



Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem<http://www.journals.elsevier.com/journal-of-energy-chemistry/>

Zirconium-containing UiO-66 as an efficient and reusable catalyst for transesterification of triglyceride with methanol

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ARTICLE INFO

Article history:

Received 26 February 2016

Revised 29 April 2016

Accepted 20 June 2016

Available online xxx

Keywords:

Metal organic frameworks

Solid acid

Transesterification

UiO-66

Catalyst

ABSTRACT

Zirconium-based MOFs of the UiO family have attracted considerable attention due to their high thermal, chemical and mechanical stability. With the aim of further exploring the applications of zirconium-based UiO-66 in acid-catalyzed reactions and elucidating the effects of the defects in UiO-66 materials on their catalytic performances, in this work, a series of zirconium-containing UiO-66 samples were synthesized by varying the synthesis temperatures and BDC/Zr (terephthalic acid/ZrCl₄) ratios in the synthesis system. The synthesized UiO-66 samples were characterized by X-ray diffraction (XRD), N₂ adsorption-desorption, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), temperature-programmed desorption of NH₃ (NH₃-TPD). Their catalytic performances were investigated in transesterification of tributyrin and soybean oil with methanol. The results showed that UiO-66 samples with different amounts of defects could be successfully prepared by varying the synthesis temperatures and/or the BDC/Zr ratios used in the synthesis system. The catalytic activities of the UiO-66 materials greatly depended on their linker defects and enhanced with the increase of the defect amount. The UiO-66 was an efficient catalyst for transesterification of tributyrin and soybean oil with methanol under mild reaction conditions and its catalytic activity was comparable to other solid acid catalysts reported in the literatures. The UiO-66 catalyst was relatively stable and could be reused.

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1. Introduction

Biodiesel is defined as alkyl esters of fatty acids derived from renewable biological products such as vegetable oils and animal fats. Biodiesel contains no sulfur and aromatic species, contributes much less to global warming than fossil fuels, and thereby is an attractive alternative to diesel usually produced from petroleum. Biodiesel can be produced by transesterification of triglycerides to methyl esters with homogeneous or heterogeneous strong base or acid as catalysts [1–3]. Compared with acid catalysts, alkaline catalysts are more effective and less corrosive, thus, commercially, homogeneous alkaline catalysts, such as NaOH or KOH are usually employed [4]. Nevertheless, homogenous alkaline catalysts suffer from many disadvantages, including catalyst separation, alkaline wastewater neutralization, and the salt (coming from neutralization step) contamination on glycerol by-product [5]. In addition, alkaline catalyst is sensitive to acid and cannot be used to treat low quality feedstock with high FFA content (>0.5 wt% of free fatty

acids (FFA)) [6,7]. Therefore, the use of solid acid catalysts instead of homogeneous alkaline catalysts is preferred [8,9]. Sulfated or tungstated zirconia and supported heteropolyacids are the most used solid acids for biodiesel production by transesterification [10–12]. However, these solid acid catalysts often face the following problems: (1) large mass transfer resistance due to lack of large textural properties; (2) facile deactivation under the reaction conditions; (3) the difficulty in catalyst reuse. Sulfonic functionalized ion-exchange resins are also attractive solid acid catalysts but their low thermal stabilities limit their use at high reaction temperatures [13]. Hence, the development of an efficient and reusable heterogeneous solid acid catalyst for biodiesel production is highly desirable.

Metal organic frameworks (MOFs) are a class of interesting three-dimensional crystalline porous materials constructed by copolymerization of multidentate organic ligands with transition metal ions or metal ion clusters. MOFs, due to their inherent large surface areas, uniform but tunable cavities and tailorable chemistry, have shown wide potential applications in gas storage and separation, molecular recognition and catalysis [14–16]. Among a large number of MOFs, zirconium-based MOFs of the UiO family have attracted considerable attention due to their high thermal, chemical and mechanical stability [17–20]. UiO-66 with inorganic

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Table 1. The names of the synthesized UiO-66 samples and the synthesis conditions.

Sample	ZrCl ₄ (mmol)	Terephthalic acid (mmol)	Synthesis temperature (°C)
UiO-66-100-1	5	5	100
UiO-66-100-2	5	10	100
UiO-66-160-2	5	10	160
UiO-66-220-2	5	10	220

[Zr₆O₄(OH)₄]¹²⁺ brick and terephthalate linkers is considered to be the parent of the other UiO members, from which other members are derived via isorecticular synthesis [17]. Zr-containing UiO-66 type MOFs usually display well Lewis acid character and have exhibited excellent catalytic performances in various acid-catalyzed reactions [21–25]. For example, Vermoortele and his co-workers have used UiO-66 as catalyst for citronellal cyclization [22]. Cirujano and his co-workers have demonstrated that UiO-66 and UiO-66-NH₂ are active and stable catalysts for the acid-catalyzed esterification of various saturated fatty acids with MeOH and EtOH with activities comparable (in some cases superior) to other solid acid catalysts previously reported in literature [24]. These exciting results inspire us to further explore the application of zirconium-based MOFs in other acid-catalyzed reactions.

In this work, we synthesized a series of UiO-66 samples with different amounts of linker defects by varying the synthesis temperatures and BDC/Zr (terephthalic acid/ZrCl₄) ratios in the synthesis system and investigated their catalytic performances in transesterification of tributyrin and soybean oil with methanol. The results show that UiO-66 is an efficient and reusable catalyst for transesterification reaction and the ligand defects have a great influence on its catalytic performance.

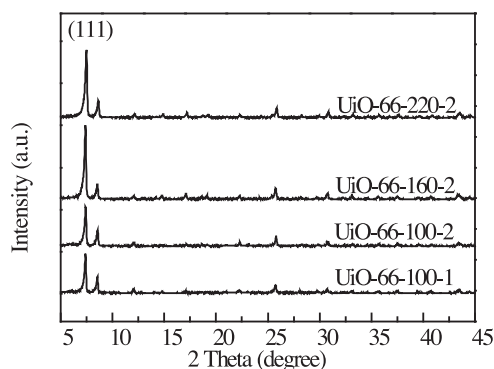
2. Experimental

2.1. Synthesis of UiO-66 samples

The UiO-66 samples were synthesized according to the method reported in the literature [26]. Typically, ZrCl₄ (1.17 g, 5 mmol), HCl (0.8 mL, 37%) and terephthalic acid (BDC, 0.83 g, 5 mmol) were added to 30 mL of DMF (N,N'-dimethyl formamide). The resulting mixture was transferred to a 100 mL Teflon-liner stainless steel autoclave. The autoclave was sealed and heated at 120 °C for 20 h. The material recovered by filtration was firstly washed thoroughly with fresh DMF for three times, and then extracted with methanol to completely remove residue DMF. Finally, the obtained solid was dried under vacuum at 200 °C for 3 h. The other samples were also prepared according to the similar procedure except for the different synthesis temperatures or the BDC/Zr ratios. Table 1 summarized the sample names and the synthetic conditions. The synthesized samples were denoted as UiO-66-x-y, in which x was the synthesis temperature and y was the BDC/Zr ratios in the synthesis system.

2.2. Characterization of sample

Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max-2500 diffractometer with Cu K α radiation. Thermogravimetric measurement was performed on a Netzch SAT449 F3 thermal analysis system with an elevating rate of 10 °C/min from 50 °C to 700 °C in air atmosphere. N₂ physisorption isotherms were performed at -196 °C using a Quantachrome Nova 1200e. Prior to measurement, the sample was evacuated at 300 °C for 3 h. The surface area was calculated by BET method at relative pressure of P/P₀ = 0.05–0.25. Scanning electron microscopy (SEM) was performed using a Hitachi 4800. NH₃-TPD measurement was performed using AutoChem 2720 instrument with He as the carries

**Fig. 1.** XRD patterns of the different UiO-66 samples.

gas (30 mL/min). First, 0.1 g of catalyst was charged into a quartz tube, and then pretreated at 300 °C for 3 h. After being cooled to 50 °C, the sample was saturated with dried NH₃, and then blown with He to remove the physical-adsorbed NH₃. Finally, desorption process was started from 50 °C to 350 °C at a heating rate of 10 °C/min and monitored by a thermal conductivity detector.

2.3. Catalytic reaction

The transesterification of tributyrin was carried out in a Teflon-lined autoclave in an oil bath. For transesterification of tributyrin, 1.3 mmol of tributyrin (Aldrich, 98%) was dissolved in a specified quantity of methanol, and then the mixture was put into the reactor containing 0.1 g of catalyst. The reaction mixture was magnetically stirred at 800 rpm at the designed temperature. The product analysis was conducted on a SHIMADZU GC-2014 gas chromatograph equipped with a FID detector and an Rtx-1 capillary column with chlorobenzene as the internal standard.

The transesterification of soybean oil were also conducted in a Teflon-lined autoclave. 1.41 g (44 mmol) of methanol, 0.9 g (about 1.1 mmol) of soybean oil and 0.1 g of catalyst were added into the reactor, and then the reaction mixture was magnetically stirred at 800 rpm at 140 °C for 5 h. After finishing the reaction, the solid catalyst was quickly removed from the reaction mixture by filtration. The un-reacted methanol in the reaction mixture was removed via vacuum distillation. The glycerol and methyl fatty esters were analyzed by the gas chromatograph equipped with a FID detector and an Agilent-DB-5ht capillary separation column.

3. Results and discussion

3.1. Sample characterization

For UiO-66 material, its catalytic activity is mainly ascribed to missing linkers in the structure [27,28]. As missing linkers create open Zr sites which are accessible for catalytic transformations, different procedures, including utilizing modulator molecules (such as acetic acid and formic acid) and varying synthesis conditions, are developed to increase these structural defects within the UiO-66 type materials [28,29]. Recently, Shearer and his co-workers systematically studied the effect of synthesis temperatures and linker concentrations on the stability and defects of UiO-66 and found that increasing the synthesis temperatures and/or the BDC/Zr ratios aided the “ironing out” of linker defects [29]. Based on their results, in this work, we synthesized a series of UiO-66 samples at different synthesis temperatures and BDC/Zr ratios with the aim of elucidating the defects in UiO-66 materials on their catalytic performances in transesterification. The XRD patterns (Fig. 1) of all the samples were in good agreement with the previous reports [17], confirming the formation of pure crystalline UiO-66 phase.

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