Chapter 8

Substituted Indium Titanates - Enhanced Photocatalytic Hydrogen Generation and Favorable Redox Properties

8.1 Introduction

In the previous chapter (Chapter 7) we have seen the suitability of indium titanate as a photocatalyst for hydrogen generation by virtue of its proper band gap and photocatalytic activity for hydrogen generation. First principle investigations revealed the band structure showing the distribution of valence states of the constituent atoms near the Fermi level of the indium titanate. The band gap of bulk indium titanate was also estimated from DRUV experiments and was found to be 3.02 eV. Both the bulk and nano indium titanate were photoactive for hydrogen generation from water-methanol mixture. The interesting photoactivity results on pristine indium titanate prompted us to investigate the effect of transition metal like Ni$^{2+}$ on the photocatalytic properties of indium titanate as transition metals with partly filled d-orbital (e.g. Ni$^{2+}$, Cr$^{3+}$, Fe$^{3+}$) are known to add impurity levels near the conduction band of titanates thereby decreasing its band gap and increasing its photoactivity [1-4]. It is a well-known fact that the light absorption by the material and the migration of the light-induced electrons and holes are the key factors controlling a photocatalytic reaction (Chapter 1), which is related to the electronic structure characteristic of the material [1-4]. The ionic radius of Ni$^{2+}$ (0.69 Å) being much smaller than
that of In$^{3+}$ (0.81 Å), substituting In$^{3+}$ by Ni$^{2+}$ should reduce the volume of the InO$_6$ octahedra, and hence the cell volume in InTiO$_5$. This should in turn affect the direct metal-metal bonding in the crystal, with the In-In distance shortened, resulting in profound alterations of the electronic properties of the compounds and consequent modifications in the photocatalytic properties [5].

So, in the present Chapter, we report the A-site substitution of Ni$^{2+}$ induced effects on the photocatalytic behavior of indium titanate. For this purpose, In$_{2(1-x)}$Ni$_{2x}$TiO$_5$-$\delta$ ($0.0 \leq x \leq 0.2$) mixed oxide catalysts were synthesized using solid-state reaction and characterized by powder X-ray diffraction (XRD), the light absorption properties was studied by recording the DRUV spectra and finally the photocatalytic splitting of water was investigated under UV-visible light irradiation. The photocatalytic activity was also compared with other A- (Nd) and B- site (Fe, Cr) doped indium titanates to compare the effect of dopant to indium titanate lattice.

The redox properties of the Ni substituted indium titanates were also studied. The important considerations in designing an oxide catalyst are its thermal, chemical stability, reducibility and oxidizability. So, it is imperative to study their interesting physicochemical properties the knowledge of which finds them utilized in suitable applications. The thermal and chemical stability and redox behavior of these titanates would play a vital role in determining their catalytic properties for various redox processes (even photocatalytic redox reactions).

8. 2. Experimental:

8.2.1 Material Synthesis

Mixed oxides with nominal composition, In$_{2(1-x)}$Ni$_{2x}$TiO$_5$-$\delta$ for $0.0 \leq x \leq 0.2$, were synthesized through ceramic route using pre-dried In$_2$O$_3$, TiO$_2$ and NiO (99.99% purity) as starting materials, mixing them in appropriate stoichiometry as depicted by following equation:

$$(1-x)\text{In}_2\text{O}_3 + \text{TiO}_2 + 2x\text{NiO} \rightarrow \text{In}_{2(1-x)}\text{Ni}_{2x}\text{TiO}_5-\delta$$
The pellets of homogeneous mixtures were calcined at 900 °C for 24 h, 1000 °C for 24 h and finally at 1250°C for 12h, with intermittent grindings so as to ensure the uniformity and the completion of the reaction.

8.2.2 Catalyst Characterization

The Powder XRD patterns were recorded on a Philips diffractometer (model PW 1710), equipped with a graphite monochromator and Ni-filtered Cu-Kα radiation. Structural analysis has been done by using Rietveld refinement program Fullprof-2005 [6]. First of all, the background parameters and scale factor were adjusted. The background was fitted with sixth order polynomial. The diffraction peak profile was fitted with Pseudo-Voigt profile function and then the FWHM parameters were adjusted. No absorption parameter was considered during refinement. Subsequently, individual thermal parameters were refined. Finally, positional parameters were refined. Consequently, individual cell parameters with position of individual atoms in the Ni-substituted In2TiO5 crystal lattice were derived. Band gap measurements of all semiconductor oxide samples was estimated by recording their Diffuse reflectance UV-Visible spectra using spectrophotometer of JASCO model V-530, Japan, scanned in range of 200-1000 nm at the scanning speed of 200 nm/min.

8.2.3 Redox properties

Redox behavior of catalyst was studied by recording temperature programmed reduction/oxidation (TPR/TPO) profiles on a TPDRO-1100 analyzer (ThermoQuest, Italy) in temperature range of 25-1100 °C under the flow of H2(5%)+Ar, gas mixtures at a flow rate of 20 ml min⁻¹, with a heating rate of 6 Kmin⁻¹. The samples were pretreated at 350°C for about 2.5 hrs in helium, prior to recording of the first TPR run. A thermal conductivity detector (TCD) is employed to monitor the change in composition of reactive gas mixture with time. The water
formed during reduction process was removed from the flowing gas by the help of a soda lime trap placed just before the detector. Hence the signal obtained was primarily due to change in thermal conductivity of the flowing gas by consumption of hydrogen. The amount of hydrogen consumed by the sample during a TPR run corresponded to the area under the TPR profile. The calibration factor (µmoles of H₂ per mV of TCD signal) for the H₂ was calculated using the standard sample. This factor has been employed in all the substituted samples and the experimental amount of H₂ consumed was obtained. The calculated value of H₂ consumed by the sample was compared with the experimental value. XPS studies were carried out on electron spectrometer using Mg-Kα X-rays (hv=1253.6 eV) as the primary source of radiation. The appropriate corrections for charging effect were made with the help of a C 1s signal appearing at 285.1 eV.

8.2.4 Photocatalytic activity

The photocatalytic activities of the samples were carried out under irradiation of a medium-pressure mercury lamp (Hg, Ace Glass Inc., 450W) placed in an outer irradiation–type quartz cell surrounded with water circulation jacket to absorb IR irradiation. The rectangular quartz cell (2.1x2.1x8 cm³) was equipped with sampling and evacuation ports and placed horizontally in a chamber close to a water-cooled medium pressure mercury vapor lamp (400 W) (shown in Fig. 2.21, Chapter 2). The said lamp exhibits very broad range emission spectra having maxima at both UV and the visible range with the UV part being only 16% of the whole spectra (shown in Fig. 2.20, Chapter 2). The catalyst (0.1g) was suspended in distilled water (10 ml) and methanol (5ml). The reaction mixture was evacuated and irradiated under the medium pressure mercury lamp. After irradiation, the amount of Hydrogen evolved was analyzed by gas Chromatograph (TCD, Molecular sieve, 5m length and Ar carrier). The number of photons falling on the reaction
cell or flux of the light was determined by a calibrated light flux meter (Cal light 400), where the flux observed in horizontal geometry was $19 \times 10^4$ lux or 278.2 watts/m$^2$.

8.3 Results and discussions

8.3.1. XRD

Table-8.1 lists the abbreviations and phases identified from XRD patterns of all the $\text{In}_2(1-x)\text{Ni}_2x\text{TiO}_5-(0.0 \leq x \leq 0.2)$ samples prepared by solid state method. Henceforth, in this Chapter, the samples will be designated by their abbreviations. The XRD patterns of all samples were recorded and analyzed. Fig. 8.1 shows the powder XRD patterns of $\text{In}_2\text{TiO}_5$ and corresponding patterns observed due to aliovalent substitution of $\text{Ni}^{2+}$ in place of $\text{In}^{3+}$ at A-site. The XRD pattern of $x = 0$, composition matches well with that of orthorhombic $\text{In}_2\text{TiO}_5$ (JCPDS card No.30-0640, space group Pnma). The XRD patterns of ITN05 ($\text{In}_{1.95}\text{Ni}_{0.05}\text{TiO}_5$) and ITN1 ($\text{In}_{1.9}\text{Ni}_{0.1}\text{TiO}_5$) compositions match with the XRD patterns of unsubstituted indium titanate sample as shown in Fig. 8.1. Thus, lower extent of Ni substitution resulted in single phase material comprised of $\text{In}_2\text{TiO}_5$ phase due to formation of solid solution of Ni with the lattice of the parent compound. However, for the nickel doped indium titanates, the peaks are shifted slightly towards higher 2-$\theta$ values as compared to those of the pristine samples, which is attributed to the decrease in lattice spacings due to substitution of smaller $\text{Ni}^{2+}$ ions in place of larger $\text{In}^{3+}$ ions. On further Ni substitution i.e. samples having Ni content $x \geq 0.1$ in $\text{In}_2(1-x)\text{Ni}_2x\text{TiO}_5-(0.0 \leq x \leq 0.2)$ a very low intensity line (marked with #) was observed which corresponds to the 100 % peak of $\text{NiO}$ (JCPDS card No.47-1049). Thus for these compositions in addition to parent phase there was segregation of unreacted NiO phase in very small proportion. Moreover, for samples having higher Ni content i.e. $x \geq 0.15$, a third phase of $\text{NiTiO}_3$ (JCPDS card No.33-0960, peaks marked with *) was observed in addition to the unreacted nickel oxide phase (Fig. 8.1).
It is pertinent to mention here that the presence of a small amount of these secondary phases in the samples, as mentioned above, was taken into consideration for Rietveld analysis. The reliability factors of the Rietveld refinement of the substituted and unsubstituted indium titanates, $\chi^2$, were within the range of 2.8 to 3.6.

Table-8.1 Identification of phase in $\text{In}_{2(1-x)}\text{Ni}_{2x}\text{TiO}_5$ ($0.0 \leq x \leq 0.2$) samples and their abbreviations.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Ni content (x in $\text{In}<em>{2(1-x)}\text{Ni}</em>{2x}\text{TiO}_5$)</th>
<th>Abbreviation</th>
<th>Phase identification by XRD and weight fraction (in %) of each phase calculated from Reitveld refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{In}_2\text{TiO}_5$</td>
<td>0.00</td>
<td>ITO</td>
<td>$\text{In}_2\text{TiO}_5$ (100)</td>
</tr>
<tr>
<td>$\text{In}<em>{1.95}\text{Ni}</em>{0.05}\text{TiO}_5$</td>
<td>0.025</td>
<td>ITN05</td>
<td>$\text{In}_2\text{TiO}_5$ (100)</td>
</tr>
<tr>
<td>$\text{In}<em>{1.9}\text{Ni}</em>{0.1}\text{TiO}_5$</td>
<td>0.05</td>
<td>ITN1</td>
<td>$\text{In}_2\text{TiO}_5$ (100)</td>
</tr>
<tr>
<td>$\text{In}<em>{1.8}\text{Ni}</em>{0.2}\text{TiO}_5$</td>
<td>0.1</td>
<td>ITN2</td>
<td>$\text{In}_2\text{TiO}_5$ (97.3) &amp; NiO (2.7)</td>
</tr>
<tr>
<td>$\text{In}<em>{1.7}\text{Ni}</em>{0.3}\text{TiO}_5$</td>
<td>0.15</td>
<td>ITN3</td>
<td>$\text{In}_2\text{TiO}_5$ (97.19), NiO (1.28) &amp; NiTiO$_3$ (1.52)</td>
</tr>
<tr>
<td>$\text{In}<em>{1.6}\text{Ni}</em>{0.4}\text{TiO}_5$</td>
<td>0.2</td>
<td>ITN4</td>
<td>$\text{In}_2\text{TiO}_5$ (94.76), NiO (2.48) &amp; NiTiO$_3$ (2.76)</td>
</tr>
</tbody>
</table>

To determine the crystal structure under investigation and to confirm the site of dopant cation Ni$^{2+}$ in the crystal lattice Rietveld refinement of the diffraction patterns were carried out and the results are shown in Fig. 8.2. The detailed crystal structure of the parent $\text{In}_2\text{TiO}_5$ phase has already been discussed in Chapter 7. The substituted samples were found to be iso-structural with the parent indium titanate phase and Ni$^{2+}$ was found to substitute only at one of the 4c In$^{3+}$
The typical variation in cell parameters and cell volume as a function of nickel content in In$_{2(1-x)}$Ni$_{2x}$TiO$_{5-\delta}$ ($0.0 \leq x \leq 0.2$) phases in indium titanate samples, as deduced from the Rietveld analysis of corresponding powder XRD reflections, is shown in Fig. 8.3. As seen in Fig. 8.3d, the cell volume decreases as a function of nickel content ($x$ in In$_{2(1-x)}$Ni$_{2x}$TiO$_{5-\delta}$) as long as $x \leq 0.15$. Thereafter, the cell expands when Ni content $x = 0.2$. Also, the decrease in cell volume is large from $x = 0$ to $x = 0.05$ and then there is a small linear decrease up to $x \leq 0.15$. The lattice parameters $a$, $b$ and $c$ also show a similar trend. Due to incorporation of smaller cation Ni$^{2+}$ by substitution of a larger cation In$^{3+}$ there is a linear decrease in the values of cell parameters and cell volume up to $x \geq 0.15$. Thereafter, the impurity phase of NiTiO$_3$ also appears and increases its volume fraction significantly with further increase in Ni-content. The offset from linearity and then an increase in lattice parameters can be explained from the segregation of this impurity phase. Although, the occupancy of Ni$^{2+}$ increases with doping but the parent lattice has a maximum capacity to substitute a large cation by a smaller cation as the structure destabilize by such a substitution and when the maximum capacity for such substitution exceeds, secondary phases appear keeping the parent crystal phase as the major phase. Such, segregation of secondary phases and its growth, due to substitution of In$^{3+}$ by Ni$^{2+}$ in oxide lattices was also observed in InTaO$_4$ by Zou et al [5].

As discussed in Chapter 7, the presence of InO$_6$ and TiO$_6$ polyhedra in the In$_2$TiO$_3$ lattice has a marked effect on the charge transport properties and consequently on photocatalytic properties. The perturbation of these polyhedral units due to substitution of Ni was also evaluated from the Rietveld refinement results and is tabulated in Table 8.2. We can see from Table 8.2 the shrinkage of both the Ti-O and In2-O bond distances in the TiO$_6$ and InO$_6$ which is in accordance to the decrease in cell parameters with Ni-doping shown in Fig. 8.3. The decrease
in bond distances in the polyhedral can have a profound influence on the photocatalytic properties. This can be understood from the point of view that since the edge shared TiO$_6$ and InO$_6$ polyhedral assist in charge conduction to the surface the reduced distances can enhance this rate of charge transfer to the surface and increase the photoactivity of the semiconductor photocatalyst.

Fig. 8.1. XRD patterns of In$_2$(1-x)Ni$_2$xTiO$_{5-δ}$samples, # indicates peaks due to unreacted NiO phase and * indicates the peaks arising from NiTiO$_3$ phase.
Fig. 8.2. Rietveld refined profiles of X-ray diffraction data of In$_{2(1-x)}$Ni$_{2x}$TiO$_{5-δ}$ samples, where $x =$ a) 0.0, b) 0.025, c) 0.05, d) 0.1 e) 0.15 and f) 0.2. The dots represent the observed data, while the solid line through dots is the calculated profile, and vertical tics represent Bragg reflections for the phase. The difference pattern is also shown below the vertical tics in each case.
Fig. 8.3. Changes in crystal structure with doping where A, B and C are the variation of lattice parameters with Ni doping and D shows Ni-content dependence of the cell volume.

Table-8.2. Selected bond distances and angles in TiO$_6$ and InO$_6$ polyhedra

<table>
<thead>
<tr>
<th>Name of phase</th>
<th>Ti-O distances</th>
<th>In1-O distances</th>
<th>In2-O distances</th>
<th>O-In-O distances</th>
<th>O-In-O angles</th>
<th>O-Ti-O angles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Å</td>
<td>Å</td>
<td>Å</td>
<td>Å</td>
<td>degrees</td>
<td>degrees</td>
</tr>
<tr>
<td>In$_2$TiO$_5$</td>
<td>1.8087, 1.8230 (×2), 2.0323, 2.0386, 2.1853</td>
<td>2.1748, 2.2127 (x2), 2.2145 (x2), 2.2316</td>
<td>2.1024, 2.2040, 2.2130 (x2), 2.2421 (x2)</td>
<td>75.56-176.37, 76.01-171.9, 75.35-179.95</td>
<td>73.53-179.52</td>
<td></td>
</tr>
<tr>
<td>In$<em>{1.9}$Ni$</em>{0.1}$TiO$_{5-δ}$</td>
<td>1.8049 (x2), 1.8291, 2.0390, 2.0569, 2.3077</td>
<td>2.2000, 2.2005, 2.2133 (x2), 2.2445 (x2)</td>
<td>2.0709, 2.1418, 2.2003 (x2), 2.2017 (x2)</td>
<td>76.73-175.95, 74.56-172.76</td>
<td>75.35-179.95</td>
<td></td>
</tr>
<tr>
<td>Compounds</td>
<td>TPR Profiles</td>
<td>( \Delta H_{\text{red}} ) (kJ/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>-----------</td>
<td>-------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>In(<em>{1.8})Ni(</em>{0.2})TiO(_5)</td>
<td>1.8494 (x2) 1.8563 1.9655 2.0686 2.1688</td>
<td>2.1275 2.1958 2.2237 (x2) 2.2430 (x2) 2.0552 2.1398 2.1836 (x2) 2.2381 (x2) 77.70-178.87 (O-In1-O), 75.43-174.00 (O-In2-O) 70.86-178.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In(<em>{1.7})Ni(</em>{0.3})TiO(_5)</td>
<td>1.7928 (x2) 1.8826 2.0205 2.0263 2.3201</td>
<td>2.1839 2.1920 (x2) 2.2203 (x2) 2.2353 2.1731 2.1192 2.1745 (x2) 2.2041 (x2) 75.24-175.04 (O-In1-O), 73.59-171.09 (O-In2-O) 76.80-177.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In(<em>{1.6})Ni(</em>{0.4})TiO(_5)</td>
<td>1.7839 1.9740 1.8276 (x2) 2.0604 2.2250</td>
<td>2.1921, 2.1900, 2.3299, 2.2148, 2.1921, 2.2148. 2.0862 2.1739 2.1946 (x2) 2.2246 (x2) 74.91-173.92 (O-In1-O), 75.32-173.95 (O-In2-O) 72.97-177.18</td>
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</tbody>
</table>

With these modifications in the crystal structure of In\(_2\)TiO\(_5\) by Ni-doping, we were interested to investigate the effect of doping on both the photocatalytic properties and redox properties of indium titanate. First we depict the results of photocatalytic properties then the redox properties.

### 8.3.2 Redox properties

The typical first temperature programmed cycle (TPR) of substituted samples and unsubstituted sample are shown in Fig. 8.4. The TPR profile of unsubstituted, In\(_2\)TiO\(_5\) sample as seen in Fig. 8.4 comprises of a prominent band with onset at ~625 °C and extending beyond 1000 °C. This indicated the predominant reduction of one of the species, identified to be In\(^{3+}\), in the temperature range of 600-1100 °C over other reducible species in In\(_2\)TiO\(_5\) sample. The temperature maximum (\(T_{\text{max}}\)) of the reduction bands corresponds to ~1070 °C. However, Ni\(^{2+}\) substitution at In\(^{3+}\) site has induced considerable changes in the reduction profile of indium titanate. In case of compositions having higher content of Ni, viz., ITN2 and ITN4, TPR profiles (Fig. 8.4), exhibit two-three weak bands in low temperature range of 450-800 °C in addition to
main reduction band. The presence of these bands is probably attributed to reduction of Ni$^{2+}$ → Ni$^{0}$ along with reduction of In$^{3+}$. At the same time, the $T_{\text{max}}$ of the individual peaks was found to be lower in the case of substituted samples. For instance, we observe the lowering of $T_{\text{max}}$ around by 80 °C for ITN4 in Fig. 8.4, as compared to the TPR profile of an un-substituted phase. Also the onset reduction temperature of 625 °C in unsubstituted phase has considerably decreased by Ni substitution as shown in Fig. 8.4.

![Fig. 8.4. Typical first TPR cycle of In$_{2(1-x)}$Ni$_{2x}$TiO$_{5-s}$ samples as a function of Ni substitution](image)

The TPR profile as a whole has shifted to lower temperature as a result of Ni substitution. Thus, Ni$^{2+}$ substitution has undoubtedly facilitated the reduction of In$_2$TiO$_5$ phase. These changes in the TPR profiles can be ascribed to the nonstoichiometry and imperfections generated in the single phased compositions as a result of A-site substitution.
Both substituted and unsubstituted samples did not show any weight loss in TG when recorded in O₂ (5%) + Ar, thus indicating that all substituted In_2(1-x)Ni_2xTiO_5-δ oxide samples are stable in air upto 1000 °C. So the In_2(1-x)Ni_2xTiO_5-δ, (x = 0.0-0.4) samples once formed, do not pick up either moisture or CO₂, and are thermally stable compositions till 1000 °C. Although, in O₂ (5%) + Ar atmosphere these compositions are stable whereas in H₂ (5%) + Ar, the corresponding TG exhibits substantial weight loss. A representative TG-DTA plot of ITN4 in H₂ (5%) + Ar atmosphere is shown in Fig. 8.5. The weight loss in TG plot starts above ~ 500 °C and continues upto ~ 1050 °C in the 20 % Ni-substituted sample. As revealed by temperature programmed reduction profiles (Fig. 8.5) of these oxides, we can infer that this weight loss is due
to reduction of these oxides in H\textsubscript{2} atmosphere. Mainly the weight loss is attributed to reduction of species, In\textsuperscript{3+} and Ni\textsuperscript{2+}, to In\textsuperscript{0} and Ni\textsuperscript{0} respectively. The evidence of the above inference comes from temperature programmed reduction profiles of In\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} oxides. TPR profiles of In\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} reactant oxides (exhibited as inset in Fig. 8.5) suggests that In\textsuperscript{3+} species reduces above 600 °C with T\textsubscript{max} at 670 °C, whereas TiO\textsubscript{2} does not reduce upto 1000 °C recorded in the range of 25-1000 °C under H\textsubscript{2} flow (5 % H\textsubscript{2} in Ar).

### 8.3.2.1 Ex situ characterization of reduced residue samples

![Figure 8.6](image_url)

Fig. 8.6 shows the XRD patterns of reduced residue of In\textsubscript{2}TiO\textsubscript{5}, ITN\textsubscript{2} and ITN\textsubscript{4} samples obtained after recording TPR. In the reduced In\textsubscript{2}TiO\textsubscript{5} and ITN\textsubscript{2} samples the presence of prominent lines at 2\(\theta\) = 32.98\(^\circ\), 39.2\(^\circ\) conforms to reported pattern of In\textsuperscript{0} (JC-PDS No.05-0642). Other strong lines at 27.44\(^\circ\), 36.08\(^\circ\) and 54.32\(^\circ\) match well with rutile TiO\textsubscript{2} phase (JC-PDS No.21-1276). Thus, both metallic indium and rutile titania were present in these two reduced samples. There was no other phases present in the reduced In\textsubscript{2}TiO\textsubscript{5} sample. No prominent additional lines were also observed in the reduced ITN\textsubscript{2} sample, except for a weak hump at 41.2\(^\circ\). This peak can be attributed to the formation of an alloy of Ni and In namely δIn\textsubscript{3}Ni\textsubscript{2} (JCPDS No. 070298). The small amount of nickel present in the sample was initially reduced at a lower temperature with an onset at ~ 450 °C and subsequently In\textsuperscript{3+} was also reduced (refer fig. 8.4). The reduced metallic nickel then reacted with the reduced In metal to form the In-Ni alloy.

An interesting feature was observed in the XRD pattern of reduced ITN\textsubscript{4} sample. The intensity of the peaks due to reduced Indium metal was reduced drastically, along with the appearance of prominent lines (marked by *) at 2\(\theta\) = 28.9, 41.0, 41.3 and 59.8. These peaks are attributed to the presence of δIn\textsubscript{3}Ni\textsubscript{2} phase. Remaining line in the residue were at 2\(\theta\) = 41.5\(^\circ\). An alloy formation of Ni-Ti is indicated by this peak as 2\(\theta\) = 41.57\(^\circ\) corresponds to 100% peak due to reflection...
from 511 plane of Ti$_2$NI alloy (JCPDS No. 180898). This suggests that Ti$^{4+}$ an otherwise stable cation towards reduction got reduced within 1100 °C. The formation of Ni-Ti alloy on reduction of ITN4 sample is quite plausible as revealed by the XRD pattern (Fig. 8.6), as secondary phase of NiTiO$_3$, also got reduced along with major indium titanate phase. This new phases possibly would have facilitated the reduction of Ti$^{4+}$ along with reduction of Ni$^{2+}$. Any of the lines in the spent samples do not match with the reported XRD pattern of Ni metal alone (JC-PDS. No. 04-0850). So, Ni metal formed by reduction was very active and reacted with other reduced phases to form alloys. Further, the presence of Ni facilitated the reduction of In$^{3+}$ as the T$_{\text{max}}$ of the individual peaks due to reduction of In$^{3+}$ was found to be lowered in the case of substituted samples. In addition to this, the otherwise non-reducible cation Ti$^{4+}$ also got reduced in the 20% substituted sample which might probably be due to autocatalytic effect of Ni$^{2+}$. This phenomenon can be referred to as an incident of hydrogen spillover in mixed metal oxide. The Ni metal initially formed by reduction of the cation was active enough to dissociate and activate the hydrogen, which in turn could even reduce Ti$^{4+}$ cation in addition to facilitating the reduction of In$^{3+}$. It could also be suggested that the extent of reduction of Ti$^{4+}$ and subsequent alloy formation would depend on the content of secondary phase. In ITN2 sample In$^{3+}$ was replaced partially by Ni$^{2+}$ and the reduced Ni metal facilitated the reduction of In$^{3+}$ cation and then an alloy formation took place. This fact is evident from the TPR curve where the whole reduction pattern including T$_{\text{max}}$ for reduction of In$^{3+}$ shifts to lower temperature. Further in the ITN4 sample the reduction of partially substituted Ni$^{2+}$ cation generated Ni metal which dissociated and activated the hydrogen which eased the reduction of In$^{3+}$ cation and also reduced Ti$^{4+}$. This process of reduction of Ti$^{4+}$ if continued would have resulted in the reduction of all Ti$^{4+}$ but the formation of the Ti$_2$Ni alloy prevented further hydrogen activation and that further reduction of
the Ti$^{4+}$ was hindered. So, only partial reduction of Ti$^{4+}$ was feasible. The presence of NiTiO$_3$ phase might have assisted the above process. Thus, Ni substitution at In-site of In$_2$TiO$_5$ had a drastic effect on the reduction behavior of indium titanates. TPR results in conjunction with XRD studies reveal the reduction of In$^{3+}$ → In$^0$, while Ni$^{2+}$ facilitated the reduction of otherwise non-reducible cation Ti$^{4+}$ and resulted in formation of Ni-Ti alloy (Ti$_2$Ni).

![XRD patterns of spent In$_{2(1-x)}$Ni$_{2x}$TiO$_{5-ac}$ samples after recording TPR in H$_2$(5%) + Ar atmosphere of ITO, ITN2 and ITN4 compositions. The peaks due to δIn$_3$Ni$_2$ alloy are marked by *.

In Fig. 8.7 a-b, the X-ray photoelectron (XPS) spectrum of fresh, and completely reduced ITN4, sample are shown, which were recorded in order to identify the oxidation states of indium and titanium metal ions present in the spent samples after the reduction. Table-8.3 lists the elements identified and their oxidation states in the fresh and reduced samples. The binding
energies at 445.9 eV and 457.5 eV corresponding to In (3d₅/₂) and Ti (2p₃/₂) which matches with the reported binding energies for In in +3 and Ti in +4 oxidation state present in fresh ITN4 sample as shown in Figs. 8.7a and 8.7b. But, the binding energy at 445.9 eV as observed in the fresh sample in Fig. 8.7a is shifted to lower binding energies of 444.1 eV in completely reduced ITN4 sample. XPS spectra suggest the existence of indium in +3 oxidation state in the fresh sample and In(0) in completely reduced sample. The changes in oxidation states of Ti present in the fresh and reduced sample are shown in Fig. 8.7b. In the reduced sample, in addition to major peak at 457.5 eV a shoulder is observed at 453.7 eV corresponding to Ti(0) state. The appearance of this shoulder peak confirms the reduction of Ti⁴⁺ to Ti metal during the temperature programmed reduction (TPR) experiments. In addition, in Figure 8.7a, a shoulder appears at higher binding energy in the XPS spectra of Indium ion for the fresh sample, but it completely disappears in the spectra recorded after the complete reduction. The appearance of shoulder is attributed to the interaction of In³⁺ with other ions present in the compound. Thus as process of reduction proceeds, the interaction of Indium with other ions decreases or it gets segregated out from the sample. However, presence of In¹⁺ in the reduced sample is not observed. Intensity of In (3d) peak is considerably increased in Fig 8.7a, after complete reduction as compared to fresh sample. Thus, ITN4, sample on reduction, deposits the metallic Indium on the surface and hence the peak intensity due to Indium on surface increases. It is well known that the catalytic properties of a sample are sensitive to its surface composition; therefore this observation may play a crucial role in deciding its performance for redox reactions. The XPS results in accordance with TPR and thermogravimetry results suggests the formation of metallic Ti(0) along with Ti⁴⁺ and In (0) when ITN₄ was reduced in H₂ upto 1100 °C whereas unsubstituted In₂TiO₅ did not
reveal any reduction of Ti$^{4+}$ species. Thus presence of Ni influenced the reduction behavior of Ti$^{4+}$ species present in the sample by activating H$_2$ molecules.

Fig. 8.7. Binding energies of different metal ions in partially reduced sample of ITN4 obtained after recording TPR up to 1000 °C of (a) In (3d), (b) Ti (2p).

Table. 8.3: Representative XPS binding energy values of different elements in ITN4 samples obtained before and after the first TPR cycle in temperature range of 25-1100 °C.

<table>
<thead>
<tr>
<th>BE of XPS Signal (eV)</th>
<th>Before TPR</th>
<th>After TPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>elements</td>
<td>In 3d$<em>{5/2}$ Ti 2p$</em>{3/2}$ In 3d$<em>{5/2}$ Ti 2p$</em>{3/2}$</td>
<td></td>
</tr>
<tr>
<td>B.E</td>
<td>445.9</td>
<td>457.5</td>
</tr>
<tr>
<td>Oxidation state</td>
<td>+3</td>
<td>+4</td>
</tr>
<tr>
<td>In$^{3+}$</td>
<td>No peak due</td>
<td>In$^{0}$</td>
</tr>
<tr>
<td>to Ti$^{0}$ metal</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
8.3.2.2 Discussion

The reduction of In$_{2(1-x)}$Ni$_{2x}$TiO$_5$-δ oxide samples is represented by following equation:

$$\text{In}^{3+}_{2(1-x)}\text{Ni}^{2+}_{2x}\text{Ti}^{4+}_5\text{O}_{5-δ}(s) + (3-δ)\text{H}_2(g) \rightarrow 2(1-x)\text{In}^0(s) + 2x\text{Ni}^0(s) + \text{Ti}^{4+}_2\text{O}_2(s) + (3-δ)\text{H}_2\text{O}(g)$$

490-1100°C

Table 8.4. H$_2$ consumption data of In$_{2(1-x)}$Ni$_x$TiO$_5$-δ samples obtained from the first TPR cycle in temperature range of 25-1100 °C.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Calculated</th>
<th>Experimental #</th>
<th>Residue as identified by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$TiO$_5$</td>
<td>8390</td>
<td>8404</td>
<td>In$_0$ &amp; TiO$_2$ rutile</td>
</tr>
<tr>
<td>In$<em>{1.95}$Ni$</em>{0.05}$TiO$_5$-δ</td>
<td>8396</td>
<td>9009</td>
<td></td>
</tr>
<tr>
<td>In$<em>{1.9}$Ni$</em>{0.1}$TiO$_5$-δ</td>
<td>8401</td>
<td>8358</td>
<td></td>
</tr>
<tr>
<td>In$<em>{1.8}$Ni$</em>{0.2}$TiO$_5$-δ</td>
<td>8412</td>
<td>9528</td>
<td>In, TiO$_2$ &amp; δIn$_3$Ni$_2$</td>
</tr>
<tr>
<td>In$<em>{1.7}$Ni$</em>{0.3}$TiO$_5$-δ</td>
<td>8424</td>
<td>10514</td>
<td></td>
</tr>
<tr>
<td>In$<em>{1.6}$Ni$</em>{0.4}$TiO$_5$-δ</td>
<td>8436</td>
<td>10153$^*$</td>
<td>In, TiO$_2$, δIn$_3$Ni$_2$ &amp; Ti$_2$Ni</td>
</tr>
</tbody>
</table>

* stoichiometry determines δ as x. # TCD signal for manual injection of standard hydrogen has been used for calibration to find out the H$_2$ consumption. $^*$ is the difference observed in experimental values (higher) of H$_2$ consumed as compared to calculated values is attributed to reduction of Ti$^{4+}$ metal ions to Ti metal driven by presence of Ni$^{2+}$ ions.

H$_2$ consumption data calculated as well as that observed from the areas under TPR peak, for all samples for the first reduction cycle (TPR) is listed in Table-8.4. The comparison shows
that except for ITN1 for all other samples experimental values are higher than calculated values. This discrepancy increases with increase in Ni content as observed from the Table-8.4. It can be explained on the basis of autocatalytic reduction of the samples in the presence of Ni\(^{2+}\) cations. Ti\(^{4+}\) cation is stable in H\(_2\) up to 1000 °C in TiO\(_2\) samples as evident from inset of Fig. 8.5. As such, to obtain the TPR profiles of some simple oxides, TiO\(_2\) and Cr\(_2\)O\(_3\), are difficult because the standard approximate free energy change (ΔG\(^\circ\) in KJ/mol) for the process: MO + H\(_2\) → Metal + H\(_2\)O are respectively ~ 220 and ~140 [7]. However for In\(_{2(1-x)}\)Ni\(_{2x}\)TiO\(_{5-δ}\) samples, in addition to the normal nucleation and growth process, during reduction the presence of Ni\(^{2+}\) in even a minor amount modifies the reduction. Ni metal initially formed by reduction dissociates and activates hydrogen. This hydrogen then reacts and reduces the oxide (even Ti\(^{4+}\)). This phenomenon is termed as hydrogen spillover. In oxide catalysts the presence of metal cations, which after reduction generates the active metal that can dissociate and activate the hydrogen for facilitating an otherwise difficult reduction phenomenon. It is reported [8-9] that hydrogen spillover can be broken into three primary steps: (i) dissociative chemisorption of gaseous H\(_2\) on a transition metal catalyst; (ii) migration of H atoms from the catalyst to the substrate and (iii) diffusion of H atoms on substrate surfaces and/or in the bulk materials. In this case the metallic Ni formed after reduction is the transition metal catalyst. The substrate is the remnant oxide from which Ni\(^{2+}\) cation gets eliminated and then the reduction of bulk In\(^{3+}\) occurs by diffusion of H-atoms into the remnant oxide material and thus the reduction profile shifts to lower temperature. Diffusion of H atoms and subsequent reduction of Ti\(^{4+}\) is definitely easier in NiTiO\(_3\) that the indium titanate phase so we observe higher amount of Ti\(^{4+}\) reduction in the sample. This is further corroborated by the TPR results where we observe increased hydrogen consumption discrepancy with an increase in Ni content. Alloy formation of the transition metal catalyst Ni with In and Ti

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prevented further reduction of Ti\(^{4+}\) but In\(^{3+}\) being reducible was completely reduced. Such phenomenon of hydrogen spillover has been noticed over nickel metal used as catalyst in hydrogen storage materials like activated carbon, where hydrogen spillover is mainly responsible in increasing the storage capacity [10]. Recently, pioneering studies by Yang et al revealed novel processes to store substantial quantities of hydrogen via hydrogen spillover [11-13].

8.3.3 Photocatalytic properties

8.3.3.1 DRUV

Figure 8.8 illustrates the light absorption properties of In\(_{2(1-x)}\)Ni\(_{2x}\)TiO\(_{5-\delta}\) (0.0 \(\leq x \leq 0.2\)), showing that the UV-visible absorption spectra of these compounds are characteristic of photocatalysts able to respond to UV-visible light. It is also evident from Fig. 8.8, that with the substitution of Ni, there is a progressive red shift in the absorption pattern of the titanates. The band gap of these compounds can be estimated from plots of the square root of Kubelka-Munk functions \(F(R)\) versus photon energy. One of the most characteristic features is that the bandgap is narrowed with Ni doping. This decrease in band gap is considered largely to be a consequence of the presence of Ni 3d level. The Nickel 3d levels might sit at a forbidden level in the band gap of indium titanate and function as an impurity level, lowering the effective band gap. The bandgap change in Ni-doped compounds is generally to internal transitions in a partly filled Ni d shell [5, 14]. Some authors [5, 14] support this fact by the appearance in the Ni-doped compounds of an ultraviolet-visible absorption band at 420-520 nm. But, it is not established how a Ni d-d internal transition can play a role in photoactivity. In our case such internal transitions were not noticed but the overall shift of the band edge towards higher wavelength was evident. The smaller bandgap will anyway facilitate excitation of an electron from the valence band to the conduction
band in the doped oxide semiconductors, thus increasing the photoresponse and is expected to increase photocatalytic efficiency of the material.

Fig. 8.8. DRUV spectra of the indium titanate samples which shows a progressive red shift in absorption with an increase in Ni content

8.3.3.2 Photoactivity

Results of photo-activity of unsubstituted In$_2$TiO$_5$ and Ni substituted Indium titanates, In$_{2(1-x)}$Ni$_{2x}$TiO$_{5-δ}$ (0.0 ≤ x ≤ 0.2) samples for hydrogen generation by water splitting in presence of methanol as a sacrificial agent, under UV-vis irradiation are shown in Fig. 8.9. The hydrogen yield was found to increase with irradiation time for all the samples upto an experiment of 6 h. It is observed from Fig. 8.9 that the 10% doped sample having composition In$_{1.8}$Ni$_{0.2}$TiO$_5$. $δ$ exhibited highest photoactivity. The pristine indium titanate sample was significantly photoactive for hydrogen generation but the rate decreased initially with low Ni substitution upto x < 0.1 but on further substitution the rate increased showing highest photoactivity at x = 0.2
followed by a drastic decrease on further increase in Ni content. Our present work clearly demonstrates the fact that indium titanate is able to generate hydrogen photocatalytically by water splitting in presence of sacrificial agent methanol. Further, Ni doping modifies the photoactivity to a great extent. On Ni-doping the photoactivity for hydrogen generation increases initially and the reaches a maximum at 10% doping and the again falls with the highest Ni-content sample of 20% doping showing lower activity than the base ITO itself.

Fig. 8.9. The time dependent H$_2$-yield from water-methanol solution using different indium titanate samples. Reaction conditions: 0.1 g catalyst, 10 ml distilled water, 5 ml methanol. Light source; UV-visible medium-pressure mercury lamp (Hg, Ace Glass Inc., 450W) surrounded with water circulation jacket to absorb IR irradiation.

The increase in photocatalytic activity can be attributed to a decrease in band gap of indium titanate on Ni-doping. The smaller bandgap as seen from DRUV result facilitated the photoinduced electron excitation from the valence band to the conduction band in the doped oxide semiconductor, thus increasing the photocatalytic activity of the material. But, Ni-doping
had an effect on the crystal structure as well which has been depicted in the XRD and Reitveld refinement results. The formation of secondary phase NiO was seen in ITN2 sample but it was not detrimental to the photocatalytic activity. Further substitution of Ni resulted in formation of other phase NiTiO$_3$ which could have a negative effect on photoactivity of indium titanate. The combination of a proper band gap and crystal structure was present in the ITN2 sample for having the highest photocatalytic activity among these semiconductor oxides.

The results are compared with other A-site and B-site cationic doped samples in indium titanate In$_2$TiO$_5$ (A = Nd$^{3+}$; B = Fe$^{3+}$ and Cr$^{3+}$; extent of doping 10 % - all prepared by solid state route) as shown in Fig 8.10. Among all the catalysts, 10% Nd substituted indium titanate photocatalysts was found to be the most active under UV-vis irradiation. A site substitution with Nd$^{3+}$ ions yielded hydrogen typically in range of ~1600 $\mu$moles/g in 4 h as compared ~ 1100 $\mu$moles g$^{-1}$ for Ni$^{2+}$ substituted sample. B site doped with Fe/Cr ions showed much lower photoactivity. The higher photoactivity of Nd substituted samples can be attributed again on the basis of band structure and crystal structure. The band structure contribution comes from the role played by 4f orbital of Nd in the band structure of In$_2$TiO$_5$ which is much more prominent than those of 3d orbitals of Ni. Further Nd substitution was an isovalent substitution at A-site creating negligible anionic vacancies or defects as compared to an aliovalent Ni substitution. As we have discussed in Chapter 1 that defect in the crystal lattice can acts as sites for electron-hole recombination thus decreasing photocatalytic activity.
Fig. 8.10. Photocatalytic activity of substituted indium titanate samples. $H_2$ yield is plotted as a function of time over $\text{In}_2\text{TiO}_5$, $\text{In}_{1.8}\text{Nd}_{0.2}\text{TiO}_5$, $\text{In}_{1.8}\text{Ni}_{0.2}\text{TiO}_5$, $\text{In}_2\text{Ti}_{1-x}\text{M}_x\text{O}_5$ ($M = \text{Fe}^{3+}$ and $\text{Cr}^{3+}$; $x = 0.2$), photocatalyst samples. Reaction conditions: 0.1 g catalyst, 10 ml distilled water, 5 ml methanol. Light source; UV-visible medium-pressure mercury lamp (Hg, Ace Glass Inc., 450W) surrounded with water circulation jacket to absorb IR irradiation.

8.4. Conclusion

A-site substitution by a divalent Ni$^{2+}$ cation at In$^{3+}$ site of $\text{In}_2\text{TiO}_5$ resulted in single phase compositions at low extent of substitution (upto 5%), biphasic at a higher substitution (10%) with very low impurity phase of unreacted NiO and triphasic at even higher Ni content (15-20%), having very low concentrations of NiO and NiTiO$_3$ phase. Highly crystalline phase of indium titanate was obtained which on Ni doping at the In site exhibited lattice contraction. The redox properties, were investigated by recording temperature programmed reduction in...
temperature range of 450-1100 °C in all the samples. Ni substitution induced considerable ease in reducibility (T<sub>max</sub>) of substituted samples as compared to In<sub>2</sub>TiO<sub>5</sub> phase. The substitution-induced non-stoichiometry and the microstructural defects may cause the distortion in the lattice, thus facilitating the reduction of oxides. The interesting observation was the reduction of otherwise non-reducible cation Ti<sup>4+</sup>, in the 20% substituted sample, ITN4. Ni metal initially formed by the reduction of Ni<sup>2+</sup> dissociate and activate the hydrogen which eased the In<sup>3+</sup> reduction and even facilitated the reduction of Ti<sup>4+</sup>. The optical measurements showed that Ni-doping induced a lowering in band gap of these semiconductor oxides. All the samples were active for hydrogen generation by water splitting in presence of methanol as a sacrificial agent, under sunlight type irradiation. The photocatalytic activity increased with Ni-doping with the In<sub>1.8</sub>Ni<sub>0.2</sub>TiO<sub>5.8</sub> sample showing the highest rate of hydrogen evolution. This increase in photocatalytic activity can be attributed to the favorable crystal structure i.e. reduction in cell parameters and bond distances and better light absorption properties. Further increase in Ni-doping reduced the rate of hydrogen evolution probably due to segregation of secondary phases and also an increase in non-stoichiometric defects.

References: