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Phosphotungstic acid on silica with modified acid sites as a solid catalyst for selective cleavage of *tert*-butyldimethylsilyl ethers

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ABSTRACT

The strength and nature of acid sites of bulk phosphotungstic acid could be modified after dispersing it on silica support which was characterized by XRD, ammonia TPD and ^{31}P MAS NMR techniques. This solid acid catalyst was found to be highly selective for the cleavage of *tert*-butyldimethylsilyl ethers at room temperature. The catalyst was easily recovered by filtration and could be reused for several times without loss of any activity giving a TON of 9.5×10^5.

1. Introduction

Heteropolyacids (HPA) possess strong acidity hence, they are widely applied as solid acids for several acid-catalyzed reactions in liquid phase such as ether cleavage, transesterification, hydration, rearrangements, etc. [1–5]. Acidity of HPA can be even higher than the protonic acids such as sulfuric and *p*-toluenesulphonic acids due to dispersion of the negative charge over several atoms of a heteropoly anion and the polarization of the negative charge of oxoanion [6]. Usually supported HPAs are used for catalyst applications than the bulk HPAs as the later have a low surface area ($<10\ m^2\ g^{-1}$). Among various supports, silica has been the most commonly used owing to its relative inertness towards HPAs [7,8]. However, recent ^{31}P MAS NMR investigations of phosphotungstic acid ($H_2PW_{12}O_{40}$, PTA) revealed the interaction of PTA with SiO_2 leading to a decrease in acid strength of PTA [9]. In several chemical transformations, mild acidity is more useful for obtaining selectively desired product. Selective cleavage of Si–O bond of *tert*-butyldimethylsilyl (TBDMS) ether group which is extensively used as a protecting group for hydroxyl functionality in various organic transformations, is one such example where a solid catalyst with appropriately designed acidity is desired. Several Lewis acids such as tetra-butyl ammonium fluoride (TBAF), tri-methylsilyl chloride (TMSCl), Zn $(BF_4)_2$, Scandium triflate (Sc $(OTf)_3$), BCl_3, $InCl_3$, $ZnBr_2$, Cerium triflate (Ce $(OTf)_4$), $SbCl_3$, $ZrCl_4$, Ni (II)$Cl_2 \cdot 6H_2O$ and tetra-butyl ammonium tribromide (TBATB) and $TiCl_4$–Lewis base complexes have been reported for the cleavage of TBDMS ethers [10–15]. Among solid acids, sulfonic acid fuctionalized nanoporous silica and $NaHSO_4$ on silica have also been reported for the cleavage of TBDMS ethers [16,17]. However, the most of these methods require hazardous reagents and cumbersome workup procedures that are detrimental to the environment. Moreover, in nearly all cases the reagent cannot be recovered and recycled except sulfonic acid functionalized nanoporous silica and $NaHSO_4$ on silica, which also requires special reagents and reaction conditions to prepare the catalyst and the catalyst to substrate weight ratio was also very high (>0.2). The main challenge in these approaches is to decrease the catalyst loading to ensure high efficiency, which leads to green process that emphasizes atom economy and the elimination of hazardous wastes. Hence, we prepared PTA supported on silica catalyst with the aim of modifying the acid sites of bulk PTA and it was found that the change in strength and nature of acid sites of bulk PTA after dispersion on silica support catalyzed the selective cleavage of several TBDMS ethers in methanol as a solvent (Scheme 1).

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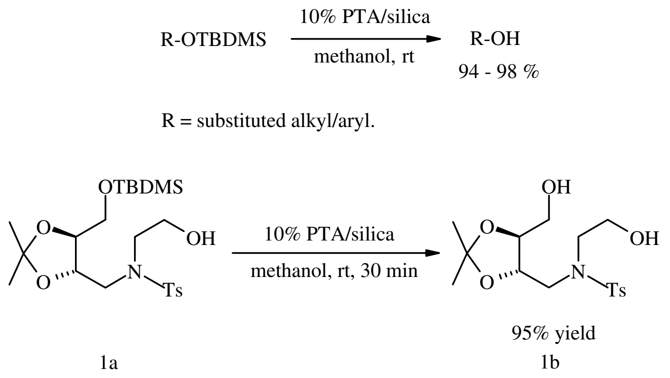

Scheme 1. Cleavage of alkyl/aryl tert-butyldimethylsilyl ethers at room temperature using 10%PTA/silica in methanol (catalyst to substrate mole ratio is 0.01).

2. Experimental

2.1. Materials

Phosphotungstic acid, $H_3PW_{12}O_{40}$ (PTA hydrate), fumed silica and protecting reagents such as *tert*-butyldimethyl chlorosilane (TBDMSCl), benzyl bromide (BnBr), methoxymethyl chloride (MOMCl), benzyl chloroformate (CbzCl), dimethoxy propane and tosyl chloride (TsCl) were procured from Aldrich, India Ltd. Solvent methanol was procured from M/s Loba Chemie, Mumbai with >99.9 purity.

2.2. Preparation 10%PTA/SiO_2 catalyst

To a solution of $H_3\,PW_{12}O_{40} \cdot 24H_2O$ (100 mg, 1 equivalent by weight) in methanol (10 ml) was added slowly fumed silica (900 mg, 9 equivalent by weight), and the mixture was stirred at room temperature for 6 h. Evaporation of methanol under reduced pressure gave a dry white 10%PTA/silica catalyst.

2.3. Preparation of TBDMS ethers

Several structurally varied TBDMS ethers with different functional groups and protections can be easily prepared using reported method available in the literature [10].

2.4. Catalyst activity measurement

A mixture of TBDMS ether **1a** 0.473 g (1 mmol) and 10%PTA/silica 0.288 g (0.0288 g and 0.01 mmol based on PTA and catalyst to substrate weight ratio of 0.038) in methanol (5 ml) was stirred at room temperature. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure, and the crude compound was purified by column chromatography over silica–gel (100–200 mesh) to afford the pure alcohol **1b** (95%). In a similar manner, activity of 10%PTA/silica was evaluated for various substrates and the recovered products were confirmed by ^1H NMR. Yields are based on the pure isolated products.

2.5. Catalyst characterization

2.5.1. Surface area measurements

BET analysis was performed by CHEMBET 3000 instrument supplied by Quantachrome. 30% nitrogen: Helium gas was used as adsorption and desorption gas. The gas flow rate was kept at 100 ml/min, and pure 99.999% nitrogen was used as a standard calibration gas.

2.5.2. Pulse titration/TPD measurements

Ammonia chemisorption measurements were performed on Quantachrome instrument to determine surface acidity of the catalyst. 0.045 g of freshly vacuum dried catalyst sample loaded in the sample tube was preheated at 150 °C for 4 h to remove moisture under nitrogen atmosphere. Then it was heated in a flow of nitrogen at 500 °C for 1 h. The catalyst was then cooled to room temperature in nitrogen flow. Then 3000 μL pulses of pure NH_3 were injected by using gas tight syringe at certain intervals until the peak areas reached the saturation point.

For TPD measurements, NH_3 chemisorbed catalyst sample was heated from initial temperature 30 to 700 °C with heating rate of

Table 1
Surface area and ammonia desorption measurement of silica, PTA and 10%PTA/silica

Entry	Catalyst	Surface area (m^2/g)	Ammonia desorbed (mmol/g)
1	Silica	241.1	0.41
2	PTA	9.1	1.7
3	10%PTA/silica	182.4	1.12

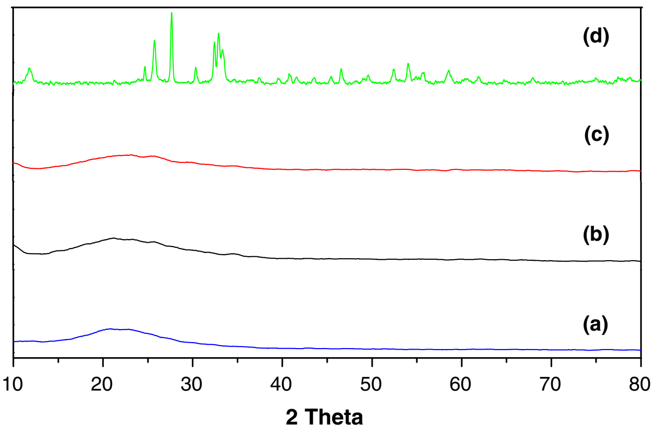

Fig. 1. XRD pattern of (a) silica; (b) 10%PTA/silica after the reaction; (c) 10%PTA/silica before the reaction and (d) bulk PTA.

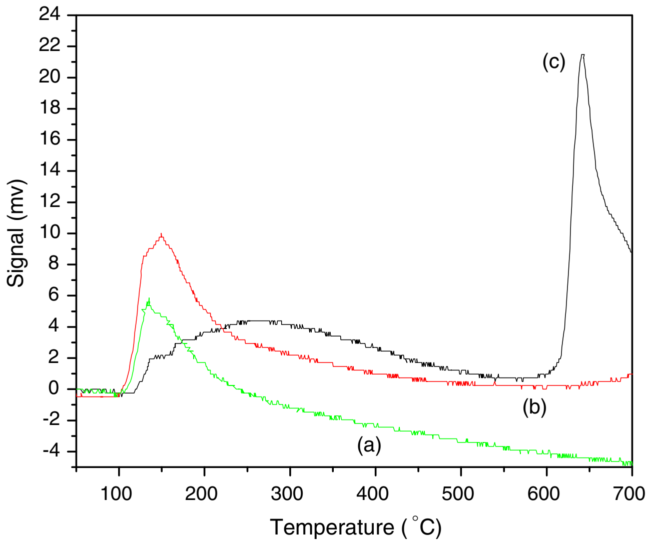

Fig. 2. Ammonia TPD studies of (a) silica; (b) 10%PTA/silica and (c) bulk PTA.