Polymer Bulletin 36, 1-5 (1996)

Polymer Bulletin

Magnesium oxide-supported polytitazane cobalt(III) complex for catalytic epoxidation of α-pinene with molecular oxygen

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Received: 27 July 1995/Revised version: 8 September 1995/Accepted: 12 September 1995

Summary

Magnesium oxide-supported polytitazane cobalt complex has been prepared and found to be a very effective catalyst for the epoxidation of α-pinene in the presence of an aldehyde as a reductant. XPS data show that the high valent cobalt(III) was stabilized by the mutidentate nitrogen ligand of polytitazane. The α-pinene oxide can be obtained in 96.0% yield with 96.6% selectivity at 25°C under an atmospheric pressure of molecular oxygen. Isobutyraldehyde is an effective reductant and only 1.2 equivalent of isobutyraldehyde to α-pinene is needed to ensure high yield of α-pinene oxide. The catalyst is also very stable and can be reused at least eight times without loss of its activity.

Introduction

Epoxidation of organic substrates using molecular oxygen as the final oxidant to substitute the stiochiometric oxidants has been a tendency from both the increased safety and economic point of view(1) . In this connection, much effort has so far been made to develop the direct and selective epoxidation of olefins by use of molecular oxygen, however, only several effective catalysts have been reported(2,3) . The recently reported Mukaiyama method for alkene epoxidation with an aldehyde as a reductant in the presence of acetylacetonate metal complex catalyst under an atmospheric pressure of oxygen was a successfully efficient one(4) . However, such a homogeneous catalyst was difficult to be recovered and reused. Within the framework of our researches for heterogenizing the homogeneous complexes, a variety of inorganic polymer supported metal complexes with nitrogen functional groups as chelating ligands have been found to be active catalysts in the organic reactions such as oxidation(5), hydrogenation(6) and hydroformylation(7). The exciting results prompt us to extend the catalytic properties of inorganic polymer supported metal complexes further to the area of epoxidation. The epoxidation of α-pinene with molecular oxygen catalyzed by magnesium oxide-supported polytitazane cobalt (III) complex (MgO-Ti-N-Co) is found an efficient alternative to the Mukaiyama's method. The catalyst is very stable and can be reused, so it is superior to the homogeneous catalyst reported.

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Experimental

Preparation of magnesium oxide-suported polytitanazane (MgO-Ti-N)

The Preparation of magnesium oxide supported polytitazane was similar to the previous method(7). Magnesium oxide (commercial product from Beijing Reagent Corporation, specific area 120m^2/g) was heated at 200°C under reduced pressure for 20hr prior to use. 20.20g pre-dried magnesium oxide, 6.27mL titanium tetrachloride and 500mL petroleum ether were placed in a 1000mL three-necked flask equipped with a stirrer, a gas inlet tube and a gas outlet tube. The mixture was stirred above an ice-bath and ammonia was bubbled into the flask for about 28h until the system became alkaline. The mixture was filtered, dried under the infrared lamp, then heated in a special furnace at 450°C to sublime the by-product ammonium chloride. Thus obtained 26.31g yellow powder product with nitrogen content calculated to be 8.70% by weight.

Preparation of magnesium oxide supported polytitazane cobalt complex (MgO-Ti-N-Co) and its XPS characterization.

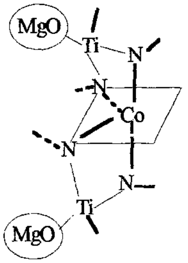
Several MgO-Ti-N-Co complexes with different amount of supported cobalt were prepared. For a typical example, $CoCl_2 \cdot 6H_2O$ (0.6215mmol) was dissolved in ethanol (20mL) in a 50mL flask, then MgO-Ti-N (1g) was added. The mixture was refluxed under nitrogen protection for about 18h until the solution became transparent and the solid became grey. After filtered and dried, the cobalt complex of magnesium oxide supported polytitazane was ready for use. XPS data were recorded on the PHI 5300 ESCA System (Perkin-Elmer). The system energy calibration was based on the binding energy of the adventitous carbon (284.60eV).

Epoxidation of α-pinene

A typical example is given for the epoxidation of α-pinene: The epoxidation was carried out at 25°C under an atmospheric pressure of oxygen. The 31mg (0.019mmol Co) catalyst sample, 0.159mL α-pinene, 0.109mL isobutyraldehyde and 2mL 1,2-dichloroethane were placed in a 50mL flask equipped with a condenser and a Teflon-coated magnetic stirring bar. The reaction was started by purging the solution with O_2 for several times. The catalyst was completely suspended in the mixture under vigorous stirring for 5hr reaction time. The mixture was then analyzed with methyl stearate as an internal standard in a ShangFen GC103 using a 2m stainless column of SE30. The products were identified using Shimadzu GC 17A-QP5000 MS technique.

Results and discussion

The XPS data for MgO-Ti-N, MgO-Ti-N-Co, $Co(NH_3)_6Cl_3$ and $CoCl_2 \cdot 6H_2O$ are listed in Table 1. The O_{1s} binding energy of MgO-Ti-N remains unchangeable after MgO-Ti-N complexing with cobalt. However, the 0.3eV N_{1s} binding energy of MgO-Ti-N-Co higher than that of MgO-Ti-N and 0.5eV difference between the Co_{2p} binding energy of $CoCl_2 \cdot 6H_2O$ and that of MgO-Ti-N-Co indicate that the electron density on nitrogen is shifted to the cobalt atom for coordination. The binding energy of Cl_{2p} (199.1eV) in $CoCl_2 \cdot 6H_2O$ declines to 198.4eV in MgO-Ti-N-Co and 197.9eV in $Co(NH_3)_6Cl_3$. Similar trend for the change of Cl_{2p} binding energy was observed after the inorganic polystannazane coordinating with copper chloride(8). The coordination of multidentate nitrogen ligand with cobalt in the present system may loose the Co-Cl bond of $CoCl_2{\cdot}6H_2O$. The shift of binding energy of Cl_{2p} may stand for the degree of the loose of Co-Cl bond caused by coordination of nitrogen ligand with cobalt. The Co-Cl bond of MgO-Ti-N-Co is therefore an intermediate between the Co-Cl bond of $CoCl_2{\cdot}6H_2O$ and that of $Co(NH_3)_6Cl_3$. The same binding energy of cobalt in two complexes $Co(NH_3)_6Cl_3$ and MgO-Ti-N-Co may infer the existence of high valent cobalt(III) in the MgO-Ti-N-Co. Actually, the stabilizing of high valent cobalt with multidenta nitrogen ligand was previously reported(9). The structure of MgO-Ti-N-Co(III) is thus proposed as follows:



(Structure of MgO-Ti-N-Co)

Table 1 XPS data for MgO-Ti-N, MgO-Ti-N-Co, $Co(NH_3)_6Cl_3$ and $CoCl_2{\cdot}6H_2O$

	Binding Energy (eV)			
Element	MgO-Ti-N	MgO-Ti-N-Co	$Co(NH_3)_6Cl_3$	$CoCl_2{\cdot}6H_2O$
O_{1s}	529.9	529.9		529.8
Ti_{2p}	458.5	458.2		
N_{1s}	399.4	399.7	400.1	
Cl_{2p}		198.4	197.9	199.1
Co_{2p}		781.1	781.1	781.6

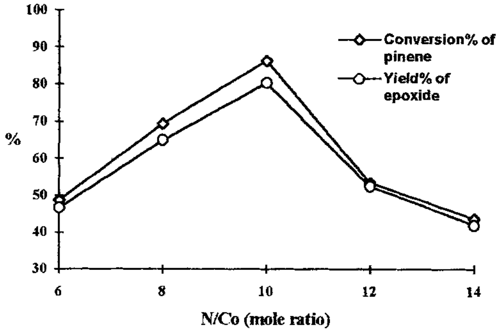


Figure 1 Influence of the N/Co mole ratio in magnesium oxide supported polytitazane cobalt (III) complexes on the epoxidation of α-Pinene
Conditions: N%=8.7wt%; dichloroethane, 2mL; α-Pinene, 1mmol; Co, 0.02mmol; n-hexanal, 2mmol; 25°C, O_2, 60h

The Influence of mole ratio of N/Co in the magnesium oxide supported polytitazane cobalt (III) complex on the epoxidation of α-pinene is illustrated in Figure 1. The N/Co mole ratios greatly affect the activities of the complexes. The yield of α-pinene oxide is 46.6% when the apparent N/Co mole ratio is 6. The 80.3% yield of α-pinene oxide is obtained at the apparent N/Co mole ratio of 10 when n-hexanal was used as a reductant. Both the lower and the higher N/Co mole ratios may not facilitate the formation and stabilization of the unsaturated coordinative cobalt intermediate.

Aldehyde was regarded as the reductant in the activation of molecular oxygen(4). With the MgO-Ti-N-Co complex, the effect of aldehydes on epoxidation of α-pinene are examined in Table 2. The oxygenation of α-pinene with n-hexanal as the reductant gives chemoselective epoxide product without allylic oxidation of α-pinene though conversion of α-pinene is relatively lower than that with isobutyraldehyde. Crotonaldehyde, cinnamaldehyde and p-anisaldehyde are all poor reductants in the present system. The branched isobutyraldehyde works best with the epoxide obtained 96.0% yield within 5h.

The two or more equivalent of the aldehyde to alkene typically used in the homogeneous Mukaiyama system is an urgent problem needed to be improved. As magnesium oxide-supported polytitazane cobalt (III) complex is tested as a new type of catalyst, the influence of aldehyde/α-pinene mole ratio on epoxidation of α-pinene is listed in Figure 2 . The epoxide is obtained in 61.6% yield at the aldehyde/α-pinene mole ratio 1.0. When a little excess of aldehyde is used, say at the aldehyde/α-pinene mole ratio 1.2, the yield of epoxide is improved to 94.4%. This may highlight the potential usage of magnesium oxide-supported polytitazane cobalt (III) complex as the catalyst in large-scale production of epoxides from cyclic alkenes.

Table 2 Effect of aldehydes on epoxidation of α-pinene

Aldehyde	C% of pinene	S% for epoxide	Y% of epoxide
i-butyraldehyde	99.4	96.6	96.0*
2-ethylhexanal	99.4	93.7	93.1
n-hexanal	61.7	98.6	60.8
crotonaldehyde	8.4	90.5	7.6
p-anisaldehyde	0	0	0
cinnamaldehyde	0	0	0

Conditions: MgO-Ti-N-Co (N/Co=10, 0.02mmolCo), 1.0mmol α-pinene, 25°C, 2.0mmol aldehyde, 2mL 1,2-dichloroethane, 1atm. O_2, 20h, *5h.

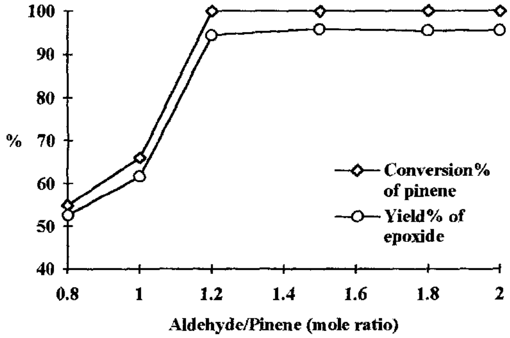


Figure 2 Influence of aldehyde/substrate mole ratio on the epoxidation of α-pinene
Conditions: MgO-Ti-N-Co (N/Co=10), dichloroethane 2mL, α-pinene 1mmol, Co 0.02mmol, 25°C, 5hr

The Stability of MgO-Ti-N-Co(III) complex in the epoxidation of α-Pinene was investigated in the following way: the polymer complex was recovered by filtration at the end of the epoxidation of α-pinene after washing with 1,2-dichloroethane three times, then the complex was used in successive runs under identical conditions. The conversion of α-Pinene and selectivity to α-Pinene oxide were determined after each run as described before. The data in Table 3 show that MgO-Ti-N-Co(III) complex is as active as the initial one after sixth recycling. After eighth recycling of the complex, the yield of the epoxide is still comparable with that of the homogeneous catalyst(10). The MgO-Ti-N-Co(III) complex therefore is very stable in the epoxidation of α-pinene.

Table 3 Stability of MgO-Ti-N-Co(III) complex in the epoxidation of α-Pinene

Entry	1	2	3	4	5	6	7	8
conversion of α-pinene, %	100	99.4	99.8	100	99.5	100	85.1	83.2
yield of the epoxide, %	96.7	95.3	95.7	94.7	95.3	95.5	75.2	70.4

Conditions: MgO-Ti-N-Co (N/Co=10, 0.02mmolCo), dichloroethane 2mL, α-pinene 1mmol, i-butyraldehyde 1.2mmol, 25°C, 5hr/each run.

Conclusions

Magnesium oxide-supported polytitazane cobalt complex has been prepared and characterized by XPS. It is a very effective catalyst for the epoxidation of α-pinene with molecular oxygen. The α-pinene oxide can be obtained in 96.0% yield with 96.6% selectivity at 25°C under an atmospheric pressure of molecular oxygen. Isobutyraldehyde is the most effective reductant and only 1.2 equivalent of isobutyraldehyde to α-pinene can make the oxygenation of α-pinene with the 94.4% yield of the corresponding epoxide. The catalyst is also very stable and can be reused at least eight times without loss of its activity.

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