Oxidation of Glycerol by Gold Catalysts

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A variant for the capitalization of glycerol resulting from biodiesel production consists in the synthesis of functional derivatives with high demand in the market like oxygenated fuel additives. One class of such compounds is the organic carboxylic esters of acids obtained by oxidation of glycerol, respectively tartronic acid and glyceric acid, with fatty alcohols. The catalysts used in the oxidation of glycerol was Au / activated charcoal powder, Au / Al_2O_3 powder and Au / diatomite powder. Preparation of catalyst was carried out by impregnation by the pore filling method, and activating by reduction in the presence of hydrazine hydrochloride and treated in a hydrogen atmosphere. The catalysts prepared were characterized by determining the metal content and the distribution of active metal centers on the catalyst surface. Experimentation of glycerol oxidation process was performed in a batch mode at high partial pressures of oxygen. Gold deposited on carbon catalyst showed higher activity in oxidation of glycerol than when deposited on alumina or diatomaceous earth.

Keywords : glycerol, oxidation, gold catalyst, activated charcoal, diatomaceous earth

Glycerol excess on market was caused by biodiesel introduction in diesel, given that in the process of biodiesel production, it is obtained at a proportion of approx. 10% compared to biodiesel. The main features of glycerol like total solubility in water, absence of toxicity and high biodegradability recommend as a raw material for production of various pharmaceutical products, food, etc.

Glycerol oxidation was studied systematically in recent years [1-4]. The oxidation process of glycerol can be achieved in various catalyst systems [5-8]. Concerns are directed toward identifying of catalysts with high activity and selectivity in products with market demand. The reason for this concern is given by the high functionality of this chemical compound. Note that the nature of the substrate catalytic influence the performance of the catalyst [9,10]. It is noted that in a basic conditions is favored the oxidation of the primary alcohol function, while in the acidic conditions is promoted the oxidation of the secondary alcohol function.

Glycerol is not used as such in the preparation of fuel additives due to low solubility and risk of acrolein formation because of its incomplete combustion. A variant of interest applied to exploit the results of glycerol in biodiesel production is the synthesis of functional derivatives with high demand in the market such as dispersant additives for fuels. A class of organic compounds with a higher dispersing ability is the carboxylic derivative of glycerol that can be obtained by oxidation thereof, respectively esters of glyceric acid and acid tartronic with long chain aliphatic alcohols.

Experimental part

The raw materials used in experiments were glycerol puriss. p.a. (Sigma-Aldrich), chloroauric acid (Sigma-Aldrich), ammonium heptamolybdate tetrahydrate (Sigma-Aldrich), sodium hydroxide reagent grade (Sigma-Aldrich), activated charcoal powder, diatomite powder, γ-alumina powder and oxygen from Linde Company.

Preparation of catalyst was carried out by impregnation of the powdered activated carbon supports, γ-alumina and diatomaceous earth with an aqueous solution of chloroauric acid.

Impregnation of the catalyst was achieved by the method of filling the pores. The gold content for the three catalysts was 1 wt%. After the catalysts impregnation were dried at 160°C for 5 h. Prepared catalysts were activated in two stages. In the first stage activation was carried out by treatment with a hydrazine hydrochloride solution in hydrazine excess of 10% of the stoichiometric amount, at a temperature of 80°C for 4 h. After the aqueous solution removal and drying, the catalysts were activated in hydrogen atmosphere for 5 h. Setting activation temperature was based on thermal reduction curves. Measurements were performed on a device type ChemBET PULSAR ™ TPR / TPD.

Acid strength distribution of prepared catalysts was performed by thermal desorption diethyl amine in the temperature range 20-700°C. Thermal analyzes (ATG) were performed on a DuPont Instruments “Thermal Analyst 2000/2100” coupled with a module “951 Thermogravimetric Analizer”. Evaluation of catalysts surface appearance and distribution of the active component clusters on the internal surface of the catalyst was performed by scanning electron microscopy (SEM). Measurements were performed on a FEI Quanta 200 (tungsten filament).

The oxidation process was carried out in a batch system, in a stainless steel autoclave type reactor of useful capacity 500 mL, electrically heated jacket with temperature control, provided with a turbine stirrer with rpm up to 2000 rpm/min, a temperature pressure and speed sensor.

Operating parameters was: (i) operating pressure 40 atm, (ii) temperature 75°C, (iii) weight ratio of glycerol / water / sodium hydroxide: 4/8/1 and (iv) catalyst to glycerol concentration 1% gr.

Characterization of the reaction product was achieved by determining the yield of compound carboxylic and of the freezing point of the reaction product. The yield of carboxylic compound was determined by potentiometric

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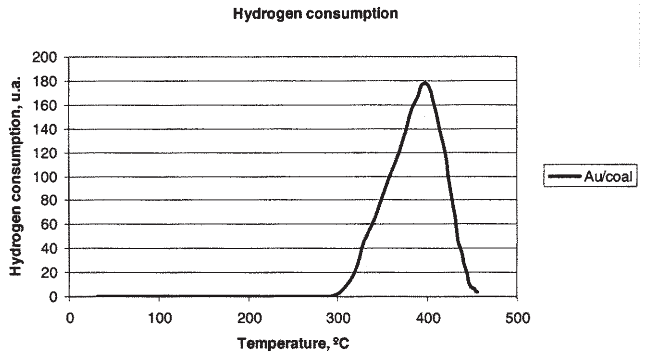

Fig. 1. Thermal reduction curve of Au / C catalyst

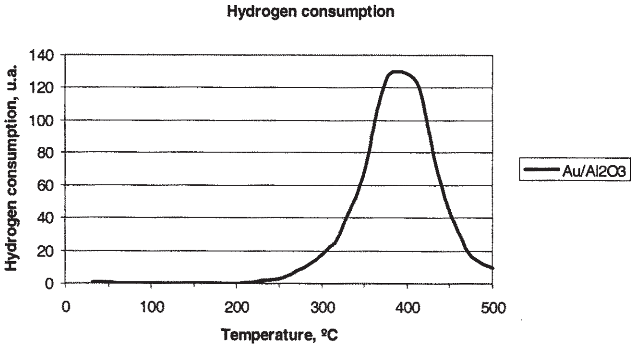

Fig. 2. The curve of thermal reduction of Au / γ-Al_2O_3 catalyst

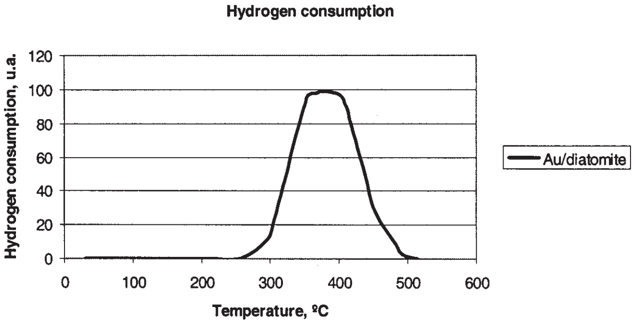

Fig. 3. Thermal reduction curve of Au / diatomite catalyst

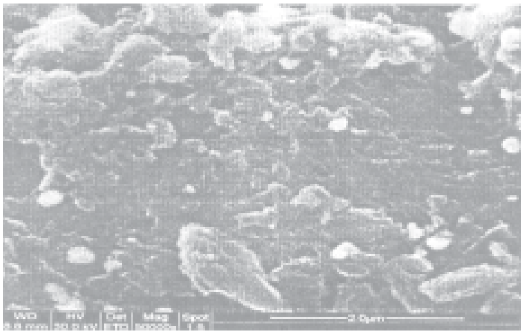

Fig. 4. The distribution of the active metal sites of Au / charcoal by scanning electron microscopy

back titration of unreacted NaOH with 0.1 n HCl solution, using a combined glass electrode.

Results and discussions

In figures 1-3 are shown the curves of thermoreduction of the three catalysts.

Thermal reduction curve of Au/C catalyst shows a maximum of hydrogen adsorption at approx. 400°C. In order to avoid sintering of the catalyst we have chosen of the activation temperature of catalyst at a value corresponding to the consumption of hydrogen of approx.20% of the maximum value. Thus, the activation temperature was approx. 325°C.

Thermal reduction curve of Au /γ-Al_2O_3 catalyst shows a maximum of hydrogen adsorption at approx. 380°C. The activation temperature of the catalyst is 300°C, this value corresponding to a hydrogen consumption of approx. 20% from the maximum value.

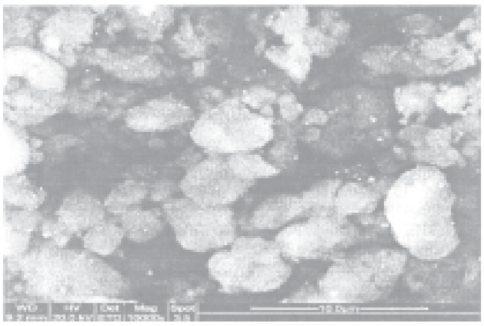

Fig. 5. The distribution of the active metal sites of Au / γ-Al_2O by scanning electron microscopy

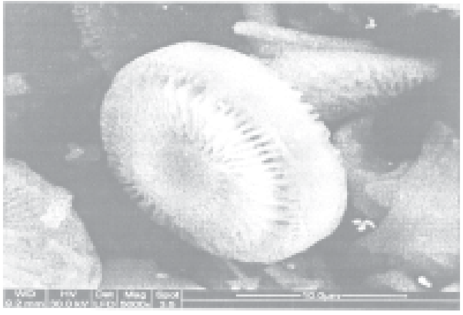

Fig. 6. The distribution of the active metal sites of Au / diatomite by scanning electron microscopy

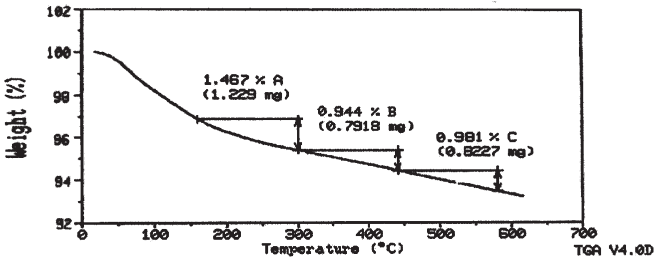

Fig. 7. Distribution of strength acidic sites of Au / C catalyst

In the case of the Au / diatomite catalyst it distinguish a sharp increase in consumption of hydrogen at temperatures above 300°C, registering maximum consumption at approx. 375°C. In order to avoid sintering of active sites, the activation of the catalysts was carried out at a temperature of approx. 320°C.

Images of catalysts samples determined by scanning electron microscope are shown in figures 4-6.

The distribution of the active metal sites by scanning electron microscopy of Au/charcoal catalyst highlights an advanced dispersion of gold clusters and an approximately equal size of it.

The distribution of the active metal sites on Au /γ-Al_2O_3 catalyst shows an approximately equal sized of gold clusters and a homogeneous distribution of its on the surface of the pores.

Advanced dispersion is observed at gold clusters of Au / diatomaceous earth catalyst. Distribution of active metal centers shows a approximately equal size of gold clusters and their homogeneous distribution on the surface of the pores.

The distribution of acid strength of the catalysts prepared is shown in figure 7-9. Note that the acid strength and acid strength distribution are different for the three catalysts.

In figure 7 is observed a higher content in weak acidic centers of the catalyst 1% wt. Au / C (17 meq./g) and a lower concentration of acid centers of medium strength (11 meq./g) and of strong acid centers (11.5 meq./g).

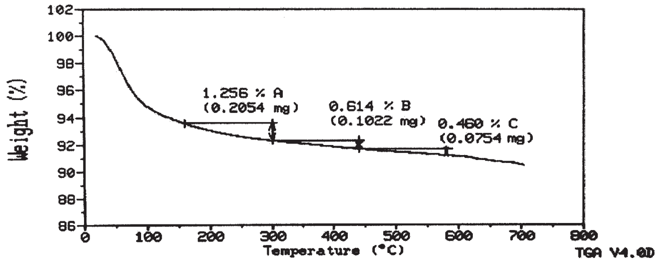

Fig. 8. Distribution of strength acidic sites of Au / γ-Al_2O_3 catalyst

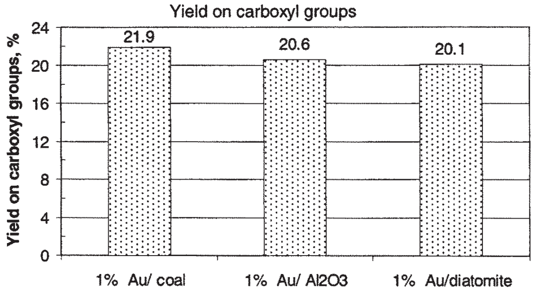

Fig. 10. Yield in the carboxyl groups

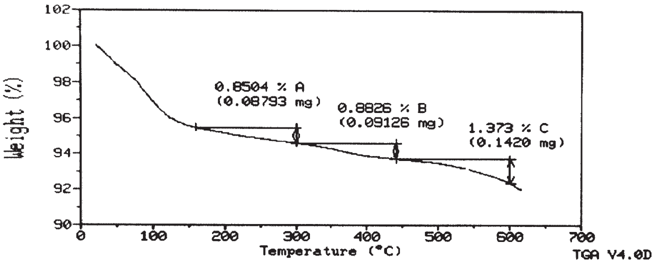

Fig. 9. Distribution of strength acidic sites to 1 wt% Au / diatomite catalyst

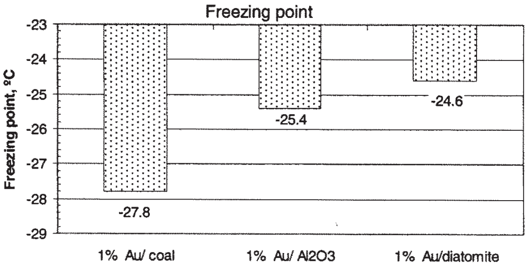

Fig. 11. Freezing point of oxidized glycerol

Distribution of acidic sites in the catalyst Au / γ-Al_2O_3 shows a concentration of medium strength acidic two times lower than the concentration of weak acidic sites and a concentration of strong acids centers around three times smaller than a weak acidic centers.

The catalyst 1% Au / diatomite shows a lower concentration of acid sites. The content of weak acidic sites was 1.2 meq./g, the content of acid sites of medium strength was 1.3 meq./g and the content of strong acid sites was 2 meq./g (fig. 9).

The yield in the carboxylic acid groups of the solutions of glycerol oxidized and its freezing point variation with the nature of the catalytic support used in the preparation of the catalysts are shown in figures 10 and 11.

There is a variation in yield carboxyl groups and the freezing point with the type of catalytic support. Thus Au / C catalyst shows a higher activity than the other two catalysts, which was evidenced by a higher yield in carboxyl groups. The Au / diatomite catalyst showed a lower activity than the other two, the yield in the carboxyl groups being reduced with 2.4% compared to Au / γ-Al_2O_3 and with 8.2% compared to Au / C.

The efficiency of the three catalysts was evaluated by determining the freezing point of glycerol samples oxidized in the presence of the three catalysts. Thus

the oxidized glycerol on Au / charcoal showed a lower freezing point than in the case of Au catalysts deposited on alumina and diatomaceous earth.

Conclusions

Glycerol oxidation in heterogenous catalyst was carried out at relatively low temperatures. The reaction was carried out in the gas-liquid-solid system on gold catalysts.

Impregnation and activation methods selected have led to high dispersion of metal clusters.

The oxidation process of glycerol was carried out in a batch system at high partial pressures of oxygen.

Yield in carboxyl groups and the pour point of the oxidation products varies with the type of catalytic support. Thus Au / charcoal has a higher activity than Au deposited on alumina or diatomaceous earth.

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