Efficient allylic oxidation of cyclohexene with oxygen catalyzed by chloromethylated polystyrene supported tridentate Schiff-base complexes

Yue Chang [a,b,*], Yurong Lv [a], Feng Lu [a], Fei Zha [a], Ziqiang Lei [a,b]

[a] College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, Gansu, China
[b] Key Laboratory of Eco-environment-related Polymer Materials Ministry of Education, Lanzhou 730070, Gansu, China

ARTICLE INFO

ABSTRACT

Four novel chloromethylated polystyrene supported tridentate Schiff-base metal complexes (PS–DA–M, M = Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+}, respectively) were prepared by chloromethylated polystyrene and tridentate Schiff-base ligands, which were synthesized by 2,4-dihydroxyacetophotone with 2-aminopyridine. The complexes were characterized by the methods of ICP, FT-IR, XPS and TG/DTA. The catalytic activity of the complexes in the oxidation of cyclohexene with molecular oxygen was determined. The results showed that oxidation reaction was occurred in the allylic carbon atoms. The products are cyclohexene oxide, 2-cyclohexene-1-ol, 2-cyclohexene-1-one and 2-cyclohexene-1-hydroperoxide. Although all of four complexes showed good catalytic activity, PS–DA–Cu exhibited the best. The conversion of cyclohexene can be reached to 51.9% under the temperature of 343 K when using 2 mg of PS–DA–Cu to catalytic oxidation of 2 ml of cyclohexene. The influences of reaction temperature, the amount of catalyst, the reaction time were investigated, and the mechanism of cyclohexene oxidation was also discussed.

1. Introduction

Transition metal complexes as catalysts for the oxidation of cyclohexene have attracted a deal of attention in recent years, mainly for the oxidation products of cyclohexene and the derivatives present the highly reactive carbonyl groups in the cycloaddition reactions [1–3]. Of the variety of ligands employed so far, the noteworthy examples include porphyrin derivatives, macrocyclic, phthalocyanine, and Schiff-base [1,2,4–12]. Among these substrates, Schiff-base transition metal complexes are the attractive oxidation catalysts. It can be prepared simply and cheaply for industrial applications. However, homogenous catalyst is difficult to be separated from reaction system, and thus influence the recycle. To overcome these disadvantages, Schiff-base complexes were immobilized with zeolite [11], modified silica [13], chitosan [14], and chloromethylated polystyrene [15–18].

In addition, during the process of catalytic reaction, these catalysts need a mono-oxygen source such as H, PhIO, NaClO, to carry out oxygen transferring to the olefin. However, these oxidants were not environmental friendly. With much attention has been directed toward the development of environmental, molecular oxygen as a cheap, environmentally clean and convenient oxidant is suitable

[5,7,10,19–24]. Meanwhile, it was observed that the oxidation efficiency of molecular oxygen is poor. 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 [25–28].

In this work, chloromethylated polystyrene supported tridentate Schiff-base metal complexes (PS–DA–M, M = Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+}, respectively) were prepared by chloromethylated polystyrene and tridentate Schiff-base ligand, which was synthesized by 2,4-dihydroxyacetophotone with 2-aminopyridine. It was found that cyclohexene could be effectively catalyzed by these complexes under mild conditions using oxygen without reductant. The allylic hydroperoxide was obtained as an important product, which was suggested as an efficient allylic oxidation pathway.
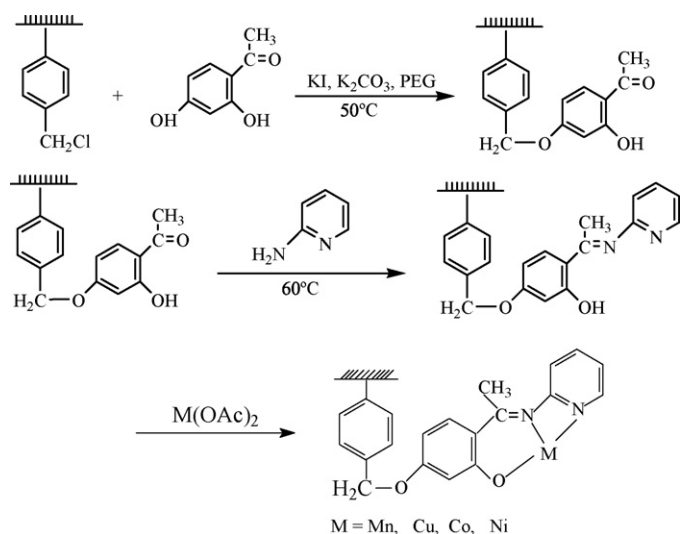
2. Experimental

2.1. Materials and instruments

Chloromethylated polystyrene (PS) contains 4.5 mmol of Cl/g and of 10% cross-linked di-vinybenzene. Cyclohexene was of chemical purity. Other chemicals used were of analytical purity. ICP measurements were carried out using a Perkin-Elmer ICP/6500. FT-IR spectra were recorded on a Digilab Merlin FTS 3000 FT-IR spectrophotometer in KBr pellets. The reaction products of oxidation were determined by a HP 6890/5973 GC/MS instrument and analyzed by a Shimadzu GC-16A gas chromatograph

* Corresponding author at: College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, Gansu, China.
Tel.: +86 931 797 1533; fax: +86 931 797 1261.
E-mail addresses: cy1126@nwnu.edu.cn, cy70@sina.com (Y. Chang).

Scheme 1. The synthesis routine of PS–DA–M.

Fig. 1. IR spectra of complexes (a) PS–DA, (b) PS–DA–Cu, (c) PS–DA–Mn, (d) PS–DA–Ni, and (e) PS–DA–Co.

(GL-16A gas chromatograph with a 5 m × 3 mm OV-17 column, 80–200 °C (10 °C/min, Inj. 220 °C, Det. 220 °C). The thermal data were recorded on a Perkin-Elmer TG-DTA 6300 instrument at a heating rate of 15 °C/min.

2.2. Synthesis of chloromethylated polystyrene supported tridentate Schiff-base metal complexes (PS–DA–M)

The method of preparation of 2,4-dihydroxyacetophotone was the same as mentioned in Ref. [29]. The yield of 2,4-dihydroxyacetophotone is 65% and m.p. is 417.4 K.

Chloromethylated polystyrene (5.0 g, equivalent to 22.5 mmol of Cl) was added into 50 ml of acetone. Then acetone solution (30 ml) of 2,4-dihydroxyacetophotone (3.42 g, 22.5 mmol) was added to the above suspension followed by anhydrous K_2CO_3 (2.0 g), KI (0.2 g) and PEG (0.05 g), respectively. The reaction mixture was stirred and refluxed for 48 h under a nitrogen atmosphere. After cooling, an orange polymer precipitated out, which was filtered and washed with water and anhydrous ethanol, respectively. The solid was dried in vacuum at 323 K for 24 h to obtain chloromethylated polystyrene supported 2,4-dihydroxyacetophotone.

Chloromethylated polystyrene supported 2,4-dihydroxyacetophotone (2 g, 9.0 mmol) was added to 2-aminopyridine (0.84 g, 9.0 mmol) in 50 ml of anhydrous ethanol. The mixture was heated and refluxed for 24 h and then cooled to room temperature. The products obtained were filtered off and washed with ethanol and dried at 323 K in vacuum for 24 h to give polymer-supported tridentate Schiff-base (PS–DA).

PS–DA was added to Cu^{2+} solution dissolved in 50 ml of absolute ethanol, and then the mixtures were refluxed for 24 h. After the reaction, the solids were collected by filtration, washed with ethanol and dried at 353 K in vacuum to give chloromethylated polystyrene supported tridentate Schiff-base copper (II) complex (PS–DA–Cu). The synthesis routine of PS–DA–M was shown in Scheme 1. PS–DA–Co, PS–DA–Ni and PS–DA–Mn were prepared as the same way, respectively.

2.3. Oxidation reaction

Typical oxidation of substrate was performed according to the procedure described in the literature [30]. The substrate and the catalyst (chloromethylated polystyrene supported tridentate Schiff-base metal complexes) were added to the special glass reactor. The oxygen was filled from the gauge glass and the atmosphere
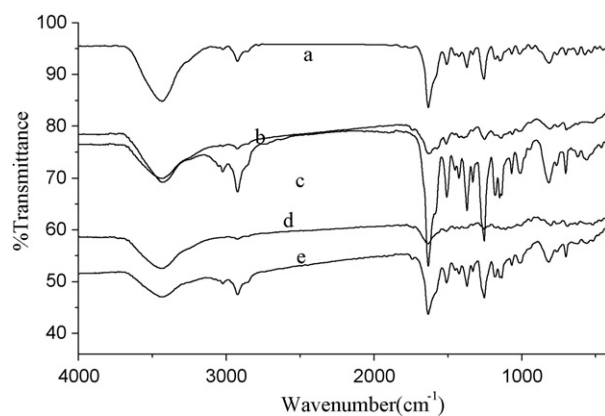
was discharged out of the glass reactor with the gas outlet tube. After the gas outlet tube was closed, the reactor was put into a paraffin oil path and heated to certain temperature. The consumption of oxygen was measured by the gauge glass. After the reaction, the products were analyzed by gas chromatograph and GC/MS.

3. Results and discussion

3.1. Characterization

The IR spectra of chloromethylated polystyrene supported tridentate Schiff-base ligand show sharp bands around 3428 cm^{-1} due to the ν_{O-H} vibrations. It gets a shift of 11–12 cm^{-1} to the lower wave number after chelated with metal ions, showing coordination is through phenol oxygen atom in the complexation (Fig. 1). Meanwhile, the band 1642 cm^{-1} due to $\nu_{C=N}$ in the free ligand gets shifted to the lower wave number ($\delta\nu = 11$–20 cm^{-1}) in the metal complexes, indicating coordination is through pyridine nitrogen. Several new bands in the complexes at 489–520 cm^{-1}, 411–419 cm^{-1} are due to ν_{O-M} and ν_{N-M}, respectively, which are absent in the spectrum of the ligand, further supporting the participation of the oxygen atom and the nitrogen atom in complexation.

In order to prove the coordination of polymer-supported tridentate Schiff-base ligand with metal ion, corresponding small area X-ray photoelectron spectroscopy of copper acetate, ligand and its complex have been studied (Fig. 2). Compared to copper acetate, the binding energy of $Cu_{2p3/2}$ of complex increases 3.0 eV. The change of binding energy of the $Cu_{2p3/2}$ means a decrease of its election density. On the other hand, binding energy of $N_{1s1/2}$ of polymer complex decreases 5.1 eV than that of the corresponding ligand of PS–DA. The electronic state of the nitrogen atom in the polymer complex is of higher electron density and, therefore, the electrons in the copper atom may flow into the nitrogen atom to form an N–Cu coordination bond. The $O_{1s1/2}$ binding energy of the polymer complex is raised of 0.6 eV than that of the corresponding support, which indicates that oxygen atom in hydroxy group is bound with metal ion. The structure of complex can be ensured as in Scheme 1.

The thermogravimetric analyses (TG) of the PS–DA and PS–DA–Cu were measured under nitrogen atmosphere in the temperature range from 293 K to 1023 K in order to investigate the thermal stability. It was showed that degradation of the polymer ligand (PS–DA) was from 484 K to 1023 K (Fig. 3). And the polymer-supported copper complex (PS–DA–Cu) was gradually from 462 K to 1023 K. The corresponding weight loss for PS–DA, PS–DA–Cu in above temperature range was 86%, 67%, respectively.
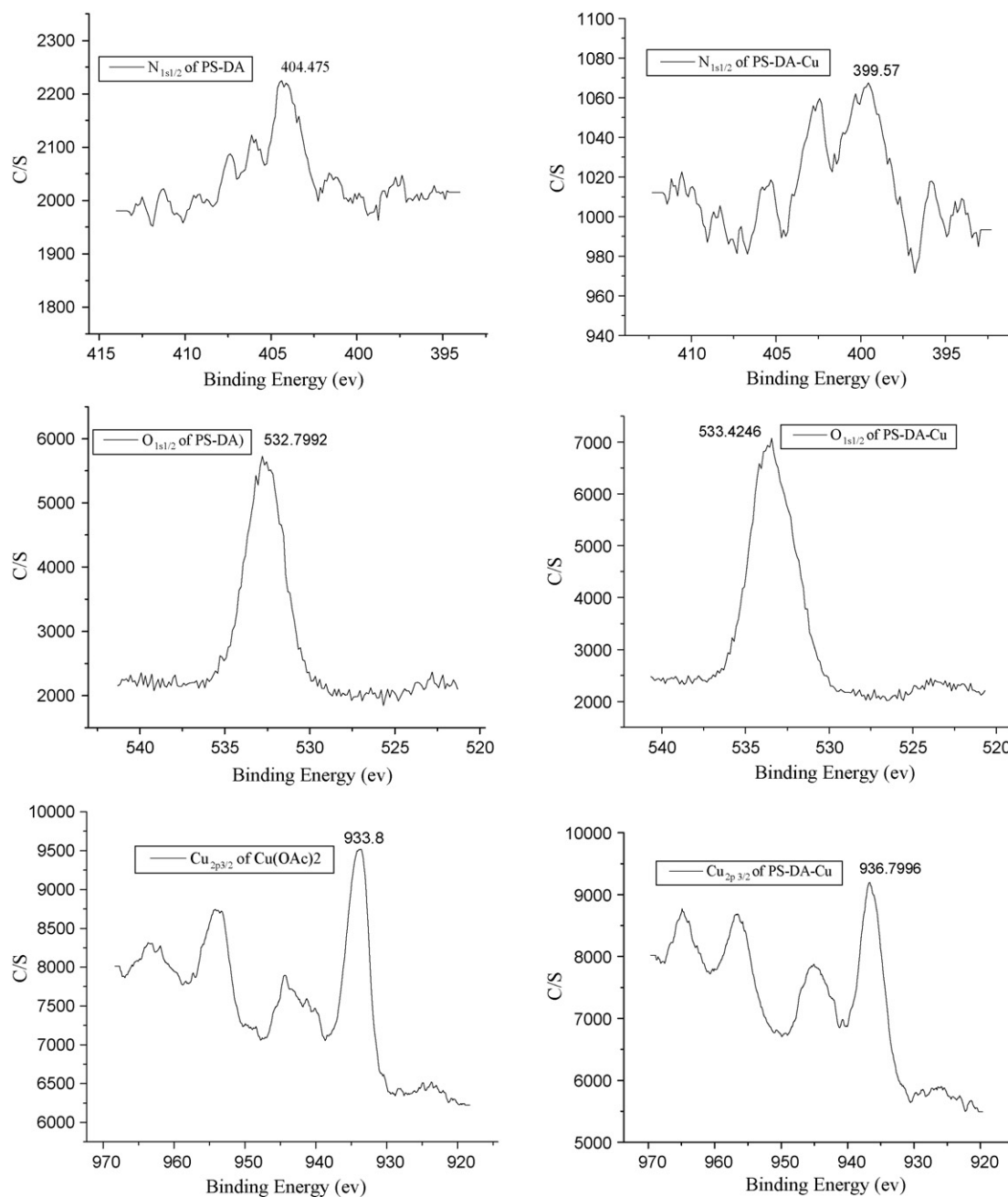
Fig. 2. XPS spectrum of Cu(OAc)$_2$, PS–DA and PS–DA–Cu (Ref. C$_{1s}$ = 284.80 eV).

3.2. Oxidation of cyclohexene

The results of cyclohexene oxidation catalyzed by chloromethy-lated polystyrene supported tridentate Schiff-base metal com-plexes were listed in Table 1. As can be seen, all of the four polymer-supported tridentate Schiff-base metal complexes have catalytic activity for the oxidation of cyclohexene and high turnover numbers have been obtained. Oxidation reactions occurred in

Table 1
Effect of various metal ions on oxidation.

Complexes	ICP (%)	Conversion[a] (%)	TON[b] ($\times 10^4$)	Selectivity of products (%)			
				EXO	–OH	C=O	–OOH
PS–DA–Mn	0.68	38.1	3.1	8.7	17.2	25.3	48.7
PS–DA–Cu	7.23	51.9	0.47	1.5	33	40.9	24
PS–DA–Co	0.78	22.2	2.29	12.5	22.7	10.6	54.1
PS–DA–Ni	1.64	32.4	1.17	10.6	26	14.7	48.6

Temperature 343 K; catalyst, 2 mg; cyclohexene, 2 ml; 1 atm O$_2$ and 10 h.

[a] Conversion and selectivity were determined by GC.

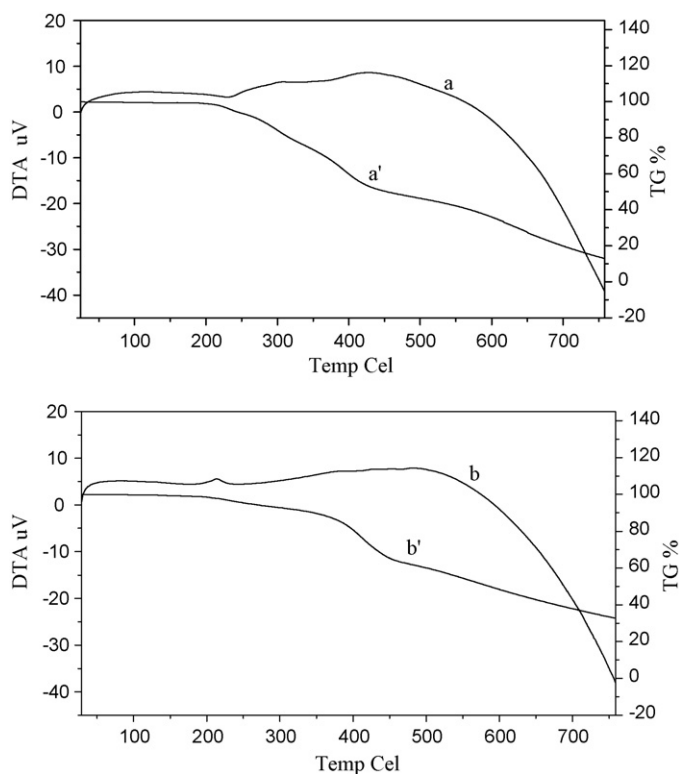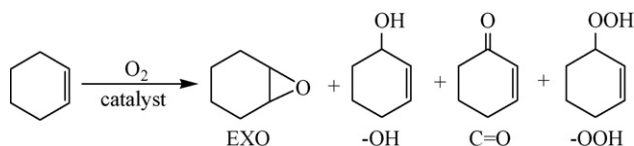[b] Moles of substrate converted per mole of metal in the catalyst.

Fig. 3. TG/DTA of PS–DA (a) and PS–DA–Cu (b).
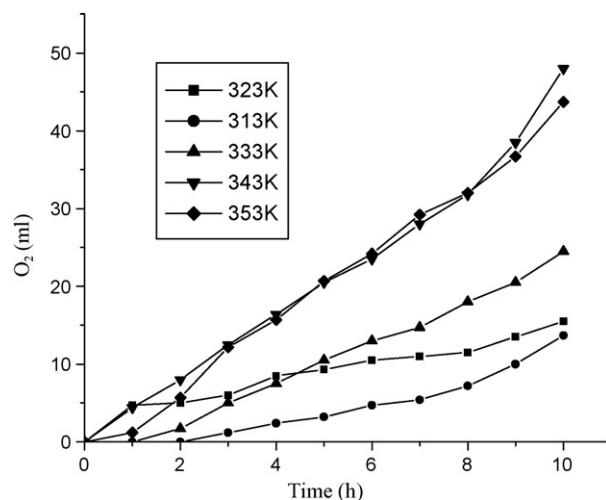

Fig. 4. Relationship between consumption of O_2 and the reaction time at the different temperature (catalyst: 2 mg; cyclohexene: 2 ml).

Table 2
Effect of reaction temperature on oxidation.

Temperature (K)	Conversion (%)	Selectivity of products (%)			
		EXO	–OH	C=O	–OOH
313	12	11.1	26.1	13.8	48.9
323	19	9.3	18.8	14.5	57.2
333	32	7.8	27.6	24.6	37.4
343	51.9	1.5	33	40.9	24
353	39.7	2.5	44.3	48.6	4.5

Substract 2 ml; catalyst 2 mg; 10 h.

allyl carbon atoms and the products are cyclohexene oxide (EXO), 2-cyclohexene-1-ol (–OH), 2-cyclohexene-1-one (–C=O) and 2-cyclohexene-1-hydroperoxide (–OOH) (Scheme 2). The conversion of cyclohexene catalyzed by PS–DA–Cu is higher than that of others, but the highest turnover numbers were obtained in the presence of PS–DA–Mn. In the same conditions, the selectivity of 2-cyclohexene-1-hydroperoxide in the presence of PS–DA–Co is the highest.

In order to investigate the catalytic activity of PS–DA–M, a series of experiments were carried out by choosing PS–DA–Cu as catalyst to investigate the influence of reaction temperature, amount of catalyst and reaction time.

3.2.1. Effect of reaction temperature

The consumption of oxygen with 2.0 mg of PS–DA–Cu as a function of the temperature was shown in Fig. 4. It is clear that the low temperature has the longer induce period and lower rate of oxygen consumption. With the temperature rising, the consumption of oxygen has increased and reaches the highest at the temperature of 343 K. After that, the consumption of oxygen decreases. At the low temperature, the energy was not sufficient for the activation of oxygen molecules or the catalytic circulation. So raising temperature is beneficial to the oxidation reaction. The conversion and selectivity at the different temperatures were collected in Table 2. The conversion of cyclohexene at 343 K is 4.3 times than at 313 K. Although the conversion of cyclohexene increases quickly with the increase of the temperature, the selectivity of 2-cyclohexene-1-hydroperoxide

(–OOH) decreases. It is clear that oxidation of cyclohexene is a free radical reaction mechanism.

3.2.2. Effect of catalyst amount

Effect of catalyst amount on oxidation at temperature of 343 K was shown in Table 3. Although the conversion of cyclohexene and the selectivity for EXO are nearly unchangeable with the increasing amount of catalyst, it is beneficial for the transformation of 2-cyclohexene-1-hydroperoxide to 2-cyclohexene-1-one and 2-cyclohexene-1-ol.

3.2.3. Effect of reaction time

The effect of reaction time on the oxidation was also investigated in this system. As the reaction time is prolonged, the cyclohexene conversion and the selectivity of 2-cyclohexene-1-one increased, while the selectivity of cyclohexene oxide and 2-cyclohexene-1-ol decreased (Fig. 5). For 2-cyclohexene-1-hydroperoxide, the selectivity increases at first and then decreases. This phenomenon is similar to the literature [14,31]. Additionally, the conversion of cyclohexene maintained constant after 10 h reaction. It can be explained that substantial decrease in the concentration of the reaction mixture.

Table 3
Effect of the amount of catalyst on oxidation.

Cat. (mg)	Conversion (%)	Selectivity of products (%)			
		EXO	–OH	C=O	–OOH
1	28	9	26.2	24	40
2	51.9	1.5	33	40.9	24
3	31.5	5.6	38	42.5	13.7
4	32.9	5.2	37.7	48.2	11.7
5	33.8	4.8	35.6	37	22.4

Temperature 343 K, substract 2 ml, 10 h.
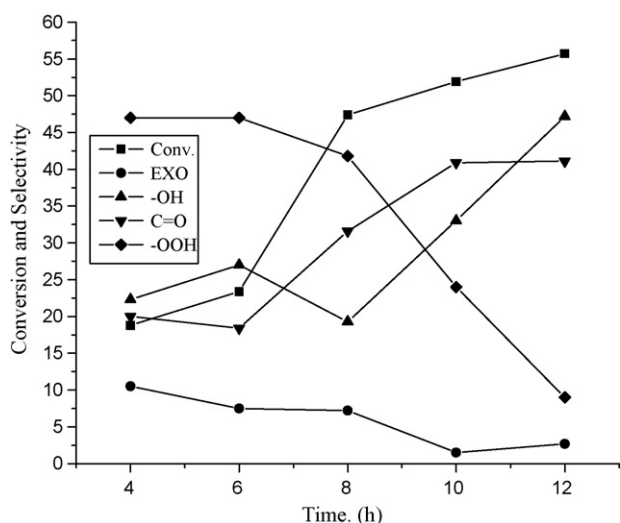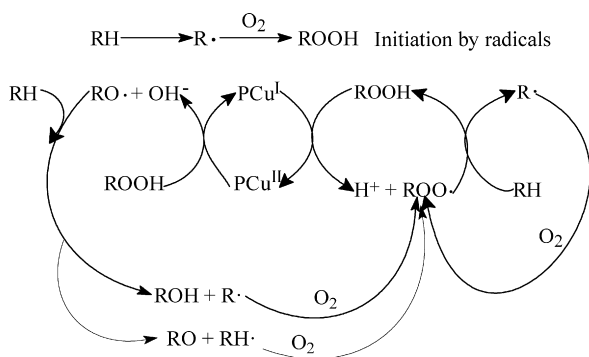

Scheme 2. The products of the reaction.

Fig. 5. The effect of reaction time on oxidation of cyclohexene (catalyst: 2 mg; cyclohexene: 2 ml; 343 K).

Scheme 3. The mechanism for the oxidation of cyclohexene.

3.3. The proposed mechanism for the oxidation process

Based on the experimental results and other reports [15,31], the mechanism for the oxidation of cyclohexene by the PS–DA–Cu was proposed as shown in Scheme 3 and the formation of the products according to the proposed mechanism was shown in Scheme 4. Firstly, the oxidation of cyclohexene with
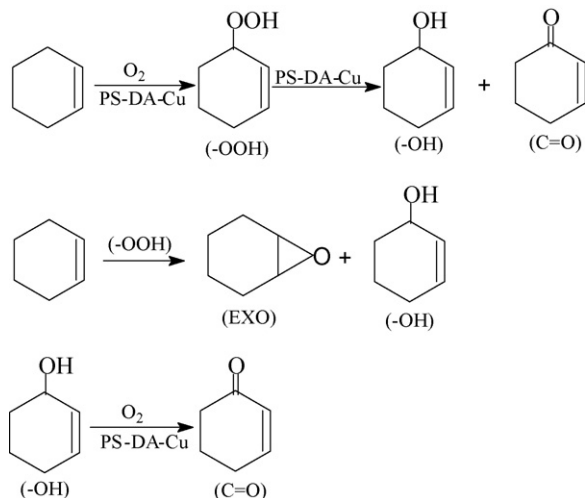
Scheme 4. The formation of the products according to the proposed mechanism.

Table 4
Reuse of the catalyst.

Recycling times	ICP (%)	Conversion (%)	Selectivity of products (%)			
			EXO	–OH	C=O	–OOH
1	7.23	51.9	1.5	33	40.9	24
2	6.0	47.2	7.9	35.7	33.7	22.6
3	–	46.4	4.4	23.5	32.8	39.1
4	–	45.5	2.4	34.3	31.6	31.5
5	5.2	41.6	4.6	31.8	32.5	30.9

Temperature 343 K; catalyst 2 mg; substract 2 ml; 10 h.

molecular oxygen forms 2-cyclohexene-1-hydroperoxide. Then, 2-cyclohexene-1-hydroperoxide is decomposed to 2-cyclohexene-1-ol and 2-cyclohexene-1-one in the presence of catalyst. Meanwhile, 2-cyclohexene-1-hydroperoxide can form cyclohexene oxide and 2-cyclohexene-1-ol by epoxidation of cyclohexene. As the rate of the formation of 2-cyclohexene-1-ol is faster than the formation of 2-cyclohexene-1-one, the selectivity of 2-cyclohexene-1-ol is higher than that of 2-cyclohexene-1-one at reaction initial stage or at low temperature (Table 2 and Fig. 5). At high temperature, 2-cyclohexene-1-ol can be continually oxidized to 2-cyclohexene-1-one in the presence of catalyst. So the selectivity of 2-cyclohexene-1-one is higher than that of 2-cyclohexene-1-ol in final stage.

3.4. Reuse of the catalyst

To investigate the reusability of PS–DA–Cu, the catalyst was separated by filtration after the first run, it was dried at 353 K under vacuum and then used for the next run under the same conditions. The data obtained were listed in Table 4. The conversion of cyclohexene dropped from 51.9% to 47.2% after first use and then kept relatively constant after next three runs, which could be mainly attributed to the loss of the content of Cu on PS–DA–Cu during the first use (from 7.23% to 6.0%). The selectivity of the products had no great changes after four runs.

4. Conclusions

Chloromethylated polystyrene supported tridentate Schiff-base metal complexes (PS–DA–M, M = Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+}, respectively) were prepared and characterized. These complexes were proved to be active and reusable catalysts for the oxidation of cyclohexene with oxygen in the absence of reducing agents. The products are ensured to be cyclohexene oxide (EXO), 2-cyclohexene-1-ol (–OH), 2-cyclohexene-1-one (–C=O) and 2-cyclohexene-1-hydroperoxide (–OOH). The catalytic activity of PS–DA–Cu was highest among the four metal complexes. The conversion of cyclohexene can be reached to 51.9% under the temperature of 343 K when using 2 mg of PS–DA–Cu to catalytic oxidation of 2 ml of cyclohexene. The oxidation mechanism differs from the literature. And the catalyst could be reused for at least four reaction cycles without considerable loss of reactivity which endow chloromethylated polystyrene supported tridentate Schiff-base metal complexes with a bright future in industrial applications.

References

[1] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Catal. 202 (2001) 245.

[2] N. Sehlotho, T. Nyokong, J. Mol. Catal. A: Chem. 209 (2004) 51.

[3] A.B. Smith, J.P. Konopelski, J. Org. Chem. 49 (1984) 4094.

[4] A. Sakthivel, S.E. Dapurkar, P. Selvam, Appl. Catal. A: Gen. 246 (2003) 283.

[5] H. Kameyama, F. Narumi, T. Hattor, H. Kameyama, J. Mol. Catal. A: Chem. 258 (2006) 172.

[6] J.P.M. Niederer, W.F. Hölderich, Appl. Catal. A: Gen. 229 (2002) 51.

[7] X.G. Han, Z.Q. Lei, Y.X. Tao, Y.P. Wang, J. Mol. Catal. A: Chem. 159 (2000) 139.

[8] J. Połtowicz, E.M. Serwicka, E. Bastardo-Gonzalez, W. Jones, R. Mokaya, Appl. Catal. A: Gen. 218 (2001) 211.

[9] E.M. Serwicka, J. Połtowicz, K. Bahranowski, Z. Olejniczak, W. Jones, Appl. Catal. A: Gen. 275 (2004) 9.

[10] R.M. Wang, X.D. Li, Y.F. He, Chin. Chem. Lett. 17 (2006) 265.

[11] S.M. Mahajani, M.M. Sharma, T. Sridhar, Chem. Eng. Sci. 54 (1999) 3967.

[12] M. Salavati-Niasari, M. Shaterian, M.R. Ganjali, P. Norouzi, J. Mol. Catal. A: Chem. 261 (2006) 147.

[13] S. Mukherjee, S. Samanta, B.C. Roy, A. Bhaumik, Appl. Catal. A: Gen. 301 (2006) 79.

[14] J.H. Tong, Y. Zhang, Z. Li, C.G. Xia, J. Mol. Catal. A: Chem. 249 (2006) 47.

[15] Z.W. Yang, Q.X. Kang, Z.Q. Lei, J. Mol. Catal. A: Chem. 213 (2004) 169.

[16] K.C. Gupta, A.K. Sutar, Polym. Adv. Technol. 19 (2008) 186.

[17] Z.Q. Lei, React. Funct. Polym. 39 (1999) 239.

[18] E.A. Prasetyanto, S.E. Park, Bull. Korean Chem. Soc. 29 (2008) 1033.

[19] K.M. Jinka, J. Sebastian, R.V. Jasra, J. Mol. Catal. A: Chem. 274 (2007) 33.

[20] Y. Chang, Y.P. Wang, F. Zha, Polym. Adv. Technol. 15 (2004) 284.

[21] S.E. Dapurkar, H. Kawanami, K. Komura, T. Yokoyama, Y. Ikushima, Appl. Catal. A: Gen. 346 (2008) 112.

[22] M. Salavati-Niasari, Polyhedron 27 (2008) 3132.

[23] J.H. Tong, Z. Li, C.G. Xia, J. Mol. Catal. A: Chem. 231 (2005) 197.

[24] S. Kulkarni, M. Alurkar, A. Kumar, Appl. Catal. A: Gen. 142 (1996) 243.

[25] V.B. Sharma, S.L. Jain, B. Sain, J. Mol. Catal. A: Chem. 212 (2004) 55.

[26] D.M. Boghaei, A. Bezaatpour, M. Behzad, J. Mol. Catal. A: Chem. 245 (2006) 12.

[27] M. Salavati-Niasari, J. Mol. Catal. A: Chem. 263 (2007) 247.

[28] Y. Chang, X.L. Shi, D.M. Zhu, Y. Liu, Polym. Adv. Technol. 19 (2008) 877.

[29] N.T. Fan, Dictionary of Organic Synthesis, Beijing institute of technology press, Beijing, 1992.

[30] R.M. Wang, S.B. Li, Y.P. Wang, Y. Chang, Y.F. He, Z.Q. Lei, H.X. Feng, React. Funct. Polym. 42 (1999) 87.

[31] R.M. Wang, T.Z. Yu, Y.F. He, Y.P. Wang, B.H. Xie, C.G. Xia, J.S. Suo, Chem. J. Chin. Univ. 11 (1999) 1772.