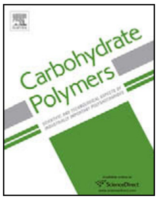
Carbohydrate Polymers 115 (2015) 146–151

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Catalytic hydrothermal conversion of carboxymethyl cellulose to value-added chemicals over metal–organic framework MIL-53(Al)

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A R T I C L E I N F O

Article history:
Received 3 April 2014
Received in revised form 9 July 2014
Accepted 13 August 2014
Available online 2 September 2014

Keywords:
Metal–organic framework
MIL-53(Al)
Biomass conversion
Carboxymethyl cellulose
5-Hydroxymethyl-furaldehyde

A B S T R A C T

Catalytic hydrolysis of biomass over solid catalysts can be one of the most efficient pathways for a future sustainable society dependent on cellulose biomass. In this work metal–organic framework MIL-53(Al) without any functionalization was directly employed as an efficient heterogeneous catalyst for the hydrolysis of carboxymethyl cellulose (CMC) to 5-hydroxymethyl-furaldehyde (5-HMF) in aqueous phase. A 5-HMF molar yield of 40.3% and total reducing sugar (TRS) molar yield of 54.2% were obtained with water as single solvent at 473 K for 4 h. The catalyst could be reused three times without losing activity to a greater extent. With the remarkable advantages such as the use of water as single solvent and MIL-53(Al) as a novel heterogeneous green catalyst, the work provides a new platform for the production of value added chemicals and liquid fuels from biomass.

1. Introduction

Efficient conversion of renewable biomass to useful chemicals and biofuels is one of the most popular topics in green and sustainable chemistry (Guo, Lian, Yan, Qi, & Smith, 2013). Hydrothermal treatment is quite promising in this process because water under high temperature and high pressure behaves as a reaction medium having outstanding properties (Takeuchi, Jin, Tohji, & Enomoto, 2007). In general, carboxymethyl cellulose (CMC) is a water-soluble derivative of cellulose which is quite economic and promising as raw materials in the conversion of biomass. (Paljevac, Primožič, Habulin, Novak, & Knez, 2007). And as a versatile intermediate between biomass-based carbohydrate chemistry and petroleum-based industrial organic chemistry, 5-hydroxymethylfurfural (5-HMF) can be used to synthesize a broad range of chemicals currently derived from petroleum. Therefore, conversion of biomass to 5-HMF has been extensively studied.

Most of the previously reported studies have employed carbohydrates such as fructose, glucose, sucrose, inulin and even cellulose, as feedstock for the synthesis of 5-HMF (Deng et al., 2012). Common inorganic acids such as HCl, H_2SO_4 have been used as catalysts for the dehydration of biomass but suffers a number of drawbacks (Guo et al., 2013). In order to minimize those negative environmental impacts, new green approaches have been developed, such as the use of cellulose enzymes (Percival Zhang, Himmel, & Mielenz, 2006), microwave irradiation (De, Dutta, & Saha, 2011), and solid catalysts. Indeed, various solid acid catalysts including heteropolyacids (Ogasawara, Itagaki, Yamaguchi, & Mizuno, 2011), layered transition-metal oxides (Tagusagawa et al., 2010), and sulfonated hierarchical H-USY zeolite (Zhou et al., 2013), have been proposed. Despite these pioneering studies, it is likely that the main obstacle to using these conventional heterogeneous mesoporous and microporous catalysts for "bulky" biomass is the limited accessibility of the reactive sites, which results in inefficient biomass conversion (Kuo, Suzuki, Yamauchi, & Wu, 2013).

Moreover, some researchers described the use of a mixed-solvent or ionic liquids for the hydrolysis of biomass (Liu, Xiao, Xia, & Ma, 2013; Moreau, Durand, Pourcheron, & Razigade, 1994; Qi, Watanabe, Aida, & Smith, 2008b). However, ionic liquids have high viscosities and their high cost may limit some applications. So far reports of hydrolysis cellulose to produce 5-HMF using water as the only solvent have been very limited in the literature as we know. Furthermore, the yield of reducing sugar (glucose) for cellulose conversion was in the range of 40.5–74.5% in most of systems and few studies concerned about the formation of 5-HMF by using water as the only solvent (Guo et al., 2013; Tian et al., 2010). For example, the yield of total reducing sugar (TRS) 54% was reported, while only 1.6% 5-HMF was obtained over $H_3PW_{12}O_{40}$

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http://dx.doi.org/10.1016/j.carbpol.2014.08.065
0144-8617/

catalyst (Tian et al., 2010). Although considerable efforts have been made, it is still a major challenge to have a heterogeneous catalyst with high yield of 5-HMF by direct conversion of cellulose in water.

Metal–organic frameworks (MOFs) possess several advantages such as high surface areas, well-defined structures, the ease of processability, and structural diversity, which make them very attractive for catalysis (Li, Eddaoudi, O'Keeffe, & Yaghi, 1999; Phan, Nguyen, Luu, & Nguyen, 2012). Recently, phosphotungstic acid (PTA) encapsulated in MIL-101(Cr) was used as a solid acid catalyst for dehydration of carbohydrates to 5-HMF in ionic liquids or DMSO, an HMF yield of 63% was obtained in DMSO (Zhang, Degirmenci, Li, & Hensen, 2011). However, a major effort has been required to functionalize these porous frameworks with specific sites or acid groups for carrying out the catalytic reactions. And catalytic studies on MOFs without any functionalization as solid acid catalysts for conversion of CMC to 5-HMF in single aqueous solvent system has not been reported so far as we know.

MIL-53(Al) with 1D lozenge-shaped tunnels built up from chains of octahedra sharing OH vertices is appropriate for a Brønsted-type acid catalyst (Farrusseng, Aguado, & Pinel, 2009; Ferey, 2008). And many researchers also reported that acid catalysts are helpful for accelerating the production of HMF under hydrothermal condition (Kuo et al., 2013; Takeuchi et al., 2007). Therefore, these properties have inspired potential applications of MIL-53(Al) in catalysis for hydrolysis of biomass. Moreover, water can still be considered as a preferred solvent for biomass conversion since the actual biomass can contain a substantial amount of water, and its properties are tunable with the variation of its temperature and pressure (Qi, Watanabe, Aida, & Smith, 2008a). Herein, MIL-53(Al) without any functionalization was employed as an acid catalyst for the hydrothermal conversion of CMC to 5-HMF using water as single solvent for the first time.

2. Experimental

2.1. Synthesis of MIL-53(Al)

MIL-53(Al) was synthesized via a hydrothermal method according to Loiseau et al.'s (2004) previous report. 1,4-benzenedicarboxylic acid (H_2BDC, 2.88 g) $Al(NO_3)_3{\cdot}9H_2O$ (13.0 g), and deionized water (50 mL) were added into a 100 mL Teflon-lined steel autoclave and heated at 473 K for 72 h. The product was filtered and washed with water to ensure the removal of nitric acid formed during the synthesis. The powder obtained was dried overnight at 353 K in air. The as-synthesized dry powder was denoted as MIL-53$(Al)_{as}$. As-synthesized MIL-53$(Al)_{as}$ was activated according to the previous literature procedure (Rallapalli et al., 2009). The product was filtered and washed with *N*,*N*-dimethylformamide (DMF) to remove the unreacted BDC, and dried under vacuum for 2 h. Further it was treated with methanol in order to replace the DMF molecules trapped inside the cavities of the product. Finally, it was filtered, washed with methanol, and dried in an air oven at 353 K for 2 h (Rallapalli et al., 2009). Then, the sample was further activated at 423 K under vacuum overnight to ensure complete removal of solvent molecules. The obtained product was calcined in conventional manner at 603 K for 72 h and the calcined product was denoted as MIL-53(Al).

2.2. Characterizations

Wide angle X-ray powder diffraction (XRD) experiments were conducted on a Rigaku TTRAX III spectrometer with Cu $K\alpha$ radiation from 5° to 40°. The Fourier transform infrared spectra (FI-IR) measurements were performed on a Thermo Nicolet 8700 instrument. Pore size distributions, BET surface areas and pore volumes were measured by the nitrogen adsorption/desorption measurements using a Beishide 3H-2000PM2 Surface area and porosity analyzer. Scanning electron microscopy (SEM) images were taken on a FEI Quanta200 FEG microscope at an accelerating voltage of 15 kV with the pressure in the sample chamber of 1 Torr. High-resolution transmission electron microscopy (HRTEM) imagines were taken on a TEM (JEM-2100). To investigate the acidic properties of the samples, NH_3 Temperature-Programmed Desorption (NH_3-TPD) was carried out using a chemisorption analyzer system (ChemBET 3000).

2.3. Carboxymethyl cellulose hydrolysis

A typical catalytic reaction procedure was as follows: 100 mg of CMC and 75 mg catalyst were dispersed into 80 mL of water under stirring. Then the solution was transferred and sealed in a Teflon-lined steel autoclave and heated to a given reaction temperature at autogenous pressure. After cooling the autoclave in an ice-water bath to room temperature, the reaction mixture was filtered through a Millipore filter (pore size, 0.45 μm) and analyzed by UV–vis spectrometer (Shimadzu UV-2401PC photometer) over 200–400 nm. The determined wavelength is 282 nm (Fig. S4), which is the maximum absorption wavelength of 5-HMF detected by UV–vis spectrometer. The concentration of 5-HMF was calculated based on a standard curve obtained with 5-HMF. In addition to Ultra-performance liquid chromatography analysis (UPLC, Waters) (Fig. S3), the structure of final product was also analyzed by ^{1}H NMR spectroscopy (Bruker Avance 300 spectrometer, 300 MHz, $CDCl_3$) in order to confirm it is HMF. ^{1}H NMR peaks at d (ppm): 4.660 (s, 2*H*), 6.447–6.459 (d, $J = 3.6$ Hz, 1*H*), 7.140–7.152 (d, $J = 3.6$ Hz, 1*H*), 9.546 (s, 1*H*).

The total reducing sugar (TRS) content was determined using the 3,5-dinitrosalicylic acid (DNS) method. A mixture contained 1 mL of 3,5-dinitrosalicylic acid (DNS) regent, 3 mL of reaction sample, and 3 mL of H_2O, was heated for 15 min in a boiling water bath, then cooled to room temperature, and mixed with 5 mL of deionized water. The color intensity of the mixture was measured in a UV-2401 Model spectrophotometer. The concentration of TRS was calculated based on a standard curve obtained with glucose.

2.4. Fast hot catalyst filtration experiments

100 mg of CMC and 75 mg catalyst were dispersed into 80 mL of water and loaded into a stainless steel autoclave with a 100 mL Teflon container. Then, the autoclave and its contents were heated to 473 K at autogenous pressure for 30 min, then quickly filtrated the catalyst. The filtrates obtained from the fast hot catalyst filtration was detected by ICP-AES analyzer (Shimadzu SEQUE-NTIAL PLASMA SPETROMETER ICPS-1000II).

3. Results and discussion

3.1. The characterization of catalyst

The diffraction patterns of MIL-53$(Al)_{as}$ and MIL-53(Al) samples clearly indicates that the materials are well crystalline, and the obtained peaks of MIL-53$(Al)_{as}$ and MIL-53(Al) are in good agreement with the literature patterns reported earlier by Ferey et al. (Fig. 1) (Loiseau et al., 2004). The diffraction patterns are obviously different, since the guest removal by heating leads to an expansion of the cell for MIL-53(Al).

The FT-IR spectra of MIL-53$(Al)_{as}$ and MIL-53(Al) (Fig. 2) exhibit vibration bands in the region 1400–1700 cm^{-1} for the carboxylic functional groups (Loiseau et al., 2004). The FT-IR of MIL-53$(Al)_{as}$ samples exhibits bands at 1601 cm^{-1} and 1512 cm^{-1} corresponds to —COO asymmetric stretching whereas the bands at 1413 cm^{-1}

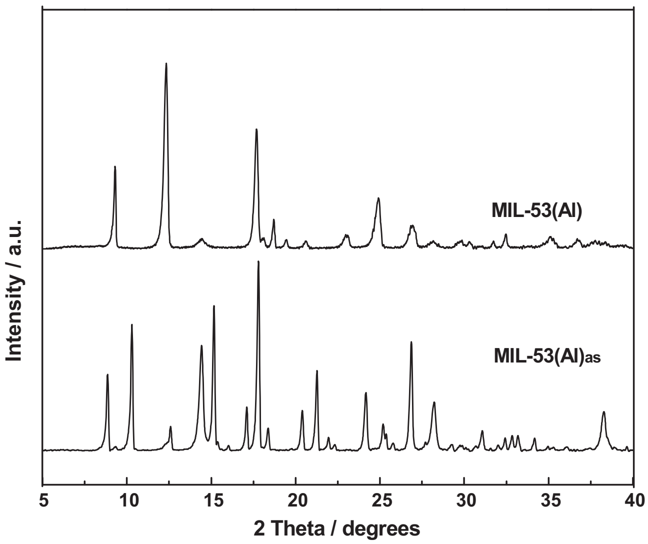


Fig. 1. XRD patterns of as-synthesized, MIL-53(Al)$_{as}$; purified, MIL-53(Al).

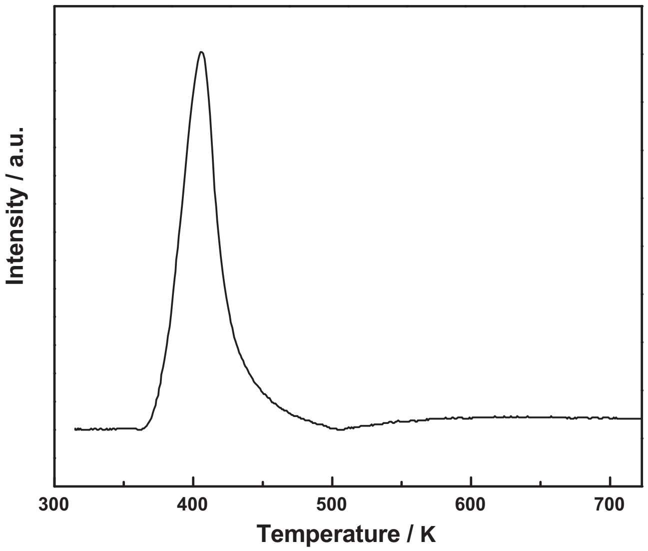


Fig. 3. NH_3-TPD patterns of MIL-53(Al).

attribute to —COO symmetric stretching (Loiseau et al., 2004). An additional absorption peak is observed at 1699 cm^{-1}, which can be attributed to —COOH group of unreacted free BDC acid that trapped in the cavities of MIL-53(Al)$_{as}$ also seen by XRD data. But for MIL-53(Al), any absorption bands are not observed at 1699 cm^{-1} indicating removal of free BDC molecules after calcination.

From the typical type I nitrogen adsorption–desorption isotherm (see the Supporting information Fig. S1), the BET surface area have been measured to be 1233.4 m^2 g^{-1} (Langmuir surface area: 1335.3 m^2 g^{-1}) with a corresponding micropore volume of 0.45 cm^3 g^{-1}. The SEM and TEM images reveal that MIL-53(Al) is composed of rods with a size of about 5 μm assembled by the lozenge shaped crystals (Fig. S2). The definite crystal shape is not observed and the size distribution is relatively wide, most probably due to the polycrystalline agglomerate nature of the crystals.

MIL-53(Al) built up from 1D lozenge-shaped tunnels created by chains of octahedrae sharing OH vertices that are linked in the two other directions may exhibt acidic property. The acidic property of MIL-53(Al) was determined by means of NH_3 temperature-programmed desorption (NH_3-TPD) as shown in Fig. 3. Low temperature peak at ca. 404 K, indicated the presence of relatively weak acidic sites which was probably Brønsted acid sites. MIL-53(Al) exhibited acidic amounts of 0.38 mmol g^{-1} and suggested its potential applications in acid catalysis for hydrolysis of biomass.

3.2. Catalytic performance

MIL-53(Al) catalyst was then tested for hydrothermal conversion of CMC. The reaction conditions, such as catalyst dosage, reaction time and temperature were optimized in advance. Influence of catalyst dosage on the activity was investigated by varying the amount of catalyst in the range of 25–150 mg in 80 mL of H_2O solution under the same condition. As shown in Fig. 4, an initial steep increase in the yield of 5-HMF was observed when the amount of the catalyst was increased up to 75 mg. Beyond this amount, the yield of 5-HMF slightly decreased. It is probable that large catalyst dosages provide excess active sites in the system that accelerate side reactions (including rehydration or condensation, etc.) (Tian,

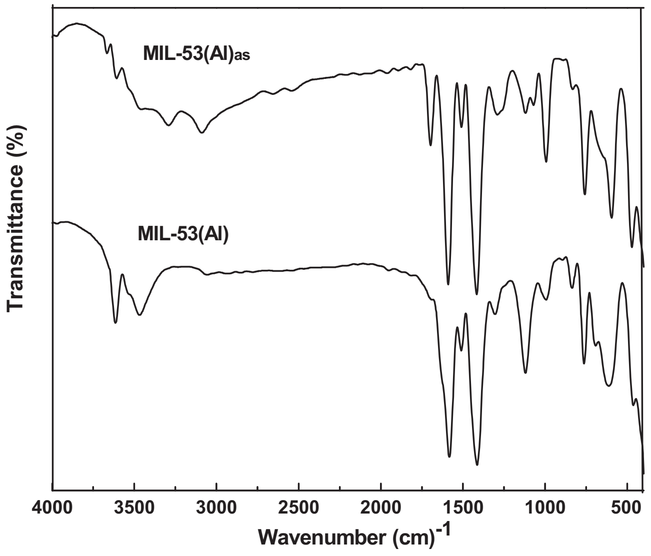


Fig. 2. FT-IR spectra of as-synthesized, MIL-53(Al)$_{as}$; purified, MIL-53(Al).

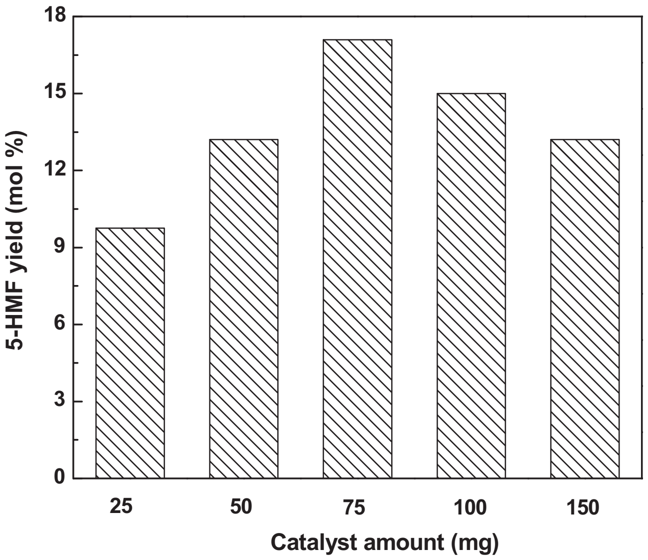


Fig. 4. Effect of catalyst dosage on the CMC hydrolysis by MIL-53(Al) catalyst. (Note: Reaction condition: substrate, 100 mg CMC; reaction time, 11 h; reaction temperature, 423 K; solvent, H_2O 80 mL.)

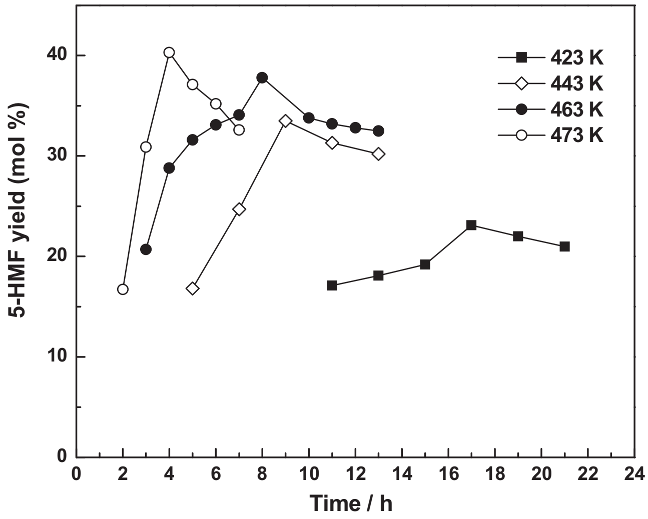


Fig. 5. Effect of reaction temperature and reaction time on the CMC hydrolysis by MIL-53(Al) catalyst.
(Note: Reaction condition: substrate, 100 mg CMC; catalyst, 75 mg; solvent, H_2O 80 mL.)

Tong, Cheng, & Xue, 2013). Therefore, 75 mg was selected as the suitable amount of the catalyst for the CMC hydrolysis.

For heterogeneous catalytic reactions, a sufficient reaction time and temperature are critical for achieving adequate mass transportation in the reactions (Kuo et al., 2013). Fig. 5 shows that MIL-53(Al) catalyst is efficient for CMC hydrolysis, and the reaction temperature and time had a great effect on the 5-HMF yield. The yield of the 5-HMF increased as the reaction temperature was increased. However, when reaction temperature passed 473 K, CMC converted to other products and 5-HMF was not detected. It has been reported that 5-HMF is not very steady in high temperature water, and can be transformed into other substances (Lü, Li, & Zhang, 2008). Therefore, 473 K was selected as the suitable reaction temperature. Furthermore, it is clear that the yield of the 5-HMF increased as the reaction time rose and passed through a maximum at each temperature, respectivety. A further increase in the reaction time resulted in significant decrease in the yield of the 5-HMF, probably owing to 5-HMF being further converted to by-products. The decomposition of 5-HMF to some products was also reported (Chheda, Román-Leshkov, & Dumesic, 2007). The generation of by-products was more rapid than that of 5-HMF at that time. Thus, we suggest the optimal reaction temperature is 473 K and reaction time to be 4 h in aqueous solvent system.

The hydrolysis of CMC to 5-HMF over different MOF catalysts under same conditions are summarized in Table 1. Possible products, 5-HMF and TRS, were identified, and their calibration curves were depicted beforehand. Generally, the hydrolysis of cellulose occurs by two consecutive reactions: conversion of cellulose into reducing sugars (glucose) and the further decomposition of the formed sugars into other products such as 5-HMF, levulinic acid, furfural and so on (dos Santos et al., 2013). The yield of TRS was determined by the equilibrium between CMC hydrolysis and glucose decomposition. Obviously, all the used MOFs have the ability to convert CMC to sugars and 5-HMF with certain yields except Zn-MOFs. This did remind us the potential applications of MOFs in the cellulosic conversion. It is also apparent that MIL-53(Al) exhibits highest yield of 5-HMF and TRS among the used catalysts in this work and it is even superior to those systems relevant to the formation of TRS and 5-HMF in the literatures using water as solvents. Since it is believed that acid catalysts are helpful for accelerating the hydrolysis of cellulose (Kuo et al., 2013), the well-isolated acid sites of MIL-53(Al) catalyst observed by NH_3-TPD can facilitate converting CMC directly to 5-HMF. And the presence of this —COOH groups in MIL-53(Al) materials also promote the adsorption of CMC and water molecules through hydrogen bonding, resulting in efficient hydrolysis of CMC (Guo et al., 2013; Suganuma et al., 2008).

Since aluminum was the active component, further comparison was made between MIL-53(Al) and other Al doped mesoporous materials such as, dodecylamine templated titania (Al–TiO_2/DDA) (Yao, Fang, Ou, Wang, & Yan, 2006), rubber latex bio-templated silica (Al–SiO_2/RL) (Ma et al., 2011; Yao et al., 2006), rubber latex bio-templated alumina (Al_2O_3/RL) (Ma et al., 2011) and commercial Al_2O_3 (Table 1). Again, MIL-53(Al) exhibited significantly higher activity. This may suggest that the large micropores, well-isolated acid sites of MIL-53(Al) catalyst allow fast diffusion of the reactants and thereby facilitating its catalytic reactivity (Lee et al., 2009). Besides, compared to conventionally used mesoporous inorganic materials, MOFs exhibit the potential for more flexible rational design, by controlling the size and the functionalization of the organic linkers (Li, Eddaoudi, O'Keeffe, & Yaghi, 1999). The well-dispersed and effective catalytic sites can be introduced during MOF's framework construction, in the metal sites or organic links (Song et al., 2011). Therefore, MOFs offer a new platform upon which to generate a high density of active catalytic centers, achieve good mass transport (Dau & Cohen, 2013).

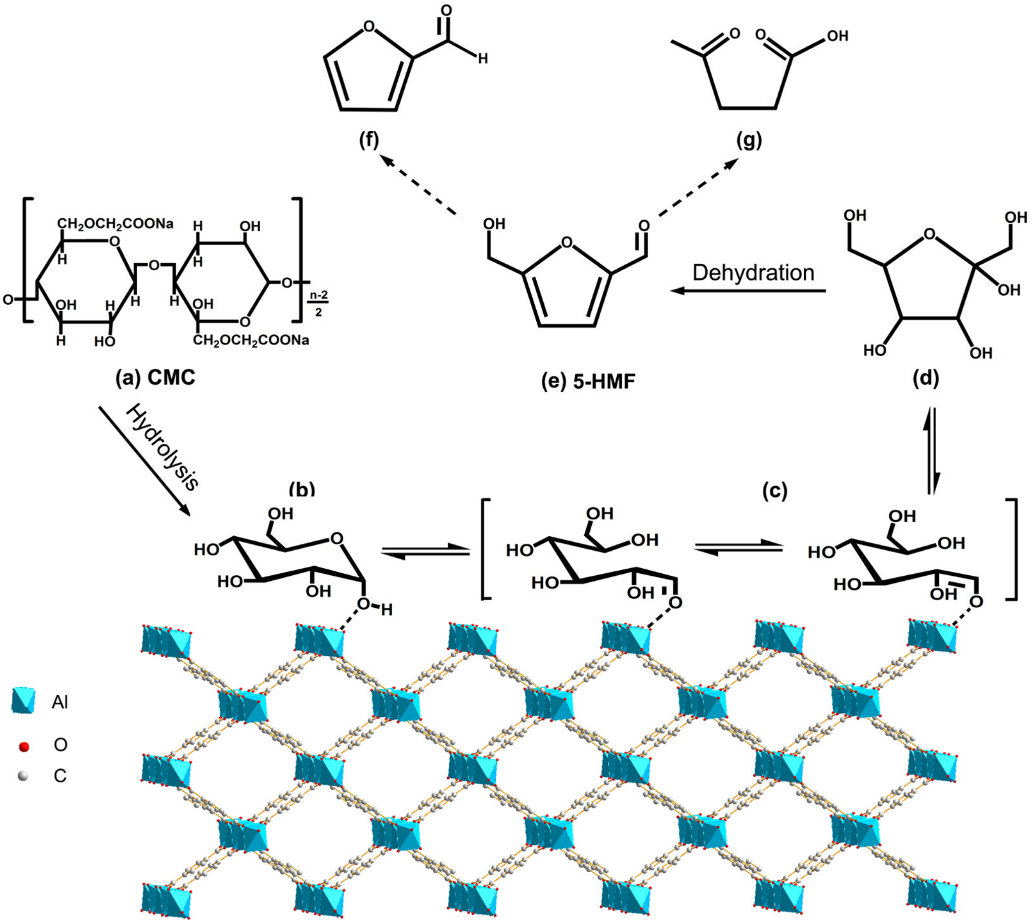
In order to prove whether the catalyst is a heterogeneous one, experiments with fast hot catalyst filtration had been done by a modified process as Ma et al. (2011). The ICP-AES analysis of the filtrates obtained from the fast hot catalyst filtration with negligible amount of leaching of active aluminum species ($\leq$0.001 wt%) was detected. This indicated that the active component (aluminum) did not leach to the solution and MIL-53(Al) did act as a heterogeneous catalyst.

To study the recycling ability of MIL-53(Al) under the optimum reaction conditions, recycling experiments were carried out. The typical recycling procedure was as follows: after the initial reaction,

Table 1
Comparison of catalytic activities of different MOF catalysts for the hydrothermal decomposition of CMC to 5-HMF[a].

Catalyst	Temperature [K]	Time [h]	5-HMF yield [mol%]	TRS yield [mol%]
MIL-100(Cr)	473	4	25.8	38.9
MIL-101(Cr)	473	4	25.3	40.3
ZIF-8(Zn)	473	4	–	36.7
MOF-5(Zn)	473	4	–	29.9
UiO-66(Zr)	473	4	24.5	34.2
MIL-53(Al)	473	4	40.3	54.2
MIL-125(Ti)	473	4	30.9	32.4
HKUST-1(Cu)	473	4	31.8	42.1
Al–SiO_2/RL	473	4	24.0	31.2
Al–TiO_2/DDA	473	4	28.6	34.7
Commercial Al_2O_3	473	4	18.6	35.2
Al_2O_3/RL	473	4	18.4	38.1

[a] Note: Reaction condition: substrate, 100 mg CMC; reaction time, 4 h; reaction temperature, 473 K; catalyst, 75 mg; solvent, H_2O 80 mL.



Scheme 1. A possible reaction pathway for the hydrolysis of carboxymethyl cellulose over MIL-53(Al) catalyst.

the catalyst was separated from the reaction mixture by centrifugation and washed with deionized water and ethanol, followed by dryness at 473 K in an oven under vacuum for 12 h. Next, fresh CMC and water were added to the recovered catalyst and then the second run started. Similarly, the third run was also performed by using the same procedure. The 5-HMF molar yield only slightly dropped from the 40.3% to 39.1% and 38.4% with the first, second and third run, respectively. The decrease of 5-HMF yield in the recycle experiments can be attributed to the mass loss of the catalyst in the washing steps and the blockage of active acid sites by humins products. And the X-ray diffraction patterns of the fresh and used MIL-53(Al) were almost similar verified the crystallinity and stability of MIL-53(Al) after the catalytic reactions (Fig. 6). The high thermal stability of MIL-53(Al) is in good agreement with the literature (Loiseau et al., 2004).

Based on the above experimental results and the mechanisms proposed for the hydrolysis of the cellulose in references (Deng et al., 2012; dos Santos et al., 2013), a possible reaction pathway for the hydrolysis of carboxymethyl cellulose over MIL-53(Al) catalyst was depicted in Scheme 1. In the presence of a Brønsted acid sites and water, a possible reaction mechanism could involve coordination of carboxymethyl cellulose oxygen species to the metal center activating bonds for subsequent reactions, such as hydrolysis and degradation. First, the polymer chains of carboxymethyl cellulose (a) are broken down into low molecular mass fragments and ultimately to Al–glucose complex (b) by the action of an acid MIL-53(Al) catalyst. Then, Al species could coordinate with the hydroxyl groups of glucose to form an enediol structure (c), which is considered as the key intermediate in the isomerization of glucose to fructose (d). Finally, 5-HMF (e) can be obtained by dehydration of fructose. Moreover, furfural (f) and levulinic acid (g) are possible by-product.

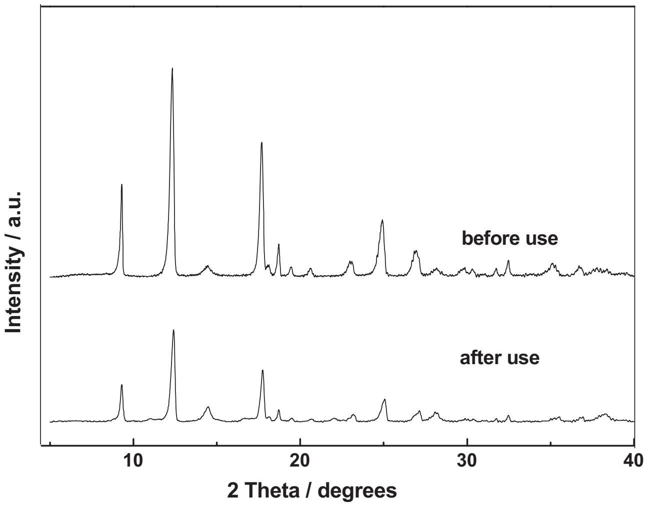


Fig. 6. XRD patterns of MIL-53(Al) (before use and after use).

4. Conclusions

In conclusion, the hydrolysis of CMC catalyzed by unfunctionalized MIL-53(Al) with an environment-friendly chemical process has been firstly studied. MIL-53(Al) with Brønsted acid sites has been shown to be an efficient heterogeneous catalyst for the hydrolysis of CMC to 5-HMF. At optimal reaction conditions, a 5-HMF molar yield of 40.3% and TRS molar yield of 54.2% were obtained. The use of MOF catalyst in simple aqueous solvent system opens up new opportunities to convert biomass resources to high-value added chemical under relatively mild reaction conditions. Moreover, MIL-53(Al) catalyst demonstrated here would be extended to other acid-catalyzed reactions.

Acknowledgments

The authors thank the National Natural Science Foundation of China (Project NSFC-YN U1033603, 21263027, 21063016), and Program for Innovative Research Team (in Science and Technology) in University of Yunnan Province (IRTSTYN) for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.08.065.

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