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Adsorption and Hydrogenation of Ethylene on Pure and Doped Zinc Oxide: Studies by Proton Magnetic Resonance

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Adsorption and hydrogenation of ethylene were studied on pure ZnO and on ZnO doped with Li^+ or Ga^{3+} ions. It was found by NMR measurements that Li^+ weakens and Ga^{3+} strengthens the chemisorption of ethylene. The hydrogenation reaction is first order in adsorbed ethylene in the presence of excess hydrogen. Since the isotherms are concave downward, this implies an order of less than 1 with respect to gaseous ethylene. Li^+ doping decreases the rate, while small amounts of Ga^{3+} increase it. Larger amounts of Ga^{3+}, however, cause a decrease in rate.

INTRODUCTION

Woodman and Taylor (*1*) discovered that zinc oxide is an effective catalyst for olefin hydrogenation. Since that time, many studies have been made of olefin hydrogenation on this catalyst (*1–11*). Attempts have been made (*6–10*) to correlate catalytic activity with the electronic structure of the oxide. The latter can be controlled in a systematic manner by doping with altervalent ions (*12, 13*). To date, a satisfactory correlation has not been established, due in part, at least, to conflicting experimental results.

In recent years, the studies of Kokes and his colleagues (*4–6, 14–16*) have led to a great increase in our understanding of olefin adsorption on ZnO. These infrared studies were directed mainly at understanding the nature of the interaction of the olefin with the surface. Kokes and co-worker have shown that there are two typical modes of adsorption, an associative mode leading to a surface π-complex, and a dissociative mode leading to a π-allyl surface species. In the case of ethylene, only the former type of adsorption can occur. This has been verified by proton NMR spectroscopy (*17, 18*).

In addition to permitting a study of the state of adsorbed species, NMR spectroscopy is useful for studying the kinetics of catalytic reactions. In favorable cases, it enables the reaction to be followed in the adsorbed phase (*19, 20*), without complications of transport to and from the gas phase.

The studies of Kokes and Dent and our previous NMR studies were all carried out using Kadox-25 ZnO from New Jersey Zinc Company. This oxide is prepared by high-temperature oxidation of zinc vapor. Since we wished to extend our studies to doped ZnO, a wet preparation of the oxide is implied. It is, of course, not self-evident that wet-prepared ZnO will have similar adsorption properties to the Kadox oxide. The first part of this study, therefore, comprises an investigation of methods of preparation of ZnO. We have studied various preparations by adsorption and NMR methods to find a wet preparation giving adsorption properties for ethylene similar to those found for Kadox ZnO. We have then carried out a study of the proton chemical shift of ethylene adsorbed on pure ZnO and on oxide doped with Li^+ or Ga^{3+} ions. We have also studied by NMR the kinetics of hydrogenation of ethylene on these catalysts.

EXPERIMENTAL

All NMR spectra were measured on a Varian XL-100 spectrometer, incorporating

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a TTI Fourier transform modification. Normally each spectrum resulted from the accumulation of 300 scans, using approximately 60° pulses at a repetition interval of 0.5 sec. Proton spin–lattice relaxation times were typically 0.1 sec or less. Chemical shifts were measured relative to a sample of tetramethylsilane (TMS) physically adsorbed on ZnO from the same preparation. This measurement was carried out by substitution using the external fluorine lock. A bulk-susceptibility-corrected value of the shift relative to gaseous ethylene was then obtained as follows: (a) the results of Whitney (*18*) show that after susceptibility correction, physically adsorbed TMS at high coverage has no chemical shift relative to the liquid. (b) We measure the gas-phase shift between ethylene and TMS in a mixed sample, which requires no susceptibility correction. (c) We use the literature value (*21*) for the gas–liquid shift of TMS. The obvious combination of these values yields the corrected shift for adsorbed ethylene relative to the gas. Our ZnO samples have such a low specific area that there is no significant change in overall sample susceptibility between the adsorbed TMS and adsorbed ethylene samples. We believe that the corrected shifts reported herein are accurate to ±0.1 ppm.

The hydrogenation experiments were performed *in situ* in the NMR probe at a temperature of 28°C. In each experiment, a fresh sample of 0.7 g was used. This was first exposed to ethylene at a pressure of 40 Torr. The sample with adsorbed ethylene was then placed in the spectrometer, an initial spectrum recorded, and 400 Torr of hydrogen added. The amount of adsorbed ethylene and the volume of the NMR tube were such that this constituted a large excess of hydrogen in all cases. The reaction was then followed by recording spectra at suitable intervals. Typically 1 to 2 days elapsed between the adsorption of ethylene and the subsequent admission of hydrogen.

The specific surface area of each preparation was obtained by the BET method, using nitrogen at relative pressures of 0.05 to 0.35. Ethylene adsorption isotherms were obtained by standard gas-volumetric methods.

Materials

Zinc oxide was prepared by the pyrolysis of zinc oxalate dihydrate. The oxalate was prepared by mixing equal volumes of 0.5 *M* zinc nitrate and sodium oxalate solutions. The precipitate was filtered, washed several times with distilled water, and air-dried for 5–6 hr at 60°C. The oxalate was then processed in various ways. Letters in parentheses in the following description identify preparations for future reference.

The first set of Zno samples was prepared by pyrolysis of the oxalate at 350°C either *in vacuo* (A) or in air (B) for 3 hr. This time is sufficient for complete decomposition of the oxalate (*22*). Another sample (C) was prepared by pyrolysis *in vacuo* at 400°C, heating in O_2 at 150 Torr and 400°C for 1 hr, degassing 1 hr at the same temperature, cooling to room temperature in 150 Torr O_2, and pumping for 6 hr.

A second series of samples was prepared by pyrolysis of the oxalate at 400°C under the vacuum of a water aspirator. Doped samples were prepared by impregnating this oxide with a measured amount of a solution of lithium or gallium nitrate. The impregnated samples were dried overnight in air at 100°C and then heated *in vacuo* at 400°C for 4 hr. These samples are identified subsequently by the mole percentage of dopant metal with respect to zinc. Pure ZnO samples (D) in this series were treated in the same way, using distilled water in place of the metal nitrate solution. Analysis by atomic absorption showed a residual sodium impurity of 3.5 ppm in the finished catalysts. In addition to the above samples, a sample (K) of Kadox 25 from the New Jersey Zinc Company was used for comparison.

A question to be considered is whether uniform doping can be achieved at the temperatures used here. There is evidence in the literature (*13*, *24*) to indicate that Li diffusion is sufficiently rapid to achieve equilibrium under our conditions. The situation is less clear for Ga, and our samples may well contain excess nonequilibrium amounts of Ga in the surface region. While a higher annealing temperature would be desirable in this case, such temperatures lead to a loss of area which makes the NMR experiments impossible, and we are therefore forced to compromise on this point.

RESULTS AND DISCUSSION

1. Adsorption Measurements

Nitrogen adsorption isotherms were measured at 77°K on all samples. the resulting surface areas are given in Table 1.

Ethylene adsorption isotherms measured at 20°C are presented in Figs. 1–3. It can be seen that increased activation temperature of the oxide leads to a marked increase in ethylene adsorption. A small amount of Ga^{3+} doping increases the ethylene adsorption, while heavier doping causes a subsequent decrease. Li^+ doping seems, however, to decrease the ethylene adsorption in a monotonic manner. A similar trend of coverage with doping has been observed (*23*) for butenes on ZnO. In this case, Ga^{3+} enhances both the strong and weak modes of adsorption, while Li^+ causes corresponding decreases. Our isotherms appear to be only partially reversible at room tem-

TABLE 1

Sample	Pressure (Torr)	Coverage (cm^3/m^2)	Area (m^2/g)	Shift[a]	Width (Hz)
A	65	0.002	130	0.0	16
B	160	0.006	34	0.0	14
C	30	0.010	53	0.5	76
D	10	0.016	34	1.0	100
K	13	0.051	10	0.9	90
1% Li	15	0.016	32	0.3	40
2% Li	16	0.017	30	−0.1	30
3% Li	70	0.011	11	−0.2	24
0.5% Ga	10	0.017	32	0.9	95
1% Ga	10	0.015	38	1.1	110
2% Ga	11	0.017	30	1.2	208
3% Ga	15	0.016	38	1.3	300

[a] Shifts are in ppm with respect to gaseous ethylene, corrected as described in the text. Positive shifts are to low field.

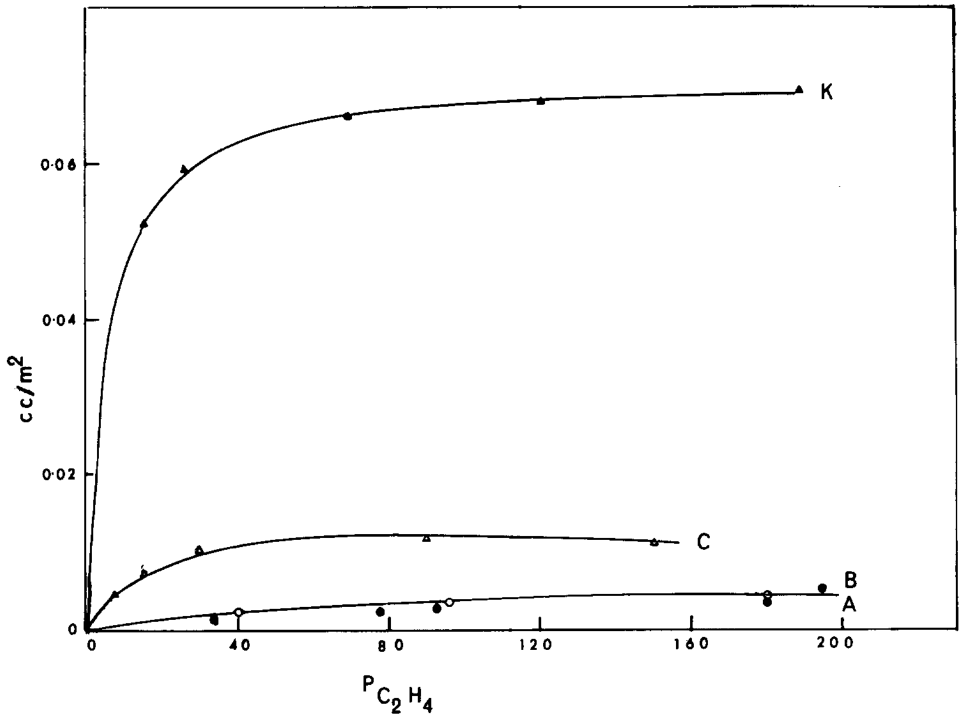

FIG. 1. Isotherms for ethylene adsorption on pure ZnO. ●, Sample A; ○, sample B; △, sample C; ▲, sample K.

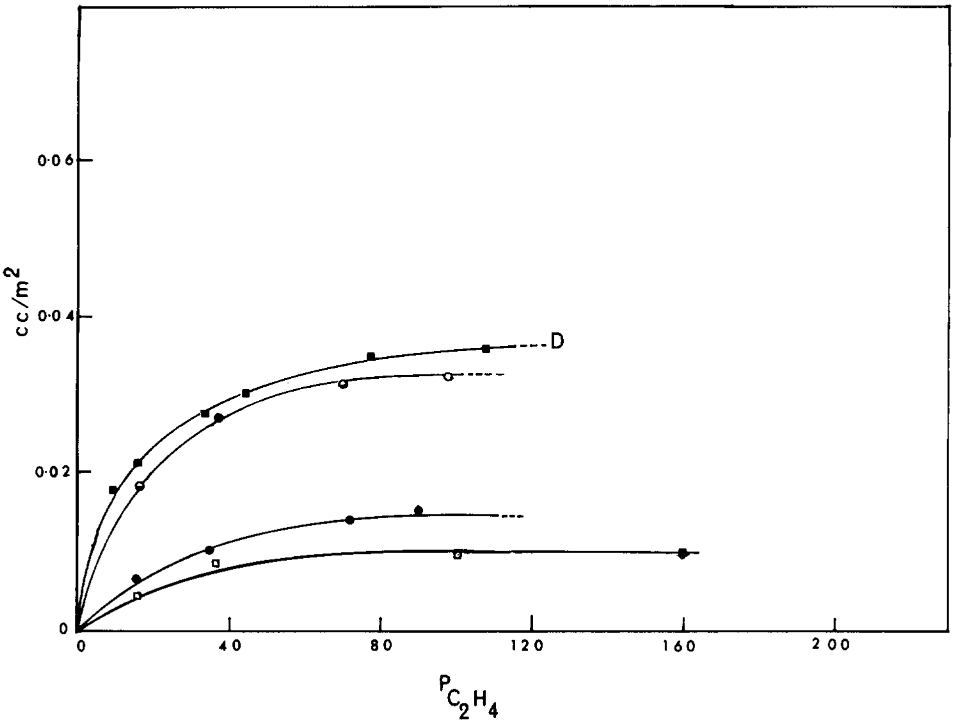

FIG. 2. Isotherms for ethylene adsorption on pure (D) and Li-doped ZnO. ○, 1% Li; ●, 2% Li; □, 3% Li.

perature. This is probably for kinetic reasons, since, in the case of Kadox oxide which we have studied more fully, complete reversibility is found at temperatures of 100–150°C.

It is difficult to make a meaningful direct comparison with adsorption on the Kadox oxide. It appears that this latter oxide varies somewhat from one lot to another. Thus the present isotherm on Kadox oxide lies slightly below that measured by Whitney (*18*) and appreciably above that of Dent and Kokes (*4*). These differences are probably due to variations in the coverage dependence of the heat of adsorption between various lots. Dent and Kokes (*6*) found an initial isosteric heat of about 14 kcal/mole, falling off rapidly at coverages above 0.02 cm^3/m^2. On Whitney's samples, this falloff did not occur until coverages of about 0.07 cm^3/m^2, and on the present lot, it occurs at about 0.05 cm^3/m^2. For all of these measurements, the same standard oxygen/vacuum pretreatment (*6*) was used. Clearly this variation can lead to substantial variations in the adsorption isotherm. In spite of this, it appears clear that none of our wet-prepared oxides have an adsorption capacity for ethylene as large as that of Kadox oxide. Our best sample (D) has about 53% as great capacity.

2. *NMR Measurements*

Table 1 also contains the proton chemical shifts and linewidths for adsorbed ethylene, measured at 28°C. The chemical shifts are with respect to gaseous ethylene, corrected as noted above. The widths reported are full widths at half-maximum height.

It can immediately be seen that those samples of ZnO which are poor adsorbers of ethylene (A, B) have a negligible chemical shift relative to the gas phase. It is probable that on these samples ethylene is only physically adsorbed. As the samples become more active in adsorption (C, D),

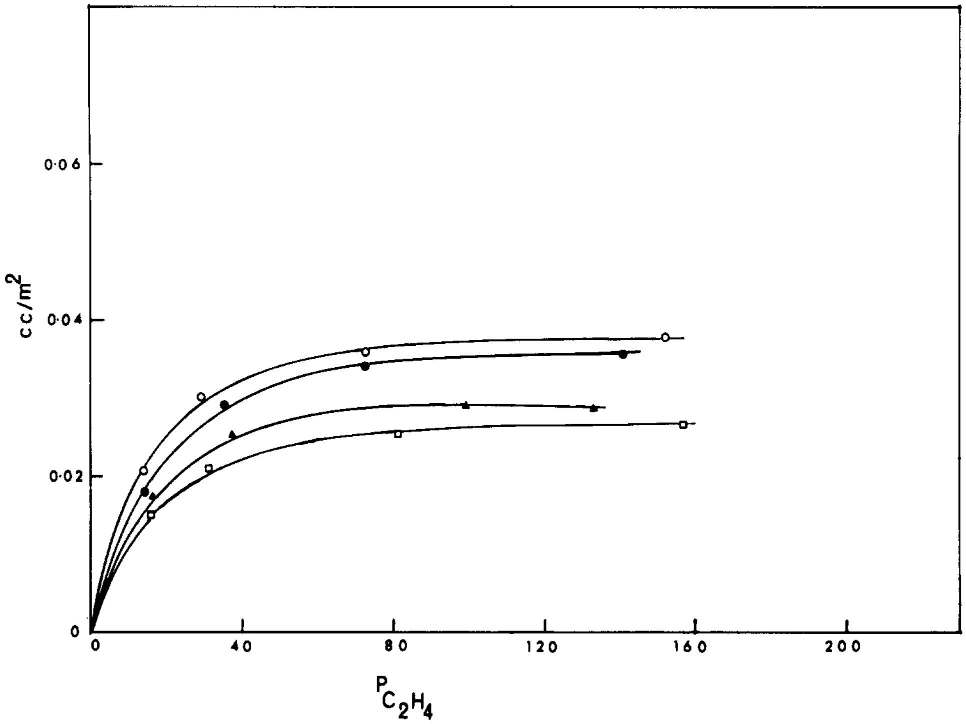

FIG. 3. Isotherms for ethylene adsorption on Ga-doped ZnO. ▲, 0.5% Ga; ○, 1% Ga; ●, 2% Ga; □, 3% Ga.

an increasing downfield shift appears, which for sample D is as large as for the Kadox oxide. This shift is characteristic (*17, 18*) of weakly chemisorbed ethylene in the "π-complex" form of Kokes and Dent. It appears that our preparation D produces chemisorption sites for ethylene which are similar to those found on Kadox ZnO, but in smaller numbers. The shifts observed on samples D and K are in good agreement with the results obtained by Whitney (*18*) at low coverage.

Doping with Li^+ has a drastic effect on the chemical shift. In all cases it is reduced to a value near the gas-phase value, and it seems that chemisorption sites have been effectively eliminated. If one accepts the simple view (*12*) that the effect of Li^+ is to lower the free-electron concentration in ZnO, it would appear that these electrons are necessary to the weak chemisorption of ethylene. This weakens the interpretation of the adsorption as π-complex formation, since if such a complex is formed by donation of electrons into the conduction band of ZnO, a decrease in free-electron concentration should enhance the adsorption. Nevertheless, the downfield shift on adsorption would seem to imply that electrons are leaving the ethylene molecule. Doping with Ga^{3+} has the opposite effect and leads to small increases in the chemical shift of adsorbed ethylene. This is what one would expect if electronic structure of the adsorbent is important to the chemisorption, and lends support to this view.

The question of electron transfer on olefin adsorption is scarcely clarified by the existing conductivity data. Bozon-Verduraz *et al.* (*9*) found that ethylene adsorption causes a small decrease of conductivity in ZnO containing excess Zn. An increase in conductivity was found on a stoichiometric oxide. However, these workers could find no infrared bands for ethylene on the stoichiometric oxide, in marked contrast to the results of Dent and Kokes (*6*), which suggests a fundamental difference in the nature of their oxide. Uematsu *et al.* (*23*) report a conductivity increase for adsorption of butenes on ZnO. Thus the balance of evidence does suggest a donation of electrons from olefins into the conduction band, at least for pure ZnO.

It will be noted in Table 1 that the width of the proton resonance line varies in a parallel manner to the chemical shift. The width of the line reflects mainly the rotational correlation times of the adsorbed molecule. Whitney showed (*18*) that the motion of adsorbed ethylene on ZnO is complex and requires at least two correlation times for its description. Thus the present linewidths are not susceptible to a quantitative explanation. However, it is qualitatively correct to say that the narrowest lines are those arising from molecules with the fastest motions. These are exactly those whose chemical shifts are smallest, supporting the view that they are only physically adsorbed. The widest lines are found for the Ga-doped samples, where the chemical shift is also the largest, and the chemisorption presumably the strongest.

3. *Hydrogenation of Ethylene*

The results of a typical kinetic run are shown in Fig. 4. As can be seen, the peak due to adsorbed ethylene falls in time, while that of ethane rises. Although hydrogen certainly adsorbs on zinc oxide (*4*), no resonance is observable on a high-resolution spectrometer (*18*). This is presumably because the hydrogen is so tightly bound that the NMR line is unobservably broad.

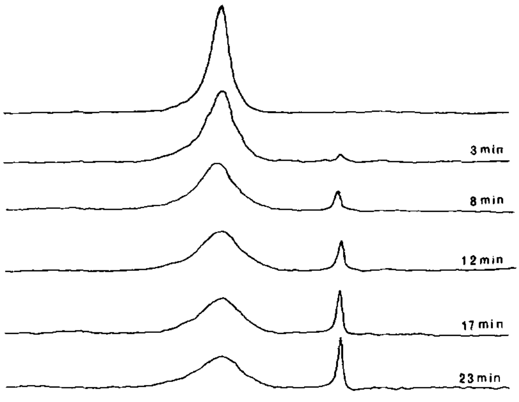

FIG. 4. NMR spectra during hydrogenation of ethylene on 1% Ga-doped ZnO. Top spectrum before admission of hydrogen, remainder after reaction for the indicated time.

The data were analyzed by reading the peak height and width at half-height for each spectrum. The product of these quantities produces a number proportional to the peak area. This was then taken to be proportional to the total number of protons giving rise to the peak in question.

It was found that on all catalysts the reaction was first order with respect to concentration of adsorbed ethylene. This is verified by the linearity of plots of $\ln(A(t)/A(0))$ vs time, where $A(0)$ and $A(t)$ are the peak areas at times 0 and t, respectively. These plots are shown in Fig. 5, and the derived first-order rate constants are reported in Table 2.

Two additional observations were made in the course of kinetic runs on the doped oxides. Firstly, on the Li-doped samples, the ethane peak was small, and for the more heavily doped samples, not observable. Analysis of the gas phase after completion of the reaction nevertheless showed the presence of ethane and the absence of any other reaction products. It thus appears that Li doping weakens the physical adsorption of ethane, as well as the chemisorption of ethylene. On the Ga-doped samples, it was found that the linewidth of ethylene increased during the course of the reaction. This probably indicates that the surface is heterogeneous, with some tendency for the more loosely bound ethylene to react first, notwithstanding the overall first-order kinetics. There is some evidence (*13*) that Ga, in contrast to Li, may not be uniformly distributed throughout the catalysts at the preparation temperatures used here. This could well be a source of heterogeneity.

Dent and Kokes (*5*) observed the reaction kinetics to have a complex dependence

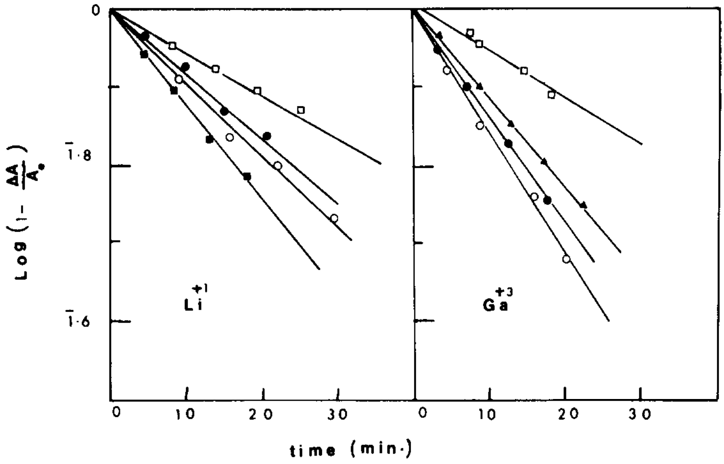

FIG. 5. Kinetic plots for the hydrogenation of ethylene. Left: ■, sample D; ○, 1% Li; ●, 2% Li; □, 3% Li. Right: ▲, 0.5% Ga; ○, 1% Ga; ●, 2% Ga; □, 3% Ga.

on ethylene pressure. By making the assumption that the ethylene isotherm in the presence of hydrogen was the same as that measured with pure ethylene, they were able to show that the reaction was first order in adsorbed ethylene concentration. The present results, in which the adsorbed phase is observed directly, may be interpreted as evidence in support of this assumption, for the case of pure ZnO. It thus appears that ethylene and hydrogen adsorption must be independent (not competing) steps in the overall reaction mechanism.

Our kinetic results (Table 2) show a uniform decrease in the rate constant for Li^+ doping. Small amounts of Ga^{3+} cause an increase, whereas larger amounts lead to a decrease. It should be noted that the trends in activity with doping are parallel to those in ethylene adsorption capacity (Figs. 2 and 3). Thus if kinetics had been followed by gas-phase measurements, the variation of rate would have appeared larger, due to the variation of ethylene adsorption coefficients.

TABLE 2

Rate constants for hydrogenation

Sample	K (min^{-1} × 100)
D	1.20
0.5% Ga	1.30
1% Ga	1.53
2% Ga	1.32
3% Ga	0.55
1% Li	1.10
2% Li	0.85
3% Li	0.56

The variation in surface rate constants observed here could be due either to variation in surface hydrogen concentration or to changes in the intrinsic reaction rate. Clearly more work is required to give a complete account of the reaction rate. The decrease in rate at high Ga^{3+} levels could be due to poisoning by strongly bound ethylene, as revealed by the NMR measurements.

Hydrogenation of ethylene on doped ZnO has been studied by Teichner and his co-workers (*7*, *8*, *10*, *11*). It was first reported (*7*, *8*) that Li^+ or Ga^{3+} doping had no effect on either the rate or the activation energy. Later (*11*) an acceleration by Ga^{3+} and a decrease in rate by Li^+ were found in the temperature range 80–125°C. An acceleration by both types of ions was found for $T > 150°C$. Our results appear to be in qualitative agreement with the later low-temperature results, although the significance of this is not clear, since Teichner and his co-workers find, on pure ZnO, major differences in kinetics and in the effect of O_2 treatment from those reported by Dent and Kokes (*4*, *5*).

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