Chapter 6 (I)

Epoxidation of Styrene with Molecular $O_2$ over Yttria Stabilized Zirconia (YSZ) based Solid Catalysts
1. **Introduction**

   Epoxidation of olefins is a field of great interest as epoxides are industrially important chemicals and are largely used as intermediates for several perfumery chemicals, plasticizers and sweeteners [1]. Moreover, styrene oxide is an important organic intermediate for fine chemicals and pharmaceuticals and has been prepared conventionally by epoxidation of styrene using stoichiometric amounts of peracids as the oxidizing agent [2]. Generally, H$_2$O$_2$, urea-H$_2$O$_2$ adduct and tert-butyl hydroperoxide (TBHP) are commonly used oxidizing agents for epoxidation of styrene. Although, H$_2$O$_2$ results into high conversion of styrene, but poor selectivity for styrene oxide; on the other hand TBHP [3] and urea-H$_2$O$_2$ adduct [4] yields high styrene oxide selectivity (>80%), but low styrene conversion (9-18%). In most of the cases, a sacrificial co-reductant (oxygen acceptor), usually aldehyde, is used to achieve reasonable yields and selectivities. These oxidizing agents are corrosive and hazardous in nature leading to either low conversion or selectivity with undesirable waste. Therefore, from environmental and economical stand point, molecular oxygen is the most desirable oxidant for the epoxidation of alkenes.

   Cobalt ions and their complexes are well known conventional homogeneous catalysts for the selective oxidation of alkenes using TBHP and O$_2$ as oxidizing agents [5,6]. Ruthenium complexes have also been reported [7] without the need for a co-reductant. However, the homogenous catalysts are difficult to separate from the product and are not re-usable. An attempt of heterogenization of chiral salen complexes on solid
supports such as modified MCM-41 and SBA-15 has proved to be effective for epoxidation of styrene, though NaOCl and PyNO were used as oxidizing agent and co-reductant, respectively [8]. Therefore, styrene epoxidation over environmental friendly and reusable solid catalysts, using molecular O\textsubscript{2} as oxidant is desirable. Consequently, attempts have been made to use solid catalysts such as Ti/SiO\textsubscript{2} [9], TS-1 [4], Ti-MCM-41 [10], Fe/SiO\textsubscript{2} [11], Au/Al\textsubscript{2}O\textsubscript{3} [12], MgO [13], BaO and CuO [14,15] with H\textsubscript{2}O\textsubscript{2}, urea-H\textsubscript{2}O\textsubscript{2} adduct and TBHP as oxidizing agents. However, studies of solid catalysts using molecular oxygen without the need of a co-reductant are sparse [16-19]. First example of aerobic epoxidation of styrene without a co-reductant was reported by Tang et al. [16] using Co(OAc)\textsubscript{2} supported on zeolite NaX resulting into 44% styrene conversion with 60% epoxide selectivity.

Ytria-stabilized zirconia (YSZ) is a well known structural ceramic being widely used in electrochemical devices such as solid oxide fuel cell [20] and oxygen sensor [21]. Though it has been widely studied as ceramic material, studies of its catalytic activity are sparse; to the best of our knowledge it has only been reported as oxidation catalyst for partial oxidation of methane to syngas [22-24]; though Zr-HMS [25], Zr-MSU-V [26] and Zr-Mn-MCM-41 [27] have been reported for oxidation of styrene/alkene, however, with H\textsubscript{2}O\textsubscript{2} and TBHP.

In the present chapter, we have studied the application of YSZ as a solid catalyst for the epoxidation of styrene using molecular O\textsubscript{2} in presence of DMF as a solvent and in absence of a sacrificial reductant. YSZ catalysts have been prepared by sol-gel technique; the addition of transition metal co-cations namely Co and Fe to YSZ has been done to study the effects of these cations on its catalytic activity. The acidity of the YSZ based
samples has been enhanced by modification with sulfate anions as a sulfating agent. A
detailed systematic study including effect of sulfation and co-cations, catalyst and DMF
concentration, presence of water and calcination temperature of the catalyst has been
undertaken. To the best of our knowledge it is the first report of epoxidation of styrene
using molecular O₂ in absence of a sacrificial reductant over non-sulfated and sulfated
YSZ based catalysts

2. Experimental

2.1) Materials

Zirconium n-propoxide, (70 wt % in n-propanol), yttrium nitrate hexahydrate
(99.9%) and styrene was procured from Sigma-Aldrich, Germany; ferric nitrate
nynhydrate, n-propanol (99%) and tridecane was procured from s.d. fine chem. Ltd.,
India; cobalt nitrate hexahydrate was from Loba Chemie Pvt. Ltd., India; N-N
dimethylformamide was from Qualigens fine chemicals Ltd., India; and aqueous
ammonia solution (25%) was purchased from Rankem, India. Oxygen (99.9% purity) was
procured from Inox Air Product Ltd., Vadodara. All the chemicals were used as such.

2.2) Catalyst synthesis

2.2.1) Synthesis of ZrO₂ and YSZ

All catalysts have been prepared by sol-gel technique. Zirconium n-propoxide
[Zr-P] diluted to 30 wt% was used as zirconium precursor in all the synthesis. ZrO₂ was
prepared as described in chapter 2. In a typical experiment, 0.025 M solution of Zr-P
was hydrolyzed by drop wise addition of aqueous ammonia till the pH became ~10.5
under constant magnetic stirring. After completion of the hydrolysis, the sol was
continuously stirred for 2h at ambient temperature for condensation of the gel. The gel
was oven dried at 110°C for 12h followed by calcination at 500°C for 4h under static air. The resulted white powder is designated as ZrO₂.

YSZ catalysts were prepared by doping 8 and 16 mol% yttria. 8 mol% YSZ were prepared as described in chapter 5. In a typical experiment, for Y (8 mol%)-ZrO₂, the composition of the solution of Y-nitrate: Zr-P = 16:84 (as two molecules of Y(NO₃)₃.6H₂O will result into one molecule of Y₂O₃) and thus the molar ratio of Y-nitrate: Zr-P in 0.025 M solution =0.004:0.021 (0.025M x 0.16 =0.004M (Y(NO₃)₃.6H₂O) and (0.025M x 0.84 = 0.021M Zr-P). Typically, alcoholic solution of Y(NO₃)₃.6H₂O (1.53 g) in n-propanol (4 ml) and Zr-P (14.9 g of 30wt%) in n-propanol (35ml) were added under constant magnetic stirring and then hydrolyzed, polymerized, dried and calcined at 500°C for 4h as described above. The resulted white powder was designated as 8YZr. For Y (16 mol%)-ZrO₂, the composition of the solution of Y-nitrate: Zr-P = 32:68 and thus 0.025 M solution was having the molar ratio of Y-nitrate: Zr-P = 0.008:0.017. The resulted white powder was designated as 16YZr.

2.2.2) Synthesis of transition metal doped YSZ

The catalysts have been prepared by doping Co or Fe (8 mol%) transition metal cations in 8YZr. Typically, for Co-Y-ZrO₂, the molar ratio of Co:Y: Zr in 0.025 M solution = 0.002:0.004:0.019M. The procedure of hydrolysis and condensation of the precursors to get polymerized gel was similar as described above. The resulted light violet color powder was designated as 8CoYZr, which was changed to light grey after calcination at 500°C for 4h. Similarly, light yellow colored 8FeYZr was obtained, which remained light yellow colored after calcination at 500°C for 4h.
Chapter 6 (I)

For comparison with 16YZr, Co and Fe(16 mol\%)–ZrO$_2$ have also been prepared. The resulted light violet color powder of 16CoZr was changed to dark grey after calcination at 500°C for 4h. Similarly, light yellow colored 16FeZr was obtained, which remained of same color after calcination at 500°C for 4h.

2.2.3) Synthesis of sulfated ZrO$_2$ and YSZ

All catalysts prepared as described above were sulfated by H$_2$SO$_4$ (1g catalyst/ 15 ml 1N H$_2$SO$_4$) under constant stirring for 30 minutes. The sulfated powder was oven dried at 120°C for 12h followed by calcination at 600°C for 4h. The resulted catalysts were designated with S- as initial, e.g., sulfated Y (8mol\%)-ZrO$_2$ was designated as S-8YZr.

For comparison with sulfated Y-ZrO$_2$, pure sulfated zirconia (SZr) has also been prepared by two-step sol-gel technique [28]. Typically, in the first step, Zr(OH)$_4$ was obtained by hydrolyzing 0.025 M solution of Zr-P by drop wise addition of aqueous ammonia till the pH =10.5 under constant stirring. After hydrolysis, the sol was continuously stirred for 2 h at ambient temperature. The obtained gel was oven dried at 110°C for 12 h and treated with H$_2$SO$_4$ (1g catalyst/ 15 ml 1N H$_2$SO$_4$) under constant stirring for 30 minutes in the second step. The sulfated powder was oven dried at 120°C for 12h followed by calcination at 600°C for 4h. The resulted white powder was designated as S-Zr.

2.3 Catalyst characterization

2.3.1. Structural Characterization

2.3.1.1 Powder X-ray diffraction (PXRD)
All prepared non-sulfated and sulfated catalysts after calcination at 500 and 600 °C, respectively were analyzed with X-ray powder diffractometer (Philips X’pert) using CuKα radiation (λ=1.5405 Å). The samples were scanned in 2θ range of 2 to 80° at a scanning rate of 0.4 degree sec\(^{-1}\). The crystallite size was determined by Scherrer formula [29] as shown below:

\[
\text{Crystalline size} = \frac{K \cdot \lambda}{W \cdot \cos \theta}
\]

where K (shape factor) =0.9, \(\lambda = 1.5405 \text{ Å}\), and \(W = (W_b - W_s)\), the difference of the broadened profile width of the experimental sample and the standard width of reference silicon sample.

2.3.1.2 Bulk sulfur

The bulk sulfur (wt%) present in sulfated samples before and after calcination at 600°C was analyzed by elemental analyzer (Perkin–Elmer, 2400, Sr II, USA).

2.3.2. Textural Characterization

Specific surface area, pore volume and pore size of samples were determined from nitrogen adsorption–desorption isotherms at 77.4K (ASAP 2010, Micromeritics, USA). Surface area and pore size were determined using BET equation. The samples were degassed under vacuum at 120°C for 4 h, prior to measurement, to evacuate the physisorbed moisture.

2.3.3. Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectroscopy (DRS) studies of non-sulfated and sulfated samples were performed with a Shimadzu UV-3101PC equipped with an integrating sphere. BaSO\(_4\) was used as the reference material. The spectra were recorded at room
temperature in the wavelength range of 200–800 nm with slit width 3 nm and medium scan speed.

2.3.4. Total Surface Acidity

The total surface acidity of sulfated samples was measured by TPD-NH\textsubscript{3} (Micromeritics Pulse Chemisorb 2720, USA) method. The sample (0.05 g) was taken in the reactor and activated \textit{in-situ} at 120°C for 2 h under helium (He) gas flow. After bringing down the reactor temperature to 40°C, a mixture of 10% NH\textsubscript{3} with He gas was passed for 30 min. The excess physisorbed NH\textsubscript{3} was flushed out with pure He gas flow at 40°C for 30 min. The sample was then heated at a rate of 10°C min\textsuperscript{-1} up to 800°C and the volume of desorbed NH\textsubscript{3} per gram was measured using a thermal conductivity detector.

2.3.5. Morphological Characterization

The scanning electron microscopic (SEM) study was done with a scanning electron microscope (Leo series VP1430, UK). The samples were coated with gold using a Polaron Sputter Coater.

2.4 Catalytic activity for Epoxidation of styrene using molecular O\textsubscript{2}

The various non-sulfated and sulfated Y-ZrO\textsubscript{2} based catalysts along with transition metal co-cations have been investigated for the liquid phase epoxidation of styrene using molecular O\textsubscript{2} in presence of DMF solvent and in absence of any sacrificial reductant. Typically, a 50 ml round bottom flask equipped with an efficient water condenser was kept in a constant temperature oil bath. Then styrene (10 mmol), DMF (10 ml) and catalyst (100 mg), which was pre-activated at 450 °C for 4 h were added to the flask. The reaction was started by bubbling O\textsubscript{2} at atmospheric pressure into the reaction mixture at the rate of 7-10 ml min\textsuperscript{-1}. Tridecane was used as an internal standard. The
reaction mixture was magnetically stirred at 600 rpm. After 8 h of reaction, the catalyst was separated by filtering the reaction mixture, and the liquid organic products were quantified using a gas chromatograph (Hewlett Packard 6890) with a flame ionization detector, capillary column (HP-5), a programmed oven (temperature range 50-250 °C) and N₂ as a carrier gas. Reaction products were confirmed by analyzing the reaction mixture with gas chromatograph-mass spectrometer (GC-MS, Shimadzu GCMS-QP-2010) having a programmed oven (temperature range 50-250 °C), He as a carrier gas and MS in the EI mode with a 70-eV ion source. The reaction kinetics was monitored by withdrawing small amounts of the reaction mixture at 1 h intervals. The conversion was calculated on the basis of molar percent of styrene and tridecane (internal standard) variation; the initial molar percent of styrene and tridecane was divided by their GC peak area percent to get their response factor. The unreacted moles of styrene and tridecane were calculated by multiplying the response factor by their GC peak area percent after the reaction. Tridecane variation was calculated by dividing the initial molar percent of tridecane with remaining molar percent of tridecane. The unreacted moles of styrene after the reaction were multiplied with tridecane variation to get the final mol percent of styrene. The conversion and selectivity were calculated as below:

Styrene conversion (mol%) = [(Initial mol% - Final mol%) / Initial mol%] x 100

Styrene oxide selectivity = [GC peak area of styrene oxide / GC peak area of all products] x 100

2.4.1) Catalyst regeneration

The spent catalyst was recovered from the reaction mixture by filtration and thoroughly washed with acetone to remove the adsorbed organic species on the surface of
the catalyst and dried at room temperature. The dried catalyst was activated at 450 °C for 4 h and was used for further reaction cycle under the similar reaction conditions. The catalyst was regenerated after every reaction cycle in a similar way.

3. Results and Discussions

3.1) Catalyst characterization

3.1.1 Structural Properties

3.1.1.1 PXRD studies

All non-sulfated samples were found to be crystalline in nature, having cubic crystalline phase after calcination at 500°C (Fig. 1). The light violet color of 8CoYZr and 16CoZr samples was changed to light and dark grey, respectively, after calcination at 500°C.

All sulfated samples were found to be amorphous in nature after calcination at 600°C (Fig. 2a) due to the presence of sulfate ions. As higher thermal energy is required for the dehydroxylation of zirconia in the presence of sulfate ions, the crystallization temperature was increased and the samples were amorphous after calcination at 600°C. However, calcination at higher temperature of 700 and 800°C resulted in crystalline sample (S-8CoYZ) having cubic phase (Fig. 2b). The pink color of sulfated 8CoYZr changed to violet, dull grey and dark grey after calcination at 600, 700 and 800°C, respectively.

3.1.1.2 Bulk sulfur

The bulk sulfur (wt.%) present in all sulfated samples after calcination at 600°C was in the range of 14.4–19.7 % (Table 1). Such a high amount of sulfur content was
Fig. 1. PXRD patterns of non-sulfated catalysts after calcination at 500°C

Fig. 2. PXRD patterns of (a) sulfated catalysts after calcination at 600°C and (b) S-8CoYZr catalyst after different calcination temperatures.

responsible for the amorphous nature of sulfated samples after calcination at 600°C. However, calcination at 700°C resulted in drastic decline in sulfur content (3.60 wt.%) of S-8CoYZr, which further decreased to 0.59 wt.% after calcination at 800°C.
3.1.2 Textural Properties

Non-sulfated samples exhibited high BET surface area (240–475 m$^2$/g), pore volume (0.28–0.61 cm$^3$/g) and pore diameters (51–102 Å). The surface area and pore volume decreased and pore size increased as the pore walls collapse during thermal treatment after calcination at 500 °C (Table 1). The as such sulfated sample (S-8CoYZr) showed poor textural properties in terms of very low surface area (2.5 m$^2$/g) and pore volume (0.002 cm$^3$/g). The pore diameter of the samples was also found to decrease (from 78 to 49 Å) after sulfation. This may be attributed to the filling of pores by sulfate species; this would make them inaccessible for nitrogen gas adsorption, resulting in very low surface area and pore volume. After calcination at 600°C, some loss of sulfate species occurred, resulting in a significant increase in pore size (137 Å). Therefore, surface area and pore volume slightly increased after calcination. The other calcined sulfated samples also showed low surface area in the range of 2.2–3.09 m$^2$/g.

3.1.3. Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance studies clearly demonstrated the doping of Co cations in Y–ZrO$_2$ samples. Pure Y–ZrO$_2$ showed a spectral band around 240 nm in the UV region similar to pure ZrO$_2$, whereas 8CoYZr exhibited an additional broad band at around 545 nm in the visible region (Fig. 3a), which was attributed to octahedral Co(II) cations bonded with the Y–ZrO$_2$ surface. However, the sample after calcination at 500°C showed the broadening of the 240 nm band and disappearance of the 545 nm band due to the formation of cobalt-oxide, which has also been observed by its color change from light violet to light grey. 16CoZr catalyst also showed similar spectral behavior before and after calcination at 500°C.
Table 1: Characterization of non-sulfated and sulfated Y–ZrO₂ based catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite phase</th>
<th>Sulfur (wt. %)</th>
<th>Total acidity (mmol NH₃/g)</th>
<th>Surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8YZr</td>
<td>Cubic</td>
<td>-</td>
<td>-</td>
<td>89</td>
<td>0.53</td>
<td>175</td>
</tr>
<tr>
<td>8CoYZr</td>
<td>Cubic</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16YZr</td>
<td>Cubic</td>
<td>-</td>
<td>-</td>
<td>107</td>
<td>0.16</td>
<td>57</td>
</tr>
<tr>
<td>16CoZr</td>
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<td>-</td>
<td>94</td>
<td>0.25</td>
<td>135</td>
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<tr>
<td>S-Zr</td>
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<td>7.24</td>
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<td>-</td>
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<tr>
<td>S-8YZr</td>
<td>Amorphous</td>
<td>18.2</td>
<td>7.77</td>
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<td>40</td>
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<tr>
<td>S-8CoYZr-600</td>
<td>Amorphous</td>
<td>15.9</td>
<td>8.21</td>
<td>3.85</td>
<td>0.011</td>
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<td>S-8CoYZr-700</td>
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<td>3.60</td>
<td>2.10</td>
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<tr>
<td>S-8CoYZr-800</td>
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<td>0.93</td>
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<td>7.52</td>
<td>3.09</td>
<td>0.003</td>
<td>106</td>
</tr>
<tr>
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<td>17.1</td>
<td>7.90</td>
<td>-</td>
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</tr>
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<td>19.7</td>
<td>-</td>
<td>2.45</td>
<td>0.002</td>
<td>125</td>
</tr>
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</table>

* Values after calcination; non-sulfated samples after 500°C; sulfated samples after 600°C

DR spectra of sulfated 8CoYZr (Fig. 3b), recorded after the calcination at different temperatures (200–800°C), showed that the octahedral coordination of Co(II) has changed to tetrahedral coordination after sulfation followed by calcination. Initially sulfation resulted in a blue shift (504 nm) in octahedral coordination of Co(II) with a color change to pink due to the formation of cobalt–water complex, [Co(H₂O)₆]²⁺, as the color change in Co(II) is influenced by the degree of hydration. After calcination at 200°C a red shift to 543 nm, for octahedral Co(II), was observed. The increase in calcination temperatures from 400 to 600°C resulted in the appearance of the bands of tetrahedral (629 and 582 nm) along with octahedral (531 nm) Co(II) ions [30] with a color change from pink to violet. This indicated a change in octahedral coordination to tetrahedral coordination of Co(II). However, further increase in calcination temperature to 700°C showed the absence of the tetrahedral Co(II) band at 629 nm, only very broad
bands at around 240 and 551 nm for octahedral Co(II) were observed. A color change of the sample from violet to dull grey showed the formation of cobalt-oxide at 700°C. Further calcination at 800°C resulted in the formation of cobalt-oxide of dark grey color, which showed no bands in the visible region.

![Diffuse reflectance spectra of (a) ZrO₂, 8YZr, 8CoYZr (as such) and 8CoYZr (500) and (b) sulfated catalyst (S-8CoYZr) before and after calcination at different temperatures.](image)

**Fig. 3.** Diffuse reflectance spectra of (a) ZrO₂, 8YZr, 8CoYZr (as such) and 8CoYZr (500) and (b) sulfated catalyst (S-8CoYZr) before and after calcination at different temperatures.

### 3.1.4. Total Surface Acidity

The total surface acid site concentration of the calcined sulfated samples measured was in the range of 7.24 to 8.21 mmol/g. Among all the sulfated samples, S-8CoYZr, calcined at 600°C, showed the highest surface acidity (8.21 mmol/g). Further calcination of the sample at higher temperature of 700 and 800°C resulted in significant decrease in the total surface acidity (2.10 and 0.93 mmol/g, respectively) (Table 1).
3.1.5. Morphological Characterization

The microscopic study revealed a spherical surface morphology of Y–ZrO₂. Doping with Co resulted in agglomerization. Sulfated samples also exhibited agglomerated spherical morphology (Fig. 4).

**Fig. 4.** SEM images of 8YZr, 8CoYZr and S-8CoYZr

3.2 Catalytic activity: Epoxidation of styrene using molecular O₂

The catalytic activity of various non-sulfated and sulfated Y–ZrO₂ based catalysts have been evaluated for the epoxidation of styrene using molecular O₂ in the presence of DMF solvent. All catalysts yielded only two major products; styrene oxide and benzaldehyde, as confirmed by GC–MS of the reaction mixture. The mass data showed standard fragmentation patterns corresponding to styrene epoxide (m/z = 119, 91, 65, 51) and benzaldehyde (m/z = 106, 77, 51) products in the reaction mixture.
3.2.1) Non-sulfated and sulfated Y–ZrO$_2$ based catalysts

Table 2 shows epoxidation of styrene over non-sulfated and sulfated catalysts. Pure ZrO$_2$ showed lower conversion (7%) of styrene with 57% selectivity for styrene oxide. 8YZr resulted in sharp increases in styrene conversion to 25% and in styrene oxide selectivity to 65%. The increased catalytic activity of 8YZr may be attributed to the presence of oxygen vacancies; doping Zr$^{4+}$ with Y$^{3+}$ resulted in the oxygen vacancies, which favored the adsorption and activation of O$_2$ during the oxidation reaction. However, further increase in yttria doping (16 mol%) did not increase the catalytic activity. This hints towards the saturation in the formation of oxygen vacancies. 16YZr showed similar styrene conversion (27%) but lower (48%) selectivity for styrene oxide.

Sulfated samples showed significant enhancement of styrene conversion. Pure sulfated zirconia (S-Zr) resulted in 25% styrene conversion with 50% selectivity for styrene oxide. It is noteworthy that non-sulfated 8YZr also showed similar styrene conversion (25%) with higher (65%) selectivity for styrene oxide than pure S-Zr, whereas S-8YZr resulted in higher conversion (35%) and selectivity (64%) compared to pure S-Zr catalyst. The enhancement of catalytic activity of sulfated zirconia occurs due to the electron withdrawing effect of sulfate species. Though all sulfated samples were amorphous in nature, having poor surface area and pore volume, these properties did not seem to take part in the catalytic activity for styrene oxidation under the reaction conditions studied. However, addition of sulfate species plays a significant contribution in the enhancement of catalytic activity of the samples. In sulfated Y–ZrO$_2$, a combined effect of sulfate species and the presence of oxygen vacancies may accelerate the oxidation reaction, thus resulting in further enhancement of conversion and selectivity.
Table 2: Epoxidation of styrene over non-sulfated and sulfated Y–ZrO\textsubscript{2} based catalysts using molecular O\textsubscript{2} \textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Styrene conversion (%)</th>
<th>Selectivity (%)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Styrene oxide</td>
</tr>
<tr>
<td>ZrO\textsubscript{2}</td>
<td>7</td>
<td>57</td>
</tr>
<tr>
<td>8YZr</td>
<td>25</td>
<td>65</td>
</tr>
<tr>
<td>8CoYZr</td>
<td>26</td>
<td>68</td>
</tr>
<tr>
<td>8FeYZr</td>
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<td>58</td>
</tr>
<tr>
<td>16YZr</td>
<td>27</td>
<td>48</td>
</tr>
<tr>
<td>16CoZr</td>
<td>19</td>
<td>48</td>
</tr>
<tr>
<td>16FeZr</td>
<td>24</td>
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<td>50</td>
</tr>
<tr>
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<td>53</td>
</tr>
<tr>
<td>No catalyst</td>
<td>15</td>
<td>58</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: Temp. = 120 °C, time=8h, styrene=1g, catalyst = 0.1 g, DMF = 10 ml, Tridecane (internal standard) = 0.1 g, O\textsubscript{2} flow=7ml min\textsuperscript{-1}. Non-sulfated samples calcined at 500°C and sulfated samples at 600°C.

3.2.2) Effect of co-cations

8YZr having Co or Fe co-cations also showed styrene conversion (26–27%) and selectivity (68–58%) in the similar range as observed for 8YZr (Table 2). 16CoZr and 16FeZr samples showed lower conversion (19–24%) and similar or higher selectivity for styrene oxide (48–57%) as compared to 16YZr. Therefore, addition of Co and Fe co-cation did not seem to affect the catalytic activity of Y–ZrO\textsubscript{2} samples under the present reaction conditions. Doping with yttria resulted in similar catalytic activity to that obtained after doping with well known oxidizing transition metals Co and Fe co-cations. This may be explained by the transformation of the Co(II) ions to oxide form after
calcination at 500°C. The cobalt-oxide was not catalytically active for epoxidation of styrene, therefore the process resulted in similar conversion and selectivity to those observed by Y–ZrO₂ catalyst.

However, sulfated co-cations doped samples showed significant rise in both the conversion and the selectivity as compared to sulfated Y–ZrO₂ catalyst. Among the Co- and Fe-doped sulfated Y–ZrO₂, Co-doped sulfated Y–ZrO₂ showed higher conversion (61%) and selectivity (76–80%) for styrene oxide as compared to Fe-doped sulfated Y–ZrO₂ samples, which showed lower conversion (43–45%) and selectivity (50–53%) (Table 2). The enhancements of conversion and selectivity in sulfated co-cations doped catalysts were due to the combined effect of sulfation along with co-cations. The effect of Co(II) cations as shown by DR analysis indicated that in sulfated Co–Y–Zr samples, tetrahedral Co(II) also plays a significant role along with the sulfate species for the oxidation of styrene. Furthermore, the higher activity of S-8CoYZr (calcined at 600°C) was also evidenced by its highest surface acidity as measured by NH₃ TPD. These results clearly showed that the acid site concentration or surface acidity of the catalysts was mainly responsible for the oxidation activity for styrene. As sulfated 8CoYZr-600 showed the highest conversion and selectivity, this sample has been selected for further detailed study.

3.2.3) Effect of temperature and kinetic study

The oxidation of styrene with O₂ over S-8CoYZr sample clearly revealed that styrene conversion and styrene oxide selectivity increased from 39 to 61% and 47 to 80%, respectively, after 8 h by increasing the temperature from 110 to 120°C (Table 3). On a further increase of the temperature to 130°C, conversion remained steady (62%),
however, the selectivity for styrene oxide decreased to 45% along with an increase in benzaldehyde formation. As the maximum conversion (61%) and selectivity (80%) were obtained at 120°C, it was chosen as the optimized temperature for further study.

**Table 3:** Epoxidation of styrene at different temperatures over sulfated (S-8CoYZr) catalyst using molecular O₂.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Styrene conversion (%)</th>
<th>Selectivity (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Styrene oxide</td>
<td>Benzaldehyde</td>
</tr>
<tr>
<td>110</td>
<td>39</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td>120</td>
<td>61</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>130</td>
<td>62</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>120⁰</td>
<td>55</td>
<td>-</td>
<td>100³</td>
</tr>
<tr>
<td>120⁰</td>
<td>Nil</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>120⁰</td>
<td>Nil</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ Reaction conditions: Temp. = 120°C, time=8h, styrene=1g, catalyst = 0.1 g, DMF = 10 ml, Tridecane (internal standard) = 0.1 g, O₂ flow=7ml min⁻¹, ² Reaction in the presence of 1 ml water, ³ In the presence of hydroquinone (50 mg), ⁴ In the presence of hydroquinone (50 mg) over S-8YZr catalyst, ⁵ Not detected by G.C., identified by ring test.

The kinetic study with respect to time showed the increase in styrene conversion and styrene oxide selectivity with increasing the time until 7–8 h (Fig. 5). The styrene conversion increased from 25 to 60–61% and the styrene oxide selectivity from 60 to 79–80% from 1 to 7–8 h. Further increase in time did not affect the conversion until 12 h, however, the selectivity for styrene oxide decreased successively (65%) along with an increase in the selectivity for benzaldehyde with increasing the time to 12 h. It is noteworthy that in the present study a decrease in styrene oxide selectivity leads to an increase in benzaldehyde along with formaldehyde formation (identification of formaldehyde is discussed later) indicating that styrene oxide undergoes a ring-opening
reaction forming benzaldehyde along with formaldehyde with time. Besides the reaction parameters, the selectivity of the products is strongly influenced by the catalyst and oxidant used. For example, Meng et al. [31] obtained benzaldehyde as the main product using O₂, whereas styrene oxide was obtained as the main product when H₂O₂ was used as oxidant for epoxidation of styrene with copper hydroxyphosphate catalyst. As styrene oxide selectivity was found maximum after 7–8 h, this time has been chosen as the optimized time for further study.

![Graph](image)

**Fig. 5.** Kinetic study over S-8CoYZr catalyst with respect to time for epoxidation of styrene with molecular O₂ at 120°C

### 3.2.4) Effect of catalyst and solvent concentration

The maximum conversion (61%) of styrene and styrene oxide selectivity (80%) was obtained with substrate to catalyst weight ratio of 10:1. The reaction was also carried out in the absence of the catalyst, this showed 15% conversion and 58% selectivity for
Chapter 6 (I)

styrene oxide (Table 2). This indicated the auto-oxidation of styrene under the present reaction conditions. It is interesting that pure ZrO₂ catalyst acted as an inhibitor in the reaction and decreased the styrene conversion as compared to that obtained in the absence of the catalyst, whereas the reaction with Y–ZrO₂ catalyst resulted in the increase, both in the conversion and styrene oxide selectivity due to the availability of oxygen vacancies that accelerate the oxidation reaction. Similar inhibiting results were observed by Opre et al. [32] for hydroxyapatite [HAp] catalyst during the epoxidation of styrene using molecular O₂ whereas better results were obtained with Co–HAp catalyst.

It is well known that the solvent plays a crucial role in the epoxidation reactions; these are reported [16,18,32] to perform well in the presence of alkyl amide solvents with molecular O₂. Among the alkyl amide solvents, DMF is reported to yield the higher epoxide [32].

We have studied the reaction in the absence and in the presence of selected concentrations of DMF (Fig. 6). The low concentration of DMF (5 ml) resulted in lower conversion (54%) and selectivity (64%). On increasing the DMF concentration to 10 ml, we found that both conversion and selectivity increased to 61 and 80%, respectively. However, on further increase in DMF concentration to 20 ml, styrene conversion was decreased significantly to 27% with a slight decrease in selectivity (77%) and the value remained steady with a further increase in DMF concentration to 30 ml. It may be explained that proper dispersion of a solid catalyst was not possible in low solvent concentrations leading to lower activity. On the other hand, an increased concentration of the solvent leads to less availability of substrate molecules to the active sites of the solid
catalyst. In the present study, 10 ml of DMF solvent was found to be sufficient for proper dispersion of a solid catalyst, yielding maximum conversion and selectivity.

The reaction carried out in the absence of DMF solvent was observed to show a slightly lower conversion of styrene (57%), however, with predominant formation of benzaldehyde along with formaldehyde. We have checked the formation of gaseous products like CO$_2$ by collecting the outlet gas in limewater and also by GC analysis, but nothing could be detected even by doing the reaction with a high amount of styrene (4 g). No formation of formaldehyde could be detected by GC or GC–MS analysis. Therefore, to confirm the presence of formaldehyde, we performed a resorcinol ring test, wherein the addition of aqueous (1%) resorcinol and 5–6 drops of conc. H$_2$SO$_4$ to the reaction mixture formed a reddish brown ring along with the white flocculent precipitate underneath, which diffused upward. The formation of reddish brown ring along with the white

![Fig. 6](image_url). Effect of concentration of DMF solvent over S-8CoYZr catalyst on epoxidation of styrene with molecular O$_2$
flocculent precipitate confirmed formaldehyde in the presence of benzaldehyde, otherwise benzaldehyde forms a yellow ring and formaldehyde forms a violet one. Formation of benzaldehyde along with formaldehyde has also been observed by others [17,33,34]. Hulea and Dumitriu [33] have observed the predominant formation of benzaldehyde along with formaldehyde over mesoporous Ti-MCM-41 and Ti-beta, which may be formed either by styrene oxide or by direct oxidative cleavage of the styrene side chain double bond by H₂O₂. Ghosh et al. [34] have also observed the higher selectivity of benzaldehyde over OMS-2 (manganese oxide octahedral molecular sieves) with TBHP and have shown the possibility of formaldehyde as the other product, which could not be observed in GC–MS analyses.

The results clearly exhibited the role of DMF in the formation of styrene epoxide during the epoxidation reaction of styrene. The reaction proceeds through two different routes in the presence and absence of DMF over sulfated CoY–ZrO₂ based catalyst (Scheme 1). It is reported that DMF associates with tetrahedral coordinated Co(II) sites and activates the O₂[17]. Therefore, interaction of DMF with the catalytic sites and styrene molecule favored the formation of styrene oxide, whereas in the absence of DMF formation of benzaldehyde occurred through the second route.

**Scheme 1.** Epoxidation of styrene via two different routes in the presence and absence of DMF solvent and in the presence of water over S-8CoYZr catalyst using molecular O₂.
3.2.5) Effect of water and calcination temperature

The reaction carried out in the presence of water (1ml) did not affect the styrene conversion significantly (55%) but the predominant formation of benzaldehyde along with formaldehyde was observed (Table 3). This result was in contrast with the studies reported by others [17,35]. The effect of water molecules present in the reaction medium was found to enhance the catalytic effect of Co-exchanged zeolite-X [17] and hydrotalcite [35]. The DMF–water mixture in zeolite-X has resulted in the relocation of Co(II) ions so that more ions were available to substrate molecule at the accessible sites of the catalysts [17]. In Co-exchanged hydrotalcite [40] the catalytic activity was due to improved dispersion of Co-complex in the hydrotalcite host in the presence of DMF–water mixture. However, in the present study selective formation of benzaldehyde indicated that oxidation of styrene with O$_2$ over sulfated CoY–ZrO$_2$ catalyst occurred through a different route in the presence of water molecules (Scheme 1). Water molecules may occupy the catalytic sites and thus DMF molecules may not get the chance to interact with the catalytic sites and therefore the formation of benzaldehyde occurred through the second route.

The temperature, at which the catalyst is calcined, before undergoing any reaction, significantly influences its acidity. Fig. 7 shows the effect of calcination of the catalyst at different temperatures. The catalyst calcined at 400°C for 4 h showed 54% styrene conversion and 62% styrene oxide selectivity. The increase in conversion and selectivity was observed with an increase in calcination temperature from 400 to 600°C. The catalyst calcined at 600°C showed maximum styrene conversion (61%) and styrene oxide selectivity (80%). However, further increase in calcination temperature to 700 and
800°C resulted in the successive decreased in both conversion (61–40%) and selectivity (80–68%).

The surface acidity, i.e., acid sites concentration, is important for the catalytic activity, which in turn significantly depends on the sulfur content of the samples. Therefore, a loss in sulfur content with increasing calcination temperature resulted in a significant loss in the surface acidity, as evident from Table 1, thus in the catalytic activity of the samples. Furthermore, DR studies of S-8CoYZr also showed the absence of tetrahedral Co(II) in the sample calcined at higher temperature of 700 and 800°C, thus resulting in the decrease in styrene conversion and selectivity.

Fig. 7. Effect of calcination temperature of catalyst (S-8CoYZr) on epoxidation of styrene with molecular O₂.
3.2.6) Reusability studies of S-8CoYZr Catalyst

The spent catalyst was recovered from the reaction mixture, washed, dried, activated at 450°C and was studied for further reaction cycles under the similar reaction conditions. The regenerated catalyst showed a slightly lower conversion (54%), however with similar styrene oxide selectivity (81%) as compared to the fresh catalyst. The conversion remained steady through the next three reaction cycles without affecting the styrene oxide selectivity (Table 4).

The DR spectrum of used catalyst was recorded after each reaction cycle and was compared with that of fresh catalyst. The spectra presented the similar spectral bands of Co(II) ions in UV and visible region to those of the fresh catalyst (Fig. 8).

Table 4: Epoxidation of styrene over sulfated (S-8CoYZr) catalyst after different reaction cycles.

<table>
<thead>
<tr>
<th>Reaction Cycle</th>
<th>Styrene conversion (%)</th>
<th>Styrene oxide</th>
<th>Benzaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>61</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>II</td>
<td>53</td>
<td>81</td>
<td>19</td>
</tr>
<tr>
<td>III</td>
<td>54</td>
<td>81</td>
<td>19</td>
</tr>
<tr>
<td>IV</td>
<td>54</td>
<td>81</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 4: Epoxidation of styrene over sulfated (S-8CoYZr) catalyst after different reaction cycles.

*Reaction conditions: Temp. = 120 °C, time=7h, styrene=1g, catalyst = 0.1 g, DMF = 10 ml, Tridecane (internal standard) = 0.1 g, O₂ flow =7ml min⁻¹*
3.3) Reaction mechanism

The mechanism of styrene epoxidation by O₂ over sulfated Y–ZrO₂ based catalysts is not completely understood; however, it seems that in pure Y–ZrO₂ catalysts the oxidation occurs due to the oxygen vacancies because of the doping of Y³⁺ to Zr⁴⁺ lattice. Co-complexes are well known to bind and activate oxygen forming Co(III)–(O²⁻) species. On the other hand sulfation enhances the acid strength of Zr⁴⁺ ions and activates the O₂. DMF also associates with tetrahedrally coordinated Co(II) sites and activates the O₂. DMF also associates with tetrahedrally coordinated Co(II) sites and activates the O₂. DMF adduct, formed by the interaction of DMF with the catalytic sites, may give rise to epoxide formation, whereas, in the absence of DMF, no adduct is formed and the predominant formation of benzaldehyde along with formaldehyde occurs through second route. In the presence of water, water molecules cover the catalytic sites and thus the interaction of DMF molecules with the catalytic sites did not occur, thus resulting in the formation of benzaldehyde. Calcination at higher temperature decreases the sulfur
content of the catalyst and also deactivates the tetrahedral Co(II) species thus decreasing the activity of the catalyst. No conversion of styrene was found by the addition of free-radical scavenger hydroquinone over S-YZr and S-CoYZr (Table 3), which confirms the formation of free-radical active oxygen species.

4. Conclusions

A number of non-sulfated and sulfated Y–ZrO₂ based catalysts including Co- and Fe-doped Y–ZrO₂ catalysts were synthesized by the sol–gel technique and were studied for liquid phase epoxidation of styrene using molecular O₂ in the presence of DMF solvent and in the absence of any sacrificial reductant. All catalysts showed styrene oxide and benzaldehyde as two major products. The reaction studied in the absence of DMF solvent or in the presence of a small amount of water strongly affects the styrene oxide selectivity, resulting in benzaldehyde formation predominantly. Sulfated Co–Y–ZrO₂ showed higher styrene conversion (61%) having 80% styrene oxide selectivity due to the combined effect of sulfate species along with tetrahedral Co(II). The addition of sulfate species to enhance the surface acidity and thus the catalytic activity of Y–ZrO₂ based catalysts towards styrene oxidation plays a significant role compared to other structural and textural properties such as amorphous or crystalline nature, surface area and pore volume of the catalysts under the reaction conditions studied. Thermally regenerated catalysts showed almost similar conversion (54%) without affecting the selectivity for styrene oxide (80%) till three reaction cycles.
Chapter 6 (I)

5. References


