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A shape-selective catalyst for epoxidation of cyclic olefins: The nanoporous nickel phosphate VSB-5

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Abstract

Nickel in the form of porous nickel phosphate VSB-5 has been used as a shape-selective catalyst for epoxidation of cyclic olefins such as cyclohexene and cyclooctene using hydrogen peroxide. The VSB-5 showed high selectivity to cyclohexene oxide and cyclohexane diol, much higher productivity per catalyst weight in the epoxidation of cyclohexene, and high selectivity to cyclooctene oxide in the epoxidation of cyclooctene. The VSB-5 behaved as a heterogeneous catalyst in the epoxidation and can be used many times without structure degradation, leaching of active nickel species, or significant activity loss. It has been concluded that the epoxidation reaction with VSB-5 proceeds via a free-radical mechanism by taking into consideration a sharp activity loss in the presence of a radical scavenger, hydroquinone. The effect of radical scavengers with different molecular dimension on the catalytic activity also indicates the shape selectivity in the pores of VSB-5.
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Keywords: Epoxidation; Nanoporous nickel phosphate; VSB-5; Nickel; Hydrogen peroxide; Shape selective catalyst

1. Introduction

Recently, there has been increasing interest in the development of heterogeneous catalysts for oxyfunctionalization of hydrocarbons, such as epoxidation reactions. Epoxidation with aqueous hydrogen peroxide (H_2O_2) is important because H_2O_2 is a green oxidant that is simply converted to water [1–5]. Various transition metal ions, including Mo, Ti, V, W, Cu, Fe, Mn, and Co, have been used as suitable catalysts for epoxidation reactions [1–4,6]. Transition metal-incorporated porous materials show particularly interesting performance in oxidative reactions with H_2O_2 or organic peroxide as the oxidant. For example, shape-selective titanium-containing molecular sieves, such as titanium silicalite-1 (TS-1) and Ti-MWW, have been widely studied for various oxyfunctionalization reactions [7–12]. Molecules with a kinetic diameter equal to or larger than that of cyclohexene are practically excluded from epoxidation with TS-1 because of its limited pore size [13]. Moreover, TS-1 does not catalyze epoxidation with bulky *tert*-butyl hydroperoxide as the oxidant [13]. Various porous materials, including mesoporous titanosilicates, have been studied for epoxidation reactions of large molecules; however, their catalytic acitivities and selectivities were generally low [14,15] compared with microporous metallosilicate zeolites. Transition metal ions incorporated in the frameworks of porous materials often suffer from leaching problem of active components from the frameworks during the reaction [13]. Therefore, the development of shape selective porous materials with relatively large pore size without a leaching problem is highly desirable.

Besides titanium-containing molecular sieves, octahedral Mn or tetrahedral Fe ions incorporated into molecular sieves have also been reported to show epoxidation activity [16,17]. On the other hand, the use of heterogeneous porous Ni catalyst for epoxidation reactions has been reported only rarely. Recently, mesoporous nickel silicate has been applied to the epoxidation of styrene [18]. In this case, benzaldehyde and styrene oxide were selective products from the oxidation of styrene using hydrogen peroxide in the presence of powder and mem-

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brane catalysts, respectively. Mesoporous material containing Ni [19] or Ru–Ni [20] showed poor activity in styrene oxidation with H_2O_2 efficiency <5% and with benzaldehyde rather than epoxide as the main product. Very recently, transition metal Schiff-base complexes (e.g., M = Mn^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}) chemically anchored on Y zeolite (partially modified by *n*-octadecyltrichlorosilane) have been applied to the epoxidation of 1-octene [21]. However, these catalysts had very low reactivity (conversion <3% after 24 h at 100 °C) despite high selectivity to epoxide (96%). Homogeneous nickel complexes have been also used as epoxidation catalysts only in the presence of aldehyde/oxygen [22] or hypochlorite [23].

We have recently discovered the porous nickel phosphate VSB-5 and its possible applications, including hydrogen storage and selective hydrogenation [24,25]. The VSB-5 structure (hexagonal, space group $P6_3/m$) is based on a three-dimensional network of octahedrally coordinated nickel atoms and tetrahedral phosphorous atoms containing large, unidimensional channels. In this work, we report VSB-5 as a new shape-selective catalyst for the epoxidation of cyclic olefins with hydrogen peroxide. We also confirm that the VSB-5 truly behaved as a heterogeneous catalyst without leaching of active nickel species during epoxidation.

2. Experimental

2.1. Synthesis and silylation of catalyst

The VSB-5 was hydrothermally synthesized with microwave irradiation, which imparts advantage of fast and efficient crystallization, as described previously [26,27]. A typical synthesis was carried out at 180 °C for 2 h in weakly basic condition (pH = 7–8) using aqueous ammonia. The reactant composition was 0.63 H_3PO_4:1.0 $NiCl_2$:3.0 NH_3:100 H_2O. After crystallization, the VSB-5 was recovered by centrifugation, washing with distilled water, and drying.

Surface silylation of VSB-5 was performed by an anaerobic reaction to increase the surface hydrophobicity of the catalyst as described previously [28,29]. Silylation was carried out by the reaction between hydrophilic hydroxyl groups with methoxytrimethylsilane (MTMS; Aldrich, 99%) as a silylating agent under a mild condition at 55 °C instead of reflux conditions, to avoid a drastic change in pore size and pore volume, because a large reduction of pore volume tends to significantly decrease the conversion. One gram of dehydrated VSB-5 was added to the mixture of toluene (50 ml) and MTMS (1 ml) in a round-bottomed flask. The mixture was stirred for 15 h at 55 °C under the nitrogen blanket. After cooling, the silylated product was separated and washed with toluene (3 times with 100 ml) and then acetone (3 times with 100 ml). The silylated VSB-5 was dried at 60 °C for 12 h and at 110 °C for 4 h.

2.2. Catalyst characterization

The structure and crystallinity of as-synthesized and dehydrated samples were determined by powder X-ray diffraction (XRD) using a Rigaku D/MAX IIIB with Cu-K_α radiation. Scanning electron microscopy (SEM) images were collected with a JEOL 630-F microscope. The Fourier transform infrared (FTIR) spectra of VSB-5 were obtained with a Nicolet FTIR spectrometer (Magna 560) at ambient conditions after palletizing using KBr. The UV/vis diffuse reflectance spectra (DRS) were recorded under ambient conditions using an UV/vis spectrophotometer (Shimadzu UV-2501PC) equipped with a quartz flat cell. N_2 adsorption–desorption isotherms were obtained using a Micromeritics ASAP 2040 apparatus at −196 °C. Cyclohexane sorption experiments were performed at room temperature in a glass vacuum manifold equipped with a diffusion pump. The amount of adsorption was calculated using the ideal gas law. Before the adsorption experiments, the sample was dehydrated at 300 °C for 4 h.

2.3. Catalytic epoxidation

The epoxidation of cyclohexene was performed in a conventional glass reactor with a condenser and stirrer. In a typical run of catalytic measurement, the reactor was loaded with 0.01–0.5 g of catalyst, 5 ml of cyclohexene, 18 ml of acetonitrile, and a proper amount of 30% aqueous H_2O_2. The catalyst was dehydrated at 300 °C for 4 h before being loaded into the glass reactor. Unless specified otherwise, the reaction was carried out at 60 °C under vigorous stirring. The products, such as cyclohexene oxide, 1,2-cyclohexane diol, and 2-cyclohexen-1-one (hereinafter designated as epoxide, diol, and cyclohexenone, respectively) were analyzed by gas chromatography (GC) using an Acme 6000 gas chromatograph with a DB wax capillary column. *o*-Dichlorobenzene added to the product mixture after reaction was used as an internal standard for the GC analysis. The H_2O_2 concentrations before and after reaction were measured by iodometric titration.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD pattern of VSB-5 synthesized by microwave irradiation. This pattern is not noticeably different than that of original nickel phosphate VSB-5 [26,27]; the structure is hexagonal, space group $P6_3/m$, $a = 18.209(1)$ Å and $c = 6.3898(7)$ Å, and the composition is $Ni_{20}[(OH)_{12}((H_2O)_6)$–$[(HPO_4)_8(PO_4)_4]\cdot 12H_2O]$. The VSB-5 used for the epoxidation reactions had a rod-like morphology with an aspect ratio of around 10 (Fig. 1). N_2 adsorption–desorption isotherms of the dehydrated sample revealed type I behavior below a relative pressure (P/P_0) of 0.8 (Fig. 2a), which is typical of microporous materials. Analysis of the data in the relative pressure (P/P_0) range of 0.04–0.20 gave a BET surface area of 350 m^2/g and a pore volume of 0.15 cm^3/g. The surface area per gram was comparable to that of a large-pore zeolite, considering that VSB-5 (~2.6 g/cm^3) is ~2 times more dense than a typical zeolite. An adsorption isotherm of cyclohexane at room temperature indicates that cyclohexane was sufficiently accessible to the pores of VSB-5 (Fig. 2b). The adsorption volume of cyclohexane was 0.09 cm^3/g at P/P_0 of 0.75, corresponding

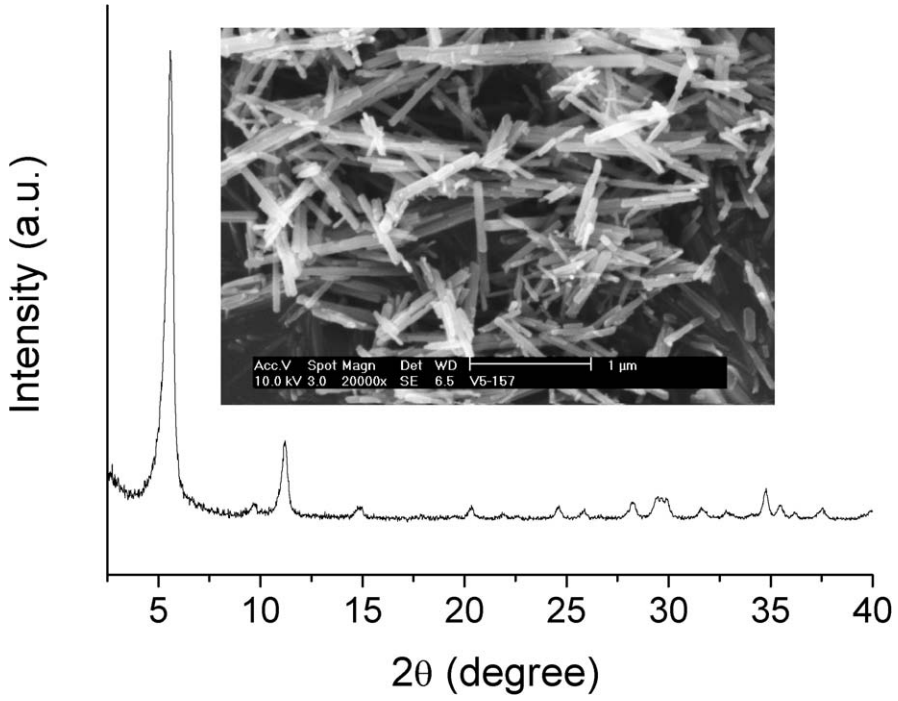

Fig. 1. XRD pattern of VSB-5. Inset shows an SEM image of VSB-5.

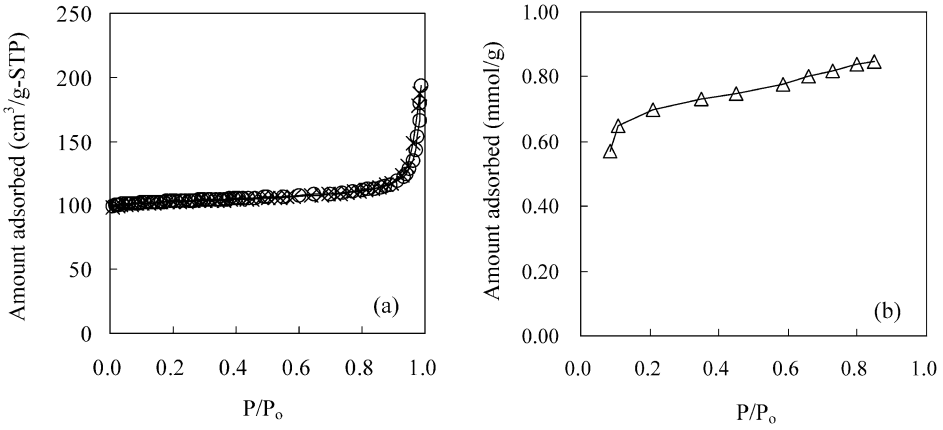

Fig. 2. Sorption isotherms on VSB-5: (a) nitrogen adsorption (◯) and desorption (×) isotherms at −196 °C; (b) cyclohexane adsorption isotherm at 23 °C.

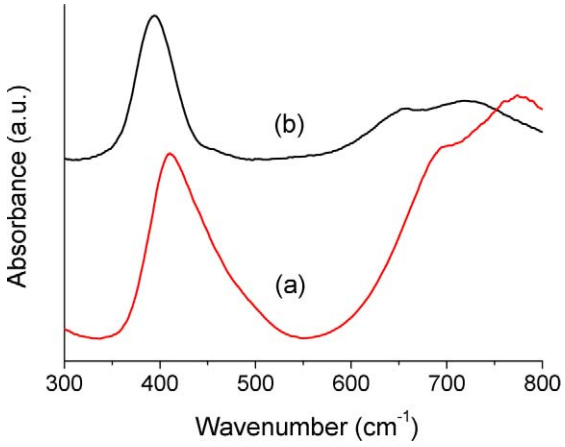

Fig. 3. UV/vis diffuse reflectance spectra of (a) VSB-5 and (b) 0.01 M nickel chloride in an aqueous solution.

to about 60% of the micropore volume. The UV/vis DRS spectrum (Fig. 3a) shows typical absorption bands of octahedrally coordinated nickel(II) ions with framework oxygen anions at 405, 705, and 790 nm, in agreement with the VSB-5 structure [24]. As shown in Fig. 3b, the bands at ∼400 and 750 nm have been assigned to the transitions of octahedral Ni(II) ions, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), respectively [30,31].

3.2. Epoxidation of cyclic olefins

In the epoxidation of cyclohexene with H_2O_2 over VSB-5, the main products were cyclohexene oxide and 1,2-cyclohexane diol (>90%). The diol concentration increased with increasing reaction time, illustrating the conversion of epoxide to diol, in accordance with previous results [15]. The cyclohexene conversion and total selectivity to epoxide and diol ($S_{\text{epoxide+diol}}$) increased steadily with increasing H_2O_2/cyclohexene ratio

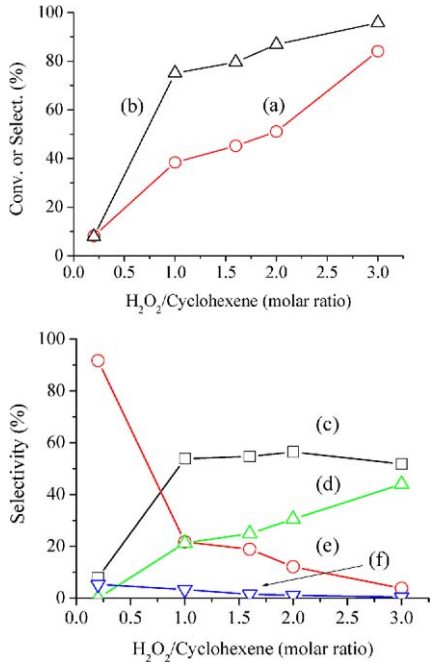

Fig. 4. Effect of H_2O_2/cyclohexene ratio on the epoxidation of cyclohexene over VSB-5 catalyst: (a) cyclohexene conversion, (b) total selectivity to epoxide and diol ($S_{epoxide+diol}$), (c) epoxide selectivity, (d) diol selectivity, (e) cyclohexenone selectivity, and (f) cyclohexenol selectivity. Reaction conditions: 60 °C, 8 h, acetonitrile 18 ml, cyclohexene 5 ml and catalyst 0.35 g.

(Fig. 4). In this case, the diol can be considered to be a further hydrolysis product via the epoxidation reaction [15]. The H_2O_2 efficiency (conversion of cyclohexene to oxygenates/conversion of H_2O_2) was 50–60% and remained constant or decreased slightly with increasing H_2O_2 concentration. In contrast, cyclohexenone selectivity decreased sharply with increasing H_2O_2 concentration. After 8 h of reaction, the cyclohexene conversion and $S_{epoxide+diol}$ were about 84.1 and 95.8%, respectively, with a H_2O_2/cyclohexene ratio of 3. It has been reported that epoxidation selectivity decreases with increasing H_2O_2/substrate ratio [15,17,32]. In general, an increased H_2O_2 concentration facilitates the decomposition of H_2O_2 to form oxygen and hence the side reactions, including allylic oxidation [15,17, 32]. Because the H_2O_2 efficiency in this work is nearly constant, it appears that VSB-5 does not accelerate the formation of active species responsible for allylic oxidation, especially at high concentrations of H_2O_2. However, further work is needed to fully understand why VSB-5 exhibits an unprecedented

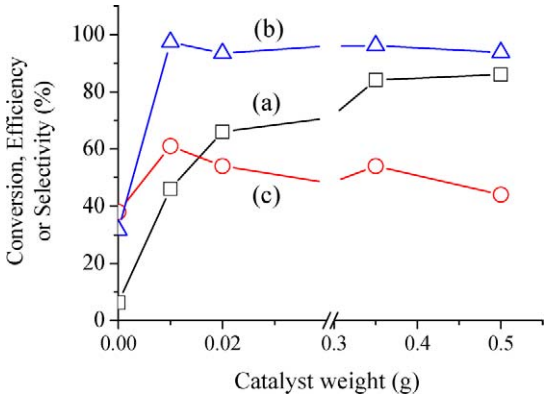

Fig. 5. Effect of catalyst weight on the epoxidation of cyclohexene: (a) cyclohexene conversion, (b) total selectivity to epoxide and diol ($S_{epoxide+diol}$) and (c) H_2O_2 efficiency. Reaction conditions: 60 °C, 8 h, acetonitrile 18 ml, cyclohexene 5 ml and H_2O_2/cyclohexene = 3.

effect of H_2O_2 concentration on the selectivity of epoxidation.

The effect of catalyst amount in the reaction is shown in Fig. 5. The conversion increased sharply with increasing catalyst concentration up to about 0.5 wt% (20 mg) based on cyclohexene but increased only slightly with further increases in catalyst concentration. Even 0.5 wt% catalyst in the reaction mixture can efficiently catalyze the epoxidation reaction to give about 68% conversion, confirming that VSB-5 is very active in epoxidation [33].

Leaching of active metal components has been a serious problem in oxyfunctionalization using transition metal-containing porous materials [13]. However, VSB-5 can be reused many times (Table 1) after separation, washing, and drying without significant catalyst deactivation due to either leaching of active species or degradation of the structure. When the separated catalyst was reused successively after drying, a slight decrease of conversion (up to 72.5%) occurred only in the first reuse, probably due to partial pore blocking with oligomeric products. No further deactivation was observed after the second reuse; the conversion (73.0%) and $S_{epoxide+diol}$ (94.0%) after the second reuse were nearly constant. The VSB-5 structure remained intact after four consecutive uses, as confirmed by XRD and FTIR (Figs. 6 and 7). In the liquid phase of the reaction mixture, no nickel could be detected with ICP analysis; thus VSB-5 can be considered to be a true heterogeneous epoxidation catalyst.

Table 1
Epoxidation of cyclohexene using H_2O_2 with porous nickel phosphate, VSB-5 to show the recyclability of the catalyst[a]

No.	Catalyst	Cyclohexene conversion (%)	H_2O_2 efficiency (%)[b]	Selectivity (mol%)			
				Cyclohexene oxide	1,2-Cyclohexane diol	2-Cyclohexene-1-one	2-Cyclohexene-1-ol
1	VSB-5	84.1	53.7	51.8	44.0	3.8	0.4
2	Recovered from No. 1	72.5	48.3	56.3	37.0	6.2	0.5
3	Recovered from No. 2	74.0	48.0	48.6	44.9	6.1	0.4
4	Recovered from No. 3	73.0	51.3	54.8	40.1	4.8	0.3

[a] Reaction conditions: 60 °C, 8 h, acetonitrile 18 ml, cyclohexene 5 ml, H_2O_2/cyclohexene = 3, catalyst 0.35 g.
[b] H_2O_2 efficiency (%) = 100 × [oxygenated products (moles)]/[total H_2O_2 (moles) converted].

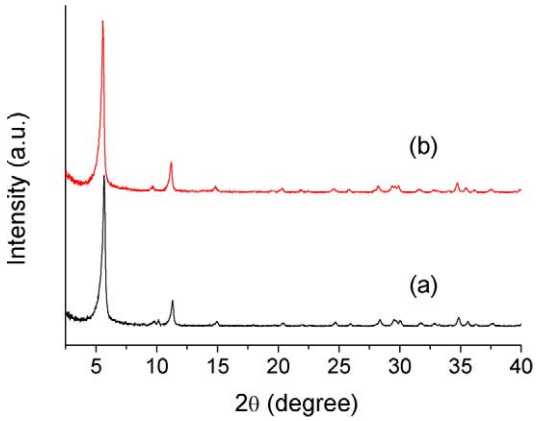

Fig. 6. XRD patterns of VSB-5 after epoxidation reactions: (a) after first reuse and (b) third reuse.

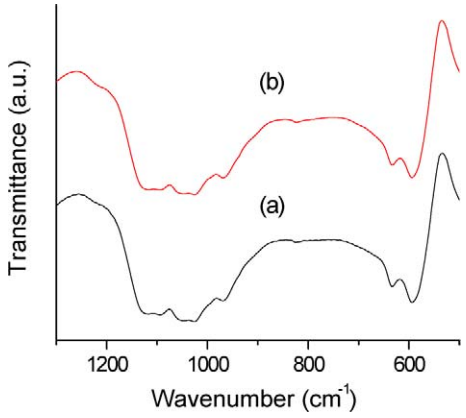

Fig. 7. FTIR spectra (in framework region) of (a) fresh VSB-5 and (b) used VSB-5 after third reuse.

As summarized in Table 2, only VSB-5 showed significant conversion and selectivity among the various nickel-containing solids or salts. With H_2O_2 as the oxidant, the soluble nickel salts, including nickel chloride and nickel acetate, revealed very low epoxide selectivity and cyclohexene conversion, indicating that soluble nickel species are ineffective in epoxidation using H_2O_2. The low conversion on NiO is probably related to the low surface area of NiO. We believe that an active site of VSB-5 for the epoxidation can be assigned to Ni^{2+} species in the framework, taking into consideration that there are no cations

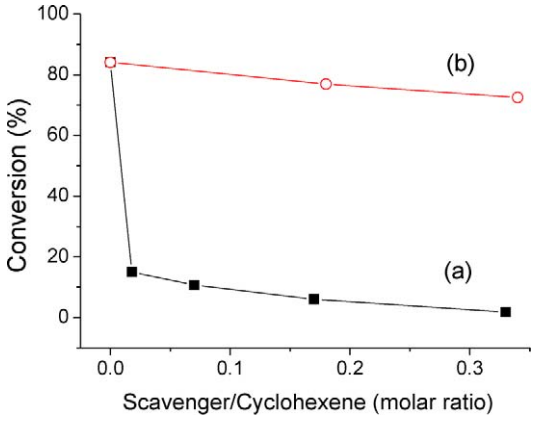

Fig. 8. Effect of radical scavenger on the epoxidation of cyclohexene: (a) hydroquinone and (b) di-tertiarybutylmethylphenol. Reaction conditions: 60 °C, 8 h, acetonitrile 18 ml, cyclohexene 5 ml and H_2O_2/cyclohexene = 3.

except Ni^{2+} and P^{5+} in VSB-5 and that the epoxidation activity over microporous aluminophosphate AlPO-5 (which does not contain nickel ions) is as low as the conversion without catalyst. Moreover, unsaturated Ni(II) sites present in VSB-5 [24,25] may be possible active species for epoxidation of cyclic olefins. However, further work is needed to clarify how nickel species catalyze the reaction.

To shed light on the reaction mechanism, hydroquinone was added to the reaction mixture as a radical scavenger [34]. As shown in Fig. 8a, the conversion decreased sharply compared with that in the absence of hydroquinone when even a small amount of hydroquinone (hydroquinone/cyclohexene = 0.02 mol/mol) was added to the reaction mixture at an early stage of the reaction. This finding indicates that the epoxidation mechanism might be of a primarily free-radical nature, similar to the epoxidation with Ni complexes in the presence of aldehyde/oxygen [22] or hypochlorite [23]. Similarly, conversion was not increased with further increases in reaction time after the addition of hydroquinone during the reaction. In contrast, cyclohexene conversion was hardly affected by another radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol [17,35,36], as illustrated in Fig. 8b, probably because the bulky scavenger did not penetrate the pores of VSB-5, which has an estimated pore diameter of 6.4 Å (from micropore analysis using argon gas [24]). This finding clearly demonstrates the shape selec-

Table 2
Epoxidation of cyclohexene using H_2O_2 with porous nickel phosphate, VSB-5 and nickel-containing compounds[a]

Catalyst	Catalyst weight (g)	Ni content[b] (wt%)	Ni conc.[c] (wt%)	S_{BET} (m^2/g)	Conversion (%)	H_2O_2[d] efficiency (%)	Selectivity (mol%)			
							Cyclohexene oxide	1,2-Cyclohexane diol	2-Cyclohexene-1-one	2-Cyclohexen-1-ol
VSB-5	0.35	41.0	3.5	350	84.1	53.7	51.8	44.0	3.8	0.4
NiO	0.35	78.6	6.8	<5	13.3	7.1	58.5	0.0	40.5	1.0
$NiCl_2{\cdot}6H_2O$	1.00	24.7	6.1	–	21.3	16.0	8.5	14.9	73.0	3.6
$Ni(OAc)_2{\cdot}4H_2O$	1.00	23.6	5.8	–	27.7	18.5	3.6	0.0	91.6	4.8
None[e]	–	–	–	–	6.3	38.0	31.7	0.0	68.3	0.0

[a] Reaction conditions: 60 °C, 8 h, acetonitrile 18 ml, cyclohexene 5 ml, H_2O_2/cyclohexene = 3.
[b] Ni content in the VSB-5 or Ni-containing compounds.
[c] Ni concentration based on the substrate cyclohexene.
[d] H_2O_2 efficiency (%) = 100 × [oxygenated products (moles)]/[total H_2O_2 (moles) converted].
[e] Results in the absence of catalyst.

Table 3
Shape selective epoxidation of cyclic olefins over VSB-5[a]

Substrate	Conversion (%)	H_2O_2 efficiency[b] (%)	Selectivity (mol%)			
			Cycloolefin oxide	1,2-Cyclo-alkane diol	2-Cyclo-olefin-1-one	2-Cyclo-olefin-1-ol
Cyclohexene	84.1	53.7	51.8	44.0	3.8	0.4
Cyclooctene	49.2	32.0	91.7	0.9	4.5	2.9
Cyclododecene	12.4	27.0	7.1	0.0	89.3	3.6

[a] Reaction conditions: 60 °C, acetonitrile 18 ml, cyclohexene 5 ml, H_2O_2/cyclohexene = 3, catalyst 0.35 g. The reaction time was 8 h (cyclohexene and cyclododecene) or 7 h (cyclooctene).

[b] H_2O_2 efficiency (%) = 100 × [oxygenated products (moles)]/[total H_2O_2 (moles) converted].

tivity of VSB-5 in epoxidation reactions; however, further investigations are needed to provide insight into the mechanistic aspects of this reaction system.

As illustrated in Table 3, VSB-5 has shape-selective properties in the epoxidation of several cyclic olefins with differing molecular diameters. VSB-5 exhibited remarkably high epoxide selectivity in the epoxidation of cyclooctene (91.7%) compared with that in the epoxidation of cyclohexene (51.8%), but with decreased conversion in the epoxidation of cyclooctene (49.2%). The low conversion of cyclooctene may be related not only to the low reactivity of cyclooctene [37,38], but also to the slow diffusion of the substrate through the pores of VSB-5. This result is also consistent with previous reports indicating that despite the free-radical mechanism, the epoxidation or oxidation of cyclooctene is quite slow compared with the cyclohexene reaction [37,38]. However, VSB-5 revealed only poor activity in oxidation of cyclododecene as a bulky cyclic olefin molecule, indicating that this porous material behaved as a shape-selective catalyst (Table 3). Cyclododecene-1-one was a main product from the oxidation of cyclododecene, representing the noncatalytic oxidation on exterior surface of VSB-5. Likewise, we have reported that Pd-exchanged VSB-1 exhibited shape selectivity for competitive hydrogenation of 1-octene, cyclohexene, and cyclododecene [39]. H_2O_2 efficiency in the epoxidation reactions was the highest in cyclohexene (53.7%) among cycloolefins. It is interesting that in these experiments a certain amount of H_2O_2 (about 50% of the initial concentration) remained even after epoxidation reactions without full consumption, revealing the slow decomposition of H_2O_2 over VSB-5.

The reaction temperature was varied between 50 and 65 °C (Fig. 9a) to obtain the reaction rate constants at different temperatures and the apparent activation energy in the epoxidation of cyclohexene. The cyclohexene conversion and the reaction time can be related through the following expressions of pseudo-first-order kinetics [16]:

$$-\mathrm{d}[\text{cyclohexene}]/\mathrm{d}(t) = k[\text{cyclohexene}] \quad (1)$$

and

$$-\ln(1 - X) = k(t), \quad (2)$$

where X and k represent the conversion of cyclohexene at time t and the apparent rate constant, respectively.

Fig. 9b displays the graph of $\ln k$ obtained from expression (2) within 3 h versus the inverse of the reaction temperature

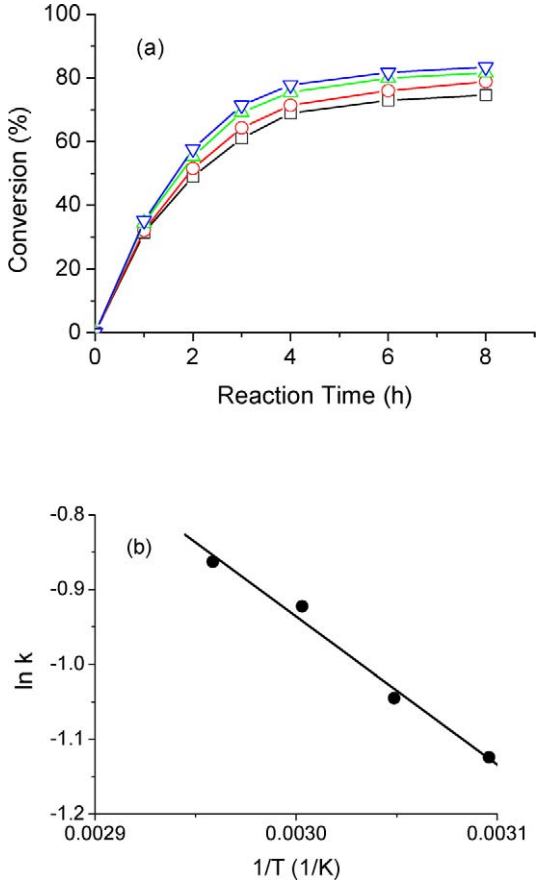

Fig. 9. Kinetics of cyclohexene epoxidation with hydrogen peroxide over VSB-5: (a) conversion of cyclohexene with time and temperature and (b) ln(apparent rate constant) vs. inverse of reaction temperature (Arrhenius plot of pseudo-first-order kinetics for the epoxidation). Reaction conditions: acetonitrile 18 ml, cyclohexene 5 ml, H_2O_2/cyclohexene = 3.0 and catalyst 0.35 g. The reaction temperature from bottom to top in (a) are 50, 55, 60 and 65 °C, respectively.

for each temperature. The apparent activation energy (E_a) calculated from the Arrhenius plot (Fig. 9b) was ca. 4.0 kcal/mol, similar to the value reported for the epoxidation of cyclooctene [40].

As mentioned above, 1,2-cyclohexane diol is considered a further hydrolysis product of cyclohexene oxide. Moreover, high diol selectivity of VSB-5 is believed to stem from the presence of surface hydroxyl groups and/or hydroxide anion in the framework. It has been reported that the hydrolysis of epoxide to diol can be decreased by increasing the surface hydrophobic-

ity of the catalyst or by removing water in the reaction [15,41–44]. In this work, to increase the surface hydrophobicity of VSB-5, silylation of VSB-5 was carried out by the anaerobic reaction of the surface hydrophilic hydroxyl groups with methoxytrimethylsilane [28,29] as a silylating agent, leading to the formation of $–O–Si(CH_3)_3$ group on the surface. The surface area of VSB-5 was decreased only slightly (by 20 m^2/g) after surface silylation from 350 m^2/g. There was no destruction of the VSB-5 structure, as confirmed by XRD and FTIR; however, the silylated VSB-5 showed weak C–H stretching vibration bands at 2855 and 2925 cm^{-1}, indicating the presence of methyl groups in $–Si(CH_3)_3$ (Fig. 10). The silylated VSB-5 clearly showed a decrease in further conversion of epoxide to diol, resulting in increased epoxide selectivity at the expense of decreased cyclohexene conversion after surface silylation (Fig. 11). The decreased activity of the silylated VSB-5 may be due to slight pore blocking or partial reduction of surface area.

For cyclooctecene, additional activity tests of the silylated VSB-5 were not needed, because fresh VSB-5 exhibited high epoxide selectivity along with very low diol selectivity in the epoxidation. Applying silylated VSB-5 to the oxidation of styrene with hydrogen peroxide at 60 °C further confirmed that the selectivity of 1-phenyl-1,2-ethandiol as a hydrolysis product

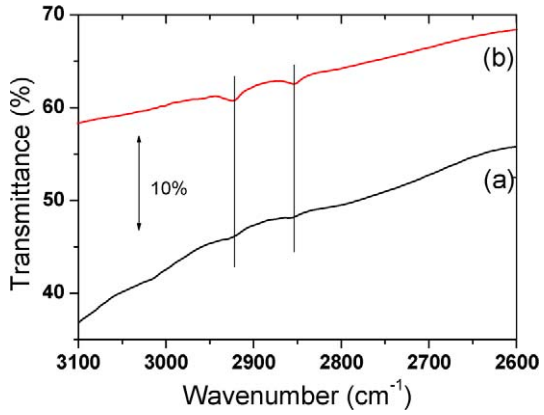

Fig. 10. FTIR spectra of VSB-5 (a) and silylated VSB-5 (b) in the range of 2600 and 3100 cm^{-1}.

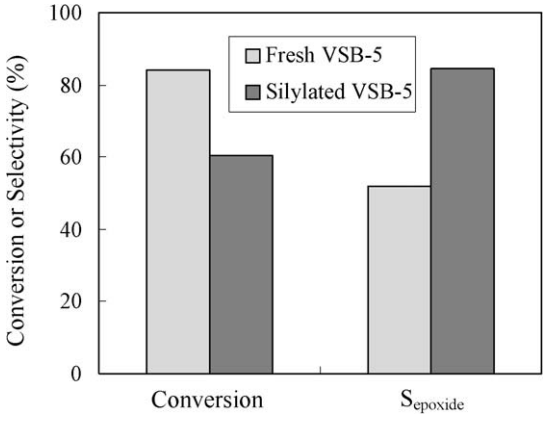

Fig. 11. Effect of surface silylation of VSB-5 on the cyclohexene conversion and epoxide selectivity.

[45] was significantly reduced (<0.1%) compared with that of fresh VSB-5 (29.7%). In this reaction, however, the main products over VSB-5 were benzaldehyde (55.3%) and 1-phenyl-1,2-ethandiol (29.7%) instead of styrene oxide (9.1%), and the decreased selectivity of the hydrolysis product in the silylated VSB-5 led to an increase in selectivity toward styrene oxide (18.5%) and benzaldehyde (70.4%).

These results indicate that the hydrolysis of the epoxide can be retarded by decreasing the hydrophilicity of VSB-5 [15,41–44]. Silylation and epoxidation using hydrophobic catalyst will be reported elsewhere in more detail.

4. Conclusion

We have demonstrated that the porous nickel phosphate VSB-5 can be used as a shape-selective catalyst for epoxidation of cyclic olefins using hydrogen peroxide, possibly via a free-radical mechanism. The VSB-5 behaved as a heterogeneous catalyst, being easily recovered after separation and drying without significant catalyst deactivation due to either leaching of active species or degradation of the structure. This new catalyst exhibits shape selectivity for the epoxidation of cyclohexene, cyclooctene, and cyclododecene and shows a negligible oxidation rate for larger substrates such as cyclododecene, clearly demonstrating the sieving properties of the catalyst. The catalyst shows high epoxidation activity with high selectivity to cyclohexene oxide and cyclohexane diol, as well as high throughput per catalyst weight. A silylation of the VSB-5 was found to improve the epoxide selectivity in the epoxidation of cyclohexene through the retardation of further hydrolysis to the diol. The efficacy of VSB-5 for epoxidation reactions points to the availability of active sites associated with framework Ni atoms.

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