

Metal-Organic Framework as Catalyst in Esterification of Oleic Acid for Biodiesel Production

Kui Zhou and Somboon Chaemchuen

Abstract—Applying metal-organic frameworks (MOFs) as a solid catalyst in esterification of oleic acid and methanol for model of biodiesel production were investigated. Taking an advantage on high surface area, chemical/thermal stability and surface chemistry (acid/basicity) properties on MOF materials (MOF-808, ZIF-8, MIL-125) applied for catalyzed reaction of carboxylic acid to ester compound. Those MOF materials showed the catalytic properties higher than the reported alumina compound at same reaction condition. Their recyclability properties in heterogeneous catalyst were investigated. The characteristic properties of MOF materials such as crystal structure, porosity, surface area and functional group (chemical bonding) on spend catalyst after reaction were studied on this work.

Index Terms—Metal-organic frameworks, biodiesel, esterification, heterogeneous catalyst.

I. INTRODUCTION

Esterification plays an important with numerous application for industrial e.g. polymer, paints, varnishes, lacquers, medicines, dyes and synthetic rubber, including energy relative such as the production of biodiesel [1]. This reaction was also used to produce the bio-fuel or biodiesel from vegetable oil and/or animal fats. The product of biodiesel can utilized as fuel which their represent a safe, non-toxic and renewable energy source [2]. The catalyst is requirement to transformation the triglyceride (TGs) into fatty acid methyl esters (FAMES) with ethanol. The source of biodiesel production are usually low cost feed stock *such as* waste cooking oils, by products of the vegetable oil refining, some non-edible oils, and animal fats *etc.*, however, these source should contained free fatty acids (FFAs) less than 1% since an excess of FFAs causes side reaction (saponification) and problem in process of product purification (reduced the production yield and emulsion formation) [3], [4]. Whereas, the acid catalyst is very important for the industrial production since can convert FFAs to ester product and non-side reaction generated.

Generally, the most common catalyst widely used in biodiesel production are base catalyst *such as* NaOH or KOH *etc.* and acid catalyst *such as* H₂SO₄ or HCl *etc.*, which those homogeneous catalyst have been proven as the most affective for acceleration reaction [5]. However, the homogeneous catalyst was several drawback for using in commercial scale in view of economic and environmental view point e.g. critical step to wash biodiesel product, waste of water and

water treatment, corrosive in metal devices of reactor and also increasing the cost of production, non-reusable catalyst and so on. Therefore, the developing in heterogeneous catalyst comes to replace with reducing the biodiesel production cost and more environmental friendly since the catalyst easy removable, non-corrosive, the recovery reused possible. During the last decades, several diverse heterogeneous catalyzed esterification have already been investigated. Some of the examples are ion-exchange resins having sulfonic acid groups [6], sulfated or mixed oxides [7], heteropoly acids [8], metal-containing molecular sieves [9], acid functionalized silica/mesoporous silica [10], carbonaceous acidic materials [11], zeolites [12] and so on. Moreover, the acidity combining or functionalized in high porosity in materials influenced to enhance the performance in catalytic activity [13], [14]. However, a serious drawbacks have been reported *such as* leaching of species in recyclability [15], high condition in term of temperature and reaction time on, the low diffusion of oil due to the small pore size, swelling tendency in solvent, low active site involve of low surface area *etc* [16]. On the basis of these considerations, the catalyst improvement of the esterification could represent one of the key points through which the whole process can result in being economically convenient.

High porosity materials like metal-organic frameworks (MOFs) which constructed framework from inorganic (metals cluster/nodes) with organic (ligand/linker) offer tremendous possibilities for catalyst application since their properties in high porosity, surface area, and enable for tailor design for tuning the acidity/basicity properties [17-19]. Here, we proposed to use MOFs which their high stability in chemical, physical and thermal properties in reaction condition to investigate on esterification. Further to understand the fundamental reasons, the oleic acid was used to study since there is a typically high content in feedstock oil of biodiesel production.

II. METHODOLOGY

A. Synthesis MOFs

The ZIF-8-SV synthesis was analogous as that reported elsewhere [1]. 0.42g (1.606 mmol) of Zn (NO₃)₂·4H₂O (metal source) and 0.12g (1.462 mmol) of 2-methylimidazole (2-MIM) were dissolved in 32 ml of DMF. The solution was transferred to a Teflon-lined stainless-steel autoclave (35ml) and heated in programmable oven at 5°C/min to 140°C and held for 24 h. The light yellow solid product was separated from mother liquor and washed with *N,N'*-dimethylformamide (DMF) three times, immersed in methanol for 3 days and dried at room temperature under

vacuum for 12h. The dried material was transferred into a vacuum desiccator for further use.

The MOF-808 was synthesised using a conventional solvothermal heating method. A teflon liner 35 mL with 116.5 mg (0.50 mmol) of ZrCl_4 and 35.3 mg (0.168 mmol) of 1,3,5-benzenetricarboxylic acid. Thereafter, 2.8 mL (49 mmol) of acetic acid and 5 mL of DMF were introduced. The mixture was sonicated for an additional 20 minutes before being sealed and heated at 135 °C for a period of 24 h. The mixture was subsequently cooled to room temperature in the oven before the precipitate was isolated by vacuum filtration and washed with DMF (2 x 30 mL), acetone (2 x 30 mL) and methanol (3 x 30 mL). The resulting powder was dried in air.

The MIL-125 has been synthesized by a solvothermal method using a solvent mixture of DMF and methanol. In a typical synthesis, terephthalic acid (7.6 mmol) and titanium isopropoxide ($\text{Ti}(\text{OiPr})_4$, 5.1 mmol) were dissolved in the mixture of DMF (40 mL) and dry methanol (10 mL, 99.9 %) and loaded into a three-neck round bottom flask (100 mL) equipped with a reflux condenser at 20°C. The resulting mixture was crystallized by stirring under reflux conditions at 100 °C for 72 h. After the reaction, the mixtures were allowed to cool down to room temperature, leading to the formation of a white crystalline product in the solution. It was further filtered and then washed with DMF. For further purification, the as-synthesized product was re-dispersed at 60°C in DMF for 2h (100 mL of DMF per 1g of product) and then in methanol for 2h (100 mL of DMF per 1g of product). Finally, it was dried overnight at 90°C under nitrogen.

B. Characterizations

Activation of the materials was done by *in-situ* evacuation under vacuum at 110 °C overnight to obtain porous materials ready for the characterizations. The powder X-ray diffraction spectra (XRD) were collected using an Empyrean instrument from PANalytical applying a monochromatic Cu K radiation at ambient conditions. The low-pressure gas adsorption isotherms were measured by the volumetric method on a Micromeritics instrument (ASAP2020). In all gas adsorption measurements 60-100 mg of sample was used. For the N_2 gas adsorption analyses gases of purity > 99.999% were applied. Prior to the adsorption measurements, the samples were evacuated at 180 °C under vacuum (initial activation) for about 3 h. The micro pore surfaces were calculated by the Brunauer-Emmett-Teller (BET) and Langmuir method. The linearized BET and Langmuir equation were fit to the data within the range $0.02 < P/P_0 < 0.2$.

III. RESULTS AND DISCUSSION

The alumina compound was considered first as catalyst in this work since their Lewis acid was reported for active side of trans/esterification reaction [20], [21]. Herein, the high stability on chemical (moisture, water and weak acid etc.) and temperature of several series in MOF materials were selected for alternative solid catalyst of oleic acid esterification. ZIF-8 is first of MOFs which this work involved a comparative evaluation since there are previous studies to use as a catalyst in transesterification of vegetable oil [22]. Consequently, solid catalyst involved a comparative on this study of the

catalyst activity in esterification of oleic acid with methanol, in all cases under the same operation condition. The different result in percentage yield of methyl oleate observed using the solid catalyst of MOFs comparable to meso-alumina and blank experiment (non-catalyst) as shown in Fig.1. The result present all MOFs catalyst obtained higher percentage of yield than meso-alumina catalyst at the same reaction condition.

Regarding recovery catalyst at the end of the esterification which is advantage of heterogeneous or solid catalyst, were determined on the MOFs catalyst. In view of high activity (% yield of methyl oleate) obtaining on the first reaction test, afterward, the recycle experiment was obtained. The result on all the MOFs catalyst observed remain catalytic activity after second and third recycle experiment (the percentage yield on methyl oleate obtained closely or stable value). Furthermore, the weight of catalyst after reaction was evaluated after washed material with methanol and dried at 120°C under vacuum for 12 h before analysis. The MOF-808, MIL-125 and meso alumina were found weight loss less than 3% after third recycles of experiment reaction. Whereas weight loss more than 10% observed on ZIF-8 on every recycle reaction which represent in partial decomposed on this material during reaction.

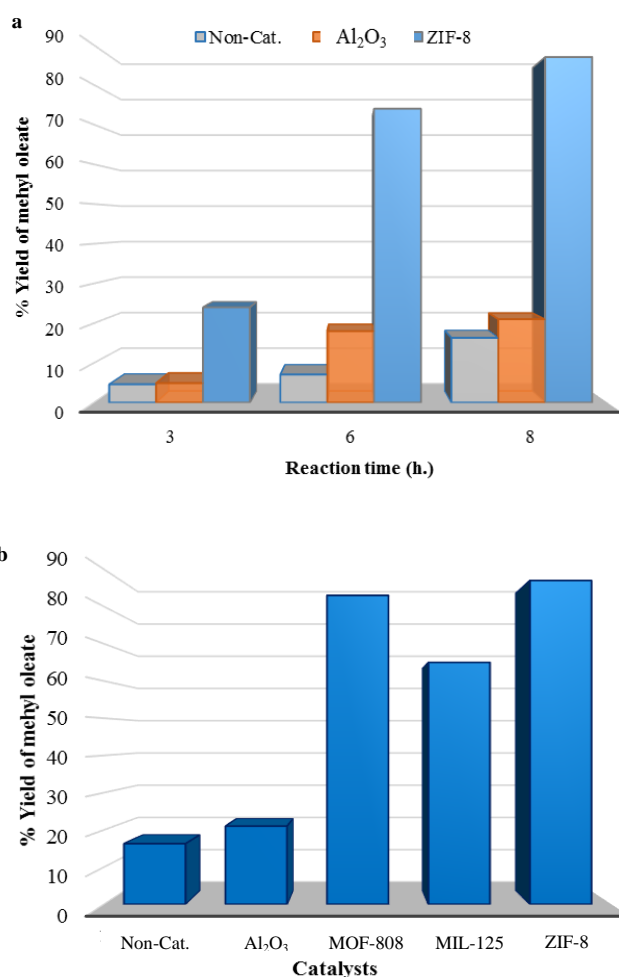


Fig. 1. The catalytic activity on Oleic acid esterification (% Yield of methyl oleate) at 130°C, 0.1g oleic acid, 1ml methanol and 10 mg of catalyst; (a) the comparable % yield of Non-catalyst and reposed solid catalyst (Al_2O_3 and ZIF-8) with time of reaction, and (b) the comparable activity in variance MOF catalyst after reaction 8h.

The properties of solid catalyst after reaction comparable to fresh sample were characterized such as the crystal

structure (powder X-ray diffraction), the porosity and surface area (gas adsorption, ASAP 2020) and chemical bonds or molecular structure (FT-IR) etc. The crystal structure of ZIF-8 after third recycle obtained similar as the fresh sample (Fig.2). However, the intensity was reduced which represent the lower in crystallinity of material. Whereas the absolutely change on XRD pattern was observed on MOF-808 and MIL-125 (Fig.2). Consequently, the analysis in chemical bonding or functional group of spend materials were investigated *via* FT-IR (Fig.3). The new spectrum (2800-2950 cm^{-1}) were found on catalyst material after reaction. The $\nu_{\text{O-H}}$ stretch vibration band was reported a

spectrum at 2500-3000 cm^{-1} which two of new spectrum (2845 and 2920 cm^{-1}) were matching on $\nu_{\text{O-H}}$ stretch vibration band [23]. Therefore, these result could evident that O-H group in carboxylic group of oleic acid was bonding on solid catalyst during the reaction and still remain after reaction. Moreover, the reducing in porosity and surface area of materials after reaction also confirm that the carboxylic group (O-H group) of oleic acid coordinated and blocked the pore of material since spend catalysts showed non porous material. However, this results could not big effect to catalytic activity since the materials (MOFs) still shown remaining in catalytic activity (recycle ability).

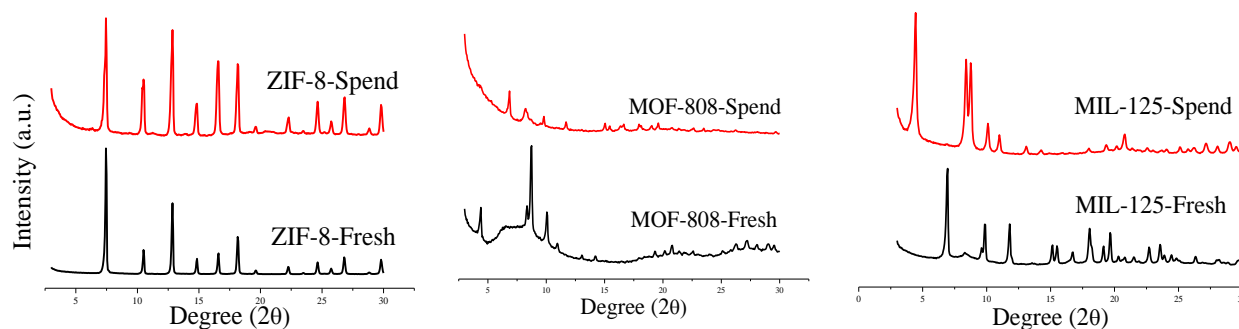


Fig. 2. The XRD pattern of MOFs on before (Fresh) and after (spend) catalytic reaction for 3rd of reaction experiment.

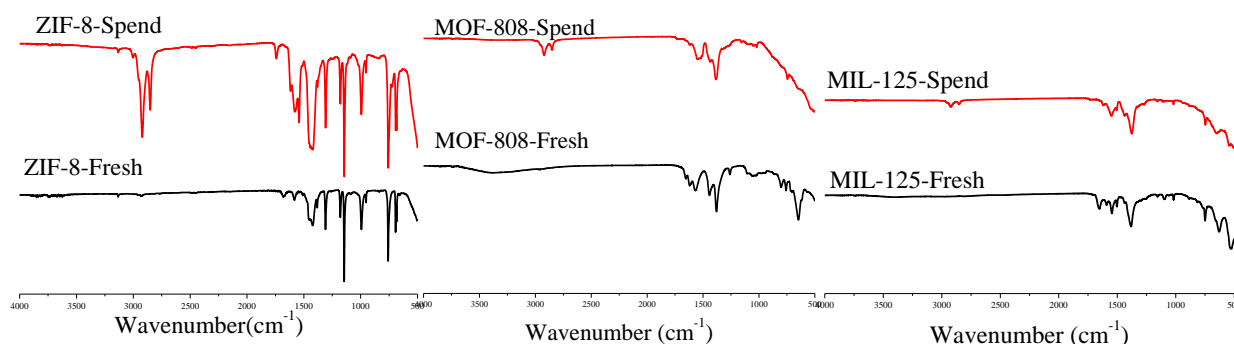


Fig. 3. The FT-IR spectrum of MOFs on before (Fresh) and after (Spend) catalytic reaction for 3rd of reaction recycles.

IV. CONCLUSION

The experimental addressing the oleic acid esterification using MOFs as a catalyst appears alternative for heterogeneous phase/solid catalyst which simple separation process. Moreover, those materials have ability to recycle catalyzed reaction in several times which high potential to use for catalyzed for biodiesel product in up-scale or industrial in further. The opportunity making biodiesel as the alternative fuel competition with traditional fossils fuel, the decreasing process cycle and costs is essential aspect in the biodiesel production. However, these material still required at high temperature which there are big challenging to improve or functionalize materials (MOFs) to achieve in requirement in industrial.

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