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Silica Supported Methyltrioxorhenium Complex of γ-(2,2'-Dipyridyl)-aminopropylpolysiloxane as a Novel Catalyst for Epoxidation of Alkenes

T. -J. Wang[a]; D. -C. Li[a]; J. -H. Bai[a]; M. -Y. Huang[a]; Y. -Y. Jiang[a]
[a] Institute of Chemistry Chinese Academy of Sciences, Beijing, China

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NOTES

SILICA SUPPORTED METHYLTRIOXORHENIUM COMPLEX OF γ-(2,2'-DIPYRIDYL)-AMINOPROPYLPOLYSILOXANE AS A NOVEL CATALYST FOR EPOXIDATION OF ALKENES

Tie-Jun Wang,* De-Chang Li, Jun-Hong Bai,
Mei-Yu Huang, and Ying-Yan Jiang
Institute of Chemistry
Chinese Academy of Sciences
Beijing 100080, China

ABSTRACT

Silica supported methyltrioxorhenium complex of γ-(2,2'-dipyridyl)-aminopropyl polysiloxane (III) has been synthesized and demonstrated as a novel catalyst of high activity, stability and improved selectivity for epoxidation of alkenes with hydrogen peroxide at room temperature. The catalyst can be recycled at least five times.

INTRODUCTION

Methyltrioxorhenium (MTO) has been found to be the most active catalyst for alkene oxidation with hydrogen peroxide [1-3]. In comparison with other metal-containing epoxidation catalysts, MTO shows high activity at room temperature and even below, and affects no decomposition of hydrogen peroxide [4, 5]. Till now, numerous organorhenium oxides have been tested as homogeneous catalysts for olefin epoxidation, but few related on the heterogeneous side [6]. It is generally known that polymeric support can concentrate the ligand on its backbone and inorgano-organo hybrid polysiloxanes are both oxidatively-resistant and of high specific surface area [7]. Those intrinsic properties of inorgano-organo hybrid polysiloxanes encourage us to explore a new kind of epoxidation catalyst by immobilizing MTO on inorgano-organo hybrid polysiloxanes. Nitrogen base such as 2,2'-bipyridine is reported to form adduct with MTO to suppress the side reactions in epoxidation reaction [8]. In the present paper, silica-supported γ-(2,2'-dipyridyl)aminopropyl derivative is synthesized and used for immobilizing MTO. With hydrogen peroxide as an oxidant, the immobilized MTO catalyst indeed exhibits high activity and improves selectivity for epoxidation of alkenes at room temperature. Furthermore, it can be recycled at least five times and also makes the epoxidation process easy to work up.

EXPERIMENTAL

THF was deprived of water prior to use. 2,2'-dipyridylamine was purchased from Aldrich. All the alkenes were of analytical grade and used as given. The precipitated silica (surface area 370 m^2/g) was modified by γ-chloropropyltriethoxysilane according to the previous method [9] (Cl%=6.31% by weight). MTO was synthesized according to the method described in the literature [1]. IR spectra were recorded on a Bruker 130 FT-IR spectrophotometer using KBr pellet.

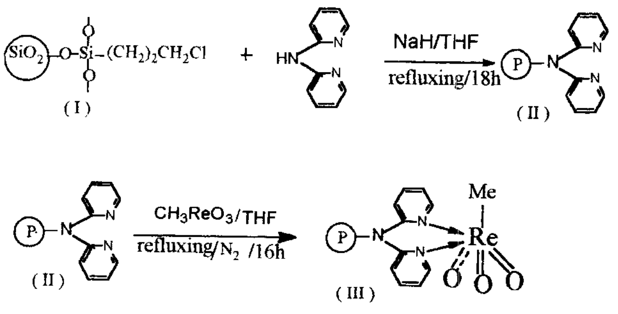
Preparation of Silica Supported MTO Complexes of γ-(2,2'-dipyridyl)-aminopropyl Derivative

To a flask were added 1.149g of 2,2'-dipyridylamine (DPA), 5 g of modified silica (I) and 0.2818 g of NaH in 200 mL of anhydrous THF. The mixture was stirred at 50°C for 18 hours followed by filtration. The product (II) was extracted in a Soxhlet extractor with mixture of benzene/water (4:1) for a day, then dried for nitrogen analysis. Its nitrogen content amounted to 1.50 mmol/g calculated from nitrogen element analysis. Silica supported methyltrioxorhenium complexes of γ-(2,2'-dipyridyl)-aminopropyl derivative (III) with different N/Re mole ratio were prepared. For a example, complex (III) with N/Re of 2 was prepared by stirring 0.5 g (II) in 5mL anhydrous THF solution of 0.0934 g MTO under nitrogen protection for 16 hours. Then, the collected compounds were washed several times with anhydrous THF and dried under vacuum at room temperature for use. The synthesis of methytrioxorhenium complex (III) of silica-supported γ-(2,2'-dipyridyl)aminopropyl derivative is illustrated in Scheme 1.

MTO Complex (III) Catalyzed Oxidation of Alkenes

Preparation of Oxidation Solution

80 mL of t-butanol was kept at 25°C and mixed with 24 mL 30% hydrogen



SCHEME 1

peroxide. The solution was stirred with 35 g of anhydrous $MgSO_4$ for 3 hours and then filtered for use.

Catalytic Oxidation of Alkenes

The oxidation with H_2O_2 was carried out at room temperature with t-butanol as solvent. The prepared oxidation solution was added at the H_2O_2/substrate mole ratio of 3 and substrate/Re mole ratio of 30. At the end of the reaction, the reaction mixture was analyzed by GC-103 using a 2m stainless column of 10% SE30 on Chromsob and identified by comparing with those of authentic samples.

Evaluation of the Stability of Complex (III)

The stability of the complex (III) was determined in recycling experiments. The polymer complex was recovered by filtration at the end of the oxidation reaction after washing with t-butanol several times, and was used in successive runs under identical conditions.

RESULTS AND DISCUSSION

The IR spectrum of (II) in Scheme 1 shows new bands at 1598.76, 1526.47, 1481.4, 1439.24 cm^{-1}, which are indicative of the attachment of DPA on chloropropylsilica (I) [10]. Stretching vibration at 1598.76, 1526.47, 1481.40, 1439.24 cm^{-1} changes to 1658.70, 1607.14, 1561.74 and 1455.06 cm^{-1} respectively, while 965 cm^{-1} representing the Re-O stretching vibration mode in MTO [11] descends to 914.78 cm^{-1} after silica immobilized DPA(II) reacting with MTO. Such a Re-O vibration at 914.78 cm^{-1} is close to that at 916 cm^{-1} of the structure

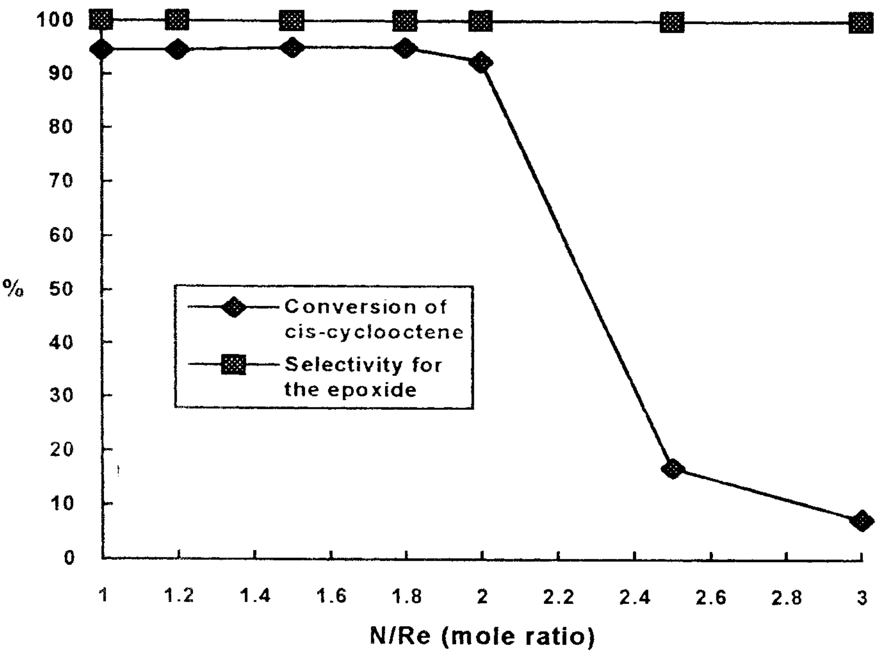


Figure 1. Influence of N/Re in complex (III) on the epoxidation of cis-cyclooctene Conditions: SiO_2-γ-DPA-$MeReO_3$ (1.50mmolN/g) 0.0454 g, cis-cyclooctene/Re (mol ratio)=30, H_2O_2/Substrate (mole ratio)=3, r. t., 4 hours, 2 mL t-Butanol.

characterized complex [3-(N,N-diethylamino)-n-propyl]trioxorhenium, where complex forms through nitrogen coordination to rhenium atom [1]. Since MTO, a strong Lewis acid, easily forms adduct with 2,2'-bipyridine [8] and DPA has been observed to coordinate to a variety of metal ions in a bidentate fashion forming a six-numbered chelate ring despite of its potential tridentate coordinated ability [12], it is suggested and as illustrated in Scheme 1 that a six-numbered ring complex (III) was formed with electron donated from nitrogen atom in pyridyl ring to rhenium atom in MTO.

Epoxidation of alkene with hydrogen peroxide catalyzed by supported methyltrioxorhenium complex (III) was investigated with cis-cyclooctene as the model substrate. The influence of N/Re mole ratio in methyltrioxorhenium complex (III) on the epoxidation of cis-cyclooctene is illustrated in Figure 1. When the N/Re mole ratio range from 1 to 2, the complex (III) displays both high activity and selectivity. However, completely chelated coordination of DPA to Re, where

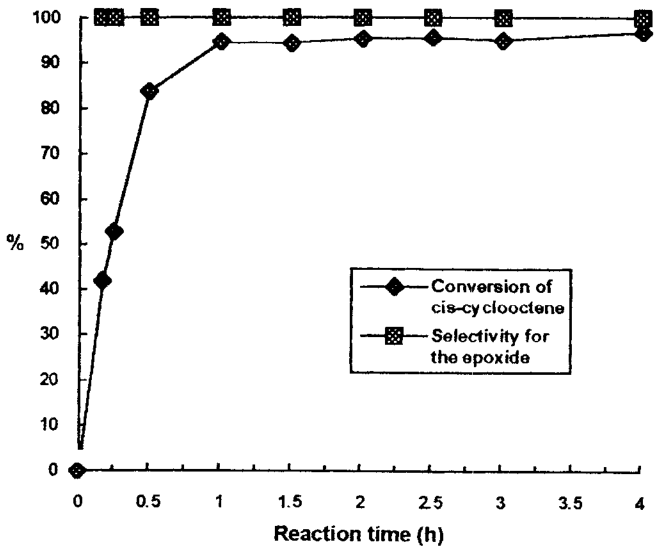
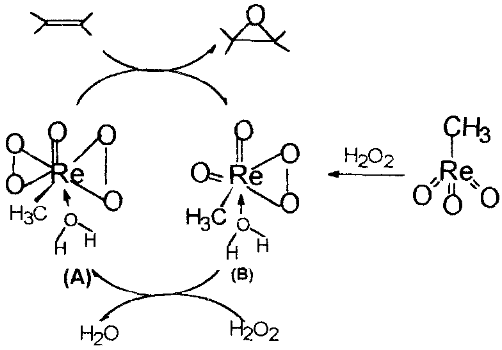


Figure 2. Influence of reaction time on the epoxidation of cis-cyclooctene Conditions: SiO_2-γ-DPA-$MeReO_3$ (1.50 mmolN/g, N/Re=2) 0.0454 g, r. t., 2 mL t-Butanol, cis-cyclooctene/Re (mol ratio)=30, H_2O_2/Substrate (mole ratio)=3.

N/Re=3, inhibits the catalytic activity. The strong inhibition effect of saturated nonaromatic tertiary amines and remarkable acceleration effect of pyridine on MTO activity have been confirmed very recently [13]. We attribute the loss of activity of the DPA coordinated MTO complex (N/Re=3) to the further coordination of the potential tertiary amine to MTO. When N/Re mole ratio ranges from 1 to 2, the maintained high activity of DPA coordinated MTO complex may be at the expense of coordination of another MTO molecule to the tertiary amine, thus shielding its detrimental effect towards activity of DPA coordinated MTO complex.

The catalytic behavior of the complex (III) is investigated in determining the time dependence of oxidation of cis-cyclooctene. Figure 2 shows a sharp increase in epoxide yield within 0.5 hours. The epoxide yield levels off at 94.7% one hour later with 100% selectivity. To our knowledge, no supported complexes with such a high activity have been reported for catalyzing epoxidation under mild conditions. The effective oxygen transfer reactivity of complex (III) can be attributed to the fact that reactivities of intermediates, monoperoxide-Re (B) and diperoxide-Re (A) are not inhibited by the presence of basic pyridine ligands [10].



Epoxidations of alkenes with H_2O_2 catalyzed by the complex (III) were investigated comparing with homogeneous MTO catalyzed reaction. The results are listed in Table 1. In comparison with the MTO catalyzed homogeneous reaction, the complex (III) shows somewhat decrease in activity but with considerably improved selectivity, especialy in cases of indene, cyclohexene, whose corresponding epoxide is believed easily to give ring-opening product respectively [8, 14]. However, the ring-opening reactions of nonbornene oxide and cyclopentene oxide are still serious. In the case of styrene, the oxidative cleavage of carbon-carbon double bond also takes place with benzaldehyde as the by-product. Design of other supported MTO complexes with high selectivity is being undertaken in the laboratory.

TABLE 1. Epoxidation of Alkenes with H_2O_2 Catalyzed by Complex (III) *versus* MTO

Alkenes	Conversion of Alkene, %	Selectivity (Yield) for the Epoxide, %	Selectivity (yield) for the Trans-1,2-diol, %
styrene	100	54.3 (54.3)	*42.7 (42.7)
cyclopentene	94.2	44.1 (43.7)	49.6 (46.7)
indene	72.4	100 (72.4)	0 (0)
norbornene	100	35.9 (35.9)	64.1 (64.1)
cyclohexene	83.8	62.1 (52.0)	35.2 (29.5)
cis-cyclooctene	94.6	100 (94.6)	0 (0)

Conditions: Complex (III) (N/Re=2, 0.075 mmolRe/g) 0.314 g (MTO 5.9 mg), Substrate/Re(mole ratio)=30, H_2O_2/Substrate(mole ratio)=3, r.t., 4 hours, 2 mL t-Butanol. * benzaldehyde

Data given are for SiO_2-(-N-DPA-$MeReO_3$ and (MTO) respectively.

TABLE 2. Stability of the Complex (III) in Epoxidation of Cis-cyclooctene*

Run No.	1	2	3	4	5
Conversion, %	96.2	95.4	94.9	89.5	87.6

Conditions: SiO_2-(-N-DPA-$MeReO_3$ (N/Re=2, 0.75 mmolRe/g) 0.03 g, r.t., Substrate/Re (mole ratio)=30, H_2O_2/Substrate (mole ratio)=3, 2 mL t-Butanol, 1 hour/each, * no trans-1,2-diol product was found during the recycling experiment.

The stability of the complex (III) was studied in the recycling experiments with epoxidation of cis-cyclooctene as model reaction. The results in Table 2 indicate that a slight decrease in activity occurs during the recycling experiments. Nevertheless, in the fifth recycling of the complex (III), the yield is still as high as 87.6%. Thus, the complex (III) is a stable catalyst in epoxidation of alkenes.

CONCLUSION

A novel modified silica supported methyltrioxorhenium complex (III) was prepared and characterized by IR. The complex with N/Re mole ratio of 2 is found an effective catalyst for the epoxidation of cis-cyclooctene with H_2O_2 in t-butanol at mild conditions. The yield of cis-cyclooctene oxide can amount to 94.7% within one hour. Selectivities for epoxides are improved with methyltrioxorhenium supported. The complex can be recycled at least five times.

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