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Dissociation of Nitrous Oxide over Zinc Oxide Samples with Different Excess Zinc Contents

The present Note reports an attempt to study the influence of zinc oxide defect structure on the decomposition of nitrous oxide, using well-defined samples of zinc oxide as catalyst. Nonstoichiometric zinc oxide with excess zinc is an *n*-type semiconductor. In previous work (*1*) a reproducible method of preparing zinc oxide has been described. The excess zinc content, in the range 0–90 ppm by weight, has been determined both by chemical titration and by investigation of esr spectra. The difference between results obtained by these two methods is assigned to metallic zinc, which is detected only by chemical titration. Actual excess interstitial zinc dissociates, in our experimental conditions, according to the following reactions:

$$\mathrm{Zn}_i{}^0 \rightarrow \mathrm{Zn}_i{}^+ + e^-,$$

or

$$V_\mathrm{O}{}^0 \rightarrow V_\mathrm{O}{}^+ + e^-.$$

From the analysis of the temperature dependence of the paramagnetic susceptibility, it was concluded that χ is due to localized magnetic moments ($\mathrm{Zn}_i{}^+$ or $V_\mathrm{O}{}^+$) a part of them corresponding to defects involved in electronic exchanges with oxygen chemisorbed during the preparation of oxide (*2*).

Three samples of zinc oxide, corresponding to different excess zinc contents, have been used. Their characteristics, determined after outgassing during 16 hr at 300°C, are reported in Table 1. Surface areas were measured by krypton adsorption. Physical and chemical titrations are described elsewhere (*1*).

Before each experiment, N_2O was purified by condensing in liquid N_2 and pumping. Measurements were carried out in the temperature range 200–300°C in a static system, using a conventional volumetric apparatus, zinc oxide being protected from grease vapors by a trap cooled at −78°C. After outgassing, a pressure of 3 Torr N_2O was introduced in contact with ZnO, and we observed that the pressure remained constant during the whole experiment, for all the temperatures and all the samples investigated. The reaction was followed by measuring the pressure of noncondensable gas product with a McLeod gauge, after having condensed the unreacted N_2O at −195°C. Mass spectrometric analysis of the product gas showed, in accordance with previous work, that it was N_2 (*3, 4*). After each experiment, chemical titration and esr measurements at room temperature were carried out on samples having been in contact with N_2O.

Results showing the increase of the volume of N_2 formed per square meter of zinc oxide with time of contact of this oxide with N_2O are summarized in Fig. 1. For a given temperature, the rate and extent of the reaction do not depend on the zinc excess content of the oxide, except for sample 3, which is the least stoichiometric: in this case the amount of N_2 formed is lower than that for samples 1 and 2, especially at 300°C. But for a given sample, the time course of nitrogen evolution varies markedly with temperature. This dependence is shown in Figs. 2, 3, 4 where $\log_{10} dV/dt$ is plotted as a function of the volume V of N_2 formed. At 200°C, for all the samples investigated, the plot is linear: the

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TABLE 1

Experimental Results[a]

Sample No.	Surface area (m^2 g^{-1})	Treatment	Excess zinc content (ppm)		θ_1	θ_2	θ_3
			Chemical titration	Physical titration by esr			
1	29.5	Before N_2O contact	14	7			
		N_2O decomposed at					
		200°C	12	3	0.16		0.3
		250°C	10	3	0.16	0.12	1.02
		275°C	10	4	0.12	0.3	5.23
		300°C	9	4	0.12		5.23
2	16	Before N_2O contact	36	25			
		N_2O decomposed at					
		200°C	34	22.5	0.10		0.4
		250°C	33.5	22	0.12	0.4	1.4
		280°C	28	21	0.16	0.75	5.23
		300°C	23	17	0.32		5.23
3	10	Before N_2O contact	60	40			
		N_2O decomposed at					
		200°C	40	35	0.20		0.2
		250°C	40	38	0.08	0.26	0.8
		300°C	40	34	0.24	1.2	2

[a] θ_1, percentage coverage of the surface from physical titration results after N_2O contact; θ_2, percentage coverage of the surface corresponding to the Elovich plot discontinuity; θ_3, percentage coverage of the surface corresponding to the end of decomposition.

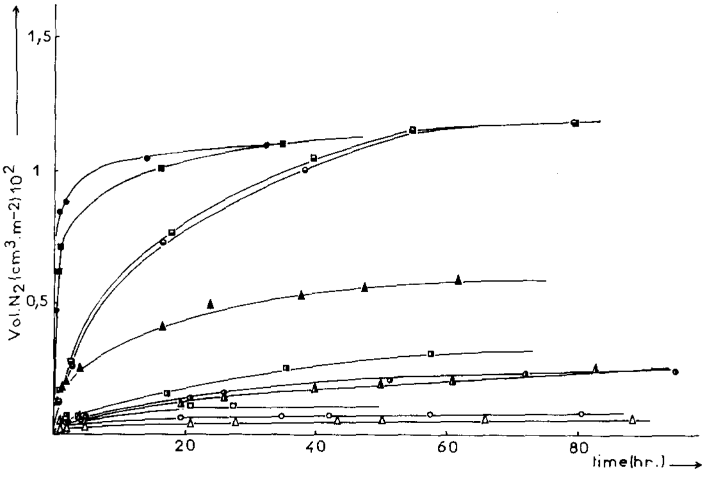

FIG. 1. Volume of N_2 produced as a function of contact time between N_2O and oxide surfaces. Sample 1: (○) 200°C, (◑) 250°C. (◒) 275°C, (●) 300°C; sample 2: (□) 200°C, (◨) 250°C, (⬓) 280°C, (■) 300°C; sample 3: (△) 200°C, (▲) 250°C, (▲) 300°C.

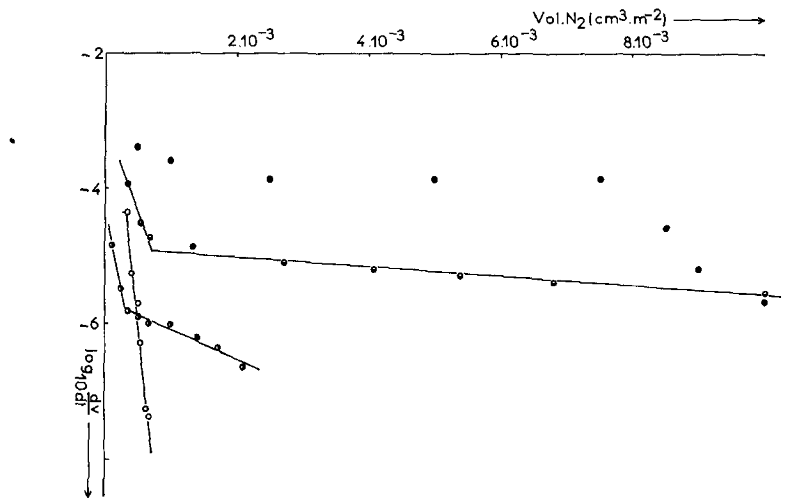

FIG. 2. Elovich plot of N_2O decomposition on sample 1. (○) 200°C, (◑) 250°C, (⊖) 275°C, (●) 300°C

process seems to satisfy the Elovich equation:

$$\frac{dV}{dt} = ae^{-bV}.$$

At 250 and 280°C, two linear segments can be observed. At 300°C, the kinetics of decomposition of N_2O on samples 1 and 2 no longer obey the Elovich equation. Assuming that each molecule of N_2 formed corresponds to one molecule of N_2O adsorbed and dissociated, the percentage coverage of the surface has been calculated for the discontinuity in the Elovich plot, and for the end of the reaction [a monolayer is supposed to contain 6×10^{18} molecules m^{-2} (*5*)]. Results are recorded in Table 1.

Values obtained from esr spectra show that N_2O decomposition leads to a slight decrease of excess zinc content (Table 1). The difference between the results of the chemical and the physical titration gives the metallic zinc content. For samples 1 and 2, containing lower concentrations of defects and metallic zinc, a decrease of

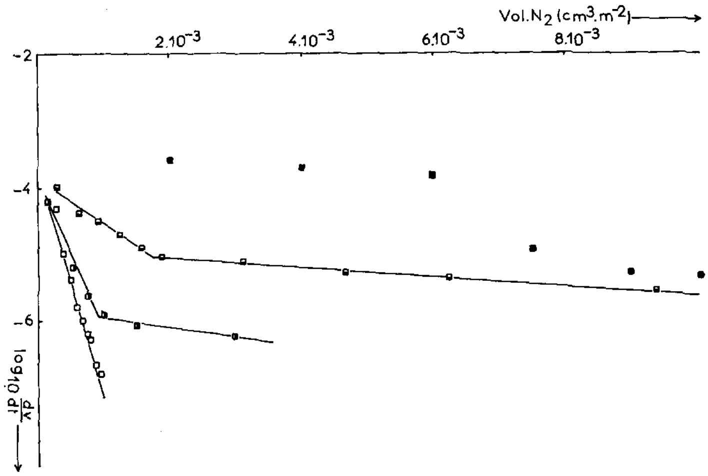

FIG. 3. Elovich plot of N_2O decomposition on sample 2. (□) 200°C, (◧) 250°C, (⬓) 280°C, (■) 300°C.

metallic zinc content is only observed for temperatures above 250°C, although for sample 3, containing more metallic zinc, this decrease already occurs at 200°C.

The results are in agreement with the assumption generally made for such experiments that the reaction proceeds through dissociative adsorption of N_2O, nitrogen being evolved and oxygen remaining in the solid phase for temperatures below 350°C. But two problems are still to be solved, namely, what is the role of the oxide defects in this decomposition and what is the form of produced oxygen remaining in the solid phase?

From the results reported in Table 1 (column 5) we can observe that the slight decrease of excess interstitial zinc content produced by N_2O decomposition is practically independent of the temperature of the experiment, as well as of the initial stoichiometry of the oxide. The same titrations were performed on samples 2 and 3 after a time of contact with N_2O of 30 min, that is to say a very short time compared with that which is necessary for the maximum extent of the decomposition (80 hr). The results are very similar to those obtained at the end of the reaction: the decrease of excess zinc content corresponds to an initial step of decomposition. Moreover, if each defect involved is assumed to be a site for the adsorption of one molecule of N_2O, the percentage coverage of the surface corresponding to this decrease of defect concentration can be calculated. The values are very small compared with those corresponding to the full extent of the reaction, or even to the discontinuity in the Elovich plot (Table 1): the initial step of decomposition cannot be observed on our kinetic plots. However, excess interstitial zinc concentrations disappearing during the decomposition are quite similar to the concentration of defects involved in electronic exchanges with oxygen chemisorbed during the preparation of zinc oxide (*2*).

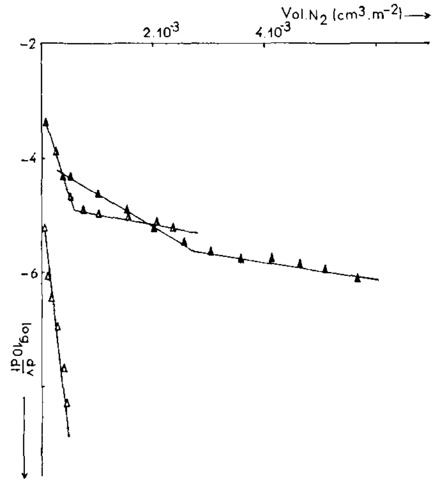

FIG. 4. Elovich plot of N_2O decomposition on sample 3. (△) 200°C, (▲) 250°C, (▲) 300°C.

Therefore, we propose that the same sites are available for chemisorption of O_2 during the preparation of the ZnO samples, and for N_2O dissociative adsorption. The initial step of the decomposition would then be the departure of chemisorbed oxygen toward other defects, which could lead to the oxidation of localized centers, following the scheme,

$$Zn_i^{+} + O^{-} \rightarrow Zn_i^{2+}O^{2-},$$

according to our observation of a slight decrease of paramagnetic susceptibility produced by the reaction. N_2O decomposition on these sites would then proceed without any electronic exchange, following the scheme already proposed by several authors (*4–6*),

$$N_2O + \text{site} \rightarrow N_2O_{\text{ads}} \rightarrow N_2 + O_{\text{ads}},$$

in accordance with the fact that, except for the slight decrease of excess zinc content at the beginning of reaction, no dependence on stoichiometry can be observed.

However, as the number of adsorption sites is very small compared with the total number of N_2O molecules dissociated, we have to assume that the rate determining step of the decomposition is the diffusion of oxygen in the solid phase. The Elovich plot suggests the possibility of two processes obeying different kinetics. One of them would already occur at 200°C. Between 250 and 280°C, as well as at 300°C for sample 3, as two linear segments are observed, we think that a second process appears after the first one. At 300°C, decomposition of N_2O on samples 1 and 2 no longer obeys Elovich kinetics, and one may expect that the two processes are occurring simultaneously.

The lower reactivity of sample 3 towards N_2O decomposition may result from enhanced difficulty for oxygen diffusion due to the higher excess zinc content of this sample. Although the ways of fixation and diffusion of oxygen produced are still difficult to elucidate, our results suggest that one of them most probably proceeds through metallic excess zinc oxidation.

Our general conclusion is that N_2O decomposition on ZnO is initiated by adsorption on a few active centers, oxygen produced diffusing in the solid phase, and that this reaction does not include an electron transfer process.

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