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Biofuel Additives: Conversion of Glycerol with Benzyl Alcohol over SBA-15 with Sulfonic Acid Groups

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Abstract

The etherification of glycerol with benzyl alcohol was carried out over mesostructured silica, SBA-15, with sulfonic acid groups. The products of glycerol etherification are ethers (glycerol mono-ether, glycerol di-ether and tri-glycerol ether). It was prepared with different catalysts, consisting of SBA-15 with different amounts of sulfonic groups (SBA-15, [SO₃H]1-SBA-15, [SO₃H]2-SBA-15, and [SO₃H]3-SBA-15). It was observed that the activity increased with the amount of sulfonic acid groups on SBA-15 until a maximum ([SO₃H]2-SBA-15). However, with high amount of acid groups, a decrease in catalytic activity was observed. The effect of different parameters, such as catalysts loading, temperature, and initial concentration of glycerol, was studied in order to optimize the reaction conditions. Catalyst [SO₃H]2-SBA-15 showed good activity after four uses.

Keywords: biodiesel, glycerol, benzyl alcohol, SBA-15-SO₃H, etherification

1. Introduction

Biodiesel is defined as mono-alkyl esters of fatty acids, which can be obtained from different feedstocks (animal fats and vegetable oils) [1–7]. Biodiesel is a renewable, biodegradable fuel with lower sulfur content, environmentally less toxicity, and better lubrication.

Biodiesel production can be carried out by transesterification of triglycerides or by esterification of free fatty acids with methanol or ethanol in the presence of base or acid catalysts [1–7]. **Figure 1** represents the transesterification of triglycerides with different alcohols.

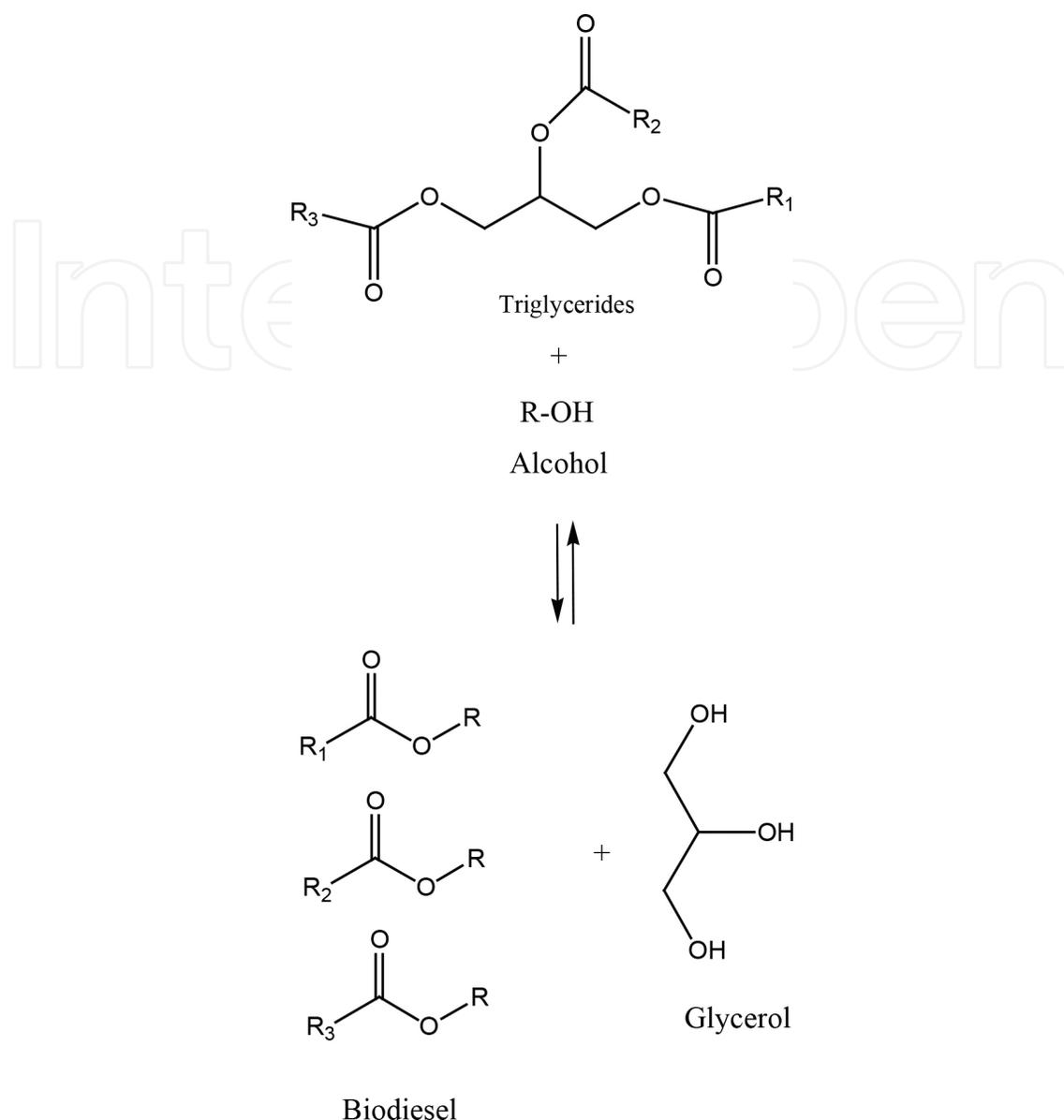


Figure 1. Representation of transesterification of triglycerides with alcohols into biodiesel and glycerol.

In the previous years, an increase in biodiesel production has been observed, and consequently, a large amount of glycerol has been produced. So, it is imperative to develop different processes to produce glycerol as a product with high commercial value. The main use of glycerol is in personal care and cosmetics, but its use as a valuable feedstock for new products and processes is growing in importance [8–13]. Glycerol ethers have many potential uses, such as fuel additives, solvents, and cryogenics. Reactions of glycerol with isobutene or *tert*-butanol under acid catalysis conditions afford *tert*-butyl-glycerol ethers, which have potential for blending with diesel [12].

Traditionally, strong homogeneous acid catalysts have been used. In order to become the process a “green process,” the homogenous catalysts have been replaced by heterogeneous ones [13].

Gu et al. [14] reported the etherification of glycerol with different alcohols catalyzed by acid-functionalized silica. They reported yields varying from 61 to 96% of the mono and di-glycerol ethers, using batch reaction conditions. These results prompted us to report some preliminary data of glycerol benzylation with benzyl alcohol, using different types of heterogeneous acid catalysts, aiming to produce mono, di, and tribenzyl glycerol ethers (**Figure 2**).

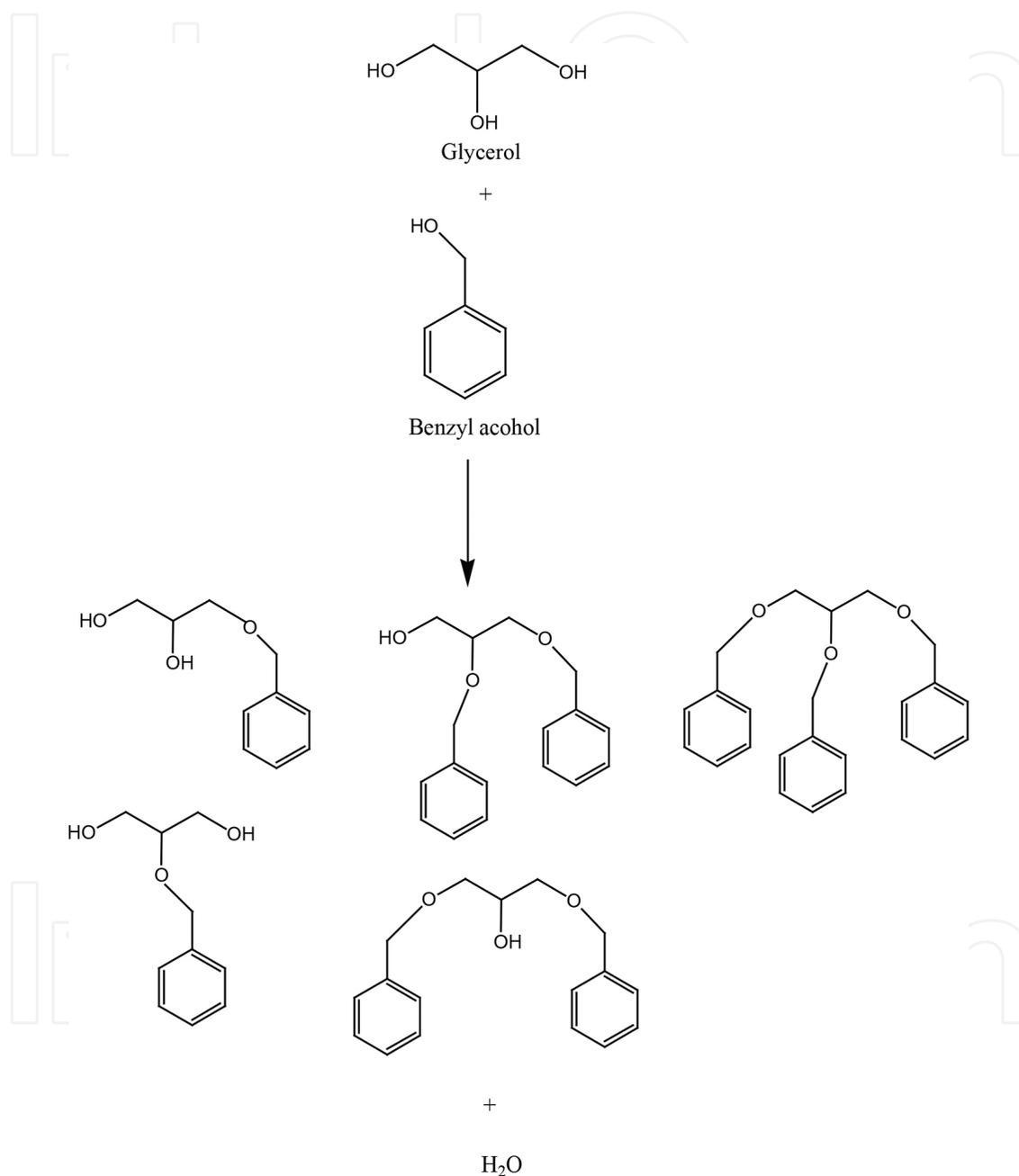


Figure 2. Etherification of glycerol with benzyl alcohol.

Etherification of glycerol with benzyl alcohol was carried out in the presence of zirconia modified with sulfuric acid (1 and 2 mol dm^{-3}). The products were mono- and dibenzyl glycerol ethers. The catalytic tests were carried out at different temperatures and initial reactant mass

ratios. The catalyst prepared with the highest sulfuric acid concentration showed the highest activity [15].

Due to high surface areas and controlled pore sizes, mesoporous materials, such as SBA-15, PMO, and MCM-41, have been used in heterogeneous catalysis as catalyst supports. This kind of materials can be functionalized with different organic groups on the surface. There are different techniques to change the materials: by grafting or co-condensation. These modified materials can be used as catalysts in different chemical reactions [16–18].

In the present work, we studied the etherification of glycerol with benzyl alcohol over SBA-15 with sulfonic acid groups.

2. Experimental

2.1. Preparation of catalysts

The catalyst samples were prepared according to Grieken et al. [19].

2.2. Catalysts characterization

Micromeritics ASAP 2010 apparatus was used to determine the nitrogen adsorption isotherm at 77 K.

A CHNS Elemental Analyser 1112 series Thermo Finnigan instrument was used to determine the amount of sulfur present in SBA-15.

Cation-exchange capacities of catalysts were determined by potentiometrical titration. An aqueous solution of sodium chloride (NaCl, 2M) was used as a cationic-exchange agent.

X-ray diffraction (XRD) patterns of the catalysts were obtained by using a Rigaku powder diffractometer.

2.3. Catalytic experiment

The catalytic experiments were carried out in a stirred batch reactor at 80°C. In a typical experiment, the reactor was loaded with 10 mL of benzyl alcohol, 4 g of glycerol, and 0.2 g of catalyst.

The catalytic stability of [SO₃H]₂-SBA-15 was carried out in the same conditions with the same sample. The catalyst was separated from reaction mixture by centrifugation. After this operation, the catalyst was washed with acetone, and it was dried at 80°C overnight.

Undecano was used as the internal standard. Samples were taken periodically and analyzed by GC, using a Hewlett Packard instrument equipped with a 30 m × 0.25 mm HP-5 column.

3. Results and discussion

3.1. Catalyst characterization

SBA-15 and SBA-15 with sulfonic acid groups show a typical IV adsorption isotherm, according to the IUPAC classification. **Table 1** reports the physicochemical characterization of materials. It was observed that the surface area (S_{BET}) and the pore volume decreased with the amount of sulfonic acid groups immobilized on SBA-15. It can be also observed that the amount of sulfur, determined by elemental analysis, is similar to the amount of sulfonic acid groups, determined by acid-base titration (**Table 1**).

Material	Amount of S (mmol/g)	H ⁺ (meq/g)	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	Vp^{b} (cm ³ /g)
SBA-15	–	–	950 ± 3	0.99 ± 0.02
[SO ₃ H]1-SBA-15	0.06 ± 0.01	0.05 ± 0.01	935 ± 5	0.95 ± 0.03
[SO ₃ H]2-SBA-15	0.14 ± 0.02	0.13 ± 0.01	875 ± 2	0.88 ± 0.01
[SO ₃ H]3-SBA-15	0.20 ± 0.01	0.19 ± 0.02	820 ± 4	0.83 ± 0.02

^a BET.

^b (p/p°) = 0.98.

Table 1. Physicochemical characterization of materials.

Figure 3 shows the powder X-ray diffraction patterns of SBA-15 and SBA-15 with sulfonic acid. It can be observed that the materials with sulfonic acid exhibit a hexagonal pore structure, characteristic of SBA-15 materials:

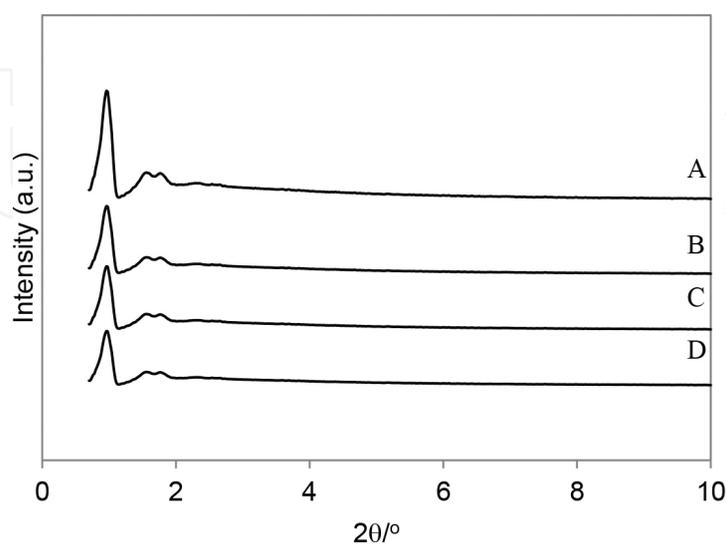


Figure 3. X-ray diffraction of materials. (A) SBA-15; (B) [SO₃H]1-SBA-15; (C) [SO₃H]2-SBA-15; and (D) [SO₃H]3-SBA-15.

3.2. Catalytic experiments

Figure 2 shows the products obtained in the glycerol etherification with benzyl alcohol. The products resulting from glycerol etherification reaction are mono-glycerol ether, di-glycerol ether, and tri-glycerol ether.

Figure 4 shows the initial activity of the catalysts in the glycerol etherification reaction with benzyl alcohol. It is observed that the catalytic activity increases from the material SBA-15 to the catalyst sample [SO₃H]2-SBA-15, which can be explained by the amount of sulfonic acid groups present on the SBA-15 surface (**Table 1**). However, when the amount of sulfonic acid groups increases (from catalyst sample [SO₃H]2-SBA-15 to [SO₃H]3-SBA-15) the catalytic activity decreases, which can be explained by the decrease of accessibility to the active centers. In fact, a decrease in S_{BET} and total pore volume with the amount of sulfonic acid groups were observed (**Table 1**).

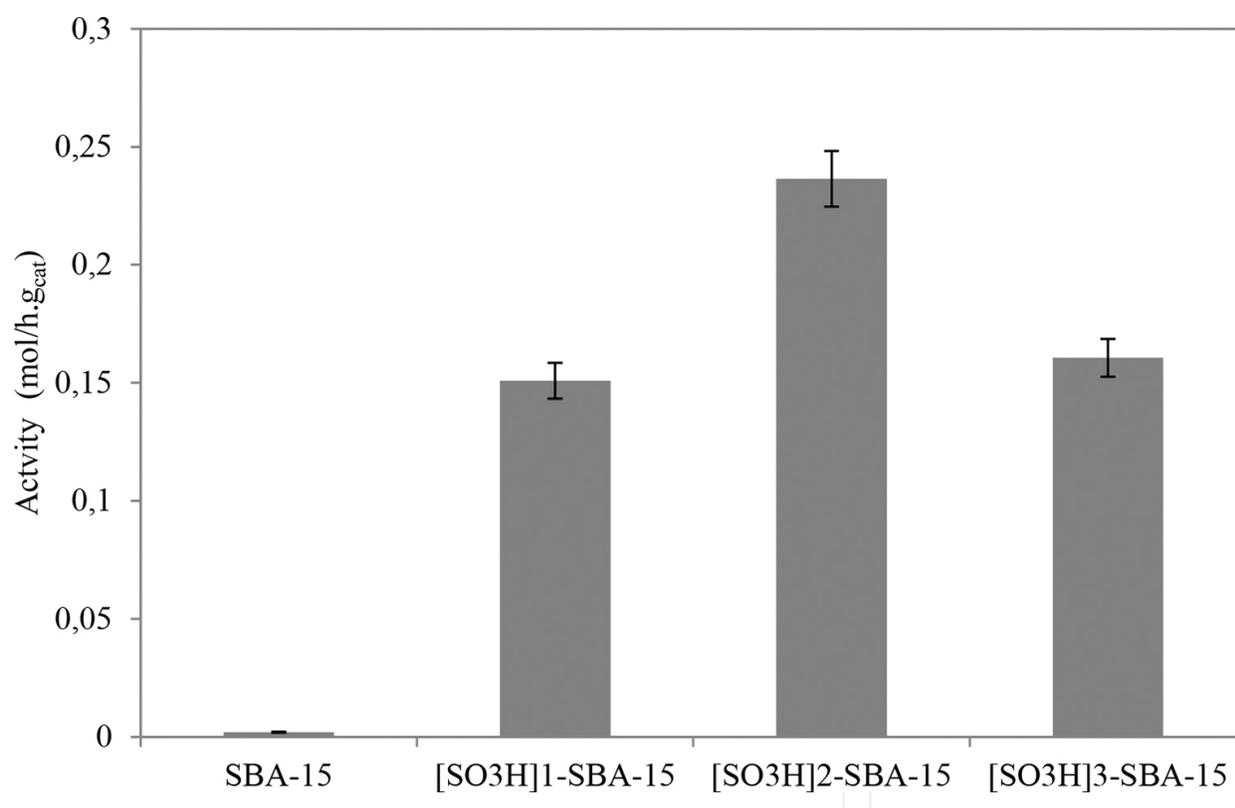


Figure 4. Etherification of glycerol with benzyl alcohol over [SO₃H]-SBA-15 catalysts.

Table 2 shows the values of glycerol conversion and selectivity of catalysts for the different products obtained from glycerol etherification with benzyl alcohol, after 7 h of reaction. It is observed that the sample of [SO₃H]2-SBA-15 got the highest conversion.

The selectivity mono-ether ranges from 72%, in the presence of SBA-15, to 78%, in the presence of the catalyst [SO₃H]1-SBA-15. It is observed that the selectivity for tri-ether is reduced. This behavior of this compound may be explained by obtaining consecutive reactions.

Catalysts	Conversion (%) ^a	Selectivity		
		Mono-ether	Di-ether	Tri-ether
SBA-15	5 ± 0.1	72 ± 1	20 ± 1	8 ± 1
[SO ₃ H]1-SBA-15	73 ± 2	78 ± 2	16 ± 2	6 ± 1
[SO ₃ H]2-SBA-15	89 ± 1	70 ± 1	20 ± 1	10 ± 1
[SO ₃ H]3-SBA-15	86 ± 0.5	71 ± 1	18 ± 1	11 ± 1

^a Glycerol conversion after 7 h of reaction.

Table 2. Conversion of glycerol and selectivity to the glycerol etherification products over sulfonic acid groups presents on SBA-15 surface.

The effect of different parameters (catalyst loading, initial glycerol concentration, and temperature) in etherification reaction with [SO₃H]2-SBA-15 catalyst was also studied in order to optimize the reaction.

3.2.1. Effect catalyst loading

In order to study the effect of catalyst loading [SO₃H]2-SBA-15 in glycerol conversion, at 80°C, different experiments were carried out. The amount of catalyst ranges from 0.05 to 0.20 g. The initial concentration of glycerol (2.9 mol dm⁻³) was kept constant. **Figure 5** shows the conversion of glycerol versus time. It was observed that when the catalyst loading increases, equilibrium conversion can be obtained faster. This behavior could be explained by the total number of active sites, with the increase in the amount of catalyst used in the reaction. However, when the catalyst amount increases from 0.1 to 0.2 g, only a slight increase in the glycerol conversion was observed.

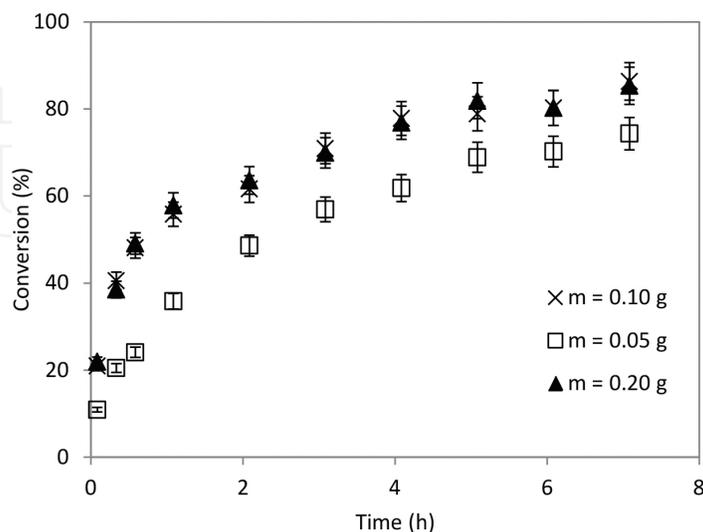


Figure 5. Etherification of glycerol with benzyl alcohol in the presence of SBA-15 with sulfonic acid groups (catalyst [SO₃H]2-SBA-15). Effect of catalyst amount. Conversion (%) versus time (h).

It was also observed that the increase in catalyst loading has no effect on the equilibrium conversion (**Figure 5**).

The amount of effect of catalyst [SO₃H]2-SBA-15 on selectivity to the different compounds was also studied. In all catalyst tests with the sample [SO₃H]2-SBA-15, similar values of selectivity to mono-ether (70%, at 70% of glycerol conversion) were observed.

3.2.2. Effect of the initial glycerol concentration

The initial concentration of glycerol ranged between 1.7 and 2.9 mol dm⁻³, while the reaction temperature ($T = 80^{\circ}\text{C}$) and the catalyst amount ($m = 0.10$ g) were kept constant. The etherification reaction of glycerol was performed with the catalyst [SO₃H]2-SBA-15. The results are shown in **Figure 6**. It was found that the conversion of glycerol increases with the increase in the initial glycerol concentration under the same reaction conditions. This behavior may be explained by the increased reaction rate with the concentration of glycerol.

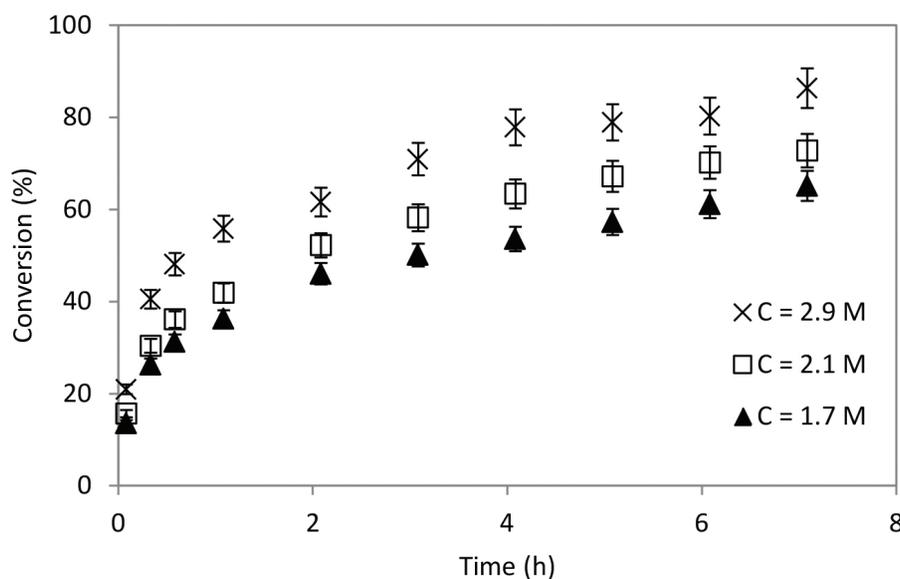


Figure 6. Etherification of glycerol with benzyl alcohol in the presence of SBA-15 with sulfonic acid groups (catalyst [SO₃H]2-SBA-15). Effect of catalyst amount. Conversion (%) versus time (h).

The effect of glycerol initial concentration for the different compounds was also studied. Similar values of selectivity to mono-ether (about 72%, 70% glycerol conversion) were observed.

3.2.3. Effect of temperature

In this work, we also studied the effect of temperature on the glycerol etherification. Catalytic tests with the catalyst [SO₃H]2-SBA-15 were performed at different temperatures, whereas the initial concentration of glycerol (2.9 mol dm⁻³) and the catalyst amount ($m = 0.10$ g) were kept constant. **Figure 7** shows the effect of temperature on the glycerol conversion. An increase in glycerol conversion with temperature was observed.

The effect of temperature on catalyst selectivity [SO₃H]2-SBA-15 for the different compounds was also studied. Increasing the temperature resulted in a decrease in the selectivity to mono-ether (about 81%, 70% glycerol conversion ($T = 55^{\circ}\text{C}$) to 60%, the glycerol conversion ($T = 110^{\circ}\text{C}$)). This behavior can be explained by the increase in the reaction rate.

The catalytic stability of [SO₃H]2-SBA-15 catalyst was also studied. Different catalytic experiments were also carried out. A slight decrease in catalytic activity was observed after the second run (Figure 8).

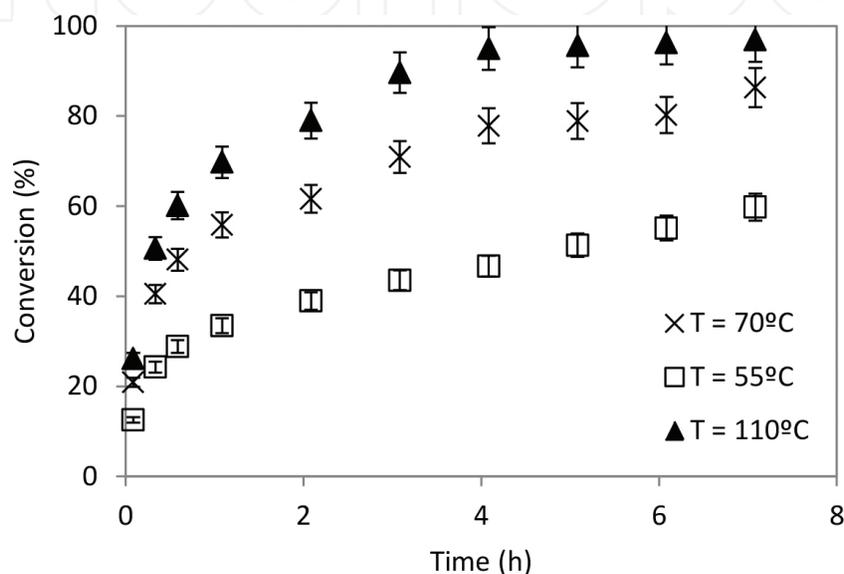


Figure 7. Etherification of glycerol with benzyl alcohol in the presence of SBA-15 with sulfonic acid groups (catalyst [SO₃H]2-SBA-15). Effect of temperature. Conversion (%) versus time (h).

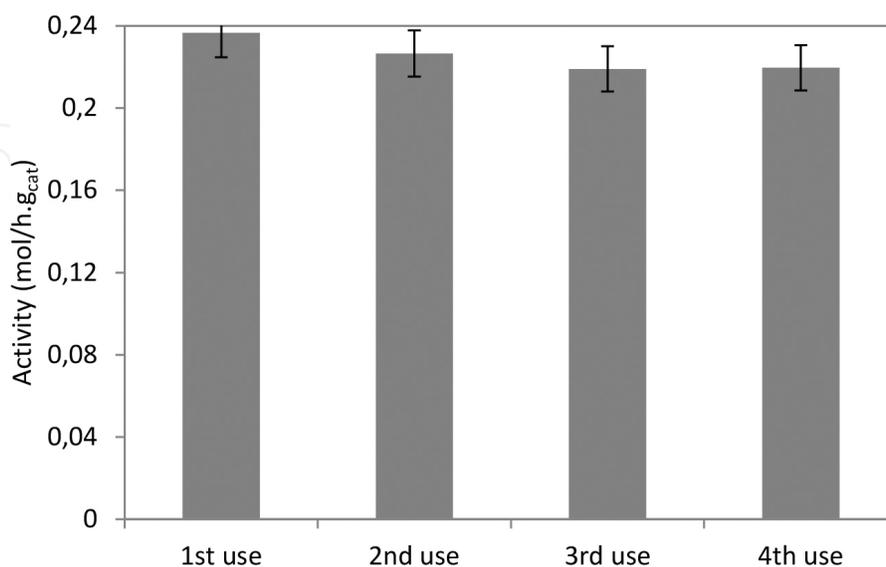


Figure 8. Catalytic stability of [SO₃H]2-SBA-15 catalyst in etherification of glycerol with benzyl alcohol.

4. Conclusions

The etherification of glycerol with benzyl alcohol can be achieved with the use of heterogeneous acid catalysts, consisting in SBA-15-SO₃H. The products of the glycerol etherification reaction are mono-glycerol ether, di-glycerol ether, and tri-glycerol ether.

The catalytic activity increased with the amount of sulfonic acid groups on SBA-15 surface, until a maximum. After this value, the catalytic activity decreases.

Different reaction parameters were optimized. It was observed that increasing the catalyst loading allows faster equilibrium conversion. However, the increases in catalyst loading do not affect the equilibrium conversion. Another conclusion is that the glycerol conversion increased with increase in the initial glycerol concentration. An increase in the glycerol conversion with temperature was observed.

After the second use ([SO₃H]₂-SBA-15), the catalyst tends to stabilize.

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