Using $ZnFe_2O_4@ZnO$ as an efficient heterogeneous catalyst for silylation of alcohols with HMDS

Mahdi Heidari-Golafzani, Mahboubeh Rabbani*, Rahmatollah Rahimi, Alireza Azad

Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran.

E-mail: m_rabani@iust.ac.ir

Abstract

A mild, efficient and eco-friendly protocol for the chemoselective protection of benzylalcohol and primary alcohols is developed in presence of $ZnFe_2O_4@ZnO$ as the catalyst. Easy work-up, relatively short reaction times, excellent yields, low cost and reusability of the catalyst are the striking properties of this methodology, which can be considered to be one of the best and general routs for the protection of alcohols.

Keywords: $ZnFe_2O_4@ZnO$; Protection of alcohols; silylation; Benzylalcohol**.**

1. Introduction

Protection of organic functions are important processes during multi-step organic synthesis [1,2]. The choice of a method for the functional group's transformations depends on its simplicity, high yields of the desired products, short reaction times, low cost of the process and ease of the work-up procedures. Trimethylsilylation of labile hydroxyl groups is one of the most important strategies for the protection of alcohols [3]. These functional organosilyl ethers are stable under different conditions, soluble in non-polar solvents, have high thermal stability and are easy to eliminate under acid or base hydrolytic conditions [4]. They also help to increase the volatility for analysis in gas-chromatography and mass spectrometry (GC–MS) [5]. A variety of reagents have been used for the introduction of the trimethylsilyl group [6–13], among which hexamethyldisilazane (HMDS), as a cheap and commercially available reagent [14,15], is the most widely used. Its handling does not need special precautions, and the work-up is not time consuming, as the by-product of the reaction is ammonia, which is simple to remove from the reaction medium. Although, the main drawback is the poor silylating capacity of HMDS which is a deterrent in its application.

2. Experimental

2.1. General

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All yields refer to the isolated products. Determination of the purity of the substrate and monitoring of the reaction were accomplished by thinlayer chromatography (TLC) on a silica-gel polygram SILG/ UV 254 plates.

2.2. Preparation of $ZnFe_2O_4$@ZnO

In first step, the $ZnFe_2O_4$ was prepared by adding iron (III) chloride and zinc chloride to 70 mL ethylene glycol. The solution was stirred in a mechanical stirrer to achieve a clean solution. Then, 2.312 g NH_4Ac was added to the above solution during stirring. With continued practice of mixing, the color turns to dark yellow and foam appeared. This solution was sonicated for 40 min. Subsequently, the mixture was put into a Teflon-lined stainless steel autoclave of 120 mL capacity and sealed and maintained at 215 ˚C for 48 h. Finally, the system was allowed to cool to room temperature. The resulting black precipitate was collected by magnetic field decantation and washed by ethanol and distilled water in sequence for several times. The final products were dried in a vacuum system at 60 ˚C for 12 h.

In last step, $ZnFe_2O_4$@ZnO core-shell was synthesized as follows:

The 0.080 g of resulting $ZnFe_2O_4$ was re-dispersed in deionized water and 0.078 g zinc acetate was added to it, then sonicated for 2 h and ammonia added drop wise until the pH reached 11. The precursor solution was transferred into a round-bottom flask and refluxed for 3 h. After cooled to room temperature, the precipitate was placed in an oven at temperature of 80 ºC for 24 h and then placed into a vacuum oven at 80 ºC for 24 h.

2.3. Trimethylsilylation of alcohols

To a stirring mixture of the substrate (alcohol) (1 mmol), and catalyst (0.020 g) in CH_3CN (12 mL), HMDS (0.75 mmol, 0.120 g) was added at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the residue was washed with acetonitrile (5 mL). Evaporation of the solvent gave almost pure product(s). Further purification proceeded by bulb-to-bulb distillation under reduced pressure or re-crystallization to obtain pure silyl ether.

3. Results and discussion

3.1. Morphological characterization

Fig. 1.shows TEM image of $ZnFe_2O_4$@ZnO composite. As is clear in this figure, $ZnFe_2O_4$ particles have size about 120 nm, while $ZnFe_2O_4$@ZnO composite size is about 150 nm. Furthermore, as observed in TEM image indicated that a layer of ZnO with 30 nm thickness coated on $ZnFe_2O_4$ core. These results illustrated that the composite structure has been formed.

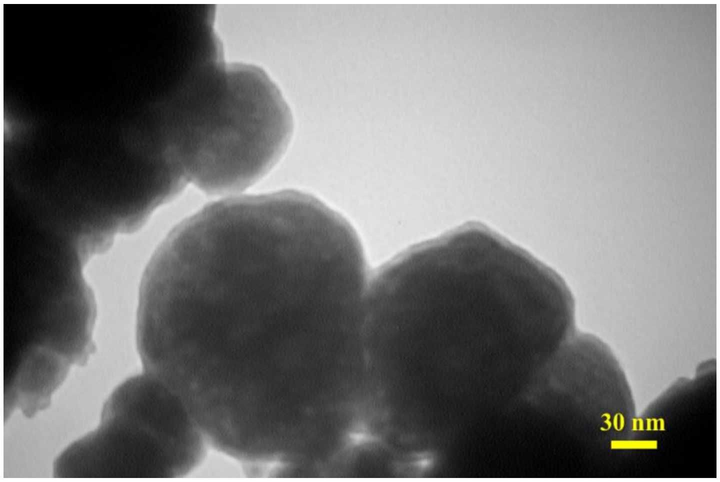


Fig. 1. The TEM image of $ZnFe_2O_4$@ZnO.

3.2. The X-ray powder diffraction

The XRD pattern of ZnO, $ZnFe_2O_4$ and $ZnFe_2O_4$@ZnO composite was illustrated in Fig. 2. As can be seen the peaks of the ZnO particles are in good agreement with hexagonal (wurtzite) ZnO (JCPDS Card, No. 36-1451). Also, at the XRD pattern of the prepared $ZnFe_2O_4$, the position of all diffraction peaks match well with those of lattice cubic system of $ZnFe_2O_4$ peaks (with standard card JCPDS No. 22-1012) at $2\theta=29.86^\circ, 35.21^\circ, 56.68^\circ, 62.25^\circ$. At the XRD patterns of $ZnFe_2O_4$@ZnO, it can be seen that in addition to $ZnFe_2O_4$ peaks, all added peaks are in good agreement with hexagonal ZnO [16].

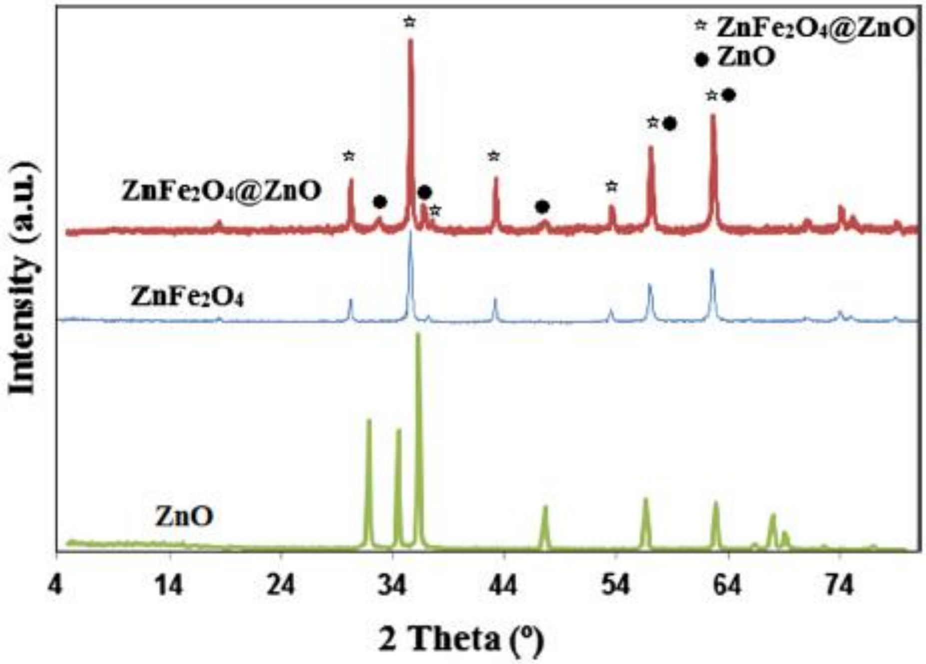


Fig. 2. The XRD pattern of ZnO, $ZnFe_2O_4$ and $ZnFe_2O_4$@ZnO.

3.3. Magnetic characterization

Vibrating sample magnetometer of pure $ZnFe_2O_4$ spheres and $ZnFe_2O_4$@ZnO composite were shown in Fig. 3. It indicated that all samples are superparamagnetic. The magnetic saturation (Ms) values of $ZnFe_2O_4$ and $ZnFe_2O_4$@ZnO were 76 and 29 emu/g, respectively. The Ms value of the composite spheres decreased because of the addition of non-magnetic components. The relatively high Ms value of the composites indicates that the spheres can be efficiently removed and recycled from the liquid reaction system, suggesting their promising applications as renewable photocatalyst.

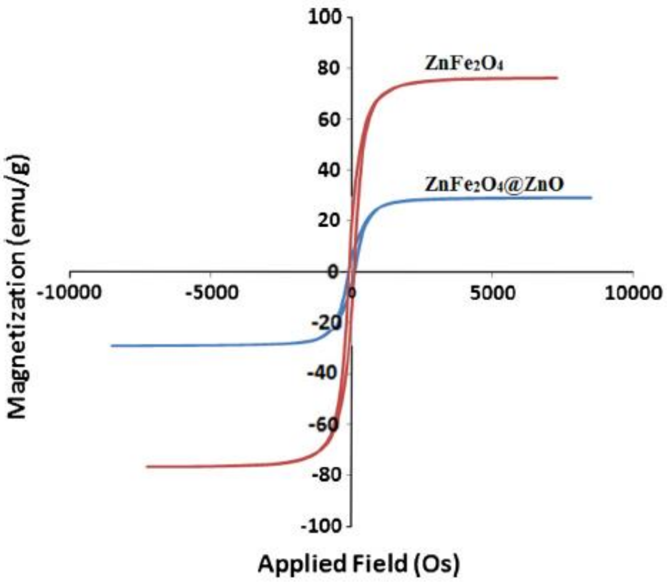
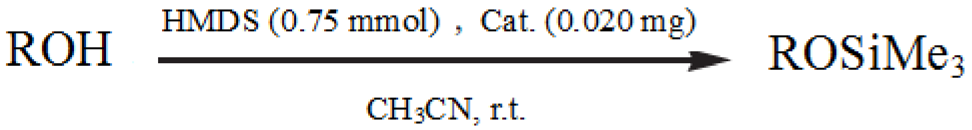


Fig. 3. The magnetic properties of $ZnFe_2O_4$ and $ZnFe_2O_4$@ZnO.

3.4. Catalytic study

In this study, we were interested to investigate the applicability of $ZnFe_2O_4$@ZnO in the promotion of the other organic reactions. Our investigations clarified that $ZnFe_2O_4$@ZnO is efficiently able to catalyze the trimethylsilyl protection of alcohols with HMDS. Initially, the standardization of the silylation reaction conditions was studied with investigating the effect of different molar ratio of reactants and different solvents (CH_2Cl_2, n-hexane, H_2O and CH_3CN) on the reaction, in terms of time and product yield. Our investigations illustrated that the best results can be obtained under the conditions showed in Scheme 1.



Scheme 1. Trimethylsilylation of alcohols.

After optimization of the reaction conditions, different types of alcohols were subjected to trimethylsilylation using this method (Table 1).

The obtained results showed that the trimethylsilylation of benzyl alcohol, proceeded efficiently with high isolated yields under the selected conditions (Table 1, entries 1). Also, para derivatives have excellent conversion relative to ortho derivatives, because para derivatives have minimum inhibitory Space in comparison to ortho substituent (Table 1).

Table 1 Trimethylsilylation of alcohols and phenols catalyzed by $ZnFe_2O_4@ZnO^{a,b}$.

Entry	Substrate	Product	Time (min)	Yield (%)
1	$PhCH_2OH$	$PhCH_2OSiMe_3$	5	94
2	$2\text{-}ClC_6H_4CH_2OH$	$2\text{-}ClC_6H_4CH_2OSiMe_3$	5	88
3	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CH_2OSiMe_3$	5	80
4	$2\text{-}MeC_6H4CH_2OH$	$2\text{-}MeC_6H_4CH_2OSiMe_3$	5	90
5	$4\text{-}Me_2CHC_6H_4CH_2OH$	$4\text{-}Me_2CHC_6H_4CH_2OSiMe_3$	5	85

[a] Products were identified spectroscopically and in comparison with authentic samples.

[b] Isolated yield.

4. Conclusions

In conclusion, we have developed an efficient method for the O-silyl protection of alcohols, producing remarkable high yields under very mild conditions. In contrast to some existing methods using potentially hazardous catalysts/additives, this new method offers the advantages such as low cost, availability and reusability of the reagent, avoidance of the use of any base, metal, or Lewis acid catalysts, relatively short reaction times, easy and clean work-up, high chemoselectivity, and no side reactions.

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