available at www.sciencedirect.com

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

Article

***N*-Sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate as a novel, efficient, and reusable solid acid catalyst for acylation under solvent-free conditions**

Nader Ghaffari Khaligh^{a,b,*}, Parisa Ghods Ghasem-Abadi^{c,d}^a Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, 47651-61964, Iran^b House Research of Professor Reza, Education Guilan, Rasht, District 1, 41569-17139, Iran^c Department of Chemistry, College of Science, University of Mohaghegh-Ardabili, Ardabil, Iran^d Department of Chemistry, Memorial University, St. John's, NL, A1B 3X7, Canada

ARTICLE INFO

Article history:

Received 1 January 2014

Accepted 10 February 2014

Published 20 July 2014

Keywords:

Solid acid

Functionalized poly(4-vinylpyridine)

Anion effect

Acetylation

1,1-Diacetylation

Solvent-free conditions

ABSTRACT

N-Sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate has been developed as a recyclable solid acid catalyst for the acetylation of alcohols, phenols, thiols, and amines, as well as the 1,1-diacetylation of aldehydes under solvent-free conditions at room temperature. The acetylated products were formed in good to excellent yields over short reaction times, and the catalyst could be readily recovered by filtration and used several times without any discernible loss in activity. The hydrogen sulfate anion of the catalytic system was found to play a critical role in enhancing the reaction time and yield of the acetylation reaction.

© 2014, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Various different solid acids have been prepared during the course of the last two decades as replacements for mineral liquid acids such as sulfuric acid and hydrochloric acid in organic synthesis. Solid acids have attracted considerable attention from organic chemists because they exhibit many advantages over liquid mineral acids, in that they can be readily recovered and reused, show enhanced levels of selectivity and reactivity, allow for facile product isolation, can be less harmful to the environment, present no corrosion or effluent disposal issues, and can be readily used in continuous and micro-reactor reaction systems [1–8]. The leaching of the catalytic species from solid catalysts, however, can lead to a decrease in their

catalytic activity [9]. The introduction of Brønsted-acidic functional groups, such as SO₃H and SO₄H moieties, can enhance the acidity and polarity properties of solid acid catalysts and allow them to be used under solvent-free conditions. There has recently been an increase in the amount of research being reported in the literature directed towards the development of environmentally friendly solid acid catalysts containing halogen-free anions.

Organic processes for the construction of synthetic intermediates or target materials are generally conducted in the presence of toxic and volatile solvents, which can have an adverse impact on the environment. For this reason, there has been an increase in research directed towards the development of organic reactions that can be conducted in environmentally

* Corresponding author. Tel: +98-2166431738; Fax: +98-2166934046; E-mail: ngkhaligh@guilan.ac.ir, ngkhaligh@gmail.com

DOI: 10.1016/S1872-2067(14)60052-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 7, July 2014

friendly media. Effective techniques for minimizing the cost and environmental impact of chemical transformations can also lead to improvements in the health and safety issues associated with the use of traditional organic solvents in reactions, and research directed towards the use of non-toxic solvents or solvent-free conditions is becoming increasingly important [10–13].

Traditional organic synthesis often requires the use of protecting groups, and the acetylation of alcohols, phenols, thiols, and amines represents a standard protecting group strategy in organic synthesis [14–17]. For this reason, a broad range of methods have been developed for the acetylation of these functional groups using a variety of different Brønsted and Lewis acid catalysts [14–31].

The 1,1-diacetylation of aldehydes has been used as a standard protection group strategy for the protection of aldehydes because of the remarkable stability of the 1,1-diacetylated products to neutral and basic conditions [32]. 1,1-Diacetates (acylal) have been used in a variety of different applications in both academic and industrial chemistry [33–39]. Acyals themselves are generally formed by the reaction of an aldehyde substrate with acetic anhydride in the presence of a suitable catalyst, and various different catalysts have been developed specifically for the activation of acetic anhydride in this context [40–47].

Unfortunately, however, the acetylation and 1,1-diacetylation methods described above suffer from several disadvantages, such as their requirement for high temperature reaction conditions, as well as expensive, hygroscopic and thermally unstable catalysts, and the use of halogenated solvents and strong acids. Furthermore, these methods generally require long reaction times and lead to the formation of by-products, as well as providing low yields of the desired products. With all of these issues in mind, there is clearly an urgent need for the development of new reagents and methods to overcome these limitations.

We recently became interested in the preparation of solid acid catalysts based on poly(4-vinylpyridine) [30,48–50]. As part of ongoing work in this area, we have developed a new solid acid functionalized poly(4-vinylpyridine) (SAFPVP) analogue known as *N*-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate (NSPVPHS) and investigated the use of this material as a new solid acid catalyst for the acetylation of alcohols, phenols, thiols, and amines at room temperature under solvent-free conditions (Schemes 1 and 2). The catalyst could be readily separated and reused several times without any significant loss in its catalytic activity.

Scheme 1. Preparation of *N*-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate (NSPVPHS).

Scheme 2. Acetylation reactions in the presence of NSPVPHS at room temperature under solvent-free conditions.

2. Experimental

2.1. Materials

Unless specified, all of the chemicals used in the current study were purchased as the analytical grade from Merck, Aldrich, and Fluka Chemical Companies and used without further purification. The reaction products were characterized on the basis of their physical properties and by comparison with authentic samples. The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel plates (SIL G/UV 254 plates).

2.2. Instrumentation

The purities of the products were determined by GC-MS on an Agilent 6890 GC-MS system (USA) under ionization conditions of 70 eV. Fourier transform infrared spectra (FT-IR) were recorded on a Perkin Elmer 781 spectrophotometer (USA) in the range of 4000–400 cm^{-1} . The solid samples were analyzed as KBr disks, whereas the liquid samples were analyzed neat. ^1H NMR spectra were recorded on 400 and 300 MHz Bruker Avance instruments (USA) using deuterated chloroform as the solvent. ^{13}C NMR spectra were collected on Bruker Avance 100 and 75 MHz instruments. All of the chemical shift data were quoted relative to TMS, which was used as an internal reference standard. Microanalyses were performed on a Vario EL III CHNOS Elemental Analyzer (Germany). Melting points were recorded on a Büchi B-545 apparatus (Germany) in open capillary tubes. The thermal stability characteristics of the catalyst were evaluated by thermal gravimetric analysis (TGA) using a Shimadzu Thermo-gravimetric Analyzer-50 (Japan) in a temperature range of 20–700 $^{\circ}\text{C}$. All of the experimental measurements were conducted under nitrogen.

2.3. Procedure for the preparation of the solid acid catalyst

Chlorosulfonic acid (2.0 mL, 30 mmol) was added in a drop-wise manner to a suspension of powdered poly(4-vinylpyridine) (5.0 g; cross-linked with 2% divinylbenzene (DVB), ~60 mesh, MW 60000; Fluka Chemicals) in dry CH_2Cl_2 (10 mL) at 0 $^{\circ}\text{C}$ over a period of 5 min, and the resulting mixture was stirred at room temperature for 6 h. The CH_2Cl_2 was then decanted from the mixture, and the residue was washed with dry CH_2Cl_2 (3 $\times$ 10 mL) before being dried under vacuum to afford *N*-sulfonic acid poly(4-vinylpyridinium) chloride (NSPVPC, 7.29

g) as a pale yellow powder [48]. Sulfuric acid (1.6 mL, 30 mmol, 100%) was then added in a drop-wise manner to a suspension of NSPVPC (7.29 g) in dry CH_2Cl_2 (10 mL) over a period of 3 min at room temperature, and the resulting mixture was vibrated and stirred for 2 h at 50 °C under a continuous flow of nitrogen to remove the hydrogen chloride gas. The mixture was then heated at the same temperature under high vacuum for 30 min to give *N*-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate (NSPVPHS, 8.52 g) as a yellow powder.

2.4. General procedure for the acetylation and 1,1-diacetylation reactions

A mixture of the substrate (1 mmol), acetic anhydride (2–3 mmol), and NSPVPHS (5 mg) was stirred at room temperature under solvent-free conditions. Upon completion of the reaction, as determined by TLC, the mixture was diluted with ethyl acetate (15 mL). The solid acid catalyst was then collected by filtration and washed sequentially with ethyl acetate (5 mL) and acetone (5 mL) before being dried under vacuum at 40 °C. The recovered catalyst could then be used for the same reaction. The organic layer of the filtrate was washed sequentially with a saturated solution of NaHCO_3 (5 mL), brine (10 mL), and water (20 mL) and then dried over MgSO_4 . The solvent was then removed under vacuum to give a residue, which was purified by column chromatography over silica gel to give the desired product in good to high yield.

2.5. Spectral data of selected products

The structure of several selected products is shown in Scheme 3.

A12. FT-IR (neat) ν_{max} = 2952, 1716, 1450, 1365, 1248, 1153 cm^{-1} ; $[\alpha]_{\text{D}}^{25}$ = +41.5°, neat, 96% e.e.; ^1H NMR (400 MHz, CDCl_3) δ = 0.82 (s, 3H), 0.88 (s, 3H), 0.92 (s, 3H), 1.26 (m, 4H), 1.72 (m, 2H), 2.08 (s, 3H), 2.36 (m, 1H), 4.89 (d, J = 9.8 Hz, 1H); ^{13}C (100 MHz, CDCl_3) δ = 13.4, 18.7, 19.6, 21.2, 27.0, 28.0, 36.7, 44.8, 47.7, 48.6, 79.8, 171.3.

A16. FT-IR (neat) ν_{max} = 2953, 1770, 1476, 1374, 1186, 1039, 907, 815 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 2.31 (s, 6H), 2.31 (s, 3H), 7.14 (d, J = 8.0 Hz, 2H), 7.28 (dd, J = 8.8, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ = 20.2, 20.7, 120.7, 125.9, 134.7, 143.6, 167.0, 167.9.

A19. FT-IR (neat) ν_{max} = 3070, 3075, 3025, 1765, 1679, 1577, 1492, 1445, 1370, 1337, 1238, 1214, 1194, 1091, 954,

821, 747, 705, 689, 612 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 2.33 (s, 3H), 2.45 (s, 3H), 7.24 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ = 20.7, 26.2, 120.7, 125.9, 130.2, 134.7, 143.5, 167.0, 171.9.

A20. FT-IR (neat) ν_{max} = 3121, 2974, 2848, 2570, 1696, 1592, 1416, 1218, 1158, 1070, 1012, 927, 808, 741, 596 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 2.36 (s, 3H), 4.29 (s, 2H), 6.01 (d, J = 2.8 Hz, 1H), 6.23 (dd, J = 2.8 and 0.8 Hz, 1H), 7.22 (d, J = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ = 22.4, 29.7, 107.2, 110.7, 141.7, 152.7, 194.3.

A25. FT-IR (neat) ν_{max} = 3295, 3051, 3018, 1635, 1554, 1505, 1341, 1284, 1021, 775, 726 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 2.30 (s, 3H), 7.45–7.87 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ = 22.8, 118.5, 122.3, 122.8, 125.2, 126.1, 127.3, 127.8, 128.4, 128.5, 133.1, 169.9.

A28. FT-IR (neat) ν_{max} = 3316, 2952, 2994, 1743, 1653, 1451, 1377, 1267, 1199, 1128, 715 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 1.97 (s, 3H), 2.02 (s, 3H), 2.11 (s, 3H), 2.20 (s, 3H), 3.47 (t, J = 6.0 Hz, 2H), 3.61 (t, J = 5.6 Hz, 2H), 4.11 (t, J = 6.0 Hz, 2H), 4.19 (t, J = 5.6 Hz, 2H), 4.59 (s, 2H), 4.62 (s, 2H), 7.14–7.36 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ = 20.7, 20.8, 21.5, 21.6, 45.0, 46.1, 48.2, 53.1, 61.2, 62.2, 126.2, 127.5, 127.7, 127.9, 128.6, 128.9, 136.6, 137.2, 170.5, 170.8, 171.1, 171.5.

A29. FT-IR (neat) ν_{max} = 3320, 1730, 1682, 1540, 1502, 1354, 1310, 1240, 1196, 1020, 992 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 2.16 (s, 3H), 2.36 (s, 3H), 7.14–7.17 (m, 2H), 7.22–7.25 (m, 1H), 7.39 (br s, 1H), 8.11 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ = 20.6, 22.7, 117.8, 120.7, 123.9, 125.9, 130.7, 140.5, 167.0, 167.9.

B9. White solid, m.p. 65–67 °C; FT-IR (KBr) ν_{max} = 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, $\text{DMSO}-d_6$) δ = 2.13 (s, 6H), 3.38 (s, 3H), 7.02 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.60–7.66 (m, 2H), 8.04 (s, 1H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ = 21.00, 21.93, 87.83, 123.53, 125.12, 127.94, 133.82, 135.42, 147.74, 167.55.

B19. White solid, m.p. 96–98 °C; FT-IR (KBr) ν_{max} = 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, $\text{DMSO}-d_6$) δ = 2.10 (s, 12H), 7.52 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 8.17 (s, 1H), 8.43 (dd, J = 7.6, 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ = 22.55, 102.33, 126.32, 128.82, 129.62, 141.19, 167.00.

B20. White solid, m.p. 164–166 °C; FT-IR (KBr) ν_{max} = 3020,

Scheme 3. The structure of the selected products.

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, 12H), 7.41 (s, 4H), 8.26 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ = 21.55, 104.33, 129.82, 141.19, 167.00.

3. Results and discussion

3.1. Characterization of the solid acid catalyst

The structure of the NSPVPHS synthesized in the current study was determined by FT-IR spectroscopy, elemental analysis, TGA and DTGA (differential thermogravimetry).

Figure 1 shows the FT-IR spectra of poly(4-vinylpyridine) (PVP) and NSPVPHS. The broad band between 3250 and 3750 cm^{-1} in the spectrum of NSPVPHS was attributed to the stretching OH vibration of the sulfonic acid and hydrogen sulfate groups in the solid acid catalyst. The other characteristic absorption bands at 1288, 1165, 1035, and 808 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the SO_2 group, as well as the bending and symmetric stretching vibrations of the S–OH and N– SO_2 groups, respectively [51–56]. The characteristic bands of the pyridine rings at 1505 and 1412 cm^{-1} disappeared from the spectrum, and a new band developed at 1637 cm^{-1} , which was attributed to the pyridinium ion. The in and out of plane bending of the pyridine C–H groups (994 cm^{-1}) is shown in Fig. 2 [57–59]. The spectra in Fig. 1 contained peaks that were characteristic of the pyridine ring vibrations at 1600 cm^{-1} for free unsulfonated rings in PVP and at 1637 cm^{-1} for the sulfonated rings in NSPVPHS at different loadings of the chlorosulfonic and sulfuric acids.

The solid acid catalyst was subjected to elemental analysis (Table 1). The amount of chloride was determined to be 3.98 mmol Cl per gram of polymer using gravimetric and potentiometric titration methods [60]. Using a previously reported method [61], the chloride content of NSPVPHS was found to be less 260 ppm. The densities of the SO_3H and SO_4H groups were measured by acid-base potentiometric titration using NaOH (0.01 mol/L) as a titrant. In a separate experiment, a suspension of NSPVPHS in benzene was titrated using *n*-butylamine as an indicator. This method allowed for the amount of Brönsted acid to be determined, but is very rarely applied to highly colored or dark samples because the color change can be difficult to observe under these conditions. The acid loading of the NSPVPHS was found to be in the range of 3.91–3.94 mmol/g using these parallel experiments.

TGA was used to develop a deeper understanding of the degradation kinetics of NSPVPHS. The TGA experiments were conducted over a temperature range of 30 to 700 $^{\circ}\text{C}$, with the samples being heated at a rate of 10 $^{\circ}\text{C}/\text{min}$. The derivative weight loss with respect to temperature (DTGA) revealed that

Fig. 1. FT-IR spectra of PVP and NSPVPHS in the range of 4000–400 cm^{-1} .

Fig. 2. FT-IR spectra of PVP and NSPVPHS in the range of 2000–400 cm^{-1} .

the decomposition of the NSPVPHS involved five distinct stages (Fig. 3). The first decomposition stage was observed around 100 $^{\circ}\text{C}$, whereas the second, third, fourth, and fifth weight loss events occurred at 320, 390, 510, and 630 $^{\circ}\text{C}$, respectively, with the second and third events representing significant weight losses. The first, second, third, and fourth weight loss stages were attributed to the expulsion of water molecules from the catalyst matrix, the decomposition of the sulfonic acid and hydrogen sulfate groups of the catalyst, and the splitting of the main DVB chain followed by the decomposition of the polymer backbone at temperatures above 550 $^{\circ}\text{C}$, respectively. These data therefore demonstrate that the NSPVPHS was thermally stable up to 320 $^{\circ}\text{C}$. In a separate control experiment, all of the bulk PVP was lost at 410 $^{\circ}\text{C}$ under an atmosphere of nitrogen [62,63].

The acidity of the solid acid was evaluated using the Hammett acidity functions, which were derived by UV-visible spec-

Table 1
Elemental analysis data of the initial polymer and modified poly(4-vinylpyridine).

Entry	Compound	Calcd (%)				Found (%)				Conversion (%)
		C	H	N	Cl	C	H	N	Cl	
1	PVP	80.29	6.69	13.01	—	80.14	6.64	13.22	—	—
2	NSPVPC	38.55	3.66	6.24	15.84	43.08	3.96	6.95	14.16	~80
3	NSPVPHS	30.25	3.22	4.90	—	34.53	3.50	5.62	—	~80

Fig. 3. TGA-DTGA curves of the NSPVPHS.

troscopy (Hammett method) using a basic indicator to trap the dissociative proton [64–66]. In the presence of the solid acid, the absorbance of the unprotonated form of the indicator, which could be observed at 349 nm, decreased (Fig. 4). These results clearly demonstrated that a dichloromethane solution of NSPVPHS was more acidic than a dichloromethane solution of poly(4-vinylpyridinium) hydrogen sulfate (PVPHS) or *N*-sulfonic acid poly(4-vinylpyridinium) chloride (NSPVPC). Based on this result, the acidities of the catalysts under our experimental conditions were determined to be of the order NSPVPHS > PVPHS > NSPVPC (Table 2).

3.2. Catalytic activity of the solid acid catalyst

The reaction of benzyl alcohol with acetic anhydride to give benzyl acetate was selected as a model reaction for the optimization of the catalytic conditions using NSPVPHS. The reaction was initially evaluated using different amounts of NSPVPHS at room temperature under solvent free conditions. The results showed that the reaction could be carried out in the presence of as little as 5 mg of NSPVPHS under solvent-free conditions, with the desired product being formed in high yield. The reaction was also conducted in a variety of different solvents (i.e., CH₂Cl₂, CH₃CN, MeOH, EtOH, and H₂O), but the reaction time became longer. Furthermore, when the reaction was conducted

Fig. 4. Absorption spectra of 4-nitroaniline (1), NSPVPC (2), PVPHS (3), and NSPVPHS (4) in CH₂Cl₂.

Table 2

Calculated Hammett acidity functions (H_0) of NSPVPC, PVPHS, and NSPVPHS.

Catalyst	$A_{\max}$	$[I]_s$ (%)	$[IH^+]_s$ (%)	H_0
—	2.9839	100	0	—
NSPVPC	1.4387	48.2	51.8	0.96
PVPHS	1.0942	36.7	63.3	0.75
NSPVPHS	0.6831	22.9	77.1	0.46

UV-vis spectroscopy conditions: CH₂Cl₂ solvent with 4-nitroaniline $pK(I)_{aq} = 0.99$ as the indicator at 1.44×10^{-4} mol/L. PVPHS or NSPVPHS (2 mg) was used as the catalyst at 20.9 °C. Calibration curves with a linearity of greater than 0.999 for the indicator in the unprotonated form were constructed using a CH₂Cl₂ solution of the indicator.

in the absence of the catalyst, none of the desired product was formed.

To confirm the importance of the NSPVPHS catalyst to the success of the acetylation reaction, we also conducted two control experiments, which involved the protection of 1-adamantanol and 4-methoxy benzyl alcohol with Ac₂O under similar reaction conditions in the presence of 5 mg of the chlorosulfonic acid and sulfuric acid used in the preparation of the solid acid catalyst. The results of these experiments are shown in Table 3. The results clearly show that when the acetylation reactions were carried out in the presence of ClSO₃H or H₂SO₄, they gave rise to a mixture of products that were observed by GC-MS. Interestingly, however, when the same substrates were acetylated in the presence of NSPVPHS, the desired products were formed in high yields without the formation of any side products.

Following on from these preliminary experiments, we proceeded to investigate the use of a catalytic amount of NSPVPHS (5 mg, 0.018 mmol) for the acetylation of a variety of different functional groups, including functionalized alcohols, phenols, thiols, and amines with acetic anhydride at room temperature under solvent-free conditions (Table 4). As shown in Table 4, a variety of different benzylic alcohols (including those bearing electron-donating or -withdrawing groups) and aliphatic alcohols underwent the acetylation with 1.0 equivalent of Ac₂O in the presence of a catalytic amount of NSPVPHS under solvent-free conditions at room temperature. The mild nature of the current reaction conditions meant that they did not have an adverse impact on acid sensitive functional groups such as the methoxy group (Table 4, entry 8). Furthermore, no competitive dehydration reactions were observed under the current condi-

Table 3

Acetylation of 1-adamantanol and 4-methoxy benzyl alcohol with Ac₂O using chlorosulfonic acid, sulfuric acid, or NSPVPHS as the catalyst.

Catalyst	1-Adamantanol		4-Methoxy benzyl alcohol	
	Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)
Chlorosulfonic acid (neat)	10	mix. ^b	5	mix. ^b
Sulfuric acid (100%)	10	mix. ^b	5	mix. ^b
NSPVPHS	10	89	5	97

Reaction conditions: Substrate (1.0 mmol) and Ac₂O (1.0 mmol) in the presence of catalyst (5 mg).

^a GC-MS yield of the corresponding acetylated product.

^b Mixture of compounds.

Table 4

NSPVPHS catalyzed acetylation of alcohols, phenols, thiols and amines.

Entry	Substrate	Product	Time (min)	Yield ^a (%)	Entry	Substrate	Product	Time (min)	Yield ^a (%)
1	C ₆ H ₅ -CH ₂ OH	C ₆ H ₅ -CH ₂ OAc	2 (2,2,3,5) ^b	98 (98,97,97,96) ^b	17	C ₆ H ₅ -SH	C ₆ H ₅ -SAC	8	92
2	2-Me-C ₆ H ₄ -CH ₂ OH	2-Me-C ₆ H ₄ -CH ₂ OAc	2	96	18	C ₆ H ₅ -CH ₂ SH	C ₆ H ₅ -CH ₂ SAC	8	93
3	2-Cl-C ₆ H ₄ -CH ₂ OH	2-Cl-C ₆ H ₄ -CH ₂ OAc	2	95	19	2-OH-C ₆ H ₄ -SH	2-OAc-C ₆ H ₄ -SAC	15	90 ^g
5	2-NO ₂ -C ₆ H ₄ -CH ₂ OH	2-NO ₂ -C ₆ H ₄ -CH ₂ OAc	12	86	20			10	84
7	4-Cl-C ₆ H ₄ -CH ₂ OH	4-Cl-C ₆ H ₄ -CH ₂ OAc	2	94	21	C ₆ H ₅ -NH ₂	C ₆ H ₅ -NHAc	2	90
8	4-MeO-C ₆ H ₄ -CH ₂ OH	4-MeO-C ₆ H ₄ -CH ₂ OAc	5	95	22	2-Me-C ₆ H ₄ -NH ₂	2-Me-C ₆ H ₄ -NHAc	1	96
9	(CH ₂) ₄ CHOH	(CH ₂) ₄ CHOAc	4	92	23	4-Br-C ₆ H ₄ -NH ₂	4-Br-C ₆ H ₄ -NHAc	2	86
10	(CH ₂) ₅ CHOH	(CH ₂) ₅ CHOAc	4	92	24	4-NO ₂ -C ₆ H ₄ -NH ₂	4-NO ₂ -C ₆ H ₄ -NHAc	1	93
11			8	86 ^c	25			2	90
12			5	95 ^d	26	C ₆ H ₅ -CH(OH)-CH ₂ OH	C ₆ H ₅ -CH(OAc)-CH ₂ OAc	10	93 ^e
13			10	89	27	2-(OH)-C ₆ H ₄ -CH ₂ OH	2-(OAc)-C ₆ H ₄ -CH ₂ OAc	4	98 ^e
14	C ₆ H ₅ -OH	C ₆ H ₅ -OAc	8	94	28	C ₆ H ₅ -CH ₂ -NH-CH ₂ CH ₂ OH	C ₆ H ₅ -CH ₂ -N(Ac)-CH ₂ CH ₂ OAc	10	98 ^e
15	1,2-(OH) ₂ -C ₆ H ₄	1,2-(OAc) ₂ -C ₆ H ₄	5	93 ^e	29	2-OH-C ₆ H ₄ -NH ₂	2-OAc-C ₆ H ₄ -NHAc	2	98 ^e
16	1,2,3-(OH) ₃ -C ₆ H ₄	1,2,3-(OAc) ₃ -C ₆ H ₄	8	92 ^f					

Reaction conditions: Substrate (1.0 mmol) and Ac₂O (1.0 mmol) in the presence of catalyst (5 mg).^a Isolated yield of the corresponding acetylated product.^b Results obtained using recycled catalyst.^c Substrate: [α]_D = -49.0°, c = 10 in 95% ethanol, 99% e.e.; product: [α]_D = -73.0°, neat, 98% e.e.^d Substrate: [α]_D = +37.9°, c = 5 in ethanol, 99% e.e.; product: [α]_D = +41.5°, neat, 96% e.e.^e Molar ratio of Ac₂O: substrate was 2.0:1.0 and isolated yield of the corresponding di-acetate.^f Molar ratio of Ac₂O: substrate was 3.0:1.0 and isolated yield of the corresponding tri-acetate.

tions (Table 4, entries 9–13). It is noteworthy that optically active alcohols reacted enantioselectively in the presence of NSPVPHS with complete retention of configuration, with the corresponding products being formed as single enantiomers in high yield (Table 4, entries 11 and 12). The optical rotations of the products were determined and compared with those reported by Aldrich.

The characteristic spectroscopic properties of 2-(*N*-benzylacetamido)ethyl acetate are worthy of additional comment (Table 4, entry 28). Shirini et al. [67] recently conducted a study aimed at developing a deeper understanding of the unusual ¹H and ¹³C NMR spectra of 2-(*N*-benzylacetamido)ethyl acetate. In the current study, conformers **I** and **II** were proposed as possible structures and optimized computationally with the Gaussian 98 set of programs at the Hartree Fock level with analytical gradients using the 6-31G* basis sets (Scheme 4). These results suggested that the two conformers could become trapped in the shown conformation until enough energy was available to overcome the high interconversion barrier (data not shown).

The results of our study have also shown that NSPVPHS can be used as a catalyst to catalyze the acetylation of phenols, thiols, and amines in good to high yields under the same reaction

conditions (Table 4, entries 14–29). In some cases, substrates bearing two or even three nucleophilic groups were successfully acetylated under the optimized reaction conditions (Table 4, entries 19 and 26–29). Furyl mercaptan, which is particularly acid sensitive, was also smoothly converted to the corresponding acetate derivative under the standard conditions without any decomposition (Table 4, entry 20). One of the principle objectives of the current study was to develop a recyclable solid acid catalyst. With this in mind, we investigated the recyclability of the NSPVPHS catalyst. Pleasingly, the catalytic activity of the recycled NSPVPHS towards the acetylation of benzyl alcohol with acetic anhydride was found to be almost the same as that of the fresh catalyst after five runs (Table 4, entry 1). This result showed that there was no significant reduction in the activity of catalyst, with the reactions using the recycled catalyst providing yields in the range of 96% to 98% in an average

Scheme 4. Conformational heterogeneity of 2-(*N*-benzylacetamido)ethyl acetate.

reaction time of approximately 4 min. It is noteworthy that the FT-IR spectra of the recovered catalyst was the same as that of the freshly prepared catalyst and that pH analysis of the reused NSPVPHS catalyst showed nearly the same loading of H^+ as the fresh catalyst. The leakage of sulfuric acid from the catalyst matrix was studied under the optimized conditions, and an activity loss of 10% was observed following the tenth use of the catalyst (in this case, a small amount of sulfuric acid leakage was detected in the reaction medium and wash solutions). These observations suggested that the catalyst remained largely intact after each run with only minor leaching of the acid species during the course of the reaction.

To highlight the efficiency of the anion exchange process observed in the current reaction, we have compared our results for the acetylation of pyrocatechol, pyrogallol, and 2-nitrobenzylalcohol with acetic anhydride in the presence of NSPVPHS with those conducted in the presence of NSPVPC (Table 5). This comparison clearly shows that the replacement of the chloride anion in NSPVPC with a hydrogen sulfate anion led to a significant increase in the acidity of the catalyst, and considerable improvements in the reaction times and product yields. These results therefore clearly demonstrate that the hydrogen sulfate anion plays a critical role in promoting the

Table 5

The impact of the exchange of the chloride anion with a hydrogen sulfate anion on the reaction time and yields.

Substrate	Product	NSPVPC		NSPVPHS	
		Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)
Pyrocatechol	1,2-(OAc) ₂ -C ₆ H ₄	50	74	5	93
Pyrogallol	1,2,3-(OAc) ₃ -C ₆ H ₃	55	82	8	92
2-Nitrobenzylalcohol	2-NO ₂ -C ₆ H ₄ -CH ₂ OAc	65	78	12	86

Reaction conditions: Substrate (1.0 mmol) and Ac₂O (1.0 mmol) in the presence of the NSPVPC or NSPVPHS catalyst (5 mg).

^a Isolated yield of the corresponding mono-, di-, and tri-acetate.

acetylation reaction.

Our result for the acetylation of benzyl alcohol with acetic anhydride in the presence of NSPVPHS was compared with the results of several other methods reported in the literature (Table 6). In the most cases, our newly developed method was found to be superior to the existing methods in terms of the reaction time, catalyst loading, or product yield.

A plausible mechanism for the current acetylation reaction is shown in Scheme 5. According to this mechanism, acetic anhydride would be activated by the solid acid NSPVPHS cation

Table 6

Comparison of NSPVPHS as a catalyst for the acetylation of benzyl alcohol with several other recently reported catalysts at room temperature under solvent-free conditions.

Entry	Catalyst	Amount of catalyst/substrate/acetic anhydride	Time (min)	Yield ^a (%)	Ref.
1	Montmorillonit KSF	100 mg/5 mmol/10 mmol	60	90	[21,22]
2	Zeolite HSZ-360	100 mg/5 mmol/10 mmol	60	84	[23]
3	Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester	2 mg/1mmol/1 mL (10.5 mmol)	6	96	[24]
4	Alumina supported MoO ₃	0.05 mmol/5 mmol/10 mmol	20	99	[25]
5	Silica-bonded N-propyl sulfamic acid	100 mg/1 mmol/1 mL (10.5 mmol)	20	98	[26]
6	Silica sulfuric acid	50 mg/1mmol/1.5 mmol	10	85 ^b	[27]
7	HClO ₄ -SiO ₂	0.01 mmol/1mmol/1 mmol	60	96	[28]
8	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	74 mg/1 mmol/1.5 mmol	75	95	[29]
9	NSPVPC	5 mg/1 mmol/2 mmol	25	92	this work
10	NSPVPHS	5 mg/1 mmol/2 mmol	2	98	this work

^a Isolated yield. ^b *n*-Hexane was used as a solvent.

Scheme 5. Proposed mechanism for the acetylation of the substrates.

and acidic hydrogen sulfate anion. The activated acetic anhydride would then be attacked by the substrate, which would ultimately be converted to the final product with the release of NSPVPHS for the next catalytic cycle.

The selectivity of this method was evaluated using a competitive acetylation reaction involving the simultaneous acetylation of benzyl alcohol, phenol, aniline, and thiophenol (Table 7). The results showed that the current procedure could be used as a practical method for the selective acetylation of amines in the presence of alcohols, phenols, and thiols.

In a separate study, NSPVPHS was used to efficiently catalyze the conversion of aldehydes to the corresponding 1,1-diacetates with acetic anhydride (Scheme 2). As shown in Table 8, NSPVPHS was used to catalyze the 1,1-diacetylation of a variety of different aromatic aldehydes bearing a range of different substituents such as NO₂, Cl, Br, CN, Me, and MeO in good to high yields (Table 8, entries 1–12). Aromatic aldehydes bearing a phenolic functionality were also acetylated to the phenol under the current conditions (Table 8, entries 13 and 14). The acid sensitive substrate furfural was also successfully acetylated under the current conditions in high yield without the formation of any side products, which are normally observed under strongly acidic conditions (Table 8, entry 15). The current method could also be used for the protection of aliphatic and α,β -unsaturated aldehydes (Table 8, entries 16–18). No isomerization reactions were observed when conjugated aldehydes were used in the presence of NSPVPHS, and the application of these conditions to iso-phthalaldehyde and terephthalaldehyde gave the *tetra*-acetylated products in high yields (Table 8, entries 19 and 20).

To evaluate the intra- and intermolecular chemoselectivity of the current method, we conducted two competitive reactions involving the 1,1-diacetylation of aldehydes in the presence of

Table 7

Competitive acetylation of benzyl alcohol, phenol, thiophenol, and aniline catalyzed by NSPVPHS.

Entry	Substrate	Product	Time (min)	Yield ^a (%)
1	C ₆ H ₅ -NH ₂ +C ₆ H ₅ -SH	C ₆ H ₅ -NHAc+C ₆ H ₅ -SAC	5	100+0
2	C ₆ H ₅ -NH ₂ +C ₆ H ₅ -OH	C ₆ H ₅ -NHAc+C ₆ H ₅ -OAc	5	100+0
3	C ₆ H ₅ -CH ₂ -OH+C ₆ H ₅ -OH	C ₆ H ₅ -CH ₂ -OAc+C ₆ H ₅ -OAc	5	88+12
4	C ₆ H ₅ -CH ₂ -OH+C ₆ H ₅ -SH	C ₆ H ₅ -CH ₂ -OAc+C ₆ H ₅ -SAC	10	85.6+14.4
5	C ₆ H ₅ -OH+C ₆ H ₅ -SH	C ₆ H ₅ -OAc+C ₆ H ₅ -SAC	10	64+36

Reaction conditions: Substrate (1.0 mmol) and Ac₂O (1.0 mmol) in the presence of catalyst (5 mg).

^a Determined by GC-MS of the corresponding acetylated products.

ketones using NSPVPHS. The results of these experiments revealed a high level selectivity towards the conversion of aldehydes to the corresponding 1,1-diacetates in the presence of ketones (Table 8, entries 21 and 22).

The NSPVPHS catalyst could be effectively recovered from the reaction mixture during the work-up procedure (Table 8, entry 5). The percentage recovery of the catalysts was greater than 98% in most cases, and subsequent reuse of the catalyst revealed that there was no significant loss in its catalytic activity.

To highlight the merits of our current 1,1-diacetylation method, we have compared our results for the 1,1-diacetylation of benzaldehyde and cinnamaldehyde with other results reported in the literature using different catalysts (Table 9). These results of this comparison clearly show that NSPVPHS is superior to all of the other reported catalysts in terms of the yield or reaction time.

A possible mechanism for this reaction could involve either the intermolecular or intramolecular transfer of the second acetate group following the initial attack of the activated alde-

Table 8

NSPVPHS catalyzed 1,1-diacylation of aldehydes^a.

Entry	Substrate	Product	Time (min)	Yield ^b (%)	Entry	Substrate	Product	Time (min)	Yield ^b (%)
1	C ₆ H ₅ -CHO	C ₆ H ₅ -CH(OAc) ₂	5	98	12	4-MeO-C ₆ H ₄ -CHO	4-MeO-C ₆ H ₄ -CH(OAc) ₂	8	90
2	2-NO ₂ -C ₆ H ₄ -CHO	2-NO ₂ -C ₆ H ₄ -CH(OAc) ₂	5	95	13	2-OH-C ₆ H ₄ -CHO	2-OAc-C ₆ H ₄ -CH(OAc) ₂	5	90
3	4-NO ₂ -C ₆ H ₄ -CHO	4-NO ₂ -C ₆ H ₄ -CH(OAc) ₂	4	98	14	4-OH-C ₆ H ₄ -CHO	4-OAc-C ₆ H ₄ -CH(OAc) ₂	8	91
4	2-Cl-C ₆ H ₄ -CHO	2-Cl-C ₆ H ₄ -CH(OAc) ₂	5	91	15			6	94
5	4-Cl-C ₆ H ₄ -CHO	4-Cl-C ₆ H ₄ -CH(OAc) ₂	5 (5, 5, 6) ^c	90 (90, 90, 90) ^c	16	C ₆ H ₅ -CH ₂ -CHO	C ₆ H ₅ -CH ₂ -CH(OAc) ₂	5	91
6	2-Br-C ₆ H ₄ -CHO	2-Br-C ₆ H ₄ -CH(OAc) ₂	6	92	17	CH ₃ (CH ₂) ₄ -CHO	CH ₃ (CH ₂) ₄ -CH(OAc) ₂	10	95
7	4-Br-C ₆ H ₄ -CHO	4-Br-C ₆ H ₄ -CH(OAc) ₂	8	94	18	C ₆ H ₅ -CH=CH-CHO	C ₆ H ₅ -CH=CH-CH(OAc) ₂	5	94
8	4-NC-C ₆ H ₄ -CHO	4-NC-C ₆ H ₄ -CH(OAc) ₂	8	84	19			5 ^d	89
9	2-Me-C ₆ H ₄ -CHO	2-Me-C ₆ H ₄ -CH(OAc) ₂	4	90	20			5 ^d	96
10	4-Me-C ₆ H ₄ -CHO	4-Me-C ₆ H ₄ -CH(OAc) ₂	5	92	21	CH ₃ CO-C ₆ H ₄ -CHO	CH ₃ CO-C ₆ H ₄ -CH(OAc) ₂	5	92
11	2-MeO-C ₆ H ₄ -CHO	2-MeO-C ₆ H ₄ -CH(OAc) ₂	7	88	22	4-Cl-C ₆ H ₄ -CHO + C ₆ H ₅ -COCH ₃	4-Cl-C ₆ H ₄ -CH(OAc) ₂ + C ₆ H ₅ -COCH ₃	5	100 ^f + 100 ^e

^a Products were characterized by their physical properties and IR and NMR spectra.

^b Isolated yield.

^c Results obtained using recycled catalyst.

^d 3 mmol of acetic anhydride was used.

^e Starting material recovered intact.

^f Conversion.

Table 9

Comparison of the effect of different catalysts in the synthesis of the 1,1-diacetates of benzaldehyde and cinnamaldehyde.

Entry	Catalyst	Benzaldehyde		Cinnamaldehyde		Ref.
		Time (min)	Yield (%)	Time (min)	Yield (%)	
1	Saccharin sulfonic acid	48	90	—	—	[40]
2	NBS	360	95	1200	48	[41]
3	<i>p</i> -TSA	25	96	35	92	[42]
4	Silica sulfuric acid	30	84	15	81	[43]
5	Copper methane-sulfonate-HOAc	78	94	120	67	[44]
6	1,3-Dibromo-5,5-dimethyl hydantoin	90	98	48	92	[45]
7	Zirconium sulfophenyl phosphonate	12	84	180	72	[47]
8	NSPVP	32	92	25	83	[48]
9	SuSA	12	98	5	93	[67]
10	NSPVPHS	5	98	5	94	this work

Scheme 6. Proposed mechanism of the 1,1-diacetylation of aldehydes.

hyde by acetic anhydride (Scheme 6). The role of NSPVPHS in the reaction could be to activate the carbonyl group towards these nucleophilic attacks.

4. Conclusions

We have developed *N*-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate as a novel, efficient, and reusable solid acid catalyst for the acetylation of alcohols, phenols, thiols, and amines, as well as the 1,1-diacetylation of aldehydes under solvent-free conditions at room temperature. This study also revealed the importance of the hydrogen sulfate anion for enhancing the reaction times and yields of the acetylation reactions. Our newly developed method provides a simple and efficient platform for the acetylation of a variety of different functional groups and does not require inert or anhydrous conditions. Furthermore, the NSPVPHS catalyst was found to be sta-

ble to both air and moisture. The introduction of a Brønsted-acidic functional group (SO₃H) as the anion of the catalyst enhanced its acidity and allowed it to be used under solvent-free conditions. Because the NSPVPHS catalyst allowed for the acetylation reaction to be conducted under mild and neutral conditions, side reactions resulting from strongly acidic or basic conditions were avoided. Furthermore, the catalyst could be readily recovered and reused without any significant loss in its activity. Further work towards explore the use of this novel catalyst in other organic transformations is currently underway in our laboratory.

Acknowledgments

The authors gratefully acknowledge the partial support of this work by the House Research of Professor Reza, Education Guilan, Rasht, District 1 and the Research Affairs Office of Guilan University.

References

- [1] Smith K. Solid Supports and Catalysis in Organic Synthesis. New York: Ellis Horwood and PTR Prentice Hall, 1992
- [2] Riego J M, Sedin Z, Zaldivar J M, Marziano N C, Tortato C. *Tetrahedron Lett*, 1996, 37: 513
- [3] Turro N J. *Tetrahedron*, 1987, 43: 1589
- [4] Zolfigol M A, Chehardoli G, Dehghanian M, Niknam K, Shirini F, Khoramabadi-Zad A. *J Chin Chem Soc*, 2008, 55: 885
- [5] Chehardoli G, Zolfigol M A, Faal-Rastegar T, Mallakpour S, Ghorbani-Choghamaranid A. *J Chem Sci*, 2009, 121: 441
- [6] Khaligh N G, Shirini F. *J Mol Catal A*, 2011, 348: 20
- [7] Khaligh N G. *Ultrason Sonochem*, 2012, 19: 736
- [8] Khaligh N G. *Tetrahedron Lett*, 2012, 53: 1637
- [9] Cole-Hamilton D J. *Science*, 2003, 299: 1702
- [10] Curzons A, Constable C C, Cunningham V L. *Clean Prod Process*, 1999, 1: 82
- [11] Tanaka K. Solvent-Free Organic Synthesis. Weinheim: Wiley-VCH, GmbH and KGaA, 2004
- [12] Gani R, Jiménez-Gonzalez C, ten Kate A, Crafts P A, Powell M J, Powell L, Atherton J H, Cordiner J L. *Chem Eng*, 2006, 113: 30
- [13] Shaabani A, Ghadari R, Rahmati A, Rezayan A H. *J Iran Chem Soc*, 2009, 6: 710
- [14] Greene T W, Wuts P G M. Protective Groups in Organic Synthesis. 3rd Ed. New York: John Wiley and Sons, 1999. 306
- [15] Otera J. Esterification: Methods, Reactions and Applications. Weinheim: Wiley-VCH, 2003
- [16] Sun X L, Kai T, Takayanagi H, Furuhashi K. *Synlett*, 1999: 1399
- [17] Yadav J S, Narsaiah A V, Basak A K, Goud P R, Sreenu D, Nagaiah K. *J Mol Catal A*, 2006, 255: 78
- [18] Scriven E F V. *Chem Soc Rev*, 1983, 12: 129
- [19] Höfle G, Steglich V, Vorbrüggen H. *Angew Chem Int Ed*, 1978, 17: 569
- [20] Cope A C, Herrich E C. Organic Synthesis Collective. Vol. IV. New York: Wiley, 1963. 304
- [21] Li A X, Li T S, Ding T H. *Chem Commun*, 1997: 1389
- [22] Hagiwara H, Morohashi K, Suzuki T, Ando M, Yamamoto I, Kato M. *Synth Commun*, 1998, 28: 2001
- [23] Ballini R, Bosica G, Carloni S, Ciaralli L, Maggi R, Sartori G. *Tetrahedron Lett*, 1998, 39: 6049
- [24] Niknam K, Saberi D. *Appl Catal A*, 2009, 366: 220
- [25] Joseph J K, Jain S L, Sain B. *J Mol Catal A*, 2007, 267: 108

Graphical Abstract

Chin. J. Catal., 2014, 35: 1126–1135 doi: 10.1016/S1872-2067(14)60052-8

N-Sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate as a novel, efficient, and reusable solid acid catalyst for acylation under solvent-free conditions

Nader Ghaffari Khaligh*, Parisa Ghods Ghasem-Abadi

Qaemshahr Branch, Islamic Azad University, Iran; House Research of Professor Reza, Education Guilan, Iran; University of Mohaghegh-Ardabili, Iran; Memorial University, Canada

Poly(4-vinylpyridinium) hydrogen sulfate (NSPVPHS) has been developed as a new recyclable solid acid catalyst for the acetylation of alcohols, phenols, thiols, and amines, and the 1,1-diacetylation of aldehydes under solvent-free conditions at room temperature. The acetylated products were obtained in good to excellent yields over short reaction times without the formation of any side products. The hydrogen sulfate anion was determined to be critical to enhancing the reaction time and product yield.

- [26] Niknam K, Saberi D. *Tetrahedron Lett*, 2009, 50: 5210
- [27] Shirini F, Zolfigol MA, Mohammadi K. *Bull Korean Chem Soc*, 2004, 25: 325
- [28] Chakraborti A K, Gulhane R. *Chem Commun*, 2003: 1896
- [29] Heravi M M, Behbahani F K, Bamoharram F F. *J Mol Catal A*, 2006, 253: 16
- [30] Khaligh N G. *J Mol Catal A*, 2012, 363-364: 90
- [31] Khaligh N G. *RSC Adv*, 2013, 3: 99
- [32] Trost B M, Lee C B. *J Am Chem Soc*, 2001, 123: 3687
- [33] Gregory M J. *J Chem Soc B*, 1970: 1201
- [34] Sandberg M, Sydnes L K. *Org Lett*, 2000, 2: 687
- [35] Held H, Rengstle A, Mayer D. In: Gerhartz W Ed. *Ullman's Encyclopedia of Industrial Chemistry*. 5th Ed. Vol. A1. New York: VCH, 1985. 68
- [36] Freeman F, Karchefski E M. *J Chem Eng Data*, 1977, 22: 355
- [37] Van Heerden F R, Huyser J J, Bradley D, Williams G, Holzapfel C W. *Tetrahedron Lett*, 1998, 39: 5281
- [38] Sandberg M, Sydnes L K. *Tetrahedron Lett*, 1998, 39: 6361
- [39] Sanderson W R. EP Patent 125 781. 1984
- [40] Shirini F, Mamaghani M, Mostashari-Rad T, Abedini M. *Bull Korean Chem Soc*, 2010, 31: 2399
- [41] Karimi B, Seradj H, Ebrahimi G R. *Synlett*, 2000, 1: 623
- [42] Manjula K, Pasha M A. *Synth Commun*, 2007, 37: 1563
- [43] Desai U V, Thopta T S, Pore D M, Wadgaonkar P P. *Catal Commun*, 2006, 7: 508
- [44] Wang M, Gong H, Jiang H, Wang Z C. *Synth Commun*, 2006, 36: 1953
- [45] Aggarwal V K, Fonquerna S, Vennall G P. *Synlett*, 1998: 849
- [46] Karimi B, Maleki J. *J Org Chem*, 2003, 68: 4951
- [47] Negron G E, Palacios L N, Angeles D, Lomas L, Gavino R. *J Braz Chem Soc*, 2005, 16: 490
- [48] Shirini F, Jolodar O G. *J Mol Catal A*, 2012, 356: 61
- [49] Shirini F, Khaligh N G, Jolodar O G. *J Iran Chem Soc*, 2013, 10: 181
- [50] Khaligh N G, Shirini F. *Ultrason Sonochem*, 2013, 20: 26
- [51] Roeges N P G. *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*. New York: Wiley, 1994
- [52] Philip D, Eapen A, Aruldas G. *J Solid State Chem*, 1995, 116: 217
- [53] Chackalackal S M, Stafford F E. *J Am Chem Soc*, 1966, 88: 4815
- [54] Silverstein R M, Bassler G C, Morrill T C. *Spectrometric Identification of Organic Compounds*. New York: John Wiley and Sons, 1991
- [55] Kemp W. *Organic Spectroscopy*. London: MacMillan, 1996
- [56] Suwan J, Zhang Z, Li B, Vongchan P, Meepowpan P, Zhang F, Mousa S A, Mousa S, Premanode B, Kongtawelert P, Linhardt R J. *Carbohydrate Res*, 2009, 344: 1190
- [57] Grzyb B, Machnikowski J, Weber J V. *J Anal Appl Pyrol*, 2004, 72: 121
- [58] McCurdie M P, Belfiore L A. *Polymer*, 1999, 40: 2889
- [59] Gill N S, Nuttall R H, Scaife D E, Sharp D W A. *J Inorg Nucl Chem*, 1961, 18: 79
- [60] Williams W J. *Handbook of Anion Determination*. London: Butterworth, 1979. 416
- [61] Villagran C, Deetlefs M, Pitner W R, Hardacre C. *Anal Chem*, 2004, 76: 2118
- [62] Wu K H, Wang Y R, Hwu W H. *Polym Degrad Stab*, 2003, 79: 195
- [63] Pardey A J, Rojas A D, Yáñez J E, Betancourt P, Scott C, Chinea C, Urbina C, Moronta D, Longo C. *Polyhedron*, 2005, 24: 511
- [64] Duan Z Y, Gu Y L, Zhang J, Zhu L Y, Deng Y Q. *J Mol Catal A*, 2006, 250: 163
- [65] Xing H B, Wang T, Zhou Z H, Dai Y Y. *J Mol Catal A*, 2007, 264: 53
- [66] Thomazeau C, Olivier-Bourbigou H, Magna L, Luts S, Gilbert B. *J Am Chem Soc*, 2003, 125: 5264
- [67] Shirini F, Khaligh N G. *Chin J Catal* (催化学报), 2013, 34: 695