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Metal ion-exchanged zeolites as solid acid catalysts for the green synthesis of nopol from Prins reaction

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The application of metal ion-exchanged zeolite as highly active and selective catalyst for the synthesis of nopol from Prins reaction of β-pinene is reported. The catalysts were prepared by ion-exchange method and characterized by XRD, pyridine-FT-IR, AAS, NH_3-TPD and SEM. The Zn-beta catalyst showed the best performance among different types of zeolites. The acidity of Zn-beta zeolite was correlated with amount of zinc and activity of the reaction. For different metal ion-exchanged beta catalysts, the yield of nopol increased with decrease in Brönsted to Lewis acidity (B/L) ratio. The influence of solvents on the Prins reaction in terms of acceptor and donor number was investigated. The degree of Zn loading, amount of solvent, temperature, catalyst amount, mole ratio and recyclability of the catalyst were investigated.

1. Introduction

The terpenes find their wide application in the synthesis of variety of products such as food additives, pharmaceuticals, agrochemicals and aromas. Pinene, a major composition of pine tree, is an inexpensive and worldwide available terpine.[1] Therefore, conversion of these pinenes into value added chemicals is one of the interesting areas of research. Nopol is a condensation product of β-pinene and paraformaldehyde, generally used in the agrochemicals as a pesticide and as an aroma in soaps, detergents and polishes.[2] The synthesis of nopol is an acid catalyzed C-C bond forming reaction between alkene and aldehyde known as Prins reaction.

Prins reaction is usually catalyzed by acids and proceeds with electrophillic addition of activated aldehyde to alkene. The conventional method to synthesize nopol by homogeneous catalyst involves high energy consumption, low yield and formation of monocyclic isomers as side products.[3] In accordance with the insight of green chemistry; heterogeneous catalysts were widely investigated in the past few decades and also applied for the Prins reaction. The most widely explored catalysts for Prins reaction are Sn-beta,[4] Sn-MCM-41,[5] Sn-SBA-15,[6] Zr- SBA-15[7] and Zn-MCM-41[8], where the metal ions are doped by isomorphous substitution, wet impregnation, ion-exchange and chemical vapor deposition methods.[4-9] A good to moderate yield for nopol has been observed for the aforementioned catalysts. However, the application may be limited due to tedious synthesis procedures, leaching of metal ions and use of toxic metal tin. In addition to these metal ion based catalysts, some other catalysts like sulfated zirconia,[10] mesoporous iron phosphate,[1] Fe-Zn double cyanide complex,[11] Sn(OH)Cl,[12] metal organic framework[13] and MWW type zeolite[2] have been applied for the Prins reaction to produce nopol. Most of the above catalysts indicate the requirement of strong Lewis acid sites or weak Brönsted acid sites for the selective synthesis of nopol.[4-13]

The presence of AlO_4 in zeolite framework induces a negative charge and compensation of this charge by proton gives rise to Brönsted acidity. Ion-exchange has been used to introduce different metal cations into zeolites, which creates new Lewis acidic and redox properties in the zeolites.[14] The transition metal exchanged zeolites have been extensively studied for the various organic transformations such as reduction of NO by ammonia,[15, 16] steam reforming of ethanol,[17] isomerization and ring opening of styrene oxide,[18] oxidative dehydrogenation of propane and epoxidation of alkenes.[19] The zinc ion-exchanged zeolite effectively catalyzes hydroamination reactions ,[20] aromatization of ethylene,[21] dehydrogenation of propane[22] and for the synthesis of 2-methyl pyrazine.[23] The ion-exchange of zinc in zeolites generates Lewis acid sites, by replacing strong Brönsted acid sites. Zeolite beta with its high acidity and large pore size was found to be an outstanding catalyst for variety of organic transformations. Lewis acidity generated in beta zeolite by ion-exchange has been reported to improve the product activity and selectivity in some organic transformations.[24, 25]

We previously reported sulfated zirconia and Sn(OH)Cl as efficient catalysts for Prins reaction to produce dioxane derivative and nopol respectively.[12, 26] Many of the industrial processes prefer the catalyst based on zeolite due to its low cost, high thermal stability and tunable acidity. In this regard, an effort is made to synthesize the nopol by Prins reaction using different modified zeolites. To the best of knowledge, zeolites and their ion-exchanged form have not been studied so far for Prins condensation reaction. The present study describes the synthesis

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of nopol by Prins condensation of β-pinene with paraformaldehyde using zinc exchanged zeolites such as Zn-BEA, Zn-ZSM-5, Zn-MOR, Zn-Y and Zn-X catalysts. The effects of different metal cations, nature of solvents and different loading of zinc by ion exchange on beta zeolite have been studied. The physicochemical properties of the catalyst were correlated with the activity and selectivity of the Prins reaction.

2. Experimental Details

2.1 Materials

The zeolites H-ZSM-5 (SAR 38), H-Y (SAR 16), H-mordenite (SAR 32) were kindly donated by Süd-Chemie India Pvt Ltd. India. The H-beta (SAR 30) and Na-X zeolites were purchased from Nankai, China and, Zeolites and Allied products Pvt Ltd. India, respectively. The paraformaldehyde and different metal salts in the form of nitrates and acetates were purchased from Merck India. The ß-pinene, nopol, camphene, α-pinene and limonene were procured from Alfa Aesar, USA. The chemicals were used without further purification.

2.2 Catalyst preparation

The metal ion-exchanged zeolites were prepared by ion-exchange method using 0.5 molar solutions of respective metal salts of nitrates or acetates. In a typical procedure, zeolite was treated with 0.5 M aqueous solution of metal salts (unless otherwise mentioned), keeping the liquid to solid weight ratio of 10. The solution was refluxed for 8 h, followed by filtration, washing with water and finally drying at 120 °C for 8 h. The above described procedure was repeated twice to achieve maximum ion-exchange for all the metal ions. Finally the catalyst was calcined at 550 °C for 4 h. These calcined metal ion-exchanged catalysts were designated as M-beta, where M represents the exchanged metal ion. In case of silver, the ion-exchange was carried out 4 times in a dark environment using 0.05 M silver nitrate solution.

Different zinc containing H-beta zeolites were prepared by using aqueous solutions of different molar concentrations and are designated as MZn-beta, where M is the molarity of solution used for the ion-exchange. The zinc loaded beta catalysts were prepared by impregnation method for comparison. The required amount of zinc acetate (corresponding to 1.0 or 1.5 mmol of Zn /g) was dissolved in 20 ml of distilled water. To this solution, H-beta was added and stirred at 80 °C for 4 h. Solvent was evaporated, dried at 120 °C followed by calcination at 500°C for 4 h.

2.3. Catalyst characterization

The phase purity of all the ion-exchanged zeolites were determined by the X-ray diffractometer instrument (Bruker D-2 Phaser) with Cu K-α Source (λ-1.542 A°). The samples were analyzed in the 2θ range of 5-60° with scanning rate of 1.2 degrees per minute.

To investigate the nature of acid sites on the surface of zeolites, FT-IR (alpha-T, Bruker) pyridine adsorption technique was employed and spectra were recorded in the range of 1400–1700 cm^{-1} as reported previously.[12, 26] The samples were prepared in the form pellets and saturated with small amount of pyridine followed by degassing at 150 °C for 30 min. The FT-IR spectra in absorbance mode after pyridine treatment were measured. The difference in FT-IR spectra before and after pyridine absorption gave the spectra due to acid-pyridine interaction. The metal contents of Zn^{2+}, Cu^{2+}, Fe^{2+}, Na^{+}, Ca^{2+}, K^{+} ion exchanged zeolites were determined by Perkin Elmer AAnalyst 200 atomic absorption spectrophotometer (AAS) using standard solutions. Metal contents of Ag^{+}, Ni^{2+}, Cs^{+} and Mn^{2+} ion-exchanged zeolites were determined by ICP-OES using Thermo-iCAP 6000 series.

Temperature programmed desorption (TPD) of ammonia was performed in the temperature range of 100-600 °C with ramp rate of 12.5 °C /min followed by 20 minutes hold time at 600 °C. Before the TPD measurements, zeolite samples were calcined at 550 °C for 2 h in flow of He gas. Then samples were saturated with anhydrous ammonia (10 % NH_3 + 90 % He) at 100 °C for 45 minutes and finally He gas was flushed for an hour to remove the physically adsorbed ammonia.

Nitrogen sorption measurements were carried out at 77 K in Nova 1000 Quantachrome instrument. Prior to the analysis, the samples were degassed at 250 °C for 4 h. Specific surface areas of catalysts were determined by Brunauer–Emmett–Teller (BET) equation.

2.4. Catalytic activity studies

The Prins reaction of ß-pinene with paraformaledye (hereafter PF) was carried out in a batch reactor in liquid phase. In a typical experiment, required amounts of ß-pinene (10 mmol) and paraformaldehyde (20 mmol) were taken in a 100 ml glass reactor containing solvent (5 ml) and appropriate amount of catalyst (20 wt% of total reactants). The glass reactor was heated over silicone oil bath equipped with a condenser. The required temperature of the oil bath was controlled and monitored by the PID temperature controller and thermometer respectively. During the course of reaction, the products were withdrawn at certain time intervals, centrifuged and were analyzed by gas chromatograph (Shimadzu-2014, FID detector) equipped with RTX-5 column (0.25 mm X 0.25 µm X 30 m). The oven temperature programme was 50 °C (5 min), 50–240 °C (15 °C /min), and 240 °C (5 min). Pure ß-pinene, α-pinene, limonene, nopol, and camphene were identified by the injection of standard samples and were further confirmed by the GCMS.

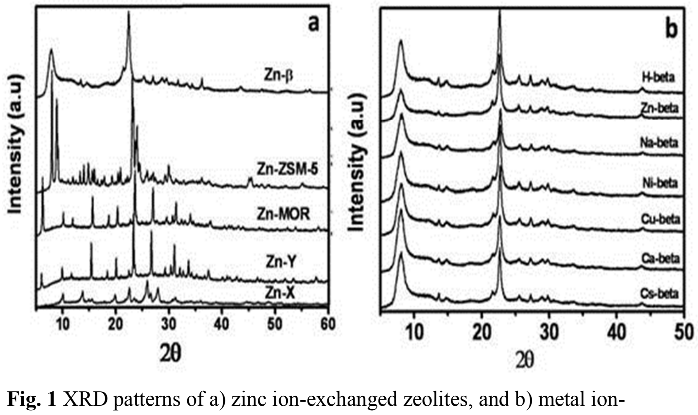


Fig. 1 XRD patterns of a) zinc ion-exchanged zeolites, and b) metal ion-exchanged beta zeolites.

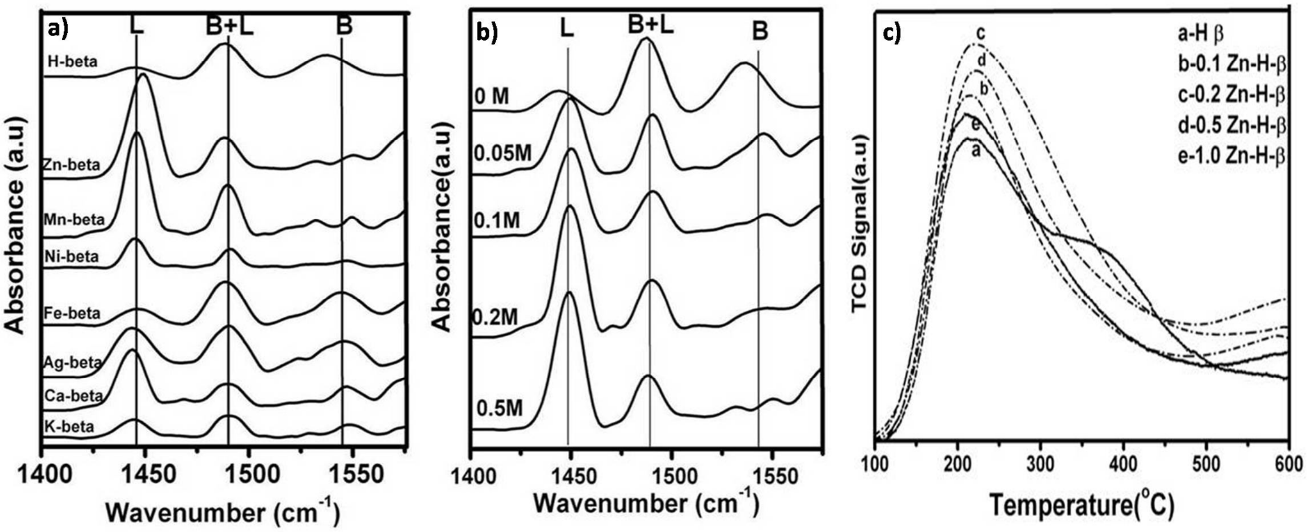


Fig. 2 a) Pyridine FT-IR spectra of metal ion-exchanged beta zeolites, b) Pyridine FT-IR spectra of Zn- H-beta catalysts prepared by different molar solutions, c) NH_3-TPD profile Zn-H-beta catalysts of different zinc contents.

3. Results and discussion

3.1 Characterization of catalysts

The X-ray diffraction patterns of the all the zeolites after ion-exchange with zinc showed the characteristic peaks in the 2θ range of 5 to 60°, which correspond to the respective zeolite patterns (Fig. 1a). The ion-exchange of H-beta zeolite with different metal ions did not affect the crystal structure of beta zeolite which can be inferred by the XRD patterns as shown in Fig.1b.

The amount of metal content in the ion-exchanged zeolite was determined by the atomic absorption spectroscopy. The amounts of Zn^{2+} exchanged in all the zeolites were shown in Table 1.The degree of ion-exchange differed based on the size and the charge of the metal ion. The degree of ion- exchange of the metal ions with H-beta zeolite decreased in the order; $Na^+ > Cu^{2+} > Ca^{2+} > Mn^{2+} > Fe^{2+} > Zn^{2+} > Ni^{2+} > K^+ > Cs^+ > Ag^+$ (Table 2). Ag^+, Cs^+ and K^+ ions showed low ion exchange probably due to their large ionic size. The extent of ion exchange of Zn^{2+} in H-beta increased with increase of molar concentration from 0.05 to 1M. The amount of zinc content was low (0.14 mmol Zn / g) for 0.05 M solution and increased to 0.57 mmol/g for 1M solution (Table 3). The lower zinc content (Zn/Al < 0.15) of Zn-beta catalyst is attributed to the sites associated with Zn^{2+} ions, whereas higher zinc content (Zn/Al = 0.15-0.26) is assigned to Zn-O-Zn active site.[20] The surface area of H-beta zeolite marginally decreased at low zinc content (0.18 mmol Zn /g) by ~3 % (465 to 450 m^2/g). It further decreased with increase in zinc content and reduced to 388 m^2/g at high concentration of zinc (0.57 mmol Zn /g) due to the blocking of micro pores by Zn^{2+} ions.

The adsorption of basic pyridine on solid acid catalyst is one of the characterization techniques to measure the nature of acid sites present on the catalyst. FT-IR spectroscopy is applied to detect adsorbed pyridine on the catalyst to distinguish Brönsted and Lewis acid sites. The interaction of pyridine with Brönsted and Lewis acid sites gives rise to the bending vibrations at 1540 and 1450 cm^{-1} respectively. To study the role of these acid sites on the Prins reaction, pyridine FT-IR spectra were measured for all the metal ion-exchanged zeolites and were depicted in Fig. 2a. The intensities of vibrations corresponding to 1540 and 1450 cm^{-1} were measured and B/L ratio for each catalyst was calculated. H-beta and most of the metal ion exchanged zeolites showed both Brönsted and Lewis acidity. The B/L ratio of M-beta zeolites increased in the following trend $Zn^{2+} < Mn^{2+} < Ni^{2+} < Ca^{2+} < Na^+ < Ag^+ < K^+ < Cs^+ < Fe^{2+} < Cu^{2+} < H^+$. The Zn^{2+} (B/L = 0.13) and Mn^{2+} (B/L = 0.18) exchanged beta gave least B/L ratio compared to other M-beta catalysts.

To explore further on the acidity of Zn-beta, pyridine FT-IR spectra of Zn-beta catalysts with different Zn contents (prepared by different molar solutions) were measured as shown in Fig. 2b. As the concentration of the zinc solutions used for the ion-exchange increased from 0.05 to 0.5 M, the amount of zinc content of beta zeolite increased. As a result, the intensity of peak due to Lewis acidity increased and that of Brönsted acidity decreased. The B/L ratio of beta zeolites prepared by different molar zinc solutions increased in the following trend, 1 M~ 0.5 M < 0.2 M < 0.1 M <0.05 M < 0 M. This indicates that the ion exchange with zinc increased the Lewis acidity in the catalyst. However, small amount of Brönsted acidity could be present even after multiple ion-exchanges.

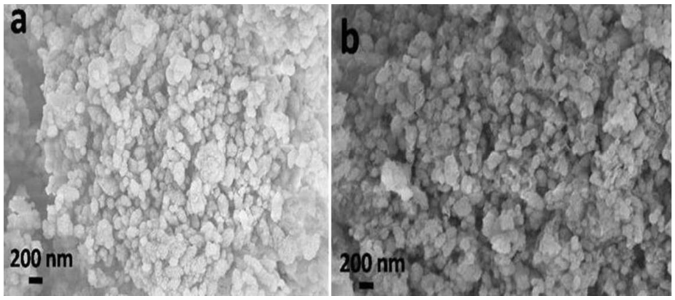


Fig. 3 SEM images of a) H-beta b) Zn-H-beta.

Table - 1. Physicochemical properties of Zn^{2+} exchanged zeolites and their catalytic activities for Prins reaction.

Zeolite	SAR (SiO_2/Al_2O_3)	Amount of Zn (mmol/g)	Pore size (A°)	Nopol yield (mol %)	TON*
Zn-Na-X	2	1.58	7.4*7.4	65.7	20.8
Zn-H-Y	16	1.58	7.4*7.4*7.4	83.7	26.5
Zn-H-BEA	30	0.31	5.6 *5.6 & 7.7*6.6	85.5	138
Zn-H-ZSM-5	38	0.35	5.1*5.6	35.2	50.3
Zn-H-MOR	32	0.63	6.5*7 & 2.9*5.7	17.8	14.1

[a] Reaction conditions: β-pinene = 10 mmol, PF = 20 mmol, solvent = 5 ml, catalyst amount = 20 wt %, temp =90 °C, time= 10 h *TON calculated by moles of nopol formed per mole of zinc

To determine the strength and amount of acid sites, temperature programmed desorption of ammonia (NH_3-TPD) of Zn-beta catalysts with different zinc contents were measured (Fig. 2c). The TPD profile of H-beta zeolite showed a major desorption peak at 220 °C with a shoulder at 350 °C indicating the presence of two types of acid sites with different strengths.[14] The peak at 220 °C could be due to the interaction of the NH_3 with weak Lewis and Brönsted acid sites and a peak with maximum at 350 °C corresponds to strong Brönsted acid sites. The TPD profile of all the Zn-beta catalysts showed only one major peak at 220 °C with increased intensity, indicating the increase of Lewis acidity in the catalyst as supported by the pyridine FT-IR measurements. The total amount of acidity measured by NH_3-TPD for Zn-beta catalysts represented in Table 3. As the amount of zinc content increased up to 0.25 mmol /g, the amount of acid sites also increased, whereas further increase of zinc content (>0.25 mmol/g) decreased the acidity as shown in Fig. 2c. The decrease in peak intensity for 0.5Zn-beta (0.31 mmol of Zn/g) could be due to the formation of ZnO. It is interesting to note that, higher amount of NH_3 molecules gets adsorbed on Zn-beta compared with H-beta.[27]

To study the textural properties of H-beta and Zn-beta zeolites, SEM images were taken as shown in Fig. 3. Both H-beta and Zn-beta contained spherical shaped particles with an average size of 150 nm. From SEM images, it can also be seen that there was no agglomeration of particles after ion-exchange with zinc.

3.2 Catalytic activity study

3.2.1 Screening of the zeolite catalyst

The Prins reaction of β-pinene with PF was carried out over different unmodified and ion-exchanged H-ZSM-5, H-mordenite, H-beta, Na-X and H-Y zeolites. The influence of different pore structure of these zeolites on the catalytic activity and selectivity were correlated. The H-form of all the zeolites showed lower conversion and selectivity compared to their Zn^{2+} exchanged counterparts (Fig. 4a). Zeolites, H-Y and H-beta showed higher conversions (43.7 and 57.7 % respectively) compared to H-MOR (6.4 %) and HZSM-5 (14 %) which could be due to the easy diffusion of reactant and product molecules in HY and H-beta compared with the later. The Na-zeolites (synthesized in Na-form) showed lower activity compared with H-form of zeolites except for Na-ZSM-5 and Na-mordenite. The low conversions in case of Na-zeolites could be due to the presence of weak acidic sites as observed in case of Na-MCM-22 and Na-ITQ-2 zeolites.[2] Furthermore, two different zinc ion-exchanged zeolites were prepared separately using H and Na forms of zeolite (Zn-H-Zeolite and Zn Na-zeolite respectively). Since there was no appreciable difference in activity between Zn- Na-zeolite and Zn-H-zeolite catalysts, all the further ion exchanges were carried with H-form of zeolite.

Overall, 12 membered ring zeolites like Zn-H-Y, Zn-Na-X and Zn-H-beta showed good yields for nopol, whereas Zn-H-ZSM-5

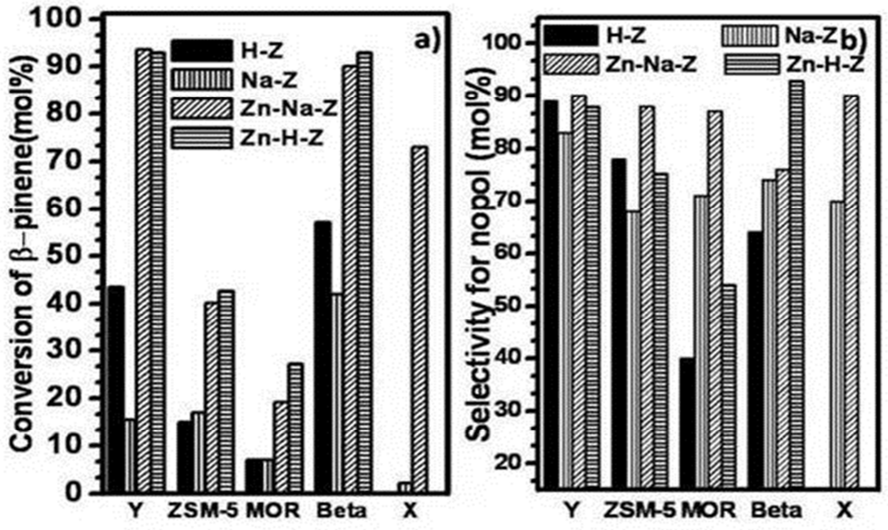


Fig. 4. Conversion of ß-pinene (a) and selectivity for nopol (b) with different zeolites, Reaction conditions: ß-pinene = 10mmol, PF= 20 mmol, benzonitrile = 5ml, catalyst amount = 20 wt %, temp =90 °C, time = 10 h, Z = Zeolite.

Table 2 Physico-chemical properties and activity of M-beta catalysts.

Metal exchanged zeolite-beta	Amount of metal (mmol/g)	Acidity (B/L ratio)	Nopol yield (mol %)
Zn^{2+}	0.31	0.13	85.5
Mn^{2+}	0.40	0.18	56.8
Ni^{2+}	0.32	0.28	48.9
Ca^{2+}	0.50	0.30	45.6
Na^{+}	0.78	0.54	44.4
Ag^{+}	0.013	0.65	32.9
K^{+}	0.23	0.87	43.4
Cs^{+}	0.12	1.26	38.2
Cu^{2+}	0.52	1.54	31.9
Fe^{2+}	0.35	1.75	34.8
H^{+}	--	2.39	36.4

[a] Reaction conditions: β-pinene = 10 mmol, PF=20 mmol, benzonitrile = 5 ml, catalyst amount = 20 wt %, temp = 90 °C, time = 10 h.

and Zn-H-MOR with 10 and 8*12 membered ring containing zeolites showed low yield for nopol as shown in Table 1. Zn-H-beta zeolite showed around 92 % conversion and 93 % selectivity for nopol with highest TON (138) among the catalysts. Hence, further optimization of reaction conditions were performed over the H-beta zeolite.

3.2.2 Effect of different metal ions

The effect of different metal ion-exchanged H-beta zeolite on the Prins reaction was performed. The various metal ions like alkali (Na^{+} ,K^{+} ,Cs^{+}), alkaline (Ca^{2+}) and transition metal ions (Mn^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Cu^{2+}, Ag^{+}) were exchanged with protons of H-beta zeolite. Only monovalent and divalent cation exchanged zeolites were studied because the trivalent ions are not really exchanged and are mainly present as oxide like clusters.[28]

Even though the same ion-exchange procedure was applied, the extent of ion-exchange was different for different metal ions (Table 2). Due to this diverse degree of ion-exchange and inherent properties of metal ions, M-beta catalysts showed different ratios of Brönsted and Lewis acid sites (B/L) as depicted by pyridine FT-IR spectroscopy. There was an interesting correlation of B/L ratio of different M-beta zeolites with nopol yield. As the B/L ratio of M-beta catalysts decreased, the yield for nopol increased (except the Ag-beta) as shown Table 2. The Zn-beta and Mn-beta with low B/L ratio showed high yield for nopol whereas Fe-beta, Cu-beta and H-beta with high B/L ratio showed low yield. The high Brönsted acidity (high B/L ratio) resulted in more side products whereas high Lewis acidity (low B/L ratio) increased both conversion and selectivity for nopol. Zn-H-beta with relatively higher Lewis acidity (B/L=0.13) gave highest conversion (92 %) and selectivity (93 %) among the other M-beta catalysts.

3.2.3 Effect of different zinc content

The catalysts with different zinc contents were prepared by ion-exchange of H-beta zeolite with aqueous zinc acetate solutions of different concentrations; 0.05, 0.1, 0.2, 0.5 and 1M. As the amount of zinc content increased, the conversion and selectivity also improved due to the increase of Lewis acidity as supported by pyridine FT-IR and NH_3-TPD results. With increase in zinc loading from 0.14 to 0.25 mmol/g, conversion of β-pinene increased from 66.6 to 91 % and selectivity also increased from 78 to 92 %. The activity and selectivity increased marginally with further increase in zinc loading from 0.25 to 0.31 mmol /g. At higher Zn loadings (> 0.31mmol/g), the conversion decreased due to decrease in acidity as shown in Table 3. The measurement of B/L ratio of different zinc containing beta catalysts gave better understanding on the role of Lewis and Brönsted acid sites in the Prins reaction. As the B/L ratio decreased from 2.4 to 0.06, both conversion and selectivity for nopol increased as shown in Table 3. The H-beta with high B/L ratio (2.4) showed low conversion (50 %) and low nopol selectivity (64 %) whereas 0.5M-Zn-beta catalyst with low B/L ratio (0.06) gave improved ß-pinene conversion of 92 % with 93% selectivity for nopol. The lower B/L ratio increased selectivity for nopol by decreasing the formation of side products like α-pinene, terpines terpinolenes, camphene and limonene.This clearly indicates that most of the strong Brönsted acid

Table 3 Properties of Zn-beta catalysts and their catalytic activity for Prins reaction.

Catalyst	Concentration of solution (M)	Amount of M (mmol /g)			Surface area (m^2/g)	Acidity (mmol of NH_3/g)	Acidity (B/L ratio)	Conversion of ß-pinene (mol %)	Selectivity (mol %)				
		Zn	Al	Zn/Al					Nopol	A	B	C	D[b]
H-beta	0	0	0.96	0	465	1.56	2.4	57.0	64	3.8	5.4	3.3	23.5
Zn-beta	0.05	0.14	0.96	0.14	450	1.62	0.45	66.6	78	2.2	3.5	2.8	13.7
Zn-beta	0.1	0.18	0.94	0.19	450	2.10	0.20	75.6	87	0.9	2.4	1.7	7.9
Zn-beta	0.2	0.25	0.92	0.27	427	2.23	0.08	91.0	92	0.6	1.6	1..0	6.8
Zn- beta	0.5	0.31	0.86	0.36	419	1.97	0.06	92.0	93	1.0	1.5	1.1	3.4
Zn-beta	1	0.57	0.84	0.67	388	1.75	0.07	87.0	94	1.0	1.5	1.0	3.5
[a]Zn/H-beta	--	1.0	--	--	--	1.64	--	58.0	91	1.0	1.8	1.2	4.9
[a]Zn/H-beta	--	1.5	--	--	--	1.52	--	52.0	89	1.1	1.9	1.4	6.6
ZnO	--	--	--	--	--	--	--	10.1	40	1.0	2.3	4.0	52.7
$ZnCl_2$	--	--	--	--	--	--	--	100	86	0.2	2.4	0.5	10.8

Reaction conditions: β-pinene = 10 mmol, PF=20 mmol, benzonitrile = 5ml, catalyst amount = 20 wt %, temp = 90 °C, time= 10 h. [a] Catalyst prepared by impregnation, A= α-pinene, B= Limonene, C= Camphene, D= Mixture of β-pinene isomerized products such as terpinenes and terpinolenes.

Table 4 Influence of solvents on Prins reaction.

Solvent	Dielectric Constant (DC)	Acceptor Number (AN)	Donor Number (DN)	ß-pinene conversion (mol %)	Product selectivity (mol %)				
					Nopol	A	B	C	D
No solvent	--	--	--	100	20.0	14.4	22.1	2.6	60.9
Cyclohexane	2.0	0	0	94.0	16.0	13.3	20.5	2.1	48.1
Toluene	2.4	8.2	0	99.6	12.0	8.9	17.6	2.6	58.9
Dichloroethane	10.4	16.7	0	100	8.2	4.8	14.8	2.4	69.8
Nitrobenzene	34.8	14.8	4.4	99.0	35.0	4.5	10.4	1.7	48.4
Benzonitrile	26.0	15.5	11.9	76.4	89.0	1.0	1.5	0.9	7.6
Acetonitrile	37.5	18.9	14.1	69.5	80.7	0.6	1.5	2.4	14.8
Dimethylformamide	36.7	16.0	26.6	5.0	39.0	0.2	0.5	0.3	60
Triethylamine	2.4	1.4	61	0	0	0	0	0	0

[a] Reaction conditions: β-pinene = 10 mmol, PF=20 mmol, solvent = 5 ml, catalyst = Zn-H-beta, catalyst amount = 20 wt %, temp =80 °C, time= 10 h. A= α-pinene, B= Limonene, C= Camphene, D= It includes β-pinene isomerized products such as terpinenes and terpinolenes.

sites of the zeolites were replaced by Lewis acidic zinc ions. The zinc content of 0.31 mmol /g in Zn-H-beta catalyst (prepared with 0.5 M Zn solution) was enough to get high conversion and selectivity.

The Zn-beta catalysts prepared by impregnation method (with 1.1 and 1.5 mmol Zn/g) were also screened for Prins reaction, but resulted into low activity (Table 3). This could be due to the presence of Zn in the form of oxide which is not active for this reaction. Pure ZnO as a catalyst also showed low conversion (10 %) and low selectivity (40%). This clearly indicates that ZnO present in Zn-beta catalyst does not contribute much to the catalytic activity. The homogenous catalyst, $ZnCl_2$ gave around 86 % of selectivity with complete conversion within 1 h. These results clearly indicate that ion-exchanged zinc is the active site for Prins reaction and not zinc as ZnO.

3.2.4 Study on the nature of solvents

The Prins reaction of ß-pinene with PF in the absence of solvent resulted in low nopol yield (20 %) which could be due to the low formaldehyde generation from PF. This indicates that a proper solvent is essential to facilitate the reaction towards high nopol yield. Hence, the effect of different solvents on the Prins reaction of ß-pinene over a Zn-beta zeolite was studied in detail. The various solvents were screened for the Prins reaction and the results are represented in Table 4. The role of dielectric constant (DC), acceptor number (AN) and donor number (DN) of solvents on the Prins reaction were studied. Initially, the effect of DC on the activity was studied by choosing solvents with similar dielectric constants. Solvents such as DMF (DC=36.7), acetonitrile (DC=37.5) and nitrobenzene (DC=34.8) with comparable DC showed different yields for nopol. The presence of solvents, toluene (DC=2.4), cyclohexane (DC=2.02) and triethylamine (DC=2.42) also gave different activity profiles. This indicates that dielectric constant of a solvent has no influence on the catalytic activity of Zn-beta for Prins reaction. .

Further study on the solvent parameters like AN and DN gave better understanding on the role of solvent in the reaction. The AN and DN were first proposed by Gutman, which assess the acidic and basic properties of solvents, respectively.[29] Subsequently, these values have been well accepted and applied by several researchers.[12, 30-31] As AN of the solvents increased (DN = 0) from cyclohexane to dichloroethane, the conversion improved from 94 to 100 % whereas selectivity were low and decreased from the 16 to 8.2 %. Further increasing the DN of the solvents (having similar AN) from dichloroethane to benzonitrile, conversion dropped from 100 to 76.4 % but selectivity increased substantially from 8.2 to 89 %. However, increase of DN from benzonitrile to DMF decreased both conversion and selectivity. Finally, triethylamine solvent with highest DN (AN = negligible) showed no activity for Prins reaction.

Solvents with both AN and DN values in the range of 10 to 20 (acetonitrile and benzonitrile) are the best to give high yield for nopol. The AN of a solvent represents its acidic property, which activates the Brönsted acid sites of the catalyst. These acid sites facilitate the isomerization of ß-pinene to give predominantly limonene, terpinolenes and terpines. As a result, high conversion of ß-pinene with low selectivity for nopol are obtained under solvents with high AN (DN = 0). The DN of solvent represents the basic property of the solvents. Therefore the solvent with DN in the range 10 to 20 could bind to the strong Brönsted acid sites of the catalyst resulting in low conversions and high selectivity. Further increase of DN (>14), solvent may preferentially bind to most of the acid sites of the Zn-H-beta catalyst leading to the low conversion. The low activity in presence of solvent with only high DN (triethylamine) could be due to the preferential adsorption on the acid sites leading to low generation of formaldehyde from PF.

Hence, solvents with both AN and DN in the range 10 to 20 are suitable to facilitate reaction by balancing Brönsted acidic sites of catalyst and decomposition of PF. Among all the solvents taken in this study, benzonitrile with AN (15.5) and DN (11.9) exhibited good conversion and selectivity.

3.2.5 Influence of reaction conditions

Effect of reaction temperature was studied using Zn-H-beta zeolite with β-pinene: PF mole ratio of 1:2 using 20 wt% of catalyst. The β-pinene conversion increased with increase in temperature as shown in Fig. 5a. The lower conversion of ß-pinene at low temperature (60 °C) is due to less in-situ generation of formaldehyde from paraformaldehyde. At 100 °C, the formation of formaldehyde was faster and as a result higher conversion was achieved. The temperature also had an effect on the selectivity of nopol. With increase in temperature from 70 to 90 °C, nopol selectivity increased whereas at 100 °C the selectivity decreased due to formation of side products. The reaction at 90 °C which gave good conversion and selectivity was used for further studies.

Further, to study the effect of different concentrations of reactants, Prins reaction was carried out with β-pinene : PF mole ratios of 1:1 to 1:4 as shown in Fig. 5b. The conversion and selectivity improved with increase in β-pinene: PF ratio from 1: 1 to 1: 2 and further increase of mole ratio did not have any effect on the catalyst performance. The low conversion of β-pinene at low PF concentration is due to the presence of less availability of active reactant, formaldehyde. The β- pinene: PF molar ratio of 1: 2 showed high conversion (92 %) and selectivity (93 %).

The effect of catalyst concentration on Prins reaction of β-pinene was studied by taking different catalyst weights with respect to the total weight of the reactant (Fig. 5c). As the catalyst concentration was increased from 10 to 20 %, the conversion increased from 70 to 92 % and marginal improvement in selectivity was also observed. Further addition of the catalyst could not improve the conversion or selectivity indicating saturation point of the reaction. Amount of solvent for the Prins reaction was studied using solvent to substrate ratio (v /w) of 1.5, 2.5, 3.5 and 4.5 at 90 °C with β-pinene: PF mole ratio of 1: 2 using Zn-H-beta catalyst (Fig. 5d).

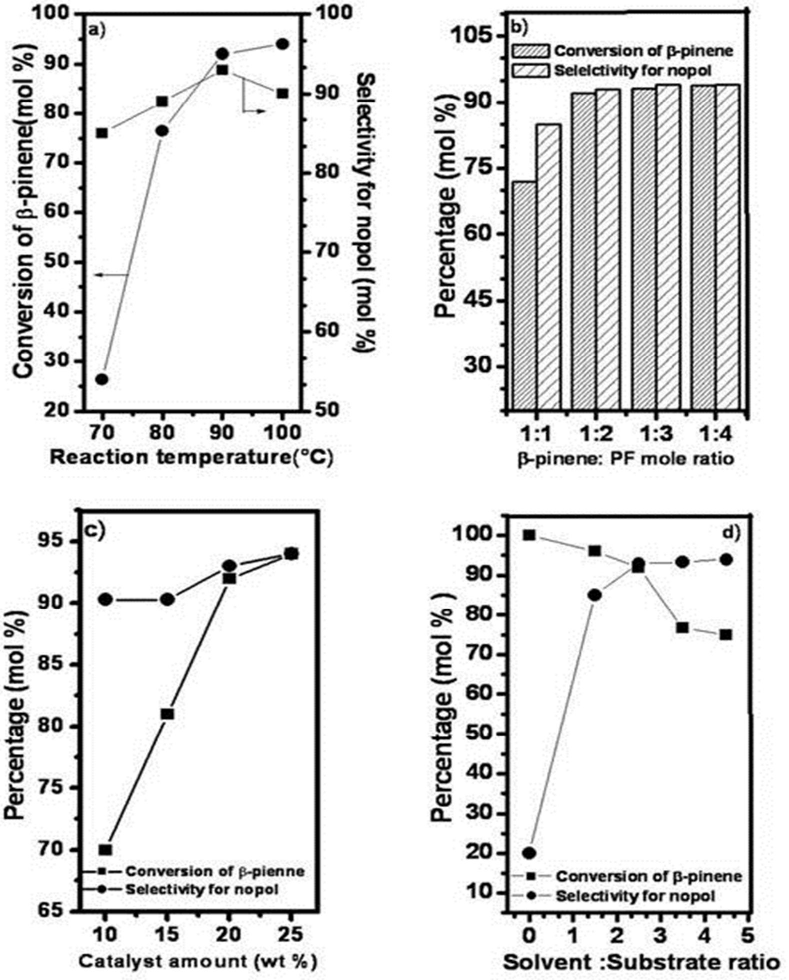
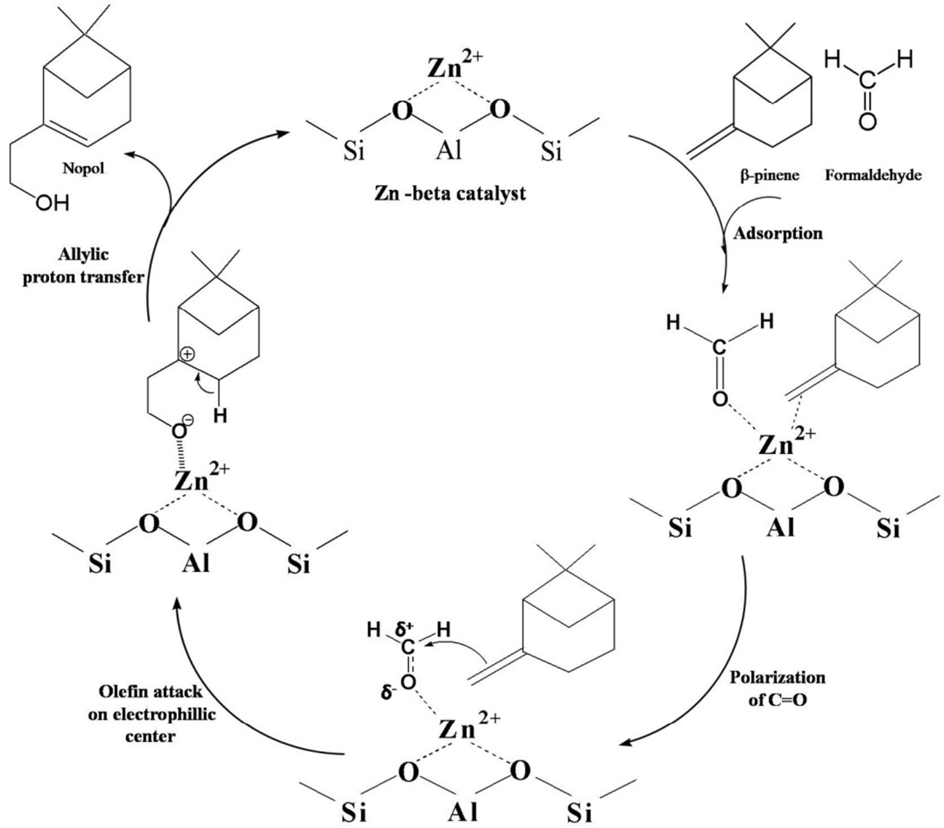


Fig. 5 Influence of reaction conditions on ß-pinene conversion and nopol selectivity
a) Effect of temperature. Conditions: ß-pinene = 10 mmol, PF= 20 mmol, benzonitrile =5ml, Catalyst = Zn-H-beta, catalyst amount = 20 wt %, time =10 h. *b) Effect of β-pinene: PF mole ratio*. Conditions: benzonitrile = 5ml, catalyst amount = 20 wt %, temp = 90 °C, time =10 h. *c) Effect of catalyst amount*. Conditions: ß-pinene = 10 mmol, PF=20 mmol , benzonitrile = 5ml, Catalyst = Zn-H-beta, temp =90 °C, time = 10 h. *d) Effect of solvent to substrate ratio.* Conditions: ß-pinene = 10mmol, PF= 20 mmol, solvent = benzonitrile, catalyst = Zn-H-beta, temp = 90 °C, time = 10 h.)



Scheme 1. Plausible reaction mechanism for the synthesis of nopol over Zn-beta catalyst.

As the amount of solvent to substrate ratio increased from 0 to 4.5, the conversion decreased from 100 to 76 % whereas selectivity increased from 20 to 94 %. The decrease in the conversion could be due to a decrease in number of collisions of the reactant with the catalyst. The increase in the selectivity is due to the smooth formation of formaldehyde in solvent media and blocking of some of the Brönsted acid sites as explained in solvent effect study. Solvent to substrate ratio of 2.5 was sufficient to get good conversion and selectivity for nopol.

3.2.6 Reaction mechanism

The plausible reaction mechanism for the condensation of ß-pinene with paraformaldehyde to produce nopol over Zn^{2+} exchanged zeolite is shown in Scheme 1. The Lewis acidic Zn^{2+} brings ß-pinene and formaldehyde molecules closer by coordinating with the π electrons of olefin and carbonyl groups. Once the molecules are adsorbed and coordinated to Zn sites, the reaction is initiated by polarization of C=O bond thereby generating an electrophilic center which then attacked by ß-pinene to give an intermediate. Further allylic proton transfer to the oxygen site forms a double bond resulting into nopol. In presence of strong Brönsted acid sites, ß-pinene easily forms carbenium ion by extracting the proton, which rearranges to form monocyclic and bicyclic isomers such as α-pinene, limonene, camphene and terpinolenes. The ion-exchange of these protons by zinc decreases the Brönsted acidity which in turn lowers the formation of side products and improves both conversion and selectivity in Prins reaction.

3.2.7 ***The heterogeneity and recycling study***

The heterogeneity test was carried out for Prins reaction by investigating the leaching of active sites of the catalyst into the reaction media. The Reaction was carried out using Zn-H-beta catalyst at a reaction temperature of 90 °C with β-pinene to PF mole ratio of 1:2. Reaction was stopped after 1 h (conversion = 37 %) and hot reaction mixture containing catalyst was filtered. To the filtrate, required amount of PF was added the reaction was continued for next 10 h. the conversion remained almost constant for the span of 10 h, indicating no leaching of active sites into the reaction mixture**.** This test confirms that the catalyst is truly heterogeneous without the leaching of active sites. It is further confirmed by the analysis of filtrate using AAS which showed the absence of zinc under the detection limit of $\geq$ 1 ppm.

For the recycling test, the catalyst was filtered after the completion of reaction, washed with acetone followed by drying at 120 °C and finally calcined at 500 °C for 2 h. The calcined catalyst was further used for the Prins reaction with fresh reaction

Table 5 Catalyst recycle study.

Catalyst cycle	Nopol yield
1	85.5
2	83.7
3	81.8
4	80.4

Reaction conditions: β-pinene = 40 mmol, PF = 80 mmol, solvent = benzonitirle =20ml, catalyst amount = 20 wt %, temp =90 °C, time= 10 h mixture. The catalyst showed good recyclability with minimal decrease in the activity after 3 recycles (Table 5). As there was no loss of Zn after catalyst recycle, the marginal loss of activity (~ 5%) may be attributed to the impurities remained after post-reaction work-up, recovery and regeneration steps.

3.2.8 *Comparison of Zn-beta catalyst with reported solid acid catalysts*

Table 6 shows the comparison of catalytic activity of Zn-beta with other reported solid acid catalysts. The tin based catalysts like Sn-SBA-15, Sn-MCM-41 and Sn(OH)Cl showed high conversion and selectivity for nopol. However, tin being toxic, makes the catalyst environmentally hazardous. Hence, there were efforts to utilize other comparatively non-toxic metals like Zn as active sites for nopol synthesis from Prins reaction. Zn-montmorillonite catalyst showed slightly higher nopol yield (87 %) compared to Zn-beta (present work).However, the leaching of the Zn was observed during the reaction.[31] Prins reaction with sulfated zirconia was reported to give high nopol yield (98 %). Zn-beta catalyst in present work exhibited higher nopol yield with lower amount of catalyst than previously reported catalysts such as Sn-MCM-41, Zn-MCM-41, Zr-SBA-15, Na-ITQ, Sn-kenyaite. The catalyst designed in the present work was prepared by non-toxic metal with environmentally friendly zeolite as its backbone and thus made synthesis of nopol, a green process.

Table 6 Comparison of catalytic activity of the Zn-beta catalyst with other reported solid acid catalysts.

Catalyst	Catalyst amount (wt %)[a]	ß-pinene conversion (mol %)	Nopol Yield (mol %)	Reference
Sn-SBA-15	13	99.8	98.7	[6]
Sn-MCM-41	51	99.3	98.0	[5]
Sn-kenyaite	50	50.8	49.8	[5]
Sn(OH)Cl	12	98	97.0	[12]
Sulfated zirconia	11	99	98.0	[10]
Na-ITQ	25	60	52.2	[2]
Zr-SBA-15	25	74	74	[7]
Zn-Montmorilionite	41	90	87.3	[32]
Fe-Zn metal cyanide	10	52	49.9	[11]
Zn-MCM-41	50	91	75.5	[8]
Zn-Beta	20	92	85.5	Present work

[a] Catalyst amount is calculated on the basis of total weight of catalyst with respect to total weight of the reactants.

4. Conclusions

Metal ion-exchanged zeolite is reported as highly efficient and selective catalyst for Prins reaction of β-pinene with paraformaldehyde to give nopol. Large pore zeolites like Zn-beta, Zn- X and Zn-Y exhibited high activity compared to Zn-ZSM-5 and Zn-mordenite. Among different metal ions screened, Zn^{2+} showed highest activity and selectivity for Prins reaction. As the Brönsted to Lewis acidity (B/L) ratio of metal ion-exchanged beta catalyst decreased, the yield of nopol increased indicating that Lewis acidic metal ion is the active site for Prins reaction. The Zn^{2+} exchange was facilitated by increase in concentration of molar solution leading to increase in total acid sites of the catalyst. Solvents like acetonitrile and benzonitrile with both acceptor and donor numbers in the range of 10 to 20 are necessary to enhance the performance of the catalyst. Zn-beta catalyst with 0.31 mmol Zn/g gave 92 % β-pinene conversion with 93 % selectivity for nopol under optimized reaction conditions. In conclusion, Zn^{2+} exchanged beta zeolite is an inexpensive and highly efficient catalyst for Prins reaction of β-pinene to produce nopol.

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