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Excess Electron Concentration of Pure and Doped Zinc Oxides

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The concentration of excess electrons in zinc oxide catalysts was determined by hydrogen-evolution method and the effect of doping with mono- and trivalent cations was studied. The amount of excess electrons of doped and nondoped zinc oxides increased remarkably by evacuation above 300°C. The addition of trivalent cations increased the excess electron concentration, while the monovalent cation seemed to decrease it. Such behavior is consistent with the observation in electron conductivity measurement, and can be interpreted in terms of the substitution of impurity cations for the lattice zinc. It was found, however, that the catalytic activity for the isomerization of butenes over these catalysts is independent of net excess of electrons detected by this method.

I. INTRODUCTION

Zinc oxide is a typical n-type semiconductor and considered to have nonstoichiometric excess zinc in the bulk and the surface layer, especially when it is treated in a reductive atmosphere or evacuated at high temperatures. The excess zinc produced by the removal of the lattice oxygen either from the surface or from the inner bulk of the oxide can easily be ionized by a thermal process, into the interstitial cation and the free electron. Thus, the nonstoichiometry of the oxide is directly associated with the electronic properties and, moreover, may be responsible for the behavior in adsorption of gases, catalysis, solid phase reaction and sintering.

In the earlier experiments to estimate the nonstoichiometry, several indirect methods using electronic devices were employed (*1*). However, chemical methods were expected to provide more direct and precise information on the nonstoichiometry and on the concentration of excess electrons (*2*). Allsopp (*3*) developed a "hydrogen evolution method" in which the oxide is dissolved in an acidic solution. Norman (*4*) reported a similar but simpler method using a photometric technique.

In the present paper, the concentration of excess electrons in pure and doped zinc oxides are reported, and the effects of pretreatment temperatures and gas adsorption are also discussed, in connection with the catalytic activity for butene isomerization.

II. EXPERIMENTAL METHODS

1. *Samples*

Basic zinc carbonate ($ZnO \cdot 2CO_3 \cdot 4H_2O$) was first decomposed in a dry air flow at 400°C for 5 hr. Doped zinc oxides, ZnO(I) series and ZnO(II) series, were prepared from the resultant oxide by impregnation into a solution of metal nitrate which contained the desired amount of the dopant cation. The samples were heated at the melting point or at the decomposition temperature and then calcined at 400°C for 5 hr [ZnO(I) series] or at 500°C for 3 hr

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[ZnO(II) series], in a dry air flow. Pure zinc oxides, ZnO(I)-pure and ZnO(II)-pure, were also treated in a similar manner using decationized water instead of the nitrate solution. Cation-doped zinc oxides are represented, for example, as ZnO(I)–Li-10, in which the last two numerals denote the cationic fraction of the dopant Li (atm%).

2. Principles and Procedures of Hydrogen Evolution Method

This method applied to determine the small amount of excess zinc or the electron concentration in zinc oxide is similar to that described by Allsopp (*3*). The principle of the analysis is based on the following reactions, viz,

$$ZnO + 2HCl = ZnCl_2 + H_2O, \quad (1)$$

$$Zn^0(\text{excess}) + 2HCl = ZnCl_2 + H_2(g), \quad (2)$$

$$Zn^+(\text{excess}) + e + 2HCl = ZnCl_2 + H_2(g). \quad (3)$$

The excess zinc, Zn^0(excess), is considered to be produced by the removal of the lattice oxygen from the surface layers and dissolved presumably into the interstitial position of the oxide lattice:

$$ZnO = Zn^0(i) + \tfrac{1}{2} O_2. \quad (4)$$

Further, most of the interstitial zinc, Zn^0(i) is singly ionized at around room temperature and doubly at higher temperatures as given in Eqs. (5) and (6) (*1*b, *5*).

$$Zn^0(i) = Zn^+(i) + e, \quad (5)$$

$$Zn^0(i) = Zn^{2+}(i) + 2e. \quad (6)$$

However, since these free electrons formed can also act to reduce proton in the acidic solution according to Eq. (7),

$$e + H^+ = \tfrac{1}{2} H_2. \quad (7)$$

The amount of the hydrogen evolved corresponds to the sum of those of the free electron and of the metallic zinc. In this sense, in the case of the pure oxide, the hydrogen evolution method can be a measure of the excess zinc in the oxides as well as that of the free electron concentration. In other words, the nonstoichiometry of the oxide can be determined by this analysis. However, in the case of doped zinc oxides, the free electron concentration may not necessarily correspond to the amount of excess zinc, Zn^0(i), and thus, it may be said that, the amount of the hydrogen evolved can be ascribed to the net amount of the reductive species over those of oxidative species. Therefore, it can be denoted as the concentration of the excess electrons including those free in the conduction band and those of quasi-free trapped in the interstitial zinc or the substituted cations which form the impurity levels.

The sensitivity of this method was ca. 0.1 ppm as reported by Allsopp (*3*) or Norman (*4*). The reproducibility of this method altered depending on the process of the preparation of the sample and also on the conditions of the pretreatment, since zinc oxide is unstable, especially when it is treated in a reductive atmosphere, or in a vacuum at high temperatures. In the first attempt to avoid the complexity and errors caused by the use of a solution of hydrochloric acid, dry gas of hydrogen chloride was employed. The result, however, proved to have little effect and rather difficult to complete the reduction-reaction. Thus, the solution method was adopted with a special care to purge out O_2 in the solution by N_2 flow and by repeated evacuation.

III. RESULT AND DISCUSSION

1. Effect of Evacuation Temperature

It is confirmed by DTA and X-ray analysis that the sample obtained by the thermal decomposition was completely zinc oxide. The specific surface areas for the ZnO(II) series were in the range 11.3–19.9 m^2/g (*6*). In Fig. 1, the effect of evacuation temperature for ZnO(II) series is shown. As for pure zinc oxide, it is evident

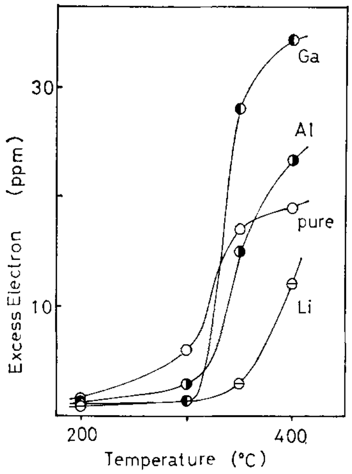

FIG. 1. Effect of the evacuation temperature on the excess electrons of variously doped zinc oxides. (Ga) ZnO(II)-Ga-0.2; (Al) ZnO(II)-Al-0.2; (pure) ZnO(II)-pure; (Li) ZnO(II)-Li-0.2. The samples were evacuated for 3 hr under a vacuum of 10^{-4} mm Hg.

that the concentration of the excess zinc increased remarkably with the rise of evacuation temperature above 300°C. This is consistent with an increase in the electron conductivity and a decrease in the optical transparency of these samples (*7*). The concentration of excess zinc observed for ZnO(I) calcined at 400°C (Eq. (1)) was rather low, compared with that for ZnO(II). The acceptable explanation for this difference might be that ZnO(II) was calcined at a higher temperature (500°C), so that the thermal dissociation reactions given in Eqs. (4), (5), and (6), might proceed to a further extent than for ZnO(I).

2. Effect of Doping

Figure 1 also shows the effect of "small" doping (0.2 at.%) on the concentration of the excess electrons. The excess electrons increase remarkably above 300°C. However, the electron concentration seems to be supressed by Li-doping, while it is increased remarkably by doping with Ga^{3+} or Al^{3+} at the higher temperature range. The temperature-dependent features might be due first to the desorption of oxidative (or acceptor) species from the surface by evacuation. Second, at higher temperatures, some of the lattice oxygen might be removed. The difference in the doping effect of mono- and trivalent cation on the electronic properties of ZnO are well known and interpreted in terms of so-called "valence control theory" (*8*). The effect of doping observed here by the hydrogen evolution method was quite consistent with the facts reported for the conductivity measurement and for the surface properties (*9*). If impurities of a trivalent cation such as Ga^{3+}, were substituted for Zn^{2+} in the zinc oxide lattice with the ratio of 1:1, it would be accompanied by electronic defect centers of reducing nature to preserve the charge neutrality as shown in Eq. (8),

$$Ga_2O_3 = 2Ga^{+}_{(Zn)} + 2e + 2ZnO + \tfrac{1}{2}O_2. \quad (8)$$

Here, $Ga^{+}_{(Zn)}$ denotes trivalent gallium ion in the zinc position of the lattice, and $(\ )^{2-}_{(Zn)}$ denotes the zinc vacancy. The former may probably trap an electron at lower temperatures and thus forms a

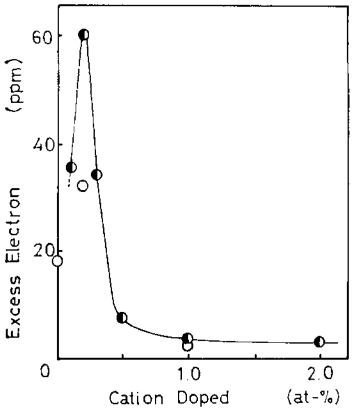

FIG. 2. Effect of the cation concentration of dopant. ZnO(I)-Ga series. The samples were evacuated at 450°C under a vacuum of 10^{-3} mm Hg for 3 hr. Ga(II)-Ga series (O) were evacuated at 400°C under a vacuum of 10^{-4} mm Hg for 3 hr.

donor level, viz,

$$(\ )^{2-}{}_{(\mathrm{Zn})} + \mathrm{Ga}^{3+} + \mathrm{e} = \mathrm{Ga}^{+}{}_{(\mathrm{Zn})} + \mathrm{e} = \mathrm{Ga}^{+}{}_{(\mathrm{Zn})}\cdot\mathrm{e}. \quad (9)$$

On the other hand, when monovalent cation, like Li^+, was substituted, the electron concentration would decrease as given:

$$\mathrm{Li_2O} + \tfrac{1}{2}\mathrm{O_2(g)} + 2\mathrm{e} = 2\mathrm{Li}^{-}{}_{(\mathrm{Zn})} + 2\mathrm{ZnO}, \quad (10)$$

$$\mathrm{Li}^{-}{}_{(\mathrm{Zn})} = (\ )^{2-}{}_{(\mathrm{Zn})} + \mathrm{Li}^{+} - \mathrm{e}, \quad (11)$$

where $Li^-{}_{(Zn)}$ represents a lithium cation substituted for lattice zinc. As for the interstitial zinc, however, the amount may decrease by doping with trivalent cations, if the reverse reaction of Eq. (6) is induced by the increase of the electron concentration. The reverse is true for doping with monovalent ones. However, Fig. 2 shows very clearly that these effects of doping on the electron concentration were evidently influenced by the cation concentration introduced and that there is an optimum concentration of Ga^{3+} at around 0.2–0.3 at.%. Further addition decreased it by factor of 10. Similar effects of large amount of impurities were also observed for pure and doped ZnO(II) series as given in Table 1. It seems evident that the level of the electron concentration was quite low compared with that for pure zinc oxide. In Fig. 3, the effects of the cation concentration are shown. These results are quite consistent with the reported observation for the samples fired at higher temperatures that the electronic conductivity increased by doping with Al_2O_3 or Cr_2O_3 and decreased by that of Li_2O, and that the former has a maximum and the latter has a minimum value at around 1–3 wt% of the impurity (*9*). Lithium ion doped from the vapor or in a solution was found to diffuse easily and to substitute for zinc above 300°C (*10*).

TABLE 1

Excess Electron Concentration of Doped Zinc Oxides (ppm)

Catalyst	Evacuation temp (°C)			
	200	350	400	450
ZnO(II)-Li-10	0.43	0.30	1.61	2.6
ZnO(II)-pure	1.52	16.6	19.1	—
ZnO(II)-Al-10	0.48	0.80	2.5	3.6
ZnO(II)-Ga-10	0.47	0.62	2.6	3.7

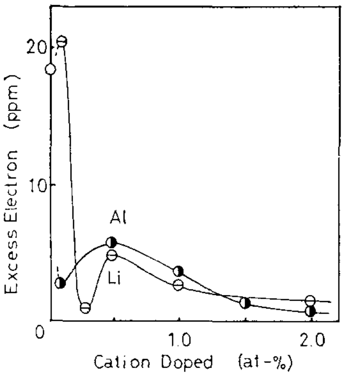

FIG. 3. Effects of cation concentration of dopant. ZnO(I)–Al series and ZnO(I)–Li series. The samples were evacuated at 450°C under a vacuum of 10^{-3} mm Hg for 2 hr.

It was reported also that the amount of hydrogen evolved was about 900 ppm, when zinc oxide was sintered with 0.5% of Ga_2O_3 at a high temperature, for example at 1100°C, to accomplish the substitution reaction of Ga^{3+} for the lattice zinc. If 0.1 at.% of Ga^{3+} introduced is assumed to completely substitute for zinc according to Eq. (8), the electron concentration would increase by 1000 ppm over that of pure zinc oxide.

In the present case, however, the result was different from the above expectation. The primary reason would be that, as for the trivalent cations the temperature of calcination was too low to complete the substitution or diffusion into the inner bulk of the lattice. The difference between the ZnO–Al series and the ZnO–Ga series might be due to the difference in reactivity and diffusion. Second, it should be noticed that, according to Eq. (8), the substitution by trivalent cations may produce oxygen. If

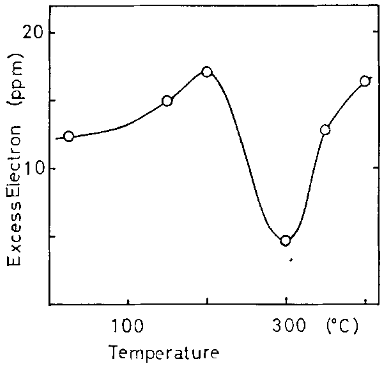

FIG. 4. Effect of O_2 adsorption at various temperatures. Sample: ZnO(II)-pure; pretreatment: evacuation at 450°C, 10^{-4} mm Hg for 2 hr; adsorption: 100 mm Hg of O_2 was introduced at each temperature, kept for 1 hr, and evacuated at the same temperature for 30 min (10^{-4} mm Hg).

the oxygen formed cannot be desorbed by evacuation and is present in an active form, hydrogen would not be produced. In fact, in the cases of ZnO–Al-10 and ZnO–Ga-10, a considerable amount of oxygen was detected after dissolving the sample in the acid, while, in contrast, ZnO–Li series did not produce any detectable oxygen. Third, when the excess impurity was introduced above the limit of solubility, it may probably be present as the "single" oxide on the surface of the crystals or as double oxide formed by solid phase reaction with zinc oxide.

However, if the substitution of Ga^{3+} for the lattice zinc took place by the stoichiometric ratio of $Ga^{3+}:Zn^{2+} = 2:3$ instead of "1:1 substitution," to form a zinc cation defect, hydrogen could not evolve as given in Eq. (12). Further, if it is assumed that the ratio is altered by some reason to a lower value, such as 2:4, the electron concentration would be decreased to conserve neutrality by accepting oxygen from the gas phase as shown in Eq. (13),

$$Ga_2O_3 = 2Ga^{+}{}_{(Zn)} + 3ZnO + (\ )^{2-}{}_{(Zn)}, \quad (12)$$

$$Ga_2O_3 + \tfrac{1}{2}O_2 + 2e = 2Ga^{+}{}_{(Zn)} + 4ZnO + 2(\ )^{2-}{}_{(Zn)}. \quad (13)$$

These circumstances might be realized as the result of the modification of the mother oxide by the impurities.

3. *Effect of Absorbed Gas on Electron Concentration*

It should be emphasized that the amount of excess electrons titrated by this method does not necessarily represent the total interstitial zinc in zinc oxide. The result obtained may represent the electron concentration over that of chemisorbed oxygen or oxidative species which are present in a form capable of taking part in the oxidation–reduction process in the acid solution.

In order to elucidate the role of oxygen on the surface, the effect of preadsorption of oxygen was examined. ZnO(II)-pure was preevacuated at 450°C for 3 hr and then oxygen (100 mm Hg) was introduced at various temperatures. The result is shown in Fig. 4. It seems that the electron concentration was lower in the two different temperature regions, below 100°C and around 300°C, which may be ascribed to the adsorption of oxygen. These facts were quite consistent with the following experimental results: when ZnO(II) was evacuated at above 450°C, a metal-like behavior was observed in the temperature dependency of electron conductivity, and when it was heated above room temperature in the presence of oxygen ($>10^{-1}$ mm Hg) the conductivity decreased stepwise at 170–300°C and 375–400°C, and then it increased

TABLE 2

Effect of Pretreatment by Various Gases on the Excess Electron Concentration (ppm)

Gas	Excess electron
H_2	55.9
CO	41.0
CO_2	17.7
O_2	16.4
No treatment	19.1

again with the desorption of the oxygen from the different sites. These facts may suggest that these adsorbed oxygens might trap the electron, and are consistent with the results detected by ESR (*11*) or TPD measurement (*12*).

The excess electron concentration obtained by this method corresponds to the net of the following electrons, provided that they can reduce protons in the acid solution: (a) those, in the bulk or the surface, free or trapped on the interstitial zinc [Zn^{2+}(i), Zn^{+}(i)] and on the impurity cation; (b) those trapped on oxygen vacancies (O_v); (c) those connected to the excess oxygen of adsorbed state (O_2^-, O^-, O^{2-}).

The effect of the pretreatment by other oxidative or reductive gases was studied over the samples where they were adsorbed at 400°C for 1 hr and evacuated at the same temperature. The result is given in Table 2. The order of the excess electron concentrations is reasonably ranged in the order of the reducing power of the gases. Thus, this fact implies that the electron concentration of these catalysts are very sensitively affected by their redox reaction.

4. Correlations between Catalytic Activity and Electron Concentration

It was reported that in the hydrogenation of ethylene over zinc oxide, no effect of doping was observed (*13*). While in the case of N_2O dissociation, a correlation between the kinetic behavior and that of the electron conductivity was interpreted in terms of the participation of the conduction electron in the rate determining step (*14*). As for the isomerization of *cis*-2-butene, the catalytic activity and the selectivity were increased by doping with Ga^{3+} and Al^{3+}, and decreased by doping with Li^{+} (*6*). Figure 5 appears to show that no simple quantitative relation is present between the catalytic activity or the selectivity, and the excess electron concentration over the whole range of the impurity content. However, if it was taken into consideration that the excess dopant added decreased the electron concentration due to the other factors accompanied as discussed above, the result for the samples of high impurity content could be excluded. Consequently, it may be probable that the excess electrons also play a role in the isomerization reaction over the surface.

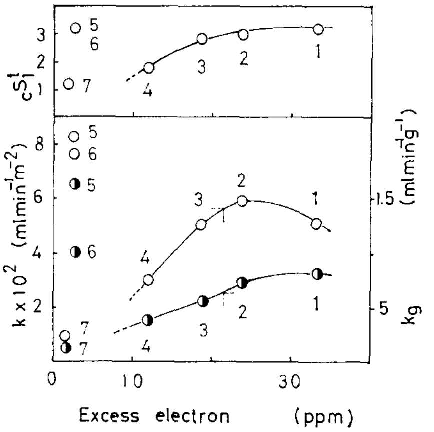

FIG. 5. Plots of catalytic activity and selectivity vs excess electron concentration. Reaction: *cis*-2-butene isomerization at 320°C in a flow system, *cis*-2-butene: 1 ml(NTP)/min; N_2(carrier gas): 10 ml(NTP)/min; pretreatment: evacuation at 400°C for 3 hr. k: first order rate constant for unit surface area; k_g: that for unit weight of the catalyst; $cS_1{}^t$: the initial selectivity by the ratio (*trans*-2-/1-). (1) ZnO(II)-Ga-0.2; (2) ZnO(II)-Al-0.2; (3) ZnO-(II)-pure; (4) ZnO(II)-Li-0.2; (5) ZnO(II)-Ga-1.0; (6) ZnO(II)-Al-1.0; (7) ZnO(II)-Li-1.0.

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