ALUMINA/SILICA AEROGEL WITH POTASSIUM-OXIDE AS HETEROGENEOUS CATALYST FOR BIODIESEL SYNTHESIS

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Certain disadvantages of conventional processes of biodiesel, i.e. fatty acid methyl esters (FAME) synthesis could be avoided by applying new technologies which are based on using heterogeneous catalyst. In this study a new type of heterogeneous catalyst with potassium-oxide as active component on alumina/silica support was synthesized using sol-gel method which was followed by drying the "dense" wet gel with the supercritical carbon dioxide to obtain aerogel. Prepared catalysts were used in the methanolysis of sunflower oil. The effects of various reaction variables such as reaction time, temperature and methanol to oil molar ratio on the yield of FAME were investigated. Aerogel catalysts with potassium-oxide as active component on alumina/silica support exhibited good activity in the methanolysis of sunflower oil, with the yield of FAME above 92 % after 15 min of reaction.

INTRODUCTION

Biodiesel, consisting of FAME, produced by alcoholysis of vegetable oils or animal fats, is an excellent substitute for conventional diesel fuels. It is non toxic, biodegradable and made from renewable sources. Increasing biodiesel consumption requires optimized production processes allowing high production capacities, simplified operations, high yields, and the absence of special chemical requirements and wastes. The utilization of a successful heterogeneous catalyst will cope with most of the economical and environmental drawbacks of a homogeneous process, such as technically difficult neutralization of catalysts after reaction and creation of large amount of wastewater produced during washing and separation of final products.
Nowadays only one industrial application, developed by the IFP, uses heterogeneous base catalyst for the transesterification of vegetable oils to produce biodiesel [1]. At the laboratory scale, many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oils, such as alumina loaded with alkali metal salts or different potassium compounds [2-4], CaO [5,6], MgO [7,8], commercial hydrotalcite [9], zeolites and modified zeolites [10,11] etc.
In this study a new type of heterogeneous catalyst with potassium-oxide as active component on alumina/silica support was synthesized using sol-gel method which was followed by drying wet gel with the supercritical carbon dioxide.

MATERIALS AND METHODS

Commercial edible sunflower oil (Sunce, Sombor, Serbia) was used for experimental studies. Catalysts were synthesized by one step sol-gel synthesis. Aluminium tri-sec-butoxide, tetraethoxy orthosilane (TEOS), 1-butanol, anhydrous potassium carbonate (all Fluka) were used as reagents. Aluminium tri-sec-butoxide (29.1 g, 0.12 mol) was mixed with 1-butanol (200 cm^3) and then TEOS (8.32 g, 0.04 mol) was added. The mixture was stirred vigorously and heated to 343 K for 5 minutes until a clear solution was obtained. Solution was cooled down to room temperature. Then, it was hydrolyzed with the water (37.5 cm^3, 2.08 mol) containing dissolved potassium carbonate (2.86 g; 0.021mol). The solution was stirred for 15 min and left to stand overnight (gelation). Water and certain amount of 1-butanol (excess) were then removed by heating the gel to 423 K, and a "densed" wet gel was obtained. The above procedure describes the wet gel synthesis of samples with ratio Al/Si = 3/1. Aerogel was obtained by drying the "dense" wet gel in a 150 cm^3 tubular extractor (Autoclave Engineers SCE Screening System), with the supercritical carbon dioxide. During the supercritical drying, first the extractor was filled with liquid CO_2, than the pressure was raised above the value of critical point for CO_2 and finally the temperature was raised to the desired value. After reaching the working conditions of pressure and temperature, the flow of CO_2 is maintained and kept constant at about 100 g CO_2/h. This procedure was necessary to avoid the presence of two-phases of CO_2 in the extractor. Duration of supercritical drying (SCD) depended on the drying conditions. The parameters of sol-gel synthesis and gel drying are presented in Table 1.

Table 1 The parameters of gel drying

	AG1	**AG2**	**AG3**	**AG4**
SCD T, ˚C (p=100 bar)	40	40	200	200
Time of SCD, h	9	9	5	5
Temperature of calcination , ˚C (t = 12h)	600	300	600	300

The XRD measurements were performed on a Philips PW1710 powder X-ray diffractometer using Cu Kα radiation, over a 2θ range of 4 - 90 º in the scan mode (step size 0,02 º, counting 0,5 s per step).
FTIR spectra were obtained using Nicolet 6700 spectrometer in the wavenumber range from 400 to 4000 cm^{-1}.
The BET surface area, overall pore volume and the pore size distribution (calculated using BJH method) of the catalyst samples were obtained from nitrogen adsorption-desorption at 77 K on Sorptomatic 1990 Thermo electron corporation instrument.
Synthesized catalysts were tested in the methanolysis of sunflower oil. Experiments were performed in the 150 cm^3 tubular extractor (Autoclave Engineers SCE Screening System) equipped with two heaters and a mixer. Prior to reaction, the catalyst samples (fraction < 500 μm) were activated by heating in an oven at 393 K for 2 h. Defined amounts of sunflower oil, methanol and catalyst were used for synthesis performed in a batch autoclave. All catalyst samples were tested at 200 ˚C and 37 bar, with molar ratio of sunflower oil to methanol of 1:30 and with 2 wt % of catalyst (based on oil). The reaction samples were withdrawn periodically, and after filtration and separation of the residual methanol using rotational evaporator, analyzed by gas chromatography (Varian 3400) with a FID detector and fused silica capillary column (5 m x 0.53 mm film thicknes 0.5 μm). One aerogel was used to study the influence of different working conditions (temperature, ratio of methanol to oil) on the effect of FAME sinthesys.

RESULTS

The X-ray diffraction analysis was conducted to investigate the structure and crystallinity of the catalysts. The results showed that all synthesized catalysts were amorphous, and none of characteristic peaks of K_2O was observed, indicating the good dispersion of K_2O in the structure of the support.
The measured BET surface area, the overall pore volume, the size and distribution of mesopores and micropores volume, and the maximum pore diameter and median pore diameter are shown in Table 2, and pore size distribution in Fig. 1.

Table 2 Textural properties of the catalysts

	S_{BET}, m^2/g	V_{pore}, cm^3/g	V_{mezo}, cm^3/g	V_{micro}, cm^3/g	D_{max}, nm	D_{med}, nm
AG2	107.47	0.144	0.137	0.036	3.764	3.838
AG4	113.05	0.162	0.172	0.035	3.786	4.427

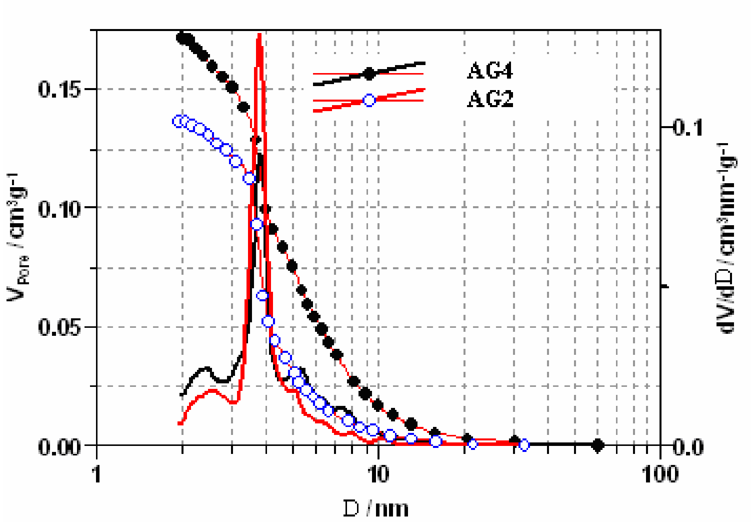

Figure 1 Pore size distribution of aerogel catalysts AG2 and AG4

The results of BET analysis indicated that synthesized catalysts are mesoporous, while the maximum pore diameters, D_{max}, has similar values around 3.7 nm not depending on SCD temperature. Aerogel AG2 has also very similar value of the median pore diameter, which means that in this case all pores are equally distributed, while a shift of a pore sizes to larger pore diameters is observed for the catalyst AG4 dried at 200 ^{o}C. On the basis of BET information one can conclude that SCD conditions have only slightly influenced the porous structure of aerogels. At higher SCD temperature porosity was increased, as well as the average pore diameter. Although it might be expected that aerogels dried at the lower temperatures, when density of CO_2 is higher, will posses a lower activity due to extraction of some amount of active component K_2O during SCD process, this effect was not observed. Both catalysts are very active in the methanolysis of sunflower oil thus leading to the general conclusion that applied SCD conditions don't observably change the catalytic activity of synthesized K_2O/Alumina-Silica aerogel.

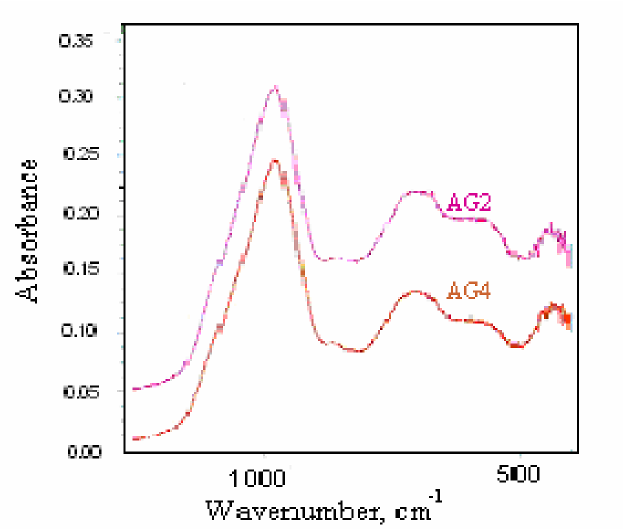

Figure 2 FTIR spectra of prepared catalyst

FTIR spectra of catalyst samples are shown in Fig. 2. Characteristic bands are: a band at about 1000 cm^{-1} attributed to Si-O stretching vibration, band at around 460 cm^{-1} attributed to Si-O bending, wavenumbers in the range of 500-700 cm^{-1} attributed to octahedral Al-O, and 700-900 cm^{-1} attributed to tetrahedral Al-O. A shift of the Si-O stretching vibration absorption band from 1000 cm^{-1} to lower wavenumbers indicates the presence of Al-O-Si bonds in the investigated samples. The intensity of shifting indicates the level of mixing of Al and Si in the alumina/silica network. A shift of the Si-O stretching vibration for both aerogels can be observed (972 cm^{-1}), which indicates that they have Al-O-Si bonds in the structure of alumina/silica support.
Yield of FAME achieved in the methanolysis reaction is shown in the Fig. 3.

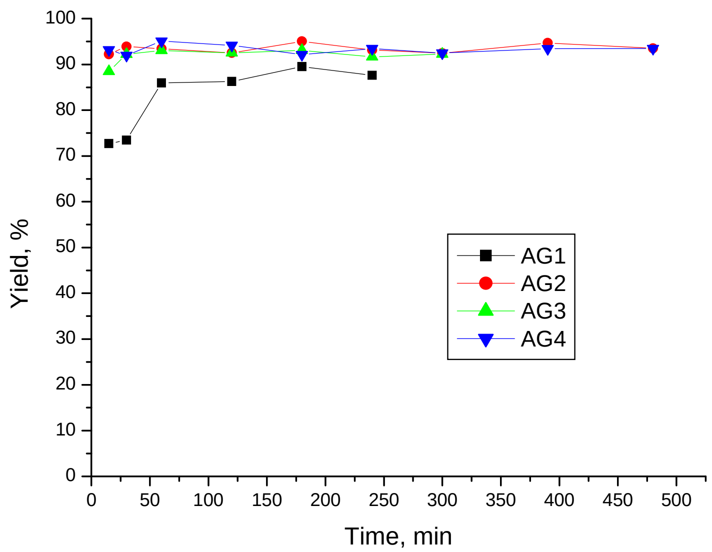

Figure 3 Effect of reaction time on the yield of FAME synthesized FAME at 200 ˚C and under 37 bar, using molar ratio of methanol:oil=30:1 and 2 wt % of catalyst (AG1-AG4; Table 1) based on oil

As can be seen from the Fig. 3, all catalysts with K_2O as active component showed very good catalytic activity, with yield of FAME over 90 % after 15 minutes for all catalysts except for AG3, which expressed a little bit lower activity.

Influence of the reaction temperature on the yield of FAME in the methanolysis performed using catalyst AG2 is shown in Fig. 4. The rate of methanolysis reaction of vegetable oil is strongly influenced by the reaction temperature and yield of FAME was increased with increasing temperature. At lower temperature (80 ˚C) much longer time is necessary for achieving desired and high yield of FAME. For almost complete conversion of triglycerides temperature of 120 ˚C is acceptable, when the yield of FAME can be 92 % and higher after 15 minutes of methanolysis.

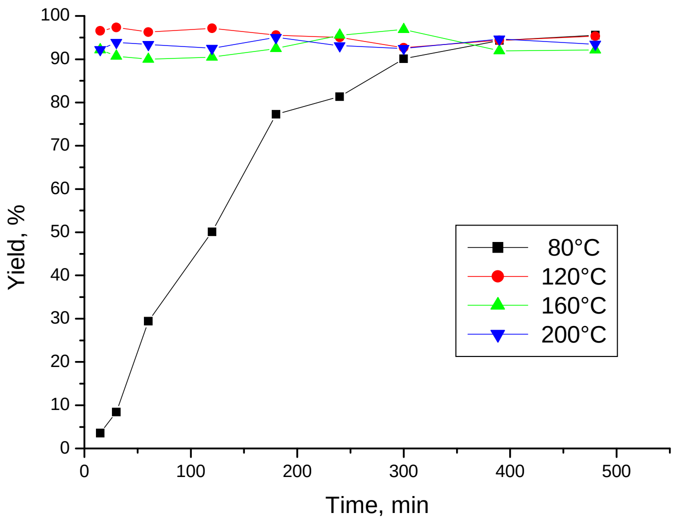

Figure 4 Influence of reaction temperature on the yield of FAME (catalyst AG2) synthesized using methanol to oil molar ratio of 30:1 and 2 wt % of catalyst (based on oil)

Very important working parameter which influences the conversion of sunflower oil (triglycerides) to methyl esters is the molar ratio of methanol to vegetable oil. Influence of molar ratio was examined in the methanolysis of sunflower oil with aerogel AG2 at 120 ˚C and with 2 wt % of catalyst and obtained results are shown in Fig. 5.

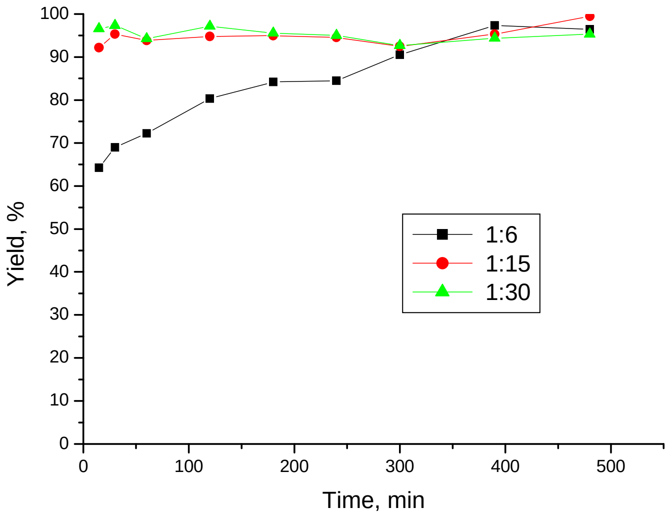

Figure 5 Influence of methanol to oil molar ratio on the yield of FAME (catalyst AG2)

Stoichiometrically, the methanolysis of vegetable oil requires three moles of methanol for each mole of oil. However, in practice a higher molar ratio is employed in order to shift the reaction equilibrium towards the products side and produce more methyl esters. As shown in the Fig. 5, synthesis realized by a larger methanol to oil ratio (15:1 and 30:1) was followed by a higher rate of FAME reaction and thus desired and high conversion of triglycerides was observed for shorter period of time. According to the results of this study one can conclude that molar ratio of methanol to oil of 15:1 was quite enough for achieving a good yield of FAME for a relatively short reaction time (less than 100 min).

CONCLUSION

Experiments performed in this study showed that heterogeneous catalyst with potassium-oxide as active component on alumina/silica support exhibited good activity in the methanolysis of sunflower oil. Achieved conversion of vegetable oil to FAME (92 % and more) was realized after 15 minutes of reaction. The results of this preliminary investigation showed that this type of catalyst could be potentially very good in heterogeneous reaction of biodiesel synthesis. The analysis of different working conditions indicated that the temperature of the reaction and methanol:oil molar ratio also affect the methanolysis reaction rate. It has been determined that 120 ˚C and 37 bar, as well as the methanol:oil molar ratio of 15:1, are optimal conditions for biodiesel synthesis with 2 wt% of K_2O/Alumina-Silica heterogeneous catalyst.

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REFERENCES

[1] BOURNAY, L., CASANAVE, D., DELFORT, B., HILLION, G., CHODORGE, J.A., Catal. Today, Vol. 106, **2005,** p. 190
[2] XIE, W., LI, H., J. Mol. Catal. Chem, Vol. 255, **2006**, p. 1
[3] XIE, W., PENG, H., CHEN, L., Appl. Catal. Gen., Vol. 300, **2006**, p. 67
[4] EBIURA, T., ECHIZEN, T., ISHIKAWA, A., MURAI, K., BABA, T., Appl. Catal. Gen, Vol.283, **2005**, p. 111
[5] LOPEZ GRANADOS, M., ZAFRA POVES, M. D., MARTIN ALONSO, D., MARISCAL, R., CABELLO GALISTEO F., MORENO-TOST R., SANTAMARI J., FIERRO J.L.G., Appl. Catal. B Environ., Vol. 73, **2007**, p. 327
[6] DEMIRBAS, A., Energ. Convers. Manag., Vol. 48, **2007**, p. 937
[7] DI SERIO, M., LEDDA, M., COZZOLINO, M., MINUTILLO, G., TESSER, R., SANTACESARIA, E., Ind. Eng. Chem. Res.,Vol. 45, **2006,** p. 3009
[8] WANG, L., YANG, J., Fuel, Vol. 86, **2007**, p. 328
[9] XIE, W., PENG, H., CHEN, L., J. Mol. Catal. Chem., Vol. 246, **2005**, p. 24
[10] SUPPES, G. J., DASARI, M. A., DOSKOCIL, E. J., MANKIDY, P. J., GOFF, M. J., Appl. Catal. Gen., Vol. 257, **2004**, p. 213
[11] XIE, W., HUANG, X., Li, H., Bioresource Technology, Vol. 98, **2007**, p. 936