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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

Amin Rostami [a,b,*], Bahareh Atashkar [a]

[a] Department of Chemistry, Faculty of Science, University of Kurdistan, 66177-15175 Sanandaj, Iran
[b] Research Centre of Nanotechnology, University of Kurdistan, P.O. Box 416, Sanandaj, Iran

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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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[*] Corresponding author at: Research Centre of Nanotechnology, University of Kurdistan, P.O. Box 416, Sanandaj, Iran. Tel.: +98 9183730910; fax: +98 8716624004.
E-mail address: a_rostami372@yahoo.com (A. Rostami).

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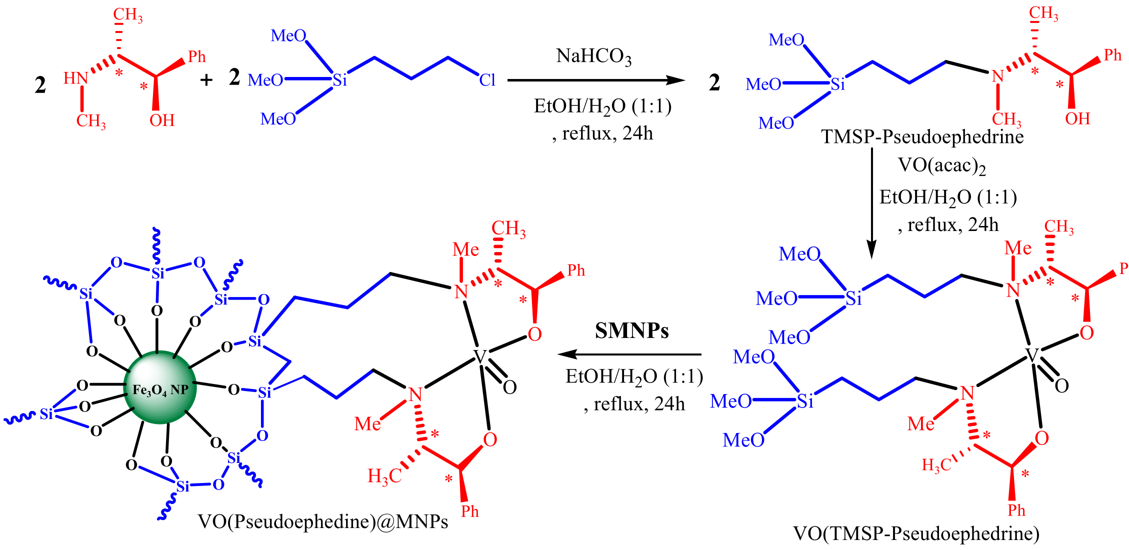


Scheme 1. Synthesis of VO(Pseudoephedrine)@MNPs.

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).

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

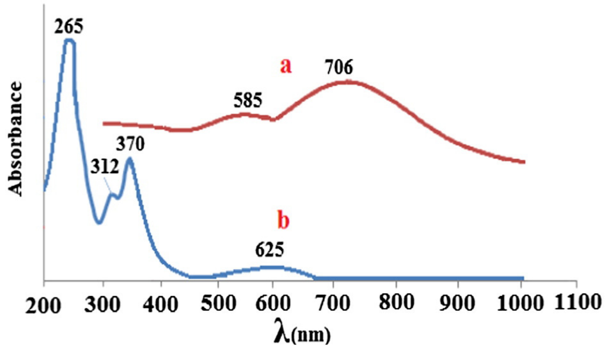


Fig. 1. UV–vis spectra of a) $VO(acac)_2$ and b) VO(Pseudoephedrine)@MNP complex.

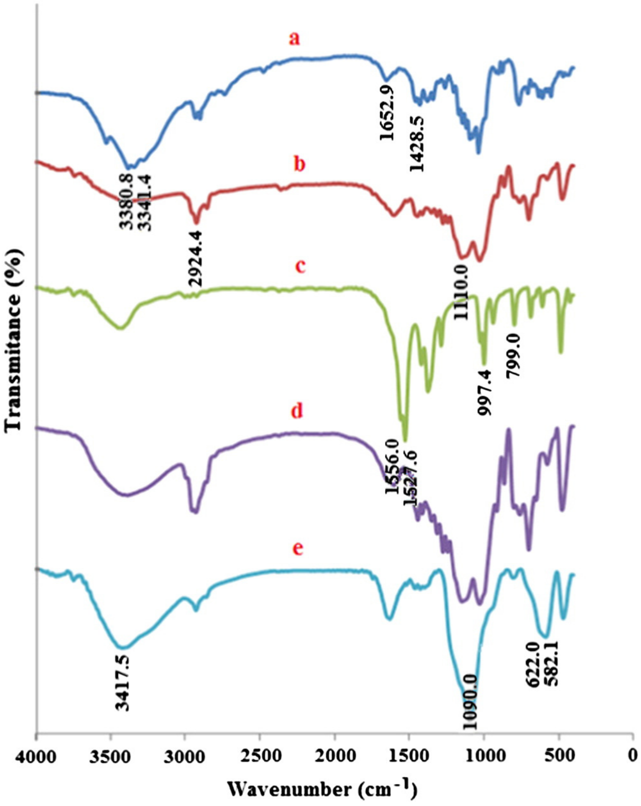
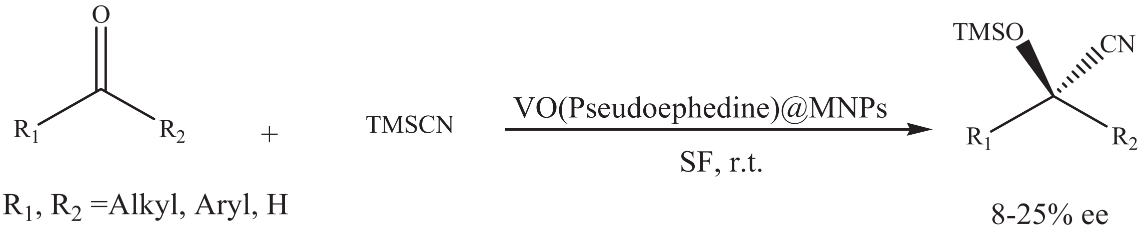


Fig. 2. FTIR spectra of (a) (+)-Pseudoephedrine hydrochloride, (b) TMSP-Pseudoephedrine, (c) $VO(acac)_2$, (d) VO(TMSP-Pseudoephedrine) complex and (e) VO(Pseudoephedrine)@MNPs.



Scheme 2. VO(Pseudoephedrine)@MNPs catalyzed the synthesis of silylated cyanohydrins.

beneath a high intensity charge transfer band (or more accurately the low energy tail of that band), and when it is observed it is generally a shoulder [25]. These bands differ from that of the $VO(acac)_2$ (Fig. 1) [26].

The SEM image of VO(Pseudoephedrine)@MNPs confirmed that the catalyst was made up of uniform nanometer-sized particles 28–32 nm (Fig. S1).

The position and relative intensities of all peaks in the XRD pattern of VO(Pseudoephedrine)@MNPs conform well with the standard XRD pattern of Fe_3O_4 (Fig. S2) [27], indicating retention of the crystalline cubic spinel structure during functionalization of MNPs. The interlayer spacing (d_{hkl}), calculated using the Bragg equation, agrees well with the data for standard magnetic (Table S1).

The TGA curve of the VO(Pseudoephedrine)@MNPs shows a weight loss of about 19% from 260 to 600 °C, resulting from the decomposition of the complex grafting to the silica-coated magnetic nanoparticle (SMNP) surface (Fig. S3). The loading of the complex in VO(Pseudoephedrine)@MNPs can be calculated from TGA and quantitative elemental analysis, which confirmed a loading of approximately 0.35 mmol/g.

EDX spectrum shows the elemental composition (V, O, C, N, Si and Fe) of the VO(Pseudoephedrine)@MNPs (Fig. S4).

Successful functionalization of the SMNPs can be inferred from FT-IR techniques. The FTIR spectrum of VO(Pseudoephedrine)@MNPs shows peaks that are characteristic of a functionalized VO(Pseudoephedrine) group, which clearly differs from that of the (+)-Pseudoephedrine hydrochloride, TMSP-Pseudoephedrine, $VO(acac)_2$ and VO(TMSP-Pseudoephedrine) complex (Fig. 2). The interpretation of FTIR spectra has been provided in the Supplementary data.

Superparamagnetic particles are beneficial for magnetic separation, the magnetic measurements of MNPs and VO(Pseudoephedrine)@MNPs were carried out in an AGFM (Fig. S5). As expected, the bare MNPs showed the higher magnetic value (saturation magnetization, Ms) of 74.3 $emug^{-1}$ [28], and the Ms value of VO(Pseudoephedrine)@MNPs is decreased due to the silica coating and the layer of the grafted catalyst (30.4 $emug^{-1}$). It has been reported that the Fe_3O_4 nanoparticles with a value of coercivity (coercive field, Hc) lower than 20 Oe could be called superparamagnetic. VO(Pseudoephedrine)@MNPs have an Hc of 1.12 Oe and the remanent magnetization (Mr) of 1.23 $emug^{-1}$ respectively. As a result, the modified MNPs have a typical superparamagnetic behavior [29] and can be efficiently attracted with a small magnet.

Table 1
Evaluation of the effect of the catalyst on the cyanosilylation reaction between benzaldehyde (1 mmol) and TMSCN (1.2 mmol) under solvent-free conditions at room temperature.

Entry	Catalyst (mg)	Time/min	Converted yield (%)[a]
1	Catalyst-free	24 h	20
2	Fe_3O_4 NP (50)	24 h	30
3	VO(Pseudoephedrine)@MNPs (40)	300	100
4	VO(Pseudoephedrine)@MNPs (45)	250	100
5	VO(Pseudoephedrine)@MNPs (50)	180	100
6	VO(Pseudoephedrine)@MNPs (55)	180	100
7	VO(Pseudoephedrine)@MNPs (60)	175	100

[a] Conversion was determined by GC.

All together, the aforementioned results confirmed the formation of a silica layer around the Fe_3O_4 nanoparticles and the VO(Pseudoephedrine)-functionalization of this core–shell structure. Unfortunately, due to the magnetic properties of VO(Pseudoephedrine)@MNPs it is actually impossible to further characterize this material by using solid-state NMR spectroscopy.

3.2. The catalytic applications of VO(Pseudoephedrine)@MNPs in the cyanosilylation of carbonyl compounds

VO(Pseudoephedrine)@MNPs was tested as a magnetically separable heterogeneous nanocatalyst for the cyanosilylation of carbonyl compounds using TMSCN under solvent-free conditions at room temperature (Scheme 2).

In order to optimize the reaction conditions, we evaluated the influence of different amounts of catalyst on the cyanosilylation of benzaldehyde as a model compound under solvent-free conditions at room temperature (Table 1). As shown in Table 1, the reaction was incomplete in the absence of a catalyst even after 24 h (Table 1, entry 1). 50 mg of VO(Pseudoephedrine)@MNPs was found to be ideal for complete reaction of benzaldehyde with TMSCN (1.2 mmol).

In order to generalize the scope of the reaction, a series of structurally diverse carbonyl compounds was subjected to the cyanosilylation reaction under the optimized reaction conditions, and the results are presented in Table 2. The overall yields of products are in the range of 75–99% and an enantiomeric excess (ee) of 8–25% silylated cyanohydrins was obtained (Table 2, entries 1–17). The effect of temperature, solvents and different amounts of catalyst and TMSCN in the cyanosilylation of benzaldehyde on the enantiomeric excess were evaluated; in all cases the observed enantiomeric excess was low.

The ability to easily recover and recycle of VO(Pseudoephedrine)@MNPs was investigated. We have found that this catalyst was rapidly recovered and demonstrated remarkably excellent recyclability; after the first use of catalyst in the cyanosilylation reaction of benzaldehyde, the catalyst was separated by an external magnet (Fig. 3), washed thoroughly with ether, and reused for subsequent experiments under similar reaction conditions. As shown in Fig. 4, the catalyst was reusable without any significant loss of activity and enantioselectivity for the 15th recycling experiment (corresponding to a total TON = 850).

The comparison of the activity and enantioselectivity of soluble oxo-vanadium complex bearing pseudoephedrine ligand [VO(TMSP-Pseudoephedrine)] and VO(Pseudoephedrine)@MNPs (heterogenized complex) in the model reaction was investigated (Table 3).

As shown in Table 3, the homogeneous complex shows more activity and selectivity than the heterogenized complex. However, two major advantages of the magnetically heterogenized complex as catalyst are: (a) easily separation and (b) high reusability.

4. Conclusion

In conclusion, the first magnetic nanoparticle-supported VO(Pseudoephedrine) for use as a robust heterogeneous catalyst was designed. The VO(Pseudoephedrine)@MNPs was used as an efficient and reusable catalyst in the cyanosilylation of carbonyl compounds using TMSCN under solvent-free conditions at room temperature. In these reactions,

Table 2
VO(Pseudoephedrine)@MNPs (50 mg) catalyzed the cyanosilylation of aldehydes and ketones using TMSCN (1.2 mmol) under solvent-free conditions at room temperature.

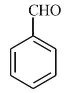
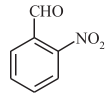
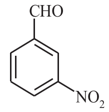
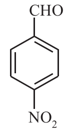
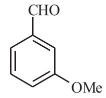
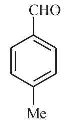
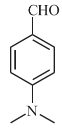
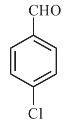
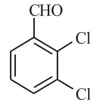
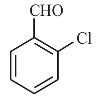
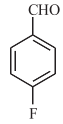
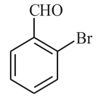
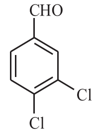
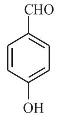
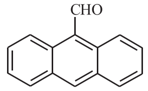
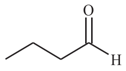
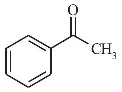
Entry	Substrate	Time (min)	Isolated yield (%)[a]	ee (%)[b]
1		180	97	25
2		200	96	18
3		195	92	20
4		182	99	22
5		205	95	20
6		240	94	19
7		540	89	9
8		180	98	23
9		180	97	20
10		190	98	18
11		205	89	18
12		180	97	15
13		180	98	20
14		195	90	10
15		190	96	8
16		180	75	15
17		300	85	17
18		220	88	–

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Fig. 3. A reaction mixture in the absence (left) or presence of a magnetic field (right).

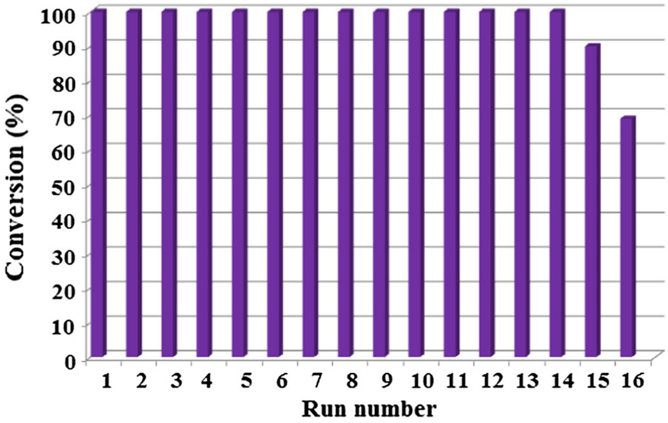

Fig. 4. The recycling experiment of VO(Pseudoephedrine)@MNPs for the cyanosilylation of benzaldehyde (1 mmol) using TMSCN (1.2 mmol) under solvent-free conditions at room temperature.

Table 3
Comparison of the activity and enantioselectivity of VO(TMSP-Pseudoephedrine) and VO(Pseudoephedrine)@MNPs in the cyanosilylation of benzaldehyde using TMSCN under solvent-free conditions at room temperature.

Entry	Catalyst	Time (min)	Converted yield (%)[a]	ee (%)
1	VO(TMSP-Pseudoephedrine)	100	100	30
2	VO(Pseudoephedrine)@MNPs	180	100	25

[a] The converted yield was determined by GC.

an enantiomeric excess (ee) of 8–25% silylated cyanohydrins was obtained. Furthermore, the catalyst combines high reactivity with facile catalyst recovery and excellent reusability of up to 15 runs, which makes it a promising material for practical and large-scale applications. Studies to further explore the potential of this powerful immobilization strategy for the preparation of other magnetically recoverable chiral catalysts are underway.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.08.029.

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