



Catalytic activity of an economically sustainable fly-ash-metal-organic-framework composite towards biomass valorization

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ABSTRACT

Low thermal stability and insufficient Brønsted acidity are the deficiencies of conventional metal-organic-frameworks (MOFs), which would greatly limit their applications particularly for high temperature and pressure reactions such as dehydration of carbohydrates. This work has successfully demonstrated the development of a composite of MOF and activated fly ash, and their catalytic application in the xylose-to-furfural dehydration process. The composite is capable of maintaining high stability under severe hydrothermal conditions and even in the acidic medium. In addition, the composite shows its excellent catalytic performance for ten consecutive reaction cycles, which is much better than the bare MOF catalyst, MIL-101 (Cr), obtaining the furfural yield and selectivity of 71% and 80%, respectively. It is proposed that such catalytic activity is mainly attributed to the mutual contribution from the Cr atoms of MIL-101 (Cr) and hydroxyl groups of activated fly ash, acting as Lewis acid centers and Brønsted acid sites, respectively. Besides, the effect of salt concentration on the efficiency of xylose conversion has been studied. The product yield can be enhanced to 78% in the presence of trace amount of sodium chloride solution (35 ppt). This provides a promising direction towards the applications when seawater is used as the reaction media. In summary, the work shows that the incorporation of fly ash as the composite material not only reduces the cost of synthesis, but also mitigates the fly ash disposal problems to some extent.

1. Introduction

The progressive scarcity of the non-renewable fossil fuels has initiated the exploration of viable and economic fuel alternatives. Carbohydrates, which are one of the abundant sources in biomass community, are the promising candidates to be the alternative energy resources. Furfural is the only biomass-derived fine chemical that has been successfully produced in an industrial scale. Besides, the furfural is of utmost importance in terms of industrial usage, because of its versatility of applications. They are one group of the key building blocks for synthesis of the various value-added chemicals like alcohols, esters, biodiesel, pesticides, and paints. Synthesis of furfural using mineral acids as homogeneous catalyst is the conventional approach in the industrial mass production. However the problems of separation and downstream processing of the homogeneous catalyst have encouraged researchers to develop the heterogeneous solid acid catalysts, particularly maximizing the product yield as well as reducing the cost of operation [1,2]. Some promising heterogeneous catalysts have been developed including SAPO-44, zeolites, Nafion NR-50 and so on [3–7]. The furfural yield obtained by heterogeneous catalyzed xylose

dehydration at a reaction temperature below 200 °C is between 30 and 78% [8].

Metal organic frameworks (MOFs) have attracted research interests as potential heterogeneous catalysts in recent decades due to their high surface areas, pore volumes and flexibility for engineering the properties of the catalytic sites, as well as pore dimensions. In addition, the inorganic metal clusters typically act as catalytic sites with Lewis acidity or redox properties, while the organic ligands can hold the desired functional groups for catalytic purpose [9]. Of those catalysts utilizing acidic sites for organics transformations, the MOF is an evolving one. Both MIL-101 (Cr) and MIL-53 (Al) have successfully catalyzed fructose and carboxymethyl cellulose, respectively to a similar product, 5-hydroxymethylfurfural (5-HMF) [10,11]. Moreover, the MIL-101 (Cr) is effective in dehydration of 1,4-butanediol to tetrahydrofuran (THF) as well as 1-phenylethanol to styrene [12].

The practical use of MOF is limited and sporadic due to its low hydrothermal and mechanical stability particularly in the acidic environment. Yaghi et al. has demonstrated the sulfation of MOF-88 for enhancement of Brønsted acidity and such modified catalysts are capable for three reaction cycles in the studied recyclability tests [13].

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However, the modification step requires a robust MOF to withstand the post-synthesis modification. Another example has been reported by Ponomareva et al. that the acid impregnated MIL-101 (Cr) suffered from significant content leaching after the reaction [14]. To avoid those drawbacks from post-treatment modification as well as maintain the hydrothermal stability, preparing composites between the MOF and other porous carriers is one of the solutions for catalyst synthesis. Materials, such as activated carbon, graphite oxide, SBA-15, CNT, zeolite or clay, have been successfully used for preparing hydrothermally stable MOF composites and used in electrodes, synthesis of 2-methoxy-2-phenylethanol from styrene oxide, benzene adsorption, hydrogen storage, hydrolyzing benzaldehyde dimethyl acetal to benzylidene malononitrile and Friedel-Crafts alkylation reactions accordingly [15–20].

Coal fly ash is one of the abundant waste materials generated from the coal combustion in power plants. It was estimated in 2012 that approximately 750 million tons of fly ash was generated annually throughout the world [21]. Although the fly ash has been used in the manufacture of cement and concrete, such a huge amount of solid waste problem cannot be simply solved by the disposal into the landfill. Therefore, several attempts have been conducted to utilize the fly ash as a carrier of the heterogeneous catalyst for production of value-added fine chemicals. The rationale of using the coal fly ash as the catalyst carrier is mainly due to its enhancement of the Brønsted acidity by chemically activating with sulfuric or perchloric acids. Several cases have shown that they are effective in various esterification and dehydration reactions [22–24]. Cerium-triflate or sulfated zirconia supported on fly ash are catalytically active for Friedel-Crafts acylation and benzylation reaction, respectively [25,26]. The increasing use of fly ash as a green solid acid catalyst for organic transformation has already been established in the past years.

This work aims to develop a stable MOF-based MIL-101 (Cr)-fly ash composite containing rich Brønsted acid sites, as well as high hydrothermal stability. Effect of different weight ratio of the fly ash to the MOF, as well as the effect of salt concentration on the distribution of acid sites and the performance of the prepared catalysts will be investigated. In addition, the kinetics of the reaction will be finally studied and discussed.

2. Experimental

2.1. Materials

The reagents used are coal fly ash [Class F-type ($\text{SiO}_2 + \text{Al}_2\text{O}_3 > 70\%$)] obtained from Durgapur steel plant (Kolkata, India), sulfuric acid (95% ACS reagent), chromium (III) nitrate nonahydrate (99%), terephthalic acid (98%), glacial acetic acid (99.7% ACS reagent), ethanol (96%), d-xylose (minimum 99%), toluene (AnalaR Normapur ACS grade), furfural (99% ACS grade), sodium chloride (> 99% ACS reagent). All these reagents are obtained from Sigma Aldrich and have been used without further purification unless otherwise stated.

2.2. Catalyst preparation

2.2.1. Synthesis of MIL-101 (Cr)

MIL-101 (Cr) is synthesized by a modified hydrothermal method without using the corrosive hydrofluoric acid. The procedure involves mixing 4 g $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, 1.66 g terephthalic acid, 0.58 mL glacial acetic acid and 50 mL water in a Teflon container, and heating the solution for 8 h at 220 °C. The material obtained is filtered by a large pore fitted glass filter ($n^{\circ}2$), followed by refluxing with ethanol at 80 °C for 24 h with the ethanol-to-solid ratio of around 200 mL ethanol/1 g of material. The as-synthesized MIL-101 (Cr) is further dried at 150 °C in vacuum to remove the moisture content in the pores. A total of 70% of the product is recovered based on the weight of precursors used [27].

2.2.2. Chemical activation fly ash (AFA)

The raw coal fly ash (Raw FA) is chemically treated with 4 times the weight of sulfuric acid at 110 °C under constant stirring for 120 h. The acid treated sample is recovered and washed with water unless physically attached acid is completely removed. It is then allowed to undergo calcination at 400 °C for 4 h to complete the chemical activation and obtain the activated coal fly ash, namely as AFA [22].

2.2.3. Synthesis of fly-ash-MOF-composite (MF)

To prepare the composite material, certain amount of activated coal fly ash is mixed into a 50 mL aqueous solution containing 1.66 g terephthalic acid and 0.58 mL glacial acetic acid. After 30 min of stirring, 4 g of $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ is added to the solution and heated at 220 °C for 8 h. The washing procedure followed is the same as that of synthesis of MIL-101 (Cr). Three catalysts are developed with the mass ratio of AFA to $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ as 0.25, 0.625 and 1 and named as MF-1, MF-2, and MF-3, accordingly.

2.3. Characterization of the developed catalysts

The bulk elemental analysis of the material is performed by the X-ray fluorescence instrument JEOL JSX-3201Z. The corresponding crystalline structures of the prepared catalysts are determined from X-ray diffraction (XRD) patterns, which are conducted by a PANalytical powder X-ray diffractometer equipped with a Cu-K α radiation source (wavelength of 1.54 Å) operating at 40 kV and 40 mA. Chemical states of the elements are determined from X-ray photoelectron spectroscopy (XPS) using Kratos Axis Ultra DLD. The time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is performed by ToF-SIMS V spectrometer (Münster, Germany) using Bi_3^+ as primary ions. Fourier-transform infrared (FTIR) spectroscopy is performed in a Bruker Vertex 70 instrument using KBr in the sample preparation. The BET areas and pore volumes of the developed catalysts are determined by nitrogen physisorption measurement at 77 K using a Coulter SA 3100 surface area and pore size analyzer. The samples are degassed at 150 °C for 2 h prior to nitrogen adsorption. Thermal gravimetric analysis (TGA) is done in Setaram TGA 92-16.18, where the sample is placed under N_2 flow and heated from ambient conditions to 800 °C with a heating rate of 10 °C/min. For morphological study, transmission electron microscopy (TEM) analyses are conducted by the unit of JEOL-2010. To determine the total number of acid sites in the developed catalysts, ammonia temperature-programmed-desorption (NH_3 -TPD) is performed by Micromeritics AutoChem II 2920 using NH_3 -16 as the probe molecule. Prior to adsorption of NH_3 , the samples are degassed with helium at 180 °C. To further identify the distribution of the acid sites, the Fourier transform infrared spectroscopy with pyridine as probe molecule has been used for identification of Brønsted and Lewis acid sites. The FTIR measurement is performed by Nicolet 6700. The samples are first degassed at 180 °C for 2 h, followed by pyridine adsorption at 25 °C for 1 h. Removal of physisorbed pyridine is performed at 150 °C for 30 min and the spectra is collected after conducting desorption at 150 °C for 1 h. The metal leaching of spent catalyst is examined by characterizing the reacted effluent by inductively coupled plasma with mass spectroscopy (ICP-MS Varian 820). The aqueous phase after the desired reaction run is collected and filtered to separate the spent catalyst. Following the filtration, 1 mL of 2 vol.% nitric acid is added to the aqueous phase.

2.4. Catalytic evaluation of organic transformation of D-xylose to furfural

The catalytic dehydration of xylose has been performed in a batch mode operation using a 100-mL Teflon-lined stainless steel reactor. In a typical experiment, a total of 300 mg of D-xylose, pre-determined amount of catalyst, 3 mL of water and 7 mL of toluene are added to the reactor. It is heated to 150 °C in an oven and kept at the same temperature for 3 h [28]. When the reaction finished, the reaction mixture

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