Nano magnetic sulfated zirconia ($Fe_3O_4@ZrO_2/SO_4^{2-}$) as a solid acid and reusable catalyst for the protection of hydroxyl groups under solvent-free condition

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Abstract: Nano magnetic sulfated zirconia ($Fe_3O_4@ZrO_2/SO_4^{2-}$) can be used as a magnetic solid acid catalyst for the conversion of alcohols to their corresponding trimethylsilyl ethers with hexamethyldisilazane (HMDS) at room temperature under solvent-free condition. Various advantages associated with this protocol include simple work up procedure, short reaction times, high product yields and easy recovery and reusability of the catalyst.

Keywords: Nano magnetic sulfated zirconia ($Fe_3O_4@ZrO_2/SO_4^{2-}$), Trimethylsilyl ethers, Hexamethyldisilazane, Protection, Solvent-free condition.

Introduction

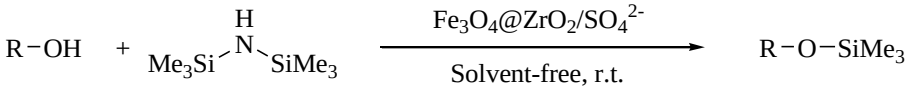
Protection of hydroxyl groups have received attention in recent years because of their role in synthetic organic [1] and analytical chemistry [2, 3]. Many multistep syntheses involve at least one step of hydroxyl group protection [4, 5]. Conversion of alcohols into their corresponding silylethers is one of the most popular and widely used strategy for protecting the hydroxyl groups [6]. 1,1,1,3,3,3-hexamethyldisilazane (HMDS) has emerged as the most versatile reagent in recent years for trimethylsilyl (TMS) protection of alcohols and phenols. HMDS is a stable, commercially available and inexpensive reagent. Its handling does not require special precautions, and the workup is convenient, because the only byproduct of the reaction is ammonia, which is simple to remove from the reaction medium [7]. However, the low silylation power of HMDS is the main drawback to its application [8], therefore several catalytic system have been developed to active of this reagent, such as $(CH_3)_3SiCl$ [9], I_2 [8], K-10 montmorillionite [10], ZnCl2 [11], cupric sulfate pentahydrate [12], lithium perchlorate supported on silica gel [13] and trichloroisocyanuric acid [14]. But, in most of these cases a long reaction time, drastic reaction conditions, or tedious workup is needed. In this communication we report an efficient nano magnetic sulfated zirconia solid acid catalyst for protection of hydroxyl groups with HMDS under solvent-free conditions at room temperature. Nano magnetic sulfated zirconia is an ecofriendly and inexpensive catalyst with high surface acidity and reusable capacity [15].

Experimental

To a mixture of alcohol (1.0 mmol) and HMDS (1.5 mmol) was added $Fe_3O_4@ZrO_2/SO_4^{2-}$ (80 mg) and the mixture was stirred at room temperature for an appropriate time (Table 1). After completion of the reaction, as indicated by thin-layer chromatography (TLC), the catalyst was separated by an external magnet and products were obtained by evaporation of the volatile portion under reduced pressure.

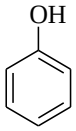
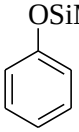
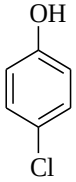
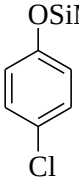
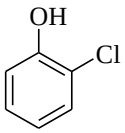
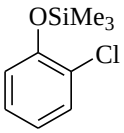
Result and discussion

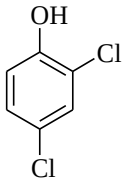
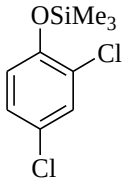
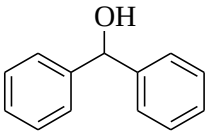
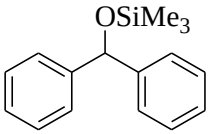
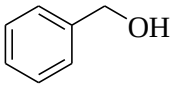
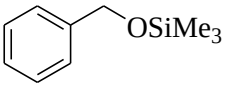
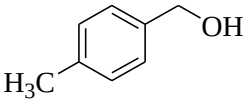
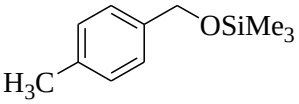
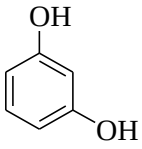
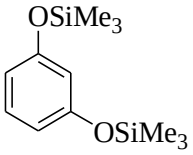
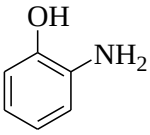
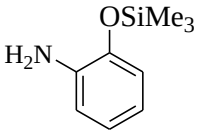
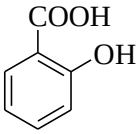
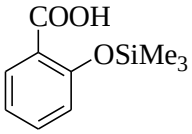
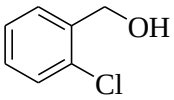
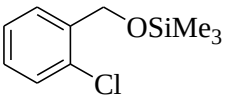
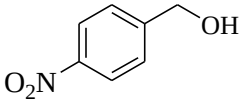
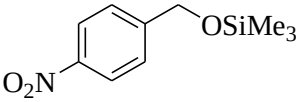
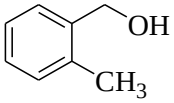
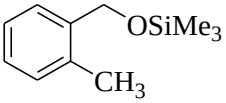
To assess the catalytic activity of $Fe_3O_4@ZrO_2/SO_4^{2-}$, it was applied in protection of alcohols with HMDS. In order to optimize reaction conditions, the reaction of benzyl alcohol and HMDS (mole ratio 1:1.5) as model reaction was chosen and the effects of the different amounts of solid acid catalyst $Fe_3O_4@ZrO_2/SO_4^{2-}$ were investigated (Scheme 1). Reaction of benzyl alcohol and HMDS in the presence of 80 mg of $Fe_3O_4@ZrO_2/SO_4^{2-}$ was completed after 15 min in solvent-free conditions; therefore, these conditions were applied to the trimethylsilylation of other hydroxyl groups.

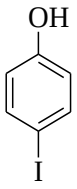
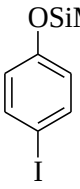
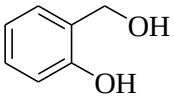
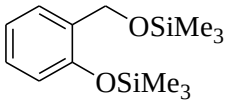


Scheme 1.

Table 1. $Fe_3O_4@ZrO_2/SO_4^{2-}$ catalyzed silylation of alcohols using HMDS at optimized conditions

Entry	Substrate	Product	Time (min)	Isolated yield (%)
1			40	95
2			50	95
3			75	90

4			100	94
5			30	90
6			15	90
7			12	88
8			34	90
9			20	90
10			20	90
11			25	88
12			25	90
13			12	90

14			120	87
15			100	85

Conclusion

In conclusion, we have demonstrated that sulfated zirconia supported on magnetic nanoparticles can acts as a novel, heterogeneous, efficient nano catalyst for the protection of hydroxyl groups through a green and facile method. This method offers several advantages including high yields, short reaction times, easy workup procedure, reusability of catalyst and environmentally benign reaction conditions.

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