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Transesterification of Canola Oil with Methanol using Nano Zinc Oxide Supported Catalysts

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Nano zinc oxide supported catalysts were prepared by an impregnation method with an aqueous solution of K_2CO_3 (3-10 wt. %) and tested for the transesterification of canola oil with methanol. Several operating variables were used in order to assess their influence on the methyl ester yield, namely, the weight ratio of K_2CO_3 over ZnO (3-10 %), the reactant feed ratio (alcohol/oil: 6/1-18/1), the reactor temperature (298, 318, 333 and 338 K), reaction time (1-9 h) and the catalyst concentration (varied between 1-7 wt. %). 10 wt. % K_2CO_3 impregnated on nano particles of zinc oxide were found to be the active catalysts resulting in high conversion of 97.83 ± 1.82 % for transesterification of canola oil at 338 K with methanol/oil ratio of 9/1 and using 5 wt. % catalysts.

Keywords: Biodiesel, Nano zinc oxide, Transesterification, Canola oil.

INTRODUCTION

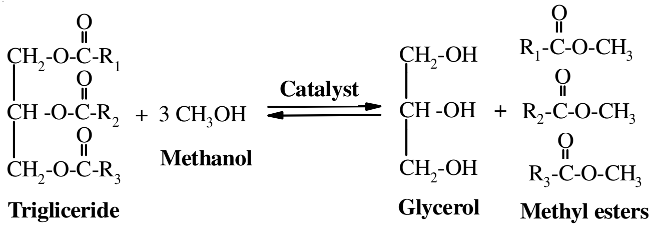
Biodiesel is considered as an alternative fuel over fossil based fuels, due to its biodegradability, non-toxicity and low emissions. Biodiesel as known fatty acids methyl ester (FAME) is conventionally produced transesterification of vegetable oils with methanol over an alkali base catalyst, mostly NaOH and KOH or acidic catalysts (**Scheme-I**).

Reaction time is very short about 1 h in the homogeneous alkali-catalyzed production of biodiesel. However, removal of basic catalysts from the reaction medium was not that easy at the end of the transesterification reaction and need a large amount of wastewater to clean the catalysts and the products[1,2]. Acidic catalysts are preferred if the vegetable oil or waste cooking oil have high free fatty acid contents and water avoiding the soap formation during the transesterifica-tion. However, the reaction time is longer than base-catalyzed transesterification and need a high molar ratio of alcohol/oil[3]. Enzymatic transesterification of triglycerides is also a good alternative for biodiesel production. However, the high production price and instability of enzymes render the commercialization of enzyme-catalyzed systems prohibitive[4,5]. Because of the disadvantages of homogeneous catalyzed system in biodiesel production, removal of the catalyst from the reaction medium, purity of biodiesel, soap formation problem in the presence of water and free fatty acids, researcher are focused on the heterogeneous catalyzed system showed that high yield and selectivity[6-12].

Zinc oxide is widely used as a catalyst support material for transesterification reaction[13-17]. Zinc oxide loaded with $Sr(NO_3)_2$[13], with iyot[14], with KF[15] and with lithium[16] has been reported as an active heterogeneous basic catalyst for soybean oil transesterification.

In recent years, nano size particles were used as catalyst support materials for transesterification reaction. Several researchers have investigated the important reaction conditions and parameters for transesterification of vegetable oil with alcohol over the nano size catalytic solid catalysts such as nano alumina with KF[6], nano calcium oxide[18], nano zirconia loaded with potassium bitartrate[19], nano CaO-ZnO mixed oxides[20], nano TiO_2-ZnO mixed oxides[21].

It is well known that relatively high conversion rates of vegetable oil to biodiesel can be achieved provided that the catalyst particles exhibit relatively high surface/volume ratios and relatively high basicity. Therefore in the present study, nanocrystalline ZnO particles were used as catalyst supports upon being impregnated with different loading concentrations of K_2CO_3 (K_2CO_3/nano ZnO) followed by calcination at 873 K. The synthesized catalysts were then characterized using XRD, SEM, EDS, BET techniques. Basic strengths of the synthesized catalysts were characterized following a Hammett indicator procedure. The transesterification reaction was carried out under different sets of reaction conditions in an effort to investigate whether biodiesel of acceptable yield and purity could be obtained with the nanoparticles of ZnO impregnated with K_2CO_3.



Scheme-I: Transesterification reactions of triglyceride with methanol

EXPERIMENTAL

Methanol with a purity of 99.8 vol. % was supplied by Riedel-de Haën. The canola oil was procured locally. Analytical-grade potassium carbonate that was used for impregnation was obtained from Merck. The ZnO nanoparticles (98 % purity) were obtained from Sigma-Aldrich Company (product ID: 544906 with a reported particle size < 100 nm). The water absorbance of the nanocrystalline ZnO was characterized as 1.67 g per g of nano ZnO. The free fatty acid concentration and the acid value of the canola oil were characterized by following the AOCS official method Cd 3a-63[22] and were determined to be 0.085 wt. % and 2.08 mg KOH g^{-1}, respectively.

Catalyst preparation and characterization: The solid base catalysts used in this work were prepared by the incipient-wetness impregnation of zinc oxide with the solution of potassium carbonate. The incipient-wetness impregnation utilizes an amount of water that is less than or equal to that required to fill the pores of the support material. The aqueous solutions of K_2CO_3 at different concentrations of K_2CO_3 were prepared based on the water absorbance of nanocrystalline ZnO (determined to be 1.67 g per g of nanocrystalline ZnO). In the impregnation step nanocrystalline ZnO was placed into a 250 mL flask which was kept in an ultrasonic water bath. Vacuum was applied in order to open the pores of nanocrystalline ZnO. For each impregnation step the pre-prepared K_2CO_3 solution was added drop-wise onto the nanocrystalline ZnO using a peristaltic pump. The impregnate was then dried for 24 h at 393 K. Finally, the impregnated and dried ZnO nanoparticles were subjected to calcination for 5 h at 873 K. The procedure of the catalyst preparation including the calcination conditions were kept the same for all K_2CO_3 impregnation solutions.

The catalyst particles were characterized by nitrogen absorbance method using a multipoint BET sorptometer in order to determine the BET surface area values. Prior to each surface area measurement, all samples were kept in an oven overnight under vacuum at 383 K. The characterization of the basic strength and basicity of the synthesized catalysts were performed using a Hammett indicator procedure, outlined by Boz *et al.*[6-8], Yang *et al.*[13], Li *et al.*[14] and Xie *et al.*[15,16].

Powder X-ray diffraction (XRD) patterns of various catalyst samples were collected at room temperature using a Rigaku/ D/MAX 2200 diffractometer with 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°. SEM images of ZnO and the K_2CO_3 impregnated nanocrystalline ZnO particles were obtained using a Jeol_JSM_6400 Scanning Microscope.

Transesterification reaction: The canola oil is converted to biodiesel *via* the transesterification reaction of the triglycerides with methanol to fatty acid methyl esters (**Scheme-I**). The transesterification reaction was carried out in a jacketed 1000 mL batch reactor equipped with a reflux condenser and a magnetic stirrer. First, the impregnated catalyst particles and methanol were well-mixed in the reaction vessel. Following the addition of the canola oil the reaction mixture was heated to the desired temperature. The speed of the agitator of the reactor was kept constant at 600 rpm during reaction. The reaction was timed as soon as the desired amount of canola oil was added to the reactor and it continued for 9 h. After transesterification reaction whole reaction mixture was transferred to the separatory funnel, allowing glycerol and biodiesel to separate by gravity for overnight. The yield of the methyl ester content of the biodiesel phase was performed using an Agilent 6890 gas chromatograph that was equipped with a flame ionization detector (FID) and with a Carbowax 20M capillary column. The methyl ester determination was performed by following the procedure of the European Standard EN 14103[23]. All data points were reproduced at least three times and 95 % confidence intervals, determined according to Student's- t distribution, are reported.

RESULTS AND DISCUSSION

Catalyst characterization: The physical properties of pure nanocrystalline ZnO and supported catalysts were prepared by the impregnation of different amount of potassium carbonate into nano particles of zinc oxide used in this work are summarized in Table-1.

The BET surface area of pure nano zinc oxide without any treatment was about 12.07 m^2/g. However, the BET surface area values of the synthesized catalysts were found to be low. This reduction was an expected result, since surface and pores of zinc oxide were covered by potassium compounds during the impregnation step.

Pore size distributions of the zinc oxide and synthesized catalysts are illustrated in Fig. 1. Most of the pores are in the 2-200 nm range, indicating macropores structure. Nitrogen adsorption isotherms obtained with zinc oxide and zinc oxide impregnated with 10 % K_2CO_3 catalysts are shown in Fig. 2.

TABLE-1
PHYSICAL PROPERTIES OF NANOCRYSTALLINE ZnO and K_2CO_3 IMPREGNATED NANOCRYSTALLINE ZnO CATALYSTS*

		BET area (m^2/g)	Basic strength (H_)	Basicity (mmol/g)
1	Nano ZnO	12.07 ± 0.18	H_< 7.2	-
2	K_2CO_3(3 %)/nano ZnO	5.59 ± 0.43	9.8 < H_ < 15	0.95 ± 0.03
3	K_2CO_3(5 %)/nano ZnO	5.18 ± 0.38	9.8 < H_ < 15	1.02 ± 0.04
4	K_2CO_3(7 %)/nano ZnO	3.19 ± 0.41	9.8 < H_ < 15	1.13 ± 0.03
5	K_2CO_3(10 %)/nano ZnO	3.17 ± 0.25	9.8 <H_ < 15	1.32 ± 0.05

*Preparation conditions: ZnO impregnated with K_2CO_3 was dried at 393 K for 24 h. Calcination temperature and time: 873 K and 5 h

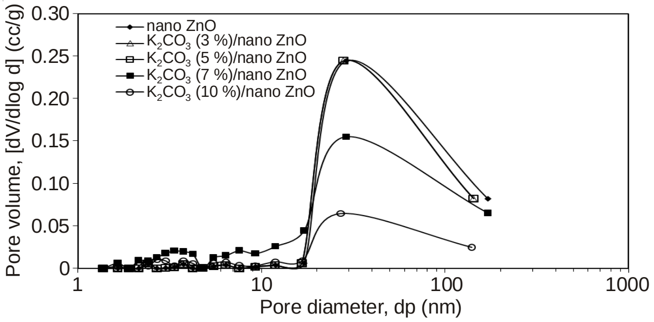


Fig. 1. Pore size distributions of nano ZnO and nano ZnO following impregnation with K_2CO_3 and calcination (prior to the transesterification reaction)

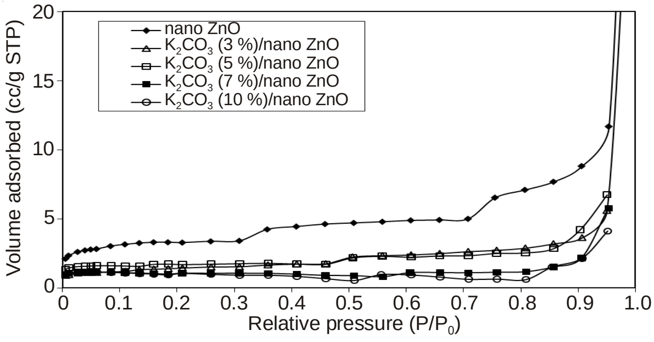


Fig. 2. Nitrogen adsorption isotherms of nano ZnO and nano ZnO catalysts impregnated with different amounts of K_2CO_3 following calcination but prior to the transesterification reaction

The SEM images of pure zinc oxide (Fig. 3a), 10 wt. % potassium carbonate doped nano ZnO before transesterification reaction (Fig. 3b) and after transesterification reaction are shown in Fig. 3. Support material of ZnO was consisting of the nano flakes and particles. The nano ZnO particles exhibit a hexagonal structure and the wide range of the diameter of the synthesized catalyst particles was observed (about 10-200 nm) (Fig. 3a-b). Upon impregnation and calcination the structure of the catalyst particles become attached to each other (Fig. 3b). After transesterification reaction the catalyst particles become smaller in diameter and attached to each other with sticky surface (Fig. 3c-d).

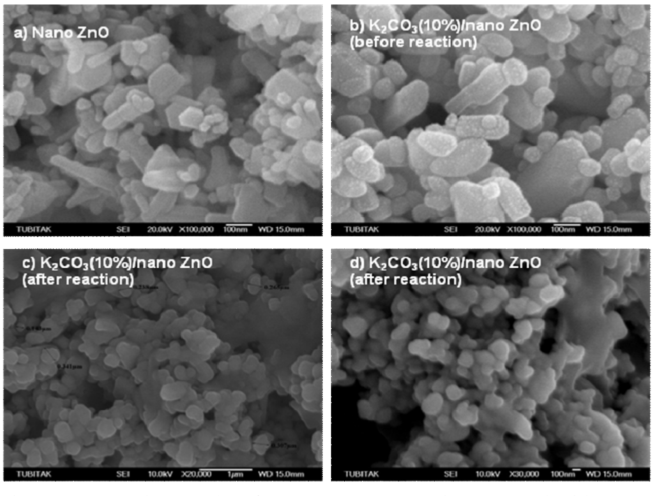


Fig. 3. SEM micrographs of pure ZnO (a); ZnO impregnated with 10 % K_2CO_3 prior to transesterification (b); ZnO impregnated with 10 % K_2CO_3 after the transesterification reaction (c & d)

Powder diffraction techniques are widely used to analyze the surface phenomena[24,25]. X-ray diffraction analysis of pure nano zinc oxide, pure K_2CO_3 and synthesized catalysts with different K_2CO_3 loadings (3-10 wt. %) are shown in Fig. 4. The X-ray diffraction pattern of the nano zinc oxide particles was observed at the Bragg angles, $2\theta = 31.44$, 34.48, 36.24, 47.86, 56.24, 62.78, 66.22, 67.86, 69.00° (JCPDS card 89-7102) (Fig. 4a). K_2CO_3 XRD patterns were observed at the Bragg angles, $2\theta = 27.06°$, 30.74°, 33.16°, 38.68.0°, 42.16°, 43.68°, 46.34°, 49.14° and 67.52° (Fig. 4b). The crystal structure of the ZnO particles doped with K_2CO_3 was not altered much by increasing the K_2CO_3 loading (range between 3-10 %) (Fig. 4c-f). The basic sites are based on Zn-O-K groups which serve as the active sites.

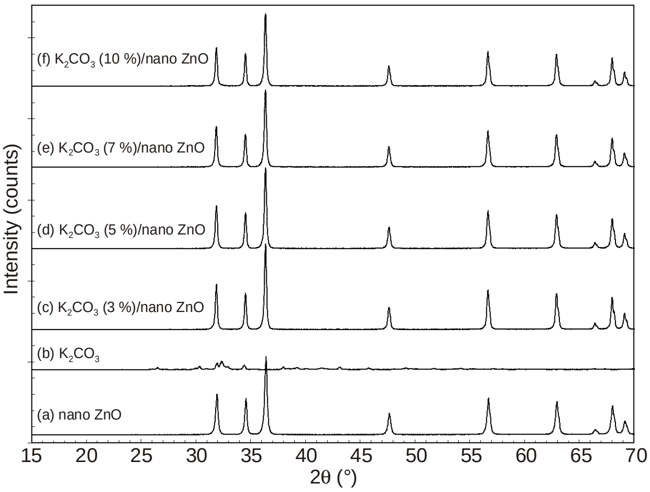


Fig. 4. XRD patterns of nano ZnO, K_2CO_3 and nano ZnO catalysts that were impregnated with K_2CO_3

Effects of transesterification reaction variables: The activity of K_2CO_3/nano ZnO catalyst on the transesterification of canola oil with methanol was investigated by conducting a series of experiments.

The variables affecting the methyl ester yield during the transesterification reaction, such as K_2CO_3 loading into nano ZnO, the molar ratio of methanol to canola oil, reaction time, reaction temperature and the catalyst content were investigated. The stirrer speed was kept constant at 600 rpm in order to increase the dispersion of the mixture.

Effect of K_2CO_3/nano ZnO ratio: The catalytic effect of K_2CO_3/nano ZnO loading on transesterification was investigated. The experimental conditions for studying the effect of K_2CO_3/nano ZnO loading on transesterification reaction were: the amount of catalyst at 5 % (based on the weight of canola oil), methanol to oil molar ratio of 9/1, reaction time of 9 h and the reaction temperature at 338 K. The results clearly indicate that the amount of K_2CO_3 loaded into nano ZnO affected the yield of methyl ester (Fig. 5). Increasing the loading amount of K_2CO_3 from 3 to 7 wt. % increased the yield of methyl esters. However, further increase of the loading amount of K_2CO_3 from 7 to 10 wt. % did not significantly affect the yield of methyl esters. The highest yield of methyl esters about 97.83 % was obtained at 10 wt. % K_2CO_3 loading into zinc oxide.

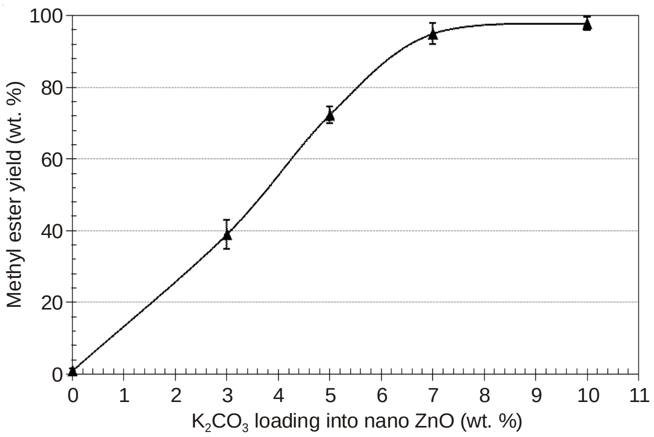


Fig. 5. Yield of methyl ester *versus* the K_2CO_3 loading into nano ZnO (for methanol/oil molar ratio: 9/1, T: 338 K, catalyst amount: 5 wt. %, reaction time: 9 h)

Effect of alcohol to oil ratio: The stoichiometric molar ratio of methanol to canola oil was 3/1. In the transesterification reaction the methanol/canola oil ratio was always chosen higher than the stoichiometric molar ratio in order to shift the equilibrium towards the formation of esters. To investigate the effects of the alcohol to oil ratio, the transesterification experiments were conducted by systematically changing the molar ratio of alcohol to oil, *i.e*., from 6/1 to 18/1, while keeping the temperature (338 K), catalyst amount of 5 wt. % and duration of 9 h constant. Fig. 6 suggests that altering the methanol/oil molar ratios that are > 9/1 does not significantly affect the methyl ester yield. A maximum yield of methyl ester yield 97.83 ± 1.82 wt. % could be reached at a molar methanol/oil ratio of 9/1.

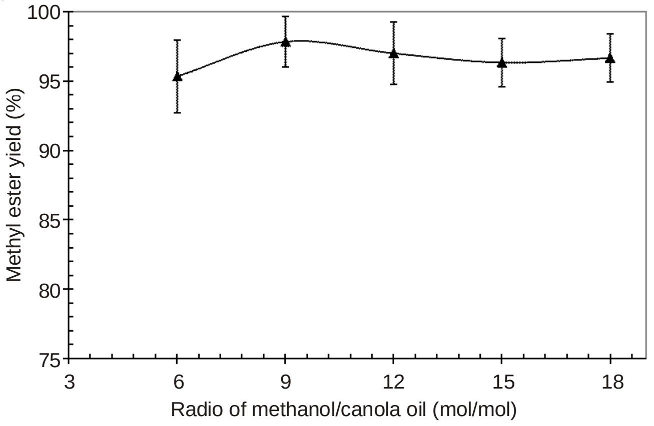


Fig. 6. Dependence of the yield of methyl ester on the methanol to canola oil molar ratio for synthesized K_2CO_3(10 %)/nano ZnO catalyst (T: 338 K, catalyst amount: 5 wt. %, reaction time: 9 h)

Effect of reaction time: Time dependence of methyl ester yield was investigated for the transesterification reaction of canola oil with methanol using 10 wt. % K_2CO_3 loaded into nano ZnO catalyst (Fig. 7). Collected 1 h time interval samples were centrifuged and the upper biodiesel phase was used for chemical analysis. Methyl ester yield increases very fast within the first hour but the rate of increase of the yield is getting slower after the first hour. A maximum yield of 97.83 ± 1.82 was reached at about 9 h of reaction time.

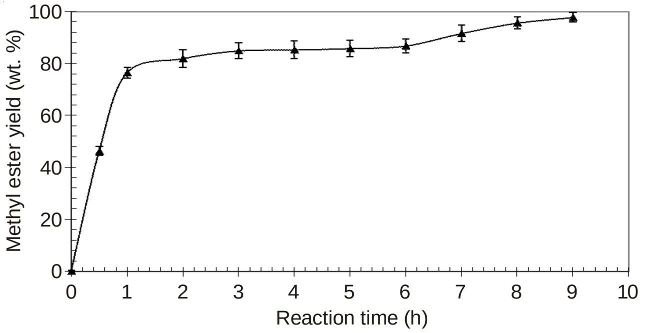


Fig. 7. Dependence of the yield of methyl ester on the reaction time for synthesized K_2CO_3(10 %)/nano ZnO catalyst (for the methanol/oil molar ratio: 9/1, catalyst amount: 5 wt. %, reaction temperature: 338 K)

Effect of reaction temperature: Reaction temperature can influence the reaction rate and the methyl ester content because the intrinsic rate constants are strong functions of temperature. The effects of the reaction temperature on the yield of methyl ester were investigated for K_2CO_3(10 %)/nano ZnO catalyst at four temperatures (298, 318, 333 and 338 K) while keeping constant the catalyst concentration at 5 wt. % and the methanol to oil ratio at 9/1 (Fig. 8). The highest methyl ester content was observed at the maximum temperature studied 338 K which is the reflux temperature of methanol as expected.

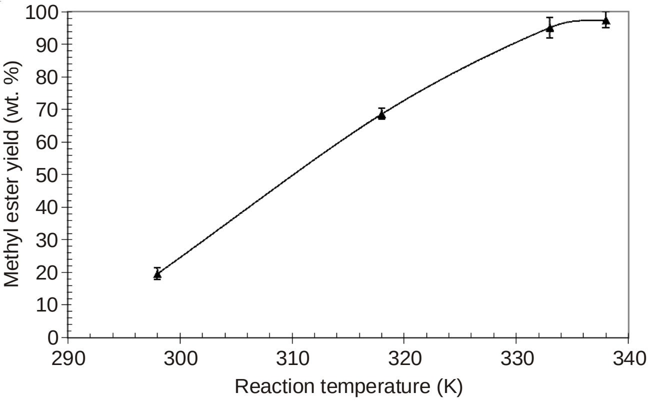


Fig. 8. Dependence of the methyl ester yield on the reaction temperature for synthesized K_2CO_3(7 %)/nano ZnO catalyst (for the methanol/oil molar ratio: 9/1, catalyst amount: 5 wt. %, reaction time: 9 h)

Effect of catalyst concentration: The effects of the catalyst concentration on methyl ester yield were investigated for K_2CO_3 (10 %)/nano ZnO catalyst. The mass ratio of the synthesized catalyst to canola oil varied within the range of 1-7 % (Fig. 9). The methyl ester content was increased with increasing catalyst amount and then reached a plateau value at a catalyst weight percent of about 5 %. Beyond the value of five weight percent yield of methyl ester did not vary much. The methyl ester yield of 97.83 % was obtained at the optimum catalyst concentration of 5 wt. %

Stability of K_2CO_3(10 %)/nano ZnO catalyst: Recovery of catalyst from the reaction mixture was an important operational parameter. Reuse of the 10 wt. % K_2CO_3 into nano ZnO catalyst was tested for transesterification of canola oil with methanol. Three successive runs were carried out under the same operating conditions (methanol/canola oil: 9/1, catalyst amount: 5 wt. %, reaction time: 9 h, reaction temperature:

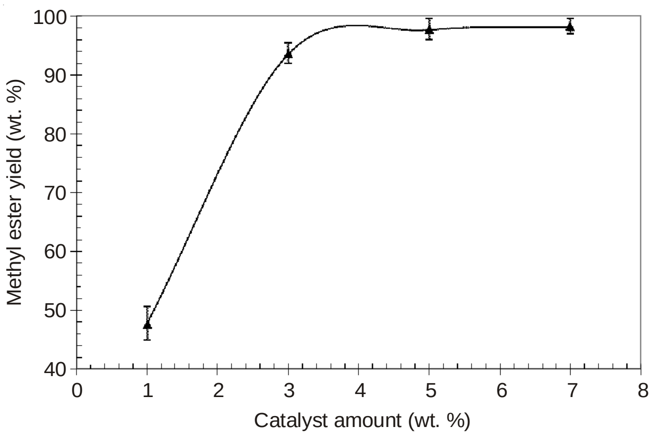


Fig. 9. Effects of the weight percent of the catalyst in the reaction mixture over synthesized K_2CO_3(10 %)/nano ZnO catalyst (for the methanol/oil molar ratio: 9/1, reaction temperature: 338 K, reaction time: 9 h)

338 K). Yield of methyl ester was reported as 97.83 wt. % (1^{st} use), 96.53 wt. % (2^{nd} use) and 96.45 wt. % (3^{rd} use), respectively. No difference of conversion in the second and third runs indicated the stability of the catalyst after the second run. The initial catalytic activity of the synthesized catalyst could be maintained for at least three reaction cycles.

Conclusion

The catalytic activity of nano zinc oxide was significantly enhanced by introducing some amount of potassium carbonate (range 3-10 % by weight) by the impregnation method. A methyl ester yield of 97.83 % ± 1.82 was achieved at a temperature of only 338 K over the K_2CO_3(10 %)/nano ZnO catalyst (alcohol/oil: 9/1, the catalyst based on the weight of the mass of oil in the amount of 5 %, reaction time: 9 h). The catalysts were recycled and reused three times without significant loss in activity. Results indicated that interaction of methanol with the catalyst surface.

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