



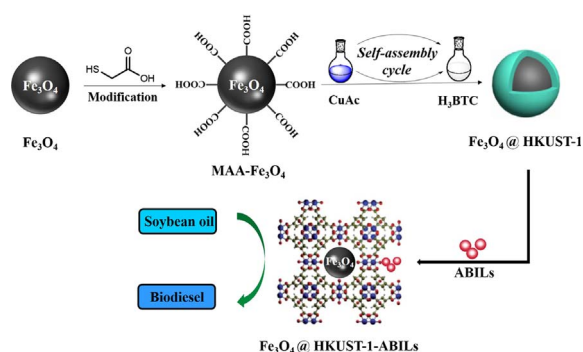
Full Length Article

Basic ionic liquid functionalized magnetically responsive Fe_3O_4 @HKUST-1 composites used for biodiesel production

Wenlei Xie*, Fei Wan

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Heterogeneous catalyst
Basic ionic liquid
Metal-organic framework
Magnetic nanoparticle
Transesterification
Biodiesel

ABSTRACT

The main purpose of this present work is to fabricate a magnetically recyclable solid catalyst for the production of biodiesel to meet the demand of green and clean production. To accomplish this, the core-shell structured Fe_3O_4 @HKUST-1 composites with a magnetic core and a porous metal-organic framework shell were fabricated by using a versatile Layer-by-Layer assembly method, and then basic ionic liquids were encapsulated within the core-shell magnetically responsive material, resulting in a solid hybrid base catalyst. Various techniques such as XRD, TEM, FT-IR, VSM and nitrogen adsorption-desorption were employed to characterize the as-prepared solid base catalyst. The characterization results revealed that Fe_3O_4 nanoparticles were well coated with metal-organic framework HKUST-1 with the formation of core-shell structured nanocomposites, and moreover the basic ionic liquid had been successfully encapsulated within the magnetic nanocomposites. Furthermore, the solid base catalysts possessed superparamagnetic behavior and high saturation magnetization, allowing them to be facilely separated from the reaction mixture by using an external magnetic field. The solid base catalyst appeared to be an efficient and environmentally benign catalyst for the transesterification of soybean oil with methanol for the production of biodiesel, giving 92.3% oil conversion to methyl esters within 3 h with a catalyst loading of 1.2 wt% and a methanol/oil molar ratio of 30:1 at reflux temperature of methanol. The solid catalyst could be readily recovered by simple magnetic decantation and reused for several times without significant degradation in its catalytic activity.

* Corresponding author.

E-mail address: xwenlei@163.com (W. Xie).

1. Introduction

The development of clean and renewable energy is recognized as a viable solution for the ever-increasing energy crisis and environmental pollution [1]. Biodiesel, consisting of long-chain fatty acid methyl esters (FAMEs) derived by the transesterification of triglycerides with methanol, is known to be a green and sustainable fuel to replace the dwindling fossil fuel owing to the advantages of its renewability, non-toxicity, low sulfur content, high biodegradability, and low combustion pollution emissions [1,2]. Industrially, biodiesel is usually produced in the presence of homogeneous alkaline catalysts, such as NaOH, KOH or CH_3ONa , since they are high efficiency at relatively low temperature and low cost [3–5]. However, the difficulties in the catalyst recovery together with the undesirable wastewater yielded in the downstream purification processes, are the major constraints to the homogeneous base-catalyzed transesterification process [4]. Such disadvantages of homogeneous catalysts can increase the cost of biodiesel production. To solve these problems, the recyclable and readily separable solid catalysts for the production of biodiesel have been widely investigated, so that the utilization of harmful substances as catalysts and formation of toxic waste water can be thus avoided [5,6]. The solid catalyst can offer an opportunity to reduce the impact of environmental pollution and to increase industrial interest for biodiesel production. Examples of solid base catalysts include CaO/ZrO_2 , $\text{MgO/MgAl}_2\text{O}_4$, KOH/NaX , CaO/SnO_2 , $\text{CaO/MoO}_3/\text{SBA-15}$, $\text{Sr}_3\text{Al}_2\text{O}_6$, KNa/ZIF-8 , and biguanide-functionalized nanocomposites [7–15], which were shown to have high catalytic activities in the transesterification reaction. However, for some heterogeneous base catalysts, leaching of active components could be generally observed during the transesterification process especially when excess methanol was applied to shift the reaction equilibrium towards the direction of biodiesel formation [9,16]. These leached catalytic species yield some homogeneous catalytic activities and require removal from the final product, and accordingly it could hinder the industrial application in biodiesel production as a heterogeneous catalyst, and inevitably leading to both homogeneous and heterogeneous pathway. In view of this, it is of great interest to improve the stability of the active species for developing a more stable solid catalyst from a sustainable chemistry point.

Despite the distinct advantages of heterogeneous catalysts, the drawbacks originated from heterogeneous catalysts are their difficulties in recovering them by filtration or centrifugation from the liquid reaction mixture due to their small diameter and their inevitable loss of solid catalysts during the separation processes, thus severely precluding their wide applications in an industrial scale [17]. To further address the issue of recyclability and reusability, magnetic nanoparticles are particularly attractive as proper support materials for the heterogeneous catalysts due to their advantages of fast and facile catalyst separation from the reaction mixture by applying an external magnetic field, thereby eliminating process steps such as conventional centrifugation and filtration [18]. However, the magnetic nanoparticles always tend to aggregation into large clusters and lose the single-domain owing to their magnetic dipole-dipole attraction [19], which can restrict the dispersion of the nanoparticles in the reaction mixture. Encapsulation of magnetic nanoparticles into porous matrix could generate a multifunctional catalyst support with magnetic properties, which is considered as an effective way to improve their chemical stabilities and prevent their aggregations [20]. For example, a coat of porous material can be deposited onto the surface of magnetic nanoparticles with the formation of core-shell structured magnetic nanocomposites. These composites possess the magnetic responsiveness, high stability, and chemical liable surface, making them ideal support candidates for the heterogeneous catalysts.

Over the past several years, metal-organic frameworks (MOFs), as a class of crystalline hybrid materials prepared by using self-assembly of metal ions or metal clusters with organic linkers, have attracted tremendous attention due to their huge specific surface area, tunable pore

size and versatile architecture. Such unique features make MOFs as promising porous materials for their utilizations such as gas storage, separation process, and catalyst materials [21]. In particular, some efforts are reported to prepare the MOFs with a desired functionality for performing catalytic reactions [22]. The post-synthesis modification (PSM) of MOFs has been demonstrated to be a promising strategy for the construction of advanced MOFs catalyst materials [23]. In this regard, the encapsulation of active sites or species within MOFs can be achieved by the PSM method at the metal or organic components.

Nowadays, functionalized ionic liquids (ILs) have been commonly utilized as an efficient catalyst for the organic transformation [24,25]. Unfortunately, their difficulties in the recovery and unendurable viscosity have restrained their wide applications in the catalytic reactions [26,27]. With this respect, the heterogenization of ILs on appropriate porous carriers would be a viable and appealing approach to fabricate the efficient solid catalyst [27]. To date, varieties of strategies for the synthesis of core-shell magnetic nanoparticles are under investigations [19,20,28]. And, the preparation of core-shell structured magnetic architecture on the basis of MOFs is also reported in the open published literature [29,30]. Very recently, Guan and coworkers synthesized a series of magnetic hybrid nanocomposites functionalized by Brønsted acidic ILs and investigated their catalytic activities in the esterification of oleic acid with methanol for the biodiesel production [31–33]. So far as we know, the application of supported basic ILs, especially those based on the core-shell structured magnetic MOFs materials and as a solid catalyst for the transesterification reaction, has seldom been disclosed for the production of biodiesel in the literatures [34].

Based on the above considerations, the main purpose of the present research is to prepare the core-shell structured magnetic $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ materials, on which the basic ILs are immobilized, thus allowing the favorable combination of the advantages of ILs and porous supports. For this purpose, Fe_3O_4 nanoparticles were firstly prepared by the solvothermal method, then the coating of Fe_3O_4 core with HKUST-1 type MOFs was performed through a Layer-by-Layer stepwise assembly procedure for the formation of the core-shell magnetic $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ materials. Thereafter, the basic ILs were immobilized onto the magnetically responsive $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ support by a coordination bond to prepare the solid base catalyst. The $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ support and so-prepared solid catalyst were thoroughly characterized by means of transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectra, X-ray powder diffraction (XRD), vibrating-sample magnetometer (VSM), and nitrogen adsorption-desorption techniques. The catalytic activities were tested in the heterogeneous transesterification of soybean oil with methanol for the production of biodiesel. Furthermore, the operational durability and reusability of the solid base catalyst were also investigated in the current research.

2. Materials and methods

2.1. Materials

Commercial soybean oil, with an average molecular mass for triacylglycerols of 873 g/mol, was purchased from a local grocery store, having the following fatty acid compositions: 12.3% palmitic acid, 5.8% stearic acid, 26.5% oleic acid, 49.4% linoleic acid, and 5.9% linolenic acid. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ethylene glycol, mercaptoacetic acid, copper acetate hydrate (CuAc , $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), and imidazole, were of analytical grades and purchased from Tianjin Kermel Chemical Reagent Company (Tianjin, China). Benzene-1,3,5-tricarboxylic acid (H_3BTC), 1-methylimidazole (99%), 2-bromoethylamine hydrobromide (99%) were procured from Aladdin Biological Technology Company (Shanghai, China). All other chemicals were commercially available and used without further purification.

Download English Version:

<https://daneshyari.com/en/article/6631652>

Download Persian Version:

<https://daneshyari.com/article/6631652>

[Daneshyari.com](https://daneshyari.com)