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Novelties of combustion synthesized and functionalized solid superacid catalysts in selective isomerization of styrene oxide to 2-phenyl acetaldehyde

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ABSTRACT

Combustion synthesis leads to very interesting characteristics to inorganic oxides which could be further modified to render them catalytic properties. Several new approaches were studied to make a novel superacidic sulfated zirconia called fuel lean sulfated zirconia (FLSZ), by combustion synthesis. FLSZ was fully characterized and used in a reaction of industrial relevance. The isomerization of styrene oxide to 2-phenyl acetaldehyde was studied by using several solid acid catalysts. 2-Phenyl acetaldehyde finds applications in the synthesis of fine chemicals, intermediates, speciality chemicals, flavors and fragrances. Among various catalysts studied FLSZ was found to give the best activity and selectivity to 2-phenyl acetaldehyde at 100 °C using cyclohexane as a solvent. Process parameters were optimized by conducting a systematic investigation. The kinetics of the reaction was also studied. The catalyst is robust, recyclable and found to be highly active and selective. The overall process is 100% atom economical, green and clean.

1. Introduction

The design and application of new catalysts and catalytic systems are at the hub of environmental protection and economic benefit. Green Chemistry aims at developing more environmentally friendly routes for organic transformations by adopting new methodologies which are mainly based on atom economy, catalysis and renewable resources [1–3]. Solid acid catalysts are widely used for the development of green technology to replace the traditional polluting catalysts in organic process industries [1–5]. Zeolites [6], acid treated clays [7], supported heteropoly acids [8–14], modified heteropolyacids [15,16,13,17], sulfated zirconia [5,18–22], UDCaTs [23–25] and ion exchange resins [26–28] have been investigated by several researchers including our group for their applications in pharmaceutical, perfumery, agro-chemicals, dye-stuffs, intermediates and specialty chemical industries. Our laboratory has been engaged in novel applications and modeling of catalysis by sulfated zirconia [5,18–25]. However, catalyst synthesis with tailored properties has always been a daunting task.

Combustion synthesis leads to very interesting characteristics to inorganic oxides, which could be further modified to render them interesting catalytic properties. It is a self propagating high temperature synthesis and is an effective and low cost method for synthesis of materials [29,30]. In combustion synthesis, a thermally induced redox reaction takes place between an oxidant and a fuel [31]. In general, the metal nitrates acting as cation sources are used as oxidants, whereas organic compounds such as citric acid, urea and glycine are employed as fuels [32–34]. Glycine-nitrate system has been a very popular combustion method for the preparation of metal oxide powders [35–38]. The combustion characteristics are closely related to the selection of fuel. A good fuel should react non-violently and act as a complexant for metal cations [36]. Various metal oxides and mixed metal oxides are prepared by combustion synthesis method. They can be used as catalysts [39,40]. Application of acid treated ZrO_2 has been quite promising in catalysis and many other areas due to its versatile structural and surface chemical properties as well as good thermal stability [5,41–44]. It has been reported as a better catalyst and catalyst support [44,45]. The present study describes the synthesis of nanocrystalline zirconia using combustion method, which has been functionalized to get sulfated zirconia, and its bulk and surface characterization studied by employing various techniques [46,47]. By using this catalyst, more shape selectivity was achieved towards bulkier organic molecule synthesis [48]. Recently we synthesized novel sulfated zirconia through combustion synthesis [49,50].

Epoxides are one of the most useful and versatile substrates in organic synthesis due to their high reactivity and easy availability. Isomerization of styrene oxide over solid acid catalyst results in the formation of 2-phenyl acetaldehyde, which finds applications in the synthesis of fine chemicals, intermediates, speciality chemicals,

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Nomenclature

A	styrene oxide
B	2-phenyl acetaldehyde
C	byproduct, 1-phenylethyloxy-2-phenyl ethanol
C_A	concentration of A (mol/cm^3)
FLSZ	fuel lean sulfated zirconia
k_1	apparent rate constant at constant w, min^{-1}
k	first order rate constant, cm^3 min^{-1} g-cat^{-1}
w	catalyst loading (g/cm^3)
X_A	fractional conversion of styrene oxide

flavors and fragrances. It can also be selectively hydrogenated to 2-phenyl ethanol, which is a high value perfumery compound. One of the most frequently used atom economical reactions of epoxide is their rearrangement to carbonyl compounds. This is an efficient method for the regioselective rearrangement of epoxide to either aldehyde or ketones.

In the current work, the isomerization of styrene oxide to phenyl acetaldehyde was studied using a novel solid superacid sulfated zirconia which was prepared using combustion and functionalized to get maximum sulfur content in the solid. The method of preparation of solid superacid is also novel. The reaction is 100% atom economical, clean and green. A mechanistic model was developed and the kinetics of the reaction established.

2. Catalyst Synthesis and Characterization

2.1. Chemicals

Styrene oxide, K10 clay, and Amberlyst-15 were procured from Sigma–Aldrich, USA. Cyclohexane and zirconyl nitrate hexahydrate from Thomas Baker Chemicals, Mumbai, India. Chlorosulfonic acid, 1,2-dichloroethane, *n*-dodecane were procured from M/s S.D. Fine Chemicals Ltd., Mumbai, India. Indion-130 was obtained from Ion Exchange (India) Ltd., Mumbai, India. Amberlyst-15 was a commercial cation exchange resin. K-10 clay was purchased from Fluka, Germany. Heteropolyacids were procured from S.D. Fine Chemicals Pvt. Ltd., Mumbai, India. All other chemicals were analytical reagent (AR) grade, which were used as received without any further purification.

2.2. Catalyst preparation

20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs-DTP)/K-10 [16], sulfated zirconia and UDCaT-5 [23] were prepared by well developed procedures and characterized in our laboratory.

Fuel lean sulfated zirconia (FLSZ) was prepared by the following procedure. For synthesis of catalyst, glycine and zirconium nitrate hexahydrate were taken in 1:2 mole ratio. Fig. 1 depicts the procedure of combustion synthesis to get zirconium oxide developed in our laboratory [49]. Zirconium dioxide powder was then washed with ethylene dichloride and the floating particles were separated out by decantation. The material was acidified with 15 cm^3/g of 1 M chlorosulfonic acid in ethylene dichloride. Acid treatment was carried out under nitrogen gas to avoid moisture absorption on the material. The material was transferred to a preheated muffle furnace at 120 °C for 24 h to evaporate the solvent. Then temperature was raised to 550 °C by using a ramp rate of 4 °C min^{-1} and calcined. Calcination was carried out for 3 h to get the active solid catalyst FLSZ. It was a white crystalline powder.

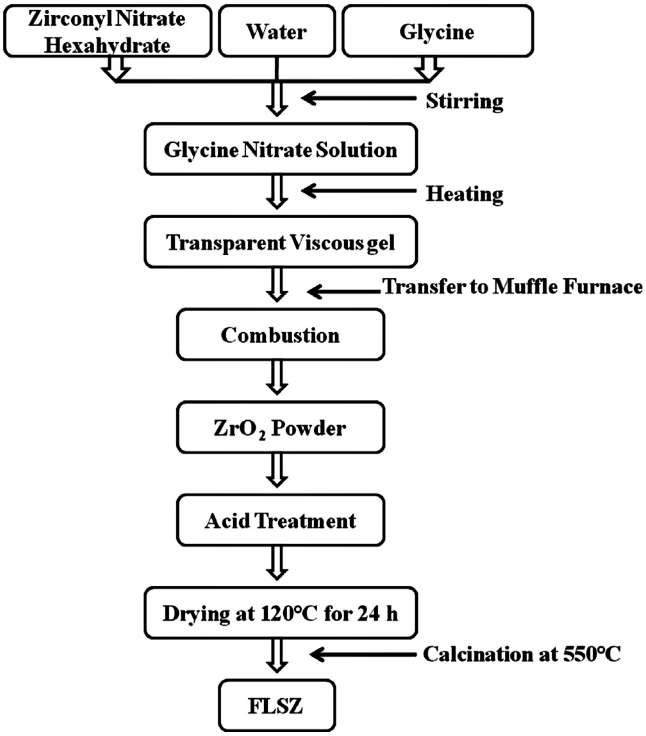


Fig. 1. Process flowsheet for catalyst synthesis.

2.3. Catalyst characterization

Crystallinity and textural patterns of the catalysts were predicted from XRD data, which were recorded using a Rigaku – miniflex powder diffractometer with Cu-Kα (1.54 Å) radiation. FTIR was recorded by using Perkin-Elmer – Spectrum BX instrument. Infrared spectra of the samples pressed in KBr pellets were obtained at a resolution of 2 cm^{-1} between 4000 cm^{-1} and 350 cm^{-1}. Ammonia TPD experiments were performed in a Micromeritics (Autochem-II chemisorptions analyzer) instrument equipped with TCD detector. Ammonia-TPD was used to determine the acid strength of FLSZ. Nitrogen adsorption–desorption for BET surface area, pore volume and pore size distribution were determined by BJH and multipoint BET method by using a Micromeritics ASAP-2010 instrument. SEM (scanning electron microscope) micrographs and energy dispersive X-ray spectroscopy (EDXS) data for the catalysts were obtained on a JEOL – JSM 6380 LA instrument.

3. Experimental

3.1. Experimental setup

All experiments were carried out in an autoclave (Amar Equipments, Mumbai) of 100 ml capacity. It was equipped with a 45° inclined-four-bladed-pitched turbine impeller, temperature controller (±1 °C), pressure indicator and speed regulator (±5 rpm). Predetermined quantities of reactants and the catalyst were charged into the autoclave under nitrogen gas. After charging the batch of reaction mass, nitrogen blanketing was done to avoid moisture. The reaction mixture was heated to the required temperature and an initial sample was taken. Samples were withdrawn at specific intervals of time. In this reaction autogenous pressure of about 0.8–1 atm was developed.

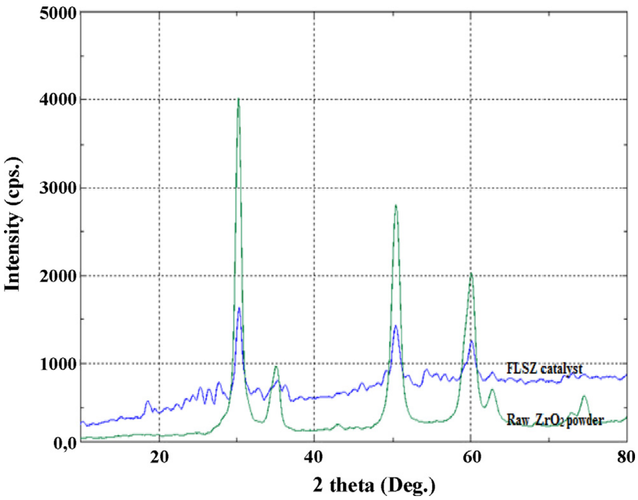


Fig. 2. XRD diffraction pattern for FLSZ catalyst and S-ZrO_2.

3.2. Reaction procedure

The catalysts used for the reaction were dried at 110 °C for 2 h before use. Styrene oxide (0.0527 mol), *n*-dodecane (0.0044 mol) as a internal standard and 0.21 g catalyst were added to the reactor containing cyclohexane as solvent. The total organic phase volume was made with cyclohexane to 30 cm^3. Addition of all materials was done under nitrogen gas to achieve inert atmosphere and the reactor was blanketed by nitrogen gas. The catalyst loading thus was 0.007 g/cm^3. Then it was heated to 100 °C. After attaining the desired temperature, the reaction mass was agitated with a mechanical stirrer at 1000 rpm and samples were withdrawn periodically.

3.3. Method of analysis

Analysis of the samples was performed by GC (Chemito model 1000, FID detector) using a BPX-50 capillary column (0.22 mm × 30 m). Nitrogen was used as a carrier gas. Samples were diluted four times by cyclohexane before analysis to get separation of reactant and products. The products were confirmed by IR spectroscopy (Perkin Elmer – Spectrum BX) and GC–MS (Perkin-Elmer, Clarius Model 500) by using BPX-1 capillary column (0.25 mm × 30 m) packed with methyl polysiloxane.

4. Results and discussion

4. Results and discussion

4.1. Catalyst characterization

4.1.1. X-ray diffraction (XRD)

The XRD study confirmed the presence of zirconia as tetragonal phase along with monoclinic phase (Fig. 2). The 2θ values close to 30, 50 and 60° show planes (1 1 1), (2 2 0), (3 1 1) corresponding to tetragonal phase while rest of the lower intense peaks denote the monoclinic phase present in the material [46]. Zirconia exhibits pure tetragonal phase at low sulfur content, whereas at higher sulfur content ($S > 4\%$), its crystallinity is strongly affected and a monoclinic phase is formed in addition to the tetragonal phase [49–51].

The XRD pattern of FLSZ does not contain sharp reflections like ZrO_2, which indicates that crystallinity of ZrO_2 decreases with increase in loading of sulfur. Crystal size of FLSZ was about 16 nm [23].

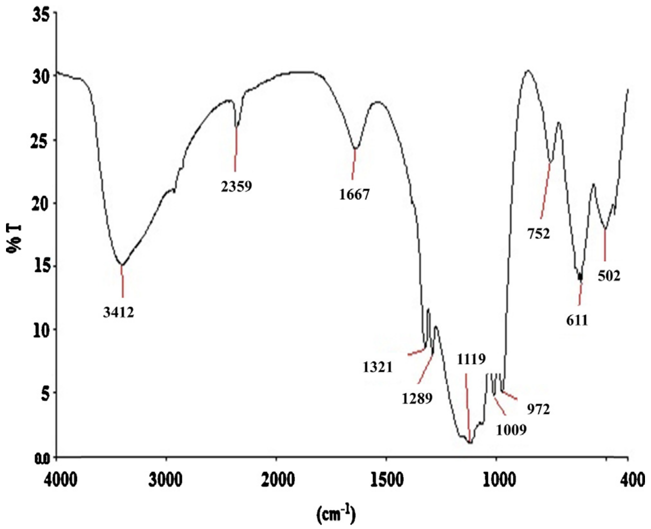


Fig. 3. IR spectra of FLSZ catalyst.

4.1.2. Fourier transform infrared spectroscopy (FTIR)

IR spectra indicated the presence of the bidentate chelating sulfate group coordinated to zirconia (Fig. 3). It also confirmed that the chlorosulfonic acid was decomposed during calcination at 550 °C, and sulfate ions were retained on the surface of FLSZ. The IR spectra of FLSZ shows a broad peak having shoulder peaks at 1321, 1289, 1119, 1009 and 972 cm^{-1}, which are typical of a chelating bidentate sulfate ion (SO_4^{-2}) coordinated to metal cation. The feature particularly at 752 cm^{-1} is due to Zr–O_2–Zr asymmetric and Zr–O stretching modes, which confirm the formation of ZrO_2 phases [42]. The IR bands between 450 and 800 cm^{-1} are characteristic of crystalline zirconia.

4.1.3. Temperature programmed desorption (NH_3-TPD)

Ammonia-TPD analysis showed the presence of maxima at 110 and 230 °C representing weak and strong acid sites, respectively (Fig. 4). In addition to weak and strong acid sites, very strong

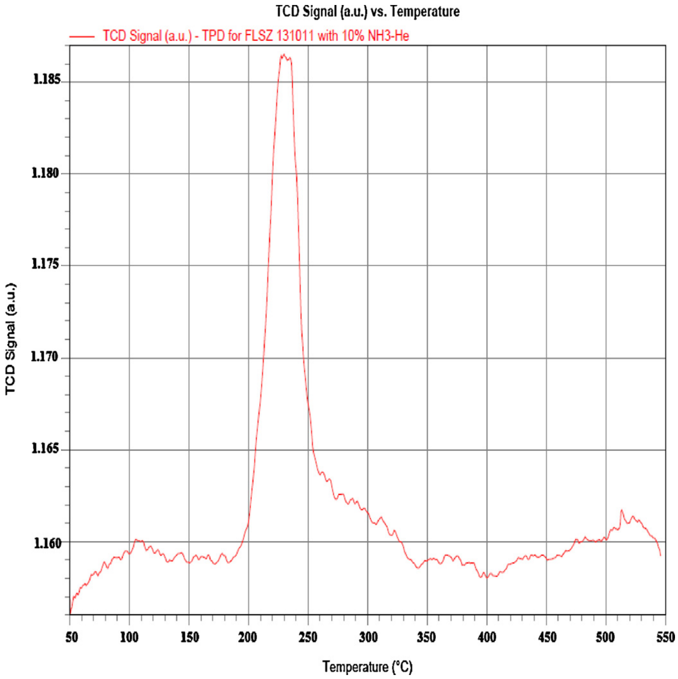


Fig. 4. Ammonia-TPD of FLSZ.

Table 1
Acidity of catalyst by ammonia–TPD.

Catalyst	FLSZ	S-ZrO_2
Acidity by NH_3-TPD (mmol g^{-1})	0.664	0.433

Table 3
Elemental analysis of catalyst by EDXS.

Element	Oxygen	Sulfur	Zirconia	Total
Mass (w/w, %)	48.47	26.51	25.02	100

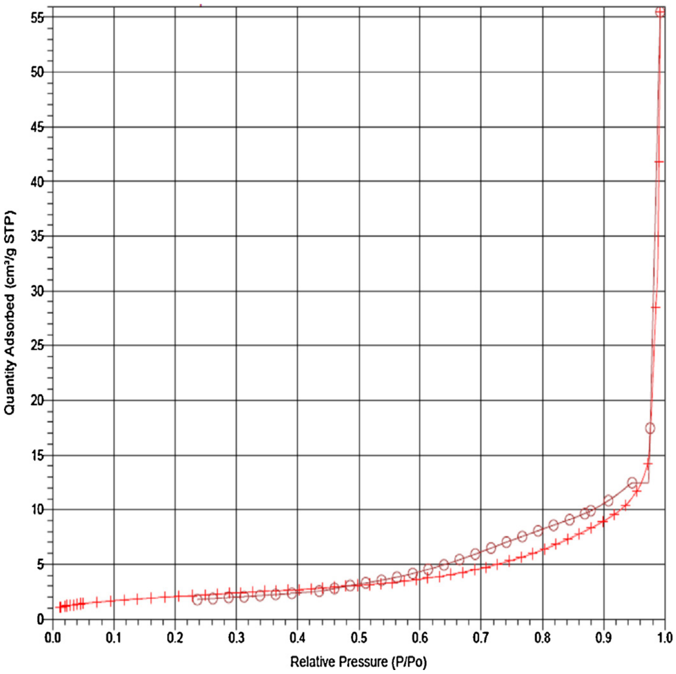


Fig. 5. N_2 adsorption desorption isotherm at temperature 77 K.

acid sites (525 °C) were also observed. Thus FLSZ contained the superacidic sites (Table 1) in comparison with sulfated zirconia.

4.1.4. BET surface area and pore size analysis

The surface area of ZrO_2 gradually increases at low sulfate contents but it decreases abruptly at the maximum sulfate content of due to the migration of sulfate ions from bulk phase to zirconia matrix (Fig. 5). Thus the amount of sulfur present on surface of the catalyst decreases its surface area (Table 2) [49,50]. FLSZ has some unburnt carbon present before the acid treatment. When the oxide is calcined at 550 °C in presence of air after acid treatment, this carbon is burnt and escapes from the inner crust of oxide in the form of CO_2. It results into violent changes in the surface of oxide, generating large numbers of pores and surface defects [49,50]. Therefore, FLSZ is superacidic in nature due to the presence of very high sulfur content present on the zirconia matrix with preservation of the tetragonal phase of zirconia.

4.2. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS)

SEM images of FLSZ clearly indicate the formation of tetragonal and monoclinic crystals of zirconia (Fig. 6a and b). EDXS was done to confirm complete decomposition of chlorosulfonic acid in synthesized catalyst and to find out the elemental composition of O, S and Zr (Table 3). Chlorosulfonic acid may get decomposed to sulfuryl chloride, pyrosulfuryl dichloride, sulfuric acid, sulfur dioxide, chlorine and water. The result showed complete absence of chloride species and that sulfate was retained on the surface of FLSZ, which is highest as compared to that reported so far in the literature.

4.3. Catalytic activity

Scheme 1 represents the isomerization reaction. whereas Scheme 2 presents the catalytic cycle for isomerization of styrene oxide to 2-phenyl acetaldehyde over FLSZ catalyst. There is an initial adsorption of styrene oxide on strong acidic surface (electrophilic activated sites) of the catalyst. This leads to cleavage of bond between C_2 and O of epoxide ring. Then there is a simultaneous migration of hydride from C_3 to C_2 (1, 2 hydride shift, i.e. concerted mechanism). Next step is the rearrangement of molecule on the catalyst surface to give 2-phenyl acetaldehyde. The final step is the desorption of the product from catalyst surface to regenerate the site. The whole reaction is rearrangement of epoxide to aldehyde involving 1, 2 hydride shift.

4.4. Effect of solvent

Different solvents were used to carry out the isomerization including toluene, acetonitrile, cyclohexane, amines and alcohols. The isomerization reaction in toluene, alcohols and amines as solvent gives ring alkylation, substituted hydroxyl ether and amino alcohols, respectively. Because of availability of strong Lewis acid sites on FLSZ catalyst, acetonitrile also gives 2-oxazolidine as a heterocyclic product to a minor extent. Beside these solvents, 2-phenyl acetaldehyde, the product itself, was also used as a solvent; however, it led to byproducts such as condensation product with styrene oxide, self condensation and polymerization. Formation of condensation products was confirmed by LC–MS and GC–MS. Since styrene oxide is highly reactive it reacts with nucleophilic solvents and gives various products. It is also important to use dilute styrene oxide in an inert solvent. Thus, cyclohexane was used as a solvent which did not show byproducts.

4.5. Efficacies of various catalysts

Various catalysts such as Indion-130, Amberlyst-15 (both ion exchange resins having all Bronsted sites), 20% (w/w) Cs-DTP/K10, UDCaT-5, cs-ZrO_2 were used to compare their efficacies in this reaction (Fig. 7). cs-ZrO_2 was the combustion synthesized (cs) zirconia without any acid treatment. Reactions were also carried out in absence of catalyst. A 0.007 g/cm^3 loading of catalyst based on the organic volume of the reaction mixture was employed at 100 °C at speed of agitation 1000 rpm. Catalyst screening of the reaction was carried out in 1 h. Among all catalysts FLSZ gives the best conversion and selectivity. The order was as follows:

$$\text{FLSZ (max)} > 20\%\ \text{Cs-DTP/K10} > \text{UDCaT-5} > \text{Indion-130} >$$
$$\text{Amberlyst-15} > \text{cs-ZrO}_2 > \text{No catalyst (min)}$$

Table 2
Textural characteristics of FLSZ.

Material	BET surface area (m^2/g)	Average pore diameter (Å)	Pore volume (BJH) (cm^3/g)
S-ZrO_2	103	41	0.11
cs-ZrO_2 (before acid treatment)	17	85	0.14
FLSZ (after acid treatment)	7.66	422	0.08

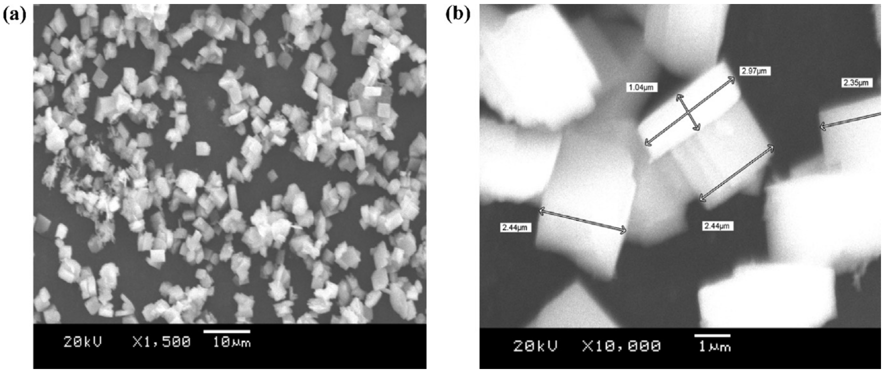
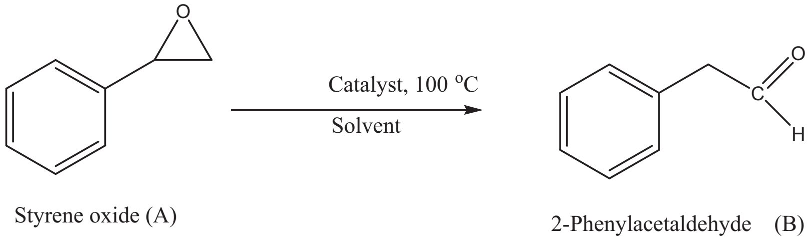


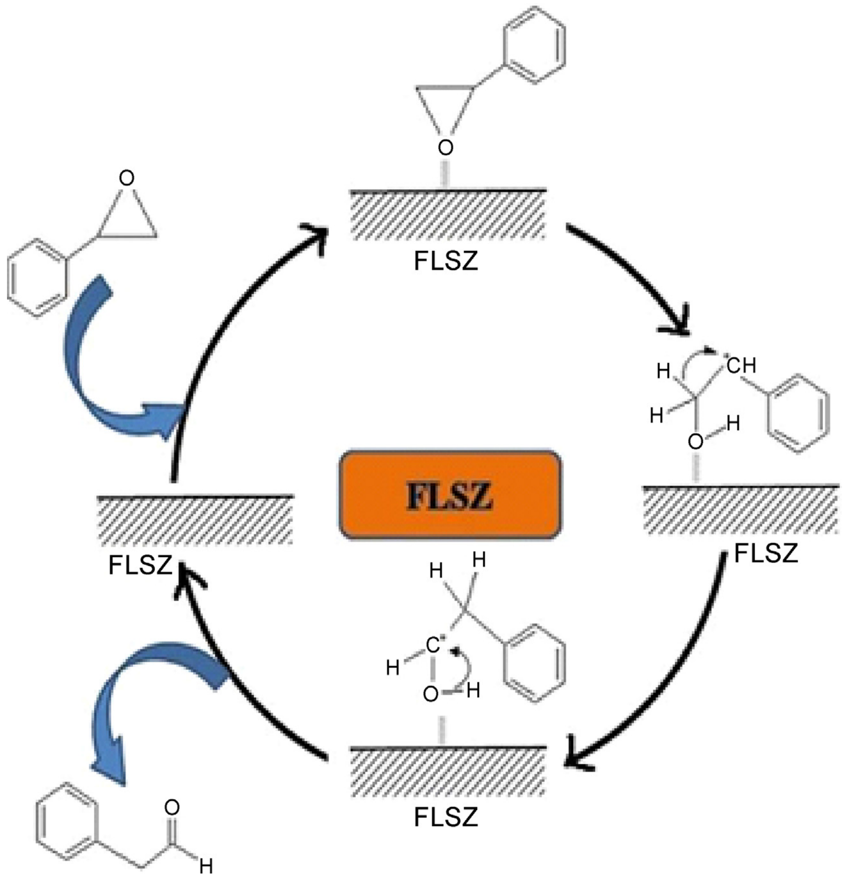
Fig. 6. (a) SEM images of FLSZ catalyst at 1.5k× magnification; acceleration voltage: 20 kV. (b) SEM images of FLSZ catalyst at 10k× magnification; acceleration voltage: 20 kV.



Scheme 1.

The first five catalysts mentioned above gave high conversion with different selectivities.

In the absence of catalyst very low conversion was observed. In the absence of catalyst, there is thermally induced isomerization of styrene oxide to a small extent. cs-ZrO_2 has some basic sites and can isomerize styrene oxide but the conversion was marginal. Bronsted acids give better conversions as has been observed with ion exchange resins. Indion-130 and Amberlyst-15 are similar cation



Scheme 2. Catalytic cycle for isomerization of styrene oxide to 2- phenyl acetaldehyde over FLSZ.

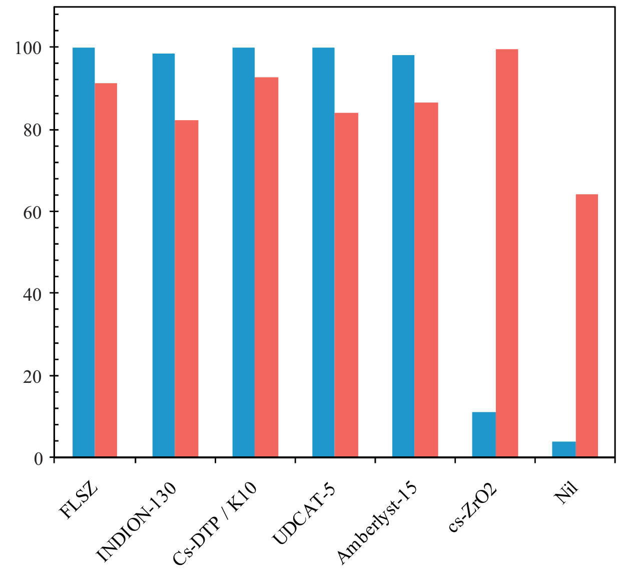


Fig. 7. Efficacies of various catalysts in isomerization of styrene oxide. Reaction conditions: Temperature: 100 °C; catalyst loading: 0.007 g/cm^3; speed of agitation: 1000 rpm, reaction volume 30 cm^3 and reaction time: 60 min. (🟦) Conversion (%); (🟥) selectivity (%).

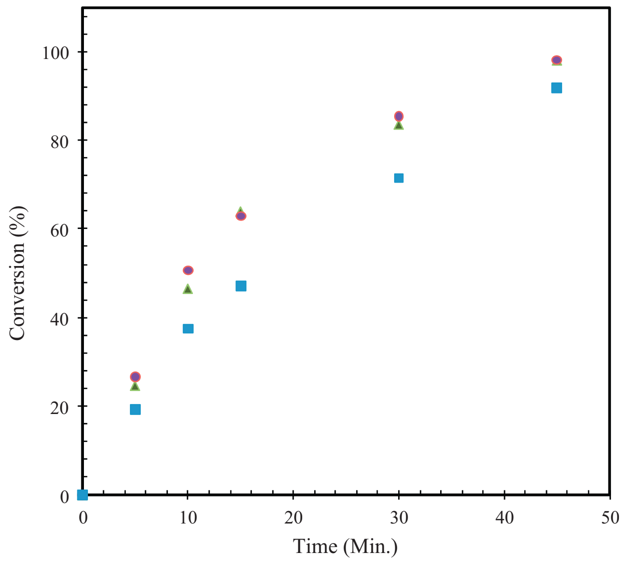


Fig. 8. Effect of speed of agitation on conversion of styrene oxide. Reaction conditions: Temperature: 100 °C; catalyst loading: 0.007 g/cm^3; catalyst: FLSZ, reaction volume 30 cm^3. (●) 1200 rpm; (▲) 1000 rpm; (🟦) 800 rpm.

exchange resins manufactured by different companies. There was only marginal increase in conversion with Amberlyst-15 giving a little higher selectivity than Indion-15. Although 20% Cs-DTP/K10 showed good conversion towards desired product, it gave polymerization product which was not detectable on GC. Polymerized product was confirmed by LC–MS. With FLSZ, the conversion was 100% with 92% selectivity in 1 h. The concentration profiles showed that there was an onset of self-condensation towards the completion of reaction. Hence FLSZ was the catalyst of choice for further studies.

4.6. *Effect of speed of agitation*

To assess the role of external mass transfer on the reaction rate, the effect of the speed of agitation was studied from 800 to 1200 rpm. It was observed that the conversion of styrene oxide practically remained the same in all the cases (Fig. 8). Also there was no effect on the selectivity. Thus, external mass transfer effects did not influence the reaction. Hence, all further reactions were carried out at 1000 rpm.

4.7. *Effect of catalyst loading*

In the absence of external mass transfer resistance and intraparticle diffusion limitation, the rate of reaction is directly proportional to catalyst loading based on the entire liquid phase volume. The catalyst loading was varied over a range of 0.005–0.009 g/cm^3 on the basis of total volume of the reaction mixture. Fig. 9 shows the effect of catalyst loading on conversion. The conversion increased with increase in catalyst loading, which is due to the proportional increase in the number of active sites. Catalyst loading of 0.007 g/cm^3 was found to be optimum. Hence all further experiments were carried out at this catalyst loading.

4.8. *Effect of temperature*

The effect of temperature was studied in the range of 80–100 °C (Fig. 10). The conversion was found to increase substantially with increasing temperature, which suggested that the reaction was intrinsically kinetically controlled and the activation energy values should be determined to ascertain this observation. Reaction temperature above 100 °C gives polymerized product and this temperature was selected for further study.

4.9. *Catalyst reusability studies*

The reusability of the catalyst was studied by refluxing the used catalyst in cyclohexane for 15 min in order to remove any adsorbed material from within the pores. It was separated and dried at 110 °C for 15 min. This material was then calcined at 550 °C for 3 h after every use. This reactivation was done to remove the molecules adsorbed on active sites from the catalyst surface. There was no loss of activity. Recyclability of catalyst was studied for three cycles (Fig. 11). About 90–95% catalyst was recovered at the end of the reaction. Out of the total recovered catalyst from previous batch, 75% catalyst used for next reaction with 25% fresh catalyst so as

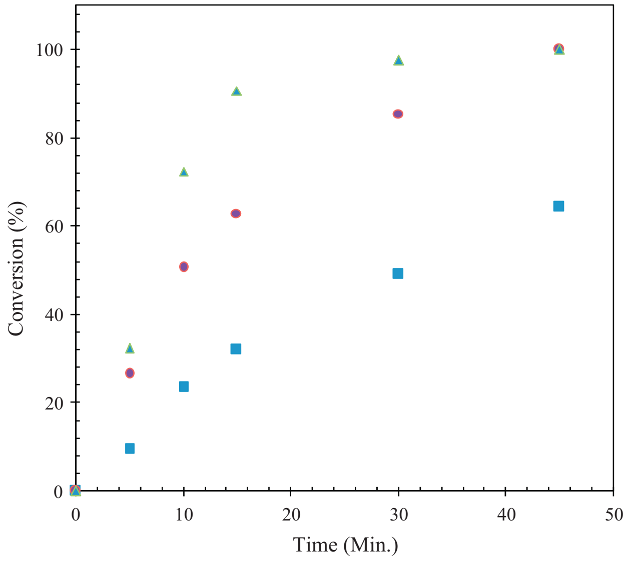


Fig. 9. Effect of catalyst loading on conversion of styrene oxide. Reaction conditions: Temperature: 100 °C; speed of agitation: 1000 rpm, catalyst: FLSZ; reaction volume 30 cm^3. (▲) 0.009 g/cm^3; (●) 0.007 g/cm^3; (🟦) 0.005 g/cm^3.

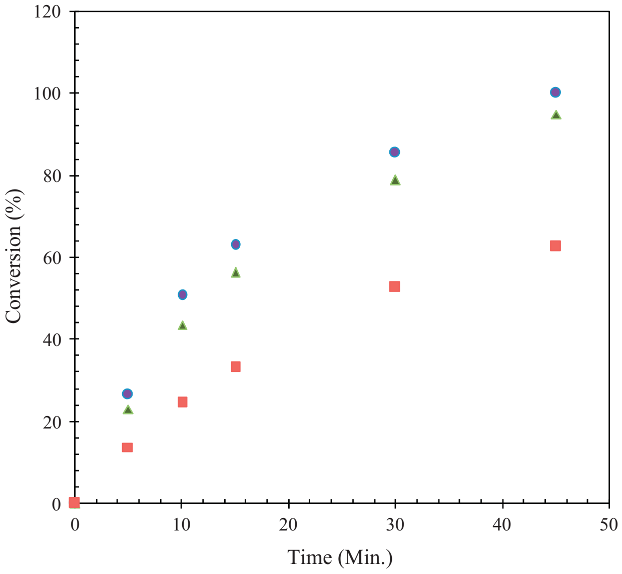


Fig. 10. Effect of temperature on conversion of styrene oxide. Reaction conditions: Speed of agitation: 1000 rpm, catalyst: FLSZ; catalyst loading: 0.007 g/cm^3; reaction volume 30 cm^3. (●) 100 °C; (▲) 90 °C; (🟥) 80 °C.

to make desired quantity of standard batch. The catalyst could be reused without any significant decrease in activity and selectivity, for three cycles after fresh use. Thus, FLSZ was proved to be highly versatile catalyst for isomerization reaction.

5. Development of mathematical model

The above results were used to build a kinetic model. The effect of change in catalyst loading shows that increasing the number of active sites increases the conversion of styrene oxide. Thus the LHHW type model was used to fit the reaction data. All sites are of the same type. There was 100% conversion with 92% selectivity with to 2-phenyl acetaldehyde (B) and 8% to 1-phenylethyloxy-2-phenyl ethanol (C) by the reaction of 2-phenyl acetaldehyde with styrene oxide. It was observed that the adsorption constants for all species were small and thus it leads to a power law model. The development of such a model is straight forward and is omitted. The overall rate of reaction of styrene oxide (A) is given by the following equation:

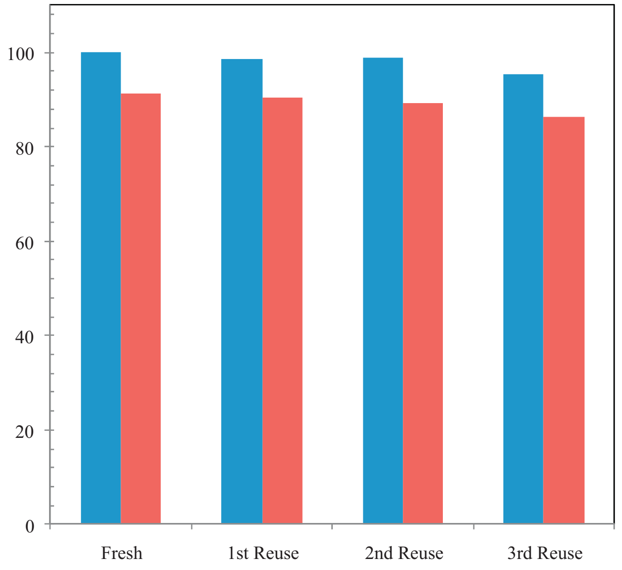


Fig. 11. Effect of catalyst reusability on conversion of styrene oxide. Reaction conditions: Temperature: 100 °C; speed of agitation: 1000 rpm, catalyst: FLSZ; catalyst loading: 0.007 g/cm^3; reaction volume 30 cm^3. (🟦) Conversion (%), (🟥) selectivity (%).

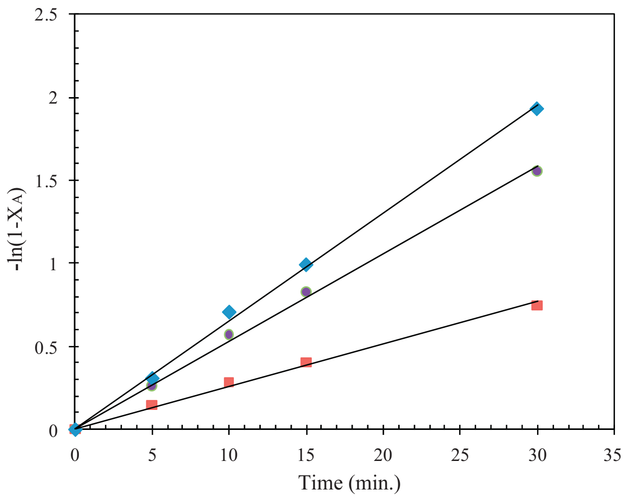


Fig. 12. Kinetic plots for various temperature. Reaction conditions: Catalyst loading: 0.007 g/cm^3; speed of agitation: 1000 rpm; catalyst: FLSZ; reaction volume 30 cm^3. (🟦) 100 °C; (●) 90 °C; (🟥) 80 °C.

$$-\frac{dC_A}{dt} = kwC_A \tag{1}$$

In terms of fractional conversion X_A, the above equation leads to the following:

$$\frac{dX_A}{dt} = kw(1 - X_A) \tag{2}$$

which upon integration gives

$$-\ln\,[1 - X_A] = kwt = k_1 t \tag{3}$$

where w is catalyst loading, k is the first order rate constant.

The values of rate constants at different temperature were calculated by plotting the $\ln[1 - X_A]$ against time (Fig. 12). The values of k_1 were also found at the different temperatures at the same w and the Arrhenius plot was made (Fig. 13), from which the activation energy was calculated as 12.26 kcal mol^{-1}. The high value of

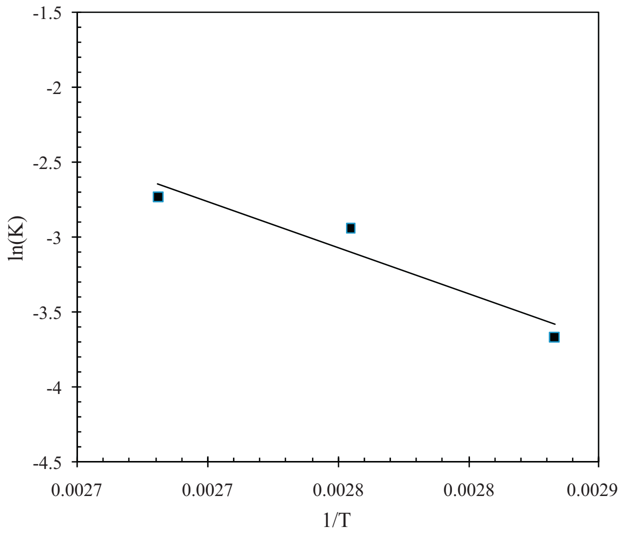


Fig. 13. Arrhenious plot for isomerization of styrene oxide. Catalyst loading: 0.007 g/cm^3; speed of agitation: 1000 rpm; catalyst: FLSZ; reaction volume 30 cm^3.

activation energy also supported the fact that the overall rate of reaction is not influenced by either external mass transfer or intraparticle diffusion resistance and it is intrinsically kinetically controlled.

6. Conclusion

The isomerization of styrene oxide was studied using a novel combustion synthesized superacidic catalyst FLSZ. The effects of various parameters on the reaction rate were studied. The optimum conditions were: concentration of styrene oxide: 0.0527 mol, catalyst loading of 0.007 g/cm^3 at 100 °C and speed of agitation 1000 rpm in cyclohexane solvent. Process parameters were optimized by conducting a systematic investigation. The kinetics of the reaction was also studied. The catalyst is robust, recyclable and found to be highly active and selective in comparison with others. The catalyst was found to be very effective and can be recycled for number of reactions without loss of activity and selectivity. The whole process is clean and green.

Acknowledgments

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