

Research Article

Hydrothermal Catalytic Conversion of Glucose into Lactic Acid with Acidic MIL-101(Fe)

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MIL-101(Fe) was explored for the first time for the catalytic conversion of glucose into lactic acid (LA). The as-synthesized MIL-101(Fe) was successfully characterized, and its higher specific surface area, porosity, and feasible acid properties were confirmed to determine the remarkable catalytic activity in glucose-to-LA conversion (up to 25.4% yield) compared with other catalysts like MIL-101(Cr, Al) and UiO-66(Zr). The reaction parameters including temperature, reaction time, and substrate species as well as catalyst reusability were discussed.

1. Introduction

Lactic acid (LA), the most versatile biomass-derived platform molecule, has made numerous contributions in the food industry, cosmetic, and chemical industries [1, 2]. It is also a significant building block for the formation of largescale noticeable intermediates, such as propylene glycol, 2,3pentanedione, pyruvic acid, and alkyl lactates [3]. Furthermore, LA is the feedstock for the manufacture of biodegradable plastics such as polylactic acid, a potential candidate to supersede petroleum-derived polymers.

Currently, LA is primarily prepared through the conventional biotechnological process via the fermentation of carbohydrates [1]. For the sake of conquering the detriments including high enzyme cost, low space-time yield, undesirable waste effluents, and large complexity in purification of the bio-fermentation technology, significant efforts have been paid for the effective chemical catalytic processes for obtaining LA from biomass-based material with satisfactory yield and selectivity under moderate conditions [4–8].

In comparison with homogeneous catalysts, solid catalysts can be readily recovered without any substantial change in catalytic effectiveness. Metal-organic framework (MOF) catalysts showed excellent catalytic efficiency [9–11] in the transformation of carbohydrates to LA due to their structural properties. MOFs drew notable attention on account of the unique properties, such as extremely high surface areas, tunable pore volumes, adjustable pores, and multi-functionalization [12–15]. The existence of coordinatively unsaturated metal sites (CUS) in MOFs facilitates their interactions with substrates, the metal ion, or cluster serving as Lewis acid or redox center [16, 17]. MIL-101 as an efficient Lewis acid catalyst is able to catalyze the benzaldehyde cyanosilylation reaction [18], carboxylation of epoxides [19], and benzylic oxidation of tetralin [20].

For all we know, rare investigation has been conducted on the preparation of LA from glucose with MOFs as catalysts. Herein, we demonstrated the catalytic performance of MIL-101(Fe, Cr, Al) and UiO-66(Zr)s in the one-pot transformation process of glucose to LA in H_2O .

2. Experimental

2.1. *Materials*. All the reagent raw materials were directly used, and no further purification was needed. Fructose (99%), glucose (99%), sucrose (AR), cellobiose (98%), inulin

and LA (99%), formic acid (FA, 98%), 5-hydroxymethylfurfural (HMF, 99%), CrO_3 (99%), $Cu(NO_3)_2$ ·3H₂O (99%), $FeCl_3$ ·6H₂O (AR), and hydrofluoric acid (49%) were obtained from the Aladdin Industrial Corporation. 1,3,5-Benzenetricarboxylic acid (H₃BTC), acetic acid (AA, 99.8%), and levulinic acid (LeA, 99%) were bought from the J&K Scientific Ltd. Ethanol (AR grade) was gained from Chongqing Chuandong Chemical co., Ltd. Distilled water has been made by the Milli-Q Advantage A10 (USA) ultrapure water purification system.

2.2. Analysis. The analysis of sugars was achieved by using HPLC (Agilent 1100 instrument with a refractive index detector) with an Aminex HPX-87H (300 mm × 7.8 mm I.D., Bio-Rad Laboratories, Inc.) column. LA, FA, and AA were analyzed by using the Agilent HPLC with an Agilent TC-C18 column and applied 0.05 wt% H₃PO₄ aqueous solution (A) and methanol (B) $(V_A: V_B = 90:10)$ as an eluent. The UV detector was set at 210 nm and was operated with a flow rate of 0.6 mL·min⁻¹. The LeA detection chose 0.05 wt% H₃PO₄ aqueous solution (C) together with acetonitrile (D) ($V_{\rm C}$: $V_{\rm D} = 90:10$), and the detector was set at 254 nm with 0.6 mL min⁻¹ flow rate. With HMF, the mobile phase was composed of MeOH (E) and H_2O (F) ($V_E: V_F = 65:35$), 1.0 mL·min⁻¹, at 280 nm. For the HPLC analyses, 0.5 mL of the reaction mixture was diluted to a total volume of 5.0 mL with the eluent. The products and by-products were identified by using UV (210 nm) detectors by comparing them with the original samples. Sugars were analyzed by using an Agilent 1100 HPLC fitted with an Aminex HPX-87H column.

2.3. Catalyst Preparation and Characterization

2.3.1. The Synthesis of MIL-101(Fe). The synthesis of MIL-101(Fe) by using the solvothermal method was proceeded, according to the published literature [21] with slight modifications. In a typical procedure, iron(III) chloride (FeCl₃·6H₂O; 2.63 g, 9.73 mmol) and 1,4-benzene dicarboxylic acid (H₂BDC; 0.808 g, 4.865 mmol) were located in 60 ml N, N-dimethylformamide (DMF). Then, the mixture was stirred at room temperature for 20 min and introduced into a solvothermal bomb which is held at 110°C for 20 h in an autoclave.

2.3.2. The Synthesis of MIL-101(Al). The synthesis of MIL-101(Fe) by using the solvothermal method was proceeded [22]. In a typical procedure, aluminum(III) chloride (AlCl₃; 0.282 g, 2.11 mmol) and 1,4-benzene dicarboxylic acid (H₂BDC; 0.514 g, 3.09 mmol) were located in 30 ml DMF. Then, the mixture was stirred at room temperature for 20 min and introduced into a solvothermal bomb which is held at 130°C for 72 h in an autoclave.

2.3.3. The Synthesis of MIL-101(Cr). The synthesis of MIL-101(Cr) by using the hydrothermal method was carried out [23]. In a typical procedure, chromic nitrate nonahydrate

 $(Cr(NO_3)_3.9H_2O; 2.4 \text{ g}, 6 \text{ mmol}), 1,4$ -benzene dicarboxylic acid $(H_2BDC; (0.99 \text{ g}, 6 \text{ mmol}), \text{ and } HF(49\%, 0.2 \text{ mL})$ were located in 30 ml H₂O. Then, the mixture was stirred at room temperature for 20 min and introduced into a solvothermal bomb which is held at 220°C for 8 h in an autoclave.

2.3.4. The Synthesis of UiO-66(Zr)-1. The synthesis of UiO-66(Zr)-1 by using the solvothermal method was proceeded [24]. In a typical procedure, zirconium tetrachloride (ZrCl₄; 0.35 g, 1.5 mmol) and 1,4-benzene dicarboxylic acid (H₂BDC; 0.25 g, 1.5 mmol) were located in 15.5 ml DMF. Then, the mixture was stirred at room temperature for 20 min and introduced into a solvothermal bomb which is held at 120°C for 24 h in an autoclave.

2.3.5. The Synthesis of UiO-66(Zr)-2. The synthesis of UiO-66(Zr)-2 by using the solvothermal method was carried out [25]. In a typical procedure, zirconium tetrachloride (ZrCl₄; 0.16 g, 0.686 mmol), 1,4-benzene dicarboxylic acid (H₂BDC; 0.114 g, 0.686 mmol), and AcOH (2.8 mL) were located in 35 ml DMF. Then, the mixture was stirred at room temperature for 20 min and introduced into a solvothermal bomb which is held at 120°C for 24 h in an autoclave.

2.3.6. The Synthesis of UiO-66(Zr)-3. The synthesis of UiO-66(Zr)-3 by using the solvothermal method was proceeded [26]. In a typical procedure, zirconium tetrachloride (ZrCl₄; 0.287 g, 1.233 mmol), 1,4-benzene dicarboxylic acid (H₂BDC; 0.205 g, 1.233 mmol), and trifluoroacetic acid (1.15 mL) were located in 33 ml DMF. Then, the mixture was stirred at room temperature for 20 min and introduced into a solvothermal bomb which is held at 120°C for 72 h in an autoclave.

2.3.7. The Synthesis of UiO-66(Zr)-4. The synthesis of UiO-66(Zr)-4 by using the solvothermal method was carried out [26]. In a typical procedure, zirconium tetrachloride (ZrCl₄; 0.431 g, 1.85 mmol), 1,4-benzene dicarboxylic acid (H₂BDC; 0.308 g, 1.85 mmol), and trifluoroacetic acid (5.2 mL) were located in 66 ml DMF. Then, the mixture was stirred at room temperature for 20 min and introduced into a solvothermal bomb which is held at 120°C for 72 h in an autoclave.

2.3.8. The Synthesis of UiO-66(Zr)-5. The synthesis of UiO-66(Zr)-5 by using the solvothermal method was proceeded [27]. In a typical procedure, zirconium tetrachloride (ZrCl₄; 0.125 g, 0.54 mmol), 1,4-benzene dicarboxylic acid (H₂BDC; 0.126 g, 0.756 mmol), and HCl (1 mL) were located in 15 ml DMF. Then, the mixture was stirred at room temperature for 20 min and introduced into a solvothermal bomb which is held at 80°C for 24 h in an autoclave.

The X-ray powder diffraction (XRD) patterns were recorded by using an XPD-6000 diffractometer with Cu monochromatic K α radiation ($\lambda = 0.1541$ nm) in a scanning range of 5–35° at a scanning rate of 1°min⁻¹. The N₂ adsorption experiments were performed in a static volumetric

apparatus (Micromeritics ASAP 2020); prior to the adsorption measurement, the sample was degassed in vacuum at 150°C for 12 h. The specific surface areas of the explored samples have been calculated using the multiple-point Brunauer–Emmett–Teller (BET) method in the relative pressure range of $p/p_0 = 0.05-0.20$, and the total pore volumes were determined at a relative pressure of 0.95. The thermogravimetric analysis (TGA) was conducted on a NETZSCH STA 449 C apparatus with 10°C min⁻¹ heating rate under N₂ flow (40 mL·min⁻¹). The acid properties of MOFs were characterized by using NH₃-TPD conducted on an AutoChem 2920 chemisorption analyser with a heating rate of 10°C/min.

2.4. Catalytic Reactions. All tests were conducted in a 25 mL Teflon-lined autoclave. Generally, reactant (50 mg), catalyst (50 mg), and H_2O (10 mL) were poured into the vessel; then, the vessel was placed into a preheated oil bath at 190°C for 2 h with magnetic stirring. The autoclave was sunk in the oil, and the time was recorded immediately. The reactor was quickly put into cold water, and the test ends. Afterward, the catalyst was recovered via centrifugation and the reaction liquid was filtered with a 0.45 mm syringe filter, and then the catalyst was detected by HPLC.

Furthermore, blank trials with no catalyst and tests with our published report catalyst MIL-100(Fe) were conducted. Four recycle tests were also conducted to check the catalyst stability. After each run, the retrieved solid was washed with EtOH.

3. Results and Discussion

3.1. Catalyst Characterization. The as-prepared XRD pattern of MIL-101(Fe) is presented in Figure 1, which shows the explored catalyst is in accordance with the simulated one and in accordance with the literature [21], implying the synthesis of MIL-101(Fe).

The textural characters of the prepared MIL-101(Fe) evaluated by the N₂ adsorption isotherm are shown in Figure 2. The as-prepared MIL-101(Fe) provided high BET surface area (2743.6 m² g⁻¹) and pore volume (0.83 cm³ g⁻¹).

Figure 3 demonstrates that the MIL-101(Fe) is steady up to 230°C, as verified by the TG analysis, and the weight loss proceeds in steps in the range of 0 to 550°C. The first step (about 12 wt%) between 23 and 100°C is ascribed to the desorption of free solvent DMF molecules existed in the pore volume. The second step (about 15 wt%) in the range of 100–310°C is because of coordination of water to the iron trimers. The final weight loss, between 310 and 460°C (about 38 wt%), is regard as the decomposition of the H₂BDC.

3.2. Catalytic Activity

3.2.1. Conversion of Glucose into LA Catalyzed by Different Catalysts. The product distribution derived from catalyzation of glucose by different solid materials was analyzed, and the consequences are displayed in Table 1. 8.5% LA yield was achieved with no catalyst. The blank experiment was



15

Intensity (a.u.)

5

FIGURE 1: XRD diffraction patterns of as-synthesized and simulated standard MIL-101(Fe).

 2θ (degrees)

10



FIGURE 2: N₂ isotherm of the synthesized MIL-101(Fe).



FIGURE 3: TG graph of the synthesized MIL-101(Fe).

20

Entry	Catalyst	Conv. (%)	Yield (%)					
			LA	HMF	FA	AA	LeA	Total
1	_	62.6	8.5	26.4	3.4	4.5	4.0	46.8
2	UiO-66(Zr)-1	52.1	21.6	6.0	7.3	3.2	0	38.1
3	UiO-66(Zr)-2	55.3	18.6	4.6	5.9	5.1	6.1	40.2
4	UiO-66(Zr)-3	55.4	20.0	9.6	6.2	4.8	0	40.6
5	UiO-66(Zr)-4	41.1	18.8	7.5	5.9	3.0	0	28.2
6	UiO-66(Zr)-5	40.9	16.6	3.5	6.2	1.6	0	27.9
7	MIL-101(Cr)	62.5	14.1	19.4	5.3	1.2	6.6	46.6
8	MIL-101(Al)	62.1	13.4	23.1	7.0	2.8	0	46.3
9	MIL-101(Fe)	70.8	25.4	17.1	9.4	1.8	0	53.7
10^{b}	MIL-100(Fe)	87.0	32	17	9	7	6	71

TABLE 1: Conversions and yields for catalytic conversion of glucose into LA over various solid catalysts^a.

^aReaction conditions: glucose 50 mg and catalyst 50 mg, 190°C, 2 h. ^bRef. [28].

compared to the catalytic activity of MIL-101(Fe) confirming the particular material processed potential to synthesize LA.

Experiments with multiple UiO-66(Zr) were carried out in order to verify whether the defects of the UiO-66(Zr) by different acids can improve the Lewis acidity and even the production of LA (entries 2-6; Table 1). The catalytic performances of various MIL-101(Cr, Al, Fe) and MIL-100(Fe) were examined for the conversion of glucose into LA. Apparently, Table 1 shows that LA combined with HMF, FA, AA, and LeA is the main product distributed in the reaction medium. MIL-101(Fe) is the optimum catalyst during investigation of MOFs, achieving 25.4% yield of LA, which ascribed to its superior morphological and textural characters with higher specific surface area $(S_{BET} = 2743.6 \text{ m}^2 \text{ g}^{-1})$. In addition, thermal stability is a significant parameter for good catalytic activity in accordance with the previous findings [28].

The previous research has shown that Lewis acid acted as the active center illustrating good performance [28]. To explore the crucial factors for the performance difference of the MOFs, the acid strength was further compared (Table 2). As acidity was obtained from the metal centers and M-OH (M = Zr, Cr, Al, Fe), NH₃-TPD illustrated the disparity of MOFs that UiO-66(Zr)-2~5 has more medium acid, while UiO-66(Zr)-1 and MIL-101(Fe) have much weak acid and minor medium acid, respectively [29]. The optimal performance of MIL-101(Fe) could be attributed to the appropriate acid strength and content.

3.2.2. Influence of Reaction Temperature on the Production of LA. To clarify the important effect of reaction temperature on glucose conversion catalyzed by MIL-101(Fe) (Figure 4), the subsequent experiments were carried out under 150° C, 170° C, and 190° C, respectively. The glucose conversion was enhanced sharply from 34.8% to 70.8%. With the extension of reaction temperature, the LA yield increased up to 25.4% at 190°C, while the FA, AA, and LeA yields were as well increased with elevated temperature. According to the published report, the yield of HMF went up to 15.6% at 170°C and went down to 11.5% at 190°C. The process of HMF formation is parallel to that of the synthesis of LA,

TABLE 2: The acid content distribution of MOFs.

Enters	Catalwata	Acid content (mmol/g)				
Entry	Catalysis	<200°C	200-300°C	Total		
1	UiO-66(Zr)-1	0.47	1.96	2.43		
2	UiO-66(Zr)-2	0.67	1.15	1.82		
3	UiO-66(Zr)-3	0.66	1.73	2.39		
4	UiO-66(Zr)-4	0.58	3.14	3.72		
5	UiO-66(Zr)-5	0.41	3.58	3.99		
6	MIL-101(Cr)	0.28	4.51	4.79		
7	MIL-101(Al)	0.18	0.95	1.13		
8	MIL-101(Fe)	1.28	0.52	1.80		



FIGURE 4: Reaction temperature effect on the LA yield. Reaction conditions: glucose 0.05 (g), MIL-101(Fe) 0.05 (g), and water 10 mL, 2 h.

which explained the 10.5% augmentation of LA augment compared to 170°C [30].

3.2.3. Effect of Reaction Time on the Conversion of Glucose into LA. The LA yield is significantly influenced by reaction time (Figure 5). The results indicated that the yield of LA increased first and then decreased with prolonging the



FIGURE 5: Reaction time effect on the LA yield. Reaction conditions: glucose 0.05 (g), MIL-101(Fe) 0.05 (g), and water 10 mL, 190°C.



FIGURE 6: Different substrates converted into LA using MIL-101(Fe) as a catalyst. Reaction conditions: substrate 0.05 (g), catalyst 0.05 (g), H_2O 10 mL, 190°C, 2 h.

reaction time. MIL-101(Fe) could provide a maximum LA yield of 25.4% when the reaction was terminated at 2 h in the one-pot process over the MIL-101(Fe) catalyst, which is comparable with those published results with the same reaction time [31]. Hence, 2 h was chosen as the optimal time for further investigation.

3.2.4. Various Sugars Converted into LA under MIL-101(Fe). The catalytic activities of the MIL-101(Fe) catalyst hydrothermally convert various biomass-derived feedstocks, including glucose, fructose, sucrose, inulin, and cellobiose, into LA. The results presented in Figure 6 implies that the monosaccharides are easily converted and the substrate glucose shows better LA yield than fructose, which depend on the



FIGURE 7: Reusability of MIL-101(Fe) for the conversion of glucose into LA. Reaction conditions: glucose 0.05 (g), MIL-101(Fe) 0.05 (g), and water 10 mL, 190° C, 2 h.

appropriate acid strength and content and further proved the aforementioned view. When sucrose, cellobiose, and inulin are as feedstocks, good LA yield requires higher temperature and longer reaction time than the present reaction condition.

3.3. Catalyst Reusability. To make uttermost study of the catalysts, the reusability of the MIL-101(Fe) catalyst was also evaluated in the conversion of glucose into LA by the hydrothermal reaction with fourth consecutive cycles. The catalytic activity results of reusable catalysts are presented in Figure 7. The glucose conversion decreased from 70.8% to 54.9%, and LA yield dropped from an initial value of 25.4% to 18.5% after four recycles. The decrease of LA yield may be due to the partial deposition of some oligomeric byproducts in pores that lead to the blocking of the active sites and partial ingredient changes within the catalyst, which are consistent with our published work [28].

4. Conclusions

In summary, the prepared MIL-101(Fe) catalyst was successfully characterized and applied in the production of LA from glucose with good catalytic performance. The optimal LA yield reached 25.4% ascribing to the catalyst structure properties and appropriate acid strength. The optimal experiments indicated that reaction temperature and time determined the catalytic activities and reduced the by-products, which further influence the reusability of catalyst. Hence, MOFs are promising materials for biomass valorization and particularly for the LA preparation by chemical processes.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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