Journal of Catalysis 365 (2018) 36–42

Contents lists available at ScienceDirect

Journal of Catalysis

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

L-proline modulated zirconium metal organic frameworks: Simple chiral catalysts for the aldol addition reaction

Xiao Feng, Himanshu Sekhar Jena, Karen Leus, Guangbo Wang, Judith Ouwehand, Pascal Van Der Voort *

Department of Chemistry, Center for Ordered Materials, Organometallics and Catalysis (COMOC), Ghent University, 281 Krijgslaan (S3), B-9000 Ghent, Belgium

ARTICLE INFO

Article history:
Received 18 April 2018
Revised 8 June 2018
Accepted 12 June 2018

Keywords:
Modulation synthesis
Defect
Zr-MOFs
L-proline
Aldol reaction

ABSTRACT

Three L-proline modulated zirconium based MOFs denoted as UiO-66, Zr-NDC (NDC = 2,6-Naphthalene dicarboxylate) and UiO-67 were synthesized, characterized and explored as heterogeneous catalyst in diastereoselective aldol addition reactions between 4-nitrobenzaldehyde and linear/cyclic ketones. Upon L-proline modulation, chirality was introduced into these Zr-MOFs which were consequently explored as chiral catalysts for asymmetric reactions. A systematic study was conducted to look into the effect of the synthesis temperature on the modulation in each Zr-MOF. The modulated UiO-66 material synthesized at 120 °C exhibited full conversion and a good diastereoselectivity whereas the homogeneous L-proline catalyst showed only 61% conversion and a reversed diastereoselectivity. The catalyst exhibited no leaching of the catalytically active species and was reused for at least three additional cycles. The observed high catalytic activity is a result of the electron withdrawing nature of the Zr-node coordinated to L-proline.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

In catalysis, both homogeneous and heterogeneous catalysts have their own advantages and disadvantages. Homogeneous catalysts exhibit high catalytic activity and selectivity but are difficult to recover and reuse. Heterogeneous catalysts are easy to recover and reuse but it is difficult to identify the active site that is responsible for the catalytic activity. Researchers are trying to bridge this gap between homogeneous and heterogeneous catalysis by designing different kinds of supports having active catalytic binding sites [1,2]. Among them, Metal Organic Frameworks (MOFs) have shown great potential because they display many properties of an ideal heterogeneous catalyst such as crystallinity, active-site uniformity, high surface area, and permanent porosity [3–6]. Therefore, MOFs are intensively explored for a variety of catalytic applications [6,7], including hydrogenations, oxidation reactions and asymmetric catalysis. Generally, three approaches are used to design catalytic active MOFs, (i) MOFs having unsaturated metal sites, (ii) post-synthetic modifications of linker/functional organic sites, (iii) encapsulation of transition metal complexes or metal nanoparticles into the channels/cages [6]. Specifically, for chiral catalysis, MOFs are integrated with chiral ligands, by either direct grafting them onto the linker or post-synthetic modification of the achiral linker. However, functionalization of MOFs by grafting or post synthetic modifications of the linkers demands complex reaction protocols, expensive multistep synthesis and several instrumental methods for their characterization.

Asymmetric aldol reactions are very important C-C coupling reactions in organic chemistry and are catalyzed by proline as a homogenous catalyst [8,9]. Recently, proline functionalized MOFs were explored for such applications [10–15]. For example, Kaskel et al. [10], reported proline functionalized Zr-MOFs (UiO-67 and UiO-68) by pre-synthetic modification of the organic linker and achieved good diastereoselectivity after 10 days of reaction. Subsequently, the same group reported another L-proline functionalized zirconium-MOF [16], denoted as DUT-67 as heterogeneous catalyst for asymmetric Michael addition reaction in which the parent monocarboxylic ligand was exchanged with L-proline after five days of treatment.

The term "coordination modulation", introduced in 2009 by Kitagawa et al. [17], refers to the use of mono-functional modulators (e.g. monocarboxylic acids) as competitive coordination agents in the synthesis of MOFs. Importantly, modulators not only regulate the pore size and morphology of the crystals [18,19], but also promote the formation of defects [20–23], which in turn allows the sophisticated tuning of the porosity, stability and catalytic reactivity [24–26]. Nowadays, the modulation synthesis has become a common approach for defect engineering in MOFs [20]. Modulated MOFs to create defect sites were used in

* Corresponding author.
E-mail address: Pascal.VanDerVoort@UGent.be (P. Van Der Voort).

https://doi.org/10.1016/j.jcat.2018.06.013
0021-9517/© 2018 Elsevier Inc. All rights reserved.

heterogeneous Brønsted [27] and Lewis acid [28] catalysis. Recently, Lillerud et al. introduced a "functionalized modulator" – a monocarboxylic acid having other functionalized groups – and exploited post-synthetic ligand exchange for CO_2 adsorption [29]. Therefore, designing functionalized modulators presents a new opportunity to create highly active and functionalized low-cost catalysts with less effort.

In this work, we synthesized three L-proline functionalized modulated zirconium MOFs denoted as UiO-66, Zr-NDC and UiO-67 at three different synthesis temperatures and explored their catalytic activity in diastereoselective aldol addition reactions. In these Zr-MOFs, L-proline is not only used as a modulator but is also employed to introduce the chiral active site. Moreover, a systematic study was conducted to examine the influence of the temperature on the number of defects and the density of modulator present in the framework.

2. Experimental details

2.1. General procedures

All chemicals were purchased from Sigma Aldrich, ABCR, TCI Europe and used without further purification. X-ray powder diffraction (XRPD) patterns were collected on an ARL X'TRA X-ray diffractometer operating at 40 kV/40 mA using Cu-Kα radiation (λ = 0.15418 nm) and a solid-state detector. Nitrogen adsorption experiments were carried out at 77 K using a Belsorp-mini II gas analyzer. Prior to adsorption measurements, the samples were activated under vacuum at 150 °C for 16 h to remove the adsorbed solvent. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449 F3 Jupiter in a temperature range of 20–600 °C in air and a heating rate of 5 °C/min. For ^{1}H NMR, the samples were dissolved in a heated mixture of D_2SO_4 and [D_6] DMSO (1:6). Spectra were recorded on a Bruker 300 MHz ADVANCE spectrometer.

2.2. Synthesis of the catalysts

The proline modulated Zr-MOFs were synthesized following the procedure of Gutov et al. and Marshall et al. [30,31] Briefly, $ZrO_2Cl_2{\cdot}8H_2O$ (485 mg, 1.51 mmol), the dicarboxylic acid (251 mg, 1.51 mmol), HCl (0.625 mL, 7.55 mmol) and L-proline (866 mg, 7.55 mmol) were dissolved in 20 mL DMF in an ultrasonic bath for 30 min. The resulting mixture was placed in a Teflon-lined autoclave at 150 °C, 120 °C or 70 °C for 4 days, and successively cooled to room temperature. The solid was collected by filtration, subsequently stirred in DMF at 70 °C for 24 h followed by stirring in methanol for 24 h to remove unreacted linker, modulator and DMF. The final purified product was dried under vacuum at 65 °C before use in catalysis.

2.3. General procedure for the catalytic reactions

The catalysts (20 mol% regarding the amount of proline groups with respect to the 4-nitrobenzaldehyde concentration) were placed in a 15 mL screwed glass vial under vacuum at 150 °C for 16 h. Afterwards, a mixture of 4-nitrobenzaldehyde (0.03 mmol/mL^{-1}), methyl 4-nitrobenzoate (internal standard, 0.022 mmol/mL^{-1}), acetone (50 vol%) and a solvent (50 vol%) were added and stirred at 20 or 45 °C for 24 h. The conversion and selectivity was determined by means of HPLC (Shimadzu LC-20AT) having a C18 column equipped with a SPD-M20A UV detector and LC-Solution software. The HPLC apparatus was operated at a column temperature of 30 °C by using a gradient method with water (0.1% trifluoroacetic acid) and acetonitrile (HPLC grade) as solvents. In this gradient method, the volumetric percentage of acetonitrile was changed from 30 to 62% over a period of 7 min. The chirality of the aldol products was analyzed by chiral HPLC (Chiralpak AS-H; hexane/ethanol, 90:10). Besides acetone also two other substrates were examined. For these substrates 4-nitrobenzaldehyde (0.3 mmol) and cyclohexanone (3 mmol) or cyclooctanone (3 mmol) was placed in a 15 mL screwed glass vial and stirred in 1.5 mL solvent at 45 °C for 24 h. The conversion and diastereoselectivity were determined using the same non-chiral column under equal conditions. Enantioselectivities were measured by chiral HPLC (LUX® 5 μm Amylose-1, 250x4.6 mm, hexane/iPrOH, 91:9). After the first run, the catalyst was removed by filtration, repeatedly washed with acetone and dried at 150 °C under vacuum before reuse in the subsequent runs.

3. Results and discussion

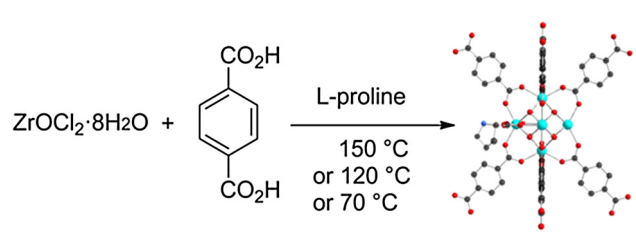
3.1. Effect of temperature on the synthesis of L-proline modulated Zr-MOFs

Three zirconium based MOFs, UiO-66 [32], Zr-NDC [33] and UiO-67 [34], were synthesized in the presence of L-proline as modulator. Each MOF was synthesized at three different temperatures (70 °C, 120 °C and 150 °C) to explore the temperature effect on the density of defects in the resulting framework (Scheme 1). The experimentally obtained ratio of L-proline and linker in each Zr-MOF was calculated by means of ^{1}H NMR analysis by digesting the sample in a mixture of D_2SO_4 and DMSO (Figs. S6–S8). Furthermore, the number of defects was calculated using TGA analysis (Table 1, Figs. 3, S4 and S5) in accordance to Lillerud's method [35]. The powder X-ray diffraction patterns of the obtained L-proline modulated Zr-MOFs corresponds well with the non-modulated Zr-MOFs reported in the literature demonstrating that the crystalline structure is preserved during the modulation approach (Figs. 1, S1). The nitrogen adsorption analysis confirmed that the porosities of these materials depend on the densities of defects and modulator as can be seen from Figs. 2, S2 and S3).

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.06.013.

UiO-66-LP-120 and UiO-66-LP-150 (LP = L-proline) exhibited a similar Langmuir surface area, whereas the Langmuir surface area of the UiO-66-LP-70 is slightly higher (Table 1). As shown in Table 1, UiO-66-LP-120 and UiO-66-LP-150 have an equal amount of missing BDC linkers and a quasi-similar number of L-proline modulators whereas UiO-66-LP-70 has a higher number of missing BDC linkers which results into a higher surface area. Furthermore, one can see an increase of the ratio of modulator and linker with decreasing synthesis temperature, whereas a similar trend is observed for the number of missing linkers.

Similarly, a series of Zr-NDC-LP MOFs were obtained at three different temperatures. Based on the defect analysis, it was found that Zr-NDC-LP-70 has the largest number of missing NDC linkers and highest amount of defects (Table 1). As can be seen from Table 1, the number of missing linkers and ratio of modulator and linker increased with decreasing temperature which was also



Scheme 1. Synthesis of UiO-66 using L-proline as modulator.

Download English Version:

https://daneshyari.com/en/article/6526499

Download Persian Version:

https://daneshyari.com/article/6526499

Daneshyari.com