Thermochimica Acta 516 (2011) 40–45

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Influence of Ni substitution on redox properties of $In_{2(1-x)}$ $Ni_{2x}TiO_{5-\delta}$ oxides

A.M. Banerjee[a], M.R. Pai[a], Jagannath[b], S.R. Bharadwaj[a,*]

[a] *Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*
[b] *Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*

ARTICLE INFO

Article history:
Received 13 August 2010
Received in revised form
15 December 2010
Accepted 7 January 2011
Available online 18 January 2011

Keywords:
Temperature programmed reduction
Reducibility
Alloy
Hydrogen spillover
XPS

ABSTRACT

The thermal behavior of mixed metal oxides with nominal compositions of $In_{2(1-x)}Ni_{2x}TiO_{5-\delta}$ where $0.0 \le x \le 0.2$, were investigated by recording their temperature programmed reduction (TPR). The samples were synthesized by ceramic route and analyzed for phase composition using powder X-ray diffraction. The TPR profile of pristine In_2TiO_5 indicated the reduction of In^{3+}, which takes place predominantly over the other species Ti^{4+} in In_2TiO_5 sample. Ni substitution at In^{3+} site induced ease in reducibility as indicated by lowering of onset reduction temperature and T_{max}. Moreover, it also facilitated the reduction of otherwise non reducible cation, Ti^{4+}. Ni metal initially formed by reduction, dissociates and activates hydrogen which then reacts and reduces the oxide (even Ti^{4+}), a case of hydrogen spillover. The metallic Ni forms an alloy Ti_2Ni with reduced Ti metal and δIn_3Ni_2 alloy with the reduced In metal as evident by XRD and XPS results of the reduced residue of 20% Ni doped ($In_{1.6}Ni_{0.4}TiO_{5-\delta}$) sample. Due to formation of new alloy phases of δIn_3Ni_2 and Ti_2Ni, the rate of hydrogen adsorption diminishes which slows down further hydrogen activation and consequent further Ti^{4+} reduction.

1. Introduction

The physico-chemical properties of ceramic ternary oxides ($A_xB_yO_z$) having perovskites, spinel or any other structure have been investigated in great detail both because of fundamental scientific knowledge and its widespread technological applications in various fields. Specifically the ternary oxide that arise when one of the cation is titanium are titantes which are high performance materials having applications in various fields. Some of the recent applications include catalysts [1–3], sensors and actuators [4,5], solar cells [6] SOFC materials [7] and so on. So, it is imperative to study their interesting physicochemical properties the knowledge of which finds them utilized in suitable applications.

One of the interesting applications of these titanates is as catalyst for various reactions. The important considerations in designing an oxide catalyst are its thermal, chemical stability, reducibility and oxidizability [8–13]. The thermal and chemical stability and redox behavior of these titanates would play a vital role in determining their catalytic properties. Further, it is well known that substitution by transition metal cations at A or B sites of these oxide systems, further tailor their physico-chemical properties which in turn results in modified catalytic behavior.

So, with the objective to study the thermal and reduction behaviors of certain titania and indium oxide based single phased compositions, which can serve as prospective catalyst for redox reactions and as photocatalysts particularly for water splitting reactions, studies have recently been taken up in our laboratories on In_2O_3–TiO_2 system resulting in formation of indium titanate, In_2TiO_5. The thermo-physical characteristics and redox behavior of In–Ti–O system was monitored. The catalytic properties of many titanates have been shown to be dependent on their physicochemical properties and the thermal properties of some titanates have been investigated [14–16]. We have also investigated the redox properties of Fe-doped lanthanum titanates ($La_2Ti_{2(1-x)}Fe_{2x}O_{7-\delta}$, $0.0 \le x \le 1.0$) and correlated its thermophysical properties with catalytic activity for $CO + N_2O$ reaction [17,18]. The crystal structure and luminescent properties of indium titanate oxide, In_2TiO_5 have been reported [19]. The structure of In_2TiO_5, belongs unambiguously to In_2VO_5 type. The two independent In^{3+} ions are octahedrally coordinated with six oxygen atoms, resulting in InO_6 octahedra, which by edge sharing forms infinite ribbons. Three corner connected $(In_2O_4)_n{}^{2n-}$ infinite ribbons forms the tunnels where O–Ti–O–Ti–O chains are inserted. In each tunnel formed by four ribbons one finds two chains of TiO_5 distorted square pyramids oppositely oriented. In order to perturb this structure and to modify catalytic properties, in the present study, an aliovalent substitution by transition metal Ni^{2+} at A-site was attempted, introducing thereby some micro-structural changes in the lattice. It

---

* Corresponding author at: Fuel Cell Materials and Catalysis Section, 3-193 H, Chemistry Division, Modular Labs, Bhabha Atomic Research Centre, Mumbai 400085, India. Tel.: +91 22 25595100; fax: +91 22 25505151.
E-mail addresses: shyamala@barc.gov.in, shyamala@apsara.barc.ernet.in (S.R. Bharadwaj).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.01.009

is apparent that the substitution of a smaller lower-valent Ni^{2+} ion (ionic radius = 0.69 Å) in place of In^{3+} (ionic radius = 0.81 Å) is likely to form an anion deficient solid solution with partial loss of oxygen in the lattice (δ).Recently we have studied the effect of B-site (Ti^{4+}) substitution by Fe^{3+} (ionic radius = 0.64 Å) and Cr^{3+} (ionic radius = 0.063 Å) on thermal properties and reduction behavior of In_2TiO_5. $In_2Ti_{1-x}Fe_xO_{5-\delta}$ and $In_2Ti_{1-x}Cr_xO_{5-\delta}$ ($0.0 \le x \le 0.2$) compositions were prepared by solid state route and the effect of substitution on redox behavior was reported [20]. In the present study, we report the A-site substitution-induced effects on indium titanate. For this purpose, $In_{2(1-x)}Ni_{2x}TiO_{5-\delta}$ ($0.0 \le x \le 0.2$) mixed oxide catalysts were synthesized using solid-state reaction and characterized by powder X-ray diffraction (XRD). The thermal and reduction behaviors were studied by recording thermogravimetric (TG), and temperature-programmed reduction (TPR) profiles. The chemical oxidation states of individual metal ions of multi-component oxides after reduction were identified using XRD and X-ray photoelectron spectroscopy (XPS).

2. Experimental

Mixed oxides with nominal composition, $In_{2(1-x)}Ni_{2x}TiO_{5-\delta}$ for $0.0 \le x \le 0.2$, were synthesized through ceramic route by mixing reactant oxides in appropriate stoichiometry as depicted by following equation:

$$(1-x)In_2O_3 + TiO_2 + 2xNIO \rightarrow In_{2(1-x)}Ni_{2x}TiO_{5-\delta}$$

The pellets of homogeneous mixtures were calcined at 900 °C for 24 h, 1000 °C for 24 h and finally at 1250 °C for 12 h, with intermittent grindings so as to ensure the uniformity and the completion of the reaction.

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 behavior of these samples (~20 mg) was monitored by recording their TG profiles both in air and 5% H_2 + Ar atmospheres, in the temperature range of 25–1000 °C at a heating rate of 10 °C min^{-1} on Setaram TGA-92 instrument.

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 H_2 (5%) + Ar, gas mixtures at a flow rate of 20 ml min^{-1}, with a heating rate of 6 K min^{-1}. The samples were pretreated at 350 °C for about 2.5 h 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 H_2 per mV of TCD signal) for the H_2 was calculated using the standard sample. This factor has been employed in all the substituted samples and the experimental amount of H_2 consumed was obtained. The calculated value of H_2 consumed by the sample was compared with the experimental value.

XPS studies were carried out on electron spectrometer using Mg Kα X-rays ($h\nu$ = 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.

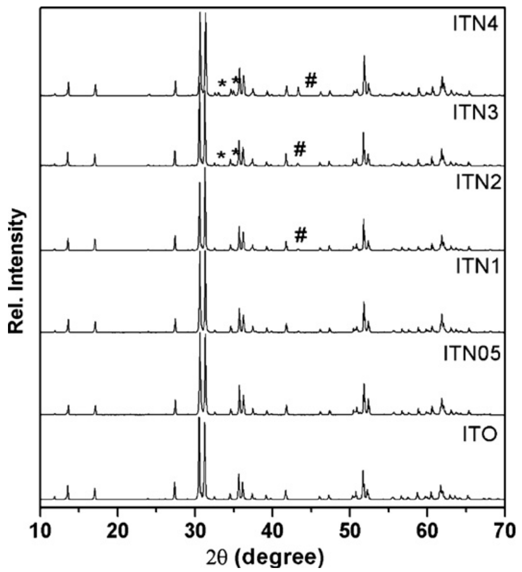

Fig. 1. XRD patterns of $In_{2(1-x)}Ni_{2x}TiO_{5-\delta}$ samples, # indicates peaks due to unreacted NiO phase and * indicates the peaks arising from $NiTiO_3$ phase.

3. Results

3.1. XRD

Table 1 lists the abbreviations and phases identified from XRD patterns of all the $In_{2(1-x)}Ni_{2x}TiO_{5-\delta}$ ($0.0 \le x \le 0.2$) samples prepared by solid state method. Fig. 1 shows the powder XRD patterns of In_2TiO_5 and corresponding patterns observed due to aliovalent substitution of Ni^{2+} in place of In^{3+} at A-site. From Fig. 1, it is observed that the XRD pattern of $x = 0$, composition matches well with that of orthorhombic In_2TiO_5 (JCPDS card No. 30-0640) oxide. The lines due to reactant oxides are missing in these patterns thus confirming the completion of the solid-state reaction. In_2TiO_5 is isostructural with In_2VO_5. It crystallizes in the orthorhombic space group, with a = 0.7241 nm, b = 0.3427 nm, c = 1.4878 nm, cell volume = 0.3692 nm^3 and Z = 4. The XRD patterns of ITN05 ($In_{1.95}Ni_{0.05}TiO_{5-\delta}$) and ITN01 ($In_{1.9}Ni_{0.1}TiO_{5-\delta}$) compositions match with the XRD patterns of unsubstituted indium titanate sample as shown in Fig. 1. Thus, lower extent of Ni substitution resulted in single phase material comprised of In_2TiO_5 phase due to formation of solid solution of Ni with the lattice of the parent compound. But for samples having Ni content $x \ge 0.1$ in $In_{2(1-x)}Ni_{2x}TiO_{5-\delta}$ a very low intensity line (marked with #) was observed which corresponds to the 100% peak of 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. $x \ge 0.15$, a third phase of $NiTiO_3$ (JCPDS card No. 33-0960, peaks marked with *) was observed in addition to the unreacted nickel oxide phase (Fig. 1). This phenomenon of segregation of secondary phases in the Ni doped samples can be attributed to the large difference in ionic radii between the substituent cation Ni (0.069 Å) and the parent cation In (0.081 Å).

3.2. Temperature programmed reduction behavior (TPR)

The typical first temperature programmed cycle (TPR) of substituted samples and unsubstituted sample are shown in Fig. 2. The TPR profile of unsubstituted, In_2TiO_5 sample as seen in Fig. 2 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