Article

Sulfonic Acids Supported on UiO-66 as Heterogeneous Catalysts for the Esterification of Fatty Acids for Biodiesel Production

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Abstract: Zr-MOF (UiO-66) catalysts PTSA/UiO-66 and MSA/UiO-66 bearing supported sulfonic acids (*p*-toluenesulfonic acid and methanesulfonic acid, respectively) were prepared through a simple impregnation approach. The UiO-66-supported sulfonic acid catalysts were characterized by X-ray diffraction (XRD), N₂ adsorption-desorption, fourier transform infrared spectroscopy (FT-IR) and elemental analysis. The prepared heterogeneous acid catalysts had excellent stability since their crystalline structure was not changed compared with that of the original UiO-66. Zr-MOF MSA/UiO-66 and PTSA/UiO-66 were next successfully used as heterogeneous acid catalysts for the esterification of biomass-derived fatty acids (e.g., palmitic acid, oleic acid) with various alcohols (e.g., methanol, *n*-butanol). The results demonstrated that both of them had high activity and excellent reusability (more than nine successive cycles) in esterification reactions. Alcohols with higher polarity (e.g., methanol) affected the solid catalyst reusability slightly, while alcohols with moderate or lower polarity (e.g., *n*-butanol, *n*-decanol) had no influence. Thus, these developed sulfonic acids-supported metal-organic frameworks (UiO-66) have the potential for use in biodiesel production with excellent reusability.

Keywords: metal-organic frameworks; UiO-66; heterogeneous acid catalyst; sulfonic acids; esterification; biodiesel

1. Introduction

Fatty acid esters are derivatives of fatty acids that play an important role in daily life and industrial production [1,2]. The main applications of fatty acid ester products are industrial washing solvents, lubricants, surfactants, plastic processing additives, cosmetic additives and so on [3–5]. More importantly, fatty acid esters, including fatty acid methyl esters, fatty acid ethyl esters and fatty acid butyl esters, are a class of biodiesel, used as a renewable energy source [6–8]. One of the main processes to produce fatty acid esters (biodiesel) is the esterification of fatty acids with short chain alcohols (e.g., methanol, ethanol, butanol) [9,10].

Preparation of fatty acid esters through esterification reaction commonly uses acid catalysts. Though homogeneous acid catalysts, such as mineral acids (e.g., H₂SO₄) have higher catalytic activity in fatty acid esters preparation, they cannot be separated easily from the products and can lead to equipment corrosion [11,12]. Other homogeneous organo-acid catalysts (e.g., *p*-toluenesulfonic acid) cannot be reused easily and lead to environmental pollution as well. With the development of sustainable and green chemistry, solid acid catalysts are highly desirable [13]. The solid acid

catalysts not only have high catalytic activity, but also can be readily recycled [6,14,15]. For instance, sulfonic acid functionalization of porous materials is considered as one of the most efficient strategies to produce solid acid catalysts, such as sulfonic acid-functionalized metal-organic frameworks (e.g., UiO-66) [16], sulfonic acid-functionalized porous organic polymers (HO₃S-POP) [17], sulfonic acid-functionalized mesoporous silica (SBA-15-SO₃H) [18], sulfonic acid-functionalized mesoporous zeolites (e.g., ZSM-5) [19] and so on.

Porous materials with excellent ion exchange, adsorption and catalysis ability owing to their high surface area and pores [20] include SiO₂ [21], activated carbon [22], zeolites [23] and metal organic frameworks [24], etc. Compared with other porous materials, metal organic frameworks (MOFs) are inorganic-organic materials consisting of inorganic nodes (metal ions or clusters) coordinated with organic linkers (e.g., terephthalate) to form a 3D coordination network [24–26]. They have the largest surface area (up to 10,400 m²/g) and pores ranging from approximately 0.5 to 9.8 nm [24,27,28]. In recent years, MOFs have been widely used in catalysis [29,30], adsorption [31] and as drug carriers [32,33], etc. For example, MIL-101-NH₂ exhibited excellent adsorption capacity for 1,5-naphthalenedisulfonic acid (NDS) and 2-naphthalenesulfonic acid (NSA) acids from water (NDS, 188.1 mg/g; NSA, 285.0 mg/g) [31]. When the pores closely match the size of the adsorbates, they will have the best interactions [34], implying that the pore size of MOFs play a vital role in adsorption. UiO-66, as a Zr-MOF, consists of Zr and terephthalate [34]. The building blocks [Zr₆O₄(OH)₄] are connected with 12 terephthalate ligands in UiO-66 under ideal conditions, and then a face-centered cubic close packing framework is formed [35,36]. That is the highest coordination of organic ligand and metal cluster. Thus UiO-66 is regarded as a high stability crystalline porous solid. In addition, the stability of UiO-66 is also enhanced by Zr-O [37]. The crystalline structure of UiO-66 can tolerate temperatures up to 500 °C, while it has strong acid resistance and a certain alkali resistance [36,38]. UiO-66 has been chosen as a support due to its higher stability. For example, sulfonic acid-functionalized UiO-66, as a catalytic transfer hydrogenation catalyst, has been prepared with sulfonic acid (-SO₃H) groups tethered on a UiO-66 framework [16].

Up to now, examples of the use of sulfonic acids-on-UiO-66 prepared through impregnation approaches as esterification catalysts are rare [39,40]. In this work, an impregnation approach was used to prepare UiO-66 MOF-supported organosulfonic acids (PTSA, MSA) which were evaluated in esterification reactions for biodiesel production, and the reusability of the solid catalyst was investigated.

2. Results and Discussion

2.1. Characterization of UiO-66 and UiO-66-Supported Acids

The degree of crystallinity of the UiO-66 and the UiO-66-supported sulfonic acid species MSA/UiO-66 and PTSA/UiO-66 was evaluated by XRD (Figure 1).

Figure 1. X-ray diffraction (XRD) patterns of the prepared UiO-66 and acids supported UiO-66.

The results demonstrated that Zr-O bonds were formed. The degree of crystallinity of the obtained UiO-66 matched well with the simulated XRD pattern, and the peak shape, position and relative size was also consistent with the results in previous reports [28,34]. The XRD patterns of the sulfonic acids supported on UiO-66 (MSA/UiO-66 and PTSA/UiO-66) were almost the same as the original UiO-66. The above results indicate that the obtained UiO-66 catalysts had a good crystalline structure, which was not affected significantly by the immobilized PTSA or MSA molecules.

FT-IR analysis was used to evaluate the PTSA and MSA supported on UiO-66 (Figure 2). The results showed that the characteristic absorption peak of the proton carboxyl group ($1760 \sim 1690 \text{ cm}^{-1}$) in UiO-66 did not appear, while the carboxyl symmetric stretching vibration (1398 cm^{-1}) and asymmetric stretching (1576 cm^{-1}) vibration absorption peak of the carboxyl ligand were present, indicating that the carboxyl acid existed in a complex form in the UiO-66. The absorption frequency at 1205 cm^{-1} and 1050 cm^{-1} in both PTSA/UiO-66 and MSA/UiO-66 were ascribed to the stretching vibration of $-\text{SO}_3$ groups, implying PTSA and MSA were successfully supported in UiO-66.

Figure 2. Fourier transform infrared spectroscopy (FT-IR) spectra of prepared UiO-66 and UiO-66-supported acids.

The porosity of UiO-66, PTSA/UiO-66 and MSA/UiO-66 was evaluated with N_2 adsorption-desorption analysis (Figure 3).

Figure 3. N_2 adsorption-desorption isotherms of UiO-66-supported acids.

The results showed that the N_2 adsorption-desorption isotherms of UiO-66, PTSA/UiO-66 and MSA/UiO-66 were similar to type I isotherms (according to BDDT classification [41]) with a sharp increase at tail end. The Langmuir surface area of UiO-66 was $1285 \text{ m}^2/\text{g}$ with the total pore volume

and average pore width were $0.46 \text{ m}^3/\text{g}$ and 1.9 nm , respectively, which were close to the previously reported values [35,38]. The surface area, total pore volume and average pore width of PTSA/UiO-66 and MSA/UiO-66 were $959 \text{ m}^2/\text{g}$ and $1059 \text{ m}^2/\text{g}$, $0.34 \text{ m}^3/\text{g}$ and $0.36 \text{ m}^3/\text{g}$, 1.87 nm and 1.79 nm , respectively (Table 1). Compared with original UiO-66, Langmuir surface area, total pore volume and average pore width of the UiO-66-supported acids PTSA/UiO-66 and MSA/UiO-66 were all decreased. It was thus concluded that PTSA and MSA were mainly within the cavities of UiO-66.

Table 1. Physicochemical properties of the prepared catalysts.

Catalyst	$S_L^a/(\text{m}^2/\text{g})$	$V_{\text{total}}^b/(\text{m}^3/\text{g})$	$W_{\text{average}}^c/\text{nm}$
UiO-66	1284.8	0.46	1.90
PTSA/UiO-66	958.5	0.34	1.87
MSA/UiO-66	1058.9	0.36	1.79

^a Langmuir surface area. ^b Total pore volume. ^c Average pore width.

2.2. Effect of Immersion Time on the Content of Organo-Sulfonic Acids in Catalysts

The amount of organosulfonic acids (PTSA or MSA) in the UiO-66-supported acids (PTSA/UiO-66 and MSA/UiO-66) was evaluated through determination of sulphur in UiO-66 by elemental analysis. The adsorption capacity of PTSA and MSA on UiO-66 was also successfully tested by elemental analysis (Figure 4). The sulphur contents in UiO-66 increased as the impregnation time increased (0–5 h), indicating the contents of PTSA or MSA in UiO-66 increased. Absorption equilibrium of PTSA and MSA was achieved at about 5 h, and the average content of PTSA and MSA supported in UiO-66 were $258.9 \pm 5.6 \text{ mg/g}$ and $247.1 \pm 2.1 \text{ mg/g}$, respectively.

Figure 4. The effect of impregnation time on the content of acids in the catalysts.

2.3. The Catalytic Activity of Acids Supported UiO-66 towards the Esterification of Palmitic Acid with Methanol

Solid acid catalysts are suitable to catalyze the esterification reaction of fatty acids. Therefore, the esterification reaction of palmitic acid (PA) with methanol was selected as the model reaction to evaluate the catalytic activity of the UiO-66-supported organosulfonic acid catalysts PTSA/UiO-66 and MSA/UiO-66 (Table 2). To our delight, the conversion of PA was up to 88.2% with PTSA/UiO-66 as solid acid catalyst (Table 2, entry 1). Because esterification is a reversible process, the conversion of PA can be promoted by increasing the amount of methanol. Indeed, the conversion of the esterification increased from 88.2% to 97.1% when the mole ratio of MeOH/PA was increased from 3:1 to 8:1 (Table 2, entries 1–3). By continuing to increase the mole ratio of MeOH/PA to 12:1, the conversion of esterification could not

be improved further. Moreover, a decreased conversion (from 97.1% to 93.5%) was observed when the reaction temperature was lowered from 100 °C to 80 °C (Table 2, entry 6).

Table 2. Esterification of palmitic acid (PA) with methanol ^a.

Entry	Catalyst	MeOH/PA (mol/mol)	Time (h)	Temp. (°C)	Conv. (%) ^b
1	PTSA/UiO-66	3	4	100	88.2
2	PTSA/UiO-66	5	4	100	94.6
3	PTSA/UiO-66	8	4	100	97.1
4	PTSA/UiO-66	12	4	100	97.1
5	PTSA/UiO-66	8	2	100	92.8
6	PTSA/UiO-66	8	4	80	93.5
7	PTSA/UiO-66-Br	8	4	100	95.5
8	PTSA/UiO-66-NO ₂	8	4	100	97.0
9	PTSA/UiO-67	8	4	100	97.7
10	MSA/UiO-66	8	4	100	97.0
11	PTSA/C	8	4	100	44.0
12	MSA/C	8	4	100	37.5
13	UiO-66	8	4	100	25.2

^a Palmitic acid (PA) was 2 mmol, catalyst was 25 g/mol. ^b The conversion was determined by gas chromatography (GC).

Furthermore, PTSA supported on other UiO-66 types of Zr-MOF (UiO-66-Br, UiO-66-NO₂ and UiO-67) was prepared and used as solid acid catalysts towards the esterification reaction as well (Table 2, entries 7–9). The results showed that PTSA/UiO-66-Br, PTSA/UiO-66-NO₂ and PTSA/UiO-67 also had high catalytic activity towards the esterification reaction and afforded conversions of 95.5%, 97.0% and 97.7%, respectively. MSA/UiO-66 also had excellent catalytic activity towards the esterification reaction with excellent conversion (97.0%) (Table 2, entry 10). Owing to their low porosity and specific surface area, PTSA and MSA supported on activated carbon (C) both had low catalytic activity with low conversions of 44.0% and 37.5%, respectively (Table 2, entries 11–12). The control experiment showed that UiO-66 alone had a poor catalytic activity (Table 2, entry 13). In general, PTSA/UiO-66 and MSA/UiO-66 both presented excellent catalytic activity towards the esterification reaction with high conversions (PTSA/UiO-66, 97.1%; MSA/UiO-66, 97.0%).

To examine the substrate scope of long chain fatty acids, PTSA/UiO-66 was used as solid acid catalyst for the esterification of different long chain fatty acids with methanol. To our delight, PTSA/UiO-66 also exhibited excellent catalytic activity and the conversions of stearic acid and oleic acid, which reached to 96.7% and 95.8%, respectively. The results suggested that this developed solid acid catalyst (e.g., PTSA/UiO-66) had potential for biodiesel production.

2.4. The Reusability of Acids Supported UiO-66 towards the Esterification of Palmitic Acid with Methanol

Reusability is a vital property of any solid catalyst. Considering high polarity methanol was always used as an exchange solvent to remove organic ligands from the cavities of MOF [42,43], it was proposed that methanol would also accelerate the leaching of organosulfonic acids (PTSA or MSA) from the developed solid catalysts. Thus, separating methanol firstly might improve the reusability of PTSA/UiO-66 and MSA/UiO-66. Then multiple recovery tests were performed through two different processing approaches to verify the reusability of the UiO-66-supported acids (Figure 5). The reusability results are shown in Figures 6 and 7. The esterification reaction conditions were as follows: PA, 2 mmol; reaction temperature, 100 °C; reaction time, 4 h; the amount of solid catalyst, 25 g/mol; the molar ratio of methanol to PA, 8:1.

Figure 5. Two different approaches in the catalyst recovery tests.

Figure 6. Reusability of solid catalysts in the esterification of PA with methanol.

Figure 7. Reusability of solid catalysts in the esterification of PA with methanol.

The results of approach 1 showed that the conversions of PA with PTSA/UiO-66 and MSA/UiO-66 as catalysts decreased to 80.0% and 91.0%, respectively, after recycling four times (Figure 6). Based on the elemental analysis, the contents of PTSA and MSA in PTSA/UiO-66 and MSA/UiO-66 were decreased to 184.5 mg/g and 115.5 mg/g, respectively. It seems that UiO-66-supported organosulfonic acids lose the organosulfonic acids (PTSA and MSA) partially, which will lead to moderate reusability in

the esterification reaction. Under the approach 2 conditions (Figure 7), the conversion of PA decreased to 84.3% when PTSA/UiO-66 was reused nine times. Significantly, the conversions of PA were almost unchanged (96.9–97.0%) when MSA/UiO-66 was reused as catalyst nine times. The elemental analysis indicated that the PTSA and MSA contents in the final solid catalysts were 213.4 mg/g and 199.0 mg/g, respectively. It was thus confirmed that PTSA/UiO-66 and MSA/UiO-66 had excellent reusability under approach 2 conditions (removing methanol first). Indeed, separating methanol firstly reduced the leaching of the organosulfonic acids (PTSA or MSA) from UiO-66, which enhanced the solid catalysts' recovery effect.

The stability of PTSA/UiO-66 and MSA/UiO-66 catalysts (used 10 times) were determined by XRD (Figure 8). The XRD patterns of the used catalysts (PTSA/UiO-66 and MSA/UiO-66) were almost identical to the fresh PTSA/UiO-66 and MSA/UiO-66, indicating that PTSA/UiO-66 and MSA/UiO-66 had high stability in the esterification of PA with methanol. The N_2 adsorption-desorption of PTSA/UiO-66 and MSA/UiO-66 (used 10 times) was also determined (Figure 9 and Table 3). After reuse 10 times, the Langmuir surface area and total pore volume of catalysts showed no change, while the average pore width of catalysts were a little bigger than the original catalysts (Table 3). The above results indicated that the solid catalysts using UiO-66 as platform retained its original crystalline structure and exhibited strong stability in the esterification reaction.

Figure 8. XRD patterns of the used PTSA/UiO-66(A) and MSA/UiO-66(B).

Figure 9. N_2 adsorption-desorption of used solid catalysts.

Table 3. Physicochemical properties of the used catalysts.

Catalyst	$S_L^a/(m^2/g)$	$V_{total}^b/(m^3/g)$	$W_{average}^c/nm$
UiO-66	1284.8	0.46	1.9
PTSA/UiO-66 (used 10 times)	1032.9	0.38	1.94
MSA/UiO-66 (used 10 times)	1056.3	0.43	2.16

^a Langmuir surface area. ^b Total pore volume. ^c Average pore width.

2.5. The Catalytic Activity of Acids Supported UiO-66 towards the Esterification of Palmitic Acid with *n*-Butanol

Methanol is an alcohol with high polarity, which will slightly decrease the recycling effect of the developed solid acid catalysts (PTSA/UiO-66 and MSA/UiO-66). Therefore, lowering the polarity of short chain alcohols will reduce the leaching of organosulfonic acid from the solid catalysts. The fatty acid esters of *n*-butanol were also found to act as emollient and solvent/diluent in chemical products and cosmetics [44]. *n*-Butyl biodiesel is also considered as an environmentally friendly fuel because of *n*-butanol can be produced by biological fermentation [45]. Thus, the esterification reaction of palmitic acid with *n*-butanol was selected to examine the catalytic activity of solid acid catalyst (MSA/UiO-66). As shown in Table 4, MSA/UiO-66 presented a preferable catalytic activity with the conversion of PA up to 99.2% under the typical reaction conditions (temperature, 100 °C; time, 2 h; amount of catalyst, 25 g/mol; molar ratio of *n*-butanol to PA, 3:1). The results of recycling experiments through approach 1 are shown in Figure 10. The esterification conversion decreased to 93.1% after 9 reuses without any post-processing. The elemental analysis demonstrated that the MSA content in the MOF catalyst was 204.7 mg/g after 10 runs. These results indicated that MSA/UiO-66 had preferable catalytic and recycling activity towards esterification reaction of palmitic acid with *n*-butanol.

Table 4. Esterification of palmitic acid (PA) with *n*-butanol.

Entry	Content of Catalyst (g/mol)	<i>n</i> -butanol/PA (mol/mol)	Time (h)	Temp. (°C)	Conv. (%)
1	20	3	2	80	64.1
2	20	3	1	100	91.3
3	20	3	2	100	98.7
4	20	3	3	100	99.0
5	20	3	3	100	99.0
6	25	3	2	100	99.2
7	25	1.5	2	100	93.3
8	20	3	2	110	98.8

Figure 10. Reusability of MSA/UiO-66 in the esterification of PA with *n*-butanol.

2.6. The Catalytic Activity of Acids Supported UiO-66 towards the Synthesis of *n*-Decyl Palmitate

A long chain fatty alcohol such as *n*-decanol was also examined as esterification partner with palmitic acid in the presence of UiO-66-supported acid (MSA/UiO-66). The results showed that MSA/UiO-66 also had good catalytic activity in the esterification of *n*-decanol with palmitic acid. Notably, a 99.9% conversion of palmitic acid (PA) was detected under the conditions of temperature, 120 °C; time, 2 h; amount of catalyst, 25 g/mol; ratio of *n*-decanol to PA, 2:1. The conversion of PA was decreased to 91.4% with the reaction temperature decreasing to 100 °C. The recycle verification experiments were conducted at 100 °C under Approach 1 method conditions (separating the catalyst first). The results showed that a little decline after 10 runs was observed and the conversions of PA were around 90% (Figure 11), indicating that MSA/UiO-66 had both excellent catalytic activity and recycling activity in the esterification reaction of PA with *n*-decanol. In addition, elemental analysis showed that the content of MSA in the solid catalyst was 209.3 mg/g after ten runs. These results verified that low polarity of alcohols (e.g., *n*-decanol, *n*-butanol) decreased the leaching of organo-sulfonic acids in the esterification reaction, which resulted in better recoverability of MSA/UiO-66.

Figure 11. Reusability of MSA/UiO-66 in the esterification of PA with *n*-decanol.

Moreover, the results of XRD analysis showed that the crystal structure of UiO-66 remained unchanged after 9 times reuse for the esterification reactions (PA with *n*-decanol, *n*-butanol) (Figure 12). Therefore, UiO-66 is indeed a stable carrier for strong organic acid (e.g., MSA, PTSA) in the esterification reactions.

Figure 12. XRD patterns of the used catalyst in the esterification of PA with *n*-decanol (C) or *n*-butanol (D).

2.7. Reaction Mechanism for Acids Supported UiO-66 towards the Esterification

To gain insight into the catalytic role of the UiO-66-supported organosulfonic acids catalysts, the roles of UiO-66 and organosulfonic acids (PTSA or MSA) in the esterification were examined. Firstly, UiO-66 adsorbed PTSA or MSA through an impregnation approach to generate the solid acid catalysts PTSA/UiO-66 and MSA/UiO-66. Compared with the original UiO-66, N₂ adsorption-desorption analysis (Figure 3 and Table 1) showed that Langmuir surface area, total pore volume and average pore width of UiO-66-supported organosulfonic acid catalysts PTSA/UiO-66 and MSA/UiO-66 were all decreased, indicating that PTSA and MSA were mainly within the cavities of UiO-66. During the reaction mixture heating, the organosulfonic acid (PTSA or MSA) was partially released. After reaction mixture cooling to room temperature, the free sulfonic acids could be recycled partially by the UiO-66 and then the solid acid catalysts were recovered for the next esterification reaction batch.

3. Experimental

3.1. Materials

Zirconium chloride (ZrCl₄, 98%), terephthalic acid (H₂BDC, 99%), *p*-toluenesulfonic acid monohydrate (PTSA) (C₇H₈O₃S·H₂O, 99%) and methanesulfonic acid (MSA, 99%) were obtained from Shanghai Macklin Biochemical Co. Ltd. (Shanghai, China). 2-Bromoterephthalic acid (97.5%), 2-nitroterephthalic acid (98%), biphenyl-4,4'-dicarboxylic acid (98%) were purchased from Beijing J&K Scientific Co. Ltd. (Beijing, China). N,N-dimethylformamide (DMF, 99.5%) and *n*-hexane (HPLC grade) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. (Tianjing, China). Palmitic acid (99%), stearic acid (99%) and oleic acid (98%) were obtained from Sigma-Aldrich Chemical Co. Ltd. (Shanghai, China). Methanol (HPLC grade) was purchased from VBS biologic Co. Ltd. (Goleta, CA, USA) *n*-Butanol (99%) and *n*-decanol (>98%) were obtained from Alfa Aesar (Tianjin) Co. Ltd. (Tianjing, China). Methanol, *n*-butanol and *n*-decanol were desiccated by activated molecular sieves (4 Å) for 24 h before use.

3.2. Preparation of Supported Catalyst

UiO-66 and other UiO-66 (Zr) types of MOF (UiO-66-Br, UiO-66-NO₂ and UiO-67) were synthesized by a solvothermal method according to previous reports [35,38]. ZrCl₄ (15 mmol) and organic ligands (e.g., H₂BDC, 15 mmol) were dissolved in DMF (90 mL) at room temperature under ultrasonic conditions until a well-distributed solution was afforded. Then HCl (37%, 3 mL) was added. Then the mixture was transferred into a Teflon-lined autoclave and reacted at 120 °C for 24 h. The products were obtained by filtration under vacuum after washing three times with DMF and chloroform. The precipitates were put into 30 mL volumes of fresh chloroform for 3 days for solvent exchange to eliminate residual organic ligands further. Finally, the solid was collected by filtration under vacuum and dried at 60 °C under vacuum for 12 h. The obtained white powder solid was UiO-66. UiO-66-Br, UiO-66-NO₂ and UiO-67 were prepared in the same method (Figure S1).

The organosulfonic acids (MSA or PTSA) were dissolved in methanol, respectively. Then UiO-66 (50 mg) was added to 50 mL of methanol solutions of the sulfonic acid (1 mol/L) through an impregnation method at room temperature without stirring. The UiO-66-supported sulfonic acids supported were obtained through filtration under vacuum. The products were washed with methanol three times to remove the free acids (MSA or PTSA), and then dried at 50 °C under vacuum for 12 h. The UiO-66-supported acids named MSA/UiO-66 or PTSA/UiO-66 were thus obtained.

3.3. Characterization of Sulfonic Acid Supported UiO-66

The crystalline structure of UiO-66 and sulfonic acids supported UiO-66 were determined by X-ray diffractometry (XRD), using a MiniFlex 600 system (Rigaku Ltd., Japan) equipped with Cu K_{α1} radiation (λ = 1.54059 Å). Fourier transform infrared (FT-IR) spectra were recorded on a WQF-510 spectrophotometer (Rayleigh Ltd., Nanjing, China). Nitrogen adsorption-desorption measurements at

77 K were performed on a TriStar II 3020 analyzer (Micromeritics, Norcross, GA, USA). In addition, the specific surface areas were calculated with the Langmuir method, the total pore volumes were determined at a relative pressure of ($P/P_0 = 0.97$), and the pore sizes were calculated according to the Barrett-Joyner-Halenda method from the adsorption branch. A Flash EA 1112 elemental analyzer (Thermo, Waltham, MA, USA) was used to detect the sulphur content in UiO-66 after adding the supported PTSA and MSA.

3.4. Esterification Reactions of Fatty Acid

Fatty acid, catalyst and alcohols were added into a 35 mL thick wall pressure-resistant reaction tube, respectively. Then the mixture was reacted at a certain temperature for a certain time under magnetic stirring. After the reaction was finished, the mixture was cooled to room temperature, and then the catalyst was isolated by high speed centrifugation. The products were collected into a separating funnel filled with *n*-hexane, and the organic phase (esterification products) were washed with distilled water for three times. Finally, *n*-hexane was removed under vacuum by a rotary evaporator. The conversion of fatty acid was determined by gas chromatography (7890B, Agilent, Santa Clara, CA, USA) equipped with a hydrogen flame ionization detector (FID) and DB-1ht capillary column (29.0 m $\times$ 250 μ m $\times$ 0.1 μ m) using *n*-hexadecane as the internal standard. And the corresponding fatty acid esters were identified by $^1\text{H-NMR}$ (Figure S2). The solid catalyst was recovered by high speed centrifugation method. The recovered catalyst was washed with *n*-hexane for three times, dried at 60 $^\circ\text{C}$ for 1 h and reused for the next cycled reaction.

4. Conclusions

In summary, novel solid UiO-66-supported sulfonic acid (PTSA and MSA) catalysts have been prepared successfully through a simple impregnation method. The developed solid catalysts PTSA/UiO-66 and MSA/UiO-66 are active, stable and reusable in the esterification of biomass-derived fatty acids (e.g., palmitic acid, oleic acid) with various alcohols. Noteworthy, the conversions of esterification of palmitic acid with various alcohols (methanol, *n*-butanol, *n*-decanol) were excellent in the presence of PTSA/UiO-66 and MSA/UiO-66. Additionally, the UiO-66 supported sulfonic acid catalysts (e.g., MSA/UiO-66) developed in this work were reusable for at least nine successive cycles without loss of catalytic activity. The present study provides a new insight into the use of the MOF materials as heterogeneous acid catalysts for various organic transformations.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/11/1271/s1>, Figure S1: XRD patterns of UiO-66-Br, UiO-66-NO₂ and UiO-67, Figure S2: $^1\text{H-NMR}$ of the esterification products.

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