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Short Communication

Synthesis, characterization and catalytic property of chiral oxo-vanadium (+)-pseudoephedrine complex supported on magnetic nanoparticles Fe_3O_4 in the cyanosilylation of carbonyl compounds

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ABSTRACT

Vanadium complex of pseudoephedrine immobilized on magnetic nanoparticle Fe_3O_4[VO(Pseudoephedrine)@MNPs] was prepared and characterized by UV–vis, SEM, XRD, TGA, EDX, FT-IR, AGFM and elemental analysis techniques. VO(Pseudoephedrine)@MNPs was found to catalyze the cyanosilylation of carbonyl compounds using TMSCN in good yields with 8–25% enantiomeric excesses under solvent-free conditions at room temperature. The catalyst was recycled up to 15 times with little loss of activity and enantioselectivity.

1. Introduction

Magnetic nanoparticles (MNPs) have gained a significant place in catalysis as a magnetically separable catalyst. The separation of magnetic nanoparticles from the reaction mixtures is driven by an external magnet, which makes the recovery and reusability of the catalyst easier and avoids loss of catalyst associated with traditional methods. Also, the activity and selectivity of magnetic nanocatalysts can be manipulated by their surface modification. In addition to these points, the magnetic properties of nanoparticles are stable and can tolerate the chemical environment except those that are acidic/corrosive [1–3].

Recently, an increasing interest has been focused on catalytic activity of the vanadium Schiff base complexes derived from chiral and achiral amino alcohols [4–9]. The main disadvantage of a catalyst based on vanadium is their separation from the products which needs tedious work-up processes in many reactions. This drawback can be overcome by immobilizing these catalysts on MNPs, which can be easily removed from the reaction mixture by magnetic separation.

The cyanosilylation of carbonyl compounds to form new C–C bonds and to protect alcohol functions is an important reaction as the *O*-protected cyanohydrins can be transformed into a wide range of important intermediates such as α-hydroxy acids, α-amino acids, β-amino alcohols, vicinal diols, 1,2-diamines and other valuable building blocks [10–12]. The main synthetic route for the preparation of silylated cyanohydrins is the addition reaction of TMSCN to carbonyl compounds. The reaction is mostly catalyzed by Lewis acids or base catalysts [13–20], although these protocols represent considerable progress, however recover and reuse of catalysts are difficult.

In continuation of our studies on magnetic nanocatalysts [21–23], herein, we report the synthesis, characterization and catalytic property of new chiral VO(Pseudoephedrine)@MNPs in the cyanosilylation of carbonyl compounds.

2. Experimental

2.1. Instruments

The X-ray powder diffraction (XRD) data were collected on an X 'Pert MPD Philips diffractometer. The SEM image was obtained by VEGA TESCAN. The thermogravimetric analysis (TGA) was carried out on a Bähr STA 503 instrument (Germany). The magnetic measurements were carried out in an Alternating Gradient Force Magnetometer (AGFM). UV–vis spectra were recorded on a JASCOV-550 UV–vis spectrophotometer. The conversion and optical rotation were determined by an Agilent GC system and a Perkin Elmer Model 341 Polarimeter respectively.

2.2. General procedure for the cyanosilylation of carbonyl compounds

VO(Pseudoephedrine)@MNPs (50 mg, 1.75 mol%) was added to a mixture of carbonyl compound (1 mmol) and TMSCN (0.119 g,

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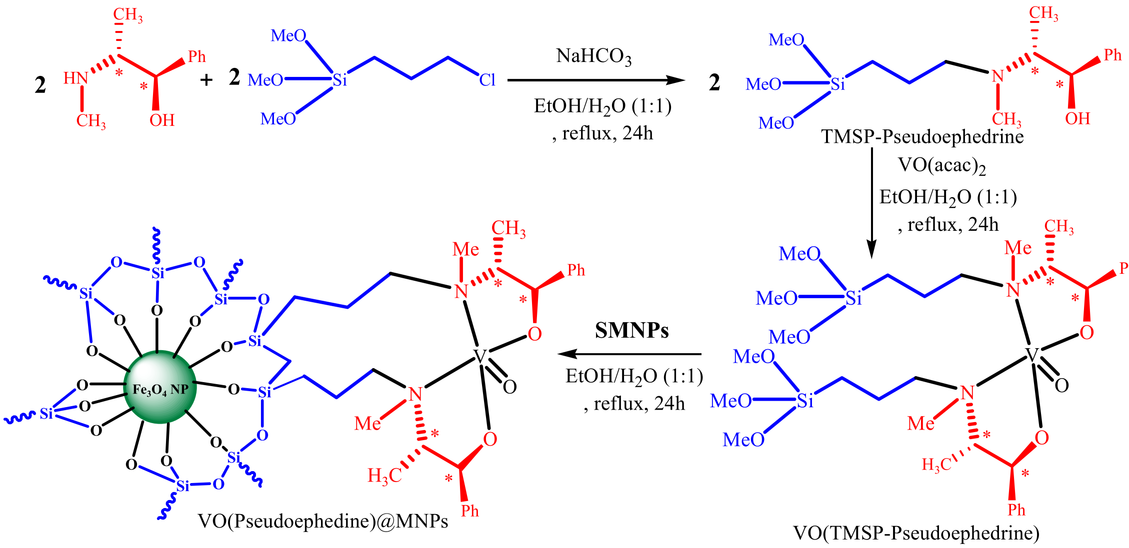

Scheme 1. Synthesis of VO(Pseudoephedrine)@MNPs.

1.2 mmol) under solvent-free conditions at room temperature and stirred for the appropriate time. The progress was monitored by TLC. After completion of the reaction, the catalyst was separated by an external magnet and the mixture was washed with CH_2Cl_2 (2 × 5 mL). The evaporation of CH_2Cl_2 under reduced pressure gave the pure products in 75–99% yields.

3. Results and discussions

3.1. Preparation and characterization of VO(Pseudoephedrine)@MNPs

To prepare the catalyst, first, (+)-Pseudoephedrine hydrochloride was reacted with (3-chloropropyl)-trimethoxysilane to give *N*-(3-trimethoxysilane) propyl pseudoephedrine (TMSP-Pseudoephedrine) ligands. The resulting TMSP-Pseudoephedrine ligand was then allowed to react with vanadium acetyl acetonate to produce the VO(TMSP-Pseudoephedrine) complex. Finally, the reaction of silica-coated Fe_3O_4 ($Fe_3O_4@SiO_2$, SMNPS) which can be easily prepared according to the reported procedure [24] with obtained VO(TMSP-Pseudoephedrine) complex nanoparticles led to VO(Pseudoephedrine)-functionalized magnetic $Fe_3O_4@SiO_2$ nanoparticles [VO(Pseudoephedrine)@MNPs]. The process of the preparation of VO(Pseudoephedrine)@MNPs is shown in Scheme 1 (experimental details were provided in the Supplementary data).

The characterization of the catalyst was carried out by UV–vis, SEM, XRD, TGA, EDX, FT-IR, AGFM and elemental analysis (see Supplementary data).

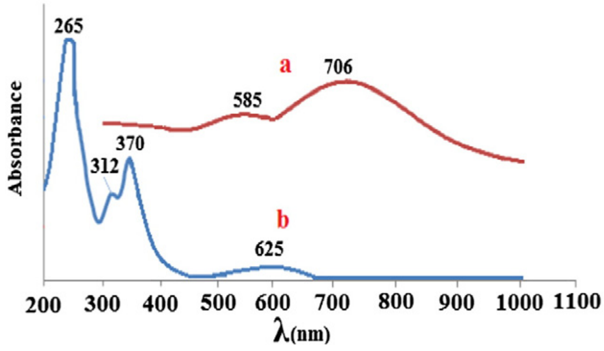

Fig. 1. UV–vis spectra of a) $VO(acac)_2$ and b) VO(Pseudoephedrine)@MNP complex.

UV–vis spectroscopy was applied to the characterization of oxovanadium *N*-(3-trimethoxysilane) propyl pseudoephedrine [VO(TMSP-Pseudoephedrine)] complex. UV–vis spectrum of the VO(TMSP-Pseudoephedrine) complex (Fig. 1) shows three bands at 265–312 (π–π* transition of phenyl ring on ligand), 320–420 (may be assigned as a ligand-to-metal charge transfer (LMCT) transition originating from the oxygen and nitrogen on pseudoephedrine ligand to the empty d orbital at the vanadium center) and 420–650 nm (d–d transition), this band is not always observed, being often buried

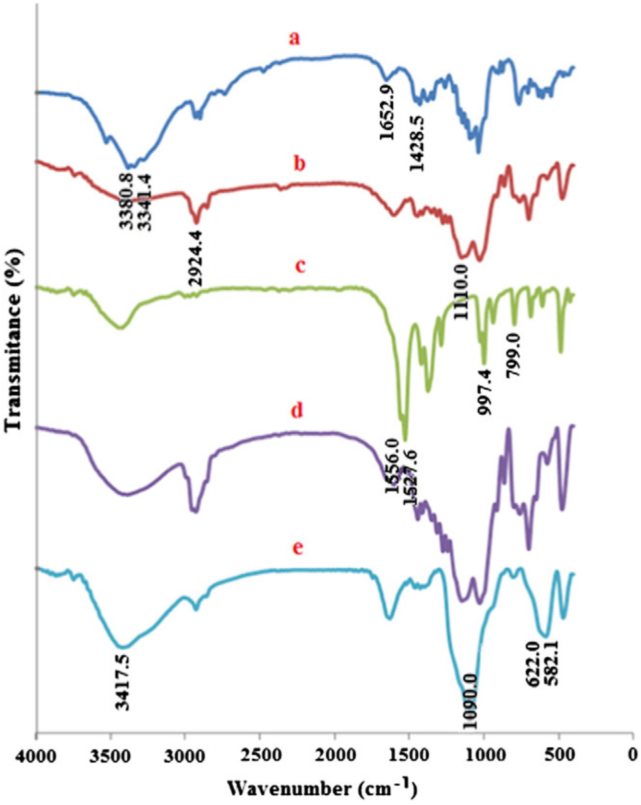

Fig. 2. FTIR spectra of (a) (+)-Pseudoephedrine hydrochloride, (b) TMSP-Pseudoephedrine, (c) $VO(acac)_2$, (d) VO(TMSP-Pseudoephedrine) complex and (e) VO(Pseudoephedrine)@MNPs.