



## Ni<sup>2+</sup>-containing ionic liquid immobilized on silica: Effective catalyst for styrene oxidation with H<sub>2</sub>O<sub>2</sub> at solvent-free condition

Gang Liu, Minqiang Hou, Jiyuan Song, Zhaofu Zhang, Tianbin Wu, Buxing Han\*

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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### ABSTRACT

In this work we synthesized Ni<sup>2+</sup>-containing ionic liquid (IL) 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride (TMICl) immobilized on silica to catalyze styrene oxidation with H<sub>2</sub>O<sub>2</sub> for producing benzaldehyde. The catalyst was characterized by Fourier transform infrared (FT-IR) spectroscopy, UV–vis spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen sorption techniques. The effects of reaction time, reaction temperature, and molar ratio of styrene and H<sub>2</sub>O<sub>2</sub> on the conversion and selectivity were studied at solvent-free condition and in acetonitrile. It was demonstrated that the catalyst was very effective for the reaction. The unique advantage of the catalyst was that the reaction could be carried out at solvent-free condition. This advantage resulted mainly from the fact that both of the reactants, styrene and H<sub>2</sub>O<sub>2</sub>, are miscible with the IL, and the Ni<sup>2+</sup> was coordinated by the immobilized IL that allowed both reactants to access to active sites of the catalyst effectively.

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### 1. Introduction

Benzaldehyde is a very important chemical, which are widely used in different fields, such as pharmaceutical industry, resin additives, dyes, flavors, and organic synthesis as an intermediate. Benzaldehyde can be produced by gas phase or liquid phase oxidation of toluene or benzyl alcohol. In gas phase oxidation, metal oxides such as MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> are used as the catalysts [1–3]. The operation temperature of this route is high and the selectivity to benzaldehyde is low. In liquid phase oxidation homogeneous metal complexes of Cr, Co, Ru [4–6] are often used as the catalysts, which makes separation process complex in most cases and expensive ligands have to be used, and the reaction is usually conducted in solvents.

In recent years, production of benzaldehyde by oxidation of styrene using H<sub>2</sub>O<sub>2</sub> as oxidant (Scheme 1) has attracted much attention. In principle, the by-products of the reaction are water and CO<sub>2</sub>. Design of effective catalysts is crucial for this reaction, and some promising catalysts have been fabricated and used [7–13]. Recently, Gao and Gao synthesized microporous nickel phosphates VSB-5 and CoVSB-5 under hydrothermal conditions [14]. Maurya et al. encapsulated V<sup>4+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> complexes of Schiff bases into the nano-cavities of zeolite-Y [15]. Shi and co-workers fabricated highly ordered Fe-containing mesoporous silica

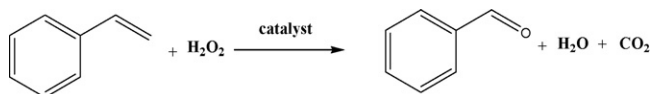
SBA-15 using physical-vapor-infiltration method [16]. Lu and co-workers synthesized lanthanum-doped MCM-48 molecular sieves [17]. Ramanathan and Sugunan fabricated gadolinium substituted nickel ferrites by co-precipitation method [18]. All of these catalysts have been used to catalyze this reaction with satisfactory results. However, the reaction has to be carried out in organic solvents such as acetone, acetonitrile, DMF. The reason is that the miscibility of styrene and hydrogen peroxide is very poor, which limits the application of the catalysts under solvent-free condition.

Ionic liquids (ILs), which are salts with melting point of below 100 °C, have attracted much attention in catalytic reactions. Recently, ILs have been used to immobilize catalysts on different supports. Supported ILs containing different metal particles or ions have been used as catalysts in different reactions such as Heck reaction [19,20], hydrogenation [21–23]. Sasaki et al. prepared immobilized metal ion-containing ionic liquid catalysts, the immobilized copper catalyst (Imm-Cu<sup>2+</sup>-IL) was very active for the Kharasch reaction between styrene and CCl<sub>4</sub> [24].

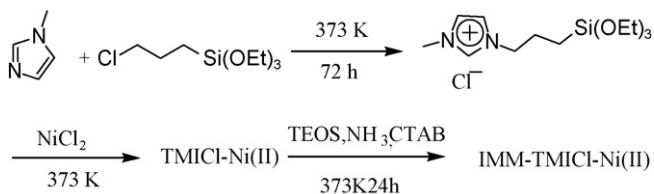
Reaction processes at solvent-free condition are desirable. Carrying out the oxidation reaction of styrene using H<sub>2</sub>O<sub>2</sub> as the oxidant at solvent-free condition is very interesting, but is challenging because, as discussed above, the miscibility of the two reactants is very poor. Enhancing the miscibility of styrene and H<sub>2</sub>O<sub>2</sub> near the active sites is the key for this reaction at solvent-free condition. In this work we synthesized Ni<sup>2+</sup>-containing TMICl immobilized on silica to catalyze the reaction at solvent-free con-

\* Corresponding author. Fax: +86 10 62562821.

E-mail address: [Hanbx@iccas.ac.cn](mailto:Hanbx@iccas.ac.cn) (B. Han).



**Scheme 1.** Oxidation of styrene with H<sub>2</sub>O<sub>2</sub>.



**Scheme 2.** Synthesis of TMICI, TMICI-Ni(II), and IMM-TMICI-Ni(II).

dition, and satisfactory results were obtained. This work utilized the advantages that both styrene and H<sub>2</sub>O<sub>2</sub> have good solubility in the IL and the IL can stabilize the metal ion by coordination force. Therefore, both the hydrophobic and hydrophilic reactants, styrene and H<sub>2</sub>O<sub>2</sub>, can reach the active sites effectively, which can avoid the use of solvents. We believe that this idea can also be used to enhance the reaction rate of some other reactions at solvent-free condition.

## 2. Experimental

### 2.1. Materials

1-Methylimidazol (99%), hydrogen peroxide (30 wt%), styrene, aqueous ammonia (25 wt%), anhydrous ether, tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), NiCl<sub>2</sub>·6H<sub>2</sub>O, anhydrous methanol, hydrochloric acid, silica (200–300 mesh) were all analytical grade reagents purchased from Beijing chemical company. 3-Triethoxy-silylpropyl chloride (97%) was purchased from Aldrich. NiCl<sub>2</sub>·6H<sub>2</sub>O was dehydrated to NiCl<sub>2</sub> in a muffle furnace at 523 K for 3 h before use.

### 2.2. Synthesis of the IL

The IL 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride (TMICI, **Scheme 2**) was synthesized according to method reported by other authors [25]. In the experiment, 1-methylimidazole (0.82 g, 0.01 mol) and (3-chloropropyl) triethoxysilane (2.41 g, 0.01 mol) were dissolved in toluene (20 ml), and the solution was refluxed at 373 K for 72 h under N<sub>2</sub> atmosphere. The TMICI layer was separated from the organic layer. Then the yellow IL layer was thoroughly washed with ether (20 ml 3×) three times and dried under vacuum for 24 h. The TMICI was characterized by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.80(s, 1H, NCHN), 7.39(s, 1H, NCHCH), 7.30(s, 1H, NCHCH), 4.37(t, 2H, CH<sub>2</sub>N), 4.12(s, 3H, NCH<sub>3</sub>), 3.80(q, 6H, OCH<sub>2</sub>), 2.02(q, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.21(t, 9H, CH<sub>3</sub>CH<sub>2</sub>), 0.60(t, 2H, SiCH<sub>2</sub>).

### 2.3. Synthesis of IL-containing Ni<sup>2+</sup>

Anhydrous NiCl<sub>2</sub> (0.65 g, 0.05 mol), TMICI (3.23 g, 0.10 mol) and anhydrous acetonitrile (100 ml) were added into a 250 ml round-bottom flask and the mixture was refluxed at 363 K for 24 h under N<sub>2</sub> atmosphere until a transparent blue solution was obtained. After cooling down, acetonitrile was evaporated under vacuum. A blue viscous liquid was obtained after washed by toluene (20 ml 3×), and was dried under vacuum for 24 h and TMICI-Ni(II) was obtained (**Scheme 2**).

### 2.4. Synthesis of mesoporous silica immobilized TMICI-Ni(II)

The method was similar to that reported in the literature to prepare porous materials by post-synthesis derivatization of materials from Si-based MCM-41 with bidentate nitrogen ligands [26,27]. In the experiment, aqueous ammonia was added to the stirring solution of CTAB, then a mixture of TEOS, TMICI-Ni(II) and neat TMICI dissolved in the methanol was added dropwise, and the final molar ratio of TEOS/TMICI-Ni(II)/TMICI/CTAB/NH<sub>3</sub>/methanol/H<sub>2</sub>O was 1:0.01:0.08:0.14:8:2:100. The mixture was stirred for 4 h at ambient condition, then aged at 373 K for 24 h. The light green product was obtained by filtration, washed with water, and dried under vacuum for 24 h. The resulting solid was added in a solution of 250 ml methanol and 6 ml HCl (37%) at 323 K and the mixture was stirred for 6 h to remove the surfactant. The pale green solid was then filtered and washed with methanol (20 ml 3×) three times and dried at 333 K for 24 h. The Ni content determined by ICP-AES technique was 0.67%. The solid catalyst containing Ni<sup>2+</sup> was denoted as IMM-TMICI-Ni(II). The solid catalyst without Ni<sup>2+</sup> was synthesized by the similar method using the TMICI to replace TMICI-Ni(II) and IMM-TMICI was obtained. To prepare the catalyst without the TMICI, anhydrous NiCl<sub>2</sub> (0.65 g, 0.05 mol) and silica (3.00 g) were added into acetonitrile (100 ml), and the mixture was refluxed at 343 K for 12 h. The light green solid was filtered and washed with methanol (20 ml 3×), and then dried at 333 K for 24 h. The solid catalyst was denoted as SiO<sub>2</sub>-Ni(II).

### 2.5. Characterization

The FT-IR spectra were collected on a Bruker Tensor 27 spectrometer in KBr pellet form. The UV-vis spectra were recorded on a TU-1201 UV-vis spectrometer. SEM examination was carried out on a scanning electron microscope (JEOL JSM-4300) operated at 15 kV. The surfaces of nanoparticles were coated with gold before observation. TEM (Philips, Tecnai F30) observation was performed at a operating voltage of 300 kV, and the images were electronically captured using a CCD camera. The surface area and pore size were calculated from nitrogen sorption data using Brunauer-Emmett-Teller (BET) Procedure of automatic surface area and pore size analyzer (ASIMP, USA).

### 2.6. Catalytic reaction

The catalytic oxidation of styrene was carried out in a 25 ml flask with stirring in an oil bath. In a typical reaction, 0.5 g styrene and 2.170 g H<sub>2</sub>O<sub>2</sub> (30 wt.%) were added in the flask, then the catalyst (0.150 g) was added. After the reaction was finished, the catalyst was separated by centrifugation. The product was analyzed by gas chromatography (Agilent 6820) using a flame ionization detector. Diphenyl was used as an internal standard substance. The formation of product was confirmed by GC-MS (QP2010).

## 3. Results and discussion

### 3.1. Synthesis and characterization of the catalyst

The routes to synthesize TMICI, TMICI-Ni(II), and IMM-TMICI-Ni(II) are presented in **Scheme 2** and the detailed procedures have been described in Section 2. The TMICI-Ni(II) was characterized by UV-vis and FT-IR. **Fig. 1** shows the UV-vis spectrum of TMICI-Ni(II) in ethanol. The spectrum has two peaks at about 705 and 660 nm that results from the transition of <sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>T<sub>1</sub>(P), indicating that the blue-coloured tetrahedral anion NiCl<sub>4</sub><sup>2-</sup> was formed [28,29].

**Fig. 2** shows the FT-IR spectra of the TMICI and TMICI-Ni(II). Comparing with the spectrum of TMICI, a new peak at about 3100 cm<sup>-1</sup> can be observed in the spectrum of TMICI-Ni(II). This

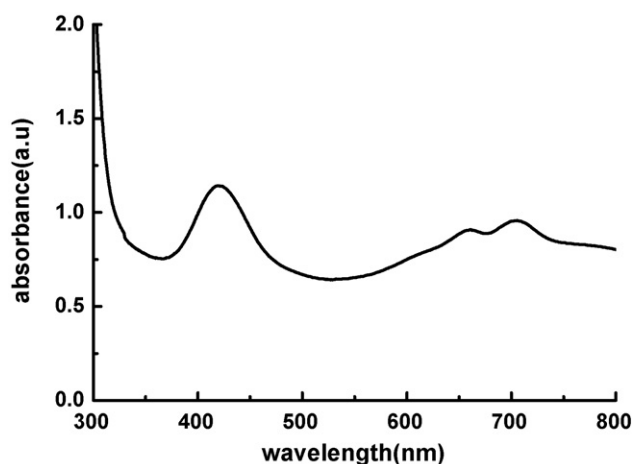


Fig. 1. UV-vis spectrum of TMICI-Ni(II) in ethanol.

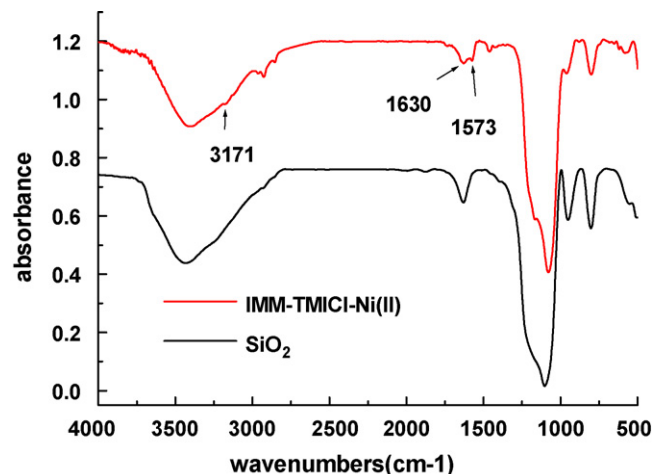


Fig. 3. FT-IR spectra of SiO<sub>2</sub> and IMM-TMICI-Ni(II).

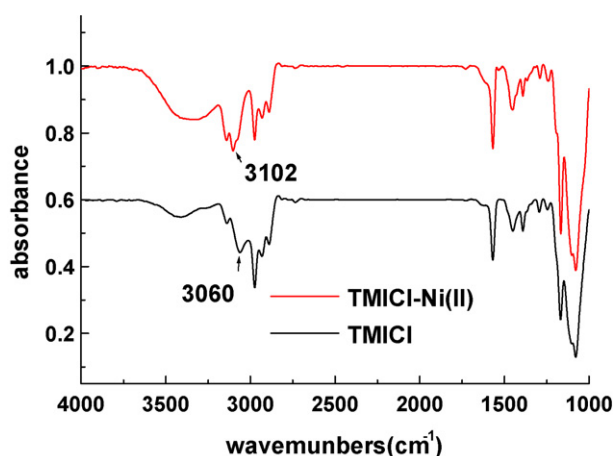


Fig. 2. FT-IR spectra of TMICI and TMICI-Ni(II).

indicates the formation of hydrogen bonding (C–H...Cl interaction), which has been observed in analogous compounds containing 1-ethyl-3-methylimidazolium cation [EmIM]<sup>+</sup> and NiCl<sub>4</sub><sup>2-</sup> ([EmIM]<sub>2</sub>[NiCl<sub>4</sub>]) [30]. Therefore, we can deduce that TMICI-Ni(II) has a structure of (TMICI)<sub>2</sub>[NiCl<sub>4</sub>], which is formed from two TMICI and one NiCl<sub>2</sub>.

IMM-TMICI-Ni(II) was characterized by SEM, TEM, FT-IR and nitrogen sorption, respectively. Fig. 3 gives the FT-IR spectra of SiO<sub>2</sub> and IMM-TMICI-Ni(II). The peak at 1573 cm<sup>-1</sup> in the spec-

trum of IMM-TMICI-Ni(II) can be attributed to the C=C stretching of imidazole ring [20], indicating the existence of the IL in IMM-TMICI-Ni(II). The SEM and TEM images of IMM-TMICI-Ni(II) are shown in Fig. 4. It can be known that the particles existed as big aggregates with diameter from 500 nm to 1 μm, and the catalysts had highly ordered pore structure with pore diameter of about 3.8 nm. To determine the surface area and porous characteristics of the IMM-TMICI-Ni(II), the sample was characterized by N<sub>2</sub> sorption analysis (Fig. 5). The pore size was about 3.9 nm, which agreed with that obtained from the TEM image. The specific surface area of catalyst determined was 561.8 m<sup>2</sup>/g. On the basis of these characterizations, we can deduce that IMM-TMICI-Ni(II) has structure schematically shown in Fig. 6 [24].

### 3.2. Reaction under solvent-free condition

The miscibility of styrene and H<sub>2</sub>O<sub>2</sub> is very poor. Therefore, a solvent that can dissolve both of them is required to carry the reactants to the active sites of the catalysts [16,31]. Using the specially designed catalyst IMM-TMICI-Ni(II) of this work, we conducted the reaction under solvent-free condition, and the results are listed in Table 1. The conversion of styrene can reach 16.3% and the selectivity to benzaldehyde is as high as 95.9%. In order to get some evidence to explain this promising result, we determined the miscibility of styrene and H<sub>2</sub>O<sub>2</sub> with IL 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride separately. It was shown that both of the reactants are miscible with the IL. Fig. 6 shows that the Ni<sup>2+</sup> is coordinated by the immobilized IL. Although

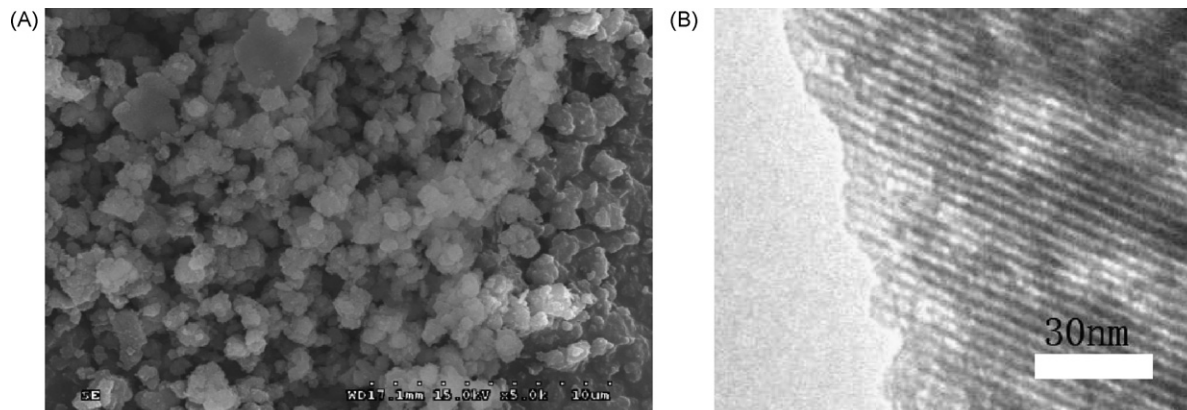


Fig. 4. SEM (A) and TEM (B) images of IMM-TMICI-Ni(II).

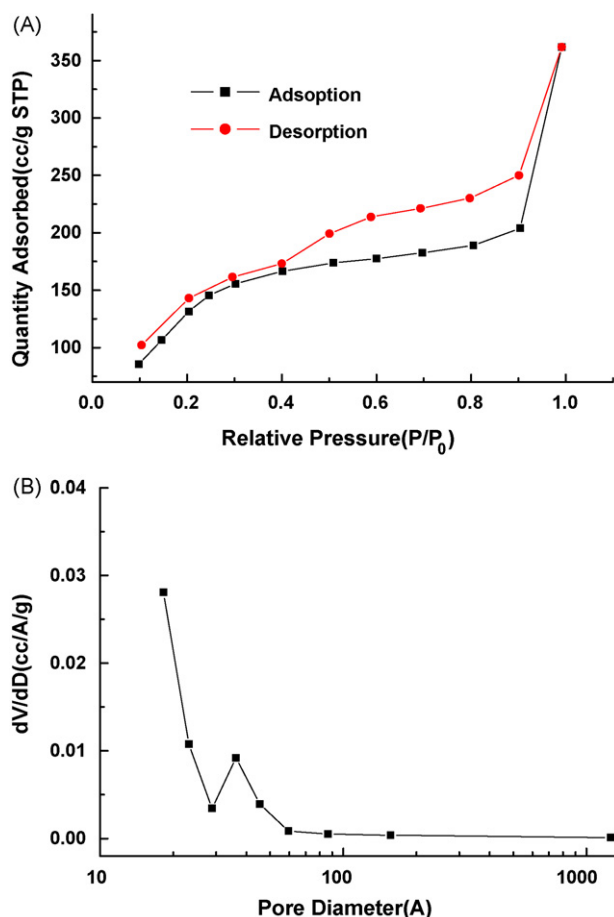


Fig. 5. Nitrogen sorption isotherms (A) and pore size distribution (B) of IMM-TMCl-Ni(II).

the miscibility of the IL with the two reactants may be changed after immobilization, it still remains the amphiphilic nature. Therefore, H<sub>2</sub>O<sub>2</sub> and styrene can diffuse into the IL layer containing the Ni<sup>2+</sup> which served as catalytic center. So the oxidation of the styrene with H<sub>2</sub>O<sub>2</sub> using IMM-TMCl-Ni(II) can be conducted at solvent-free condition. We also conducted the reaction catalyzed by NiCl<sub>2</sub>, SiO<sub>2</sub>-TMCl, and SiO<sub>2</sub>-Ni(II) separately, and it was shown that the conversions were very low (entries 5–7), similar to the blank experiment. This further indicated that the special structure of IMM-TMCl-Ni(II) is crucial for effectively catalyzing the reaction at solvent-free condition.

Table 1

Conversion and selectivity at different conditions<sup>a</sup>.

Entry	Catalyst	Styrene:H <sub>2</sub> O <sub>2</sub> (mol/mol)	Solvent	T (K)	Conv. (%)	Sel. (%) <sup>b</sup>
1	IMM-TMCl-Ni(II)	1:4	Solvent-free	333	7.5	96.2
2	IMM-TMCl-Ni(II)	1:4	Solvent-free	343	16.3	95.9
3	IMM-TMCl-Ni(II)	1:2	Solvent-free	343	15.4	95.1
4	IMM-TMCl-Ni(II)	1:1	Solvent-free	343	10.3	93.4
5	NiCl <sub>2</sub>	1:4	Solvent-free	343	2.4	80.2
6	SiO <sub>2</sub> -Ni(II)	1:4	Solvent-free	343	<1	–
7	SiO <sub>2</sub> -TMCl	1:4	Solvent-free	343	<1	–
8	Blank test	1:4	Solvent-free	343	<1	–
9	IMM-TMCl-Ni(II)	1:4	Acetonitrile <sup>c</sup>	323	3.2	>99
10	IMM-TMCl-Ni(II)	1:4	Acetonitrile <sup>c</sup>	333	23.9	94.7
11	IMM-TMCl-Ni(II)	1:4	Acetonitrile <sup>c</sup>	343	36.8	93.6
12	IMM-TMCl-Ni(II)	1:2	Acetonitrile <sup>c</sup>	343	34.5	88.7
13	IMM-TMCl-Ni(II)	1:1	Acetonitrile <sup>c</sup>	343	33.6	82.4

<sup>a</sup> Reaction condition: catalyst 0.150 g with Ni content of 0.67%, styrene 0.500 g, 6 h.

<sup>b</sup> The by-products are styrene oxide, acetophenone and phenylacetaldehyde.

<sup>c</sup> Solvent 8 g.

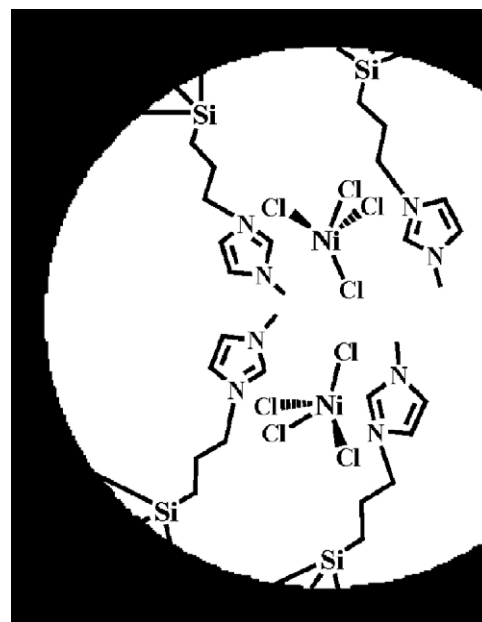
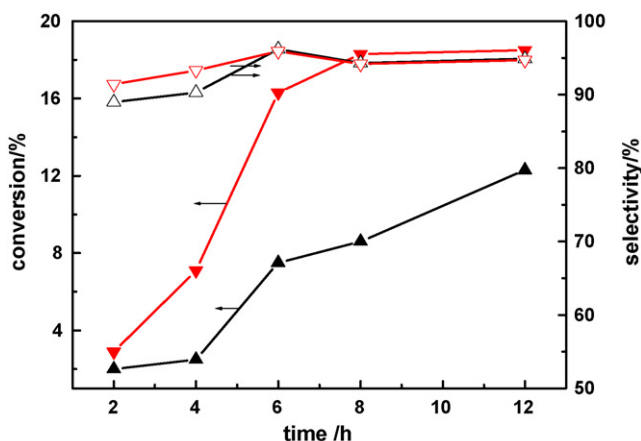
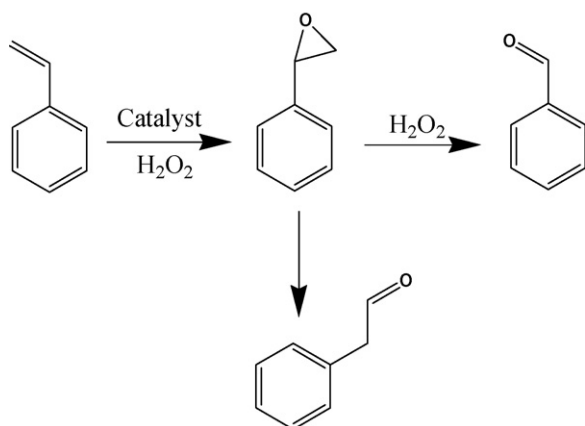


Fig. 6. Schematic structure of the catalyst IMM-TMCl-Ni(II) [24].

The effect of reaction time on the oxidation of styrene at the solvent-free condition is shown in Fig. 7. As the reaction time increased from 2 to 12 h, the conversion of styrene increased from 2.0% to 12.3% at 333 K and from 2.9% to 18.5% at 343 K. It can be known from the conversion curves that at 333 K the conversion increased with increasing time even the reaction time was 12 h. At 343 K, however, the conversion was nearly unchanged after the reaction exceeded 8 h. This can be explained by the effect of temperature on the decomposition rate of hydrogen peroxide. The higher temperature can accelerate the decomposition rate which hinders the increase in conversion. The selectivity of benzaldehyde decreased slightly after about 6 h. The decrease of selectivity can be explained by the proposed reaction mechanism (Scheme 3) [18]. The production of benzaldehyde was due to the later nucleophilic attack of H<sub>2</sub>O<sub>2</sub> on the styrene oxide, which was formed in the former reaction between styrene and H<sub>2</sub>O<sub>2</sub> [16,18]. The concentration of H<sub>2</sub>O<sub>2</sub> reduced continuously with the reaction going on, and less amount of H<sub>2</sub>O<sub>2</sub> was not favorable to further oxidation of styrene oxide formed in the first step. Therefore, more by-product was produced with increasing time, and the selectivity to benzaldehyde was decreased. The trend of selectivity is consistent with the result reported by other researchers [17]. As shown in Fig. 7, the



**Fig. 7.** Effects of reaction time on the oxidation of styrene in the solvent-free condition; (▲) conversion of styrene at 333 K; (▼) conversion of styrene at 343 K; (△) selectivity of benzaldehyde at 333 K; (▽) selectivity of benzaldehyde at 343 K. Reaction condition: catalyst (IMM-TMCl-Ni(II)) 0.150 g; styrene 0.500 g; H<sub>2</sub>O<sub>2</sub> 2.170 g.



**Scheme 3.** The possible reaction mechanism of styrene oxidation.

increase in temperature can increase the selectivity because the rate for nucleophilic attack is also enhanced at the higher temperature, which finally leads to the increase of selectivity at higher temperature. Table 1 also shows that the selectivity increased with increasing the content of H<sub>2</sub>O<sub>2</sub> (entries 2–4), which further supports the argument discussed above.

### 3.3. Reaction in acetonitrile

We also conducted the reaction in acetonitrile, and the results are listed in Table 1. The effect of temperature on the oxidation of styrene in acetonitrile over the catalyst of IMM-TMCl-Ni(II) for 6 h is shown in entries 9–11. As the temperature changed from 323 to 343 K, the conversion of styrene increased from 3.2% to 36.8%. A conversion of 36.8% was among the highest ones reported in the literature, while the selectivity of benzaldehyde was as high as 93.6% even at the high conversion. Meanwhile, as shown in Table 1, the selectivity was relatively lower in acetonitrile than at solvent-free condition. This may be explained by the fact that the presence of acetonitrile can decrease the rate of open-ring reaction of styrene oxide to benzaldehyde and result in an increase in the selectivity to styrene oxide [17]. In addition, in this work the reaction time

was short and the amount of catalyst used was relatively small, indicating high activity of the catalyst.

## 4. Conclusions

Ni<sup>2+</sup>-containing IL TMCl immobilized on the porous silica has been synthesized and is used as a heterogeneous catalyst for oxidation of styrene with H<sub>2</sub>O<sub>2</sub> to produce benzaldehyde. Under solvent-free condition, the conversion of styrene could reach 18.5% and the selectivity to benzaldehyde could be as high as 95.9%. The promising result is originated from the special structure of catalyst IMM-TMCl-Ni(II). With the aid of the IL, both hydrophobic reactant and the hydrophilic reactant were accessible to the active sites of the catalyst. The catalyst was also very effective for the reaction in acetonitrile. The conversion and selectivity could reach 36.8% and 93.6%, respectively, which are among the highest reported in the literature. In addition, the reaction time was short and the amount of catalyst used is relatively small.

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