CHAPTER 3
RESULTS AND DISCUSSIONS

3.1 INTRODUCTION

The characterization results obtained by various instrumental techniques such as X-ray diffraction (XRD), BET surface area, UV- Diffuse reflectance spectroscopy (UV-DRS), Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS, Transmission Electron Microscopy (TEM), Atomic Absorption Spectrophotometry (AAS) and X-ray photoelectron spectroscopy (XPS) for all the synthesized catalysts are discussed in this chapter.

3.2 CHARACTERIZATION OF TITANIA AND STRONTIUM TITANATE CATALYSTS

3.2.1 X-Ray Diffraction Studies

The XRD patterns of bare TiO₂, Ni/TiO₂ (0.5%, 1% & 3%) and Ru/TiO₂ (0.5%, 1% & 3%) catalysts are shown in Figure 3.1. All the peaks were identified and indexed using the data available from the Joint Committee for Powder Diffraction studies (JCPDS) and the corresponding planes were indicated. XRD patterns indicate high crystallinity for all the catalysts. The reflections at 2θ = 25.3°, 48.2° and 37.8° confirmed the presence of anatase phase (JCPDS No. 89-4921), the absence of peak at 27.4° and 30.8° confirm that both rutile and brookite phases were absent (Hermann et al 1997).
No observable peaks were obtained for the presence of impregnated metals such as Ni and Ru over TiO$_2$. This may be due to the less amount of loading of these metals over titania (He et al 2010).

The XRD patterns of bare SrTiO$_3$ (ST), (1%) Ni-SrTiO$_3$ (NiST) and (1%) Ru-SrTiO$_3$ (RuST) is given in Figure 3.2. Both bare and metal doped titanates showed sharp and intense XRD peaks indicating high degree of crystallinity. All the X-ray diffraction patterns indicate the presence of single oxide cubic (Pm3m) phase. The sharp peaks at $2\theta = 32.5^\circ$, 46.5$^\circ$, 57.8$^\circ$ & 40.01$^\circ$ corresponding to (1 1 0), (2 0 0), (2 1 1) & (1 1 1) planes confirm the cubic (Pm3m) phase of strontium titanates.
Figure 3.2 XRD patterns of (a) ST (b) NiST and (c) RuST

The patterns match with Joint Committee for Powder Diffraction Studies (JCPDS) file available in the literature (File No: 35-0734) (Battisha et al 2002). Due to the very low level doping (<1 mol %) of Ni/Ru over strontium titanate, separate peaks for their presence were not observed in the XRD patterns of Ni and Ru doped strontium titanate catalysts.

The average crystallite sizes of all the catalysts were calculated by Scherrer’s formula (Equation 3.1) and given in Table 3.1.

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(3.1)
where, $D =$ crystallite size, $K =$ constant $(0.89)$, $\lambda =$ wavelength of the CuK$\alpha$ radiation, $\beta =$ Full width at half height, $\theta =$ diffraction angle. The crystallite sizes of TiO$_2$ and SrTiO$_3$ in the synthesized catalysts were found to be around 20 and 40 nm respectively.

Table 3.1  **Average crystallite sizes of bare, metal impregnated titania and metal doped strontium titanate catalysts**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>21.0</td>
</tr>
<tr>
<td>(0.5%)Ni/TiO$_2$</td>
<td>22.0</td>
</tr>
<tr>
<td>(1%)Ni/TiO$_2$</td>
<td>22.0</td>
</tr>
<tr>
<td>(3%)Ni/TiO$_2$</td>
<td>22.5</td>
</tr>
<tr>
<td>(0.5%)Ru/TiO$_2$</td>
<td>22.0</td>
</tr>
<tr>
<td>(1%)Ru/TiO$_2$</td>
<td>22.5</td>
</tr>
<tr>
<td>(3%)Ru/TiO$_2$</td>
<td>22.5</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>43.0</td>
</tr>
<tr>
<td>(1%)Ni-SrTiO$_3$</td>
<td>39.0</td>
</tr>
<tr>
<td>(1%)Ru-SrTiO$_3$</td>
<td>38.0</td>
</tr>
</tbody>
</table>

### 3.2.2 BET Surface Area

The specific surface area of bare, Ni/Ru impregnated titania and Ni/Ru doped strontium titanate catalysts were determined and the values are listed in Table 3.2.

Sol-gel method of syntheses of both titania and strontium titanate led to the formation of highly crystalline compounds. However they differ much in their surface area values.
Table 3.2  BET surface area values of titania and strontium titanate catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>93</td>
</tr>
<tr>
<td>(0.5%)Ni/TiO₂</td>
<td>87</td>
</tr>
<tr>
<td>(1%)Ni/TiO₂</td>
<td>62</td>
</tr>
<tr>
<td>(3%)Ni/TiO₂</td>
<td>41</td>
</tr>
<tr>
<td>(0.5%)Ru/TiO₂</td>
<td>81</td>
</tr>
<tr>
<td>(1%)Ru/TiO₂</td>
<td>72</td>
</tr>
<tr>
<td>(3%)Ru/TiO₂</td>
<td>60</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>11</td>
</tr>
<tr>
<td>(1%)Ni-SrTiO₃</td>
<td>16</td>
</tr>
<tr>
<td>(1%)Ru-SrTiO₃</td>
<td>19</td>
</tr>
</tbody>
</table>

Increase in the impregnation of either nickel or ruthenium decreased the surface area (Houskova et al 2009). However doping of these metals into SrTiO₃ lattice increased the surface area slightly. The lowering of surface area with increase in the impregnation of Ni or Ru may be attributed to the increasing coverage of a lower surface area material over higher surface area material. Since the nitrogen is used as a probe molecule in the BET measurement area, its entry into titania surface is prevented by the Ni and Ru metals (Rupa et al 2011). The lower surface area (11-19 m²/g) obtained in the case of SrTiO₃ may be due to the high calcination temperature (1050°C) employed during the synthesis.

3.2.3  UV – Visible Diffuse Reflectance Spectral Data

UV- Visible Diffuse reflectance spectroscopy generally provides some insights into the interaction of photocatalytic materials with photon energies (George et al 2009). Figure 3.3 and 3.4 show the DRS and Kubelka-Munk spectra of bare & metal impregnated titania and bare & metal doped titanate catalysts.
Figure 3.3  (A) UV- Visible DRS spectra and (B) – (H) Kubelka-Munk spectra of (a) bare TiO$_2$, (b) (0.5%)Ni/TiO$_2$, (c) (1%) Ni/TiO$_2$, (d) (3%)Ni/TiO$_2$, (e) (0.5%)Ru/ TiO$_2$, (f) (1%) Ru/ TiO$_2$ and (g) (3%) Ru/TiO$_2$
The band gap of all the catalysts were determined using the formula $E_g = \frac{1240}{\lambda}$, where $\lambda$ is the cut-off wavelength (Table 3.3). This cut-off wavelength is calculated by converting the absorbance into reflectance by performing Kubelka-Munk transformation using the following equation,

$$k/s = (1-R)^2/2R \Rightarrow F(R)$$ (3.2)

where $k/s$ is reflectance transformed according to Kubelka-Munk, $R$ is reflectance (%R) and $F(R)$ is Kubelka-Munk function.

Figure 3.4 (A) UV- Visible DRS absorption spectra (B) – (D) Kubelka-Munk spectra of (a) ST, (b) NiST and (c) RuST
Table 3.3  Band gap values of titania and strontium titanate photocatalysts

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Band gap energy, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.20</td>
</tr>
<tr>
<td>(0.5%)Ni/TiO$_2$</td>
<td>3.04</td>
</tr>
<tr>
<td>(1%)Ni/TiO$_2$</td>
<td>2.95</td>
</tr>
<tr>
<td>(3%)Ni/TiO$_2$</td>
<td>2.97</td>
</tr>
<tr>
<td>(0.5%)Ru/TiO$_2$</td>
<td>2.79</td>
</tr>
<tr>
<td>(1%)Ru/TiO$_2$</td>
<td>2.80</td>
</tr>
<tr>
<td>(3%)Ru/TiO$_2$</td>
<td>2.48</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>3.17</td>
</tr>
<tr>
<td>(1%)Ni-SrTiO$_3$</td>
<td>1.9</td>
</tr>
<tr>
<td>(1%)Ru-SrTiO$_3$</td>
<td>2.13</td>
</tr>
</tbody>
</table>

Impregnation or doping of nickel or ruthenium over/into titania and strontium titanate lattices resulted in decrease in the bandgap value. Larger decrease in the bandgap value is observed for the doped catalysts than impregnated catalysts. Catalysts showing such red shift are generally photocatalytically active in the visible region (Faughnan 1971).

3.2.4  Raman Spectral Studies

As anatase and rutile forms are very sensitive to Raman scattering, with the help of the Raman spectra one can distinguish whether titania exists in anatase or rutile phase. From Raman studies crystallinity, phase compositions and oxygen vacancy defects can also be analysed. Figure 3.5 shows the Raman spectra of the most active catalysts such as (1%) Ni/ TiO$_2$ and (1%) Ru/ TiO$_2$ and compared with that of bare TiO$_2$. 
Figure 3.5 Raman spectra of (a) bare TiO$_2$, (b) (1%) Ni/TiO$_2$ and (c) (1%) Ru/TiO$_2$

Raman spectra of the synthesized and metal impregnated titania catalysts exhibit Raman scatterings at 144 cm$^{-1}$ confirming the presence of pure anatase phase in all the three catalysts and absence of Raman scattering at 447 cm$^{-1}$ confirm the absence of rutile phase.

Chen et al (2007) reported that the anatase TiO$_2$ has six Raman-active fundamental vibrations in its spectrum: three E$_g$ modes centered around 144 cm$^{-1}$, 200 cm$^{-1}$, and 639 cm$^{-1}$ (designated as E$_g$(1), E$_g$(2) and E$_g$(3) respectively), two B$_{1g}$ modes at 399 cm$^{-1}$ and 519 cm$^{-1}$ (designated as B$_{1g}$(1) and B$_{1g}$(2)) and A$_{1g}$ mode at 513 cm$^{-1}$. Raman scatterings around 144 cm$^{-1}$ (E$_g$(1) the strongest), 200 cm$^{-1}$ (E$_g$(2)), 399 cm$^{-1}$ (B$_{1g}$(1)), 519 cm$^{-1}$ (B$_{1g}$(2)) and 639 cm$^{-1}$ (E$_g$(3)) and absence of Raman scatterings around 447 cm$^{-1}$ confirm that TiO$_2$ is in anatase phase only. The doped catalysts also exhibit similar Raman scatterings which confirm that
there is no phase transformation due to the impregnation of metals. No additional peaks were observed for the doped metals. This may be due to less amount of loading of metals over titania (1%). However a slight broadening and shifting of Raman scattering for $E_{g(3)}$ was observed which may be due to incorporation of metal atoms into the lattice of titania. Similar observation was also made by Karthik & Jaya (2011). Senthilnanthan et al (2010) also have reported similar shifting of Raman modes (146, 199, 400, 519 and 636 cm$^{-1}$) for anatase TiO$_2$ and the non – metal doped TiO$_2$ catalysts and attributed to different crystallite sizes of bare and doped titania.

Raman spectra of strontium titanate catalysts are shown in Figure 3.6.

![Figure 3.6 Raman spectra of (a) ST, (b) NiST and (c) RuST](image)
SrTiO$_3$ has an ideal cubic perovskite structure with the space group Pm3m with the vibration mode of 3F$_{1u}$+F$_{2u}$. In this compound the first order Raman modes are forbidden at room temperature, however Du et al (2004) have reported the first order Raman modes caused by strain effects, oxygen vacancies and external conditions. Each of the F$_{1u}$ modes splits into a doubly degenerate E mode and a nondegenerate A$_1$ mode, while the F$_{2u}$ mode splits into E and B$_1$ modes. Thus, the vibration modes are 3(A$_1$ + E) +E + B$_1$. The presence of long-range electrostatic forces further splits each of the A$_1$ and E modes into transverse optical (TO) and longitudinal optical (LO) modes.

Luo et al (2008) observed the Raman modes at 484, 547 and 797 cm$^{-1}$ and assigned to LO$_3$, TO$_4$ and LO$_4$ modes. The synthesized strontium titanate catalysts also exhibited Raman modes at 476, 549 and 802 cm$^{-1}$ due to the above mentioned modes. However for the nickel and ruthenium doped strontium titanate catalysts these modes were obtained around 472, 514 and 740 cm$^{-1}$ respectively.

3.2.5 FT-IR Spectra

FTIR spectra of bare and 1% metal doped titania catalysts are shown in Figure 3.7. All the peaks for bare and metal doped titania catalysts look alike. Owing to low impregnation levels of nickel and ruthenium over titania no additional peaks were observed. The sharp peaks observed at 1600 cm$^{-1}$ for all the catalysts may be attributed to the bending vibrations of adsorbed water molecules whereas the peaks observed around 650 cm$^{-1}$ are due to the vibrational modes of Ti-O-Ti (Bezrodna et al 2004). Stretching vibration of adsorbed water molecules are evidenced by the appearance of broad peak around 3400 cm$^{-1}$. 
Figure 3.7  FTIR spectra of (a) bare TiO$_2$, (b) (1%) Ni/ TiO$_2$ and (c) (1%) Ru/ TiO$_2$

FTIR spectra of bare and metal doped strontium titanate catalysts are shown in Figure 3.8. The strong peaks around 650 cm$^{-1}$ are due to crystal lattice vibrations of Ti-O-Ti within the TiO$_6$ octahedra in titanate catalysts, whereas the other peaks appear around 1400-1600 cm$^{-1}$ and 3400 cm$^{-1}$ are due to bending and stretching vibrations of adsorbed water molecules (Ohno et al 2005, Simoes et al 2010 and Liang et al 2011).
3.2.6 Scanning Electron Microscopy with Energy Dispersive Spectra (EDS)

SEM images and Energy Dispersive Spectra of bare titania and titanate catalysts are shown in Figures 3.9 & 3.10 respectively. Bare titania particles are highly agglomerated. However the shape and size of synthesized titania were found to be almost the same. Both bare and metal doped titanate catalysts show particles of different shape and size.
Figure 3.9  SEM images of (a) bare TiO$_2$, (b) (1%) Ni/TiO$_2$, (c) (1%) Ru/TiO$_2$, (d) bare SrTiO$_3$, (e) (1%) Ni-SrTiO$_3$ and (f) (1%) Ru-SrTiO$_3$
Figure 3.10  EDS spectra of a) TiO\textsubscript{2}, b) (1\%) Ni/TiO\textsubscript{2}, c) (1\%) Ru/TiO\textsubscript{2}, d) ST, e) NiST and f) RuST

The peaks in the EDS spectra between 4.5-5 keV, 1.5-2 keV, 7.5-8.4 keV and 2.3-2.9 keV confirm the presence of different elements such as Ti, Sr, Ni and Ru respectively (Tseng et al 2009, Tsumura et al 2009 and Yousefpour & Shokuhy 2012).

3.2.7  Transmission Electron Micrographs (TEM)

TEM images of bare titania and metal impregnated titania catalysts are shown in Figure 3.11 (a-h). TEM images indicated that the titania particles are agglomerated and have different shapes and sizes. The particle sizes of
both bare and metal impregnated titania particles ranged from 15-20 nm which is in consistent with the XRD data.

Figure 3.11 TEM images of (a) bare TiO$_2$, (b) HRTEM image of TiO$_2$ (Inset- SAED pattern), (c) (0.5%) Ni/ TiO$_2$, (d) (1%)Ni/ TiO$_2$, (e) (3%)Ni/ TiO$_2$, (f) (0.5%) Ru/ TiO$_2$, (g) (1%) Ru/ TiO$_2$ and (h) (3%)Ru/ TiO$_2$.
HRTEM image of titania shows fringes with lattice spacing of 0.35 nm which corresponds to (101) plane of the anatase phase and its SAED pattern indicate the different planes such as (101), (200), (004), (105) and (211) of anatase phase (Figure 3.11b) (Li et al 2006 and Shu et al 2008). Sajjad et al (2010) also reported the lattice fringe value of 0.35 nm for anatase TiO$_2$ in WO$_3$/TiO$_2$ composite catalyst. This study also confirms high degree of crystallinity of titania. When the % of impregnation of metal over titania was increased from 0.5% to 3%, the black spots and the dispersion of nickel and ruthenium metals over TiO$_2$ catalysts were also increased (Figure 3.11 (a-h)). TEM images of strontium titanate, nickel and ruthenium strontium titanates are shown in Figure 3.12.

**Figure 3.12** TEM images of (a) bare SrTiO$_3$, (b) HR TEM image of SrTiO$_3$ (Inset its SAED pattern), (c) NiST and (d) RuST
The TEM images of metal doped strontium titanates show particles with particle size of 5 nm. The fringe and SAED patterns of strontium titanate catalyst are shown in Figure 3.12 (b) which confirm their crystallinity. Inter planar distance \((d)\) was calculated for strontium titanate \((1\ 1\ 0)\) and was found to be 0.28 nm. The TEM images also revealed that the incorporation of Ni and Ru into SrTiO\(_3\) lattice has not altered the morphology. Similar observation was made elsewhere (Bui et al 2013 and Setinc et al 2013).

### 3.2.8 Atomic Absorption Spectral Data (AAS)

The synthesized catalyst samples were analysed by AAS technique to determine the actual metal content present in it. The % metal content values determined by AAS are given in Table 3.4. These results are in close agreement with the theoretical values.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Metal content (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.5%)Ni/TiO(_2)</td>
<td>0.48</td>
</tr>
<tr>
<td>(1%)Ni/TiO(_2)</td>
<td>0.97</td>
</tr>
<tr>
<td>(3%)Ni/TiO(_2)</td>
<td>2.95</td>
</tr>
<tr>
<td>(0.5%)Ru/TiO(_2)</td>
<td>0.49</td>
</tr>
<tr>
<td>(1%)Ru/TiO(_2)</td>
<td>0.99</td>
</tr>
<tr>
<td>(3%)Ru/TiO(_2)</td>
<td>2.96</td>
</tr>
<tr>
<td>NiST</td>
<td>0.98</td>
</tr>
<tr>
<td>RuST</td>
<td>0.96</td>
</tr>
</tbody>
</table>

### 3.2.9 X-ray Photoelectron Spectral Studies (XPS)

The presence of different elements and their oxidation state can be known from XPS spectra. Overall and individual elemental XPS spectra of nickel and ruthenium doped titania catalysts are shown in Figure 3.13 (a-f).
Figure 3.13 (a & b) show the presence of different elements in the impregnated titania catalysts.

Figure 3.13  Overall XPS spectra of (a) (1%) Ni/TiO$_2$, (b) (1%) Ru/TiO$_2$ and individual spectra of (c) Ni 2p, (d) Ru 3d, (e) Ti 2p in (1%) Ni/TiO$_2$ (upper) & in (1%) Ru/TiO$_2$ (lower) and (f) O 1s in (1%) Ni/TiO$_2$ (upper) & in (1%) Ru/TiO$_2$ (lower) catalysts
The binding energies of Ti (2p$_{1/2}$), Ti (2p$_{3/2}$), O (1s), Ni (2p), Ru (3d) are located at 465.4, 459.5, 530.3, 853.5 and 285.6 eV. Ni (2p) peaks were observed at the binding energies of 855.5, 853.5 and 852.1 eV (Figure 3.13 c). These binding energies correspond to oxides of nickel and metallic nickel respectively. The binding energy of Ru 3d$_{3/2}$ is observed at 285.6 eV (Figure 3.13 d). Ti (2p$_{1/2}$), Ti (2p$_{3/2}$) binding energies were observed at 465.45, 459.5 eV confirming the presence of Ti$^{4+}$ (Figure 3.13 e). The binding energy at 530.3 eV is attributed to O$^{2-}$ ions of TiO$_2$ frame work (Ti-O-Ti) (Figure 3.13 f) (Elmasides et al 1999 and Zubavichus et al 2002).

Figure 3.14 (a-c) show the overall spectra of strontium titanate, nickel/ruthenium strontium titanate catalysts and Figure 3.14 (d-h) show the individual spectra of the elements present in the synthesized catalysts.

The XPS overall spectra indicated the presence of all the components of strontium titanate (Sr, Ti, O) including the carbon from adsorbed gaseous molecules (Li et al 2013). The binding energies at 458.1, 458.6, 269.1 and 357.6 eV for Ti (2p$_{1/2}$), Ti (2p$_{3/2}$), Sr (2p) and Sr (3s) respectively (Huang et al 2013). The binding energy at 529.6 eV is for O$^{2-}$ ions (Sr-O-Ti) of SrTiO$_3$ frame work. The characteristic Sr 3d doublet line located around 132- 134 eV confirms the presence of strontium as Sr$^{2+}$ in strontium titanate catalyst. Ni (2p$_{3/2}$) peak was observed at 855.8 eV which confirms the presence of nickel. The binding energy located at 280.6 eV for the presence of ruthenium in Ru (3d$_{5/2}$).
Figure 3.14  Overall XPS spectra of (a) ST, (b) NiST, (c) RuST and individual XPS spectra of (d) Sr 3d, (e) Ni 2p, (f) Ru 3d, (g) Ti 2p and (h) O 2p