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

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Using newly developed mesoporous Mg–Fe bi-metal oxides as supports, a novel kind of high performance transesterification catalysts for biodiesel production has been synthesized. More importantly, the impregnation solvent was for the first time found to substantially affect the structures and catalytic performances of the resultant transesterification catalysts.

Due to the rapid depletion of fossil fuels and increasing environmental concerns, biodiesel, a sort of environmentally-friendly and renewable energy, has attracted increasing attention in recent years.[1] The main content of biodiesel is C_{12}–C_{22} fatty acid monoalkyl esters (FAMEs), fabricated mainly by transesterification reactions between renewable triglycerides and short-chain alcohols in the presence of catalysts. Currently, homogeneous base catalysts, *e.g.* KOH, are generally being utilized in industry.[2] Difficult catalyst separation and consequently high cost for product purification are the major drawbacks of homogeneous catalysis systems.[3] To solve these problems, much attention has been paid to solid bases, *e.g.* KF-loaded materials.[4] Nevertheless, extremely high KF loading amounts (70–100% (wt/wt support))[4b–f] and poor recyclability[4f,i,j] are their main defects. Moreover, few studies have concerned the leaching properties of elements in the biodiesels obtained from KF-loaded catalysts,[4g–i] which are actually very important and highly restricted by relevant standards, such as the EN14214 standard.[4h]

Mesoporous materials have been used extensively in catalytic applications due to their high specific surface areas and largely uniform pore channels, which are favor the dispersion of active species and transportation of rapid molecules.[5] Previously, our group has synthesized magnetically separable mesoporous Mg–Fe bi-metal oxides, which showed high activities and good recyclability for Knoevenagel reactions due to their mesoporous structures, basicity and strong interactions between MgO and $MgFe_2O_4$.[6] However, these materials showed poor activities in transesterification reactions for biodiesel production. On the other hand, very recently a kind of KF-loaded mesoporous Ca–Al bi-metal oxides has been synthesized by us and used as transesterification catalysts.[4h] An interesting result is that the leaching amount of Ca and K in the obtained biodiesel product either meets or is only a little higher than the corresponding items of EN 14214 standard. However, their catalytic activity and recyclability need further improvement.

Herein, by loading/dispersing KF in the newly developed mesoporous Mg–Fe bi-metal oxides with a Mg/Fe molar ratio of 2 (*m*-Mg$_2$Fe), a novel kind of high performance transesterification catalyst, xKF/*m*-Mg$_2$Fe (x stands for the KF·2H$_2$O loading amount (%)), has been synthesized (Fig. 1). Encouragingly, when methanol (-M) was used as the impregnation solvent, the resultant 20KF/*m*-Mg$_2$Fe-M composite, under the
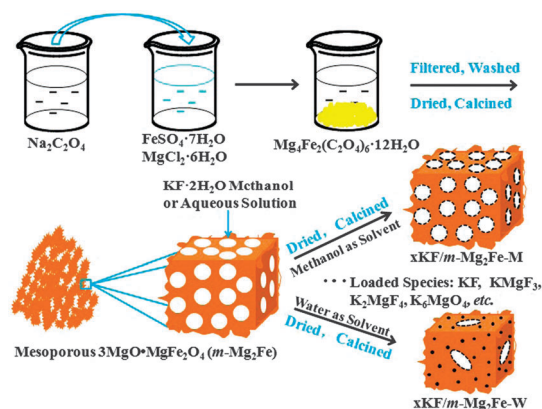
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Fig. 1 Schematic diagram of the synthesis process of xKF/*m*-Mg$_2$Fe composites with methanol or water as the impregnation solvent.

mild reaction conditions, demonstrated almost 100% yield of FAMEs in 1 h of reaction duration, extraordinarily low leaching amounts of K and Mg as well as high recyclability. Moreover, for the first time, it is found that the impregnation solvent significantly affects the catalytic performances of supported transesterification catalysts for biodiesel production, which has been ignored before.

Wide-angle X-ray diffraction (XRD) patterns (Fig. S1, ESI†) demonstrate that, compared to the m-Mg$_2$Fe support, xKF/m-Mg$_2$Fe composites present a series of new diffraction peaks belonging to KMgF$_3$, K$_2$MgF$_4$ and K$_6$MgO$_4$, as a result of reactions between KF and the nano-crystallized MgO phase in the m-Mg$_2$Fe support (eqn (1) and (2)).[4a,g,7]

$$9KF + 4MgO \rightarrow 3KMgF_3 + K_6MgO_4 \qquad (1)$$

$$12KF + 4MgO \rightarrow 3K_2MgF_4 + K_6MgO_4 \qquad (2)$$
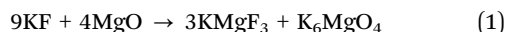
N$_2$ sorption results are shown in Table 1 and Fig. S2 (ESI†). Due to the introduction of KF, the specific surface areas (S_{BET}) and pore volumes (V_{BJH}) of xKF/m-Mg$_2$Fe-M are smaller than those of m-Mg$_2$Fe and decrease gently with increasing KF·2H$_2$O loading amounts. Unexpectedly, the lowest S_{BET} and V_{BJH} were obtained with 20KF/m-Mg$_2$Fe-W (W = water, impregnation solvent) among xKF/m-Mg$_2$Fe composites. Since the XRD pattern of non-calcined 20KF/m-Mg$_2$Fe-W (Fig. S3, ESI†) showed the characteristic peaks of Mg(OH)$_2$ while those of the MgO phase in the m-Mg$_2$Fe support almost completely disappeared, it is postulated that the hydration reaction between the solvent H$_2$O and nano-crystallized MgO in m-Mg$_2$Fe during impregnation seriously destroyed the mesoporous structure of the support.

Being consistent with N$_2$ sorption results, SEM and TEM images (Fig. 2; Fig. S4 and S5, ESI†) depict that all xKF/m-Mg$_2$Fe-M keep well-defined 3-D wormlike mesoporous structure very similar to that of m-Mg$_2$Fe, which favors the high dispersion of KF and its subsequent interaction/reaction with the support, and finally leading to the generation of numerous highly dispersed active sites accessible to reactants. In contrast, the 3-D wormlike mesoporous structure is no longer dominant in 20KF/m-Mg$_2$Fe-W due to the hydration of nano-crystallized MgO during the impregnation process, which makes part of the generated active sites unaccessible to reactants.

All CO$_2$-TPD profiles of xKF/m-Mg$_2$Fe and m-Mg$_2$Fe (Fig. S6, ESI†) present three broad desorption bands with desorption temperatures of 100 °C to 340 °C, 360 °C to 590 °C and 590 °C to 820 °C, resulting from the interactions between CO$_2$ and the weak, medium and strong basic sites, respectively.[8] Compared to m-Mg$_2$Fe, xKF/m-Mg$_2$Fe possesses far lower amounts of weak basic sites but much larger amounts of medium and strong ones due to the introduction of KF, and the reactions between KF and nano-crystallized MgO and calcination. Moreover, the CO$_2$ desorption temperatures maximized at around 481 °C and 624 °C of xKF/m-Mg$_2$Fe, belonging to the medium and strong basic sites, respectively, are higher than those of m-Mg$_2$Fe at around 442 °C and 613 °C, which may result from the highly basic species such as K$_6$MgO$_4$,[4g,7b,d] coordinately unsaturated F$^-$,[4a,f,7d,9] low-coordination O^{2-} anions and oxygen in Mg^{2+}-O^{2-} pairs of strong basicity due to the insertion of K$^+$ into the vacancy sites of the m-Mg$_2$Fe support.[10]

On the other hand, compared to 20KF/m-Mg$_2$Fe-M, 20KF/m-Mg$_2$Fe-W has much higher amounts of medium basic sites and slightly higher amounts of strong ones. As proved by XRD results (Fig. S3, ESI†), it is believed that when water was used as the impregnation solvent, nano-crystallized MgO particles in m-Mg$_2$Fe would gradually hydrate to form the Mg(OH)$_2$ phase, which would simultaneously mix with the solute KF in aqueous solution. Accompanying the solvent evaporation, homogeneous mixtures of Mg(OH)$_2$ and KF would re-deposit on m-Mg$_2$Fe. During the following calcination, more KF would react with Mg(OH)$_2$ or MgO decomposed from Mg(OH)$_2$, generating more medium and strong basic sites in 20KF/m-Mg$_2$Fe-W.

The transesterification reaction results between soybean oil and methanol (Scheme S1, ESI†) catalyzed by xKF/m-Mg$_2$Fe and m-Mg$_2$Fe are summarized in Fig. 3 and Table 1. As expected, all xKF/m-Mg$_2$Fe exhibit much higher activities than m-Mg$_2$Fe due to their larger amounts of medium and strong basic sites (Fig. S6, ESI†).[8b,11] Very encouragingly, the yields of biodiesel obtained with xKF/m-Mg$_2$Fe are higher than 88% in only 1 h of reaction duration, and noticeably they reached 100.00 ± 0.53% with 20KF/m-Mg$_2$Fe-M. These biodiesel yields are considerably higher than those obtained with our recently reported meso-structured KF/Ca–Al bi-metal oxides, which only showed 59.71 ± 0.90% and 97.82 ± 0.93% yields in the reaction durations of 1 h and 5 h, respectively,[4h] as well as those obtained with other supported catalysts, such as KF/MgO,[4a] potassium compound/Al$_2$O$_3$,[12] and CaO/Al$_2$O$_3$.[13] Moreover, with an equal amount of K (in moles) as in 20KF/m-Mg$_2$Fe-M, KOH, a homogeneous base catalyst used industrially, even shows lower catalytic activity than 20KF/m-Mg$_2$Fe-M. Thus, 20KF/m-Mg$_2$Fe-M is a highly efficient transesterification catalyst and m-Mg$_2$Fe might be one of the best reported supports for biodiesel production so far due to its excellent basic properties and well-defined mesoporous structure that

Table 1 Texture properties and FAME yields with the xKF/m-Mg$_2$Fe and m-Mg$_2$Fe support

Materials	S_{BET} [m^2 g^{-1}]	V_{BJH} [cm^3 g^{-1}]	FAMEs yield[a] [%]
m-Mg$_2$Fe	187	0.52	25.17 ± 0.63
20KF/m-Mg$_2$Fe-W	37.9	0.19	88.95 ± 1.07
10KF/m-Mg$_2$Fe-M	151	0.40	92.16 ± 0.73
20KF/m-Mg$_2$Fe-M	106	0.35	100.00 ± 0.53
30KF/m-Mg$_2$Fe-M	74.4	0.25	100.48 ± 0.10
KOH	—	—	96.74 ± 0.24

[a] A reaction temperature of 60 °C, an alcohol to oil (A/O) molar ratio of 12:1, a catalyst amount (catalyst/oil weight ratio) of 3 wt% and a reaction duration of 1 h.
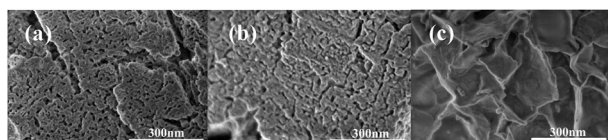

Fig. 2 SEM images of the m-Mg$_2$Fe support (a), 20KF/m-Mg$_2$Fe-M (b) and 20KF/m-Mg$_2$Fe-W (c) (M = methanol, W = water, impregnation solvent).
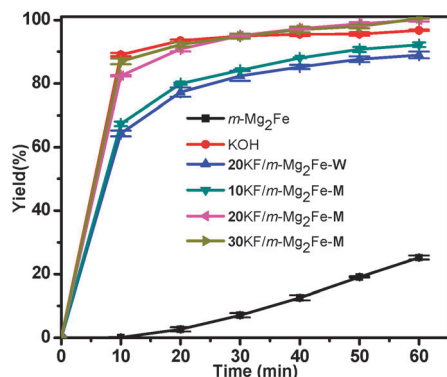
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Fig. 3 Yields of FAMEs catalyzed by xKF/m-Mg$_2$Fe-M, 20KF/m-Mg$_2$Fe-W (M = methanol, W = water, impregnation solvent), m-Mg$_2$Fe and KOH.

favor the generation of numerous highly dispersed active sites accessible to reactants when KF was loaded. In addition, all xKF/m-Mg$_2$Fe samples present almost 100% product selectivity of FAMEs and could be magnetically separable due to their near zero remanence and coercivity (Fig. S7, ESI†).

Notably, though 20KF/m-Mg$_2$Fe-W even has larger amounts of medium and strong basic sites (Fig. S6, ESI†) than 20KF/m-Mg$_2$Fe-M, 20KF/m-Mg$_2$Fe-M still demonstrates distinctively higher yield of biodiesel (100.00 ± 0.53%) than 20KF/m-Mg$_2$Fe-W (88.95 ± 1.07%) due to its well-reserved mesoporous structure that made the active sites easily accessible. In contrast, the collapsed mesoporous structure of 20KF/m-Mg$_2$Fe-W made it much less catalytically active. Moreover, attempts have been made to improve the catalytic performances of xKF/m-Mg$_2$Fe-W, and no appealing improvements were obtained (Table S1, ESI†). Thus, it is believed that the impregnation solvent plays a vital role in affecting the catalytic performances of these KF-loaded catalysts, which, however, was commonly ignored before.

Table S2 (ESI†) shows that, for 20KF/m-Mg$_2$Fe-M, the leachings of K and Mg into biodiesel are only a little higher than the corresponding items of EN 14214 standard, which makes the post-purification process for biodiesel products simple and cost-effective. This also indicates the good stability and the heterogeneous catalytic mechanism of this catalyst. Moreover, the recyclability of 20KF/m-Mg$_2$Fe-M (Table S2, ESI†) is better than that of 20KF/m-Mg$_2$Fe-W (Table S1, ESI†), mesostructured KF/Ca–Al bi-metal oxides (Table S1, ESI†)[4h] and other KF-loaded catalysts.[4j,14] We are confident that higher yields can be obtained with recycled 20KF/m-Mg$_2$Fe-M at higher A/O molar ratios, catalyst amounts and/or prolonged reaction durations. The influences of the KF·2H$_2$O loading amount, the A/O molar ratio and the catalyst amount on the yield of biodiesel were also investigated and the results are shown in Fig. 3 and Fig. S8 (ESI†).

In conclusion, a novel kind of magnetically separable high performance transesterification catalysts, KF-loaded mesoporous Mg–Fe bi-metal oxides, has been synthesized. Interestingly, for the first time, the impregnation solvent has been found to affect the catalytic performance of the transesterification catalysts significantly. The synthesized 20KF/m-Mg$_2$Fe-M composite, under mild reaction conditions, demonstrated almost 100% yield of FAMEs in 1 h reaction duration, extraordinarily low leaching amounts of K and Mg as well as good recyclability.

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