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# Synthesis and Catalytic Activity of Magnesium Hydroxide Fluorides for Production of Biodiesel: Influence of Different Mg/F Ratios

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The magnesium hydroxide fluorides having formula $MgF_x(OH)_{2-x}$ with diverse Mg/F ratios were prepared by fluorolytic sol-gel method. The XRD, FT-IR, SEM, nitrogen adsorption-desorption, TG/DTG and pyridine FT-IR were performed to study properties and characteristics of samples. Based on the characterization results, the samples show dissimilar structure, thermal stability, porosity, surface acidity and morphology. In addition, the average pore diameter and total pore volume of the $MgF_x(OH)_{2-x}$ decrease with increase in fluorine contents. The activity of solids as heterogeneous catalyst for production of biodiesel from used frying oil exhibits that $MgF_x(OH)_{2-x}$ with Mg/F ratio of 1:2 gives higher yield of biodiesel (75.29 %) compared to $MgF_x(OH)_{2-x}$ ($x < 2$). The higher activity of $MgF_x(OH)_{2-x}$ ($x = 2$) catalyst for biodiesel production can be attributed to acid sites (Lewis and Brønsted), average pore diameter and total pore volume. Moreover, performance of catalyst decreases after three cycles.

**Keywords: Magnesium hydroxide fluorides, Sol gel method, Heterogeneous catalyst, Biodiesel, Used frying oil.**

## INTRODUCTION

The biodiesel, containing methyl esters, became one of the potential subtitute to diesel fuel. It has many advantages such as a renewable, biodegradable and non-toxic fuel. The biodiesel could be obtained from triglycerides of animal fats or vegetable oils by transesterification and FFA (free fatty acids) by esterification reaction in the existence of base and acid materials as catalyst. However, the use of these feedstocks increased the price of production. Therefore, the low-quality oils such as used frying oils has been recently considered as the most potential raw material for the production of biodiesel in previous years [1-4].

Usually, the methyl ester from non-edible oils could be produced by chemical method of homogeneous catalyst [5,6]. However, several disadvantages related to homogeneous catalysts such as non-separatibility, non-reusability and corrosiveness that create new matters to the environment. Moreover, the use of this catalyst in the reaction to produce biodiesel requires additional step for the neutralization, which generates additional costs [7]. Therefore, the use of homogeneous catalyst for biodiesel production became unfavourable. The heterogeneous catalyst system could be an attractive solution to solve these disadvantages because the heterogeneous catalyst could be easily separable, reusable and inexpensive [8-10]. There are several heterogeneous catalysts have been studied to yield biodiesel from used frying oil [11-16]. Nevertheless, the solid catalysts exhibited some disadvantages such as expensive, not active, mass tranfer limitation and easily deactivated. Currently, few studies that investigate the magnesium hydroxide fluoride as catalyst to produce biodiesel using used frying oil.

Thus, the aim of the study is to observe the behaviour of magnesium hydroxide fluoride, especially the effect of diverse Mg/F ratios as heterogeneous catalyst for production of biodiesel using used frying oil *via* simultaneously reaction of transesterification and esterification. The influence of Mg/F ratios in the biodiesel production have also been investigated and discussed.

## EXPERIMENTAL

Metallic magnesium (98 % powder) was purchased from Aldrich Co. The acetone, dried methanol and HPLC, 48 %wt.-hydrofluoric acid and ethanol were purchased from Merck Co. The used frying oil with 13 % FFA was gained from Local Restoran, Indonesia. The phase and structure of resulting materials were studied by XRD at 2θ about 20-80° with Cu-$K_\alpha$ radiation source with $\lambda = 1.54056$ nm. The diffractogram patterns were compared with the data base of JCPDS-PDF. The FTIR were recorded with Shimadzu spectrometer equipped with KBr windows in the range 4000-350 $cm^{-1}$. The porosity of samples was investigated by adsorption isoterms of $N_2$ using a Quantachrome Instruments. The TG/DTG were performed by METTLER TOLEDO in $N_2$ with thermocouple. The SEM images were obtained by ZEISS EVO MA 10 apparatus. The acidic sites of samples were determined by FTIR with pyridine as probe at range 1600-1300 $cm^{-1}$.

**General procedure of synthesis of magnesium hydroxide fluorides [$MgF_x(OH)_{2-x}$]:** The $MgF_x(OH)_{2-x}$ with different ratios of Mg/HF were prepared by sol-gel technique and metallic magnesium as precursor [17]. First of all, metallic magnesium (98 % powder obtained from Aldrich Co.) (0.77 g) was dissolved in dried methanol (50 mL). The amount of hydrofluoric acid dissolved water, 48 % aquous HF (x = 0.5; 1; 1.5; and 2) was added. The formed gel was aged and the solven was removed under reduce pressure. The resulting powder was dried and the samples were referred to hereafter as 1:0.5; 1:1; 1:1.5 and 1:2, indicating the different of Mg/F molar ratios.

**Catalytic tests:** The catalytic activity of $MgF_x(OH)_{2-x}$ was applied as heterogeneous catalyst in the reaction of the used frying oils and metanol. The reaction was done in a Teflon-lined reactor. First, the used frying oil (10 g), methanol (48 mL) and catalyst (0.5 g) were stirred and heated to 150 °C for 5 h. Then, the mixture was cooled down and obtained biodiesel was analyzed with gas chromatography (HP6890). The product of biodiesel (yield) was determined using equation used by Torres-Rodríguez *et al.* [18].

In this study, the reusability of sample as catalyst in the reaction to yield biodiesel was also investigated. The reaction was carried out under the same reaction conditions and catalyst. After the reaction finished, the material used as heterogeneous catalyst was separated and washed (ethanol, acetone and distilled water). Then, the regenerated catalyst was used for the subsequent runs [19].

## RESULTS AND DISCUSSION

The structure and phase of samples obtained from sol gel process were investigated by X-ray diffraction. The XRD characterization results of materials are presented in Fig. 1. As shown in Fig. 1, all samples show a high structural disorder and very broad. The XRD patterns of solids ($x \leq 1$) in Fig. 1a-b. exhibit the same pattern with main peaks at 2θ = 60° and 35° that indicate typical for polymeric magnesium methoxide (○). However, the increase in the amount of HF ($x \geq 1.5$) gives different patterns than the previous peaks. The peaks at 2θ = 27.29, 40.56 and 53.47° indicate main peak of $MgF_2$ (◇) as shown in Fig. 1.

The resulting materials with different molar ratios of Mg/F are also characterized by FT-IR. This characterization aims to determine the bonding of $MgF_x(OH)_{2-x}$. The spectra are used to study the model of its chemical bonding. The $MgF_x(OH)_{2-x}$ spectra are presented in Fig. 2. The bands about 3700-3000 $cm^{-1}$ (♠) are correlated to bridged OH grups, while the H-O-H vibration of water molecules are shown at 1640 $cm^{-1}$ (●). Furthermore, the FTIR spectra of samples in the Fig. 2a-c. show the similar vibration at wave number about 2930 and 2700 $cm^{-1}$ (■) that indicate ν(C-H) vibration and ν(Mg-O) band at 550 $cm^{-1}$ (★). The increase in fluorine contents are followed by decreasing of intensities. Besides, there are also

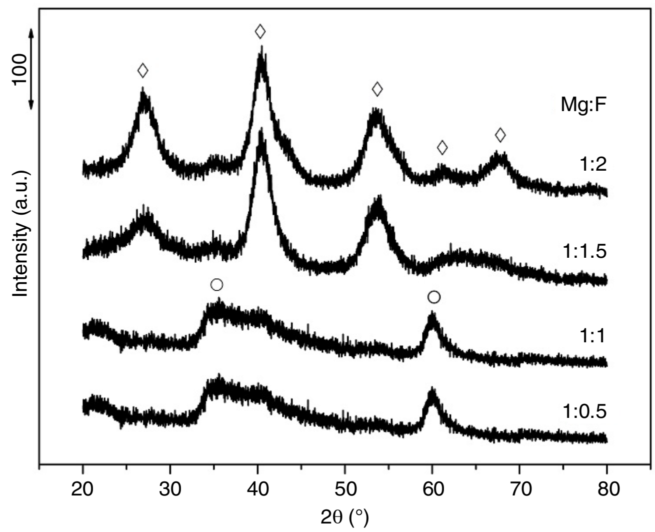

Fig. 1. XRD patterns of $MgF_x(OH)_{2-x}$ with diversed Mg/F ratios

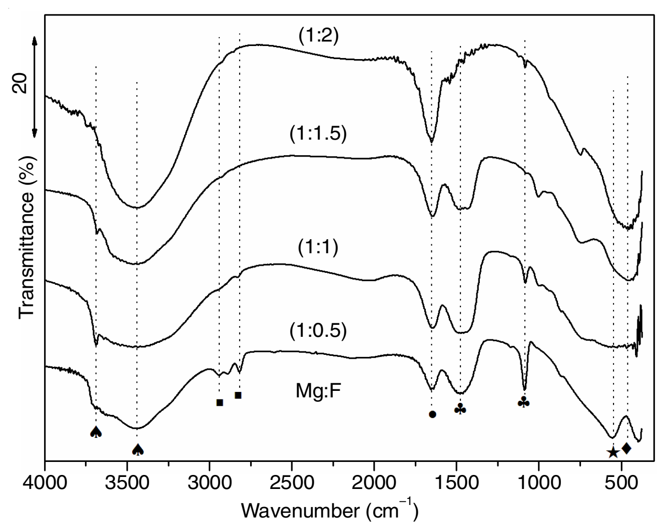

Fig. 2. FT-IR spectra of $MgF_x(OH)_{2-x}$ with diversed Mg/F ratios

ν(CO) band (♣) at 1460 and 1100 $cm^{-1}$, which showed Brønsted basic on magnesium hydroxide fluoride. Except of $MgF_2$, all samples show this band happened by the bonding between $CO_2$ and OH group of surfaces. Finally the band appearing about 490 $cm^{-1}$ (◆) is attributed to Mg-F vibrations. The intensity of this band increased with increase in fluorine content as shown in Fig. 2.

The thermal analysis of $MgF_x(OH)_{2-x}$ was performed in order to study the stability of samples, particularly the effect of diverse molar ratios of Mg/F. The curves TG and DTG of the sample are shown in the Fig. 3A and B. As shown in Fig. 3 (x = 0.5), mass loss is calculated for simple dihydroxide due to a large methoxide content, while in Fig. 3 ($0.5 < x < 2$) demonstrates stronger and structured TG/DTG traces. Moreover, except $MgF_2$, in the temperature intervall between 400 and 500 ºC, dominantly thermal decomposition and release of carbonate and hydrogen carbonate taked place. Furthermore, $MgF_{2-x}(OH)_x$ with x = 2 (Fig. 3) shows one-step decay phase (80-300 ºC) that indicated the reduction of methoxides from $Mg(OCH_3)_2{\cdot}2CH_3OH$ and -OH groups of sample. Besides, there is not decomposition of HF which appearing about 600-700 °C. It is clear that the samples are thermally stable.

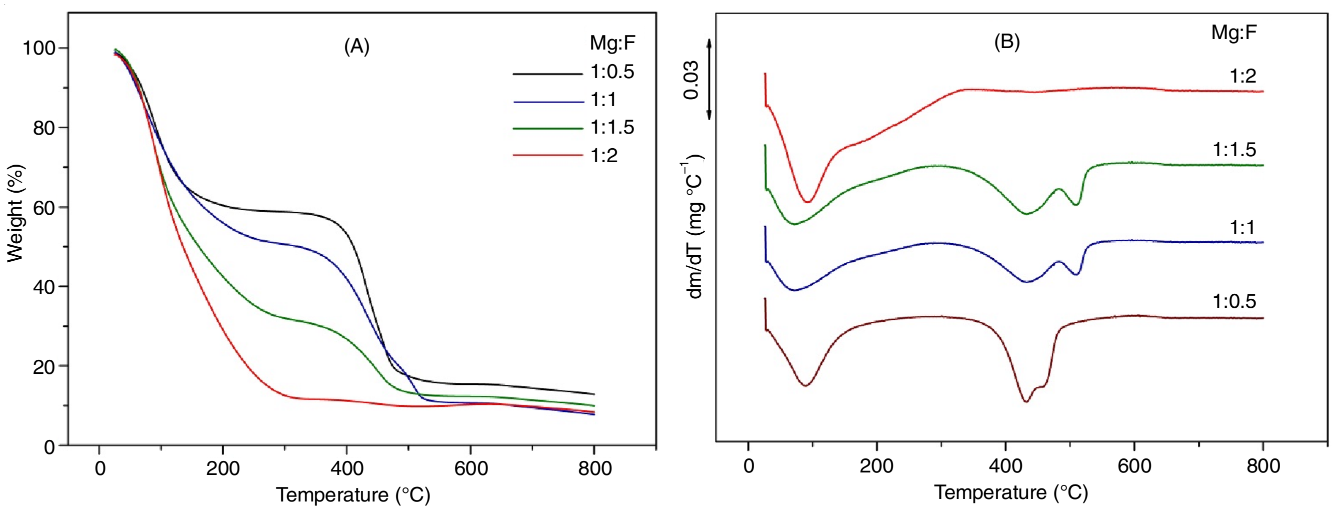


Fig. 3. TG/DTG (A and B) curves of $MgF_x(OH)_{2-x}$ with diversed Mg/F ratios

The $N_2$ isotherms of $MgF_x(OH)_{2-x}$ with diverse molar ratios of Mg/F are presented in Fig. 4. The materials show a typical type IV isotherm (according to the IUPAC classification) with a cylindrical pore (HI hysteritic loop). Moreover, based on the adsorption-desorption of nitrogen result, the average pore diameter and total pore volume calculated by Barret-Joyner-Hallender (BJH) method decrease from 40.40 to 3.02 nm and from 0.27 to 0.100 $cm^3/g$ after increase in fluorine content as shown in Table-1, respectively. Clearly, the increasing of fluorine concentration can decrease the pore diameter and total pore volume of material. Beside, the surface area of samples calculated by Brunauer-Emmett-Teller (BET) method increases with decreasing of fluorine contents. Especially for $MgF_2$, the specific surface area is 110.97 ($m^2/g$) as displayed in Table-1.

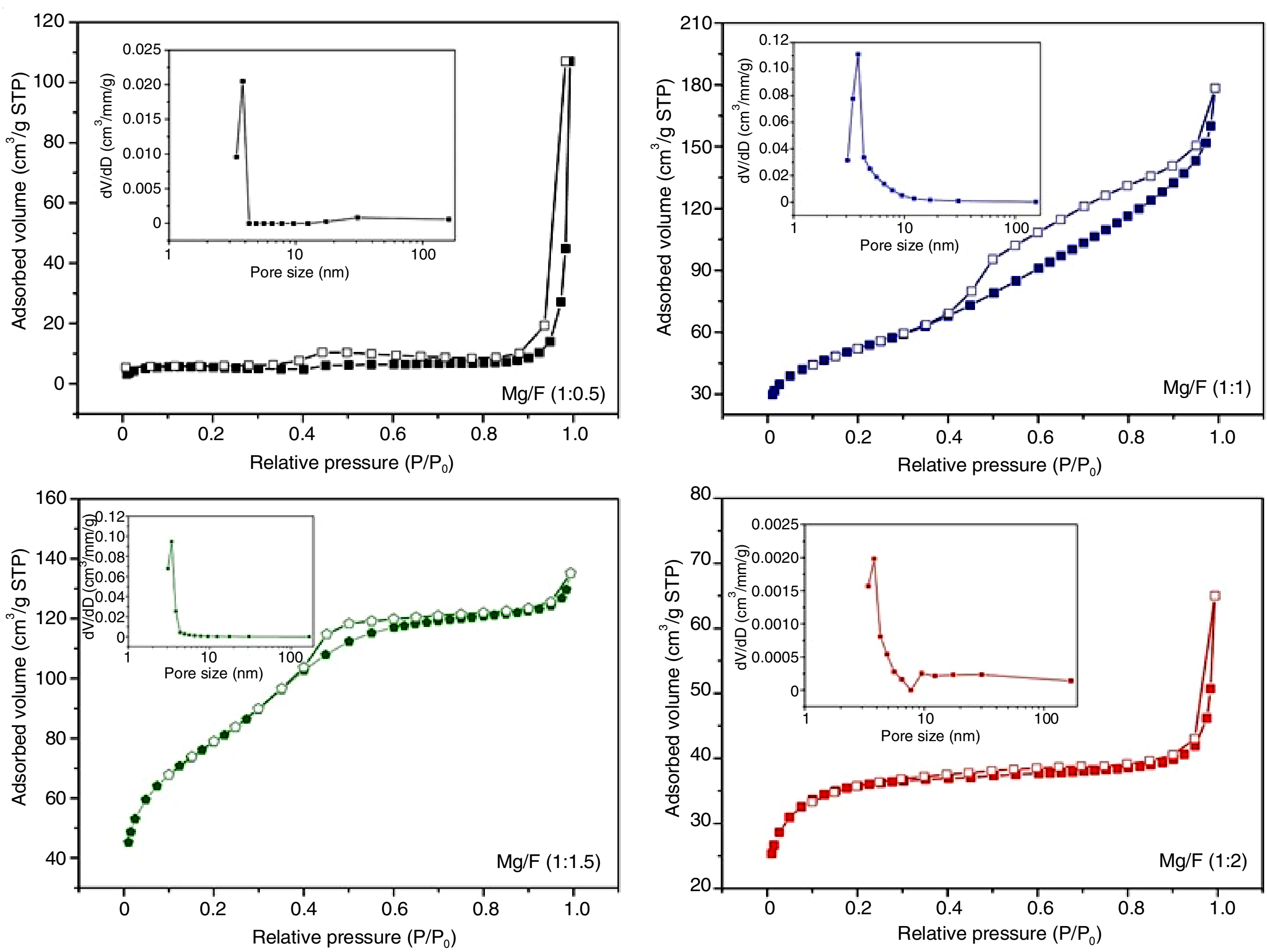


Fig. 4. Adsorption-desorption of $N_2$ and the pore size distribution of $MgF_x(OH)_{2-x}$ with diversed Mg/F ratios

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF MATERIALS

| Mg/F ratios | $S_{BET}$ ($m^2/g$) | Pore size (nm) | Pore volume ($cm^3/g$) | Surface acidity | |
|---|---|---|---|---|---|
| | | | | Lewis (mmol/g) | Brønsted (mmol/g) |
| 1:0.5 | – | 40.40 | 0.17 | – | – |
| 1:1 | 183.95 | 6.01 | 0.27 | – | – |
| 1:1.5 | 150.66 | 3.02 | 0.20 | – | – |
| 1:2 | 110.97 | 3.63 | 0.10 | 0.973 | 1.198 |

This result showed that an increase in fluorine contents decrease the specific surface area of samples.

The type and amount of acid sites of the materials are generally observed and determined using pyridine adsorption by FT-IR. Therefore, the investigation about the acid site of the resulting samples was studied by this method. The FTIR spectra using pyridine as probe of $MgF_x(OH)_{2-x}$ with diverse Mg/F ratios displayed in Fig. 5. Except of $MgF_2$, there were no absorption peaks at 1450-1442, 1500-1490 and 1550-1540 $cm^{-1}$ of the resulting samples, indicating the existance of acid sites *i.e.* Lewis and Brønsted acid as shown in Fig. 5. This result exhibited that these samples did not have the Lewis and Bronsted acid sites, similar to the FT-IR result.

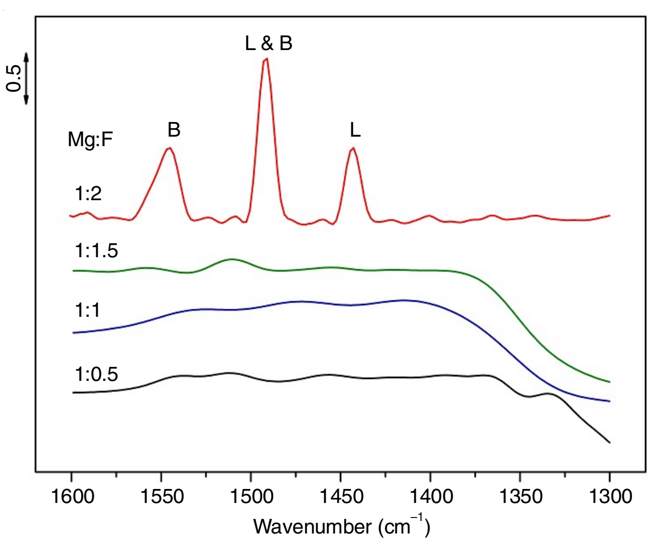


Fig. 5. FTIR spectra using pyridine as probe on $MgF_x(OH)_{2-x}$ with diversed Mg/F ratios

The SEM image was used to investigate topography or morphology of the magnesium hydroxide fluoride, $MgF_x(OH)_{2-x}$ with different fluorine contents. Fig. 6 displays the SEM images of the resulting samples prepared from sol gel technique with diverse molar ratios of Mg/F. It is clear that the texture of the resulting materials are different from each other. The shape of particle appears more spherical by increase in fluorine. Moreover, the aglomerate also increased with increasing fluorine. Furthermore, the greater of fluorine content, the smaller of particle size. This result demonstrates that the increase in fluorine content decreases particle size, correspond to decrease in the pore size diameter by $N_2$ adsorption-desorption measurements. Furthermore, the particle size of these samples ranges from 0.2 to 3 µm.

To study the performance of magnesium hydroxide fluorides as catalyst, the reaction between the used frying oil (containing 13 % FFA) with methanol to produce biodiesel was applied as

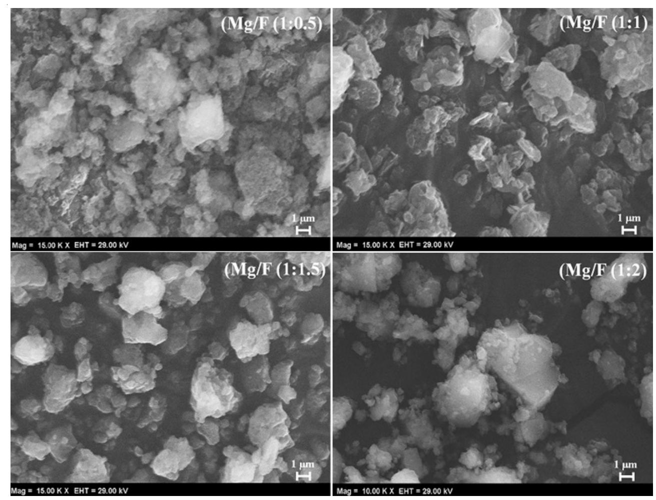


Fig. 6. SEM images of $MgF_x(OH)_{2-x}$ with diversed Mg/F ratios

probe reaction. The reaction was evaluated under the optimum condition with that of the resulting samples as catalyst. The result of performance of $MgF_x(OH)_{2-x}$ with various fluorine content for production of biodiesel using used frying oil as feedstock was presented in Fig. 7.

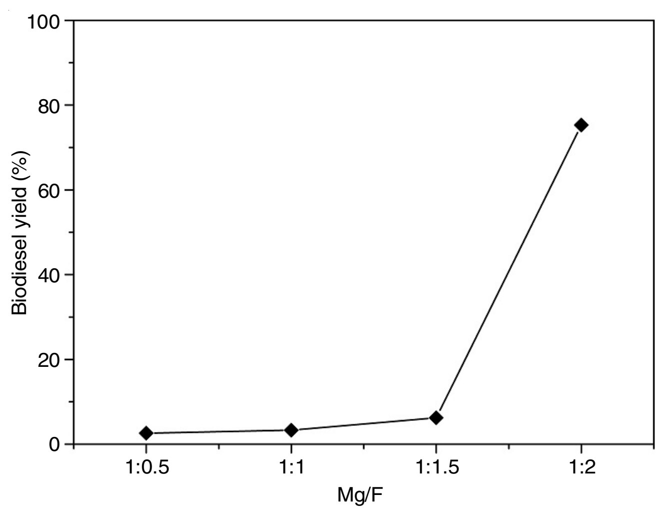


Fig. 7. Catalytic activity of $MgF_x(OH)_{2-x}$ with diversed Mg/F ratios in the reaction for biodiesel production

As shown in Fig. 7, the biodiesel yield increases from 2.61 to 3.31, 6.24 and 75.29 % with increase in fluorine contents, respectively. This result shows that $MgF_x(OH)_{2-x}$ (x = 2) catalyst is very tolerant to free fatty acids (13 %) in used frying oil. The existance of acidic sites, both Lewis and Brønsted is believed to increase the yield of biodiesel. The acidic sites can capture a large amount of free fatty acids so that it is able to produce biodiesel in large quantities. Although the surface area of $MgF_x(OH)_{2-x}$ (x < 2) is greater than $MgF_x(OH)_{2-x}$ (x = 2), but it can not help contact beetwen used frying oil and methanol. This indicate that the activity of materials as catalyst is not correlated with surface area. Furthermore, the combination of average pore size and acid sites of catalyst give a high value of biodiesel yield. According to this result, the acid sites and pore size are influence in simultaneous esterification and transesterification reaction of used frying oils for production of biodiesel.

To investigate the reusability of the catalyst, the durability of catalysts is tested at the same reaction condition and material as heterogeneous catalyst. The values of the reusability of catalyst to yield biodiesel are shown in Fig. 8. The biodiesel yield decreases after being used for three runs. Clearly, the performance of material decreases linearly with longer usage.

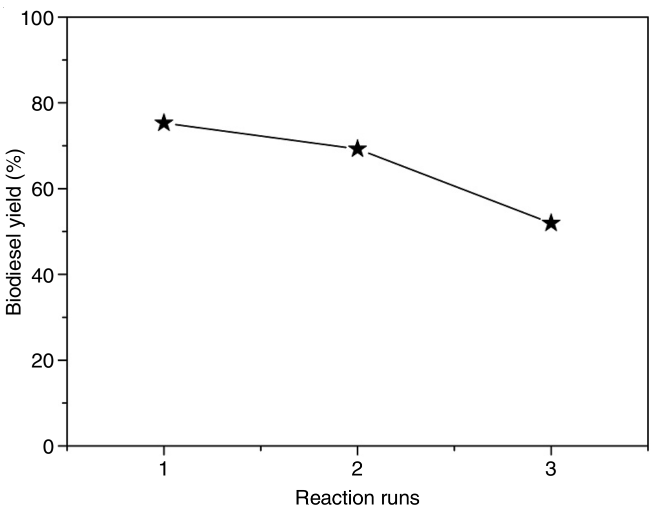


Fig. 8. Durability of catalyst for three runs. The experiments were investigated under the same reaction conditions and catalyst (Mg/F = 1:2)

## Conclusion

The magnesium hydroxide fluorides [$MgF_x(OH)_{2-x}$] with diverse Mg/F molar ratios were prepared by the sol-gel technique. The resulting materials show dissimilar structure, thermal stability, porosity, shape and surface acidity. Moreover, the average pore size and volume decrease with increase in fluorine contents. The catalytic activity of the resulting materials as solid catalyst to yield biodiesel through reaction between the used frying oils and methanol exhibit that $MgF_x(OH)_{2-x}$ with x = 2 shows higher yield of biodiesel (75.29 %) compared to $MgF_x(OH)_{2-x}$ (x < 2) from 2.61 to 3.31 and 6.24 %, respectively. The best catalytic activity of $MgF_x(OH)_{2-x}$ (x = 2) sample for biodiesel production from used frying oil can be attributed to acidic sites (Lewis and Brønsted), pore diameter and volume of the catalyst. In addition, the activity of catalyst decreases after being used for three runs.

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