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Efficient and green oxidation of alcohols with *tert*-butyl hydrogenperoxide catalyzed by a recyclable magnetic core-shell nanoparticle-supported oxo-vanadium ephedrine complex

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ABSTRACT

A novel method for the oxidation of alcohols to the corresponding carbonyl compounds has been successfully developed using *tert*-butyl hydrogenperoxide (TBHP) in the presence of a catalytic amount of recyclable magnetic nanoparticle-supported oxo-vanadium ephedrine complex (VO(ephedrine)₂@MNPs) in PEG as a green solvent at 80 °C. The catalyst can be magnetically recycled and successfully reused in six subsequent reaction cycles with only slight decreases of its catalytic activity.

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1. Introduction

Recently, magnetic nanoparticles (MNPs) have been used as a new alternative to porous materials for supporting catalytic transformations [1–7]. Their simple magnetically driven separation from a liquid-phase reaction makes catalyst recovery and recycling much easier than by cross-flow filtration and centrifugation. Additionally, the MNP-supported catalysts also show high dispersion and reactivity with a high degree of chemical stability. By utilizing these advantages of magnetic nanoparticles over other supporting materials, various catalysts and ligands have been immobilized on these nanoparticles [8–12].

The selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is one of the

most challenging reactions in organic chemistry [13], because aldehydes and ketones are important intermediates in the synthesis of other organic compounds and they are utilized particularly in the manufacture of medicines, flavors, fragrances and aniline dyes [14]. Traditionally, oxidation of alcohols has been performed with a stoichiometric amount of metal oxidants, such as Cr(VI) salts [15], permanganate [16] and bromate [17] reagents. However, these reagents show poor atom efficiency and generate a large amount of environmentally ill-disposed heavy-metal waste. Therefore, catalytic oxidation methods, which employ a variety of transition metals such as Cu (I) [18], Ni (II) [19], Co (II) [20], Pd (II) and manganese oxides [21–24] using molecular oxygen [25,26], H₂O₂ [27] and TBHP [28,29] as oxidizing agents are well explored. Vanadium based catalytic systems also have shown potential for alcohol oxidation, in some cases proving effective for substrates where palladium catalysts display limited activity [30–35]. However, the major disadvantage of metal-based catalyst systems is their separation from the

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reaction solution by classical methods; they may possibly leave toxic traces of heavy metals in the products. Also, the reuse of the catalysts is difficult. These drawbacks can be overcome by immobilization of these catalysts on MNPs.

2. Experimental

2.1. General procedure for the oxidation of alcohols to carbonyl compounds

The alcohol (1 mmol) was added to a mixture of TBHP (1 mmol) and VO(ephedrine)₂@MNPs (50 mg) in PEG (1 mL), and then the mixture was refluxed at 80 °C for the time specified. The progress was monitored by TLC (EtOAc/*n*-hexane, 1/2). After completion of the reaction, the catalyst was separated from the product by an external magnet (within 5 s), and the mixture was washed with EtOAc (2×5 mL) and decanted. The decanted mixture was washed with 30% NaOH (5 mL) and the organic layer was dried over anhydrous Na₂SO₄. The evaporation of EtOAc under reduced pressure gave the pure products in 85–98% yields.

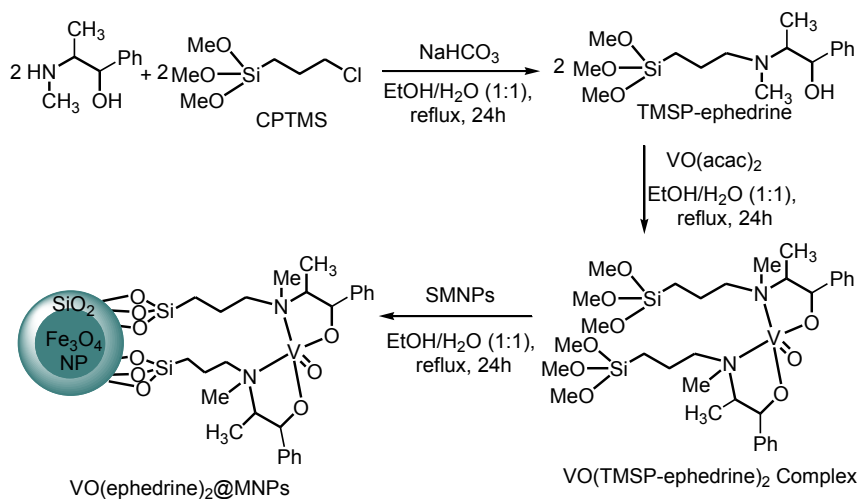
3. Results and discussions

In continuation of our studies on the synthesis and application of magnetic nanocatalysts [36–39], herein, we

report the catalytic properties of VO(ephedrine)₂@MNPs in the selective oxidation of alcohols to carbonyl compounds using TBHP as an oxidant. VO(ephedrine)₂@MNPs were synthesized according to our recently reported protocol for the preparation of the chiral oxo-vanadium (+)-pseudoephedrine complex supported on magnetic nanoparticles [38]. The process of the preparation VO(ephedrine)₂@MNPs shown in Scheme 1 (See the Supporting information for experimental details). The characterization of the catalyst was carried out by FT-IR, SEM, TGA and EDX techniques.

The explanation of characterization techniques has been provided in the Supporting information.

In order to optimize the reaction conditions, the oxidation reaction of benzyl alcohol to benzaldehyde was selected as a model reaction, and various parameters including solvent, temperature and the amount of catalyst were optimized to develop the scope of this reaction further (Table 1). We have conducted the reaction in different solvents such as CH₂Cl₂, CH₃CN, H₂O and PEG in the presence of 50 mg of the catalyst and 1 mmol of TBHP at room temperature (Table 1, entries 1–4), as shown in Table 1, in PEG, benzaldehyde was produced in 100% yield after 15 h. Therefore, PEG was chosen as the best reaction solvent. When the reaction was carried out at 80 °C, the rate of reaction was increased and the reaction was completed



Scheme 1. The preparation of VO(ephedrine)₂@MNPs

Table 1

The selective oxidation of benzyl alcohol to benzaldehyde using TBHP under different conditions.

Entry	Solvent	T (°C)	Catalyst (mg)	Time (h)	Conversion (%)
1	CH ₂ Cl ₂	rt	VO(ephedrine) ₂ @MNPs (50)	24	No Reaction
2	CH ₃ CN	rt	VO(ephedrine) ₂ @MNPs (50)	24	No Reaction
3	H ₂ O	rt	VO(ephedrine) ₂ @MNPs (50)	24	No Reaction
4	PEG	rt	VO(ephedrine) ₂ @MNPs (50)	15	100
5	PEG	80	VO(ephedrine)₂@MNPs (50)	3	100^a
6	PEG	80	None	24	20
7	PEG	80	VO(ephedrine) ₂ @MNPs (30)	8	100
8	PEG	80	VO(ephedrine) ₂ @MNPs (40)	7	100
9	PEG	80	Fe ₃ O ₄ MNPs (50)	15	50

^a The bold letters represent the most effective reaction conditions.

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