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Dealuminated BEA Zeolite for selective synthesis of five-membered cyclic acetal from glycerol under ambient conditions

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Abstract: BEA zeolite was treated with phenoldisulfonic acid (PDSA) of different concentrations from 0.1 M to 1.0 M to obtain dealuminated zeolites. Treated BEA samples were characterized by XRD, ²⁷Al-MASNMR, SEM-EDX, TPD NH₃, pyridine-FTIR and BET measurements. Modified zeolites showed increase in surface area and pore volume and a decrease in acid amount with increase in PDSA concentration. Untreated BEA sample catalyzed reaction between glycerol and acetone to form glycerol acteals to yield two products, five-membered dioxalane and six-membered dioxane. Under optimized reaction conditions, untreated BEA sample showed 83% dioxalane and 17% dioxane while the modified samples showed an increase in dioxalane selectivity with increase in acid concentration used for treatment. 1MPDSA treated sample exhibited 100% selectivity for dioxalane. This is attributed to increase in pore volume and decrease in acid amount of modified BEA samples with increase in PDSA concentration. Combined effect of pore volume and acidity in determining dioxalane selectivity is discussed.

Keywords: BEA zeolite, dealumination, phenoldisulfonic acid, dioxalane.

1. Introduction

The condensation of glycerol with aldehydes or ketones gives mixture of cyclic acetal products, 1,3 dioxalane, a 5-membered solketal and 1,3 dioxane, a 6-membered solketal with an excess of one product or approximately in equimolar amounts^{1,2}. This phenomenon seems to be related to the nearly identical reactivity of the primary and secondary hydroxyl group in glycerol and to similar tendencies for the formation of the 5- and 6-membered ketals. Only by changing their physical properties by converting them into their derivatives, an isolation of one or both of the

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acetals on a large scale is feasible³. However, this procedure is disadvantageous because of expensive purification steps which result in considerable loss of the target $product^{3-5}$.

Selective protection of carbonyl groups by glycerol during the manipulation of multifunctional organic molecules⁶ is employed in production of fragrances, food and beverage additives, pharmaceuticals, detergents, lacquers and also as fuel additives by blending with petrol to reduce the cost and enhance efficiency by controlling the knocking⁶⁻¹⁰.

The general method for acetal synthesis involves reaction of carbonyl compounds with an alcohol or an orthoester in the presence of protic or Lewis acid catalysts. Protic acids such as pTSA, HCl, H₃PO₄, H₂SO₄¹¹ and Lewis acids such as AlCl₃, FeCl₃, ZnCl₂, SnCl₂^{12,13} are largely used in the homogeneous medium for acetal synthesis. These acids, however, have limitations which include tedious work-up procedure and production of undesired wastes in addition to their costs. Heterogeneous acid catalysts have obvious advantages over homogeneous acids such as their easy separation, product selectivity, solventless conditions and reusability^{13,14}. There are several reports available on the synthesis of glycerol acetals by different carbonyl compounds like formaldehyde, cinnamaldehyde, benzaldehyde, furfural, acetone, benzophenone, cycloheaxanone^{1,7,9,14-16} using various catalysts such as, Amberlyst, MCM, Nafion-H¹, alumina¹⁷, montmorillonite^{18,19}, zeolites^{9,20-22}, mesoporous aluminosilicates^{23,24}, ion exchange resins^{12,25}, [Cp*IrCl₂]₂, Lu(OTf)₃²⁶ and supported silica²⁷⁻²⁹.

Modified zeolites have been used as heterogeneous acid catalysts for organic synthesis. Post synthesis modification of zeolites is commonly practiced to vary their catalytic activity. Dealumination of zeolites is an effective post synthesis method of varying the Si to Al ratio (SAR) and acidity. Mineral acids such as HCl, HNO₃, H₂SO₄^{30,31} and organic acids like pTSA³², citric acid, oxalic acid, acetic acid and dicarboxylic acid³³⁻³⁶ have been used as dealuminating agents for zeolite samples. When treated with mineral acids, dealumination is caused by the acid hydrolysis of Al-O-Si bonds whereas organic acids essentially remove Al by complexation³²⁻³⁶. In both cases, post modification results in a zeolite having steady catalytic performance for a long period in acid catalyzed reactions such as alkylation, acylation, esterification and hexane cracking reactions³²⁻³⁶.

In the recent years, microwave heating is used in the post synthesis modification like dealumination of zeolite. Microwave heating brings about the dealumination considerably faster. Apart from saving energy, it also results in more pronounced effect on the surface and acidic

properties compared to conventional heating. Thus, use of microwave in the zeolite modification is a valuable green chemistry process^{32, 37, 38}.

In the present study, dealumination of BEA zeolite sample was brought about by treatment with organic acids such as phenoldisulfonic acid (PDSA), methanesulfonic acid (MSA) and paratoluenesulfonic acid (pTSA). The objective was to investigate the catalytic activity of the dealuminated samples for the reaction between glycerol and acetone to form glycerol acetals. Selectivity aspect of five and six membered cyclic acetals formed as a result of dealumination is also examined.

2. Experimental

2.1 Materials and methods:

The BEA zeolite sample having Si to Al ratio (SAR) 25 was obtained from Süd chemie, Vadodara, Gujarat, India. Commercial zeolite obtained is in Na⁺ form, which was further converted into H⁺ form by ion exchanging with 1M NH₄NO₃ solution followed by calcination at 540 °C. MSA and pTSA were obtained from SD fine chemicals, PDSA was procured from Loba chemicals, glycerol was supplied by Merck chemicals and acetone was received from CDH chemicals. Glycerol formal [mixture of dioxalane (64%) and dioxane (36%)] and dioxalane were procured from Sigma Aldrich.

2.2 Catalyst preparation:

The modification of zeolite samples by organic acid treatment was performed under microwave irradiation. Milestone, "START-S" microwave lab station for synthesis, Italy has been used. This has a facility to control reaction temperature with the aid of infrared sensor by regulating microwave power output has been used. Variable power up to 1200 W was applied by microprocessor-controlled single-magnetron system.

Acid treatment of zeolites was performed by following the procedure reported elsewhere³². PDSA solution of different concentrations (0.1M, 0.25M, 0.5M and 1.0M) were prepared using deionized water in 100 cm³ volumetric flasks. BEA zeolite samples (10 g each, H-form) was separately dispersed with continuous stirring in PDSA solutions of different concentrations. The suspensions were subjected to refluxing under microwave irradiation for 30 min initially by applying 800 W of energy to reach 110 °C. Then the same temperature was maintained for 29

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min by applying the energy in the range of 200-450 W. After that the mixture was cooled to ambient temperature, centrifuged and repeatedly washed to remove the excess of acid from the sample. The centrifuged solid sample was dried at 120 °C, finely ground and subjected to calcination at 540 °C for 6 hours. Similarly, BEA was treated with 1M each of pTSA and MSA. The samples were designated as 0.1PDSABEA, 0.25PDSABEA, 0.5PDSABEA, 1.0PDSABEA, 1.0PDSABEA, 1.0PDSABEA.

2.3 *Characterization:* Different acid treated zeolite samples were characterized using various techniques such as pyridine adsorbed by FTIR, NH₃-TPD, ²⁷Al MASNMR, powder XRD, SEM-EDX and BET analyses.

Acidity of samples was recorded before and after organic acid treatment of the zeolite. All the samples were activated by degassing at 150 °C for 2 hours, then cooled under vacuum and saturated with liquid pyridine for 1 hour. Samples were again heated to 110 °C to remove physisorbed pyridine. Spectra of the samples were recorded by KBr pellet technique using Shimadzu, IRAffinity-1 instrument with 4 cm⁻¹ resolution of 40 scans in the wavenumber range 1700-1400 cm⁻¹.

Surface area and pore characteristics of the parent and modified zeolite samples were characterized under liquid nitrogen temperature using Quanta Chrome Nova-1000 surface analyzer instrument. BET and de Boer t-plot methods were used to determine surface area and pore volume.

Structural integrity of the catalyst samples was checked by powder XRD. The data were recorded by step scanning at $2\theta = 0.020^{\circ}$ per second from 3° to 80° on PANalytical X'Pert PRO MPD X-ray diffractometer with graphite monochromatized Cu K α radiation ($\lambda = 0.15406$ nm).

²⁷Al MAS NMR spectra of untreated and dealuminated BEA zeolites were recorded using Joel-ECX instrument having 8mm rotor of speed 10k.

Morphology and Si/Al ratio of BEA and acid treated zeolite samples were recorded using ZEISS ULTRA-55 Field Emission Scanning Electron Microscope (FESEM) having Energy Dispersive x-ray Analysis (EDXA) under high vacuum mode.

Strength of the zeolite acid sites was evaluated by NH_3 -TPD method. Typically it involved around 0.1g of sample, which was placed in a U-shaped quartz sample tube. Prior to the TPD measurement, the catalyst was pretreated with He at 120 °C for 2 h. A mixture of NH_3 in He

(10%) was passed at the rate of 30 cm³/min at 150 °C for 30 min. The sample was then flushed with He (30 cm³/min) at 150 °C for 1 h. The TPD measurements were carried out in the range of 100-600 °C at a heating rate of 10 °C/min. Ammonia concentration in the effluent was measured with a gold-plated filament thermal conductivity detector.

Molecular dimensions of the reactant and product molecules were calculated using Chem Bio 3D (version 7) and Gaussian software theoretically.

2.4 Catalytic activity tests

Ten mmol each of glycerol and acetone were mixed with 0.5 g catalyst sample in 50 ml reaction vessel and stirred on a magnetic stirrer for 30 min. Reaction temperature was maintained using a thermostat. After the reaction, the mixture was extracted by stirring with 4 ml of n-pentanol for 5 minutes and filtered to remove the catalyst. The reaction mixture was analyzed using Chemito GC-1000 gas chromatograph with TR-Wax capillary column and flame ionization detector. The cyclic acetal products [5-membered cyclic ketal (2,2-dimethyl-1,3-dioxolan-4-yl) methanol simply called dioxalane and 6-membered cyclic ketal (2,2-dimethyl-1,3-dioxan-5-ol)] simply called dioxane were analyzed using n-heptane as internal standard. The products were also confirmed by GC-MS analysis. The conversion and selectivity of products were quantified with respect to standard samples of dioxalane, glycerol formal and glycerol. Reaction occurring is shown in scheme 1.



Scheme 1: Reaction carried out using dealuminated BEA zeolite samples

3. Results and discussion:

Table 1 gives the surface characteristics and acidity of zeolite samples before and after modification with organic sulfonic acids. BEA zeolite having SAR 25 was used for the experiments. Before modification, it possessed a measured surface area of 538 m²/g. Surface area and pore volume of BEA zeolite, before and after modification, are also presented in table 1. Three different organic sulfonic acids such as pTSA, MSA and PDSA were used for

modification. All the three organic acids caused removal of structural Al accompanied by increase in surface area and pore volume; the changes observed was in the sequence PDSA > MSA > pTSA.

Catalyst	Si/Al	Surface	Pore	Average Pore	Pyridin	e FT-IR
samples	ratio	area,	volume,	diameter	acidity	
		$S_{BET}(m^2/g)$	V (cm ³ /g)	(Å)	mm	ol/g
					В	L
BEA	25	538	0.307	31.04	0.644	0.394
1.0pTSABEA	48	579	0.364	30.9	0.626	0.372
1.0MSABEA	69	628	0.388	30.01	0.602	0.366
1.0PDSABEA	96	674	0.412	29.24	0.531	0.347

Table 1 Surface characteristic and acidity of acid treated and other zeolite samples

Standard deviation values: Si/Al-±1%, S_{BET}-± 2.1%, V-±0.35%, Average pore diameter-±1.2%, Pyridine FT-IR acidity-±0.42%

Si/Al ratio was calculated using SEM-EDX analysis

3.1 Acidity: Acidity in zeolite is mainly due to isomorphous substitution of aluminum, generating a negative charge on the framework. This charge is compensated by H^+ ions in H-form of BEA and is responsible for Bronsted acidity. Aluminum present on the framework edges is the Lewis acid site. Organic sulfonic acid treatment of the zeolite removes aluminum from the framework and also from edges of the framework. This causes decrease in both Bronsted and Lewis acidity. The changes in the Bronsted (B) and Lewis (L) acidities of different organic sulfonic acid treated BEA samples were measured by the pyridine adsorption using FTIR method reported elsewhere^{39, 40}. The results are given in table 1 and the pyridine-FTIR patterns are shown in Fig 1.

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Fig 1 pyridine adsorbed FT-IR spectra of the catalyst samples

Both the methods of acidity measurement showed a decrease in the acid amounts of BEA on treatment with organic acids. The decrease in the Bronsted and Lewis acid amounts due to dealumination was found to be in the order PDSA>MSA>pTSA. Different organic acids have the ability to remove structural (tetrahedral) Al to different extents thereby altering the Si/Al ratio of the treated BEA zeolite. PDSA is able to remove more Al than the other two acids. This is confirmed by decrease in the intensity of the band at 60 ppm in the ²⁷Al MAS NMR spectra corresponding to the tetrahedral aluminum present in the zeolite framework ((Fig 2). From the ²⁷Al MAS NMR spectra it can be seen that the decrease in the Al content of the organic acid treated zeolite follows the order PDSA>MSA> pTSA. Consequently, among the organic acid treated zeolites, PDSA treated zeolite shows the lowest acid amounts and pTSA treated zeolite shows the highest acid amount. Al removal from the zeolite structure is expected to cause enhancement in surface area and pore volume. This is supported by the fact that the increase in surface area, pore volume and Si/Al ratio for the treated zeolites is in the order pTSA< MSA<PDSA (table 1). Also there is no change in structural integrity of the acid treated BEA samples, as evident from the XRD patterns (Fig 3). Morphology of zeolite samples, as shown by FESEM images, does not show any major change upon organic acid treatment (Fig 4).

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Fig 2 ²⁷Al-MAS NMR plots of (a) BEA (b) 1.0pTSABEA (c) 1.0MSABEA and (d) 1.0PDSABEA



Fig 3 XRD pattern of BEA and acid treated BEA samples



Fig.4 FESEM images of (a) BEA (b) 1.0pTSABEA (c) 1.0MSABEA and (d) 1.0PDSABEA samples

3.2 Reaction parameter studies with untreated BEA

The effect of different reaction parameters such as temperature, catalyst amount, mole ratio and reaction time on conversion and selectivity was carried out in the presence of untreated BEA catalyst. Each experiment was performed three times and the mean of the obtained values was considered for the calculation of standard deviation. Internal and external diffusion effects were calculated under similar experimental conditions using Mear criteria (3.54×10^{-7}) for external diffusion and Weisz-Prater (2.984×10⁻⁷) and Koros-Nowak criteria for internal diffusion. Both the diffusion effects are found to be negligible. The results of variation of reaction parameters on catalytic activity are discussed in the ensuing sections.

3.2.1 Effect of catalyst amount:

There is a significant effect of catalyst amount on the glycerol conversion and the product selectivity. In the absence of catalyst, reaction does not proceed and in the presence of the catalyst reaction proceeds slowly with gradual increase in conversion of glycerol with the amount of the untreated BEA catalyst (Fig 5). At lower catalyst amounts up to 0.5 g there is a

substantial increase in conversion which gets stabilized beyond 0.5 g. Fig 5 also shows the effect of catalyst amount on the selectivity of the two products. The selectivity of five-membered dioxalane increased accompanied by decrease in the six-membered dioxane. At 0.1 g of catalyst, the selectivity of dioxalane, 72% and dioxane, 28% was observed. Further increase in catalyst amount beyond 0.5 g, the selectivity distribution was found to be 94% dioxalane and 6% dioxane.



Fig 5 Effect of untreated BEA catalyst amount on acetalization of glycerol with acetone and product selectivity Reaction conditions: mole ratio 1:1 of glycerol to acetone, temperature; 30 °C, reaction time; 30 min.

3.2.2 Effect of reaction time:

Effect of reaction time was studied in the range of 5 to 100 min (Fig 6). As the reaction time increases from 5 to 30 min, glycerol conversion also increased and reached a maximum around 40 min. Beyond 40 min, a slight decrease in conversion was observed, but the selectivity distribution of the two products remained almost the same. The decrease in the conversion of glycerol is explained due to hydrolysis of cyclic acetals⁴¹⁻⁴³. In the present study, it is noticed that, when the glycerol conversion reaches a point (around 78%), the hydrolysis of cyclic acetals becomes significant.



Fig 6 Effect of reaction time on acetalization of Glycerol with acetone in presence of BEA as catalyst

Reaction conditions: mole ratio 1:1 glycerol to acetone, temperature, 30 °C, catalyst amount; 0.5g.

3.2.3 Effect of temperature:



Fig 7 Effect of reaction temperature on acetalization of Glycerol with acetone Reaction conditions: mole ratio 1:1 of glycerol to acetone, reaction time; 30 min, catalyst amount; 0.5 g.

Fig 7 shows effect of temperature variation on the acetalization of glycerol with acetone. Effect was studied from ambient temperature (30 °C) to 65 °C. At the ambient temperature, conversion was 61% with selectivity 83% for dioxalane and 17% for dioxane. Increase in temperature caused an increase in conversion and reached a maximum at 50 °C, with 96% dioxalane and 4%

dioxane. Beyond 50 °C, conversion slightly decreased possibly because of the hydrolysis of the cyclic acetals formed but again there was no change in product selectivity.

3.3 Comparison with dealuminated BEA samples:

Under similar reaction conditions catalytic reactions using organic sulfonic acid treated BEA samples were carried out to study their behavior in catalytic activity and selectivity in acetalization of glycerol with acetone. Untreated BEA sample showed 76% conversion with selectivity 83% for dioxalane and 17% for dioxane. Conversion and selectivity of products were found to be higher in modified BEAs (Table 2). 1.0MSABEA and 1.0pTSABEA showed almost the same conversion and selectivity. 1.0PDSABEA however showed 100% selectivity for the dioxalane with no formation of dioxane. This is perhaps due to the rearrangement of dioxane to dioxalane over 1.0PDSABEA.

Catalytic acetalisation reaction mainly occurs on the internal surface (pores) of the zeolite. Molecular dimensions of the dioxane and dioxalane computed theoretically are given below (Fig 8). It can be seen that dimensions of both reactant and product molecules are smaller than internal pore dimensions. Further, most of the active sites are located within the pores.



Dioxalane dimension 6.29×4.99Å _{Dioxane dimension 6.49×4.37Å} Glycerol dimension 5.56 ×4.08Å Acetone dimension 4.36×3.11Å Fig 8 Molecular dimension and 3D structures of reactant and product molecules

Generally glycerol acetalization reaction is a Bronsted acid catalyzed reaction but also can take place to a lesser extent in the presence of a Lewis acid. The rearrangement of dioxane to dioxalane however, can take place only in the presence of Bronsted acid sites. Accordingly, selectivity is only dependent on the Bronsted acid sites.

Strength of the acid sites was studied by using NH₃-TPD method. Desorption of ammonia at different temperatures could be seen in the TPD profile (Fig 9). It indicates desorption of ammonia at lower temperature range (T1 = 100-300 °C) corresponding to weak acid sites and desorption at higher temperature (T2 = 325-550 °C) corresponding to the stronger acid sites. The amounts of NH₃ desorbed are given in table 2.

On treatment with organic acids, BEA zeolite showed changes in strength of the acid sites- a decrease in weaker acid sites and a moderate increase in stronger acid sites (Fig 9). Increase in strength of the acid sites enhanced the selectivity of dioxalane from dioxane with insignificant change in conversion of glycerol in the acetalization reaction.

Table.2 comparison of conversion of glycerol and dioxalane selectivity in glycerol acetalization with acetone using BEA samples dealuminated with different acids

Catalyst	%	%	%	Amount	of NH ₃ -	Total
samples	Conversion	selectivity	selectivity	desorbed	(mmol)	acidity
	of glycerol	of	of	T_1	T ₂	(mmol)
		dioxalane	dioxane			
BEA	76	83	17	0.64	0.47	1.11
1.0pTSABEA	82	90	10	0.45	0.51	0.96
1.0MSABEA	84	93	07	0.29	0.58	0.87
1.0PDSABEA	80	100	00	0.19	0.49	0.68

Reaction conditions: time; 30 min, temperature; 30 °C, catalyst amount; 0.5 g, mole ratio 1:1 of glycerol and acetone. T₁= temperature range 100-300 °C, T₂ = temperature range 325-550 °C Standard deviation values: Glycerol conversion- \pm 1.6%, dioxalane selectivity- \pm 2.1%, dioxane- \pm 1.35%, Amount of NH3 desorbed - \pm 0.52%,



Fig 9 NH₃- TPD profiles of HBEA and acid treated BEA zeolite samples.

3.4 Selective dioxalane formation:

Catalytic activity with 1.0PDSABEA was carried out by varying reaction conditions such as temperature, catalyst amount and reaction time. The results obtained are shown in table 3A-3C. Though the glycerol conversion varied under different conditions, 1.0PDSABEA sample gave dioxalane as the single product. This shows that only catalyst characteristics are responsible for the selectivity and not the reaction conditions. Further studies were made with the catalyst samples dealuminated with 0.1 M to 0.5 M PDSA. This was to investigate the changes in acid amounts and pore volumes that arise upon acid treatment and their relation with dioxalane selectivity.

Table.3A Effect of catalyst amount on the conversion of glycerol and product selectivity with 1.0PDSABEA catalyst

	2		
Catalyst	% conversion	Selectivity of	Selectivity
amount (g)	of glycerol	dioxalane	of dioxane
0.1	35	≜	≜
0.2	48		
0.3	62		
0.4	76		I
0.5	81	100	00
0.6	82		
0.7	84		
0.8	85		
0.9	85		
1.0	86	★	★

Reaction conditions: Time; 30 min, temperature; 30 °C, mole ratio 1:1 glycerol: acetone. Standard deviation values: Glycerol conversion-±1.8%, dioxalane selectivity-±0.15%, dioxane-±0.2%,

Table.3B	Effect of	reaction	temperature	on the	conversion	of glycerol	and produc	t selectivity
with 1.0P	DSABEA	catalyst						

Temperature	% conversion	Selectivity of	Selectivity
$(^{\circ}C)$	of glycerol	dioxalane	of dioxane
30	56	▲	♠
35	66		
40	71		
45	76		I
50	80	100	00
55	82		
60	84		
70	85		
80	85] ↓	. ↓

Reaction conditions: Time; 30 min, catalyst; 0.5 g, mole ratio 1:1 glycerol: acetone.

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Standard deviation values: Glycerol conversion-±1.48%, dioxalane selectivity-±0.09%, dioxane-±0.17%,

Table.3C Effect of reaction time on the conversion of glycerol and product selectivity with 1.0PDSABEA catalyst

1.0FDSADI	EA Catalyst		
Reaction	% conversion	Selectivity of	Selectivity
time (min)	of glycerol	dioxalane	of dioxane
5	39		
10	48		
20	62		
30	76		I
40	80	100	00
50	78		
60	80		
90	82		
120	84	↓	+

Reaction conditions: Catalyst; 0.5 g, temperature; 30 °C, mole ratio 1:1 glycerol: acetone. Standard deviation values: Glycerol conversion-±1.84%, dioxalane selectivity-±0.16%, dioxane-±0.20%.

3.5 Reusability of the samples

The reusability of the catalyst samples was checked for four cycles. The results (table 4) are similar to fresh catalyst samples indicating negligible changes in catalyst characteristics after use in the reaction. Further catalyst samples were recovered after the reaction and subjected to pyridine FT-IR, XRD and BET analysis. These results do not show any significant change in catalyst characteristics before and after use in the reaction indicating there is no deactivation of zeolite sample.

Table 4 Recyclability of 1.0PDSABEA catalyst and their surface and acidity characteristics after the reaction

Cycles	% Conversion	% selectivity	% selectivity	Surface	Pore	Pyridine
	of glycerol	of dioxalane	of dioxane	area	volume	FT-IR
				(m^2/g)	(cm^3/g)	acidity
						(mmol/g)
1^{st}	80	100	00	673	0.410	0.875
2^{nd}	78	100	00	671	0.409	0.869
3 rd	79	100	00	672	0.411	0.872
4 th	77	100	00	670	0.410	0.870

Reaction conditions: time; 30 min, temperature; 30 °C, catalyst amount; 0.5 g, mole ratio 1:1 of glycerol and acetone.

Standard deviation values: Glycerol conversion- $\pm 2\%$, dioxalane selectivity- $\pm 0.2\%$, dioxane- $\pm 0.25\%$, S_{BET}- $\pm 2.4\%$, V- $\pm 0.28\%$, Pyridine FT-IR acidity- $\pm 0.38\%$,

The possible reaction mechanism for dioxalane formation is shown in scheme 2. The mechanism of formation of glycerol acetals involves protonation by Bronsted acid site or Lewis acid

coordination to carbonyl oxygen of acetone generating positive charge on the carbonyl carbon (scheme 2). The carbocation thus formed gets attacked readily by nucleophilic hydroxyl group of glycerol giving hemi acetal. This is further attacked by another hydroxyl group resulting in cyclic acetal with the elimination of a molecule of water. When 1,2 hydroxy groups are involved dioxalane [5-membered] is formed and dioxane [6-membered] is formed when 1,3 hydroxy groups are involved. Further, in the presence of Bronsted or Lewis acid sites, dioxane gets rearranged to dioxalane.



Scheme 2 Possible reaction mechanism for dioxalane formation

3.5 Role of pore volume and acidity in dioxalane selectivity:

The selectivity for dioxalane and dioxane in presence of untreated BEA and selectivity for those treated with different concentrations of PDSA are shown in Table 5. It reveals that the selectivity for the dioxalane increased with the increase in PDSA concentration from 0.1 M to 1.0 M. The selectivity for dioxalane with 0.1PDSABEA was the same as that of untreated BEA catalyst (83%) but the selectivity increased to 100% with 1.0PDSABEA. Since this increase of 17% has significance with respect to mechanism, its relation with changes in various parameters observed in the catalyst samples upon acid treatment was studied.

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Catalyst	Conversi	%	%	Si/Al	Acidity	Pore	Surface
samples	on of	selectivity	selectivity	ratio	(Pyr-	volume	area
	glycerol	of	of dioxane		FTIR)	(V) cm^3/g	(S_{BET})
	(%)	dioxalane			(A)		m ² /g
					mmol/g		
0.1PDSABEA	72	83	17	48	0.992	0.345	556
0.25PDSABEA	75	86	14	63	0.953	0.364	589
0.5PDSABEA	76	95	05	84	0.928	0.392	635
1.0PDSA-BEA	80	100	00	96	0.878	0.412	674
R	-	-	_	-	-0.963	0.994	0.993

Table 5 Comparison of glycerol conversion and product selectivity for BEA zeolite treated with different concentrations of PDSA

Reaction conditions: time, 30 min; temperature, 30 °C; catalyst amount, 0.5 g; glycerol and acetone mole ratio, 1:1.

Standard deviation values: Glycerol conversion- $\pm 1.6\%$, dioxalane selectivity- $\pm 2.1\%$, dioxane- $\pm 1.35\%$, Si/Al- $\pm 1\%$.

It could be seen from Table 5 that the catalyst properties that change on increase in the acid concentration used for treatment are surface area, pore volume and acidity. Increase in pore volume is evidently due to the removal of structural Al causing decrease in acid amount (table 5). Acidity (A) was calculated by summing up the Bronsted and Lewis acidities by the pyridine-FTIR method. In order to know whether the change in pore volume and acidity are responsible for the increase in dioxalane selectivity, these characteristics were correlated with the increase in selectivity. The correlation coefficients are given in table 5. The correlation coefficient (r) values show good correlation for the dioxalane selectivity with all the parameters. Surface area and pore volume showed very nearly the same r value. This is expected because these two parameters are caused due to dealumination and therefore there exists a good proportionality between surface area and pore volume. Since both pore volume and acidity appear to be responsible, some combination of both have to be considered in explaining the rearrangement of dioxane leading to 100 % dioxalane selectivity.

3.6 Volume space acidity (VSA):

Increase in pore volume (by about 25%) on organic acid treatment is caused by the removal of framework Al thereby diminishing the acid amount (by about 14%) in the enhanced pore volume. A combination of both these factors, that is, acidity and pore volume, apparently determines the rearrangement of dioxane. Extent of rearrangement is dependent on the

progressive removal of Al which causes decrease in acid amounts and increase in pore volume. The combination of both these factors is expressed as volume space acidity factor (VSA). VSA, described as the product of pore volume (V) and inverse acidity (A⁻¹), provides a measure of volume space for each acid site available for the dioxane molecule to orient and undergo rearrangement.

In the present work, the rearrangement of the dioxane to dioxalane is facilitated by the pore volume to approach the acid sites in such a way that the molecule readily orients to rearrange itself. With the increase in acid concentration used for treatment, the pore volume increases with proportional decrease in the acid amounts (or increase in VSA) till it reaches an optimum value to achieve 100 % dioxalane selectivity with 1.0PDSABEA catalyst (Fig 10). Correlation coefficient (r) between VSA and the dioxalane selectivity for catalysts treated with different acid concentrations also showed a high correlation (r = 0.989). Thus, combination of increase in pore volume and decrease in acid amounts favoring the rearrangement of the dioxane to dioxalane is probable.



Fig 10 Representation of relation between VSA and selectivity of dioxalane

Reaction conditions: time, 30 min; temperature, 30 °C; catalyst amount, 0.5 g; glycerol and acetone mole ratio, 1:1

3.7 Acidity, hydrophobicity and dioxalane selectivity:

Increase in acid amounts is known to cause the hydrolysis of dioxane/dioxalane favoring the reverse reaction giving back the reactant molecules^{20,26,29,41-45}. On the contrary, decrease in framework Al brings down the acidity and consequently hydrolysis of the dioxane/dioxalane is

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reduced. Furthermore, Al removal causes increased hydrophobicity in the zeolite channels. Increased hydrophobicity prevents the dioxane molecules to hydrolyze back into the reactants thereby favoring the rearrangement of the dioxane molecules to dioxalane. This results in 100% selectivity for dioxalane in 1.0PDSABEA. High correlation factor observed between VSA and dioxalane selectivity is not surprising. On the other hand VSA correlation of acid amount of higher strength (as measured by the ammonia desorbed at higher temperature T2) with dioxalane selectivity showed a poor correlation (r = 0.846). It appears that variation of acid strength as measured by TPD-NH₃ has no influence on the dioxalane selectivity. And also VSA of average pore diameter when correlated with the selectivity of dioxalane showed r value 0.953.

4. Conclusion:

Removal of Al from the framework on treatment with PDSA modifies the characteristics of BEA zeolite. Increase in PDSA concentration for treatment results in dealuminated zeolite with gradual increase in surface area and pore volume but decrease in acid amounts. Untreated BEA zeolite catalyzes the reaction between glycerol and acetone to form six-membered dioxane and five membered dioxalane, the maximum selectivity of the latter being 83%. BEA sample treated with 1MPDSA, however, is found to exhibit complete rearrangement of six-membered dioxane into the five-membered dioxalane. Augmented selectivity for the five membered species is attributed to the increase in pore volume and decreased acid amount. A factor called volume space acidity (VSA) described as the product of pore volume (V) and inverse acidity (A⁻¹), provides a measure of volume space available for molecular rearrangement on each acid site. VSA correlates well with the dioxalane selectivity exhibited by the modified BEA zeolite.

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Graphical Abstract:

