

SYNTHESIS, CHARACTERIZATION AND CATALYTIC STUDIES OF NON-STOICHIOMETRIC MIXED OXIDES OF CERIUM.

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Abstract : Mixed transition metal oxides of cerium with ABO₃ structure and stoichiometry were synthesized by solid state reaction technique at 700°C, 800°C, 900°C and 1000°C. Characterization was done by XRD, surface area, surface acidity etc. methods. Catalytic properties of different samples were determined and correlated. Nickel containing oxide sample was found more catalytic active than the copper and Zinc containing ones. Existence of Cerium (Ce) and Metal (M) as Ce⁺³ M³⁺ O₃⁶⁻ with greater electron mobility was labelled as the reason of greater activities.

IndexTerms - Nonstoichiometric mixed oxides, Cerium, XRD, Surface and catalytic properties.

I. INTRODUCTION

The most interesting non-stoichiometric oxides are found in transition metal and rare earth oxides at higher temperatures [1]. Transition metal non stoichiometric oxides of different structures have been the subject of intensive investigations because of their interesting electrical, magnetic and catalytic properties [2-5]. The role of solid state properties in the catalysis using mixed metal oxides as catalyst have wide applications in petrochemical, fertilizer, pharmaceutical and food stuff industries. Such types of oxides or ceramic materials as are formed by the solid-state reactions at very high temperature >1000C have not only high thermal stability but also resistive towards acids and alkalis [6]. Presently the physico-chemical and catalytic properties of non-stoichiometric oxides of cerium with copper zinc and nickel of ABO₃ structure prepared at 700°C, 800°C, 900°C and 1000°C are reported. Thermal decomposition of Urea in presence of different oxides samples was employed as a model reaction for comparing their catalytic activities

II. RESEARCH METHODOLOGY

Nitrates of Ce, Ni, Cu and Zn and urea as starting materials of 99.99% purity (L.R. Sarabhai M. Chemicals Ltd. and CDH Ltd.) were used as such for catalyst preparation and catalytic reaction. The mixed oxide catalysts were prepared by the ceramic method [12,14]. Metallic nitrates were heated to produce oxides. The oxides were then mixed in the proper ratio by weight. The mixture of oxides thus prepared was subjected to the heat treatment in vacuum. To prepare Cerium Nickelate about 10gm of the oxide mixture of Cerium oxide and Nickel oxide was put in a small silica tube of 30mm diameter closed at one end. The other end of the tube was connected with a vacuum line. To avoid moisture and CO₂ entering into the pump two traps, one containing potassium hydroxide pellets and the other fused calcium chloride were put into the vacuum line. The vacuum in the line was measured with vacuscope. The silica tube was heated in an electric tube furnace supplied by International Commercial Traders 18 Ezra Street, Calcutta-1. The rate of heating was 10°/minute i.e. the switch of the pyrometer of the furnace was so tuned that temperature always increased by 10°C at the interval of one minute till the desired temperature (700°C, 800°C, 900°C & 1000C) was reached for 18-20 hrs at desired temperature. The temperature of the furnace was measured with a pyrometer attached to the furnace itself. The heating duration was completed in three or four steps. At the end of every step the material was cooled to room temperature with the vacuum pump running on. The sample was taken out of the silica tube. It was then grounded in the agate mortar sieved to roughly 100mesh and stored in a vacuum desiccator over fused calcium chloride. The samples obtained at 700°C, 800°C, 900°C and 1000°C were labelled as M₁N₁, M₂N₂, M₃N₃ and M₄N₄ respectively.

Cerium cuprate was prepared by the same method as adopted by Goodenough². The samples were subjected to heat treatment at 700C, 800°C, 900°C and 1000°C by the same process as described above³ and the oxides were labelled M₁C₁, M₂C₂, M₃C₃ and M₄C₄ respectively.

Cerium cuprate and Cerium Zincate were prepared similarly. Cerium Zincate samples were labelled as M_1Z_1 , M_2Z_2 , M_3Z_3 and M_4Z_4 and cerium cuprate samples as M_1C_1 , M_2C_2 , M_3C_3 and M_4C_4 respectively. Metals in the oxide samples were estimated gravimetrically by reported methods.⁸ The Imperial formulae of the catalysts samples were derived.

X-ray powder diffraction pattern of the samples under investigation at room temperature were taken using an automatic X-ray powder diffractometer (Philips Pw1877 and / or Rigaku MiniFlex II) with a scan speed of 2° min^{-1} at a scan step of 0.02° using CuK_α radiation. In the present structural investigation of these compounds, the diffraction peaks detected within the measured 2θ range 20° - 100° of the present compounds were indexed and the lattice parameters were determined using the least-squares method with the help of standard computer programme (crysfire). X-Ray diffraction pattern of the sample of CeNiO_3 prepared at 900°C has been shown in figure -1

Measurement of excess surface oxygen was done by the method described by Voltz et. al.^[8]. Arora et. al.^[9] method was employed for the measurement of acidity of the oxide samples. Surface areas of samples were measured by the BET method^[11]. The results were recorded in Table 2. The process and apparatus used for the kinetic study of degradation of urea were similar to those adopted by the previous workers^[11]. Commercial sample of urea was used. The decomposition of mixture of urea and the catalyst (20:1) was performed at three different temperatures viz 140°C , 150°C and 160°C . Volume of ammonia released vs. time graph is shown in figure -2.

IV. RESULTS AND DISCUSSION

The X-ray diffraction pattern (XRD analysis) of the polycrystalline sample of CeNiO_3 (as an example) using CuK_α radiation with wave length of 1.54184\AA is shown in figure -1. All XRD patterns of sample are very similar. The intensity peaks are quite sharp with little background absorption, which indicates that the samples are made of well-grown crystalline, mostly in single phase. The XRD data for each sample was analysed through standard computer programme called, crysfire with an accuracy of 10-3 and on that basis the best structural information derived are as follows. For $[\text{CeCuO}_3]$, $[\text{CeNiO}_3]$ and $[\text{CeZnO}_3]$ are found to $a=3.3109\text{\AA}$, $b=9.3393\text{\AA}$, $c=2.6252\text{\AA}$, $v=81.17$; $a=3.2737\text{\AA}$, $b=20.6505\text{\AA}$, $c=2.8107\text{\AA}$, $v=190.01$ and $a=3.7981\text{\AA}$, $b=6.2412\text{\AA}$, $c=3.8415\text{\AA}$, $v=97.06$ respectively showing that all samples have an orthorhombic structure, though there are significant change in cell volume. The computer program takes diffraction angle (2θ) as input parameter and evaluates d-values, which are reproduced using a set of (hkl) index for the given (input) structure type. The rate constants of the urea degradation reaction catalysed by samples were calculated from the initial slopes of the rate curves. $\text{Log}(V_\infty - V_t)$ vs t (time) and energy of activation and frequency factor were calculated from the Arrhenius plots ($\text{Log } k$ vs t, Table 2. From the data it is clear that all the oxides samples activated at different temperatures, catalyse the degradation of urea though their degrees of catalytic activities seem to be different. An observation of specific rate constants shows that there is a regular pattern between the catalytic activities of the samples and their activation and reaction temperature (table 2). Specific rate goes on increasing with activation and also with reaction temperatures in all the three oxides, the only unusual behaviour is seen for CeNiO_3 sample activated at 1000°C where it is lower than the one at 900°C , though this increases with increasing reaction temperature. Comparing specific rates at 900°C it comes in the order as $\text{CeZnO}_3 > \text{CeNiO}_3 > \text{CeCuO}_3$. However the order of energy of activation, EA and frequency factor $\text{log}_{10} A$ comes in the order as

$$\text{CeNiO}_3 < \text{CeZnO}_3 < \text{CeCuO}_3$$

$$6.84/3.75 \quad 9.51/5.15 \quad 14.02/7.51 \quad (E_A / \text{Log}_{10} A)$$

This shows that the CeNiO_3 samples is the most activating oxide.

An analysis of the physico-chemical data of the samples (Table 1) it is seen that all the three parameters excess surface oxygen (E.S.O), surface area and acidity go on a gradual decrease with activation temperature in all the samples^[12,13,14]. E.S.O is responsible for surface acidity which in turn is responsible for luring the catalytic activity by trapping the mobile electrons. So, the activity can best be explained in terms of surface area and surface acidity. There is a linear decrease of surface acidity and surface area with activation temperature (not shown here) but both maintain the same order for all the samples as $\text{CeNiO}_3 > \text{CeZnO}_3 > \text{CeCuO}_3$. As per the established norm the surface area determines the potentiality if catalytic activity of the, mixed oxides of Perovskite type, the magnitude of the acidity \ acidic sites would be responsible for the ease mobile electrons taking part in the reaction(activation). So, the surface area together with acidity would certainly account for the total catalytic activity of the samples. Though the surface area gradually decreases from going the activation temperature of 700°C to 1000°C , the difference is small in comparison to their corresponding gradual decrease in the acidity values. The combination of both these

factors determines the serial increase of activity among these samples and thus the results can best explained. Moreover, presence heterogeneity in Cerium Nickelate in terms of presences of traces, steps, kinks, vacancies, electronic and other solid-state defects might have added to its greater activity.^[15]

However, the unusual catalytic behaviour of cerium nickelate activated at 1000°C seems to be due to more distortion and more oxygen vacancies created in the oversized unit cell which may cause loss of some active nickel sites

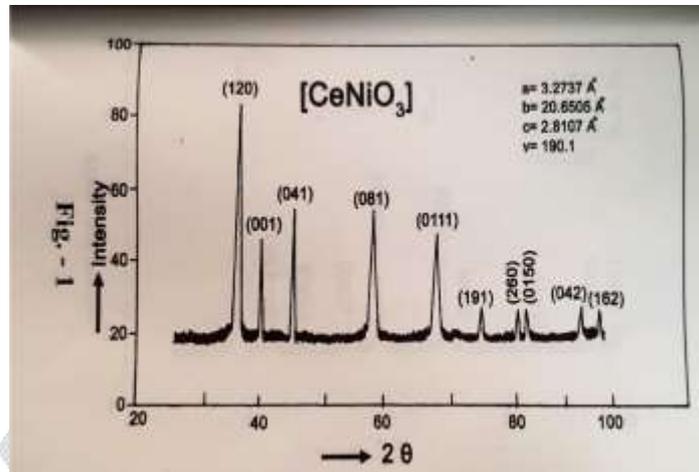


Fig-1 XRD of CeNiO₃

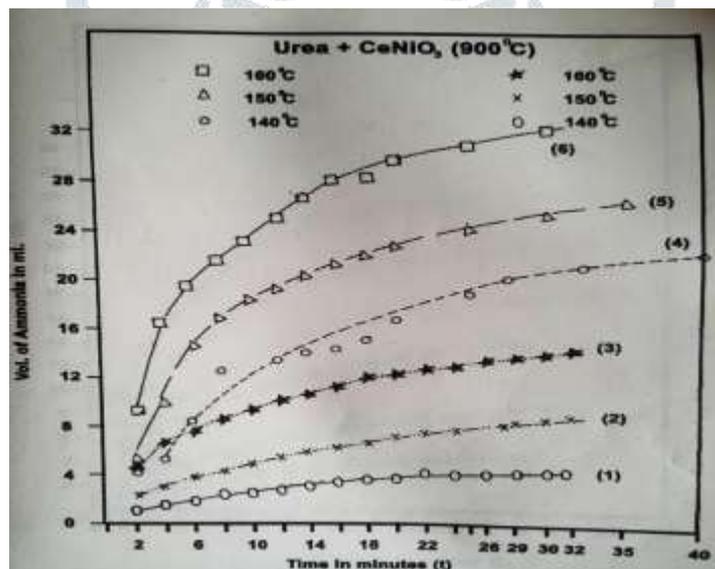


Fig-2 Kinetics degradation of urea :

(1), (2), (3) and (4), (5), (6) for (Urea + M₃N₃) at 140°C , 150°C and 160°C respectively

Table-1, Physic-Chemical data of the samples

Sample	Activation Temp. ^o C	Excess surface Oxygen per 100gms of the Sample X 10 ⁻²	Surface Area m ² /gm	Acidity M.eq/gm
CeNiO ₃	700	17.50	23.78	170.20
	800	11.42	21.93	152.00
	900	10.40	20.60	137.05
	1000	9.90	18.41	120.30
CeZnO ₃	700	14.10	22.24	151.75
	800	9.82	18.48	139.00
	900	8.52	16.40	130.00
	1000	7.68	14.41	105.00
CeCuO ₃	700	12.84	19.12	134.00
	800	7.82	17.10	111.55
	900	5.51	14.66	92.85
	1000	4.50	12.87	67.80

Table-2,kinetic data for the solid state decomposition of Urea alone and in presence of mixed oxide samples

Sample	symbols	Activation Temp. ^o C	Specific rate (X10 ⁻² min ⁻¹) at			E _A Kcal/mol	Log10 ^A
			140 °C	150 °C	160 °C		
Carbamide alone			1.65	3.34	4.48	16.416	8.64
CeNiO ₃	M ₁ N ₁	700	2.30	4.15	5.35	8.38.	4.49
	M ₂ N ₂	800	3.90	5.88	7.77	7.18	3.85
	M ₃ N ₃	900	5.29	5.98	8.79	6.38	3.52
	M ₄ N ₄	1000	3.50	5.40	7.17	6.84	3.75
CeZnO ₃	M ₁ C ₁	700	1.95	3.68	5.88	15.00	8.05
	M ₂ C ₂	800	2.50	3.78	6.38	14.75	7.91.
	M ₃ C ₃	900	3.21	4.167	6.76	14.02	7.51
	M ₄ C ₄	1000	3.85	4.36	6.91	13.75	7.40
CeCuO ₃	M ₁ Z ₁	700	5.45	7.15	9.48	12.25	6.51
	M ₂ Z ₂	800	6.88	9.00	11.69	11.20	6.05
	M ₃ Z ₃	900	8.59	10.36	12.897	9.51	5.15
	M ₄ Z ₄	1000	9.10	11.30	13.20	9.25	5.00

From the different catalytic activity values, it is clear that it is the Ni⁺², Zn⁺² and Cu⁺² active ionic centres on the surface of catalyst that are responsible for activity. Not only that the catalytic activity of these binary ions is enhanced by presence of Ni³⁺, Zn³⁺ and Cu³⁺ ions formed due to valance defects at higher temperatures of mixed oxide preparation. Unlike in ABO₃ and ABO₄ where the central atom would be less reactive transition metals like Nd, Ho, Pr, Dy etc.^[3,4,7] in the present case cerium is also highly reactive along with Ni, Zn, Cu and form oxygen vacancies and valances defects so, presence of Ce(III) - Ce(IV) cannot be ruled out in the samples.^[10] So it is not only the Ni⁺²/Ni³⁺, Zn⁺²/Zn³⁺, Cu⁺²/Cu³⁺ ions as active centres but also the central atom of the ABO₃ structure Ce³⁺/Ce⁴⁺ make greater mobility of electrons possible from the system to the reactant(Carbamide) and vice versa causing the greater catalytic activity.

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