Research Article

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Fabrication of silicotungstic acid immobilized on Ce-based MOF and embedded in Zr-based MOF matrix for green fatty acid esterification

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Abstract: In the present study, a facile solvothermal method was used for the synthesis of silicotungstic acid (HSiW) immobilized on Ce-based metal organic framework (Ce-BDC) and embedded in Zr-based metal-organic framework (UiO-66(Zr)) composite catalyst, namely, Ce-BDC@HSiW@UiO-66 for the production of biodiesel through green fatty acid esterification. The obtained hybrids were characterized by various characterization technologies, including Fourier transform infrared, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, N₂ physisorption, X-ray photoelectron spectroscopy, and temperature-programmed desorption of NH₃ (NH₃-TPD) analysis. The characterization analyses showed that the hybrids have been successfully synthesized. Also, the volume and pore size of UiO-66(Zr) were changed by introducing HSiW@Ce-BDC, and the resulting Ce-BDC@HSiW@UiO-66 possessed the mesoporous structure and relatively high surface area. Simultaneously, the NH₃-TPD analysis of

Ce-BDC@HSiW@UiO-66 reveals that the acid strength was increased in comparison with HSiW@Ce-BDC. In addition, the composite Ce-BDC@HSiW@UiO-66 demonstrated high catalytic activity, and the oleic acid esterification gave 81.5% conversion at optimum conditions of 0.2 g catalysts, 1:30 oleic acid to methanol molar ratio at 130°C for 4 h. More interestingly, after six recycling cycles, the reduction in the conversion rate was only 4.6%, indicating that Ce-BDC@HSiW@UiO-66 has excellent reusability. Our study provides an effective approach to synthesize multifunctional hybrids for green biofuel production.

Keywords: silicotungstic acid, metal-organic framework, hybrid catalyst, esterification, biodiesel

1 Introduction

Recently, with the rapid growth of world population and the development of industrialization, the growing consumption of energy, especially fossil fuels, is increasing [1]. However, the depletion and the widespread use of fossil fuels bring a series of environmental pollution which has gotten much attention [2]. In the views of the above concerns, it is urged to develop the alternative efficient green fuels. Among the alternative fuels, biodiesel is considered to be a potential substitute fuel for its biodegradable, nontoxic, higher cetane index, and sulfur free properties [3]. Generally, biodiesel is able to be produced from fatty acid, various edible oils, and non-edible oils with small-chain alcohol via esterification/transesterification over acid/base catalyst [4].

The production of biodiesel by esterification process is an interesting choice via using low-cost feedstock with high fatty acid contents, which may be the best solution for cost reduction [5]. Currently, liquid inorganic acids (sulfuric acid, hydrochloric acid, phosphoric acid, etc.) are usually preferred as they present a high-level conversion rate of fatty acids in a shorter reaction time [6]. However, liquid acid catalysis suffers from the severe

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corrosion of the vessel with large amount of wastewater from neutralization steps, and the impossibility of reuse [7]. In contrast, many efforts have been devoted to study the different types of solid acid catalysts, such as heteropolyacids [8,9], zeolites [10], metal oxides [11], ionic liquid [12,13], and carbon-based acid catalyst [14], because it can reduce the problem of the reactor's corrosion, and it can be easily separated and reused [15]. Heteropolyacids are certainly regarded as the most famous solid acid catalysts and catalyze a wide variety of reactions due to their stronger Brønsted acids and thermal stability [16]. Unfortunately, heteropolyacids have a low surface area ($<10\text{ m}^2\text{g}^{-1}$) and can be easily soluble in polar solvent that lead to obtain a homogeneous catalysis [17]. Then, heteropolyacids may require an appropriate support with high surface area and chemical stability for corresponding impregnation or anchoring [18,19].

Lately, metal-organic framework (MOF) has the desirable structure and excellent properties, such as adjustable structure, high porosity, and high accessible surface area, that can be used as catalysts or extended by encapsulation of other functional species within MOF [20,21]. Up to now, UiO-66(Zr), Cu-BTC, MIL-100(Fe), and Ni-BDC have widespread and versatile applications as supported [22–24].

In this work, we prepared a novel Ce-BDC@HSiW@UiO-66 composite synthesized by the simple solvothermal method. In the preparation process, the synthesized Ce-BDC acted as the supporting material, and the silicotungstic acid was immobilized on Ce-BDC to form HSiW@Ce-BDC. Afterwards, the HSiW@Ce-BDC was embedded in UiO-66(Zr), forming the Ce-BDC@HSiW@UiO-66 hybrids. The physical and structural properties of the obtained hybrids were characterized by using Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 physisorption, X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption of NH_3 (NH_3 -TPD). Meanwhile, the hybrids were used for esterification of green fatty acid. Furthermore, the recycling and leaching test were applied to study the stability and heterogeneous nature of the synthesized hybrids. This work presents an effective approach to obtain the multifunctional hybrids for green biofuel production.

2 Experimental methods

2.1 Chemicals and reagents

The chemicals were procured from the following sources: Absolute ethanol, oleic acid, stearic acid (98%), anhydrous methanol, and *N,N*-dimethylformamide (DMF) are obtained

from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Zirconium (IV) chloride (ZrCl_4), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), benzene-1,4-dicarboxylic acid (H_2BDC), silicotungstic acid (HSiW, $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$), lauric acid (98%), methanol (>99%), myristic acid (98%), and palmitic acid (98%) were obtained from Shanghai Aladdin Industrial Inc. (Shanghai, China). All chemicals were of analytical grade and used without further purification, unless otherwise noted.

2.2 Catalyst preparation and characterization

The silicotungstic acid impregnation on Ce-BDC (denoted as HSiW@Ce-BDC) and embedded in UiO-66(Zr) was synthesized by solvothermal technique. Initially, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.87 g) was dissolved in 40 mL of DMF and then commercial silicotungstic acid (0.8 g) and terephthalic acid (0.5 g) were added into the above solution under magnetic stirring for 1 h, and placed on an oil bath at 150°C and allowed to stir for 3 h. The product was then washed two times with DMF and deionized water to obtain the HSiW@Ce-BDC sample. After that, the HSiW@Ce-BDC was added to 30 mL of DMF, and ultrasonic reaction was carried out for 30 min, followed by the addition of ZrCl_4 (0.51 g) and terephthalic acid (0.33 g), and the mixture was slowly stirred for 1 h and then placed in a 50 mL Teflon-lined stainless-steel autoclave at 120°C for 6 h. Finally, the attained product was centrifuged and washed with DMF and deionized water two times, dried at 80°C for 12 h in an oven. This sample was coded as Ce-BDC@HSiW@UiO-66. For comparison, the Ce-BDC and UiO-66(Zr) samples were also prepared following the same method.

FTIR spectra were analyzed on a PerkinElmer spectrum100 using KBr pellet technology ($4,000\text{--}400\text{ cm}^{-1}$). XRD spectra was performed using D8 ADVANCE (Germany) with $\text{CuK}\alpha$ ($1.5406\text{ \AA}$) radiation. Nitrogen adsorption-desorption isotherms were examined using a Quantachrome Quadrasorb EVO apparatus (Quantachrome Instruments, Boynton Beach, USA). XPS (Thermo ESCALAB 250XI) was used to measure the elemental compositions of the sample. The morphological features of the synthesized samples were observed by SEM (Hitachi S4800) and TEM (FEI Tecnai G2 20). The NH_3 -TPD (Micromeritics, AutoChem II 2920 instrument) was performed to measure the acid value of the sample.

2.3 Esterification experiments

Esterification experiments on conversion of fatty acid was carried out by a 50 mL high-pressure autoclave reactor,

using the Ce-BDC@HSiW@UiO-66 catalyst. Initially, calculated amount of Ce-BDC@HSiW@UiO-66 catalyst was fed into the autoclave reactor and the reactants (fatty acid and methanol) were added. Then, the reactor was allowed to stir for an appropriate time via magnetically operated stirrer at 120–140°C on an oil bath. After the accomplishment of the esterification process, the catalyst was collected by centrifugation, and the residual methanol and by-products of water were rotary evaporated under reduced pressure. The acid value of the resulting product was measured according to the method described in ISO 660-2009 standard, and the fatty acid conversion was estimated as the reduction in acid value before and after the reaction [25].

3 Results and discussion

3.1 Characterization of the hybrids

The FTIR spectra of HSiW, Ce-BDC, and UiO-66(Zr) along with Ce-BDC@HSiW@UiO-66 are shown in Figure 1. For HSiW sample, the four peaks were observed at 980, 927, 884, and 804 cm^{-1} , which corresponded to Keggin ion structure of HSiW [26]. In the infrared spectra of Ce-BDC, UiO-66(Zr) and Ce-BDC@HSiW@UiO-66 samples, the absorption bands attributed to the asymmetric and symmetric stretching of carboxyl ($\text{O}=\text{C}-\text{O}$) are observed at 1,583 and 1,397 cm^{-1} , and the obvious bonds at 1,000–1,200 cm^{-1} are representing the stretching vibration of $\text{C}-\text{O}$ [27,28]. Simultaneously, the

absence of peak at 745 cm^{-1} was believed to be the $\text{O}-\text{H}$ vibrations in the H_2BDC ligand. These results indicate the presence of the organic ligands terephthalic acid in the synthesized samples. Notably, the obvious bonds in 553 cm^{-1} attributed to $\text{Zr}-(\text{OC})$ asymmetric stretch found in the UiO-66(Zr) and Ce-BDC@HSiW@UiO-66 samples [29]. Moreover, the bands' absorption at 450–550 cm^{-1} were attributed to $\text{Ce}-\text{O}$ vibration [30], indicating the existence of the bonds of $\text{Zr}-\text{O}$ and $\text{Ce}-\text{O}$ in the Ce-BDC@HSiW@UiO-66 sample. However, the intensity of the characteristic peaks of Ce-BDC@HSiW@UiO-66 showed to be weaker, which was caused likely by the interaction between HSiW, Ce-BDC, and UiO-66(Zr). Surprisingly, the peaks at 980 and 804 cm^{-1} are observed from Ce-BDC@HSiW@UiO-66 sample, which indicates that HSiW was embedded within the Ce-BDC and UiO-66(Zr) and the synthesis of the hybrids was successful.

The XRD diffraction patterns of the HSiW, Ce-BDC, HSiW@Ce-BDC, and UiO-66(Zr) along with Ce-BDC@HSiW@UiO-66 samples are depicted in Figure 2. Ce-BDC exhibits several major characteristic peaks at $2\theta = 9.1^\circ, 14.5^\circ, 15.3^\circ, 18.1^\circ, 28.1^\circ, 29.1^\circ,$ and 30.0° [31], and similar patterns were observed for HSiW@Ce-BDC and Ce-BDC@HSiW@UiO-66 samples, indicating that the Ce-BDC is kept almost intact in the synthesis process. Additionally, the major characteristic peaks of HSiW could not be found from the XRD patterns of HSiW@Ce-BDC, which proves that HSiW is uniformly dispersed on the Ce-BDC, similar observations have been reported by Wang *et al.* [32]. When HSiW@Ce-BDC is embedded in UiO-66(Zr), some diffraction peaks of UiO-66(Zr) partially disappeared from Ce-BDC@HSiW@UiO-66 sample, and the intensity of the characteristic diffraction

Figure 1: FTIR spectra of HSiW, Ce-BDC, UiO-66(Zr), and Ce-BDC@HSiW@UiO-66 hybrids.

Figure 2: XRD patterns of HSiW, Ce-BDC, HSiW@Ce-BDC, UiO-66(Zr), and Ce-BDC@HSiW@UiO-66 hybrids.

peaks of HSiW@Ce-BDC in Ce-BDC@HSiW@UiO-66 was weakened. This may be related to UiO-66(Zr)-encapsulated HSiW@Ce-BDC samples and the existence of the strong interaction between HSiW@Ce-BDC and UiO-66(Zr), which was also evident in the FTIR results.

The surface morphology of HSiW, Ce-BDC, HSiW@Ce-BDC, UiO-66(Zr), and Ce-BDC@HSiW@UiO-66 hybrids were investigated through SEM imaging. As reported in Figure 3, the HSiW sample (Figure 3a) presents irregular sizes of massive structure, and Ce-BDC (Figure 3b) presents collectively packed irregular block-like particles. After the introduction of HSiW, the shape of HSiW@Ce-BDC was similar to those of Ce-BDC as shown in the SEM image in Figure 3c, but the irregular sizes became smaller, suggesting HSiW has successfully incorporated into Ce-BDC and the framework structure of Ce-BDC has good stability. UiO-66(Zr) sample (Figure 3d) exhibited relatively regular sizes of near-cubic particles. Obviously, the addition of HSiW@Ce-BDC provoked significant morphological changes in the structure of UiO-66(Zr) due to its electrostatic interaction with HSiW@Ce-BDC. Simultaneously, the Ce-BDC@HSiW@UiO-66 sample (Figure 3e) consists of blocky-shaped agglomerates with varying sizes, and the aggregated blocky-shaped particles have also formed many pores, suggesting that the porous structure is favorable to catalyze esterification reaction. The TEM characterization of Ce-BDC@HSiW@UiO-66 sample is also taken. As provided in Figure 4, Ce-BDC@HSiW@UiO-66 presents aggregated blocky-shaped particles, and its size is not uniform. Moreover, lots of mesopores are also clearly visible from the TEM images, which is consistent with SEM analysis.

The textural properties of UiO-66 and Ce-BDC@HSiW@UiO-66 were studied by nitrogen physisorption, and the isotherms and corresponding pore size distribution profiles are depicted in Figure 5. The isotherm curve of UiO-66(Zr) shows typical type I adsorption isotherms, implying the existence of micro-pore structure [33]. By contrast, the isotherm curve of Ce-BDC@HSiW@UiO-66 hybrids displays a type IV curve with a hysteresis loop at $P/P_0 = 0.45\text{--}0.95$, demonstrating that it is a typical mesoporous material [34], and that the introduction of HSiW@Ce-BDC has a significant effect on the micro-pore structure of the UiO-66(Zr). Remarkably, the calculated BET surface areas and pore volume decreased from $667.2\text{ m}^2\cdot\text{g}^{-1}$ and $0.431\text{ cm}^3\cdot\text{g}^{-1}$ of UiO-66 to $251.2\text{ m}^2\cdot\text{g}^{-1}$ and $0.215\text{ cm}^3\cdot\text{g}^{-1}$ of Ce-BDC@HSiW@UiO-66, respectively, it is due to the pore blockage by HSiW@Ce-BDC guest embedded into UiO-66(Zr) host. From Figure 5b, compared to UiO-66(Zr) sample, the main peaks located at 3.9 nm are observed in Ce-BDC@HSiW@UiO-66 sample, demonstrating that the pore size is amplified to mesoporous scale. Meanwhile, the average pore size increased from 2.58 nm of UiO-66 to 3.42 nm of Ce-BDC@HSiW@UiO-66 because of the blockage of micropores and the presence of some mesoporous in the original Ce-BDC sample [35], which further indicates that the Ce-BDC@HSiW@UiO-66 hybrid has been successfully synthesized, similar to the result obtained in SEM and TEM. Moreover, the mesoporous Ce-BDC@HSiW@UiO-66 material is also in favor of reducing mass transfer resistance during catalytic esterification.

The XPS analysis of the synthesized hybrids is conducted to measure the element composition information. Figure 6a shows the survey XPS spectrum of as-prepared

Figure 3: SEM images of (a) HSiW, (b) Ce-BDC, (c) HSiW@Ce-BDC, (d) UiO-66(Zr), and (e) Ce-BDC@HSiW@UiO-66 hybrids.

Figure 4: TEM images of Ce-BDC@HSiW@UiO-66 hybrids.

catalyst, implying the existence of O, Ce, Zr, C, and W in the Ce-BDC@HSiW@UiO-66 hybrids. Moreover, NH_3 -TPD experiments were also carried out for HSiW@Ce-BDC and Ce-BDC@HSiW@UiO-66 samples. As reported in Figure 6b, the HSiW@Ce-BDC showed the formation of weak acidity with a strong acidity desorption peak at 113°C and 570°C, respectively, and this is due to the desorption of NH_3 adsorbed on weak acid sites, and the strong acidic nature of HSiW. Note that the Ce-BDC@HSiW@UiO-66 sample displayed a sharper peak at about 570°C with a shoulder. The peak at 579°C is due to the high Brønsted acid of HSiW. In addition, the slight decrease in desorption temperature at 545°C is due to the introduction of UiO-66(Zr), which led to the existence of the strong interaction between HSiW@Ce-BDC and UiO-66(Zr) and might be created due to the Lewis acidity (Zr^{4+}) in the sample surface. Thus, it is

expected that the Ce-BDC@HSiW@UiO-66 hybrids will be effective for green fatty acid esterification.

3.2 Catalytic activity evaluation

3.2.1 Effect of reaction temperature and time

The effects of reaction temperature and time on oleic acid were evaluated at the conditions of 0.2 g of Ce-BDC@HSiW@UiO-66 catalyst and 1:30 oleic acid to methanol mole ratio. Generally, there is an important effect of temperature on the endothermic reaction, and the conversion of oleic acid increased with elevated reaction temperature. As shown in Figure 7, the catalytic activity is gradually improved with the increase in reaction

Figure 5: Nitrogen physisorption curves (a) and pore diameter distributions (b) of UiO-66(Zr) and Ce-BDC@HSiW@UiO-66 hybrids.

Figure 6: (a) XPS survey spectrum of Ce-BDC@HSiW@UiO-66 hybrids; (b) NH₃-TPD curves of HSiW@Ce-BDC and Ce-BDC@HSiW@UiO-66 hybrids.

temperature from 120 to 140°C. For instance, the conversion of oleic acid jumped up from 21.8 to 53.7% at 2 h as the reaction temperature raised from 120 to 140°C. Likewise, when reaction temperature was 120°C, 130°C, and 140°C after 4 h of reaction, the oleic acid conversion was 53.1%, 81.5%, and 85.1%, respectively, indicating that the increase in temperature from 130°C to 140°C had no considerable alteration in the conversion of oleic acid, as well the conversions significantly increased with increasing reaction time. However, with progression in reaction time from 4 to 5 h at a temperature of 130°C, the conversion increased from 81.5% to 85.2%, respectively, indicating that no significant change was observed with prolonged reaction time. Taking this into account, 4 h and 130°C was decided as the optimum reaction time and temperature.

Figure 7: Evaluation of effects of reaction temperature and time on catalyst for the conversion of oleic acid.

3.2.2 Effect of catalyst amount

The influence of catalyst amount on the conversion has been studied for Ce-BDC@HSiW@UiO-66 catalyst at the conditions of 1:30 oleic acid to methanol mole ratio, and 130°C of reaction temperature. In Figure 8a, the conversion increased with increase in the amount of Ce-BDC@HSiW@UiO-66 catalyst from 0.15 to 0.20 g, this is owing directly to the increase in catalytic active sites available for the esterification reaction system. However, when the amount of catalyst was 0.25 g, a slight decrease in conversion was observed. It may be due to the decrease in mass transfer between reactants and catalyst with excessive catalyst amount, which led to reduction in interactions between them [36]. According to these results, 0.2 g was selected as the optimum catalyst amount.

3.2.3 Effect of the mole ratio of the reactants

Generally, the mole ratio of the reactants was another important factor for esterification. As esterification is reversible, the excess of methanol is required to shift the reaction in a forward direction. Hence, the effect of amount of methanol on the reaction was investigated at the conditions of 0.2 g of Ce-BDC@HSiW@UiO-66 catalyst and 130°C of reaction temperature. As shown in Figure 8b, as the ratio increases from 1:20 to 1:30, the conversion of oleic acid is significantly improved. And the conversion could reach 81.5% as the mole ratio of oleic acid to methanol was 1:30. Further enhancing the mole ratio to 1:40 resulted in the oleic acid conversion tending to decrease slightly, similar results were found in

Figure 8: Study of effects of (a) amount of Ce-BDC@HSiW@UiO-66 and (b) mole ratio on the conversion of oleic acid.

the literature [37]. Therefore, the mole ratio of oleic acid/methanol of 1:30 is considered to be the optimum condition for the reaction.

3.3 The reusability and heterogeneity of catalyst

The reusability of HSiW@Ce-BDC and Ce-BDC@HSiW@UiO-66 were studied by six recycling experiments and the results are provided in Figure 9a. After each reaction, the used catalyst was removed by centrifugation and then used for the next experiment. According to Figure 9a, the oleic acid conversion obtained by Ce-BDC@HSiW@UiO-66 (81.5%) is higher than that of HSiW@Ce-BDC (21.9%) in the first used

cycle. Afterward, the conversion of oleic acid is still around 20% in the third cycle by HSiW@Ce-BDC catalyst. In contrast, after the 6th usage cycle, the conversion of oleic acid decreased only by 4.6% compared to the conversion in the first used cycle, indicating that the Ce-BDC@HSiW@UiO-66 hybrids are an efficient catalyst and can be recycled. This is maybe due to the strong interaction between HSiW@Ce-BDC and UiO-66(Zr), resulting in its synergistic effect enhancing the catalytic activity and stability, similar results were also found by Pithadia and Patel [38]. FTIR and XRD analyses of fresh and recycled Ce-BDC@HSiW@UiO-66 are shown in Figures A1 and A2 (in Appendix), it revealed that there were no discernible differences in the XRD patterns and FT-IR spectra between them, confirming its stability. However, the observed decline in catalytic activity might be due to the loss of catalyst occurred during the recycling process [39].

Figure 9: Recycling (a) and leaching (b) test results for Ce-BDC@HSiW@UiO-66 catalyst.

Table 1: Reactivity of different fatty acids and methanol by Ce-BDC@HSiW@UiO-66 catalyst

Free fatty acids (FFAs)	Reaction conditions				Activity (%)
	Temperature (°C)	FFA:Methanol molar ratio	Amount of catalyst (g)	Time (h)	
Lauric acid	130	1:30	0.2	4	56.8
Myristic acid	130	1:30	0.2	4	79.8
Palmitic acid	130	1:30	0.2	4	96.3
Stearic acid	130	1:30	0.2	4	77.3
Oleic acid	130	1:30	0.2	4	81.5

Leaching test for the Ce-BDC@HSiW@UiO-66 catalyst was also performed by removing the catalyst from the system after 2 h, and the reaction was continued for further 3 h. As displayed in Figure 9b, it is observed that no substantial increase in the oleic acid conversion was observed after the removal of the catalyst, confirming the heterogeneous nature of the Ce-BDC@HSiW@UiO-66 catalyst. Hence, it could be clearly seen that the developed Ce-BDC@HSiW@UiO-66 solid catalyst had a long-term catalytic esterification activity.

3.4 Catalytic performance of Ce-BDC@HSiW@UiO-66 for esterification of other fatty acids

Interestingly, the different fatty acid carbon chain lengths in the reaction with methanol was also investigated for Ce-BDC@HSiW@UiO-66 hybrids, and the results are presented in Table 1. It was found that the Ce-BDC@HSiW@UiO-66 catalyst showed good catalytic performance in these reactions, suggesting that Ce-BDC@HSiW@UiO-66 hybrids could be used as an efficient solid catalyst for other esterification or pre-esterification of low-quality oils.

4 Conclusion

In this research, we have successfully fabricated silicotungstic acid immobilized on Ce-BDC and embedded in UiO-66(Zr) forming hybrids (Ce-BDC@HSiW@UiO-66) via a simple solvothermal strategy. The existence of the UiO-66(Zr) led to an interaction between HSiW@Ce-BDC and UiO-66(Zr), endowing the prepared hybrids with mesoporous structure, large BET surface areas, and high acidity. Meanwhile, the prepared Ce-BDC@HSiW@UiO-66 hybrids showed better catalytic activity in comparison to HSiW@Ce-BDC for esterification of oleic acid. The conversion of 81.5% was attained under mild reaction conditions,

catalyst amount of 0.2 g, 1:30 oleic acid to methanol molar ratio at 130°C for 4 h, and the Ce-BDC@HSiW@UiO-66 hybrids could be reused 6 times with a decrease in catalytic activity only by 4.6% in the reaction, indicating higher catalytic activity and better stability. Therefore, the reasonable design of the MOF-based catalyst in this work results in outstanding properties, which may provide a way for the synthesis of other multifunctional hybrids for green biofuel production in the future.

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Appendix

Figure A1: FTIR spectrum of fresh and used Ce-BDC@HSiW@UiO-66 catalysts.

Figure A2: XRD patterns of fresh and used Ce-BDC@HSiW@UiO-66 catalysts.