SURFACE PROPERTIES MEASUREMENTS STUDY OF ABO₃ PEROVSKITE TYPE MIXED METAL OXIDES OF CERIUM.

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Abstract : The potential of using new mixed metal oxides of the type $LnMO_3$ with Ln = Ce and M = Ni, Cu, and Zn have been prepared by ceramic methods and to find out as a suitable oxidative catalyst . The surface properties (Surface area, Excess surface oxygen and Acidity) of these new mixed oxides of $CeNiO_3$, $CeCuO_3$ & $CeZnO_3$ based on perovskite at different temperatures   (600,700 and 900^0C) have been studied choosing the thermal degradation of urea as a model reaction .From the surface properties measurements it is observed that Surface area and acidity variation goes on decreasing linearly whereas excess surface oxygen (E.S.O) goes on decreasing exponentially with temperatures. Catalytic activity of $CeNiO_3$ at higher activation temperature ($900°c$) is more in comparion to $CeZnO_3$ & $CeCuO_3$. Examination of the X-ray diffraction pattern are used to confirm these new mixed metal oxides of Cerium for its commercial application.

IndexTerms - Perovskite materials, Surface area, Excess surface oxygen(E.S.O) & Acidity.

I. INTRODUCTION

Solid state chemists, material scientists and theorists have become interested in the role of solid state properties in the catalysis using mixed metal oxides as catalyst. At present mixed metal oxides of perovskite type, especially substituted with small amount of nobel metals have been chosen emphatically for the purpose. Thus, the mixed metal oxides are now being studied as nobel catalysts in their own right. The direct co-relation between bulk properties and catalysis may be conveniently studied for some particular series of iso-structural compounds. Mixed metal oxides seem to offer such series.

In 1982 Baythoun and Sale[18] prepared Mn_2O_3, Mn_3O_4 , $LaMnO_3$, $SrMnO_3$ and strontium substituted $LaMnO_3$ by following the amorphous citrate process. They determined the surface area and the residual carbon content of the strontium substituted $LaMnO_3$. On the analysis of the result they observed that the experimental condition corresponding to the maximum surface area are not necessarily required for optimum yield and homogeneity.

2. MATERIALS AND 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 prerparation and catalytic reaction. The mixed oxide catalyst were prepared by ceramic method at 700 °C, 800 °C, 900 °C, 1000 °C. Estimation of metals in the samples is to be done by following the usual classical methods and then formula of mixed oxides would be derived.Excess surface oxygen present in the sample would be determined by the Voltz [11] methods.The acidity measurements would be carried out as followed by Arora[17] etal.Surface area of the samples are plant to be determined by adsorption by Nitrogen at liquid Nitrogen temperature (-195 °C) and using the BET equation.

2.1 A EXCESS SURFACE OXYGEN

Samples of Cerium Nickelate , Cerium Cuprate, Cerium Zinckate , were synthesized and were subjected to heat treatment with a view to make the samples catalytically active. Consequently, it is within the expectation that the samples would show the varying catalytic activities owing to their different surface characteristics. One of the factors affecting surface properties is the excess surface oxygen and the specificity of the method of sample preparation would certainly enrich the samples with different amount of excess surface oxygen resulting in the surface heterogeneity to the varying extent. Thus, it becomes vital to measure the amount of excess surface oxygen of the

samples prepared. From the previous works recorded in the literature it has become obvious that surface excess oxygen has been found to be one of the factors responsible for the activity. Sahay et al [1] have observed that acidity and excess surface oxygen are related with activity for hydrogen peroxide decomposition. After an extensive investigation on oriental adsorption of normal aliphatic alcohols on perovskite type oxides, Madhok [2] came to the conclusion that the change in excess surface oxygen with the decomposition temperature of the catalysts should be related with the catalytic activity. He discussed the important role of excess surface oxygen in the partial oxidation processes. M.N.Ra [3] prepared the different samples of nickel oxide form nickel nitrate with several precipitant and estimated the excess surface oxygen. He explained clearly the role of excess surface oxygen for enhancing the catalytic activities of the sample for the decomposition of hydrogen peroxide. Bhagat and Saha [4] measured the excess surface oxygen of non-stoichiometric oxides of Yttrium, Praseodymium and Gadolinium and made an attempt to correlate the excess surface oxygen with the catalytic activity. Further, they have recorded that the samples of Yttrium oxide with high value of excess surface oxygen showed considerable activity indicating the positive tendency of the excess surface oxygen to enhance the activity.

Kumar R. and Bhagat [5] and Pankaj, A.K. and Indu[6] also observed that catalytic activity of mixed metal oxides of $LnMO_3$ and Ln_2MO_3 type is related to the amount of excess surface oxygen.

Thus in view of the above mentioned facts the estimation of excess surface oxygen vis-à-vis its role in catalytic activity seems to be an indispensable part of the present programme. Since all our samples are mixed metal oxides it was thought fruitful to estimate excess surface oxygen, if any present in the samples and to study its role in the activity of our samples for decomposition of urea. Previously, several workers [2,4] have used the aqueous hydrazine solution for the selective reduction of excess surface oxygen. In the present study the iodometric method[7] has been employed to estimate the excess surface oxygen.

2.1 B SURFACE ACIDITY

It becomes now very clear that surface acidity might play a crucial role in the process, catalyzed especially by metallic oxides. Clark[8] and Fischer[9] did extensive investigations regarding the effect of acidic nature of the surface and have pointed out that there is an increase in acidity of Silica-Alumina catalyst with the addition of metal oxides. Pines et al[10] have concluded that Rany nickel or even precipitated nickel owing to their acidic nature dissociate a hydrogen molecule into a hydrogen ion. It has been found that Sulpher containing compounds show prominently the acidic character of their surface and consequently they interact with strong bases like pyridine and aniline. On account of the acidic nature of the supported nickel oxide the carbon liberation becomes a problem.

Bhagat et al[4] measured the acidity and excess surface oxygen of the oxide samples of the inner transition metals. As a result of experimental observations they concluded that excess surface ocygen varies exponentially with acidity.

Although transition metal oxides as reformation catalyst have been extensively studied but it does lack in throwing light on the mechanism of liberation of oxygen in case of rare earth oxides. It has also not taken account of the surface characterization which must have bearing on the electronic catalytic behaviours. Recently, R. Kumar [6] has done the schematic work on the surface characterization of perovskite type oxides. He observed that the acidic sites control the surface characteristics of the catalyst affecting the catalytic behaviours.

To provide the support for the observations recorded by the previous workers [4.5] the thermal decomposition of urea catalyzed by provskite type oxide, Cerium as inner transition metal component, Nickel, Copper and Zinc as transition metal components have been studied.

2.1 C SURFACE AREA

Bhatt [12] made the experimental study on the surface area and acidity of clay samples and alumina and has been able to correlate the physico-chemical properties to the catalytic activity. Further, he noted that the alumina has the large surface area and less acidity. He also observed that acidity decreases with the increase in temperature. Yadav et al [13] during the course of their study on surface properties of low temperature co-conversion catalyst have shown that surface area of all the catalysts decreases invariably on reduction.

It was recorded that loss in surface area occurs with thermal shock. Madhok [14] has measured the surface area of perovskite type oxide by orientation absorption of several aliphatic alcohols. He came to an interesting conclusion. The value of surface area increases at first instant, if the temperature of activation is increased from 350°c to 450°c. Further increase in temperature decreases the specific surface area of the samples. However, it was observed that in all the samples heated at 350°c, 450°c and 500°c the values of specific surface area obtained for the alcohols are practically the same, if oriental adsorption perpendicular to the surface of the linear alcohol molecule is assumed.

Ramchandra Reddy [15] and his Co-workers established that the phenolic group present on the surface appears to be responsible for the catalytic activity. Poddar P. and Bhagat S [5 -6] utilized the adsorption method to calculate the relative surface area of the oxide samples of Yttrium (Y_2O_3), Proseodymium (Pr_2O_3), and Cerium (Ce_2O_3), obtained by the solid state decomposition of their compounds on the assumption of monomolecular layer adsorption of acetic acid. They have shown that there is a reciprocal relationship in between activation temperature

and surface area. B.L. Bishwas [5] during his research work concluded that the catalytic activity is directly proportional to surface area.

Thus, it is notable that surface area forms an essential feature of the surface characteristics and hence, its measurement for mixed metal oxides is of prime importance in the catalytic science. Measurement of surface area was done in PDIL sindri (Bihar) by the same method as adopted by Dr. M.N. Roy[3] and B. Yadav[13].

2.1 D X-RAY ANALYSIS

The X-ray photographs of our samples obtained from the decomposition of nitrates of Cerium and others(Ni, Cu, Zn) at desired temperatures were taken at IIT Kharagpur, using CuK_α radiation.

Structural Study:-

The X-ray diffraction pattern (XRD analysis) of the polycrystalline samples ($CeCuO_3$, $CeNiO_3$ & $CeZnO_3$) using Cuk_α radiation with wave length of 1.54184A° .. 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 analyzed through standard computer programme called, crysfire with an accuracy of 10^{-3} and on that basis the best structural information derived are as fallows. For [$CeCuO_3$], [$CeNiO_3$] and [$CeZnO_3$] are found to a=3.3109A° b=9.3393 c=2.6252A° v=81.17; a=3.2737A° b= 20.6505 c=2.8107A° v=190.01 and a= 3.7981A° b=6.2412 c=3.8415 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. It is found that the same d-values can be generated sometimes by different structure and so, the result should be accepted with careful consideration.

3.3 RESULTS AND DISCUSSION

3.1 A ROLE OF EXCESS SURFACE OXYGEN

The experimental results of the excess surface oxygen measurements have been recorded. The Plate 3.1 represents the variation of the excess surface oxygen with the change in activation temperature of the samples. it appears that

(i) the excess surface oxygen values of all the samples of Cerium Nickelate, Cerium Cuprate and Cerium Zincate activated at 700°C are considerably greater than the values of samples activated at higher temperatures viz. 800°C,900°C and 1000°C .

(ii) the values of excess surface oxygen of the samples show regular and smooth decrease with rise in activation temperature.

This type of reciprocal relationship in between the values of excess surface oxygen and activation temperature as indicated in the plate 3.1 has also been reported by Pankaj A. K.[16] while working on the catalytic activities of transition metal mixed oxides. This observation has also been supported by the experimental findings of earlier workers [2,4]. The quantitative analysis of the values of excess surface oxygen recorded and shown in plate 3.1 led us to the conclusion that in both magnitude and variation the value of excess surface oxygen of all the samples of Cerium Nickelate, Cerium Cuprate and Cerium Zincate are quite comparable with one another.

For the catalytic activity measurement of the samples the solid state degradation of urea has been taken as the model reaction. From the perusal of the experimental results obtained on the catalytic degradation of urea.

All these samples of mixed oxides with one exception, activated at 800°C and 900°C have been found to be comparatively more active than the samples activated at 700°C and 1000°C. Surprisingly enough these samples however, possess relatively small values of excess surface oxygen. This observation strongly concludes that the excess surface oxygen extends no contribution at all towards the activities of the samples. Obviously our samples are active catalytically owing to some other factors that are to be ascertained.

The surface of solid samples is heterogeneous on atomic scale, especially on account of the preparative procedures resulting in the presence terraces, steps, kinks, vacancies and atoms with unusual oxidation states. In fact, the differences in catalytic activities must be attributed to the defferent degree of heterogeneity of the surface of mixed oxides under consideration. Consequently, the mixed oxide activated at different temperatures would have different B.E.T. parameters, porous structure, particle size and surface morphology. A rougher surface should show the higher catalytic activities.

3.3 B ROLE OF SURFACE ACIDITY

The results of acidity measurements by the method of Arora et al[17] have been recorded in plates 3.2 and 3.3. The Plate 3.2 represents the variation of acidity of the different samples with that of activation temperatures. How does acidity vary with the change in excess surface oxygen has been shown in the Plate 3.3. When Plate 3.2 is examined it becomes obvious that acidity of the samples increases with decrease in activation temperature. Now it can be concluded that the rise in activation temperature to which the samples have been subjected, is somehow detrimental to the acidic sites available at the surface of the samples. Hence there is a decreasing tendency in acidity value with rise in activation temperature. This trend of variation in acidic values with activation temperature is recorded in case of all samples namely Cerium Nickelate, Cerium Cuprate and Cerium Zincate (Plate 3.2). However, the acidity value of the samples activated at 700°C, 800°C, 900°C and 1000°C are found in the following sequence: Cerium Nickelate > Cerium Zincate > Cerium Cuprate. In all the series of samples the ones activated at 700°C have got the maximum value of acidity. The Plate 3.3 which represents the variation of acidity with that of excess surface oxygen leads us to the interesting conclusion. The acidity values seem to be the function of excess surface oxygen. It is very clear that keeping the magnitude aside both have the decreasing tendency with the rise in activation temperature of the samples thus indicating a parallelism in the surface characteristic. It is to be pointed out that this would have certainly some bearing on the catalytic properties of the samples in the event when these two would be the controlling factors. Saha et al[4] after the critical examination of the results on the measurement of acidity and excess surface oxygen of the samples of inner transition metal oxides have noted that the excess surface oxygen varies exponentially with acidity which is also seen in Plate 3.3.

The increase in activation temperature leads to the reduction in acidic values as well as the values of excess surface oxygen. It is supported unambiguously that activation temperature controls the surface characteristic of the samples. Further, if in any way the acidity and excess surface oxygen affect the catalytic behavior of the samples, this would be certainly shown by experimental results. In view of these concluding points the thermal degradation of urea in presence of these samples as catalyst has been carried out.

3.3C ROLE OF SURFACE AREA

The surface area measurements of the samples were done in PDIL, Sindri by the method as adopted by M.N. Rao[3]. The results on the surface area have been represented in the Plate 3.4. On account of adsorption of very small amount of nitrogen by the samples particularly by those activated at high temperatures, the measurement of surface areas has been, in fact a troublesome task. The surface area data represented in plate 3.1 are the average of two measurements made for each samples.

A perusal of the Plate 3.4 makes it obvious that the values of surface area of the sample of Cerium Zincate are a little higher in comparison to that of the samples of Cerium Cuprate and the surface area of the samples of Cerium Nickelate are much higher than that of the samples of Cerium Zincate:

$$CeCuO_3 < CeZnO_3 << CeNiO_3$$
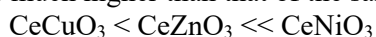
The value of surface area of the samples in case of all the three series is reduced regularly and linearly as the activation temperature increases (Plate 3.4). It is worth mentioning that exactly the same observation pertaining to the variation of surface area with the rise in activation temperature was noted by Baythoun and Sale[18] who measured the surface area of lanthanum magnanite perovskite at various temperatures, surface area has been supposed to be the key factor in the performance of catalytic action and consequently the sample of highest surface area would be most active potentially than other samples provided other factors remain the same in all the cases. In view of the trend recorded in between surface area and activation temperature it can be predicted that the samples activated at lower temperature would show higher activities and there would be gradual fall in activity as the activation temperature would rise.
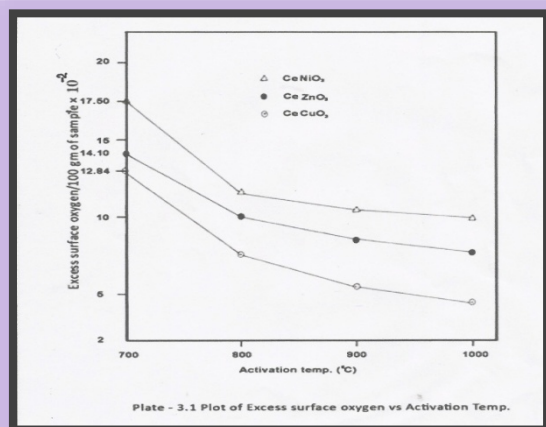
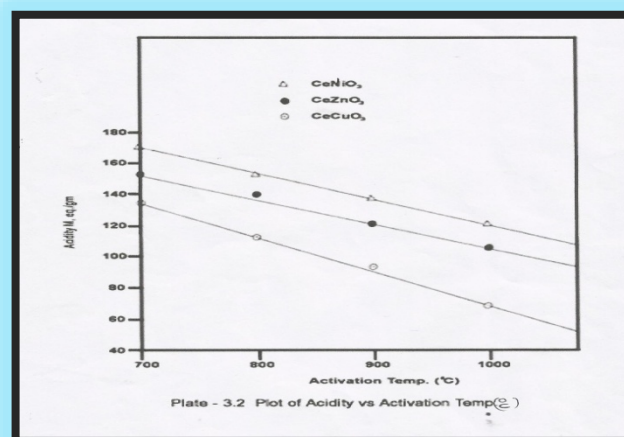Plate - 3.1 Plot of Excess surface oxygen vs Activation Temp.
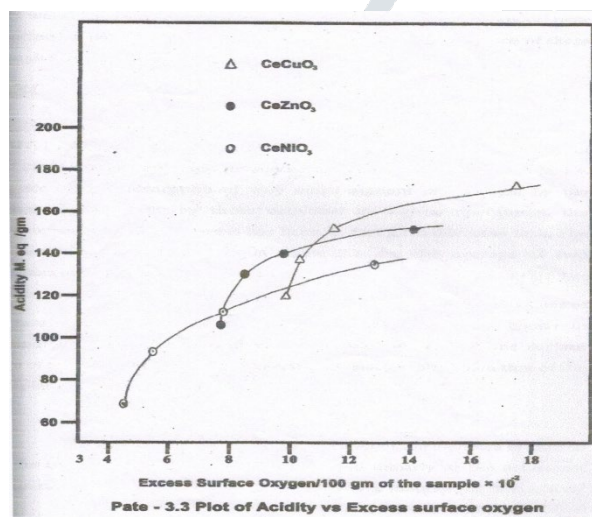

Plate - 3.2 Plot of Acidity vs Activation Temp.
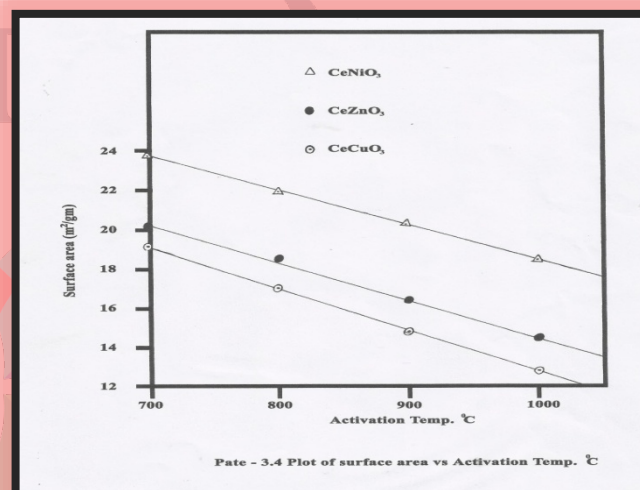

Pate - 3.3 Plot of Acidity vs Excess surface oxygen

Pate - 3.4 Plot of surface area vs Activation Temp. °C

IV.　ACKNOWLEDGMENT

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