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Heterogenization of chiral molybdenum(VI) dioxo complexes on mesoporous materials and their application in catalysis

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Abstract

Optically active molybdenum(VI) dioxo complexes bearing hydrosalen derivatives as ligands were synthesized, grafted on the surface of MCM-41 and MCM-48 and examined as catalysts for asymmetric epoxidation. In case of *cis*-β-methylstyrene and *trans*-β-methylstyrene moderate enantiomeric excesses of up to 31% can be reached when the reaction is carried out at room temperature. The catalysts can also be applied for non-chiral oxidation reactions.

Keywords: Catalysis; Chirality; Mesoporous materials; Molybdenum; Epoxidation

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1. Introduction

Enantiopure epoxides are highly valuable chiral molecules, useful for the synthesis of various biologically active molecules [1]. For the preparation of chiral epoxides, transition metal-catalyzed enantioselective epoxidation of different organic substrates is of high importance and has been widely studied over the past decades [2]. The generally good catalytic activities of several molybdenum(VI) dioxo complexes in oxidation reactions make this type of complexes – in principle – promising candidates for asymmetric catalysis by using chiral ligands [3]. 2′-Pyridyl alcohols and phosphinoalcohols [4] have been reported to induce enantiomeric excesses of 20–40% for functionalized olefins when coordinated to dioxo or peroxo molybdenum(VI) fragments. In this context, we and others have reported on the synthesis of a variety of *cis*-MoO_2^{2+} epoxidation catalysts bearing chiral ligands, such as bis-oxazoline, *cis*-diol and *cis*-8-phenylthiomenthol [5]. Recently we reported also the synthesis of some molybdenum(VI)-*cis*-dioxo complexes bearing sugar derived chiral Schiff base ligands of general formula $MoO_2(L)(Solv)$, which showed moderate enantiomeric inductions of ca. 30% ee for the epoxidation of *cis*-β-methylstyrene [6].

During the last years significant efforts were dedicated to the heterogenization of homogeneous catalysts in order to combine the advantages of heterogeneous catalysts such as easier product/catalyst separation with the advantages of homogeneous catalysts, e.g. higher selectivity [7]. Among the various supporting materials studied, the mesoporous silicates, designated as MCM-41 and MCM-48 by Mobil scientists [8] with regular pore size, large surface areas, large number of surface silanol groups, and high chemical and thermal stability are potential and promising candidates as both catalysts and catalyst supports [9]. In this regard, very recently modified MCM-41 and MCM-48 materials were synthesized by grafting MoO_2X_2 (X = Cl, Br), [7] the latter being quite efficient homogeneous epoxidation catalysts [10]. Additionally, surface-fixed bidentate Lewis bases have been used to bind catalytically active Mo(VI) complexes as described by Gonçalves and co-workers [7,11] and Thiel and co-workers [12]. Silylation using halosilane to remove residual Si–OH groups, which were considered to be

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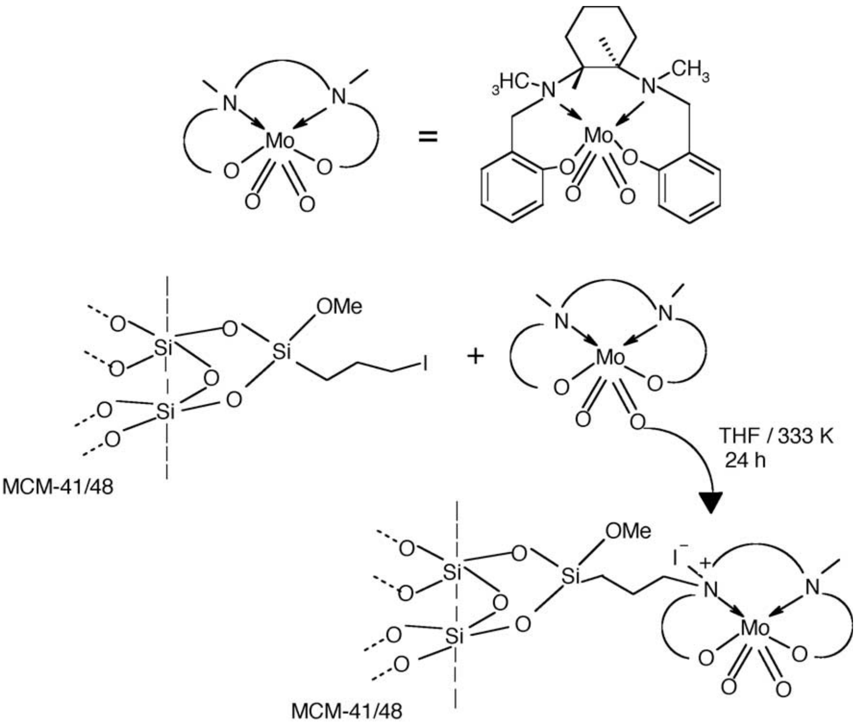

Scheme 1.

favourable for the catalytic reaction on the surface of the mesoporous material, reduced the catalyst leaching significantly [12].

The above mentioned homogeneous chiral molybdenum(IV) dioxo complexes bearing hydrosalen derivatives as ligands with one or more *N*-methyl groups were found to be – among other applications – interesting candidates as catalysts [6]. One of the *N*-methyl groups on the chiral homogenous complex can be reacted with halosilane modified MCM-41 and MCM-48 surfaces, yielding chiral heterogeneous catalysts, as depicted in Scheme 1.

Similar reactions are known and have been reported previously [13,14]. In the present work the MCM-41 and MCM-48 surface are thus modified with trimethoxy iodo propyl silane and then the chiral catalysts are grafted by reaction of the iodo-groups on the silylated surface materials with the *N*-methyl groups present on the homogeneous chiral catalysts.

2. Experimental

Mesoporous molecular sieves were synthesized following the procedures described earlier [7,9] with molar gel compositions of 1.0 SiO_2:0.2 NaOH:0.27 TMAOH:0.27 CTABr:60 H_2O for MCM-41, and 5.0 SiO_2:2.5 NaOH:0.87 CTABr:0.13 Brij30:400 H_2O for MCM-48, respectively. Solvents were dried by standard procedures (THF with Na/benzophenone ketyl; CH_2Cl_2 with CaH_2), distilled under argon and kept over 4 Å molecular sieves. All preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. The chiral homogeneous Schiff base ligated catalysts were synthesized by a procedure described earlier [6]. First the mesoporous molecular sieves (MCM-41 and MCM-48) were silylated with iodo-propyl trimethoxy silane using dry toluene (30 mL) as solvent under an argon atmosphere at 383 K (reaction time: 24 h). The excess silane was then removed by filtration followed by repeated washing with dichloromethane. The resulting solid was dried under vacuum at room temperature. Grafting experiments were carried out using standard Schlenk techniques under argon atmosphere applying the following procedure: first the silylated mesoporous molecular sieves MCM-41/48 were pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove physisorbed water. The activated sample was treated with 0.2 mmol of the chiral complex in 30 mL dry THF under argon atmosphere. The mixture was stirred at 339 K for 24 h. The resulting solution was filtered off and the pale yellow solid was then washed repeatedly with CH_2Cl_2 until all physisorbed complex was removed from the surface. The washed samples were dried under vacuum at RT. For sake of comparison achiral complexes were also grafted in an analogous manner. The resulting material prepared from chiral and achiral complexes on MCM-41 and MCM-48 are designated as SM-41ccg, SM-48ccg, SM-41accg and SM-48accg, respectively.

Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and