford the pure aldehyde.

Table 1
Acid strength of NSPVPC.

Catalysts	Indicator and H_0		
	Anthraquinone	*p*-Nitrotoluene	4-Chloronitrobenzene
NSPVPC	−8.2	−11.35	−12.70
	+	±	−

+, color changed clearly; −, color unchanged; ±, color changed unclearly.

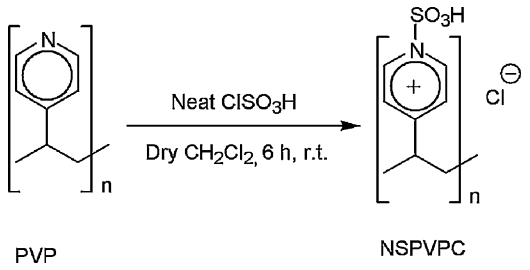
Table 2
The effect of different amounts of NSPVPC on the reaction of 4-chlorobenzaldehyde and acetic anhydride.[a]

Entry	Catalyst (mg)	Time (min)	Yield (%)[b]
1	5	60	80
2	10	5	93
3	15	4	93
4	20	4	91

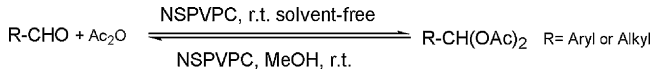
[a] Reaction conditions: 4-chlorobenzaldehyde (Table 5, entry 6) (1 mmol), acetic anhydride (2 mmol), room temperature, and solvent-free.
[b] Isolated yields.

3. Results and discussion

Very recently and in continuation of our ongoing research program on the development of new methods and reagents for the functional group transformations [65–68], we have reported the preparation of poly(4-vinylpyridinium) hydrogen sulfate salt and its application in the promotion of the acetylation of aldehydes using acetic anhydride [69]. Even though the activity of Ac_2O has been increased drastically in the presence of this reagent, this method suffers from disadvantages such as use of an excess amounts of sulfuric acid for the preparation of the catalyst, and non-reusability of the catalyst (in this method poly(4-vinylpyridine) is recovered at the end of the reaction and used for the preparation of the catalyst during a long reaction time). In view of this, we decided to overcome these limitations by the preparation of *N*-sulfonic acid (poly(4-vinylpyridinuim) chloride and conducting the acetylation of aldehydes in the presence of this catalyst. *N*-sulfonic acid poly(4-vinylpyridinium) chloride is prepared from the reaction of poly(4-vinylpyridine) [PVP], as a cheap and commercially



Scheme 1. Preparation of the catalyst.



Scheme 2. The protection and deprotection of aldehydes.

Table 3
The effect of different solvents on the reaction of 4-chlorobenzaldehyde with Ac_2O in the presence of NSPVPC.[a]

Entry	Solvent	Time (h)	Yield (%)[b]
1	Dichloromethane	1	25
2	Acetone	1	35
3	Methanol	1	40
4	Acetonitrile	1	44
5	Solvent-free	5 min	93

[a] Reaction conditions: 4-chlorobenzaldehyde (Table 5, entry 6) (1 mmol), acetic anhydride (2 mmol), NSPVPC (10 mg), room temperature, and solvent-free.
[b] Isolated yields.

available reagent, and neat chlorosulfonic acid at room temperature. The reaction is easy and clean, and needs no special work-up procedure (Scheme 1).

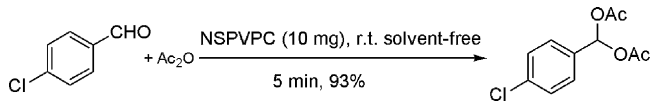
The structure of NSPVPC assured us to accept that this reagent can act as an efficient catalyst in reactions that need acidic reagents to speed up. Our investigations clarified that this prediction is correct and the conversion of aldehydes to their corresponding 1,1-diacetatesis efficiently promoted in the presence of NSPVPC (Scheme 2).

In order to optimize the reaction conditions, we conducted the acetylation of 4-chlorobenzaldehyde (1 mmol) with acetic anhydride (2 mmol) using different amounts of NSPVPC in various solvents and in the absence of solvent at different temperatures. The results are shown in Tables 2–4. On the basis of these Tables, the best result can be obtained under the conditions shown in Scheme 3. To illustrate the efficiency of NSPVPC in these reactions, protection of 4-chlorobenzaldehyde was also carried out in the absence of the catalyst and in the presence of poly(4-vinylpyridine).

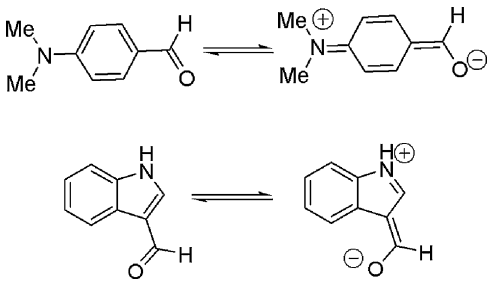
Table 4
The effect of temperature on the reaction of 4-chlorobenzaldehyde with Ac_2O in the presence of NSPVPC and in the absence of solvent.[a]

Entry	Temperature (°C)	Time (min)	Yield (%)[b]
1	25	5	93
2	50	4	96
3	60	4	96

[a] Reaction conditions: 4-chlorobenzaldehyde (Table 5, entry 6) (1 mmol), acetic anhydride (2 mmol), NSPVPC (10 mg), and solvent-free.
[b] Isolated yields.



Scheme 3. Acetylation of 4-chlorobenzaldehyde.



Scheme 4. Inactivity of 4-dimethylamino benzaldehyde and indole-3-carbaldehyde against 1,1-diacetate protection.

The reactions were not completed after 6 h. Obviously the sulfontion of PVP is important for the reaction.

After optimization of the reaction conditions various aromatic, aliphatic and heterocyclic aldehydes were subjected to acylation with Ac_2O under the selected conditions. The results were summarized in Table 5. Obviously, the present method is quite general and found to be very effective for the acylation of the above mentioned aldehydes. The reaction conditions were mild enough not to induce any damage to moieties like methoxy group (Table 5, entries 11 and 12) which often undergo cleavage in the presence of strong acids or certain Lewis acids. Aromatic aldehydes bearing electron withdrawing substituents such as nitrobenzaldehydes (Table 5, entries 2–4) also gave good results under the presented conditions. Mention must be made here that the hydroxyl groups were also protected as acetates in aromatic aldehydes containing this functionality (Table 5, entries 13 and 14). In addition, the hindered aldehydes (Table 5, entries 2, 5, 9, 11, 13 and 21) gave good yields of the requested products. Furfural, as an acid sensitive substrate (Table 5, entry 18) was also diacetylated by this procedure, giving the corresponding 1,1-diacetate in good yield without the formation of any side products, which are normally observed under strongly acidic conditions. Moreover, the protocol could also equally work with aliphatic aldehydes (Table 5, entries 15–17). In our experiments, cinnamaldehyde, as an α,β-unsaturated aldehyde (Table 5, entry 19), was diacetylated smoothly without the isomerization of double bond.

Attempted acetylation of benzenedicarbaldehydes, gave the tetracetylated products in good to moderate yields for phthaldialdehyde, iso-phthaldialdehyde and tere-phthaldialdehyde. The tetracylated products were obtained in 86, 88 and 97% yields, respectively (Table 5, entries 21–23).

In accordance with the fact reported in the literature [39d], 4-dimethylamino benzaldehyde and indole-3-carbaldehyde (Table 1, entries 27 and 28) failed to give the corresponding 1,1-diacetates and the starting materials were quantitatively recovered after prolonged reaction times (Table 5, entries 27 and 28). This result may be due to the strong electron donation of dimethylamino and NH groups. Also, a degree of tautomerization may occur with formation of a quininoid structure as shown in Scheme 4, which decreases the reactivity of the aldehydic carbonyl group [44].

Under the selected conditions acylation of ketones was not successful and the starting material was recovered unchanged (Table 5, entry 20).

Selectivity of a method determines the importance of its application in organic reactions. Therefore, the chemoselectivity of this method was also investigated and the results were reported in Table 5 (entries 20 and 26).

We have also found that NSPVPC can be easily recovered by filtration, washing with EtOAc and acetone and drying at 100 °C. The reusability of this reagent is exemplified by acylation of 4-chlorobenzaldehyde in the presence of recycled reagent, which gave the requested product in 93, 92, 92 and 90% yields after four

Table 5
Acylation of aldehydes and deprotection of acylals in the presence of NSPVPC.

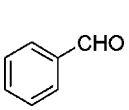
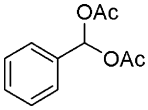
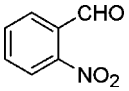
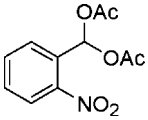
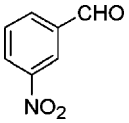
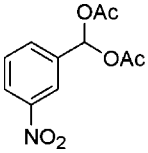
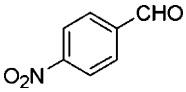
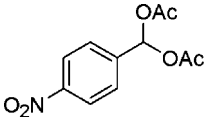
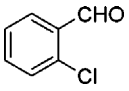
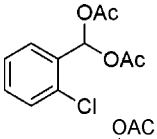
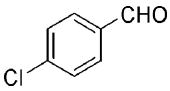
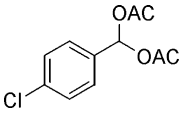
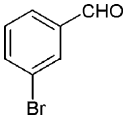
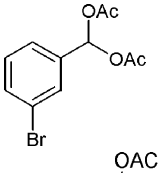
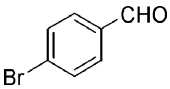
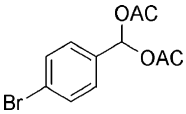
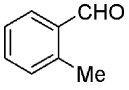
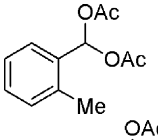
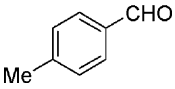
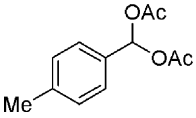
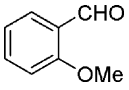
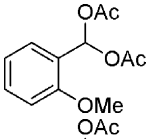
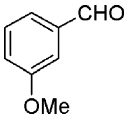
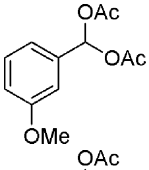
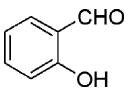
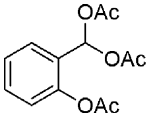
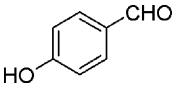
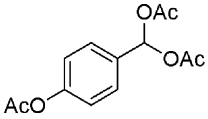
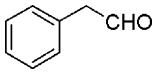
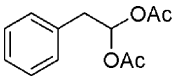
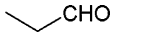
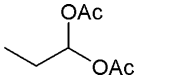
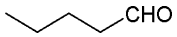
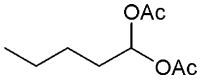
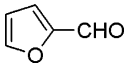
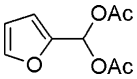
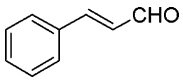
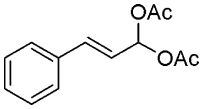
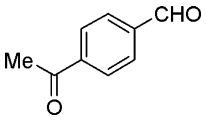
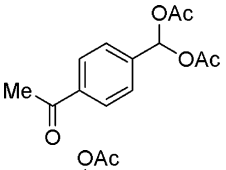
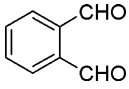
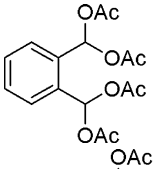
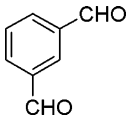
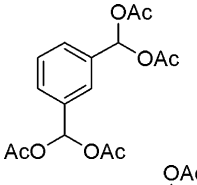
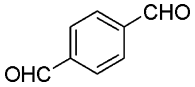
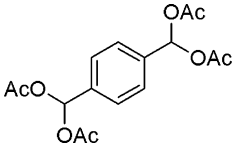
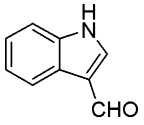
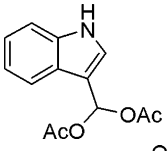
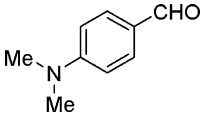
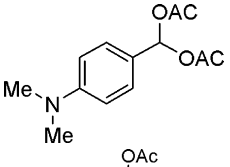
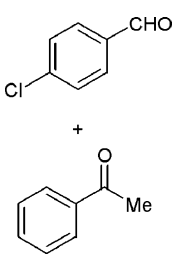
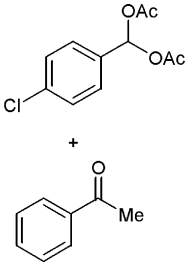
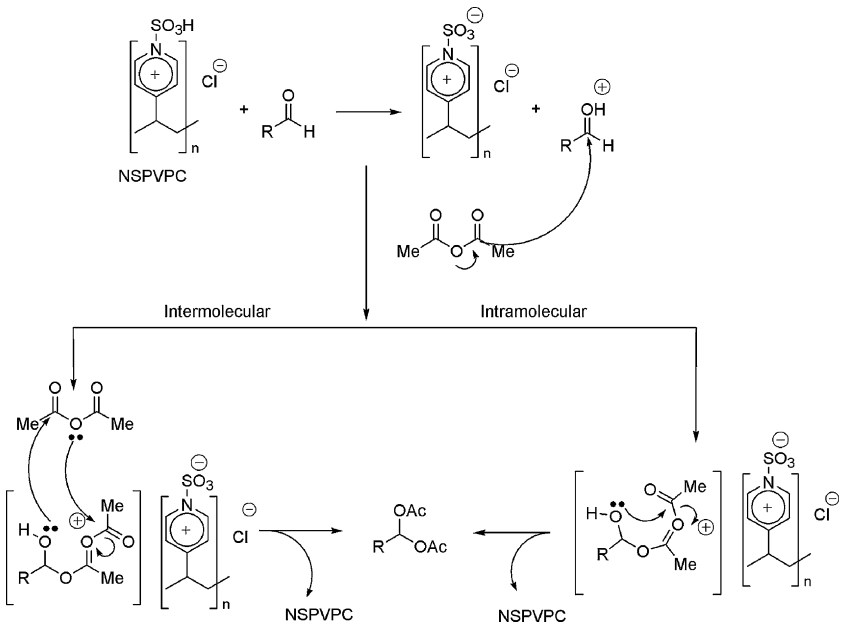
Entry	Substrate	Product	Protection		Deprotection	
			Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]
1			6	92	32	88
2			5	90	35	85
3			15	92	40	88
4			10	98	35	85
5			12	88	45	83
6			5	93	25	82
7			7	92	35	88
8			5	90	25	87
9			15	85	55	89
10			2	94	5	92
11			15	88	55	82
12			7	91	32	89
13			5	88[b]	45	86
14			10	88[b]	35	85

Table 5 (*Continued*)

Entry	Substrate	Product	Protection		Deprotection	
			Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]
15			12	85	32	84
16			10	92	25	90
17			15	89	40	88
18			12	86	45	88
19			5	93	12	92
20			10	92	35	90
21			10	86[c]	35	82
22			5	88[c]	35	87
23			5	97[c]	35	87
24			6 h	–	–	–
25			6 h	–	–	–
26			1 h	93 97	–	–

[a] Yields refer to pure isolated products and the products were characterized by m.p., IR, ^{1}H NMR.
[b] 4 equiv. acetic anhydride was used.
[c] 6 equiv. acetic anhydride was used.



Scheme 5. Proposed mechanism of the acetylation of aldehydes in the presence of NSPVPC.

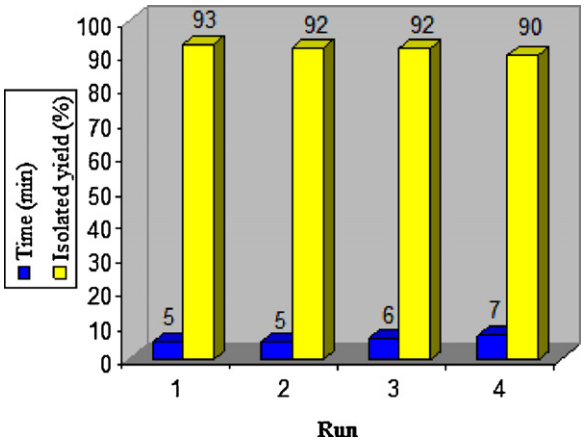


Fig. 5. Reusability of NSPVPC.

runs. The average time for four consecutive runs was 5.7 min and 100% conversion for all, which clearly demonstrates the practical recyclability of this catalyst (Fig. 5).

The possible mechanism for the acylation of various aldehydes in the presence of NSPVPC as a promoter is shown in Scheme 5. On the basis of this mechanism, NSPVPC catalyzes the reaction by the electrophilic activation of the aldehyde to form a zwitterionic species, making the carbonyl group susceptible to nucleophilic attack by Ac_2O. Successive intermolecular or intramolecular transfer of the second acetate group results in the formation of 1,1-diacetate derivatives and regenerates NSPVPC in the reaction.

We have also found that the conversion of 1,1-diacetates to their corresponding aldehydes can be easily catalyzed in the presence of NSPVPC in methanol. All reactions were performed at room temperature in good to high yields (Scheme 2 and Table 5).

4. Conclusion

In conclusion, we have developed a simple, efficient and chemoselective protocol for the acylation of various aldehydes and deprotection of the obtained 1,1-diacetates using NSPVPC as a novel heterogeneous catalyst. The protocol is highly chemoselective offering potential in different applications. The methodology also has several other advantages such as: high reaction rates and excellent yields, no side reactions, ease of preparation and handling of the catalyst, cost efficiency and effective reusability of the catalyst, use of inexpensive catalyst with lower loading and simple experimental procedure. Further work to explore this novel catalyst in other organic transformations is in progress.

Acknowledgment

We are thankful to the University of Guilan Research Council for the partial support of this work.

References

[1] D. Choudhary, S. Paul, R. Gupta, J.H. Clark, Green Chem. 8 (2006) 479–482.
[2] A. Ghorbani-Choghamarani, S. Sardari, J. Sulfur. Chem. 32 (2011) 63–69.
[3] R. Dalpozzo, G. Bartoli, L. Sambri, P. Melchiorre, Chem. Rev. 110 (2010) 3501–3551.
[4] A.K. Chakraborti, B. Singh, S.V. Chankeshwara, A.R. Patel, J. Org. Chem. 74 (2009) 5967–5974.
[5] G. Sharma, R. Kumar, K.C. Asit, Tetrahedron Lett. 49 (2008) 4272–4275.
[6] R. Kumar, D. Kumar, K.C. Asit, Synthesis (2007) 299–303.
[7] K. Tanabe, W.F. Hölderich, Appl. Catal. A 181 (1999) 399–434.
[8] D.J. Cole-Hamilton, Science 299 (2003) 1702–1706.
[9] A. Chakrabarti, M.M. Sharma, React. Polym. 20 (1993) 1–45.
[10] J.M. Riego, Z. Sedin, J.M. Zaldivar, N.C. Marziano, C. Tortato, Tetrahedron Lett. 37 (1996) 513–516.
[11] N.J. Turro, Tetrahedron 43 (1987) 1589–1616.
[12] M.A. Zolfigol, G. Chehardoli, M. Dehghanian, K. Niknam, F. Shirini, A. Khoramabadi-Zad, J. Chin. Chem. Soc. 55 (2008) 885–889.
[13] G. Chehardoli, M.A. Zolfigol, T. Faal-Rastegar, S. Mallakpour, A. Ghorbani-Choghamaranid, J. Chem. Sci. 121 (2009) 441–447.
[14] (a) T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, 3rd ed., John Wiley and Sons, New York, 1999, pp. 306–307;
(b) M.J. Gregory, J. Chem. Soc. B (1970) 1201–1207.
[15] F.R. Heerden, J.J. Huyser, D.B.G. Williams, C.W. Holzapfer, Tetrahedron Lett. 39 (1998) 5281–5284.
[16] B.M. Trost, C. Lee, J. Am. Chem. Soc. 123 (2001) 12191–12201.
[17] M. Sandberg, L.K. Sydnes, Tetrahedron Lett. 39 (1998) 6361–6364.
[18] K.S. Kochhar, B.S. Bal, R.P. Deshpande, S.N. Rajadhyaksha, H.W. Pinnick, J. Org. Chem. 48 (1983) 1765–1767.
[19] (a) M. Tomita, T. Kikuchi, K. Bessho, T. Hori, Y. Inubushi, Chem. Pharm. Bull. 11 (1963) 1484–1490;
(b) R. Wegscheider, E. Spath, Monatsh. Chem. 30 (1909) 825–869.
[20] (a) W. Davey, J.R. Gwilt, J. Chem. Soc. (1957) 1008–1014;
(b) F. Freeman, E.M. Karchetski, J. Chem. Eng. Data 22 (1977) 355–357.

[21] J.A. Marshall, P.G.M. Wuts, J. Org. Chem. 42 (1977) 1794–1798.
[22] (a) G.A. Olah, A.K. Mehrotra, Synthesis (1982) 962–967;
(b) T.S. Jin, G.Y. Du, Z.H. Zhang, T.S. Li, Synth. Commun. 27 (1997) 2261–2262;
(c) T.S. Li, Z.H. Zhang, C.G. Fu, Tetrahedron Lett. 38 (1997) 3285–3288;
(d) B.M. Reddy, P.M. Sreekanth, A. Kahn, Synth. Commun. 34 (2004) 1839–1845.
[23] (a) N. Deka, D.J. Kalita, R. Borah, J.C. Sarma, J. Org. Chem. 62 (1997) 1563–1564;
(b) J.M. Thomas, Angew. Chem. Int. Ed. Engl. 27 (1998) 1673–1691.
[24] N. Daka, R. Borah, D.J. Kalita, J.C. Sarma, J. Chem. Res. (1998) 94–95.
[25] I. Scriabire, Bull. Soc. Chim. Fr. (1961) 1194–1198.
[26] (a) B.M. Trost, C.B. Lee, J.M. Weiss, J. Am. Chem. Soc. 117 (1995) 7247–7248;
(b) C.D. Wang, M.H. Li, Synth. Commun. 32 (2002) 3469–3473.
[27] (a) T.S. Jin, G.Y. Du, T.S. Li, Indian J. Chem. B 37 (1998) 939–940;
(b) X.Y. Zhang, L.J. Li, G.S. Zhang, Green Chem. 5 (2003) 546–548.
[28] J.K. Michie, J.A. Miller, Synthesis (1981) 824–825.
[29] J.S. Yadav, B.V.S. Reddy, C. Srinivas, Synth. Commun. 32 (2002) 1175–1180.
[30] L. Yin, Z.-H. Zhang, Y.-M. Wang, M.-L. Pang, Synlett (2004) 1727–1730.
[31] B.F. Mirjalili, M.A. Zolfigol, A. Bamoniric, N. Sheikhan, J. Chin. Chem. Soc. 53 (2006) 955–959.
[32] M.M. Heravi, K. Bakhtiari, T. Benmorad, H.A. Oskooie, J. Chin. Chem. Soc. 54 (2007) 273–275.
[33] B.P. Bandgar, N.S. Joshi, V.T. Kamble, J. Chin. Chem. Soc. 54 (2007) 489–492.
[34] V.K. Aggarwal, S. Fonquerna, G.P. Vennall, Synlett (1998) 849–852.
[35] K.L. Chandra, P. Saravanan, V.K. Singh, Synlett (2000) 359–360.
[36] M.D. Carrigan, K.J. Eash, M.C. Oswald, R.S. Mohan, Tetrahedron Lett. 42 (2001) 8133–8135.
[37] B. Karimi, J. Maleki, J. Org. Chem. 68 (2003) 4951–4954.
[38] R. Ghosh, S. Maiti, A. Chakraborty, R. Halder, J. Mol. Catal. A: Chem. 215 (2004) 49–53.
[39] (a) M.V. Joshi, C.S. Narasimhan, J. Catal. 141 (1993) 308–310;
(b) D. Karmakar, D. Prajapati, J.S. Sandhu, J. Chem. Res. (1998) 382–383;
(c) Z.H. Zhang, T.S. Li, C.G. Fu, J. Chem. Res. (1997) 174–175;
(d) T.S. Li, Z.H. Zhang, Y.J. Gao, Synth. Commun. 28 (1998) 4665–4671.
[40] T.S. Jin, Y.R. Ma, Z.H. Zhang, T.S. Li, Synth. Commun. 27 (1997) 3379–3383.
[41] (a) P. Kumar, V.R. Hedge, T.P. Kumar, Tetrahedron Lett. (1995) 601–602;
(b) C. Pereira, B. Gigante, M.J. Marcelocurto, H. Carreyre, G. Perot, M. Guisnet, Synthesis (1995) 1077–1078;
(c) R. Ballini, M. Bordoni, G. Bosica, R. Maggi, G. Sartori, Tetrahedron Lett. 39 (1998) 7587–7590.
[42] B. Karimi, H. Seradj, G.R. Ebrahimian, Synlett (2000) 623–624.
[43] S.C. Roy, B. Banerjee, Synlett (2002) 1677–1678.
[44] T.S. Jin, G. Sun, Y.W. Li, T.S. Li, Green Chem. 4 (2002) 255–256.
[45] B. Karimi, G.R. Ebrahimian, H. Seradj, Synth. Commun. 32 (2002) 669–673.
[46] H. Firouzabadi, N. Iranpoor, F. Nowrouzi, K. Amani, Tetrahedron Lett. 44 (2003) 3951–3954.
[47] G.P. Romanelli, H.J. Thomas, G.T. Baronetti, J.C. Autino, Tetrahedron Lett. 44 (2003) 1301–1303.
[48] M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, M. Nocchetti, Tetrahedron Lett. 43 (2002) 2709–2711.
[49] G. Smitha, C.S. Reddy, Tetrahedron 59 (2003) 9571–9576.
[50] (a) N. Sumida, K. Nishioka, T. Sato, Synlett (2001) 1921–1922;
(b) J.S. Yadav, B.V.S. Reddy, C. Venugopal, T. Ramalingam, Synlett (2002) 604–606.
[51] H.M.S. Kumar, B.V.S. Reddy, P.T. Reddy, J.S. Yadav, J. Chem. Res. (2000) 86–87.
[52] B.C. Rana, J. Dutta, A. Das, Chem. Lett. (2003) 366–367.
[53] A.K. Chakraborti, R. Thilagavathi, R. Kumar, Synthesis (2004) 831–833.
[54] D.H. Aggen, J.N. Arnold, P.D. Hayes, N.J. Smoter, R.S. Mohan, Tetrahedron Lett. 60 (2004) 3675–3679.
[55] A. Ziyaei, N. Azizi, M.R. Saidi, J. Mol. Catal. A: Chem. 238 (2005) 138–141.
[56] G.E. Negron, L.N. Palacios, D. Angeles, L. Lomas, R. Gavino, J. Braz, Chem. Soc. 16 (3A) (2005) 490–494.
[57] B. Grzyb, J. Machnikowski, J.V. Weber, J. Anal. Appl. Pyrolysis 72 (2004) 121–130.
[58] M.P. McCurdie, L.A. Belfiore, Polymer 40 (1999) 2889–2902.
[59] L.N. Karklin, M.W. Kluev, A.D. Pomogailo, Kin. Kat. 24 (1983) 408–410.
[60] N.S. Gill, R.H. Nuttall, D.E. Scaife, D.W.A. Sharp, J. Inorg. Chem. 18 (1961) 79–87.
[61] N.P.G. Roeges, A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures, Wiley, New York, 1994.
[62] D. Philip, A. Eapen, G. Aruldhas, J. Solid State Chem. 116 (1995) 217–223.
[63] S.M. Chackalackal, F.E. Stafford, J. Am. Chem. Soc. 88 (21) (1966) 4815–4819.
[64] Y.X. Jiang, X.M. Chen, Y.F. Mo, Z.F. Tong, J. Mol. Catal. A: Chem. 213 (2004) 231–234.
[65] P. Salehi, M.A. Zolfigol, F. Shirini, M. Baghbanzadeh, Curr. Org. Chem. 10 (2006) 2171–2181.
[66] F. Shirini, M.A. Zolfigol, P. Salehi, M. Abedini, Curr. Org. Chem. 12 (2008) 183–202.
[67] E. Kolvari, A. Ghorbani-Choghamarani, P. Salehi, F. Shirini, M.A. Zolfigol, J. Iran. Chem. Soc. 2 (2007) 126–174.
[68] F. Shirini, M. Mamaghani, S.V. Atghia, Catal. Commun. 12 (2011) 1088–1094.
[69] N. Ghaffari Khaligh, F. Shirini, J. Mol. Catal. A: Chem. 348 (2011) 20–29.