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Host (nanocavity of zeolite-Y)–guest (molybdophosphoric acid) nanocomposite materials: An efficient catalyst for solvent-free synthesis and deprotection of 1,l-diacetates

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ABSTRACT

In the present work, a mild and efficient method has been developed for the synthesis of acylals from aldehydes with acetic anhydride in the presence of molybdophosphoric acid encapsulated into dealuminated zeolite Y (MPA-DAZY) as a catalyst under solvent-free conditions at 45–55 °C in good to excellent yield. The deprotection of acylals has also been attained using this catalyst in acetonitrile. The catalyst was reused several times without efficient loss of its catalytic activity.

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1. Introduction

Protection of functional groups plays an important role in multi-step synthesis of natural products. However, selective protection and deprotection of carbonyl groups are substantial steps in synthetic organic chemistry [1]. Acylals (1,1-diacetates) are appropriate candidates to this aim due to their stability in basic and neutral reaction media as well as in aqueous acids [2]. Meanwhile, gem-diacetates derived from α,β-unsaturated aldehydes are useful as dienes for Diels–Alder cycloaddition reactions. Moreover, acylals are used as cross linking reagents for cellulose in cotton [3].

Several methods have been used for the synthesis of 1,1-diacetates from strong acids including sulfuric acid [4], methane sulfuric acid [5], sulfamic acid [6], Lewis acids as lithium bromide [7], aluminum chloride [8], anhydrous ferrous sulfate [9], PCl_3 [10], $FeCl_3$ [11], NBS [12], Nafion-H [13], sulfated zirconia [14], montmorillonite clay [15], expansive graphite [16], aluminum dodecatungstophosphate [17], Well–Dawson acid ($H_6P_2W_{18}O_{62}$ $.24H_2O$) [18] zeolite HSZ-360 [19], $Cu(OTf)_2$ [20], $Sc(OTf)_3$ [21], $Bi(OTf)_3$ [22], $Zn(BF_4)_2$ [23], $Bi(NO_3)_3.5H_2O$ [24] and $ZrCl_4$ [25] which are also efficient for this conversion. However, many of these methodologies have drawbacks, and involve strongly acidic conditions, corrosive reagents, long reaction times, high temperature and high toxicity. Recently, solvent-free reactions were developed because of their ecological and low-cost advantages. Some of these catalysts are P_2O_5/Al_2O_3 [26], dodecamolybdophoshporic acid [27], SO_4^{2-}/SnO_2 [28], bromodimethylsulfonium bromide [29], solid lithium perchlorate [30], $[bmim]BF_4$ [31], $[Hmim]HSO_4$ [32] zirconium sulfophenyl phosphonate [19] and Zeolite Y [33].

In this article, we report a new and efficient method for solvent-free conversion of aromatic aldehydes to their corresponding 1,1-diacetates with acetic anhydride and their deprotection in acetonitrile using encapsulated molybdophosphoric acid in dealuminated Y zeolite (MPA-DAZY) as a reusable catalyst (Scheme 1).

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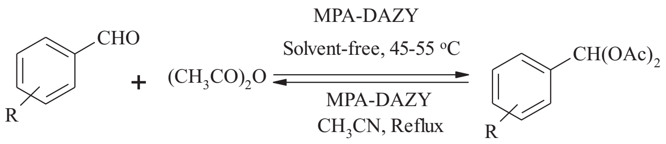

Scheme 1. Synthesis of 1,1-diacetates under solvent-free conditions and their deprotection in acetonitrile using encapsulated molybdophosphoric acid in dealuminated Y zeolite (MPA-DAZY).

2. Experimental

All solvents and reagents were of the commercial reagent grade and obtained from Merck or Fluka. All of reaction mixtures were monitored by TLC. Melting points were recorded on a Barnstead Electrothermal 9200 apparatus, and are uncorrected. The NaY-zeolite was purchased from Sigma-Aldrich Chemical Company. The framework of NaY-zeolite contains aluminum atoms are basic and therefore, increase the decomposition of MPAs, or disturb the formation of MPA into the supercages of zeolite. Therefore, the modified DAZY (dealuminated zeolite Y) as support, was prepared by hydrothermal treatment [34]. Dealumination of NaY zeolite not only improves the zeolite stability but also yields a secondary pore system in zeolite matrix for deposition of the large MPA species [35]. Therefore, zeolite Y was dealuminated. The method reported by Mukai was used for the synthesis of $H_3PMo_{12}O_{40}$ encapsulated into dealuminated zeolite (MPA-DAZY) [36,37]. All products were known compounds and identified by comparing their physical data by their authentic samples.

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

In a round bottom flask equipped with a magnetic stirrer, aldehyde (1 mmol), acetic anhydride (3 mmol) and catalyst (250 mg, 0.01 mmol) were mixed and stirred at 45–55 °C for an appropriate time. The progress of the reaction was monitored by TLC (ethyl acetate/*n*-hexane 7:1). After the reaction was completed, saturated $NaHCO_3$ (5 ml) was added and the catalyst was filtered. The product was extracted with diethyl ether (2 × 15 ml) and the etherates were dried over Na_2SO_4. The solvent was evaporated to give the corresponding 1,1-diacetate.

2.2. Catalyst recovery and reuse

The reusability of catalyst also was investigated in the multiple sequential reaction of 3-nitrobenzaldehyde as a model substrate. At the end of each reaction, the catalyst was filtered, activated by washing with ethyl acetate and drying at 120 °C for 3 h, and reused with fresh aldehyde and acetic anhydride.

2.3. General procedure for the deprotection of 1,1-diacetates

In a typical procedure, 1,1-diacetates (1 mmol) in acetonitrile (3 ml) and MPA-DAZY (500 mg, 0.02 mmol) were mixed and refluxed for an appropriate time. The progress of reaction was monitored by TLC (ethyl acetate/*n*-hexane 7:1). After completion of the reaction, the reaction mixture was diluted with ethyl acetate and filtered. The organic layer was washed with $NaHCO_3$ (10%, 2 × 5 ml) and dried over Na_2SO_4. The organic solvent was evaporated to produce the crude aldehyde. The residue was purified by plate chromatography (*n*-hexane/ether 4:1) to give the corresponding aldehyde.

3. Results and discussion

3.1. Catalytic performance in the protection of aldehydes

The MPA-DAZY catalyst was synthesized and characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD), differential thermal gravimetry (DTG) and atomic absorption spectroscopic (AAS) techniques. The content of MPA in the synthesized sample, obtained by dissolving a small amount of the washed catalyst in hydrofluoric acid and hot concentrated hydrochloric acid, was determined by atomic absorption spectroscopy (AAS) [37].

The results showed that the catalyst loading was about 0.043 mmol/g of encapsulated catalyst. The reaction of aldehydes with acetic anhydride in the presence of MPA-DAZY produces the correponding 1,1-diacetates (Scheme 1). First, the amount of catalyst was optimized in the reaction of 3-nitrobenzaldehyde with acetic anhydride. The results showed that highest yield was obtained with 250 mg (0.01 mmol) of catalyst (Table 1). For optimization of the reaction media, the same reaction was performed in

Table 1
Optimization of the catalyst amount in the reaction of 3-nitrobenzaldehyde with acetic anhydride under solvent-free conditions after 1 h.[a]

Entry	Catalyst amount (mg)	Yield[b] (%)
1	100	40
2	150	65
3	200	84
4	250 (0.01 mmol of MPA)	95

[a] Reaction conditions: 3-nitrobenzaldehyde (1 mmol), acetic anhydride (3 mmol).
[b] Isolated yield.

Table 2
The effect of solvent on the protection of 3-nitrobenzaldehyde with acetic anhydride catalyzed by MPA-DAZY after 1 h.[a]

Entry	Solvent	Yield[b] (%)
1	CH_3CN	44
2	CH_3COCH_3	35
3	CH_3OH	40
4	CH_2Cl_2	25
5	Solvent-free	95

[a] Reaction conditions: 3-nitrobenzaldehyde (1 mmol), acetic anhydride (3 mmol), catalyst (250 mg, 0.01 mmol).
[b] Isolated yield.

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