Chapter 4

PALLADIUM SUPPORTED ON STRONTIUM FLUORIDE: SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY FOR ALCOHOLYSIS OF EPOXIDES
Abstract

Palladium supported on strontium hydroxyl fluoride has been synthesized by one-pot fluorolytic sol-gel method. The prepared catalyst was characterized by various physicochemical techniques including PXRD, BET-surface area measurements, acidity measurements, SEM and TEM etc. The sol-gel method has led to formation of high surface area (57 m² g⁻¹), mesoporous (pore diameter = 13.0 nm) catalysts with uniform dispersion of Pd nanoparticles of size ~7 nm on surface of strontium hydroxyl fluoride. The catalyst was used for alcoholysis of epoxide to form β-alkoxy alcohols at room temperature. The epoxides were reacted with a range of alcohols under mild reaction conditions. The catalyst could recycle up to three catalytic cycles. The filtration test of catalyst indicated no Pd leaching which confirmed true heterogeneous nature of catalyst. Further the mechanism of alcoholysis was proposed on the basis of products of the catalytic reaction.
4.1. Introduction

Epoxides are resourceful and vital intermediates in organic synthesis and undergo ring-opening reactions to give β-substituted compounds with a variety of nucleophilic species [1]. Epoxide undergoes a variety of ring-opening reactions to give β-amino alcohols [2], 1,2-diacetates [3], carbonyl compounds [4], diols [5], β-alkoxy alcohols [6], and β-alkoxy sulfides [7]. These are convenient, practical and widely employed strategies for the synthesis of important classes of intermediates in organic chemistry. The opening of epoxides with alcohols is among important transformation in the synthesis of β-alkoxy alcohols which are mainly used as valuable organic solvents, versatile synthons, and intermediates [8].

A variety of organic reactions that are catalyzed by Brønsted acids such as H$_2$SO$_4$, HCl, HNO$_3$, CH$_3$COOH, etc. or Lewis acids like AlCl$_3$, TiCl$_4$, FeCl$_3$, ZnCl$_2$, etc. have been gradually replaced by heterogeneous catalysts with more efficiency [9]. The conventional minerals acids or bases have been used for alcoholysis of epoxides, which resulted in the formation of polymerized products with low regioselectivity [10]. The use of conventional mineral acids in industrial processes is still widespread, leading to large amounts of inorganic wastes and often imposing drastic reaction conditions.

Various catalysts have been employed to accomplish this transformations including Lewis acids such as FeCl$_3$ [11], Cu(BF$_4$)$_2$·nH$_2$O [12], InCl$_3$ [13], Mg(HSO$_4$)$_2$ [14] and heterogeneous catalysts like polymer supported FeCl$_3$ [15] and AlPW$_{12}$O$_{40}$ [16]. Recently, the use of triflates Yb(OTf)$_3$ [17] and perchlorates Fe(ClO$_4$)$_3$ [18] have been reported along with other catalysts such as Cp$_2$ZrCl$_2$ [19], K$_5$[CoW$_{12}$O$_{40}$]·3H$_2$O [20], CBr$_4$ [21], tin(IV)porphyrinato trifluoromethanesulfonate [22], Amberlyst-15 [23] for the alcoholysis of epoxides. Although there are currently a number of methods available for epoxide ring opening, they have one or more disadvantages, such as long reaction time, high catalyst loading, high reaction temperature, tedious method of catalyst synthesis, and low selectivity. However in spite of high catalytic activity, perchlorates and triflates are less favored because of their explosive and expensive nature.

The use of harsh reaction conditions is necessary owing to poor nucleophilicity of alcohols, which led to decrease in regioselectivity of product [24].
Furthermore, a significant and important progress has been made in the development of efficient catalytic methods which are successful under mild conditions [25].

The novel nanoscopic partially hydroxylated inorganic fluoride materials with bi-acidic (Lewis/Brønsted) properties were developed for catalytic applications [26]. The materials were synthesized using classical sol–gel route from metal alkoxide via fluorination with aqueous/nonaqueous HF which led to high surface area metal fluorides [27]. These types of catalysts have been already applied successfully for various catalytic applications viz. synthesis of (all-rac)-[α]-tocopherol [28], Friedal-Crafts reaction [29], Suzuki coupling reaction [30], synthesis of menthol [31], synthesis of vitamin K-1 and K-2 chromanol [32], oxidation of ethylbenzene [33], dehydrohalogenation of 3-Chloro-1,1,1,3,-tetrafluorobutane [34], catalytic C-H bond activation [35] and glycerol acetylation [36].

Recently, the palladium supported catalyst was used for phenolysis of epoxides at high temperature in presence of bases [37]. The Pd supported on alkaline earth metal fluorides are known for its duel (acidic/basic) properties. These properties play an important role in determining not only activity but selectivity of the catalytic reactions. Therefore, the study of synthesis and characterization of palladium supported strontium fluoride and its catalytic activity for alcoholysis of epoxides has been described in this chapter.

4.2. Experimental

4.2.1. Materials

All chemicals were purchased from Aldrich Chemical Co. USA and used as received. Hydrofluoric acid (71% aqueous solution) and solvents were procured from Merck Chemicals, Germany and used as obtained.

4.2.2. Catalyst synthesis

Cautions: 1. HF is a highly toxic and irritant compound causing severe burns if it comes in contact with the skin.

2. Strontium is highly reactive with methanol to generate hydrogen hence the rate of reaction need to be controlled by keeping reaction flask in ice bath.
Catalyst preparation was carried out under inert atmosphere of argon using standard Schlenk technique. In 250 mL round bottom flask, metallic strontium (2.103 g, 24 mmol) was treated with dry methanol (300 mL) at room temperature for 16 h in Schlenk flask to form strontium methoxide solution. A stoichiometric amount (Sr/F: 1/2) of 71% aqueous solution of hydrofluoric acid (5.3 mL, 48 mmol) was added to the solution of strontium methoxide followed by the addition of alcoholic solution of palladium acetate (0.630 g, 1 wt% loading of Pd metal, dissolved in 15 mL of methanol). This solution turned into a grey colored gel which was kept for 16 h for ageing. Then the grey gel was dried under vacuum at room temperature and 70 °C to remove solvents (methanol and water). The solid product was further calcined at 250 °C for 5 h. The prepared catalyst is referred hereafter as Pd-SrF$_2$-71 indicating 71% aqueous concentration of HF used for synthesis.

4.2.3. Catalyst characterizations

The Pd-SrF$_2$-71 was characterized using various physicochemical techniques as mentioned in chapter 2A, section 2A.2.6.

4.2.4. Typical procedure for catalytic reaction

In a sample tube equipped with a magnetic needle, an epoxide (1.0 mmol), alcohol (2.0 mL) and catalyst (10 wt % with respect to epoxide) was added. The reaction mixture was stirred at room temperature for the given time. The progress of the reaction was monitored by thin layer chromatography (TLC) and gas chromatography (GC). After the completion of the reaction the catalyst was separated by filtration and washed with alcohol and diethyl ether. The combined organic fractions were dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The reaction was monitored by gas chromatographic analysis using Agilent 6890 Gas Chromatograph equipped with a HP-5 dimethyl polysiloxane capillary column (60 m length, 0.25 mm internal diameter, 0.25 µm film thickness) with flame ionization detector. Products were confirmed by comparison with GC spectra of the authentic samples. Further the structure was confirmed by FTIR (Nicolet Nexus spectrometer equipped with DTGS detector), $^1$HNMR (Bruker AC 200, 200MHZ spectrometer) spectral analysis and matched with the literature (only for representative reaction alcoholysis of cyclohexene oxide, styrene oxide and epichlorohydrin using ethanol).
4.2.5. Procedure for catalytic recycle study

To study the recyclability of the catalyst, after completion of the first reaction, the catalyst was separated using centrifugation followed by filtration through Whatmann filter paper (no. 1), washed with ethanol (5 mL X 3 times), and finally dried at 80 °C for 30 min. A fresh charge of reactants was taken with the dried catalyst and subjected under the similar reaction conditions. The same procedure was repeated for successive three catalytic run with same catalyst.

4.2.6. Procedure for filtration experiment study and ICP analysis

To verify the Pd leaching in the reaction mixture the filtration test was carried out at room temperature. A 0.05 g of catalyst was stirred with 0.5 g of cyclohexene oxide in 6 mL of ethanol under typical reaction conditions at room temperature. After 1 h, the catalyst was separated from liquid phase by centrifugation followed by filtration through Whatmann filter paper no. 1. Further the reaction was continued without catalyst at room temperature.

The separated catalyst was further tested for ICP-AES analysis to determine Pd content in the catalyst. The ICP-AES samples were prepared using similar procedure as mentioned in chapter 2 section 2A.2.7.

4.3. Results and discussion

4.3.1. Catalyst synthesis

The one pot synthesis of Pd-SrF$_2$-71 catalyst by fluorolytic sol-gel route using aq. HF (71%), resulted in simultaneous fluorolysis and hydrolysis of M-OR bond to form M-F and M-OH bonds respectively [38, 39]. Though the molar ratio of Sr:HF was adjusted to 1:2, the hydrolysis of strontium methoxide becomes competitive with the fluorination due of water content in the fluorinating agent. This reaction generates the composition in which both fluorine and hydroxide are attached to strontium in a solid structure and this led to the formation of strontium hydroxyl fluorides [SrF$_{12-x}$($\text{OH}$)$_x$] material, which upon further addition of methanolic solution of palladium acetate forms Pd-SrF$_{2-x}$($\text{OH}$)$_x$ (henceforth mentioned as Pd-SrF$_2$-71) catalyst as represented in scheme 4.1. The addition of alcoholic solution of palladium acetate led to formation of light red colored gel initially which upon aging turned to light gray. Typically Pd$^{II}$ get partially reduced to Pd$^0$ due to dissolved hydrogen liberated during
the formation of strontium methoxide from metallic strontium to give gray color to the gel. In contrast to the non-aqueous sol gel route which results in the formation of clear sols and transparent gels, the aqueous route results in opaque gels of grey color due to presence of partially reduced palladium nanoparticles [40]. The bulk and surface structure of this material was characterized using various physicochemical techniques.

![Scheme 4.1](image)

**Scheme 4.1:** Schematic representation for sol-gel synthesis of Pd-SrF<sub>2</sub>-71 catalyst.

### 4.3.2. PXRD

The PXRD pattern of the prepared sample is shown in fig. 4.1. The diffraction peaks can be indexed as the peak corresponding to metal fluorides and metal hydroxides on comparison with strontium fluoride (JCPDS 06-0262) and strontium hydroxide (JCPDS 27-847).

![Figure 4.1](image)

**Figure 4.1.** PXRD pattern of Pd-SrF<sub>2</sub>-71 catalyst.

Furthermore, PXRD showed broad peaks which may corresponds to strontium fluoride and sharp peaks to strontium hydroxide. Additionally few less intense peaks
were observed, these peaks indicates the formation of mixed phases of strontium hydroxyl fluorides. However no diffraction for Pd\textsubscript{111} was detected because of very low content of Pd with high order of dispersion of Pd particles over the surface of catalyst.

4.3.3. FTIR

The FTIR spectrum of the Pd-SrF\textsubscript{2}-71 catalyst showed of the bands at 3450.1, 3007, 1631.5, 1402, 1083, 742.7, and 484.1 cm\textsuperscript{-1} (fig. 4.2). The high intense bands at 484.1 and 742.7 cm\textsuperscript{-1} can be related to v(Sr-F) and v(Sr-O) respectively. The bands around 3450 and 1650 cm\textsuperscript{-1} corresponds to presence of surface hydroxyl groups or moisture. The band at 3007 and 1083 cm\textsuperscript{-1} observed due to v(C-H) and v(C-O) stretching vibrations could be due to hydrocarbon residue in prepared catalysts. The presence of Sr-O and O-H band confirms the formation of partially hydroxylated strontium fluorides catalyst in the final catalyst.

![FTIR spectrum of Pd-SrF\textsubscript{2}-71 catalyst](image)

**Figure 4.2.** FTIR spectrum of Pd-SrF\textsubscript{2}-71 catalyst

4.3.4. BET surface area

Nitrogen sorption studies were performed to study the surface area, pore diameter and pore volume (Fig. 4.3). The isotherms showed type IV character typical for mesoporous materials with a H1 type hysteresis loop and porous texture. The BET surface area and total pore volume of the catalyst was found to be 57 m\textsuperscript{2} g\textsuperscript{-1} and 0.11 cc.g\textsuperscript{-1} respectively.
Typically the surface area of Pd-SrF$_2$-71 was observed to be intermediate between metal fluorides from same group in periodic table like Pd-MgF$_2$-71 (140 m$^2$g$^{-1}$) and Pd-BaF$_2$-71 (8 m$^2$g$^{-1}$) prepared under identical conditions. The average pore size was determined using Barrett-Joyner-Halenda (BJH) analysis and found to be 13.1 nm which confirms the mesoporous nature of the catalyst.

### 4.3.5. Acidity measurements

**A. Ammonia- Temperature programmed desorption (NH$_3$-TPD)**

The total acidity as well as the strength of acidic sites on the surface of the catalysts was determined by ammonia-temperature programmed desorption (NH$_3$-TPD) technique as shown in fig. 4.4.
The NH₃ desorption studies indicated the presence of weak, moderate and strong acidic sites with peak maxima corresponds to 111, 276, and 386 °C respectively. Also the total acidity of the catalyst was found to be 0.151 mmol g⁻¹. The total acidity of the catalyst was depends on the degree of fluorination as well as on the nature of the metal alkoxide. Normally a decreasing trend in the acidity of the metal alkoxide was observed down the group in periodic table.

B. DRIFT Spectroscopy

The type of acidity present on the catalyst surface was studied by DRIFT spectroscopy of adsorbed pyridine (pKₐ = 5.25). The subtracted FTIR spectrum of adsorbed pyridine on Pd-SrF₂-71 surface is shown in fig. 4.5. The FTIR peak at 1445 and 1545 cm⁻¹ shows presence of Lewis and Brønsted acidic sites respectively while the peak at 1490 cm⁻¹ represents presence of both Lewis and Brønsted acidity on the surface of oxide materials in adsorbed pyridine spectrum [41]. Similarly, the bands in the adsorbed pyridine spectrum of Pd-SrF₂-71 are assignable to coordinately bound pyridine [41, 42]. The pyridinium ion (PyH⁺) produced by the reaction of pyridine with Brønsted acid sites showed bands around 1542 and 1640 cm⁻¹. The coordinately bound pyridine on Lewis acid sites shows bands around 1452 and 1610 cm⁻¹. This DRIFT indicated the presence of Lewis and Brønsted acidic sites on the surface of Pd-SrF₂-71 catalyst.

![Figure 4.5. FTIR spectrum of adsorbed pyridine on Pd-SrF₂-71 surface at 100 °C.](image)
4.3.6. XPS

XPS was used to derive surface compositional information of the Pd-SrF$_2$-71 catalyst in fig. 4.6. The montage of survey scan after analysis of Pd-SrF$_2$-71 catalyst is shown in fig. 4.6 - A. The peaks were annotated to the Sr, F, O and Pd with their core levels. The peaks were standardized with respect to carbon peak at 284.6 eV on surface. Due to non-conductive nature of strontium fluoride some charging of sample was observed. In order to determine the effect of the support on the oxidation state of palladium of the as synthesized samples, the region of Pd was studied further (fig. 4.6-B). Palladium showed presence of two oxidation states namely Pd$^0$ and Pd$^{2+}$.

**Figure 4.6.** XPS of the Pd-SrF$_2$-71 catalysts (A) Survey scan and (B) scan for binding energy of palladium species.

The two different values of Pd$^{2+}$ may be due to variable coordination of Pd$^{2+}$ species. The peak at 335.1 corresponds to Pd$^0$ and peaks at 338.9 and 340.4 relates to Pd$^{2+}$ species from palladium acetate and palladium oxide respectively. The ratio of relative abundance (Pd:Pd$^{2+}$) was observed to be 1:2 approximately. The presence of Pd$^0$ can be attributed to partial reduction of palladium acetate in presence of dissolved hydrogen which was produced during catalyst synthesis.

4.3.7. SEM and EDAX

The morphology of Pd-SrF$_2$-71 catalyst was studied by SEM. The representative micrograph of Pd-SrF$_2$-71 is shown in fig. 4.7. It showed the particles of SrF$_2$-71 to be of oval shaped of 1.5- 2.0 μm in length and 0.5-1.0 μm in width. The Pd particles were spread throughout evenly on the strontium hydroxyl fluoride
surface. Further the surface composition of catalyst was also determined by EDAX spectroscopy. The results showed the surface palladium composition to be approximately 1.1 wt%.

![Figure 4.7. SEM image of Pd-SrF$_2$-71 catalyst.](image)

4. 3.8. HRTEM

The Particle size of palladium was determined by HRTEM analysis. The representative micrograph of Pd-SrF$_2$-71 is shown in fig. 4.8. The particle size distribution studied by TEM clearly showed the majority of particles with ~7 nm diameter though the particle size distribution spreads up to 20 nm. The palladium particles were found to be in 111 plane as identified from d spacing (d$_{111}$ = 0.223 nm).

![Figure 4.8. Representative HRTEM image of Pd-SrF$_2$-71 catalyst with SAED pattern.](image)
4.3.9. Catalytic activity for alcoholysis of epoxides

The catalytic activity of Pd-MF$_2$-71 (where, M = Mg, Sr, Ba) was studied for alcoholysis of epoxide at room temperature initially with cyclohexene oxide as model substrate and ethanol as nucleophile (scheme 4.2). The results obtained with various catalysts are given in table 4.1. In absence of catalyst reaction did not take place even after 2 h time (table 4.1, entry 1). Further a series of palladium supported metal fluoride catalysts were evaluated for catalytic reactions. The Pd-MgF$_2$-71, Pd-SrF$_2$-71, Pd-BaF$_2$-71 catalysts showed 43, 100 and 20% conversion respectively (table 4.1, entry 2-4). It is well known that the Lewis acidity of the catalyst decreases from Pd-AlF$_3$ to Pd-BaF$_2$ with increase in basicity [43]. In case of highly acidic catalyst higher conversion has been reported but the higher order of acidity is responsible for decrease in selectivity and generation of byproduct like 1,6-hexandiol. Moreover Pd-BaF$_2$ showed less conversion with 100% selectivity due to its basic nature. In case of Pd-SrF$_2$, the acidic and basic sites were found to be balanced to get optimum conversion and selectivity. The catalytic activity of the Pd-AlF$_3$ was compared which showed 59% conversion under identical reaction conditions (table 4.1, entry 5).

![Scheme 4.2. Alcoholysis of epoxides.](image)

**Table 4.1. Results of alcoholysis of epoxide$^a$**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. $^b$ (%)</th>
<th>Sel. $^b$ (%)</th>
<th>Activity $(\text{mmol h}^{-1} \text{g}^{-1}) \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Pd-MgF$_2$-71</td>
<td>43</td>
<td>93</td>
<td>3.18</td>
</tr>
<tr>
<td>3</td>
<td>Pd-SrF$_2$-71</td>
<td>100</td>
<td>96</td>
<td>7.00</td>
</tr>
<tr>
<td>4</td>
<td>Pd-BaF$_2$-71</td>
<td>20</td>
<td>96</td>
<td>1.27</td>
</tr>
<tr>
<td>5</td>
<td>Pd-AlF$_3$-71</td>
<td>59</td>
<td>80</td>
<td>2.86</td>
</tr>
</tbody>
</table>

$^a$ **Reaction conditions**: Cyclohexene oxide: 1 mmol; Ethanol: 2 mL; Catalyst: 0.01 g (10 wt%, 1.0 wt% of Pd loading); Temperature: RT (27 °C). $^b$ Conv. and Sel. was determined based on GC.
4.3.10. Effects of various reaction parameters

A. Catalyst loading effect

The effect of catalyst loading on alcoholysis of cyclohexene oxide was studied at room temperature in fig. 4.9. The conversion increased with gradual increase in catalyst loading. The 1 wt% catalyst loading gave 9% conversion which was increasing to 70% for 15 wt% loading in 1 h at room temperature. There was marginal decrease in selectivity at high catalyst loading.

![Figure 4.9. Catalyst loading effect using Pd-SrF$_2$-71 catalyst.](image_url)

**Reaction conditions**: Cyclohexene oxide: 5 mmol (0.54 g); Ethanol: 2 mL; Temperature: RT (27 °C). Time: 1 h.

B. Temperature effect

Epoxide ring opening of cyclohexene oxide was studied at various temperatures ranging from room temperature to 70 °C in ethanol with 10 wt% loading of Pd-SrF$_2$-71 catalyst as shown in fig. 4.10. It was observed that with gradual increase in reaction temperature from room temperature (27 °C) to 70 °C, the time for 100% conversion of cyclohexene oxide decreased from 120 to 30 min without much decrease in selectivity. The increase in rate of reaction revealed to increase in rate of intermolecular collision. Although the rate of reaction was higher at 70 °C, room temperature is always preferred. Therefore room temperature was considered as optimum temperature for carrying out further reactions.
C. TIME PROFILE STUDY

The conversion of the cyclohexene oxide increased with increase in reaction time at room temperature in ethanol as shown in fig. 4.11. A virtually linear time-conversion profile has been observed for ethanolation of cyclohexene oxide. The selectivity of the 2-ethoxycyclohexanol decrease to 96% after complete conversion of cyclohexene oxide after 2 h which was found to be constant up to 2.5 h at room temperature.

Figure 4.11. Time profile study using Pd-SrF$_2$-71 catalyst.

**Reaction conditions**: Cyclohexene oxide: 2 mmol (0.196 g); Catalyst (Pd-SrF$_2$): 0.02 g; Ethanol: 2 mL; Temperature: RT (27 °C).
4.3.11. Substrate scope study

After optimizing the reaction conditions for ethanol as a nucleophile with cyclohexene oxide as a model reaction, the applicability of the catalyst to other epoxides and alcohols was evaluated. The reaction of cyclohexene oxide with methanol and ethanol gave 98 and 96% yield respectively (table 4.2, entry 1-2). The reaction of 2-propanol gave lower yield (57%) as compared to ethanol as a nucleophilic source (table 4.2, entry 3). This may be due to the steric effect of two methyl groups, which hinders the reaction site resulting in the lowering of cyclohexene oxide conversion into the desired product. Similar behavior was also observed when the reaction was carried out with t-butyl alcohol which showed 25% yield (table 4.2, entry 4). This observation can be explained by the fact that tertiary butyl alcohol is even more bulky, having three methyl groups which increases the steric hindrance and which lower the activity in nucleophilic substitution reaction.

When benzyl alcohol was used as nucleophile 99% yield was observed (table 4.2, entry 5). Although the steric hindrance in benzyl alcohols is higher than t-butyl alcohol, the higher nucleophilicity may be responsible for increment in the rate of the reaction. Further styrene oxide was used as substrate to check the effect of catalyst on regioselectivity (table 4.2, entry 5-10).

The rate of the reaction was found to be depending on nucleophilicity of the alcohol but also on steric hindrance of epoxide. The yields of β-alkoxyalcohols were decreased from methoxyl to t-butoxyl (92-18%) due to increase in bulkier nature of nucleophile (table 4.2, entry 5-9), which increased to 72% in case of benzyl alcohol (table 4.2, entry10). The reaction of epichlorohydrin with methanol and ethanol showed 89 and 78% yields respectively (table 4.2, entry 11-12). When bulkier alcohols like 2-propanol and 2-methyl-2-propanol was used as nucleophile, the yield decreased to 53 and 36% respectively (table 4.2, entry 13-14) which again increased to 65% with benzyl alcohol as nucleophile (table 4.2, entry 15). Remarkably formation of a single regioisomer was observed in all the cases. This formation of stable intermediate in each case led to formation of single regioisomer. In styrene because of formation of stable benzylc carbocation, the reaction follows SN¹ pathway and formed 2 as preferable regio-isomer. In epichlorohydrin, the reaction follows SN² pathway due to attack of nucleophile from backside of ring opening, yielding 3 as preferable regioisomer.
Table 4.2. Substrate scope study using Pd-SrF$_2$-71 catalyst.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxide</th>
<th>Alcohol</th>
<th>Products ratio (2:3)</th>
<th>Yields$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>MeOH</td>
<td>Trans</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>EtOH</td>
<td>Trans</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>i-PrOH</td>
<td>Trans</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>t-BuOH</td>
<td>Trans</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>BnOH</td>
<td>Trans</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>MeOH</td>
<td>100:0</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>EtOH</td>
<td>100:0</td>
<td>73</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>i-PrOH</td>
<td>100:0</td>
<td>49</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>t-BuOH</td>
<td>100:0</td>
<td>18</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>BnOH</td>
<td>100:0</td>
<td>72</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>MeOH</td>
<td>0:100</td>
<td>89</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>EtOH</td>
<td>0:100</td>
<td>78</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>i-PrOH</td>
<td>0:100</td>
<td>53</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>t-BuOH</td>
<td>0:100</td>
<td>36</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>BnOH</td>
<td>0:100</td>
<td>65</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: Substrate: 0.2 g; Catalyst (Pd-SrF$_2$-71): 0.02 g (10 wt% w.r.t. substrate); Alcohols: 2 mL; Temperature: RT (27 °C). Time: 2 h. $^b$ Yields were determined based on GC.

4.3.12. Catalyst recycle study

The recyclability of Pd-SrF$_2$-71 was studied for optimized ring opening of cyclohexene oxide in ethanol under reaction conditions. After completion of the reaction, the catalyst was separated from reaction mixture by centrifugation followed by filtration using Whatmann filter paper no.1. The catalyst was washed with ethanol (5 mL X 2) and acetone (5 mL) and allowed to dry at 80 °C and used it for subsequent catalytic runs. The same procedure was repeated for three times. However even after three runs, the catalyst exhibited excellent activity as shown in fig. 4.12. It implied that the catalytic system can be used even for three cycles without significant loss of activity.
Figure 4.12. Recycle study using Pd-SrF$_2$-71 catalyst.

**Reaction conditions:** Cyclohexene oxide: 5 mmol (0.54 g); Pd-SrF$_2$-71: 0.05 g (10 wt% w.r.t. substrate); Ethanol: 2 mL; Temperature: RT (27 °C). Time: 2 h.

4.3.13. TEM and ICP analysis of recycled catalyst

The TEM image of recycled catalyst after 3$^{rd}$ cycle revealed no agglomeration of Pd on the catalyst surface as shown in fig. 4.13.

Figure 4.13. TEM image of Pd-SrF$_2$-71 catalyst after 3$^{rd}$ catalytic recycle.

The size of Pd nanoparticle was found to be in the same range of 6-8 nm when compared with the fresh catalyst (refer fig. 4.8). There was no decrease in the catalytic activity in successive cycles for alcoholysis of epoxides. Filtration test was used to check the Pd leaching in reaction mixture. It was observed that in absence of
catalyst, no further change in cyclohexene oxide conversion was observed even after additional 3 h which confirms no Pd leaching which were also confirmed by ICP-AES analysis of catalyst. The Pd concentration was found to be 0.986 % before reaction and 0.978% after the reaction. Therefore Pd-SrF₂-71 catalyst acts as true heterogeneous catalytic system.

4.3.14. Possible reaction mechanism

Based on the results obtained during catalytic reactions and by comparison with the literature reports, the mechanism for the alcoholysis of epoxide using Pd-SrF₂-71 catalyst has been proposed in scheme 4.3. In case of styrene oxide, nucleophilic alkoxy group attacks in such a way to produce 2-phenyl-2-alkoxy ethanol. While in epichlorohydrin case, the alkoxy group attacks epoxide ring to get 3-chloro-1-alkoxy-2-propanol as only product. Initially the adsorption of epoxide on surface of catalyst takes place which activates epoxide via partial transfer of electrons of oxygen to empty orbital of oxidized palladium to get intermediate B (Step 1).

![Scheme 4.3. Possible reaction mechanism for regioselective alcoholysis of epoxide using Pd-SrF₂-71 catalyst.](image)

Further attack of nucleophilic oxygen led to open the epoxide ring in two possible ways depending on the nature of alkyl group. In case of electron withdrawing alkyl group, the reaction follows SN₂ pathways to generate intermediate C which undergoes simultaneous C-O bond cleavage and backside attack of nucleophilic O-atom of alcohol followed by proton transfer to produce product 3. In case of electron donating alkyl group, the reaction follows SN₁ pathways to generate...
intermediate carbocation C’ by cleavage of C-O bond. This C’ carbocation intermediate gets stabilized via resonance and inductive effect which undergoes nucleophilic attack by nucleophilic O- atom of alcohol followed by proton transfer to generate product 2. The high regioselectivity is due to stabilization of intermediate on species the catalyst surface and results in two different nucleophilic substitution reactions

4.4. Conclusions

In conclusion, Pd-SrF2-71 proved to be novel and efficient catalyst for room temperature alcoholsysis of epoxide. Due to very less acidic nature of catalyst, it may find application for ring opening of epoxides containing acid sensitive functional groups. The catalyst showed very high regioselectivity which depends on the nature of alkyl group of the substrate. One pot method of synthesis, ease of procedure, high order of recyclability, regioselectivity and mild reaction condition showed a new synthetic applications of heterogeneous metal fluoride supported palladium catalyst in synthetic chemistry.

4.5. References


