Dendrimeric silanes for formation of metallosilicates: new heterogeneous catalysts for the epoxidation of alkenes with *tert*-butylhydroperoxide

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New metallosilicate catalysts were prepared by reacting a silanol capped dendrimer, $Si[CH_2CH_2Si(CH_3)_2OH]_4$ with MCp_2Cl_2 (M = Ti^{IV}, Mo^{VI}, W^{VI} and V^{V}). The resulting $Si[CH_2CH_2Si(CH_3)_2OMCp_2Cl]_4$ compounds were incorporated in a silica matrix by the sol–gel method. The catalytic activity of the metallosilicates after calcination revealed excellent activity and selectivity towards epoxidation of alkenes with *tert*-butylhydroperoxide. Maximum activity was observed with molybdenum-containing materials. Analysis of the catalytic activity revealed that the catalysts were truly heterogeneous.

KEY WORDS: epoxidation; dendrimer; metallosilicate

1. Introduction

Amorphous catalytic silicate based materials containing metal oxides are now commonly synthesized by the sol–gel procedure based on the hydrolysis and condensation of alkoxide precursors [1]. An important limitation of this technique is the difficulty in homogeneously dispersing transition metals within the silicate matrix, due to the large disparity in the rate of hydrolysis of the precursors [2]. In the area of catalytic oxidation with peroxides, it is especially highly desirable to achieve high surface area by formation of aerogels [3], or effective dispersion and homogeneity of high valent transition metals, M, such as Ti^{IV}, V^{V}, Mo^{VI}, and W^{VI} in silicate matrices since polymeric MO_x are catalytically less active or even inactive [4]. In the past, one approach that has been effective was based on grafting a titanium metallocene complex onto mesoporous silica MCM-41 [5]. Alternatively, a non-aqueous molecular route whereby $M[OSi(O^tBu)_3]_4$ species were heated to form MO_x–$4SiO_2$ materials has also been effective [6]. By design the metal oxide is surrounded by four silicate units. High catalytic activity has been observed in several cases [7].

In this paper, we present a new method to achieve high dispersion of metal oxides within a silicate matrix and show that the materials obtained have high activity for alkene epoxidation with *tert*-butylhydroperoxide. The catalyst preparation is based on the functionalization of a dendrimeric silanol with bis(cyclopentadienyl)metal dichlorides yielding $Si[CH_2CH_2Si(CH_3)_2OMCp_2Cl]_4$, **1**, with isolated metal centers, scheme 1. $Si[CH_2CH_2Si(CH_3)_2OMCp_2Cl]_4$ was then encapsulated in a silicate sol–gel matrix and activated by calcination.

2. Experimental

The preparation of $Si[CH_2CH_2Si(CH_3)_2OMCp_2Cl]_4$ was under Schlenk conditions. THF, DMSO and Et_3N were dried and distilled before use. The starting material $Si[CH_2CH_2Si(CH_3)_2OH]_4$ [8], was prepared according to the literature procedure; Cp_2MCl_2 was from Aldrich. **1a** [8] was prepared under argon as follows: $Si[CH_2CH_2Si(CH_3)_2OH]_4$ (0.315 mg, 0.72 mmol) dissolved in 10 ml THF was added dropwise at room temperature to a solution of Cp_2TiCl_2 (717 mg, 2.88 mmol) in 50 ml THF. After stirring for an additional 30 min Et_3N (350 mg, 3.5 mmol) in 5 ml THF was slowly added. The solution was stirred for 20 h whereupon the color changed from dark red to light orange and white precipitate was formed. The precipitate, Et_3NHCl, was filtered off and the filtrate was left to stand for an additional three days. Additional solid that was formed was discarded and volatile components were evaporated off; an orange powder was obtained, yield 87%. ^1H NMR (DMSO-d_6) δ 0.15 ppm, m, 6H; δ 0.54 ppm, m, 4H, δ 6.35 ppm, s, 10H. **1b**, **1c** and **1d** were prepared in an analogous manner using DMSO instead of THF as solvent. For molybdenum the solution changed from dark green to red-brown, yield 82%; for tungsten the solution changed from green to light brown-orange, yield 83% and for vanadium the solution turned from green to brown, yield 80%. **1b** ^1H NMR (DMSO-d_6) δ −0.65 ppm, m, 6H; δ 1.04 ppm, m, 4H, δ 5.60 ppm, bs, 10H; **1c** ^1H NMR (DMSO-d_6) δ −0.53 ppm, m, 6H; δ 1.11 ppm, m, 4H, δ 5.77 ppm, bs, 10H; **1d** ^1H NMR ($CDCl_3$) δ 0.33 ppm, m, 6H; δ 1.15 ppm, m, 4H, δ 6.45 ppm, d, 10H. **1** was encapsulated in a silicate matrix as follows: $Si(n\text{-}OPr)_4$ (10 mmol, 2.64 g) and 100 mmol water as 0.05 N HCl were dissolved in 20 ml *n*-PrOH and kept at 60 °C for

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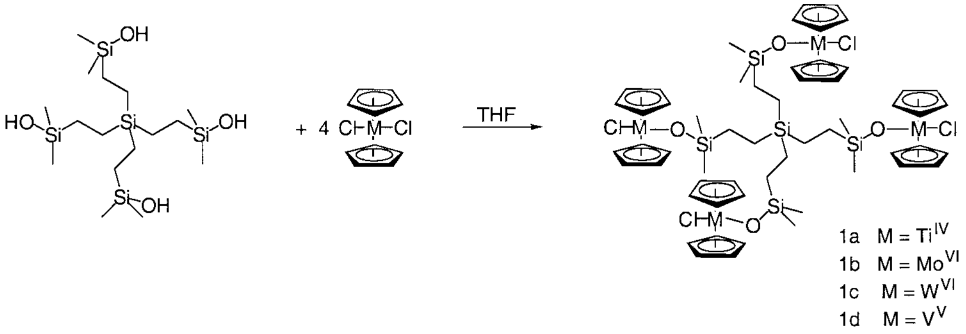

Scheme 1.

1.5 h. Then 0.25, 0.5 or 1.25 mol% **1** dissolved in THF or DMSO were added along with 100 mmol H_2O as 0.05 N HCl and kept at 60 °C for another 4 h. The solution was cooled and the *n*-PrOH was allowed slowly to evaporate off for a period of 72 h. The solids obtained were dried at ~100 °C overnight and then calcined under air at 500 °C for 4 h. White to off-white powders were obtained. The IR spectrum for all three materials Ti–SiO_2, Mo–SiO_2 and W–SiO_2, were essentially the same with peaks at 1635, 1235, 1029, 908, and 580–610 cm^{-1}. Typically, oxidation reactions were carried out by mixing 1 mmol substrate, 2 mmol 2 M *tert*-butylhydroperoxide (TBHP) in decane and 12 mg catalyst at 60 °C for 8 h in a pressure tube. The reaction mixtures were analyzed using gas chromatography. Oxidation reaction products were identified using reference standards and GC-MS (HP-5973) equipped with a 30 m × 0.32 mm 5% phenylmethylsilicone (0.25 μm coating) capillary column. Quantification was by GLC (HP 5980) equipped with a flame ionization detector and the same column.

3. Results and discussion

The metal containing dendrimers, **1**, prepared as indicated in scheme 1 were encapsulated into a silica sol–gel and calcined to yield metal containing silicates represented as M–SiO_2. A preliminary assay to determine catalytic activity for epoxidation of alkenes with hydrogen peroxide and TBHP was carried out using cyclooctene, a highly reactive alkene, as a probe substrate. From the results as described in table 1, it is clear that TBHP is more effective than H_2O_2 and that Mo–SiO_2 > Ti–SiO_2 > V–SiO_2 > W–SiO_2. When using aqueous H_2O_2, there was visible leaching and some dissolution of the silicate. On the other hand, when using anhydrous TBHP, leaching was very limited for Mo–SiO_2 and Ti–SiO_2 but significant for V–SiO_2 and W–SiO_2. Leaching was tested by mixing the catalyst under reaction conditions (table 1) without substrate for 8 h at 60 °C. The suspension was filtered hot over a 25 μm filter and the filtrate and solid tested for catalytic activity. For Mo–SiO_2 and Ti–SiO_2 the filtrate gave about 5% conversion (no catalyst gave 2% conversion). The solid was active. The catalytic activity for the Mo–SiO_2 compound is comparable to the activity described for other amorphous silicates [3–5]. Notably for titanium grafted on mesoporous MCM-41 [6], and also molybdenum complexes grafted on MCM-41 [9] catalyst deactivation is fast under similar reaction conditions.

Table 1
Epoxidation of cyclooctene catalysed by metallosilicates.[a]

Metallosilicate	Conversion (selectivity) (mol%)	
	Oxidant 30% H_2O_2	Oxidant 6 M TBHP
None	0	2
Ti–SiO_2	39 (98)	95 (99)
V–SiO_2	12 (94)	81 (95)
Mo–SiO_2	46 (99)	>99 (99)
W–SiO_2	51 (85)	20 (99)

[a] Reaction conditions: 1 mmol cyclooctene, 12 mg metallosilicate catalyst (2 mol% M on SiO_d), 2 mmol 30% H_2O_2 + 1 ml methanol or 1 ml 2 M TBHP in *n*-decane, 60 °C, 8 h.

Table 2
Epoxidation of alkenes catalyzed by Ti–SiO_2 and Mo–SiO_2 with *tert*-butylhydroperoxide.[a]

Substrate	Conversion (selectivity) (mol%)	
	Ti–SiO_2	Mo–SiO_2
Cyclooctene	95 (99)	>99 (99)
Cyclohexene	44 (92)	71 (93)
1-octene[b]	25 (81)	56 (95)
1-decene[b]	17 (76)	61 (95
2-octene	21 (97)	62 (98)
2-methyl-2-heptene	29 (90)	90 (90)

[a] Reaction conditions: 1 mmol substrate, 12 mg metallosilicate catalyst (2 mol% M on SiO_d), 1 ml 2 M TBHP in *n*-decane, 60 °C, 8 h.
[b] 100 °C.

Since Mo–SiO_2 and Ti–SiO_2 were both active and quite stable to reaction conditions when using anhydrous TBHP as oxidant, these materials were further tested for activity in epoxidation of a series of alkenes by TBHP, table 2. As may be expected, reactivity was clearly a function of the nucleophilicity of the alkene. Thus, the least nucleophilic terminal alkenes such as 1-octene and 1-decene were least reactive and required higher reaction temperatures for reasonable yields. In the epoxidation of cyclohexene, a substrate sensitive allylic oxidation by *tert*-butyloxy and *tert*-butylperoxo radical species, selectivity was high indicating only a minor amount of radicals were formed. In this context it is valuable to note that for Mo–SiO_2 the catalyst is light blue indicating some formation of Mo^V species. Additionally, yields calculated for TBHP were high. 2-methyl-2-heptene was more

Table 3
Epoxidation of alkenols catalyzed by Mo–SiO_2 with *tert*-butylhydroperoxide.[a]

Substrate	Conversion (selectivity) (mol%)
Cis-2-hexen-1-ol	74 (96)
Trans-2-hexen-1-ol	87 (97)
Cis-3-hexen-1-ol	60 (>99)
Trans-3-hexen-1-ol	85 (>99)
5-hexen-1-ol	6 (>99)

[a] Reaction conditions: 1 mmol substrate, 12 mg metallosilicate catalyst (2 mol% Mo on SiO_d), 1 ml 2 M TBHP in *n*-decane, 60 °C, 8 h.

reactive than 2-octene but there was some loss of selectivity when the former was used as substrate. Further optimization was carried out by changing the load of the transition metal on the silica and by varying the silicate precursor. Using cyclohexene as a probe substrate we found for Mo–SiO_2 and Ti–SiO_2 that (a) 2 mol% M > 5 mol% M > 1 mol% M and (b) $Si(n\text{-}OPr)_4 > Si(n\text{-}OBu)_4 > Si(OMe)_4 > Si(OEt)_4$ and precursors for SiO_2. This would appear to indicate that at the 1–2 mol% Ti or Mo substitution most of the metal sites are site isolated and accessible to the oxidant and substrate, whereas at higher loadings accessibility and site isolation are perhaps more limited.

The molybdenum containing silicate Mo–SiO_2 was also surveyed for activity in the epoxidation of alkenols with anhydrous TBHP, table 3. Rather unusually the allylic alcohols were only slightly more reactive than the homoallylic alcohols, whereas 5-hexen-1-ol reacted like a terminal alkene. Selectivity was high; in the case of allylic alcohols 3–4% of the allylic aldehyde was formed as by-product. Also rather unusual was the greater reactivity of the *trans* isomers as compared to the *cis* isomers as typically the latter are more reactive with peroxo type complexes. We have as yet no explanation for this phenomenon.

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