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Surface characterization and catalytic activity of $Ln_2Ti_2O_7$ (Ln = Y, Sm, Gd and Tb)

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The surface of the catalyst, $Ln_2Ti_2O_7$ where Ln = Y, Sm, Gd and Tb was analysed by X-ray photoelectron spectroscopy. Terbium is found to be present in 3^+ and 4^+ states while Y, Sm and Gd are present in the 3^+ state. The catalytic activity of these oxides was tested using decomposition of N_2O as the test reaction and the catalytic activity was correlated to the surface properties.

1. Introduction

Extensive studies have been made to evaluate the catalytic activity of mixed metal oxides crystallizing in spinel, perovskite and related structures for various reactions. In recent years, attention has also been focused on other ternary oxides to select materials which can be used as catalysts for various reactions. It has been found that oxides having pyrochlore structure with the general formula $A_2B_2O_7$, are emerging as good catalysts for reactions like NO reduction [1], CO oxidation [2, 3] and oxidative cleavage of vicinal diols [4]. In electrocatalysis, ruthenium containing pyrochlores are found to be superior to any other oxygen evolution catalysts and their performance was as good as any other available oxygen reduction catalysts [5]. These oxides perform well as catalysts because the crystal structure can tolerate vacancies at the cationic and anionic sites to a certain extent and also stabilize unusual and mixed valence states of transition metal ions. In our earlier communication [6], we reported the catalytic activity of titanate pyrochlores with the composition $Ln_2Ti_2O_7$ (Ln = Y, Sm and Tb) using N_2O decomposition as the test reaction and correlated the activity with the bulk properties. In the present investigation an attempt has been made to correlate the catalytic activity with surface properties of these titanates.

2. Experimental procedure

Pyrochlores with the composition $Ln_2Ti_2O_7$ (Ln = Y, Sm, Gd and Tb) were synthesized by solid state reaction between oxides of Ti and Ln as reported by Brixner [7]. Formation of the single phase was confirmed by XRD. Experimental procedure for measuring conductivity and magnetic moment are given elsewhere [6]. XPS studies were performed in an ESCA LAB Mark II (Vacuum Generator, UK). The spectra were recorded using AlK_α ($h\nu = 1486.6$ eV) radiation and the normal operating pressure inside the analyser chamber was 5×10^{-9} mbar. The peak positions were assigned by setting the C 1s contamination peak to a binding energy value of 285.0 eV. XP spectra were recorded at room temperature without additional treatment. Catalytic decomposition of N_2O was carried out in a static recirculatory reactor at 50 and 200 torr pressures of N_2O. Details of experimental procedure are discussed elsewhere [6].

3. Results

Table I summarizes the lattice parameters, electrical, magnetic properties and surface area of the titanate pyrochlores. The structural and solid state properties of these compounds are in agreement with the results reported in literature [8].

Kinetic studies showed that $Y_2Ti_2O_7$ and $Sm_2Ti_2O_7$ are less active for the decomposition of N_2O. On both the catalysts the conversion was poor (5% at 480 °C) and hence kinetics could not be followed in the temperature range 400 to 480 °C [6]. On the other hand $Tb_2Ti_2O_7$ showed good conversion and the detailed kinetic runs were made at 50 and 200 torr initial pressure of N_2O while $Gd_2Ti_2O_7$ showed measurable conversions only at 200 torr. The kinetics of decomposition on these catalysts obeyed a first-order equation and Table II summarizes the kinetic and Arrhenius parameters for the decomposition of N_2O. The variation in the catalytic activity of $Ln_2Ti_2O_7$ (Ln = Y, Sm and Tb) has been explained based on solid state properties [6]. Correlation of catalytic activity with surface properties is more meaningful because reactions take place on the surface of the catalysts and hence the surface of these catalysts was characterized by XPS.

The surface of these catalysts was analysed by XPS to get an idea about the active sites, valence state of the metal ions and also to explain the observed activity for the decomposition of N_2O. XP spectral features of these compounds are summarized in Table III.

XP spectra of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ regions are shown in Fig. 1. It is reported [9–15] that titanium in the 4^+ state is found to have a binding energy value between 458 and 460 eV for the Ti $2p_{3/2}$ level. Since a

TABLE I Physico-chemical properties of $Ln_2Ti_2O_7$

Property	$Y_2Ti_2O_7$	$Sm_2Ti_2O_7$	$Gd_2Ti_2O_7$	$Tb_2Ti_2O_7$
Structure	Cubic	Cubic	Cubic	Cubic
Lattice parameter (nm)	1.0049	1.0206	1.0165	1.0133
Specific resistivity (Ω cm) (30 to 500 °C)	$< 10^7$	$< 10^7$	$< 10^7$	$10^7 - 10^5$
Magnetic moment (B.M.)	–	1.5	8.1	11.2
$E^{\circ}_{Ln^{3+} \rightarrow Ln^{4+}}$ (V)	Very high	-5.2	-7.9	-3.4
Surface area ($m^2 g^{-1}$)	1.2	0.8	1.0	1.0

TABLE II Kinetic and Arrhenius parameters for the decomposition of N_2O on $Tb_2Ti_2O_7$ and $Gd_2Ti_2O_7$

Catalyst	P_{N_2O} (torr)	Temperature (°C)	Rate constant $k \times 10^3$ (min^{-1})	Activation energy E_a ($kcal\ mol^{-1}$)	ln A
$Tb_2Ti_2O_7$	50	420	0.56	26.6	11.7
		440	1.20		
		460	1.54		
		480	2.05		
	200	420	0.36	20.0	6.5
		440	0.53		
		460	0.86		
		480	1.09		
$Gd_2Ti_2O_7$	200	440	0.70	24.3	9.8
		460	1.33		
		480	1.75		

TABLE III XPS results[a] of $Ln_2Ti_2O_7$

Region	$Y_2Ti_2O_7$		$Sm_2Ti_2O_7$		$Gd_2Ti_2O_7$		$Tb_2Ti_2O_7$	
	Core level	Satellite	Core level	Satellite	Core level	Satellite	Core level	Satellite
C 1s	289.75		291.00		292.00		291.75	
O 1s	530.00		530.25		530.25		530.50	
	532.00		531.75		531.75		532.25	
Ln $3d_{5/2}$	157.50		1083.50	1081.0	1187.50	1185.25	1240.75	1238.75
$3d_{3/2}$	159.40		1109.00	1107.0	1219.75	1216.75	1276.75	1274.50
4d	–		broad		broad		broad	
Ti $2p_{3/2}$	458.40	462.25	458.50	463.35	459.00	463.50	458.90	463.25
$2p_{1/2}$	464.10	469.75	464.00	470.0	464.75	469.25	464.50	470.75
		471.25		471.5		471.25		472.00
3p	37.00		37.25		37.25		37.25	
BE(O 1s–Ti $2p_{3/2}$)	71.60		71.75		71.25		71.60	
Ln–Ti	2.38		2.27		1.82		4.57	
FWHM (Ti $2p_{3/2}$)	1.80		1.90		1.85		1.90	

[a] Binding energy in eV.

wide range of binding energies, E_b, is reported for Ti^{4+} ion the separation energy between O 1s and Ti $2p_{3/2}$ (ΔE_B) has been considered for determining the valence state of titanium. Sayers and Armstrong [15] have analysed samples of TiO_2 obtained from various sources by XPS and ΔE_b (O 1s–Ti $2p_{2/3}$) is found to be in the range 71.2 to 71.9 eV. In the present investigation, ΔE_b (O 1s–Ti $2p_{3/2}$) is found to be in the range 71.5 ± 0.25 indicating that titanium is present in the 4^+ state in $Ln_2Ti_2O_7$. The FWHM (Ti $2p_{3/2}$) values are in the range 1.8–1.9 which are in agreement with the values reported in the literature [9, 13, 15].

The spectra also show satellite peaks next to the main peaks. There exists satellites at ~ 4.5 eV and ~ 12.5 eV away from the $2p_{3/2}$ peak. The satellite peak observed at ~ 4.5 eV away from $2p_{3/2}$ peak overlaps with the $2p_{1/2}$ main peak which results in an asymmetry as can be seen from Fig. 1. $2p_{1/2}$ level of

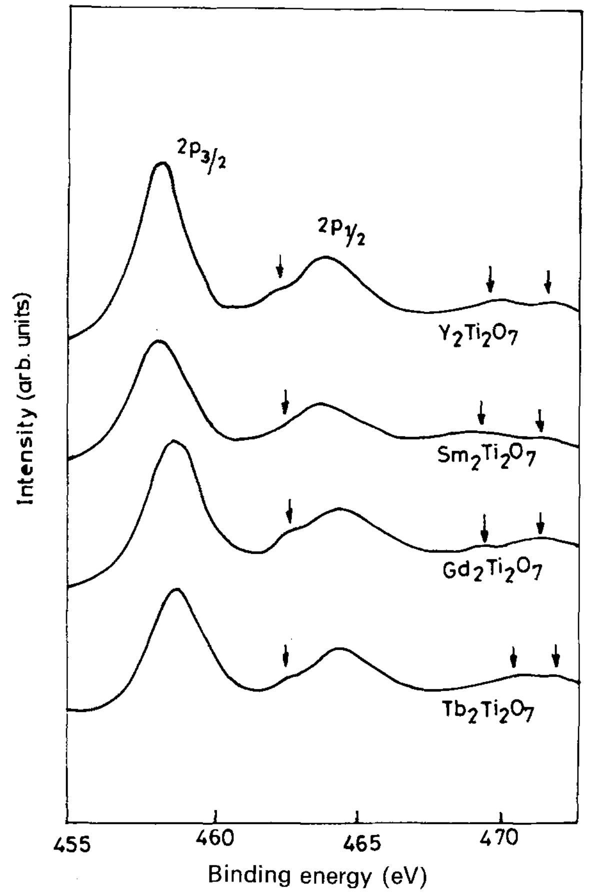

Figure 1 XP (Ti 2p) spectra of $Ln_2Ti_2O_7$.

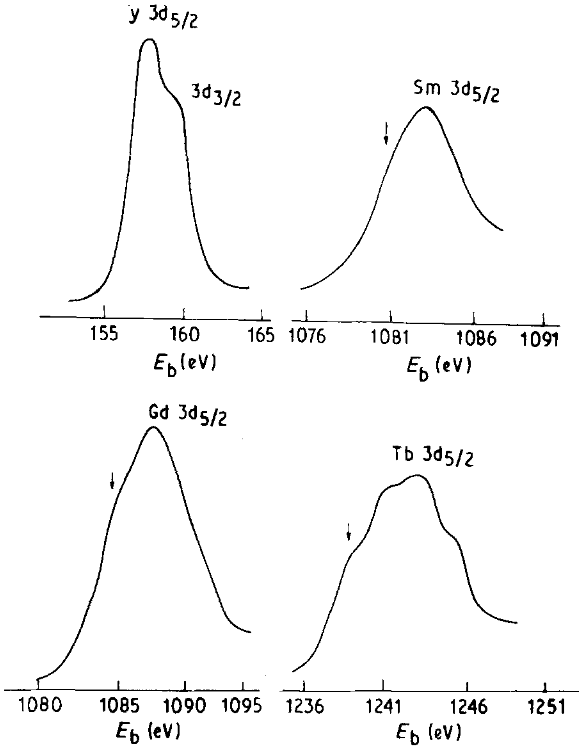

Figure 2 XP (Ln 3d) spectra of $Ln_2Ti_2O_7$.

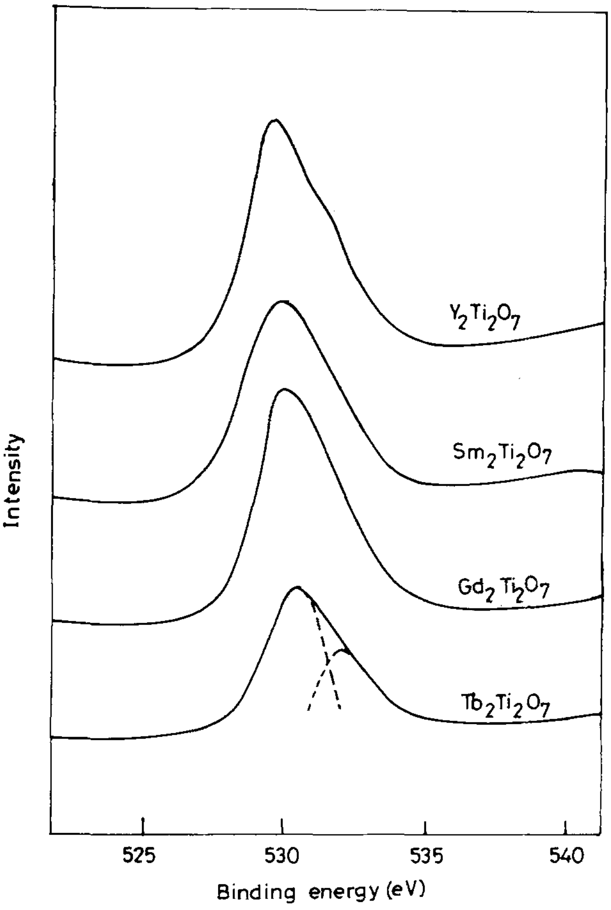

Figure 3 XP (O 1s) spectra of $Ln_2Ti_2O_7$.

titanium also shows a satellite at ~ 4.5 eV next to its core level. The satellites at 4.5 and 12.5 eV are normally due to charge transfer excitations from oxygen 2p levels to empty 3d orbitals, namely $O(2p)t_{2g} \rightarrow M(3d)t_{2g}^*$ and $O(2p)e_g \rightarrow M(3d)e_g^*$ transitions. These results are in agreement with the earlier reports of TiO_2 and related oxides [10]. It has also been suggested that the occurrence of lower energy shake up satellite is due to charge transfer transition, $t_{2g} \rightarrow t_{2g}^*$ in π bonding and the appearance of higher energy shake up satellite is due to charge transfer excitation, $e_g \rightarrow e_g^*$ in σ bonding [10–12].

Fig. 2 shows the XP spectra of the rare earth 3d level in $Ln_2Ti_2O_7$. XP spectra of Y, Sm and Gd showed that the rare earths ions are present in the 3^+ state as evidenced from the binding energy values at 157.5, 1083.5 and 1187.5 eV, respectively, for the $3d_{5/2}$ level as given in Table III. These values are in good agreement with the values reported for corresponding rare earth oxides and ternary oxides [16–20]. The surface of $Tb_2Ti_2O_7$, however, showed the presence of terbium in 3^+ and 4^+ states (Fig. 2). Similar kind of spectrum has been reported for $Tb_2Ti_2O_7$ by Vander Lean *et al.* [21] using XAS studies. The satellite features observed in the case of Sm^{3+}, Gd^{3+} and Tb^{3+} (indicated by arrows in Fig. 2) can be due to the charge transfer processes from O(2p) to Ln (4f) [19]. The satellites are attributed to the shake down processes as reported by Sharma *et al.* [18].

Fig. 3 shows the XP(O 1s) spectra of $Ln_2Ti_2O_7$. The spectra show two kinds of oxide ions present on the surface. The two peaks with binding energy values at 530 and 532 eV generally observed for oxide systems are due to the presence of O^{2-} and O^- or OH^-, respectively [22, 23]. These two peaks can also, however, be attributed to the presence of non-equivalent oxygen in these systems. It is known that pyrochlore is often written as $A_2B_2O_6O'$ indicating the presence of crystallographically non-equivalent oxygen.

XPS studies thus reveal that titanium is present in the 4^+ state in all these compounds while Y, Sm and Gd are present in trivalent state. On the other hand, the XP spectra of $Tb_2Ti_2O_7$ showed the presence of terbium in the 3^+ and 4^+ states on the surface.

4. Discussion

Nitrous oxide decomposition is a typical suprafacial reaction [24] and the electron transfer from the catalyst in the initial adsorption step (step 1) and electron transfer to the catalyst in the final desorption step (steps 3–4) determine the kinetics of the reaction

$$N_2O + e^- \rightarrow N_2O^-_{ads} \quad (1)$$

$$N_2O^-_{ads} \rightarrow N_2 + O^-_{ads} \quad (2)$$

$$O^-_{ads} \rightarrow O_2 + 2e^- \quad (3)$$

$$O^-_{ads} + N_2O \rightarrow N_2 + O_2 + e^- \quad (4)$$

The presence of large density of filled localized electronic states at the surface is essential for the adsorption of N_2O and availability of localized empty d-orbitals are necessary for the oxygen desorption step. From quantum mechanical analysis it is inferred that at low pressure, the adsorption of N_2O preferentially occurs at specific sites and at higher pressures of N_2O, the adsorption of N_2O occurs in a multi-centre fasion on normal lattice sites so that the M–O bond is stronger and the oxygen desorption step becomes rate controlling [25]. In the present investigation at both pressures of N_2O, the kinetic studies revealed that adsorption of N_2O is rate limiting. The adsorption of N_2O on $Ln_2Ti_2O_7$ may thus be of single site.

In our earlier communication [6], the low activity of $Y_2Ti_2O_7$ and $Sm_2Ti_2O_7$ were explained on the basis of the type of conductivity, magnetic and electronic structure of component metal ions. In the titanium pyrochlores, titanium is present in the 4^+ state, as evidenced from XPS studies, which is very stable due to its closed-shell electronic configuration ($Ti^{4+}: d^{10}$). For the decomposition of N_2O to take place, there must be transfer of an electron from the catalyst to the N_2O molecule which is essential for the adsorption of N_2O. Since titanium in $Ln_2Ti_2O_7$ is in the 4^+ state, it cannot donate an electron to the reactant gas and hence adsorption of N_2O is not facile on Ti^{4+}. This is also supported by the results reported for the decomposition of N_2O on TiO_2 [26, 27] and $MTiO_3$ (M = Ca, Sr or Ba) [28]. TiO_2 and $MTiO_3$ were reported to be active only at very high temperatures for the decomposition of N_2O and a high energy of activation has been observed.

Similarly XPS studies showed the presence of Y and Sm in the trivalent state. Y^{3+} and Sm^{3+} cannot go to a higher valence state as evidenced from the high oxidation potential reported for $M^{3+} \rightarrow M^{4+}$ in Table I, thus, adsorption is not facile on Y^{3+} and Sm^{3+}.

Korf *et al.* [3] explained the high activity observed for $Tb_2Ti_2O_7$ for CO oxidation based on

$$Tb^{3+} \rightleftharpoons Tb^{4+}$$

A similar kind of equilibrium can also be assumed in the present investigation. XPS studies on $Tb_2Ti_2O_7$ confirmed the presence of Tb^{3+} and Tb^{4+} in this system. Tb^{3+} can donate an electron to N_2O and facilitates the adsorption of N_2O. This is also evidenced from the low oxidation potential value (-3.4 eV) reported for $Tb^{3+} \rightarrow Tb^{4+}$, thus, the high activity observed for $Tb_2Ti_2O_7$ is due to the presence of mixed valence of terbium. It is also known that the desorption of oxygen will be easier on catalysts with a high magnetic moment [6]. Both $Gd_2Ti_2O_7$ and $Tb_2Ti_2O_7$ have high magnetic moments and hence showed higher activity than $Y_2Ti_2O_7$ and $Sm_2Ti_2O_7$.

The concentration of rare earth ions on the surface was calculated using [29]

$$\frac{n_B}{n_B} = \frac{I_a \sigma_b}{I_b \sigma_a}\left(\frac{KE_b}{KE_a}\right)^{1/2}$$

The relative concentrations of Ln–Ti are given in Table III. The higher concentration of rare earth ion on the surface indicates the preferential segregation of rare earth to the surface which has a lower surface energy ($< 1000\,\mathrm{mJ\,m^{-2}}$) than titanium ($2050\,\mathrm{mJ\,m^{-2}}$) [30]. Comparing ratios of Ln–Ti on the surface of $Ln_2Ti_2O_7$ catalysts, it is seen that $Tb_2Ti_2O_7$ contains a higher concentration of terbium on the surface (the ratio being 4.57 as against 2.0 expected for the bulk). The higher activity observed for $Tb_2Ti_2O_7$ can thus be attributed to the higher concentration of Tb on the surface which is the active site for the decomposition of N_2O. This is also evidenced from the observed E_a values for $Tb_2Ti_2O_7$ which is found to be in the range (25–$30\,\mathrm{kcal\,mol^{-1}}$) reported for rare earth oxides [26].

5. Conclusions

The following conclusions can be drawn from the above study

(i) XPS studies on $Ln_2Ti_2O_7$ indicated the presence of terbium in mixed valent states namely 3^+ and 4^+ and Y, Sm and Gd in the trivalent state.

(ii) Catalysts containing mixed valence states on the surface are more active in the decomposition of N_2O.

(iii) The participation of rare earth ion, in the case of titanates, in determining the catalytic activity is established.

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