Electronic Supplementary Information (ESI)

KF-loaded mesoporous Mg-Fe bi-metal oxides: high performance transesterification catalysts for biodiesel production

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Fig. S8. Influence of alcohol to oil molar ratios and the catalyst amounts on the yield of biodiesel catalyzed by **20**KF/*m*-Mg_2Fe-**M**.

Experimental details

Materials: Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium oxalate ($Na_2C_2O_4$), potassium fluoride dihydrate ($KF \cdot 2H_2O$), potassium hydroxide (KOH) were obtained from Sinopharm Chemical Reagent Co.. Methyl laurate was purchased from TCI. Soybean oil was obtained from the local supermarket. Methanol (MeOH) was purchased from Sigma-Aldrich. All regents were used without further purification. Deionized water was used in all synthesis experiments.

Synthesis of KF/m-Mg_2Fe composites: The support, mesoporous Mg-Fe bi-metal oxides with a Mg/Fe molar ratio of 2 (*m*-Mg_2Fe), was synthesized by the simple template–free strategy according to our previous report [1] with a modified calcination duration of 1 h. Then, the obtained *m*-Mg_2Fe was wetted by $KF \cdot 2H_2O$ methanol or aqueous solutions with different concentrations corresponding to the loading amounts of $KF \cdot 2H_2O$ (10, 20, and 30% (wt/wt *m*-Mg_2Fe support)) by incipient wetness impregnation. After ultrasonically treated for 5 min, the slurries were placed statically for 6 h and further dried at 100 °C overnight after the solvents were evaporated under reduced pressure in a rotary evaporator at room temperature for methanol or 40 °C for water. Prior to use, these dried materials were activated by calcining at 400 °C for 1 h. The resultant composites are denoted as **x**KF/*m*-Mg_2Fe-**M** or **x**KF/*m*-Mg_2Fe-**W**, where '**x**', '**M**' and '**W**' are the nominal $KF \cdot 2H_2O$ loading amount, **M**ethanol (the impregnation solvent) and **W**ater (the impregnation solvent), respectively. The whole synthesis process of the mesostructured KF/*m*-Mg_2Fe composites with different impregnation solvents is shown in Fig. 1.

Characterization: Wide-angle X-ray diffraction patterns were recorded on a Rigaku D/Max 2200PC diffractometer with CuKa radiation (40 kV and 40 mA) and a scanning rate of 4 ° min^{-1}. N_2 adsorption/desorption measurements were performed by

using Micromeritics Tristar 3000 at 77 K and the mesoporous specific surface area, pore size distributions were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. A vibrating-sample magnetometer (PPMS Model 6000 Quantum Design, San Diego, USA) was used to study the magnetic properties. Transmission electron microscopy (TEM) images and field emission scanning electron microscopic (FE-SEM) images were obtained by a JEOL-2010F electron microscope operating at 200 kV and a Hitachi S-4800, respectively. Carbon dioxide temperature-programmed desorption (CO_2-TPD) was performed on a ChemiSorb 2750 instrument (Micromeritics, USA). About 50 mg of sample was put into a quartz "U" tube and pretreated under a helium stream at 350 °C for 1 h (10 °C min^{-1}, 25 ml min^{-1}). The sample was then cooled to room temperature, and a flow of CO_2 gas (25 ml min^{-1}) was subsequently introduced into the quartz "U" tube for 1 h. Then the temperature was raised to 100 °C and the gas flow was changed to the helium gas flow again for 1 h to remove loosely adsorbed carbon dioxide molecules from the catalyst surface. The sample was then heated to 850 °C under helium flow (25 ml min^{-1}) to desorb CO_2, which was detected using an online thermal conductivity detector. The product of the transesterification reaction was analyzed by a GC-MS (Agilent, 6890/5973N), with the injector and detector temperatures being maintained at 240 °C and 260 °C, respectively. The oven temperature in the GC-MS was increased to 195 °C from 60 °C at a heating rate of 5 °C min^{-1} and further to 205 °C at 1 °C min^{-1}. The leaching amounts of K and/or Mg species of catalysts into biodiesel were evaluated by measuring the K and Mg concentrations in the biodiesel after evaporating methanol with ICP-OES (Vista AX).

Transesterification reactions: The transesterification reaction of soybean oil with methanol was carried out in a three-necked flask equipped with a condenser and a magnetic stirrer under mild conditions: stirring at 200 rpm, atmospheric pressure, and 60 °C without protecting gas. Typically, 5.0 g of soybean oil, 0.8 g of methyl laurate (internal standard) and a specified volume of methanol were added into the flask. Then, a certain amount of catalyst was added into the above mixture after it reached

60 °C. The product was collected with a micro syringe per 10 min and analyzed by the GC-MS. The yield of biodiesel was determined by the following equation:

Yield (%) = actual weight of total FAMEs * 100% / weight of soybean oil (4)

In which the actual weight of total FAMEs (fatty acid monoalkyl esters, main content of biodiesel) was determined by GC-MS.

After each reaction, the catalyst was separated from the reaction mixture with a magnet, washed with cyclohexane, dried under vacuum at room temperature for 4 h and calcined at 400 °C for 1 h before reuse.

Reference

1 Z. Gao, J. Zhou, F. Cui, Y. Zhu, Z. Hua and J. Shi, *Dalton Trans.*, 2010, **39**, 11132.

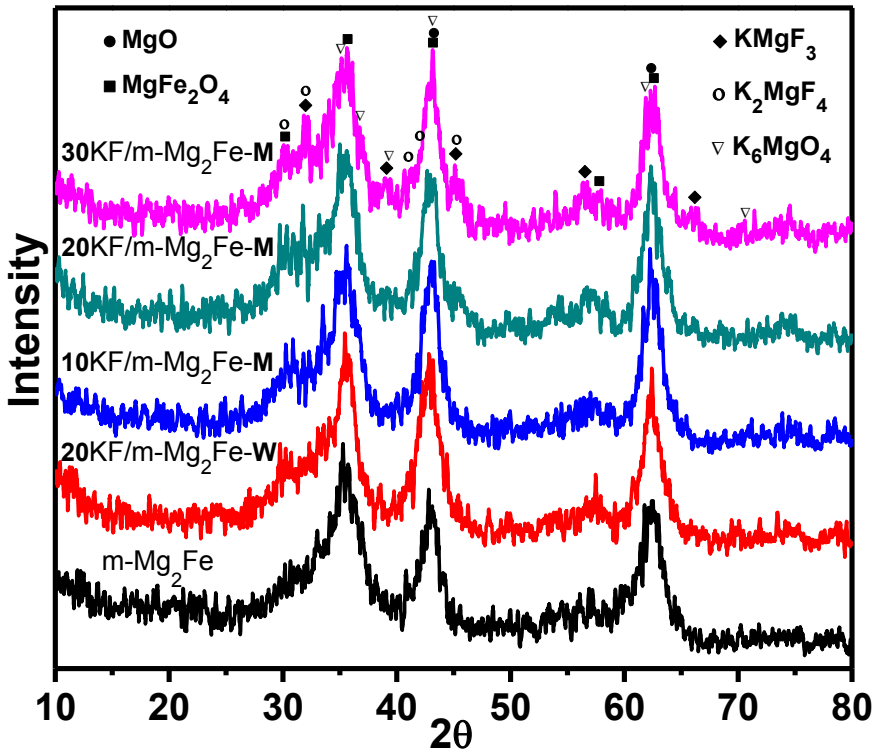


Fig. S1. Wide-angle X-ray diffraction patterns of **x**KF/*m*-Mg_2Fe-**M**, **20**KF/*m*-Mg_2Fe-**W** (**x** = **10**, **20**, or **30**, the loading amounts (%) of $KF{\cdot}2H_2O$; **M** = **M**ethanol, **W** = **W**ater, the impregnation solvent) and *m*-Mg_2Fe support.

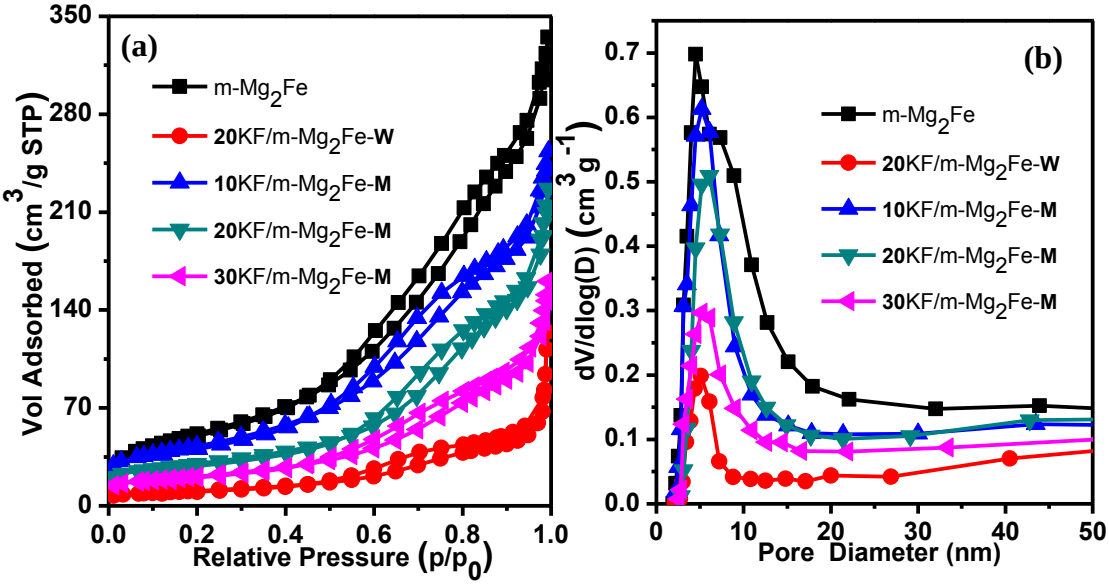


Fig. S2. N_2 adsorption–desorption isotherms (a) and their corresponding pore-size distributions (b) of **x**KF/*m*-Mg_2Fe-**M**, **20**KF/*m*-Mg_2Fe-**W** (**x** = **10**, **20**, or **30**, the loading amounts (%) of $KF{\cdot}2H_2O$; **M** = **M**ethanol, **W** = **W**ater, the impregnation solvent) and *m*-Mg_2Fe support.

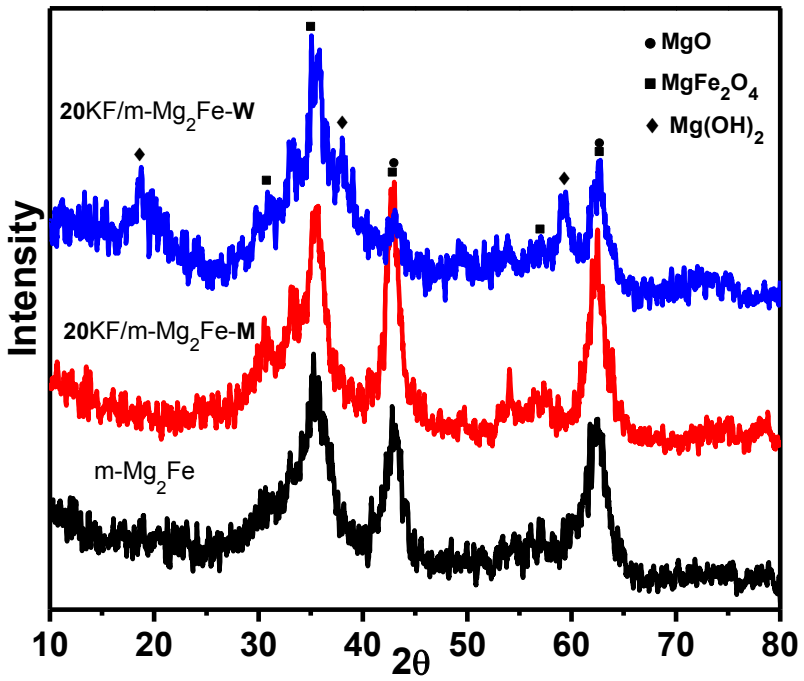


Fig. S3. Wide-angle X-ray diffraction patterns of non-calcined **20**KF/*m*-Mg_2Fe-**M** and **20**KF/*m*-Mg_2Fe-**W** (**M** = **M**eOH, **W** = **W**ater, the impregnation solvent) as well as calcined *m*-Mg_2Fe support.

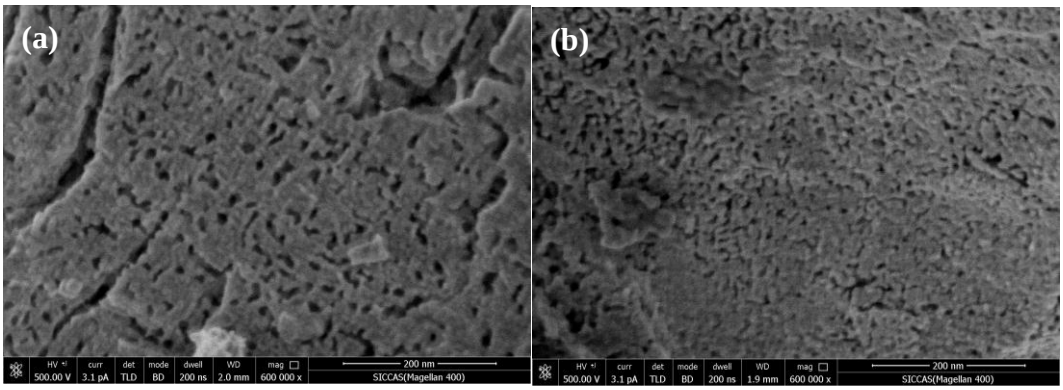


Fig. S4. SEM images of **10**KF/*m*-Mg_2Fe-**M** (a) and **30**KF/*m*-Mg_2Fe-**M** (b) (**M** = **M**ethanol, the impregnation solvent).

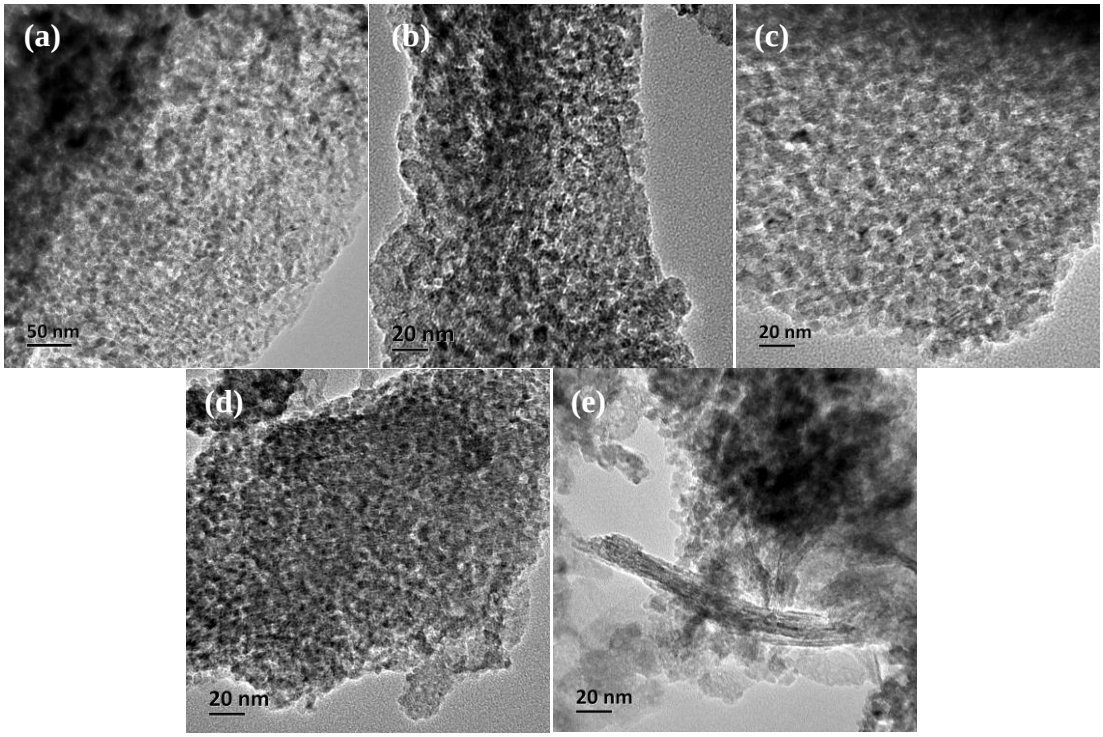


Fig. S5. TEM images of *m*-Mg_2Fe support (a), **10**KF/*m*-Mg_2Fe-**M** (b), **20**KF/*m*-Mg_2Fe-**M** (c), **30**KF/*m*-Mg_2Fe-**M** (d) and **20**KF/*m*-Mg_2Fe-**W** (e) (**M** = **M**ethanol, **W** = **W**ater, the impregnation solvent).

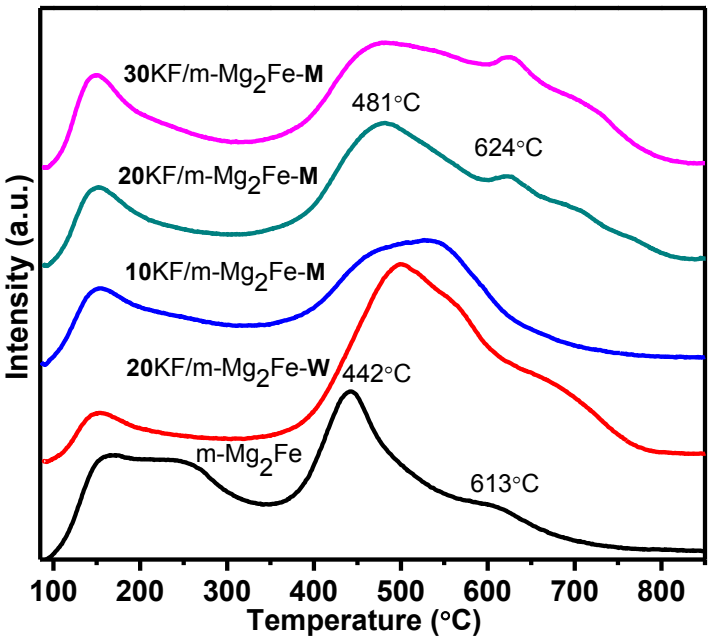
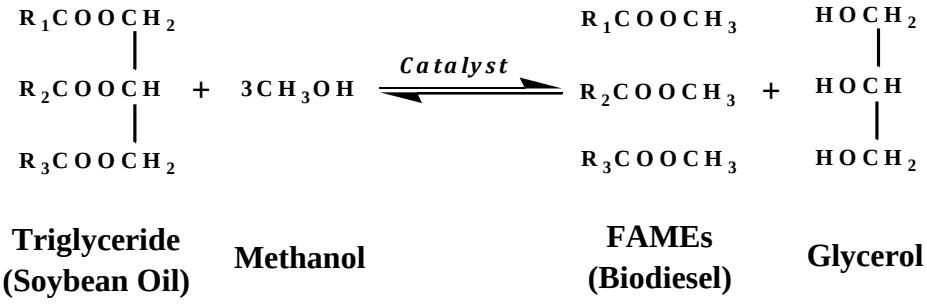


Fig. S6. CO_2-TPD profiles of **x**KF/*m*-Mg_2Fe-**M**, **20**KF/*m*-Mg_2Fe-**W** (**x = 10**, **20**, or **30**, the loading amounts (%) of $KF{\cdot}2H_2O$; **M** = **M**ethanol, **W** = **W**ater, the impregnation solvent) and *m*-Mg_2Fe support.



Scheme S1. The transesterification reaction schematic diagram between soybean oil and methanol (FAMEs: fatty acid monoalkyl esters).

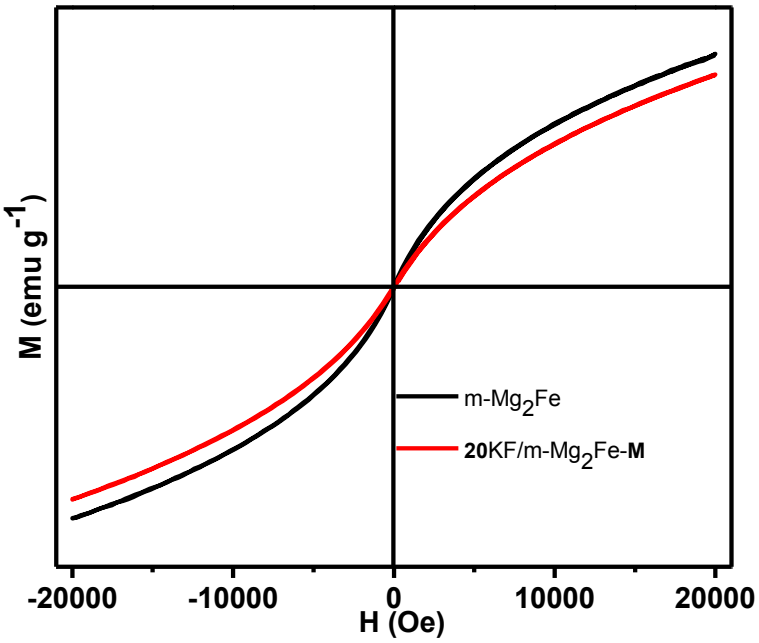


Fig. S7. Magnetization curves of *m*-Mg_2Fe support and **20**KF/*m*-Mg_2Fe-**M** composite (as a representative; **M** = **M**ethanol, the impregnation solvent).

Table S1. Yields of FAMEs with fresh **x**KF/*m*-Mg_2Fe(**y0z**)-**W**-**a0b** (**x** is the loading amount (%) of KF·$2H_2O$; **W** = **W**ater, the impregnation solvent; '**y0z**' indicates that *m*-Mg_2Fe support was calcined at 'y' °C for 'z' h and '**a0b**' means that the supported catalyst was activated at 'a' °C for 'b' h) as well as 1st recycled **20**KF/*m*-Mg_2Fe-**W** and 30KF/*m*-CaAl4(700)-700-3 (our previous reported mesostructured KF/Ca-Al bi-metal oxides).

Materials	FAMEs Yield [%]
20KF/*m*-Mg_2Fe(**401**)-**W-503**[a)]	91.10±0.50
48.6KF/*m*-Mg_2Fe(**401**)-**W-401**[a)]	91.40±0.71
20KF/*m*-Mg_2Fe(**403**)-**W-403**[a)]	86.90±0.98
30KF/*m*-Mg_2Fe(**403**)-**W-403**[a)]	91.46±0.96
1st recycled **20**KF/*m*-Mg_2Fe-**W**[a)]	77.14±0.42
1st recycled 30KF/*m*-CaAl4(700)-700-3[b)]	70.38±0.13

[a)]Reaction conditions: reaction temperature of 60 °C, alcohol to oil (A/O) molar ratio of 12:1, catalyst amount (catalyst/oil weight ratio) of 3 wt%, reaction duration of 1 h and stirring at 200 rpm; [b)]Reaction conditions: reaction temperature of 60 °C, A/O molar ratio of 18:1, catalyst amount of 3 wt%, reaction duration of 5 h and stirring at 200 rpm.

Table S2. Recyclability and stability of **20**KF/*m*-Mg_2Fe-**M** (**M** = **M**ethanol, the impregnation solvent).

Recycle times	1st use	1st recycle	2nd recycle	3rd recycle	4th recycle	EN 14214 Standard
FAMEs yield [%][a)]	100.00±0.53	93.34±1.78	84.10±1.62	77.13±1.40	59.57±0.16	≥ 96.5
Leached K [mg kg^{-1}][a)]	23.37±0.30	8.00±1.06	13.03±0.81	25.50±0.60	20.17±0.80	≤ 5
Leached Mg [mg kg^{-1}][a)]	<1	<1	1.30±0.17	1.37±0.15	5.47±0.15	≤ 5
Leached Fe [mg kg^{-1}][a)]	<2.5	<2.5	<2.5	<2.5	<2.5	-

[a)]Reaction conditions: reaction temperature of 60 °C, A/O molar ratio of 12:1, catalyst amount of 3 wt%, reaction duration of 1 h and stirring at 200 rpm.

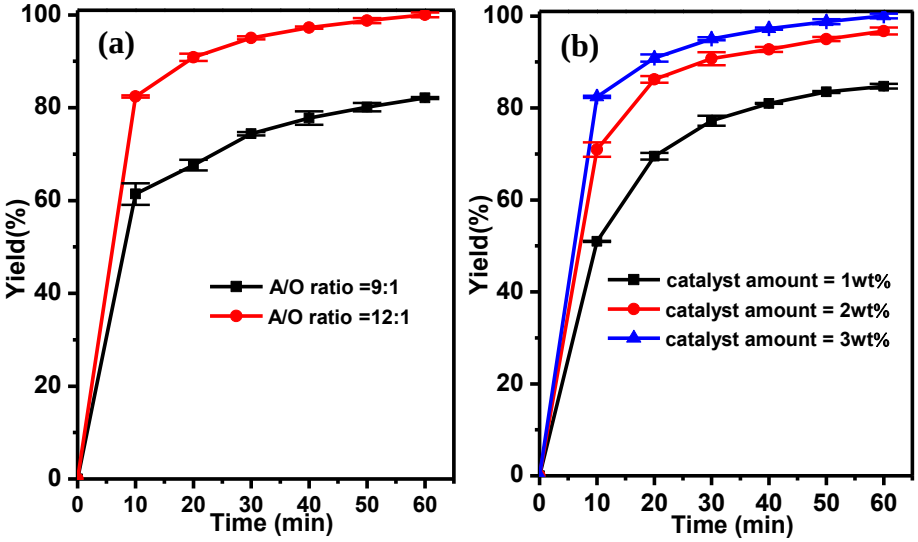


Fig. S8. Influence of alcohol to oil (A/O) molar ratios (a) and the catalyst amounts in catalyst/oil weight ratio (b) on the yield of biodiesel catalyzed by **20**KF/*m*-Mg_2Fe-**M** (**M** = **M**ethanol, impregnation solvent).