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Selective Heterogeneous Epoxidations with Cp-Titanium Chloride Derived Microporous Silica Glasses

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Abstract : A new heterogeneous epoxidation catalyst is prepared by the copolycondensation of cyclopentadienyl titanium chlorides with tetraethoxysilane by a modified sol-gel procedure. Epoxidations of non-activated olefins in the presence of these new heterogeneous catalysts are described.

Introduction

The development of new heterogeneous catalysts for selective oxidation reactions is driven by increasing ecological and economical pressure on industrial processes.[1,2] The preparation of epoxides of higher olefins, which are useful synthons for multistep synthesis,[3] is still problematic and dominated by homogeneous catalysis. Chiral epoxidation activity is reported with bis(1-indenyl)titanium dichloride.[4] Heterogeneous catalysts of comparable activity and selectivity still remain a desirable goal in catalysis. Crystalline titanium silicalites have been found to be good epoxidation catalysts, but only at low alkene conversion.[1] Lau et al. have reported the preparation of a polystyrene divinylbenzene-supported titanocene.[5] Here the titanium atom is attached to the support by a η^5-interaction with a cyclopentadienyl group covalently bond to the organic polymer. These polymer-attached titanocene chlorides isomerise allyl benzene and 1,5-cyclooctadiene and catalyse the epoxidation of cyclohexene and cyclooctene. We report here the preparation of new heterogeneous epoxidation catalysts by a modified sol-gel procedure from tetraethoxysilane (TEOS) and cyclopentadienyl titanium chlorides.

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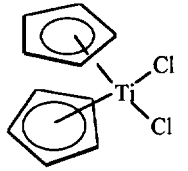
Sol-gel chemistry is a powerful method for the preparation of metal oxides under very mild conditions.[6] It also allows to obtain mixed metal oxides with good homogeneity of the components.[7] During our work on catalysed epoxidations with amorphous silicon-titanium materials prepared by the sol-gel method, we have examined the incorporation of titanocene derivatives into a silica matrix as an alternative preparation procedure. The commercial monoatomic Cp_2TiCl_2 **1** and the dimeric $(CpTiCl_2)_2O$ **2** have been used as titanium source for the preparation of mixed Si-Ti oxides.



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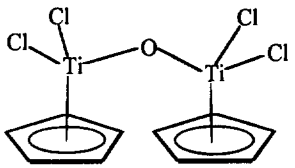

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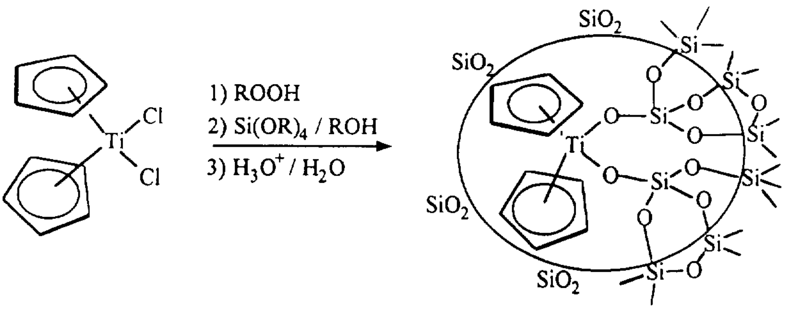
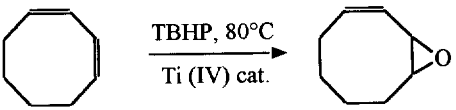
Results and discussion

Poor solubility and reactivity of **1** under our sol-gel conditions have been the main difficulties. Solubilisation with halogenated solvents ($HCCl_3$ or CH_2Cl_2) was possible, but after polycondensation by the sol-gel method, the obtained xerogels were covered with non-incorporated Cp_2TiCl_2. Since cyclopentadienyl titanium compounds are commonly activated with tertiary butyl hydroperoxide (TBHP) or H_2O_2,[5] we decided to activate the titanocene **1** by an *in situ* reaction with these oxidating agents. Addition of an excess of TBHP and / or H_2O_2 (2-10 eq.) to an alcoholic solution of **1** followed by addition of TEOS and concentrated hydrochloric acid allowed the preparation of translucent homogeneous orange xerogels. The assumed reaction is shown in Scheme 1. In contrast to **1**, dimer **2**, prepared according to Gorsich[8] and Corradini and Allegra[9] respectively, dissolved directly in the sol and was easily incorporated into the silica matrix. After evaporation of the volatile material, a clear homogeneous glass was obtained.



Scheme 1. Preparation of amorphous silica-titania materials.

The gels were calcined at 250°C to provide the final xerogels (glasses). Ar- and N_2-adsorption isotherms showed BET surface areas of 200-500 m^2/g and a narrow pore size distribution with a maximum at 0.7-0.9 nm pore diameter. High resolution transmission electron microscopy (HR-TEM) shows the materials to be amorphous and continuous even at atomic resolution, no evidence for particle formation or crystallinity was obtained. Statistical selected area EDX (energy dispersive X-ray) analyses from nm to µm scale confirmed a uniform distribution of Ti in the silica matrix. No evidence for SiO_2- or TiO_2-domain formation could be obtained, confirming the formation of a homogeneous material. The epoxidation activities of the gels and xerogels have been tested with the non-activated olefins 1-octene, cyclohexene, cyclooctene and 1,3-cyclooctadiene (COD) (see Scheme 2).



Scheme 2 . Titanium-catalysed epoxidations

Although **1** is reported to be inactive for epoxidation reactions,[5] under our reaction conditions it displayed remarkable activity. The activity of the homogeneously catalysed epoxidation of 1,3-COD with pure dicyclopentadienyl titanium dichloride is shown in Table 1. In epoxidations with 1 and 3 mol% homogeneous titanocene catalysts yields of up to 60% have been obtained. Turnover numbers are low and the selectivity decreases significantly for titanium contents higher than 0.3 molar%. Higher turnover numbers up to 100 are obtained for concentrations below 1%, but yields decrease significantly. The heterogeneously catalysed reactions were carried out under conditions identical to the homogeneous reactions and the results are summarised in Table 2. Removal of the catalyst from the mother liquor by centrifugation early in the reaction results in complete loss of activity confirming heterogeneous catalysis. With the xerogel catalysts based on **1** a similar influence of the titanium content on the 1,3-COD epoxidation is observed. A higher TON was obtained with the gel prepared with a ratio Si/Ti of 200 (entry 5). In this case, the yield is significantly lower than for a ratio Si/Ti of 50 (17 respectively 42%).

Table 1 . Homogeneously catalysed epoxidations of 1,3-cyclooctadiene with Cp_2TiCl_2

Entry	% Ti	% Yield[a]	Selectivity[a]	TON[b]
1	0	3	100/0	autoxidation
2	0.1	9	100/0	92
3	0.3	30	93/7	100
4	1.0	50	86/14	50
5	3.2	59	79/21	18

a) Yields and selectivity are determined by GLC. Selectivity : monoepoxidation versus diepoxidation and degradation.
b) TON : Turnover number, number of converted olefins per titanium atom

In comparison to homogeneously-catalysed epoxidations, dilution of the titanium in the silica matrix prevent deactivation of the active center. For similar titanium contents in the reaction, turnover numbers are higher for heterogeneous catalysts than for homogeneous catalysts (entries 2, 3 Table 1 and 1, 5 Table 2). Epoxides of cyclohexene and cyclooctene are obtained with 29 and 41% yield respectively, the corresponding TONs approach 500.

Table 2 . Heterogeneously catalysed epoxidations.

Entry	Olefin	Ti source	Si/Ti	Ti mol %	Yield %*	TON
1	1,3-cyclooctadiene	**1**	50	0.3	42[a]	136
2	1,3-cyclooctadiene	**1**	100	0.16	15[b]	93
3	1,3-cyclooctadiene	**2**	100	0.16	13[b]	95
4	1,3-cyclooctadiene	**2**	150	0.11	17[b]	185
5	1,3-cyclooctadiene	**1**	200	0.08	17[a]	200
6	1-octene	**2**	100	0.16	30	220
7	1-octene	**2**	150	0.11	31	338
8	cyclohexene	**1**	200	0.08	29	341
9	cyclooctene	**1**	200	0.08	41	482

*Yields and selectivity determined by GLC. a) presence of 15% diepoxide.b) monoepoxide only

The catalysts prepared with **2** also show high activities and TONs comparable to those obtained with **1** (table 2, entries 3,4). The activity and TONs obtained with 1-octene (entries 6,7) are also similar to those with COD and cyclohexene. Since Ti-O-Ti units seem to be inactive for epoxidation,[10] we assume that the Ti-O-Ti bond is cleaved during the polycondensation reaction to give isolated titanium atoms with exclusive Ti-O-Si bonds.

Conclusion

In this work we have studied the preparation and the reactivity of some mixed cyclopentadienyl titanium-silica materials prepared by the sol-gel method. Use of TBHP or H_2O_2 allows to prepare clear, yellow-orange xerogels from TEOS and the halogenated titanocene **1**. Highly acidic conditions and addition of 2 to 4 equivalents of water relative to silicon are important to obtain a good tridimensional polymer network active for epoxidation. TEM studies have confirmed the highly homogeneous dispersion of the titanium in the silica matrix. The final catalysts have surface areas up to 500 m^2/g with a narrow pore size distribution in the sub-nm-range. We have shown that these amorphous glasses are good catalysts for the epoxidation of non-activated olefins. The xerogels reveal higher activity than the corresponding soluble titanocene compounds and can be recycled after epoxidation without loss of activity.

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EXPERIMENTAL

General methods: BET surfaces and pore-size distributions were measured with a Coulter Omnisorp 360 with argon and nitrogen as probe gases. TEM-EDX examinations were performed on a Hitachi HF 2000 FE-TEM with an acceleration energy of 200kV. Melting points were determined with a Shimadzu DSC 50 differential scanning calorimeter. The GLC examinations were obtained on a Shimadzu GC-14 A gas chromatograph equipped with a FID. Epoxidation products were characterised by GLC-coinjection and GLC-MS coupling, respectively.

Typical preparation of an amorphous glass: In a polypropylene-beaker, to a solution of cyclopentadienyltitanium chloride (Merck 803036, 64 mg, 0.26 mmol) in ethanol (99%, 12.8 mL), aqueous H_2O_2 (1.56 mmol in a 30 weight% solution) was added. After 15 min tetraethoxysilane (TEOS, Fluka 86580, 11 mL, 52 mmol) and hydrochloric acid (1.6 mL 8 N HCl) were added dropwise. A temperature increase up to 40-50°C was observed. Subsequently 2 mL of distilled water were added and the red-orange solution was stirred for 1 h. Without further stirring the loosely covered solution solidified within 3-4 days. The glassy material was submitted to a programmed heat treatment: the material was heated from room temperature to 65°C (rate 0.5K/min), kept there for 3 h, then heated to 250°C (rate 0.2K/min), kept there for 3 h and finally cooled down to room temperature. The calcined material was ground in a ball mill.

Typical procedure for an epoxidation reaction: to a heterogeneous mixture of olefin (2.5 mmol) and catalyst (25mg, 1 to 3 Ti molar%, depending on Si/Ti ratio) tert.-butylhydroperoxide (TBHP, Fluka 19998, 3molar solution in isooctane, 1 eq.) was added. The reactor was closed and the well stirred solution was heated to 80°C. The development of the reaction was followed by GLC. Maximum epoxide formation was observed during the first 2 h, the reaction was carried out for an extended period of 10 h.

Regeneration: The materials were regenerated after the use as epoxidation catalysts via the following procedure. The reaction mixture was centrifuged and the mother liquor was removed. The remaining solid was washed three times with diethyl ether followed by centrifugation and once with n-pentane. After drying at room temperature the material was submitted to a heat treatment (30 min at 200°C).

Control experiments: To distinguish between heterogeneous and homogeneous catalysis the mother liquor was removed from the reaction mixture by centrifuging 15 min after the reaction had started at the reaction conditions given above. There was no further increase in conversion in the mother liquor excluding homogeneous catalysis. The rates of the examined reactions are not dependent on the particle size of the powdered catalysts, which excludes rate control by transport phenomena.

Preparation of **2** ($CpCl_2Ti$-O-$TiCl_2Cp$): A solution of cyclopentadienyltitanium chloride (Merck 803036, 6g, 24 mmol, melting point 289°C) and titanium tetrachloride (13 g, 69 mmol) in 45 mL dry p-xylene were refluxed for 4 h under inert gas. The reaction mixture was cooled down to room temperature. The resulting residue ($CpTiCl_3$, melting point 205-209°C) was filtered off and immediately diluted in n-heptane. The solution was boiled under ambient conditions for 2 h. Concentration of the solution resulted in yellow crystalls with a melting point of 145°C. Recrystallisation from CCl_4 gave 3.0 g of **2** (65% overall yield) with a melting point of 149-150°C in agreement with that of the literature.[8] IR and ^1H NMR data are identical with those of the literature.[11]

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