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Highly Selective Oxidation of Styrene Over $FeCl_3$-Imidazolium Ionic Liquid Grafted SBA-15

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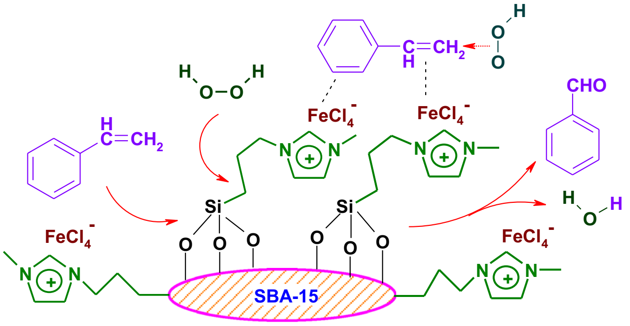
Abstract

A composite material (FeSIL) prepared by $FeCl_3$-imidazolium ionic liquid grafted on SBA-15 exhibited effective catalytic activity for solvent-free oxidation of styrene into benzaldehyde with high selectivity using H_2O_2 oxidant and it presented easy recovery and reusability. In situ DRIFTS spectra for styrene and H_2O_2 adsorption showed that an intermediate Fe^{3+}–π surface complex on the catalyst surface was responsible for the activation of styrene and its reaction with H_2O_2 molecules on the surface or in the bulk phase.

Graphic Abstract

Iron-chloride immobilized ionic liquid (FeSIL) was prepared by *N*-methylimidazole reacting with chloropropylsilane grafted on SBA-15 and coordinating of $FeCl_3$ to the imidazolium on the surface. The higher catalytic activity of the catalyst for effective oxidation of styrene under solvent-free condition were achieved The catalyst can be easily recovered and effectively reused without a significant loss in its activity.



Keywords $FeCl_3$-ionic liquid grafted SBA-15 · Fe^{3+}–π surface complex · Styrene · Oxidation

1 Introduction

Oxidation of benzene and its derivatives such as toluene, styrene to produce phenols, alcohols, aldehydes and carboxylic acids is one of the most significant functional group transformations in organic synthesis. As a derivative, styrene can be oxidized into styrene oxide, benzaldehyde (BzH) and benzoic acid depending on the allylic oxidation, or even cleavage of the C=C double bond. Among these products, BzH is an important chemical applied as feedstock for producing intermediates in perfumery, pharmaceutical, dyestuff and agrochemical industries. As a traditional

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technology, hydrolysis of benzal chloride was widely used for BzH production in industry. This method encountered the main problem, traces of chlorine inevitably exist in the product BzH, which limited its application in perfumery and pharmaceutical. In order to overcome this limit, attempts on liquid-phase oxidation of toluene or styrene into BzH have been carried out. Several catalysts for styrene oxidation such as $Ce_{0.3}Co_{0.7}Fe_2O_4$ [1], Cu-doped hydrotalcites [2], W/SiO_2 [3], Pt/TiO_2 [4] and $H_3PW_{12}O_{40}$/SBA-15 [5] etc. have been investigated and good results were received including higher conversion of styrene and selectivity to BzH. Recently, the Ti-based zeolites like TS-1, Ti-MCM-41, Ti-substituted SBA-15 have gained considerable development for selective oxidation of propylene, cyclohexene and styrene [6–9]. Among them, TS-1 has an effectively catalytic activity for propylene oxidation in fixed bed reactor and cyclohexene liquid-phase oxidation using H_2O_2 as oxidant. Chen et al. and Eimer et al. reported the catalytic performance of Ti-MCM-41 and Ti-substituted SBA-15 for oxidation of styrene with good activity. Nonetheless, most of above catalytic processes are usually conducted in organic solvents such as acetone, acetonitrile, methanol and 1,4-dioxane, which causes environmental pollution due to loss of solvents by the evaporation. Besides, other drawbacks such as complicated synthesis process and high cost remain continually existed. Thus, solvent-free oxidation of styrene to BzH using environment-benign and cheap-metal catalysts needs to be widely developed. Fe based catalysts involving $FeCl_4^-$-imidazolium ionic liquid, nano iron oxide, Fe-based hydrotalcites and iron supported micro or mesoporous molecular sieves [10–15] have been reported by our and other groups in recent years. Although $FeCl_4^-$-imidazolium ionic liquid exhibited good catalytic activity for solvent-free oxidation of toluene into BzH, this process encountered a problem that is the separation of the ionic liquid catalyst from the reaction mixture. Therefore, mesoporous silica SBA-15 grafted $FeCl_4^-$-imidazolium ionic liquid was prepared and catalytic performance of this prepared composite material for solvent-free oxidation of styrene using H_2O_2 aqueous medium as oxidant was estimated. The effect of reaction conditions like reaction temperature, reaction time and catalyst dose on the oxidation was discussed. However, the reusability of the catalyst, adsorption of styrene on the catalyst and the reaction mechanism were explored and these obtained results were reported in this paper. This catalytic progress using highly efficient and environment friendly heterogeneous catalysts has always been pursued by green or sustainable chemistry.

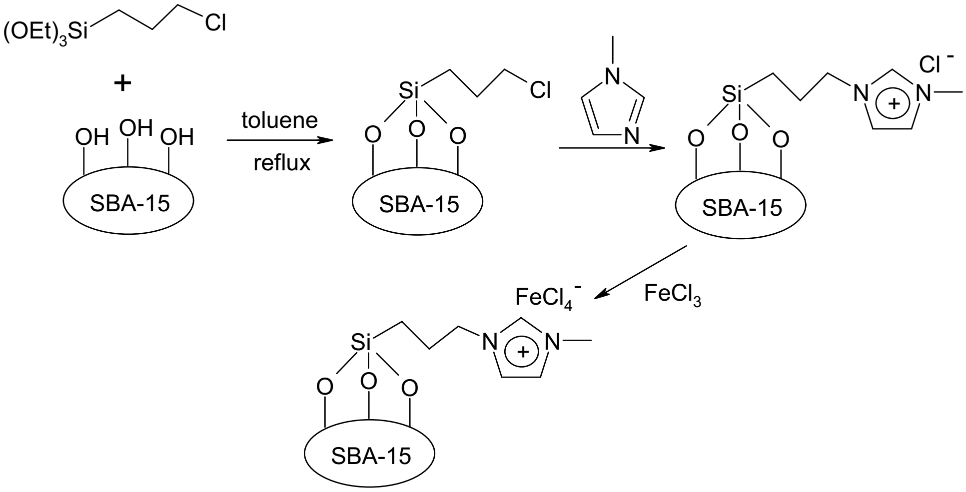
2 Experimental

2.1 Chemicals

TEOS, styrene, H_2O_2 (30%), toluene, hydrochloric acid and anhydrous iron trichloride are all analytical grade and purchased form Sinopharm Chemical Reagent Co. Ltd. Chloropropyltriethoxysilane (A.R.) *N*-methyl-imidazole (A.R.) and P123 (polyethylene oxide-polypropylene oxide-polyethylene oxide) are purchased from Aladdin Chemical Reagent Co. Ltd, Beshine Chemical Science and technology Co. Ltd and Tianjin Fuchen Chemical Reagent Co. Ltd, respectively. All above chemicals were directly used without any purification.

2.2 Preparation of the Catalyst

SBA-15 was prepared depending to the reported method [16]. SBA-15 grafted ionic liquid 1-methyl-3-(chloropro pyltriethoxysilane) imidazolium-$FeCl_4^-$ (designated as FeSIL) was prepared according to our previous work [17] as shown in Scheme 1.



Scheme 1 Preparation progress of FeSIL

2.3 Catalytic Test

Three mL of styrene and 0.2 g of FeSIL was added into a three-necked flask fitted with magnetic stirrer and a condenser. The flask was heated in water bath to 80 °C under stirring, and then 8.1 mL of 30% H_2O_2 was slowly dripped into the reaction mixture and the resulting mixture had been reacted at 80 °C for 5 h. After the reaction completed, the mixture solution was filtered to remove the catalyst FeSIL. The reaction mixture was extracted by 5 mL of toluene. The extracted organic phase was analyzed by GC (Agilent GC7820) and GC–MS (Agilent GC7890-MS5975C) using HP-5 column (30 m × 0.32 mm × 0.25 µm) and FID detector (GC).

2.4 Adsorption of Styrene and H_2O_2

In situ DRIFTS spectra were recorded by an FT-IR spectrometer (Brucker TENSOR II) equipped with a diffuse reflectance optics accessory (Harrick Scientific products Inc.). The FeSIL sample was heated to 400 °C for 2 h in vacuo before measurement. The styrene and/or H_2O_2 species were introduced onto the catalyst surface by high-pure N_2 gas (purity 99.99%) for 2 h, followed by evacuating from the system to about 9.8×10^{-4} Pa. After that, the DRIFTS spectra were measured at 80 °C half an hour under vacuo condition.

3 Results and Discussion

3.1 Catalytic Activity of FeSIL

The catalyst FeSIL was prepared by $FeCl_3$-1-methyl-3-(chloropro pyl-triethoxysilane) imidazolium ionic liquid grafted on SBA-15. The characterization results in previous report [17] indicated that Fe loading was determined to be 11.58% of $FeCl_3$ average content (0.71 mmol/g) by ICP-MS with the nonuniform distribution of $FeCl_3$ on FeSIL surface. This prepared FeSIL was used for free-solvent oxidation of styrene with H_2O_2 as oxidant. Its catalytic performance was reported as the following.

The influence of reaction temperature on the oxidation of styrene with H_2O_2 oxidant was conducted and the results were depicted in Fig. 1. It was clear that the conversion was gradually increased as the reaction temperature going up. The increment extent of the conversion with the temperature was so smooth that it approached to 37.5% at 60 °C and 45.0% at 100 °C, indicating that the effect of the reaction temperature on the catalytic process was slight. This phenomenon was likely related to rapid decomposition of H_2O_2 over Fe-containing catalyst. According to the previous report [15], oxidizing action of H_2O_2 for organic substrates could be homolytic decomposition into ·OH radicals or heterolytic dissociation into ·OOH radicals by the interaction of various metal compound catalysts [18]. In any case, the radicals played a key role for oxidizing the organic substrates. Meanwhile, some transition metal compound catalysts, especially iron compounds could effectively catalyze rapid decomposition of H_2O_2 into O_2 and H_2O, especially at higher reaction temperature [13]. It was the rapid decomposition of H_2O_2 carrying out that caused slight effect of the reaction temperature. Besides, higher selectivity to benzaldehyde (BzH) was observed in this progress and only one byproduct was benzoic acid (BzA), which was in agreement with our previous reported work using Fe_3O_4 as catalyst [13]. The high selectivity for Fe containing catalysts was ascribed to Fe active species limiting BzH further oxidation to phenol [12]. Certainly, the temperature raising was advantageous to the selectivity to BzA.

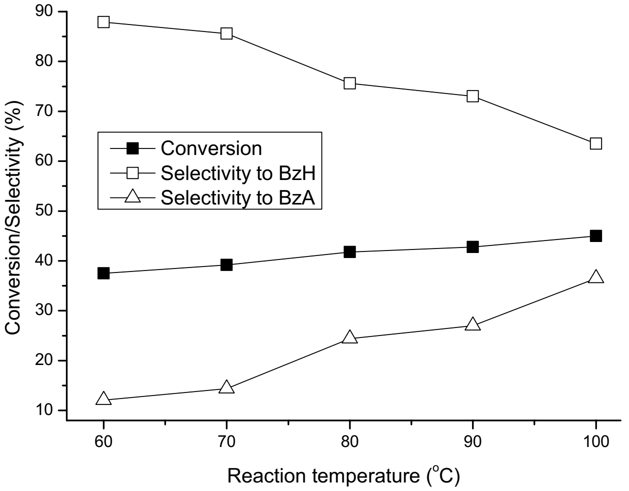


Fig. 1 Effect of reaction temperature on the oxidation. Reaction condition: reaction time 5 h, catalyst 0.2 g, molar ratio of H_2O_2 to styrene 4:1

Influence of catalyst dose on the oxidation was remarkable. As shown in Fig. 2, the sharp increase in the conversion from 7.0 to 43.1% was observed as the catalyst dose increasing from 0.1 to 0.2 g, followed by smooth increment of the conversion from 43.1 to 47.5% when continuously increasing the catalyst amount from 0.2 to 0.3 g. Moreover, the selectivity to BzH was decreased from 95.7 to 68.9% as the catalyst dose raising from 0.1 g to 0.3 g, which was attributed to BzH further oxidized into BzA. The increase in dose of the catalyst used in this system would lead to increase in amount of active sites on the catalyst surface. These excess active sites promoted the oxidation of styrene into BzH. Certainly, they could enhance BzH further oxidized into benzoic acid (BzA), for example, the selectivity to BzA was raised from 4.3 to 31.1% when the dose of the catalyst raising from 0.1 to 0.3 g, which necessarily led to

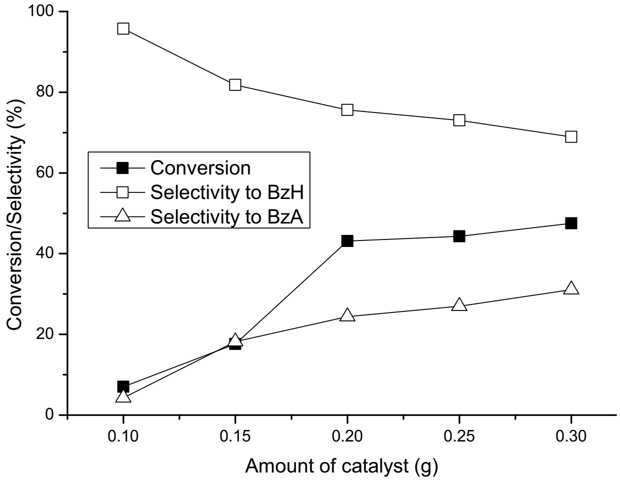


Fig. 2 Effect of the catalyst dose on catalytic activity. Reaction condition: reaction time 5 h, temperature 80 °C, molar ratio of H_2O_2 to styrene 4:1

the decrease in the selectivity to BzH due to the active sites increasing on the catalyst surface.

The dependence of the styrene conversion on reaction time was depicted in Fig. 3. Two stages for the conversion and selectivity curves were found. The conversion was remarkably increased as the reaction time prolonged from 2 to 5 h, and then slight increase in the conversion was observed as the reaction time prolonging from 5 to 7 h. On the contrary, the selectivity to BzH was smoothly decreased from 2 to 5 h of the time. At the same time, the selectivity to BzA was increased in this time range. However, the remarkably decreasing for selectivity to BzH and the increasing for that to BzA also meant the further conversion of BzH into BzA with the time prolonging. In addition, dependence of $\ln(C_0/C_t)$ on the reaction time was made and depicted in Fig. 4, where C_0 represents initial concentration of styrene and C_t stands for the concentration of remanent styrene in the system at some time. As seen from the figure, the relationship between $\ln(C_0/C_t)$ and reaction time almost approaches to a straight line, suggesting that the oxidation reaction of styrene is quasi-first order in styrene and the first order rate constant calculated from the plot is $k = 0.1428\ h^{-1}$.

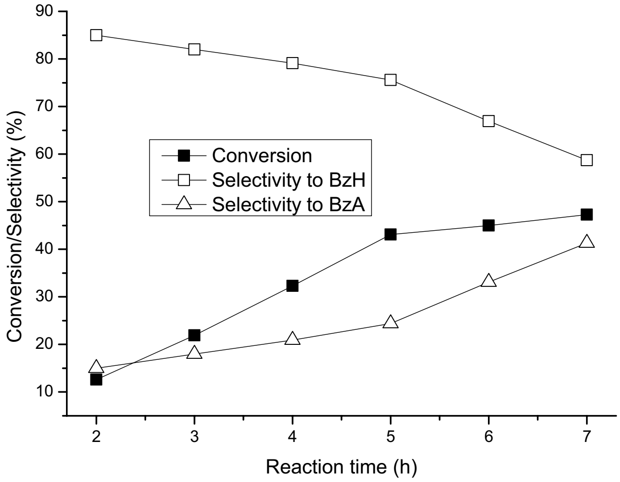


Fig. 3 Dependence of reaction time on the catalytic performance. Reaction condition: reaction temperature 80 °C, catalyst 0.2 g, molar ratio of H_2O_2 to styrene 4:1

3.2 Reusability of the Catalyst

In order to gain application prospect of the catalyst in industry, recovery and reuse of the catalyst were performed. The catalyst FeSIL was recovered by filtration after first run, and then it was reused in the next run under the same reaction conditions. It was as shown in Fig. 5 that the activity of FeSIL was unaffected even at the seventh run. This indicated that the prepared FeSIL was highly stable within seven repeated runs. In addition, ICP-MS analysis was used for examining if there is a leaching of active species to the reaction medium. 18.9 and 17.3 ppb of Fe^{3+}, corresponding to 0.055 and 0.050 ppm of $FeCl_3$ in the solution were found after the first and seventh run, respectively. This result exhibited that the leaching extent of immobilizing $FeCl_3$ species from the composite was negligible. Besides, this also proved this oxidation was a heterogeneous catalysis reaction and the linking and/or coordinating of the IL-$FeCl_3$ on the SBA-15 surface was very stable.

3.3 The Adsorption Behavior of Styrene and H_2O_2

In situ DRIFTS spectra for styrene adsorption on FeSIL at various time were measured and shown in Fig. 6. The bands observed at 3737.5 and 3624.5 cm^{-1} were ascribed

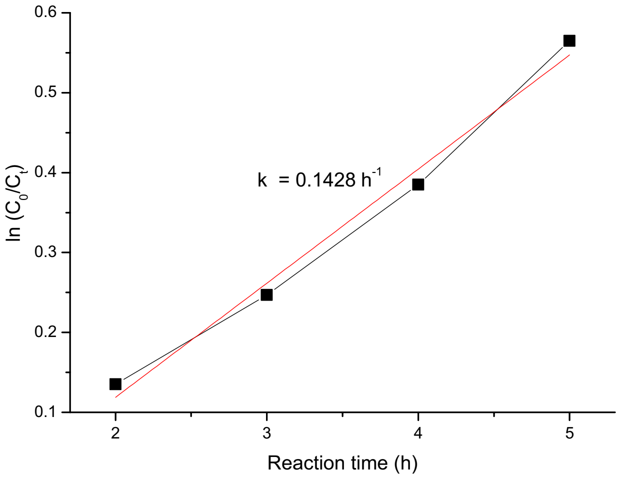


Fig. 4 Kinetic curve of the oxidation

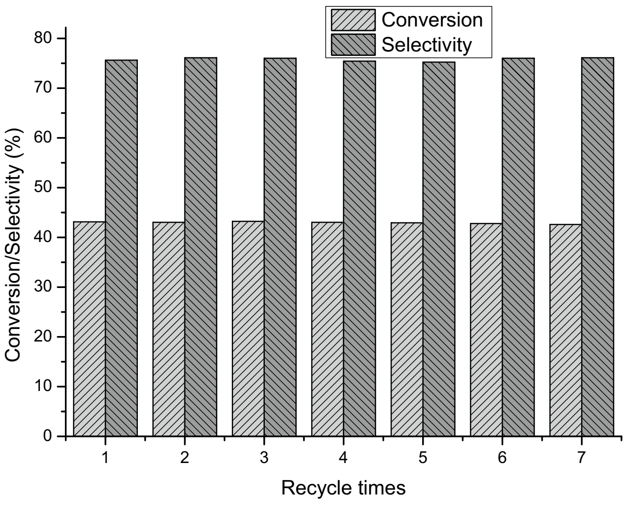


Fig. 5 The reusability of FeSIL

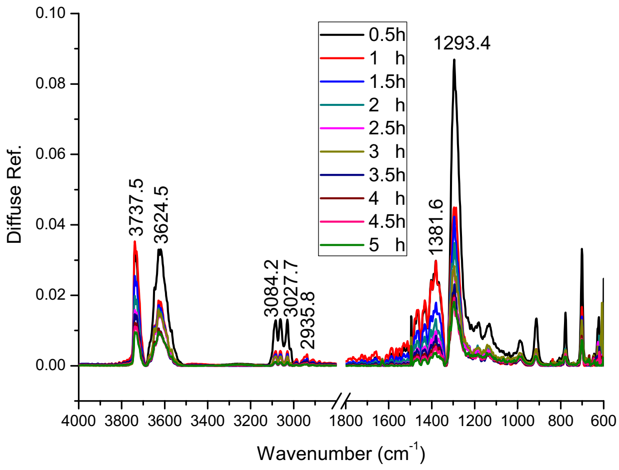


Fig. 6 DRIFTS spectra of styrene adsorbed on FeSIL

to stretching vibration of free Si–O–H bonds on the surface, and the strength of the bands was obviously decreased as the adsorption time prolonged. Meanwhile, the bands around 3000 and 2900 cm^{-1} assigned to stretching vibration of C–H bonds in benzene ring and $–CH_2=CH_2$ species were also decreased with the adsorption time, so were the bands at 1381.6 and 1293.4 cm^{-1} that were related to bending vibration of C–H bonds in aromatic ring and vinyl groups. Besides, no any band around 1600–1700 cm^{-1} corresponding to C=C double bonds was observed at adsorption time of 5 h. These findings indicated that the vinyl group almost disappeared when styrene was adsorbed on the catalyst surface via interaction between the active sites and olefinic bonds or aromatic ring [19] to form intermediate complexes, which certainly had a effect on vibrations of C–H bonds. Besides, introduction of H_2O_2 into the adsorption system effectively influenced the adsorption of styrene on the surface. As shown in Fig. 7, a new and wide band around 3240 cm^{-1} was found, which was attributed to stretching vibration of associated hydroxyls caused by adsorption of $H_2O_2+H_2O$ on the surface. The appearance of the band at 1628.8 cm^{-1} that was related to bending vibration of H–O–H further confirmed the $H_2O_2+H_2O$ adsorption. This finding indicated that adsorption of $H_2O_2+H_2O$ had an influence on the adsorption of styrene on the catalyst surface. The associated hydroxyls may be attributed to their decomposition into $^{\cdot}OH$ or $^{\cdot}OOH$ radicals, which resulted in oxidation of styrene. Therefore, the activation of styrene on the catalyst surface was mainly considered to generate surface active complexes via interaction between Fe^{3+} species and π electrons in aromatic ring or/and $–CH_2=CH_2$ species, which led to π electrons deviating from styrene molecule, further causing intensity of C=C bonds weakened, even broken [20]. As a result, styrene was easily oxidized by $^{\cdot}OH$ or $^{\cdot}OOH$ on the surface or in the bulk phase.

4 Conclusions

A composite material (FeSIL) prepared by $FeCl_3$-imidazolium ionic liquid grafted on SBA-15 exhibited effective catalytic activity for solvent-free oxidation of styrene into benzaldehyde using H_2O_2 oxidant, giving 43% conversion and ca. 100% selectivity to benzaldehyde (76.0%) and benzoic acid (24.0%). This catalyst indicated a heterogeneous catalysis nature and the linking or coordinating of the IL-$FeCl_3$ on the SBA-15 surface was very stable, providing easy recovery and reusability. In this oxidation process, an intermediate Fe^{3+}–π surface complex was found on the catalyst surface by means of in situ DRIFTS spectra analysis for styrene and H_2O_2 adsorption. It was the

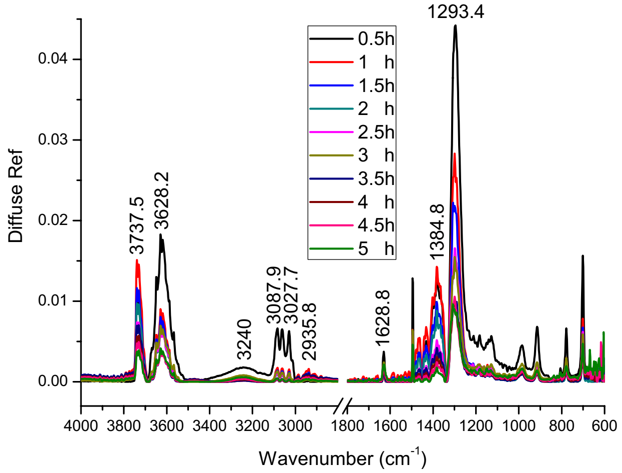


Fig. 7 DRIFTS spectra of styrene and H_2O_2 adsorbed on FeSIL

formation of this active intermediate that was responsible for the activation of styrene and its effective reaction with H_2O_2 molecules on the surface or in the bulk phase.

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