THE SIGNIFICANCE OF TEXTURAL AND STRUCTURAL PROPERTIES OF POTASSIUM LOADED γ -ALUMINA CATALYST ON THE FINAL CATALYTIC EFFICIENCY IN THE TRANSESTERIFICATION OF SUNFLOWER OIL

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The preparation of γ - Al_2O_3 catalyst support by the modified hydrothermal method and synthesis of $\text{Kl}/\gamma\text{-Al}_2\text{O}_3$ catalyst, as well as the investigations of their activities in the reaction of transesterification of sunflower oil were performed in this study. The effect of various process parameters on the transesterification reaction of sunflower oil with methanol and their impacts on the reaction conversions were examined. The $\gamma\text{-Al}_2\text{O}_3$ support and $\text{Kl}/\gamma\text{-Al}_2\text{O}_3$ catalysts were characterized by BET, XRD and SEM methods. The physico-chemical properties (surface, textural, structural and morphological) of the catalyst were correlated with its catalytic efficiency. The obtained results implicate that textural and structural properties of the catalyst and also the catalyst activity in the reaction of transesterification essentially depend on textural and structural properties of the $\gamma\text{-Al}_2\text{O}_3$ support. From the optimization of the process parameters, it was found that the optimal conditions for transesterification reaction are: molar ratio of methanol to oil 12:1; stirring speed 600 rpm; the reflux temperature of methanol; the reaction time 5h; the amount of catalyst in the reaction 3 wt. %.

Keywords: biodiesel, catalytic efficiency, potassium loaded alumina, process parameters

Introduction

In present time, there is the increased requirement for all types of energy. Energy is necessary in order to maintain the development and progress of the humanity [1]. Main sources of energy are all types of fossil fuels, but they are related to problems such as environmental pollution and the effects of greenhouse gases emissions. Due to the increased population, industry, economic growth, and negative effects of fossil fuels consumption, there is a constant need for new and alternative energy resources [2]. Unfortunately, the excessive use of fossil fuels has negative consequences on the environment, so there is a need of finding adequate environmentally acceptable replacements for fossil fuels. Biodiesel is a clean-burning renewable fuel prepared by using natural vegetable oils and/or fats and it can be used for the replacement of fossil fuels. It can be used for diesel-engine without modifications and it is biodegradable, easy handled, has lower toxicity and reduced exhaust emissions comparing to fossil fuels [3]. The reaction of transesterification can be carried out over base or acid catalysed process, depending on the quality and chemical composition of the used oil and/or fat samples [4]. One of the most applied technologies for the biodiesel production is transesterification of vegetable oils [5]. The most widely used industrial method for the commercial production

of biodiesel from vegetable oils is the base-catalyzed transesterification process using KOH or NaOH as the homogeneous catalyst and methanol. Main advantages of the base catalyzed homogeneous transesterification process are high conversions of triglycerides to methyl esters under (relatively) mild reaction conditions and a short reaction time [6]. Regardless of the fact that there are advantages of the homogeneous catalysis for the biodiesel production, a need for complete washing by water and catalyst pre-neutralization by acid, resulting in the production of the additional waste-water, which presents an important environmental concern makes this technology inappropriate. These limitations can be overcome by using a heterogeneous catalyst. Smaller volumes of waste waters produced during the process, much easier separation of products/phases and also the facts that a catalyst can be reused are main advantages of heterogeneous catalytic transesterification [7, 8]. Some of the solid catalysts applied in heterogeneous catalytic transesterification of plant oils are: modified zeolites, hydrotalcites, doped/modified oxides, doped γ -alumina, etc. Most commonly used solid base catalysts are alkali metal oxides and derivatives [9-12], alkaline earth metal oxides and derivatives [13-16], transition metal oxides and derivatives [17, 18], mixed metal oxides and derivatives [19-21].

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Loading of potassium iodide on alumina can lead to a high activity of the catalyst in the transesterification reaction, as it was shown by recent studies [22-24]. Marinkovic et al. [24] have found that the catalysts prepared by loading 37 wt.% of KI onto Al_2O_3 and calcinated at 1043 K for 3h resulted in the highest conversions of 99.99% to fatty acids methyl-esters under relatively mild conditions [24].

The subject of this work was to synthesize a (new) heterogeneous base catalyst by using the improved, modified hydrothermal method; it is expected that the catalyst should be characterized with advantageous physico-chemical properties, and it is planned to test its catalytic efficiency in the reaction of biodiesel synthesis. The aim of this study was to determine whether the physico-chemical properties of the catalyst support and the catalyst affect the final catalytic performance of the catalyst in the transesterification reaction of sunflower oil with methanol, and additionally to determine the influence of selected process parameters/reaction conditions on the conversion of sunflower oil to methyl-esters. For this purpose, the catalyst support was synthesized by the modified hydrothermal method of the synthesis in order to obtain the nano-sized well-crystallized material, as well as the final catalyst.

Experimental

Catalyst preparation

Preparation of nano-crystalline alumina support by the modified hydrothermal method

In the present work, modified hydrothermal method of the synthesis of nano-crystalline alumina was conducted in order to obtain a well-crystallized material [25]. A precursor solution was prepared by dissolving the adequate amount of aluminum isopropoxide (Aldrich Co., purity $\geq 98\%$) in 2-propanol (Aldrich Co., 99.5%) at the temperature of 50 °C in an ultrasonic bath. The precursor solution was mixed with the solution made from the appropriate volumes of 2-propanol and water. The mixing of the solutions was performed drop by drop with vigorous stirring continuously for 1 h on a magnetic stirrer, and pH value was maintained at 12.0 with 0.1 M NaOH solution. The resulting gel was then subjected to the hydrothermal treatment, which was carried out at 200 °C for 2 h in a 150 ml stainless steel autoclave lined with Teflon. Inside the autoclave, the pressure was the autogenous water vapor pressure. The precipitate was then washed several times with the solution consisting of deionized water and 2-propanol (1 : 1 volume ratio) and dried at 120 °C for 3 h. Two samples (*i.e.* the support and promoted catalyst) were separated and calcinated at 750 °C. The calcinations of the catalyst samples were carried out by thermal treating at 750 °C with the temperature rate of 10 °C/min for 3 h.

Preparation of potassium iodide $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts

The KI/ Al_2O_3 catalysts were prepared by incipient wet-impregnation of $\gamma\text{-Al}_2\text{O}_3$ with desired amounts of potas-

sium iodide aqueous solutions to the nominal amount of KI 37 wt.%. This procedure was conducted for 2 h. After that, the catalysts were dried at 120 °C for 3 h, and then the catalysts were activated by heating at 770 °C with the temperature rate of 10 °C/min for 3 h [24].

Catalyst characterization

Brunauer-Emmett-Teller (BET) surface area was calculated using the BET method based on the adsorption/desorption of liquid nitrogen in the range of relative pressures $p/p_0=0.05\text{-}0.25$. Pore volume was calculated from the volume adsorbed at the relative pressure of 0.99 by using the desorption branch of isotherms, by Barrett-Joyner-Halenda (BJH) method. The results concerning textural properties of the catalysts were obtained by using a Micromeritics ASAP 2010 instrument [24].

X-Ray diffraction (XRD) measurements were conducted on Philips AMD 1011 X-ray diffractometer with a radiation source Cu K $_{\alpha}$ ($\lambda = 0.154$ nm) at 40 kV and 50 mA. Data were collected over the 2θ range 10 – 80 °C with the step size of 0.017° at a scanning speed of 5° min $^{-1}$ [24].

Scanning electron microscope SEM JOEL 101 with an accelerating voltage of 20 kV was used to obtain SEM micrograms of the catalysts samples [24].

Transesterification reaction

A commercial edible grade sunflower oil ("Sunce") was obtained from the local market. According to GC-MS analysis (Shimadzu DC-9A), the fatty acid contents consisted of linoleic acid 61.21%, oleic acid 19.27%, and palmitic acid 9.19%, stearic acid 6.43%, and linoleic acid 5.9%. The acid number of the sunflower oil was determined as less than 0.1 mg KOH/g, and the average molecular weight was 880 g/mol [24]. A 250 mL one-necked glass flask equipped with a water cooled condenser and a magnetic stirrer was charged with the adequate volume of sunflower oil, different volumes, exactly molar ratios of anhydrous (from 6:1 to 21:1) and various amounts of the catalyst, *i.e.* 1.0 - 5.0 wt.%. Each mixture was stirred at various mixing speeds, *i.e.* 300-900 rpm and the reflux temperature of methanol (65 °C) for the required reaction time of (5 h). After the separation of reaction products, the product determination was conducted by ^1H NMR spectroscopy (Bruker, 400MHz). A reaction mixture was separated from the heterogeneous catalyst by filtration and dissolved in chlorophorm. Afterwards, the solution was added to a separation funnel, and the mixture was washed with water several times. The organic phase was separated by a decantation, dried with anhydrous magnesium sulfate and submitted to NMR analysis in CDCl_3 using TMS as an internal standard [24].

The conversion of the sunflower oil to the mixture of methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of methyl esters) and 2.30 ppm (-carbon CH_2 groups of all fatty acid derivatives) according to previously reported data [24,29].

Results and discussion

Catalyst characterization

Textural properties

In Table 1, selected textural properties of the γ - Al_2O_3 catalyst support prepared by the modified hydrothermal synthesis method and KI/ Al_2O_3 -based catalyst samples are presented. Based on the results regarding the obtained BET surface areas and pore volumes that were obtained in this study, and comparing them with the previously conducted research [24], it can be seen that

there is a significant relationship between the catalytic efficiency in the transesterification reaction of sunflower oil and textural properties of the heterogeneous KI/ Al_2O_3 -based catalyst. It is presumed that the decreased catalytic activity is in line with the reduction of the specific surface area in the case of unmodified nano-crystalline alumina. It can also be observed that there is a connection between textural properties of the catalyst support and the catalyst, and the preparation method used and the applied calcinations temperatures [24].

Table 1. Textural properties of the catalyst samples

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	BJH cumulative desorption pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter (nm)
γ - Al_2O_3	181.75	0.38	6.32
KI/ Al_2O_3	7.59	0.18	32.95

In comparison with the results of other authors [23], the determined BET surface areas of the analyzed KI/ Al_2O_3 -based catalyst sample and γ - Al_2O_3 support possess somewhat lower values of the BET surface areas, and greater values of average pore diameters. Such differences may be related to a different origin of the γ - Al_2O_3 support and the used precursors and the preparation procedure, as well as calcination temperatures applied for the final KI/ Al_2O_3 catalyst preparation in different researches.

Based on presented results, it is evident that after impregnation of KI onto the γ - Al_2O_3 support, a significant reduction of the BET surface area occurred. In addition, a slighter decrease in the pore volume values between the support and the corresponding catalyst after the introduction of KI can also be noted. These facts may be explained by the potential formation of a deposit of KI-based compound onto the support surface, thus affecting the reduction of the pore volume. This assumption is similar to the previously published one [23,24].

Because of the presence of meso-pores in the KI/ Al_2O_3 catalyst, no internal diffusion restrictions for a transport of reactants (ex. methyl-oleate molecule) and/or transesterification products can be expected during the reaction-run, similarly to the previously reported opinions [24,30].

Structural properties

In Figure 1., the XRD patterns of the γ - Al_2O_3 support and the corresponding KI/ Al_2O_3 catalyst are given. Similarly to the previously published results [24], and the results reported by other authors in literature [23], the XRD patterns of the γ - Al_2O_3 support show diffraction peaks of a smaller intensity at $2\theta = 20.5^\circ$; 37.0° ; 46.0° and 66.7° , which are appropriate to different phases: the amorphous phase, tetragonal and mono-phase structure. The fact that the peaks are not clearly registered at XRD patterns of γ - Al_2O_3 support leads to the conclusion of the potential amorphous structure of the gained material even

after the applied calcination temperature of 750°C .

Some differences can be observed both in the intensity of the XRD peaks and their broadening in comparisons between KI/ Al_2O_3 and γ - Al_2O_3 samples. Probably, these peaks in the case of the support sample are broadened due to potential crystal defects and deformations. Structural differences of various γ - Al_2O_3 supports obtained by varied methods of syntheses lead to further differences in structural properties of the obtained KI/ Al_2O_3 catalysts. Impregnation of KI onto γ - Al_2O_3 support led to the formation of sharp and clearly defined intense XRD lines that can be related to the well-crystallized material. KI residual crystals were determined by additional diffraction lines which appeared at: $2\theta = 21^\circ$; 25° and 35° . Additional diffraction lines which appeared at $2\theta = 51^\circ$; 56° ; 69° and 76° are assigned to the formation of a new potential phase, K_2O species. The intermediate structure K_3AlI_6 was characterized by characteristic peaks at $2\theta = 58.0^\circ$ and 64° . Alkaline iodine-based compounds, and especially K_2O species, are catalytically active in the transesterification reaction, as previously claimed by groups of authors [22-24]. Moreover, the formation of K_2O species and intermediate structure K_3AlI_6 onto the KI/ Al_2O_3 catalyst could be additionally correlated with the increase in the number of catalytically active basic sites that are essential in the biodiesel production. From comparisons of structural properties of the catalyst in this study and the previous one [24], a decrease in the relative intensity of the peaks of the catalyst active phase(s) can be noted. All these data together lead to the observation that final catalytic performance of the KI/ Al_2O_3 catalyst significantly depends on the structural properties of the catalyst, as well as final structural properties of the catalyst highly depend on the structural properties of the γ - Al_2O_3 support [24, 31].

Figure 1. XRD patterns of $\gamma\text{-Al}_2\text{O}_3$ and $\text{KI}/\text{Al}_2\text{O}_3$ samples

(a)

(b)

Figure 2. SEM micrographs of the catalyst samples: a) $\gamma\text{-Al}_2\text{O}_3$, b) $\text{KI}/\text{Al}_2\text{O}_3$

Morphological properties

SEM micrographs of the $\gamma\text{-Al}_2\text{O}_3$ support and the corresponding $\text{KI}/\text{Al}_2\text{O}_3$ catalyst are shown in Figure 2. and they represent morphological properties of the catalyst $\text{KI}/\text{Al}_2\text{O}_3$ and the support. On the material surface of the $\gamma\text{-Al}_2\text{O}_3$ support, there is an insignificant number of primary particles that are up to 100 nm in size, and numerous secondary particles distributed as aggregates char-

acterized with the diameter from 0.5 to 1.5 μm (Figure 2a). After loading of the dopant (KI), the bulk morphology of the $\text{KI}/\text{Al}_2\text{O}_3$ catalyst stayed globally unchanged comparing to the alumina support. Thermal treatments at a relatively high temperature of 770 $^\circ\text{C}$ and the incorporation of the dopant in the corresponding $\text{KI}/\text{Al}_2\text{O}_3$ catalyst led to the additional agglomeration of materials particles (Figure 2b)). These findings of the occurred sintering process during thermal treatments are consistent with the studies of other authors [33] and a previously conducted research [24]. The obtained results are consistent with the textural properties obtained by using the BET method (Table 1) and with the XRD data (Figure 1). Despite a significant reduction of the BET specific surface in the case of the $\text{KI}/\text{Al}_2\text{O}_3$ catalyst caused by a sintering process, the other textural properties such as pore volume and pore diameter remained as acceptable values in the case of the $\text{KI}/\text{Al}_2\text{O}_3$ catalyst for application as a heterogeneous catalyst in the transesterification of the sunflower oil (Table 1).

Biodiesel production

Influence of process parameters on the conversion of reactants to the main product

The influence of molar ratio (methanol to sunflower oil) on the conversion of reactants in the transesterification reaction is presented in Figure 3. As it was previously reported [24, 34], the molar ratio of methanol to sunflower oil has been reported as significant parameter which influenced the conversion of the reactants to the final product(s) in the biodiesel production. In order to shift the reaction equilibrium towards the final products, higher molar ratios than the stoichiometrically determined (3:1 = methanol:sunflower oil) were tested. As expected, an excess of methanol increased conversions of the reactants up to the molar ratio of 12:1, which is adequate to the previously published results of other authors [22,23]. The fact that this excess of methanol up to the molar ratio of 12:1 increased conversions of the reactants can be explained by diminishing of different limitations in the catalyst bulk and inside the reaction mixture.

Figure 3. Influence of the molar ratio (methanol to sunflower oil) on the conversion of the reactants

Figure 4. Influence of the catalyst loading on the conversion of the reactants

Different catalyst loadings between 1 and 5 wt.% were tested in the transesterification reaction of the sunflower oil with methanol. As presented, the use of larger catalyst loadings in the reaction mixture caused higher conversions to products. This can be explained by the fact that greater amounts of catalysts provided a greater number of catalytically active sites and more effective contacts between reactants and catalytically active sites. In addition, a further increase of the catalyst loadings results in shortening of the reaction time in order to achieve the same conversions.

The influence of the stirring speed in the reaction is shown in Figure 5. The increase in the reaction stirring speed up to 600 rpm results in the increase of conversions up to the maximum conversion and furthermore, the increase in the reaction stirring speed (greater than 600 rpm) has a somewhat negative effect on the conversions of the reactants. This slightly negative effect may occur due to the reversible effect of thermodynamic equilibrium in the reaction mixture on the products.

Figure 5. Influence of the stirring speed on the conversion of the reactants

In contrast to the results of other authors [22,23] and previously published researches [24], in this paper the obtained results indicate a lower catalytic activity of the alumina-supported potassium iodide catalyst in the

transesterification reaction of sunflower oil and methanol. This lower catalytic activity of the catalyst can be in line with a different origin of the support and dissimilar preparation treatments among the mentioned previously published results. Despite the fact that a relatively high calcination temperature was applied in order to gain the adequate crystal phase(s) of the alumina support, based on the previously published temperatures of crystal phase transitions [35], the resulting catalyst showed slightly different structural properties in terms of reducing the total amount of the active phase(s). Additionally, the authors of this investigation also suggest that textural and structural properties of the support and catalyst have a decisive influence on the catalytic performance of the final KI/Al₂O₃ catalyst in the transesterification reaction of sunflower oil and methanol.

Conclusions

Potassium iodide impregnated γ -Al₂O₃ showed to be an active catalyst in the transesterification of sunflower oil with methanol under relatively mild reaction conditions, standard operating temperature and atmospheric pressure, molar ratios of reactants (12:1), relatively short contact time (5 h), and reasonably small catalyst loadings (3 wt.%).

The results of the experiments showed that the preferred properties of the KI/Al₂O₃ catalyst such as the presence of desirable crystal phases of K₂O, K₃AlI₆ and γ -Al₂O₃, the acceptable pore volume and average pore diameter, the absence of external and internal diffusion restrictions, and the complete amount of surface basic sites all together may depend on structural and textural properties of the γ -Al₂O₃ catalyst support. Structural and textural properties of the catalyst have a vital impact on the final catalytic efficiency of the KI/Al₂O₃ catalyst in the transesterification reaction of the plant oil with methanol. In addition, it was observed that process parameters, as well as physico-chemical properties of the catalyst have a great impact on the conversion of the biodiesel product in the transesterification reaction of sunflower oil over potassium iodide promoted γ -Al₂O₃.

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Izvod

ZNAČAJ TEKSTURALNIH I STRUKTURALNIH SVOJSTAVA KALIJUMOM -PROMOTOVANOG γ -ALUMINA KATALIZATORA NA KONAČNU KATALITIČKU EFIKASNOST U TRANSESTERIFIKACIJI SUNCOKRETOVOG ULJA

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Priprema γ - Al_2O_3 nosača katalizatora modifikovanom hidrotermalnom metodom i sinteza KI/γ - Al_2O_3 katalizatora, kao i određivanje njihove aktivnosti u reakciji transesterifikacije suncokretovog ulja izvedeni su u ovom radu. Efekat različitih procesnih parametara na transesterifikaciju suncokretovog ulja i metanola i njihov uticaj na konverziju je ispitan. Nosač katalizatora γ - Al_2O_3 i katalizator KI/γ - Al_2O_3 su karakterisani BET, XRD i SEM instrumentalnim metodama. Fizičko-hemijska svojstva (površina, teksturalna, strukturalna i morfološka) katalizatora dovedena su u korelaciju sa njihovom katalitičkom efikasnošću. Dobijeni rezultati impliciraju da teksturalna i strukturalna svojstva katalizatora i katalitička aktivnost bitno zavise od teksturalnih i strukturalnih svojstava γ - Al_2O_3 nosača katalizatora. Optimizacijom procesnih parametara, utvrđeno je da su optimalni uslovi za reakciju transesterifikacije sledeći: molarni odnos metanola prema ulju 12:1; brzina mešanja 600 rpm; refluks temperatura metanola; vreme reakcije 5 h; maseni udeo katalizatora u reakciji 3%.

KLjučne reči: biodizel, katalitička efikasnost, kalijumom dopirana alumina, procesni parametri