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Epoxidation of soybean oil by *insitu* formation of peracid in the presence of zeolites

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The catalytic epoxidation of soybean oil with hydrogen peroxide as oxidant has been accomplished using HZSM-5-, HY- and Hß- zeolite catalysts. The prepared catalysts are characterized by XRD, FTIR, and BET surface area. The catalytic epoxidation of soybean oil is studied as a function of time. The results show that all three catalysts exhibit higher conversion and selectivity of epoxidized soybean oil. Optimized protocol provides 85 %, 83 % and 70.55 %, conversion, selectivity and yield, respectively with HZSM-5 catalyst. The reaction occurs inside the pores of the zeolite framework via *insitu* formation of performic acid which further catalyzed by acid sites.

Keywords: Epoxidation, Heterogeneous catalysts, Soybean oil, Zeolite

Vegetable oils (VOs) are considered as biodegradable, non toxic and non corrosive renewable materials use for production of various chemicals and new materials. Phthalates have been used in polyvinyl chloride (PVC) industry as plasticizers for many years. But due to associated environmental problems, it is essential to find an alternative for them[1,2]. Among the various reactions such as oxidation, epoxidation, halogenation, hydroxylation, carboxylation, and hydrogenation; epoxidation of VOs has gained significant attention owing to high reactivity of produced epoxy group[1]**.**

According to the United States Department of Agriculture (European Commission, 2017) data, worldwide production of different oilseeds enhanced to 450 million tonnes in 2016 from 300 million tonnes in 2012, among them soybean production was highest and its represent more than 50% of total oil production[3]. Epoxidized soyabean oil (ESBO) is consider as important product obtained through epoxidation reaction of soybean oil (SO) and can be used as replacements of phthalates which have adverse effect on human health i.e. reproductive, developmental toxicities, allergic diseases or pose a carcinogenic threat etc[4-6]. Apart of these, it can also be used to produce polymers such as polyesters and polyurethane and a variety of chemicals like alkanolamines, polyoils etc[7]. Its worldwide and European production accounted to 200 ktons/year and 9 ktons/year in the 2011, respectively[8].

Epoxidation of vegetable oils (EVOs) carried out in homogeneous phase by the Prilezhaev reaction in the industry[9-11]. In the reaction, peracid is *insitu* generated by the reaction between organic acids mostly formic acid and acetic acid with mineral acids in aqueous phase. There are several problems associated with this process: (i) use of acids caused corrosion and pollution related issues associated with them, (ii) low selectivity of epoxide due to *insitu* formation of peracids occurred in aqueous phase that difficult to diffuse in VOs (organic phase), and (iii) mineral acid and regenerated acid made reaction media more acidic which prone to openized epoxide ring[12,13]. Hence, to circumvent these problems, various acidic ion exchange resins, polyoxometalates and heterogeneous catalysts were widely studied as summarized by Jiang *et al*[1]. Among them, zeolite was found most suitable system that of ionic resin and polyoxometalates as advocated by Turco *et al.*[14]. In zeolites, *insitu* formation of peracids probably happened inside the pore of zeolites, because of small size of reactants (organic acids and water) easily facilitated reactions inside the pore of zeolites. The formed peracids diffused directly organic phase (vegetable oil) which could be enhanced the selectivity and nullified ring opening of epoxide[1,14]. A very few examples are reported in literature for EVOs *via insitu* formation of peracids in the presence of zeolites and other solid inorganic materials. For instance, HY – zeolite exhibited higher conversion and yield in epoxidation of soyabean oil (ESBO)[14], Sienkiewicz and Czub reported ESBO in the presence of zeolite-Y and obtained 44 % conversion and low epoxy selectivity[15] and Yunus *et al*. reported TiO_2 and ZSM-5 for epoxidation of palm oil (EPO) and concluded that ZSM-5 exhibited higher relative conversion to oxirane as compared to TiO_2 at higher temperature[16]. Various heterogeneous catalyst i.e silicalite-1 (TS-1)[4], amorphous Ti/SiO_2[13], Nb_2O_5–SiO_2[17], and Ti-HMS and Mn-HMS[18] have explored for this reaction. However, less conversion, low selectivity, higher reaction time, reusability etc. are major concerns associated with them. Metal complexes such as zirconium poly (styrene-phenylvunyl-phosphonate)-phosphate (ZPS-PVPA)-SO_3H[19], phosphotungstic@halloysite nano tube[20], TS-1 and Cd@TS-1[21] have also been reported for ESBO. Whereas, Nb(V) over mesoporous molecular sieves[22] and Ti(IV)@silica[23] were used for fatty acid methyl esters (FAMEs) epoxidation and rapeseed oil, and epoxidation of mixture of unsaturated FAMEs obtained from vegetable source, respectively.

Zeolites are microporous crystalline material known of its shape selectivity and are available in various types, shapes and sizes and widely used as important heterogeneous catalysts in petrochemical, oil-refining industries, as ion exchangers, detergents, and adsorbents in various chemical industries, and in production of important chemicals. They are also known for their low production costs, unique shape selective properties, and hydro-thermal stability[24,25]. In this work, HZSM-5-, HY- and Hß- zeolite are reported as efficient heterogeneous catalyst for epoxidation of soybean oil by *insitu* formation of peracids.

Experimental Section

Materials and catalyst preparation

The soybean oil was procured from local food-store having an Iodine Number (I.N.) in 120 - 128 (g_{I2}/100 g_{oil}) range. Hydrogen peroxide (30 % w/v), formic acid (85 % by wt) and the other organic compounds and chemicals were procured from Finar chemicals and used as received, without any pre-treatment. Zeolites used in present work were obtained from Sud-chemie, Vadodara.

Pre synthesized zeolites are converted into Na-form by removing the occluded organic templates in flowing air for 6 - 8 h at 540°C. Later on, exchange of Na-form zeolite with 10 % NH_4NO_3 (ammonium nitrate, 15 mL) per gm of a catalyst resulted into NH^{4+} form of zeolite. This exchange process was performed under total reflux for 3 times for 4 h each followed by washed with distilled water. Later on, NH^{4+} form of zeolite was converted to H^+ form of zeolite *via* calcinations at 540 °C[26].

Catalyst characterization

The phase composition of catalysts was examined on a Bruker-D8 Discover X-ray diffraction (XRD) using CuKα radiation (λ = 1.542 Å) in the 10 - 90° range of 2θ (with 0.02°2θ/s scan rate) at 40 kV and 30 mA. The catalysts framework was obtained by Fourier transform infrared (FTIR) spectra, using a Bruker Alpha Eco-ATR spectrometer in a range of 4000 - 500 cm^{-1} with a resolution of 4 cm^{-1} and 24 scans. The surface area was calculated using the Brunauer–Emmett–Teller (BET) technique.

Epoxidation reaction

Experimental setup and procedure

Three neck 250 mL round bottom flask (RBF) was used to carried out soybean oil epoxidation reaction which is furnished with a thermometer, condenser and mechanical stirrer. The reaction mixture was heated at 70°C and kept constant during reaction. (Figure S1, supportive information)

Experimental procedure

In experiment, 3 g of zeolites and 50 g of soyabean oil (about 0.2510 moles of double bonds) mixed in the reactor. Reaction mixture was stirred and heated at 70 °C. A mixture of 18.36 g of H_2O_2 and 2.68 g of formic acid subsequently added to the reaction mixture at continuous flow rate of 0.18 cm^3/min. The whole reaction mixture stirred at 70°C for 4 h of reaction time.

During reaction, at different time intervals, samples of reaction mixture were obtained from the reactor. Later on, the separated aqueous phase treated with 5 wt % $NaHCO_3$ solution to neutralize acidity. Then, dried with anhydrous $MgSO_4$ and analyzed to determine the Iodine Number (I.N.) and Oxirane Number (O.N.).

Analytical method

The double bond conversion, yield to epoxide and selectivity with epoxidation reaction time, were determined by evaluating both I.N. (I_2 g/100 g of oil) and O.N. (epoxy oxygen g/100 g of oil). The I.N. and O.N. were calculated by Wijs method[17] and potentiometric method[14], respectively. The double bond conversion, yield to epoxide and selectivity were calculated by following equations.

$$Double\ bond\ conversion\ (\%) = \frac{(\boldsymbol{I.N.})_i - (\boldsymbol{I.N.})_f}{(\boldsymbol{I.N.})_i} * 100 \qquad \ldots(1)$$

where, I.N. = iodine number

$$Yield\ (\%) = \frac{(O.N.)_f * MW_{I2}}{(I.N.)_i * MW_{oxygen}} * 100 \qquad \ldots(2)$$

where, O.N. = oxirane number

MW_{I2} = molecular weight of iodine, MW_{oxygen} = molecular weight of oxygen

$$selectivity\ (\%) = \frac{Yield\ to\ epoxide}{Double\ bonds\ conversion} * 100 \qquad \ldots(3)$$

The subsctript i and f represent initial and final value, respectively.

Results and Discussion

XRD patterns of zeolite

XRD patterns of Hß, HY and HZSM-5 are shown in Fig 1. The diffraction peaks observed at 2θ = 13.96°, 23.98°, 24.57°, and 45.44° confirmed the crystalline structure of HZSM-5. The obtained diffractogram is similar to earlier reported by literature[27-29]. The characteristic peaks at HY at 2θ of 15.8° and 23.1° confirmed the crystalline structure of HY[29-31]. XRD patterns of Hβ catalysts shows similar pattern to that of the parent Hβ as indicated by the diffraction angle at 2θ = 16.5°, 22.5°, 25.3°, 26.9° and 29.5°[29,32-33].

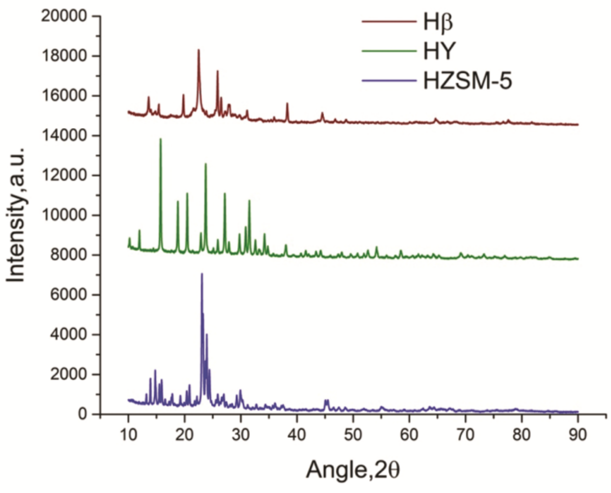

Fig 1 — XRD pattern of HZSM-5, HY and Hß

Fourier transform infra red of zeolite

Fourier transform infra red (FTIR) spectrum of HZSM-5, HY and Hß in the range of 4000-500 cm^{-1} are demonstrate in Fig. 2. The absorption band observed at 540 cm^{-1} belonged to double 5-member ring tetrahedral vibration for HZSM-5[26]. The band observed at 795 cm^{-1} and 1075 cm^{-1} were assigned to symmetric and asymmetric stretching vibrations, respectively[34] While, IR bands at 1625 cm^{-1} assigned to H-OH vibrations of adsorbed water molecules. This suggests the existence of water molecule in the catalysts[26,34-36].

Catalytic activity of HZSM-5, HY and Hß

The catalytic activities of HZSM-5, HY and Hß catalysts were tested for epoxidation reaction of soybean oil using H_2O_2 and HCOOH at different time on stream. As seen in Fig. 3, bond conversion was

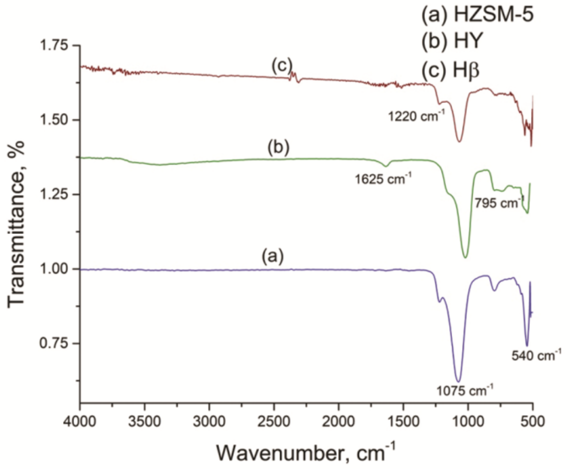

Fig. 2 — FTIR of HZSM-5, HY and Hß

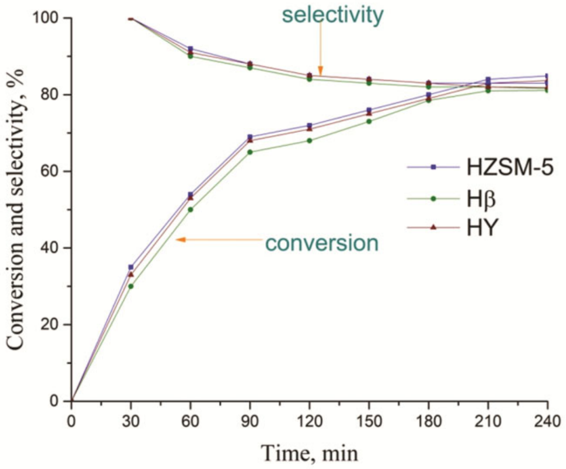

Fig. 3 — Double bonds conversion and selectivity vs. reaction time; Reaction conditions: oil – 50 g; HCOOH - 2.68 g; H_2O_2 - 18.36 g; catalyst - 3 g; temp – 70°C; rpm- 550

increased with reaction time. Initially, it was around 35, 30 and 33 % at 30 min for HZSM-5, HY and Hß, respectively. This was increased to 80, 77, and 79 % for HZSM-5, HY and Hß, respectively at 240 min. The selectivity decreased initially and eventually it remains constant around 83 % for HZSM-5 and about for 80 % for both HY and Hß.

The conversion was about (77 – 80 %) with all three catalysts suspected that the catalysts might be deactivated after 4 h time on stream. Further to check whether catalyst was deactivated only after 4 h, the same catalysts were reused for several times (5 times) and the results showed that bond conversion augmented to 85, 81 and 83 % for HZSM-5, HY and Hß, respectively, whereas remains constant for all three catalysts. In general, acidic strength of zeolite crystal structure as follows: HY < Hβ < HZSM-5 [24,37]. In this case, HZSM-5 displayed higher conversion as compared HY and Hß which may be due to its higher acidic strength. The calculation of oxirane number, iodine number, and yield % can be seen in table S1 (supportive information).

This revealed that the disappearance of reactants (H_2O_2 or HCOOOH) halt the reactions not the deactivation of catalysts. The enhanced catalytic activity can be due to slower decomposition of oxidizing reagents at the external surface of catalysts[4,14,38].

In this reaction, first reaction occurs between formic acid and H_2O_2 (aqueous phase) led to form percarboxylic acid (HCOOOH) and H_2O. The formed HCOOOH reacted with soybean oil to produce ESBO and formic acid (organic phase). The generated formic acid returns to reaction for next cycle. Herein, HCOOH and HCOOOH are in equilibriums and moderately soluble in the organic phase.

Turco et al. studied the decomposition of H_2O_2 and mixture of HCOOH and H_2O_2 in absence of soybean oil by contacting with HY catalyst and concluded that mixture of HCOOH and H_2O_2 decomposed very fast as compared to H_2O_2 and produced a large volume of gas in lesser time[14]. While in the presence of soybean oil, reactant (HCOOH and H_2O_2) was consumed during epoxidation reaction and the reaction stopped at the complete decomposition of reactants. This is supporting our earlier assumption that disappearances of reactants halt the reactions. The direct contact between HCOOOH and H_2O_2 aqueous solution with catalysts surface led to promotes the decomposition of oxidizing agents. Similar observation of ease of decomposition of H_2O_2 when contacted with solid powders surface was made by Ebrahimi *et al.*[38]. In the presence of soybean oil, decomposition rate of mixture of HCOOH and H_2O_2 was much lower as compared to absence of soybean oil that may be due to presence of oil surrounding zeolite particles. The oil surrounding zeolite particles may be blocking the active sites located at external surface which are responsible for decomposition of oxidizing agents. Similar argument was made by turco et al.[14] for soybean oil epoxidation reaction. They demonstrated the absorptions of ESBO on external surface of HY catalyst during the reaction.

In order to investigate the role of HZSM-5, HY and Hß catalysts, a blank kinetic study was carried out at same reaction conditions in absence of catalyst and results showed that double bond conversion after 30 min was significantly lower about 8 %. This indicated that an initiation time around 25- 30 minutes required for producing performic acid, possibly, due to weak acidity of formic acid resulted in slower reaction rate between HCOOH and H_2O_2. However, with catalysts, no initiation time was observed and 35 % conversion was obtained after 30 min. Therefore, it can be concluded that HZSM-5, HY and Hß catalysts plays an important role to enhance double bond conversion by selectively produced performic acid. These could be possible due to narrow channels of zeolite which do not allow triglycerides bulky molecules to enter, while aqueous reactant substances and reaction products can easily access its framework[1,14]. Hence, it can be said that reaction occurs inside pores of zeolite and after attaining the equilibrium there, performic acid can disseminate outside pores and react in oil the phase to produce to ESBO as discussed earlier. Further, the high selectivity of ESBO confirms preventions of undesired side reaction of ring opening. Herein, acid sites of zeolite play an important role to selectively produce performic acid which subsequently reacted with soybean oil to produce ESBO.

The double bond conversion and selectivity for the catalyst used in this work and other reported works in this area are complied in Table 1. However, direct comparison of catalytic activities cannot be made owing to different feed composition, catalyst amount, reaction time, temperature and oxidant. As apparent in Table 1, different catalysts have been utilized for the epoxidation of soybean oil with varying feed composition, and reaction condition. The results show that the highest SO conversion (85 %) ESO selectivity (83 %) and yield (70.55 %) are obtained with HZSM-5 in this study at a reaction temperature of 70 °C. As

Table 1 — Comparison of catalytic activity of present work and that of earlier reported work

Catalyst	Feed composition	Temp, °C	Reaction time, h	X, %	S, %	Yield, %	Ref
$5Nb_2O_5$-SiO_2	5 g - SO, 6.9 g - H_2O_2, 20 mL- Ethyl acetate	80	5	23	38	8.77	[17]
Ti-HMS	10 g -SO, 5 mmol -THBP, 5 mL- 1,2-dichloroethane	60	24	42.60	51	21.77	[18]
TS-1-40	5 g - SO, 6.8 g - H_2O_2, 4 g - tert-butanol	80	24	65.27	90	58.89	[4]
Ti/SiO2 (2.5 wt %)	20 g - SO, 4 g - H_2O_2, 5.81 g- tert-butanol	80	31.3	65.95	65	42.88	[13]
HY	50 g - SO, 18.36 g - H_2O_2, 2.68 g - Formic acid	70	4	81	80	64.80	This work
ZPS–PVPA–SO_3H (10 wt %)	10 g - SO (),5 mmol – THBP, 5 mL- 1,2-dichloroethane	80	6	81.6	73.2	60.06	[19]
HY	50 g - SO, 18.36 g - H_2O_2, 2.68 g - Formic acid	70	3	83	82	-	[14]
Hß	50 g - SO, 18.36 g - H_2O_2, 2.68 g - Formic acid	70	4	83	80	67.20	This work
HZSM-5	50 g - SO, 18.36 g - H_2O_2, 2.68 g - Formic acid	70	4	85	83	70.55	This work

compared to reported work[4,13,17-19], the catalyst used in earlier[14] and this work, demonstrated high ESO selectivity and this could be owing to characteristics of zeolite as discussed earlier. In general, catalysts used in this work shown superior performance in terms of double bond conversion, ESO yield and selectivity, and stability.

Conclusion

It is shown that HZSM-5, HY and Hß catalysts are effectively promoting reaction between H_2O_2 and HCOOH to produce *insitu* performic acid in the soybean oil epoxidation. All the three catalyst are active and gave 85, 81 and 83 % conversion for HZSM-5, HY and Hß, respectively. The catalyst exhibited excellent activity and its remains intact up to five cycles. The high conversion and selectivity can be due to narrow crystalline pores of zeolite which are accessible to aqueous phase reactants only not for bulky molecules (triglycerides). The above catalysts are cost effective, recyclable, and environmental friendly. Further, the high selectivity of ESBO confirms preventions of undesired side reaction of ring opening.

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Conflict of Interest

The authors declare no conflict of interest.

Abbreviations

ESBO - Epoxidized soyabean oil
VOs - Vegetable oils
SO - Soybean oil
EVOs - Epoxidation of vegetable oils,
EPO - Epoxidation of palm oil

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