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Temperature-controlled selectivity in oxidation of 1-octene by using aqueous hydrogen peroxide in phase-boundary catalytic system



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ABSTRACT

Temperature-controlled selectivity in oxidation of 1-octene by using aqueous hydrogen peroxide in phase-boundary catalytic system was demonstrated by using alkylsilylated-Ti(IV) salicylaldimine complex at a series of temperature (25-90 °C). The catalyst was synthesized by titanium(IV) sulfate solution, salicylaldehyde, and 3-aminopropyltrimethoxysilane as the precursors and followed by the attachment of octadecyltrimethoxysilane. It was found that the reaction system resulted in high selectivity at low temperature. One suggests that the high selectivity in the oxidation of 1-octene by aqueous hydrogen peroxide was related to partitioning of alkylsilylated-titanium(IV) salicylaldimine complex in immiscible liquid–liquid phase boundary which is temperature dependent.

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1. Introduction

Nowadays, heterogeneous liquid-phase which is involving immiscible liquid-liquid phase and solid catalyst is widely utilized in chemical processing and for environmental control. Cosolvent and stirring are adopted in the catalytic system in order to generate homogeneous solution (biphasic condition) which can enhance the interaction among reactants and solid catalyst. However, cosolvent brings the problem to the separation of the products from the mixture of reactants and cosolvent. Besides, leaching effect and producing unnecessary byproducts might be obtained after stirring. Thus, phase-boundary catalysis (PBC) has been proposed with the aim of solving the above problems with neither stirring nor adding cosolvent in this triphasic condition [1–4].

Previously, phase-boundary catalysis (PBC) system with titania impregnated on sodium zeolite solid particles along with surface modified by octadecyltrichlorosilane (OTS) to form amphiphilic structure solid particles has been reported [1–4]. The catalyst is located in between the interphase of organic and aqueous phases and then generates the mass transfer from bulk reactants to the catalysts, resulting in high affinity for both 1-octene and aqueous hydrogen peroxide, followed by improving the rate of reaction of

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0926-860X/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2013.04.016 the system. It can be deduced that amphiphilic structure is significant in relation to the catalytic behavior.

On the other hand, numerous heterogeneous transition metal Schiff base complexes have been used in the epoxidation or oxidation of olefins [5-7] by utilization of hydrogen peroxide. Aqueous hydrogen peroxide (H₂O₂) is highly adopted due to it gives water as byproduct, more accessible, and less expensive compared to other oxidizing agents, such as organic peracids or hydroperoxides. Moreover, the challenging and common phenomenon of nowadays is the conversion of organic substrate is very high, but, the selectivity to products is quite low [8].

Herein, we would like to demonstrate the temperaturecontrolled selectivity in oxidation of 1-octene by using aqueous hydrogen peroxide (H_2O_2) in phase-boundary catalytic system by using alkylsilylated-Ti(IV) salicylaldimine complex as catalyst. It is worth noting that the selectivity to 2-octanone and 2-octanol was quite high up to a point although the reaction was carried out at high temperature at certain time.

2. Experimental

2.1. Synthesis of alkylsilylated-Ti(IV) salicylaldimine complex

The synthesis of Ti(IV) salicylaldimine complex was done in the following steps. Ti(IV) sulfate solution (1.0 mmol, 0.89 ml, Kanto Chemical) in absolute ethanol (10 ml, Hayman) was added dropwise into salicylaldimine ligand (2.0 mmol, 0.57 g) in absolute ethanol (10 ml, Hayman). The ligand was previously prepared by salicylaldehyde (5.0 mmol, 0.54 ml, Acros Organics) in absolute ethanol (10 ml, Hayman) and 3-aminopropyltrimethoxysilane (5.0 mmol, 0.96 ml, Aldrich-Sigma) in absolute ethanol (10 ml, Hayman), both were mixed under flow of nitrogen gas and then vacuumed to remove the solvent. The weight of ligand was obtained before adding with Ti(IV) sulfate solution. After that, the titanium(IV) mixture solution was stirred for 24h to complete the hydrolysis and condensation reaction. It was followed by centrifugation of Ti(IV) salicylaldimine complex at 4000 rpm for 10 min to separate the solid complex and liquid layer (solvent) in the solution. Then, the solid complex was washed by ethanol and hexane, each for twice, to wash out the excess ligand and water. The weight of Ti(IV) salicylaldimine complex was 0.71 g. Now, the procedures for the synthesis of phase-boundary catalysts were as follows. Ti(IV) complex (0.50 g) was ground with 0.25 ml doubled distilled water thoroughly. After that, it was put into the beaker containing octadecyltrimethoxysilane (OTMS, 500 µmol per 1 g of solid Ti(IV) salicylaldimine complex, 0.12 ml, Merck) in 10 ml toluene. It was shaken for 5 min and stirred until dry for 3-4 days. Then it was washed by toluene and hexane, twice for each solvent. This catalyst was known as phase-boundary catalyst. The procedure to make phase-boundary solid particles was adopted from the previous reports [1–4].

2.2. Characterizations of alkylsilylated-Ti(IV) salicylaldimine complex

The solid catalysts obtained were characterized by Fourier transform infrared (FTIR) spectrometer, diffuse reflectance ultraviolet–visible spectrometer (DR UV–vis), scanning electron microscope (SEM) and ²⁹Si solid state magic angle spinning (MAS) nuclear magnetic resonance NMR.

Samples were preheated at 60 °C for few hours as a precaution step to ensure that the dried samples mixed well with KBr powder and get a compact and transparent disk for infrared analysis. The FTIR spectra were collected on a Perkin Elmer Spectrum One spectrometer with 15 scans and resolution of 4 cm^{-1} , in the range of 4000–400 cm⁻¹. Potassium bromide (KBr) pellet technique was used to examine the presence of alkylsilyl groups on Ti(IV) salicylaldimine complex after modified by octadecyltrimethoxysilane (OTMS) (alkylsilylated-Ti(IV) salicylaldimine complex). The samples were mixed with KBr in the weight ratio of 1:100 and ground thoroughly. Then, it was put in the pellet die to make a very thin pellet for analysis.

The solid yellow samples were also recorded by Perkin Elmer Ultraviolet-visible Spectrometer Lambda 900 and plotted using Kubelka–Munk function, in the range of 200–800 nm, using barium sulfate as the standard.

The morphology of the solid particles was observed under low vacuum scanning electron microscope (LVSEM). The solid particles were fixed on carbon tape and then coated with platinum for 4–5 times under conventional sputtering techniques. Then, the sample morphology was shown under 15 kV accelerating voltage.

The ²⁹Si MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4T spectrometer. The spectra were recorded at 79.44 MHz using 4 μ s radio frequency pulses, a recycle delay of 60 s and spinning rate of 7.0 kHz using a 4 mm zirconia sample rotor. ²⁹Si MAS NMR chemical shifts were referred to external TMS at 0 ppm.

2.3. Catalytic activity of alkylsilylated-Ti(IV) salicylaldimine complex

The reactions were carried out at a series of temperature to investigate catalytic activities of oxidation of 1-octene (10 mmol, 1.56 ml, Merck) by 30% aqueous H_2O_2 (30 mmol, 3.06 ml, Merck).

(a) Ti(IV) salicylaldimine complex



 $\frac{4000}{3600} \frac{3200}{2200} \frac{2800}{2400} \frac{2400}{2000} \frac{1800}{1800} \frac{1800}{1800} \frac{1400}{1200} \frac{1200}{1000} \frac{1000}{800} \frac{800}{600} \frac{400}{400}$ Wavenumber / cm⁻¹

 $\label{eq:Fig.1.} FIIR spectra of (a) Ti(IV) salicylaldimine complex and (b) alkylsilylated-Ti(IV) salicylaldimine complex.$

The alkylsilylated–Ti(IV) complex (0.05 g) was examined at 25, 30, 40, 50, 60, 80 and 90 $^{\circ}$ C to observe the relationship of solubility and temperature. We used the sealed and closed system in order to prevent the evaporation of the reactants. The apparatus used is 10 ml bottle sample with screw cap equipped with induction seal liner in order to avoid leaking of the system.

The products of reaction were analyzed by Shidmazu Gas Chromatography model GC-2014 equipped with BPX-5 column (30 m length, 0.25 mm inner diameter, 0.25 μ m film thickness and a flame ionization detector (FID). The catalytic reactions were conducted without organic solvent. The program temperature of the column oven was performed at the initial temperature, 50 °C, held for 1.0 min, ramp temperature is 10 °C min⁻¹ till 200 °C and it was held for 3 min to elute the products left. Total program time is 12.40 min. The equilibration time is 1.0 min.

3. Results and discussion

The result of IR spectra Ti(IV) salicylaldimine complex and alkylsilylated-Ti(IV) salicylaldimine complex is presented in Fig. 1. The solid Ti(IV) salicyladimine complex was successfully formed because the imine group (C=N) is at lower frequency, 1610 cm^{-1} , compared to free azomethine group which was assigned at 1647 cm^{-1} [9]. In our infrared results, there are two absorption bands have been assigned to Ti–N and Ti–O bonds with 601 cm^{-1} [10] and 697 cm^{-1} [11], respectively (Fig. 2).

It is found that the stretching mode of Si–OH functional group at ca. $3427 \,\mathrm{cm}^{-1}$ [11,12], meanwhile, its bending mode located at $984 \,\mathrm{cm}^{-1}$. However, Yan Luo et al. [13] suggested that this region frequency ($984 \,\mathrm{cm}^{-1}$) might be assigned to Ti–O–Si bonds. The absorption bands presented at $1125 \,\mathrm{cm}^{-1}$ and $1035 \,\mathrm{cm}^{-1}$ are attributable to Si–O–Si asymmetric and symmetric stretching modes, respectively [9]. We observed that OH bending from water molecules at the $1661 \,\mathrm{cm}^{-1}$ [14] for complexes due to the complexes comprised of terminal silanol groups. This hydrophilic silanol group, Si–OH, can attract moisture containing water molecules onto it.

Before the solid complex was modified by octadecyltrimethoxysilane (OTMS), there is no apparent peak at around 2920–2850 cm⁻¹ and 1470–1460 cm⁻¹. After the modification, there are evident peaks shown by this phase-boundary catalyst due to attachment of octadecylsilyl groups on the complexes, hence, absorption bands of symmetric and asymmetric CH₂ vibration at 2850 and 2918 cm⁻¹ and CH₂ bending peak at 1468 cm⁻¹ and 1504 cm⁻¹ were observed [15]. Furthermore, the peak at ca.



Fig. 2. Diffuse reflectance UV–vis spectra of (a) alkylsilylated-Ti(IV) salicylaldimine complex and (b) Ti(IV) salicylaldimine complex.

818 cm⁻¹ was attributed to symmetric deformation vibration of Si–C stretching [16].

In the diffuse reflectance of spectra Ti(IV) salicylaldimine complex and alkylsilylated-Ti(IV) salicylaldimine complex, both displayed that a shoulder band in the range of 200–250 nm, it is owing to association of π – π * transitions of aromatic ring and imine (C=N) group [17]. It is found that there is an absorption at 315–317 nm because of Laporte – allowed LMCT of oxygen from phenyl group (substituted phenol) to Ti(IV) was successfully formed [18]. Shifting of n– π * transition of imine group, C=N (400 nm) [16] to lower frequency, ca. 360 nm, was due to the

nitrogen from imine group has successfully coordinated to metal to form complexes [19,20]. It is a typical electronic transition in transition metal Schiff base complexes which consist of the aromatic ring and -C=N imine conjugation $(n-\pi^* \text{ transition})$ [20]. Furthermore, we observed that the alkylsilylated-Ti(IV) salicylaldimine complex displayed more intense absorption band at ca. 360 nm compared to Ti(IV) salicylaldimine complex. It is because of the addition of octadecyltrimethoxysilane (OTMS) to the metal complex. This argument was supported by the previous reported literature [21].

²⁹Si MAS NMR has been used for the structural characterization of silica surface modification as described in Fig. 3. It is depicted in Fig. 3 that the presence of $T^3 = R - Si(OSi)_3$ with -66 ppm [22] in the complex is due to hydrolysis and condensation of the alkylsilylane group of Ti(IV) salicylaldimine complex. It can be seen that the hydrolysis and condensation processes were completed with high degree of cross-linking on the complexes. After anchoring the octadecyltrimethoxysilane (OTMS) to the complexes, it is interesting to note that the appearance of new signal at -57 ppm [22], which is attributed to partial cross-linking with terminal silanol groups, $T^2 = R - Si(OH)(OSi)_2$. The results suggest that the OTMS has been successfully attached on the complexes. Thus, this analysis can be complementary to FTIR, diffuse reflectance UV-vis spectra and SEM image in determining the proposed structure as shown in Fig. 4b. The SEM micrograph displayed the particles are in small sizes (ca. 100-700 nm) and this particles can be well-dispersed in the consolute layer of the immiscible liquid-liquid system at 90 °C after 24 h as depicted in Fig. 4a.

Fig. 5a shows the phase-boundary catalyst was well suspended and located at the immiscible liquid/liquid interface. Octadecylsilyl group was partially attached onto the Ti(IV) salicylaldimine complex to form hydrophobic —Si—O—R groups, on the other hand, the complex is hydrophilic due to the presence of Si—OH groups after the hydrolysis and condensation process of salicylaldehyde and 3-aminopropyltrimethoxysilane (APTMS). This amphiphilic



Fig. 3. ²⁹Si MAS NMR spectra and proposed structures of Ti(IV) salicylaldimine complex.

(b)





Fig. 4. (a) Photograph of the solid complex can be stabilized at the consolute liquid–liquid phase boundary after 24 h at 90 °C and (b) SEM image of alkylsilylated-Ti(IV) salicylaldimine complex.



25 Product Yield: □ others ■1,2-epoxyoctane 10 77 □2-octanol 20 ■2-octanone 4 78 0.08 Conversion / % 15 5 32 9 50 10 5 6.33 32 0 25 30 40 50 70 80 90 60 Temperature / °C

Fig. 5. (a) The photograph of the consolute liquid–liquid layers increases with elevating temperatures and (b) the conversion of 1-octene and the product yields of 2-octanone, 2-octanol, 1,2-epoxyoctane and other products after catalytic reaction. The reactions were carried out for 1 h with 1-octene (10 mmol, 1.56 ml), 30% aqueous H_2O_2 (30 mmol, 3.06 ml) and catalyst (50 mg) under static conditions.

characteristic is such an advantage for the solid catalyst to be located at the interphase of both organic and aqueous phase, and thus, it can contact with both phases effectively. It is worth to notice that the immiscible liquid–liquid boundary phase formed consolute liquid layer at low temperature, however, it is near to the upper consolute point (partially miscible) with increasing temperature. It is clearly seen in Fig. 5a. According to Sinko [23], there are three types of systems in describing the liquid–liquid solubility: upper critical solution temperature (UCST), lower critical solution temperature (LCST), last but not least, upper and lower critical solution temperature. Our reaction system can be categorized as upper critical solution temperature (UCST) system. It is owing to organic 1-octene is partially miscible to aqueous hydrogen peroxide by increasing the temperature to a certain extent. This consolute layer gives effect to the conversion and selectivity of the reaction system.

Fig. 5b summarizes the product selectivity of the reaction between 1-octene and aqueous H_2O_2 in the presence of alkylsilylated-Ti(IV) salicylaldimine complex as the phaseboundary catalyst. From previous research, 1,2-epoxyoctane was the main product at room temperature with high selectivity [1,2], however, in this reaction system; 2-octanone was the main product instead. It might due to the concentration of hydrogen peroxide adopted is higher than previous researches and the characteristic of the catalyst system is different [1-4], which can trigger the faster reactivity of the 1,2-epoxyoctane to open the oxirane ring and then form 2-octanone. At higher temperature (60 °C), products of 2-octanol are predominant than others and it was observed that selectivity to 2-octanone decreased with increasing of the selectivity to 2-octanol along the temperature from 25–60 °C. One suggests that the 2-octanone can act as a substrate to undergo further oxidation reaction by aqueous hydrogen peroxide assisted by the catalyst. To prove this argument, the oxidation of 2-octanone with aqueous H_2O_2 was conducted at 25 and 90 °C as shown in Table 1. It was observed that the yield of 2-octanol in the oxidation reaction decreased when the temperature increased. It is because 2-octanone was converted to other products at higher temperature. It is in agreement with the results shown in the oxidation of 1-octene by aqueous H₂O₂ (Fig. 5b) over alkylsilylated-Ti(IV) salicylaldimine complex, in which the selectivity to 2-octanone decrease with increasing temperature.

On the other hand, it is an interesting phenomenon to note that the conversion was maintained approximately in 15-18% with duration of 1 h. Generally, the rate of reaction depends on the temperature and concentration of reactants. Increasing temperature and concentration of reactants will increase the frequency of collisions between reactants and hence increasing the reaction rate [24]. However, in our phase-boundary catalytic system, as shown in Fig. 5a, increasing temperature will increase the consolute layer. The presence of the consolute layer can reduce the concentration of reactants at the liquid-liquid interfacial layer at relatively high temperatures. One suggests that although an increase in the reaction rate, the concentration of reactants decreases at higher temperatures. The compensation effect between increasing the reaction rate and lowering the concentration of reactants in the consolute layer at relatively high temperature is the reason why the conversion of reactants is almost the same at low and high

Table 1	
Catalytic oxidation of 2-octanone. ^a	

Temperature (°C)	The yield of 2-octanol (%)
25	6.7
90	3.7

 a The oxidation reaction was examined by 2-octanone (10 mmol, 1.56 ml), $\rm H_2O_2$ 30% (30 mmol, 3.00 ml), and 50 mg catalyst. It was carried out at the selected temperatures, 25 and 90 $^\circ$ C for 1 h.



Fig. 6. The effects of static, stirring and adding cosolvent in the phase-boundary catalytic system at $25 \,^{\circ}$ C. Reaction conditions are the same as given for Fig. 4. To examine the effect of cosolvent, the homogeneous mixture was made. It contains 1-octene (8%), aqueous H₂O₂ (8%), ethanol (84%) and catalyst (50 mg).

temperatures. Due to the products from oxidation of 1-octene, i.e. 2-octanone, 2-octanol and 1,2-epoxyoctane, are more hydrophobic than aqueous H_2O_2 and more hydrophilic than 1-octene, one suggests that they can easily dissolve in the consolute layer which is also more hydrophilic and hydrophobic compared with 1-octene and aqueous H_2O_2 , respectively. It suggests that the consolute layer can act as a medium for the reaction products to react with the catalyst to produce other products. Subsequently, it has resulted in low selectivity.

Furthermore, it is widely known that the cosolvent can greatly influence the conversion and selectivity in a reaction system [25], however, Fig. 6 proves that vigorous stirring and addition of ethanol as cosolvent in this system do not give much effect to the selectivity. The reaction solution included homogeneous mixture containing 1-octene (8%), aqueous H_2O_2 (8%), ethanol (84%) and catalyst (50 mg). The selectivity to 2-octanone at 25 °C is 67% and 61% for stirring and adding cosolvent, respectively. The obtained results were near to the selectivity of 2-octanone by phase-boundary catalysis, i.e. 79%. However, the conversion increased remarkably for both conditions, which vigorous stirring resulted in 64% conversion and addition of cosolvent produced 72% conversion. It is reasonable

Table 2

Reaction rates of the oxidation of 1-octene.^a

Entry	Temperature (°C)	Reaction rate ^b (mmol h^{-1})
1	25	3.3
2	30	3.7
3	40	3.3
4	50	3.4
5	60	3.2
6	70	3.0
7	80	3.4
8	90	4.1

 a The reaction was conducted at 1 h with the oxidation 1-octene (10 mmol, 1.56 ml), H_2O_2 30% (30 mmol, 3.00 ml), and 50 mg catalyst.

^b Reaction rate is the average rate of a reaction over a time interval by dividing the change in concentration of products over that time period by the time interval.

due to the contact area between the reactant and catalyst is thoroughly increased, hence, it results in increasing of conversion and reaction rate. Moreover, Table 2 displays that the reaction rates of alkylsilylated-Ti(IV) salicylaldimine complex at a series of temperatures are ca. $3.30-4.12 \text{ mmol h}^{-1}$. Hence, the selectivity can be compared under the similar conversion percentage by varying the temperatures. At 90 °C, the reaction rate is the highest amongst all due to increase of liquid–liquid miscibility of 1-octene and aqueous hydrogen peroxide or consolute phase-boundary layer.

4. Conclusions

Temperature-controlled selectivity in oxidation of 1-octene by using aqueous hydrogen peroxide in phase-boundary catalytic system over alkylsilylated-Ti(IV) salicylaldimine complex catalyst has been demonstrated. In conclusion, there are two properties that make the selectivity of the oxidation of 1-octene by using aqueous hydrogen peroxide can be temperature-controlled in phase-boundary catalytic system. The first property is the presence of catalyst that can be located at liquid–liquid boundary. Secondly, the ability of the catalyst to well-disperse and stabilize after 24 h at 90 °C in the consolute layer of the liquid–liquid phase due to an increase in the miscibility between organic and aqueous phases at relatively high temperature.

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