

# Preparation and catalysis of NaY-encapsulated Mn(III) Schiff-base complex in presence of molecular oxygen

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## Abstract

The new NaY zeolite (DMY), whose cages' size had been expanded, was used as supports for encapsulating the large Schiff-base complexes. The catalysts were used in the aerobic epoxidation of 1-octene. The catalyst showed high activity and selectivity for the substrate and products. These catalysts proved to be more active than other kind of metal ion or supports. The effect of temperature, organic acid or base, and the amount of catalyst was discussed. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Epoxidation; Zeolite encapsulated catalyst; Mn-Schiff-base

## 1. Introduction

One of the major current challenges in synthetic organic chemistry is the partial, i.e., selective oxidation of organic compounds using molecular oxygen in the presence of transition metal catalysts [1–12]. Epoxides are one of the most useful synthetic intermediates for the preparation of oxygen-containing natural products or the production of epoxy resins, etc. Much effort has been made to develop the direct and selective epoxidation reaction of olefins by use of molecular oxygen [13]. A few epoxidation reactions of long-chain linear aliphatic olefins with O<sub>2</sub> combining transition metal complexes with reducing agents have recently been studied, for example, bis(1,3-diketonato)-nickel complex/isovalveraldehyde [14]. However, the reducing agents will make cost price increase or make oxides to be easily decomposed. We have reported the aerobic epoxidation of linear aliphatic olefins using amino acid Schiff-base complexes [15], which is a new methodology for synthesis of 1,2-epoxy alkane with the linear aliphatic olefins in presence of molecular oxygen.

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Comparing with a natural catalyst, such as cytochrome *P*-450, zeolites are very interesting supports for oxidation with metal complexes [16,17], because the zeolite framework could prevent entrapped metal complexes from dimerizing and degrading [18]. However, in the natural faujasite and synthetic zeolites X and Y, the inner diameter and channel diameter are in the range of 0.4 to 1.3 nm. They are not available for big complexes because the limited pore size of these catalysts make it difficult for big complexes, substrates and products to diffuse into or out of the narrow channel of the microporous inorganic solid [19]. Up to now, some mesoporous solids have been produced and are characterized by pore diameters that could be adjusted to between 1.8 and 20.0 nm [20]. But the H<sub>2</sub>O<sub>2</sub> was used as oxidant in catalytic oxidation with MCM-41-supported complexes [21]. In this paper, the new NaY zeolite (DMY), whose cage size had been expanded, was used as supports for encapsulating the large complexes which synthesized by stable aromatic ring (such as pyridine and nitro-substituted benzene). The DMY encapsulated Schiff-base complexes were applied in the aerobic epoxidation of olefin.

## 2. Experimental

### 2.1. Material and equipment

2,6-Diaminopyridine and *m*-nitrobenzaldehyde were purchased from CTD of Sweden. MCM-41 was synthesized in our lab [22,23]. The Zeolite-Y of expanding cage (DMY) was obtained from Lanzhou Lianyou General Factory. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 83/13 (g/g) × 1–3 nm: 8.2%. All other reagents used were of AR grades of purity.

IR spectra were recorded in KBr disks with a Alpha-centauri FT-IR spectrophotometer. Elemental analysis performed on Itali Carbo-Erba 1106 elemental auto-analyzer. The thermal analysis was recorded on Shimadzu DT-40 Thermal Analyzer (15°C/min); ICP was measured on an American ARL-3520 Inductivity-coupled plasmas atomic emission spectrometry. The reaction products of oxidation were determined and analyzed by Shimadzu GC-16A gas chromatograph, QP-1000A GC/MS system, and GC-IR system (HP 5890 II GC and Bio-Rad 65A FTS IR system).

### 2.2. Synthesis and characterization of the catalyst

The Schiff-base ligand (NBPY) was synthesized by condensing of one 2,6-diaminopyridine with two *m*-nitrobenzaldehyde, which was characterized by infrared spectra, mass spectra, element analysis.

Table 1  
IR data of small molecular and zeolite encapsulated Schiff-base complex (cm<sup>-1</sup>)

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N}); \nu(\text{C}=\text{C}); \nu(\text{C}-\text{N})$	$\nu_{\text{as}}(\text{NO}_2) \nu_{\text{s}}(\text{NO}_2)$	$\nu_{\text{as}}(\text{Si}-\text{O}) \nu_{\text{s}}(\text{Si}-\text{O})$	$\nu(\text{M}-\text{O}) \nu(\text{M}-\text{N})$
NBPY		1701vw, 1662sh, 1595vs, 1477, 1451s	1526vs;1348	–	
MnNBPY		1701vw, 1603vs, 1478m, 1453m, 1384w	1526vs; 1349vs	–	519w
MnNBPY/DMY	3651vs br	1672; 1663, 1438;	1529; 1389	1209 ~ 1009vs br, 816	460, 376
CoNBPY/DMY	3608vs br	1659vs, 1588m	1498, 1386	1185 ~ 1018vs br, 815	457, 390
FeNBPY/DMY	3677vs br	1672s, 1664vs, 1497, 1438, 1420	1528s, 1389s	1205 ~ 1010vs br, 816	456, 390
MnNBPY/MCM	3408vs br	1658; 1497, 1439	1529, 1388	1126, 1087vs br, 813	460, 380
MnNBPY/NaX	3500vs br	1663; 1647	1558, 1390	1220 ~ 919vs br, 774	391, 358
DMY	3481vs br	–	–	1223vs br, 820	
MCM	3491vs br	–	–	1078vs br, 798	



Table 3

Catalytic activity of the MnNBPY/DMY in oxidation of linear olefins by molecular oxygen

Substrate	Conv (%)	Product	Selectivity (%)
1-Octene	63	1,2-epoxy octane	75
1-Decene	26	1,2-epoxy decane	74
1-Dodecene	–	–	–

Substrate: 1 ml; Cat: 10 mg. Temp: 100°C, Time: 12 h.

determined and analyzed by Shimadzu GC-16A gas chromatograph with a 5 m × 3 mm OV-17 column, Shimadzu QP-1000A GC/MS system, and GC-IR system (HP 5890 II GC and Bio-Rad 65A FTS IR system, Interface: GC/C 32 GC-IR; Column: SE54 (25 m × 0.32 mm); FID; Inj. temp. 260°C, Dect. temp. 260°C; Init. temp. 100°C, Init. time: 3 min, Rate 10°C/min, Final temp. 220°C, Flow rate: 1.41 ml/min).

### 3. Results and discussion

The linear aliphatic olefins **1**, such as 1-octene, 1-decene, can be directly oxidized by molecular oxygen without any reductants or solvents, which afford the 1,2-epoxy alkane **2**.

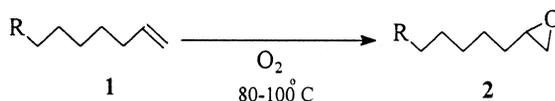


Table 3 shows the data of catalyzed by MnNBPY/DMY. In general, the selectivity of 1,2-epoxy alkane is about 70%. When the conversion of linear aliphatic olefins increased by extending the reaction time or increasing oxidation temperature, the selectivity of 1,2-epoxides will be decreased.

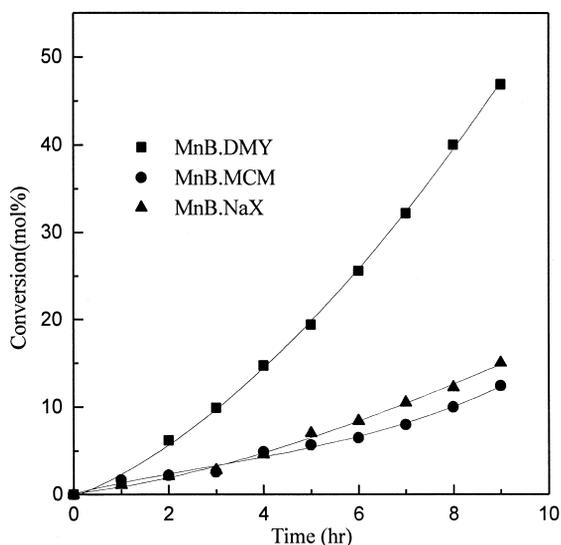


Fig. 1. Catalytic activity of different supports in oxidation of the 1-octene (1 ml, 100°C) (MnB: MnNBPY).

Table 4  
The influence of metal ion in epoxidation of 1-octene

Catalyst	Temp. (°C)/time (h)	Conversion (%)	Selectivity (%)
MnNBPpy/DMY	100/12	63	75
CoNBPpy/DMY	100/9	31	72
FeNBPpy/DMY	100/10	14	64

Condition: Sub: 1 ml; Cat 10 mg.

The catalytic activity decreases along with length of olefin and the 1-dodecene could not be a catalytic aerobic epoxidation by MnNBPpy/DMY. It shows that the longer the alkyl of olefin, the more obstructed are they from reaching the center of catalyst.

The catalytic activity and selectivity of MnNBPpy/DMY are higher for the substrate and product of epoxide than that of amino acid Schiff-base complexes [15].

### 3.1. The effect of the zeolite type

Fig. 1 shows the relationship between the conversion of substrate and the reaction time for different supports in the epoxidation of 1-octene. The reactive rates of MnNBPpy/DMY is higher than the others. The selectivity for 1,2-epoxy octane of MnNBPpy/DMY is 75%. It is also higher than that of MnNBPpy/MCM and MnNBPpy/NaX.

### 3.2. The influence of metal ion

Table 4 shows the influence of metal ion in the epoxidation of 1-octene. It indicates that the order of catalytic activity of different metal ions is Mn > Co > Fe. A much lower activity for FeNBPpy/DMY is observed as compared to the others because of its very low amount of catalytic center.

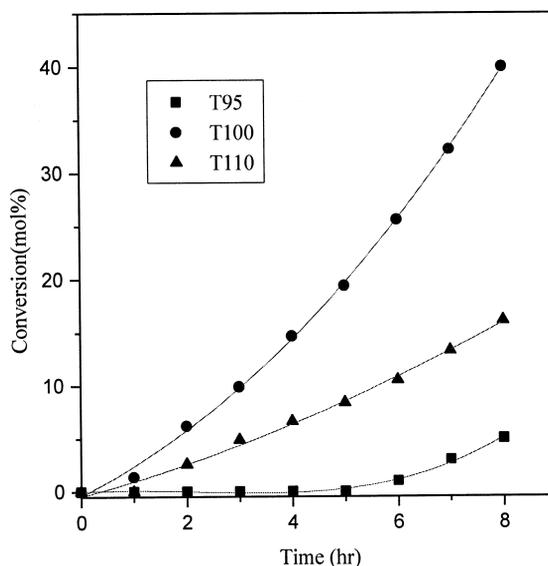


Fig. 2. Effect of temperature in catalytic oxidation of the 1-octene (1 ml) by MnNBPpy/DMY [ $T$ , °C].

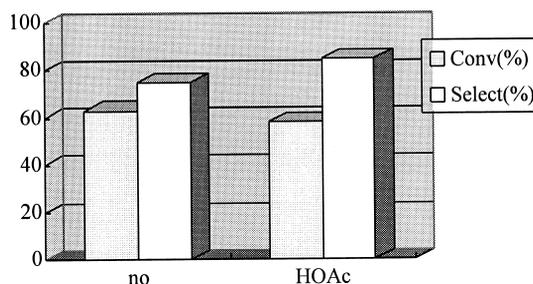


Fig. 3. Effect of HOAc in oxidation of 1-octene catalyzed by MnBNPy/DMY (Sub: 1 ml; Cat: 10 mg, 100°C; 1 atm O<sub>2</sub>, 12 h)

### 3.3. The influence of reaction temperature

Fig. 2 shows the relationship between the conversion of substrate and the reaction time for different reactive temperatures in the epoxidation of 1-octene. The reactive rates decrease when the reactive temperature was higher than 110°C or lower than 95°C. It indicates that the mechanism of the catalytic epoxidation was radical reaction. When the temperature was too low, it was difficult to initiate reaction. When the temperature was too high, it was difficult to contact with active center for oxygen molecular. Another reason is partly the polymerization of olefins on the surface of the supports.

### 3.4. The influence of organic acid and base

When the organic base, pyridine, was added into catalytic oxidation system, the reaction stopped. The selectivity increased with the addition of HOAc in catalytic oxidation system, shown in Fig. 3.

### 3.5. The influence of the catalyst amount

Fig. 4 shows the relationship between conversion of substrate and the amount of catalyst in the epoxidation of 1-octene. It indicates that the catalytic activity of MnBNPy/DMY increase with

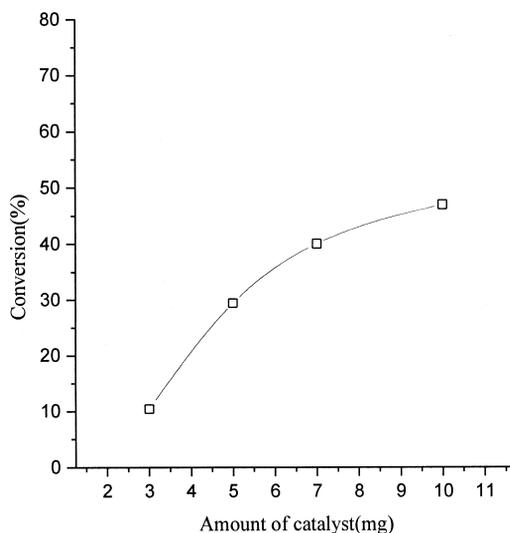


Fig. 4. Relationship between conversion and amount of catalyst in oxidation of 1-octene by O<sub>2</sub> (Sub: 1 ml; 100°C).

increasing amount of the catalyst, but not of same rate. It may be caused by too many cages which absorb the radical group.

#### 4. Conclusion

The new kind of Y-Zeolite, whose cage was expanded, encapsulated Mn-NBPy catalysts and was an active catalyst in the epoxidation of 1-octene, which afforded 1,2-epoxy octene. It was proved to be more active than other kinds of metal ion or supports. This suggests that the reaction is a radical mechanism, which will be discussed in detail in the future.

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