

# Preparation and catalysis of porous silica supported metal Schiff-base complex

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## Abstract

A series of porous silica support metal Schiff-base complexes was synthesized with amino porous silica, salicylaldehyde and metal ion, which characterized by IR spectra, elemental analysis, and SEM. The catalytic property for oxidation of olefins in the presence of molecular oxygen has been investigated. The major product of the aerobic oxidation without reductant was the epoxy. The influence of reaction temperature and additive for epoxidation had been studied. The selectivity and the conversion of epoxidation varied with reaction time, different additives and different catalysts. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Catalytic oxidation; Schiff-base complexes; Porous silica

## 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 [1–8]. Many efforts have been made to develop the direct and selective epoxidation reaction of olefins by use of molecular oxygen [9–14]. We have reported the aerobic epoxidation of olefins using Schiff-base complexes [15]. Application of these materials, especially in selective oxidation has mostly been focused on ligands whose structures were similar to porphyrins, such as Schiff-base ligands.

These trans-coordinating ligands impose a stable, planar coordination sphere on the metal, and the redox catalytic reaction often takes place in the axial position of the complex. Here, the Schiff-base complexes have been supported on the porous amino silica bead, which were used as catalysts for oxidation of olefins. It was found that olefins could be effectively epoxidized by molecular oxygen, catalyzed by porous silica support metal Schiff-base complexes.

## 2. Experimental

### 2.1. Material and equipment

Salicylaldehyde and *m*-nitro-benzaldehyde were purchased from CTD of Sweden. All other reagents used were of AR grades of purity.

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Table 1  
IR and element analysis data of the porous silica supported metal Schiff-base complexes ( $\text{cm}^{-1}$ )

Compound	$\nu_{(\text{O}-\text{H})}$	$\nu_{(\text{C}=\text{N})}$	$\nu_{(\text{C}-\text{N})}$	$\nu_{\text{Si}-\text{O}}$	$\nu_{\text{C}-\text{N}}$	$\nu_{\text{M}-\text{O}}$	$\nu_{\text{M}-\text{N}}$	M (%)
Si-NH <sub>2</sub>			1120	802				
MnmN/SiN 3500	1594	1395	1097	805	647	478	6.8	
MnSal/SiN 3500	1654	1383	1108	804	650	471	5.9	
ComN/SiN 3209	1645	1383	1064	805	679	479	3.2	
CoSal/SiN 3383	1656	1383	1106	804	650	473	0.2	

IR spectra were recorded in KBr disks with an Alpha-centauri FT-IR spectrophotometer. Elemental analysis performed on Itali Carbo-Erba 1106 elemental auto-analyzer. ICP was mea-

sured on an American ARL-3520 Inductivity coupled plasmas atomic emission spectrometry. The electron micrograph was measured on JEM-100SX electron micrograph.

## 2.2. Synthesis and characterization of the catalyst

Firstly, 1.0 g of porous silica condensed with 100 ml of a 5-mmol organic aldehyde solution of alcohol for 24 h at room temperature. Then the products were filtered, and washed with alcohol until the filtrate become colorless. Secondly, the obtained solid was mixed with 3-

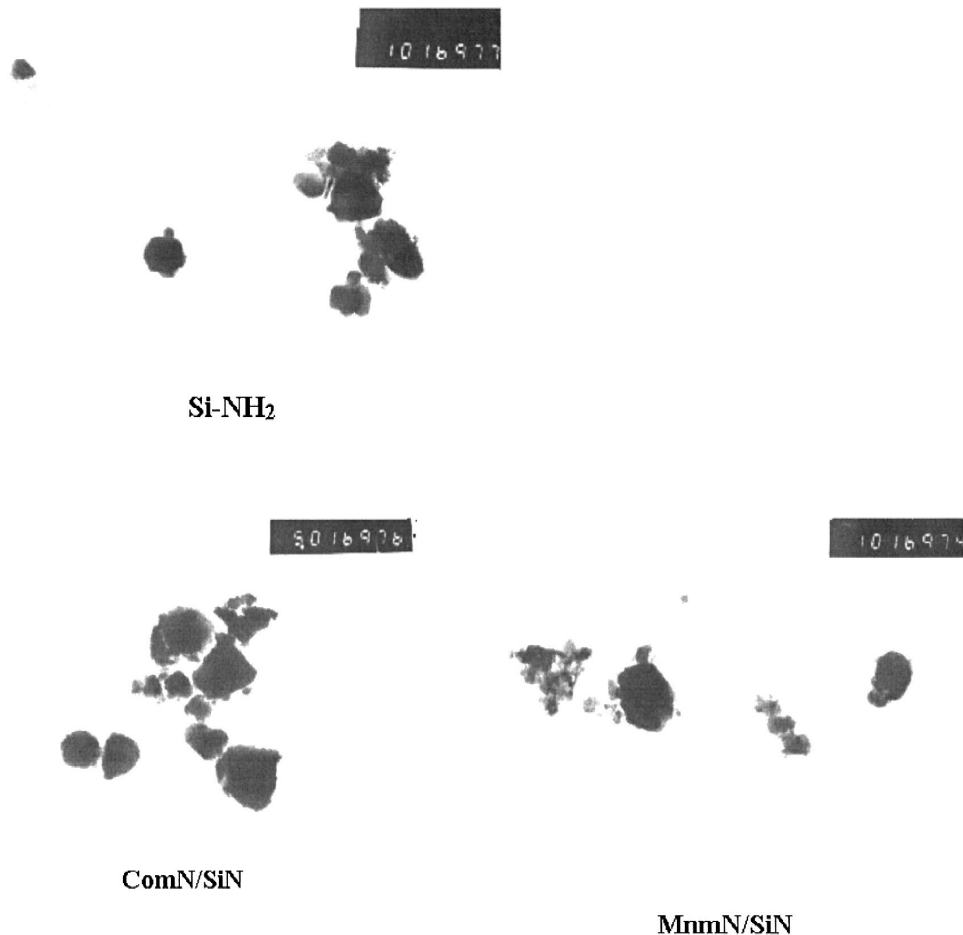
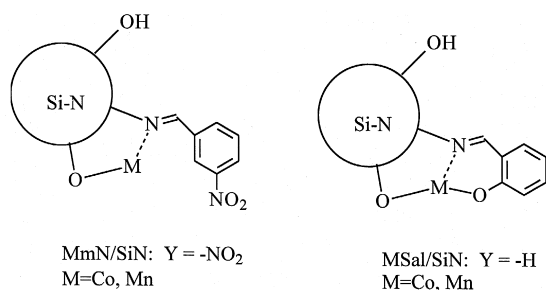


Fig. 1. The electron micrograph of amino porous silica (SiN-NH<sub>2</sub>) and its supported complexes (ComN/SiN, MnmN/SiN).



Scheme 1.

mmol solution of metal ion in alcohol for 24 h at room temperature. The products were filtered and washed thoroughly until the filtrate become colorless. The obtained solid was dried at 100°C for 2 h, which afforded MSal/SiN. The porous silica supported metal Schiff-base complexes were characterized by IR and element analysis (Table 1), and electron micrography.

IR spectra data show that the stretching vibration absorption band of Si–O appears at 1120 cm<sup>-1</sup>,  $\nu_{C-N}$  is at 802 cm<sup>-1</sup> for the amino porous silica (Si–NH<sub>2</sub>). The stretching vibrations of C=N appear at 1645–1694 cm<sup>-1</sup> for the porous silica supported metal Schiff-base complexes. The M–N bond and M–O bond appear in these complexes.

Fig. 1 shows the electron micrograph of amino porous silica (SiN–NH<sub>2</sub>) and its supported cobalt complex (ComN/SiN), and manganese complex (MmnN/SiN). It can be concluded that the crystalline state of amino porous silica has not evidently changed after supporting complexes.

Table 2  
Catalytic activity of ComN/SiN in oxidation of different substrates

Substrate: 1 ml; temperature: 100°C; catalyst: 10 mg.

Substrate	Conversion (%)	Selectivity (%)
1-octene <sup>a</sup>	36.6	75.0
1-decene <sup>a</sup>	33.2	75.0
1-dodecene <sup>b</sup>	98.5	82.0

<sup>a</sup>Time: 10 h.

<sup>b</sup>Time: 12 h.

Table 3

Catalytic activity of the different complexes in oxidation of 1-dodecene

Substrate: 1 ml; temperature: 100°C; time: 12 h.

Compound	Conversion (%)	Selectivity (%)
ComN/SiN	98.5	82.0
MmnN/SiN	5.4	50.0
MnSal/SiN	17.6	50.0

According to the spectra data, it is considered that Schiff-base complexes were supported on the porous silica with the following structure (Scheme 1).

### 2.3. Procedure of oxidation

Typical oxidation procedure of the linear aliphatic olefins was described as the literature [16]. 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).

## 3. Results and discussion

### 3.1. Catalytic activity of the porous silica supported metal Schiff-base complex in oxidation of linear aliphatic olefins

The linear aliphatic olefins, such as 1-octene, 1-decene, and 1-dodecene, can be directly oxi-

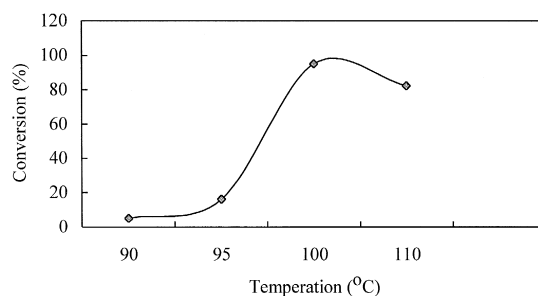


Fig. 2. Effect of temperature in catalytic oxidation of the 1-dodecene catalyzed by Com/SiN. Substrate: 1 ml; catalyst: 2.0 mg; time: 12 h.

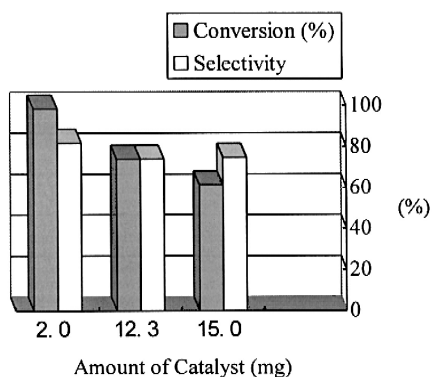


Fig. 3. Effect of the catalyst amount in oxidation of the 1-dodecene catalyzed by ComN/SiN (Substrate: 1 ml, time: 12 h, temperature: 100°C.)

dized by molecular oxygen without any reductant and solvent, which afford the 1,2-epoxy alkanes. The component products were analyzed after the reaction by the gas chromatograph and the GC–MS system. The structure was determined by comparing with the standard spectra of the compound and fragmentation pattern. The results of the different substrates were listed in Table 2. It shows that the conversion of 1-dodecene catalyzed by ComN/SiN reached to 98.5%, and the selectivity of epoxidation was reached to 82.0%.

Table 3 shows the catalytic activity of the different complexes in oxidation of 1-dodecene. The conversion of 1-dodecene catalyzed by Mn-Sal/SiN is more than 17%, and its selectivity reach to 50.0%. But no catalytic activity is measured for CoSal/SiN. It is accounted to be very low content of metal ion in the catalyst.

### 3.2. The influence of reaction temperature

Fig. 2 illustrate the variation of the conversion of substrate with different reaction temperature in the epoxidation of 1-dodecene. It was found that the conversion increased with rising of temperature in the range of 90–100°C. When the temperature was lower, it was difficult to initiate the reaction.

### 3.3. The influence of the catalyst amount

Fig. 3 shows the effect of the amount of catalyst in epoxidation of 1-dodecene. The optimum amount of catalyst is 2.0 mg. When the catalyst amount was too small, its catalytic center was short of it, which was difficult to initiate reaction. However, when the catalyst amount was too much, it inhibited oxidation reaction.

## 4. Conclusion

It was demonstrated that the porous silica supported metal Schiff-base complexes are effective catalysts for epoxidation of olefins by O<sub>2</sub> without reductant. The major products of the reaction were 1,2-epoxy alkane under appropriate reaction condition.

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