

Synergetic Effect of Oxide Catalysts with Different Dopants on Catalytic Activity

I. Nickel Oxide and Zinc Oxide for Carbon Monoxide Oxidation

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The catalytic activity of pure, doped nickel oxide, and mixtures of nickel oxides with different dopants was investigated by the reaction of carbon monoxide oxidation. The incorporation of lithium ions in the oxide enhanced the activity and the addition of indium lowered the activity. The activity of mixtures increased to several times greater than would be predicted by simple additive effect of single doped catalysts. For zinc oxide, the incorporation of lithium or indium ions, respectively, decreased or increased the activity. Mixtures of zinc oxides with different dopants were also more active than expected from the simple additive effect. The mechanism of the enhanced activity of mixtures was discussed from the viewpoint of synergetic action of doped catalysts with different Fermi levels.

INTRODUCTION

The effect of dopants on the chemical properties of semiconductors has been discussed from two standpoints. First, attention has been given to the reactivity of solids which is controlled by vacancy and interstitial ion concentration. The second group of studies has been concerned with catalytic property of solids. Here, by contrast, the ionic factors are suppressed and the observed effects are primarily due to the variations in electron hole and electron concentration.

Effect of dopants on the catalytic activity of nickel oxide for carbon monoxide has been studied by many authors (1-7). Unfortunately, the results are diverse and sometimes contradict each other. A few workers studied on the same effect for zinc oxide and the apparent discrepancies among the results are also recognized (2), (8-10).

No attention, however, has so far been confined to the chemical properties of mixture of semiconductive oxides with different dopants. Komatsu and co-workers (11)

have already found an enhanced reactivity of solids when solids with different dopants were mixed. Powder mixtures of lithium doped and indium doped nickel oxides were found to show the greatest sinterability among pure, lithium doped, indium doped nickel oxide, and the mixture.

This result may be explained by a consideration of the band structure of the two oxides. Fermi levels of the two oxides will be different; the Fermi level of lithium doped oxide may be lower than that of indium doped. When the two oxides are brought in contact directly or indirectly through adsorbed oxygen ions on the surfaces, an electron rearrangement will occur in such a way as to equalize Fermi levels at the interface. Electrons are transferred from indium doped oxide to lithium doped oxide, exhibiting a positive space charge in indium doped oxide and negative space charge in lithium doped oxide. This electrostatic field, caused by the space charge, is responsible for the enhancement of sinterability of nickel oxide with different dopants. The same result was also obtained for the free sintering of powder mixtures

of lithium doped and indium doped zinc oxide (12).

The aim of present work is to develop the effect of mixing of oxides with different dopents (henceforth called the mixing effect) in the field of catalysis such as carbon monoxide oxidation. In the paper we report, first, on a reinvestigation of CO oxidation over doped and undoped-nickel oxide and-zinc oxide and then, on the mixing effect for nickel oxide and zinc oxide.

EXPERIMENTAL

Preparation of Catalysts

Nickel oxide. Nickel nitrate (G.R.) was decomposed at low temperature on a sand bath and the resulting oxide (black) was further fired at 600°C for 15 hours. The nickel oxide obtained was greenish gray and was doped in the following: To solutions of known quantities of lithium nitrate (G.R.) or indium nitrate (G.R.) the oxide was added. The suspension was stirred for 30 minutes and was evaporated to dryness with an infrared lamp. The solid mixture was lightly ground and fired at 650°C for 3 hours. The following oxides were prepared: Nickel oxide with 0.1%, 1.0%, and 3.0% (atom %) lithium or indium. Pure nickel oxide, as a reference, was also treated with nickel nitrate solution and fired at 650°C for 3 hours. The oxides with and without dopent were granulated to 20-30 mesh and finally fired at 950°C for 3 hours. Pure nickel oxide, lithium doped, and indium doped oxide (henceforth represented NiO-Li₂O and NiO-In₂O₃) were greenish gray, black, and green, respectively.

Zinc oxide. Basic zinc carbonate (G.R.) was slowly dehydrated at 250°C for 3 hours in air and then decomposed in vacuum at 300°C for 30 hours. The resulting oxide was doped in the same way described above and granulated to 20-30 mesh and fired at 950°C for 3 hours. Amounts of dopents were 0.05%, 0.1%, and 1.0% for lithium and 0.1%, 1.0%, and 3.0% for indium, respectively. The resulting pure and lithium doped zinc oxide

were white and the indium doped was pale yellow.

Mixed catalyst. Mixed catalyst was prepared as follows: NiO-Li₂O (1%) and NiO-In₂O₃ (1%) were taken into the reactor and mixed lightly by shaking the reactor several times. Total amount of mixture was 1.500 g and mixed ratios of NiO-Li₂O to NiO-In₂O₃ were 3/1, 1/1, and 1/3 by weight, respectively. As for mixed catalyst of zinc oxide, total amount of mixture was 3.000 g and mixed ratios of ZnO-Li₂O (1%) to ZnO-In₂O₃ (1%) were 2/1, 1/1, and 1/2, respectively. When liquid nitrogen trap was used to remove carbon dioxide formed from the reaction system, amounts of single catalyst of doped nickel oxide and the mixed catalyst (ratio of 1/1) were 0.500 g and 1.000 g, respectively. Surface areas of the catalysts were obtained by BET plots of nitrogen isotherms at -195°C.

The Reaction System

Carbon monoxide, from a commercial cylinder, was purified by passing it through glass wool, soda lime, and liquid nitrogen trap. Oxygen, from a commercial cylinder, was purified by passing it over calcium chloride, Pd-asbestos, and liquid nitrogen trap.

Stoichiometric mixture of carbon monoxide and oxygen was primarily used, while mixtures of various compositions were also used in order to determine the rate equation of reaction. The total pressure of premixed gas was 150-240 torr.

Rates of oxidation were measured in all Pyrex glass, completely closed system having a total volume of 256 cc. Weighed amount of catalyst was loaded on a sintered Pyrex glass disc in the small reactor (inner diameter = 18 mm) in a furnace. Reactor temperature was controlled ($\pm 0.5^\circ\text{C}$) by a regulator.

Premixed carbon monoxide and oxygen was circulated to pass through the catalyst by means of a circular pump. The flow rate of about 1 l/min was adopted to obtain data, independent of diffusion effect. The reactions were carried out without and with the trap. Changes in pressure due to the

TABLE 1
 SURFACE AREA OF CATALYST

Catalyst	$S(\text{m}^2/\text{g})$	Catalyst	$S(\text{m}^2/\text{g})$
NiO-Li ₂ O (0.1 at%)	1.3	ZnO-Li ₂ O (0.05 at%)	0.7
(1.0 at%)	0.9	(0.1 at%)	0.8
(3.0 at%)	0.7	(1.0 at%)	0.9
NiO	1.0	ZnO	1.1
NiO-In ₂ O ₃ (0.1 at%)	1.2	ZnO-In ₂ O ₃ (0.1 at%)	1.1
(1.0 at%)	1.9	(1.0 at%)	1.5
(3.0 at%)	1.6	(3.0 at%)	1.4

reaction were recorded by means of a mercury manometer.

The activity of catalyst decreased during the course of each run, new catalyst, therefore, was used for each run. Before the experiments, nickel and zinc oxide catalysts were evacuated at 250°C for 40 min and at 500°C for 1 hour, respectively. Temperatures of the reaction were 142°–270°C (without the trap) and 40°–130°C (with the trap) for nickel oxide catalysts and 375°–500°C (without the trap) for zinc oxide, respectively.

RESULTS

Surface areas of the catalysts obtained by BET method are recorded in Table 1.

On nickel oxide catalysts, the rate of CO oxidation was found to obey the first order reaction with respect to partial pressure of carbon monoxide; $-dp_{\text{CO}}/dt = kp_{\text{CO}}$, where p_{CO} is partial pressure of carbon monoxide

at time t and k (1/min) is a rate constant. With indium doped nickel oxide, the first order equation failed to express the data at high conversion (>50%).

For zinc oxide catalysts many kinetic equations have been proposed (2, 9, 10, 13, 14). Changing the composition and the initial pressure of gaseous mixture, we tested these equations. Our results, however, could not obey the rate expressions of above authors. Therefore, the initial rate of CO consumption, V (torr/min), was taken as the activity of zinc oxide catalysts.

In the case of the reaction system without the trap, the rate constants reduced to unit area of 1 m², k/S , and V/S , were plotted against $1/T$ in Figs. 1 and 2. Arrhenius plots for nickel oxide catalysts, obtained with the reaction system having the trap, were recorded in Fig. 3 with the plots for mixed catalysts. The rate constants (without the trap) for the mixed catalysts

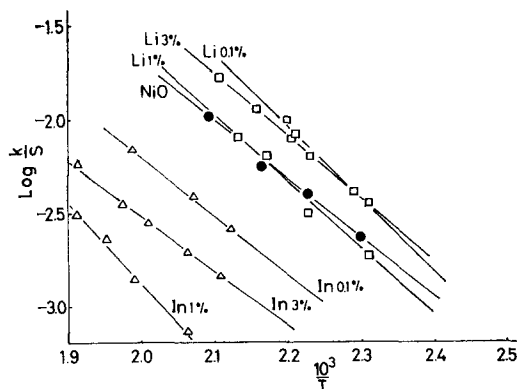


FIG. 1. Arrhenius plots for pure, lithium doped and indium doped nickel oxide catalyst (without the trap).

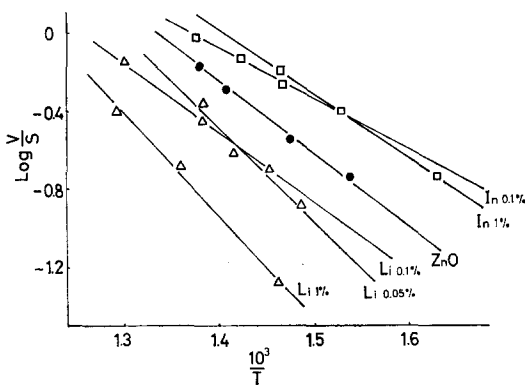


FIG. 2. Arrhenius plots for pure, lithium doped and indium doped zinc oxide catalyst (without the trap).

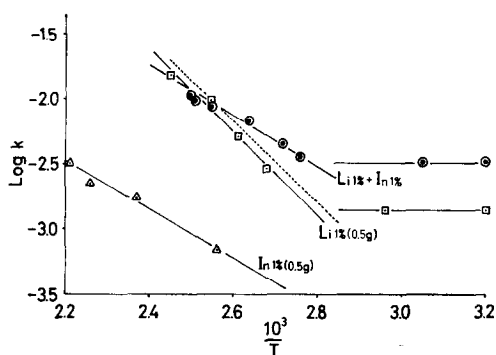


FIG. 3. Arrhenius plots for lithium doped, indium doped nickel oxide catalyst and mixed catalyst (with the trap).

of doped nickel oxide, k obs, were given in Fig. 4.

DISCUSSION

The results of the surface area measurements showed that the areas of both nickel oxide and zinc oxide were found to be decreased by the doping of lithium ions and that the areas to be increased by the incorporation of indium ions. These results can be explained by assuming that the sintering of nickel oxide and zinc oxide is controlled by the diffusion of electron

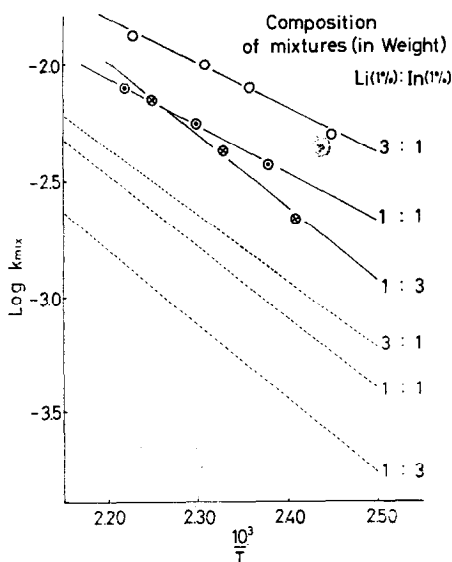


FIG. 4. Arrhenius plots for mixed catalyst of doped nickel oxide (without the trap).

holes, e.g., Ni³⁺ ions and of interstitial zinc ions, respectively (15, 16).

For the effect of dopents on the catalytic activity of nickel oxide, various results have been obtained by many authors. Parravano (1) and Keier *et al.* (3) showed that the incorporation of higher valent ions (W⁶⁺, Ce⁴⁺, Cr³⁺, Fe³⁺) led to a decrease of the apparent activation energy and the addition of univalent ions (Ag⁺, Li⁺), on the other hand, raised the energy of the reaction. Contrary to these results, Schwab and Block (2) and Dry and Stone (5) demonstrated that lithium doped nickel oxide was more active than pure oxide and thereby lowered the activation energy and chromium doped oxide was, on the other hand, less active and hence raised the energy. Matsuura *et al.* (6) expressed the opinion that both dopents of tri- and univalent ions did not affect essentially the activation energy and that the slight difference of the energy caused by the dopents should be ascribed to the different degree of poisoning of the catalyst by carbon dioxide.

The activation energies obtained for single catalysts are shown in Fig. 5 with the trends of Schwab and Block (2) and Dry and Stone (5). Accordance among these three results are satisfactory, except present results for NiO-Li₂O (0.1%) and NiO-In₂O₃ (3%). Among common experimental conditions in these experiments, that is, the high firing temperature of catalysts and the static condition for measuring the rate, of special importance may probably be the high firing temperature of catalysts which is necessary for the homogeneous incorporation of foreign ions in the oxide.

A few results have been reported on the effect of dopents on the activity of zinc oxide. Schwab and Block (2) demonstrated that the doping of gallium resulted in an increase of the activity of zinc oxide and thereby decreased the apparent activation energy and that the incorporation of lithium, on the other hand, lowered the activity and raised the activation energy. Keier and Chizhikova (8) and Chizhikova (10) showed that the addition of both

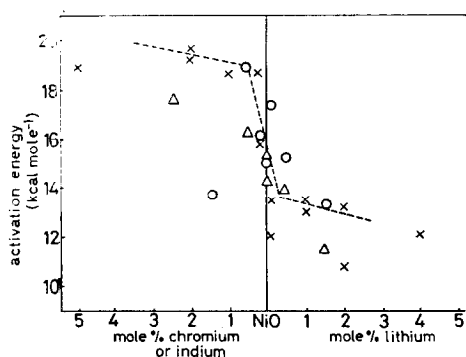


Fig. 5. Apparent activation energies for oxidation of carbon monoxide on doped nickel oxide. X Schwab and Block, Δ Dry and Stone, O Present work.

trivalent ions (Ga^{3+} , In^{3+}) and univalent ions (Li^+) suppressed the activity of oxide. Matsuura *et al.* (9) pointed out that the dopents of tri- and univalent ions had no effect on the activation energy.

The results in Fig. 2, in accordance with the trend of Schwab and Block, demonstrated that the incorporation of indium ions enhanced the activity of catalyst and that of lithium ions suppressed the activity. The absolute values of activation energies obtained, however, are lower than that of Schwab and are nearly equal to the results of Chizhikova and Matsuura as shown in Table 2.

TABLE 2
ACTIVATION ENERGY FOR ZINC OXIDE CATALYST

Catalyst	Activation Energy (kcal/mole)
ZnO-Li ₂ O (0.05 at%)	18.9
(0.1 at%)	15.2
(1.0 at%)	23.4
ZnO	16.8
ZnO-In ₂ O ₃ (0.1 at%)	16.5
(1.0 at%)	15.5
ZnO-Li ₂ O(1%):ZnO-In ₂ O ₃ (1%)	
2:1	13.4
1:1	12.4
1:2	10.7

As for mixed catalysts of doped nickel oxide, Arrhenius plots of observed rate constants k_{obs} (solid lines) are given in Fig. 4, where k_{calc} (dashed lines) are cal-

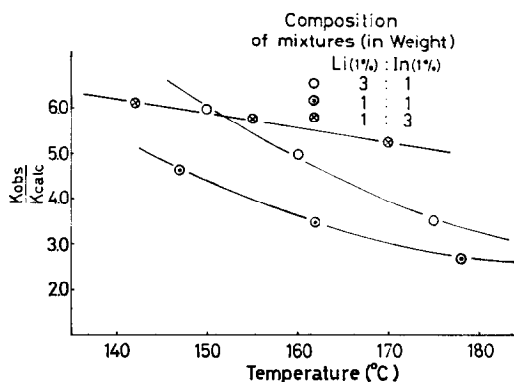


Fig. 6. Values of $k_{\text{obs}}/k_{\text{calc}}$ for mixed catalyst of doped nickel oxide (without the trap).

culated from the results in Fig. 1 by assuming the additivity of single catalyst activity. The values of k_{obs} are obviously greater than that of k_{calc} and the former values are found to be 3-6 times as great as the latter (Fig. 6). The activation energies are calculated to be 9.2, 9.2, and 16.0 kcal/mole for mixed catalysts having mixed ratios, NiO-Li₂O/NiO-In₂O₃, of 3/1, 1/1, and 1/3, respectively. The activation energies for mixed catalysts are less than that for single catalysts, except 16 kcal/mole for a mixed catalyst of mixed ratio 1/3.

When the reaction was carried out with liquid nitrogen trap, the ratios of $k_{\text{obs}}/k_{\text{calc}}$ were 1-2 as shown in Fig. 7.

Comparing the values of k in Fig. 1 with those in Fig. 3, which have been re-

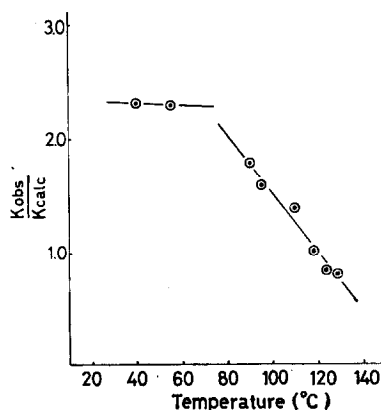


Fig. 7. Values of $k_{\text{obs}}/k_{\text{calc}}$ for mixed catalyst of doped nickel oxide (with the trap).

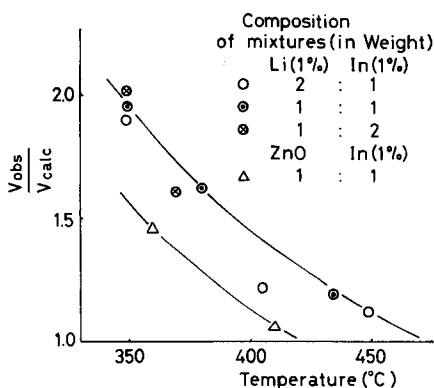


FIG. 8. Values of V_{obs}/V_{calc} for mixed catalyst of doped zinc oxide (without the trap).

duced to the values at the same temperature ($>120^{\circ}\text{C}$) and the same amount of catalyst, the values of k (with the trap) are about ten times as great as that of k (without the trap). This result shows that carbon dioxide formed adsorbs strongly on the catalyst and markedly retard the reaction. The poisoning of carbon dioxide seems to be responsible for the difference of mixing effect described above.

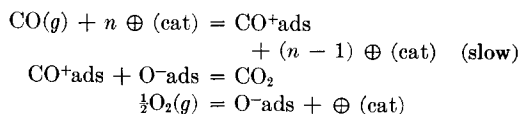
For mixed catalysts of zinc oxide, the values of V_{obs}/V_{calc} obtained from Fig. 2 are plotted vs. temperature in Fig. 8. Here, the values of 1-2 seem to be independent to the mixed ratio and the activation energies obtained are less than that for single catalysts as recorded in Table 2. Attention shall be given to the fact that the values of V_{obs}/V_{calc} for mixed catalysts consisting of ZnO and ZnO-In₂O₃ are evidently smaller than the values for mixed catalysts of ZnO-Li₂O and ZnO-In₂O₃.

Correspond to the observed lower activation energies for mixed catalysts, the mixing effect, k_{obs}/k_{calc} and V_{obs}/V_{calc} , increases obviously at low temperature as shown in Figs. 6, 7, and 8. This fact may show that the reaction over the mixed catalysts proceeds by two mechanisms, that is, the one proposed for single catalysts (2) and the other for the mixed catalysts which will be discussed later.

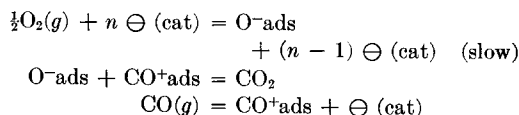
From the results obtained for the effect of doping on the catalytic activity of nickel oxide and zinc oxide, the mechanism proposed

by Schwab and Block (2) may be correct and is expressed as follows:

For nickel oxide catalysts,



and for zinc oxide,



where \oplus and \ominus represent electron hole and electron in the catalyst, respectively.

Before discussing on the mixing effect, the authors assume that the catalysts used can always be represented by the simple band structure of the host oxides, neglecting surface phases, precipitated species, and grain boundaries. Since phase diagrams of host oxides and lithium or indium systems are not still clear (17) and the solubility of indium in zinc oxide has been estimated by Thomas to be only about 10^{-18} atom/cm³ at 950°C (18). With such assumption in mind, we propose the following mechanism for the mixing effect from the results discussed above and the mechanism cited.

From the theory of semiconductor and the discussions on the mixing effect for sintering, the Fermi level of NiO-Li₂O or ZnO-Li₂O is expected to be lower than the level of NiO-In₂O₃ or ZnO-In₂O₃. When the two oxides are brought into contact in the reactor, an electron rearrangement will occur in such a way as to equalize Fermi levels at the interface, exhibiting a positive and a negative space charge in the indium doped and in the lithium doped oxide, respectively. In the discussion above, direct or indirect contact between two oxides is tacitly assumed. The assumption may be plausible in the powder mixture. Since, in addition to the observed mixing effect on sintering, the catalytic activity of the nickel oxide is found to be markedly changed when Pt-wire which itself has no observable cata-

lytic activity in our experimental conditions is added to the nickel oxide in the reactor. This fact seems to have close reference to the result obtained by Schwab (19) and may be explained by assuming electrical contact between Pt-wire and nickel oxide even when metal and the oxide are not pressed together and an electron rearrangement between Pt-wire and the oxide.

The positive charge on the indium doped oxide favors the chemisorption of carbon monoxide as CO⁺ads and the amount of CO⁺ads on the indium doped may be greater than on the single catalyst which has no positive charge and is neutral. And the negative charge on the lithium doped oxide favors the chemisorption of oxygen as O⁻ads and the amount of O⁻ads on the lithium doped is also greater than on the single catalyst. These adsorbed CO⁺ads and O⁻ads may diffuse through the contact zone from one component of the catalyst to the other and react to form CO₂, neutralizing the space charge. When the neutralization of space charge takes place, the positive and negative charge are again regenerated on the two oxides. Thus, the reaction may continue as described above. The similar mechanism was recently proposed by Schwab for the combined action of silver and zinc oxide catalyst in compact form on the oxidation of methanol (19).

The fact that the mixing effect for mixed catalyst consisting of ZnO and ZnO-In₂O₃ is less than for the catalyst of ZnO-Li₂O and ZnO-In₂O₃ may be due to the difference of ΔE_F of these two catalyst pairs. Here, ΔE_F is the difference between the higher and the lower Fermi level for each pair and determines the quantity of the space charge. Since, ΔE_F for the catalyst of ZnO and ZnO-In₂O₃ is smaller than ΔE_F for the catalyst of ZnO-Li₂O and ZnO-In₂O₃, both positive and negative charge on the former mixed catalyst is smaller than on the latter. The resulting difference in amount of adsorbed reactants

between two catalyst pairs is responsible for the difference of the mixing effect.

Further studies on the mixing effect and the application of the effect to the other reactions are now in progress.

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