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INFLUENCE OF γ-IRRADIATION ON THE CATALYTIC PROPERTIES OF ZINC OXIDE

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Abstract—Preliminary irradiation of ZnO with ^{60}Co γ-radiation in air is found to enhance its catalytic activity for the free radical oxidation reaction of secondary alcohols by CCl_4. The enhanced catalytic activity is found to be permanent and is a function of the γ-dose. The radiation damage caused in ZnO due to γ-irradiation increases the concentration of O_2^-(ads) on the surface of ZnO and this is responsible for the enhanced catalytic activity of γ-irradiated ZnO.

INTRODUCTION

ZnO is a very important *n*-type semiconductor and a catalyst for a variety of reactions like hydrogenation, dehydrogenation, disproportionation, etc.[1] The surface behaviour of ZnO can be considerably influenced by the presence of adsorbed species and other surface defects. Impurities and defects in the bulk of ZnO also influence its electronic properties which in turn influence its catalytic properties. It has been a preferred substance for studies on the influence of γ-radiation, β-radiation and neutrons on its catalytic properties,[2–4] however, in most of the cases reported so far, satisfactory explanations have not been offered to account for the changes in the catalytic properties caused by irradiation.

ZnO is chosen for the present investigation on the influence of γ-irradiation on its catalytic properties with a view to seek correlations between catalytic activity and surface properties. Free radical oxidation of secondary alcohols by CCl_4 in the presence of ZnO[5] (reaction 1)

$$(1)\qquad R_2CHOH + CCl_4 \xrightarrow[RT,Dark]{ZnO} R_2C=O + CHCl_3 + HCl$$

has been found to take place at ambient temperatures in the dark and hence is an ideal reaction to study the influence of γ-irradiation on the catalytic properties of ZnO. Hence it is used as the indicator reaction.

EXPERIMENTAL

Irradiations with γ-radiation were conducted in a 2000 Ci-^{60}Co γ-cell supplied by the Bhabha Atomic Research Centre, Bombay, India. The dose rate was measured to be 0.4 M rad/h using a Fricke dosimeter. The ZnO samples were taken in open test tubes and γ-irradiated in air. The samples were used in the reaction immediately after removal from the γ-source.

ZnO catalyst samples were prepared by the following methods:

(i) By the decomposition of basic zinc carbonate in air at 450°C for 6 h. (ZnO–C).

(ii) By the decomposition of zinc oxalate in air at 450°C for 6 h (ZnO–O).

(iii) By the decomposition of zinc formate in air at 250°C for 6 h (ZnO–F).

(iv) By the decomposition of zinc acetate dihydrate in air at 225°C for 6 h (ZnO–A).

In addition to these samples, M&B reagent grade ZnO was also used (ZnO–M&B). All the other reagents used in the investigation were of analytical reagent or equivalent grade.

The surface areas of various preparations of ZnO were measured by the BET method[6] using nitrogen adsorption at liquid nitrogen temperature. The non-stoichiometries (concentration of non-stoichiometric excess zinc) of the ZnO samples were estimated by Norman's method.[7] A Varian E4 ESR Spectrometer operating at X-band frequencies was used for recording the ESR spectra.

The reactions were carried out batch wise in pyrex glass bottles of 3 cm dia. and 30 ml volume, kept thermostated in the dark at the specified temperature, for the required period of time. The progress of the reaction (1) was followed by estimating the chloride ion formed in the reaction by Volhard's method.

RESULTS AND DISCUSSION

It has been observed that irradiation of ZnO with ^{60}Co γ-radiation prior to its use in the reaction enhances its catalytic activity significantly. Irrespective of the method of preparation of ZnO, γ-irradiation is found to enhance its catalytic activity (Figs. 1–3). The enhanced catalytic activity of γ-irradiated ZnO is noticed even 6 months after irradiation.

The surface area of the ZnO as measured by the BET method is unaffected by γ-irradiation. There is no difference in the Debye–Scherrer X-ray powder patterns of irradiated and unirradiated

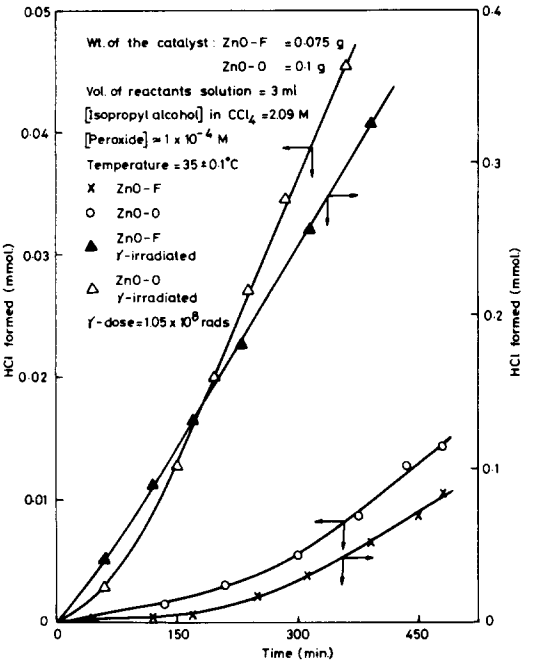

FIG. 1. Effect of γ-irradiation of ZnO on the progress of reaction.

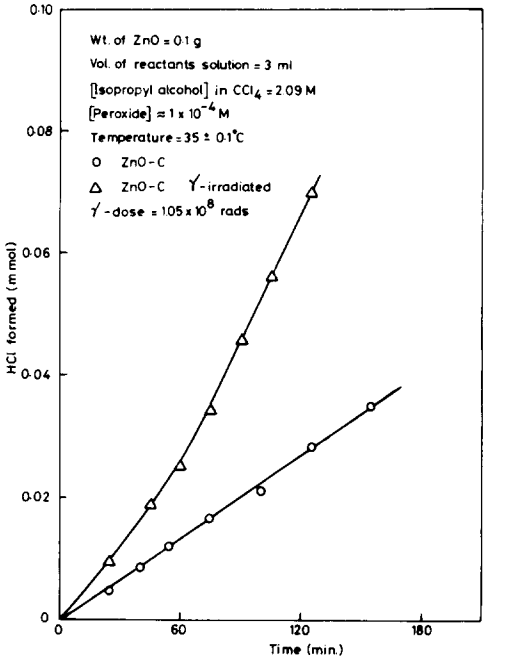

FIG. 3. Effect of γ-irradiation of ZnO on the progress of reaction.

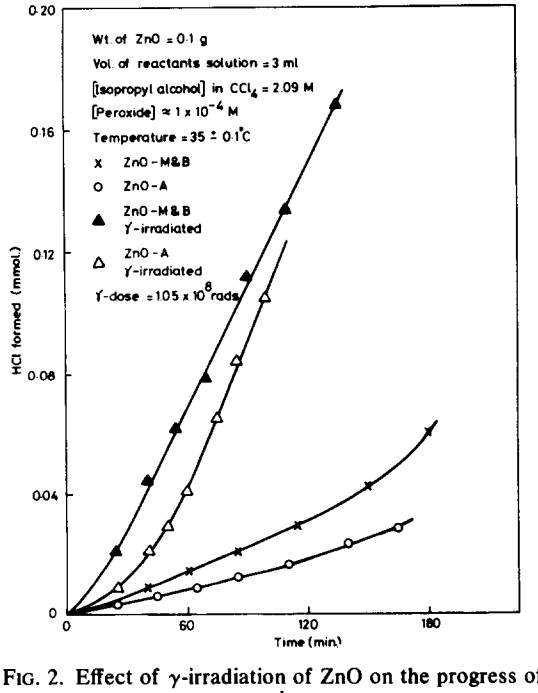

FIG. 2. Effect of γ-irradiation of ZnO on the progress of reaction.

ZnO samples. The reflectance spectrum of γ-irradiated ZnO is found to be identical with that of unirradiated ZnO, suggesting that the band gap of ZnO is not affected by γ-irradiation. This also indicates that the coordination around the Zn^{+2} ion in the bulk of ZnO is unchanged due to irradiation. The far IR spectra of γ-irradiated and unirradiated ZnO samples are found to be identical indicating that the strength of the Zn–O bond in ZnO is unchanged due to γ-irradiation.

It is known that ZnO undergoes radiolysis when it is irradiated with ^{60}Co γ-radiation and evolves oxygen.[8] If oxygen is freed from the ZnO lattice, there will be excess zinc left behind and so the non-stoichiometry of ZnO can be expected to increase due to γ-irradiation. The electronic properties of ZnO are very much dependent on its non-stoichoimetry. Since the catalytic and chemisorptive properties of a solid depend on its electronic properties, non-stoichiometry assumes an important role in determining the catalytic properties of ZnO. The concentrations of non-stoichiometric excess zinc of the ZnO samples prepared by different methods before and after irradiation with ^{60}Co γ-radiation are presented in Table 1. It can be observed from Table 1 that except in the case of M&B ZnO, there is a considerable enhancement in the concentration of excess zinc in all the cases

TABLE 1. EFFECT OF γ-IRRADIATION ON THE NON-STOICHIOMETRY OF ZnO

ZnO sample	Non-stoichiometry (ppm)	
	Before irradiation	After irradiation
ZnO-C	1.31	6.28
ZnO-A	3.27	9.81
ZnO-O	3.73	6.15
ZnO-M2B	2.09	1.70
ZnO-F	36.60	48.40

Duration of γ-irradiation = 30 days
γ-dose rate = 0.4 M rad/h

TABLE 2. EFFECT OF γ-IRRADIATION ON THE INTENSITY OF THE $g \sim 1.96$ ESR SIGNAL OF ZnO

ZnO sample	Intensity of the g~1.96 ESR signal (arbitrary units)	
	Before irradiation	After γ-irradiation
ZnO-A	4651	14420
ZnO-O	1225	1882
ZnO-M2B	237	256
ZnO-C	3997	4548

Duration of γ-irradiation = 11 days
γ-dose rate = 0.4 M rad/h

due to γ-irradiation. Thus it can be concluded that γ-irradiation of ZnO enhances its non-stoichiometry.

ZnO gives an ESR spectrum with a principal signal at $g \sim 1.96$. This signal has been variously attributed to F^+ centres,[9–12] interstitial Zn^+ ions or to the conduction electrons.[13–17] The assignment of the signal to a particular species is not yet satisfactorily resolved. However, since all the above mentioned species arise due to the non-stoichiometry of ZnO, it can be safely concluded that the ESR signal is related to the non-stoichiometry of ZnO and the intensity of the signal can be taken as a measure of the non-stoichiometry of the ZnO sample.

It was reported that the intensity of the $g \sim 1.96$ ESR signal of ZnO is enhanced if ZnO is irradiated with ^{60}Co γ-radiation after evacuation at high temperature.[14] In our study since the irradiation is done in air, it was thought worth while to see whether the intensity of the signal changes under the experimental conditions employed by us. The ESR spectra of the ZnO samples prepared by different methods were recorded at liquid nitrogen temperature before and after γ-irradiation and the intensities of the $g \sim 1.96$ signal calculated. They are given in Table 2. It can be observed from Table 2 that the intensity of the $g \sim 1.96$ ESR signal of ZnO is enhanced by γ-irradiation. If the intensity of the ESR signal is a measure of the concentration of conduction electrons then one can consider that the electrical conductivity also increases with γ-irradiation.

It is observed in the present investigation that the concentration of O_2^-(ads) on the surface of ZnO increases when it is irradiated in air with ^{60}Co γ-radiation. The O_2^-(ads) has been identified from its characteristic ESR spectrum,[13] a triplet with $g_1 = 2.045$, $g_2 = 2.009$ and $g_3 = 2.003$ (Fig. 4). Efforts were made to estimate the concentration of O_2^-(ads) on the surface of ZnO using ESR spectroscopy, but due to lack of sufficient sensitivity of the ESR spectrometer employed for measurement and since it was possible to record the ESR spectra at LNT only in air, we could not detect the signals corresponding to O_2^-(ads) with low doses of γ-radiation.

However, with larger doses (1000 Mrad), we have been able to record the spectra of samples immediately after irradiation in air at LNT and could identify the species as O_2^-(ads) on the surface of ZnO (Fig. 4). Under these conditions of measurement, quantitative estimation of O_2^-(ads) was not possible. It can be concluded that radiation induced chemisorption of oxygen (as O_2^- ads)

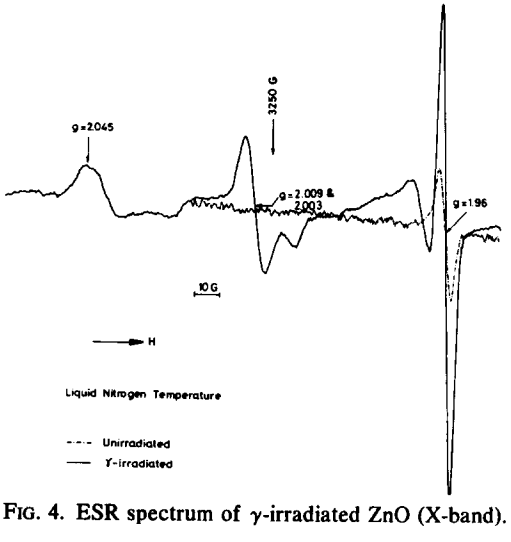

FIG. 4. ESR spectrum of γ-irradiated ZnO (X-band).

occurs on the surface of ZnO due to γ-irradiation in air. This observation is in agreement with the results of several other workers.[14, 18, 19]

The radiation damage process in ZnO due to γ-irradiation can be visualised in the following manner. ZnO undergoes radiolysis and as a result, molecular oxygen is liberated from its lattice.[8]

$$O^{=} \xrightarrow{\gamma} \frac{1}{2} O_2 \oplus 2\,e^{-}.$$

The electrons formed in this manner will be left in the ZnO lattice. Some of these electrons will occupy the oxygen ion vacancies to form F centres. A part of the remaining electrons will be taken up by the Zn^{++} ions to form Zn^{+} ions. When oxygen vacancies are formed on the surface of ZnO, the oxygen from the bulk can travel to the surface to fill the vacancies, with the result vacancies will be created in the bulk of ZnO. Fraction of the electrons present in the surface anionic vacancies will be taken up by the atmospheric oxygen molecules (since the γ-irradiation is done in air) to form O_2^-(ads). This process repeats itself during the irradiation and hence the non-stoichiometry, concentration of conduction electrons and the concentration of O_2^-(ads) are found to be higher in the case of γ-irradiated ZnO when compared to the unirradiated one.

Table 3 gives the catalytic activities (initial rates measured at 40°C in terms of m.moles of HCl formed in 1 h.), non-stoichiometries and the relative concentration of conduction electrons of the ZnO samples prepared by different methods. This temperature was chosen for convenience of measurement. It can be observed from Table 3, that the catalytic activity of ZnO is dependent neither on its non-stoichiometry nor on the concentration of conduction electrons. This leads us to the conclusion that the radiation induced chemisorbed oxygen on the surface of ZnO (O_2^- ads) is responsible for the enhanced catalytic activity of γ-irradiated ZnO. This explanation is supported by the following observations: (i) ZnO–M&B samples (0.1 g each) were irradiated for different periods of time in the ^{60}Co γ-chamber and used in the experiment. The initial rates of the reaction with these ZnO samples irradiated with different γ-doses were measured and the percentage increase in the initial rate calculated in each case. This quantity is taken as a measure of enhancement in the catalytic activity of ZnO due to γ-irradiation and it is plotted vs the γ-dose to which the ZnO samples were subjected. The plot is shown in Fig. 5. It can be noticed from Fig. 5, that the catalytic activity of ZnO increases with increasing γ-dose. The increase is very steep till a dose of 10 Mrad and, thereafter, it is gradual.

The variation of enhanced catalytic activity of γ-irradiated ZnO with the γ-dose represented in Fig. 5 is exactly similar to the plot obtained by Duck *et al.*[14] for the dose dependence of the γ-induced chemisorption of oxygen on the surface of ZnO. This observation clearly indictes that the enhanced catalytic activity is related to the concentration of O_2^-(ads) on the surface of ZnO. (ii) M&B ZnO is sealed in a glass tube in argon atmosphere and then irradiated with ^{60}Co γ-radiation to a total dose of 100 Mrad. It is observed that there is absolutely no change in the catalytic activity of ZnO due to γ-irradiation in argon atmosphere. This experimental observation clearly supports our conclusion that radiation induced chemisorption of oxygen on the surface of ZnO is responsible for the enhancement in the catalytic activity of ZnO due to γ-irradiation.

The free radical oxidation of secondary alcohols by CCl_4 on the surface of ZnO[5] (equation 1) con-

TABLE 3. CORRELATION OF THE CATALYTIC ACTIVITIES OF ZnO CATALYSTS PREPARED BY DIFFERENT METHODS TO THEIR PHYSICAL PROPERTIES

ZnO sample	Catalytic activity/m^2 (m.moles HCl/h)	Non-stoichiometry (ppm)	Relative intensity of $g \sim 1.96$ ESR signal (arbitrary units)
ZnO-C	0.58	1.31	3997
ZnO-O	0.06	3.73	1225
ZnO-A	0.08	3.27	4651
ZnO-F	0.12	36.60	29400
ZnO-M&B	0.49	2.09	237

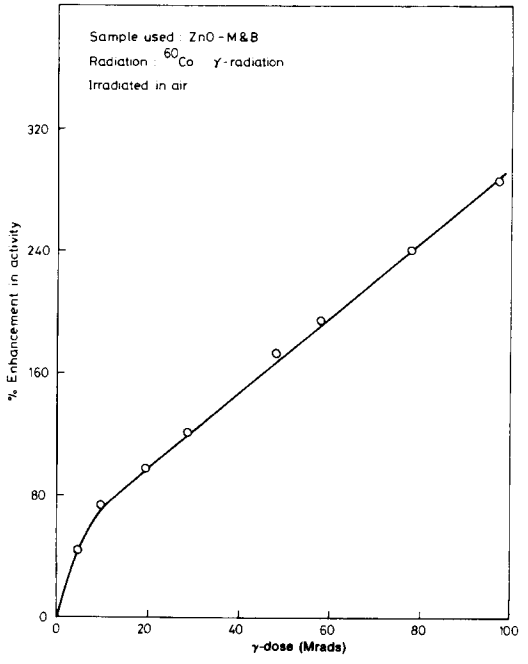

FIG. 5. Dependence of the enhanced activity of irradiated ZnO on the γ-dose.

sists of two initiation steps. They are given as follows

$$(2)\qquad R_2C(OH)OOC(OH)R_2 \xrightarrow{ZnO} 2R_2C(OH)O$$

$$(3)\qquad R_2CHOH + O_2^-(ads) \xrightarrow{ZnO} R_2C(OH)OOH + e^-$$

(to the catalyst)

$$\downarrow$$

$$R_2C(OH)O + OH.$$

The first initiation step (equation 2) is the homolytic decomposition of organic peroxide molecules (which are present as impurities in the sec-alcohol) on the surface of ZnO to yield the free radicals $R_2C(OH)O^{\cdot}$. In the second initiation step (equation 3), the chemisorbed oxygen species on the surface of ZnO (O_2^- ads) reacts with a molecule of sec-alcohol also adsorbed on the surface of ZnO to form a hydroperoxide molecule which dissociates in a fast step on the surface of ZnO to form the radicals OH and $R_2C(OH)O^{\cdot}$.

Since γ-irradiation of ZnO in air brings about an enhancement in the concentration of O_2^-(ads) on its surface, the rate of reaction (3) will be higher in the case of γ-irradiated ZnO than in the case of the unirradiated catalyst. This results in the enhancement in the rate of the overall reaction and consequent higher catalytic activity for the γ-irradiated ZnO.

Thus, it has been possible from the study of the influence of γ-irradiation on the catalytic properties of ZnO, to conclude that O_2^- adsorbed on the surface of ZnO plays an important role in the initiation of the free radical oxidation of secondary alcohols by CCl_4 on the surface of ZnO.

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