



Acetylacetonate complexes of vanadium and molybdenum supported on functionalized boehmite nano-particles for the catalytic epoxidation of alkenes



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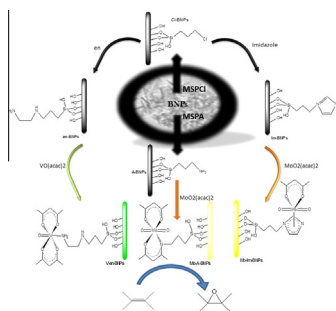
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HIGHLIGHTS

- Functionalization of BNPs with $(\text{OMe})_3\text{Si}(\text{CH}_2)_3\text{X}$, X = Cl or NH_2 .
- Replacement of the chlorine atom with ethylene di-amine or imidazole.
- Supporting of Mo and V complexes on functionalized BNPs.
- Epoxidation of different alkenes using these grafted BNPs catalysts.

GRAPHICAL ABSTRACT

Boehmite nano-particles were prepared via hydrothermal assisted sol-gel processing of aluminium 2-butoxide. The produced powder was covalently functionalized with 3-(tri-methoxysilyl) propylchloride or 3-(tri-methoxysilyl) propylamine and then the terminal chlorine groups were changed by refluxing with ethylenediamine (en) or imidazole (Im). Then all the functionalized boehmite nano-particles were used to support bis-acetylacetonato-oxo vanadium or bis-acetylacetonato-di-oxo molybdenum complexes. These catalysts were applied in epoxidation of *cis*-cyclooctene and other alkenes. The catalytic procedures with all catalysts were optimized for different parameters such as solvent, oxidant and temperature.



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ABSTRACT

Hydrothermal derived boehmite nano-particles (BNPs), with high surface area and high degree of surface hydroxyl groups, were covalently functionalized with 3-(tri-methoxysilyl) propylchloride or 3-(tri-methoxysilyl) propylamine and then the terminal chlorine groups were changed by refluxing with ethylenediamine or imidazole. Then all the functionalized boehmite nano-particles were used to support bis-acetylacetonato-oxo vanadium or bis-acetylacetonato-di-oxo molybdenum complexes. These supported catalysts were characterized by FT-IR, CHN, ICP and TEM analysis. Then these catalysts were applied in the epoxidation of *cis*-cyclooctene, and the catalytic procedures were optimized for different parameters such as the solvent and oxidant. The reactions progress was investigated by gas-liquid chromatography (GLC) analysis. The optimized conditions were found as 0.5 mmol *cis*-cyclooctene and 1.0 mmol *tert*-butylhydroperoxide (TBHP) in 0.5–1 mL CCl_4 with 20 mg catalyst at reflux temperature. Recycling experiments revealed that these heterogeneous nano-catalysts could be repeatedly applied for the epoxidation of *cis*-cyclooctene. The optimized conditions were also used for the epoxidation of some other substituted alkenes successfully.

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1. Introduction

Epoxides are known as one of the most valuable precursors for the production of some important chemicals such as chiral pharmaceuticals, pesticides, detergents, epoxy paints, agrochemicals, different polymers, surfactants, antistatic agents, corrosion protection agents, lubricating oils, textiles, sweeteners, cosmetics and perfumes [1–4].

Formerly, some soluble complexes of Cr, Mo, Re, Ni, Co, Mn, V, Cu, Ru and Ti were employed as active homogenous catalysts in epoxidation of alkenes [5–8]. However, most of these catalysts are expensive and contaminate the environment and it is desirable to immobilize them onto insoluble supports. Immobilization can also efficiently increase the reactivity of catalysts by homogeneous dispersion of active metal sites onto the surface of support and/or preventing the formation of oxo-bridged dimeric or polymeric complexes which is deleterious for the catalytic activity [9,10].

Different organic, inorganic and hybrid materials can be used as insoluble supports. Organic insoluble supports include polymers such as poly-styrene [11,12]. Hybrid organic-inorganic materials such as zirconium poly(styrene-phenylvinylphosphonate)-phosphate [13] have been used for this purpose as well. Activated carbon [14], carbon nanotubes [9,15,16], nanostructured ordered carbon material [9,17], porous silica [2,18], MCM-41 [19,3], SBA-15 [9,20–22], zeolites [1,9,23–27], and magnetic nano-particles [28] have been also used as insoluble supports. Inorganic supports generally have higher chemical stability and higher surface area. Also in the most cases, their surfaces were covered with hydroxyl groups which provide valuable sites for the modification with various functionalities. Boehmite (γ -AlOOH) is one of these inorganic insoluble supports. Besides its reactivity to catalyze some organic reactions, boehmite was widely used in our research group to anchor different metal complexes covalently, and then used as catalyst in epoxidation of *cis*-cyclooctene [29,30].

In continuation of our interest to boehmite as an insoluble support, here we used grafted boehmite nano-particles (BNPs) with 3-(Trimethoxysilyl)-propylamine (MSPA) or 3-(Trimethoxysilyl)-propylchloride (MSPCl) to anchor ethylenediamine (en) or imidazole (Im). Then they were used to support two complexes of vanadium or molybdenum and employed in epoxidation of different alkene substrates.

2. Materials and methods

Solvents and reagents were purchased from Merck or Fluka and used without any further purification. IR spectra were recorded on a Rayleigh WQF-500 FTIR instrument at 4 cm^{-1} resolution, using KBr pellets. Powder X-ray diffraction (PXRD) patterns were collected on a Phillips PW-1800 or STOE diffractometer with Cu K α radiation. Elemental analyses were carried out on a Leco TruSpec CHN Analyzer. Electron microscopy was performed on a JEOL JSM-6360LV transmission electron microscope. Gas-liquid chromatography (GLC) was carried out on a Shimadzu GC-16A instrument using a 2 m column, peaked with silicon DC-200.

3. Experimental

3.1. Preparation of boehmite nano-particles (BNPs)

Aluminium 2-butoxide was synthesized from aluminium and 2-butanol according to the general preparation procedure of aluminium alkoxides [30]. The prepared aluminium alkoxide was hydrothermally hydrolysed, according to our previous report

[29,31], and the produced powder was filtered off and dried at 100 °C overnight. Then the produced BNPs were used as catalytic support.

3.2. Preparation of supported bis-acetylacetonato-oxo vanadium complex on boehmite nano-particles functionalized with ethylenediamine

For the preparation of functionalized BNPs, 1.00 g BNPs was refluxed with MSPCl (400.0 μl , 2.2 mmol) in dry toluene (50.0 ml) for 24 h (Scheme 1). The functionalized BNPs (Cl-BNPs) as a white solid was filtered off, washed three times with dry toluene and dried at 100 °C overnight. Then 1.00 g Cl-BNPs was refluxed with en (500.0 μl , 16 mmol) in dry toluene (50.0 ml) for 48 h (Scheme 1) in order to replace the terminal chlorine atoms. During this process, in 6 h intervals, 1.2 ml triethylamine was added to the refluxed solution to ease the replacement of chlorine atom. At the end, en functionalized BNPs (en-BNPs) was filtered off, washed three times with dry toluene and dried at 100 °C overnight.

VO(acac)₂ complex was then used for supporting on en-BNPs (Scheme 1). For this purpose, 25 ml chloroform was added to VO(acac)₂ (0.3 g, 1.1 mmol) and en-BNPs (0.5 g) and the mixture was refluxed for 12 h. Then the mixture was cooled down, filtered off and the precipitate was washed several times with chloroform and dried at 100 °C overnight to give V-en-BNPs sample.

3.3. Preparation of supported bis-acetylacetonato-di-oxo molybdenum complex on boehmite nano-particles functionalized with imidazole

The chlorine functionalized BNPs (Cl-BNPs) was prepared according to the above procedure. Then 1.00 g Cl-BNPs was refluxed with imidazole (138.4 μl , 2.5 mmol) and KI (16.6 mg, 0.1 mmol) in acetonitrile (30.0 ml) for 48 h (Scheme 1) in order to replace the terminal chlorine atoms. The imidazole functionalized BNPs (Im-BNPs) was then filtered off, washed three times with acetonitrile and dried at 100 °C overnight.

MoO₂(acac)₂ complex was then used for supporting on Im-BNPs (Scheme 1). For this purpose, 15 ml toluene was added to MoO₂(acac)₂ (0.36 g, 1.1 mmol) and Im-BNPs (0.5 g) and the mixture was refluxed for 6 h. Then the mixture was cooled down, filtered off and the precipitate was washed several times with toluene and dried at 100 °C overnight to give Mo-Im-BNPs sample.

3.4. Preparation of supported bis-acetylacetonato-di-oxo molybdenum complex on boehmite nano-particles functionalized with amine

For the preparation of amine functionalized BNPs, 1.00 g BNPs was refluxed with MSPA (61 μl , 0.35 mmol) in dry toluene (50.0 ml) for 24 h (Scheme 1). The amine functionalized BNPs (A-BNPs) as a white solid was filtered off, washed three times with dry toluene and dried at 100 °C overnight.

MoO₂(acac)₂ complex was then used for supporting on A-BNPs (Scheme 1). For this purpose, 20 ml chloroform was added to MoO₂(acac)₂ (0.23 g, 0.7 mmol) and A-BNPs (0.5 g) and the mixture was refluxed for 24 h. Then the mixture was cooled down, filtered off and the precipitate was washed several times with chloroform and dried at 100 °C overnight to give Mo-A-BNPs sample.

3.5. Catalytic epoxidation of alkenes

In a typical procedure, a 25 ml round bottom flask, equipped with a magnetic stirrer bar and a condenser, was charged with an alkene (0.5 mmol), an oxidant, the catalyst (V-en-BNPs, Mo-Im-BNPs or Mo-A-BNPs) and solvent, and the mixture was then refluxed. All the reactions were performed at least two times and the reaction progress was monitored by GLC. Since different

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