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Studies of Electron Spin Resonance Spectra and Activity of Supported Zinc Oxide Catalysts for Hydrogenation of Ethylene

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The activities and ESR spectra of zinc oxide catalysts for hydrogenation of ethylene at 150°C have been studied. No catalytic activity was observed for silica- or alumina-supported ZnO at surface coverages below 2–3 nominal monolayers. The ESR signal at $g = 1.958$ from the zinc oxide was assigned to conduction electrons, and no correlation was found between this signal and the catalytic activity.

The nature of the catalytically active sites is discussed in the light of these observations, and it is concluded that the former are likely to be regions of strained dehydration rather than interstitial zinc ions.

A further ESR signal at $g = 2.000$ is also discussed. This appears in supported catalysts and shows some correlation with activity.

INTRODUCTION

In recent years the view that the catalytic activity of oxides is correlated with their bulk properties such as semiconductivity has been modified. It is now accepted that the properties of the individual components of oxides, such as the number of unpaired *d*-electrons of their cations, may be related to catalytic activity. Experimental evidence supporting this includes the characteristic twin peak activity pattern which appears for a number of reactions when the activity of the first series transition metal oxides is plotted as a function of their cation position in the transition metal group (*1–3*). This pattern bears no relation to their semiconducting properties, but can easily be explained by consideration of their electronic configuration. In other cases, dilution of the active oxide by solution in inert oxides increases the activity per ion, even at dilutions where semiconductivity is much reduced (*4*, *5*). Zinc oxide and alumina, however, are catalysts to which these considerations do not apply. ZnO in particular is active in hydrogenation yet the Zn^{2+} ion has no empty *d*-orbitals.

As a model catalytic system, hydrogenation of ethylene over zinc oxide has been investigated by various groups of workers. Much of this work has recently been reviewed by Kokes and Dent (*6*), who have contributed considerably to this field of research, concentrating particularly on the behavior of ZnO at relatively low temperatures (i.e., up to 100°C) (*7*). There have also been other studies (*8–10*) at low temperatures, while Teichner and co-workers (*11–14*) have studied the system in a higher temperature range, up to ca. 400°C, where the behavior is more complex.

Zinc oxide has to be treated before activity appears and, while various treatments are successful, they all involve the development of nonstoichiometry by re-

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moval of oxygen from the lattice. These treatments include outgassing at ⩾250°C (*3, 8, 9, 11, 14*), treatment with dry hydrogen (*15*), doping with 1,1-diphenyl-2-picryl hydrazyl (*16*) and uv or visible irradiation (*17, 18*). Most of these treatments cause ESR signals to develop. Ueda (*19*) has reviewed this latter field up to 1968, and various other ESR studies have been reported since then (*20–28*). It is generally assumed that interstitial zinc ions and oxygen lattice vacancies are formed.

The present work investigates the possibility of a link between the catalytic activity of ZnO for ethylene hydrogenation at 150°C and its ESR signals.

EXPERIMENTAL

Materials

Ethylene. High purity ethylene (99.9%) supplied by Phillips Petroleum Co. was used. The only impurity detected by mass spectrometry was ethane. Before admission to the vacuum system the ethylene was liquefied and distilled, the first and last fractions being discarded. The liquefaction was repeated from time to time to remove any possible traces of permanent gases.

Hydrogen. British Oxygen Co. cylinder hydrogen was freed from traces of oxygen by passing it over a Deoxo catalyst followed by molecular sieve type 4A to remove the water thus formed. Mass spectrographic analysis showed the impurities to be in the ppm range.

Catalysts. "Zincoid" (gift from Amalgamated Oxides Ltd.) zinc oxide was used without further purification for supported catalysts. Analysis (*29*) showed that the only significant impurity was cadmium at 100 ppm (w/w).

Catalyst supports. The silica used was Degussa "Aerosil." The partially hydrated solid was treated in boiling water for 2 hr and then dried at 120°C to produce a well-defined state of surface hydroxylation. α-Alumina was prepared by calcination of the γ-hydroxide at 980°C after the latter had been formed by hydrolysis of distilled aluminum isopropoxide.

Preparation of Supported Catalysts

These were made from aqueous solutions of Analar grade zinc acetate. The quantity of solution was adjusted such that the solid support was just wetted and the resulting mix was calcined in a stream of oxygen at 500°C. Before impregnation, the silica was hydroxylated as already described. Failure to do this resulted in the production of catalysts of considerably lower activity. This effect was not noted in the case of α-alumina-supported catalysts.

In some cases, when catalysts of high ZnO content were prepared, the impregnation treatment had to be carried out twice because of the limitation imposed by the solubility of zinc acetate in water.

Catalyst Characterization

The zinc content was determined by complexometric titration. The surface area was measured using the BET method. Catalysts were also examined by electron microscopy and electron diffraction. Finally the ESR spectra were studied.

Activation of Catalysts

In the present work the catalysts were outgassed overnight at ca 300°C. This temperature was chosen as a result of experiments discussed below (see Fig. 1).

Activity Measurements

The activity of the catalyst was measured by following the rate of hydrogenation of ethylene. In general the following conditions were adopted as standard; 50 Torr H_2, premixed with 30 Torr C_2H_4, reacting over the catalyst at a temperature of 150°C. The reaction rate was followed by pressure measurement, using a mercury manometer which was read to 0.02 mm by means of a cathetometer. A magnetically operated glass-constructed pump circulated the gases over the catalyst.

Conventional vacuum apparatus was used which could be evacuated to 10^{-6} Torr. Several silica sample tubes for ESR measurements were attached to the Pyrex reactor by means of 5 mm Pyrex to silica graded seals. The reactor assembly could

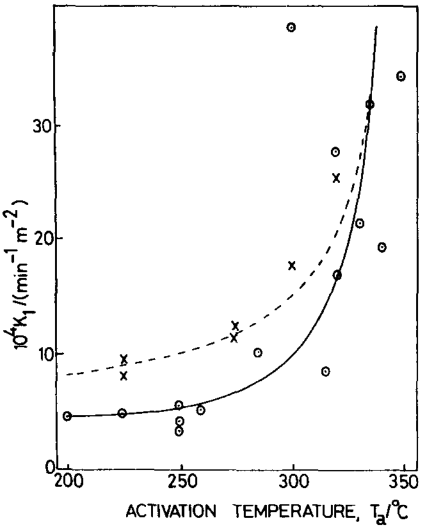

FIG. 1. Variation of the activity of zinc oxide catalysts with activation temperature, T_a. (×) Experiments in which the catalysts were treated with hydrogen before use (see text).

be detached from the apparatus under vacuum and a sample of catalyst transferred to an ESR tube. After reattachment to the apparatus, the ESR tube was sealed while pumping. The ESR tubes were calibrated for weight of ZnO so that the amount of ZnO remaining and participating in the reaction was known.

ESR Measurements

The ESR spectra were obtained on a Decca Type X 1 spectrometer with 100 kHz field modulation. Spin concentrations were calculated from the first derivative spectra by means of first moment calculations using a computer program. To allow for variations in sensitivity, a ruby crystal was fixed to the cavity wall close to the sample, and the height of one of its signals was taken as a standard for correction. Finely ground $CuSO_4 \cdot 5H_2O$ was used as an intensity standard, and the spin concentrations thus obtained were estimated to be accurate to 15–20%. Although the intensity calibration points thus obtained are much higher than those reported here for ZnO samples, a calibrated gain control on the spectrometer enabled the range to be extended sufficiently for this work. Polycrystalline 1,1-diphenyl-2-picryl hydrazyl (DPPH) was used as a standard for *g*-value measurements.

RESULTS

Under the standard conditions used (150°C, 50 Torr H_2, 30 Torr C_2H_4) the ethylene hydrogenation over ZnO was found to be first order in H_2 and zero order in C_2H_4, at least for 30–50% of the total reaction. A first order rate constant (min^{-1} m^{-2}) was therefore taken as a measure of the activity. Occasional mass-spectrometric analyses of the reacting mixture confirmed that ethane was the only product.

The choice of a suitable activation temperature for ZnO catalysts needs careful consideration. Conductivity measurements (*31*) have shown that too high a temperature leads to irreversible metallic behavior, whereas the activity of the catalyst is low without activation. In order to arrive at a satisfactory compromise, the activity of unsupported ZnO was studied as a function of activation temperature, T_a. The results are summarized in Fig. 1, which also shows the effect of adsorption of hydrogen (50 Torr at 150–170°C) for 30 min prior to hydrogenation. In the case of silica-supported catalysts, however, hydrogen adsorption prior to hydrogenation had no effect. In view of these considerations, an activation temperature of ca. 300°C was chosen for the rest of the work.

The characteristics of the various catalysts and supports are summarized in Table 1. The average diameter of individual particles was obtained from electron microscope pictures. Although there was a tendency to form clusters, the silica particles were approximately spherical. Although many were ellipsoidal, the shape (and size) of the alumina particles varied. The work described in this paper has therefore concentrated on silica-supported ZnO, though a few results for alumina-supported ZnO are quoted for comparison.

Table 1 shows that the surface area determined from electron micrographs of the alumina support material alone agrees well with that determined by the BET method.

TABLE 1
CATALYST CHARACTERISTICS

	Catalyst composition		Surface area ($m^2\ g^{-1}$)		
Ref.[a]	ZnO (monolayers)	ZnO (mole%)	BET	Electron micrograph	$10^4\ k_1$ ($min^{-1}\ m^{-2}$)
Silica	0.00	0.00	165.0	110.6	<0.05
S-1	0.10	1.35			<0.05
S-2	1.10	13.0			<0.05
S-3	1.49	16.9	98.2		<0.05
S-10	2.71	27.0	84.5		<0.05
S-7	3.28	31.0			<0.05
S-20	3.60	32.9	85.2		0.31
S-9	3.85	33.4	79.5		0.37
S-17	4.35	37.2	78.5		2.17
S-21	4.54	38.2	87.6		1.01
S-11	5.21	41.5	71.3		0.21
S-5	6.51	47.0	62.9		3.00
S-8	6.76	48.0	63.5		0.66
S-22	7.12	48.9	62.1		1.06
S-18	8.46	53.5	50.0		3.47
S-23	10.07	57.9	54.8		3.80
S-19	10.78	59.5	53.6	108.2	4.01
S-24	41.20	85.0	44.7		4.17
Alumina	0.00	0.00	4.9	4.9	<0.05
A-2	2.31	1.65			<0.05
A-3	5.15	3.66			<0.05
A-5	6.86	4.81			<0.05
A-4	8.39	5.82			6.2
A-6	11.50	7.81			2.0
A-7	17.87	11.62			6.6
A-8	50.72	27.20			9.7
A-1	94.60	41.31	4.8		11.2
ZnO	—	100	9.5	9.8	10–15

[a] S- and A-series catalysts are silica- and alumina-supported, respectively.

In the case of silica alone, the BET value is some 50% larger, indicating some microporosity. However, the BET surface areas for the ZnO–SiO_2 catalysts were only about half those obtained from the electron micrographs. This point is discussed below. The electron micrographs of ZnO–Al_2O_3 did not permit such a comparison to be made.

The ZnO–SiO_2 catalysts clearly showed electron diffraction patterns due to the crystalline ZnO on the amorphous SiO_2. These diffraction patterns disappeared completely when the catalysts were treated with concentrated HCl for determination of the ZnO content. In the case of ZnO–α-Al_2O_3, both materials being crystalline, it was not possible to distinguish between the diffraction pattern of the alumina and that of the ZnO. To exclude the possibility that ZnO reacted with SiO_2 to give a zinc silicate, which would not be soluble in concd. HCl and thus escape detection, SiO_2, after removing the ZnO with HCl, was treated in a platinum crucible with molten NaOH. On analysis of the water-soluble melt no signs of Zn^{2+} ion were detected.

Figures 2 and 3 show the activity of the catalyst as a function of molar composition, and as a function of the "nominal coverage" of the support by ZnO layers. The nominal coverage was calculated from the BET area of the support taking 1.96 Å for the Zn–O distance (*32*). In view of the microporosity, it is recognized that the

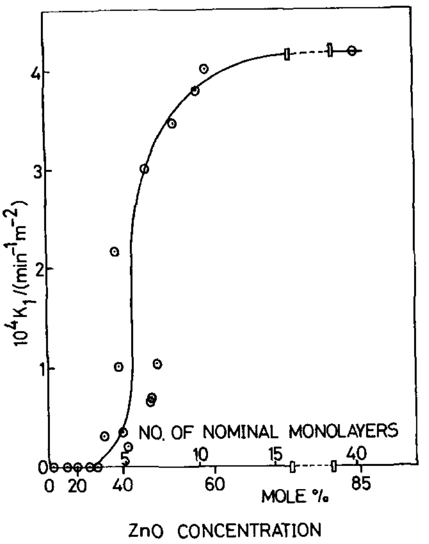

FIG. 2. Variation of the activity of ZnO-SiO_2 catalysts with ZnO concentration. The SiO_2 support material was hydrated.

nominal coverage as calculated here may deviate somewhat from the actual surface coverage, but it was found convenient to express the catalyst composition in this way. It can be seen from Figs. 2 and 3 that the catalysts are completely inactive until about 3 nominal layers of ZnO have been deposited in the case of a silica support, and 5–7 layers in the case of an alumina support. The activity then rises very rapidly until it appears to reach a limiting value. In Table 2 this limiting value is compared with the activity of unsupported ZnO which was also studied. The limiting value obtained on the alumina support agrees well with that of unsupported ZnO, but on silica the final activity was about 2–3 times smaller. This may be due to the fact that the silica had a greater tendency to agglomerate than the alumina. Therefore as the ZnO loading increased some ZnO-coated silica spheres would become completely cut off or at least only accessible by a slow diffusion process. This point is discussed below.

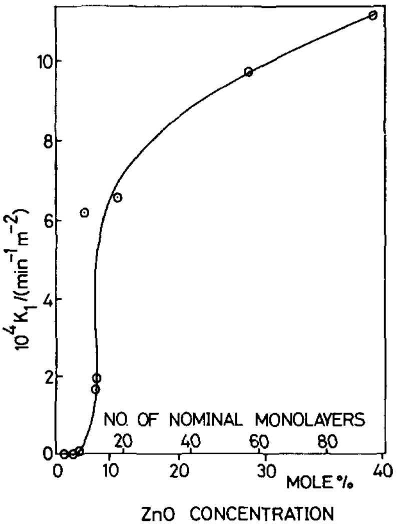

FIG. 3. Variation of the activity of ZnO-Al_2O_3 catalysts with ZnO concentration.

ESR studies revealed two signals. The first of these, at $g = 1.958 \pm 0.001$, has often been observed before (*19–26*), and was present in all our activated samples. It was nearly symmetrical with a derivative peak–peak width of 9.6 ± 0.8 G at room temperature. Exposure to a hydrogen atmosphere or uv light after activation increases the signal strength by a factor of 2–3 in the case of unsupported catalysts, but appears to cause no permanent change in this signal when the ZnO is supported on silica (*30*). The higher the activation temperature, the stronger is the signal with an upper limit of about 5×10^{15} spins/g at 350°C. A sample containing 79% of ^{67}Zn ($I = 5/2$) was examined in an attempt to find some hyperfine structure or line broadening in the $g = 1.958$ signal, but none was detected at temperatures down to 77°K. On cooling the catalyst to 77°K,

TABLE 2
RELATIVE ACTIVITIES OF ZINC OXIDE CATALYSTS AFTER ACTIVATION AT 300°C

Catalyst	Coverage (monolayers)	ZnO (mole%)	$10^4 k_1$ (min^{-1} m^{-2})
ZnO	—	100	10–15
min ZnO/SiO_2	3.0	29.0	<0.05
max ZnO/SiO_2	41.2	85.0	4.2
min ZnO/Al_2O_3	7.0	5.0	<0.05
max ZnO/Al_2O_3	94.6	41.3	11.2

a net decrease was observed in the number of centers contributing to the signal at $g = 1.958$. In view of these observations, this signal may be assigned to electrons in the conduction band in agreement with other workers (*21, 22, 24, 27*). Several attempts were made to correlate the catalytic activity of activated samples with the strength of their $g = 1.958$ signals, but a negative result was obtained with both supported and unsupported catalysts.

A second ESR signal ($g = 2.000 \pm 0.001$, width ca. 10 G) appeared in the supported ZnO samples, and in uv-irradiated pure ZnO. The signal was also of moderate intensity (10^{14}–10^{15} spins/g) but in contrast to the $g = 1.958$ signal it showed some correlation with the activity of the supported catalysts (Fig. 4) and in particular it did not appear until 2–3 nominal layers of ZnO had been deposited on silica. Unfortunately it has not been possible to examine this signal in isotopically enriched samples, but intensity considerations tend to rule out interstitial zinc ions as the source of the signal since the concentration of excess zinc in the lattice measured by different methods varies from 10^{17} to 10^{18} spins/g (*33–36*). Similar signals have been observed in ZnO samples which have been subjected to various other treatments (*23, 25, 27, 28*). It should be noted that a signal at $g = 2.00$ may be produced in ZnO exposed to ca. 10^{-1} Torr O_2. This signal usually shows some structure and has been assigned to a surface O_2^- species formed by electron transfer from the solid (*37, 38*), although more recent work tends to indicate a higher g-value for O_2^- (*39*). In the present work, however, considerable care was taken to exclude oxygen from the catalytic system, and it is considered unlikely that the signal under discussion here arises from a surface oxygen species.

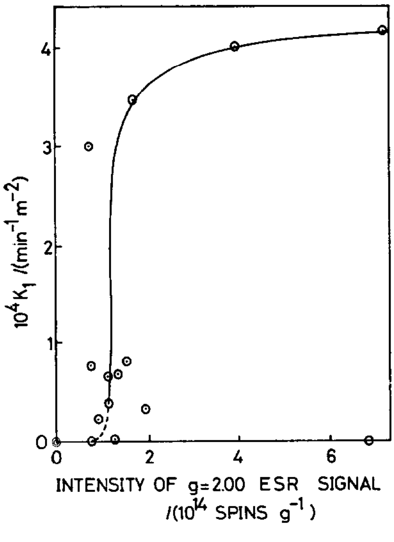

FIG. 4. Variation of the activity of ZnO–SiO_2 catalysts with the intensity of the $g = 2.000$ ESR signals after activation.

DISCUSSION

It is difficult to compare our results with those of many other workers because of differences in experimental conditions. The work most suitable for comparison with our own is that of Aigueperse and Teichner (*11*) who also worked at 150°C after vacuum activation at 250°C. They found the reaction to be approximately first order in hydrogen and zero order in ethylene for at least the early stages of the reaction. Our results confirm this.

One important aspect of the present results is that catalytic activity is only observed when the ZnO coverage is higher than 2–3 nominal monolayers in the case of a silica-supported catalyst. The values in Table 1 show that there is a large reduction of surface area on impregnating the SiO_2 support with ZnO. It is possible that clusters of SiO_2 spheres, visible on the electron micrographs, are cemented together by ZnO, and the inner part of such a cluster would then no longer be accessible to the reacting gases (H_2 and C_2H_4). Model calculations, assuming a cluster of four touching SiO_2 spheres arranged in a tetrahedron predict the observed reduction in surface area. Such a model enables one to calculate that about 0.5 of a nominal monolayer of ZnO can be contained in the volume between the four spheres. To this must be added the amount of ZnO which can be accommodated in the micropores of the silica, which is unlikely to be more than 1 nominal monolayer, leading to the result that 1.5–2 nominal monolayers of ZnO may become inaccessible to the reacting gases and therefore be ineffective catalytically. The quantity of ZnO deposited on SiO_2 at the point where it first becomes catalytically active is about 3 monolayers, which is still somewhat greater than that predicted by the above model. There is, however, an important objection to this explanation of the lack of activity in the first part of the curve. The sensitivity of the pressure method of following the reaction is high. A rate 200 times smaller than that half-way up the activity curve (Fig. 2) would have been detected. This means that, for this explanation to be valid, in this part of the curve ZnO must go quantitatively into the interstices and micropores, and practically no ZnO at all can be deposited on the outer surface of the silica particles. This condition appears highly unlikely.

Thus, although this observation gives no information about the nature of the active sites, it appears that these sites are not formed at surface coverages below 2–3 nominal monolayers. This finding is consistent with the models of active sites proposed by other authors. Kokes *et al.* (*7*) have postulated that the active sites are Zn–O pairs with the zinc ion embedded in a close-packed surface oxide layer arising from surface dehydration and consequent strain. Narayana, Lal and Kesavulu (*10*), on the other hand, propose a model consisting of isolated surface zinc atoms produced by oxygen removal. Although both these sets of authors did not work under the same conditions as the present work, their arguments may have a bearing on this work in view of the fact that the active sites postulated by both groups would not be formed until a few monolayers of ZnO have been deposited. Furthermore, either dehydrated or strained sites could be consistent with the observation that the activity increases with activation temperature up to ca. 350°C.

The uncertain geometry of the catalysts supported on alumina makes it very difficult to calculate the amount of zinc oxide which may be inffective in these catalysts. Comparison of Figs. 2 and 3 indicates a higher threshold value of ca. 7 nominal monolayers, compared to 2–3 nominal monolayers on silica. However, since the ellipsoidal particles of alumina were large, having dimensions up to 3500 Å, a considerable amount of ZnO (10–15 nominal monolayers) (*30*) could be accommodated in cementing two alumina particles together. In addition, it is possible that the impregnation technique may not have been entirely successful in creating a uniform ZnO surface. There is some evidence from the electron micrographs for the existence of particles of pure ZnO in the alumina-supported catalysts. Both of these effects would cause inaccuracies in calculating the number of monolayers of ZnO deposited, though Fig. 3 should still be qualitatively correct.

The lack of activity of supported ZnO catalysts below a coverage of at least 2–3 nominal monolayers might lead to the speculation that the catalytically active sites could be associated with nonstoichiometry such as interstitial zinc ions. However, the ESR signal at $g = 1.958$, which does not correlate with the activity, has been assigned to conduction electrons. It has been shown by the doping experiments of Aigueperse and Teichner (*11*) that conduction electrons are not directly involved in ethylene hydrogenation. The observed lack of correlation of the $g = 1.958$ signal with the catalytic activity is therefore to be expected. This lack of correlation also tends to rule out interstitial zinc as the catalytically active species, since it is likely that interstitial zinc would act as a donor for conduction electrons.

The effect of treatment with hydrogen after outgassing is worthy of note. Treatment with hydrogen at 150°C enhanced the activity of unsupported ZnO (for activation temperatures up to 325°C, Fig. 1) but had no effect on the activity of supported ZnO. A similar increase was observed in the $g = 1.958$ ESR signal ascribed to conduction electrons in the case of unsupported zinc oxide only. It is difficult to explain these observations if the role of hydrogen is merely that of a reducing agent at the catalyst surface. It seems possible that, in the case of unsupported ZnO, hydrogen is diffusing into the bulk with the liberation of conduction electrons according to the mechanism of Thomas and Lander (*40*) and helping to produce an active structure at the surface similar to that which is already present in the supported catalysts.

From the present work it therefore seems that the active sites for hydrogenation reactions on ZnO are not interstitial zinc ions, but are more probably regions of dehydration. These could correspond to either those of Dent and Kokes, or Kesavulu *et al.*, but if nonstoichiometry is involved at all it does not appear to be associated with donation of electrons to the conduction band.

The correlation of the $g = 2.000$ ESR signal with the activity of silica-supported catalysts leads to speculation as to whether this signal may arise from a species whose formation is related to that of the active zinc ions, or even from the active ions themselves. However, the failure to observe this signal in active, unirradiated, unsupported ZnO tends to preclude such a simple explanation. Further investigation of this signal is therefore planned.

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