The glycerol acetalization into fuel additive solketal over Beta zeolites: Effect of impurities and Si/Al ratio

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Abstract
The conversion of waste glycerol from the biodiesel process into solketal via acetalization reaction with the mild condition is a promising process. In this study, we studied glycerol acetalization over Beta zeolites using a batch reactor in the presence of water and NaCl impurities. We found that water and/or NaCl strongly impact the active sites of Beta zeolite resulting in a decrease in catalytic activity and product yield. Also, we found that Beta zeolite with a high Si/Al ratio showed better glycerol acetalization performance in comparison with Beta zeolite with a low Si/Al ratio due to the high hydrophobicity. Beta zeolite with Si/Al = 180 remained solketal yield (~ 80%) with 10% of water impurity, while the yield of solketal over Beta zeolite with Si/Al = 19 decreased from 83.6% to 41%. In the presence of both NaCl (2 wt.%) and water (50 wt.%), the yield of solketal was obtained at 33% and 28.5% for high (180) and low (19) Si/Al Beta zeolites, respectively. Suggesting that the hydrophobicity of zeolite with high Si/Al can be applied to prevent the effect of impurities in the acid catalytic reaction.

1. Introduction

Currently, the use of fuels decreases due to the lockdown in many countries, however, the demand for fuels will increase to conform the requirement of the industry. Therefore, the demand for diesel will increase again in the near future. Additionally, in order to reduce the greenhouse gas effect and avoid the dependence of crude oil, a limited resource, the use of renewable feedstocks for diesel production is of great interest. Biodiesel can typically be produced through transesterification of vegetable oils/animal fats with alcohol (e.g., methanol) using alkali catalysts [1-6]. Glycerol is a byproduct of the biodiesel production process, hence, a large amount of crude glycerol will become available with increasing biodiesel production.

Glycerol from biodiesel production can be upgraded valuable compounds such as propanediol, acrolein, glycerol carbonate, glyceric acid, tartonic acid, syngas, and solketal [7-15]. Among these glycerol-derived compounds, solketal ((2,2-Dimethyl-1,3-dioxolan-4-yl)methanol) is one of the most interesting compounds because it can be produced from glycerol acetalization under a mild reaction condition [16-21]. Additionally, solketal has many applications such as fuel additives [22, 23], additives and solvents for in the pharmaceutical industry [24-26], solvents in paint and ink industries [27-29], and cleaning products [30].

Solketal production via glycerol acetalization has been studied using many acid catalysts [12, 13, 17, 18, 20, 21, 31-38]. Among them, Beta zeolite is one of the great catalysts in the conversion of glycerol into solketal through acetalization reaction [36]. Beta zeolite has many advantages including possessing a large pore size (7.7 Å x 7.3 Å) can diffuse the product within the pores and high stability [36, 39]. Recently, the modified Beta zeolite with an increase in pore volume and a decrease in acid density can enhance the selectivity of solketal up to 100% [40]. Manjunathan et al. [35] reported that a small crystal size of Beta zeolite improved glycerol conversion and solketal yield. Additionally, the acidity of zeolite has an important role in the glycerol acetalization reaction [35, 36]. Continuously, we study the glycerol acetalization reaction with "crude" glycerol to elucidate the performance of Beta zeolite. This crude glycerol consists of ~80% glycerol and other impurities including methanol from adding an excess of methanol reactant, water from byproduct or washing system, and salts (e.g., NaCl) from the neutralization process in the biodiesel production process [38]. In this work, we found that water and/or NaCl hurts the glycerol conversion and solketal yield, but Beta zeolite with a high Si/Al ratio can prevent the effect of the impurities.

2. Material and Methods

2.1. Materials

Glycerol (99+%, Acros), acetone (99.8+%, Fisher), ethanol (99.8+%, Fisher), n-dodecane (extra pure, Fisher) and NaCl (99.0%, Fisher) were used without any treatment. Beta zeolites were purchased from Alfa Aesar and summarized in Table 1.

Table 1: The properties of investigated catalysts

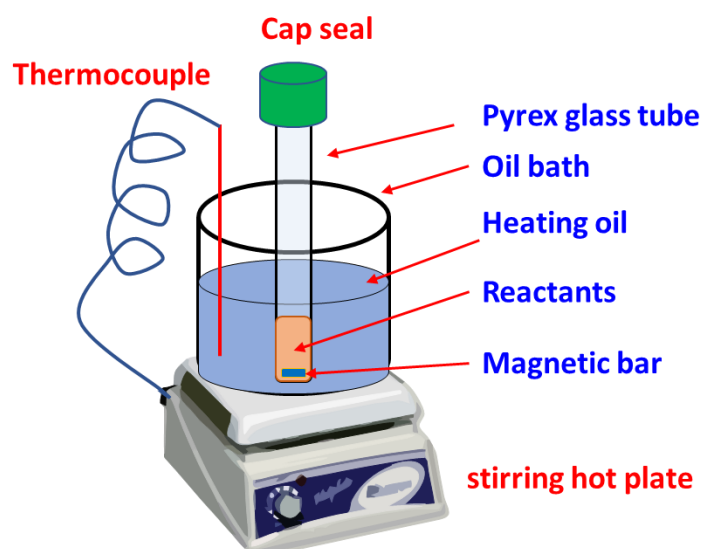| Catalyst	Si/Al	Surface area (m^2/g)*	Treatment	Low-temp. peak (µmol NH_3/g catalyst)	High-temp. peak (µmol NH_3/g catalyst)	Total acidity (µmol NH_3/g catalyst)	High-temp. peak/Low-temp. peak ratio
B19	19	710	calcined at 500ºC, 5h	351.7	253.1	604.8	0.720
B180	180	620	As received	20.7	24.9	45.6	1.203

 *data from manufacturer

2.2. Catalyst characterization

The fresh catalysts were determined the acid density by using the Ammonia-temperature programmed desorption (NH_3-TPD) method. Typically, the fresh catalyst (20 – 40 mg) was treated at 500°C for 1h under flowing He, then flushed by He at 100°C for 1h to remove the physically adsorbed ammonia. The NH_3-TPD profile was recorded with the heating rate of 10 °C/min from 100°C to 700°C under He flow (40 cc/min) using Micromeritics ChemiSorb 2720 equipped with a thermal conductivity detector (TCD).

2.3. Glycerol acetalization reaction

The screening catalytic test, glycerol (0.125 g), acetone (0.946 g), catalyst, and dodecane (internal standard) were added into a pyrex glass tube (5 mL) containing a magnetic bar (**Scheme 1**). The test tubes were sealed and performed the acetalization reaction at 30 °C for 20 min. For the testing reactions, we remained the amount of glycerol and acetone, reaction time, and temperature. The catalyst amount was adjusted to be similar acidity density for both Beta zeolites, and the impurities, water and/or NaCl were added into the reactor as a model of crude glycerol. After finishing the reaction, the reactors were quenched in ice water followed by adding ethanol (1mL) to dissolve both remaining glycerol and acetone. The solution was centrifuged, and the solid catalysts were removed. The liquid sample was then diluted with ethanol prior to analysis. The reactants and products were analyzed by a gas chromatograph (GC) Agilent 4890 equipped a DB-1701 column (30mx0.25mmx0.25µm) with a temperature ramp of 8°C/min from 50°C to 200°C. The products were identified by gas chromatography coupled with mass spectroscopy (GC-MS) Thermo Scientific with TG-SQC column (15 m x 0.25 mm x 0.25 µm).

Scheme 1. The diagram of the reaction system

3. Results and discussion

3.1. Characterization of Beta zeolites

Table 1 showed that both commercial Beta zeolites had a high surface area, and they were not too much different. However, the acidity of them was so different, the lower Si/Al ratio zeolite showed higher total acidity density than that of higher Si/Al ratio zeolite (Figure 1). The difference in acidity density can be explained based on the difference in Si/Al ratio [41, 42]. Indeed, the low Si/Al zeolite has more acid sites than that of high Si/Al zeolite. Low Si/Al zeolite means that high amount of Al_2O_3, hence, Al replaces Si in the tetrahedral framework of SiO_2 producing more Brønsted acid sites of the framework [43, 44] and Lewis acid sites of unsaturated Al^{3+} [45, 46]. The lower Si/Al zeolite also has many Lewis acid sites, whereas the Lewis acid sites decrease with increasing of Si/Al ratio due to the decrease of Al acid sites. Therefore, the ratio of the Brønsted/Lewis acid sites increase with the increase of the Si/Al ratio.
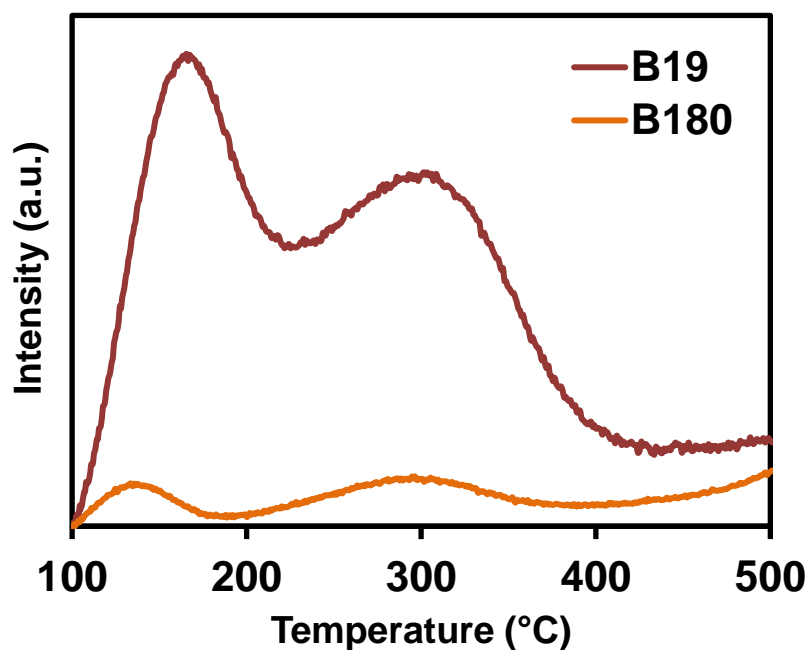

Figure 1: NH_3-TPD profile of investigated catalysts.

3.2. Activity of Beta zeolites and effect of impurities on the glycerol acetalization

The screening reactions with different catalyst loading from 2.5 to 15 wt.% were performed at 30 °C. Glycerol conversion and solketal yield increased with an increase of the catalyst loading over B180 (Figure S1). B19 zeolite yielded high glycerol conversion and solketal at very low catalyst loading (2.5 wt.%) and kept constant with increasing catalyst loading (Figure S1). This is because B19 possesses high catalytic active sites than B180 (Table 1). At high catalyst loading (15 wt.%), all Beta zeolites showed almost similar glycerol conversion and solketal yield at 15 wt.% catalyst loading. The glycerol conversion of all was near 100%, and the solketal yield was around 95% with 15 wt.% catalyst loading. In order to study the effect of different Si/Al ratio on the glycerol conversion and solketal yield, we study the glycerol acetalization in the same active sites of both zeolites. The catalyst loading of the higher Si/Al ratio (B180) is kept at 5 wt.%, while the lower Si/Al ratio is adjusted based on the total amount of acid sites as calculated from the NH_3-TPD experiment. The glycerol conversion was almost similar in the case of B19 and B180 catalysts without the addition of any impurity (Figure 2). B19 zeolite showed slightly higher glycerol conversion than that of B180 zeolite possibly due to its possession of strong acid sites than that of B180 zeolite (Figure 1). However, high Si/Al ratio (B180) zeolite presented better than lower Si/Al (B19) zeolite in the presence of NaCl impurity (Figure 2). A small amount of NaCl (2 wt.%) caused a decrease in glycerol conversion around 6% and 32% in the case of B180 and B19 zeolites, respectively. The same trend is also applied for solketal yield with a decrease of 3.2% and 26.7% over B180 and B19 zeolites, respectively.
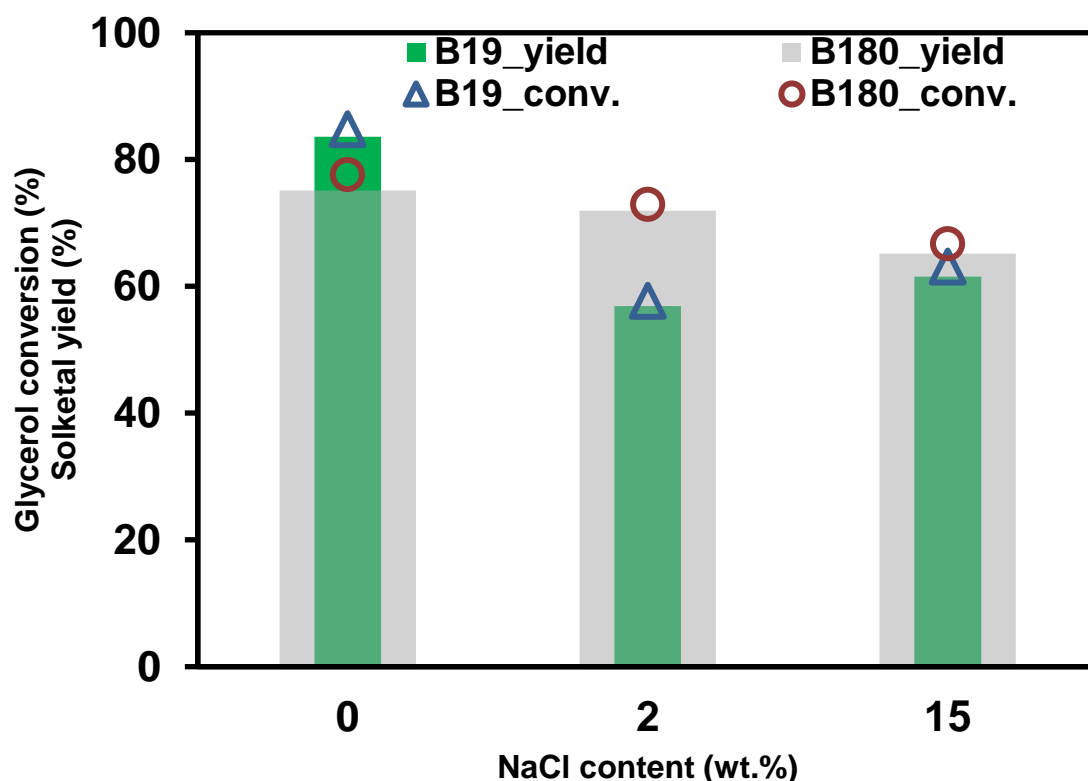

Figure 2: The effect of NaCl content on the glycerol acetalization with acetone. Reaction condition: 30˚C, 0.36 wt.% (B19) and 5 wt.% (B180) catalyst loading, 20 min.

A further increase of NaCl content (15 wt.%), glycerol conversion over B180 zeolite decreased 8% more, while it did not drop in the case of B19 zeolite. Hence, the yield of solketal decreased by 6.8% over B180 zeolite, and it almost remained in the case of B19 zeolite. This is possibly due to the high amount of NaCl killed the weak acid sites of B180 zeolite, while it just killed a part of the acid sites of B19

zeolite. In all cases, solketal is still the main product in the presence of NaCl. The remarkable drop of glycerol conversion in the presence of NaCl is possibly due to the coverage of active sites of beta zeolites by NaCl. Sodium cation from NaCl may exchange with the proton of zeolite and lower its activity. Indeed, a small amount of sodium can kill the active sites of catalysts and reduce catalytic activity in the case of Al_2O_3 oxide [47]. In the same manner, it can kill the active acid sites of Beta zeolite. Additionally, the higher hydrophobicity of the higher Si/Al ratio (B180) zeolite also helps to protect the influence of NaCl than that of B19 zeolite. In fact, higher Si/Al of zeolite enhances the hydrophobicity of zeolite [48]. But at very high NaCl content, the coverage of NaCl also affects the high Si/Al zeolite (B180), showing a slightly different with B19, but both of them decrease in comparison with the case of 2 wt.% NaCl.

In the case of water impurity, the hydrophobicity of zeolite also strongly impacts on the glycerol conversion in the presence of water (Figure 3). A high Si/Al ratio zeolite (B180) did not affect by water with water content lower than 10 wt.%, while a low Si/Al ratio zeolite (B19) dropped the glycerol conversion with only 2 wt.% water content. Indeed, the low water content below 10 wt.% in the reaction did not affect the glycerol conversion over B180 zeolite (Figure 3). A further increase in water content (i.e. > 10 wt.%), the glycerol conversion dropped in all cases. Looking at the solketal yield, it had the same trend with glycerol conversion because the selectivity of solketal was almost 100% in all cases. In other words, water hurt the glycerol conversion of B19 with low content (2 wt.%), and glycerol conversion significantly dropped with an increase in water content. Our result suggests that water hindered glycerol acetalization due to the competitive adsorption on the active sites and the potential shifting of the equilibrium toward acetal hydrolysis [49]. The adsorption of water on the active sites of catalysts possibly by hydrongen-bonding interaction [50] caused a decrease in catalytic activity. Glycerol conversion over B180 zeolite was always higher than that of B19 zeolite, indicating that B180 zeolite was more effective in the protection of the water effect. It is true, B180 zeolite with a high Si/Al ratio (180) has higher hydrophobicity than B19 zeolite with a low Si/Al ratio (19) [48]. It demonstrated that the ratio of silica to alumina in Beta zeolites have a strong effect on glycerol acetalization reaction.
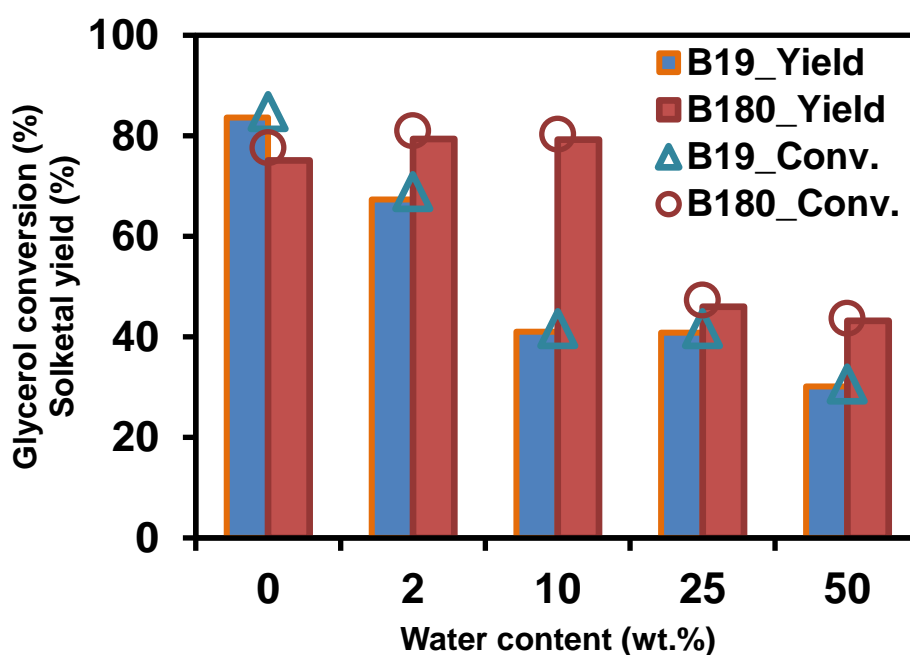

Figure 3: The effect of water content on the glycerol acetalization with acetone. Reaction condition: 30°C, 0.36 wt.% (B19) and 5 wt.% (B180) catalyst loading, 20 min.
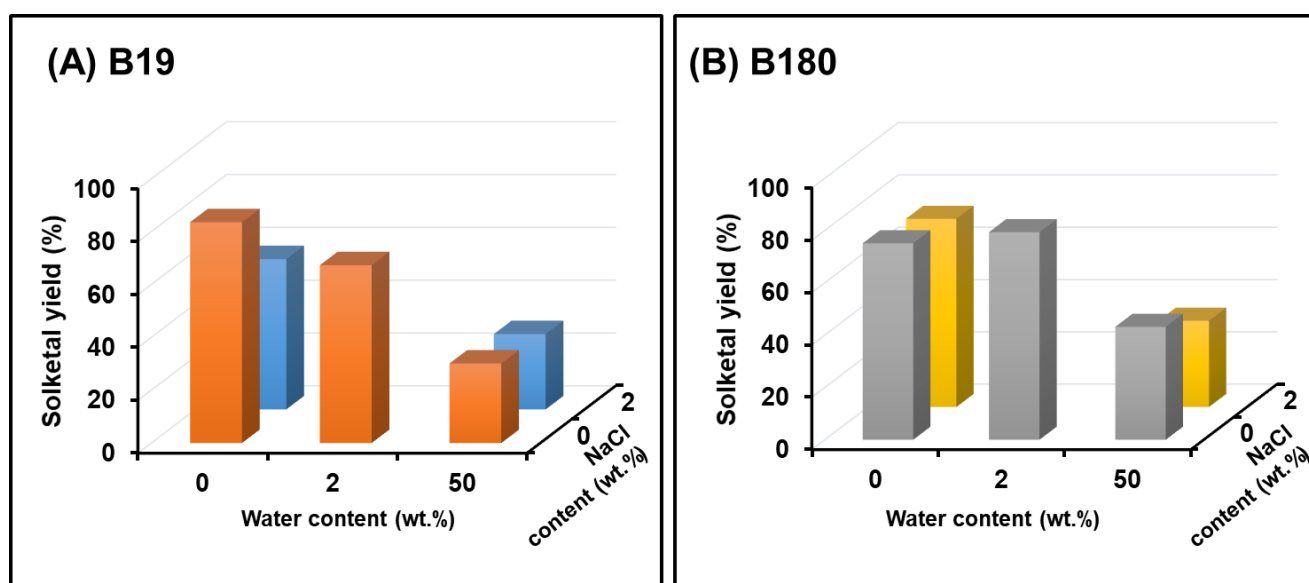
Figure 4: The influence of NaCl and/or water on the glycerol acetalization with acetone. Reaction condition: 30°C, 0.36 wt.% (B19) and 5 wt.% (B180) catalyst loading, 20 min.

For the impurities containing water and NaCl, the presence of water together with NaCl in the reaction using all Beta zeolites further lowered the solketal yield compared to that of no impurity (Figure 4). NaCl had a more prominent effect on Beta zeolites than H_2O with low content (2 wt.%). A high water content (50 wt.%) caused a significant decrease in solketal yield over B19 (53.5%) and B180 (31.9%). In all cases of impurities, solketal yield over B180 zeolite is always higher than that of B19 zeolite. The presence of both water and NaCl in the reaction strongly hurt the glycerol conversion. For example, 2 wt.% NaCl and 50% H_2O decreased in solketal yield ca. 55.1% and 42.1% respect to the reaction without impurities over B19 and B180 zeolite (Figure 4), respectively. Suggesting that the presence of both water and NaCl strongly hurt solketal yield. It is possibly due to the improvement of Na^+ exchange with the active sites of zeolite reducing the catalytic activity with the presence of both water and NaCl. However, in all cases, solketal yield over B180 zeolite was higher than that of B19 zeolite determining that high Si/Al ratio zeolite protects the effect of impurities better than that of low Si/Al ratio zeolite.

For the comparison of our results to the literature, we summarized the glycerol conversion and solketal yield of glycerol acetalization reaction over H-Beta zeolites and other catalysts (Table 2). Our catalyst showed a comparable catalytic activity with the results reported. In fact, the yield of solketal was just lower than those of H-BEA (Si/Al = 75 in ref. [48]) and H-BEA (Si/Al = 12.5 in ref. [35]), however, the catalyst loading was higher (27.2%) in the case of H-BEA (75) with respect to our catalyst loading (5% and 0.36%); or lower Si/Al (12.5) than our zeolites (Si/Al = 19 and 180). Additionally, in the case of the presence of impurities, our result (33% solketal yield) was lower than that of HR/Y-W_{20} (97.85%), but our catalyst (B180) contains very low acidity density compared to HR/Y-W_{20} (Si/Al = 6.2 in ref. [20]), which was also supported by heteropoly acid. In the case of a flow reactor, the yield of solketal (61.6%) is almost double our result (33%) in a batch reactor. It is possibly due to the high reaction temperature (40 °C vs 30 °C), high catalyst loading (10% vs 5%), and the use of H-BEA with low Si/Al (12) for the flow reactor instead of high Si/Al (180) of our catalyst. Also, a flow reactor may avoid the interaction of impurities to the active sites than that of the batch reactor. In short, our results are comparable to the results in the literature, and potentially further upgrade the high Si/Al Beta zeolite for obtaining high solketal yield from crude glycerol.

Table 2: The glycerol conversion and solketal yield of glycerol acetalization reaction over H-Beta zeolites and other catalysts.

Catalyst	Si/Al	Gly/Ace[a] molar ratio	Reaction condition					Conv. (%)	Solketal Yield (%)	Ref.
			Catalyst loading (wt.%)	NaCl (wt.%)	H_2O (wt.%)	Temp. (°C)	Time (h)			
H-BEA	16	1:1.2	21.2	-	-	70	0.33	85	-	[31]
H-BEA	16	1:2	21.2	-	-	70	1	90	-	[38]
H-BEA	16	1:2	21.2	5	10	70	1	58	-	[38]
H-BEA	12.5	1:1.5[b]	27.2	-	-	-	24	-	44	[48]
H-BEA	75	1:1.5[b]	27.2	-	-	-	24	-	96	[48]
H-BEA	255	1:1.5[b]	27.2	-	-	-	24	-	77	[48]
H-ZSM-5	75	1:1.5[b]	27.2	-	-	-	24	-	68	[48]
H-MOR	45	1:1.5[b]	27.2	-	-	-	24	-	61	[48]
ZnO_2	-	1:1.5[b]	27.2	-	-	-	24	-	61	[48]
SnO_2	-	1:1.5[b]	27.2	-	-	-	24	-	67	[48]
Nb_2O_5		1:1.5[b]	27.2	-	-	-	24	-	54	[48]
H-BEA	12.5	1:2	5	-	-	28	1	86	84.7	[35]
H-BEA	15	1:2	5	-	-	28	1	79.6	78.4	[35]
H-BEA	12	1:3	5 g [c]	-	8	50	1	85	82.5	[21]
H-ZSM-5	22.1	1:3	5 g [c]	-	8	50	1	85	82.5	[21]
H-USY	40	1:3	5 g [c]	-	8	50	1	82	77.9	[21]
H-BEA	12	1:3	5 g [c]	5.6	-		8	85	68	[21]
H-ZSM-5	22.1	1:3	5 g [c]	5.6	-		8	79.2	61.8	[21]
H-USY	40	1:3	5 g [c]	5.6	-		8	26.6	21.3	[21]
H-BEA	12	1:3	5 g [c]	5.6	8		8	~ 77	61.6	[21]
HR/Y-W$_{20}$[d]	6.2	1:10	10	*	*	40	1.5	100	97.85	[20]
HR/Y-W$_{20}$[d]	6.2	1:10	10	*	*	20	1.5	93.59	65.36	[20]
H-BEA	19	1:12	0.36	-	-	30	0.33	84.8	83.6	Our study
H-BEA	180	1:12	5	-	-	30	0.33	77.6	75.1	Our study
H-BEA	180	1:12	5	2	50	30	0.33	33.6	33	Our study

[a]Gly/Ace = glycerol/acetone
[b]Glycerol/3-pentanone
[c]flow reactor
[d]Hierarchical faujasite zeolite-supported heteropoly acid catalyst
* Crude-glycerol
H-BEA: protonic Beta zeolite; H-USY: protonic Ultra Stable Y zeolite; H-ZSM-5: protonic Mobil five zeolite; H-MOR: protonic Mordenite zeolite

Conclusion

The conclusions of this work can be summarized as follows:

- Sodium (Na) hurts the catalytic activity and solketal yield from 10 to 20% over Beta zeolite with an increasing NaCl content up to 15 wt.%.
- Water strongly hurts the active sites of Beta zeolite with a low Si/Al ratio (B19) zeolite at a low water content (< 10%), but it dramatically diminishes the glycerol conversion and solketal yield on both Beta zeolite.

- The presence of both water and NaCl as impurities remarkably damages solketal yield of glycerol acetalization reaction.
- High Si/Al ratio of Beta zeolites enhances the resistance of the effects of water and NaCl impurities.

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