

Highly effective catalysts of natural polymer supported Salophen Mn(III) complexes for aerobic oxidation of cyclohexene

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Received 9 May 2005; received in revised form 29 November 2005; accepted 31 December 2005

Available online 7 February 2006

Abstract

Three chitosan (abbreviated as CS) supported Salophen Mn(III) complexes were prepared in a simple way and characterized by FT-IR and XPS. Their abilities to catalyze allylic oxidation of cyclohexene with oxygen in the absence of solvents or reducing agents were studied. It has been revealed that the amino groups of CS coordinated with the Mn atoms of Salophen Mn(III) complexes to form CS–Salophen Mn(III) complexes, which have much better catalytic activities for allylic oxidation of cyclohexene than the corresponding unsupported Salophen Mn(III) complexes. Under reaction conditions of 343 K and ambient pressure of oxygen, after 12 h reaction, the cyclohexene oxidation catalyzed by CS–Salophen Mn(III) complex resulted in 11.03×10^4 turnover numbers (based on the manganese atom), which was about 44 times as large as that by unsupported Salophen Mn(III) complex. The influences of reaction temperature and reaction time on the oxidation of cyclohexene were also investigated.

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Keywords: Chitosan; Supported; Schiff base; Oxygen; Cyclohexene oxidation

1. Introduction

The allylic oxidation of olefin into α,β -unsaturated ketones is an important transformation in natural product synthesis [1]. In particular, the oxidation products of cyclohexene and their derivatives, viz. 2-cyclohexen-1-one, 1-methylcyclohex-1-en-3-one, etc., are important in organic synthesis owing to the presence of a highly reactive carbonyl group, which is utilized in cycloaddition reactions [2–4]. Great efforts have been devoted to the oxidation of cyclohexene in the past years [5–13]. Direct conversion of cyclohexene into adipic acid with H_2O_2 catalyzed by $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ combined with PTC has been reported by Sato et al. [14]. However, most processes reported suffer from relatively harsh conditions or poor conversions and selectivities. Awareness of environmental issues has proven a potent driving force in the development of environmentally friendly processes and technologies in the chemical industry [15,16]. In this aspect, more efficient catalytic system for oxidation of cyclohexene with molecular

oxygen without any solvents or reducing agents is particularly desirable.

Manganese Schiff base complexes are known to be active homogeneous catalysts in the epoxidation of olefins with various stoichiometric oxidants [17] such as peroxides, NaOCl or PhIO. The chiral manganese Schiff base catalysts developed by Jacobsen and co-workers are active and enantioselective epoxidation catalysts known to date [18]. Due to the inherent advantages of heterogeneous catalysts over homogeneous catalysts, much effort [19–22] has been made to immobilize these homogeneous catalysts onto solid supports, such as polymers [23], clays [24] and zeolites [22,25]. However, catalysts based on biopolymers have not received much attention.

Chitosan, the most abundant natural amino polysaccharide, is produced by the deacetylation of chitin, which is one of the key constituents of the shells of crustaceans and is a by-product of the fishing industry. It is readily formed into films or fibres for many applications [26]. The flexibility of the material, insoluble in the vast majority of solvents, but capable of being cast into films and fibres from dilute acid, along with its inherent chirality makes chitosan an excellent candidate for a support of catalyst. In this respect, several catalytic systems using chitosan as supports have been developed [27–35]. Functionalization of

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the chitosan to provide co-ordination sites has also been carried out and has provided catalysts for oxidation reactions and Suzuki and Heck reactions [36–38]. We previously reported that Schiff base copper complexes derived from chitosan and substituted salicylaldehydes were efficient catalysts for the cyclopropanation of styrene [39,40]. In this paper, we prepared chitosan supported Schiff base Mn(III) complexes and investigated their catalytic abilities in the oxidation of cyclohexene with oxygen without any solvents or reducing agents. High turnover numbers and selectivities were obtained.

2. Experimental

2.1. Materials and equipments

2,4-di-*tert*-Butylphenol was purchased from Fluka. Chitosan finely purified to a de-acetyl degree of 90.0% and with viscosity molecular weight (Mv) of 9.6×10^5 was provided by researcher Ai-Qin Wang (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences). Salicylaldehyde, cyclohexene and *o*-phenylenediamine were repurified before use. Other reagents were of analytical grade and were used as received. 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 5-nitro-2-hydroxybenzaldehyde were synthesized according to the procedure described in the literatures [41,42]. Salophen Mn(III) complexes **2a–c** were prepared as described in the literature [43] (Scheme 1). FT-IR spectra were measured on a Nexus 870 FT-IR spectrophotometer. XPS measurements were performed with a VG Scientific ESCALAB 210 instrument with Mg K α radiation (1253.6 eV). Atomic absorption results were obtained on a Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer. The reaction products of oxidation were determined by an HP 6890/5973 GC/MS instrument and analyzed by an Agilent 6820 gas chromatograph.

2.2. Preparation of chitosan supported Salophen Mn(III) complexes

Chitosan (2.0 g, equivalent to 10.80 mmol NH₂) was dissolved in 150 mL dilute acetic acid at 50 °C and stirred vig-

Table 1
The IR date of CS and CS–Salophen Mn(III) complexes

| Selective IR bands (cm ⁻¹) | Substances | | | |
|--|------------|---------------|---------------|---------------|
| | CS | CS– 2a | CS– 2b | CS– 2c |
| $\nu_{\text{N-H}}$ | 3473 | 3422 | 3427 | 3422 |
| $\delta_{\text{N-H}}$ | 1601 | – | – | – |

orously till the solution became clear. The pH of the solution was adjusted to 7 by addition of an aqueous solution of Na₂CO₃ (1%), and then, a second solution containing 0.15 mmol Salophen Mn(III) complex (**2a–c**) in 50 mL ethanol was added dropwise to the first solution. After stirred continuously for 20 h in these conditions, the mixture was separated by filtration. The solid was copiously washed with ethanol and acetone, dried at 90 °C under vacuum for 12 h to give chitosan supported Salophen Mn(III) (CS–**2a–c**) catalysts, which were then used for the oxidation of cyclohexene with molecular oxygen in the absence of solvents or reducing agents.

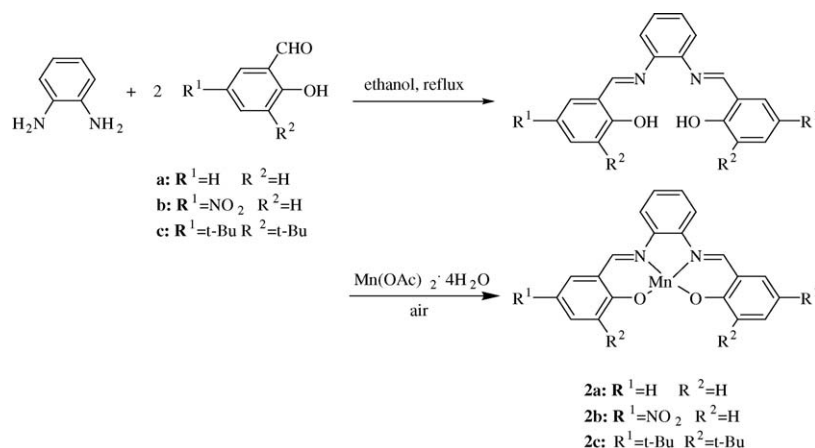
The metal contents of CS–**2a–c** determined by atomic absorption spectroscopy are 0.31, 0.59, and 0.56%, respectively.

2.3. Characterization of the catalysts

The catalysts obtained were characterized by FT-IR and XPS. The FT-IR spectrum of CS has a strong and broad absorption at 3473 cm⁻¹ which masks the N–H stretching band. However, in CS–**2a–c**, this absorption shifted to 3422, 3427, and 3422 cm⁻¹ respectively (Table 1). The absorption at 1601 cm⁻¹ on CS can be attributed to bending vibration of NH₂, but in CS–**2a–c** this absorption disappeared.

The data of XPS are shown in Table 2. It can be seen that after supporting, the binding energies of N 1s_{1/2} (in NH₂) increased and the binding energies of Mn 2p_{1/2} and Mn 2p_{2/3} decreased as expected (Table 2).

From the data of FT-IR and XPS, it can be concluded that the amino groups of chitosan coordinated with the manganese atoms of Salophen Mn(III) complexes to form CS–Salophen Mn(III) complexes.



Scheme 1. Procedure for synthesis of salophen Mn(III) complexes.

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