

# Effect of CNTs on direct oxidation of cyclohexene catalyzed by ruthenium diaminodiphosphine complex

Chun-Bo Li<sup>a</sup>, Wei-Xiong Pan<sup>a,\*</sup>, Wai-Kwok Wong<sup>b</sup>, Jin-Lu Li<sup>a</sup>,  
Xian-Qing Qiu<sup>a</sup>, Xiao-Ping Chen<sup>b</sup>

<sup>a</sup> State Key Laboratory of C<sub>1</sub> Chemistry and Technology, Department of Chemistry,  
Tsinghua University, Beijing 100084, PR China

<sup>b</sup> Department of Chemistry, HongKong Baptist University, Waterloo Road,  
Kowloon Tong, HongKong, PR China

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## Abstract

*trans*-RuCl<sub>2</sub>[κ<sup>3</sup>-1R,2R-P(NH)(NH)P](PPh<sub>3</sub>) was synthesized and used in the oxidation of cyclohexene at 80–130 °C by molecular oxygen with very high activity to the products including 2-cyclohexen-1-one, 2-cyclohexen-1-ol and 1,2-cyclohexandiols. The addition of carbon nanotubes (CNTs), which were synthesized by Fe-Cu/SiO<sub>2</sub> catalyzed decomposition of ethylene at 550 °C, can enhance the activity of the Ru complex and the selectivity of 2-cyclohexen-1-ol. It was also better for the recycling of the Ru complex, the catalytic activity and selectivity of which still held at a high level after nine times using.

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## 1. Introduction

The oxidation of cyclic alkenes by transition-metal complexes [1,2] has become a very important field in homogeneous catalysis due to its relevance in the modern synthetic chemical industry. A variety of complexes of cobalt [3–5], rhodium [6], palladium [7], ruthenium [8–10], manganese [11,12], iridium [13] and niobium [14] have been studied in the oxidation of cyclic alkenes. However, most of the reported work needs special oxidants such as hydroperoxide [10,14], iodosylbenzene [12] and *tert*-butylhydroperoxide (TBHP) [10,11], which result in difficult analyzing

and separating of products. So far, for the demand of benign environment, much effort has been devoted to the selective oxidation of cyclic alkenes with molecular oxygen catalyzed by transition-metal complexes [15,16].

As a new type of catalyst support, carbon nanotubes (CNTs) have been used in hydrogenation [17,18] and hydroformylation [19]. However, to our knowledge, there is lack of report on oxidation by using CNTs supported homogeneous catalyst. Both the effect of CNTs as support on the oxidative activity and selectivity of homogeneous catalyst and the stability of CNTs as carbon materials at severe oxidation conditions are still uncertain. In this paper, we are reporting new advances in the oxidation of cyclohexene catalyzed by new tridentate ruthenium complex with additive CNTs under severe reaction conditions.

\* Corresponding author. Tel.: +86-10-62772592;

fax: +86-10-62792122.

E-mail address: weixiongpan@yahoo.com (W.-X. Pan).

## 2. Experimental

### 2.1. Materials

Cyclohexene was purchased from commercial source, with concentration of 97% (w/w). CNTs were prepared by the catalytic decomposition of ethylene. Ruthenium complex was synthesized by the method later.

### 2.2. Synthesis of ruthenium diaminodiphosphine complex

A solution of *N,N'*-bis[2-(diphenylphosphino)benzyl]-1*R*,2*R*-diaminocyclo-hexane, 1*R*,2*R*-P(NH)(NH)P, and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> was stirred under a nitrogen atmosphere at room temperature for 4 h. After filtration and drying in vacuo, the dark red residue product, *trans*-RuCl<sub>2</sub>[κ<sup>3</sup>-1*R*,2*R*-P(NH)(NH)P](PPh<sub>3</sub>), which was analyzed by IR, NMR [<sup>31</sup>P-<sup>1</sup>H} and <sup>1</sup>H] and MS, was used as a catalyst. The tridentate nature of the P(NH)(NH)P ligand in this complex was also confirmed by X-ray crystallography. For more detailed information, please see the references [20,21] (Fig. 1).

### 2.3. CNTs preparation

CNTs were prepared by the decomposition of ethylene at 550 °C catalyzed by Fe-Cu/SiO<sub>2</sub> catalyst. Fe-Cu/SiO<sub>2</sub> was reduced in a quartz boat at 550 °C for 60 min with a mixture of hydrogen and nitrogen

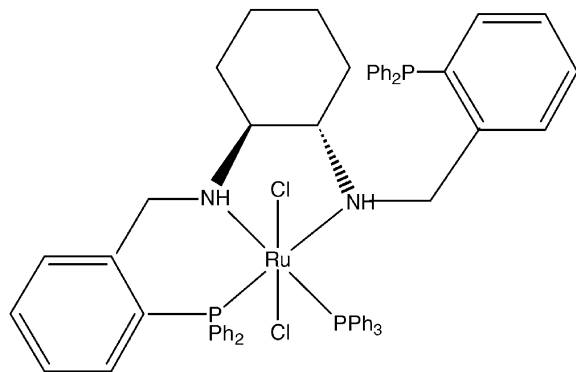


Fig. 1. Structure illustration of *trans*-RuCl<sub>2</sub>[κ<sup>3</sup>-1*R*,2*R*-P(NH)(NH)P](PPh<sub>3</sub>).

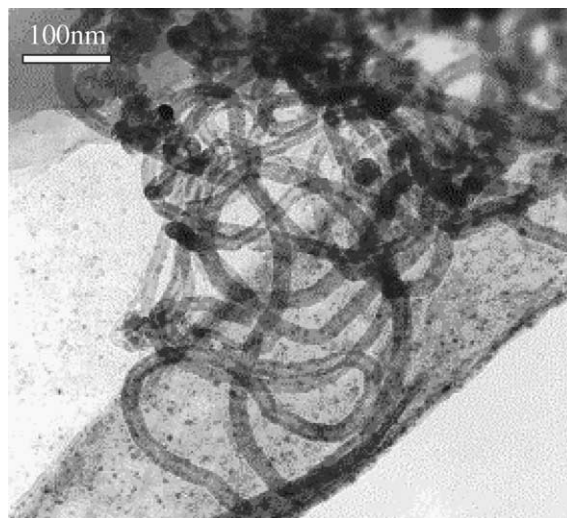


Fig. 2. TEM image of carbon nanotubes.

in a molar ratio of 1:8. Then the flowing gas was turned to a mixture of hydrogen and ethylene (7:2) and carried out the decomposition for 60 min with a flowing rate of 90 ml/min. The raw product was first immersed in an aqueous solution of HF to remove SiO<sub>2</sub>, then filtered and washed with distilled water, and refluxed in diluted HNO<sub>3</sub> for 4 h to remove the metals and amorphous carbon. The residue was filtered and washed for three times with distilled water to yield the CNT product. TEM analysis showed that the CNTs exhibited a multi-wall structure and their diameters were about 20–25 nm (Fig. 2).

### 2.4. Catalytic oxidation

The catalytic reactions were performed according to the following conditions. The reactor used was a 50 ml stainless steel autoclave with a temperature-controlling unit and a magnetic stirrer. The reaction temperatures were 80–130 °C, and the oxygen pressures were 1 and 2 MPa, respectively. The molar ratio of cyclohexene, Ru complex and CNTs was 20,274:1:570 (3 ml/29.6 mmol, 1.6 mg/0.00146 mmol and 10 mg/0.833 mmol, respectively). At the end of the reaction time, liquid samples were removed from the reactor and analyzed by HP-4890 GC (HP-5 capillary column) and HP-5890 GC-MS.

Table 1  
Effect of the reaction temperature on the oxidation of cyclohexene

Temperature (°C)	Conversion (%)	TOF <sup>a</sup> (h <sup>-1</sup> )	Product distribution (wt.%)		
			1-one	1-ol	1,2-diol
80	60.3	12225	43.5	18.9	6.5
105	80.7	16361	49.0	4.2	14.0
130	99.0	20274	42.9	13.9	10.4

Reaction conditions—oxygen pressure 2 MPa; reaction time 1.0 h; molar ratio of cyclohexene:catalyst:CNTs = 20,274:1:570.

<sup>a</sup> Defined as: converted cyclohexene mole per hour divided by the Ru catalyst mole used. The TOF obtained by this definition will be larger than that of Ru catalyst contribution alone if blank activity exists.

### 3. Results and discussion

#### 3.1. Effect of reaction temperature on cyclohexene oxidation

The oxidation of cyclohexene was carried out at several temperatures while the O<sub>2</sub> pressure was fixed at 2 MPa. Table 1 shows the results of the oxidation at reaction temperatures 80, 105 and 130 °C, respectively. It can be seen that the TOF of the catalyst was extremely high in the reaction temperature range and that with the increase of the reaction temperature, the conversion of cyclohexene increased remarkably. The reaction temperature also affected the distribution of the products. We can conclude that the reaction temperature has strong accelerative effect on the rate of the oxidation of cyclohexene.

#### 3.2. Effect of reaction time and O<sub>2</sub> pressure on cyclohexene oxidation

The oxidation of cyclohexene was carried out at pressures 1 and 2 MPa, respectively (Table 2). When the O<sub>2</sub> pressure was 1 MPa, the cyclohexene con-

version increased with the reaction time initially, but longer reaction time did not cause increasing in the conversion of cyclohexene significantly but decreasing the selectivity remarkably after 1 h. To get total conversion and better selectivity the higher O<sub>2</sub> pressure 2 MPa was preferred, where the initial reaction rate was higher than that at 1 MPa and the conversion of cyclohexene increased with reaction time too. Cyclohexene was almost totally converted after 1 h at 2 MPa. We can see that the O<sub>2</sub> pressure is also an important parameter for the oxidation of cyclohexene and 2 MPa might be a better operation pressure both for activity and selectivity.

#### 3.3. The role of Ru and CNTs in the oxidation

The results of cyclohexene oxidation with and without CNTs are presented in Table 3. For comparison, the results of the Ru catalyst with TBHP oxidant and the blank oxidation with O<sub>2</sub> are also given. We can see from the table that the TOF by using O<sub>2</sub> at higher temperature is much higher than that by using strong oxidant TBHP at room temperature. Oxidation products were also observed in blank experiments without

Table 2  
Effect of the reaction time and O<sub>2</sub> pressure on the oxidation of cyclohexene

O <sub>2</sub> pressure (MPa)	Reaction time (h)	Conversion (%)	TOF (h <sup>-1</sup> )	Products distribution (wt.%)		
				1-one	1-ol	1,2-diol
1.0	0.5	44.8	18166	36.2	27.2	1.8
1.0	1.0	83.8	16990	45.1	14.2	9.7
1.0	1.5	94.0	12705	32.6	5.0	7.1
2.0	0.5	93.8	38034	38.5	19.7	7.7
2.0	1.0	99.0	20071	42.9	13.9	10.4

Reaction conditions—reaction temperature 130 °C; molar ratio of cyclohexene:catalyst:CNTs = 20,274:1:570.

Table 3  
Catalytic activity of Ru-CNTs

Temperature (°C)	Catalysts	Oxidant	Pressure (MPa)	Time (h)	Conversion (%)	TOF (h <sup>-1</sup> )	Products distribution (%)		
							1-one	1-ol	1,2-diol
130	–	O <sub>2</sub>	1	0.5	42.0	–	26.4	35.6	2.0
130	–	O <sub>2</sub>	2	1	62.7	–	34.6	18.8	6.0
20	Ru	TBHP <sup>a</sup>	0	16	25.0	121	53.3	44.3	2.5
130	CNTs	O <sub>2</sub>	2	1	62.9	–	40.7	16.4	8.9
130	Ru	O <sub>2</sub>	2	1	81.4	16503	46.8	4.4	14.8
130	Ru-CNTs <sup>b</sup>	O <sub>2</sub>	2	1	99.0	20071	42.9	13.9	10.4

<sup>a</sup> Molar ratio of cyclohexene:catalyst = 7800:1 (0.5 ml/1.0 mg), 2.5 ml benzene as solvent.

<sup>b</sup> Molar ratio of cyclohexene:catalyst:CNTs = 20,274:1:570.

catalyst under severe oxidation conditions, though the selectivity to 2-cyclohexen-1-one, 2-cyclohexen-1-ol and 1,2-cyclohexandiol was too low and the conversion was not high enough. This agrees with the result of Sridhar and co-workers [22] to some extent.

The addition of Ru complex catalyst, which was rather active in the octane oxidation by oxygen [20], increased the selective oxidation of cyclohexene to 2-cyclohexen-1-one (see entries 2 and 5 in Table 3). From the strong dependence of the activity on the temperature the oxidation reaction of cyclohexene seems to proceed by a radical mechanism. It was easy to cause an explosion if higher reaction temperature was employed.

From the entries 2 and 4 in Table 3 we can see that CNTs alone had no activity. It demonstrated that CNTs had not been doped by some Fe and Cu, which might be active for oxidation, after washing by HF and HNO<sub>3</sub> and that CNTs had no oxidation activity itself. It can increase the conversion and selectivity to 2-cyclohexen-1-ol and decrease the selectivity of 2-cyclohexen-1-one while used together with the Ru complex. This might be due to the electronic property and the carboxyl on the coping of carbon nanotubes. Lei reported that the organic acid had similar function in the oxidation of cyclohexene at 70 °C catalyzed by PS-bipy-Ru-bipy [9], but the catalysis activity decreased very much. Differently from that result, while the CNTs were added to the reaction system the cyclohexene conversion increased obviously in our system.

The addition of CNTs also facilitates the recycle use of the catalyst. Fig. 3 shows the performance of the repeatedly used catalyst. The reactions were performed using the catalyst which had been used in the previous reaction and separated from the products by

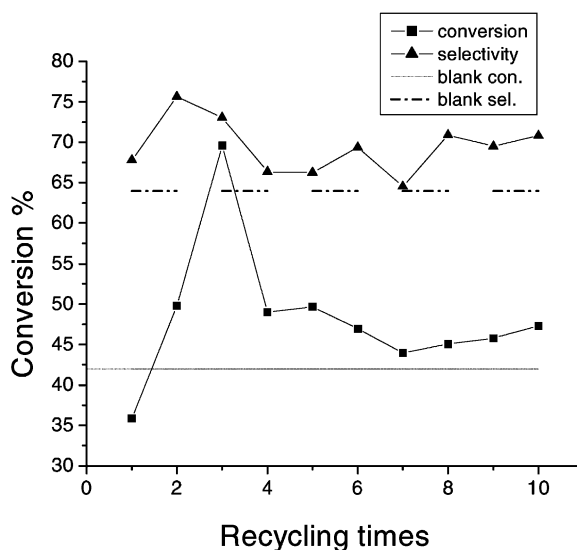


Fig. 3. Cyclohexene conversion and total products selectivity vs. recycling times (reaction conditions—reaction temperature 130 °C; molar ratio of cyclohexene:catalyst:CNTs = 20,274:1:570 (for the first time); O<sub>2</sub> pressure 1.0 MPa; reaction time 0.5 h).

filtration without supplement of any Ru complex and CNTs. The catalyst still had high activity after nine times of reuse. The increase in the conversion of cyclohexene in the second and third time reactions hints that there is an induction period. From the fourth time on, the conversion of cyclohexene maintains a level of about 45% of the original one while keeping the selectivity unchanged.

The leaching of Ru catalyst from the CNTs had not been measured for it could be hard to distinguish the leaching from CNTs or the filtration lost of the fine particles of CNTs if Ru lost was founded. From the

results of nine times using the leaching of Ru should be less. The nine time using also demonstrated that CNTs loaded homogeneous catalyst had enough stability under severe oxidation conditions.

#### 4. Conclusion

The novel tridentate Ru complex has an extremely high activity with a TOF around  $20,000 \text{ h}^{-1}$  in the oxidation of cyclohexene by molecular oxygen. Both the reaction temperature and the  $\text{O}_2$  pressure are important parameters for this reaction. The adequate reaction conditions are  $130^\circ\text{C}$ , 2 MPa  $\text{O}_2$  for 1 h.

The addition of CNTs to the Ru complex can enhance the conversion of cyclohexene and the selectivity to 2-cyclohexen-1-ol. CNTs can also take up the Ru catalysts by adsorption and thereby facilitate the reusability at a quite high conversion level.

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