

# Highly efficient catalysts of chitosan-Schiff base Co(II) and Pd(II) complexes for aerobic oxidation of cyclohexane in the absence of reductants and solvents

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## Abstract

Three chitosan-Schiff base Co(II) and Pd(II) complexes were prepared in a simple way and characterized by FT-IR, XPS and TG. Their abilities to catalyze oxidation of cyclohexane into cyclohexanone and cyclohexanol with oxygen in the absence of any solvents or reducing agents were studied. It has been revealed that the complexes had high catalytic activities for heterogeneous cyclohexane oxidation with oxygen. Especially, the oxidation of cyclohexane catalyzed by chitosan-salicylaldehyde Schiff base Co(II) complex under 1.6 MPa of initial oxygen pressure at 418 K gave excellent results with 9100 turnover numbers (based on the cobalt atom) and 96% selectivity for cyclohexanone and cyclohexanol after reaction of 4.5 h. The influences of oxygen pressure, reaction temperature and reaction time on the oxidation of cyclohexane were also investigated. It has been also revealed that the complexes were efficient for the oxidation of bulky cyclic alkanes and linear alkanes. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Chitosan-Schiff base; Co(II) and Pd(II) complexes; Oxygen; Cyclohexane oxidation

## 1. Introduction

Functionalization of hydrocarbons by selective oxidation is a very useful reaction and has been studied comprehensively over the past decade. Of particular importance is the oxidation of cyclohexane due to the large demand for cyclohexanone and cyclohexanol, which are important raw materials for the production of adipic acid and caprolactam [1–4]. Great efforts have been devoted to the oxidation of cyclohexane in the past years [5–24]. Direct conversion of cyclohexane into adipic acid with molecular oxygen catalyzed by *N*-hydroxyphthalimide combined with Mn(acac)<sub>2</sub> and Co(OAc)<sub>2</sub> has been reported by Ishii and coworkers [24]. However, owing to employment of large amounts of solvents and/or reducing agents as well as harsh reaction

conditions, it is still difficult to apply these technologies to industrial production [5–21,25]. Therefore, industrial oxidation of cyclohexane to cyclohexanone and cyclohexanol at present is still carried out using soluble cobalt catalyst or no catalyst, in which cyclohexane conversion is less than 3.9% and the selectivity for cyclohexanol and cyclohexanone is 78% [26–28]. So the great demand for these oxidation products and the high-energy intensity of the present process warrant a replacement with a more effective catalytic process. Oxidation of cyclohexane with molecular oxygen without any solvents or reducing agents is particularly desirable from both economical and environmental aspects.

Due to the inherent advantages of heterogeneous catalysts over homogeneous catalysts, a great deal of efforts have been devoted to the development of heterogeneous catalysts [8–17]. However, the majority of these reported catalysts were based on silicates and molecular sieves, catalysts based on biopolymers having not received much attention.

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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 [29]. 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 as a support for catalysis. In this respect, several catalytic systems using chitosan as supports have been developed [23,30–37]. Functionalisation of the chitosan to provide co-ordination sites has also been carried out and has provided catalysts for oxidation reactions and Suzuki and Heck reactions [38,39]. We previously reported that Schiff base copper complexes derived from chitosan and substituted salicylaldehydes were efficient catalysts for the cyclopropanation of styrene [40,41]. In this paper, we prepared chitosan-Schiff base cobalt(II) and palladium(II) complexes and investigated their catalytic abilities in the oxidation of cyclohexane with oxygen without any solvents or reducing agents. High turnover numbers and selectivities were obtained.

## 2. Experimental

### 2.1. Materials and equipments

Pyridine-2-carboxaldehyde and cyclooctane were purchased from Fluka. Chitosan finely purified to a de-acetyl degree of 90.0% and with viscosity molecular weight ( $M_v$ ) of  $9.6 \times 10^5$  was provided by researcher Ai-Qin Wang (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences). Salicylaldehyde and cyclohexane were distilled before use. Other reagents were of analytical grade and were used as received. 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 $\alpha$  radiation (1253.6 eV). Atomic absorption results were obtained on a Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer. The TG analyses were performed on a TGA7 thermogravimetric analyzer (Perkin-Elmer, USA). The oxidation products were determined by an

HP 6890/5973 GC/MS instrument and analyzed by an Agilent 6820 gas chromatograph.

### 2.2. Preparation of the chitosan-Schiff base complexes

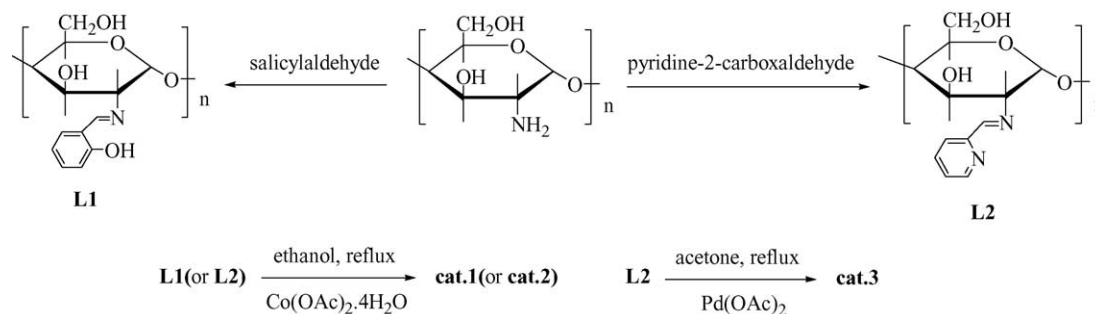
Chitosan-Schiff base Co(II) and Pd(II) complexes were prepared according to a modified procedure in the literature (Scheme 1) [39]. Chitosan (2.0 g, equivalent to 10.80 mmol NH<sub>2</sub>) and salicylaldehyde (1.319 g, 10.80 mmol) or pyridine-2-carboxaldehyde (1.157 g, 10.80 mmol) were added to ethanol (60 mL), and then the mixture was refluxed for 30 h. After the resultant mixture was cooled, the solid was separated by filtration, washed with ethanol and then dried at 50 °C under vacuum for 12 h to give **L1** or **L2**. **L1** or **L2** (1.5 g), to which were added Co(OAc)<sub>2</sub>·4H<sub>2</sub>O or Pd(OAc)<sub>2</sub> with different ratios in 60 ml ethanol or acetone and then the mixture was refluxed for 20 h under an argon atmosphere. After the reaction, the solids were collected by filtration, preconditioned by multiple washings as described in [39] to remove any loose metal species, and dried at 90 °C under vacuum to give catalysts **cat.1–cat.3**, which were then used to catalyze the oxidation of cyclohexane with molecular oxygen.

The metal contents of **cat.1–cat.3** determined by atomic absorption spectroscopy are 2.28%, 7.08% and 4.68%, respectively.

### 2.3. Characterization of the catalysts

The catalysts obtained were characterized by FT-IR, XPS and TG. FT-IR analyses were carried out using diffuse reflectance IR. The spectrum of chitosan has a strong and broad absorption centered around 3500 cm<sup>-1</sup> which masks the N–H stretching band. Diagnostic peaks appeared on **L1** and **L2** at 1635 and 1650 cm<sup>-1</sup> respectively. These bands are due to the stretching vibrations of the C=N bonds. No H-bonded or free aldehyde were evident in the range 1675–1710 cm<sup>-1</sup> on **L1** and **L2**. In **cat.1–cat.3**, however, the absorption of C=N bonds shifted to 1632, 1647 and 1648 cm<sup>-1</sup>, respectively, as previously described [39,42].

From the data of XPS (Table 1), it can be seen that the binding energies of O 1s and C=N bond N 1s in **cat.1** are 1.2 and 1.5 eV higher than those in **L1**. Binding energies of C=N



Scheme 1. Procedure for synthesis of **cat.1–cat.3**.

Table 1  
The data of X-ray photoelectron spectroscopy (XPS)

XPS peak	Binding energy (eV)						
	L1	L2	cat.1	cat.2	cat.3	Co(OAc) <sub>2</sub>	Pd(OAc) <sub>2</sub>
O 1s	531.7	532.1	532.9	531.8	531.8	–	–
N 1s	401.8	402.0	403.3	402.8	402.4	–	–
	–	398.5	–	398.8	398.5	–	–
Co 2p <sub>1/2</sub>	–	–	795.4	796.2	–	797.8	–
Pd 3d <sub>5/2</sub>	–	–	–	–	337.1	–	338.7

bond N 1s in **L2** are 402.0 eV, which are 0.8 and 0.4 eV lower than those in **cat.2** and **cat.3**, respectively. Binding energies of pyridine-2-carboxaldehyde N 1s in **L2** is 398.5 eV, which are 0.3 eV lower than those in **cat.2**. Binding energies of O 1s in **cat.2** and **cat.3** are 0.3 eV lower than those in **L2**, respectively. Co 2p<sub>1/2</sub> binding energies in **cat.1** and **cat.2** are 2.4 and 1.6 eV lower than those in Co(OAc)<sub>2</sub>, respectively. Binding energies of Pd 3d<sub>5/2</sub> in **cat.3** are 1.6 eV lower than those in Pd(OAc)<sub>2</sub>.

From the data of FT-IR and XPS, it can be concluded that Co(II) and Pd(II) coordinated with chitosan-Schiff base.

The TG data of the **cat.1–cat.3** are depicted in Fig. 1. From these results, the destruction temperatures of **cat.1–cat.3** are 256, 208 and 218 °C, respectively. The weight loss of the catalysts before the destruction is attributed to desorption of water.

#### 2.4. Oxidation of cyclohexane

The oxidation of cyclohexane was performed in a 30 mL stainless steel autoclave equipped with a magnetic stirrer and an automatic temperature controller. In a typical reaction, 2.0 mg catalyst and 7.0 mL (65.2 mmol) cyclohexane were added to the autoclave. The autoclave was flushed three times with O<sub>2</sub> and pressurized to the desired pressure, then heated to the desired temperature with stirring. After the reaction,

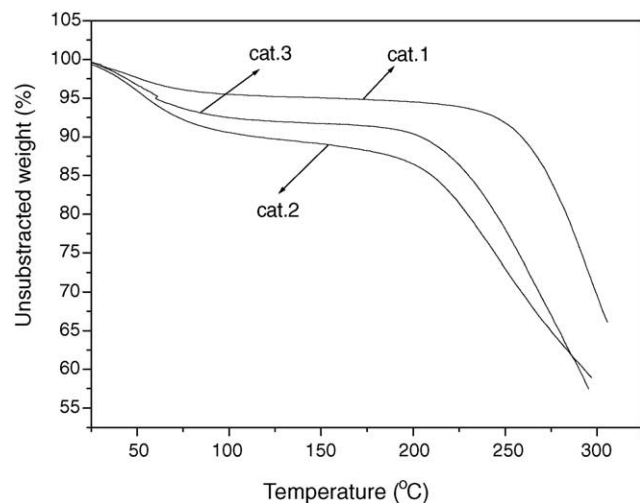
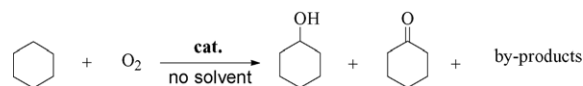


Fig. 1. The TG date of **cat.1–cat.3**.



Scheme 2. Oxidation of cyclohexane.

the autoclave was cooled to room temperature and slowly depressurized. The samples were identified by GC–MS and quantified by GC. The by-products of the reaction were di-cyclohexyl, adipic acid and esters (Scheme 2).

### 3. Results and discussion

#### 3.1. The effect of different oxygen pressure

The efficiencies of the chitosan-Schiff base Co(II) and Pd(II) complexes as catalysts for oxidation of cyclohexane at different oxygen pressure are shown in Figs. 2 and 3. It is clear that for each of the three catalysts, the conversion increased with increasing oxygen pressure (Fig. 2). For **cat.1** and **cat.3**, the selectivity for cyclohexanone increased with the increase in oxygen pressure from 0.8 to 1.6 MPa and then decreased when the oxygen pressure exceeded 1.6 MPa. For

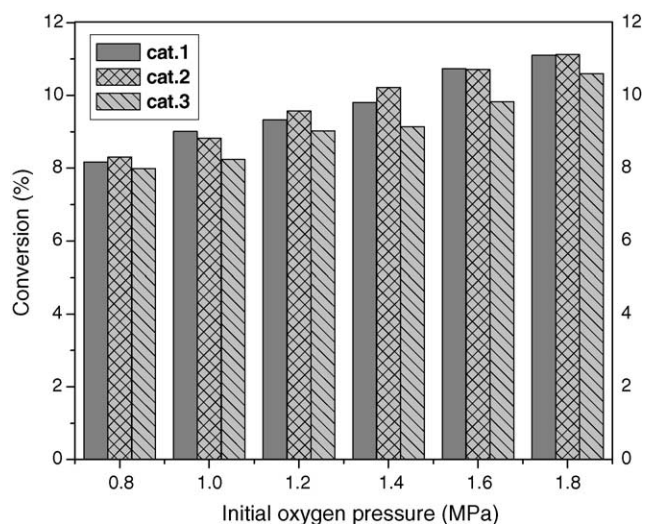


Fig. 2. The effect of oxygen pressure on cyclohexane conversion: (a) conditions: catalyst 2.0 mg, cyclohexane 7.0 mL (65.2 mmol), 145 °C, 4.5 h; (b) conversion was determined by GC; (c) caution: the reaction under such conditions is dangerous. Do be careful!

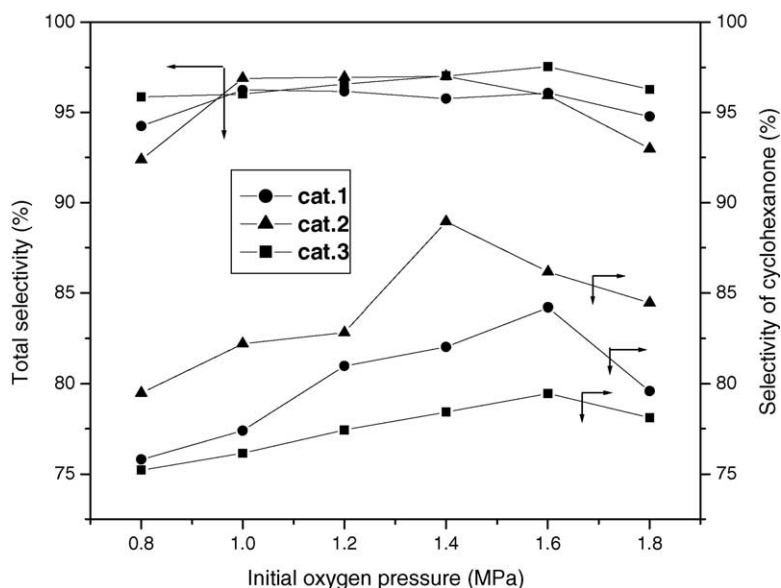


Fig. 3. The effect of oxygen pressure on total selectivity and selectivity for cyclohexanone: (a) conditions as in Fig. 2; (b) selectivity was determined by GC; (c) total selectivity = the selectivity of cyclohexanone add the selectivity for cyclohexanol.

**cat.2** the highest selectivity for cyclohexanone was obtained at 1.4 MPa. As for the total selectivity, the effect of oxygen pressure was unapparent (Fig. 3).

### 3.2. The effect of reaction temperature

As shown in Fig. 4, the conversion increased to the maximum and then decreased with the rise in the reaction temperature for each catalyst. Generally, there are two possible reasons for this decrease: the loss of the metal atoms and

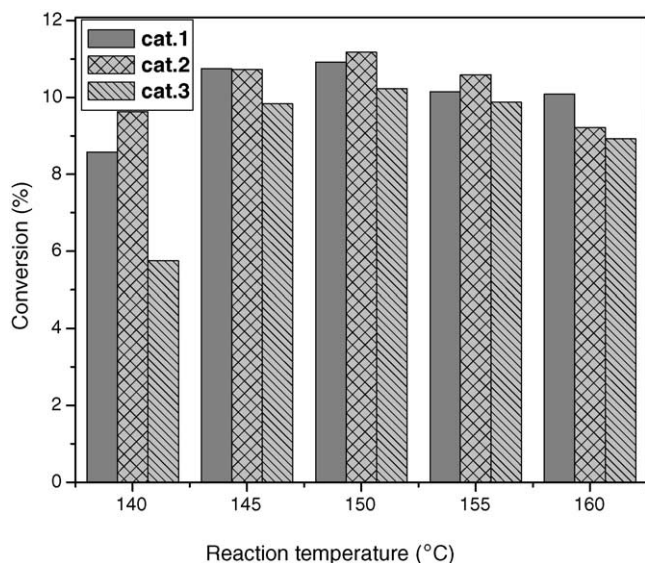


Fig. 4. The effect of reaction temperature on cyclohexane conversion. Conditions: catalyst 2.0 mg, cyclohexane 7.0 mL (65.2 mmol), initial oxygen pressure 1.6 MPa, 4.5 h.

the destruction of the catalyst at high reaction temperature. The TG data of the catalysts (Fig. 1) show that the catalysts have no apparent destruction when the temperature is below 200 °C. So progressive decreasing conversion with an increase in the reaction temperature above 145 °C for cyclohexane oxidation is mainly due to the loss of the metal atoms.

Fig. 5 shows the selectivity for cyclohexanone and the total selectivity as a function of the reaction temperature. It is clear that high temperature favors the formation of cyclohexanone. In the range of 140–160 °C, the total selectivity decreased for **cat.2**, but for **cat.1** and **cat.3**, it first increased and then decreased, with the highest values at 145 °C. Even so, **cat.2** gave higher selectivity for cyclohexanone than **cat.1** and **cat.3** under the same conditions. In addition, reaction temperature seems to have little effects on the total selectivity for **cat.3** in comparison with the other two catalysts (Fig. 5).

### 3.3. The effect of reaction time

Figs. 6 and 7 present the effects of reaction time on cyclohexane oxidation with oxygen. The reaction hardly occurred during the first 1 h, which might be the initiation period according to the generally accepted free radical mechanism [43]. After the initiation period, the cyclohexane conversion and the selectivity of cyclohexanone increased for every catalyst as the reaction time was prolonged. For **cat.2**, the total selectivity slowly increased with the reaction time going on. In the case of **cat.1** and **cat.3**, the total selectivity first increased slowly but then decreased slightly, with the highest values at 4.5 h (Fig. 7). It is obvious that the cyclohexane conversion for **cat.2** was higher than those for **cat.1** and **cat.3** between 1 and 3.5 h. After 4.0 h, the cyclohexane conversion for **cat.1** increased to the level of **cat.2** (Fig. 6). We also found

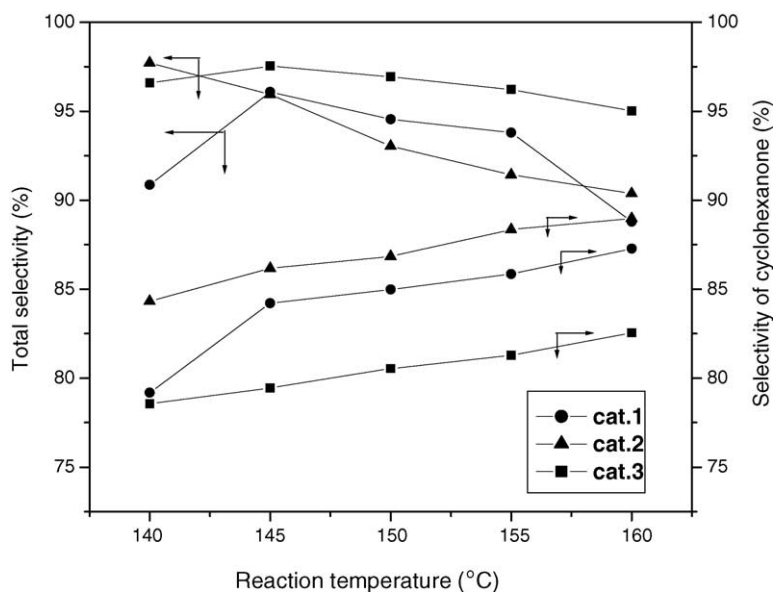


Fig. 5. The effect of reaction temperature on total selectivity and selectivity for cyclohexanone. Conditions as in Fig. 4.

that **cat.2** gave the highest cyclohexanone selectivity among the three catalysts (Fig. 7).

### 3.4. Reuse of the catalysts

To investigate the reusability of chitosan-Schiff base Co(II) and Pd(II) complexes, the catalysts were separated by filtration after the first run, dried at 90 °C under vacuum and then subjected to the second run under the same conditions. The data obtained are listed in Table 2. As shown in Table 2, the total selectivity changed only slightly for the three catalysts after four runs, but the conversion of cyclohexane and

the selectivity of cyclohexanone dropped. The decrease in the activity could be mainly attributed to the loss of metal atoms and catalyst during the reaction and filtration. From the average of the results, the activities of the three catalysts can be arranged in the following manner: **cat.2** < **cat.3** < **cat.1**. A possible explanation for high turnover numbers of Co(II) containing chitosan-salicylaldehyde complex as compared to those of chitosan-pyridine-2-carboxaldehyde complex for cyclohexane oxidation is that the oxygen atom of hydroxyl in salicylaldehyde have greater ability to coordinate than the nitrogen atom in pyridine-2-carboxaldehyde.

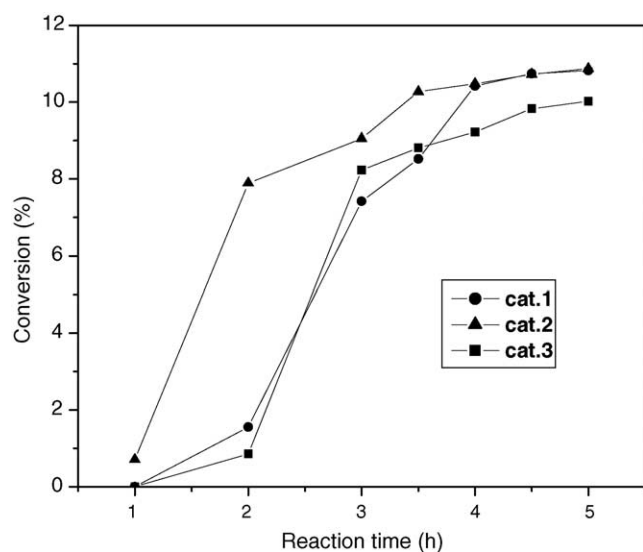


Fig. 6. The effect of reaction time on cyclohexane conversion. Conditions: catalyst 2.0 mg, cyclohexane 7.0 mL (65.2 mmol), initial oxygen pressure 1.6 MPa, 145 °C.

Table 2  
Reuse of the catalysts<sup>a</sup>

Recycle no.	Catalyst	Conversion (%)	TON <sup>b</sup> ( $\times 10^3$ )	Selectivity (%)	
				Total	Cyclohexanone
Fresh	<b>cat.1</b>	10.7	9.1	96.1	84.2
	<b>cat.2</b>	10.7	2.9	96.0	86.2
	<b>cat.3</b>	9.8	7.3	97.5	79.5
1	<b>cat.1</b>	9.6	8.1	97.2	81.7
	<b>cat.2</b>	8.9	2.4	97.6	82.5
	<b>cat.3</b>	8.5	6.3	99.2	82.1
2	<b>cat.1</b>	8.1	6.8	97.1	84.7
	<b>cat.2</b>	7.4	2.0	99.5	85.8
	<b>cat.3</b>	7.2	5.3	99.6	86.6
3	<b>cat.1</b>	7.6	6.4	98.3	88.5
	<b>cat.2</b>	6.1	1.7	99.7	86.6
	<b>cat.3</b>	6.3	4.7	99.6	88.3
Average	<b>cat.1</b>	9.0	7.6	97.2	84.8
	<b>cat.2</b>	8.3	2.2	98.2	85.3
	<b>cat.3</b>	8.0	5.9	99.0	84.1

<sup>a</sup> Conditions: catalyst 2.0 mg, cyclohexane 7.0 mL (65.2 mmol), initial oxygen pressure 1.6 MPa, 145 °C, 4.5 h.

<sup>b</sup> Moles of substrate converted per mole of metal (Co, Pd) in the catalyst.

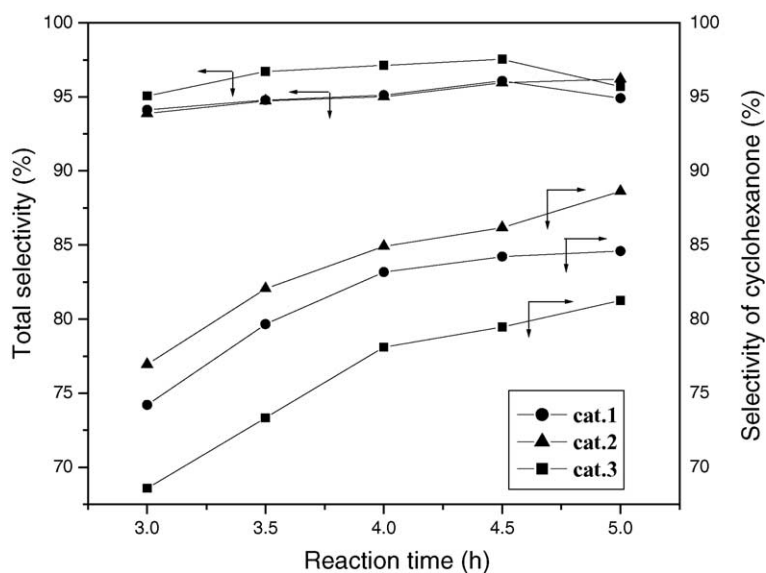


Fig. 7. The effect of reaction time on total selectivity and selectivity for cyclohexanone. Conditions as in Fig. 6.

### 3.5. Comparison of catalytic activities of chitosan-Schiff base Co(II) and Pd(II) complexes with Co(OAc)<sub>2</sub>, Pd(OAc)<sub>2</sub> and Co(acac)<sub>3</sub>

The catalytic activities of chitosan-Schiff base Co(II) and Pd(II) complexes, Co(OAc)<sub>2</sub>, Pd(OAc)<sub>2</sub>, Co(acac)<sub>3</sub> for oxidation of cyclohexane are listed in Table 3. Data obtained with no catalyst are also shown for comparison. Chitosan-Schiff base complexes gave much higher conversions, selectivities and turnover numbers than the corresponding acetates, Co(acac)<sub>3</sub> or no catalyst.

## 4. Extension to other substrates

The optimal reaction conditions were applied to other cyclic and linear alkanes. The results are listed in Table 4.

Table 4  
Oxidation of other substrates<sup>a</sup>

Substrate	Catalyst	Conversion (%)	TON <sup>b</sup> ( $\times 10^3$ )	Selectivity (%)		
				1-Cyclooctanone	1,4-Cyclohexanedione	4-Octanone
Cyclooctane	cat.1	19.0	12.8	81.8	18.2	
	cat.2	18.0	3.9	79.3	20.7	
	cat.3	21.1	12.5	82.5	17.5	
Heptane	cat.1	3.5	2.2	82.0	18.0	
	cat.2	3.4	0.7	82.5	17.5	
	cat.3	2.1	1.2	82.5	17.5	
Octane	cat.1	4.1	2.3	69.6	26.1	4.3
	cat.2	3.6	0.6	67.0	28.3	4.7
	cat.3	3.4	1.6	71.0	29.0	–

<sup>a</sup> Reaction conditions: catalyst 2.0 mg, substrate 7.0 mL, initial oxygen pressure 1.6 MPa, 145 °C, 4.5 h.

<sup>b</sup> Moles of substrate converted per mole of metal (Co, Pd) in the catalyst.

Table 3

Comparison of catalytic abilities of chitosan-Schiff base Co(II) and Pd(II) complexes with Co(OAc)<sub>2</sub>, Pd(OAc)<sub>2</sub> and Co(acac)<sub>3</sub><sup>a</sup>

Catalyst	Conversion (%)	TON <sup>b</sup> ( $\times 10^3$ )	Selectivity (%)	
			Total	Cyclohexanone
cat.1	10.7	9.1	96.1	84.2
cat.2	10.7	2.9	96.0	86.2
cat.3	9.8	7.3	97.5	79.5
Co(OAc) <sub>2</sub>	7.6	0.6	83.6	70.4
Pd(OAc) <sub>2</sub>	4.4	0.3	91.4	64.5
Co(acac) <sub>3</sub>	7.7	0.9	90.2	76.9
No catalyst	5.9	–	89.5	72.4

<sup>a</sup> Conditions: catalyst 2.0 mg, substrate 7.0 mL, initial oxygen pressure 1.6 MPa, 145 °C, 4.5 h.

<sup>b</sup> Moles of substrate converted per mole of metal (Co, Pd) in the catalyst.

It is shown that the three catalysts are more effective in the oxidation of cyclooctane than in the oxidation of cyclohexane, but for heptane and octane only low conversions were obtained.

## 5. Conclusions

Chitosan-Schiff base Co(II) and Pd(II) complexes prove to be active and reusable catalysts for cyclohexane oxidation with oxygen in the absence of reducing agents or solvents; high turnover numbers and selectivity can be obtained. The complexes are also effective for oxidation of bulky cyclic alkane and linear alkane. Chitosan is cheap and plentiful, and possesses particular microstructure, lower acidity (compared to supports such as silica) and excellent function; the catalysts are easy for preparation and can be easily separated after the reaction. These properties endow chitosan-Schiff base Co(II) and Pd(II) complexes with a bright future in industrial applications. This work, along with other published work, indicates that chitosan is a particularly interesting support for catalysts and its inherent chirality will form the basis for further applications of this fascinating material.

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