5.1. Introduction

There has been an increasing interest in recent years to develop novel solid acid catalysts and modify them for selective synthesis of fine and specialty chemicals. The major types of heterogeneous acid catalysts include zeolites (ZSM-5, H-Beta), mesoporous materials (MCM-41 and SBA-15), clays (montmorillonite K-10), heteropoly acids, anion modified oxides (WO$_3$/ZrO$_2$, SO$_4^{2-}$/ZrO$_2$), functionalized resins (Amberlyst-15) and mixed oxides (SiO$_2$-Al$_2$O$_3$). The above foremost catalysts and their modified forms were well applied in a large number of organic transformations. But still there is a thirst for the chemist to design and develop new class of catalysts which are well competent to the leading ones. It is well known that metal chlorides and their hydroxides are applied as acid and base catalysts respectively. [1, 2] However, metal hydroxychloride, which falls in between metal chloride and its hydroxide, is not well established as a catalyst. Metal hydroxychlorides are well known as minerals found in various parts of the world. One such example is tin(II)hydroxychloride, a mineral known by name abhurite.[3] The crystallographic and mineralogical properties of tin(II)hydroxychloride are well understood but its application is overlooked so far. Its insolubility in water and organic solvents generated a curiosity to study its properties and application as heterogeneous catalyst.

The Prins reaction is an important and well-known carbon-carbon bond forming reaction in organic synthesis. The condensation of olefin with aldehyde leads to the formation of 1,3-dioxanes, 1,3-diols and unsaturated alcohols.[4] The Prins reaction of β-pinene with paraformaldehyde results in the formation of nopol, an unsaturated primary alcohol. Nopol finds wide applications in agrochemical industry as a pesticide and as a fragrance in soap/detergent industries.[5] Nopol was traditionally prepared by the use of homogenous catalysts. [6] But these methods suffer from drastic reaction conditions, low yield and unwanted side products. To overcome these problems several heterogeneous catalysts like Sn-MCM-41, Sn-kenyaite, Sn-SBA-15, sulfated zirconia, Fe-Zn metal
cyanides, Zn-MCM-41, mesoporous iron phosphate, ZnCl₂ impregnated on montmorillonite and Zr-SBA-15 were designed for Prins reaction.[7-14] Most of the above catalysts indicate the requirement of Lewis acidic sites for the selective synthesis of nopol. The use of strong Brönsted acid catalyst usually results in isomerized products.[8]

In the present work, tin(II)hydroxychloride is reported for the first time as heterogeneous acid catalyst. Catalytic properties of tin(II)hydroxychloride were established for Prins condensation of β-pinene with PF to produce nopol. The uniqueness of tin(II)hydroxychloride as an acid catalyst was determined by establishing its physico-chemical properties and comparing with tin hydroxide and tin oxide.

5.2. Results and discussion

5.2.1. Catalytic activity studies

5.2.1.1. Experimental procedure

In a typical reaction procedure, β-pinene (10 mmol), paraformaldehyde (20 mmol), catalyst (0.23 g) and solvent toluene (5 ml) were taken in a 100 ml glass reactor equipped with a reflux condenser and a magnetic stirrer. The mixture was stirred vigorously at atmospheric pressure at a desired temperature and time. After the reaction, the product mixture was analyzed by gas chromatograph (Shimadzu-2041, FID detector) using RTX-5 column. The products were identified and quantified by GC-MS and standards.

5.2.1.2. Prins condensation of β-pinene with PF

The Prins reaction of β-pinene with paraformaldehyde was carried out in liquid phase at 90 °C in the presence of toluene as solvent. The catalytic activities of all the tin based catalysts were tabulated in Table 5.1. The Sn(OH)Cl exhibited high catalytic performance of 98% β-pinene conversion with 99 % nopol selectivity. On the other hand, SnO and SnO₂ showed low conversion of ~ 35%. The Sn₂(OH)₂O showed 3.8 %
conversion and 83% nopol selectivity, much lower compared to Sn(OH)Cl. The by-products are mainly α-pinene, camphene and limonene formed by the isomerisation of β-pinene. The Sn(OH)Cl exhibited good recyclability for the Prins reaction with minimal decrease in activity after 3 recycles as shown in Table 5.1.

### 5.2.1.3. Nature of active sites in Sn(OH)Cl

To correlate the catalytic activity and active sites, XRD, FT-IR and solid state $^1$H MAS NMR of the catalysts were determined. The Sn(OH)Cl, Sn$_2$(OH)$_2$O, SnO and SnO$_2$ prepared under different pH and calcination conditions were characterized by powder XRD. The XRD patterns confirmed the formation of the above tin compounds by identifying respective pure crystalline phases. [15, 16] (Fig. 5.1.)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination Temperature (°C)</th>
<th>Surface area (m$^2$/g)</th>
<th>Conversion of β-pinene (mol %)</th>
<th>Selectivity for nopol (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>--</td>
<td>--</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sn(OH)Cl</td>
<td>180</td>
<td>8</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>SnO$_2$-400</td>
<td>400</td>
<td>9</td>
<td>32</td>
<td>94</td>
</tr>
<tr>
<td>Sn$_2$(OH)$_2$O</td>
<td>180</td>
<td>18</td>
<td>3.8</td>
<td>83</td>
</tr>
<tr>
<td>SnO</td>
<td>300</td>
<td>13</td>
<td>35</td>
<td>96</td>
</tr>
<tr>
<td>SnO$_2$-500</td>
<td>500</td>
<td>16</td>
<td>32</td>
<td>92</td>
</tr>
<tr>
<td>Sn(OH)Cl –R1$^b$</td>
<td>--</td>
<td>--</td>
<td>91.4</td>
<td>96</td>
</tr>
<tr>
<td>Sn(OH)Cl –R2$^b$</td>
<td>--</td>
<td>--</td>
<td>91</td>
<td>97</td>
</tr>
<tr>
<td>Sn(OH)Cl –R3$^b$</td>
<td>--</td>
<td>--</td>
<td>88</td>
<td>94</td>
</tr>
</tbody>
</table>

Reaction conditions: β-Pinene = 10 mmol, Paraformaldehyde = 20 mmol, toluene = 5ml, Catalyst weight = 0.23 g, Temperature = 90 °C, Time = 12 h. $^b$ R = Catalyst recycle.
Chapter 5  Sn(OH)Cl: A novel solid acid catalyst

The FT-IR pyridine adsorption study was used to determine the type of acid sites by the method as reported elsewhere.[4] Initially, we assumed that Sn(OH)Cl possessed Lewis acidity due to the presence of tin. However, the pyridine FT-IR spectra of Sn(OH)Cl clearly indicated the absence of peak due to Lewis acidity at ~1445 cm\(^{-1}\). (Fig.5.2.) Instead, to our surprise, it showed a peak at 1532 cm\(^{-1}\) due to Brönsted acidity. Similar observation was made in case of Sn\(_2\)(OH)\(_2\)O but with less intense peak. On the other hand, SnO and SnO\(_2\) showed minor Lewis acidity. This indicates that the active sites of Sn(OH)Cl and Sn\(_2\)(OH)\(_2\)O are Brönsted acidic whereas for tin oxides, it is Lewis acidic. The area of peak at 1532 cm\(^{-1}\) indicated that, Sn\(_2\)(OH)\(_2\)O possessed about half the amount of Brönsted acidity compared to Sn(OH)Cl. However, Sn\(_2\)(OH)\(_2\)O exhibited very low activity in Prins reaction (3.8 % conversion). This indicated that the strength of acid sites might be different in Sn(OH)Cl and Sn\(_2\)(OH)\(_2\)O. The presence of these Brönsted acid sites could be due to the hydrogen bonded protons which is confirmed by FT-IR and \(^1\)H MAS NMR study.

To understand the difference in the strength of acid sites, FT-IR spectra of Sn(OH)Cl and Sn\(_2\)(OH)\(_2\)O were determined. The FT-IR spectra of Sn(OH)Cl showed broad peaks in the region of 3200 to 3600 cm\(^{-1}\) due to hydrogen bonded -OH groups as shown in Fig. 5.3. The peaks at 975 and 928 cm\(^{-1}\) are assigned to the deformation of -OH groups and that of peak at 623 cm\(^{-1}\) is because of Sn-O stretching. [17] The peaks at 3571 and 3409 cm\(^{-1}\) indicate the presence of non or low hydrogen bonded -OH groups whereas the band at 3296 cm\(^{-1}\) is due to -OH groups involved in strong hydrogen bonding. This different strength of hydrogen bonding might have weakened the -O-H bond to generate Brönsted acidity in these catalysts. Similar hydrogen bonded -OH groups were also found in the FT-IR spectra of Sn\(_2\)(OH)\(_2\)O and therefore it was difficult to distinguish the different strength of hydrogen-bonding between the two.

Hence, further difference in the strength hydrogen bonded protons was evaluated by \(^1\)H MAS NMR. The Sn(OH)Cl exhibited three different types of protons at 6.94, 5.43 and 0.12 ppm whereas Sn\(_2\)(OH)\(_2\)O showed only two peaks at 6.34 and 5.0 ppm. (Fig.5.4)
Fig. 5.1. XRD patterns of tin based catalysts synthesized at different pH and calcination temperature.

Fig. 5.2. Acidity measurements of tin based catalysts by pyridine FT-IR.
Scheme 5.1 Pictorial representation of Brönsted acidity in Sn(OH)Cl and Sn(OH)₂.
The chemical shift region of 3-7 ppm is generally assigned to hydrogen bonded protons. [18] The increase in chemical shift (from 6.34 to 6.94 and 5 to 5.43) for Sn(OH)Cl compared with Sn₂(OH)₂O can be related to the stronger hydrogen bonding between electronegative chlorine atom with vicinal -OH good hydrogen bond acceptors.[19] A strongly polarized character of the metal-halogen bond results in an enhanced partial negative charge on halogen. Such a halogen atom can attract hydrogen atom of -OH group resulting in weakening of O-H bond. The peak broadening in ¹H MAS NMR spectra of Sn(OH)Cl further confirms that the hydrogen atoms are loosely held due to strong hydrogen bonding. This hydrogen bonding between -OH and Cl could be responsible to generate adequate amount of Brönsted acidity to catalyze the Prins reaction with almost complete conversion.

To get more insight into the physicochemical properties of Sn(OH)Cl, thermal and morphological properties were evaluated by TG-DTA, SEM and N₂ sorption techniques. The TG-DTA profile showed weight loss in three steps as shown in Fig. 5.5. The initial weight loss below 210 °C is due to dehydration and between 200-400 °C region can be attributed to a slow dehydroxylation. The substantial weight loss in the range of 400-550 °C is due to volatilization of tin as SnCl₂ and formation of oxide.[16] It is evident that thermal stability of Sn(OH)Cl is around 200 °C and hence can be used as catalyst below this temperature. The SEM images of the Sn(OH)Cl showed the presence of thin plates arranged in spherical particles of average size of 15 μm as shown in Fig. 5.6. The N₂ adsorption measurements of all the tin based catalysts showed a low specific BET surface area (<20 m²/g) as shown in Table 5.1.

5.2.1.4. Influence of reaction conditions

The effect of reaction temperature on β-pinene conversion and nopol selectivity was studied in the range of 70 to 100 °C. The conversion increased with increase of temperature as shown in the Table 5.2. The conversion was too low around 25 % at 70 °C and reached to almost 100% conversion above 90 °C of reaction temperature. The selectivity for nopol was 100 % at 70 °C and reached to 92 % at 100 °C of reaction.
Fig. 5.3. FT-IR spectra of tin based catalysts.

Fig. 5.4. $^1$H MAS NMR spectra of a) Sn(OH)Cl  b) Sn$_2$(OH)$_2$O.
Fig. 5.5. Thermal analysis of Sn(OH)Cl.

Fig. 5.6. SEM images of Sn(OH)Cl.
temperature. The decrease in selectivity with increase of reaction temperature could be due to the isomerization of β-pinene to other side products. The reaction temperature of 90 °C was good enough to get high β-pinene conversion of 98% and selectivity for nopol (~99%) in Prins reaction.

![Image](image.png)

**Fig. 5.7.** a) Pseudo first order kinetics for the conversion of β-pinene over Sn(OH)Cl catalyst at different temperature. b) Arrhenius plot for Prins condensation of β-pinene with paraformaldehyde over Sn(OH)Cl.

The kinetic investigations results revealed a pseudo first order reaction rate dependence with respect to β-pinene concentrations as shown in Fig.5.7a. The results presented in Table 5.2. shows increase of β-pinene conversion with increase in temperature linearly with reaction time (constant $k_1$ increased from $42.5 \times 10^{-4}$ min$^{-1}$ at 70 °C to $86.2 \times 10^{-4}$ min$^{-1}$ at 100 °C). The rate constants calculated at different temperatures at 4 h reaction time are presented in Table.5.2. It is seen that rate constant increases with increase in temperature. The Arrhenius plot provides apparent activation energy of 389.6 KJ/mol or 93.11 Kcal/mol. (Fig. 5.7b.)
Table 5.2. Influence of reaction temperature on Prins condensation reaction

<table>
<thead>
<tr>
<th>Reaction temperature</th>
<th>Conversion (mol %)</th>
<th>Selectivity (mol %)</th>
<th>Rate constant ($10^{-4}$ * min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>24.9</td>
<td>100</td>
<td>42.5</td>
</tr>
<tr>
<td>80</td>
<td>64.5</td>
<td>100</td>
<td>53.1</td>
</tr>
<tr>
<td>90</td>
<td>98</td>
<td>99</td>
<td>61.1</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>92</td>
<td>86.2</td>
</tr>
</tbody>
</table>

Reaction conditions: $\beta$-Pinene = 10 mmol, Paraformaldehyde = 20 mmol, Solvent toluene = 5ml, Catalyst weight = 0.23 g, Time = 12 h.

Fig. 5.8. Influence of a) $\beta$-pinene: PF mole ratio b) Catalyst amount.

The effect of the stoichiometric ratios of $\beta$-pinene with PF on conversion and product selectivity was also studied over Sn(OH)Cl catalyst at a reaction temperature of 90 °C. The molar ratio of $\beta$-pinene with PF was varied in the range of 1-4 and the product distribution at various $\beta$-pinene to PF ratios is shown in Fig.5.8a. The results show
that the conversion of β-pinene increases from 78 to 100 % on varying the molar ratio from 1 to 4. The nopol selectivity was also increased with increase of concentration of PF. The lower selectivity at low concentration of PF (1:1) could be due to insufficient generation of formaldehyde from PF leading to formation of side products by isomerization of β-pinene. The β-pinene: PF mole ratio of 1:2 is good enough to get high conversion and selectivity for nopol.

The influence of catalyst amount on the Prins condensation of β-pinene with PF was studied by taking different catalyst weights with respect to the total weight of the reactant as shown in Fig. 5.8b. As catalyst concentration increased from 6 to 12%, the conversion increased from 69.2 to 99 % and above 12 % of catalyst amount has no effect; the selectivity for nopol almost remained constant for all catalyst concentration. The 12 wt % of catalyst amount was sufficient to give high conversion of β-pinene and nopol selectivity.

![XRD pattern of Sn(OH)Cl](image)

**Fig. 5.9.** XRD pattern of Sn(OH)Cl  a) Fresh catalyst. b) Catalyst after 3 recycles.
5.2.1.5. Recyclability study

Recyclability study was carried out to check the efficient of catalyst, the catalyst was separated by filtration after the reaction, washed with acetone and dried at 120 °C for 12 h followed by activation at 180 °C for 1 h. The dried catalyst was reused for the next cycle. The Sn(OH)Cl exhibited good recyclability for the Prins reaction with minimal decrease in activity after 3 recycles. The XRD pattern of Sn(OH)Cl after 3 recycles matched with that of fresh catalyst indicating the structural integrity of the catalyst. (Fig. 5.9.)
5.3. References