Abstract

The reduction behaviour of mixed metal oxides with nominal compositions of \( \text{In}_{2(1-x)}\text{Ni}_{2x}\text{TiO}_{5.5-x} \), where 0.0 \( \leq x \leq 0.2 \), has been investigated as a function of the value of \( x \). These compositions were synthesized by ceramic route and characterized using powder X-ray diffraction and Infrared spectroscopic techniques. The \( \text{In}_{2(1-x)}\text{Ni}_{2x}\text{TiO}_{5.5} \) samples were single-phased samples, isomorphic with \( \text{In}_2\text{TiO}_5 \) phase up to 10% Ni content. A secondary phase, identified to be \( \text{Ni}_{0.25}\text{Ti}_{0.125}\text{O} \) phase, was present along with the major phase of indium titanate in \( \text{In}_{1.6}\text{Ni}_{0.4}\text{TiO}_{5.5} \) and \( \text{In}_{2}\text{Ni}_{0.4}\text{TiO}_{5.5} \) samples. Ni substitution at \( \text{In}^{3+} \) site, induced ease in reducibility, as indicated by lowering of \( T_{\text{max}} \) and onset reduction temperature in substituted samples, as compared to the \( \text{In}_2\text{TiO}_5 \) phase. Ni facilitated the reduction of \( \text{Ti}^{4+} \) in \( \text{Ni}_{0.25}\text{Ti}_{0.125}\text{O} \) to Ni-Ti phase, as indicated by the XRD reflections in the reduced \( \text{In}_{1.4}\text{Ni}_{0.2}\text{TiO}_{5.5} \) sample.

Introduction

In view of global energy and environmental issues, photocatalytic water splitting to produce clean energy carrier \( \text{H}_2 \) has been widely regarded as one of the ideal solar energy conversion methods \cite{1}. Much effort has been made to develop the single phased photocatalysts for efficient water splitting. To our knowledge, however, the number of single phased photocatalysts capable of stoichiometric water splitting, especially under visible light irradiation, is still very limited so far \cite{2}. Uptill now, various kinds of indates such as \( \text{In}_2\text{O}_3(\text{ZnO})_m \) \cite{3}, \( \text{Mn}_x\text{O}_4 (\text{M}=\text{Ca}, \text{Sr}, \text{Ba}) \) \cite{4}, \( \text{LnIn}_2\text{O}_5 \) (\( \text{Ln}=\text{La}, \text{Nd} \)) and \( \text{Sr}_x\text{M}_m\text{In}_2\text{O}_5 (\text{M}=\text{Ca}, \text{Ba}) \), \cite{5} have been reported as photocatalysts for water splitting. However, the activities of the aforementioned \( \text{In}^{3+} \) containing photocatalysts are usually low under visible light irradiation, due to the relatively large band gaps.

Earlier, we have reported the thermal/chemical stability, redox behaviour and catalytic properties of \( \text{Th}(\text{VO}_4)_4 \) and \( \text{LaMn}_2\text{O}_5 \) oxides, as a function of multiple cationic substitutions, at both A and B sites \cite{6-9}. With the objective to study the thermal and reduction behaviours of certain titania-based single phased compositions, which can serve as prospective photocatalysts particularly for water splitting reactions, studies have been recently taken up in our laboratories on \( \text{In}_2\text{O}_3-\text{TiO}_2 \) system, resulting in formation of indium titanate, \( \text{In}_2\text{TiO}_5 \). An aliovalent substitution by \( \text{M}^{3+} \) cation \( \text{M}=\text{Fe}^{3+} (0.64 \text{ Å}), \text{Cr}^{3+} (0.63 \text{ Å}) \) at B-cation site, in \( \text{In}_2\text{TiO}_5 \) was attempted, introducing thereby some micro-structural changes in their lattice.
It is therefore apparent, that the substitution of a lower-valent ion in place of smaller Ti\textsuperscript{4+} (ionic radius = 0.68 Å), is likely to form an anion deficient solid solution with partial loss of oxygen in the lattice (δ). Recently, we studied the effect of B-Site substitution on thermal properties and reduction behaviour of In\textsubscript{1-x}TiO\textsubscript{3} (0.0 ≤ x ≤ 0.02) mixed oxide catalysts \[10\]. In the present study, we report the A-site substitution-induced effects on indium titanate. For this purpose, In\textsubscript{2(1-x)}Ni\textsubscript{x}TiO\textsubscript{5-δ}, (0.0 ≤ x ≤ 0.2) mixed oxide catalysts were synthesized using solid-state reaction and characterized by powder X-Ray Diffraction (XRD). The thermal and reduction behaviours were studied by recording ThermoGravimetric, Differential Thermal Analysis (TG/DTA) and Temperature-Programmed Reduction (TPR) profiles.

**Experimental**

Mixed oxides with nominal composition, In\textsubscript{2(1-x)}Ni\textsubscript{x}TiO\textsubscript{5-δ}, for 0.0 ≤ x ≤ 0.2, were synthesized through ceramic route, by mixing reactant oxides in appropriate stoichiometry and calcining at 1200°C. The powder XRD patterns were recorded on a Philips X-ray diffractometer (model PW 1710), equipped with a graphite monochromator and Ni-filtered Cu-Kα radiation. The thermal behaviour of these samples (~ 20 mg) was monitored by recording their simultaneous DTA/TG profiles both in air and 5%H\textsubscript{2}+Ar atmospheres, in the temperature range of 25-1000°C at a heating rate of 10°C min\textsuperscript{-1}.

TPR run was recorded on a TPDRO-1100 analyzer (ThermoQuest, Italy) under the flow of H\textsubscript{2} (5%) + Ar at a gas flow rate of 20 ml min\textsuperscript{-1}, in the temperature range of 25-1000°C, at a heating rate of 6°C min\textsuperscript{-1}. The samples were pretreated at 350°C for about 2.5 h in helium, prior to recording of the first TPR run.

**Results and Discussion**

**X-Ray Diffraction (XRD)**

Fig. 1 shows the powder XRD patterns of In\textsubscript{2}TiO\textsubscript{3} and corresponding patterns observed due to aliovalent substitution of Ni\textsuperscript{2+} in place of In\textsuperscript{3+} at A-site. The lines due to reactant oxides are missing in these patterns thus confirming the completion of the solid-state reaction. The XRD patterns, of samples with In\textsubscript{1.9}Ni\textsubscript{0.1}TiO\textsubscript{5-δ}, In\textsubscript{1.8}Ni\textsubscript{0.2}TiO\textsubscript{5-δ} and In\textsubscript{1.6}Ni\textsubscript{0.4}TiO\textsubscript{5-δ} compositions, match with the XRD pattern of unsubstituted indium titanate sample, as shown in curves b-d of Fig. 1. Thus in these samples,
Ni substitution resulted in single phase, due to formation of solid solution of Ni with the lattice of the parent compound, indium titanate. However, for samples having Ni content higher than 10% some low intensity lines (marked with *) in addition to parent phase were also observed (Fig. 1e and f). These weak lines present at 2θ = 43.33°, 35.71° and 63.02° are attributed to the formation of secondary phase in the samples having compositions of In_{1-x}Ni_xTiO_{4.8} and In_{1.6}Ni_{0.4}TiO_{5.4}. The secondary phase was identified to be NiO_{0.25}TiO_{1.125}O (JC-PDS card No. 31-0916).

**Temperature Programmed Reduction behaviour (TPR)**

The typical first Temperature Programmed Reduction cycle (TPR) of substituted samples and unsubstituted sample, are shown in Fig. 2. The TPR profile of unsubstituted In$_2$TiO$_5$ sample as seen in curve ‘a’ comprises a prominent band starting at ~600°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$_{max}$) 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., In$_{1.8}$Ni$_{0.2}$TiO$_{5.8}$ and In$_{1.6}$Ni$_{0.4}$TiO$_{5.4}$, TPR profiles (Fig. 2c-d), 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 attributed to reduction of Ni$^{2+} \rightarrow$ Ni$^{0}$ along with reduction of In$^{3+}$. At the same time, the T$_{max}$ of the individual peaks was found to be lower in the case of substituted samples. For instance, we observe the lowering of T$_{max}$ around by 80°C in Fig. 2d, as compared to the TPR profile of an unsubstituted phase (Fig. 2a). Also the onset reduction temperature of 625°C in unsubstituted phase has considerably decreased by mere 20% Ni substitution as shown in Fig. 2d. The TPR profile as a whole has shifted to lower temperature as a result of Ni substitution. These results are comparable to our earlier work [10] where Fe and Cr were substituted at B-site. Thus, M (Ni$^{2+}$, Cr$^{3+}$ and Fe$^{3+}$) 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 and B-site substitution.

XRD patterns of spent In$_{1-x}$Ni$_x$TiO$_{5.8}$ sample, obtained after recording TPR, shows the presence of prominent lines at 2θ = 33.01°, 39.0°, 54.00° which conform to reported pattern of In$^2$ (JC-PDS No.5-642). Other strong lines at 27.44°, 36.08° and 54.32°,match well with rutile TiO$_2$ phase (JC-PDS No.21-1276). Remaining lines in the residue were at 2θ = 41.27°, 43.38°, 44.23°, 39.2°. These lines do not match with the reported XRD pattern of Ni metal alone (JC-PDS. No. 04-0850). However, an alloy formation of Ni-Ti is indicated by these lines, according to JC-PDS card No. 35-1281. This is a very interesting observation as Ti$^{4+}$ is otherwise stable towards reduction, but Ni facilitated its reduction upto 1100°C. The formation of Ni-Ti alloy on reduction of In$_{1-x}$Ni$_{0.2}$TiO$_{5.8}$ sample is quite plausible, as revealed by the XRD pattern, a secondary phase of Ni$^{0.75}$Ti$^{0.125}$O, which segregated out in the fresh In$_{1.8}$Ni$_{0.2}$TiO$_{5.8}$ sample along with major indium titanate phase. This new phase possibly would have facilitated the reduction of titanium along with reduction of nickel. This also suggests that the extent of reduction of Ti and subsequent alloy formation, would depend on the content of secondary phase. Thus TPR results in conjunction with XRD studies, reveal the reduction of In$^{3+} \rightarrow$ In$^0$, while Ni$^{2+}$ facilitated the reduction of non-reducible cation Ti$^{4+}$ and resulted in formation of Ni-Ti alloy.

**Thermo-Gravimetric, Differential Thermal Analysis (TG/DTA)**

Both substituted and unsubstituted samples did not show any weight loss in TG, thus indicating that all substituted In$_{2(1-x)}$Ni$_x$TiO$_{5.8}$ oxide samples are stable in air upto 1000°C. However, in H$_2$+Ar atmosphere, corresponding TG plots exhibited substantial weight loss of all samples. The weight loss in TG plot starts above ~490°C and continues upto ~1050°C in
Ni-substituted samples. As revealed by temperature programmed reduction profiles (Fig. 2) of these oxides, we can infer that this weight loss is due to reduction of these oxides in H₂ atmosphere. Mainly the weight loss is attributed to reduction of species, In³⁺ and Ni²⁺, to In⁰ and Ni⁰ respectively. The evidence of the above inference comes from temperature programmed reduction profiles of In₂O₃ and TiO₂ oxides. Their TPR profiles recorded in the range of 25-1000°C under H₂ flow (5% H₂ in Ar) suggest that In₂O₃ gives single prominent reduction band with T_max at 670°C, whereas TiO₂ gives a very weak profile up to 1000°C. The presence of lines due to In⁰ in the XRD pattern of residue sample obtained after recording TG, confirms the above result.

Conclusions

A-site substitution by a divalent Ni²⁺ cation at In³⁺ site, resulted in single phase compositions suggesting formation of solid solution of Ni in the lattice of the parent compound, indium titanate. However, for samples having Ni content higher than 10% in indium titanate, it resulted in the segregation of secondary phase, Ni₀.75Ti₁.25O along with major phase of indium titanate, In₂TiO₅. The secondary phase, identified to be Ni₀.75Ti₁.25O, was present in the samples having compositions of In₁₋ₓNiₓTiO₂₋ₓ and In₁₋ₓNiₓTiO₂₋ₓ (x=0.4). The temperature programmed reduction and XRD studies establish reduction of In³⁺ and Ni²⁺ to In⁰ and Ni⁰ metal in the temperature range of 450-1050°C. Ni substitution induced considerable ease in reducibility (T_max) of substituted samples as compared to In₂TiO₅ phase. Presence of Ni-Ti alloy is indicated in the reduced In₁₋ₓNiₓTiO₂₋ₓ sample. The substitution-induced non-stoichiometry and the microstructural defects, may cause distortion in the lattice, thus facilitating the reduction of oxides.

References


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