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Synthesis of biodiesel from sunflower oil over potassium loaded alumina as heterogeneous catalyst: The effect of process parameters

Milos M. Marinkovic, Nikola I. Stojkovic, Marija B. Vasic, Radomir B. Ljupkovic, Sofija M. Rancic, Boban R. Spalovic, Aleksandra R. Zarubica*

Department of Chemistry, Faculty of Science and Mathematics, University of Nis,
Visegradska 33, 18000 Nis, Serbia

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*Corresponding author: Prof. Dr. A. Zarubica, e-mail: zarubica2000@yahoo.com; phone: +381 63 11 18 551; fax: +381 18 533 014

Abstract

Heterogeneous catalysis is in recent focus of research for biodiesel production from vegetable oils because of advantages such as easy separation and reuse of catalysts, although homogeneous catalysis is most commonly used method. The aim of this study was preparation of γ-Al_2O_3 support by modified sol-gel procedure, synthesis of the KI/Al_2O_3 catalyst and testing its activity in the transesterification of sunflower oil with methanol. Influences of different process parameters on conversion of sunflower oil to methyl esters were examined. The gained results implicate that the potassium iodide incorporation into/onto the structure of γ-Al_2O_3 significantly influences textural and structural properties of the catalyst. Additionally, the catalyst basic strength is increased and all together those properties are positively affecting the activity of the catalyst in the reaction of transesterification of sunflower oil with methanol. The impregnation of alumina with potassium iodide resulted in the additional formation of basic catalytically active sites. The surface properties of the catalyst have an essential impact on its catalytic performance. Under relatively mild process conditions and relatively short reaction time, the usage of the KI/Al_2O_3 catalyst resulted in very high conversion to fatty acids methyl esters (*i.e.* 99.99 %).

Keywords: biodiesel, heterogeneous catalyst, potassium loaded alumina, process parameters, sunflower oil

INTRODUCTION

Nowadays, energy demands of modern society are continuously increasing. It is known that the quantities of fossil fuels are limited, and taking in mind that the demands for them are constantly growing, it is necessary to replace them with alternative renewable energy sources. The increasing requirements for fossil and/or new alternative fuels in all sectors of human life (*i.e.* transportation, industrial processes, power generation) cause environmental concerns such as more extensive greenhouse gases emissions. Recently, biodiesel has been considered as suitable potential solution for a diesel fuel substitution. The main benefits of using biodiesel are that it is non-toxic, biodegradable; it produces reduced volumes of harmful gases emissions and can be used without modifying existing (motor) engines [1, 2]. Carbon dioxide and total CO_x gases emissions produced from the use of biodiesel are reduced for 78 % on a life-cycle basis when compared to conventional diesel fuel [3]. Moreover, the improvements on total engine exhaust emissions have also been observed, *i.e.* combustion of neat biodiesel decreases carbon monoxide (CO) emissions for 46.7 %, unburned hydrocarbons 45.2 % and particulate matter emissions 66.7 % [4].

Transesterification of vegetable oils is most commonly used technology for biodiesel production [5]. Base catalyzed transesterification process using KOH or NaOH as the homogeneous catalyst and methanol is most widely used industrial method for the commercial production of biodiesel from vegetable oils. High conversions to methyl esters, (relatively) mild reaction conditions and short reaction time are the main advantages of the process [6]. However, the need for complete washing by water and catalyst pre-neutralization by acid, resulting in the production of additional waste water, presents an important environmental concern and also increases the cost of the process. Heterogeneous catalyst can be used to avoid these limitations. The key advantages of heterogeneous catalytic transesterification are: the catalyst can be reused, separation of biodiesel from glycerol is much easier and there are smaller volumes of waste waters produced during the process [7, 8]. A great variety of solid catalysts in heterogeneous catalytic transesterification of vegetable oils have been used. These include modified zeolites, hydrotalcites, doped/modified oxides, doped γ-alumina, etc. Most of these catalysts are alkali and/or alkaline oxides supported over large surface area characterized supports. Solid basic catalysts are more active than solid acid catalysts, similar to their homogeneous counterparts.

Some of the most commonly used solid base catalysts are alkali metal oxides and derivatives [9-12], alkaline earth metal oxides and derivatives [13-15], transition metal oxides and derivatives [16, 17], mixed metal oxides and derivatives [18-20].

Vujicic et al. [15] has investigated CaO as a heterogeneous catalyst and its effect in the transesterification reaction of sunflower oil. Experiments were carried out using 1 wt. % of the catalyst loading and methanol to oil molar ratio 6 to 1 as constant parameters at 200 rpm in a commercial bench stirred tank reactor. Methyl-ester yields were reported as a function of reaction time (1.5–5.5 h), pressure (1–15 bar), and temperature (60–120 °C). Maximum methyl esters yield (91 %) was achieved at the process temperature of 100 °C, while pressure had a positive impact up to 10 bars at 80 °C. The catalyst activation in air has leading to the formation of strong basic sites as it was found to occur at 900 °C.

Xie et al. [21] have reported that catalysts, which were prepared by loading potassium on alumina were strong solid-base catalysts and active in the transesterification of soybean oil with methanol. The catalyst prepared by loading 35 wt. % of KNO_3 on Al_2O_3 and calcinated at 773 K for 5 h, showed a best performance in this reaction. The highest conversion of 87 % has been achieved when reaction was carried out at reflux of methanol, with a molar ratio of methanol to soybean oil of 15 : 1, and a catalyst amount 6.5 wt. % after 7 h of the reaction run.

Recent studies show that loading of potassium iodide on alumina can lead to even higher activity of catalyst in transesterification reaction [22, 23]. Xie et al. [22] have reported that catalysts, which were prepared by loading potassium iodide on alumina were highly active in the transesterification of soybean oil with methanol. The catalyst prepared by loading 35 wt. % of KI on Al_2O_3 and calcinated at 773 K for 3 h, gave the highest basicity and the best catalytic activity in this reaction. The highest conversion of 96 % has been achieved when reaction was carried out at reflux of methanol, with a molar ratio of methanol to soybean oil, 15 : 1, and a catalyst amount 2.5 wt. % after 8 h of the reaction run [22].

Evangelista et al. [23] have reported that catalyst, which was prepared by loading potassium iodide on alumina was active in the transesterification of rice bran oil with methanol. The catalyst was prepared by loading 35 wt. % of KI on Al_2O_3 and calcinated at 773 K for 3 h. The highest conversion of 95.2 % has been achieved when reaction was carried out at reflux of methanol, with a molar ratio of methanol to rice bran oil of 15 : 1, and a catalyst amount 5 wt. % after 8 h of the reaction run [23].

The aim of this work is to synthesize the KI/Al_2O_3 catalyst and test it in the transesterification of sunflower oil with methanol. A wide range of reaction conditions were tested in order to optimize the process and obtain the highest potential conversions to methyl esters.

To the best of our knowledge, there is no literature data concerning the identical preparation and activation procedure of the solid catalyst based on potassium iodide doped γ-alumina, then the same amount of the dopant used onto/into the γ-alumina support, and no totally equal process parameters applied. Therefore, there are no the same results on the topic in the scientific literature regarding similar catalytic systems in the process of biodiesel production.

The authors believe/suggest that the improved preparation procedures of the catalyst and the support are used, in addition the thermal activation of the support and catalyst is optimized in this investigation, and furthermore the process parameters are optimized during the experimental process performed. Additionally, physico-chemical properties of the catalysts as well as support are improved by improving the preparation procedure and activation treatment applied.

EXPERIMENTAL

Catalyst preparation

Preparation of nano-crystalline support

Synthesis of nano-crystalline alumina was conducted using somewhat modified sol-gel method [24]. During preparation procedure of the catalyst support, the adequate amount of aluminum isopropoxide (Aldrich Co., purity ≥ 98 %) was dissolved in 2-propanol (Aldrich Co., 99.5 %) at temperature of 50°C in ultrasonic bath. This solution was mixed with a solution made from the appropriate volumes of 2-propanol and water. The mixing of solutions was performed drop by drop on magnetic stirrer for 2 h. The aging of sol was conveyed for 2 h at 50°C and pH value was maintained at 12.0 with 0.1 M NaOH solution. The precipitate was washed several times with a 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 770°C. The calcinations of catalysts samples were carried out by thermal treating at 770°C with a temperature rate of 10 °C/min for 3 h.

Preparation of potassium iodide γ-Al_2O_3-supported catalysts

The KI/Al_2O_3 catalysts were prepared by incipient wet impregnation of **γ-**Al_2O_3 with desired amounts of potassium iodide aqueous solutions to 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 a temperature rate of 10 °C/min for 3 h.

Catalyst characterization

Surface properties of the catalysts, *i.e.* surface basicity of the catalyst samples were determined by using Hammett indicators [25-27]. The following Hammett indicators were used: bromothymol Blue (H_0-=7.2), phenolphthalein (H_0-=9.8), 2.4-dinitroamine (H_0-=15.0) and 4-nitroaniline (H_0-=18.4). In order to evaluate the strength of solid basic catalytically active sites, the additional FTIR analysis after adsorption of phenol was done. KBr pellet technique was used to prepare samples for FTIR spectra measurements, which were recorded on a Win Bomem Easy spectrometer with 2 cm^{-1} resolution. The scanning range was between 4000 and 400 cm^{-1}.

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/po*=0.05-0.25. Pore volume was calculated from volume adsorbed at the relative pressure of 0.99 by using desorption branch of isotherms by Barrett-Joyner-Halenda (BJH) method. The results concerning textural properties of the catalysts were obtained using a Micromeritics ASAP 2010 instrument.

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

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

Transesterification reaction

Commercial edible grade sunflower oil (“Sunce”) was obtained from a 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. A 250 mL one-necked glass flask equipped with a water cooled condenser and a magnetic stirrer was charged with adequate volume of sunflower oil, different volumes, exactly molar ratios of anhydrous methanol (from 1 : 6 to 1 : 21) and various amounts of catalyst, *i.e.* 1.0 - 3.0 wt. % of freshly prepared catalyst. Each mixture was stirred vigorously at reflux temperature of methanol for the required reaction time (5.5 h). The progress of the reaction run was monitored by ^{1}H NMR spectroscopy (Bruker, 400 MHz). The organic phase was separated by decantation, dried with anhydrous sodium sulfate and submitted to NMR analysis in $CDCl_3$ using TMS as internal standard. The conversion of the sunflower oil to a 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 [28].

RESULTS AND DISCUSSION

Catalyst characterization

Textural properties

The textural properties of the KI/Al_2O_3-based catalyst sample and γ-Al_2O_3 used as a support (BET surface area, BJH cumulative desorption pore volume and average pore diameter) are shown in Table 1. These textural properties could be important characteristics of the heterogeneous KI/Al_2O_3-based catalyst because they can affect the catalytic efficiency in the transesterification of sunflower oil. Such catalytic characteristics may also be in correlation with the precursor type of the solid state catalyst (KI/Al_2O_3), preparation method used and the applied calcinations treatments.

Table 1.

The determined BET surface areas of the analyzed KI/Al_2O_3-based catalyst sample and γ-Al_2O_3 support possess lower values of the BET surface areas and greater values of pore volumes and average pore diameters in comparison with the results of other authors [23]. These differences can be related to different origin of the final KI/Al_2O_3 catalyst regarding the used precursors and preparation procedure/calcination temperatures applied, despite the comparable/same gross chemical composition.

Figure 1.

The results show that the KI/Al_2O_3 catalyst sample possesses the BET surface area 9.86 m^2/g and an average pore diameter of 33.60 nm, while the BET surface area of γ-Al_2O_3 support is 196.82 m^2/g. 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, it is also observed a decreasing in the pore volume values between support and corresponding catalyst. These facts may be explained with potential formation of a layer or deposit of KI-based compound/K-based intermediate onto support surface, thus, affecting the reduction of the pore volume, probably of smaller pores in size. This assumption is similar to the one reported earlier [23]. The N_2 adsorption/desorption isotherms of the KI/Al_2O_3 catalyst showed a typical *s*-shape behavior of IV-type with a type-H1 of hysteresis loop that indicated the existence of meso-pores in the catalytic material (Fig 1). The pore system is in the meso-pores range between bimodal distributed pores characterized with maxima in pore size between 3-6 nm and 30-40 nm with an average pore diameter around 32 nm in size according to the BJH desorption isotherms. It is also possible that pores of smaller diameter (Table 1, Fig 1.) were present alongside of larger pores. This is based on the registered bimodal type of pore size distribution in the case of KI/Al_2O_3 catalyst. The average pore diameter of the KI/Al_2O_3 catalyst (more than ten times greater than 2.5 nm, Table 1.) may be important because of supporting effective process of mass transfer of triglycerides (namely, around 2.5 nm is methyl-oleate molecule in size, [29]) during the catalytic run of reactants conversion.

Structural properties

The XRD patterns of the catalyst KI/Al_2O_3 and corresponding γ-Al_2O_3 support are given in Fig 2. The XRD patterns of γ-Al_2O_3 (curve 1 in Fig. 2.) show diffraction peaks of smaller intensity at 2θ = 20.5°; 37.0°; 46.0° and 66.7°, which are appropriate to its amorphous phase, tetragonal and mono-phase structure similarly to the results reported by other authors in literature [23]. Especially, diffraction peaks (2θ = 37.0°; 46.0° and 66.7°) are assigned to the amorphous Al_2O_3 similarly to the XRD-results published earlier [22]. No clearly defined diffraction peak is registered at XRD patterns of Al_2O_3, however, several shoulders are detected, which are typical for the amorphous phase. The impregnation of KI onto the support has caused the formation of catalyst characterized with higher structure order. Grafting of KI into/onto γ-Al_2O_3 support (curve 2 in Fig. 2.) has led to the formation of sharp/clearly defined intense XRD lines that can be related to well crystallize material. In the case of KI/Al_2O_3 catalyst sample, additional diffraction lines, which appeared at 2θ = 21°; 25° and 35° ascribed to KI residual crystals were determined. A new phase was formed characteristic for K_2O species, which are demonstrated by typical diffraction peaks at 2θ = 51°; 56°; 69° and 76°. The formation of an intermediate structure K_3AlJ_6 was characterized by the peaks at 2θ = 58.0° and 64°. Different research groups [22, 23] have already claimed that alkaline iodine-based compounds and also K_2O species are catalytically active in transesterification reaction. Moreover, it is similarly reported that a genesis of Al-O-K groups on the catalyst surface/bulk as a result of strong metal-support interaction (MSI) may play a role of catalytically active sites in the transesterification reaction of plant oil, *i.e.* sunflower oil with methanol [22, 23]. The formation of K_2O species onto the KI/Al_2O_3 catalyst as well as the increase of the total mass fraction of K_2O species in the catalyst could be correlated with an increase in the number of catalytically active basic sites. All these together may be in line with the increase of total Hammett basicity of the catalyst. It is expected that higher Hammett basicity would cause higher catalytic activity.

Figure 2.

Onto catalyst surface (KI/Al_2O_3), there are many potential crystal defects and/or oxygen vacancies, therefore, the impregnation and dispersion of alkaline iodine-based compounds onto γ-alumina is in line with strong metal/salt-support interaction, MSI [30]. It is possible that after incorporation of KI, the KI and especially K^+-ion can be inserted into oxygen vacancies of alumina directly accelerating a decomposition of KI to form basic sites in the activation process, a phenomenon, which results in surface enrichment with basic species (*i.e.* pottasium-based) that can be considered as active sites for base-catalyzed reactions such as transesterification of sunflower oil.

Surface properties

The FTIR spectra of the catalyst KI/Al_2O_3 and support γ-Al_2O_3 are shown in Fig 3. This investigation was carried out to determine the basic/surface nature/properties of the KI/Al_2O_3 catalyst, an important catalytic feature for the transesterification of sunflower oil.

Figure 3.

The intensive broad vibration bands in the region 3400-3480 cm^{-1} (*i.e.* at approximately 3440 cm^{-1}) in both samples are attributed to OH-groups directly attached to the alumina. Moreover, broad bands at around 3480-3500 cm^{-1} could be also assigned to the stretching vibrations of Al-O-K groups, which is additional finding of the strong MSI [31–33]. Additionally, physically adsorbed water on the solid catalyst was observed and represented by bending mode of δOH group at around 1638 cm^{-1} [34]. The analysis of the catalyst KI/Al_2O_3 surface showed two additional bands at 1540 and 1410 cm^{-1} assigned to carbonates [35, 36]. The existence of potassium carbonates onto the KI/Al_2O_3 catalyst can be explained by the reaction of K_2O and CO_2 from the air during calcination activation procedure. K^+-ions could replace the protons of isolated hydroxyl groups forming Al-O-K groups during the activation process on the surface of totally hydroxylated alumina [37]. These groups are probably considered as active basic species/sites of the KI/Al_2O_3 catalyst. The authors suggest that K_2O derived from KI as well as the surface Al-O-K groups are probably the main base catalytically active sites in transesterification of sunflower oil with methanol over KI/Al_2O_3.

Total Hammett basicity

The basic strengths of the γ-Al_2O_3 support and catalyst modified with KI were evaluated by using Hammett indicators (Table 2). Particularly, the γ-Al_2O_3 support possesses the weakest basic strength in the range lower than 7.2 ($H° < 7.2$), exhibiting no catalytic activity (Table 2). The introduction of KI into/onto alumina support could cause the basic strength H° in the range from 15.0 to 18.4 (Table 2). The catalysts samples characterized with H° of their surface in the range from 15.0 to 18.4 are determined as strong solid bases according to Tanabe's definition [38].

Table 2.

It seems that expressed very high catalytic activity of the KI/Al_2O_3 catalyst is directly related to its surface basic strength. Higher surface basic strength resulted with higher conversions to biodiesel/final product in transesterification process. When potassium iodide was loaded onto alumina and catalyst material activated at high temperature, such impregnated KI/Al_2O_3 catalyst, showed extremely high catalytic activity (Table 2).

Morphological properties

SEM images that represent morphological properties of the catalyst KI/Al_2O_3 and the support are shown in Fig. 4. There is insignificant number of primary particles of the γ-Al_2O_3 support that are up to 100 nm in size on the material surface, and numerous secondary particles distributed as aggregates characterized with diameter from 0.3 to 1.9 µm (Fig. 4a)). The bulk morphology of the KI/Al_2O_3 catalyst stayed globally unchanged after loading of dopant (KI) into bare alumina support. Moreover, after calcination and activation treatments of the doped catalyst based on KI/Al_2O_3 at relatively high temperature 750 °C, these thermal treatments led to additional agglomeration of materials particles (Fig. 4b)). These findings are in line with the sintering process occurred during thermal treatments [39]. All these results are consistent with the XRD data on the registered crystal phases (Fig. 2), and with the textural properties obtained by using the BET method (Table 1). The mentioned sintering process over KI/Al_2O_3 has caused a significant reduction of its BET specific surface area. On the other side, despite feedbacks of the sintering process regarding specific surface area, the other textural properties such as pore volume and pore diameter remained suitable values in the case of the KI/Al_2O_3 catalyst (Table 1). Such a developed pore system considering pore volume and especially pore diameter has provided no internal diffusion restrictions for the penetration of reactants to catalytically active sites into the catalyst bulk. Therefore, the final catalyst KI/Al_2O_3 expressed favorable activity in the transesterification reaction performed under the process parameters applied in the investigation (Table 2).

Figure 4.

Catalytic activity in transesterification reaction of sunflower oil

Influence of the transesterification reaction parameters

Influence of molar ratio (methanol to sunflower oil) on the transesterification reaction conversion is presented in Fig. 5. Previously, the molar ratio of methanol to sunflower/plant oil has been reported as significant parameter, which has influenced the conversion of the reactants to the final product(s) in biodiesel production [23, 40, 41]. Higher molar ratios than the stoichiometrically determined (more than 3 : 1 = methanol : sunflower oil) are tested in order to shift the reaction equilibrium towards the final products. However, the excess of methanol has increased reactants conversions up to molar ratio of 12 : 1 = methanol : sunflower oil (Fig. 5). Furthermore, the increase of molar ratio over 12 : 1 has resulted in the decrease of the conversions. This fact can be explained with a formation of relatively complicated reaction system/mixture consisted of three-phases, where the excess of methanol could limit the contact between triglycerides and catalytically active sites in the catalyst bulk over internal and/or external diffusion restrictions.

Figure 5.

It is shown in Fig. 6, that the use of larger catalyst dosages in the reaction mixture has caused higher conversions to final product(s). Different catalysts loadings between 0.5 and 3.0 wt. % were tested in the transesterification reaction and determined conversions after three hours of the reaction run(s). The highest conversion was by this time achieved with 2.5 wt. % of the used KI/Al_2O_3 catalyst (Fig. 6). The explanation is in fact that greater amounts of the catalysts provided greater number of catalytically active sites and more effective contacts among both reactants and catalytically active sites in the applied reaction conditions. The authors predict that further increase of the catalyst loadings could result with a shortening of reaction time in order to achieve the same conversions.

Figure 6.

It is shown in Fig. 7 that conversions have increased when longer reaction times have been conveyed. In details, a conversion of almost 100 % (*i.e.* 99.9 %) has been achieved by using 2.5 wt. % of the KI/Al_2O_3 catalyst after three hours of the reaction run.

Figure 7.

For the difference, other authors [22] have claimed that conversions of about 90 % were obtained over 2 wt. % of the alumina-supported potassium iodide catalyst after at least eight hours of the reaction time. Higher conversions over smaller dosages of the catalyst and during shorter reaction runs in our investigation can be explained with somewhat greater amount of dopant impregnated into the alumina support, different origin of the support and dissimilar calcination temperatures applied. Here, 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 [42]. Additionally, the authors of this investigation also suggest that achieved higher conversions under relatively mild reaction conditions were obtained due to a synergism of physico-chemical properties of the KI/Al_2O_3 catalyst, such as greater pore diameter and pore volume, more favorable composition of crystal phases, higher total basicity and potentially greater number of basic active sites as well as the absence of internal and/or external diffusion restrictions under the selected process parameters.

CONCLUSIONS

Potassium iodide impregnated γ-Al_2O_3 prepared and activated at relatively high temperature has shown itself as a very active catalyst in trans-esterification of sunflower oil with methanol. The advantages of the use of this catalytic system in the process for biodiesel production are standard operating temperature (reflux of methanol) and at atmospheric pressure, acceptable molar ratios of reactants (1: 12), relatively short contact time (180 min) and reasonably small catalyst loadings (2.5 wt. %). These all together resulted in high conversions to fatty acids methyl esters and promising process for biodiesel production.

Physico-chemical properties of the KI/γ-Al_2O_3 catalyst such as acceptable pore volume and satisfactory average pore diameter, the presence of desirable crystal phases of K_2O, K_3AlI_6 and γ-Al_2O_3, strong metal-support-interaction, the high total basicity and the complete amount of surface basic sites, the absence of external and internal diffusion restrictions are all together found to be the reasons for the obtained high catalytic activity.

The results of the experiments show that the incorporation of potassium iodide into/onto the structure of γ-Al_2O_3 significantly influences textural and structural properties of the final catalyst as well as its basic strength and positively affects the activity of the KI/γ-Al_2O_3 catalyst in the reaction of transesterification of sunflower oil with methanol. The impregnated KI/γ-Al_2O_3 catalyst has a much higher Hammett basicity and greater number of base catalytically active sites, which have positively influenced biodiesel yield.

The conversions of 99.99 % to fatty acids methyl esters were achieved by using the catalyst impregnated with potassium iodide under relatively mild conditions (methanol to oil molar ratio 1 : 12, reflux temperature, reaction time 180 minutes and catalyst loading of 2.5 wt. %), while the usage of the unimpregnated material (alumina-based support) resulted with no conversion under the same process conditions.

It is obvious that the surface properties of the catalyst have the essential impact on its catalytic performance in the reaction of sunflower oil conversion to fatty acids methyl esters with methanol. High basic strength of the γ-Al_2O_3 catalyst impregnated with potassium iodide can be ascribed to the formation of K_2O species and strong MSI interactions (*i.e.* Al–O–K groups on the surface), which work as basic catalytically active sites for the reaction together with the occurrence of intermediate species of K_3AlI_6 that is also important for high basicity of the catalyst surface, and therefore, high catalytic efficiency.

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IZVOD

Sinteza biodizela iz suncokretovog ulja korišćenjem heterogenog katalizatora na bazi kalijum-jodida na alumini: Uticaj procesnih parametara

Milos M. Marinkovic, Nikola I. Stojkovic, Marija B. Vasic, Radomir B. Ljupkovic, Sofija M. Rancic, Boban R. Spalovic, Aleksandra R. Zarubica*

Departman za hemiju, Prirodno-matematički fakultet, Univerzitet u Nišu, Višegradska 33, 18000 Niš, Srbija

(Naučni rad)

Primena heterogene katalize u proizvodnji biodizela iz biljnih ulja privlači veliku pažnju istraživača, zbog prednosti koje obezbeđuje, kao što su: laka separacija/razdvajanje faza i mogućnost ponovne upotrebe katalizatora; sa druge strane, homogena kataliza je češće primenjivana u ove svrhe. Cilj ovog istraživanja je sinteza nosača na bazi γ-Al_2O_3, modifikovanom sol-gel metodom i sinteza katalizatora na bazi KI/Al_2O_3, te testiranje njegove aktivnosti u reakciji transesterifikacije suncokretovog ulja (sa) metanolom. Ispitani su uticaji različitih procesnih parametara na konverziju suncokretovog ulja u metil-estre viših masnih kiselina. Dobijeni rezultati ukazuju da ugradnja kalijum jodida u/na strukturu γ-Al_2O_3 značajno utiče na teksturalna i strukturalna svojstva katalizatora. Pored toga, povećana je jačina baznih centara katalizatora; sve fizičko-hemijske osobine katalizatora zajedno pozitivno utiču na aktivnost katalizatora u reakciji transesterifikacije suncokretovog ulja sa metanolom. Impregnacija nosača na bazi γ-Al_2O_3 kalijum-jodidom, rezultirala je dodatnim formiranjem baznih katalitički aktivnih centara. Površinske osobine katalizatora imaju ključni uticaj na njegove katalitičke radne performanse/karakteristike. Pri relativno blagim procesnim uslovima i pri relativno kratkom vremenu reakcije, upotreba KI/Al_2O_3 kao katalizatora je rezultirala (veoma) visokom konverzijom u metil-estre viših masnih kiselina od 99,99 %.

Ključne reči: biodizel, heterogeni katalizator, kalijum jodid na alumini, parametri procesa, suncokretovo ulje

Table captions:

Table 1. Textural properties of the catalyst samples

Table 2. Basicity of the catalyst samples estimated by using Hammett indicators

Figure captions

Fig. 1. N_2 adsorption/desorption isotherms of KI/γ-Al_2O_3

Fig. 2. XRD patterns of KI/γ-Al_2O_3 and γ-Al_2O_3 samples

Fig. 3. The FTIR spectra of the catalyst samples: (1) γ-Al_2O_3 and (2) KI/γ-Al_2O_3

Fig. 4. SEM micrographs of the catalyst samples: a) γ-Al_2O_3, b) KI/γ-Al_2O_3

Fig. 5. Influence of molar ratio (methanol to oil) on the conversion to the product(s)

Fig. 6. Influence of catalyst loading on the conversion to the product(s)

Fig. 7. Influence of the reaction time on the conversion to the product(s)

Tables

Table 1.

Sample	**BET surface area (m^2 g^{-1})**	**BJH cumulative desorption pore volume (cm^3 g^{-1})**	**Average pore diameter (nm)**
Al_2O_3	196.82	0.42	6.69
KI/Al_2O_3	9.86	0.23	33.60

Table 2.

Sample	**Calcination temperature (K)**	**Basic strength (H°)**	**Conversion (%)**
Al_2O_3	1043	H°< 7.2	-
KI/Al_2O_3	1043	15.0 < H° < 18.4	99.99

Figures

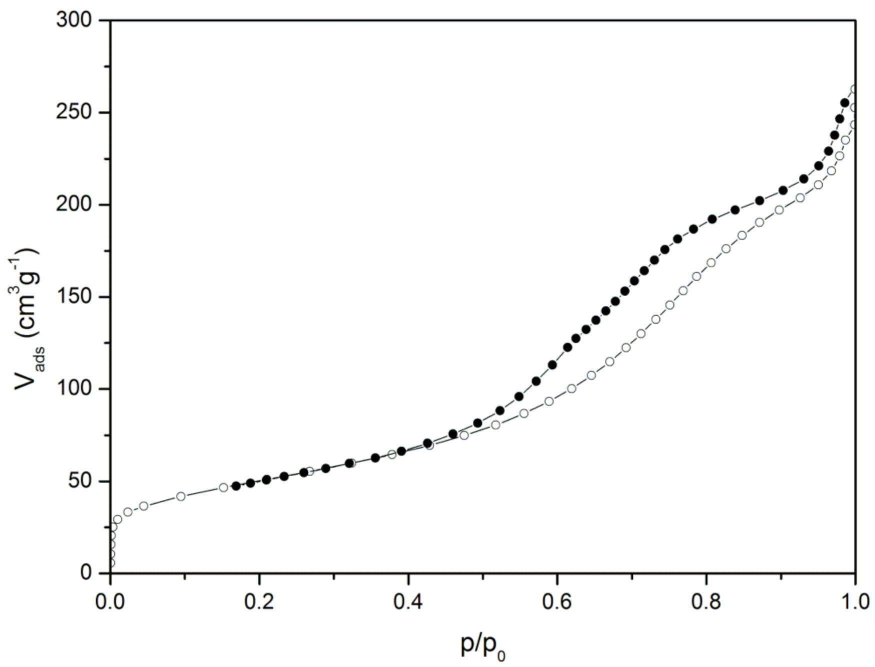


Fig. 1.

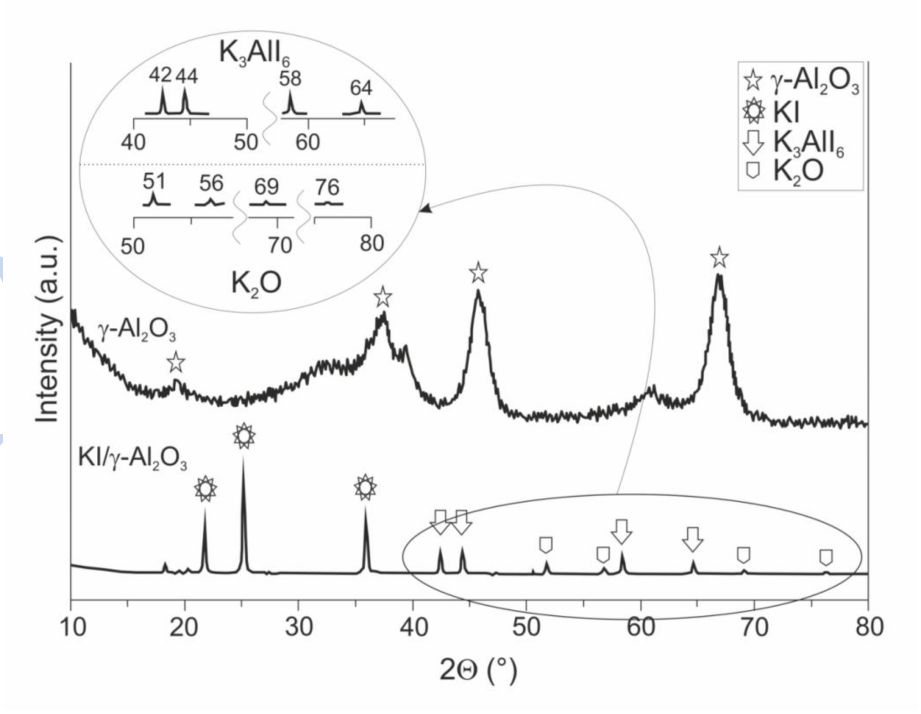


Fig. 2.

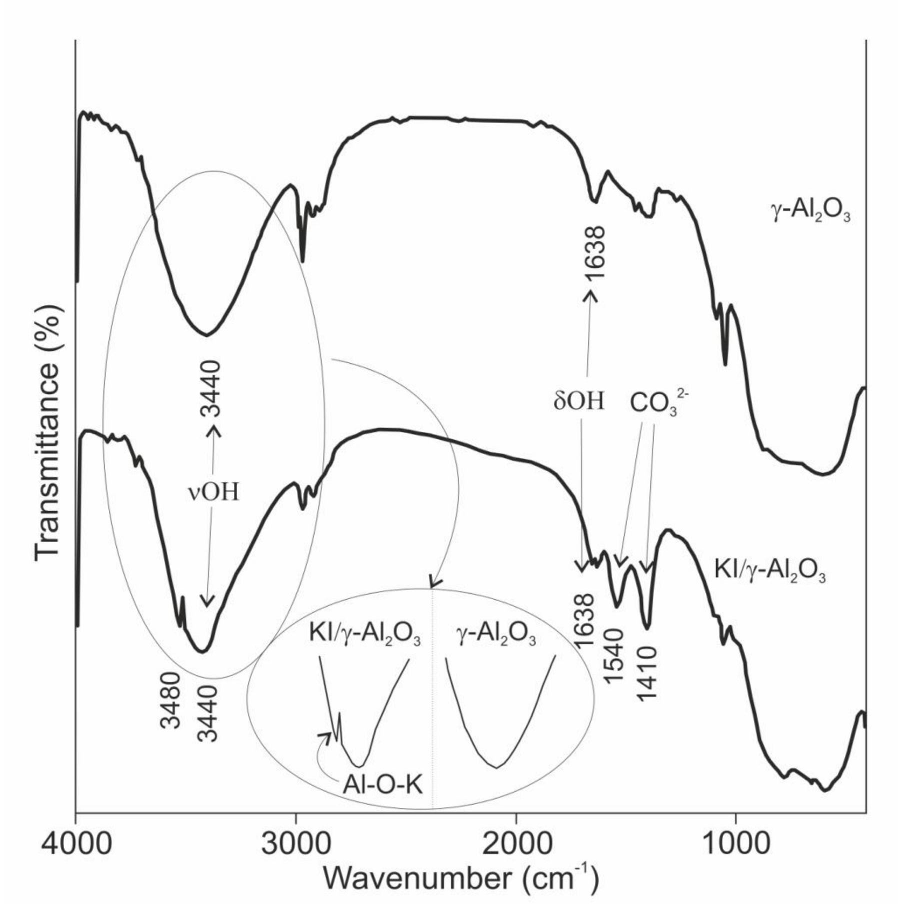

γ-Al2O3
KI/γ-Al2O3
Transmittance (%)
Wavenumber (cm-1)
4000
3000
2000
1000
νOH
3440
3480
3440
δOH
1638
1638
CO3 2-
1540
1410
KI/γ-Al2O3
γ-Al2O3
Al-O-K

Fig. 3.

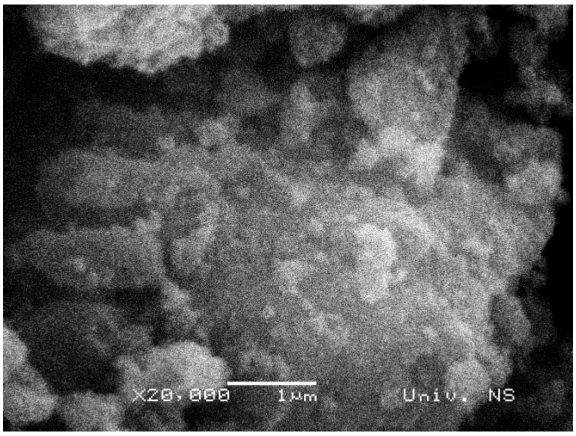


Fig. 4. a)

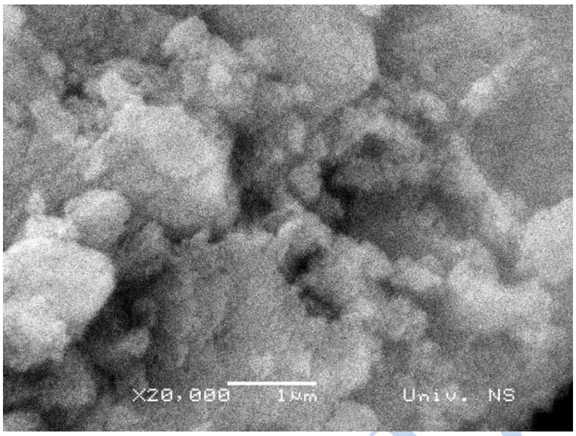
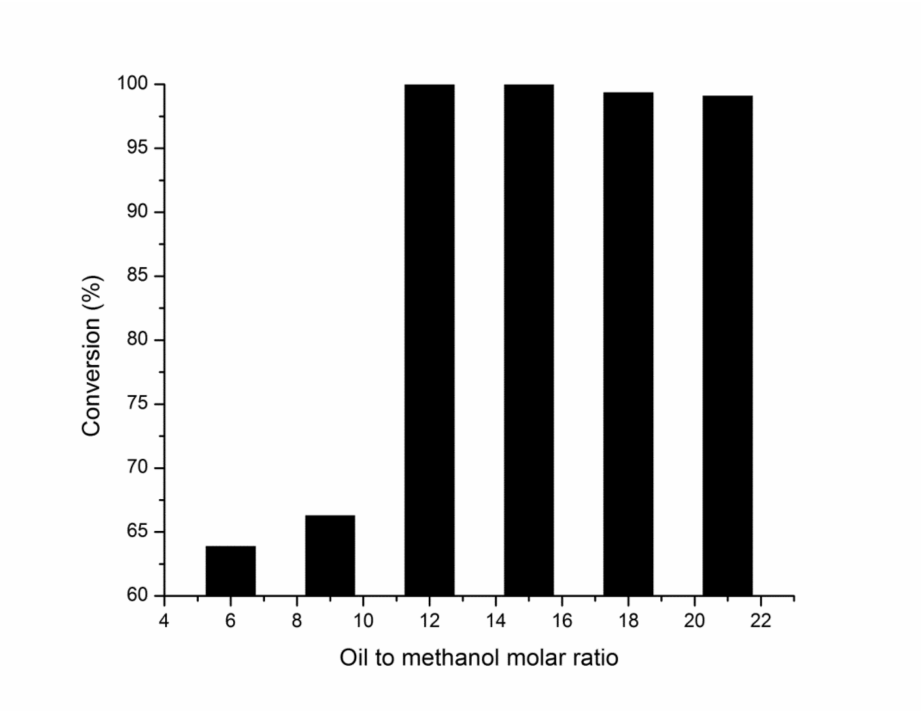
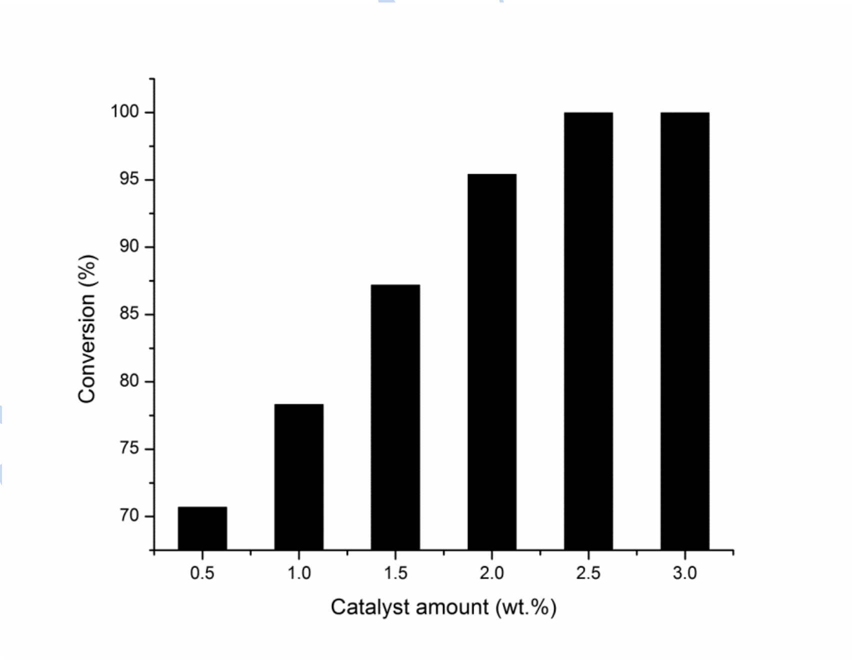


Fig. 4. b)



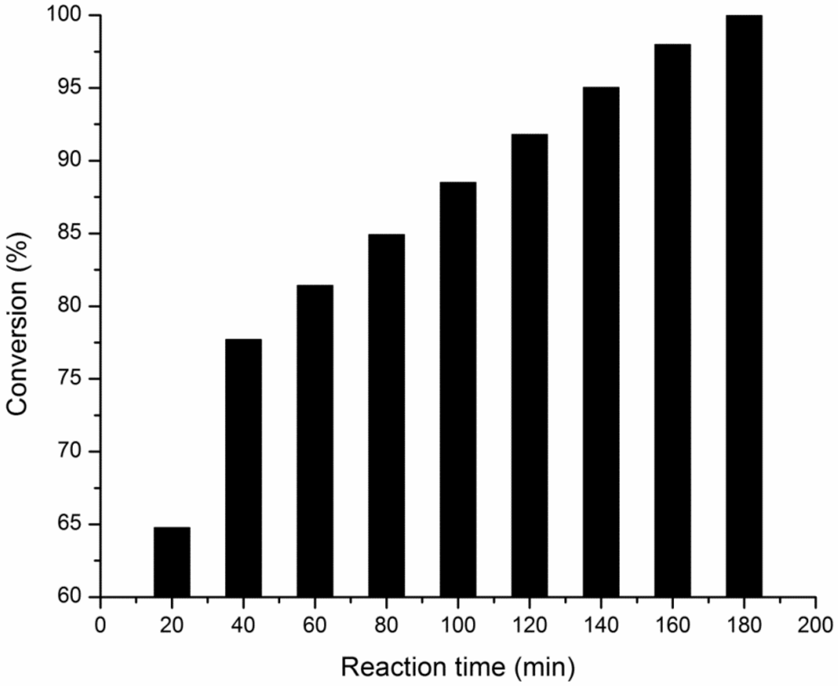
Conversion (%)
100
95
90
85
80
75
70
65
60
4
6
8
10
12
14
16
18
20
22
Oil to methanol molar ratio

Fig. 5.



Conversion (%)
100
95
90
85
80
75
70
0.5
1.0
1.5
2.0
2.5
3.0
Catalyst amount (wt.%)

Fig. 6.



Conversion (%)
100
95
90
85
80
75
70
65
60
0
20
40
60
80
100
120
140
160
180
200
Reaction time (min)

Fig. 7.