



Stable and recyclable MIL-101(Cr)–Ionic liquid based hybrid nanomaterials as heterogeneous catalyst



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ABSTRACT

Brønsted acidic ionic liquid, *N*-methyl-2-pyrrolidonium methyl sulfonate ([NMP]⁺ CH₃SO₃⁻) immobilized on MIL-101(Cr) was fabricated by simple impregnation method with a good combination of MIL-101(Cr) and IL species. The worthiness of IL/MIL-101(Cr), as a Brønsted acid catalyst, has been examined for the esterification of acetic acid with amyl alcohol and Friedel–Crafts acylation of anisole. Our findings demonstrated that IL/MIL-101(Cr) catalyst exhibited distinct catalytic activity with respect to the other catalysts towards the esterification reaction and Friedel–Crafts acylation of anisole. The Brønsted acidic catalysts loaded on MIL-101(Cr) as a new category of porous materials are probably auspicious heterogeneous catalysts for acid-catalyzed to replace the use of traditional homogeneous catalysts. Furthermore, the catalyst can be easily removed from the reactions mixtures and reuse for posterior reactions, more than six times without any considerable decay in catalytic performance.

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1. Introduction

For assorted applications, such as adsorption, membrane science, and catalysis, acid catalysts are abundantly under-exploited in the chemical industry [1]. Mineral acids as homogeneous catalysts usually have high catalytic activity, however, they have many disadvantages as side reactions, corrosion and huge amounts of harmful wastes, which can cause environmental problems [2]. Recently, the reusable rigid acidic catalysts became much significant due to their prospect to substitute harmful homogeneous acidic catalysts in industrial operations [3,4]. Acidic heterogeneous catalyzing agents can be effectively isolated from the reaction blend by filtration or centrifugation and don't require any special treatments, consequently giving an ecologically favorable process and decreasing the expense of handling [5]. Another favorability of the heterogeneous catalyst is the reusability [6,7]. The field of metal–organic frameworks (MOFs), a new category of porous materials self-assembled from metal ions or clusters and polytopic rigid organic linkers, has provided a good candidate for catalytic applications owing to (i) effective framework in comparison with other micro- and mesoporous materials. (ii) Well-defined channels with a tunable pore size that able to accommodate various species with different sizes and shape. (iii) MOF backbone can be incorporated

with multiple metals and/or organic linkers (multivariate (MTV) functionalization), leading to possible functional sites of unique distribution within the pores while the original structure is retained [8–12].

Recently, several strategies for acid sites functionalizing MOFs have been introduced, including post-synthesis and metal encapsulation to tuned framework through coordination bonds between metal center and Lewis or base guests [13], post framework sulfonation, amination, *N*-substituted aminosulfonic acids and encapsulation of heteropolyacids [14–16]. In spite of these promising approaches, the development of general and facile methods to introduce more sites within MOFs remains a challenge.

Today, an ionic liquids (ILs) as environmental-friendly acidic catalysts have received wide attention because of their unique characteristics like considerable solubility, negligible volatility, non-flammable, non-corrosive and remarkable thermal stability. Ionic liquids (ILs) are defined as salt with a melting point lower than the boiling point of water. Typically, ILs are composed of organic onium cations and inorganic anions. Additionally, the solubility of ionic liquids in various reaction media can be controlled and easily fine-tuned by changing of both cations and anions [17–24]. Ionic liquids (ILs) have emerged as alternative solvents for various organic syntheses and attracted increasing attention for various catalytic applications. However, there are some drawbacks in the catalytic field such as limited solubility in organic compounds (especially polar molecules), causing not only the loss of catalytic efficiency but also resulted in the difficulty of purification due

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to the high viscosity of the reaction media. Among attempts have been made to overcome these problems is immobilization the ILs on solid porous materials such as crosslinked polystyrene-divinylbenzene [24], mesoporous materials [7] and Fe₃O₄ nanoparticles [25]. Indeed, utilization of immobilized acidic ionic liquids (ILs) on robust backings as heterogeneous catalysts displays many advantages other than the use of acidic ILs directly. Such immobilization may lead to boost the available effective sites on the catalyst surface and reduces the used amount of ILs. The ionic liquid layer on the support surface acts as a homogeneous medium for the catalyzed processes however the catalyst macroscopically seems solid, consequently it is easily separated from the medium [2].

Despite the fact that there are abundant future prospects to apply MOFs as solid supports for ILs, ILs/MOFs composites showed considerable properties owing to the nanosizing of ILs than the bulk ionic liquid that showed the usual melting or freezing characteristics [26]. Thus, it is very interesting and significant to prepare and explore for the first time the application of chemically confinement ILs-MOFs for catalysis. As a prevalent Acidic catalyzed model reaction, Esterification is a standout among the most connected reactions in organic chemistry, with the hugeness in the synthesis of fragrances, polymers, and paints [27]. As well, Friedel–Crafts acylation of aromatics is a critical process, which is typically utilized as a part of fine synthetic, pharmaceutical commercial projects polymers, and paints, etc. [28].

Herein, we demonstrate how to chemically incorporate highly Brønsted acidic IL, *N*-methyl-2-pyrrolidonium methyl sulfonate, into porous MIL-101(Cr) to avoiding leaching of ILs through grafting the IL into the residual terephthalic species coordinated to CUS (coordinatively unsaturated metal sites) in MIL-101(Cr) by simple impregnation method under ambient conditions as a significant heterogeneous and economically acidic catalyst for esterification and Friedel–Crafts acylation reactions.

2. Experimental

2.1. Chemicals

All the used chemicals in this work were of analytical grade and used as received without further purification. Chromium (III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, 99%), hydrofluoric acid (HF, 48%), *N*-methyl-2-pyrrolidone (C₅H₉NO, 99.5%), 1-pentanol (CH₃(CH₂)₄OH, 99%), acetic acid, (CH₃CO₂H, 99%), anisole (CH₃OC₆H₅, 99.7%), acetic anhydride ((CH₃CO)₂O, 99.5%) and toluene (C₆H₅CH₃, 99.5%) were taken up from Sigma–Aldrich Chemicals. Methane sulfonic acid (CH₃SO₃H, 99%), ammonium fluoride (NH₄F, 98%), terephthalic acid (TPA, 98%), ethanol (CH₃CH₂OH, 99%), and ethyl acetate (CH₃COOC₂H₅, 99%) were purchased from ACROS Organics.

2.2. Synthesis

2.2.1. Synthesis of MIL-101(Cr)

Hydrothermal synthesis of MIL-101(Cr) from Cr(NO₃)₃·9H₂O, TPA and deionized water was in accordance with a described procedure [29]. Typically, a Cr(NO₃)₃·9H₂O (6.0 g), terephthalic acid (3.76 g) and HF (0.75 ml) were dissolved in 75 ml of H₂O in Teflon beaker, then introduced into 150-ml Teflon-line autoclave. The mixture was then heated in an oven at 220 °C for 8 h. By the end of the reaction, the temperature lowered to the ambient temperature, and the developed green-colored powder was obtained by filtration to remove the excess recrystallized terephthalic acid. The MIL-101(Cr) was first activated by suspending into 300 ml water with stirring for 5 h at 70 °C and then separated using a fine pore fritted glass filter followed by drying at 150 °C on standing overnight to take out powdered MIL-101(Cr) [30]. The second activation for the same sample was carried out by soaking the sample in 150 ml 30 mM NH₄F and stirred for 10 h at 60 °C. Finally, the solid product was separated by filtration and washed with hot water and then vacuum dried at 80 °C for 12 h.

2.2.2. Synthesis of *N*-methyl-2-pyrrolidonium methyl sulfate (IL)

The Brønsted acidic IL (*N*-methyl-2-pyrrolidonium methyl sulfonate, ([NMP]⁺ CH₃SO₃⁻) was prepared (Scheme 1) as described elsewhere [31] with slight modification. Typically, 9.9 g of *N*-methyl-2-pyrrolidone (0.1 mol) was stirred with (15 ml) ethyl acetate in a 50 ml round flask. After that, 9.6 g of methane sulfonic acid (0.1 mol) in 15 ml ethyl acetate was added dropwise within 30 min in an ice bath. The reaction continued for extra 4 h at ambient temperature. Finally, ethyl acetate was taken away under diminished pressure at 80 °C till the initial volume added.

2.2.3. Synthesis of IL/MIL-101(Cr) catalysts

The impregnation reaction encapsulation technique was used to encapsulate *N*-methyl-2-pyrrolidonium methyl sulfonate IL onto MIL-101(Cr) framework. In a typical synthesis, 2.0 g of IL was diluted with 10 times volume of ethyl acetate was added to 1 g of MIL-101(Cr) suspended in 10 ml ethyl acetate under stirring for 4 h at 45 °C. Then, the solvent was removed under vacuum at 80 °C and stirring of 150 rpm. The obtained gel was extracted in Soxhlet extractor using ethanol/toluene (1:1) as co-solvent, and the weight of the obtained solid was determined to explore the maximum capacity of MIL-101(Cr). To maximize the ratio of IL occluded in MIL-101(Cr) pores, different loading of IL behind maximum capacity are prepared and denoted as X% MIL-101(Cr) where X (5, 10, 15, 20) indicates the percent ratio of the ionic liquid on MIL-101(Cr). The elemental composition based C, N, H % only for MIL-101(Cr): C, 43.00; H, 2.26%, while after grafting the IL become C, 42.73; H, 2.46; N, 0.32% (5% IL/MIL-101(Cr)), C, 42.44; H, 2.67; N, 0.65% (10% IL/MIL-101(Cr)), C, 42.17; H, 2.87; N, 0.98% (15% IL/MIL-101(Cr)) and C, 41.96; H, 3.02; N, 1.23% (20% IL/MIL-101(Cr)). Consequently, the real grafting percent after Soxhlet extraction is of 4.6, 9.2, 13.7, and 17.2% for 5, 10, 15 and 20% IL/MIL-101(Cr), respectively.

2.3. Characterization

X-ray diffraction patterns were recorded by means of X'PERT X-ray diffractometer, equipped with Cu- α radiation (40 kV, 40 mA) ($\lambda = 1.5406 \text{ \AA}$). The diffractogram is in the 2θ range of 4 to 20°, with a scanning speed of 2° in 2/min. For the FT-IR spectra, a KBr disk containing the sample was prepared and scanned from 4000 to 500 cm⁻¹ using (Shimadzu FT-IR, Japan). The nitrogen physisorption isotherms and the specific surface area were measured at -196 °C using the Quantachrome Autosorb iQ MP gas sorption analyzer. Prior to the analysis, the samples were degassed at 150 °C for 12 h. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2010 electron microscope operating at 200 kV. The surface electronic states of the prepared catalysts were characterized by XPS (X-ray photoelectron spectroscopy) on ESCALAB 250 spectrometer. The acidity measurement of the samples was investigated using potentiometric titration [32,33].

2.4. Catalytic performance

2.4.1. Esterification reaction

The esterification reaction was carried out using a certain percent of catalyst (1, 3, 5 and 10%). Typical, a mixture of acetic acid and amyl alcohol (1:1) were stirred and heated to achieve the reaction temperature (30, 60, 80 and 100 °C). The activated catalyst was then added, and the mixture was stirred for 1 h. The reaction mixture was then collected and analyzed using GC (Varian Technologies, model 3800 GC, capillary column DHA-100).

2.4.2. Friedel–Crafts acylation

Friedel–Crafts acylation of anisole with acetic anhydride was carried out by mixing (20 mmol) anisole, (5 mmol) acetic anhydride followed by magnetically stirred and heated to achieve the reaction temperature (80–120 °C). Then activated catalyst (5 wt%) was added and the

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