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Comparative Study of Ship-in-a-Bottle and Anchored Heterogenized Mn Complexes

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Abstract Metal schiff base catalyst can be immobilized with the heteropoly acid as the anchor or by flexible ligand route. The immobilized Mn schiff base catalysts overY molecular sieves prepared by these two methods were characterized by IR, DTA-TGA thermal analysis and XPS. The catalysts were used in the oxidation of cyclohexene under ambient conditions using molecular dioxygen as oxidant and isobutyraldehyde as sacrificial reagent. For the oxidation of cyclohexene the heterogenized catalysts showed the advantages of easy handling and recycling and the immobilized catalyst with the heteropoly acid as the anchoring agent showed higher turnover number than that prepared by the flexible ligand route. Morever, the anchored catalyst was still active after reused for six times, attributed to the lower leaching speed of Mn complex from the heterogenized catalyst.

Keywords Heterogeneous catalyst · Heteropoly acid · Molecular oxygen · Cyclohexene · Catalytic oxidation

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1 Introduction

Epoxides are relevant intermediates in organic synthesis as they can be easily transformed into a large variety of compounds by means of regioselective ring opening reactions. Manganese(III) salen complexes have been demonstrated to be useful laboratory and industrial homogeneous catalysts in the epoxidation of some unfunctionalised alkenes using iodosylbenzene, sodium hypochlorite and hydroperoxides as oxygen sources. Furthermore, when the catalysts are chiral Mn(III) salen complexes high enantioselectivity is observed in the epoxidation of olefins [1, 2].

However, these homogeneous catalysts are inconvenient for industrial use. On the other hand, heterogeneous catalysts have several superiorities such as the ease of separation from the reaction system and the potential for re-use, therefore, the immobilization of the homogeneous catalyst to combine the superiorities of both homogeneous and heterogeneous catalysts will be of great importance for the industrial production [3].

There are many immobilization methods including sol–gel method [4], functional groups modification [5], flexible ligand route [6] and the zeolite synthesis [7]. Augustine [8] reported a new method using heteropoly acids as the anchors to immobilize the homogeneous Ru catalyst onto different inorganic supports for the hydrogenation of olefin. It was found that the anchored catalyst is highly active, easy to recover and could be reused for many times. Agnes Zsigmond et al. [9] compared the performances of both catalysts prepared by heteropoly acids anchoring method and ship-in-a-bottle method in the olefin hydrogenation and as the result, the turnover number of the catalyst prepared by the heteropoly acids anchoring method is 5–800 times higher than that prepared by ship-in-a-bottle method.

In our research, the manganese shiff base complex was immobilized over Y zeolite using the heteropoly acids as the anchors and characterized by IR, DTA-TGA thermal analysis and XPS. The catalytic performance and recycling of the anchored catalyst was investigated in the epoxidiation of cyclohexene with molecular oxygen as the oxidant and isobutylaldehyde as the co-reductant.

2 Experimental

2.1 Materials and Equipment

Salicylaldehyde, o-phenylenediamine, $Mn(AcO)_2 \cdot 4H_2O$, phosphomolybdicacid isobutylaldehyde were obtained from Sinopharm Group Chemical Reagent Co., Ltd. Y molecular sieves were purchased from Nankai university catalyst factory. Cyclohexene was obtained from China Shenma Group Company Limited, and re-distilled prior to use. Salophen and MnSalophen were prepared in our Lab according to the procedure described previously [10].

IR spectra were carried out on American Thermo Electron IR-200 spectrometer, (KBr pellets). The thermogravimetrical analysis was recorded on Shimadzu DTG-60 Thermal Analyzer. The metal content was determined by ICP, America Thermo Electron company. XPS spectra were recorded on a Axis Ultra electron spectroscopy, Kratos Company, U.K. The reaction products of oxidation were analyzed by GC-900 from Shanghai Kechuang Chromatograph Instrument Co., Ltd. using a 30 m × 0.53 mm × 0.25 μm SE30 capillary column.

2.2 Ship-in-a-Bottle MnSalophen/Y Catalyst Prepared with Flexible Ligand Route [11]

Stirring the mixture of 1 g of Y zeolite and 100 mL, 1 mmol/mL solution of manganese ion in water for 24 h at room temperature, the solid was filtered and washed thoroughly. Dried at 100 °C for 4 h afforded Mn/Y.The mixture of Mn/Y and Salophen in $CHCl_3/CH_3OH$ (10/1) was stirred for 24 h at room temperature. The resulting materials was filtered and washed with $CHCl_3/CH_3OH$ (10/1) until the filtrate become colorless. The solid obtained was dried at 100 °C for 4 h, and then Soxhlet extracted with acetonitrile, which afforded MnSalophen/Y. The content of Mn^{2+} in MnSalophen/Y was 2.98% according to ICP analysis.

2.3 MnSalophen/HPA/Y with the Heteropoly Acid as Anchoring Agent

1.5 g of NaY zeolite was suspended in 25 mL of ethanol, 0.1 mmol of HPA was dissolved in 30 mL of ethanol, and the HPA solution was dropped into the zeolite suspension with efficient stirring. The stirring was continued for 1 day. The mixture was filtered and the solid residue was suspended in 30 mL of $CHCl_3/CH_3OH$ (10/1). Then 0.1 mmol MnSalophen complex was dissolved in 10 mL $CHCl_3$ / CH_3OH (10/1) and the MnSalophen solution was dropped slowly, with stirring, into the suspension under nitrogen and the stirring was continued for another day. The mixture was filtered and washed with $CHCl_3/CH_3OH$ (10/1) until the filtrate become colorless. The solid material was dried at 333 K for 4 h in vacuum then Soxhlet extracted with acetonitrile, which afforded MnSalophen/HPA/Y. The content of Mn^{2+} in MnSalophen/HPA/Y was 0.95% according to ICP analysis Scheme 1

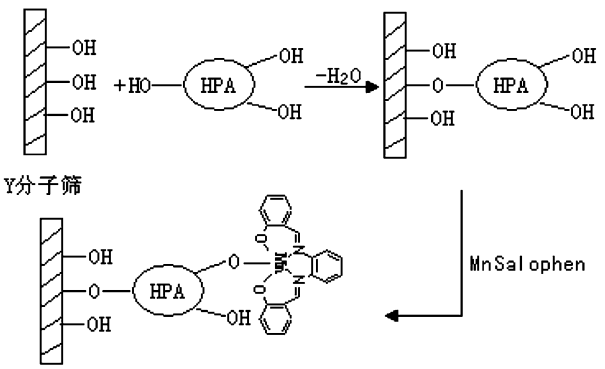
2.4 Procedure of Catalytical Oxidation

A 100 mL two-necked glass flask with water-bath jacket equipped with a reflux condenser was specially designed as the reactor for catalytical oxidation of cyclohexene. The reactor was charged with a certain amount of catalyst, 2 mL cyclohexene, 5 mL isobutylaldehyde and 20 mL acetonitrile. Oxygen was bubbled into the solution with stirring at a flow velocity of 5 mL/min. The reaction was processed in a water bath the temperature of which was 35 °C. After reaction for some time, Products were analyzed with gas chromatography by adding *n*-heptane as internal standard and conformed by comparision of the retention time with the commercial cyclohexene epoxide from Fluka.

3 Results and Discussion

3.1 Catalyst Characterization

The FT-IR spectra of the Y zeolite, the neat MnSaloph, the MnSalophen/Y and the MnSalophen/HPA/Y catalysts were



Scheme 1 Synthesis of MnSalophen/HPA/Y

shown in Fig. 1. The comparision of the spectra of the neat complex, the MnSalophen/Y and MnSalophen /HPA/Y sample showed evidence for the immobilization of the MnSalophen complex over Y zeolite and HPA modified Y zeolite, since the same bands at 1607 cm^{-1} (attributed to $\nu_{C=C}$) and at 1537 cm^{-1} (attributed to $\nu_{C=N}$) which are characteristic of the homogeneous MnSalophen complex appeared in both IR spectra of the supported catalysts.

Differential thermal analysis and thermogravimetric analysis have been used to characterize the neat complex and the immobilized samples, as shown in Fig. 2. The neat complex MnSalophen shows a weight loss at 384 °C. However, for the corresponding immobilized complexes, there are also a weight losses at about 384 °C.This showed that the neat complex was encapsulated on the Y zeolite with two methods. The expandation of the weight loss peak was due to the interaction between supports and the neat complex.

The XPS spectra also provide information on immobilization. From the data of XPS, it can be seen that Mn2p and O_{1S} binding energies in MnSalophen/HPA/Y and MnSalophen/Y are lower than those in MnSalophen. The

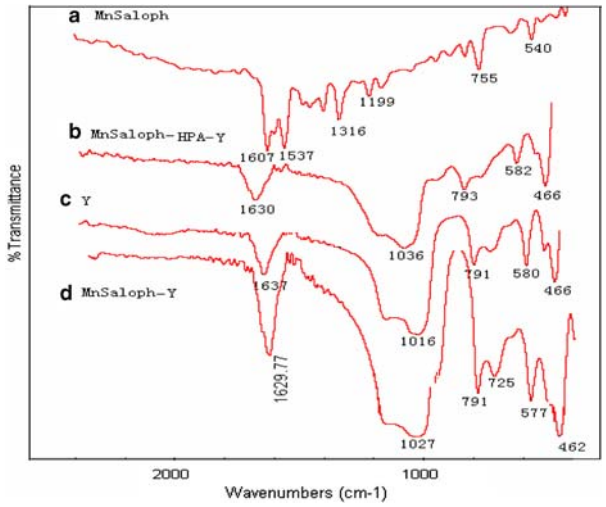


Fig. 1 FT-IR spectra of the MnSalophen complex (**a**), MnSalophen/HPA/Y (**b**), NaY zeolite (**c**) and MnSalophen/Y (**d**)

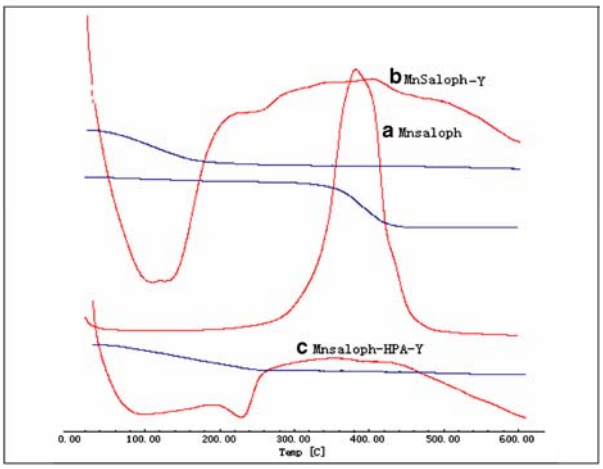


Fig. 2 Thermal analysis of MnSalophen complex, MnSalophen/Y, and MnSalophen/HPA/Y catalyst

$Mo_{2P3/2}$ and $Mo_{2P1/2}$ binding energies in MnSalophen/HPA/Y are 230.4 ev and 233.4 ev, respectively, which are lower than those of HPA/Y. The O_{1S} binding energy in MnSalophen/HPA/Y and MnSalophen/Y are 528.9 ev and 529.3 ev, respectively, which are also lower than that of HPA/Y. The difference of N_{1S} binding energies between MnSalophen/HPA/Y and MnSalophen is 0.1 ev, while 0.4 ev was observed between MnSalophen/Y and MnSalophen. These changes in binding energy can be attributed to charge transfer between Mn2p, O_{1S}, Mo_{2P}, and N_{1S}. Table 1

3.2 The Comparision of Oxidation Reaction with Different Catalysts

The performances of different catalysts were studied in the epoxidation of cyclohexene and the results were listed in Table 2. The TONs of the heterogenized catalysts were higher than those of the neat complex. This showed that the heterogenized catalysts could prevent the neat complex from dimerizing and degradation and therefore raised the turnover number. One reason for the lower activity of MnSalophen/Y than MnSalophen/HPA/Y may be the

Table 1 XPS results of Y, MnSalophen, MnSalophen/Y, HPA/Y and MnSalophen/HPA/Y

Samples	XPS data/ev				
	O_{1S}	Si_{2p}	N_{1S}	$Mo_{2P3/2}$, $Mo_{2P1/2}$	$Mn_{2P3/2}$, $Mn_{2P1/2}$
Y	532.0	102.55		–	–
MnSalophen	529.93		397.1		642.06, 651.77
MnSalophen/Y	529.3	101.8	397.5		640.06, 651.49
HPA/Y	530.35	101.2		231.4, 234.4	–
MnSalophen/HPA/Y	528.9	100.8	397.2	230.4, 233.4	641.97, 651.38

Table 2 The catalytic performances of different catalysts in the epoxidation of cyclohexene

Catalyst	Mol Mn complex/g catalyst	Conversions(selectivity)/%				Ton
		4 h	6 h	7 h	8 h	
HPA/Y	–	40(66)	64(72)	79(74)	82(75)	–
MnSalophen	0.00271	21(69)	76(76)	83(78)	88(79)	69
MnSalophen/Y	0.00054	46(86)	81(88)	87(90)	91(92)	89.5
MnSalophen /HPA/Y	0.00017	78(84)	86(89)	91(87)	97(86)	303

Reaction conditions: cyclohexene: 2 mL, isobutylaldehyde: 4 mL, acetonitrille: 20 mL, temperature: 35 °C, time: 8 h, the velocity of dioxygen: 5 mL/min,MnSalophen : 10 mg, MnSalophen/Y: 40 mg, MnSalophen/HPA/Y: 40 mg, HPA/Y: 40 mg

higher resistance when the cyclohexene molecules contacted with the active Mn complex. Surprisingly even HPA/Y is active catalyst for the epoxidation reaction while the selectivity was a little bit lower.

3.3 Reuse of the Catalysts

The recycling of the MnSalophen/HPA/Y and MnSalophen/Y catalysts were also investigated. The catalysts were reused six times. Each time when the reaction finished, the reaction mixture was deposited over night, and then the liquid layer was taken out. The residual catalysts were used directly for the next trial, and the results were given in Table 3. It clearly showed that after being reused six times, the activity of the anchored catalyst MnSalophen/HPA/Y only decrease 3.8% of its initial activity. However, the activity of the ship-in-a-bottle catalyst MnSalophen/Y decreases from 91 to 79.4%. This showed that the ship-in-a-bottle catalyst MnSalophen/Y easily lose its activity than the anchored catalyst MnSalophen/HPA/Y.

For discovering the reason for the lower activity after being reused six times, we employed ICP to determine the Mn content before and after the catalytic runs. As shown in Table 4, 0.91% of Mn was lost after six runs for the MnSalophen/Y catalyst. However only 0.06% of Mn was lost after six runs for the MnSalophen/HPA/Y catalyst. Thus we can say one reason for the activity reduction of the ship-in-a-bottle catalyst MnSalophen/Y is attributed to the leaching of the neat complex entrapped in zeolite supercage. The slight decrease in the activity of the anchored catalyst MnSalophen/HPA/Y may be the neat complex being covered with the impurities during the raction, which prevents molecular oxygen and cyclohexene from contacting the complex. This can be overcome by ultrasonic treatment [12]. From the results we conclude that the anchored catalyst MnSalophen/HPA/Y is suitable catalyst in the epoxidation of cyclohexene with molecular oxygen as oxidant.

Table 3 Recycle run results of the heterogenized catalysts

Runs	Conversion(%)		Selectivity((%)	
	A	B	A	B
1	91	97.5	92	86.6
2	88.3	94.8	93	84.5
3	82.6	95.4	89	86.1
4	85.1	94.5	91	80.6
5	78.5	91.3	87	90.3
6	79.4	93.7	84	77.4

Reaction conditions: cyclohexene: 2 mL, isobutylaldehyde: 4 mL, acetonitrille: 20 mL, catalyst: 40 mg, temperature: 35 °C, time: 8 h, the velocity of dioxygen: 5 mL/min

A: MnSalophen/Y, B: MnSalophen/HPA/Y

Table 4 The Mn content of the catalysts

Sample	Content of Mn(%)	
	A	B
Fresh	2.98	0.95
After the sixth run	2.07	0.89

4 Conclusions

We sythesized two catalysts of MnSalophen/Y by flexible ligand route and MnSalophen/HPA/Y with the heteropoly acid as the anchor. Both of them were used as catalysts for the epoxidation of cyclohexene. Besides the advantages of easy handling and recycling, they both showed better selectivity than the neat complex. The anchored catalyst had the higher activity and the lower leaching of Mn complex than the encapsulated catalyst.

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