Chapter 6 (II)

Microwave-assisted Epoxidation of Styrene
with Molecular $O_2$ over Sulfated Co-Yttria
Stabilized Zirconia Solid Catalyst
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1. Introduction

Epoxidation of styrene is a field of great interest as styrene oxide is an important organic intermediate for fine chemicals and pharmaceuticals. Besides the use of conventional thermal heating for the syntheses purposes, microwave irradiation has been employed for a number of organic syntheses to reduce the reaction time and to increase the selectivity and yields of desired products. However, studies on oxidation of styrene/alkenes with solid catalysts using microwave irradiation are few [1,2]. Balu et al. [1] obtained higher conversion (>99%) of styrene in reduced time (30 min) under microwave irradiation using mesoporous Ti-silicates catalyst and H$_2$O$_2$ as an oxidant as compared to conventional heating (90% conversion at 100°C and 24 h), but selectivity for styrene epoxide was lower (20%). Pillai et al. [2] used a hydrotalcite solid base catalyst with H$_2$O$_2$ oxidizing agent and acetonitrile solvent for olefin oxidation and achieved 62% yield of styrene epoxide. Yadav et al. [3] studied the kinetic modeling of microwave-assisted chemoenzymatic epoxidation of styrene and found that enhanced collision of molecules under microwave irradiation increased the entropy of the system.

In the previous chapter 6 (I), we have studied the liquid phase epoxidation of styrene over Y–ZrO$_2$ based solid catalysts with molecular O$_2$ in the presence of DMF as solvent, wherein we could obtain the maximum 61% styrene conversion and 80% styrene oxide selectivity at 120°C after 8 h with sulfated Co–Y–Zr catalyst. In the present chapter, part (II), we have studied the microwave-assisted epoxidation of styrene using molecular O$_2$ in DMF over sulfated Co–Y–Zr catalyst, which showed maximum styrene
conversion and styrene oxide selectivity. The aim of the present study is to enhance styrene conversion and oxide yield in reduced time and temperature under microwave irradiation. To the best of our knowledge, this is the first report of microwave assisted epoxidation of styrene using molecular O$_2$ over sulfated Co–Y–ZrO$_2$ solid acid catalyst.

2. Experimental

2.1 Catalyst synthesis and characterization

Sulfated Co–Y-doped ZrO$_2$ catalyst was prepared by the sol–gel technique followed by calcination at 600°C for 4h as described in previous chapter 6, part (I). The resulting violet colored powder was designated as S-8CoYZr. The structural, textural, morphological and acidic characterization of the catalyst are described in previous chapter 6, part (I).

2.2 Catalytic activity: Microwave-assisted epoxidation of styrene with molecular O$_2$

Microwave-assisted epoxidation of styrene with molecular O$_2$ was carried out in a Microwave system (MAS II, China) consisting of continuous microwave non-pulsed power supply, advanced IR temperature sensor and uniform temperature throughout the cavity. The system was programmed for six steps (30 min/step) at 120°C temperature for 3 h. Typically, a 50-ml three necked round bottom flask equipped with an efficient water condenser was kept at a constant temperature using a non-pulsed power supply (400 W). Then styrene (10 mmol), solvent (10 ml) and catalyst (100 mg, pre-activated at 450°C for 2 h) were added to the flask. Tridecane (0.1 g) was used as an internal standard. O$_2$ was bubbled at atmospheric pressure into the reaction mixture at the rate of 10–12 ml min$^{-1}$. The reaction mixture was magnetically stirred at 1500 rpm. After 3 h of reaction, the liquid organic products were quantified by a gas chromatograph (Hewlett Packard-HP)
6890) fit-ted with a capillary column (HP-5, 30 m). Reaction products were also confirmed by analyzing the reaction mixture with gas chromatograph-mass spectrometer (GC–MS, Shimadzu GCMS-QP-2010) having MS in the EI mode with a 70-eV ion source. The conversion was calculated as described in chapter 6, part (I) and finally 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

3. Results and discussion

3.1 PXRD studies

The catalyst was amorphous in nature after calcination at 600°C (Fig. 1). The amorphous nature of the catalyst was due to the higher amount of sulfur (15.9 wt. %) (Table 1) present in the sample as sulfate ions increase the crystallization temperature of zirconia [4].

![Figure 1. PXRD of S-8CoYZr after calcination at 600 °C](image-url)
3.2 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance studies demonstrated that the pink colored (uncalcined) S-8CoYZr catalyst has a band at 504 nm, which was attributed to octahedral coordination of Co(II). The sample after calcination at 600°C exhibited three bands at 531, 582 and 629 nm (Fig. 2) along with a change in color from pink to violet. This indicated a change in Co(II) coordination from octahedral to tetrahedral. The band at 531 nm was attributed to octahedral and 629 and 582 nm were of tetrahedral coordination of Co(II) [5].

![Figure 2: Diffuse reflectance spectra of S-8CoYZr before (as such) and after calcination at 600°C](image)

3.3 Total Surface Acidity

Among all the sulfated samples, S-8CoYZr showed the highest surface acidity (8.21 mmol/g) (Table 1).

3.4 Textural Properties

The S-8CoYZr catalyst showed poor textural properties in terms of very low surface area and pore volume (Table 1, which is attributed to the filling of pores by
sulfate species making them inaccessible for nitrogen gas adsorption, resulting in a low surface area and pore volume.

Table 1: Characterization of S-8CoYZr-600

<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>S-8CoYZr-600</td>
<td>Amorphous</td>
<td>15.9</td>
<td>8.21</td>
<td>3.85</td>
<td>0.011</td>
<td>137</td>
</tr>
</tbody>
</table>

3.5 Microwave-assisted epoxidation of styrene with molecular O₂

The results of the epoxidation of styrene with molecular O₂ at different temperatures (100–120°C) under microwave irradiation (at 400 W) are shown in Fig 3a and b. The catalyst yielded two major products, styrene oxide and benzaldehyde, as confirmed by GC-mass of the reaction mixture. The kinetic study carried out at 100 and 120°C showed that the maximum selectivity for styrene epoxide (81–82%) was achieved at 120 °C after 2 h and remained steady till 3.5 h; whereas, the conversion increased till 3 h. After 3 h at 120°C, 62% conversion with 82% selectivity was obtained (Fig 3b). The similar conversion (61%) and selectivity (80%) was obtained for epoxidation of styrene with molecular O₂ by conventional heating at 120 °C after 8 h in chapter 6, part (I). In the present study, similar conversion of styrene and epoxide selectivity was obtained in reduced time (3 h) at the same temperature, i.e., 120°C under microwave irradiation. However, enhancement in yield or reduction in temperature could not be achieved under the present reaction conditions using microwave irradiation. By decreasing the temperature to 100°C (Fig 3a), similar selectivity for styrene oxide (81%) was found in 2 h but conversion of styrene was lower (47%). By extending the reaction time to 3–4 h, the conversion increased maximum to 50% and then remained steady.
The increase in styrene oxide selectivity (Fig 3a and b) with increasing time, indicated the participation of DMF in the epoxidation of styrene oxide as also observed by others [6,8]. The interaction of DMF with the active catalytic sites and the substrate molecule may enhance the desorption of the product molecule and thus favored the formation of styrene oxide.

**Fig. 3.** Microwave epoxidation of styrene with molecular O$_2$ over S-8CoYZr catalyst at 400W at (a) 100 °C and (b) 120 °C.

We have also studied the effect of rate of increase in temperature by increasing the microwave power from 400 to 800 W. By increasing the microwave power from 400 to 800 W, styrene conversion was slightly lower (58%), however, selectivity for styrene oxide was significantly reduced from 81% to 68% along with the increase in benzaldehyde (23%), and the formation of styrene glycol (9%) (Table 2). Therefore, higher microwave power did not favor the formation of styrene oxide.
To achieve the enhanced conversion and/or selectivity, the epoxidation of styrene with molecular O\textsubscript{2} was also carried out using variable concentrations of DMF. The results (Fig. 4) showed that an enhancement in selectivity (90–91\%) for styrene oxide was achieved using the higher concentration of DMF (20–30 ml). However, the conversion of styrene was significantly decreased from 62\% to 37\% and 22\% by increasing the DMF concentration from 10 to 20 and 30 ml, respectively.

**Table 2:** Effect of microwave power on epoxidation of styrene with molecular O\textsubscript{2} over S-8CoYZr catalyst.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Microwave power (W)</th>
<th>% Conversion</th>
<th>% Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Styrene oxide</td>
</tr>
<tr>
<td>400</td>
<td>61</td>
<td>81</td>
</tr>
<tr>
<td>800</td>
<td>58</td>
<td>68</td>
</tr>
</tbody>
</table>

Reaction conditions: temp: 120°C, time: 2 h, styrene: 1 g, DMF solvent = 10 ml, catalyst: 100 mg, tridecane: 0.1 g, O\textsubscript{2} flow = 10–12 ml min\textsuperscript{-1}

It is noteworthy that when the similar reaction was carried out under conventional thermal heating in chapter 6, part (I), we obtained decrease in both styrene conversion (from 61\% to 27\%) and styrene oxide selectivity (from 80\% to 77\%) with an increase in DMF concentration from 10 to 20 and 30 ml. It showed that the polarity of DMF plays an important role in epoxide selectivity under microwave irradiation. The absorption of microwave energy by polar molecules or polar transition state intermediates formed during the course of reaction results in higher selectivity of styrene oxide. To the best of our knowledge this is the highest styrene oxide selectivity reported using a solid acid catalyst under microwave-assisted oxidation of styrene. However, the lower conversion of styrene may be attributed to the dilution effect by increasing the solvent concentration,
which resulted into less interaction of the reactant molecules with the active sites of the catalyst.

![Figure 4: Effect of DMF concentration on conversion and selectivity for microwave-assisted epoxidation of styrene with molecular O\textsubscript{2} over S-8CoYZr catalyst](image)

Besides DMF, other alkyl amide solvents like dimethyl acetamide (DMA) and dimethyl sulphoxide (DMSO) and nitrobenzene (NB) were also studied under the similar reaction conditions (Table 2). DMA resulted in higher styrene conversion (70%) but lower styrene oxide selectivity (40%) along with the formation of higher amount of methyl acetamide (53%). Though, DMSO also showed higher styrene conversion (68%) but benzaldehyde (51%) and other side products such as disulphide dimethyl (14%), 2,4-dithiopentane (10%), acetophenone (12%) and 1-phenyl 1-propanone (13%) were found without any formation of styrene oxide (Table 3). Nitrobenzene showed lower styrene conversion (22%) and oxide selectivity (18%); and higher selectivity for benzaldehyde (60%) along with the formation of phenyl acetaldehyde (22%). These results indicated
that DMF is a suitable solvent for epoxidation of styrene using O₂ as oxidant under microwave irradiation.

**Table 3:** Effect of different solvents on microwave-assisted epoxidation of styrene with molecular O₂ over S-8CoYZr catalyst.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Styrene conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Styrene Oxide</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>37</td>
<td>90</td>
</tr>
<tr>
<td>Dimethyl acetamide</td>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>22</td>
<td>18</td>
</tr>
</tbody>
</table>

*Reaction conditions: power = 400 W, temp. = 120°C, time = 3 h, styrene = 1 g, solvent = 20 ml, catalyst = 0.1 g, tridecane = 0.1 g, O₂ flow = 10–12 ml min⁻¹, SG=styrene glycol, MA = methyl acetamide, PA = phenyl acetaldehyde.³ Disulphide dimethyl (14%); 2,4-dithiopentane (10%); acetophenone (12%) and 1-phenyl 1-propanone (13%)

4. **Conclusions**

The microwave (400 W) assisted styrene oxidation reaction with molecular O₂ over sulfated Co–Y-doped ZrO₂ solid catalyst resulted in similar conversion and styrene oxide selectivity in reduced time as compared to conventional thermal heating. Higher microwave power (800 W) decreased the oxide selectivity along with the formation of styrene glycol as side product. The solvent and its concentration play an important role in the selectivity of styrene oxide during the oxidation under microwave irradiation. Among the solvents studied, DMF (20 ml) yielded maximum oxide selectivity (90–91%). From the present study, it is obvious that the microwave application is advantageous in reducing the reaction time and thus conserving energy.
5. References


