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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

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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

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[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 ^1H 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 ($\lambda = 1.542$ Å). The scanning was over a range of $2\theta = 10–70^\circ$. 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 $ClSO_3H$.

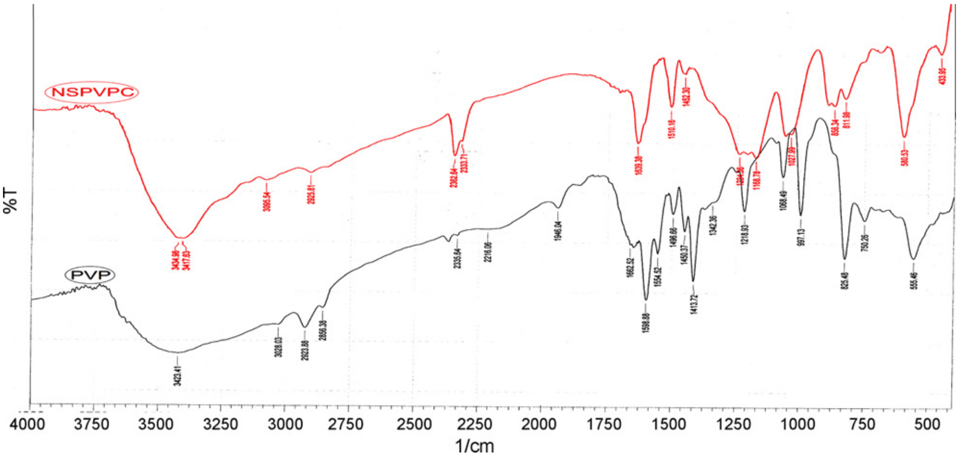

Fig. 1. FTIR spectra of PVP (down) and NSPVPC (up).