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Synthesis, Characterization and Catalytic Activity of Dialdehyde Starch-Schiff Base Co(II) Complex in the Oxidation of Cyclohexane

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Abstract Dialdehyde starch-Schiff base Co(II) complex was prepared in a simple way and characterized by FT-IR, UV–vis and XPS. Its ability to catalyze oxidation of cyclohexane with oxygen in the absence of solvents or reducing agents was studied, and its reusability of the catalyst also be investigated.

Keywords Dialdehyde starch · Schiff base Co(II) complex · Cyclohexane · Oxidation

1 Introduction

The selective oxidation of saturated hydrocarbons is one of the most challenging and promising subjects in oxidation chemistry [1]. Of particular importance is the oxidation of cyclohexane due to the large demand for cyclohexanone and cyclohexanol (KA oil), which are important raw materials for the production of adipic acid and caprolactam [2]. Traditionally, the process for cyclohexane oxidation is carried out at 423–433 K in the presence of a homogeneous catalyst. This process is low in energy efficiency and generates plenty of by-products [3, 4]. So it is necessary to find an environmentally friendly way to improve the catalytic process of oxidizing cyclohexane under mild conditions.

Schiff base transition metal complexes are a family of homogeneous oxidation catalysts for a variety of organic substrates, and have been widely applied in the area of bio-inorganic and bio-organic and catalytic chemistry [5–10]. In the field of biomimetic dioxygen carrier, the ability of Schiff base cobalt complex to bind dioxygen reversibly has been extensively examined since 1938 Tsumaki discovered that Co(Salen) could carry dioxygen reversibly [11], many Schiff base cobalt complexes were synthesized and applied in oxidation reactions.

However, difficulty of recovery is one of the major drawbacks of these homogeneous catalysts, so a great deal of efforts has been devoted to the development of heterogeneous catalysts [12–20]. The encapsulation in zeolites [16, 19, 20], the grafting on polymers [12, 18] or silica [13–15, 17] have been used as supporting methods. Application of alumina-supported catalyst also has been received attention in recent years [21]. However, the catalysts based on biopolymers have not received much attention.

Dialdehyde starch (DAS), obtained after periodate oxidative cleavage of the C_2–C_3 bonds in the anhydroglucose units of starch, is an interesting product with several viable industrial applications [22]. The insolubility in the vast majority of solvents makes dialdehyde starch an excellent candidate for a support of catalyst. In this paper, we prepared DAS-Schiff base cobalt (II) complex and investigated its catalytic ability in the oxidation of cyclohexane with molecular oxygen in the absence of any solvents or reducing agents.

2 Experimental

2.1 Materials and Equipments

Cyclohexane was redistilled before being used. The moisture of potato starch (PS) was 20 wt%. All the other reagents were analytically pure.

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IR spectra were recorded using FTS165 Spectrophotometer. Electronic spectral data was obtained on T6 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed with a VG Scientific ESCALAB 210 instrument with Mg Kαradiation (1,253.6 eV). In order to correct for possible deviations caused by electric charge of the samples, the graphitic C1s peak at 284.6 eV was taken as internal standard [23]. The metal contents of the catalysts were measured by Perkin Elmer 4100-1319 atomic absorption spectrophotometer. The products of oxidation were determined by an HP 6890/5973 GC-MS instrument and analyzed by an Agilent 6820 gas chromatograph.

2.2 Synthesis of the Catalyst

2.2.1 *Synthesis of DAS*

DAS was synthesized by sodium periodate oxidation of potato starch (PS) (Scheme 1). The oxidation was performed in a 10 wt% aqueous suspension at pH 3 and 25 °C in the dark. After filtration and washing, the products were freeze-dried. Consequently, the dried products were sieved and the granular fraction smaller than 150 pm was applied for the subsequent reaction. The degree of oxidation (DO), which corresponds with the aldehyde content (CHO), determined chromatographically according to the literature [24] was 99.12%.

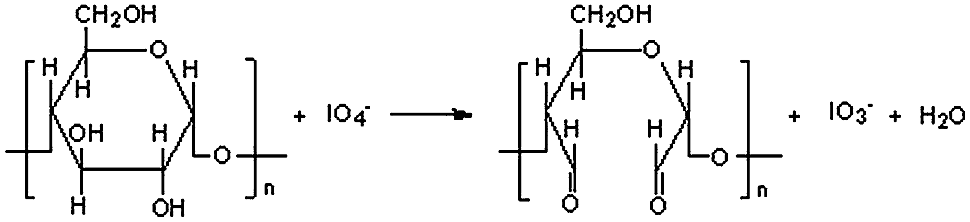
2.2.2 *Synthesis of the Catalyst*

DAS 1.6 g (equivalent to 20 mmol CHO) and 2-aminophenol 4.36 g (40 mmol) were added to 100 mL ethanol; the mixture was refluxed for 2 h and then cooled to room temperature. The solid was separated by filtration, washed with ethanol and dried at 50 °C under vacuum for 12 h to give DAS-Schiff base, to which were added $Co(OAC)_2 \cdot 4H_2O$ in 50 mL ethanol, and then the mixture was refluxed for 8 h under a nitrogen atmosphere. After the reaction, the solids were collected by filtration, preconditioned by multiple washings to remove any loose metal species, and dried at 80 °C under vacuum to give DAS-Schiff base cobalt (II) complex (Scheme 2). The metal content of the catalyst determined by atomic absorption spectroscopy was 2.08 wt%.

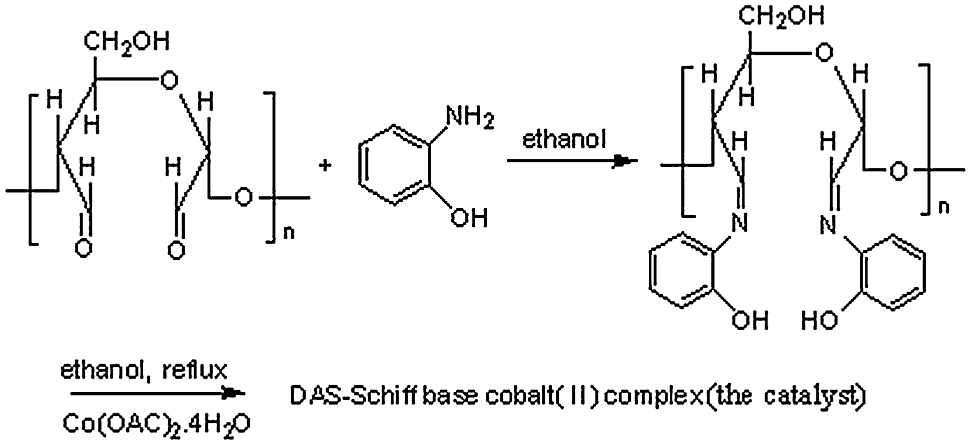
2.3 Oxidation of Cyclohexane

The oxidation of cyclohexane was carried out in a 600 mL stainless steel autoclave equipped with a magnetic stirrer and an automatic temperature controller. In a typical reaction, 200 mL cyclohexane and 0.05 g catalysts were added to the autoclave, oxygen was pressurized into the autoclave and the pressure was kept constant, and then heated to the desired temperature with stirring. After the reaction, the autoclave was cooled and slowly depressurized. The liquid phase mixture was analyzed by gas chromatography (GC), and chlorobenzene was used as internal standard. Product quantification was carried out using calibration curves obtained with standard solutions of cyclohexane, cyclohexanone and cyclohexanol as internal standard. Since cyclohexyl hydroperoxide (CHHP) decomposed in part during chromatographic analysis, CHHP contents were determined by decomposition with PPh3 [25] and quantification of the additionally formed

Scheme 1 Procedure for synthesis of DAS



Scheme 2 Procedure for synthesis of the catalyst



cyclohexanol and cyclohexanone by GC. The formation of acids was investigated by esterification of the reaction mixture with *n*-butyl alcohol and identification of the products by GC-MS.

The conversion of cyclohexane (mol%) was calculated based on moles of cyclohexane converted to cyclohexanone, cyclohexanol, cyclohexyl hydroperoxide and diacids. The selectivity of each product (%) equaled (moles of each product yielded/moles of cyclohexane converted) × 100%.

3 Results and Discussion

3.1 Characterization of the Catalyst

The catalyst obtained was characterized by FT-IR, UV–vis and XPS. FT-IR spectra were recorded on KBr pellet using FTS165 Spectrophotometer. The IR spectra of DAS showed bands at 1,730, 2,720 and 2,820 cm^{-1} corresponding to the stretching vibrations of the C=O and C–H bonds respectively. The diagnostic peaks appeared on the DAS-Schiff base at 1,636 cm^{-1}, which were due to the stretching vibrations of the C=N bonds. In the catalyst, however, the absorption of C=N bonds shift to 1,624 cm^{-1}, as previously described [21]. Furthermore, in the catalyst strong to medium intensity bands were observed at 422 and 536 cm^{-1} attributed to the stretching vibrations of Co–N and Co–O bonds, respectively.

The electronic spectrum of the catalyst was recorded in T6 spectrophotometer. The catalyst showed a shift in $\pi \rightarrow \pi^*$ transition from ~260 to ~230 nm and $n \rightarrow \pi^*$ transition from ~320 to ~280 nm. In addition, the band at ~420 nm which was assigned to d→d transition of cobalt (II) [21] also was been observed.

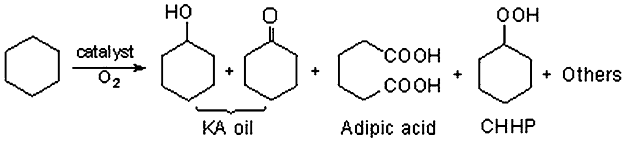
The XPS was performed with a VG Scientific ESCALAB 210 instrument with Mg Kαradiation (1,253.6 eV). The binding energy of –CHO O 1s was 531.2 eV in DAS, and –OH O 1s was 532.3 eV in starch. The binding energies of O 1s (531.9 eV) and C=N bond N 1s (401.5 EV) in the catalyst were higher than those in DAS-Schiff base (O 1s: 530.8 eV, N 1s: 399.2 eV), and Co 2p3/2 binding energy (795.9 eV) in the catalyst was lower than that in $\mathrm{Co(OAc)_2}$ (797.6 eV).

On the basis of all these studies, it could be concluded that cobalt (II) had coordinated with DAS-Schiff base.

3.2 Oxidation of Cyclohexane

Cyclohexane was oxidized by molecular oxygen to KA oil (cyclohexanol and cyclohexanone), adipic acid, CHHP, and others (Scheme 3). The reaction results were listed in Table 1.

As shown in Table 1, the conversion of cyclohexane increased with reaction temperature and time. The selectivity of KA oil reached the maximum at 120 °C for 6 h and then decreased. The selectivity of adipic acid increased all along, while the selectivity of CHHP decreased. This phenomenon could be explained by followed reason: at the lower temperature, the energy was not sufficient for the activation of oxygen molecules or the catalytic circulation, on the other hand, the oxidation reaction was incomplete in a short time. As increasing temperature and time, CHHP was apt to decompose to cyclohexanol and cyclohexanone sufficiently, so the selectivity of KA oil increased. The



Scheme 3 Oxidation of cyclohexane to KA oil, adipic acid, CHHP and others

Table 1 The oxidation of cyclohexane with molecular oxygen

Entry	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)			TON^b (×10^3)
				KA oil	Adipic acid	CHHP	
1^a	120	6	3.8	79.7	2.3	3.1	–
2	120	6	10.2(10.07) [12]	81.6	4.1	2.8	10.7
3	120	5	9.1(10.2) [13]	77.2	3.6	3.2	9.5
4	120	4	7.9(5.3) [14]	75.4	3.5	3.5	8.3
5	120	7	10.6(6.8) [15]	78.3	4.0	2.4	11.1
6	110	6	8.8(11.5) [16]	76.9	3.6	3.2	9.2
7	100	6	7.3(1.03) [17]	73.8	3.4	3.4	7.7
8	130	6	11.7(10.7) [18]	78.5	4.2	2.3	12.3

Reaction conditions: cyclohexane 200 mL, catalyst 0.05 g, 1.4 MPa O_2

[a] The reaction was carried out in the absence of any catalyst

[b] TON (turnover number) moles of substrate converted per mole metal ion

decreased selectivity of KA oil was mainly due to the continued oxidation of KA oil.

In order to further study the process, the effect of oxygen pressure on the reaction was investigated. The effect of oxygen pressure on the oxidation of cyclohexane was shown in Fig. 1. It was clear that the conversion increased with increasing oxygen pressure, while the selectivity of CHHP decreased. The selectivity of KA oil reached the maximum at 1.4 MPa and subsequently decreased. The reason was that at a lower oxygen pressure, the concentration of O_2 in cyclohexane was so low that little oxygen could be activated by catalysts which resulted in the lower conversions. The decreased selectivity of CHHP was ascribed to the decomposition of CHHP at higher oxygen pressure, which was also the reason for the increasing selectivity of KA oil. However, excessive oxygen pressure could lead to oxidize adipic acid to others.

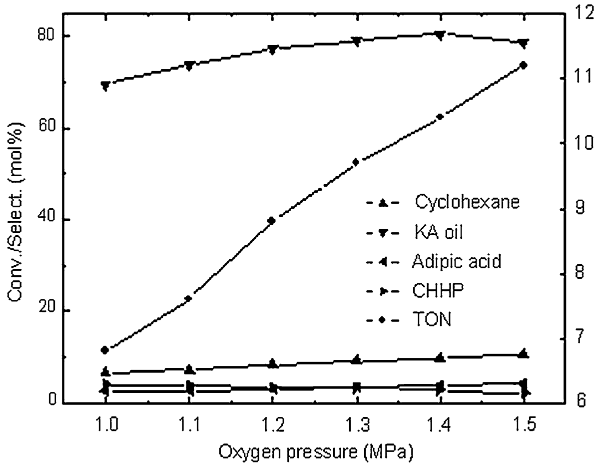


Fig. 1 The effect of oxygen pressure on the oxidation of cyclohexane. Reaction conditions: cyclohexane 200 mL, catalyst 0.05 g, 120 °C, 6 h

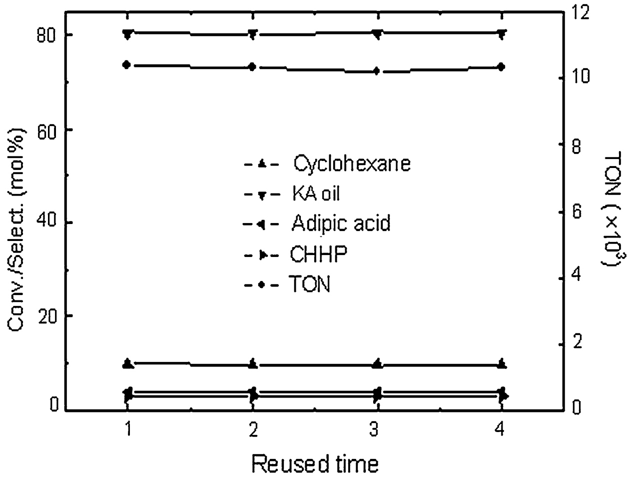


Fig. 2 Recycling study of the catalyst. Reaction conditions: cyclohexane 200 mL, catalyst 0.05 g, 120 °C, 1.4 MPa, 6 h

Recycling tests with repeated use of the catalyst in four consecutive reactions were carried out. The catalyst was removed from the reaction mixture after 6 h by filtration, washed with ether and dried at 80 °C for 5 h and subjected to the next catalytic run under the same conditions, and the results were shown in Fig. 2. As shown in Fig. 2, the reused catalyst displayed consistent reactivity and selectivity.

4 Conclusions

Dialdehyde starch-Schiff base Co(II) complex proved to be active and reusable catalyst for cyclohexane oxidation with oxygen in the absence of solvents or reducing agents, high turnover number of catalyst and the selectivity of the product could be obtained. The catalyst was easy for preparation and could be easily separated after the reaction. Furthermore, the catalyst could be reused for at least four reaction cycles without considerable loss of reactivity. These properties endowed dialdehyde starch-Schiff base Co(II) complex with a bright future in industrial applications.

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