Research Article

Bimetallic MOF-Derived Synthesis of Cobalt-Cerium Oxide Supported Phosphotungstic Acid Composites for the Oleic Acid Esterification

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The impregnation of phosphotungstic acid (HPW) with porous cobalt-cerium oxide (HPW@CoCeO) has been prepared by pyrolysis of CoCe-MOF and used for the production of methyl oleate from oleic acid and methanol. FTIR, XRD, SEM, TEM, N2 adsorption/desorption, and NH3-TPD were characterized for the prepared composites. Simultaneously, the effects of reaction time, substrate molar ratio, temperature, and catalyst loading on catalytic activity were highlighted, and the conversion of 67.2% was reached after 4 h at 60°C. Importantly, HPW@CoCeO was reusable and reused more than eight times, and the oleic acid conversion could be maintained at 61.8% without significant activity loss. Thus, the HPW@CoCeO composite could be used as acid catalysts for sustainable energy production.

1. Introduction

The increase in the environmental pollution issues and the consumption of traditional fossil fuels have enhanced the development of greener alternatives [1, 2]. As such, various alternative fuels have been examined, and biodiesel as a renewable fuel has received great attraction recently due to its nontoxicity, sustainability, and biodegradability [3, 4]. At present, the production of biodiesel is via the esterification/transesterification of free fatty acids (FFAs) or various oils over heterogeneous acid/base catalysts [5]. However, FFAs or the presence of FFAs in oils do not make them suitable for the base catalytic system because of saponification and catalyst neutralization [6]. Consequently, the study of esterification of FFAs with alcohol for biodiesel production over heterogeneous acid catalysts is desired.

A wide range of heterogeneous acid catalysts, namely, metal oxides [7–9], heteropolyacids [10], ionic liquids (e.g., ionic liquid@amphiphilic silica nanoparticles, AILs/POM/UiO-66-2COOH, and polymeric acidic IL-functionalized Fe3O4/SiO2) [11–13], and zeolites [14], have been widely investigated for catalysis. Heteropolyacids (such as phosphotungstic acid, silicotungstic acid, and phosphomolybdic acid) have received much attraction due to their superacidic features and excellent stability [15, 16]. However, owing to that low surface area leads to low catalytic reactivity and high solubility in the presence of polar solvents, there is a direct need for pure heteropolyacids as an acid catalyst [17]. Hence, the fabrication of heteropolyacids immobilized in various materials with great surface area is vital.

A variety of supports, metal-organic frameworks (MOFs), are used as potentially porous supports for catalysis [18, 19], gas storage, supercapacitors, and separation, owing to their high catalytic surface area, adjustable structure, and chemical stability [20, 21]. More interestingly, it is an effective strategy on pyrolysis of MOFs to prepare porous metal oxides [22, 23]. Recently, cobaltic oxide has shown good stability and could be alovalently substituted into
ceramic oxide to form well-defined shapes [24, 25]. Thus, bimetallic MOFs could be regarded as an excellent precursor for designing cobalt-cerium oxide with porous structure and well-defined morphology. Therefore, in this study, a simple solvothermal method is used to synthesize phosphotungstic acid-loaded CoCe-MOF and used as a self-sacrificial template to prepare the impregnation of phosphotungstic acid on the porous cobalt-cerium oxide (CoCeO) via the pyrolysis process. The textural structures and acidic properties of the composites were characterized by analysis. Additionally, reaction conditions such as substrate molar ratio, catalyst amount, and temperature were investigated. Additionally, recyclability of the catalyst was also studied.

2. Experimental

2.1. Chemicals. Cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, ≥99.9% AR), cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, ≥99% AR), 12-tungstophosphoric acid (H$_3$PW$_12$O$_40$, HPW, AR), and terephthalic acid (H$_2$-BDC) (AR) were provided by Shanghai Aladdin Industrial Inc. Oleic acid (AR), anhydrous methanol (AR), and N,N-dimethylformamide (DMF, AR) were provided by Sinopharm Chemical Regent Co., Ltd. All chemical reagents are used as received without further purification.

2.2. Syntheses. HPW@CoCe-MOF was prepared by a modified method according to the previous literature [26]. First, 2 mmol Ce(NO$_3$)$_3$·6H$_2$O and 1 mmol Co(NO$_3$)$_2$·6H$_2$O were added to 40 mL DMF under continuous magnetic stirring, followed by the addition of 0.6 g of HPW and 4 mmol of H$_2$-BDC, and the stirring was continued for 2 h. After that, the solution was sealed in a 100 mL Teflon autoclave reactor for 6 h under 150°C. After cooling to room temperature, the resultant precipitation was centrifuged and washed twice using DMF and distilled water, respectively, to get the catalyst precursor, HPW@CoCe-MOF, and washed two times using DMF and distilled water, respectively. At last, HPW@CoCe-MOF was dried at 100°C overnight under an air atmosphere. At last, to get the catalyst precursor, HPW@CoCe-MOF, and terephthalic acid (H$_2$-BDC) (AR) were provided by Shanghai Aladdin Industrial Inc. Oleic acid (AR), anhydrous methanol (AR), and N,N-dimethylformamide (DMF, AR) were provided by Sinopharm Chemical Regent Co., Ltd. All chemical reagents are used as received without further purification.

2.3. Instrumentation and Characterization.

Fourier-transform infrared spectroscopy (FTIR, PerkinElmer spectrum100), wide-angle X-ray diffraction (XRD, Bruker D8 ADVANCE (Germany) using CuKa (0.15406 nm) radiation), field-emission scanning electron microscopy (SEM, Hitachi/S-4800), nitrogen physiosorption measurements (Quantachrome, Nova 3200 S apparatus, Boynton Beach), temperature-programmed desorption with NH$_3$ as the probe gas (NH$_3$-TPD, Micromeritics, AutoChem II 2920), and transmission electron microscopy (TEM, FEI Tecnai G2 20) were used.

2.4. Catalytic Activity Measurements. A mixture of oleic acid, methanol, and HPW@CoCeO catalyst was placed in a 50 mL round flat-bottom flask, heated by using oil bath equipped with a reflux condenser for several hours at an appropriate temperature and vigorously agitated by magnetic stirring. After the reaction was over, the catalyst is collected via the centrifugal process. Meanwhile, excess methanol and water produced were evaporated from the liquid product and analyzed via the acid value to get the esterification conversion, and the acid value was determined by using the ISO 660-2009 standard.

3. Results and Discussion

3.1. Catalyst Characterization. The prepared composite catalysts were analyzed by XRD and given in Figure 1. From Figure 1, it can be seen that CoCe-MOF and HPW@CoCe-MOF samples show main characteristic peaks at 14.5°, 15.6°, 17.7°, 21.8°, 22.5°, 24.5°, 28.2°, 29.2°, and 30.0°, suggesting that they have similar crystal structure. Surprisingly, no diffraction peaks of HPW can be observed from HPW@CoCe-MOF and HPW@CoCeO samples, indicating HPW uniformly occupies the matrix frame. The result is similar to our previous reports [27]. After calcination, XRD patterns of the HPW@CoCeO sample display the intensity of the CoCe-MOF sample characteristic peaks decreased or even disappeared, and two strong diffraction peaks at 18.2° and 28.7° are assigned to cobalt oxide and cerium oxide, respectively [28], implying that the CoCe-MOF transformed to CoCeO after pyrolysis. This also indicates that the HPW@CoCeO catalyst was successfully synthesized.

The FTIR spectra for the HPW and HPW@CoCeO were also characterized to illustrate the HPW had been embedded in the CoCeO framework, and the results are presented in Figure 2. The strong spectra at 750 cm$^{-1}$ were ascribed to the Ce-O bonds [29], and the spectra in the range of 500–580 cm$^{-1}$ were assigned to the Co-O bonds [30]. Moreover, the absorption peak corresponding to Keggin-type HPW emerged at 982 cm$^{-1}$, 889 cm$^{-1}$, and 801 cm$^{-1}$ assigned to W-O, W-O-W, and W-O-W, respectively [31]. Notably, in the FTIR spectrum of HPW@CoCeO, characteristic HPW peaks can be also found. These results confirm the HPW was successfully loaded in CoCeO.

The morphological features of the HPW@CoCe-MOF and HPW@CoCeO catalysts were characterized by SEM and TEM. As depicted in Figures 3(a) and 3(b), HPW@CoCe-MOF had an irregular and long strip structure with relatively smooth surface and the approximate length of 1 μm. After the calcination of HPW@CoCe-MOF (Figures 3(c), 3(d)), the resulting particles became the stacked short rod-like morphology with rough surface and sizes of ~200 nm. This may be due to the disappearance of organic ligands after the calcination of CoCe-MOF to CoCeO [32]. Moreover, Figures 3(e) and 3(f) show the TEM images of the HPW@CoCeO catalyst, clearly indicating that the composite is porous, and it can be also observed that some irregular small particles (HPW) are embedded in the CoCeO framework, further confirming the uniform distribution of HPW within
the CoCe-MOF-derived CoCeO framework. This is in agreement with XRD and FTIR analysis results.

The specific surface area and pore size distribution of HPW@CoCe-MOF and HPW@CoCeO composites were analyzed by BET. The adsorption isotherms and pore size distribution plots of the prepared composites are illustrated in Figure 4. According to IUPAC classification, the adsorption isotherms of both HPW@CoCe-MOF and HPW@CoCeO displayed a typical type V isotherm with the hysteresis loops for H3 [33], implying the existence of a mesoporous structure, as also confirmed by the SEM and TEM results. Meanwhile, the pore size analysis was obtained by the BJH method (Figure 4(b)), and the pore size distribution of the HPW@CoCe-MOF catalyst is mainly in the range of 2–6 nm. For the HPW@CoCeO catalyst, the mesoporous structure of 4.5–6 nm is reduced and the pore size distribution is in the range of 4–5 nm. This is possibly due to the collapse of the CoCe-MOF cage during the calcination process. In addition, the HPW@CoCe-MOF possesses a relatively high BET surface area and average pore diameter of 9.9 m²/g and 24 nm, respectively. After calcination, the HPW@CoCeO composite exhibits the BET surface area is correspondingly increased to 20.5 m²/g and the average pore diameter is decreased to 16 nm, and the phenomenon is associated with the shrinkage of the HPW@CoCe-MOF in the case of the heat treatment [34].

The surface acidic properties of the HPW@CoCeO composite are probed by TPD of NH₃, and the test results are shown in Figure 5. As could be seen, distinct peaks of NH₃ desorption were observed at 80–120°C and 450–600°C. In principle, the peak of 80–120°C is correlated to the NH₃ desorption from the sites of weak acidic strengths. The peak of 450–600°C is attributed to the NH₃ desorption from medium acidic sites, and it may be related to the strong Brønsted acid of HPW from the HPW@CoCeO composite. These results suggest that the HPW@CoCeO composite is having excellent acidic strength toward catalytic esterification.
3.2. Exploration of the Optimal Esterification Conditions

3.2.1. Effect of Reaction Temperature.

Influence of the esterification temperature was also studied from 50°C to 70°C with a catalyst concentration of 10wt.% and oleic acid/methanol molar ratio of 1:30. From Figure 6, the conversion increases as esterification temperature increases from 50°C to 60°C, and the maximum conversion of 67.2% was obtained at 4h. This may be because the esterification reaction is endothermic, and increases in temperature facilitate the reaction to develop in a positive direction. Meanwhile, high temperature can enhance miscibility and interactions between reactants molecular species [35]. However, when the reaction temperature is 70°C, the conversion does not significant change. In light of the results, 60°C was selected as an optimum temperature of the esterification process.

3.3. Effect of Catalyst Amount.

As shown in Figure 7, the conversion of oleic acid depends on catalyst amount under the following conditions: 60°C, oleic acid/methanol molar ratio of 1:30. Upon increasing the catalyst amount from 5 wt.% to 10 wt.% at 4h, the conversion was enhanced from 62.9% to 67.2%. However, at a catalyst amount of 15 wt.%, the conversion was slightly decreased. At a reaction time of 5h, the conversion of oleic acid 69.2% and 62.5% was obtained when the catalyst amount was 10 wt.% and 15 wt.% respectively. This is attributed to that much catalyst amount...
would increase the viscosity and, thus, limit the diffusion of reactants to oleic acid-catalyst-methanol [36, 37]. Therefore, 10 wt.% is the suitable catalyst amount for the esterification.

3.4. Effect of Substrate Molar Ratio. Substrate molar ratio of oleic acid to methanol is one of the essential factors for oleic acid conversion to methyl oleate. According to the esterification, the theoretical value of molar ratio of oleic acid to methanol in the esterification reaction is 1:1. However, the esterification is a reversible process, and thus, excess methanol is used to promote the positive reaction. The effect of the substrate molar ratio on the oleic acid conversion over the HPW@CoCeO catalyst with 10 wt.% of catalyst and temperature of 60°C is shown in Figure 8. As evident in Figure 8, the attainable level of the conversion increased from 41.4% to 57.9% with the rise of molar ratio of oleic acid to methanol from 1:20 to 1:40 at 1 h. However, when the reaction time was 3, 4, and 5 h, the conversion does not increase and even exhibited a decrease trend. This may be because too much methanol dilution effect reduces the collision frequency of reactant molecular species [38]. Therefore, it can be concluded that the molar ratio of oleic acid/methanol of 1:30 could be chosen for esterification in this study.

3.5. Recyclability and Leaching Test of the HPW@CoCeO Catalyst. In order to evaluate the reusability feature of the catalysts, the reusability of the HPW@CoCeO and HPW@CoCe-MOF catalyst for esterification was performed under the optimized conditions in the current research. After each reaction, the catalyst was collected by centrifugation and directly reused as a catalyst for the next esterification reaction, and the test results are indicated in Figure 9(a). As could be seen, the conversion of oleic acid decreased after
each run from 45.7% (first run) to 17.9% (sixth run) for the HPW@CoCe-MOF catalyst, and the possible reasons for the reduction substantially of conversion are the blockage of the CoCe-MOF channel. On the contrary, the conversion of oleic acid decreased slightly after each run from 67.2% (first run) to 61.8% (eighth run) for the HPW@CoCeO catalyst, and the decrease in catalytic activity could be related to the adsorption of oleic acid, methanol, or water molecule on the active sites of the HPW@CoCeO composite during each run [39]. The collected catalyst from the eighth reaction cycle was characterized by FTIR (Figure 2). It can be observed that the structure of the reused catalyst did not significant change throughout the reuse cycles. Seemingly, the strong interactions existing between HPW and CoCe-MOF-derived CoCeO are responsible for the good reusability of the composite catalyst.

Moreover, the hot filtration test for HPW@CoCeO was also studied to further demonstrate the reusability, and the related results are indicated in Figure 9(b). It could be clearly seen that there was no important increase in the oleic acid conversion after removal of the HPW@CoCeO composite, demonstrating a characteristic of a heterogeneous composite catalyst. A similar study was also reported by Hu et al. [40].

**Figure 7:** The effect of catalyst amount on the oleic acid conversion over the HPW@CoCeO catalyst.

**Figure 8:** The effect of substrate molar ratio on the oleic acid conversion over the HPW@CoCeO catalyst.
4. Conclusions

In conclusion, a simple pyrolysis method strategy has been employed for the synthesis of HPW@CoCeO composite, and the characterization results showed the HPW was successfully loaded in CoCeO and the composite provided a mesoporous structure and excellent acidic strength. Moreover, the HPW@CoCeO also showed good activity and stability compared to the HPW@CoCe-MOF, and the conversion reached 67.2% under the conditions of a temperature of 60°C, time of 4h, molar ratio of oleic acid to methanol of 1 : 30, and 10 wt.% of catalyst. Furthermore, the catalyst can be reused for over eight cycles with slight activity loss. This synthesis strategy may provide a candidate route to prepare MOF-based composite catalysts for catalyzing various chemistry reactions. However, future works could include analysis of the catalyst to determine its morphology, surface area, guest molecule, and matrix interaction and an attempt to improve catalytic activity.

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 no conflicts of interest.

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