A novel magnesium oxide supported polytitazane–tin tetrachloride catalyst for aerobic epoxidation of cycloalkenes under mild conditions

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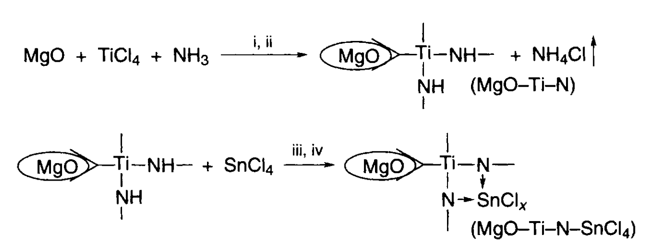
A magnesium oxide supported polytitazane–tin tetrachloride complex is found to be a novel efficient catalyst for epoxidation of cycloalkenes with molecular oxygen with 1,4-dioxane as a co-reductant under mild conditions.

While extensive efforts have been made to explore new epoxidation processes, the following aspects commonly associated with oxidation still need to be improved: (*i*) oxidative degradation of the catalyst and/or deactivation by irreversible dimerization of the metal complexes;[1] (*ii*) replacing other oxygen sources with molecular oxygen for environmental and economic concerns[2] and (*iii*) employing heterogeneous catalysts for easy operation and recycling.[3] Although various catalytic systems have dealt with one or two of the above aspects, such as using perhalogenated metalloporphyrins,[4] zeolites[5] and heteropolyoxometalates[6] to improve the oxidatively resistant stabilities of the catalytic systems, employing molecular oxygen as oxidant with[7] or without[8] co-reductants and taking advantage of heterogeneous catalytic systems,[9] to the best of our knowledge, there has been no report dealing with all three aspects in one catalytic epoxidation system. In our laboratory, a series of inorganic polymers with rigid nitrogen ligands and with thermally and oxidatively resistant properties have been synthesized.[10] We now report a magnesium oxide supported polytitazane–tin tetrachloride complex as a novel efficient catalyst for aerobic epoxidation of cycloalkenes.

The typical synthesis of magnesium oxide supported polytitazane (MgO–Ti–N) was carried out according to the method described in ref. 11 and is illustrated in Scheme 1. The preparation of the magnesium oxide supported polytitazane–tin tetrachloride complex (MgO–Ti–N–$SnCl_4$) using tin tetrachloride as precursor is also illustrated in Scheme 1 and is as follows: to 1 g MgO–Ti–N and 40 ml anhydrous carbon tetrachloride was added 2.34 ml of a carbon tetrachloride solution of anhydrous tin tetrachloride (0.0855 mol dm^{-3}). The mixture was refluxed for 18 h under nitrogen then filtered, washed several times with carbon tetrachloride and dried *in vacuo*. Other polytitazane–tin complexes were prepared by similar procedures. Catalytic epoxidations were carried out similarly to the method described in ref. 11 with the exception of the reaction conditions indicated in Table 1.

The catalytic performances of the polytitazane–tin complexes are listed in Table 1. Neither the precursor tin salts nor the MgO–Ti–N support alone or mechanical mixtures of the tin salts and the support catalyse the aerobic epoxidation of *cis*-cyclooctene. On the other hand, polytitazane–tin complexes (entries 2–4) are all active catalysts for epoxidation of *cis*-cyclooctene with selectivities for the epoxide in excess of 90% (cyclooctanone is the by-product). Among those tin complexes, MgO–Ti–N–$SnCl_4$ has the highest activity for epoxidation of *cis*-cyclooctene. The yield of *cis*-cyclooctene oxide amounts to 81.0%. GC–MS analysis of the reaction mixture reveals that some of the 1,4-dioxane was also simultaneously oxidised to ethanediol diformate/monoformate (1.17 : 1) with a total amount of 0.77 equiv. relative to the *cis*-cyclooctene oxide. When other solvents such as toluene, 1,2-dichloroethane, ethyl nitrile and ethyl benzoate were used, no epoxidation occurred. The MgO–Ti–N–$SnCl_4$ is also a versatile catalyst for the epoxidation of other cycloalkenes such as cyclohexene, indene and norbornene. The yield of norbornene oxide reaches 94.6%.

The stability of the magnesium oxide supported polytitazane–tin tetrachloride complexes were evaluated in recycling experiments. The catalyst was filtered at the end of each



Scheme 1 *Reagents and conditions*: i, light petroleum, 0 °C; ii, 450 °C; iii, N_2, 18 h; iv, CCl_4, reflux

Table 1 Aerobic epoxidation of cycloalkenes catalysed by polytitazane–tin complexes[a,b]

Entry	Catalyst	Cycloalkene	Conversion of cycloalkene (%)	Selectivity for epoxide (%)	Yield of epoxide (%)
1	Ⓟ = MgO–Ti–N	*cis*-cyclooctene	trace		
2	Ⓟ –$SnCl_2$•$2H_2O$	*cis*-cyclooctene	55.4	91.3	50.6
3	Ⓟ –$SnCl_4$•$5H_2O$	*cis*-cyclooctene	34.8	92.6	32.2
4	Ⓟ –$SnCl_4$	*cis*-cycloctene	86.9	93.2	81.0
5	Ⓟ –$SnCl_4$	cyclohexene	82.6	97.5	80.5
6	Ⓟ –$SnCl_4$	indene	81.3	86.2	70.1
7	Ⓟ –$SnCl_4$	norbornene	94.6	100	94.6

[a] Reaction conditions: 100 mg catalyst (0.02 mmol Sn), mol ratio of alkene/Sn = 50, 2.5 ml 1,4-dioxane, 1 atm. O_2, 80 °C, 20 h. [b] Products analysed by a Shimadzu GC-17A/QP-5000MS with a OV-17 capillary column.

run, washed with 1,4-dioxane and used in the successive reaction. The activities and selectivities of the catalysts are listed in Table 2. The activity of the catalyst increases slightly and then levels off upon recycling while the selectivity remains almost unchanged. The catalyst is therefore stable and can be recycled at least seven times for epoxidation of *cis*-cyclooctene without apparent loss in activity and selectivity.

While the mechanistic steps involved in the aerobic epoxidation catalysed by the polytitazane–tin tetrachloride complex have not been elucidated in any detail, several points can be made based on chemical evidence. The oxidation of cycloalkenes with high selectivity to the corresponding epoxide rules out the possibility of a free-radical mechanism in the catalytic cycle. The presence of cyclooctanone as the side product accompanying the *cis*-cyclooctene oxide indicates that a pathway involving the high-valent oxotin as found for high-valent Cr and Mn oxide systems is not likely.[12] The identification of ethanediol diformate/monoformate which have been reported as the oxidation products of 1,4-dioxane in the reaction mixture[13] and the indispensability of 1,4-dioxane as the solvent strongly supports the participation of 1,4-dioxane in the epoxidation. The co-oxygenation of cycloalkenes and 1,4-dioxane seems to be the most probable pathway. It is noteworthy that until now the use of the main group element tin as a selective oxygenation catalyst has not been reported previously, despite the fact that tin dichloride dihydrate was used to hydroxylyse alkanes with molecular oxygen in a stoichiometric reaction.[14] Some correlation of the recently reported unusual structure of a bis(1,2-μ-peroxo) bridged tin complex,[15] $[Sn\{N(SiMe_3)_2\}_2(\mu\text{-}O_2)]_2$, with the present catalytic system may help to elucidate the role of polytitazane–tin tetrachloride complexes in the aerobic epoxidation of alkenes. Further details are being investigated.

Table 2 Recycling of MgO–Ti–N–$SnCl_4$ in the epoxidation of *cis*-cyclooctene[a]

Run	1	2	3	4	5	6	7
Conversion of alkene (%)	83.4	84.7	86.6	87.0	87.6	87.6	86.7
Selectivity for the epoxide (%)	94.2	94.3	93.8	94.6	94.3	92.9	93.2
Yield of the epoxide (%)	78.6	79.9	81.2	82.3	82.6	81.4	80.8

[a] Reaction conditions identical to those in Table 1.

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