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The role of mesoporosity and Si/Al ratio in the catalytic etherification of glycerol with benzyl alcohol using ZSM-5 zeolites

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ABSTRACT

A comparative study of the influence of three different acid solids as catalysts (conventional zeolites Z15c with Si/Al = 19.5 and Z40c with Si/Al = 48.2, and a hierarchical zeolite Z40c-H with Si/Al = 50.0) for the etherification of glycerol with benzyl alcohol was performed. The catalytic activity and selectivity of these zeolites was elucidated at different catalyst contents. Three different ethers (3-benzyloxy-1,2-propanediol, which is a mono-benzyl-glycerol ether (MBG) and 1,3-dibenzyloxy-2-propanol, which is a di-benzyl-glycerol ether (DBG) and dibenzyl ether (DBz) were identified as the main products. MBG was the major product of the reaction catalyzed by the microporous Z15c zeolite with low Si/Al molar ratio, whereas DBG was formed in higher yield with the use of microporous Z40c and hierarchical Z40c-H zeolites, both of them having a similar high Si/Al molar ratio (≈50). MBG is a value-added product and it is obtained with good yield and selectivity when using the conventional zeolite Z15c as a catalyst. Under the best conditions tested, i.e., 25 mg of catalyst for 8 h at 120 °C, a 62% of conversion was obtained without the need of solvent, with an excellent 84% selectivity toward the MBG and no formation of DBz.

1. Introduction

The increasing consumption of fossil fuels over the past decades has caused severe environmental problems, climate change not being the least of them. Attempts to find alternative more sustainable energy sources have produced an unprecedented global effort in the exploration and development of renewable resources such as biomass and its derivatives (glucose, sorbitol, glycerol and lactose acid), for use as an alternative to fuels and chemicals [1,2]. The biodiesel is produced at industrial scale, generating a large amount of glycerol as a by-product (10 weight% of the total product) [3,4] which has caused a significant economic devaluation of this important triol. Glycerol has a large number of applications in the pharmaceutical, cosmetic, and food industries [5,6]. Currently, chemical efforts focus on finding new uses for glycerol to output large surplus produced by industry and turn it into products with high added value [7,8]

The catalytic transformation of glycerol into various chemicals by hydrogenolysis [9,10], polymerization [11] etherification [12,13], oxidation [14], dehydration [15,16], esterification [17] and acetalysation [18], among other, has been reported.

Catalytic etherification of glycerol is one interesting option, as glycerol ethers have many potential applications, for example, fuel additives [19] and solvents [20]. Usually, olefins as isobutene [21,22] and alcohols as *tert*-butyl alcohol [22,23] have been used for the etherification of glycerol to obtain di- and tri-*tert*-butyl ethers of glycerol in the presence of acid catalysts, the so-called higher ethers (h-GTBE), which constitute excellent additives with a great potential for diesel and biodiesel reformulation [24]. One major advantage of *tert*-butyl alcohol over isobutene is the higher solubility of glycerol in *tert*-butyl alcohol.

Different groups have studied other raw materials. For example, Gu et al. [25] evaluated the activity of silica supported sulfonic moieties in the etherification of glycerol with alkyl alcohols. Another important group of ethers is polyglycerols, which have many appli-

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cations in the food, pharmaceutical and oleochemical industries, for example, Guerrero-Urbaneja et al. [26] obtained polyglycerols from glycerol etherification with oxides derived from hydrotalcites MgFe. Benzyl alcohol has been used as solvent for hair dyes, but this compound may cause skin allergies [27]. A more suitable alternative would be the derivatives of benzyl alcohol with glycerol, more specifically monosubstituted. Pico et al. [28] and da Silva et al. [29] investigated the etherification of glycerol with benzyl alcohol using different catalyst acid ion-exchange resins, acid-functionalized mesostructured silica and zeolites, obtaining good results in most cases.

Recently, we have reported that hierarchical ZSM-5 zeolites prepared using a simple alkali treatment and subsequent HCl washing exhibit unprecedented catalytic activities in selective oxidation of benzyl alcohol under microwave irradiation [30]. The scope of this article is to study the influence of Si/Al ratio and the micro/mesoporosity of zeolites on the catalytic activity of Z15c and Z40c zeolites on the glycerol etherification reaction with benzyl alcohol.

2. Experimental

2.1. Preparation of the catalysts

Two commercial MFI zeolites in their ammonium form, CBV8014 (Zeolyst International, Si/Al molar ratio = 40) and CBV3024E (Zeolyst International, Si/Al molar ratio = 15), were transformed into the acid form by calcination at 550 °C for 5 h in air (heating rate up to 550 °C of 100 °C h^{-1}) and used as starting materials. These are denoted as Z40c and Z15c, in which Z stands for the type of zeolite (ZSM-5), the number (40 or 15) refers to the Si/Al ratio according to the manufacturer's specifications, and the letter c refers to the calcined material.

Hierarchical Z40c zeolite was prepared by desilication of the zeolite Z40c using a simple alkali treatment, followed by an acid wash with HCl [30]. Desilication treatment of Z40c zeolite was conducted following the methodology reported by Verboekend et al. [31] in which the zeolite Z40c is treated with 100 mL NaOH solution 0.8 M and for Z15c for 30 min at 65 °C and 600 rpm. The solution was then filtered off and thoroughly washed with distilled water. Desilicated zeolite was subsequently treated in 100 mL of 0.1 M aqueous HCl during 6 h to remove debris alumina and obtain the ZSM-5 porous zeolites, as recently reported elsewhere [30]. Hierarchical Z40c catalysts after acid washing is denoted as Z40c-H (see ref. [30] for further details).

2.2. Materials characterization

The porosity of the materials was measured by N_2 adsorption/desorption isotherms at 77 K in an AUTOSORB-6 apparatus. Samples were previously degassed for 5 h at 373 K at 5×10^{-5} bar. BET surface area was estimated by using multipoint BET method and the adsorption data in the relative pressure (P/P_0) range of 0.05–0.30. The pore size distribution was calculated from the adsorption branch of the N_2 isotherms using the DFT method. The mesoporous volume was calculated from the cumulative pore volume distribution curve. Micropore volume was calculated using the *t*-plot method. Pyridine (PY) and 2,6-dimethylpyridine (DMPY) titration experiments were conducted at 200 °C via gas phase adsorption of the basic probe molecules utilizing a pulse chromatographic titration methodology. Briefly, probe molecules (typically 1–2 μL) were injected in very small amounts (to approach conditions of gas chromatography linearity) into a gas chromatograph through a microreactor in which the solid acid catalyst was previously placed. Basic compounds are adsorbed until complete saturation from where the peaks of the probe molecules in the gas phase are detected in the GC. The quantity of probe molecule adsorbed by the solid acid catalyst can subsequently be easily quantified. In order to distinguish between Lewis and Brönsted acidity, the assumption that all DMPY selectively titrates Brönsted sites (methyl groups hinder coordination of nitrogen atoms with Lewis acid sites) while PY titrates both Brönsted and Lewis acidity in the materials was made. Thus, the difference between the amounts of PY (total acidity) and DMPY (Brönsted acidity) adsorbed should correspond to Lewis acidity in the materials. Diffuse Reflectance Fourier-Transform Infrared (DRIFT) spectra of adsorbed pyridine (PY) were carried out in an ABB IR-ATR instrument equipped with an environmental chamber. PY was adsorbed at room temperature for a certain period of time (typically 1 h) to ensure a complete saturation of the acid sites in the catalyst and then spectra were recorded at different temperatures ranging from 100 to 300 °C in a similar way to previous reports [32]. With this purpose, the different types of acid sites in the materials (Brönsted and Lewis) could be measured and quantified.

2.3. Catalytic experiments

a) Materials: Glycerol (100% purity), supplied by Aldrich, and benzyl alcohol (≥99.5% purity), provided by Sigma–Aldrich, were employed as reactants. All chemicals were used without further purification. Ethanol (≥99% purity), supplied by Scharlau, was used as the solvent for sample analysis. Hexadecane (≥99% purity, Sigma–Aldrich) was employed as the internal standard compound in the chromatographic analysis. Commercial (±) 3-benzyloxy-1,2-propanediol (≥97% purity), 1,3-dibenzyloxy-2-propanol (≥97% purity), and benzyl ether (≥98% purity) were used to calibrate the gas chromatograph, and supplied by Aldrich.

b) Typical procedure for etherification reactions: In a typical run, 10 mmol glycerol, 10 mmol benzyl alcohol and the catalyst (0.025–0.100 g) were placed in a ampoule with continuous stirring for 8 or 15 h at 120–140 °C. The resultant mixture was filtered off, extracted using ethanol and the products were identified by GC–MS and their ratios also. The response factors of the benzyl alcohol was determinated using hexadecane as external standard and calibrate curve. Commercial (±) 3-benzyloxy-1,2-propanediol (MBG) and 1,3-dibenzyloxy-2-propanol were employed to obtained the corresponding response factor. Dibenzyl ether was calibrated as well. Quantification of glycerol was performed taking into account the molar ratio on the chromatographic analysis of compounds derived from glycerol. Any dehydration products of glycerol or of benzyl alcohol were detected. The stirring speed was 1200 rpm to guarantee the absence of external mass-transfer resistance.

c) Analytic methods: The composition of the reaction mixture (ethers and benzyl alcohol) was analyzed by means gas chromatography using an Agilent turbo system 5975 chromatograph, integrated with a mass detector 7820A. An HP 5MS capillary chromatographic column (30 m × 0.25 mm × 0.25 μm) was utilized. The chromatographic conditions were as follows: initial oven temperature of 50 °C, final oven temperature of 230 °C, and one programmed rate of 10 °C min^{-1}. Retention times: peak at 6.20 min benzyl alcohol, at 13.36 min (±) 3-benzyloxy-1,2-propanediol (MBG), at 13.74 min hexadecane, at 14.48 min dibenzyl ether (DBz) and at 20.43 min 1,3-dibenzyloxy-2-propanol (DBG).

3. Results and discussion

Table 1 summarizes the bulk Si/Al ratio, porosity and acidic properties of both conventional zeolites as (Z15c and Z40c) well as of the hierarchical Z40c-H sample, all after calcination. As previously reported [30], the introduction of mesoporosity in ZSM-5

Table 1
Bulk Si/Al ratio, porosity and acidic properties of Z15c, Z40c and Z40c-H materials [30].

Sample	Si/Al[a]	S_{BET}[b] (m^2/g)	S_{meso}[c] (m^2/g)	V_{micro}[c] (cm^3/g)	V_{meso}[d] (cm^3/g)	Surf. acidity[e] ($\mu mol\,g^{-1}$)		
						PY	DMPY	PY-DMPY
Z40c	48.2	410	210	0.14	0.16	218	14	204
Z40c-H	50.0	610	440	0.16	1.13	264	249	15
Z15c	19.5	360	190	0.14	0.13	529	285	244

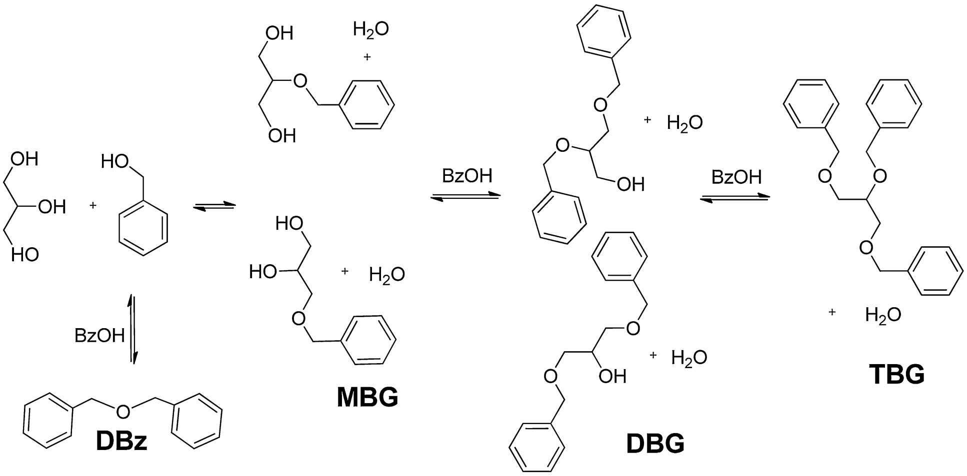
[a] Surface Si/Al mole ratio content as determined by XPS after the samples were etched. According to the manufacturer, Si/Al molar ratio in Z40 and Z15 zeolites before calcinations is 40 and 15, respectively.

[b] BET surface area obtained using multipoint BET method from the adsorption data (P/P_0 range = 0.05–0.30).

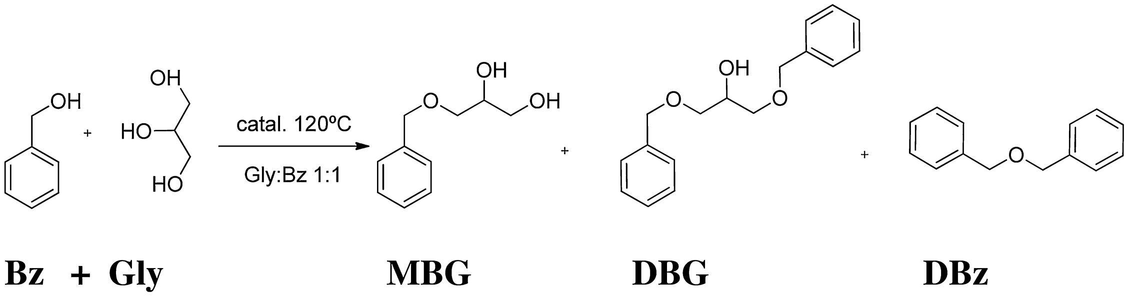
[c] External surface area and micropore volume from the isotherms using the *t*-plot method.

[d] Mesopore volume from the isotherms using the DFT method.

[e] Surface acidity measured using PY and DMPY as probe molecules at 300 °C. Lewis acidity was obtained by subtracting PY and DMPY values, by assuming that PY characterizes both B and L sites while DMPY mainly for B sites [32].



Scheme 1. Reaction equilibria of etherification of glycerol with benzyl alcohol. Legend: DBz: dibenzyl ether, MBG: mono-benzyl-glycerol ether (3-benzyloxy-1,2-propanediol and 2-benzyloxy-1,3-propanediol), DBG: di-benzyl-glycerol ether (1,3-dibenzyloxy-2-propanol and 1,2-dibenzyloxy-3-propanol), and TBG: 1,2,3-tribenzyloxypropane.



Scheme 2. Observed products in the etherification of glycerol (Gly) with benzyl alcohol (Bz) catalyzed by microporous Z15c and Z40c zeolites in comparison with hierarchical Z40c-H catalysts.

zeolites using the proposed desilication treatment followed by acid washing allows to roughly maintain the Si/Al ratio of the parent calcined zeolite. Textural parameters have been calculated from the adsorption/desorption isotherms at 77 K shown in Fig. S1 (ESI). Accordingly, microporous Z15c and Z40c samples show type I isotherms, while hierarchical Z40c-H sample shows type I + IV isotherm typical of a micro and mesoporous material, with a surface area, specially the external surface area, comparably superior to that of parent microporous Z40c catalyst. The development of mesoporosity in Z40c-H sample is related to the higher accessibility of DMPY giving rise to a material with essentially Brönsted acid sites, as shown in Table 1 (see ref. [30] for further details). It should be remembered that PY and DMPY differs also in molecular dimension and thus, while PY reaches all acid sites either in micropores or mesopores/surface, DMPY is only applicable the quantification of acid sites in mesopores or on external surface [30,32,33].

Scheme 1 shows the reaction pathway of the etherification of glycerol with benzyl alcohol, with all the possible products. This process involves a set of consecutive equilibrium reactions and it is reversible process unless water is continuously removed. The possible products of the etherification of glycerol with benzyl alcohol are MBG, two isomers: (±) 3-benzyloxy-1,2-propanediol and 2-benzyloxy-1,3-propanediol; DBG, two isomers as well: 1,2-dibenzyloxy-3-propanol and 1,3-dibenzyloxy-2-propanol and 1,2,3-tribenzyloxypropane: TBG. A side reaction could occur, namely the dimerization of benzyl alcohol, this process is undesired because it consumes benzyl alcohol. However, this product could react with glycerol to produce MBG [25].

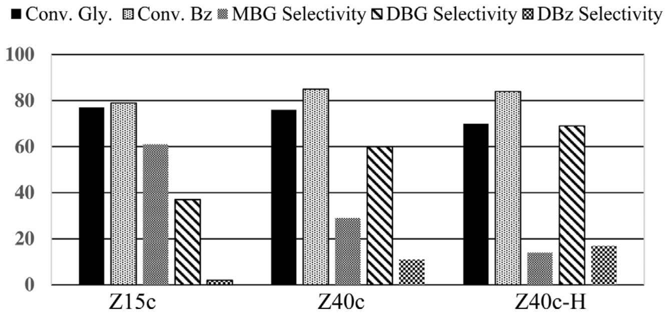


Fig. 1. Conversion (%) and selectivity (%) in the etherification of glycerol (Gly) with benzyl alcohol (Bz) catalyzed by microporous Z15c and Z40c zeolites in comparison with hierarchical Z40c-H catalysts. Reaction conditions: 120 °C, 8 h, 50 mg of catalyst, 1 mmol of glycerol, and Bz/Gly = 1/1. Legend: Gly: glycerol, Bz: benzyl alcohol, DBz: dibenzyl ether, MBG: mono-benzyl-glycerol ether and DBG: di-benzyl-glycerol ether.

Glycerol etherification with benzyl alcohol was studied over three different solid catalysts: two microporous zeolites (Z15c and Z40c) and one hierarchical Z40c-H zeolite. The experimental conditions employed for this study were an initial reactant molar ratio of 1/1, a temperature of 120 °C, and an amount of catalyst of 50 mg (number of acid sites depend on material) referred to 1 mmol of glycerol. The only products obtained under the synthetic conditions employed were MBG, DBG and DBz (see Scheme 2).

Fig. 1 shows the effect of the Si/Al molar ratio and the acidity of catalysts on the glycerol conversion and selectivity toward MBG, DBG and DBz in the presence of 50 mg of catalyst/mmol of glycerol. Despite their different acidity, Z15c (26.4 μmol of acid sites/mmol of glycerol), Z40c (10.9 μmol of acid sites/mmol of glycerol) and Z40c-H (13.2 μmol of acid sites/mmol of glycerol) the three zeolites gave a similar catalytic activity, with a glycerol conversion of 77, 76 and 70%, respectively. In other words, a high acid sites density in the zeolite doesn't translated into a higher catalytic activity as previously reported for the acid-catalysed reactions [34,35]. The

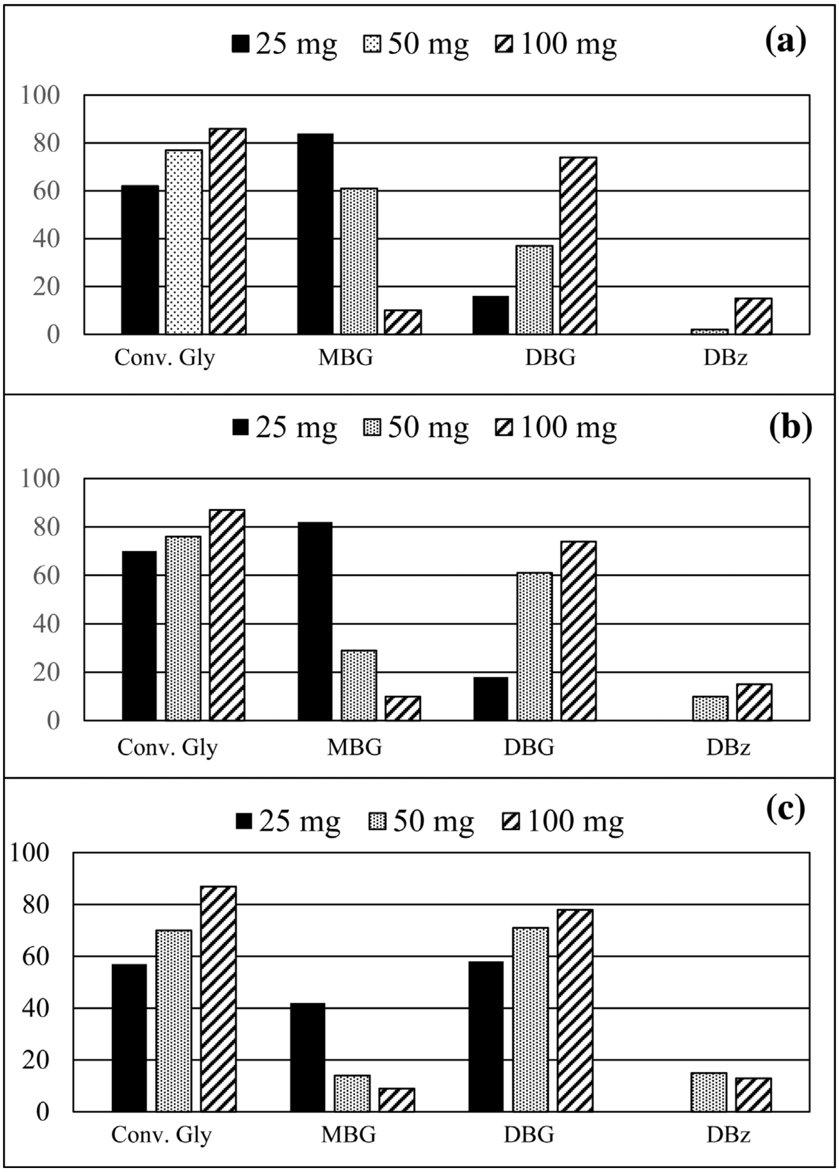


Fig. 2. Effect of catalyst concentration on conversion (%) and selectivity (%) in the etherification of glycerol (Gly) with benzyl alcohol (Bz) catalyzed by: (a) Z15c (13.2 (25 mg), 26.4 (50 mg) and 52.9 μmol (100 mg) of acid sites per mmol of glycerol), (b) Z40c (5.45 (25 mg), 10.9 (50 mg) and 26.4 μmol (100 mg) of acid sites/mmol of glycerol), and (c) Z40c-H (6.6 (25 mg), 13.2 (50 mg) and 21.8 μmol (100 mg) of acid sites/mmol of glycerol). Reaction conditions: 120 °C, 8 h, 1 mmol of glycerol, and Bz/Gly = 1/1. Legend: Gly: glycerol, DBz: dibenzyl ether, MBG: mono-benzyl-glycerol ether DBG: di-benzyl-glycerol ether.

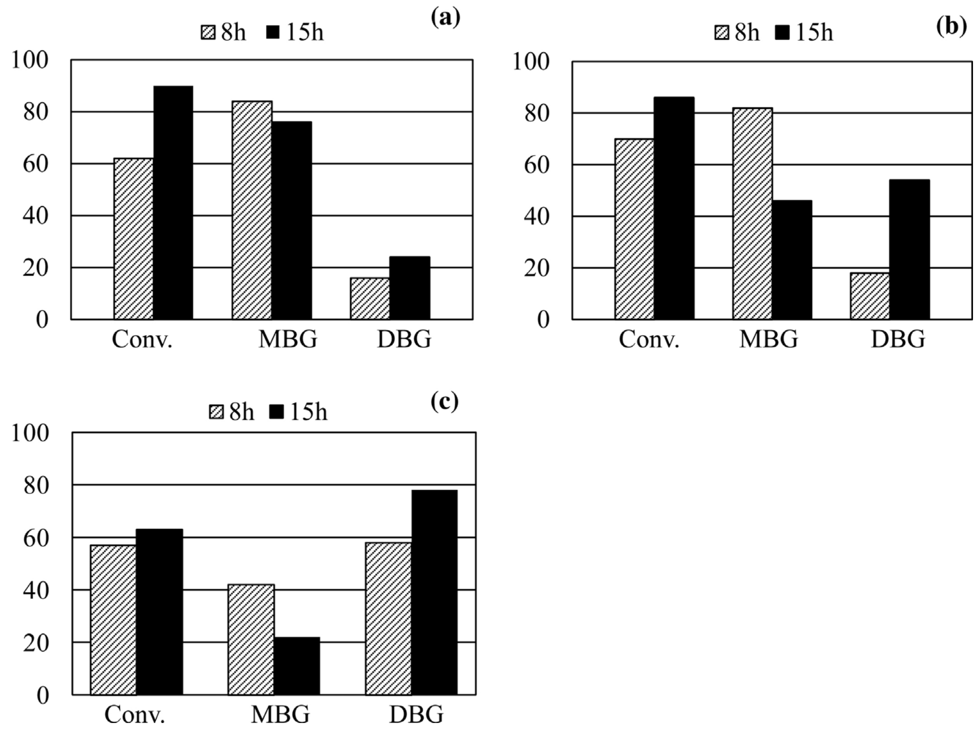


Fig. 3. Effect of reaction time on conversion (%) and selectivity (%) in the etherification of glycerol (Gly) with benzyl alcohol (Bz) catalyzed by: (a) Z15c (13.2 μmol of acid sites/mmol of glycerol), (b) Z40c (5.45 μmol of acid sites/mmol of glycerol), and (c) Z40c-H (6.6 μmol of acid sites/mmol of glycerol). Reaction conditions: 120 °C, 25 mg of catalyst and Bz/Gly = 1/1.

higher selectivity toward DBG when the hierarchical Z40c-H zeolite is used as the catalyst is likely due to its hierarchical porous structure because its mesoporous could facilitate the formation of bulk transition states [29]. The formation of DBz was detected, but in any case the conversion was >20%. Gu et al. [25] used a similar Bz/Gly ratio and did not find auto-etherification of benzyl or alkyl alcohol, and the selectivity to the TBG was zero. A blank control experiment revealed no activity in the absence of catalyst.

The effect of the catalyst concentration on the glycerol conversion and selectivity at 120 °C was also analyzed. For this purpose, the catalyst concentration was varied between 25 and 100 mg/mmol of glycerol. According to the obtained results, increasing the amount of catalyst led to the increase in the glycerol conversion and also toward the DBG selectivity (Fig. 2). MBG and DBz are intermediate products and thus, the formation of DBG is favored as the concentration of catalyst increased leading to a decrease on the MBG and DBz concentration. This performance was already observed in previous studies when using these reactants and glycerol ethers with this alcohol [28] and other ones [22].

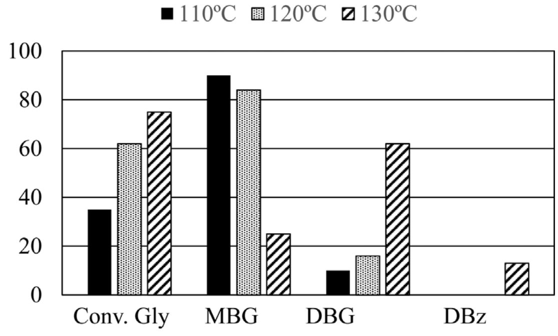


Fig. 4. Effect of temperature on conversion (%) and selectivity (%) in the etherification of glycerol (Gly) with benzyl alcohol (Bz) catalyzed by the Z15c zeolite. Reaction conditions: 8 h, 25 mg of catalyst and Bz/Gly = 1/1.

Again, DBG is the main product when the hierarchical Z40c-H zeolite is used, probably due to the higher accessibility related to the presence of mesoporous in this sample.

The influence of the reaction time on the etherification of glycerol over Z15c, Z40c and Z40c-H catalysts was studied. Based on these result, 25 mg was selected because DBz was not observed and MBG was the main product (Fig. 3), the reaction conditions were 120 °C, molar ratio glycerol/benzyl alcohol 1/1 and without solvent. The higher selectivity toward MBG at 8 h evolves toward to DBG at 15 h in the subsequent consecutive reactions, as we said before.

Finally, Fig. 4 shows the effect of the temperature on glycerol conversion and selectivity while the reaction temperature varied between 110 °C and 130 °C in the presence of 25 mg of Z15c catalyst (Bz/Gly = 1/1). The total yield of benzyl-glycerol ethers increased when temperature increased; however, the selectivity of the target compound MBG decreased. DBz is only obtained at highest temperature 140 °C, and although at 110 °C the catalyst showed the best selectivity toward MBG, the conversion was very low.

4. Conclusions

The effect in their catalytic performance of the Si/Al and the introduction of mesoporosity in ZSM-5 was studied in the etherification of glycerol with benzyl alcohol. Two conventional, Z15c (Si/Al = 19.5), Z40c (Si/Al = 48.2), and a hierarchical, Z40c-H (Si/Al = 50.0), ZSM-5 zeolites were used for this study, showing quite similar activity under the conditions used. The zeolite with higher Al content, (Z15c, Si/Al ratio = 19.5) showed slight higher selectivity to MBG, than the other samples. In the case of the hierarchical ZSM-5, Z40c-H, this showed slight higher selectivity toward DBG. This observation could be due to the higher accessibility of the reactants to the acid sites in the zeolites because of the presence of mesoporosity. The increase in catalyst concentration and time yield a higher conversion of glycerol and formation of DBG, probably because both MBG and DBz are intermediate products. The results obtained in this study led us to conclude that Z15c zeolite might be used as a good catalyst to produce MBG, with negligible formation of DBG and DBz.

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