Influence of Catalyst Porosity on the Etherification of Glycerol with Isobutene

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Transforming glycerol in oxygenated compounds presents opportunities for improving the quality of diesel. Manufacturing of glycerol ether with isobutene, represents the alternative of capitalizing by use as components for fuels. The use of an effective catalyst, having a porosity suitable, enhances the performance of the process of glycerol etherification with isobutene. Also the use of catalysts in powder form favours the contact between reactants by improving the stability of emulsions. Etherification experimental program was conducted on two catalysts with the same concentration of triflic acid supported on microporous amorphous support (γ -alumina) and mesoporous crystalline support (MCM-41). The selectivity in di- and tri-ethers, products with low polarity suitable as components for diesel fuels, is largely influenced by the porosity of the catalysts.

Keywords: glycerol etherification, isobutene, microporous and mesoporous catalyst, triflic acid

Production of biodiesel in growth, raised concerns about the use of glycerol as a byproduct resulting from its manufacture. The trend in the near future to expand the production of biodiesel will increase the production of glycerol, so it will be difficult to identify eligible options for its processing. Conversion of glycerol in value-added products presents opportunities for biodiesel price trends. The same time, to reduce dependence on non-renewable resources is essential for development processes based on biomass, which can be an alternative to obtain chemicals from other sources.

Many recent studies [1-4] are dedicated to conversion of glycerol to chemicals such as surfactants, additives for industry, cosmetics, etc., rather than to larger scale commodity chemicals. Conversion of glycerol to common chemicals like propylene glycol, propionic acid, acrylic acid, propylic alcohol, isopropyl alcohol, allyl alcohol and acrolein, does not provide a sufficient increase in the consumption of glycerin. The alternative to etherification of glycerol presented also of great interest for research in the direction of obtaining oxygenated fuel components. Thus by reacting glycerol with olefins in acid catalysis may be obtained ethers that can be used as renewable fuel components.

Many studies were dedicated to glycerol etherification with isobutene. Difficulty of etherification of glycerol with isobutene is due to high differences between the main physical characteristics of the two reactants such as density and each other solubility. Improving mass transfer between the two phases was achieved by addition of emulsifiers, helping to increase process performance [5,6]. In order to achieve the etherification process have been used various catalytic systems, such as inorganic acid catalysts, ion exchange resins and zeolites [7-9].

The etherification of glycerol with isobutene follows the formation of various ethers like 1- and 2-t-butoxy-glycerol (MTBG), 1,2- and 1,3-di-t-butoxy-glycerol (DTBG), and 1,2,3 tri-t-butoxy-glycerol (TTBG). Among these compounds only those with low polarity such as diethers and triethers, are of interest for applications in fuel. The concerns to preferentially obtain these ethers are related to the assessing of the influence of pore size on selectivity catalytic process in this direction.

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 acid (TFA or triflic acid) supported on a microporous amorphous (γ-alumina) or crystalline mesoporous (MCM 41). The γ-Al_2O_3 support was obtained from a commercial alumina sample (Sasol) by calcination in air at 500°C for 6 h. Mesoporous support MCM 41 was synthesized by Zecasin SA Bucharest. Supported catalysts were prepared by pore volume impregnation method using aqueous solutions containing triflic acid. Two samples of TFA/ γ-Al_2O_3 and TFA/ MCM 41 with the same triflic acid concentrations, respectively 10 wt%, were prepared. Characterization of the prepared catalysts was carried out by determining their 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 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.

Results and discussions

Catalysts preparation

Two series of supported trifluoromethanesulfonic acid (TFA - triflic acid, Merck) catalysts have been prepared

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Table 1
TEXTURAL CHARACTERISTICS OF γ-Al_2O_3 SUPPORT AND 10% TFA/ γ-Al_2O_3 CATALYST

Sample	BET specifc surface area (m^2/g)	Total pore volume (cc/g)	BJH pore diameter (Å)
γ-Al_2O_3 support	240	0.50	68
10%TFA/ γ-Al_2O_3	243	2.39	51

using powder γ-Al_2O_3 and pure silica MCM-41, respectively as supports. TFA was used for supported catalysts preparation. The γ - Al_2O_3 support was obtained from a commercial alumina sample (Sasol) by calcination in air at 500°C for 6 h.

The cationic surfactant assisted synthesis of the MCM-41 was performed using sodium silicate and fumed silica as silicon source, tetramethylammonium hydroxide as mineralizer agent and cetyltrimethylammonium bromide as surfactant. The hydrothermal synthesis of pure silica MCM-41 was carried out at 100°C for 48 h under continuous stirring. The solid products were separated by filtration, washed and dried at room temperature. Finally, the as-synthesized material was calcined in air at 550°C for 8 h to remove the surfactant molecules.

Supported catalysts were prepared by pore volume impregnation method using aqueous solutions containing triflic acid. Three samples of TFA/ γ -Al_2O_3 with variable triflic acid concentrations, namely 10, 20 and 30 wt%, respectively were prepared. The MCM-41 supported triflic acid sample contained 10 wt% TFA. The impregnated samples were heated at 150°C for 24 h.

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 Barett-Joyner-Halenda method (BJH).

Textural characteristics of 10% TFA/ γ-Al_2O_3 catalyst 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 m^2/g and a total pore volume of 0.5 cc/g. Specific surface area values of the 10% TFA/ γ-Al_2O_3 catalyst varies relative little compared to support (S_{BET} = 240 and 243 m^2/g) that means no important differences in comparison with the support. Also, it can be noticed that the impregnation with 10% triflic acid led to significantly higher nitrogen adsorption as compared to alumina support.

Figures 1 - 2 represent nitrogen adsorption-desorption isotherms and pore size distribution plots for 10% TFA/γ-Al_2O_3 sample in comparison with γ-Al_2O_3 support. The γ-Al_2O_3 support displays a IV type isotherm according to the IUPAC classification. The presence of H_2 type hysteresis loop in the isotherm indicates that the alumina used as catalyst support have "ink-bottle" type pores. As figures 1 shown, the nitrogen adsorption-desorption isotherm corresponding to the supported 10% triflic acid is quite different in comparison with the γ -Al_2O_3 support and illustrates two nitrogen adsorption steps. The first adsorption step occurs in the same range of relative pressure (p/p_o 0.5-0.8) as for alumina support. The second step corresponding to higher relative pressure (p/p_o>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.

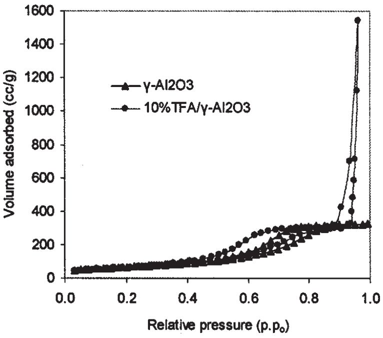

Fig. 1. Nitrogen adsorption-desorption isotherms of γ-alumina and 10% TFA/γ-Al_2O_3 samples

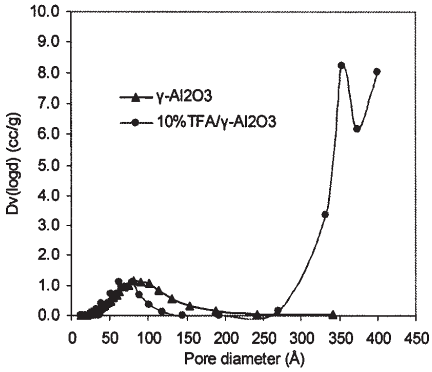

Fig. 2. Pore size distributions of γ-alumina and 10% TFA/γ-Al_2O_3 samples

Figure 2 shows a large pore size distribution for the alumina support with a maximum at 68 A°and a bimodal pore size distribution for the supported TFA catalyst corresponding to pore diameters of 67 A and 350-400 A°, respectively. The appearance of supplementary pores with diameters higher than 300 A °observed in the supported TFA sample, could indicate some modification in the structure of the alumina used as support occurring during the impregnation step, which is probably due to the high acid impregnation solution.

Table 2 gathers textural characteristics of TFA/MCM-41 catalyst synthesized. The MCM-41sample used as catalyst support has the following characteristics: BET surface area of 1252 m^2/g, total pore volume of 1.74 cc/g and micropore volume of 0.41 cc/g. High values of BET surface area (960 m^2/g) and total pore volume (1.75 cc/g) were also found in supported trific acid sample.

Figure 3 compares nitrogen adsorption-desorption isotherms of MCM-41 and TFA/MCM-41 samples. The two samples have IV type isotherms with H1 hysteresis loop, typical to mesoporous materials according to IUPAC nomenclature. The nitrogen capillary condensation in the low relative pressure range (p/p_o~ 0.28-0.35) shows the

Table 2
TEXTURAL CHARACTERISTICS OF MCM-41 SUPPORT AND 10% TFA/ MCM-41CATALYST

Sample	Specific surface area (m^2/g)		Pore volume (cc/g)		BJH pore diameter (Å)
	BET	micropore	total	micropore	
MCM-41 support	1252	667	1.74	0.41	27
10%TFA/MCM-41	960	215	1.75	0.17	26

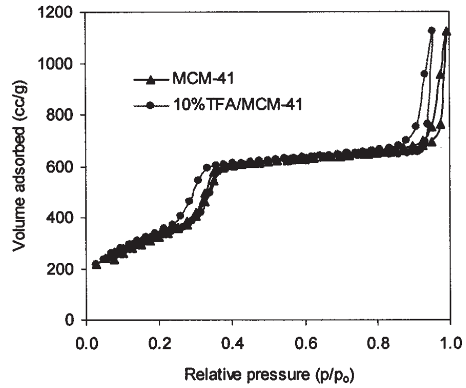

Fig. 3. Nitrogen adsorption-desorption isotherms of MCM-41 samples

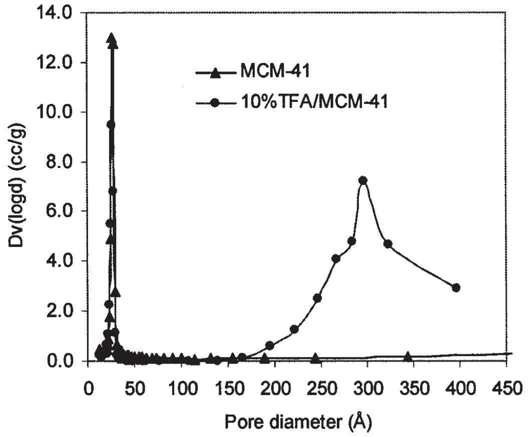

Fig. 4. Pore size distributions of MCM-41 samples

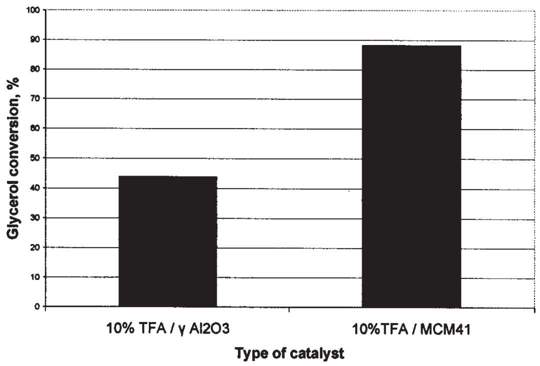

Fig. 5. Influence of the type of catalyst for the conversion of glycerol

existence of uniform small mesopores in both samples. The isotherm corresponding to the supported catalyst has a second step at a high relative pressure corresponding to the filling of large mesopores.

Figure 3 shows that the mesoporous silica support possesses a well-defined narrow pore size distribution centered at 27 A°while MCM-41 supported TFA have two distinguishable pore size distributions centerd at 26 A°and 300 A°, respectively. The first one originating from MCM-41 has a very narrow pore diameter with a maximum of lower intensity as compared to mesoporous support. Also, an additional large maximum around 300 A°appeared upon impregnation with triflic acid. Taking into account the significant decrease in microporosity and the presence of the second large mesopore system one might presume that the collapse of smaller pores occurred during the impregnation with triflic acid. Therefore, the presence of higher dimension mesopores system could explain the large adsorbed volume on triflic acid containing MCM-41sample.

This result could indicate that the bimodal pore structure of MCM-41 supported triflic acid has been induced during the catalyst preparation process. Also, the result shows that the support structure in connection with the impregnation step control are two important factors for the final structural characteristics of the MCM-41 supported catalysts. Generally, main textural properties of MCM-41 supported triflic acid prepared as described above consist of large surface area, high pore volume and bimodal mesopore size distribution indicating a good accessibility of the catalytic sites.

Influence of porosity of catalysts on the etherification of glycerol with isobutene

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-butoxi-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-butoxi-glycerol). Conversion of glycerol and isobutene, and selectivity to mono-ethers, di-ethers, tri-ether of glycerol and isobutene were calculated based on the material balance for each experiment.

Performances in the etherification of glycerol with isobutene with triflic acid catalyst supported on mesoporous zeolite MCM-41, were much higher than with microporous catalyst supported on γ-alumina (fig. 5-9). Thus glycerol conversion on the catalyst TFA /MCM-41 was over 88% wt., more than two times higher than on the catalyst TFA / γ-Al$_2$O$_3$ (fig. 5). Glycerol selectivity in monoethers had a value more than twice higher on TFA / γ-Al$_2$O$_3$ catalyst compared to TFA / MCM-41catalyst. Glycerol selectivity in diethers was over 2.6 times greater on TFA/MCM-41catalyst compared to TFA / γ-Al$_2$O$_3$ catalyst and glycerol selectivity in trieter was relatively low on the catalyst TFA / MCM-41 (5.54% gr.), while on the TFA supported on γ-Al$_2$O$_3$ catalyst was not formed practically triether (fig. 6).

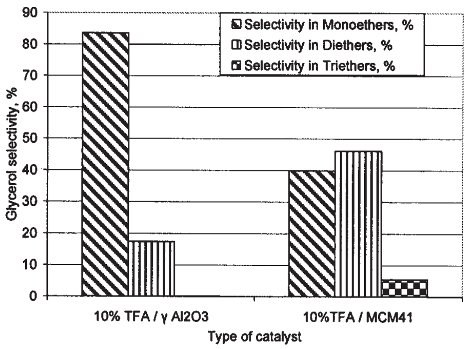

Fig. 6. The influence of the type of catalyst on selectivity of glycerol in ethers

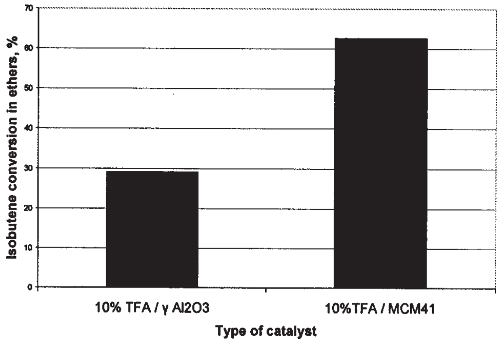

Fig. 7. Influence of the type of catalyst on the conversion of isobutene in ether

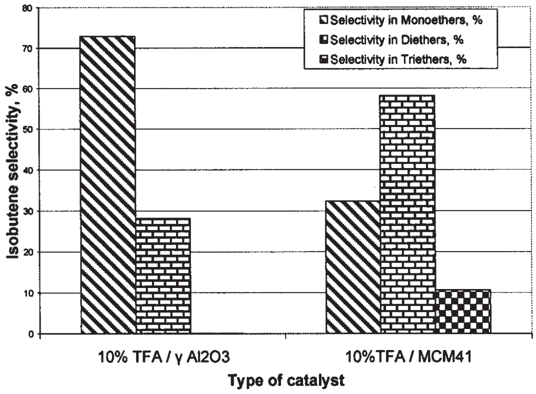

Fig. 8. Influence of the type of catalyst on selectivity of isobutene in ethers

Conversion of isobutene in ethers is more than twice higher on triflic acid catalyst supported on mesoporous zeolite MCM-41 than with TFA catalyst supported on γ-Al_2O_3 microporous (fig. 7). Isobutene selectivity in monoethers had a value of more than 2.25 times greater in TFA catalyst / γ-Al_2O_3 catalyst compared to TFA / MCM-41. Isobutene selectivity in diethers was over two times higher on the TFA/MCM-41 catalyst compared to TFA / γ-Al_2O_3 catalyst and isobutene selectivity in triether was relatively low on the catalyst TFA / MCM-41 (10.60 wt.%), while on the catalyst TFA / γ -Al_2O_3 practically no triether was obtained (fig. 8).

Much higher value on the conversion of TFA catalyst deposited on MCM-41, compared to that deposited on γ-Al_2O_3, is due both appropriate pore size distribution and perhaps improving the contacting of the two reactants by improving of the process of emulsification and thus of the contacting of the reactants by powdered MCM-41. Support pore size distribution of MCM-41, which is manifested by a higher content in mesopores is more favourable to the formation of diethers and even of triether, while the pore size distribution of the γ-Al_2O_3 support with a higher content of micropores preferentially favours monoethers formation.

Conclusions

Etherification reaction of glycerol with isobutene occurs in strong acid catalysts such as Lewis acids like TFA at relatively low temperatures (below 80 ^{0}C).

Performance process isobutene etherification of glycerol are diminished due to the low solubility of isobutene in glycerol and implicitly difficulty of contacting the two reactants.

Inorganic catalytic systems used to perform the experimental program were based on triflic acid supported on γ-Al_2O_3 or on MCM-41, at the same concentration of 10% TFA.

Textural data showed increasing specific surface area of γ -alumina after treatment with triflic acid, also adsorption isotherm and pore size distribution change after impregnation with triflic acid.

Textural changes of the support MCM-41 after impregnation with triflic acid are less highlighted by adsorption isotherm, but they are demonstrated by pore size distribution curves.

Specific surface area of the catalyst support MCM-41 decreases after impregnation with triflic acid, probably due to small pore collapse after reaction of TFA with support.

Performances obtained by triflic acid catalyst supported on mesoporous zeolite MCM-41 were much higher than with microporous alumina catalyst support.

Selectivity in monoethers had higher values on TFA catalyst deposited on the support with a higher content in micropores, ie γ -Al_2O_3.

Selectivity in more voluminous ethers (diethers and triether respectively) had higher values on TFA catalyst deposited on the support with a higher content in macropores, ie MCM-41.

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Manuscript received: 20.01.2014