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Immobilization of a thiol-functionalized ionic liquid onto HKUST-1 through thiol compounds as the chemical bridge

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Abstract:

heterogeneous catalyst [HVIm-(CH₂)₃SO₃H]HSO₄@HKUST-1 А novel (IL@HKUST-1), with both Lewis and Brønsted acid sites, was developed for the esterification of oleic acid with short-chain alcohols. HKUST-1 was chemically modified with ethanedithiol, and the vinyl-containing ionic liquid was then grafted onto the carrier through thiol groups. The catalyst IL@HKUST-1 was characterized by XRD, N₂ adsorption-desorption, FT-IR, SEM, TG, elemental analysis, and ICP. The results proved that HKUST-1 had typical microporous structure, and the thiol groups were incorporated into the channels of the carrier. Through the reaction of vinyl and thiol, the ionic liquid was successfully immobilized onto SH-HKUST-1 by chemical covalent bond. The catalyst was applied in the esterification of oleic acid with ethanol, and the optimal conditions were determined as follows: molar ratio of ethanol to oleic acid 12:1, catalyst amount 15 wt% (based on oleic acid), reaction time

4 h, and reaction temperature 90 °C. Under the conditions, the conversion of oleic acid was 92.1%. After 5 times of recycling, there was no significant decrease in conversion, showing a certain stability and good reusability of the catalyst. The catalyst also exhibited high catalytic activity in esterification of oleic acid with other short-chain alcohols.

1. Introduction

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Biodiesel is well recognized as one of the most promising substitutes for the traditional fossil-based fuels.¹ Due to its excellent properties², such as biodegradability, renewability, low viscosity and pollution emissions, biodiesel can be applied as diesel engine fuels without further modifications. Compared with regular diesel, the biodiesel shows better engine performance and is environmentally beneficial.³ Biodiesel can be obtained by the esterification of long-chain fatty acids with short-chain alcohols to mono alkyl esters in the presence of a catalyst.^{4, 5} To improve its production, an efficient and green catalyst is urgently needed, attracting more and more attention in this field.

Functionalized acidic ionic liquids play an important role in acid catalysis fields.⁶ As a class of novel environmental friendly catalysts, they combine the advantages of solid acids and liquid acids, meanwhile have the characteristics of low volatility, adjustable acidity, high acidity density, and good fluidity.⁷⁻¹⁰ However, functionalized acidic ionic liquids still have some serious defects such as high viscosity and difficult to recycle.¹¹⁻¹³ An effective solution to these problems is the immobilization of ionic

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liquid onto solid material with high surface area and certain mechanical strength,¹⁴⁻¹⁹ such as SiO₂, ZrO₂, SBA-15, and MCM-41. In this way, the performance of ionic liquid can be improved and its applications will be broadened. Meanwhile, the introduction of functionalized acidic ionic liquid can endow the solid with diversity and variability. H. Li and co-workers²⁰ designed a graphene-analogue hexagonal boron nitride (G-h-BN) supported with tungsten-based ionic liquid heterogeneous catalyst based on post-synthetic modification strategy. The prepared catalyst presented excellent activity in oxidation of dibenzothiophene, which was superior to homogeneous catalysts of ionic liquids themselves.

In recent years, metal organic frameworks (MOFs) have been the focus of academic research due to their excellent properties.^{21, 22} As new functional materials, MOFs have been applied very widely in many fields such as gas storage, adsorption separation, drug delivery, and heterogeneous catalysis.²³⁻²⁶ And as more and more MOFs with the advantages of large surface area, high porosity, stable structure, adjustable pore size, and available functionalization are synthesized,²⁷⁻²⁹ they have attracted increasing attention and shown great potential application in catalytic field. During the past decade, the study of using MOFs as carriers to support active components has been reported.³⁰⁻³³ L H Wee et al.³⁴ prepared the Cu₃(BTC)₂ (BTC = benzene tricarboxylic acid) incorporating heteropolyacid nanomaterial and evaluated its catalytic activity in esterification of acetic acid with 1-propanol. Y Pan and co-workers³⁵ reported the one-step synthesis of methyl isobutyl ketone over palladium nanoparticles deposited on a chromium terephthalate MIL-101 (MIL = material from

institute Lavoisier) catalyst. These studies strongly indicate that MOFs are a class of promising carrier materials. However, there are only a handful of reports describing the immobilization of ionic liquid onto MOFs.

Post-synthetic modification (PSM) refers to the chemical modification of MOFs after the formation of crystals, while the basic frameworks remain unchanged.^{36, 37} This is an effective way to construct interactions between MOFs and the functional guest molecules. Y K Hwang et al.³⁸ selected ethylenediamine and diethylenetriamine as grafting agents to produce the amine-grafted MIL-101 and both of them exhibited high activities in the Knoevenagel condensation. F Ke et al.³⁹ described thiol-functionalization of MOFs by a facile coordination-based post-synthetic strategy and the samples showed high adsorption capacity for Hg^{2+} from water. In these cases, the functionalization mainly relies on the coordinatively unsaturated metal centers (UMCs) of MOFs and the active species are grafted through coordinate covalent bond.⁴⁰⁻⁴² With the similar method, the immobilization of functionalized ionic liquid onto MOFs can also be realized. O Luo and co-workers⁴³ developed a functionalized MIL-101 material for acetalization, in which a Brønsted acidic quaternary ammonium salt ionic liquid was confined inside well-defined nanocages. This was the first successful attempt to combine the advantages of ionic liquid with the desirable microenvironment in MOFs. All these works and some other studies⁴⁴⁻⁴⁸ prove that the introduction of ionic liquid into MOFs is attainable and hopeful in catalytic applications.

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Herein, a novel bi-functional catalyst IL@HKUST-1 (HKUST = Hong Kong

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university of science and technology) is synthesized by a PSM strategy and applied in the esterification reaction. HKUST-1, also known as Cu₃(BTC)₂ or MOF-199, is selected as the carrier. Considering the strong coordination ability of metal centers (Cu²⁺), ethanedithiol is used as the grafting agent to introduce thiol groups. By the reaction of vinyl and thiol, the ionic liquid [HVIm-(CH₂)₃SO₃H]HSO₄ can then be immobilized onto HKUST-1 to achieve the catalyst. Although the pristine carrier exists a certain amount of Lewis acid sites, the acidity is far from enough to meet the requirement of the acid catalytic system. The introduction of ionic liquid greatly improves the Brønsted acidity of the material, thus making it an efficient catalyst for the esterification of oleic acid with ethanol. The structure and property of the prepared IL@HKUST-1 are systematically characterized by XRD, N₂ adsorption-desorption, FT-IR, SEM, TG, elemental analysis, and ICP. At the same time, the optimal reaction conditions are obtained and the reusability of the catalyst is also evaluated.

2. Experimental

2.1. Materials

All chemicals were commercially available and used without further purification. Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), benzene-1,3,5-tricarboxylic acid (H₃BTC), 1,2-ethanedithiol, 2,2-azo-bis-isobutyronitrile (AIBN), and oleic acid were of analytical reagent grade and purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. 1-Vinylimidazole (99%) was purchased from Ninghai Kaile Chemical Co., Ltd. 1,3-Propane sultone (99%) was purchased from Wuhan Fengfan Surface

Engineering Co., Ltd. Sulfuric acid, anhydrous ethanol, and ethyl acetate were purchased from Wuxi City Yasheng Chemical Co., Ltd. Diethyl ether was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Toluene (99.5%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. All other chemicals used in synthesis were of analytical grade.

2.2. Methods

The powder X-ray diffraction (XRD) experiments were carried out at the Smartlab diffractometer (RIGAKU, Japan) equipped with Ni-filtered Cu K α radiation $(\lambda=0.15418 \text{ nm})$. The X-ray tube was operated at 40 kV and 40 mA. The scanning angle was from 0.6° to 30° with scan-steps of 0.02° per second. To calculate the Brunauer-Emmett-Teller (BET) surface area, N₂ adsorption-desorption measurements were performed on the Micromeritics ASAP 2020 system model instrument at -196 °C. The samples were outgassed under vacuum at 200 °C for 8 h before measurement. Fourier transform infrared (FT-IR) spectra were recorded on the Nicolet-6700 spectrometer (Thermo Fisher Scientific, U.S.) using anhydrous KBr (Nicolet, United States) as dispersing agent. The spectra were collected after accumulation of 128 scans with a resolution of 5 cm⁻¹. Scanning electron microscopy (SEM) images were obtained with the S4800 field-emission scanning electron microscope (HITACHI, Japan). Before the test the samples were dispersed with ultrasonic treatment to remove the aggregated grains. The thermal behavior was examined by the STA 409PC thermo gravimetric (TG) analyzer. The temperature ranged from 30 °C to 600 °C with a heating rate of 10 °C/min under N₂ atmosphere. Elemental analyses were performed

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on Elementar Vario EL III system to determine the loading amount of ionic liquid in the prepared catalysts. The amount of Cu in the catalyst was analyzed by inductively coupled plasma (ICP, Optima 7000 DV, Perkin-Elmer, USA) after dissolving the sample in hydrofluoric acid.

2.3. Catalyst preparation

The acidic ionic liquid [HVIm-(CH₂)₃SO₃H]HSO₄ was synthesized referring to our previous work (Scheme 1).⁴⁹ Specifically, 9.4 g of 1-vinylimidazole was added into a 100 mL round bottom flask, adding certain amount of ethyl acetate as solvent. 1,3-propane sultone (12.2 g) was then slowly dropped into the solution under vigorous stirring condition at 0 °C and the mixture was continuously agitated for another 24 h. After suction filtration, washing with ethyl acetate, and vacuum drying, the white precipitates were collected. Then the formed products were dissolved in a small amount of deionized water, and equal molar sulfuric acid was added dropwise in an ice bath. The mixture was slowly heated up to 60 °C and reacted for 12 h with stirring. After the reaction finished, the target ionic liquid was obtained by reduced pressure distillation, washing with diethyl ether, and vacuum drying.

The thiol-functionalized HKUST-1 (SH-HKUST-1) was synthesized by a convenient post-synthetic modification method.³⁹ First, 2.174 g of Cu(NO₃)₂·3H₂O was dissolved in 30 mL deionized water, while 1.05 g of benzene-1,3,5-tricarboxylic acid was dissolved in 30 mL ethanol. The two solutions were mixed thoroughly and stirred for 30 min. Then the mixture was transferred to a 100 mL Teflon autoclave liner and heated for 12 h at 120 °C. After cooling down to the room temperature, the

blue powder was obtained by filtering, washing with deionized water and ethanol alternately, and drying under vacuum at 60 °C for 12 h. Second, the synthesized HKUST-1 sample was chemically modified with 1,2-ethanedithiol. The solid powder was activated at 150 °C for 12 h before use to remove the water molecules. Typically, 0.25 g of ethanedithiol was dissolved in 100 mL of anhydrous toluene, and 1.0 g of HKUST-1 was added into the solution gradually. The mixture was stirred at room temperature for 24 h, and then the suspension was centrifuged. The dark green solid was washed with ethanol for 5 times, and dried overnight under vacuum at room temperature.

The preparation process of IL@HKUST-1 was illustrated in Scheme 2. In a typical process, 3.0 g of the vinyl-containing ionic liquid was dissolved in 50 mL of anhydrous ethanol, and 1.0 g of thiol-functionalized HKUST-1 was subsequently dispersed to the mixture with stirring. After the temperature was increased to 80 °C, 0.03 g of AIBN was added under the protection of nitrogen and the reaction was lasted for 30 h. The product was filtered and washed with ethanol repeatedly to remove the excess ionic liquid. The target catalyst IL@HKUST-1 was obtained after drying in vacuum at 60 °C for 12 h.

2.4. Catalytic Activity Measurement

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Taking the esterification of oleic acid with ethanol as a probe reaction, the catalytic activity of IL@HKUST-1 was investigated. In a typical procedure, appropriate amounts of oleic acid and ethanol were mixed in a 50 mL round bottomed flask equipped with magnetic stirring and condensate water, and IL@HKUST-1 was

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added as the catalyst. Then the esterification was allowed to proceed at a certain temperature for a period of time. For this study, the molar ratios of ethanol to oleic acid were varied from 8:1 to 16:1, and the catalyst amounts (based on oleic acid) were set from 5 wt% to 25 wt% (the total mass of the catalyst). The reaction times ranging from 2 h to 6 h were investigated. The reaction temperatures changing from 50 °C to 130 °C were also discussed. After reaction, the upper liquid was obtained by centrifugation for further analysis and the remaining catalyst was recovered by washing with diethyl ether and drying under vacuum. The recycling experiment was carried out as the same procedure to study the reusability of the catalyst.

The conversion of oleic acid was calculated according to the literature with modification.⁵⁰ Briefly, 1.0 g of reaction liquid was accurately weighed and dissolved in 20 mL of ethanol, adding a few drops of phenolphthalein as indicator. The mixture was then titrated with 0.02 mol/L NaOH ethanol solution. The acidity index of the sample could be calculated based on the volume of NaOH solution consumed by the following equation:

$$A = (V_t - V_o) Mc / m$$
⁽¹⁾

where A is the acidity index of the sample, mg/g; V_t is the final reading of the burette, mL; V_o is the initial reading of the burette, mL; M is the molecular weight of NaOH, g/mol; c is the concentration of NaOH solution, mol/L; m is the weight of the sample used for titration, g.

According to the equation below, the conversion of oleic acid could be obtained. $Y = (A_o - A_t) / A_o \times 100\%$ (2) where Y represents the conversion of oleic acid, %; A_o represents the initial acidity index of the sample before reaction, mg/g; A_t represents the final acidity index of the sample after reaction, mg/g.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of HKUST-1, SH-HKUST-1, IL@HKUST-1, and the recovered catalyst were illustrated in Figure 1. It could be seen that the diffraction peak positions of all samples were primarily the same. The main characteristic diffraction peaks of HKUST-1 crystals appeared at 20=6.66 °, 9.50 °, 11.68 °, 13.44 °, 19.12 °, and 25.96 °, which were aligned with the data reported in literature.⁵¹ After the chemical modification with ethanedithiol (Figure 1(b)), the intensities of diffraction peaks of SH-HKUST-1 were accordingly declined, indicating the decrease in the crystallinity degree of the sample. This was because a small amount of HKUST-1 crystallites were unstable and decomposed in the functionalization process. As shown in Figure 1(c), the introduction of vinyl-containing ionic liquid did not cause further damage to the frameworks and the MOF structure remained unchanged during immobilization. The pattern of the recovered catalyst was akin to that of the fresh one, proving a good stability of the prepared catalyst in esterification reactions.

The N_2 adsorption-desorption isotherms of HKUST-1, SH-HKUST-1, and IL@HKUST-1 were shown in Figure 2. The curves of the bare HKUST-1 were typical IV-type isotherms with an H4-type hysteresis loop, which was characteristic of

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microporous materials with regular channel structure. Compared with HKUST-1, the surface area and pore volume of the thiol-functionalized sample were both declined. The surface area dropped from 1395.3 m²/g to 816.0 m²/g, while the pore volume decreased from 0.56 cm³/g to 0.40 cm³/g. The main reason for this phenomenon was that the pores of the carrier were partially occupied by ethanedithiol after modification, inferring that the thiol functional groups existed inside the channels of the framework rather than outside the surfaces. For IL@HKUST-1, the surface area and pore volume further reduced to 386.9 m²/g and 0.23 cm³/g respectively due to the partial blocking of the pores. It demonstrated that the ionic liquid was successfully immobilized onto HKUST-1 by the reaction of vinyl and thiol. As observed in Figure 2(b) and (c), the hysteresis loops of the two samples had a tendency to translate into H3-type, which could be ascribed to the slight decomposition of the framework.

The FT-IR spectra (A) and partial enlargement (B) of $[HVIm-(CH_2)_3SO_3H]HSO_4$, 1,2-ethanedithiol, HKUST-1, SH-HKUST-1, IL@HKUST-1, and recovered IL@HKUST-1 were presented in Figure 3. For vinyl-containing ionic liquid, the bands around 1643 cm⁻¹, 1565 cm⁻¹, and 3143 cm⁻¹ could be attributed to the C=C, C=N, and C-H stretching vibrations of the imidazole ring, respectively. The band corresponding to the end-group C=C shear vibration was observed at 1417 cm⁻¹, while the bands at 1176 cm⁻¹ and 1050 cm⁻¹ were assigned to the S=O asymmetric and symmetric stretching vibrations of -SO₃H group.⁵² In Figure 3(c), the characteristic peaks of bare HKUST-1 were observed around 1646 cm⁻¹ and 1375 cm⁻¹, which were related to the C=O asymmetric and symmetric stretching vibrations of carboxylic

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ligands. The characteristic vibrational band of the C=C group at 1449 cm⁻¹ was also observed corresponding to the aromatic group. The thiol-functionalized sample showed two new peaks at 2590 cm⁻¹ and 695 cm⁻¹, indicating the presence of S-H and C-S vibrations. Meanwhile, the wavenumbers of the aliphatic C-H stretching vibrations around 2800-3000 cm⁻¹ were slightly shifted to larger values in comparison with the standard spectrum of ethanedithiol (Figure 3(b)), which demonstrated that the thiol groups had been successfully grafted onto the unsaturated metal sites (Cu^{2+}) in the HKUST-1 framework through S-Cu coordination bond.³⁹ It could be found in Figure 3(d) and (e) that the characteristic adsorption peaks of S-H and end-group C=C totally disappeared after the introduction of ionic liquid.⁴⁹ Furthermore, the main peaks of HKUST-1 as well as [HVIm-(CH₂)₃SO₃H]HSO₄ occurred in curve (e). These results also confirmed that the ionic liquid was grafted onto SH-HKUST-1 by chemical covalent bond. There was no obvious difference in characteristic peaks between recovered IL@HKUST-1 and the fresh one, ensuring a considerable reusability of the catalyst. The results obtained were well accordant with the analysis of XRD.

To investigate the surface morphologies and crystalloid structures of the samples, the SEM characterization was conducted and the correlative images were given in Figure 4. The original HKUST-1 crystals had regular octahedron geometry with smooth surfaces, and the average particle size was about 15 μ m. After the thiol-functionalization, the surfaces of SH-HKUST-1 became rougher and part of the crystals ruptured. The main reason was that the HKUST-1 framework was partially

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decomposed during the process. In comparison, the dispersion of the catalyst tended to get worse after the immobilization of ionic liquid, whereas the structure was conserved. It was worth noticing that the crystal grains of IL@HKUST-1 did not massively aggregated, indicating that most of the vinyl-containing ionic liquid diffused into the pores of the carrier and reacted with thiol groups rather than self-polymerized on the outer surfaces. The results agreed well with those of XRD and N₂ adsorption-desorption. The morphology of the recovered catalyst was virtually unchanged, which revealed that the stability of the catalyst was improved owing to the introduction of ionic liquid.

The TG curves of HKUST-1, SH-HKUST-1, and IL@HKUST-1 were illustrated in Figure 5. The bare HKUST-1 exhibited two weight loss stages corresponding to the departure of the adsorbed/coordinated water inside the pores (30-200 °C) and the collapse of HKUST-1 framework (200-350 °C). For the thiol-functionalized sample, a new stage between 100 °C and 220 °C was discovered, the weight loss was related to the decomposition of ethanedithiol. The TG curve of IL@HKUST-1 could also be divided into three stages. The weight loss within 200 °C was due to the loss of adsorbed water as well as the coordinated water molecules. In the second step (200-300 °C), the weight loss was attributed to the decomposition of ionic liquid. On the final stage, the trimesic acid disintegrated and the framework collapsed, as indicated by the weight loss between 300 °C and 400 °C. It was obvious that the decomposition temperature of IL@HKUST-1 was the highest among all the samples, suggesting that the interaction between ionic liquid and the carrier could enhance the thermal stability of the catalyst to some extent.

The data of elemental analysis revealed that the loading amount of ionic liquid in the fresh catalyst was calculated to be 0.97 mmol/g. While in the catalyst reused for 5 times, the corresponding value decreased to 0.93 mmol/g. The main reason was that a small amount of crystals were decomposed during reaction due to the poor chemical stability of HKUST-1,³⁴ which might cause the loss of ionic liquid inside the grains. The results corresponded well with those of SEM.

3.2. Catalytic activity of IL@HKUST-1

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To investigate the catalytic activity of IL@HKUST-1, the esterification of oleic acid with ethanol was selected as the probe reaction. Under the standard conditions (oleic acid 5 mmol, molar ratio of ethanol to oleic acid 12:1, catalyst amount 15 wt% (based on oleic acid), reaction time 4 h, reaction temperature 90 °C), the esterification reactions were carried out with different catalysts and the corresponding results were shown in Table 1.

It was clearly that the pure ionic liquid, as a homogeneous catalyst, showed high catalytic activity for the esterification of oleic acid. By contrast, only 4.8% conversion was obtained without catalyst. The activity of HKUST-1 was slightly enhanced due to the mild Lewis acidity of the unsaturated coordinated metal center (Cu²⁺), whereas the conversion of oleic acid was still below 10%. Besides, the introduction of thiol functional groups (SH-HKUST-1) had very little impact on the reaction. After the immobilization of ionic liquid, the conversion of oleic acid reached 92.1%, much higher than that of the carrier. The possible reason was that the ionic liquid was the

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main active component, and the acidity of the catalyst was greatly improved. Moreover, the newly joined Brønsted acid sites worked together with Lewis acid sites to promote the synergistic effect, which was more conducive to the reaction.^{52, 53}

In comparison with the results reported in literature,⁵⁴⁻⁶⁰ the catalytic activity of IL@HKUST-1 was roughly equal to that of the same kind of catalysts. It indicated that the introduction of acidic ionic liquid into MOFs was feasible and effective.

3.3. Effect of reaction conditions

For esterification of oleic acid with ethanol, the main factors influenced the conversion of oleic acid were molar ratio of ethanol to oleic acid, amount of catalyst, reaction time, and reaction temperature. In order to obtain the optimum reaction conditions, the single-factor experiments were carried out.

Effect of molar ratio. To investigate the effect of molar ratio on conversion of oleic acid, the dosage of ethanol was increased whereas other conditions were invariant. As shown in Figure 6, the conversion increased rapidly with increasing molar ratio of ethanol to oleic acid from 8:1 to 12:1. However, further increase of molar ratio led to slight decrease of the conversion. This was due to the reversibility of esterification reaction, in other words, excess ethanol was unfavorable because the active sites of catalyst and oleic acid were both diluted.⁵⁹ Therefore, we could conclude that the appropriate molar ratio was 12:1, and the corresponding conversion was 92.1%.

Effect of catalyst amount. The relationship between catalyst amount and the conversion of oleic acid was given in Figure 7. It was seen that the conversion

increased in the initial stage (from 5 wt% to 15 wt%) and slowly declined in the latter part (from 15 wt% to 25 wt%). Within a certain scope, the increase of catalyst amount could provide more active centers, and thus the conversion rate was improved. Instead, excessive amount of catalyst might lead to worse dispersion and partial coverage of the active sites, thereby avoiding the contact between the reactants and catalyst.⁵⁴ The optimal catalyst amount was chosen as 15 wt%.

Effect of reaction time. Figure 8 showed the effect of reaction time on conversion of oleic acid. At first, the conversion obtained rapid increase with the reaction time extending. After reacting for about 4 h, the esterification basically achieved equilibrium and the conversion of oleic acid reached 92.1% at this point. Further prolongation of time did not show significant promoting effect on the conversion. Taking into account of energy consumption at the same time, the appropriate reaction time was selected as 4 h.

Effect of reaction temperature. The last but equally important factor we discussed here was reaction temperature. As shown in Figure 9, the conversion of oleic acid increased from 62.8% to 92.1% as the reaction temperature was raised up from 50 °C to 90 °C. When the temperature was over 90 °C, the conversion almost remained unchanged. The molecule collision was more likely to happen at relatively high temperatures, therefore the reaction rate was accelerated with temperature ascending. However, too high temperature was unnecessary because the decrease of reactant concentration caused by the volatilization of ethanol was not conducive to the reaction.⁵⁹ For this reason, the suitable reaction temperature was set as 90 °C.

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Based on the analysis above, the optimal reaction conditions were listed as follows: molar ratio of ethanol to oleic acid 12:1, catalyst amount 15 wt% (based on oleic acid), reaction time 4 h, and reaction temperature 90 °C. Under these conditions, the conversion of oleic acid could reach 92.1%, showing high catalytic activity of the prepared catalyst.

Effect of different alcohols. The influence of different alcohols (methanol, ethanol, n-propanol, and n-butanol) as the reactants were also studied in the presence of IL@HKUST-1 catalyst. The esterification reactions were conducted under the same conditions and the results were illustrated in Figure 10.

The experimental results indicated that the prepared catalyst was active in a series of esterification reactions and all of the conversions were above 90%. The slight diversity between conversions could be attributed to the different solubility of reactants. It could be concluded that IL@HKUST-1 was an efficient heterogeneous catalyst for esterification of oleic acid with short-chain alcohols.

3.4. Reusability of IL@HKUST-1 and hot filtration test

To investigate the reusability of IL@HKUST-1, the esterification of oleic acid with ethanol was repeated for several times under the optimal reaction conditions. It was observed in Figure 11 that the conversion of oleic acid decreased from 92.1% to 86.3% (dropped by 5.8%) after 5 times of recycling. The hot filtration test was carried out to clarify the reasons for deterioration in activity. After reacting for 0.5 h, the esterification was stopped and the catalyst was removed from the reaction mixture. The liquid phase was analyzed and allowed to react for another 4.5 h. A slight

increase in conversion (Figure 12) was found in the subsequent process, which might be ascribed to the leaching of active component (ionic liquid) inside the channels. To further assess the leaching phenomenon, the ICP technique was performed to examine the variation of Cu^{2+} ions. The Cu^{2+} content in the catalyst decreased by 3.12% after 5 times recycle, indicating that the HKUST-1 framework was slightly decomposed during the process. It also suggested that the decomposition of the framework was the main reason for the loss of active component. There was only a minor decrease in conversion rate, revealing that the catalyst could still remain stable under reaction conditions and the catalyst had good reusability within a certain scope.

3.5. Catalytic mechanism of esterification over IL@HKUST-1 catalyst

In this experiment, the entity relationship (ER) model was applied to illustrate the possible reaction mechanism of esterification catalyzed by IL@HKUST-1. As shown in Figure 13, the whole process could be divided into five steps. At first, the carbonyl group of carboxylic acid was protonated by the immobilized ionic liquid catalyst, which was then attacked by the nucleophilic O atom of alcohol. In the third stage, the proton from oxonium ion transferred and the activated complex 4 was formed. After loss of water and subsequent deprotonation, the product ester was obtained and the catalyst IL@HKUST-1 was regenerated.

4. Conclusions

In this study, the acidic ionic liquid [HVIm-(CH₂)₃SO₃H]HSO₄ was synthesized and successfully grafted onto the thiol-functionalized HKUST-1 by chemical covalent

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bond. The ethanedithiol bridged the gap between ionic liquid and HKUST-1, thus the vinyl-containing ionic liquid could be immobilized onto the carrier through thiol groups. Furthermore, the introduction of ionic liquid slightly enhanced the thermal stability of framework and greatly improved the acidity of the catalyst. The bi-functional IL@HKUST-1 catalyst exhibited good activity for esterification of oleic acid with ethanol, and a satisfactory conversion of 92.1% was obtained under optimal reaction conditions. The catalyst could be easily recovered and reused for at least 5 times without obvious decrease in activity. However, the chemical stability of HKUST-1 in acidic medium is still not so satisfactory. Thus, it is a crucial problem to prevent the decomposition of framework and it is worth investigating in the further. In conclusion, this work provides a new thinking for the combination between ionic liquid and MOF, which is very important for designing novel immobilized ionic liquid catalysts.

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Captions for Tables and Figures

 Table 1. Activities of various catalysts for the esterification of oleic acid with short alcohols.

Scheme 1. Preparation of the ionic liquid [HVIm-(CH₂)₃SO₃H]HSO₄.

Scheme 2. Preparation of the immobilized ionic liquid IL@HKUST-1.

Figure 1. The XRD patterns of HKUST-1 (a), SH-HKUST-1 (b), IL@HKUST-1 (c),

and recovered IL@HKUST-1 (d).

Figure 2. The N_2 adsorption-desorption isotherms of HKUST-1 (a), SH-HKUST-1 (b), and IL@HKUST-1 (c).

Figure 3. The FT-IR spectra (A) and partial enlargement (B) of [HVIm-(CH₂)₃SO₃H]HSO₄ (a), 1,2-ethanedithiol (b), HKUST-1 (c), SH-HKUST-1 (d), IL@HKUST-1 (e), and recovered IL@HKUST-1 (f).

Figure 4. The SEM images of HKUST-1 (a_1, a_2) , SH-HKUST-1 (b_1, b_2) , IL@HKUST-1 (c_1, c_2) , and recovered IL@HKUST-1 (d_1, d_2) .

Figure 5. The thermogravimetric curves of HKUST-1 (a), SH-HKUST-1 (b), and IL@HKUST-1 (c).

Figure 6. Effect of molar ratio on conversion of oleic acid. Catalyst amount = 15 wt%, t = 4 h, T = 90 °C.

Figure 7. Effect of catalyst amount on conversion of oleic acid. Molar ratio = 12:1, t = 4 h, T = 90 °C.

Figure 8. Effect of reaction time on conversion of oleic acid. Molar ratio = 12:1, catalyst amount = 15 wt%, T = 90 °C.

12:1, catalyst amount = 15 wt%, t = 4 h.

Figure 10. Esterification of oleic acid with different alcohols catalyzed by

IL@HKUST-1. Molar ratio = 12:1, catalyst amount = 15 wt%, t = 4 h, T = $90 \degree \text{C}$.

Figure 11. The recycling of IL@HKUST-1 catalyst for esterification of oleic acid

with ethanol. Molar ratio = 12:1, catalyst amount = 15 wt%, t = 4 h, T = 90 °C.

Figure 12. The hot filtration test for esterification with IL@HKUST-1 catalyst.

Figure 13. Catalytic mechanism of esterification over IL@HKUST-1 catalyst.

Entry	Catalyst	Alcohol	Alcohol/Acid	Conversion (%)	Ref.
1	without catalyst	ethanol	12:1	4.8	this work
2	[HVIm-(CH ₂) ₃ SO ₃ H]HSO ₄	ethanol	12:1	94.6	this work
3	HKUST-1	ethanol	12:1	8.2	this work
4	SH-HKUST-1	ethanol	12:1	8.7	this work
5	IL@HKUST-1	ethanol	12:1	92.1	this work
6	H_2SO_4	ethanol	12:1	90.1	54
7	H ₃ PW/ZrO ₂	ethanol	6:1	88.0	55
8	sulfonated cation exchange	ethanol	9:1	93.0	56
	resin				
9	[BMIM][FeCl ₄]	methanol	22:1	83.4	57
10	[BMIM][HSO ₄]	methanol	9:1	80.6	58
11	IL/Fe-SBA-15	methanol	6:1	87.7	59
12	MPEG-350-ILs	methanol	10:1	84.5	60

Table 1.	Activities	of various	catalysts	for the	esterification	of oleic	acid v	vith short	alcohols.
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Step 1: 0 °C, 24 h; Step 2: 60 °C, 12 h.

Scheme 1. Preparation of the ionic liquid [HVIm-(CH₂)₃SO₃H]HSO₄.



Step 1: 25 °C, 12 h; Step 2: 80 °C, 30 h.

Scheme 2. Preparation of the immobilized ionic liquid IL@HKUST-1.



Figure 1. The XRD patterns of HKUST-1 (a), SH-HKUST-1 (b), IL@HKUST-1 (c),

and recovered IL@HKUST-1 (d).



Figure 2. The N₂ adsorption-desorption isotherms of HKUST-1 (a), SH-HKUST-1 (b),

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Figure 3. The FT-IR spectra (A) and partial enlargement (B) of [HVIm-(CH₂)₃SO₃H]HSO₄ (a),

1,2-ethanedithiol (b), HKUST-1 (c), SH-HKUST-1 (d), IL@HKUST-1 (e),

and recovered IL@HKUST-1 (f).



Figure 4. The SEM images of HKUST-1 (a1, a2), SH-HKUST-1 (b1, b2), IL@HKUST-1 (c1, c2),

and recovered IL@HKUST-1 (d1, d2).



Figure 5. The thermogravimetric curves of HKUST-1 (a), SH-HKUST-1 (b),

and IL@HKUST-1 (c).



Figure 6. Effect of molar ratio on conversion of oleic acid.

Catalyst amount = 15 wt%, t = 4 h, T = 90 °C.



Figure 7. Effect of catalyst amount on conversion of oleic acid.

Molar ratio = 12:1, t = 4 h, T = 90 °C.



Figure 8. Effect of reaction time on conversion of oleic acid.

Molar ratio = 12:1, catalyst amount = 15 wt%, T = $90 \degree \text{C}$.



Figure 9. Effect of reaction temperature on conversion of oleic acid.

Molar ratio = 12:1, catalyst amount = 15 wt%, t = 4 h.





Molar ratio = 12:1, catalyst amount = 15 wt%, t = 4 h, T = 90 °C.



Figure 11. The recycling of IL@HKUST-1 catalyst for esterification of oleic acid with ethanol.

Molar ratio = 12:1, catalyst amount = 15 wt%, t = 4 h, T = 90 °C.



Figure 12. The hot filtration test for esterification with IL@HKUST-1 catalyst.



Figure 13. Catalytic mechanism of esterification over IL@HKUST-1 catalyst.



The IL@HKUST-1 catalyst was synthesized by a post-synthetic modification strategy. HKUST-1 was chemically modified with 1,2-ethanedithiol, and the vinyl-containing ionic liquid was then grafted onto the carrier through thiol groups. The introduction of ionic liquid greatly improved the acidity of the material, making it an efficient and recyclable catalyst for the esterification of oleic acid with ethanol.