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Synthesis of titanium–triazine based MCM-41 hybrid materials as catalyst for the asymmetric epoxidation of cinammyl alcohol

Ruth Ballesteros, Mariano Fajardo, Isabel Sierra*, Isabel del Hierro*

Departamento de Química Inorgánica y Analítica, E.S.C.E.T., Universidad Rey Juan Carlos, C/Tulipan S/N, 28933, Móstoles, Madrid, Spain

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ABSTRACT

A molecular precursor approach involving tethering procedures was used to produce site isolated titanium-supported asymmetric epoxidation catalysts. This was done by first modifying the support in one step with a mixture of silanes: the synthesized triazine propyl triethoxysilane as functional linker and hexamethyldisilizane as capped agent, to increase the hydrophobicity of the support and mask the remaining silanol groups. In addition, $[Ti(OPr^i)_4]$ and $[\{Ti(OPr^i)_3(OMent)\}_2]$ (MentO = 1R,2S,5R-(−)-menthoxo) complexes were heterogenized by reaction with the modified MCM-41. Finally, after $[Ti(OPr^i)_4]$ immobilization on to the organomodified support the reaction with the chiral auxiliary (+)-diethyl-L-tartrate was accomplished. All the materials were characterized by elemental analysis, X-ray diffraction, nitrogen adsorption techniques, FT-IR, ICP-MS, DR-UV–vis, ^{29}Si and ^{13}C MAS NMR and TGA. The different systems were tested in the asymmetric epoxidation of cinnamyl alcohol in order to evaluate their catalytic activity and enantioselectivity.

1. Introduction

Over the last decades, numerous catalytic reactions allowing the formation of enantiomerically pure compounds have been discovered. A family of homogeneous organometallic catalysts using, surprisingly, a small number of ligands, named “privileged structures” [1] show applicability over a wide range of different enantioselective reactions, even on an industrial scale [2]. However, the contribution of asymmetric catalysis to the overall production of chiral chemicals is still low, basically due to the difficulty of recovering the relatively expensive chiral catalyst from the bulk of the reaction. In order to overcome this problem, a great deal of work has been developed to prepare effective heterogeneous catalyst [3,4]. By far, the most widely studied systems are those prepared by immobilization of homogeneous chiral catalyst onto solid supports; by covalent bonding, adsorption, encapsulation, entrapment [5–7], etc. and lately, by sol–gel hydrolysis condensation of silylated chiral ligands or silylated chiral complexes [8,9]. The support must be thermally, chemically, and mechanically stable during the reaction process and its structure must make possible the good dispersion of the active sites, which must be also easily accessible. Organic–inorganic hybrid materials meet these criteria by exploiting the physical robustness of porous inorganic materials and the chemical functionality of organic materials. Among them, mesoporous type materials grow in importance as a result of their regular structures and tuneable pore diameters. In addition, increased activity and selectivity can also be observed upon immobilization in a confined space, due to the confinement effect originated from the weak interactions between catalyst/substrate and pore surfaces. Therefore, the enantioselectivity can be improved by careful tuning the confinement effect based on the molecular designing of the pore/surface and the immobilized catalysts according to the requirements of chiral reactions [10].

Sharpless asymmetric epoxidation of allylic alcohols has become a highlight classic in asymmetric catalysis. In this process, well understood by now, the chiral ligand plays a critical role in the enantioselectivity. The catalytically active species is titanium dimer, containing two dialkyl tartrate ligands and both the oxidant and the allylic alcohol coordinated. Nevertheless, there are few reports on the assemblies of chiral titanium complexes over solid supports in order to achieve the heterogenization of these catalyst components. Nearly two decades ago, Choudary et al. [11] carried out the immobilization of a heterogeneous chiral titanium catalyst on an inorganic support, a combination of dialkyl tartrate and titanium-pillared montmorillonite resulted in excellent ee in the epoxidation reaction of several allylic alcohols ranging from 90% to 98%. Johnson and co-workers [12] published a variety of Ti (IV) complexes, as molecular models of heterogeneous silica based systems, in which the titanium was coordinated to only one or two siloxides of a partially silylated silsesquioxane backbone in order to modify the degree of steric congestion around the titanium (IV) active site. These new complexes were performed in their chiral

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* Corresponding author. Tel.: +34 914887022; fax: +34 914888143.
E-mail address: isabel.hierro@urjc.es (I. del Hierro).

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version by reaction with BINOL but they resulted inactive epoxidation catalysts. Basset and co-workers [13] reported silica-supported tantalum catalysts for the enantioselective epoxidation of allylic alcohols in the presence of chiral tartrate derivatives with comparable results to that obtained in the homogeneous Sharpless reaction, however, the tantalum precursors were not easy to prepare. Some years later, Fu et al. [14] reported the grafting of titanium tartrate complexes onto HMS by reaction of $\mathrm{TiL_4}$ ($\mathrm{L = OPr^i}$, Cl) and D-tartaric acid with the surface OH groups. Recently, our group has reported the grafting of $[\{\mathrm{Ti(OPr^{\ddot{\imath}})_3(OMent)}\}_2]$ and $[\mathrm{Ti(OMent)_4}]$ to prepared SBA-15 based catalyst rendering medium yields and low ee. Interestingly, the chiral induction obtained was the contrary to those of the analogous homogeneous systems and similar to that prompted by the silsesquioxane complex modelling the heterogeneous systems [15]. A different strategy was followed by Li and co-workers, who grafted a chiral tartaric acid onto the surface of silica and in the mesoporous of MCM-41 providing and effective heterogeneous catalyst for asymmetric epoxidation of allylic alcohols by further reaction with $\mathrm{Ti(OPr^i)_4}$ [16].

The main objective in this study is to obtain well-defined organotitanium compounds tethered onto capped MCM-41 capable of acting as active catalyst in the Sharpless epoxidation process, in the presence of a chiral auxiliar or, in a parallel way, the synthesis of well-defined tethered organotitanium compounds in which the chiral moiety is kept bonded to titanium.

2. Experimental procedure

2.1. General remarks

All reactions were performed using standard Schlenk tube techniques under an atmosphere of dry nitrogen or argon.

2.2. Reagents and materials

Sulphuric acid 98% ($M = 98.08$, $d = 1.840\,\mathrm{g\,mL^{-1}}$) was purchased from Panreac. Sodium silicate $\mathrm{SiO_2{\cdot}NaOH}$ ($M = 242.23$, $d = 1.390\,\mathrm{g\,mL^{-1}}$), cetyltrimethylammonium bromide (CTAB) ($M = 364.46$), hexamethyldisilazane (HMDS) and 1R,2S,5R-(−)-menthol were purchased from Sigma–Aldrich and used as supplied. Titanium tetraisopropoxide $\mathrm{Ti(OPr^i)_4}$ ($0.955\,\mathrm{g\,mL^{-1}}$, 97%) was purchased from Sigma–Aldrich distilled and stored under an argon atmosphere prior to use. Cinnamyl alcohol, (+)-diethyl-L-tartrate (L-DET) and tertbutylhydroperoxide (TBHP) (5–6 M decane) were purchased from Sigma–Aldrich and stored in presence of molecular sieves. Organic solvents (toluene and dichloromethane) were purchased from SDS, distilled and dried before use according to conventional literature methods. Triazine propyl triethoxysilane ligand (CyPTS) and the modified MCM-41 (CyPTS-HMDS-MCM-41) were prepared by previously reported procedure [17]. Synthesis and characterization of $[\{\mathrm{Ti(O}i\mathrm{Pr)_3(OMent)}\}_2]$ was also reported by our group [18].

2.3. Synthesis of MCM-41 mesoporous silica

A hexagonal (plane group p6mm) material (MCM-41) was prepared according to the method of Landau et al. [19] using hydrothermal crystallization. A sodium silicate solution (65.45 g, 14% NaOH; 27% $\mathrm{SiO_2}$) was mixed with 4.20 g of 98% sulphuric acid and 140 mL of water. The mixture was stirred for 30 min at room temperature. Cetyltrimethylammonium bromide (58.66 g) dissolved in 176 mL of water was added. The resulting gel was mixed with 70 mL of water (stirred at room temperature for 30 min). The gel was transferred to a Teflon-coated autoclave and heated at 121 °C for 144 h. A solid was produced, separated by suction filtration and dried at 100 °C for 8 h. The surfactant was removed by calcination in air at 530 °C for 6 h.

2.4. Preparation of titanium modified MCM-41-supported catalyst

2.4.1. Preparation of Ti-CyPTS-HMDS-MCM-41 and TiMent-CyPTS-HMDS-MCM-41

The titanium containing mesoporous materials were prepared by reaction of $\mathrm{Ti(OPr^i)_4}$ or $[\{\mathrm{Ti(OPr^i)_3(OMent)}\}_2]$ with the chemically modified MCM-41 silica (CyPTS-HMDS-MCM-41). In a typical experiment $[\{\mathrm{Ti(O}i\mathrm{Pr)_3(OMent)}\}_2]$ or $\mathrm{Ti(OPr^i)_4}$ (4 mmol) was added to 4 g of the organomodified silica suspended in dry toluene and stirred for 24 h in order to obtain TiMent-CyPTS-HMDS-MCM-41 and Ti-CyPTS-HMDS-MCM-41 catalysts, respectively. The solid was filtered off, washed repeatedly with toluene and dried under vacuum in order to remove the volatiles.

Ti-CyPTS-HMDS-MCM-41: ^{13}C CP/MAS NMR $\delta = -6$ ($\equiv$Si–O–Si($\mathbf{C}$H$_3$)$_3$), 9 (O–CH$_2$–CH$_2$–$\mathbf{C}$H$_2$–Si), 18 (Si(OCH$_2$$\mathbf{C}H_3$)), 21.5 (O–CH$_2$–$\mathbf{C}H_2$–CH$_2$–Si), 25 (Ti–O–CH($\mathbf{C}H_3$)$_2$), 40.5 (O–$\mathbf{C}H_2$–CH$_2$–CH$_2$–Si), 58 (Si(O$\mathbf{C}H_2CH_3$)), 68 (Ti–O–$\mathbf{C}$H(CH$_3$)$_2$), 150 (N–$\mathbf{C}$–OH ($\mathbf{C}_3N_3$)).

TiMent-CyPTS-HMDS-MCM-41: ^{13}C CP/MAS NMR $\delta = -2.5$ ($\equiv$Si–O–Si($\mathbf{C}$H$_3$)$_3$), 11 (O–CH$_2$–CH$_2$–$\mathbf{C}$H$_2$–Si), 17 (Si(OCH$_2$$\mathbf{C}H_3$)), 21.5 (O–CH$_2$–$\mathbf{C}H_2$–CH$_2$–Si), 21.5 (Ti–O–CH($\mathbf{C}H_3$)$_2$), 40.5 (O–$\mathbf{C}H_2$–CH$_2$–CH$_2$–Si), 58 (Si(O$\mathbf{C}H_2CH_3$)), 68 (Ti–O–$\mathbf{C}$H(CH$_3$)$_2$), 146 (N–$\mathbf{C}$–OH ($\mathbf{C}_3N_3$)).

Ti-menthoxo unit	
C1	84
C2	53.3
C3	21.5 ($C_9 + C_7 + C_3$)
C4	32.5 ($C_4 + C_5$)
C5	32.5 ($C_4 + C_5$)
C6	46.1
C7	21.5 ($C_9 + C_7 + C_3$)
C8	28
C9	21.5 ($C_9 + C_7 + C_3$)
C10	14