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# Nanosized sulfated zinc ferrite as catalyst for the synthesis of nopol and other fine chemicals

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# 1. Introduction

To perform reactions with very high yield, reduction of byproducts and limited use of toxic solvents is a challenge of modern research in organic chemistry. In this facet, heterogeneous catalysis serves as a fundamental tool as it offers several advantages including lower energy requirements, easy separation, increased selectivity and elimination of the toxic substances [1]. Variety of inorganic compounds such as zeolites, clays, supported heteropolyacids and metal oxides are employed for the development of ideal solid acid catalyst [2].

Ferrospinel materials having general formula  $M^{2+}[Fe^{3+}_2]O_4$ , are well known for their catalytic properties [3]. Depending upon the location of metal ions in the tetrahedral and octahedral sites, ferrospinel can be normal  $M^{2+}[Fe^{3+}_2]O_4$ , inverse  $Fe^{3+}[M^{2+}Fe^{3+}]O_4$ , or mixed spinel wherein the divalent cations are distributed between both sites. The cation location and distribution in zinc ferrite significantly affects its acid–basic properties [4]. Metal oxide materials, impregnated with sulfur compounds showed remarkable enhancement in their catalytic activity [5]. From the systematic studies of sulfated metal oxide catalysts it was revealed that, sulfatation increased number of weak and strong acid sites with simultaneous decrease in the number of weak and strong base sites at the catalyst surface [6]. Nevertheless, data on the catalytic applications of SZF catalyst towards organic transformations is scanty.

# ABSTRACT

A nanosized highly ordered mesoporous zinc ferrite ( $ZnFe_2O_4$ ; ZF) was synthesized *via* co-precipitation method, further sulfated with ammonium sulfate solution to obtain sulfated ZF (SZF) and have been used for the synthesis of nopol by Prins condensation of  $\beta$ -pinene and paraformaldehyde. The NH<sub>3</sub>-TPD and pyridine sorption DRIFT-IR studies revealed the significant enhancement in Lewis acidic sites of the zinc ferrite on sulfatation. The influence of various reaction parameters such as reaction temperature, effect of substrate stoichiometry and catalyst loading has been investigated. It gave 70% conversion of  $\beta$ -pinene with 88% selectivity to nopol. The spent catalyst was regenerated and reused successfully up to four cycles with slight loss in catalytic activity. The nanosized SZF catalyst was found to be highly active towards several other commercially important acid catalyzed reactions such as isomerization, acetalization and aldol condensation.

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Nopol [2-(7,7-dimethyl-4-bicyclo[3.1.1]hept-3-enyl)ethanol], is an optically active bicyclic primary alcohol, useful in the agrochemical industry for the synthesis of pesticides and other fine chemicals including soap perfumes [7]. The conventional synthesis of nopol involves Prins condensation reaction of  $\beta$ -pinene and paraformaldehyde using either zinc chloride as a catalyst at 115–120 °C for several hours, or acetic acid as a catalyst at 120 °C to yield nopyl acetate, which is saponified to nopol; or by autoclaving a mixture of  $\beta$ -pinene and paraformaldehyde at 150–230 °C for several hours [8]. However, numerous limitations are associated with the homogeneous catalyst systems in terms of their corrosive nature, difficulty in separation, post-synthesis disposal of effluents and recovery of reaction products [9].

Current research efforts are being directed to develop ecofriendly heterogeneous catalytic routes for the synthesis of fine chemicals. Several heterogeneous catalysts have been reported for the synthesis of nopol, such as metal supported MCM-41 mesoporous molecular sieves [10], ZnCl<sub>2</sub> impregnated montmorillonite [7], mesoporous iron phosphate [11], SnCl<sub>4</sub> grafted on MCM-41 by chemical vapor deposition (CVD) [12], Sn-SBA-15 [13], Sn-MCM-41 [14], Sn and Zn loaded MCM-41 [15]. In continuation of our previous studies on sulfated zirconia catalyzed synthesis of nopol [16], herewith we report the use of nanosized sulfated zinc ferrite catalyst for the synthesis of nopol and several other commercially important fine chemicals (Scheme 1).

The SZF catalyst showed good catalytic activity towards protection reaction of carbonyl compounds through formation of corresponding acetals/ketals. Further the catalyst was evaluated for isomerization of  $\alpha$ -pinene oxide to campholenic aldehyde and cross



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Scheme 1. Prins condensation reaction of  $\beta$ -pinene and paraformaldehyde.

aldol condensation reaction of 1-heptanal and benzaldehyde to produce jasminaldehyde. The catalyst also gave promising results for Claisen–Schmidt condensation reaction for the synthesis of flavanone and chalcones. All the synthesized compounds are of industrial importance and find several applications, either directly or as synthetic intermediates [17–20].

# 2. Experimental

#### 2.1. Materials

FeCl<sub>3</sub>·6H<sub>2</sub>O and ZnCl<sub>2</sub> were purchased from S.D. Fine Chemicals, India.  $\beta$ -Pinene was procured from Sigma–Aldrich Chemical Inc., USA. Other organic substrates and solvents were of analytical grade obtained from various commercial suppliers and were used without further purification. Millipore water was used in the catalyst preparation.

#### 2.2. Preparation of zinc ferrites

Nanosized ZF catalyst was prepared by a co-precipitation method. Zinc chloride (1.775 g) and iron (III) chloride (4.225 g) were separately dissolved in distilled water (125 m) and heated to 70 °C. In another beaker 1250 ml of NaOH solution (0.6 N) was heated to 70 °C. The metal precursor solutions were then added into NaOH solution as quickly as possible with vigorous stirring. The resulting solution was stirred vigorously at 70 °C for 1 h and aged overnight at room temperature. The precipitate was filtered and washed extensively with warm distilled water until free from chloride ions (AgNO<sub>3</sub> test). The solid product was dried at 175 °C for 16 h, and finally calcined at 470 °C for 3 h to yield the spinel catalyst. The as synthesized sample dried at 175 °C and calcined ferrite sample, hereafter denoted as ZF-175 and ZF-470 respectively.

#### 2.3. Sulfatation of ZF catalysts

SZF catalysts were prepared by impregnating calcined ZF sample using 0.3 M aqueous ammonium sulfate  $((NH_4)_2SO_4)$  solution [21]. Sulfatation was done by vigorously stirring 1 g of ZnFe<sub>2</sub>O<sub>4</sub> in 20 ml of ammonium sulfate solution for 4 h. The resulting solid was filtered and washed with distilled water followed by acetone. The impregnated sample was dried overnight at 100 °C, and then it was calcined at 470 °C for 1 h to get the SZF catalyst. The sulfated zinc ferrite sample calcined at 470 °C is hereafter denoted as SZF-470.

#### 2.4. Catalyst characterizations

Catalysts were characterized by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), TEM analysis,  $N_2$  sorption and temperature programmed desorption (TPD) studies using NH<sub>3</sub> and CO<sub>2</sub> as probe molecules.

The phase purity of the calcined zinc ferrite catalysts was evaluated using PXRD (Rigaku, MiniFlex II) using Cu K $\alpha$  radiation ( $\lambda$  = 1.54178 Å) in 2 $\theta$  range of 2–80° at a scanning rate of 3° min<sup>-1</sup>.

Transmission electronic microscope (TEM) images were collected using a JEOL TEM 2100 microscope. Samples were prepared by mounting acetone-dispersed samples on lacey carbon formvar coated Cu grids.

FT-IR spectroscopic studies were performed in the range of  $4000-400 \,\mathrm{cm^{-1}}$  as KBr pellets (Perkin Elmer). The pyridine adsorbed DRIFT spectra were recorded to investigate the distribution of Lewis and Brönsted acidic sites of ZF and SZF catalysts.

The BET surface area of the catalyst was measured by nitrogen adsorption–desorption method at liquid N<sub>2</sub> temperature (Micromeritics-ASAP 2020). The calcined samples were degassed under vacuum at 200 °C for 4 h, prior to adsorption measurement.

The acidic and basic properties of the catalysts were investigated with TPD analysis using NH<sub>3</sub> and CO<sub>2</sub> as probe molecules respectively. For the TPD measurements ~0.3 g of each catalyst was charged into a tubular quartz reactor of the TPD. The catalyst was pretreated at 200 °C for 1 h under a flow of helium (40 ml/min). Then the samples were saturated with 10% ultrapure adsorbate gas (NH<sub>3</sub> or CO<sub>2</sub>, balance He; 75 ml/min) at 50 °C for 1 h. The physisorbed probe molecule was removed by evacuating the catalyst sample at 50 °C for 1 h. Furnace temperature was increased from 50 °C to 850 °C at the heating rate of 5 °C/min and the desorbed NH<sub>3</sub> or CO<sub>2</sub> were analyzed.

# 2.5. Catalytic studies

All the catalytic reactions were performed at ambient pressure in liquid phase. In a typical run, requisite quantity of catalyst (preactivated at 200 °C for 1 h) and calculated quantities of substrates were charged in an oven dried double-necked round bottom (RB) glass flask either in presence of suitable solvent or under solventfree conditions. One neck of the flask was connected to a reflux condenser and the other was blocked with a silicon rubber septum. Water at ~15 °C was circulated through the condenser and the flask was then kept in an oil bath equipped with temperature controller and magnetic stirrer.

In a typical Prins condensation reaction,  $\beta$ -pinene (5 mmol), paraformaldehyde (15 mmol) in toluene (4 ml) with 0.14g preactivated SZF catalyst was refluxed at 95 °C in the RB flask with continuous stirring. The aliquots of reaction mixture were collected periodically, cooled and centrifuged to separate the catalyst. The reaction products were analyzed by gas chromatograph (Varian GC-450), equipped with Factor-4 capillary column (30 m long and 0.32 mm internal diameter) and flame ionization detector. The oven temperature was increased from 80 °C to 220 °C at the rate of 10 °C/min. High purity nitrogen gas was used (30 ml/h flow rate) as a carrier gas for the analysis.

Product identification was done on gas chromatograph-mass spectrometer (GCMS, Shimadzu – QP-2010) with GC oven programmed in the temperature range of 40–200 °C with helium as a carrier gas, and MS in EI mode with 70 eV ion source. GC peak areas were calibrated by taking solutions of known compositions with dodecane and tetradecane as an internal standard. The conversion and selectivity were calculated as per the formulas (i) and (ii) respectively:

% Conversion<sub>Substrate</sub> = 
$$\frac{(C_i - C_f)_{Substrate}}{(C_i)_{Substrate}} \times 100$$
 (i)

% Selectivity<sub>Product</sub> = 
$$\frac{(C_f)_{Product}}{(C_i - C_f)_{Substrate}} \times 100$$
 (ii)

where *C*<sub>i</sub> and *C*<sub>f</sub> are initial and final concentration of the respective species in the reaction mixture.

The best catalyst, SZF-470 (as identified in Prins condensation reaction) was further investigated for several other catalytic reactions such as, isomerization of  $\alpha$ -pinene oxide to campholenic aldehyde, synthesis of jasminaldehyde by cross aldol condensation reaction of 1-heptanal with benzaldehyde,



Scheme 2. Organic reactions performed using ZF-470 and SZF-470 catalysts.

acetalization of ethylene glycol with carbonyl compounds to produce corresponding acetals/ketals, and synthesis of chalcone and flavanone by Claisen–Schmidt condensation reaction using 2hydroxyacetophenone and benzaldehyde (Scheme 2). However only primary investigations are carried out for these catalytic reactions and detailed studies for optimizing reaction parameters are in progress.

# 3. Results and discussion

# 3.1. Characterization of the ferrite catalysts

The X-ray diffraction studies for ZF revealed the well-matched pattern with characteristic reflections for spinel phase confirming the structural purity of the samples (Fig. 1). The atomic ratio of Fe/Zn in ZF determined with ICP-AES was found to be 2.02, in good agreement with the theoretical value of 2.0. PXRD pattern of SZF also showed the characteristic peaks for spinel phase, indicating no change in the crystallinity of the parent ferrite materials after sulfatation. Furthermore, no characteristic peak of ammonium sulfate or sulfur containing salt was observed in the SZF catalyst. It clearly revealed that sulfur was not in the form of any sulfur containing salts such as ammonium sulfate, ammonium sulfide and ammonium persulfate [22].

The TEM image of the calcined ZF at 475 °C (Fig. 2) clearly showed the presence of ZF particles (average particle size of 7–10 nm) with well-ordered cubic morphology. The consistent lattice orientation of the particles reveals the highly ordered and crystalline nature of ZF particles.

It has been reported that, S<sup>6+</sup> species presumably exists in the form of inorganic chelating bidentate complexes or organic



Fig. 1. PXRD pattern of ZF and SZF catalyst.

sulfates over the metal oxide surfaces [23]. The FT-IR spectra (Fig. 3) of calcined SZF catalyst depict the IR bands of  $SO_4^{2-}$  group in the region of 900–1200 cm<sup>-1</sup>, with peaks at 972–980, 1042–1058, and 1118–1135 cm<sup>-1</sup> (characteristics of inorganic chelating bidentate sulfate) and are assigned to asymmetric and symmetric stretching frequencies of partially ionized S=O double bonds and S=O bonds (Structure A, Fig. 3) [24]. The elemental compositions along with the corresponding BET surface areas derived from N<sub>2</sub> adsorption–desorption studies of ZF and SZF samples are presented in Table 1. The pristine ZF material had surface area of  $68 \text{ m}^2/\text{g}$  which increased to  $81 \text{ m}^2/\text{g}$  after sulfatation.



Fig. 2. TEM micrographs of (a) zinc ferrite catalyst and (b) focussed morphology of particles of ZF. (c) Lattice view and (d) SAED pattern of ZF catalyst.

#### Table 1

Textural and compositional properties of ZF and SZF samples.

Catalyst	Surface area (m <sup>2</sup> /g)	S content (wt%)	Total acidity (mmol/g)	L/B ratio <sup>a</sup>
ZF-470	68	-	0.257	1.80
SZF-175	76	0.72	0.511	1.23
SZF-470	81	0.63	0.555	1.86

<sup>a</sup> Ratio of Lewis to Brönsted acid sites.



Fig. 3. FT-IR spectrum of ZF and SZF catalyst.

To probe the nature of acidic sites over the catalyst surface, pyridine sorption DRIFT-IR analysis was performed (Fig. 4). The assynthesized sample (ZF-175) showed peaks at 1600 and 1540 cm<sup>-1</sup> corresponding to Brönsted acid sites (surface –OH), and peak at 1440 cm<sup>-1</sup> corresponding to Lewis acid sites. A peak at 1490 cm<sup>-1</sup> corresponding to combined Lewis and Brönsted sites was also observed. The calcined sample (ZF-470) showed prominent peaks at 1445 cm<sup>-1</sup> indicating the presence of strong Lewis acid sites, wherein only a small hump at ~1600–1640 cm<sup>-1</sup> due to Brönsted sites was observed [25]. This indicates that as synthesized (ZF-175) sample has surface hydroxyl groups there by resulting in higher Brönsted acid sites whereas calcined samples, ZF-470 and SZF-470 were in pure spinel phase with prominent Lewis acidic sites [26].

To probe the distribution of Lewis and Brönsted acidic sites,  $NH_3$ -TPD profiles of ZF and SZF were collected (Fig. 5). The assynthesized sample (ZF-175) showed a prominent broad peak at 350 °C attributed to Brönsted acidic sites with medium strength, arising due to the surface –OH groups; however a small hump at 100 °C indicates the presence of Lewis acidic sites. On calcination to obtain spinel phase (ZF-470) there was decrease in the number of Brönsted acidic sites due to the loss of terminal –OH species



Fig. 4. DRIFT spectrum of pyridine adsorbed ZF and SZF catalyst.



Fig. 5. NH<sub>3</sub>-TPD profiles of ZF and SZF catalyst.

which may have been converted into oxide bridges as supported with FT-IR spectra [27]. The strong acid sites pertaining to sulfate binding especially around 440–460 °C corresponding to stable Lewis site were observed in SZF-470 [28]. A desorption peak at 700 °C observed in SZF-470 was supposed to be originated due to decomposition of sulfur at elevated temperatures [29].

To investigate the effect of sulfatation on the basic properties of ZF catalyst, TPD analysis using CO<sub>2</sub> as probe molecule was performed (Fig. 6). The weak and strong basic sites at respectively 100 °C and 350 °C observed for calcined sample (ZF-470) were supposed to be originated due to surface oxygen of the ZnFe<sub>2</sub>O<sub>4</sub> catalyst. On sulfatation, significant decrease in basic sites was observed with simultaneous increase in the acid sites for SZF-470 sample (Fig. 5). These results indicate that the base sites of the catalyst were converted into acid sites due to the inductive effect of S=O bond in the sulfated ZnFe<sub>2</sub>O<sub>4</sub> catalyst [5,26].

#### 3.2. Screening of catalyst for Prins condensation

The catalyst ZF-175, ZF-470 and SZF-470 were evaluated for Prins condensation reaction of  $\beta$ -pinene and paraformaldehyde for synthesis of nopol. The ZF-175 catalyst resulted in 30% conversion of  $\beta$ -pinene with 64% selectivity to nopol (Table 2, *entry 1*), wherein the ZF-470 catalyst gave 38%  $\beta$ -pinene conversion with 84% nopol selectivity (Table 2, *entry 2*). The low values of  $\beta$ -pinene conversion and nopol selectivity with ZF-175 could be attributed to excess



Fig. 6. CO<sub>2</sub>-TPD profiles of ZF and SZF catalyst.

Brönsted acid sites. While studying the effect of sulfatation, it was revealed that sulfatation of ZF catalyst enhanced the catalytic performance, thereby improving the  $\beta$ -pinene conversion up to 70% with 88% selectivity to nopol (Table 2, *entry 5*). The other products formed in addition to nopol include camphene, pinocarveol, pinocarvone, myrtenal, myrtenol, nopyl acetate and nopadiene as detected by GC–MS analysis of the reaction products. The mass data showed standard fragmentation pattern corresponding to nopol (*m*/*z*: 166, 122, 105, 91, 79, 41), pinocarveol (*m*/*z*: 152, 135, 119, 109, 92, 83, 55, 41), pinocarvone (*m*/*z*: 150, 122, 108, 91, 81, 69, 53), myrtenal (*m*/*z*: 150, 135, 107, 93, 91, 79, 41), myrtenol (*m*/*z*: 152, 119, 108, 93, 91, 79, 41), nopyl acetate (*m*/*z*: 148, 133, 105, 91, 79, 41).

#### 3.3. Solvent effect

To study the effect of solvent on catalytic activity of SZF, the Prins condensation reaction was conducted in different solvents using  $\beta$ -pinene to paraformaldehyde molar ratio 1:3 (Table 3). Very low conversion (9%) of  $\beta$ -pinene was observed in protic solvents such as methanol (Table 3, entry 1). These results are in agreement with previous reports [30], ascribed to weak interaction of protic solvents with reactant or poor solubility of paraformaldehyde in alcohols. In case of apolar-aprotic solvents such as hexane, ethyl acetate and toluene, increase in the  $\beta$ -pinene conversion as well as nopol selectivity was observed (Table 3, entries 2, 3, and 6). MEK and acetonitrile being dipolar solvents gave low conversion (7% in the case of MEK, whereas acetonitrile gave 40%) of  $\beta$ -pinene with good selectivity to nopol (Table 3, entries 4 and 5). The reasonable conversion in acetonitrile may be attributed to stabilization of polar carbocation by interaction of positively charged species with the nitrogen lone pair of electrons, thereby favoring the  $\beta$ pinene conversion. This assumption is supported with the fact that, under the same experimental conditions on increasing the acetonitrile amount, the  $\beta$ -pinene conversion drops, may be due to competition of acetonitrile with paraformaldehyde species for their interaction with Zn<sup>2+</sup> sites, thereby blocking the catalytically active sites leading to decrease in  $\beta$ -pinene conversion [31]. On the basis of observed catalytic activity toluene was identified as best solvent for maximum  $\beta$ -pinene conversion and nopol selectivity (Table 3, entry 6).

The amount of toluene was varied using 1:3 molar ratio of  $\beta$ pinene to paraformaldehyde at 95 °C. With substrate to solvent ratio of 1:6, 70%  $\beta$ -pinene conversion and 88% nopol selectivity was

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The catalytic activity of ferrite catalysts toward Prins condensation reaction.

Entry	Catalyst	Time (h)	β-P:PF <sup>a</sup> ratio	Temperature (°C)	Conversion <sup>b</sup> (%)	Selectivity (%)
1	ZF-175	12	1:3	95	30	64
2	ZF-470	12	1:3	95	38	84
3	SZF-470	12	1:2	95	44	86
4	SZF-470	12	1:4	95	68	88
5	SZF-470	12	1:3	95	70	88
6	SZF-470	12	1:3	65	25	83
7	SZF-470	12	1:3	80	55	84
8	SZF-470	12	1:3	110	72	57
9	SZF-470 <sup>c</sup>	12	1:3	95	56	88
10	SZF-470 <sup>d</sup>	12	1:3	95	72	87
11	SZF-470 <sup>e</sup>	12	1:3	95	63	42
Catalyst recyclin	ng experiments					
12	SZF-470 (Run 1)	12	1:3	95	70	88
13	SZF-470 (Run 2)	12	1:3	95	69	87
14	SZF-470 (Run 3)	12	1:3	95	67	86
15	SZF-470 (Run 4)	12	1:3	95	64	87

<sup>a</sup> β-Pinene to paraformaldehyde molar ratio.

<sup>b</sup> Reaction conditions: β-pinene (5 mmol); catalyst (0.14 g); Toluene (4 ml).

<sup>c</sup> Catalyst quantity: 0.12 g.

<sup>d</sup> Catalyst quantity: 0.16 g.

<sup>e</sup> Reaction was performed under oxygen purged atmosphere.

#### Table 3

Effect of solvent on Prins condensation reaction of  $\beta$ -pinene and paraformaldehyde.<sup>a</sup>

Entry	Solvent	Polarity	Conversion (%)	Selectivity (%)
1	Methanol	Protic	09	73
2	Hexane	Apolar aprotic	33	81
3	Ethyl acetate	Apolar aprotic	42	89
4	Methyl ethyl ketone	Dipolar aprotic	07	86
5	Acetonitrile	Dipolar aprotic	40	89
6	Toluene	Apolar aprotic	70	88
7	Di-chloroethane	Dipolar aprotic	62	84

<sup>a</sup> Reaction conditions: β-pinene (5 mmol); paraformaldehyde (15 mmol); catalyst (0.14 g); solvent (4 ml); reflux for 12 h.



**Fig. 7.** Effect of substrate:solvent ratio on  $\beta$ -pinene conversion (reaction conditions:  $\beta$ -pinene = 5 mmol; paraformaldehyde = 15 mmol; catalyst = 0.14 g; toluene = 4 ml; reaction temperature = 95 °C).

observed. On increasing the toluene amount there was slight drop in  $\beta$ -pinene conversion, while nopol selectivity remained almost unaffected (Fig. 7).

# 3.4. Effect of reaction temperature

The effect of reaction temperature on the Prins condensation reaction was studied in the temperature range of 65–110 °C, by keeping other experimental conditions same. Reactions performed

at 65, 80, 95 and 110 °C gave 25, 55, 70 and 72%  $\beta$ -pinene conversion with 83, 84, 88 and 57% nopol selectivity respectively (Table 2, *entries* 5–8). Low conversion up to 80 °C was probably due to insufficient *in situ* formation of formaldehyde from paraformaldehyde. As the temperature increased to 110 °C  $\beta$ -pinene conversion increased to 72% with slight drop in selectivity for nopol (57%). Therefore 95 °C has been identified as optimal reaction temperature for further studies.

#### 3.5. Effect of substrate:paraformaldehyde ratio

The Prins condensation reaction was investigated with variable molar ratio of  $\beta$ -pinene to paraformaldehyde (1:2 to 1:4) in toluene at 95 °C using SZF-470 as catalyst, wherein 1:3 molar ratio gave maximum conversion (Table 2). Only 44% conversion of  $\beta$ -pinene was observed with 1:2 molar ratio of  $\beta$ -pinene to paraformaldehyde (Table 2, *entry* 3), ascribed to less availability of formaldehyde, generated *in situ* from paraformaldehyde. Conversion increased to 70% when molar ratio of substrates increased to 1:3 (Table 2, *entry* 5), while further increase in paraformaldehyde amount did not show any notable increase in  $\beta$ -pinene conversion. From the observed results, it was clear that only  $\beta$ -pinene conversion was affected with substrate to paraformaldehyde molar ratio, while nopol selectivity remained almost unaffected.

#### 3.6. Effect of catalyst amount

The effect of catalyst concentration on the conversion and selectivity was studied by varying the catalyst amount from 0.12 to 0.16 g using 1:3 molar ratio of  $\beta$ -pinene and paraformaldehyde in toluene at 95 °C. The  $\beta$ -pinene conversion increased with an increase in

#### Table 4

Comparative studies on the catalytic activity of ZF-470 and SZF-470 for various organic transformations.

Reaction	Product	Reaction conditions	% Conversion (% selectivity)	
			ZF-470	SZF-470
Prins <sup>a</sup>	Nopol	95 °C, 12 h	38 (84)	70 (88)
Isomerization <sup>b</sup>	Campholenic aldehyde	100 °C, 9 h	50 (58)	93 (64)
Cross aldol <sup>c</sup>	Jasminaldehyde	150°C, 12 h	95 (68)	81 (55)
Claisen-Schmidt <sup>d</sup>	Flavanone/chalcone	150°C, 9h	81 (70/30)	93 (72/28)
Acetalization <sup>e</sup>	1,4-Dioxa-spiro[4,5]decane	60°C, 6h	79 (99)	96 (99)

<sup>a</sup> Solvent = toluene;  $\beta$ -pinene (5 mmol); paraformaldehyde (15 mmol); catalyst (0.14 g).

<sup>b</sup> Solvent = toluene;  $\alpha$ -pinene epoxide (5 mmol); catalyst (0.10 g).

<sup>c</sup> Solvent-free; 1-heptanal (5 mmol); benzaldehyde (25 mmol); catalyst (0.075 g).

<sup>d</sup> Solvent-free; 2'-hydroxy acetophenone (5 mmol); benzaldehyde (10 mmol); catalyst (0.1 g).

<sup>e</sup> Solvent-free; cyclohexanone (5 mmol); ethylene glycol (25 mmol); catalyst (0.1 g).



Fig. 8. Proposed reaction mechanism of Prins condensation reaction for nopol production over SZF-470 catalyst.

the catalyst loading (0.12 to 0.16 g) without affecting the nopol selectivity (Table 2, *entries 9 and 10*).

#### 3.7. Reusability studies

In order to investigate the recyclability of the catalyst, the Prins condensation reaction was performed at 95 °C, with  $\beta$ -pinene to paraformaldehyde molar ratio 1:3. The catalyst SZF-470 obtained after the first catalytic cycle was washed with warm acetone to remove the adhered organics and refluxed with H<sub>2</sub>O<sub>2</sub> at 80 °C for 3 h. Finally the catalyst was regenerated by heating at 200 °C for 2 h. The PXRD and elemental analysis of the regenerated catalyst showed no significant changes in the textural and compositional properties. It was successfully recycled up to four catalytic runs with slight loss in conversion and selectivity (Table 2, *entries 12–15*).

As SZF was found to be highly effective for Prins condensation reaction, it was further used as a catalyst for the protection of carbonyl compounds using ethylene glycol, isomerization of  $\alpha$ -pinene epoxide to campholenic aldehyde, cross aldol condensation of 1-heptanal and benzaldehyde to give jasminaldehyde and Claisen–Schmidt condensation reaction of benzaldehyde and acetophenone. All these reactions were performed in solvent-free condition, except for isomerization reaction. The conversion–selectivity data for the desired compounds of the above mentioned reactions is summarized in Table 4. The catalytic activity of the synthesized nanosized SZF was quite good towards these organic transformations. To investigate the effect of sulfatation, the reactions were also carried out using ZF catalyst (catalyst without sulfatation). Table 4 represents the comparison of catalytic activity of as synthesized and sulfated zinc ferrite; from the data it is evident that, sulfatation causes pronounce effect on catalytic activity of zinc ferrite samples, in terms of conversion and selectivity of the desired substrate.

# 4. Reaction mechanism for SZF catalyzed synthesis of nopol

It was previously reported that, presence of Lewis acid sites are favorable for nopol formation [31]. The proposed structure of the ZF (Fig. 3, structure A) shows coordinatively unsaturated Zn<sup>2+</sup> species over the catalyst surface. The generation of Lewis acidic sites over the catalyst surface could be attributed to the inductive effect of SO<sub>4</sub><sup>2–</sup> species through bridging oxygen atoms, thereby generating electron deficient Zn<sup>2+</sup> species. Paraformaldehyde interacts with these Zn<sup>2+</sup> species, to form carbocation via polarization of C=O linkage, thereby generating electrophillic center.  $\beta$ -Pinene then reacts with the cationic species, followed by allylic proton transfer thus completing the reaction cycle with nopol formation (Fig. 8). The above postulated mechanism could be correlated with the surface acid-base properties of the catalyst. As we increase the extent of sulfur loading over ZnFe<sub>2</sub>O<sub>4</sub> catalyst, increased inductive effect of the sulfate species account for enhanced Lewis acidity thereby increasing the  $\beta$ -pinene conversion. Formation of minor oxidation products of  $\beta$ -pinene like pinocarveol, pinocarvone, myrtenol and myrtenal, may be ascribed to interaction of  $\beta$ -pinene molecule with Fe<sup>2+</sup> sites, as these are known to be active sites for allylic oxidation of  $\beta$ -pinene. To investigate the oxidizing properties of the ZnFe<sub>2</sub>O<sub>4</sub> catalyst, the Prins condensation reaction of  $\beta$ -pinene with paraformaldehyde under oxygen flow was also carried out. As expected, we end up with very low selectivity to nopol due to increased formation of oxidation products like pinocarveol and pinocarvone. These results were in good agreement with those of the reported results of Menini et al. [32], where they had also observed the formation of allylic oxidation products of  $\beta$ -pinene in presence of dioxygen using various iron oxide catalysts.

# 5. Conclusion

Nanosized SZF catalyst was prepared through a simple and versatile synthetic procedure. The SZF shows good catalytic activity towards Prins condensation reaction of  $\beta$ -pinene and paraformaldehyde to produce nopol. The catalyst gave 70% conversion of  $\beta$ -pinene with 88% selectivity to nopol. The conversion and selectivity were related with reaction temperature, catalyst loading and molar ratios of  $\beta$ -pinene and paraformaldehyde. Moreover, the catalyst showed good catalytic activity for several acid catalyzed reactions involving small as well as bulky molecules in solvent-free conditions. The nanosized SZF can be recycled at least four times without significant loss of catalytic activity.

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#### References

- G. Rothenberg, Catalysis: Concepts and Green Applications, Wiley-VCH, Weinheim, 2008.
- [2] R.A. Sheldon, H. van Bekkum, Fine Chemicals Through Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2001.
- [3] V.S. Reddy, A. Radheshyam, R. Dwivedi, R.K. Gupta, V.R. Chumbale, R. Prasad, J. Chem. Technol. Biotechnol. 79 (2004) 1057–1064.
- [4] T. Mathew, N.R. Shiju, K. Sreekumar, B.S. Rao, C.S. Gopinath, J. Catal. 210 (2002) 405–417.
- [5] K. Arata, Adv. Catal. 37 (1990) 165-211.
- [6] C.G. Ramankutty, S. Sugunan, Appl. Catal. A: Gen. 218 (2001) 39-51.
- [7] M.K. Yadav, R.V. Jasra, Catal. Commun. 7 (2006) 889-895.
- [8] J.P. Bain, J. Am. Chem. Soc. 68 (1946) 638-641.
- [9] R.A. Sheldon, I. Arends, U. Hanefeld, Green Chemistry and Catalysis, Wiley-VCH, Weinheim, 2007.
- [10] A.L. Villa, P.E. Alarcon, Chem. Commun. 22 (2002) 2654-2655.
- [11] U.R. Pillai, E.S. Demessie, Chem. Commun. 7 (2004) 826-827.
- [12] A.L. Villa, P.E. Alarcon, C. Montes, Catal. Today 942 (2005) 107-108.
- [13] M. Selvaraj, Y. Choe, Appl. Catal. A: Gen. 373 (2010) 186–191.
- [14] E.A. Alarcon, L. Correa, C. Montes, A.L. Villa, Micropor. Mesopor. Mater. 136 (2010) 59–67.
- [15] E.A. Alarcon, A.L. Villa, C. Montes de Correa, Micropor. Mesopor. Mater. 122 (2009) 208–215.
- [16] S.V. Jadhav, K.M. Jinka, H.C. Bajaj, Appl. Catal. A: Gen. 390 (2010) 158-165.
- [17] K. Bauer, D. Garbe, H. Surburg, Common Fragrances and Flavour Materials, 2nd edition, VCH, New York, 1990.
- [18] N. Ravasio, F. Zaccheria, A. Gervasini, C. Messi, Catal. Commun. 9 (2008) 1125-1127.
- [19] N. Sudheesh, S.K. Sharma, R.S. Shukla, J. Mol. Catal. A: Chem. 321 (2010) 77–82.
  [20] S. Saravanamurugan, M. Palanichamy, B. Arabindoo, V. Murugesan, Catal. Commun. 6 (2005) 399–403.
- [21] H. Lee, J.C. Jung, I.K. Song, Catal. Lett. 133 (2009) 321–327.
- [22] C. Whiston, X-ray Methods by F.E. Prichard, Wiley, New York, 1991.
- [23] T. Yamaguchi, T. Jin, K. Tanabe, J. Phys. Chem. 90 (1986) 3148-3152.
- [24] G.D. Yadav, J.J. Nair, Micropor. Mesopor. Mater. 33 (1999) 1-48.
- [25] J.M. Yang, F.S. Yen, J. Alloys Compd. 450 (2008) 387-394.
- [26] X. Song, A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 329-412.
- [27] K. Meguro, K. Esumi, J. Adhes. Sci. Technol. 4 (1990) 393–410.
- [28] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, A. Marinas, A. Porras, F.J. Urbano, Appl. Catal. 184 (1999) 115–125.
- [29] W.H. Chen, H.H. Ko, A. Sakthivel, S.J. Huang, S.H. Liu, A.Y. Lo, T.C. Tsai, S.B. Liu, Catal. Today 116 (2006) 111-120.
- [30] C.M. Hansen, Hansen Solubility Parameters: A User's Handbook, 2nd edition, CRC Press, Taylor and Francis Group, Boca Raton, FL, USA, 2007.
- [31] M.V. Patil, M.K. Yadav, R.V. Jasra, J. Mol. Catal. A: Chem. 273 (2007) 39-47.
- [32] L. Menini, M.J. Da Silva, M.M.F. Lelis, J.D. Fabris, R.M. Lago, E.V. Gusevskaya, Appl. Catal. A: Gen. 269 (2004) 117-121.