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MANGANESE CARBONATE-ZINC GLYCEROLATE. SYNTHESIS, CHARACTERIZATION AND APPLICATION AS CATALYST FOR TRANSESTERIFICATION OF SOYBEAN OIL

Article Highlights

- MnCO₃/Zn-glycerolate was synthesized by thermal treatment of MnCO₃/ZnO with glycerol
- MnCO₃/Zn-glycerolate was tested as catalyst for biodiesel synthesis
- Reusing of MnCO₃/Zn-glycerolat was analyzed for 13th times
- The rate of deactivation of MnCO₃/Zn-glycerolate was examined
- Comparison between activity of MnCO₃/Zn-glycerolate and MnCO₃/ZnO was done

Abstract

In this study, a mixed system containing manganese carbonate (MnCO₃) and zinc glycerolate (ZnGly) was synthesized, and tested as a solid catalyst for transesterification of soybean oil and biodiesel production. The samples of MnCO₃/ZnGly before and after usage for transesterification were characterized using different techniques: determination of basic strength, determination of specific surface area according to Brunauer-Emmett-Teller (BET), measuring the mass change using thermal gravimetric analysis (TGA), investigating the solid phase content and presence of different specific elements and groups by X-Ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). The effects of different working parameters of transesterification were also investigated: temperature (438-458 K), duration of transesterification (0-3.5 h), methanol to oil molar ratio (12:1-36:1) and used amounts of catalyst (1-5 mass%). The reusability and stability of MnCO₃/ZnGly were analyzed and obtained results showed that MnCO₃/ZnGly exhibited a good activity with 100% TG conversion and 81.5% FAME yield with fresh catalyst, and can give 95-100% TG conversion and 62-78% FAME yield after 13 repeated uses of the same amount of catalyst without regeneration processes. The contents of Mn and Zn in biodiesel and glycerol were analyzed by ICP-AAS after each reuse of catalyst.

Keywords: manganese carbonate-zinc glycerolate, biodiesel, reusability, stability.

The industrial process of biodiesel production is mainly based on the use of homogeneous basic catalysts, and nowadays some new and technically more

interesting route for biodiesel synthesis is under investigation [1-7]. Although sodium or potassium hydroxides or corresponding methoxides are applied in many processes [8,9] there has been increased and significant interest for proposing technology that can satisfy the drawbacks of homogeneous catalysis of biodiesel synthesis. These catalysts, although very active for transesterification of triglycerides, create difficulties in the process of catalyst separation from

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the products of transesterification (biodiesel and glycerol) and formation of larger wastewater amounts, which increase the cost of biodiesel production [10,11]. This problem has initiated research efforts to find the best route of biodiesel synthesis using appropriate solid catalysts that might be active and stable in the process of heterogeneous synthesis of biodiesel [12]. Unlike homogeneous catalysts, the use of heterogeneous catalysts eliminates the need of products purification process and could be easily applied for continuous biodiesel production [13,14]. Most of the heterogeneous catalysts include two types: solid acids such as $\text{SO}_4^{2-}/\text{TiO}_2\text{-SiO}_2$, $\text{Fe}_2\text{O}_3\text{-MnO-SO}_4^{2-}/\text{ZrO}_2$, $\text{RHC-SO}_3\text{H}$ [15-17], and solid bases, which are generally alkali metal oxides or alkaline-earth metal oxides [18-20], basic hydrotalcites [21], or basic zeolites [22]. These catalysts showed various catalytic activities ranging from 84 to 100% of TG conversion [23]. Unfortunately, some oxides such as CaO and MgO, although very active, are relatively unstable; they usually leach and their active sites could be easily blocked by products or reactants of transesterification [24]. In order to decrease or eventually completely suppress the leakage of the precursor, some new techniques have been applied [25]. They are based on mixed systems synthesis of precursor and other metals or dispersion of precursor on mesoporous supports [26,27-29]. However, in many cases catalysts underwent the significant deactivation due to the leaching process of the strongest base precursors [30-32]. In summary, the major drawback of solid base catalysts is their unstable chemical structures in contact with methanol, biodiesel or even glycerol. Application of such catalysts require their replacement (*e.g.*, for continuous processes) or in-city regeneration. Besides the requirement for preparation the solid catalysts with desired activity, the sustainable utilization of heterogeneous catalysts is also an important step that must be considered.

Several reports recently published in the literature were focused their attention on alkali metal glycerolate (or glyceroxide) which might be formed during catalytic process of biodiesel synthesis with metal oxide. For example Zn carboxylates could be transformed into ZnGly at 100-140 °C in the presence of glycerol [33,34]. It was also shown that ZnGly could be reused five times without deactivation enabling TG conversion of 95-97% and FAME yield of 66-76% [33-35]. Kouzu *et al.* [36] and other researchers studied calcium diglyceroxide and they found that it might be easily formed in reaction between calcium oxide and glycerol [34,37,38]. Their conclusions are instructive

and important for commercial application, and were also considered for research reported in this study.

One task of this study is to compare $\text{MnCO}_3/\text{ZnGly}$ activity to the activity of recently reported results obtained with MnCO_3/ZnO [39]. Although solid MnCO_3/ZnO was shown as a possible catalyst for continuous application under subcritical conditions for methanol, it was also suspected that the observed change of its activity and selectivity could be caused by ZnGly formation [39]. Thus, a general idea of this study is to show that during the use of MnCO_3/ZnO as catalyst for biodiesel synthesis such conversion of MnCO_3/ZnO into $\text{MnCO}_3/\text{ZnGly}$ is possible and also causes the change in MnCO_3/ZnO activity. The $\text{MnCO}_3/\text{ZnGly}$ was prepared after treatment MnCO_3/ZnO and glycerol at high temperature. Different parameters of biodiesel synthesis were investigated in order to define the catalytic behavior of $\text{MnCO}_3/\text{ZnGly}$: the temperature and duration of transesterification, the initial reaction mixture composition (methanol to oil mole ratio) and amount of used catalyst. These conditions were chosen based on the data determined as optimal for biodiesel synthesis with MnCO_3/ZnO as the catalyst. The characteristics of the catalyst, before and after usage, were determined using different analysis: determination of basic strength, BET, TGA, XRD, FTIR, SEM-EDS. The stability and reusability of catalyst were tested in series of consecutive batch processes realized with same amount of $\text{MnCO}_3/\text{ZnGly}$. The leaching of active metals (Mn and Zn) in biodiesel and glycerol were analyzed by ICP-AAS.

EXPERIMENTAL

Materials

The raw soybean oil was produced by Wuhan Baifu Oils & FatCo. Ltd. (Wuhan, China). The reagents K_2CO_3 (99%), ZnCl_2 (99%), MnCl_2 (99%), methanol (99.5%), glycerol (99%) were of analytical grade and purchased from Aopu Chemical Company (Wuhan, China). Methanol and acetone of HPLC grade were purchased from Tedia Company Inc. (Fairfield, OH, USA) and Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA), respectively.

Catalyst preparation

$\text{MnCO}_3/\text{ZnGly}$ was prepared using solid MnCO_3/ZnO obtained by co-precipitation of ZnCl_2 and MnCl_2 in K_2CO_3 [39]. The MnCO_3/ZnO powder and glycerol in excess was treated at 448 K for 2 h in batch reactor using constant intensity of mixing (200 rpm). The reaction mixture was taken out of the reactor after 2 h

of synthesis and the precipitate was separated by filtration, traces of glycerol were washed by methanol, and the solid phase was dried overnight in an oven at 323 K. Using the same procedure as above defined for $\text{MnCO}_3/\text{ZnGly}$ synthesis, two complexes, called Zn-complex and Mn-complex, using either ZnO or MnCO_3 were also prepared.

Biodiesel synthesis

The transesterification batch reaction was realized in 500 mL stainless steel autoclave [39]. The catalyst test started with the mixing of soybean oil, methanol, and $\text{MnCO}_3/\text{ZnGly}$ in a batch reactor and then reaction mixture was heated to the preset temperature and stirred at a constant speed of 200 rpm. The actual initial reaction time defined as $t=0$, was a moment when the temperature reached the value for isothermal biodiesel synthesis. All the experiments were conducted in duplicate and the obtained results for TG conversion and FAME yield were shown as average values.

Analytical methods

Triglycerides (TG), the fatty acid methyl esters (FAME) and intermediate products, monoglycerides (MG) and diglycerides (DG) were analyzed in the sample of biodiesel using Agilent 1100 Series with a C18 column (40 °C, particle size 5 μm , 200 $\text{mm} \times 4.6 \text{ mm}$ I.D.) and UV-Vis detector at 205 nm [40]. The flow rate of HPLC grade methanol used as mobile phase was 1.0 mL min^{-1} . The biodiesel samples were diluted with HPLC grade acetone and then filtered through a 0.45 μm micro-pore membrane before injection. TG conversion [41] and FAME yield was calculated based on peak areas from HPLC analysis:

$$\text{TG conversion (\%)} = 100 \left[\frac{(\text{TG}_{\text{oil}} - \text{TG}_{\text{sample}})}{\text{TG}_{\text{oil}}} \right]$$

$$\begin{aligned} \text{FAME yield (\%)} &= \\ &= 100 \left[\frac{(\text{FAME}_{\text{sample}} - \text{FAME}_{\text{oil}})}{\text{FAME}_{\text{end}}} \right] \end{aligned}$$

where TG_{oil} and $\text{TG}_{\text{sample}}$ refer to the total HPLC peak areas of triglycerides in the soybean oil and biodiesel samples, respectively, and $\text{FAME}_{\text{sample}}$ and FAME_{oil} are HPLC peak areas of fatty acid methyl esters in sample and soybean oil, while FAME_{end} is area of fatty acids methyl esters in the sample of complete conversion of TG, DG and MG into FAME.

Catalyst characterization

A detailed description of the applied procedure of basic strength of samples has been reported in the literature [32].

BET surface areas of the samples were determined according to the multipoint N_2 adsorption-desorption method using an instrument of SSA-4200 surface area & pore size analyzer (Beijing Builder Electronic Technology Co., Ltd., China). Prior to measurements, all samples were out-gassed overnight under vacuum at 373 K.

The thermal stability of the catalyst was determined using a thermogravimetric analyzer (Discovery TGA) under N_2 flow from room temperature to 800 °C (at a heating rate of 20 °C/min) [35].

XRD was performed on a D/MAX-RB powder X-ray diffractometer (Rigaku Corporation, Japan) at room temperature. $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$), with a step size of 0.02° in the 2θ range from 5 to 65°. The data were processed with the X'Pert HighScore Plus software. The peaks were identified using the Powder Diffraction File (PDF) database created by International Centre for Diffraction Data (ICDD).

FTIR spectra were recorded on a Nicolet FT-IR 5700 spectrometer (Thermo Electron Corp., USA) over the wave number range of 4000–5000 cm^{-1} , with 2 cm^{-1} resolution. The KBr pellet technique was applied for preparing samples. All measurements were conducted at room temperature.

Sample morphology and elemental chemical analysis at chosen points of samples were characterized at room temperature by a Quanta 200 SEM system equipped with an EDS detector (FEI Company, Netherlands). The accelerating voltage was 20 kV.

RESULTS AND DISCUSSIONS

Influence of different working conditions used for biodiesel synthesis

It was concluded in the previous study [39] using MnCO_3/ZnO as catalyst for soybean transesterification with methanol that the highest yield of FAME could be obtained after 1 h of isothermal operation at 448 K, with 4% of catalyst based on oil, and 18:1 methanol/oil mole ratio. According to these optimal conditions, the similar working parameters using $\text{MnCO}_3/\text{ZnGly}$ as catalyst were also tested, and the comparison of activity for two catalysts was analyzed.

Effect of reaction temperature

The influence of temperature on TG conversion and FAME yield is presented in Figure 1a. Relation between TG conversion and temperature had a typical s-curve for temperature increase from 438 to 458 K; it was changed from about 45% to more than 95% for that isothermal and 1 h operation, respectively. The maximal change of TG conversion rate was

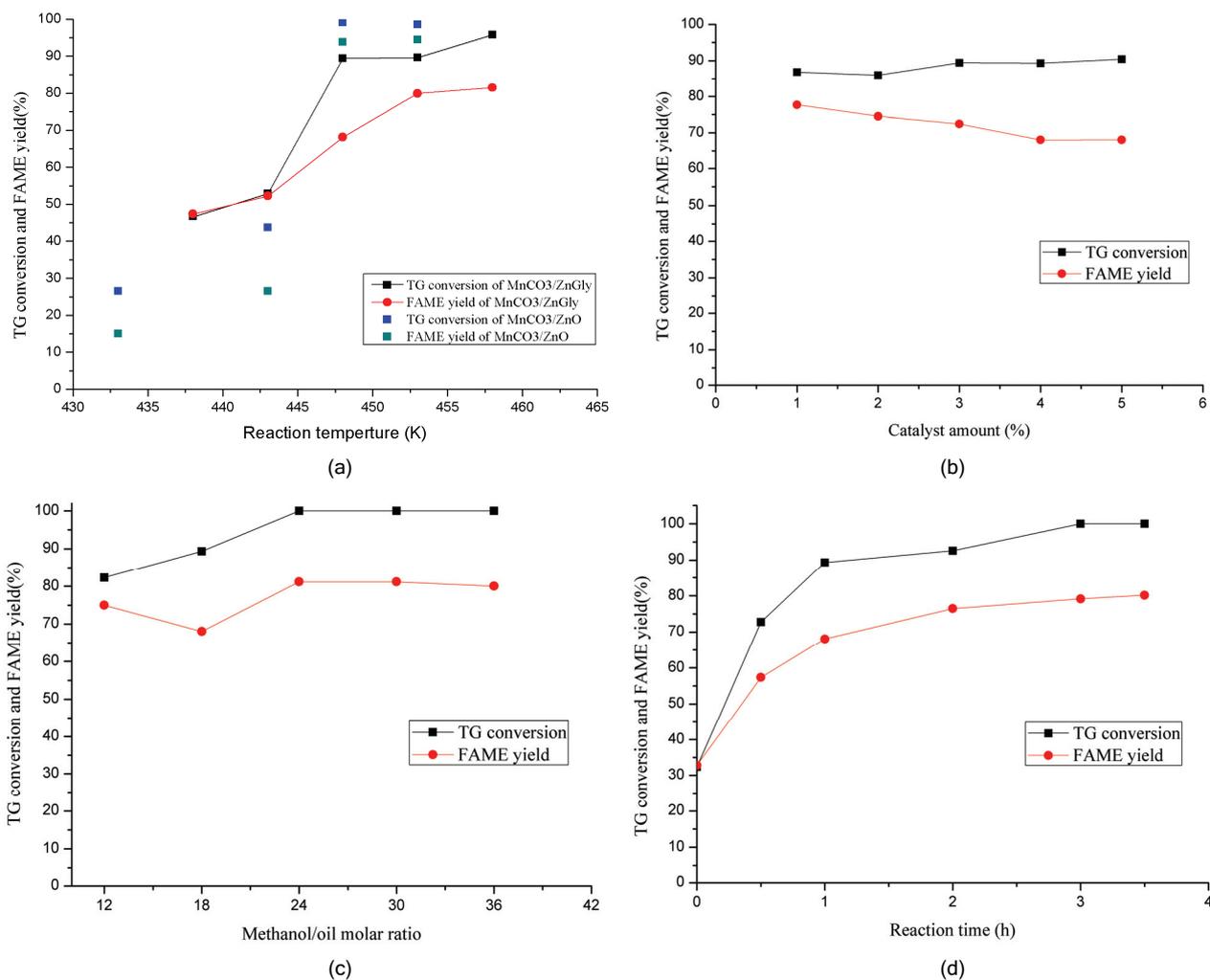


Figure 1. Effect of: a) reaction temperature, catalyst amount: 4 wt. %, methanol/oil mole ratio: 18:1 h and reaction time: 1 h; MnCO_3/ZnO [39]; b) catalyst amount, temperature: 448 K; methanol/oil mole ratio: 18:1 and reaction time: 1 h; c) methanol/oil mole ratio, temperature: 448 K, catalyst amount: 4 wt. % and reaction time: 1 h; d) reaction time, temperature: 448 K, catalyst amount: 4 wt. % and methanol/oil mole ratio: 18:1, on the TG conversion and the FAME yield.

observed for isothermal operation performed between 443 and 448 K and defined as the inflection point of the s-curve, representing the relation between TG conversion and temperature. Less expressed, but with the same s-shape curve, was the relationship between the yield of FAME and temperature. The yield of FAME was also increased at higher temperature and the highest value (81%) was determined at 458 K. It is important to point out that at lower temperature (438–443 K) only the smaller part of TG was transformed into FAME. It was changed at higher temperature where other compounds, the monoglycerides (MG) and diglycerides (DG), formed in complex reaction of TG transesterification, were also detected but in smaller amount. In the temperature range 443–453 K the increase of FAME yields was more expressed mainly as a result of DG and MG conversion. Compared to optimal activity of MnCO_3/ZnO ,

determined at 448 K [39], the $\text{MnCO}_3/\text{ZnGly}$ was also very active in the same range of temperature.

The temperature has a major effect on the state of dispersion, and formation at higher temperature provides better contact between two immiscible phases (oil and methanol) and solid catalyst. Better contact and smaller drops of oil increase the rate of transesterification with $\text{MnCO}_3/\text{ZnGly}$ and MnCO_3/ZnO used as catalyst. However, temperature beyond the optimal could also accelerate the saponification process and limit the yield of FAME [42] as shown in Figure 1a.

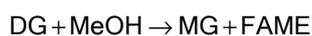
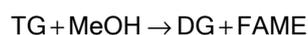
Effect of catalyst amount

The catalyst amount is an important parameter for obtaining the desired conversion of triglycerides into methyl esters. A large amount of used catalyst usually leads to higher and complete TG conversion.

The relationship between used amount of $\text{MnCO}_3/\text{ZnGly}$ and TG conversion or FAME yield is shown in Figure 1b. Contrary to the expected effect, the TG conversion was almost constant and about 88%, while FAME yield was slightly decreased. This effect is probably the result of FAME transformation either to MG in the reaction of FAME and glycerol, or the reaction of FAME and MG with formation of DG. Finally, it could be concluded that TG conversion of soybean oil with methanol using $\text{MnCO}_3/\text{ZnGly}$ was not influenced by catalyst amount, which is not observed for biodiesel synthesis with MnCO_3/ZnO catalyst applied at the same working conditions.

Effect of methanol/oil mole ratio

The stoichiometric molar ratio of methanol to triglyceride for their complete conversion into glycerol and FAME is 3:1. Transesterification of triglyceride is a complex process in which several intermediate compounds are formed (DG and MG) according to the following reactions:



However, regarding the used working condition, all three steps of complex process could be more or less reversible. Thus, a large excess of methanol shifts the equilibrium toward the forward reactions and formation of FAME and glycerol as the final products of transesterification. As shown in Figure 1c, the FAME yield and TG conversion were slightly increased when the methanol-to-oil mole ratio was changed from 12:1 to 24:1. Further increase of the methanol-to-oil mole ratio beyond 24:1 did not increase TG conversion. Namely, for 24:1 as well for other higher values of methanol to oil mole ratio the complete TG conversion (100%) and 81% yield of FAME were obtained. However, although a large excess of methanol would suppress the rate of reverse reaction, the ratio between the FAME productivity and cost of methanol recovery would define the optimal molar ratio of methanol and oil in praxis [43,44].

Comparing the results related to the influence of temperature and mole ratio of methanol and oil, a general conclusion could be derived: the increase of both parameters to some optimal value had a positive effect on TG conversion and not a significant effect on FAME yield.

A greater difference of FAME yield and TG conversion could be detected at a methanol-to-oil mole ratio less than 24:1 when the transesterification

of soybean oil was performed at the same working condition using MnCO_3/ZnO [39] or $\text{MnCO}_3/\text{ZnGly}$ catalysts. Determined TG conversion and FAME yield were 50 and 30% with MnCO_3/ZnO catalyst and mole ratio of 12:1 [39] while with $\text{MnCO}_3/\text{ZnGly}$ were about 78 and 75%, respectively. By increasing the mole ratio to 18:1, a greater increase of TG conversion and FAME yield with MnCO_3/ZnO was reported [39] and only a minor increase in the case of $\text{MnCO}_3/\text{ZnGly}$ as shown in this study.

Effect of reaction time

Both TG conversion and FAME yield curves increase from the initial value about 32% for $t=0$ (time when temperature in the batch reactor reached the set point) to almost 100% and 80% after 5 h of operation at 448 K, respectively (Figure 1d). The absence of the s-shape of both curves indicated that the mass transfer resistance during isothermal operation at 448 K could be neglected and that the resistance of reaction rate at the catalyst surface determines the overall rate of the transesterification process. Comparison to transesterification performed at that temperature without the presence of catalyst (so called "blank" experiment in which TG conversion was about 20%) indicated that $\text{MnCO}_3/\text{ZnGly}$ catalyze the soybean transesterification process.

A serious drawback of batch process at high temperature is that some time is obviously necessary to reach the final temperature at which transesterification starts to be examined under isothermal condition. The time necessary to increase the temperature of the reaction mixture from 298 to 448 K was about 60 min. For that non-isothermal period of transesterification, TG conversion (32%) and FAME yield (32%) were determined. During 1 h of isothermal operation at 448 K, the rate of transesterification process was substantially increased and TG conversion of 90% and FAME yield of 68% was obtained. The complete TG conversion (100%) and slightly higher FAME yield (76%), as shown in Figure 1d, was detected after continuing isothermal operation at 448 K for the next 3 h.

In summary, the following conclusion can be derived: temperature, duration of transesterification and molar ratio of methanol to oil had much more influence on TG conversion and FAME yield than the amount of used catalyst. Probably the most important parameter is the temperature at which transesterification is performed. Taking into account all of the above results, the applied optimal working conditions: temperature ~450 K, methanol-to-oil mole ratio 24:1, mass of catalyst 1-2% based on oil, and duration of

transesterification between 2 and 3 h at isothermal conditions, were used for biodiesel synthesis with $\text{MnCO}_3/\text{ZnGly}$ as catalyst. At these working conditions, higher conversion of TG with $\text{MnCO}_3/\text{ZnGly}$ compared to MnCO_3/ZnO [39] could be obtained, as shown. However, the conclusion is not the same if FAME yields obtained with these catalysts are compared. That fact implies that $\text{MnCO}_3/\text{ZnGly}$ catalyst increases TG conversion but not as effectively as the corresponding DG and MG conversion, or maybe that $\text{MnCO}_3/\text{ZnGly}$ increases the reversible reaction between glycerol and FAME, which in the final consequence decreases the FAME yield.

The reusability and stability of catalyst

The standards for measuring catalyst “quality” extend beyond just its initial catalyst activity. The long

life or reusability for applying in a batch process, *i.e.*, the stability of catalysts, are in many cases even more important factors. Thus, from the perspective of economy of biodiesel synthesis, the catalyst activity and its stability (“long life”) are the main factors determining optimal biodiesel production [14,45].

Repeated tests of transesterification in batch reactor were realized using the same initial amount of catalyst without its regeneration. The catalyst was separated by centrifugation of reaction mixture after finalized transesterification. TG conversion and FAME yield was analyzed, and the obtained results are shown in Figure 2a. During repeated use of catalyst, experiments showed that TG conversion and FAME yield were above 95 and 62%, respectively. A significant decrease of catalyst activity was observed

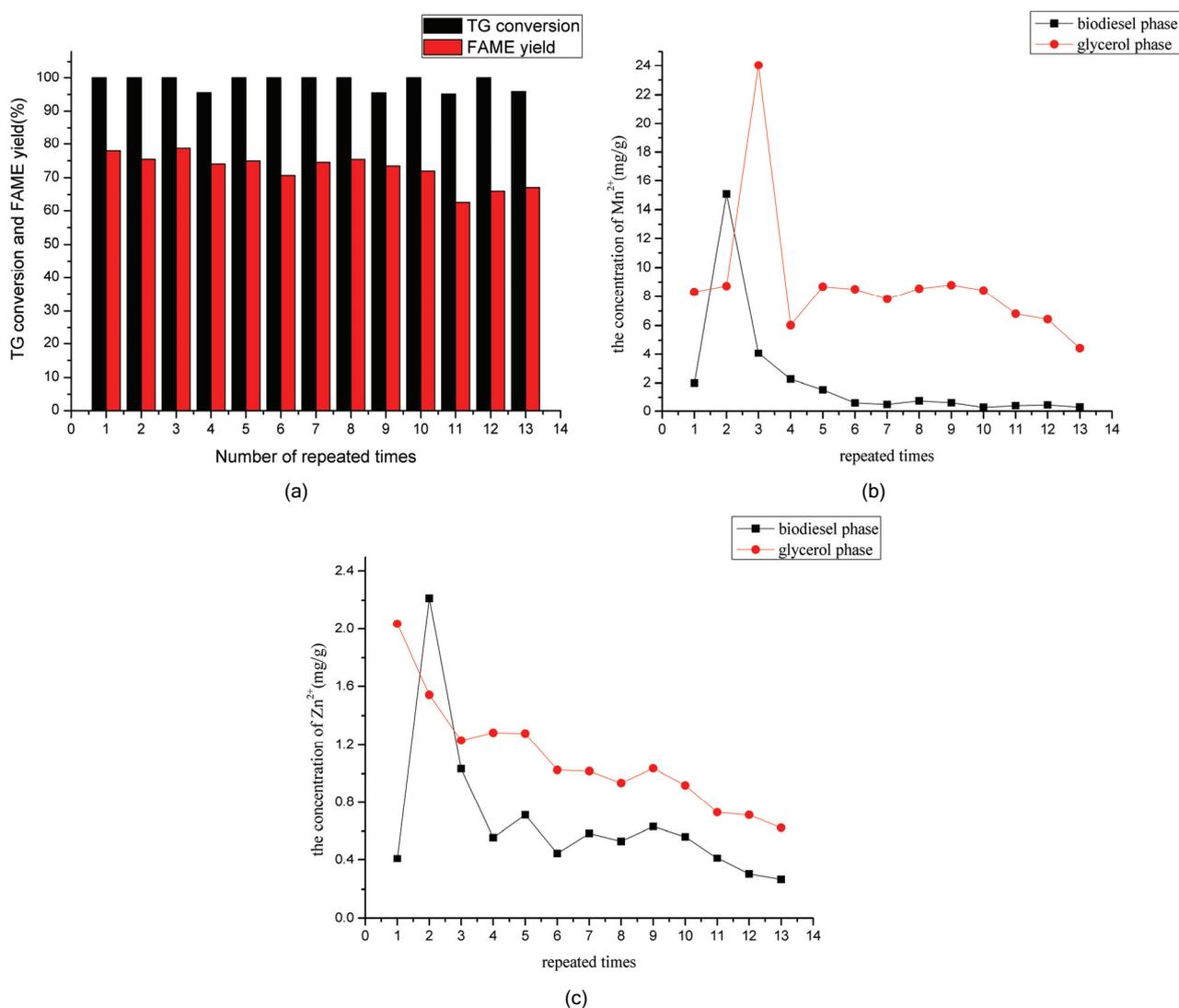


Figure 2. Effect of the repeated use of the $\text{MnCO}_3/\text{ZnGly}$ catalyst on: a) the TG conversion and the FAME yield (reaction temperature: 448 K; catalyst amount: 5%; methanol/oil mole ratio: 24:1; reaction time: 1 h), and determined concentration of b) Mn and c) Zn in biodiesel and glycerol phase.

after 13 repeated cycles of transesterification. However, a slightly higher decrease of FAME yield after 6 and 10 cycles can also be observed. Decrease of catalytic activity could be a consequence of different reasons, among them the most important being poisoning of active site of catalyst caused by adsorption of oil, or by leaching the active metals in the product of transesterification. For deactivation caused by adsorption, the catalyst can be regenerated to remove the organics from the external surface or from the pores and internal catalyst surface. However, the leaching of metal ions (Mn and Zn) and destruction of active catalyst sites is an irreversible process, and in that case the regeneration of catalyst is impossible [46].

In order to understand the mechanism of catalysts deactivation, the contents of Mn and Zn in biodiesel and glycerol phases were determined by ICP-AAS, and the obtained results are shown in Figures 2b and c. The highest values of Mn concentration in biodiesel and glycerol were after the first several catalysts reuse and they were remarkably decreased after the 4th cycle being almost constant in both phases from 4th to 13th cycles of transesterification as shown in Figure 2b. In general, content of leached Mn in the glycerol phase was found to be several times of that in the biodiesel phase.

The content of Zn in biodiesel and glycerol is shown in Figure 2c. The same trends of Zn content in biodiesel and glycerol phases after each cycle of transesterification were determined. The highest value of Zn was several times lower than detected Mn content in both phases. The content of Zn detected in the glycerol phase decreased gradually from the first to the last repeated transesterification, while the trend in the biodiesel phase was similar to that of Mn content in the same phase. These data indicated that Mn solubility in biodiesel and glycerol was much more significant compared to Zn solubility.

Catalyst characterization

The fresh catalyst and samples of catalyst after repeated use were characterized by measuring the basic strength, BET surface area, TGA, XRD, FTIR and SEM-EDS. The results of these investigations could be the starting point for proposing the mechanism of catalyst deactivation.

Basic strength

The activities of catalysts were usually related to their basic strengths, the higher base strengths of the catalyst could be responsible for the higher biodiesel yields [47]. The basic strength of fresh $\text{MnCO}_3/\text{ZnGly}$ was in the range $9.8 < H_- < 15.0$. However, the basic strength of catalyst reused for 13 times was dec-

reased to $H_- < 9.8$. The main active sites of catalyst which contain MnCO_3 and ZnGly structures gradually change their bulk and surface concentration caused by leaching into glycerol (more) and biodiesel phases. That irreversible process decreases the basic strength and catalytic activity of $\text{MnCO}_3/\text{ZnGly}$. It caused the change of TG conversion and even more the selectivity of transesterification towards FAME formation (Figure 2).

BET surface area

The BET surface area of fresh catalyst was $32 \text{ m}^2/\text{g}$, and surface area of 13th time reused catalyst was $16 \text{ m}^2/\text{g}$. At the same time, the pore volume changed from 0.14 to $0.02 \text{ cm}^3/\text{g}$, and the average pore size from 14 to 5 nm after the catalyst has been reused for 13 times.

Chemical reaction between TG and formed methoxide ions at active site of catalyst depends on value of specific surface area. From the above data related to the surface area of catalyst, and more to the pore volume and to the value of average pore size, one can conclude that TG conversion with fresh catalyst and as from the used catalyst was mainly concentrated on the external surface area. However, the significant decrease of pore volume as well as pore size means that blockage of catalyst active sites by large TG molecule was the main reason for changing the selectivity of catalyst after its reuse [48]. These data showed that complete TG, DG and MG conversion into FAME depend on the existence of large interconnected pores that would minimize diffusion resistance of molecules with long alkyl chains [48].

All above data indicated that the physical structure of the catalyst was remarkably changed; evidently, the catalyst was not only blocked by some organics, but moreover, the structure of $\text{MnCO}_3/\text{ZnGly}$ was changed as result of Mn and, to a lesser extent, of Zn dissolutions into biodiesel and glycerol. Both effects caused a decrease of $\text{MnCO}_3/\text{ZnGly}$ activity or its slow deactivation during the 13th repeated use.

TGA/DSC analysis

The TG/DTG/DSC analysis of fresh (A) and the 13 times reused catalyst (B) is shown in Figure 3. The thermal decomposition process of these samples occurred in the same temperature range $300\text{--}450 \text{ }^\circ\text{C}$ with maximum of DTG observed around $400 \text{ }^\circ\text{C}$. That process represents the ZnGly decomposition into corresponding metal oxide [35]. The differences were found only in total mass loss (TG analysis), which was for fresh catalyst about 11% less compared to 13 times reused $\text{MnCO}_3/\text{ZnGly}$ catalyst. This is evidently a result of organic compounds decomposition in used

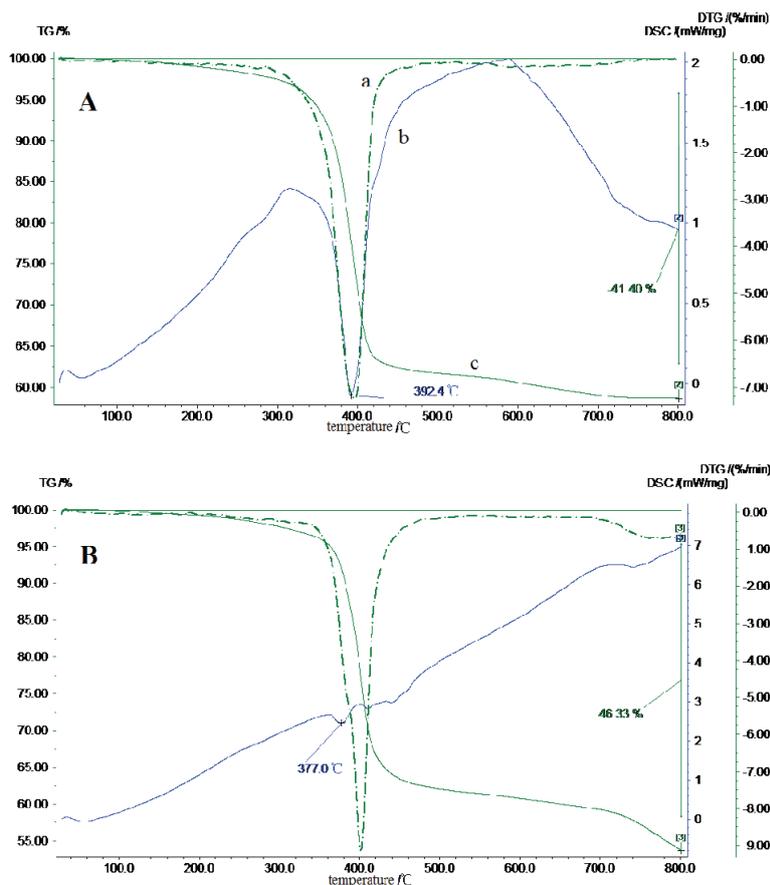


Figure 3. The curves of DTG (curve a), DSC (curve b) and TG (curve c) for the fresh $\text{MnCO}_3/\text{ZnGly}$ catalyst (A) and the same amount of the used $\text{MnCO}_3/\text{ZnGly}$ catalyst after the 13th reuse (B).

catalyst at high temperature. The DSC curves showed only a sharp endothermic peak at 392.4 °C for fresh and at 377.0 °C for used catalyst, which corresponds to decomposition of ZnGly [35]. The TG/DTG/DSC profiles indicated that both fresh and used samples of catalyst were stable up to 300 °C and that structure of $\text{MnCO}_3/\text{ZnGly}$ was not changed during transesterification of soybean oil at lower temperature (165–185 °C).

X-ray diffraction (XRD)

The X-ray diffraction analysis of fresh and 13 times reused $\text{MnCO}_3\text{-ZnGly}$, together with MnCO_3 complex is shown in Figure 4. The fresh catalyst exhibited the typical characteristic peaks of crystalline phases at 2θ 10.9, 17.12, 20.67, 27.53 and 28.6°, which were (JCPDS card No.00-23-1975) assigned to zinc glycerolate ($\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$) [35]. The peaks that correspond to MnCO_3 were also observed, which suggested that MnCO_3 was also the dominant form in fresh catalyst, besides the zinc glycerolate.

Compared to fresh catalyst, the used catalyst also showed the peaks of zinc glycerolate, as well as a single overlapping peak attributed to zinc glyce-

rolate and MnCO_3 implying existence of both constituents of $\text{MnCO}_3/\text{ZnGly}$ catalyst in unchanged form during its repeated use for soybean transesterification. However, new crystal structures were also defined at 2θ 33.1 and 47.5° showing formation of $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$. Existence of such crystal structure was not observed in fresh catalyst sample and it could be a precursor for ZnO formation (Figure 4a). It has been reported in the literature that 593 K is the temperature of $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ decomposition [49]. However, the process of soybean transesterification was realized below 473 K, thus the formation and existence of that structure might also be a reason for catalyst deactivation.

X-ray diffraction analysis of fresh $\text{MnCO}_3/\text{ZnGly}$ sample was performed after its calcinations at 200, 400 and 750 °C. It was found that dominant peaks of ZnGly exist after heating to 200 °C; their intensities were decreased after calcination at 400 °C, and finally they disappeared after calcination at 750 °C. The main peaks of the sample calcined at the highest temperature belong to MnCO_3 . These data are in

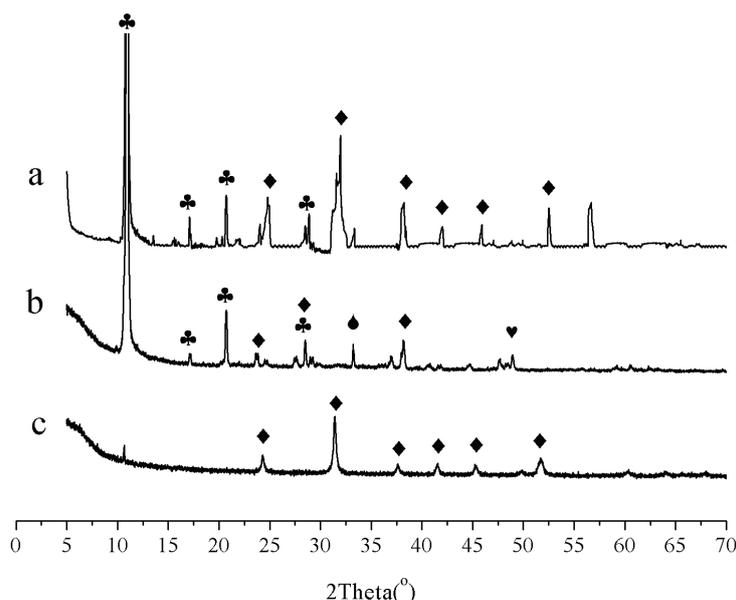


Figure 4. X-Ray diffraction patterns of: a) the fresh $\text{MnCO}_3/\text{ZnGly}$ catalyst, b) the $\text{MnCO}_3/\text{ZnGly}$ catalyst after being reused for 13 cycles, and c) MnCO_3 complex: ZnGly - *; MnCO_3 - \blacklozenge ; ZnO - \blacktriangledown and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ - \bullet .

agreement with the presented TG/DSC analysis of $\text{MnCO}_3/\text{ZnGly}$ sample.

Additional compounds were synthesized and analyzed for better explanation of the observed structure of fresh and used catalyst. The MnCO_3 -complex was prepared by mixing the MnCO_3 and glycerol using the same procedure as described for $\text{MnCO}_3/\text{ZnGly}$ synthesis. The main typical peaks of prepared Mn-complex were ascribed to MnCO_3 indicating that MnCO_3 was stable during the mixing process and that compounds like $\text{MnGly}/\text{ZnGly}$ could not be formed during thermal treatment of MnCO_3/ZnO .

Fourier transform infrared (FT-IR) spectra

FT-IR spectroscopy was used to investigate the functional groups of fresh and 13 times reused catalyst (Figure 5) [32]. The region at $3000\text{--}3500\text{ cm}^{-1}$ corresponds to physically adsorbed water, glycerol O-H stretching mode and hydrogen bonding. The broad band at 3419 cm^{-1} was observed in the fresh (Figure 5a) and used catalyst (Figure 5b). The characteristic band of C-H was present at 2881 cm^{-1} . The band at 1940 cm^{-1} assigned to C-O stretching mode, where the oxygen atom was involved in hydrogen bond, confirming the existence of a zinc glycerolate phase [35], which could be observed at 2495 cm^{-1} (hydrogen bond between two oxygen atoms), 1124 cm^{-1} (C-O stretch), 989 and 651 cm^{-1} [50]. The peak at 1465 cm^{-1} was attributed to the O-H bending mode. Typical peaks at 1419 and 867 cm^{-1} were assigned to CO_3^{2-} vibrations [51] in fresh catalyst (Figure 5a),

while both disappeared in the reused sample of catalyst (Figure 5b). It could be concluded that MnCO_3 exists in the fresh catalyst and maybe it was covered by organics after use of catalyst in soybean transesterification. The FTIR signals of zinc glycerolate revealed that it had not been more affected by the repeated use, which was consistent with other (TG and XRD) analysis of used catalyst.

Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS)

The SEM micrograph of the catalyst samples are shown in Figure 6.

It shows two types of morphologies observed for fresh catalyst: the stacked layers of laminated platelet-like structure in irregular forms (Figure 6a), and a few small spherical particles appeared scattered around the laminates (Figure 6d). The laminated structure was attributed to zinc glycerolate [35], and the globular particles were MnCO_3 . The main morphology of MnCO_3 in ample could be defined as globular form with different dimensions. The 13 times reused catalyst showed the image like plant stems around the laminates, or as stems rooted in some fragmented laminates. Distinct globe structures were not identified (Figure 6c) thus proving that reuse of catalyst led to decrease of MnCO_3 amount in catalyst sample.

Several typical points on the surface of two samples were selected for EDS analysis to determine the content of Zn, Mn, C, O. As shown in Table 1, the

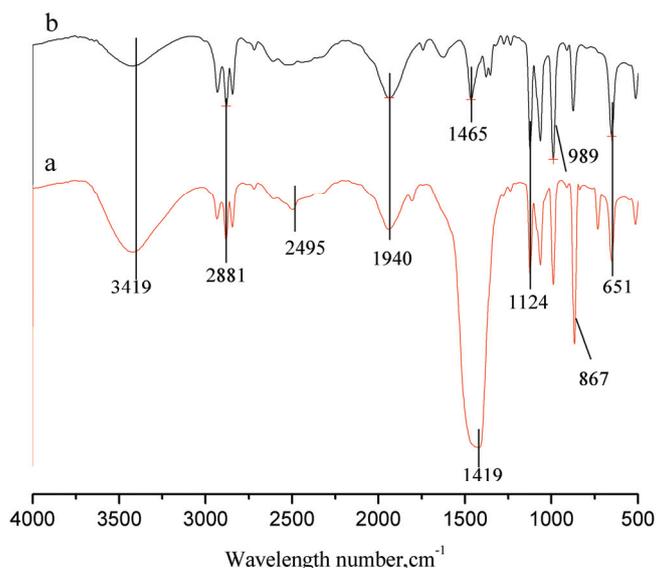


Figure 5. FTIR spectra of: a) the fresh $MnCO_3/ZnGly$ catalyst and b) the used $MnCO_3/ZnGly$ catalyst (13 cycles).

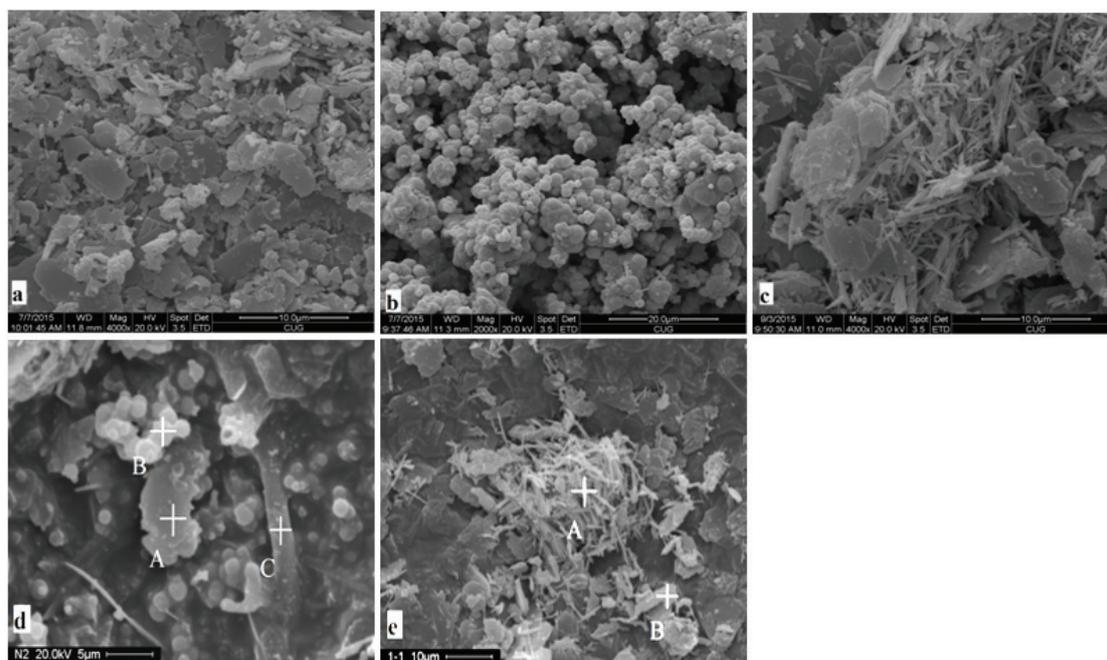


Figure 6. The SEM of the fresh $MnCO_3/ZnGly$ catalyst (a, d), the Mn complex (b) and the $MnCO_3/ZnGly$ catalyst after being reused for 13 times (c, e).

Table 1. EDS analysis of typical surface points signed in Figure 6

Pictures/catalyst	Test point	Element content, at. %			
		Zn	Mn	C	O
Figure 6d "fresh"	A	24.38	04.34	43.44	27.83
	B	10.36	09.72	30.89	49.03
	C	10.17	03.78	54.52	31.53
Figure 6e "reused"	A	08.64	09.67	60.38	21.31
	B	18.93	01.84	64.10	15.13

content of Zn was much higher than Mn in point A and C, which were chosen from the laminated structure (Figure 6d), and indirectly demonstrated that the dominating functional material was ZnGly. Otherwise, the content of Zn was almost equal to Mn in point B, which was similar with point A in Figure 6e. There is not any similar information found which might prove that the higher presence of MnCO_3 existed (Figure 6e). It has to be pointed out that Zn content was 18 times of Mn in point B and that they are very similar in point A (Figure 6e) like point B on Figure 6c. That evidence confirmed that ZnGly was the main constituent in reused catalyst, and that higher contents of C and O could be associated with presence of some organic compounds (e.g. glycerol or other). They were adsorbed on the surface of used catalyst, covering the globular structure of MnCO_3 and suppressing its catalytic activity.

Comparison of $\text{MnCO}_3/\text{ZnGly}$ and MnCO_3/ZnO reusability

Data of TG conversion and FAME yield obtained with $\text{MnCO}_3/\text{ZnGly}$ (13th repeated use), which are shown in Figure 5, and similar data recently reported for MnCO_3/ZnO (18 repeated use) [39] were analyzed using linear relationship to show activity or catalyst life in batch processes. The obtained correlations are:

$$\text{MnCO}_3 / \text{ZnGly} : \text{TG}(\%) = 100 - 0.22N \quad (\text{a})$$

$$\text{FAME}(\%) = 80 - 0.67N \quad (\text{b})$$

$$\text{MnCO}_3 / \text{ZnGly} : \text{TG}(\%) = 97 - 0.26N \quad (\text{c})$$

$$\text{FAME}(\%) = 92 - 0.48N \quad (\text{d})$$

where N is the number of repeated runs in the batch process with the same amount of catalyst or number of catalyst reuse.

Although very similar percentage of TG conversion was observed for both catalysts (coefficient of correlation is 0.22 and 0.26) one can conclude that a smaller decrease of TG conversion could be obtained with $\text{MnCO}_3/\text{ZnGly}$; 100% after the 1st use and about 98% after 10th use of same amount of catalyst compared to effect of MnCO_3/ZnO which were 97% and 94%, respectively. However, the value of FAME yield and its relation to N , the number of catalyst reuse, is not in favor of MnCO_3/Gly catalyst. The values after the first and after the 10th use of MnCO_3/Gly catalyst were 80 and 70%, while certain decrease was also observed for MnCO_3/ZnO but only from 92 to 87%. The main reason for these phenomena lies in fact that glycerolate improve miscibility of oil and methanol [52] and also suppress reaction between DG and MG

and methanol and formation of fatty acid methyl esters or biodiesel. The first phenomenon is positive and leads to higher TG conversion, while the second one increases the amount of MG and DG in complex reaction mixture thus decreasing FAME yield.

CONCLUSION

$\text{MnCO}_3/\text{ZnGly}$ was thermally synthesized from MnCO_3/ZnO and glycerol and used for soybean transesterification with methanol in a batch process. Different working parameters were studied, and showed that temperature, the methanol-to-oil mole ratio, and duration of transesterification mainly determine the rate of the transesterification process. The catalyst exhibited high activity for TG conversion even after the 13th reuse of the same amount without any regeneration. The results of this study showed that $\text{MnCO}_3/\text{ZnGly}$ improves the miscibility of oil and methanol, similarly as observed with Ca-diglyceroxide. This effect enables a high TG conversion to be achieved, but complete conversion of diglycerides and monoglycerides into FAME, expressed as fatty acid methyl esters yield, was gradually decreased after repeated use of $\text{MnCO}_3/\text{ZnGly}$. It is a consequence of dissolving effect of Mn into biodiesel and glycerol phases, which are followed by decreases of surface area, the pore volume and average pore size during catalyst reuse.

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NAUČNI RAD

SINTEZA, KARAKTERIZACIJA I PRIMENA MANGAN-KARBONATA-CINK-GLICEROLATA KAO KATALIZATORA ZA TRANSESTERIFIKACIJU SOJINOG ULJA

Sistem koji se sastoji od mangan-karbonata i cink-glicerolata (ZnGly) je sintetizovan, a zatim, u ovom radu, ispitan kao katalizator za transesterifikaciju sojinog ulja i proizvodnju biodizela. Uzorci MnCO₃/ZnGly katalizatora pre i nakon korišćenja u procesu transesterifikacije su okarakterisani uz pomoć različitih tehnika: određivanjem baznosti, specifične površine prema metodi Brunauer-Emet-Telera (BET), merenjem promene mase uzorka termijskom gravimetrijskom analizom (TGA), ispitivanjem sastava čvrste faze i utvrđivanjem specifičnih elemenata i grupa pomoću rendgenske analize (XRD), Furijeove obrade infracrvene spektroskopije (FT-IR), primenom skanirajuće elektronske mikroskopije (SEM) uz elektronsku disperzionu spektroskopiju (EDS). Analizirani su različiti radni uslovi: temperatura (438–458 K), vreme trajanja transesterifikacije (0–3,5 h), molski odnos metanola i ulja (12:1–36:1) i upotrebljena masa katalizatora (1–5 mas. %), kao i ponovljeno korišćenje i aktivnost iste mase MnCO₃/ZnGly katalizatora. Utvrđeno je da pripremljen MnCO₃/ZnGly pokazuje dobru aktivnost (100% konverziju triacilglicerola, TAG; 81,5% prinos metil-estara masnih kiselina, MEMK) dok je utvrđena 95–100% konverzija TAG i 62–78% prinos MEMK nakon 13 puta ponovljenog korišćenja iste mase katalizatora bez njegove regeneracije. Udeo Mn i Zn u biodizelu i glicerolu analiziran je pomoću atomske absorpcione spektroskopije (ICP-AAS) nakon svakog ponovljenog korišćenja katalizatora.

Ključne reči: mangan-karbonat-cink-glicerolat, biodizel, višestruko korišćenje, stabilnost.