Transition metal Schiff-base complexes chemically anchored on Y-zeolite: their preparation and catalytic epoxidation of 1-octene in the suspension and phase boundary systems

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Abstract

Synthesis procedures are described for the complexes [M(L-H)(AcO)(H$_2$O)$_2$] (M(II) = Mn, Ni), [M(L-H)Cl$_n$(H$_2$O)$_m$] (M = Fe(III), $n = 2$, $m = 2$; M = Pd(II), $n = 1$, $m = 1$; M = Ag(I), $n = 0$, $m = 2$) and [M(L-H)$_2$(H$_2$O)$_n$] (M = Co(II), $n = 2$; M = Cu(II), [WO$_2$]$^{2+}$, $n = 0$) where L is the Schiff-base derived from salicylaldehyde and 3-aminopropyltriethoxysaline (APTSsal) that is chemically anchored on Y-zeolite. Characterization of these complexes was accomplished by elemental analyses, infrared and diffuse-reflectance spectra and magnetic moment. The anchored Schiff-bases imposed stable planar coordination sphere on the metal ions, allowing epoxidation of 1-octene in the axial position in the presence of molecular oxygen. The epoxidation of 1-octene was also achieved by employing the partly modified Y-zeolite with n-octadecyltrichlorosilane (OTS) Schiff-base complexes in the presence of 30% H$_2$O$_2$ under a phase-boundary system.
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1. Introduction

Development of efficient catalysts for direct and selective epoxidation of long chain linear olefins under mild conditions remains one of the major current challenges in chemical and biological catalysis [1]. Numerous epoxidation systems based on the use of alkyl peroxides [2–4], hydrogen peroxide [4–6] or molecular oxygen [6–10] as oxidant and a catalyst which is commonly a transition metal complex have been developed. Utilizing molecular oxygen (without reductant product) or H$_2$O$_2$ (gives only H$_2$O as a product) has received much attention in recent years because of their environmental implications, low cost than other oxidizing agents [9,11–13]. It was reported that olefins could be effectively epoxidized by molecular oxygen, catalyzed by NaY-encapsulated or porous silica supported Schiff-base transition metal complexes [7–10].

Here, we report a new range of active oxidation catalysts based on chemically anchored Schiff-base transition metal complexes on Y-zeolite. This study is interesting from two points: (i) The Schiff-bases anchored on Y-zeolite which imposed stable planar coordination sphere on the metal ions that make the aerobic epoxidation of 1-octene take place in the axial position in the presence of molecular oxygen [8]. (ii) The partial modification of the chemically anchored Y-zeolite with Schiff-base transition metal compounds makes these catalysts amphiphilic and facilitate its accommodation between dilute H$_2$O$_2$ (hydrophilic phase) and organic substrate (hydrophobic phase) at the phase-boundary. This system catalyses the epoxidation of alkenes without making an emulsion containing the catalyst by stirring [11–13].

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2. Experimental

2.1. Material and equipment

All used chemicals were analytically grade and used as commercially obtained. 1-Octene was purified through a basic alumina column. 3-Aminopropyltriethoxysilane and toluene were predried on molecular sieves.

All manipulations were carried out under argon and all solvents degassed before use.

The IR spectra were recorded on a Shimadzu FTIR-8200 spectrometer as KBr discs and the diffuse-reflectance spectra on a Shimadzu UV-2200 A UV–vis instrument using $BaSO_4$ as a solid phase standard. The room temperature magnetic susceptibilities were measured using a Johnson Matthey magnetic susceptibility balance; $HgCo(SCN)_4$ was employed as a susceptibility standard. The epoxidation reaction products were determined and analysed by a Shimadzu GC-14B gas chromatograph. Elemental analyses were performed at the Micro analytical Unit, Faculty of Medicine, Hokkaido University, Japan. Conductometric measurements were carried out at room temperature on a YSI Model 32 conductance meter.

2.2. Synthesis and characterization of the catalysts

2.2.1. Preparation of the ligand

2.2.1.1. The free Schiff-base (APTSsal). The Schiff-base ligand (APTSsal) was synthesized by condensation of 3-aminopropyltriethoxysilane (APTS; 0.8 mmol) and salicylaldehyde (sal; 0.6 mmol).

2.2.1.2. The Schiff-base chemically anchored Y-zeolite (HY-APTSsal). 3-Aminopropyltriethoxysilane (APTS, 0.8 mmol) in toluene (10 cm³) was added to a suspension of activated HY-zeolite (1.0 g) in toluene (7 cm³) and the reaction mixture was stirred for 1 h. The solid HY-APTS was separated out, washed with toluene and dried at 370 K under vacuum. A suspension of HY-APTS in $CHCl_3$–EtOH (1:2; 10 cm³) was mixed with salicylaldehyde (sal, 0.6 mmol) and the mixture was stirred over night. The solid Schiff-base anchored on HY-zeolite (HY-APTSsal = HL) was separated out, washed with $CHCl_3$–EtOH (1:2) and dried at 368 K under vacuum.

2.2.1.3. The Schiff-base chemically anchored partly modified Y-zeolite (HY-OTS-APTSsal). With n-octadecyltrichlorosilane (OTS, 100 μmol) in toluene suspended in water (0.5 cm³) was impregnated activated HY-zeolite (1 g). The partly modified (HY-OTS) was separated out and dried under vacuum at ca. 368 K. A similar procedure to that used for the HY-APTSsal was employed using APTS (0.6 mmol) and sal (0.25 mmol).

2.2.2. Preparation of complexes

2.2.2.1. The free Schiff-base (APTSsal) complexes. An ethanolic solution of APTSsal (2 mmol) was mixed with an aqueous–EtOH solution of the metal salt {$FeCl_3$, $CuSO_4$ or $M(AcO)_2$ (M(II) = Mn, Co, Ni)} (1 mmol). The resulting mixture was heated under reflux for 1 h. The complexes were separated out, washed with EtOH and Et_2O and dried in vacuo.

An ethanolic solution of APTSsal (2 mmol) was mixed with an aqueous solution of the metal salts $AgNO_3$, $(NH_4)_2[PdCl_4]$ and $Na_2[WO_4]$, (1 mmol). The reaction mixture was stirred during which time the complex was obtained. The complexes were separated out, washed with water, EtOH and Et_2O and dried in vacuo.

2.2.2.2. The Schiff-base chemically anchored Y-zeolite (HY-APTSsal), (HY-OTS-APTSsal) complexes. All the reported complexes were synthesized by using the following general procedure.

Ethanolic suspension of the anchored Schiff-base HY-zeolite (1 g, 0.48 mmol) was mixed with an EtOH solution of the metal salt {$FeCl_3$, $CuSO_4$, $AgNO_3$, $(NH_4)_2[PdCl_4]$, Na_2WO_4, $M(AcO)_2$ (M(II) = Mn, Co, Ni); drops of water may be added if necessary}. The resulting mixture was stirred overnight and the complex was separated out, washed with EtOH and Et_2O and dried under vacuum at ca. 368 K.

With partly modified HY-OTS-APTSsal, a similar procedure to that used for HY-APTSsal was employed using 0.25 mmol of the metal salt.

All manipulations were carried out under argon and all solvents degassed before use to avoid the uncontrollable hydrolysis and polarization of APTS [14]. Scheme 1 shows the structures of the Schiff-base APTSsal anchored on HY and partly modified HY-OTS zeolite [14,15].

Analytical data of APTSsal and HY-APTSsal complexes are in agreement with the empirical formulae shown in Table 1. Their molar conductivities (Λ_M) in DMF at room temperature showed them to be non-electrolytes [16].

2.2.3. Infrared spectra

The IR spectral data of Schiff-base (APTSsal) complexes and the Schiff-base chemically anchored on Y-zeolite (HY-APTSsal and HY-OTS-APTSsal) are reported in Table 1. The general features are similar to those observed for NaY [7,10] and porous silica [8,17] encapsulated complexes. As expected, the vibration bands observed near the 484 (medium) and 1120–1040 cm⁻¹ region (broad and strong) are assigned to ν(Al–O) and ν(Si–O) stretching of Si(μ-O)$_2$Al bridges of zeolite [10], respectively. In the free ligands, the bands near 1650 and 1250 cm⁻¹ arise from ν(C=N) [16] and ν(C–O) [8,9] stretching, respectively. These latter stretching vibrations are shifted to lower frequencies upon coordination [7,9,10]. The medium intense bands near 2922 and 2885 cm⁻¹ are attributed to $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ stretching, respectively [18]. The bands near 1467 and 1445 cm⁻¹ are assigned to $\delta(CH_3)_{as}$ and the bands near 1380 cm⁻¹ are typical of $\delta(CH_3)_s$ vibrations, respectively [19] (the CH_3 stretches are observed in case of the APTSsal and HY-OTS-APTSsal and their complexes). In the acetato complexes (Mn(II),
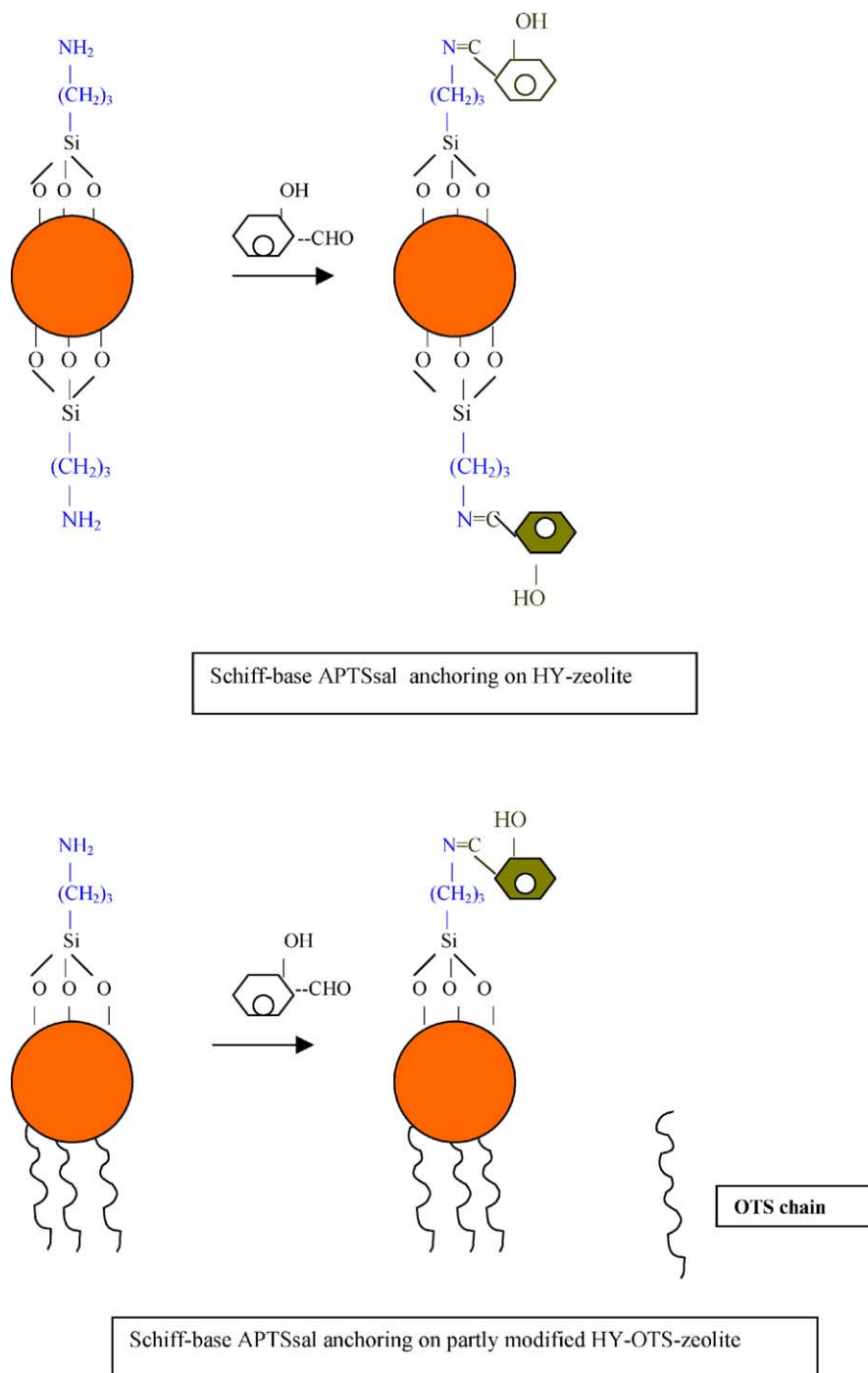
Scheme 1. Anchoring of Schiff-base APTSsal on HY and partly modified HY-OTS zeolite.

Ni(II)), two extra bands observed near 1535 and 1400 cm^{-1} are due to $\nu_{as}(OCO)$ and $\nu_s(OCO)$ of the acetato group, respectively indicating asymmetric bidentate coordination of the acetate group [9,20]. Also, two extra bands are observed in the spectra of $[WO_2]^{2+}$ complexes near 940 cm^{-1} (weak) and 890 cm^{-1} (strong) assigned to $\nu_s(WO_2)$ and $\nu_{as}(WO_2)$ stretching, respectively [21].

Most of the reported complexes show new bands near 500 and 400 cm^{-1} which probably arise from $\nu(M-O)$ and

$\nu(M-N)$ stretching, respectively [22]. The spectra of Fe(III) and Pd(II) complexes show another new band near 300 cm^{-1} arising from $\nu(M-Cl)$ stretching [23].

2.2.4. Electronic spectra

The diffuse-reflectance spectral data of the reported complexes are listed in Table 1.

The electronic spectra of ligands showed that each one has a n → π^* transition in the 270–290 nm region assignable to

Table 1

Analytical, IR and diffuse-reflectance spectroscopic data of Schiff-bases anchored on Y-zeolite and their complexes

Compound	Color	Found (calc.) (%)[a]				Vibrational spectra (cm^{-1})					Diffuse-reflectance spectra (nm)
		C	H	N	M	ν(C=N)	ν(C—O)	ν(M—O)	ν(M—N)	ν(M—Cl)	
APTSsal (L)	Yellow										410, 320
HY-APTSsal	Yellow					1650	1250				400, 295
HY-OTS-APTSsal	Yellow					1655	1240				410, 300
[Mn(L-H)(AcO)(H$_2$O)$_2$]	Yellow	45.2 (45.6)	6.8 (7.0)	2.9 (3.0)	11.4 (11.6)	1625	1220	488	402		550
HY-APTSsal-Mn(II)	Pale yellow	6.0 (6.0)	0.75 (0.76)	0.6 (0.58)	2.3 (2.3)	1630	1215	500	404		555
HY-OTS-APTSsal-Mn(II)	Pale yellow				0.92 (0.96)	1632	1217	495	397		555
[Fe(L-H)Cl$_2$(H$_2$O)$_2$]·H$_2$O	Purple	38.0 (38.0)	6.0 (6.3)	2.7 (2.8)	10.8 (11.0)	1635	1237	488	398	296	550, 375
HY-APTSsal-Fe(III)	Pale purple	5.1 (5.1)	0.63 (0.64)	0.57 (0.60)	2.2 (2.4)	1633	1234	495	385	293	550, 390
HY-OTS-APTSsal-Fe(III)	Pale purple				0.85 (0.91)	1633	1230	499	390	300	550, 385
[Co(L-H)$_2$(H$_2$O)$_2$]·H$_2$O	Dark brown	50.8 (50.4)	7.6 (7.7)	3.7 (3.7)	7.6 (7.7)	1632	1230	504	400		610, 475
HY-APTSsal-Co(II)	Pale brown	6.4 (6.4)	0.61 (0.58)	0.72 (0.75)	1.5 (1.6)	1636	1224	517	406		620, 480
HY-OTS-APTSsal-Co(II)	Pale brown				0.65 (0.64)	1637	1219	509	404		620, 480
[Ni(L-H)(AcO)(H$_2$O)$_2$]·2H$_2$O	Shine green	39.6 (39.3)	7.2 (7.5)	2.6 (2.6)	10.6 (10.7)	1629	1235	509	397		645, 410
HY-APTSsal-Ni(II)	Pale green	4.9 (4.9)	0.71 (0.75)	0.48 (0.48)	2.0 (2.0)	1633	1239	499	395		635, 390
HY-OTS-APTSsal-Ni(II)	Pale blue-green				0.92 (0.92)	1635	1241	500	400		630, 380
[Cu(L-H)$_2$]	Blue-green	53.6 (53.9)	7.3 (7.4)	3.4 (3.9)	8.8 (8.9)	1635	1215	511	408		650, 400
HY-APTSsal-Cu(II)	Pale blue-green	4.9 (4.9)	0.44 (0.41)	0.56 (0.57)	1.2 (1.3)	1636	1237	506	409		650, 395
HY-OTS-APTSsal-Cu(II)	Pale blue-green				0.77 (0.76)	1633	1237	503	401		650, 400
[Pd(L-H)Cl(H$_2$O)]·H$_2$O	Brown	38.2 (38.3)	6.0 (6.0)	2.7 (2.8)	21.0 (21.2)	1630	1238	519	399	283	460, 370
HY-APTSsal-Pd(II)	Brown	4.7 (4.7)	0.59 (0.59)	0.57 (0.55)	4.1 (4.2)	1631	1233	524	400	280	450, 380
HY-OTS-APTSsal-Pd(II)	Brown				1.80 (1.81)	1630	1237	520	400	281	450, 360
[Ag(L-H)(H$_2$O)$_2$]	Dirty white	41.2 (41.0)	6.4 (6.5)	3.0 (3.0)	22.8 (22.0)	1612	1240	533	410		550, 465
HY-APTSsal-Ag(I)	White	4.8 (4.8)	0.60 (0.61)	0.54 (0.56)	4.4 (4.3)	1610	1237	526	404		545, 470
HY-OTS-APTSsal-Ag(I)	White				2.2 (2.3)	1613	1235	520	407		545, 470
[WO$_2$(L-H)$_2$]	Yellow	44.2 (44.4)	8.0 (7.9)	3.3 (3.3)		1627	1223	909[b], 877[c]	400		470, 370
HY-APTSsal-WO$_2$$^{2+}$	Pale yellow	4.9 (4.9)	0.45 (0.45)	0.56 (0.57)		1625	1233	910[b], 875[c]	405		465, 360
HY-OTS-APTSsal-WO$_2$$^{2+}$	Pale yellow					1628	1230	905[b], 872[c]	400		470, 355

[a] The analytical data of HY-OTS-APTSsal and their complexes can only be determined for the metal ion.

[b] ν_s(WO$_2$) stretches.

[c] ν_{as}(WO$_2$) stretches.

the phenyl rings [24]; these energies are raised by ca. 10 nm in the complexes [25]. The 390–405 nm region bands are assignable to n $\rightarrow$ π^* transition of the (C=N) moiety, and are shifted to higher energies in complexes [26]. The Mn(II) complexes show broad bands near 550 nm, that is attributed to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ transition in octahedral structures [23]. The magnetic moment value of [Mn(APTSsal-H)(AcO)(H$_2$O)$_2$] (μ_{eff} = 5.1 B.M.) indicates a high-spin 3d^5 system [27]. The [Fe(APTSsal-H)Cl$_2$(H$_2$O)$_2$] complex is paramagnetic (μ_{eff} = 5.4 B.M.), indicating a high spin configuration [23]. The electronic spectra of Fe(III) complexes show two bands near 550 and 380 nm, which are due to $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(D)$ transitions, respectively in octahedral stereochemistry [28]. The Co(II) complexes have bands in the 620–610, 480–475 and 380–360 nm regions due to $^4T_{1g} \rightarrow {}^4A_{2g}$, $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and ligand to metal charge transfer (LMCT), respectively [27,29]. The magnetic moment value of [Co(APTSsal-H)$_2$(H$_2$O)$_2$] (μ_{eff} = 4.6 B.M.) together with the positions of the absorption bands suggest octahedral geometries around the Co(II) ions [22]. The electronic spectra of the Ni(II) complexes exhibit two bands near 630 and 390 nm probably arising from $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively in octahedral geometry [23]. The magnetic moment value of [Ni(APTSsal-H)(AcO)(H$_2$O)$_2$] (μ_{eff} = 3.0 B.M.) lies within the range reported for octahedral Ni(II) complexes [22].

The electronic spectra of Cu(II) complexes show two bands near 650 nm (broad) and 400 nm (shoulder), attributed to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions for the former one and charge transfer for the latter one, indicating tetragonal configuration [22]. The complex [Cu(APTSsal-H)$_2$] is paramagnetic (μ_{eff} = 2.1 B.M.) which is normal for Cu(II) complexes (d^9 system contains one unpaired electron [30]). The spectra of Pd(II) complexes have bands near 450 nm due to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition in square planar configurations [31]. The spectra of the diamagnetic Ag(I) complexes exhibit three bands near 550, 470 and 380 nm with square planar geometry [20]. The diamagnetic [WO$_2$]$^{2+}$ complexes exhibit two electronic spectral bands near 470 and 360 nm; the latter one is a shoulder and can be assigned to ligand $\rightarrow$ metal charge transfer transition in octahedral structures [32].

2.3. Procedure for catalytic oxidation of 1-octene

2.3.1. Molecular oxygen oxidant under heterogeneous system

In these oxidation processes, the catalysts used were the non modified HY-APTSsal species.

In a typical oxidation procedure, a Pyrex tube (20 cm^3) was charged with the catalyst (0.025 g) and 1-octene (2 cm^3). The molecular oxygen was filled and the reaction mixture was heated at 373 K with stirring. The reaction products were determined and analyzed after 2, 6, 12 and 24 h.

2.3.2. Hydrogen peroxide oxidant under phase-boundary system

In these oxidation processes, the catalysts were partly modified HY-OTS-APTSsal complexes.

In a typical oxidation procedure, a Pyrex bottle (10 cm^3) was charged with the catalyst (0.025 g), 1-octene (2 cm^3) and 30% aqueous H$_2$O$_2$ (0.5 cm^3). The reaction mixture was heated at 373 K with and without stirring. The reaction products were determined and analyzed after 4, 8, 12, 16, 20 and 24 h.

3. Results and discussion

3.1. Catalytic activity of HY-APTSsal complexes in the oxidation of 1-octene in the presence of molecular oxygen under heterogeneous system

Generally, the linear aliphatic olefins such as 1-octene can be directly oxidized to 1,2-epoxyoctane by molecular oxygen at 353–373 K without any reductant and solvent [7,8].

Table 2 shows the catalytic activities of HY-APTSsal complexes of Fe(III), M(II) (M = Mn, Co, Ni, Cu, Pd), Ag(I) and WO$_2^{2+}$ in the epoxidation of 1-octene. The epoxidation of 1-octene is increased by increasing the reaction temperature (368–378 K), as high temperature initiate the epoxidation [8]. All the catalysts reported in this study are found to be stable under experimental conditions as they are recovered by separation, washing with EtOH and Et$_2$O and drying under vacuum. Also, these catalysts show activity for further catalytic runs (Table 2), but they undergo some degradation over 24 h as evidenced by a slight metal loss. The same features have been observed for NaY-encapsulated M(Salen) (M = Mn, Ni) complexes [33]. The catalytic activities of the filtrates from the washing of the first time use of the catalysts for reuse was examined, but very poor activities were obtained.

As 1-octene (linear olefin) can easily approach the catalyst active sites [33], all the reported catalysts in this study are showing high selectivity of 1,2-epoxyoctane formation (94–70%) with small amounts of by-products being detected by GC [34], except for Pd(II) complex (selectivity is 35%), as the oxidation products are 1,2-epoxyoctane (104 µmol), 2-octanol (27 µmol) and 2-octanone (167 µmol). In order to explain the catalytic activity of HY-APTSsal complexes for the epoxidation of 1-octene by molecular oxygen, a radical chain mechanism have been proposed in Scheme 2 [9,34–37].

3.2. Catalytic activity of HY-OTS-APTSsal complexes in the oxidation of 1-octene in the presence of H$_2$O$_2$ under phase-boundary system

Table 3 shows the catalytic activity of the partly modified HY-OTS-APTSsal complexes of Fe(III), M(II) (M = Mn, Co, Ni, Cu, Pd), Ag(I) and [WO$_2$]$^{2+}$ in the epoxidation of 1-octene at 373 K under the phase-boundary system. The non-modified HY-APTSsal complexes are hydrophilic in nature and showed low catalytic activities towards epoxidation of 1-octene under phase-boundary conditions at different

Table 2
Catalytic activity of HY-APTSsal complexes in epoxidation of 1-octene by molecular oxygen as oxidant[a]

Compound	Loading of complexes in zeolite (mmol/1g)	1,2-Epoxyoctane (μmol)[b]		TON[d]
		First use	Second use[c]	
1-Octene		22.5		
HY-APTS		122 (75)	98 (85)	
HY-APTSsal		140 (71)	133 (92)	
HY-APTSsal-Mn(II)	0.161	283 (87)	261 (91)	70
HY-APTSsal-Fe(III)	0.170	225 (70)	204 (83)	53
[Co(L-H)$_2$(H$_2$O)$_2$]·H$_2$O	20.6	288 (93)		14
HY-APTSsal-Co(II)	0.153	356 (87)	300 (95)	93
HY-APTSsal-Ni(II)	0.145	246 (77)	205 (90)	68
HY-APTSsal-Cu(II)	0.110	282 (86)	253 (92)	103
HY-APTSsal-Pd(II)	0.163	104(35)	260(70)	26
HY-APTSsal-Ag(I)	0.152	297 (83)	255 (92)	78
HY-APTSsal-WO$_2$$^{2+}$	0.141	350 (92)	319 (94)	99

[a] All the reactions were carried out at 373 K with stirring using 1-octene (2 cm^3), catalyst (0.025 g) and O$_2$ to completion in a 20 cm^3 Pyrex tube for 24 h.
[b] Selectivity is given in parentheses.
[c] The re-use of the catalyst after separation, washing and drying.
[d] Turnover number for the first use of the catalyst (epoxide/catalyst in μmol).

temperatures. On the other hand, the partial modification of HY-zeolite by OTS before the anchoring of APTSsal complexes leads to a significant enhancement of epoxidation rate. The oxidation results seem consistent with the mechanism of phase-boundary catalysis; amphiphilic particles containing both hydrophilic (APTSsal complex) and hydrophobic (OTS) parts at the phase-boundary catalyse the epoxidation of 1-octene without stirring. In the phase-boundary system, hydrogen peroxide decomposed into oxygen and then participate in epoxidation. Also, additional description showing that the phase-boundary catalytic system decomposition of hydrogen peroxide into oxygen is a side reaction and direct oxidation of olefins to epoxide proceeds directly from hydrogen peroxide [11–13].

3.2.1. The influence of reaction temperature

Fig. 1 illustrates the epoxidation of 1-octene at different temperatures. It is clear that the epoxidation rate increases with increasing temperature from 363 to 373 K; below 363 K, it is difficult to initiate the epoxidation process [8].
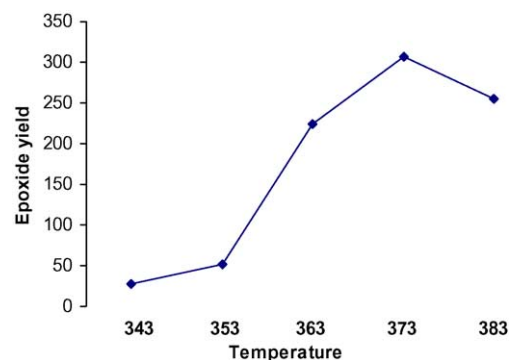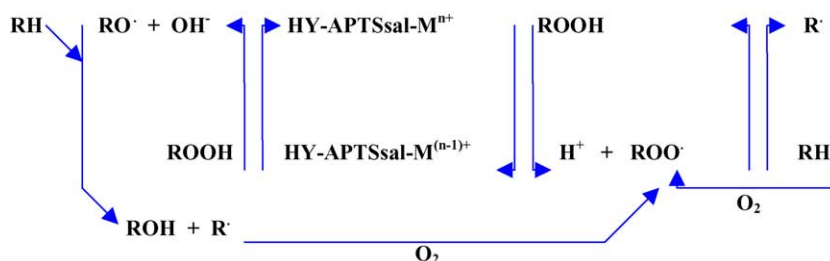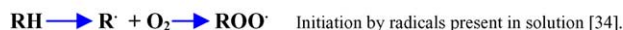

Fig. 1. Effect of temperature in the catalytic epoxidation of 1-octene by HY-OTS-APTSsal-Fe(III) complex using 1-octene (2 cm^3), catalyst (0.025 g) and 30% H$_2$O$_2$ (0.5 cm^3) in 24 h under phase-boundary system.

3.2.2. The influence of reaction time

Fig. 2 shows the relationship between the conversion of 1-octene to 1,2-epoxyoctane and the reaction time at 373 K. the catalytic activity of most of these catalysts becomes very high after 20–23 h.

Scheme 2. The mechanism for the catalysis of HY-APTSsal complexes in the epoxidation of 1-octene in the presence of O$_2$ at 373 K. Initiated by radicals.

Table 3
Catalytic activity of HY-APTSsal complexes in epoxidation of 1-octene by hydrogen peroxide as oxidant under phase-boundary system[a]

Compound	Loading of complexes in zeolite (mmol/1g)	1,2-Epoxyoctane (μmol)[b]		TON[e]
		First use[c]	Second use[d]	
HY-OTS		119 (90)		
HY-OTS-APTS		125 (79)		
HY-OTS-APTSsal		119 (86)		
HY-OTS-APTSsal-Mn(II)	0.0672	304 (94)	293 (93)	181
		157 (91)		
HY-OTS-APTSsal-Fe(III)	0.0708	307 (93)	281 (90)	173
		108 (96)		
HY-OTS-APTSsal-Co(II)	0.0640	275 (92)	251 (92)	172
		98 (86)		
HY-OTS-APTSsal-Ni(II)	0.0280	318 (93)	295 (93)	454
		152 (86)		
HY-OTS-APTSsal-Cu(II)	0.0296	265 (93)	246 (92)	358
		33 (79)		
HY-OTS-APTSsal-Pd(II)	0.0300	226 (62)	221 (81)	301
		45 (27)		
HY-OTS-APTSsal-Ag(I)	0.0332	281 (92)	280 (89)	339
		39 (53)		
HY-OTS-APTSsal-WO$_2$$^{2+}$	0.0588[f]	288 (90)	282 (89)	196[f]
		82 (72)		

[a] All the reactions were carried out at 373 K without stirring using 1-octene (2 cm^3), catalyst (0.025 g) and H$_2$O$_2$ (0.5 cm^3) for 24 h.
[b] Selectivity is given in parentheses.
[c] The underlined data is obtained by stirring.
[d] The re-use of the catalyst after separation, washing and drying.
[e] Turn over number for the first use of the catalyst (epoxide/catalyst in μmol).
[f] Metal ion concentration and TON are calculated with respect to the concentration of sal added in HY-APTSsal and HY-OTS-APTsal [WO$_2$]$^{2+}$ complexes.

3.2.3. The influence of stirring

Upon the stirring of the epoxidation reaction of 1-octene under the phase-boundary system, an obvious reduction in the production of 1,2-epoxyoctane at 373 K was observed (Table 3). This feature probably arises from the adsorption of H$_2$O (produces from the decomposition of H$_2$O$_2$ at high temperature) on the hydrophobic OTS phase and thus increases the hydrophilicity of the catalyst surface. This behavior is not observed when the reaction is carried out without stirring, presumably due to either coordination or adsorption of water molecules to the metal complex phase without affecting the OTS hydrophobic phase [11–13].
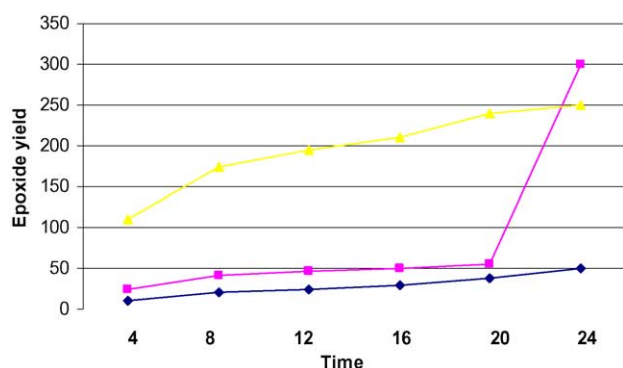
4. Conclusions

The above results show that the Schiff-base transition metal complexes chemically anchored on HY-zeolite are effective catalysts for the epoxidation of 1-octene by O$_2$ without reductant at 373 K. Also, HY-zeolite partly modified by n-octadecyltrichlorosilane and chemically anchored Schiff-base transition metal complexes located at the boundary between aqueous H$_2$O$_2$ and organic phase (a phase-boundary catalyst) act as catalysts for the epoxidation of 1-octene without stirring or the addition of co-catalyst at 373 K.

Fig. 2. Catalytic activity of HY-OTS-APTSsal-complexes: (♦) Fe(III) and (△) Pd(II) at 373 K, and (■) Fe(III) at 353 K using 1-octene (2 cm^3), catalyst (0.025 g) and 30% H$_2$O$_2$ (0.5 cm^3) in 24 h under phase-boundary system.

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