Journal of Catalysis 352 (2017) 480–490

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Selective transformation of renewable furfural catalyzed by diverse active species derived from 2D co-based metal-organic frameworks

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ARTICLE INFO

Article history:
Received 28 February 2017
Revised 11 June 2017
Accepted 13 June 2017
Available online 7 July 2017

Keywords:
Metal-organic frameworks
Catalytic species
Oxidative condensation
Furfural
Molecular oxygen

ABSTRACT

We report a facile method for gaining two different types of highly active species from the same 2D Co-based MOFs, which can effectively catalyze the selective transformation of biomass-derived furfural (FUR) in alcohols. Removal of the coordinated water molecules from the Co-based MOFs at 300 °C creates the open metal centers as catalytic active species (designated as **ACS-I** catalyst). Increasing the pyrolysis temperature to 700 °C, the derived multi-element carbon-matrix nanocomposite from the MOFs (designated as **ACS-II** catalyst) also shows highly catalytic performance. Both catalyst **ACS-I** and **ACS-II** exhibit high reactivity (84.9% conv.) and excellent selectivity (*ca.* 99.0%) in the oxidative condensation of FUR with *n*-propanol to produce 3-(furan-2-yl-)-2-methylacrylaldehyde (**2**) in the presence of molecular oxygen. The particular evidence for the role of metal Co centers in **ACS-I** and **ACS-II** is originated from the catalyst characterization and control experiments, in which **Ni-I** and **Ni-II** catalysts derived from isomorphrous 2D Ni-based MOFs show no catalytic activity on the transformation of FUR under the similar conditions.

1. Introduction

The growing concerning of the exhaustion of fossil resource and environmental deterioration has provoked the extensive interest for obtaining fine chemicals from the inexpensive and abundant biomass [1–5]. Furfural (FUR), a typical bio-based platform chemical, is regarded as versatile and important building blocks for generating a series of value-added products [6,7]. Ongoing research is mainly focusing on the catalytic transformation processes of furfural such as selective oxidation, oxidative esterification, partial hydrogenation, aldol condensation and oxidative condensation [8–11]. In particular, the carbon-chain-growth condensation is of great importance for the catalytic upgrading of furfural to produce a desirable gasoline component and stabilize furanic compounds [12]. The oxidative condensation of FUR with aliphatic alcohols-O_2 is emerging as a tandem process, which can impel two carbon molecules together to produce longer hydrocarbon chains using as low volatile liquid transport fuels [13]. In the previous report, the efficient transformation of FUR often relies on the catalysis of precious metallic Pt/Al_2O_3 [14]. Thus, developing the novel catalytic system with earth abundant metal is still challenging at present. Incorporation of redox metals into molecular sieves affords potentially interesting heterogeneous oxidation catalysts such as TS-1, in which Ti was in tetrahedral positions [15,16]. However, Roger A. Sheldon, et al. found some redox metal molecular sieves such as CrAPO-5 and CoAPO-5 are by no means heterogeneous catalysts during the course of oxidation of cyclohexane, in which the metal leaches to form an active homogeneous catalyst because metal was attached to defect sites of silicates [17–20].

Metal-organic frameworks (MOFs) have recently emerged as a novel class of tunable molecular materials with great potential applications. The key strategies for achieving catalytic active species using MOFs are as follows. (i) The catalytic active species (e.g. metal or metal oxide nanoparticles) were immobilized into the MOFs matrix [21]. There are several approaches are available, such as encapsulating the active species in the pores and cages [22], depositing metallic nanoparticles [23], and post-synthetic covalent modification [24,25]. (ii) Intrinsic catalytic active sites originating from the inorganic nodes and organic linkers can serve as the intriguing platform for developing reusable single site catalysts [26–29]. However, there are a limited number of MOFs with free coordinated sites available [30,31]. Removal of coordinated solvent from the metal nodes is a promising method to activation of the metal nodes [32]. (iii) Metal or metal oxide nanoparticles derived from the MOFs through thermolysis under the controllable atmosphere were used as catalysis [33–35]. A comparison of the

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http://dx.doi.org/10.1016/j.jcat.2017.06.017

aforementioned strategies indicates the latter two will probably be simple and cost-economic. However, the selection of metal nodes and the controlled growth of MOFs are the key factors for design and synthesis such catalysts. The discovery of earth-abundant transition metal catalyst such as Co, Ni and Cu is becoming increasingly critical for economically producing the commercial fine chemicals owing to the high cost and scarcity of some precious metals such as Ru, Pd and Au [36–39]. However, in some limited reports on the application of MOFs for biomass valorization, the earth-abundant metals such as Co, Ni-based MOFs never have been used, presumably due to the catalytic active sites are often occupied by the donor atoms from the organic ligands [40–42]. Solvent removal might be a promising way for initiating the catalytic activity of the metal nodes [32]. To the best of our knowledge, there is no report on using this approach combined with cobalt(II) ions as a strategy for the transformation of biomass [43–45]. In addition, using metal oxide nanoparticles derived from MOFs precursors as catalysts for biomass valorization remains unexplored [46–48].

Herein, we perform the oxidative condensation of FUR, a typical biomass-based platform compound, using the simple MOFs-derived material as heterogeneous catalyst. The 2D Co-based MOFs ($[Co(tia)(H_2O)_2]_n$) are evaluated as potential catalytic species for the selective transformation of FUR in the green alcohol-O_2 system [13]. For the first time, two different types of Co-based active species were obtained using the same 2D Co-based MOFs. One catalytic species with the intrinsic open-metal active sites (designated as **ACS-I** catalyst) was generated through removal of coordinated water molecules at 300 °C under argon atmosphere, promoting the oxidative condensation of FUR and *n*-propanol where a 63.4% conversion of FUR and 99% product selectivity are obtained. With the higher pyrolysis temperature at 700 °C, another derived active nanocomposite (designated as **ACS-II** catalyst) is produced and it catalyzes more efficiently the oxidative condensation in which the FUR conversion and selectivity of desired product are increased up to 84.9% and 99.7%, respectively.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

All reagents and solvents for synthesis and analysis were commercially available and used as received. H_3ctia (H_3ctia = 5-(4-carboxyl-*1H*-1,2,3-triazol-1-yl) isophthalic acid) has been synthesized according to the literature [49].

2.1.2. General methods for characterization

IR spectra were recorded in the range of 4000–400 cm^{-1} on a Perkin-Elmer spectrometer with KBr pellets. Elemental analyses for C, H, and N were carried out on a Model 2400 II, Perkin-Elmerelemental analyzer. X-ray powder diffraction (XRD) intensities of the different samples were measured on a Rigaku D/max-IIIA diffractometer (Cu Kα, λ = 1.54056 Å). TGA experiments were performed in flowing N_2 on a NETZSCH TG 209 instrument with a heating rate of 10 °C/min. Single crystal diffraction data for Co-based and Ni-based MOFs were collected with a Bruker SMART APEX CCD instrument with graphite monochromatic MoKα radiation (λ = 0.71073 Å). The data were collected at 293(2) K. The absorption corrections were made by multi-scan methods. The structure was solved by direct methods and refined by full-matrix least-square methods on all F^2 data with the program Olex2. The quantitative analyses of the products were determined on a GC apparatus with FID detector or on the Agilent 6890/5973 Gas Chromatograph-Mass Spectrometer (GC–MS) instrument. The morphology of catalytic materials was obtained by scanning electron microscope (SEM: JSM-6301F, JEOL) equipped with a JED-2300 (JEOL) EDXS spectrometer for chemical analysis and transmission electron microscope (TEM: JEM-2100, JEOL). X-ray photoelectron spectra (XPS) were recorded on a KRATOS AXIS 165 with a dual X-ray anode (Mg and Al) and all XPS spectra were recorded using the MgKα line. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES:Varian 700-ES) was used to measure the metal content of the catalytic materials.

2.2. Preparation of catalysts

2.2.1. Synthesis of 2D Co-based and Ni-based MOFs

2D Co-based MOFs has been synthesized using the similar procedure published earlier [49,50]. Briefly, $Co(NO_3)_2{\cdot}6H_2O$ (0.2 mmol, 0.0582 g) or $Ni(NO_3)_2{\cdot}6H_2O$ (0.2 mmol, 0.0582 g) and the aqueous solution of H_3ctia (15 mL) (H_3ctia = 5-(4-carboxyl-*1H*-1,2,3-triazol-1-yl) isophthalic acid, 0.2 mmol, 0.0554 g) whose pH value was adjusted to 3.5 by NaOH was added into a Teflon-lined pressure vessel, and then the mixture was heated to 170 °C and kept at 170 °C for 72 h. After cooling to room temperature at a rate of 2.5 °C/h. Red needle-shaped crystals suitable for X-ray analysis were directly obtained, collected, washed with water and ethanol, and then dried in the air. The formula for the obtained 2D Co-based MOFs is $[Co(tia)(H_2O)_2]_n$ (tia^{2-} = 5-(*1H*-1,2 ,3-triazol-1-yl)isophthalate). Yield about 99% (based on $Co(NO_3)_2{\cdot}6H_2O$). Anal.Calcd (%) for $[Co(tia)(H_2O)_2]_n$ (325.98): C, 36.83; H, 2.78; N, 12.88. Found: C, 36.50; H, 2.67; N, 12.80. Crystallographic data for the as-obtained MOFs are given in Table S1. Selected bond lengths and angles are given in Table S2 in supporting information.

The formula for the as-synthesized 2D Ni-based MOFs is $[Ni(tia)(H_2O)_2]_n$. Yield about 98% (based on $Ni(NO_3)_2{\cdot}6H_2O$). Anal. Calcd (%) for $[Ni(tia)(H_2O)_2]_n$ (324.98): C, 36.83; H, 2.78; N, 12.89. Found: C, 36.90; H, 2.69; N, 12.04. Crystallographic data for the as-obtained MOFs are given in Table S1. Selected bond lengths and angles are given in Table S3 in supporting information.

2.2.2. Preparation of the active species

As-obtained 2D Co-based MOFs were added in a quartz boat, and placed in the tubular furnace. The MOFs was heated up at different temperatures from 100 to 800 °C for 4 h under a continuous argon flow of 50 mL min^{-1}. After cooling to room temperature, the derived catalytic materials were obtained. (The derived catalytic materials at 300 °C and 700 °C were designated as **ACS-I** and **ACS-II**, respectively).

The preparation methods of **Ni-I** and **Ni-II** catalysts were similar with those for preparing **ACS-I** and **ACS-II** catalysts.

2.3. The catalytic oxidative condensation of furfural

All oxidative condensation experiments were performed in a 120 mL stainless steel autoclave equipped with the magnetic stirring and a temperature controller. A typical procedure for oxidation condensation of FUR with *n*-propanol is as follows. FUR (0.1 g, 1 mmol), *n*-propanol (15 mL), the Co-based catalyst (25 mg) and Cs_2CO_3 (25 mg) were added into the autoclave. After the reactor was sealed, the pure oxygen was pumped to replace the atmosphere for several times. Then under the pressure of 0.3 MPa, the mixture was preheated to the set temperature with magnetic stirring and kept for a certain time. After the autoclave was cooled down and the excess gas was released, the as-obtained mixture was analyzed by GC and GC–MS (The details are shown in the supporting information).