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Alkali promoted selective epoxidation of styrene to styrene oxide using TS-1 catalyst

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Abstract

The epoxidation of styrene was carried out over titanium silicalite (TS-1) and an alkali (sodium hydroxide) in the reaction medium. This system gave a very high TOF (>200 h^{-1}) and selectivity to styrene oxide ($>92\%$). It was found by EPR characterization that the local coordination of Ti centers is transformed from five fold to six fold in presence of NaOH. Also, further isomerization of styrene oxide to phenylacetaldehyde is nearly suppressed by NaOH, thereby increasing the styrene oxide selectivity remarkably.

1. Introduction

The conventional route for epoxidation of alkenes involving the use of peracids is being replaced by H$_2$O$_2$ epoxidation using reusable heterogeneous catalysts that are more environment friendly [1–5]. Among these, epoxidation of styrene to styrene oxide is of particular interest from both scientific as well as commercial point of view [6,7]. TS-1, a transition metal ion-substituted zeolite is well known for this transformation, however, the formation of the desired product (styrene epoxide) is always accompanied by the oxidative cleavage of double bond to benzaldehyde and isomerisation of styrene epoxide to phenyl acetaldehyde [8,9]. Attempts have been made to improve activity and selectivity of TS-1, with a focus mainly on generating highly isolated titanium sites by using various chemical and physical methods for preparation of TS-1, however, the maximum conversion of styrene achieved was up to 40% with a selectivity to styrene oxide up to 70% [10–12]. A highest styrene conversion (71 mol%) with maximum epoxide selectivity (87 mol%) has been reported by the use of anhydrous urea–hydrogen peroxide as an oxidant over TS-1 [13]. However, this procedure demands the use of anhydrous H$_2$O$_2$ and also the catalyst loading is as high as 20 wt % of the styrene. In the present work, we report the TOF>200 h^{-1} and selectivity of styrene oxide as high as 92% by using alkali as a promoter. The

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role of NaOH has been explained based on the characterization of TS-1 by EPR measurement. The use of alkali also caused suppression of hydrogen bonding and thereby reducing acid centers generally responsible for isomerization of styrene oxide to phenyl acetaldehyde.

2. Experimental

2.1. TS-1 synthesis

Titanium silicalite-1 molecular sieve catalyst (TS-1) was synthesized according to the literature procedure [14]. In a typical synthesis, 1.98 g of tetra butyl orthotitanate (Aldrich, US) dissolved in 20 g of dry isopropyl alcohol (S.D. Fine chemicals, India) was added to 30 g of ethylsilicate-40 (Chempalst, India) at 25 °C under stirring. Then 56 g of tetrapropyl ammonium hydroxide (TPAOH, 22.2 wt% aqueous) was slowly added to the above clear solution under vigorous stirring which was further continued at 60–70 °C for about 2 h in order to accelerate hydrolysis and evaporate the alcohol. Then the required amount of water (80 g) was added and the solution was kept stirring for further 1 h. The initial molar composition of this solution was SiO_2:0.03 TiO_2:0.33 TPA:35 H_2O. This solution was transferred to an autoclave (Parr) and was further stirred while heating at 170 °C for hydrothermal crystallization. The solid product was recovered by centrifugation, washed with doubly distilled water and dried overnight at 100 °C in an air oven. The catalyst was further calcined at 500 °C for 24 h.

2.2. Characterization

TS-1 thus prepared was characterized by XRD (Rigaku, D-Max III VC model, nickel filtered Cu-Kα radiation) and FTIR spectroscopy (KBr pellet technique, Nicolet 60 SXB). FTIR spectra were recorded after preheating the samples at 100 °C for 4 h to remove water. The chemical composition of the sample was determined by XRF (Rigaku, 3700) and energy dispersive X-ray (EDX) attached to SEM (JEOL JSM 500). The EPR spectra of the samples were recorded on a Bruker EMX spectrometer operating at X-band frequency and 100 kHz field modulation. EPR spectra at 90 K were measured using a Bruker BVT 3000 temperature controller.

2.3. Catalytic activity

The catalytic performance of TS-1 was studied for the epoxidation of styrene in a glass reactor (100 ml. capacity) equipped with a stirrer, thermometer, reflux condenser, two dropping funnels and a pH electrode. In a typical batch experiment, 10.42 g of styrene (100 mmol), 12.31 g acetonitrile (300 mmol) and 155 mg of Ts-1 catalyst were charged to the reactor. The mixture was heated to 343 K while stirring and a solution of 2.89 ml hydrogen peroxide (50 wt%, 50 mmol), and l2.82 g methanol (400 mmol) was added drop wise to the above mixture over a period of 1.5 h. Aqueous 1 N sodium hydroxide was also added simultaneously to maintain a pH of 7.5–8. After three hours of reaction, the liquid product was cooled down to room temperature and the catalyst was separated by filtration. The product was diluted with 50 ml of water and extracted with three 20 ml. portions of chloroform after which the extraction liquid was dried by adding anhydrous sodium sulfate to it. The extracted solution was concentrated and was analyzed by gas chromatograph (HP-6890) with a capillary column (HP-1, 30 m × 0.32 mm, 0.25 μm) using FID.

3. Results and discussion

3.1. TS-1 characterization

The XRD pattern (characteristic of MFI topology) confirmed the crystallinity and phase purity of the calcined TS-1 used in this work [14,15]. DRUV (absorption at $\lambda = 209$ nm), framework region IR (band at 958 cm^{-1}), confirmed the incorporation of Ti(IV) in the framework and the absence of any extra framework anatase TiO_2 species. Different TS-1 samples were prepared with varying Si/Ti molar ratio in the range of 30–90, as determined by EDX analysis. The BET surface area determined from N_2 adsorption isotherm was 489 m^2/g.

For the EPR measurement, to a sample of solid TS-1 catalyst (245 mg) soaked with acetonitrile (0.4 ml) 0.1 ml of 50% aqueous H_2O_2 was added. Soon after the addition of aqueous H_2O_2 the colour of the solid changed from white to yellow. This sample was quenched to 90 K and immediately the EPR spectrum was recorded. Figs. 1(a) and (b) show the EPR spectra of TS-1 + aq. H_2O_2 and TS-1 + aq. H_2O_2 in presence of NaOH, respectively. Activation of H_2O_2 by isolated Ti centers form three types of oxo-titanium species viz. Ti(IV)-peroxide, -hydroperoxide and -superoxide which are found to be active in oxidations catalyzed by titanosilicates. Among these, Ti(IV)-superoxide species is detected in EPR due to its paramagnetic nature and is also said to bring about the epoxi-

dation reactions [16–19]. There is a striking difference between the EPR spectra of these two samples. Two types of Ti(IV)-superoxide radicals: A and B (curve a) are seen for TS-1 treated with only aq. H_2O_2 while, only one type of -superoxide radical A is seen for TS-1 in presence of H_2O_2 and NaOH. Species A and B differ only in g_z parameter (for A: $g_z = 2.0276, g_y = 2.010, g_x = 2.0028$ and for species B: $g_z = 2.025, g_y = 2.010$ and $g_x = 2.0028$) while in case of curve b, species B is totally absent with EPR parameters as ($g_z = 2.028, g_y = 2.010, g_x = 2.0028$) which clearly indicates that upon treatment with NaOH, species B got converted to A.

3.2. Activity studies: epoxidation of styrene

Table 1 summarizes the results of epoxidation of styrene with H_2O_2 as an oxidizing agent using titanium silicalite-1 (TS-1) as a catalyst under various reaction conditions. As can be seen from this Table, TS-1 showed significantly high conversion and epoxide selectivity as high as 96% (entry 4) in presence of NaOH as against that without an alkali (entry 6). TOF obtained in our work (398 h-1) is several times higher than that reported in the recent work [13] on styrene epoxidation using UHP (anhydrous urea–hydrogen peroxide) system over TS-1. This is mainly due the fact that in our case the catalyst concentration was very small (1.5 wt% of styrene) as compared with 20 wt% used earlier and also the reaction time was about one fourth of that reported by Laha and
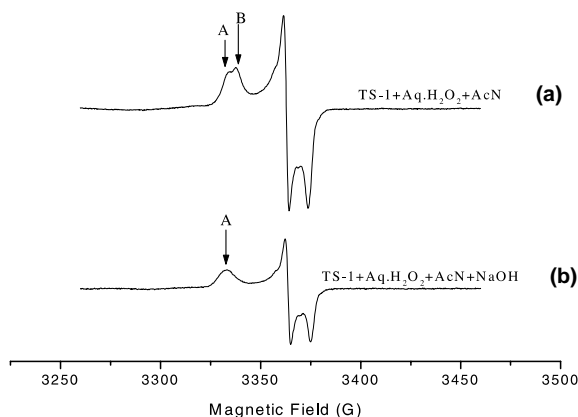

Fig. 1. EPR spectra of TS-1 in absence (a) and in presence (b) of NaOH.

Table 1
Performance of TS-1 catalyst in styrene epoxidation under various conditions

No.	Styrene:H_2O_2 mole ratio	Temp. (K)	Styrene conversion (%)	%Selectivity			
				Styrene oxide	Benzaldehyde	Phenylacetaldehyde	Others
1	1:1	323	70	85.5	14.2	0.0	0.3
2	1:1	343	80.7	95.4	3.9	0.0	0.7
3	1.1	353	54.6	81.1	17.5	0.0	1.4
4	1:0.5	343	95	96.5	3.1	0.0	0.4
5*	1.1	343	65	80.2	18.9	0.0	0.9
6**	1:1	343	45	3.0	22.7	73.8	0.5

Catalyst wt = 0.155 g (1.5 wt% of styrene); reaction time = 3 h.
* Without methanol as solvent/diluent.
** Without alkali.

Kumar [13]. A major drawback of using UHP system is its decomposition at temperatures >40 °C, which directly reflects in longer reaction times for appreciable styrene conversion thereby causing very low conversion. The conversion enhancement by about 35% in presence of NaOH (entries 2 and 6) was due to the transformation of oxo-Ti(IV) ions from five fold to sixfold coordination. Another significant effect of NaOH was that the formation of phenylacetaldehyde was completely eliminated leading to increase in selectivity of styrene oxide from 3% (without NaOH) to 96%. The role of NaOH on selectivity is discussed in more details in the following section. Fig. 2 shows the effect of temperature on styrene conversion and selectivity of styrene oxide. The conversion first increased from 45% to 51% with increase in temperature from 323 to 343 K however, with further increase in temperature to 353 K, the conversion drastically dropped to below 40%, indicating the H_2O_2 decomposition at higher temperature. Similar trend was observed in case of epoxide selectivity though the extent of drop in selectivity was not so high. The conversion and selectivity were dramatically increased when the styrene to hydrogen peroxide ratio was increased (styrene:hydrogen peroxide = 2:1). The conversion of hydrogen peroxide was increased from 52% to 83.6% while the selectivity increased upto 96.5% with a TOF of 398.4 indicating better conversion of hydrogen peroxide at this ratio. (entry 4, Table 1).
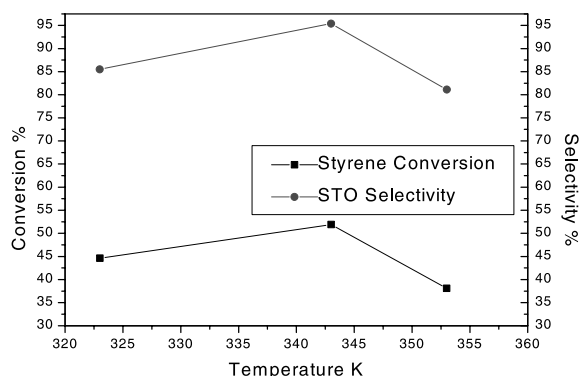
The effect of catalyst loading on activity and selectivity of TS-1 catalyst was studied in the range of 0.75–6.66 wt% at 323 K. It was found that both styrene conversion and epoxide selectivity increased with increase in catalyst loading from 0.75 to 1.5 wt% (of styrene). In case of TS-1 catalyst, formation of two types of species is proposed: isolated Ti^{3+} and Ti^{4+} ions together known as Ti(α) which catalyzes the epoxidation reaction; and Ti(β) species consisting of (TiO_2) clusters responsible for benzaldehyde formation [20]. At lower catalyst concentration, the concentration of active Ti(α) sites is low causing lower epoxidation rate while with increase in catalyst loading up to a certain value (1.5 wt%), the concentration of Ti(β) species also increases leading to a higher conversion (Fig. 3).

3.3. Role of NaOH

In this study, we observed that in presence of NaOH both the conversion and styrene oxide selectivity was higher than that in case of TS-1 alone. Pyne et al. have reported the formation of peroxycarboximidic acid intermediate as a result of reaction between H_2O_2 and nitrile at pH = 8 [21]. This peroxycarboximidic acid reacts with olefin to give an epoxide along with formation of equimolar amount of amide (acetamide in case of styrene epoxidation). Since in our work TS-1 was present as a catalyst (which was not present in the work of Pyne et al.), the interaction of framework Ti atom
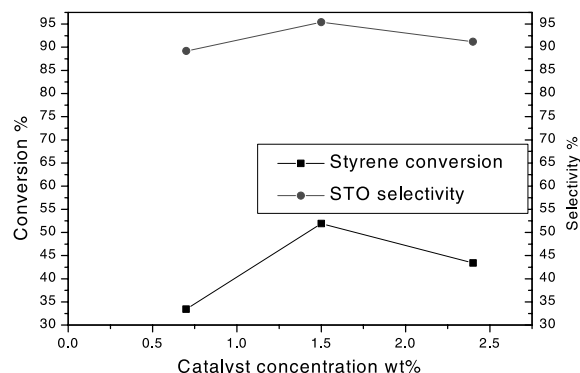

Fig. 2. Effect of temperature on conversion and selectivity.

Fig. 3. Effect of catalyst concentration on conversion and selectivity.

and H_2O_2 is expected to form a stable five membered cyclic structure such as hydroperoxo species. With NaOH as a ligand, isolated and tetracoordinated Ti centers would expand their coordination sphere up to six. Such interactions are known with ligands like water, ammonia [22,23]. The increase in coordination sphere causes change in unit cell parameter, i.e., increase in the micropore diameter which can facilitate the diffusion rate of reagent inside the channels. In the present study, different EPR signals for TS-1 in absence and in presence of NaOH has clearly established the existence of superoxo species A which is said to be responsible for epoxidation reaction. In addition to this, we have not observed formation of acetamide though, acetonitrile used was in excess. Acetonitrile along with methanol serves merely as a solvent system in the present case. It is well known that the acid centers developed by TS-1 in the presence of aqueous H_2O_2 are responsible for the epoxide ring opening and isomerisation to phenylacetaldehyde [24,25]. The enhancement in epoxide selectivity presence of NaOH is due to suppression of hydrogen bonding and acid centers and hence the isomerization to the side product phenylacetaldehyde is eliminated

4. Conclusions

Epoxidation of styrene was investigated over TS-1 catalyst in presence of NaOH in the reaction medium. A very high TOF ($>200h^{-1}$) was obtained in comparison with previous results over TS-1 for styrene epoxidation. Most important observation was the elimination of formation of commonly encountered side product, phenylacetaldehyde due to the suppression of styrene epoxide isomerisation by NaOH. An EPR study of TS-1 in presence of NaOH showed the expansion of penta-coordination to six-fold of Ti(IV) centers leading to a significantly higher activity of TS-1. Effect of other reaction parameters such as temperature, catalyst concentration, Si/Ti ratio on the catalyst activity and selectivity was also studied.

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