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Biodiesel Production from Canola Oil with Methanol in Presence of Nanocrystalline MgO-Supported Alkaline Catalysts

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Transesterification reaction of canola oil to biodiesel was performed using alkaline catalysts supported by nanocrystalline magnesium oxide with high surface area. Alkaline supported catalysts were prepared by loading aqueous solution of K_2CO_3 (5-20 wt. %) into magnesium oxide and tested for the transesterification of canola oil with methanol at the reaction conditions such as the reactant feed ratio (alcohol/oil: 6/1-15/1), the reactor temperature (298, 318, 333 and 338 K), reaction time (1-8 h) and the catalyst concentration of 5 wt. % based on oil content. The catalyst with 20 wt. % K_2CO_3 loaded into magnesium oxide gave the highest methyl ester yield of 96.85 % which meets the purity requirement of the European biodiesel standard of EN 14103. The reusability and stability of the K_2CO_3 (20 %)/MgO catalyst was tested for at least three reaction cycles. About 16 % activity lost was observed at the end of third cycles.

Keywords: Magnesium oxide, Transesterification, Heterogeneous catalyst, Biodiesel.

INTRODUCTION

In the last decade, biodiesel has gained an increasing attention of researchers because of its biodegradability, non-toxicity and low emissions [1-3]. Biodiesel (fatty acids methyl ester) is usually produced by the transesterification of the edible or non-edible oils with the excess methanol using a basic (NaOH or KOH) or acidic catalyst [4]. Activity of the alkali basic catalyst is very high and conversion is completed within 2 h. Some drawbacks of the homogeneous catalysts such as purification of product, low water tolerance and free fatty acid content of the oils makes the researchers have focus on the more environmentally friendly processes with heterogeneous catalysts [5-11].

Some metal oxides, such as zinc oxide, calcium oxide and magnesium oxide were utilized as solid base catalysts for the transesterification of vegetable oils [12,13]. In some cases ZnO and CaO were functionalized with alkali earth metals in order to increase the basicity of the support materials [14,15].

Among the metal oxides MgO can be synthesized in the form of the nano particles with high surface area [16] and can be used successfully as the catalyst and the catalyst support materials for the transesterification of vegetables [17-22]. Magnesium based heterogeneous production of biodiesel has been reported as more promising process since high methyl ester yield are attained at the mild reaction conditions [17-22]. Highest palm oil conversion of 51.8 % was obtained when the calcination temperature of 600 °C was applied [20]. Nano structured MgO has been prepared and has been tested for the transesterification of sunflower oil in autoclave conditions. Highest conversion of 80 % methyl ester yield was obtained at 493 K [23]. In the work of Yacob *et al.* [18,24], the commercial nano MgO has been prepared by hydration and dehydration method. The nanocrystalline magnesium oxide does not satisfy the requisite purity requirements of European biodiesel standard (EN-14103) [25]. Thus the surfaces of the nano particles of magnesium oxide need to be modified in order to enhance catalytic activity for the transesterification reaction.

The aim of this study was to prepare a novel catalyst for the highest methyl ester yield which satisfies the requisite purity requirements of EN-14103 [25]. By this purpose, the high surface basicity of the nano particles of MgO functionalized with potassium carbonate catalysts were prepared for the transesterification of canola oil with methanol. The influences of the K_2CO_3 over MgO ratio in the catalyst preparation, alcohol/oil ratio, reaction temperature and reaction time on the methyl ester yield were investigated to obtain the optimum reaction conditions. Reuse and regeneration of the optimized catalyst were also evaluated for the recovery of the used catalyst. X-ray diffraction, scanning electron microscopy and N_2 adsorption surface area analysis of Brunauer-Emmett-Teller method were used to characterize the synthesized catalysts. Basic strengths and the basicity of the synthesized catalysts were evaluated by following a Hammett indicator procedure.

EXPERIMENTAL

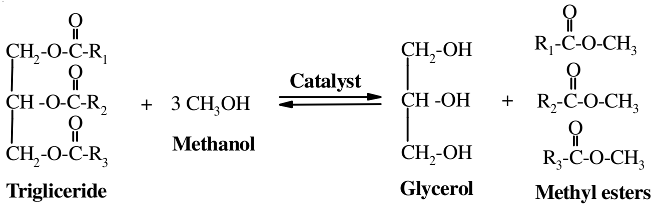
Methanol (purity of 99.8 vol. %) was obtained from Riedel-de Haën. The canola oil was obtained from a local food store. Potassium carbonate was obtained from Merck. The MgO were obtained from Sigma-Aldrich Company (product ID: 549649 with a reported particle size < 50 nm). The free fatty acid level and the acid value of the canola oil were characterized by using the AOCS Official Method Cd 3a-63 [26] and were determined to be 0.085 wt. % and 2.08 mg KOH g^{-1}, respectively.

Solid catalyst preparation and characterization: Nanocrystalline MgO particles were used as a support material in the preparation of potassium functionalized solid base catalysts. Aqueous solution of potassium carbonate was loaded into magnesium oxide by the incipient-wetness impregnation method. The water absorbance of the nanocrystalline MgO was measured as 9.81 g per g of MgO. In the catalyst preparation step MgO was placed into a 250 mL flask which was placed in an ultrasonic water bath while applying vacuum in order to open the pores of MgO particles. The prepared aqueous K_2CO_3 solution was then added drop-wise onto the MgO particles by using a peristaltic pump. The obtained impregnate was then dried for overnight at 393 K. Thereafter, the obtained particles were calcined for 3 h at 773 K. These procedures including the impregnation and the calcination conditions were kept the same in all the preparation processes of the catalysts.

The BET surface area values of the prepared catalyst particles were conducted in AUTOSORB-6B (Quanta Chrome) instrument by applying the nitrogen absorbance method using a multipoint BET sorptometer. Prior to each surface area measurement, all powdered samples were kept in an oven overnight under vacuum at 383 K in order to eliminate the water absorbance of the samples. The basicity of the synthesized catalysts was performed using a Hammett indicator procedure, outlined in detail by Boz *et al.* [6-8].

X-ray diffraction patterns of MgO, K_2CO_3 and the K_2CO_3 impregnated MgO particles were collected at room temperature using a Rigaku/D/MAX 2200 diffractometer using CuK_α radiation equipped with a CuX-ray tube running at 40 kV/40 mA. The X-ray diffraction measurements were obtained over the Bragg angle (2θ) range of 5-75°. Scanning electron micrographs of MgO and the K_2CO_3 impregnated MgO particles were conducted on a Jeol-JSM 6400 scanning microscope.

The overall transesterification reaction of canola oil with methanol to fatty acid methyl esters was given in **Scheme-I**.



Scheme-I: Overall transesterification reactions of triglyceride with methanol

The reaction was carried out in a 250 mL three-necked flask equipped with a reflux condenser, a temperature controller and a sampling port. Mixing and heating of the reaction mixture was performed with a magnetic stirrer which was placed under the three-necked flask. At the beginning of each experiment the catalyst particles and methanol were well-mixed in the reaction flask. Then the canola oil was added to the reaction mixture and it was heated to the reaction temperature. Reaction takes about 8 h and 2-3 mL of sample was manually collected for product analysis from the reactor sampling port at hourly intervals. All the reactions were carried out at 600 rpm stirring conditions in order to eliminate the mass transfer limitations. The catalytic activities of the different loading of K_2CO_3 (5-20 wt. %) into MgO catalysts were studied at the following reaction conditions: the reactant feed ratio (alcohol/oil: 6/1-15/1), the reactor temperature (298, 318, 333 and 338 K), reaction time (1-8 h) and the catalyst concentration of 5 wt. % based on oil content. After the transesterification reaction the used catalyst particles were separated from the reaction mixture by filtration. Then whole reaction mixture was separated by centrifugation. The residual methanol was evaporated. The less dense phase was biodiesel and the yield of the methyl ester content of the biodiesel was analyzed using an Agilent 6890 gas chromatograph that was equipped with a flame ionization detector (FID) and with a Carbowax 20M capillary column. European Standard EN 14103 [25] was followed in the determination of the methyl ester yield. All data points were repeated at least three times and 95 % confidence intervals according to Student's– t distribution are reported.

RESULTS AND DISCUSSION

Scanning electron microscopy images of MgO and MgO with 10 and 20 % potassium carbonate before transesterification reaction were shown in Fig. 1. Pure MgO surfaces comprise a large number of agglomerates with the particles diameters < 50 nm (Fig. 1a-b). Upon impregnation and calcination the catalyst particles become greater in diameter (about 50-200 nm) and attached to each other with sticky surface (Fig. 1c-d).

Table-1 indicates that the physical properties of the synthesized catalysts *via* the incipient wetness impregnation. All prepared catalysts were calcined at 773 K for 3 h. Pure nano MgO oxide has the highest BET surface area of 156.2 m^2/g. However, the BET surface area values of the synthesized catalysts were significantly reduced by the increasing loading potassium level. This is presumably due to the coverage of the support surface and pores by the potassium carbonate during the impregnation step. When the loading potassium level increased to 20 %, the basicity and basic strength of the catalysts was increased. A strong relation between the basicity and activity of the catalysts was found in the next section. Similar relationships between the basicity and activity of the catalysts in the biodiesel were also reported in literature [5-9,12-14].

Fig. 2 shows the pore size distributions of the magnesium oxide and synthesized catalysts. It can be seen that most of the surface area is occupied by pores of 2-200 nm range, indicating macropores structure. These macropores were involved during the impregnation step. Nitrogen adsorption isotherms obtained with magnesium oxide and potassium carbonates loading into MgO catalysts are shown in Fig. 3. Magnesium oxide and synthesized catalysts are Type II

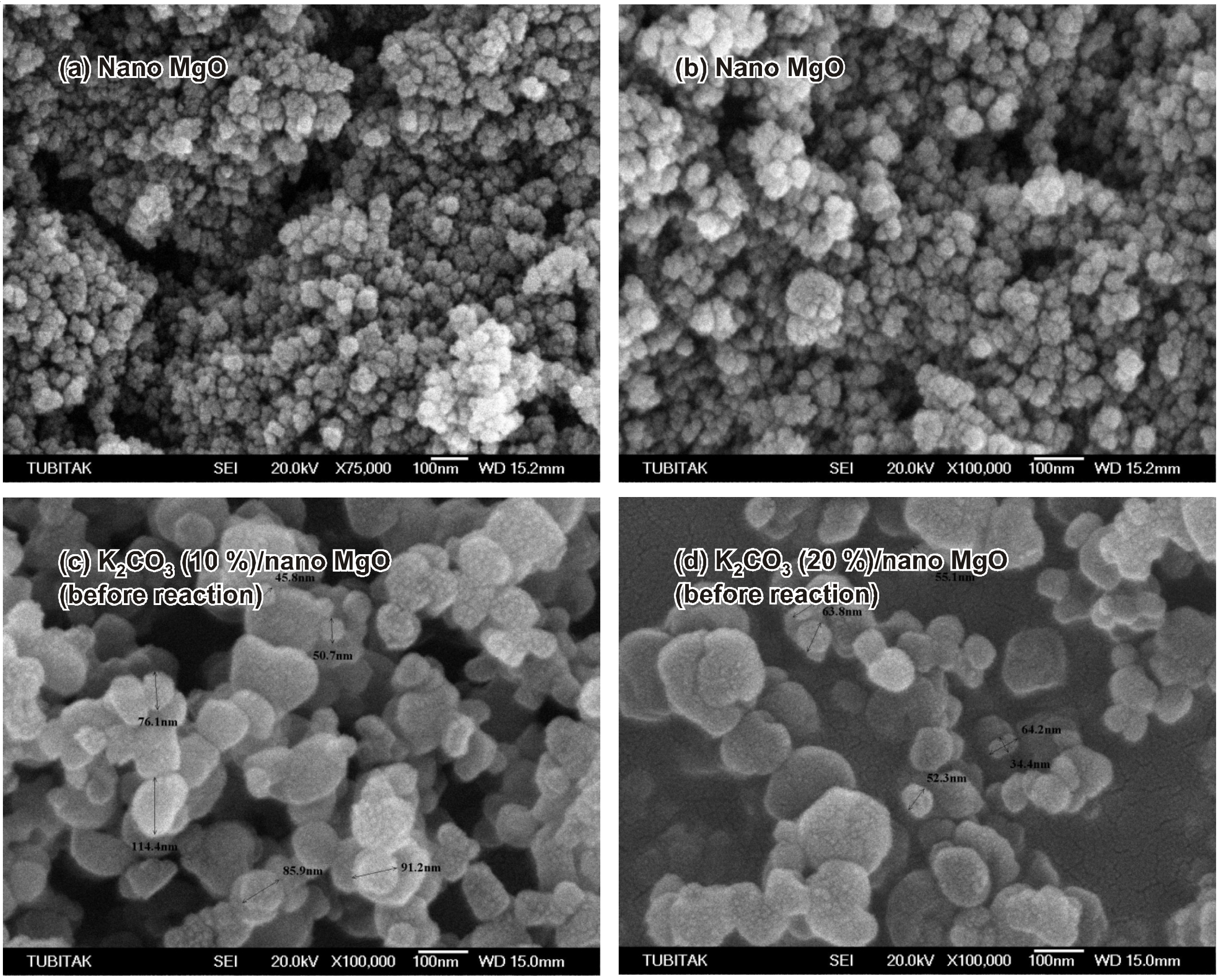


Fig. 1. SEM micrographs of pure MgO (a-b); MgO impregnated with 10 % K_2CO_3 prior to transesterification (c); MgO impregnated with 20 % K_2CO_3 prior to transesterification (d)

TABLE-1
PHYSICAL PROPERTIES OF NANOCRYSTALLINE MgO AND K_2CO_3 IMPREGNATED NANOCRYSTALLINE MgO CATALYSTS*

Entry	Name	Surface area (m^2/g)	Basic strength (H_)	Basicity (mmol/g)
1	Nano MgO	156.20	7.2 < H_< 9.8	0.75 ± 0.04
2	K_2CO_3 (5 %)/nano MgO	39.87	9.8 < H_< 15.0	1.11 ± 0.04
3	K_2CO_3 (10 %)/nano MgO	33.82	9.8 < H_< 15.0	2.13 ± 0.04
4	K_2CO_3 (15 %)/nano MgO	31.87	15 < H_< 18.4	2.84 ± 0.03
5	K_2CO_3 (20 %)/nano MgO	28.60	15 < H_< 18.4	2.93 ± 0.05

*Preparation conditions: MgO impregnated with K_2CO_3 was dried at 393 K for 24 h. Calcination temperature and time: 773 K and 3 h.

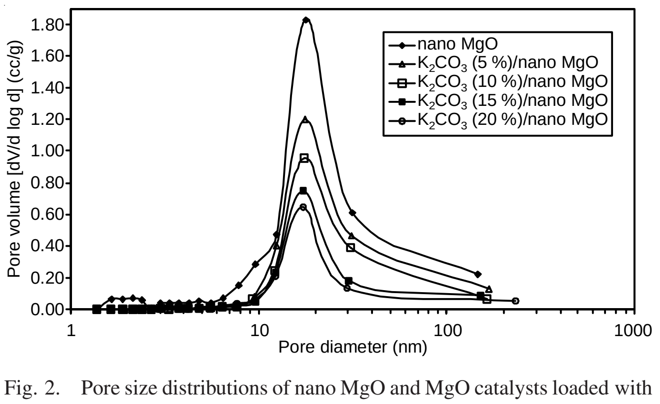


Fig. 2. Pore size distributions of nano MgO and MgO catalysts loaded with K_2CO_3 and calcination at 773 K for 3 h (prior to the transesterification reaction)

adsorption which indicates that material is possibly macroporous and has a high energy of adsorption [27].

A powder diffraction technique has extensively used for characterization the surface phenomena [28]. Fig. 4 shows X-ray diffraction analysis of pure MgO, pure K_2CO_3 and synthesized catalysts with 20 wt. % K_2CO_3 loading. The typical X-ray diffraction pattern of the nano magnesium oxide particles was observed at the Bragg angles, 2θ = 37.44°, 42.51° and 62.55° (Fig. 4a). Pure MgO structures are in the cubic form before the impregnation and the calcination step. X-ray diffraction patterns of potassium carbonate were observed at the Bragg angles, 2θ = 27.06°, 30.74°, 33.16°, 38.68.0°, 42.16°, 43.68°, 46.34°, 49.14° and 67.52° (Fig. 4b). In the XRD pattern of the MgO particles doped with 20 % K_2CO_3, new K_2O

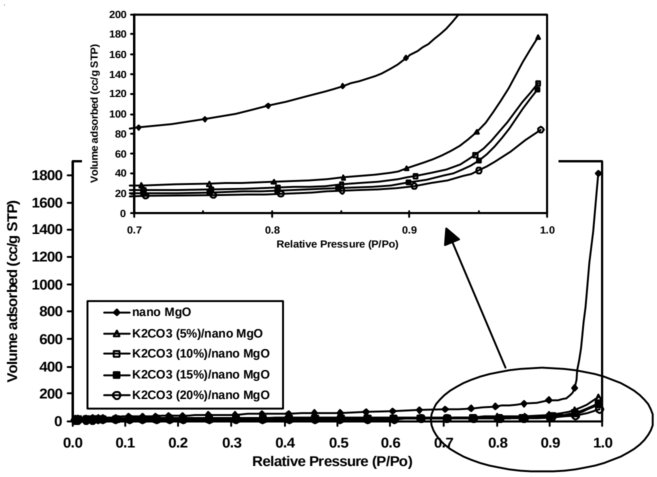


Fig. 3. Nitrogen adsorption isotherms of nano MgO and MgO catalysts loaded with K_2CO_3 and calcination at 773 K for 3 h (prior to the transesterification reaction).

phase (at 2θ = 30.74°, 42.70°, 53.40°) and $MgCO_3$ phase (at 2θ = 26.44°, 30.00° and 31.51°) were formed as shown in the Fig. 4c. The main basic sites are based on K_2O phase, $MgCO_3$ and Mg-O-K surface groups which serve as the active sites.

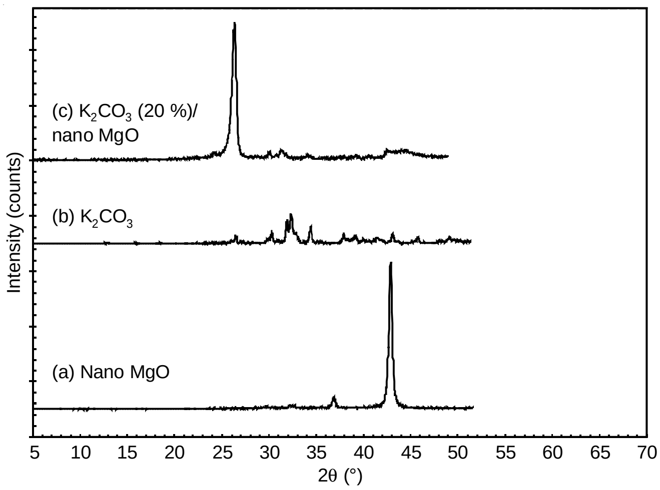


Fig. 4. XRD diffractogram of nano MgO, K_2CO_3 and nano MgO catalysts

Transesterification reaction: The effects of the loading K_2CO_3 into nano MgO, the molar ratio of methanol to canola oil and reaction temperature in biodiesel production were investigated. Reaction time was 8 h. The effect of K_2CO_3/nano MgO ratio during the impregnation step was studied at four different K_2CO_3 loading ratios (5, 10, 15, 20 wt. %). The reaction conditions were as follows: the amount of catalyst of 5 % based on the weight of canola oil, methanol to oil molar ratio of 12/1, reaction time of 8 h and the reaction temperature at 338 K. As shown in Fig. 5, the methyl ester yield was increased by the increasing K_2CO_3 loading ratios. However, the increase of the loading amount of K_2CO_3 from 15 to 20 % did not significantly alter the yield of methyl esters. The highest methyl esters yield of about 96.85 % was obtained in the presence of 20 wt. % K_2CO_3 into MgO catalyst.

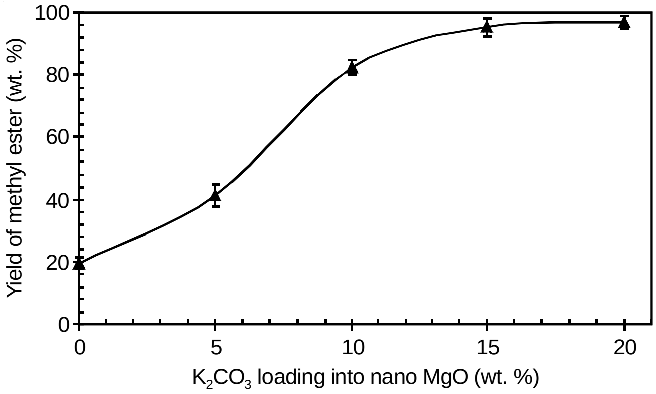


Fig. 5. Methyl ester yield *versus* the K_2CO_3 loading into nano MgO (for methanol/oil molar ratio: 12/1, T: 338 K, catalyst amount: 5 wt. %, reaction time: 8 h)

In the transesterification reaction the stoichiometric molar ratio of methanol to oil is 3/1. However, the methanol to canola oil ratio was always chosen higher than the stoichiometric molar ratio in order to shift the equilibrium towards the formation of methyl esters. The effects of the alcohol to oil ratio were studied as a function of time by systematically changing the molar ratio from 6/1 to 15/1, while keeping the temperature (338 K), catalyst amount of 5 wt. % and duration of 8 h constant. 2-3 mL of samples was collected 1 h time interval and they were then centrifuged. The upper lighter biodiesel phase was used for methyl ester analysis. Fig. 6 shows that increasing the methanol/oil molar ratios from 6/1 to 15/1 do not significantly affect the methyl ester yield when the reaction time exceeds to 5 h. A maximum yield of 96.85 % was reached at the molar methanol/oil ratio of 12/1 at the end of 8 h. The obtained value satisfies the requisite purity requirements of EN-14103. Similar results were also reported for different supported catalyst [5-9,12-14]. Above 90 % yield was observed when the molar alcohol to oil ratios were ranged between from 6/1 to 18/1 [5-9,12-14].

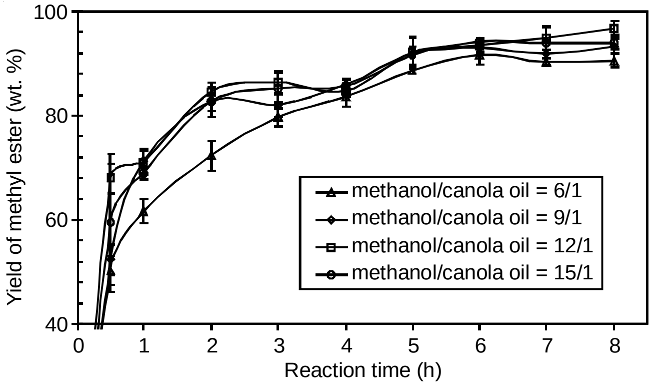


Fig. 6. Dependence of the yield of methyl ester on the methanol to canola oil molar ratio as a function of time for the synthesized K_2CO_3 (20 %)/nano MgO catalyst (T: 338 K, catalyst amount: 5 wt. %, reaction time: 8 h)

The methyl ester yield as a function of temperature for the synthesized K_2CO_3 (20 %)/nano MgO catalyst at the molar methanol/oil ratio of 12:1 is shown in Fig. 7. Reaction yield increased with increasing temperature. The methyl ester yield of 96.85 % was achieved at the reflux temperature of methanol, 338 K. Our findings are consistent with the earlier studies related with the solid base catalyzed of vegetables oil to fatty acid methyl esters [5-9,12-14].

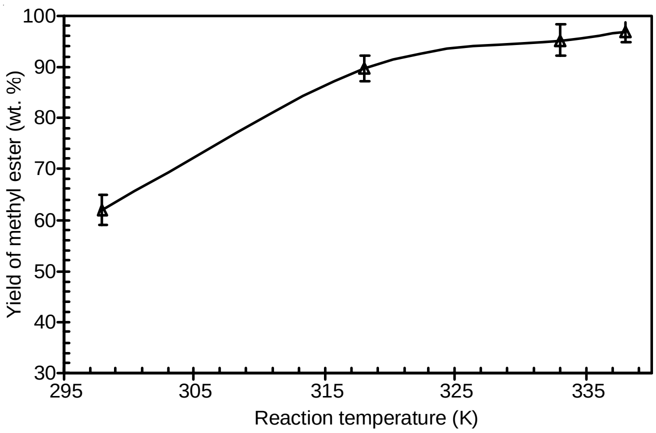


Fig. 7. Dependence of the methyl ester yield on the reaction temperature synthesized K_2CO_3 (20 %)/nano MgO catalyst (methanol/oil molar ratio: 12/1, catalyst amount: 5 wt. %, reaction time: 8 h)

Reusability and stability of K_2CO_3 (20 %)/nano MgO catalyst: The reusability of the catalyst using K_2CO_3 (20 %)/nano MgO was investigated since recovery of catalyst from the reaction mixture was an important operational parameter in the heterogeneous catalysis system. Three successive runs were performed under the same operating conditions (methanol/canola oil: 12/1, catalyst amount: 5 wt. %, reaction time: 8 h, reaction temperature: 338 K). Yield of methyl ester was obtained as 96.85 wt. % (1st use), 91.53 wt. % (2nd use) and 81.45 wt. % (3rd use), respectively. The yields of methyl ester were decreased after several usages. About 16 % activity lost was obtained at the end of third usage. Leaching of MgO and K_2O from catalyst was also reported in the literature [6,19,29]. During several usages prepared catalyst was deactivated because of the leaching phenomena of K and Mg in highly polar alcohol environment. SEM micrographs of pure MgO, MgO loaded with 20 % K_2CO_3 prior to transesterification and after first transesterification reaction was shown in Fig. 8. Recycled catalyst particles after first usage were collected and washed with methanol several times. During impregnation and calcination the structure of the catalyst particles become attached to each other (Fig. 8b). After transesterification reaction the catalyst particles become smaller in diameter and attached to each other with sticky surface (Fig. 8c).

Conclusion

The new solid base catalyst with 20 wt. % K_2CO_3 loaded into nano magnesium oxide was successfully prepared by the incipient-wetness impregnation method. The highest methyl ester yield of 96.85 % which meets the purity requirement of the European EN standard 14103 was obtained over 20 wt. % K_2CO_3 loaded into magnesium oxide catalyst at mild reaction conditions. The reusability and stability of the K_2CO_3 (20 %)/MgO catalyst was tested for at least three reaction cycles. About 16 % lost in the activity was observed at the end of the third cycles. The activity lost after first use of the catalyst could be associated with the leaching potassium and magnesium in polar phase. Generated methoxide magnesium and methoxide potassium behaves as a homogeneous catalyst and the transesterification reaction could be catalyzed both homogeneously and heterogeneously.

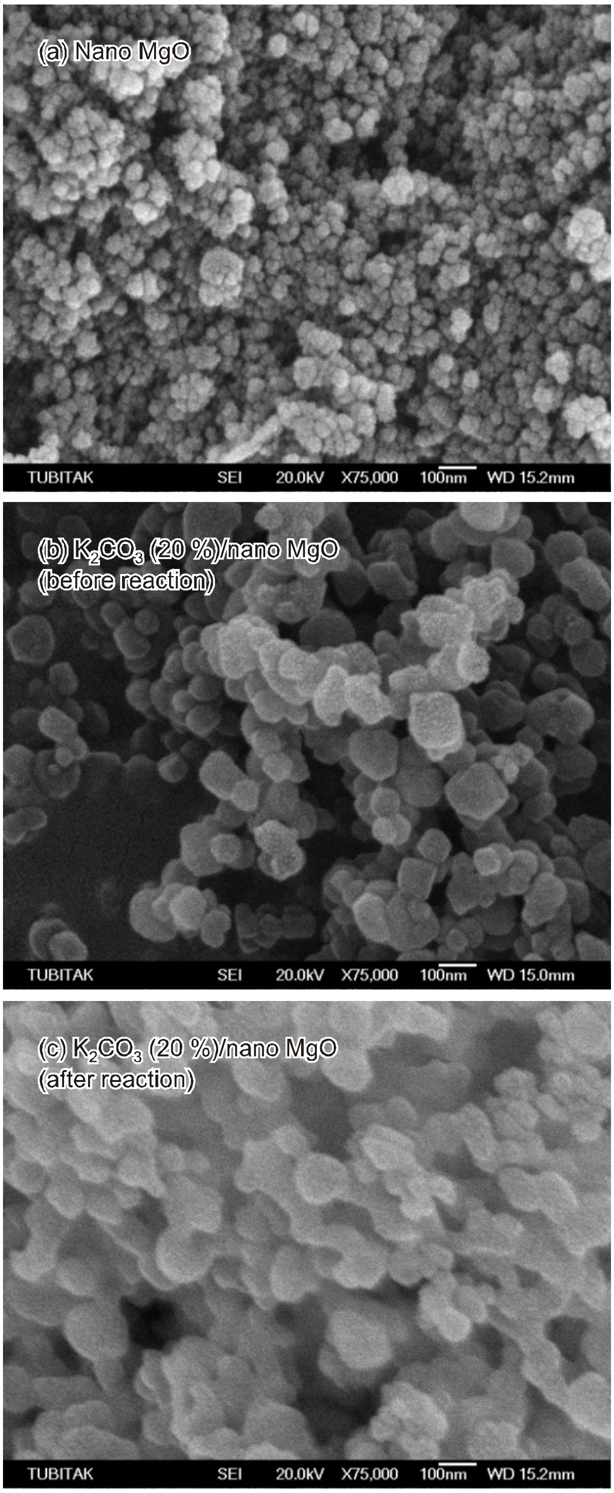


Fig. 8. SEM micrographs of pure MgO (a); MgO loaded with 20 % K_2CO_3 prior to transesterification (c); MgO loaded with 20 % K_2CO_3 after the transesterification reaction

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REFERENCES

1. Y.C. Sharma and B. Singh, *Renew. Sustain. Energy Rev.*, **13**, 1646 (2009).
2. S.B. Lee, K.H. Han, J.D. Lee and I.K. Hong, *J. Ind. Eng. Chem.*, **16**, 1006 (2010).
3. R. Alcantara, J. Amores, L. Canoira, E. Fidalgo, M.J. Franco and A. Navarro, *Biomass Bioenergy*, **18**, 515 (2000).
4. S. Chongkhong, C. Tongurai and P. Chetpattananondh, *Renew. Energy*, **34**, 1059 (2009).
5. N. Boz, N. Degirmenbasi and D.M. Kalyon, *Appl. Catal. B*, **89**, 590 (2009).
6. N. Boz and M. Kara, *Chem. Eng. Commun.*, **196**, 80 (2008).
7. N. Boz, N. Degirmenbasi and D.M. Kalyon, *Appl. Catal. B*, **138-139**, 236 (2013).
8. N. Degirmenbasi, N. Boz and D.M. Kalyon, *Appl. Catal. B*, **150-151**, 147 (2014).
9. W. Xie and X. Huang, *Catal. Lett.*, **107**, 53 (2006).
10. N. Degirmenbasi and B. Ozgun, *Monatsh. Chem.*, **134**, 1565 (2003).
11. H.B. Ozgun and N. Degirmenbasi, *J. Chem. Res. (S)*, 32 (1997).
12. M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka and J. Hidaka, *Fuel*, **87**, 2798 (2008).
13. T.F. Dossin, M.F. Reyniers, R.J. Berger and G.B. Marin, *Appl. Catal. B*, **67**, 136 (2006).
14. N. Boz and O. Sunal, *J. GUMMF*, **24**, 389 (2009).
15. P. Boey, G.P. Maniam and S.A. Hamid, *Chem. Eng. J.*, **168**, 15 (2011).
16. P. Jash, A.W. Nicholls, R.S. Ruoff and M. Trenary, *Nano Lett.*, **8**, 3794 (2008).
17. M. Verziu, B. Cojocaru, J. Hu, R. Richards, C. Ciuculescu, P. Filip and V.I. Parvulescu, *Green Chem.*, **10**, 373 (2008).
18. A.R. Yacob, M.K.A.A. Mustajab and N.S. Samadi, *World Academy Sci. Eng. Technol.*, **3**, 376 (2009).
19. Y.C. Sharma, B. Singh and J. Korstad, *Fuel*, **90**, 1309 (2011).
20. Y.H. Taufiq-Yap, H.V. Lee, R. Yunus and J.C. Juan, *Chem. Eng. J.*, **178**, 342 (2011).
21. N. Kaur and A. Ali, *Energy Sources Part A*, **35**, 184 (2013).
22. M. Manríquez-Ramírez, R. Gómez, J.G. Hernández-Cortez, A. Zúñiga-Moreno, C.M. Reza-San Germán and S.O. Flores-Valle, *Catal. Today*, **212**, 23 (2013).
23. Z. Wen, X. Yu, S. Tu, J. Yan and E. Dahlquist, *Bioresour. Technol.*, **101**, 9570 (2010).
24. A.A. Refaat, *Int. J. Environ. Sci. Technol.*, **8**, 203 (2011).
25. European Standard of EN 14103, Fat and Oil Derivatives–Fatty Acid Methyl Esters (FAME)–Determination of Ester and Linolenic Acid Methyl Ester Contents, April (2003).
26. American Oil Chemists' Society, Official Test Method Cd 3a-63 for Acid Value, In: Official Methods and Recommended Practices of the American Oil Chemists' Society, Champaign, IL (1998).
27. J.B. Condon, Surface Area and Porosity Determinations by Physisorption: Measurements and Theory, Elsevier, Amsterdam, p. 59 (2006).
28. N. Degirmenbasi, Z. Peralta-Inga, U. Olgun, H. Gocmez and D.M. Kalyon, *J. Energ. Mater.*, **24**, 103 (2006).
29. F.S.H. Simanjuntak, S.R. Lim, B.S. Ahn, H.S. Kim and H. Lee, *J. Appl. Catal. A*, **484**, 33 (2014).