

Etherification of Glycerol with Isobutene on Triflic Acid / $\gamma\text{Al}_2\text{O}_3$ Catalyst

VASILEIOS MANGOURILOS¹, DORIN BOMBOS^{1*}, MIHAELA BOMBOS², RODICA GANEA³, ION BOLOCAN¹

¹ Petrol – Gaze University of Ploiești, 30 București Blv., 100680, Ploiești, Romania

² National Research Institute for Chemistry and Petrochemistry, ICECHIM, 202 Spl. Independentei , 060021, Bucharest, Romania

³ SC ZECASIN SA., 202 Spl. Independentei , 060021, Bucharest, Romania

Transforming glycerol in oxygenated compounds by production of ether with isobutene, represents an alternative of capitalizing by using as components for fuel. The selectivity in ethers can be improved by selecting a hydrophilic catalytic support which reduces the secondary reactions of isobutene oligomerization. Etherification experiments were conducted in a batch system in the presence of a triflic acid catalyst supported on powdered $\gamma\text{-Al}_2\text{O}_3$. The distribution of the reaction products is influenced by triflic acid concentration, in the range of concentrations studied. Thus the increase of triflic acid concentration of catalyst diminishes the selectivity in monoethers and increases the selectivity in di- and tri-ethers.

Keywords: glycerol etherification, isobutene, microporous catalyst, triflic acid, $\gamma\text{-Al}_2\text{O}_3$

Glycerol is the by-product of the biodiesel manufacturing process, whose production is about 10% wt. of the value of production of biodiesel. The increase of production of biodiesel in recent years led to a proportional increase in the production of glycerol. Demand for glycerol is stationary, so that absorption of the entire amount of glycerol involves identifying new applications. Recent studies are mainly devoted to the transformation of glycerol in products with a high demand on the market. One alternative would be the synthesis of oxygenated motor fuel. Thus, by etherification of glycerol with isobutene are obtained branched oxygenated compounds which have properties suitable for use as components for fuel [1-4].

In the process of etherification can be formed five isomers of glycerol ethers, ethers of which two monosubstituted (3-tert-butoxy-1,2-propanediol and 2-tert-butoxy-1,3-propane-diol), two ethers disubstituted (2,3-di-tert-butoxy-1-propanol and 1,3-di-tert-butoxy-2-propanol) ether and trisubstituted (1,2,3-tri-tert-butoxy-propane). By-products are C8-C16 hydrocarbons obtained by the dimerization-oligomerization of isobutene. There have been many studies of etherification of glycerol with isobutene using various acid catalysts such as zeolites, ion exchange resins, homogeneous catalysts such as p-toluene sulfonic acid, et al.

The improvement of the mass transfer between glycerol and hydrocarbon phases, was achieved by emulsifying the reaction mixture in presence of a cationic or nonionic emulsifiers [5,6]. The effect of hierarchical porosity in Beta zeolite on the catalytic etherification of glycerol with tert-butanol or isobutene has been studied by Maria Dolores González et al., by comparing its catalytic behaviour with one conventionally synthesized β -zeolite with similar Si/Al ratio. Fluorination of Beta samples led to slight higher selectivity to di- and triethers of glycerol [7]. Glycerol etherification performance was improved by acid-treated HY zeolite. The catalyst showed higher selectivity than an acidic resin and was reusable [8].

In a recent paper [9] was studied the influence of reaction conditions on the ethers selectivity, at a molar ratio isobutene / glycerol of 3, at 80°C, in the presence of a cationic ion

exchange resin, Amberlyst 35 W. It was revealed that the etherification reactions can lead to various byproducts by varying the reaction conditions. The main purpose of this study was to optimize the reaction conditions of glycerine with isobutene by varying the reaction conditions. The catalyst used was an ion exchange resin (Rohm & Haas). The main mono-ether formed was 3-tert-butoxy-1,2-propanediol, and 1,3-di-tert-butoxy-2-propanol was the predominantly diether. Ether selectivity was low, which indicates that the isobutene in contact with catalyst reacts to oligomerization reactions. The methods presented shows different inconvenients. By selecting a hydrophilic catalytic support can avoid secondary reactions of oligomerization of isobutene to improve selectivity in ethers.

Experimental part

The experiments were performed in a 600 mL stainless steel Berghoff autoclave equipped with mechanical stirring. The device is electrically heated, with automatic temperature control. The stirring rate was maintained at 1300 rot/min for each experiment.

Reagent grade glycerol provided by Aldrich and 99% purity isobutene purchased from Linde were the agents used for all the experimental runs. The catalysts used in the experiments are based on trifluoro-methanesulfonic (TFA) acid supported on powdered γ -alumina. The $\gamma\text{-Al}_2\text{O}_3$ support was obtained from a commercial alumina sample (Sasol) by calcination in air at 500°C for 6 hours. Supported catalysts were prepared by pore volume impregnation method using aqueous solutions containing triflic acid. Two samples of TFA/ $\gamma\text{-Al}_2\text{O}_3$ with variable triflic acid concentrations, namely 20 and 30 wt%, were prepared. Characterization of the prepared catalysts was carried out by determining the acid strength distribution and the analysis of texture.

The experimental program of the etherification was performed for 5 h at 80°C, the isobutene/glycerol molar ratio of 1.5 / 1 and the concentration of catalyst of 5 wt %. The analyses of starting materials and reaction products were performed by gas-chromatography, using an

* email: dorin_bombos@yahoo.com

Sample	BET specific surface area (m ² /g)	Total pore volume (cc/g)	BJH pore diameter (Å)
γ -Al ₂ O ₃ support	240	0.50	68
20%TFA/ γ -Al ₂ O ₃	267	1.43	39
30%TFA/ γ -Al ₂ O ₃	286	2.16	44

instrument from Agilent Technologies with FID detector, equipped with DB-WAX polar column of 30 m length and 0.32 mm inner diameter. The chromatographic column was operated between 20-220°C, with nitrogen as carrier gas. The chromatographic analyses of reaction products have demonstrated the presence of two isomers for the glycerol mono-ether (1- and 2-t-butoxy-glycerol) and the glycerol di-ether (1,2- and 1,3-di-t-butoxy-glycerol) and of the tri-ether (1,2,3-tri-t-butoxy-glycerol). Conversion of glycerol, and yields to mono-ethers, di-ethers, tri-ether of glycerol and isoctenes were calculated based on the material balance for each experiment.

Results and discussions

Catalysts characterization

Textural measurements were performed with a Quantachrome Autosorb-1 gas sorption analyzer. The specific surface area was calculated from the linear part of the adsorption branch of the isotherms by Brunauer-Emmett-Teller (BET) method and the corresponding pore size distributions were determined from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda method (BJH).

Textural characteristics of supported TFA catalysts are given in table 1. For comparison data corresponding to the alumina support are also included in table 1. The nitrogen physisorption measurements show that the alumina support has a total specific surface area of 240 m²/g and a total pore volume of 0.5 cc/g. Specific surface area values of the triflic acid containing samples varies in a relative narrow range ($S_{BET} = 267$ and 286 m²/g) that means no important differences in comparison with the support (S_{BET} 240). Also, it can be observed that the impregnation with 20 and 30% triflic acid led to significantly higher nitrogen adsorption as compared to alumina support.

Figures 2 and 3 represent nitrogen adsorption-desorption isotherms and pore size distribution plots for 10% and 20% TFA/ γ -Al₂O₃ sample. As figures 1 - 3 shown, the nitrogen adsorption-desorption isotherm corresponding to the supported 20 and 30 % triflic acid is quite different in comparison with the γ -Al₂O₃ support and illustrates two nitrogen adsorption step. The first adsorption step occurs in the same range of relative pressure (p/p_0 0.5-0.8) as for alumina support. The second step corresponding to higher relative pressure ($p/p_0 > 0.8$) can be due to the adsorption in larger dimension pores. The adsorption in this range has a major contribution to the total pore volume of the impregnated sample.

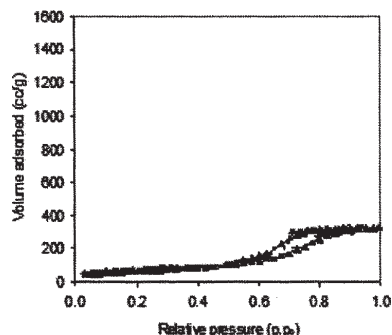


Fig. 1 Nitrogen adsorption-desorption isotherms of γ -Al₂O₃ samples

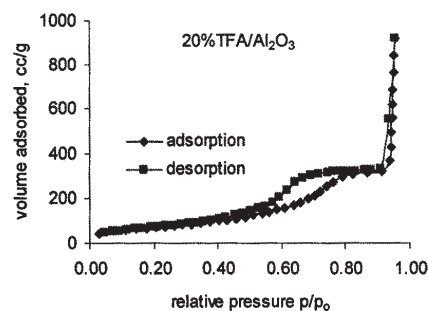


Fig. 2. Nitrogen adsorption-desorption isotherms of 20% acid triflic / γ -Al₂O₃

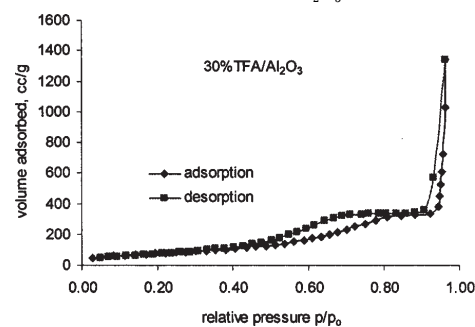


Fig. 3. Nitrogen adsorption-desorption isotherms of 30% acid triflic / γ -Al₂O₃

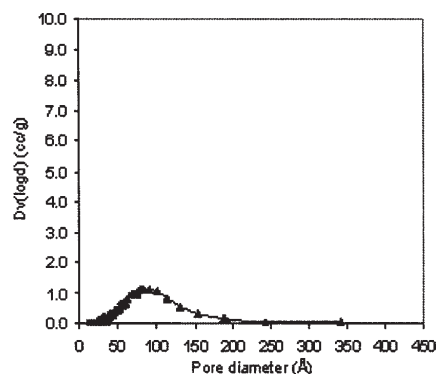


Fig. 4. Pore size distributions of γ -Al₂O₃ sample

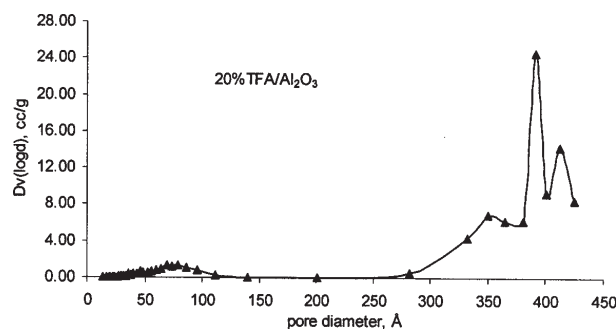


Fig. 5. Pore size distributions of 20% TFA/ γ -Al₂O₃ sample

Figures 4 - 6 show a large pore size distribution for the alumina support with a maximum at 68 Å and a bimodal pore size distribution for the supported TFA catalyst corresponding to pore diameters of 67 Å and 350-400 Å, respectively. The appearance of supplementary pores with diameters higher than 300 Å was observed in all the supported TFA samples. This result could indicate some modification in the structure of the alumina used as support

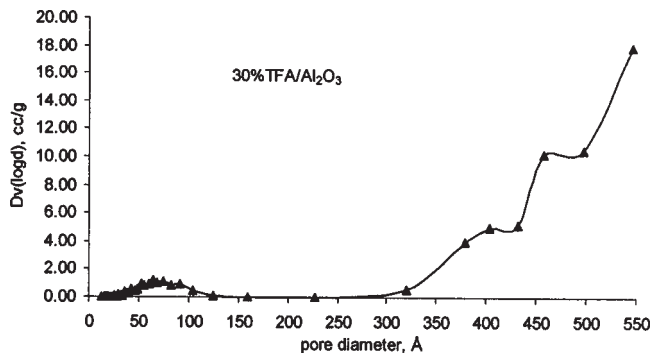


Fig. 6. Pore size distributions of 30% TFA/ γ - Al_2O_3 sample

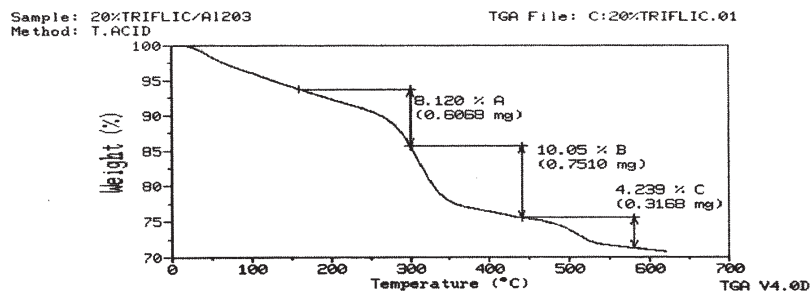


Fig. 7. The distribution of acid strength for 20% TFA/ γ - Al_2O_3 sample (A-weak centers concentration; B-concentration of medium strength centers; C - strong centers concentration)

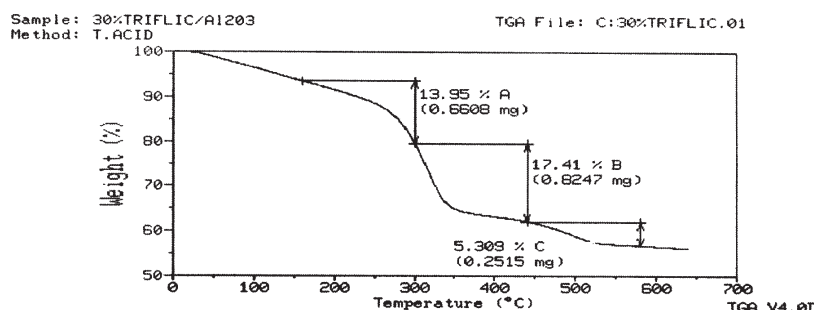


Fig. 8. The distribution of acid strength for 30% TFA/ γ - Al_2O_3 sample (A-weak centers concentration; B - concentration of medium strength centers; C - strong centers concentration)

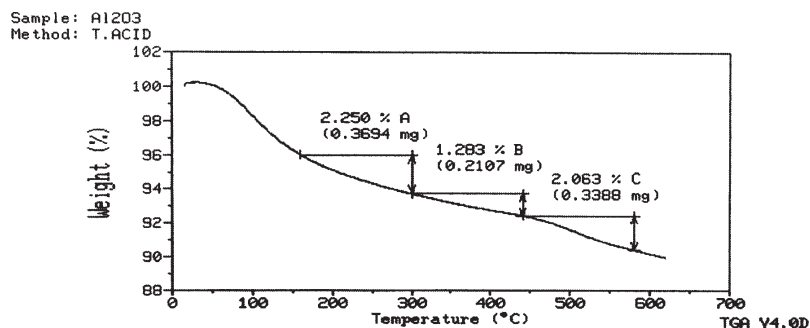


Fig. 9. The distribution of acid strength for γ - Al_2O_3 sample. (A-weak centers concentration; B-concentration of medium strength centers; C - strong centers concentration)

occurring during the impregnation step, which is probably due to the high acid impregnation solution.

The distribution of the strength of the acidic centers of the catalyst support and of the catalysts was determined by thermal desorption of diethyl amine in the temperature range 20-650 °C. Thermal analyzes (ATG, DSC) were performed on a DuPont Instruments' Thermal Analyst 2000/2100 "coupled with a module "Differential Scanning Calorimeter 912" and a module "951 Thermogravimetric Analyzer". Figures 7-10 shown the distributions of acid strength for the two catalysts prepared and for the support of catalysts.

From figures 7-9 we can see that the total concentration of the acidic centers of the catalyst 20% TFA/ γ - Al_2O_3 is about 4 times higher than γ - Al_2O_3 support, while the total concentration of acid centers on the catalyst 30% TFA/ γ - Al_2O_3 is approx. 6.5 times higher than the support. Centers strong acids on which occur etherification reactions, shows an increase in concentration over twice after impregnation with 20% TFA and over 8.4 times after impregnation with 30% TFA.

The influence of the concentration of TFA/ γ - Al_2O_3 on etherification of glycerol

The chromatographic analyses of reaction products obtained on the two catalysts, have demonstrated the presence of two isomers for the glycerol mono-ether (1- and 2-t-butoxy-glycerol) and the glycerol di-ether (1,2- and 1,3-di-t-butoxy- glycerol) and of the tri-ether (1,2,3-tri-t-butoxy-glycerol). Conversion of glycerol and isobutene, and selectivity to mono-ethers, di-ethers, tri-ether of glycerol and of isobutene were calculated based on the material balance for each experiment.

From figure 10 it is observed that glycerol conversion ranged between 32% and 40%, and decreases with the increase of TFA content. This is due, probably, to lower concentration of acidic centers available, due to unfavorable change of the pore size distribution from increasing content TFA deposited on the support (fig. 4-6). The process of glycerol etherification arising with the preferred form of the mono- and di-ether; tri-ether selectivity

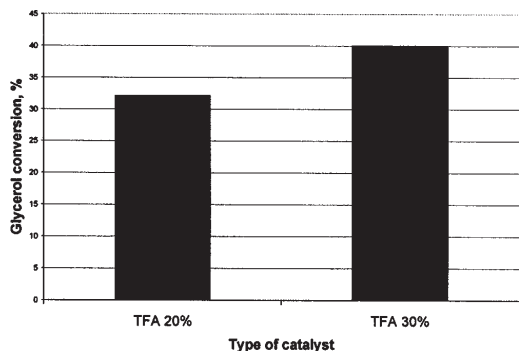


Fig. 10. The influence of the type of catalyst for the conversion of glycerol

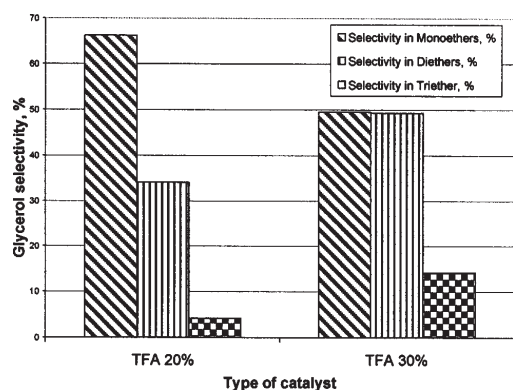


Fig. 11. The influence of the type of catalyst on selectivity of glycerol in ethers

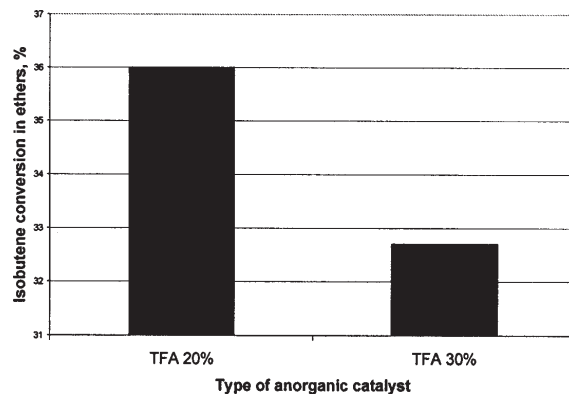


Fig. 12. The influence of the type of catalyst on the conversion of isobutene in ether

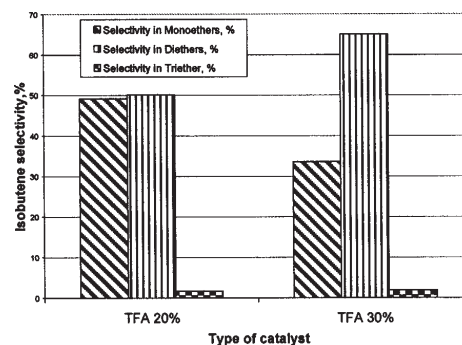


Fig. 13. The influence of the type of catalyst on selectivity of isobutene in ethers

arising with much lower probably because the pore size distribution of catalysts supported on $\gamma\text{-Al}_2\text{O}_3$.

TFA concentration also influence the process, so selectivity of glycerol in di- and tri-ethers increases with increasing TFA content of the catalyst, the increase being more pronounced in the case of tri- ether; selectivity of glycerol in mono-ether decreases with increasing TFA content of catalyst. This behaviour is due to changes in the pore size distribution after treatment of the support with triflic acid (fig. 11). The same behaviour is observed in the variation of conversion of isobutene in ethers (fig. 12) and variation of selectivity of isobutene in ethers (fig. 13), except that the selectivity of isobutene in tri-ether shows a much smaller increase with the increase in TFA of the catalyst.

Modest performance obtained on this type of catalysts is due to textural characteristics of alumina (improper porous distribution) and, probably, low emulsifying capacity of the alumina.

Conclusions

Two series of supported TFA catalysts have been prepared using powder $\gamma\text{-Al}_2\text{O}_3$ at a concentration of TFA of 20 and 30%.

Triflic acid content increases favours increasing of the specific surface area of γ -alumina, modification of adsorption isotherm and pore size distribution.

Triflic acid content increases favours increasing the concentration of acidic centers and implicitly of the concentration of strong acid centers that promote etherification reaction of glycerol with isobutene.

The catalysts prepared were used in carrying out the etherification of glycerol with isobutene. The experimental program of the etherification was performed for 5 h at 80°C, the isobutene/glycerol molar ratio of 1.5 /1 and the concentration of catalyst of 5 wt %.

Conversion of glycerol on TFA based catalysts increased with increasing triflic acid content of catalyst.

Selectivity of glycerol in monoethers had higher values than in diethers and trieter; this behaviour is probably due to steric hindrance caused by the distribution of the porous catalyst.

The increase of triflic acid concentration of catalyst diminishes the selectivity in monoethers and increases the selectivity in di-and tri-ethers.

References

1. IZQUIERDO J.F., MONTIEL M., PALÉS I., OUTÓN P.R., GALÁN M., JUTGLAR L., VILLARRUBIA M., IZQUIERDO M., HERMO M.P., ARIZA X., *Renewable and Sustainable Energy Reviews*, 16 (9), 2012, p. 6717-6724
2. LEE H. J., SEUNG D., JUNG K. S., KIM H., FILIMONOV I. N., *Applied Catalysis A: General*, 390 (1-2), 2010, p. 235-244
3. ZHAO W., YI C., YANG B., HU J., HUANG X., *Fuel Processing Technology*, 112, 2013, p. 70-75
4. FRUSTERI F., FRUSTERI L., CANNILLA C., BONURA G., *Bioresource Technology*, 118, 2012, p. 350-358
5. MANGURILOS V., BOMBOS D., JUGANARU T., BOLOCAN I., BOMBOS M., CIUPARU D., *Rev. Chim. (Bucharest)*, **60**, no. 12, 2009, p.1338
6. MANGOURILOS V., BOMBOS D., BOLOCAN I., BOMBOS M., JUGANARU T., *Rev. Chim. (Bucharest)*, **65**, no. 2, 2014, p. 219
7. GONZÁLEZ M. D., SALAGRE P., LINARES M., GARCÍA R., SERRANO D., CESTEROS Y., *Applied Catalysis A: General*, 473 (5), 2014, p. 75-82
8. XIAO L., MAO J., ZHOU J., GUO X., ZHANG SH., *Applied Catalysis A: General*, 393 (1-2), 2011, p.88-95
9. KARINEN R.S., KRAUSE A.O.I., *Applied Catalysis A: General*, 306 (7), 2006, p.128-133

Manuscript received: 6.11.2013