TRANSFORMATION OF GLYCEROL INTO SOLKETAL BY BETA AND FERRIERITE ACID ZEOLITES

Transformação de glicerol em solketal por zeólitas ácidas beta e ferrierita

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RESUMO: A transformação do glicerol em solketal através da reação de cetalização foi estudada, utilizando as zeólitas H-BEA e H-FER como catalisadores ácidos. As zeólitas foram caracterizadas por diversas técnicas analíticas como difração de raios X (DRX), Fluorescência de Raios X (FRX), Espectroscopia no Infravermelho (IV), Análise Textural (adsorção de N_2) distribuição de tamanho de partículas e medida de acidez por dessorção de piridina. A zeólita H-BEA apresenta maior área específica e maior quantidade de sítios de Lewis do que a zeólita H-FER. Ambas zeólitas apresentam atividade para a transformação de glicerol em solketal com conversão similar ao catalisador comercial (PTSA), atingindo 54 % de conversão e, aproximadamente, 98 % de seletividade para o solketal. Foi realizado um planejamento experimental e as melhores conversões, 72 %, e seletividades, 98 %, foram atingidas quando as condições reacionais foram de 60 °C, 700 rpm, 5 % de catalisador e razão molar glicerol: acetona de 1:4 para H-BEA. O catalisador H-BEA pode ser reusado por 4 vezes sem precisar de pré-tratamentos entre as reações.

Palavras-chave: Glicerol. Solketal. Zeólita H-BEA. Zeólita H-FER. Planejamento experimental.

ABSTRACT: The transformation of glycerol into solketal through the ketalization reaction was studied using H-beta and H-ferrierite zeolites as acidic catalysts. The zeolites were characterized by several techniques, such as X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Infrared spectroscopy (IR), N2 sorption, particle size distribution and acidity measurements by pyridine adsorption. The H-BEA presents a larger surface area and more Lewis acid sites than H-FER. Both zeolites presented activity for the transformation of glycerol into solketal with similar conversions to the commercial catalyst (PTSA), which has a 54% conversion, and a high selectivity to solketal around 98%. An experimental design was studied, and it could be seen that the best conditions for higher conversion (72%) with high selectivity (98%) were reached at 60°C, stirring at 700 rpm, 5% of catalyst, and molar ratio glycerol: acetone 1:4 for H-BEA. The catalyst H-BEA can be reused in 4 reactions without losing its activity.

Keywords: Glycerol. Solketal. H-BEA zeolite . H-FER zeolite. Experimental design.

Introduction

With the success of the global biodiesel industry, glycerin production also had a high growth rate. For each liter of biodiesel, approximately 100 mL of crude glycerin was obtained, i.e., 10%. (ADHIKARI et al*.,* 2007; SÁNCHEZ et al., 2010). Although many industrialized products use glycerin in their formulations, the amount used in these products is still not enough to utilize the great over-production. Therefore, it is necessary to find new technological routes to be applied to the excess glycerin for converting it into value-added products. (KIRSCHHOCK, et al*.,* 2004). The study of glycerol and its conversion into higher value-added products is usually called glycerochemistry. The transformation of glycerol into other products can be carried out by ketalization, acetylation, carbonation, dehydration, esterification, etherification, hydrogenolysis, and oxidation reactions among others. (MOTA et al*.,* 2009).

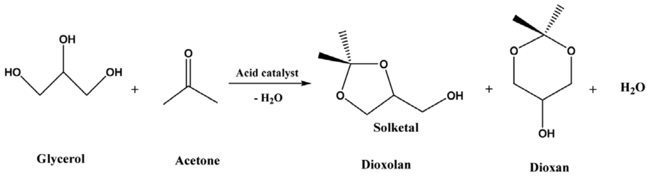
In this paper, we will focus on glycerol ketalization for the production of isopropylidene glycerol or solketal, (2,2-dimethyl-1,3-dioxolan-4-yl) methanol. This reaction is facilitated by homogeneous acidic catalysts (sulfuric acid, hydrochloric acid, phosphorus pentoxide, and p-toluene sulfonic acid) or heterogeneous acid catalysts (zeolites, clays, and Amberlyst resins). (ROYON, et al., 2011). Various glycerol ketals can be produced with a variety of ketones. (REDDY, et al*.,* 2011). These compounds have great potential when applied as fuel additives and biofuels. Solketal is an excellent component for the formation of gasoline, diesel and biodiesel. A mixture of this compound in biofuels improves their properties and the viscosity decreases. Additionally, it helps in obtaining the pre-set requirements for the flash point and oxidation stability of biodiesel. (MOTA et al., 2009; ROYON et al., 2011; REDDY et al., 2011).

Moreover, glycerol ketals are used as solvents, plasticizers, surfactants, disinfectants, and flavorings among others. They can also be used in both the pharmaceutical industry and food industry. (ROYON et al*.,* 2011; REDDY et al*.,* 2011).

The ketalization of glycerol generates branched oxygenated compounds, but when the reaction is carried out with acetone, there is greater selectivity for the molecule solketal, (2,2-dimethyl- [1,3] dioxolan-4-yl) methanol, Figure 1. (ROYON, et al*.,* 2011).

Industrially, the solketal reaction is catalyzed by p-toluene sulfonic acid (PTSA), a Brönsted acid used in homogeneous catalysis for 12 h at 100 °C. (SURIYAPRAPADILOK,

Figure 1 - Glycerol ketalization with acetone. Dioxolan: five-membered ring; dioxan: six-membered ring. Adapted from Royon, 2011.



et al., 2011). However, Brönsted acid homogeneous catalysts (hydrochloric, sulfuric and p-toluene sulfonic among others) have several drawbacks that reduce their usefulness, such as their difficulty of separation, inability to be reused and corrosion of the reactor. Menezes et al. (2013) proposed the use of Lewis acid homogeneous catalysts ($SnCl_2$, SnF_2, and $Sn(OAc)_2$), which can be recovered. The results showed that $SnCl_2$ was the most effective and selective catalyst for the synthesis of solketal at room temperature. In addition to being easily recovered from the reaction mixture in the distillation process, the catalyst may be reused up to 6 times. (MENEZES, et al., 2013). However, in industrial processes, the presence of chlorides (Cl^- from the $SnCl_2$) in the reaction medium becomes undesirable, as they cause corrosion in the reactors and in the other pipes of the plant. For this reason, several groups have investigated the use of other acidic catalysts in this reaction.

Ferreira et al (2010) studied the reaction using a heteropolyacid based on phosphorus and tungsten immobilized on silica (PW-S) and obtained a conversion and selectivity of 94 and 97%, respectively. (FERREIRA et al., 2010). Silva (2011) and his group conducted tests using β-zeolite and the polymer resin Amberlyst-15 TM resulting in conversions and selectivities of 90 and 95%, respectively. (SILVA, et al., 2011) Studies by the Reddy group (2011) for this reaction have used Zirconia (ZrO_2) impregnated with molybdenum oxide (MoO_x/ZrO_2), tungsten oxide (WO_X/ZrO_2) and sulfated zirconia (SO_4^{2-}/ZrO_2) and obtained conversions of 8, 75, 85 and 95%, respectively. (REDDY et al., 2011).

MCM-41 solid mesoporous impregnated with tin (Sn-MCM-41) and zeolite USY, as catalysts, have also been utilized reaching conversions of 42 and 36%, respectively[11]. Activated mesoporous carbon (AC) has been used as a catalyst in the ketalization reaction of glycerol with acetone. The AC was impregnated with Ni and Zr, and the best results occurred when carbon was only impregnated with 5% nickel ($CANi_{(5\%)}$), reaching a conversion and selectivity of 98 and 86%, respectively. Relying only on activated charcoal as the catalyst, 33% conversion and 81% selectivity were achieved. The results suggest that improved results occurred due to the addition of Lewis acid sites from nickel. (KHAYOON et al., 2013).

It has been observed that the Amberlyst-15 resin, β zeolite, activated carbon impregnated with Ni (CANi(5%)) and heteropolyacid (PW-S) were the most active in the ketalization reaction of glycerol with acetone. This leads us to suppose that in this reaction, the acidic strength of the catalyst is the most important factor.

The use of BEA zeolites in heterogeneous catalysis is due to their high surface area, approximately 500 m^2/g, high thermal and hydrothermal stability. This feature improves with increasing Si/Al ratio of the structure. It is easily regenerated by burning the coke between 500 and 700 ° C. The FER zeolites has a high thermal stability, high cation exchange capacity and low production cost, your surface area are 340 m^2/g, approximately. It regenerates by firing the coke between 550 and 650 ° C.

Recently our research group has already tested a similar H-BEA zeolite (ROSSA et al., 2017*),* and now in this work we aim to test and compare the catalytic activity between H-BEA and H-FER zeolites in the Solketal production.

Materials and Methods

The H-BEA (Zeolyst S. A.) and H-FER (PROCAT/UFRJ) zeolites were acquared by in their ammonium forms.

Catalysts Characterization

X-ray diffraction (XRD) was performed with a BRUKER diffractometer (model PHASER D2) over the range of 2° to 70° using Cu-Kα radiation.

Nitrogen adsorption measurements were performed on a Tristar 3000 Surface Area and Porosimetry Analyzer from Micromeritics. The specific area was obtained using the BET method (Brunauer, Emmet and Teller). The specific volume and pore diameter were obtained by the BJH method from the isotherm adsorption/desorption. The samples were weighed after being subjected to a heat drying treatment at 300°C under a vacuum of 5 x 10^{-3} Torr for a period of 24 hours. Then, they were cooled to room temperature and reweighed to start analysis at a temperature of -196 °C, thereby obtaining isotherms of N_2 adsorption/desorption for different partial pressures of N_2.

The particle size distribution of the materials was evaluated on a Mastersize 2000 (Malvern Equipment). Chemical analyses were accomplished by a Bruker XRF-S2 Ranger.

Infrared (IR) with pyridine adsorption was performed in a Nicolet 710 FTIR spectrometer using vacuum cells. The measurements were performed in self-supported wafers of 10 mg cm^{-2} that were degassed overnight under vacuum (10^{-4} to 10^{-5} Pa) at 400°C. The spectra were recorded and pyridine was admitted. After equilibration, the samples were outgassed for 1 h at increasing temperatures (150/250/350 °C). After each desorption step, the spectrum was recorded at room temperature and the background was subtracted in the pyridine case. Absorption coefficients calculated by Emeis (1993) were used. (EMEIS et al., 1993).

Preliminary Tests

First, a test was performed under industrial conditions with the industrial homogeneous catalyst p-toluene sulfonic acid. The reactions were conducted in a PARR Instruments reactor autoclave (model 4842, stainless steel 316) with a reaction volume of 300 mL. The reactor has a thermocouple, transducer, temperature controller and external mantle for the heating and stirring system.

The reactor was fed with 40 g of glycerol (0.43 mol), 62.44 g of acetone (0.65 moles) at a molar ratio of glycerol:acetone = 1:2.5 and 1% catalyst relative to the mass of glycerol. Stirring was at 400 rpm, 50 °C, and 1 atm. The reaction time was 60 min. At the end of the reaction, 5 g of sodium bicarbonate was added to the reaction mixture to neutralize the catalyst, and the reaction mixture was filtered. In order to obtain a solution, 2 g of anhydrous sodium sulfate was added for partial removal of the water formed in the reaction, and the solution was filtered again. Afterwards, the samples were stored at 15 °C for analysis by gas chromatography.

Under the same conditions, the homogeneous catalyst was replaced by the heterogeneous catalysts H-BEA and H-FER (0.4

g, 1% of catalyst relative to the weight of glycerol).

The products of the glycerol ketalization were analyzed using a Shimadzu gas chromatograph with a flame ionization detector (GC-FID) using the internal standardization method. The column used was Carbowax (30 m x 0.25 mm x 0.25 μM polyethylene glycol). The analysis parameters were as follows: detector and injector temperature were 250°C; the heating ramp of 50°C was maintained for 5 min; 50°C to 180°C with a heating rate of 16°C/min maintained for 2 min at 180°C; and 180°C to 230°C with rate of 20°C/min maintained for 2 min at 230°C. The internal calibration method was applied to the chromatographic patterns of glycerol (99.5%) and solketal (98%) using 1,4-dioxane (99.8%) as the internal standard.

The glycerol conversion, solketal selectivity and solketal yield calculations were performed using the following equations:

glycerol conversion:

$$X_A(\%) = \frac{N_{A0} - N_A}{N_{A0}}.100$$

where N_{A0} is the amount of glycerol (moles) in the beginning of the reaction and N_A is the amount of glycerol (moles) at the end of the reaction.

Selectivity:

$$Sel(\%) = \frac{A_{\text{Pr}oduct}}{A_{\text{Pr}oducts}}.100$$

where A_{Product} is the area of the desired product and A_{Prodcts} is the sum of the area of the desired product and the areas of unwanted products obtained by chromatograms.

Yield:

$$Yield(\%) = (X_A \times Sel_{\text{Pr}oduct}).100$$

where X_A is the conversion of glycerol multiplied by the selectivity of the product of interest (Sel_{Product}).

Experimental Design

The reactions were conducted in the same reactor previously used. The reactor was fed with 40 g of glycerol (0.43 moles). For each of the two types of heterogeneous catalysts, the following variables were evaluated: stirring rate (ω) (400, 550, and 700 rpm); temperature (T) (40, 50, and 60 °C); catalyst amount (C) (1 % 3 %, and 5 % relative to the glycerol weight); and amount of acetone (R) (in molar ratios of 1:2, 1:3, and 1:4). The reaction time was 1 h.

A factorial fractional design (2^{4-1}) was used, consisting of 8 experiments and 3 center points aimed at calculating the experimental error. The catalysts tested were H-BEA and H-FER, and 11 experiments for each catalyst were performed.

At the end of the reaction, the suspension was filtered to remove the catalyst. To the solution obtained, 2 g of anhydrous sodium sulfate was added for partial removal of the water formed in the reaction, and the solution was filtered again. After this, the samples were stored at 15 °C for analysis by gas chromatography.

To find the best conditions that generate the highest conversion of glycerol and higher yields and selectivities for solketal, these conditions were repeated 3 times with both catalysts and were also tested in the absence of catalyst (control condition).

Reuse Tests

The reuse study of the catalyst was carried out under the best conditions found through the fractional factorial design and using the most active catalyst.

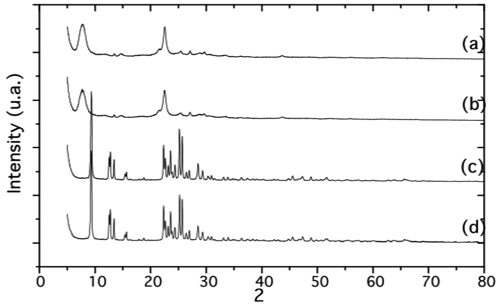
The test consisted of reusing the same catalyst 5 times after centrifugation of the suspension (catalyst/solution) without washing and/or calcinating. After each reuse test, the suspension was centrifuged for separation of the catalyst solution and returned to the reactor for the next reaction.

Results and Discussion

Catalyst Characterization

Initially, the beta (BEA-NH^{4+}) and ferrierite (FER-NH^{4+}) materials in the ammonium form were calcined at 500°C for processing into the acidic forms and so-called H-BEA and H-FER, Figure 2.

Figure 2 - XRD patterns for zeolites BEA-NH^{4+} (a), H-BEA (b), FER-NH^{4+} (c) and H-FER (d).



The BEA zeolite did not undergo changes in its structure after calcination, Figure 2. It presents as characteristic in its diffractogram high intensity peaks located between 2θ = 7-32 °, and, therefore, confirm the structure and the crystallinity of the BEA zeolite. It should be noted that the peaks located at the 2θ = 7.5 and 22.5 positions are typical of the BEA zeolite both in its sodium form and in its ammonia form. The characteristic diffraction peaks of the FER zeolites appear at 2θ = 9.5; 13.4; 17.28; 22.4; 23.5; 24.3; 25.1 and 25.6 °. According to Figure 2 the calcination process showed that the structure of the zeolite FER was maintained. Both the BEA zeolite and the FER showed similar patterns to those of the International Zeolite Association (IZA).

The sizes of crystallites for H-BEA and H-FER are 13 nm and 34 nm, respectively.

The N_2 adsorption results (Table I) demonstrate that the materials are essentially microporous and that the zeolite H-BEA has a significant contribution area and pore volume in the mesoporous region (pore size distribution not shown, presented contribution in pores in the region from 40 to 50 nm).

Table I - Results of textural analysis of the H-BEA and H-FER catalysts obtained by the N_2 adsorption technique.

	Catalysts	
Results	**H-BEA**	**H-FER**
Area$_{BET}$ [m^2/g]	535	328
Area$_{MICROPORES}$ [m^2/g]	337	309
Area$_{EXTERNAL}$ [m^2/g]	198	19
Volume$_{TOTAL}$ [cm^3/g]	0.56	0.19
Volume$_{MICROPORES}$ [cm^3/g]	0.15	0.15
Volume$_{BJH}$ [cm^3/g]	0.40	0.04

The particle diameters of the materials the BEA zeolite has a very uniform size of approximately 10 µm in agreement with the results of the nitrogen adsorption that showed a significant contribution of the area and volume between particles. Because the FER zeolite has a less uniform particle size distribution and particle sizes of 10, 70 and 400 µm, it has a smaller area of contribution and a smaller volume between particles.

The SARs (silica:alumina ratios) of the zeolite determined by XRF had values of approximately 19 for the H-BEA zeolite and 16 for H-FER zeolite.

The acidity of the materials was evaluated by adsorbed pyridine infrared spectroscopy, as shown in Table II.

The concentrations of Brönsted and Lewis acid sites of the H-BEA and H-FER zeolites were calculated from the intensity of the Py-Brönsted and Py-Lewis bands, 1555 and 1450 cm^{-1}, respectively. The concentration

Table II - Measurement of Brönsted acid sites (BAS) and Lewis acid sites (LAS) after different temperature treatments for the zeolites (μmol pyridine/g of material).

	150 °C		**250 °C**		**350 °C**	
Catalysts	**BAS**	**LAS**	**BAS**	**LAS**	**BAS**	**LAS**
H-FER	49.7	3.78	60.4	4.6	51.3	4.6
H-BEA	60.4	33.6	39.4	58.3	24.7	45.8

Table III - Results of the preliminary tests.

Catalysts	**X_A (%)**	**R_5 (%)**	**S_5 (%)**	**R_6 (%)**	**S_6 (%)**	**DP**
H-BEA	53.9	52.7	97.8	1.1	2.1	0.06
H-FER	45.4	44.2	97.5	1.1	2.5	0.08
PTSA	52.6	51.0	97.7	1.6	2.2	0.11
Control test	9.9	9.7	96.1	0.1	3.9	0.09

X_A (glycerol conversion); **R_5** (solketal yield); **S_5** (solketal selectivity); **R_6** (dioxan yield); **S_6** (dioxan selectivity); **DP** (standard deviation)

ratio of the B/L sites was calculated from the concentrations of the acid sites corresponding to their nature at each temperature.

With increasing temperature the B/L ratio tends to decrease for both H-BEA and H-FER. The B/L ratio is much higher for the H-FER zeolite than for the H-BEA zeolite, which drops to half when it has its temperature increased by 100°C, whereas for H-FER zeolite this ratio has remained constant. At 350°C the decrease of the B/L ratio in H-FER is much higher when compared to H-BEA.

It can be seen in the Table III that the H-BEA zeolite has more Brönsted acid sites and more Lewis acid sites than the H-FER zeolite at 150°C.

Acidity is a very important factor to evaluate the ketalization of glycerol with acetone, since this reaction occurs at the acid sites of the catalyst.

Preliminary Reaction Tests

First, preliminary tests were conducted in order to compare the effectiveness of the heterogeneous catalysts (H-FER and H-BEA) compared to the homogeneous catalyst (PTSA) industrially used in the ketalization reaction of glycerol with acetone.

Parameters such as the temperature, stirring rate, quantity of catalyst and molar ratio of catalyst were maintained according to the following parameters used in industry: 50 °C, 400 rpm, 1:2.5 (1 mol of glycerol to 2.5 moles of acetone) and 1% catalyst (in relation to the initial mass of glycerol).

The catalytic results obtained at the end of the preliminary tests are presented in Table III.

Table III shows that the heterogeneous catalyst H-BEA showed a glycerol conversion very close to that obtained by the industrial catalyst (PTSA), with conversions of 53.9 and 52.6%, respectively. The H-FER catalyst presented a lower glycerol conversion (45.4%) than the other catalysts studied. The absence of catalyst in the reaction medium (control test) shows the necessity of using an acidic catalyst for this reaction to occur with a higher conversion of glycerol, as it can be seen that only 9.9% of the glycerol was converted.

The selectivity to Solketal remained practically constant, 97%, for all tests. The H-BEA catalyst can be considered the ideal catalyst for this reaction, since in addition to presenting a higher yield of Solketal, 52,77%, presents lower selectivity, 2,13%, for undesirable products, such as dioxane (6-membered ring). H-BEA has higher acid strength, lower ratio of Brönsted/Lewis acid sites, higher contribution of mesopores and greater surface area than the H-FER catalyst, and these properties may help to explain its high activity in the production of Solketal.

Experimental Design

In order to maximize the values obtained in preliminary tests, a fractional factorial design (2^{4-1}) was carried out only for the heterogeneous catalysts (H-BEA and H-FER). The independent variables evaluated were process parameters such as the stirring rate, temperature, molar ratio and percentage of catalyst for the catalytic system, and the aim was to get closer to the "desired" to proceed with the kinetic studies.

The "desired" catalyst system will be whichever system presents the highest glycerol conversion (X_A) along with a high yield of solketal (R_5), a low selectivity for dioxan (S_6) and consequently, a high selectivity for solketal (S_5). Table IV shows the matrix design with the responses X_A, R_5, S_5, R_6 and S_6.

Table IV shows that the best results for X_A, R_5 and S_5 were obtained in the catalytic systems 8A and 8B for both catalysts. Entry 8 is characterized by a higher stirring rate (700 rpm), which prevents resistance to both internal and external mass transfer. The temperature directly influences the reaction rate, so the equilibrium is reached more quickly. The molar ratio of 1:4 will not introduce more problems because it is possible to recover the unreacted acetone at the end of the reaction. Lastly, the optimum amount of catalyst was found to be 5% of the initial mass of glycerol because the greater the mass of catalyst, the more acidic sites that are available for the ketalization reaction.

These results were evaluated in terms of the main effects of the process variables on the obtained responses. Tables VI-VIII present the effects of the variables on the principal responses evaluated.

Using the catalyst H-BEA, the independent variables of stirring rate (rpm), temperature (°C) and molar ratio (G:A) presented significant and positive effects on the conversion (X_A). Using H-FER, only the temperature (°C) and catalyst amount (%) showed significant and positive effects on the conversion of glycerol (X_A). A possible explanation for this behavior is that ferrierite zeolite has smaller pore sizes than beta zeolite, and thus, diffusional problems can occur. Acetone accesses the H-FER pores more easily than glycerol, which causes an excess of acetone inside the pores, making glycerol difficult to access. The surface of the H-FER is saturated with one of the reactants, in this case acetone because it is the excess reactant, molar ratio G: A = 1: 4. When there is excess reagent in the reactor this excess may be much higher at the catalyst surface in the order of 1: 6 to 1:10.

In addition to the acetone molecule having lower density and viscosity values than the glycerol molecule, another possible explanation is the affinity difference (interactions or intermolecular forces) between catalytic reagents/sites. Since, the affinity between the reactants and the catalytic sites of the H-FER zeolite is higher for acetone than for glycerol.

In terms of the solketal yield, for the H-BEA catalyst the stirring rate (rpm), temperature (°C) and molar ratio (G:A) showed significant and positive effects. For the H-FER, only the temperature (°C) and catalyst (%) showed significant and positive effects on the yield of solketal (R_5). This difference in behavior among the catalysts in the Solketal yield follows the same behavior as the glycerol conversion.

Table IV - Experimental design (coded and real values) of the factorial design 2^{4-1} and respective responses for the catalysts evaluated.

Entries	**ω**	**T**	**C**	**R**	**X_A**	**R_5**	**S_5**	**R_6**	**S_6**
H-BEA	**(rpm)**	**(°C)**	**(%)**	**(G:A)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**
1A	-1 (400)	-1 (40)	-1 (1)	-1 (1:2)	23.7	22.4	94.4	1.3	5.6
2A	-1 (400)	-1 (40)	1 (5)	1 (1:4)	42.2	41.4	98.1	0.9	1.9
3A	-1 (400)	1 (60)	-1 (1)	1 (1:4)	63.2	61.7	97.6	1.5	2.4
4A	-1 (400)	1 (60)	1 (5)	-1 (1:2)	53.1	52.1	98.1	1.0	1.9
5A	1 (700)	-1 (40)	-1 (1)	1 (1:4)	59.3	57.1	96.2	2.3	3.8
6A	1 (700)	-1 (40)	1 (5)	-1 (1:2)	59.0	57.9	98.2	1.1	1.8
7A	1 (700)	1 (60)	-1 (1)	-1 (1:2)	60.3	59.0	97.8	1.4	2.2
8A	1 (700)	1 (60)	1 (5)	1 (1:4)	72.6	71.4	98.3	1.2	1.7
9A	0 (550)	0 (50)	0 (3)	0 (1:3)	57.7	56.3	98.0	1.4	2.0
10A	0 (550)	0 (50)	0 (3)	0 (1:3)	55.5	54.3	97.8	1.2	2.2
11A	0 (550)	0 (50)	0 (3)	0 (1:3)	54.7	53.8	98.3	0.9	1.7
H-FER									
1B	-1 (400)	-1 (40)	-1 (1)	-1 (1:2)	0.6	0.4	78.3	0.1	21.7
2B	-1 (400)	-1 (40)	1 (5)	1 (1:4)	14.8	12.2	82.3	2.67	17.7
3B	-1 (400)	1 (60)	-1 (1)	1 (1:4)	14.0	10.8	77.0	3.2	23.0
4B	-1 (400)	1 (60)	1 (5)	-1 (1:2)	48.4	45.9	95.2	2.4	4.8
5B	1 (700)	-1 (40)	-1 (1)	1 (1:4)	4.6	3.4	74.5	1.2	25.4
6B	1 (700)	-1 (40)	1 (5)	-1 (1:2)	36.9	32.5	88.5	4.4	11.5
7B	1 (700)	1 (60)	-1 (1)	-1 (1:2)	36.1	34.3	86.9	1.8	13.1
8B	1 (700)	1 (60)	1 (5)	1 (1:4)	54.2	51.8	95.6	2.4	4.4
9B	0 (550)	0 (50)	0 (3)	0 (1:3)	9.5	8.0	83.7	1.5	16.3
10B	0 (550)	0 (50)	0 (3)	0 (1:3)	9.9	8.4	84.1	1.5	15.9
11B	0 (550)	0 (50)	0 (3)	0 (1:3)	4.9	3.9	84.7	1.0	15.3

X_A (glycerol conversion); **R_5** (solketal yield); **S_5** (solketal selectivity); **R_6** (dioxan yield); **S_6** (dioxan selectivity)

Table VI - Main effects of each of the variables evaluated on the response glycerol conversion (X_A) using both catalysts (H-BEA and H-FER).

Factors/H-BEA	**Effects**	**Standard deviation**	**t(6)**	**p-value**
Means	54.7	1.8	31.1	<0.05
(1) Stirring (rpm)	17.2	4.3	4.5	<0.05
(2) Temperature (°C)	16.2	4.3	4.0	<0.05
(3) Catalyst (%)	5.1	4.3	1.2	0.30
(4) Molar Ratio (G:A)	10.3	4.3	2.5	<0.05
Factors/H-FER	**Effects**	**Standard deviation**	**t(6)**	**p-value**
Means	21.3	3.3	6.4	<0.05
(1) Stirring (rpm)	13.5	7.8	1.7	0.13
(2) Temperature (°C)	23.9	7.8	3.1	<0.05
(3) Catalyst (%)	24.8	7.8	3.2	<0.05
(4) Molar Ratio (G:A)	-8.6	7.8	-1.1	0.3

Table VII - Main effects of each of the evaluated variables on the solketal yield (R_5) using both catalysts (H-BEA and H-FER).

Factors/H-BEA	**Effects**	**Standard deviation**	**t(6)**	**p-value**
Means	53.5	1.8	30.6	<0.05
(1) Stirring (rpm)	17.0	4.3	4.1	<0.05
(2) Temperature (°C)	16.3	4.3	4.0	<0.05
(3) Catalyst (%)	5.7	4.3	1.4	0.30
(4) Molar Ratio (G:A)	10.0	4.3	2.4	<0.05
Factors/H-FER	**Effects**	**Standard deviation**	**t(6)**	**p-value**
Means	19.2	3.2	6.0	<0.05
(1) Stirring (rpm)	13.2	7.5	1.7	0.13
(2) Temperature (°C)	23.5	7.5	3.1	<0.05
(3) Catalyst (%)	23.4	7.5	3.1	<0.05
(4) Molar Ratio (G:A)	-8.8	7.5	-1.1	0.29

Table VIII - Main effects of each of the evaluated variables on the solketal selectivity (S_5) using both catalysts (H-BEA and H-FER).

Factors/H-BEA	**Effects**	**Standard deviation**	**t(6)**	**p-value**
Means	97.6	0.3	350.4	<0.05
(1) Stirring (rpm)	0.6	0.6	0.8	0.44
(2) Temperature (°C)	1.5	0.6	1.7	0.12
(3) Catalyst (%)	1.6	0.6	2.6	<0.05
(4) Molar Ratio (G:A)	0.5	0.6	0.7	0.49
Factors/H-FER	**Effects**	**Standard deviation**	**t(6)**	**p-value**
Means	84.6	0.5	157.9	<0.05
(1) Stirring (rpm)	3.2	1.3	2.5	<0.05
(2) Temperature (°C)	7.7	1.3	6.2	<0.05
(3) Catalyst (%)	11.2	1.3	8.9	<0.05
(4) Molar Ratio (G:A)	-4.9	1.3	-3.9	<0.05

Table IX - Results of the effects obtained for each variable explored in the ketalization reaction of glycerol with acetone reusing the H-BEA catalyst.

Number of reactions	**X_A (%)**	**R_5 (%)**	**S_5 (%)**	**R_6 (%)**	**S_6 (%)**	**SD**
1	66,50	65,37	98,30	1,13	1,70	0,04
2	54,50	53,52	98,20	0,98	1,80	0,07
3	52,50	51,40	97,90	1,10	2,10	0,29
4	51,80	50,61	97,70	1,19	2,30	0,10
5	22,50	21,94	97,50	0,56	2,50	0,32

X_A (glycerol conversion); **R_5** (solketal yields; **S_5** (solketal selectivity); **R_6** (dioxan yield); **S_6** (dioxin selectivity); **SD** (standard deviation)

In terms of the selectivity for solketal, only the catalyst (%) showed a significant and positive effect for the H-BEA catalyst. This occurs because of the form selective property of beta zeolite, which works like a molecular sieve. Using the H-FER catalyst, the stirring rate (rpm), temperature (°C) and catalyst (%) had significant and positive effects. The molar ratio (G:A) also had a significant effect, but the effect was negative for the solketal selectivity (S_5). The behavior of the selectivity to Solketal follows the same behavior of the glycerol conversion and Solketal yield.

Reuse Tests

Table IX show the results of the reuse test, and it can be seen that the catalyst maintains its activity for 4 cycles with a high selectivity for solketal.

Conclusions

Glycerol to solketal transformation is possible to carry out using zeolite acidic catalysts. H-BEA and H-FER showed similar conversions (53%) and selectivities (98%) as the industrial catalyst PTSA. H-BEA presented a larger area and Lewis acidity than H-FER, resulting in a higher activity for glycerol ketalization. An experimental design was studied, and it can be seen that the best conditions for higher conversion (72%) with high selectivity (98%) were as follows: 60°C, stirring at 700 rpm, 5% catalyst and 1:4 for the molar ratio of glycerol:acetone. The catalytic activity increases with increasing the Brönsted acid strong sites and superficial area of catalyst. When decreasing crystallit size and particles size increases the catalytic activity. The catalyst can be used without losing its activity for 5 cycles.

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