Catalytic Decomposition of Methanol on ZnO Single-Crystal Surfaces at Low and Near-Atmospheric Pressures

MICHAEL A. VEST, KAM C. LUI, AND HAROLD H. KUNG[1]

Ipatieff Laboratory and Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60208

The catalytic decomposition of methanol at 0 to 50 mPa and 1 to 13 kPa was studied on three ZnO single-crystal surfaces: a Zn-polar (0001), a stepped nonpolar (50$\bar{5}$1) and an O-polar (000$\bar{1}$) surface. The low-pressure study was conducted in an ultrahigh vacuum chamber in which methanol was directed onto the surfaces with a doser tube. Up to 425°C, the Zn-polar surface was at least five times more active than the other two surfaces, and the stepped nonpolar surface was marginally more active than the O-polar surface. The near-atomspheric pressure study was conducted in a microreactor at 250–300°C. No measurable activities were found on the O-polar (000$\bar{1}$) surface, whereas the activities of the Zn-polar (0001) and the stepped nonpolar (50$\bar{5}$1) surfaces were comparable. The reaction rate increased with increasing methanol pressure up to about 27 mPa beyond which the reaction became zeroth order in methanol. In the zeroth order region, the activation energy was 138–161 kJ/mole for the Zn-polar surface. These values and the turnover frequencies were comparable to values obtained on powder ZnO samples under near-atmospheric pressures. In the first-order region, the activation energy decreased as the temperature was increased. The major carbon-containing product observed was formaldehyde at low pressures and CO at near-atmospheric pressures. Differences between the results obtained at the two different pressures and the importance of surface defects generated by reduction of the surfaces were discussed. © 1989 Academic Press, Inc.

INTRODUCTION

The need to understand the relationship between the atomic structure and the catalytic properties of a surface has long been recognized. In 1925 Taylor, discussing this in terms of active centers, wrote that "there will be all cases between the extremes in which all the atoms in the surface are active and that in which relatively few are so active" (*1*). Unless all surface atoms are equally active, it is important to know the atomic structures of the active sites to fully understand catalytic reactions. Advances in the application of surface science techniques to catalytic studies have led to the use of well-defined single-crystal surfaces as catalysts. To date there are many examples of metallic catalysts for which surfaces of different crystallographic orien-

tations exhibit different catalytic activities (*2–4*).

On the other hand, very few catalytic studies have been performed on single-crystal oxide surfaces. Recently we studied the catalytic decomposition of 2-propanol on different single-crystal ZnO surfaces by directing onto them a molecular flux of 2-propanol (*5, 6*). Between 200 and 300°C and with a 2-propanol pressure less than 130 mPa, the reaction rate was found to be the highest on a Zn-polar (0001) surface, intermediate on a stepped nonpolar (50$\bar{5}$1) surface, and the lowest on an O-polar (000$\bar{1}$) surface. It was concluded that the decomposition of 2-propanol on ZnO was structure sensitive. However, when 2-propanol vapor was decomposed under 1 atm pressure on ZnO powder samples, the results led to the conclusion that the reaction was structure insensitive (*7*)—every surface-exposed Zn ion was equally active. The two

[1] To whom correspondence should be addressed.

231

different conclusions could be due to the different pressures used or to a physical difference between ZnO single crystals and powders. In order to resolve these discrepancies, the decomposition of methanol on the same ZnO single-crystal surfaces was investigated in two different ranges of pressure: less than 0.1 Pa and near-atmospheric pressure.

There are also reports in the literature on results of temperature-programmed decompositon (TPDe) studies of methanol on single-crystal surfaces of ZnO (8–13). The Zn-polar surface was found to be the most active for methanol decomposition, whereas the O-polar surface was much less active. There were indications, at least on the nonpolar surfaces, that the methanol decomposition activity depended on the density of surface defects. In addition, the product distributions were different: formaldehyde was observed on the Zn-polar surface but not on the other surfaces. The methanol decomposition reaction was also accompanied by a reduction of the surface which led to the evolution of metallic Zn at a much faster rate than could be due to sublimation at the same temperature. Since these TPDe studies were not carried out under catalytic conditions, it would be interesting to see if the conclusions regarding the reaction mechanisms and the structure sensitivity can be extended to studies under catalytic conditions.

EXPERIMENTAL

I. Apparatus

Low-pressure experiments. Experiments were carried out in the same stainless-steel ultrahigh vacuum chamber as that used previously (5, 6, 14, 15). The chamber was equipped with LEED and Auger spectroscopy (PHI single-pass cylindrical mirror analyzer) and was pumped by two 220 liter s^{-1} ion pumps and a Ti sublimation pump. Background pressures as low as 1.3×10^{-8} Pa were routinely achieved prior to conducting an experiment.

The sample holder consisted of two stainless-steel legs mounted on a small ceramic block (15). A tantalum foil and two tantalum wires were spot-welded onto the steel legs. The tantalum wires were used to wrap around the ZnO single crystal and press it to a gold foil that was placed between the tantalum foil and the ZnO. The Ta foil was heated resistively. The heat was conducted to the ZnO single-crystal through the gold foil, which provided good thermal contact between the ZnO sample and the tantalum foil heat source. The temperature at the surface of the ZnO sample was measured by a chromel–alumel thermocouple that was attached to the front surface of the ZnO by a small drop of liquid colloidal silver. The liquid colloidal silver had been determined to be inactive for the methanol decomposition reaction (15). A stainless-steel plate with a 0.5-cm-diameter hole was placed between the ionizer of the mass spectrometer and the ZnO sample to discriminate the direct flux of molecules from the surface from the background gas that entered the ionizer.

Chemicals. The same ZnO single crystals as those used in previous studies were used in these experiments (5, 6, 8–10). These surfaces were about 6 × 6 mm^2, and the crystals were about 1 mm thick. Except for the surface to be studied, the rest of the crystal was covered with gold. The samples were aligned by Laue X-ray diffraction, mechanically polished, and then cleaned and ordered by repeated cycles of argon ion sputtering (6 × 10^{-3} Pa, 45 min) and annealing at 375°C for 1 h in the UHV chamber.

Liquid methanol (99.9% purity) was purified by several freeze–thaw cycles. CO (99.99%), CO$_2$ (99.995%), and doubly distilled water were used to obtain the individual fragmentation patterns of these compounds in the mass spectrometer (MS) for low-pressure experiments. The fragmentation pattern of formaldehyde was obtained from formaldehyde vapor that was generated by heating solid paraformaldehyde (95%) to 100°C. These patterns were deter-

mined in each experiment by dosing small amounts of each compound into the chamber. That of methanol was obtained from the change in the MS signals when the steady flux of methanol was changed.

Procedure. The methanol vapor, collected over liquid methanol submerged in a saturated aqueous sodium chloride–ice slurry, was introduced into the vacuum chamber via a leak valve and a 1.6-mm-o.d. stainless-steel doser tube. The opening of the doser tube was about 2 mm from the ZnO surface and the angle between the line of sight of the doser and the surface normal was about 50°. For the stepped nonpolar (50$\overline{5}$1) surface, the methanol flux was in the up-the-step direction. The methanol flux was determined from the initial rate of methanol pressure drop in a calibrated volume (*15*). This rate of pressure drop was found to be linearly proportional to the measured direct flux of methanol into the mass spectrometer (Fig. 1). The liquid methanol was changed frequently to avoid accumulating less volatile impurities in it.

In an experiment, the mass spectrometer (MS) signal due to methanol flux onto a ZnO surface at room temperature and facing the mass spectrometer (referred to as direct flux) was first determined. The direct flux was found to reach a steady state in 2 to 6 h. Afterwards, the sample was turned away from the mass spectrometer and a new steady-state MS signal was recorded, which corresponded to the indirect flux resulting from the background gases. The difference between the direct and the indirect flux was taken as the signal due to the reactant feed. This procedure to obtain the direct flux and then the indirect flux was repeated at each sample temperature after the temperature was stabilized. The difference between these two fluxes after correcting for the same difference at room temperature was taken as the MS signal due to the reaction mixture desorbing directly from the surface. Sometimes the methanol flux onto the ZnO surface was changed instead of the temperature.

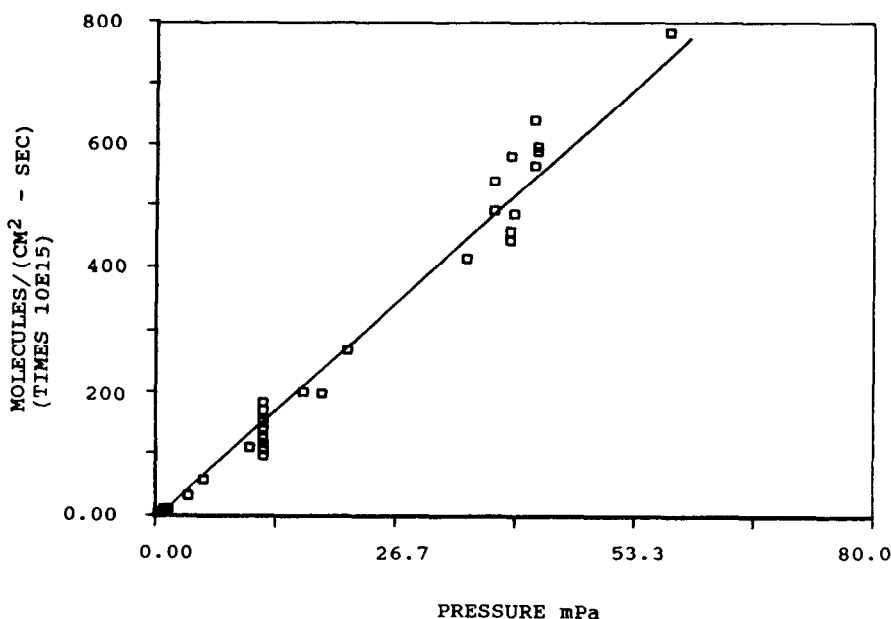The activity of the holder was deter-

FIG. 1. The intensity of mass spectrometer signal of methanol expressed as direct flux of methanol from the surface versus the average surface pressure calculated from the rate of pressure drop in the feed line.

mined in the control experiments where a gold-plated ZnO sample was used. No activity was observed when the holder temperature was raised to the highest value achieved in the experiments even though the surface temperature of the gold-plated sample was above the highest temperature of the ZnO surfaces studied (425°C).

The factor to convert the MS signal to the number density of molecules leaving the ZnO surface was determined by performing a temperature-programmed desorption of CO from a Ni(111) surface, where a saturation coverage of CO corresponds to 9.3×10^{14} molecules/cm^2 (17, 18). The relative MS sensitivities for different compounds were calculated using the formula provided by the mass spectrometer manual which took into account the fragmentation pattern, the transmission coefficient, and the spectrometer gain (15).

The effective methanol pressure at the ZnO surface was calculated from the geometry of the system and the measured methanol flux assuming that methanol effused from the open end of the doser tube (15).

Figure 2 shows the calculated pressure distribution for an average pressure of 0.93 mPa.

II. Near-Atmospheric Experiments

These experiments were conducted in a batch reactor (16) which was made from three stainless-steel flanges. The top flange contained a Pyrex window with a 2.5 cm diameter. The middle one was double-sided Vac-U-Flat flange, and the bottom one was a blank flange. The reactor was connected to the gas manifold via two valves. Its volume was 10.5 cm^3. The interior of the reactor was coated with evaporated gold to minimize its reactivity. Except for the window, the reactor was wrapped in heating tapes and heated to about 110°C during experiments to prevent condensation of the reaction mixture onto the reactor wall. The pressure of methanol in the reactor was measured by a pressure transducer.

The ZnO samples were held in place in the reactor by a piece of gold foil that was mounted on a gold-plated ceramic block 1.2 × 1.2 × 0.3 cm^3 in size (Fig. 3). The gold
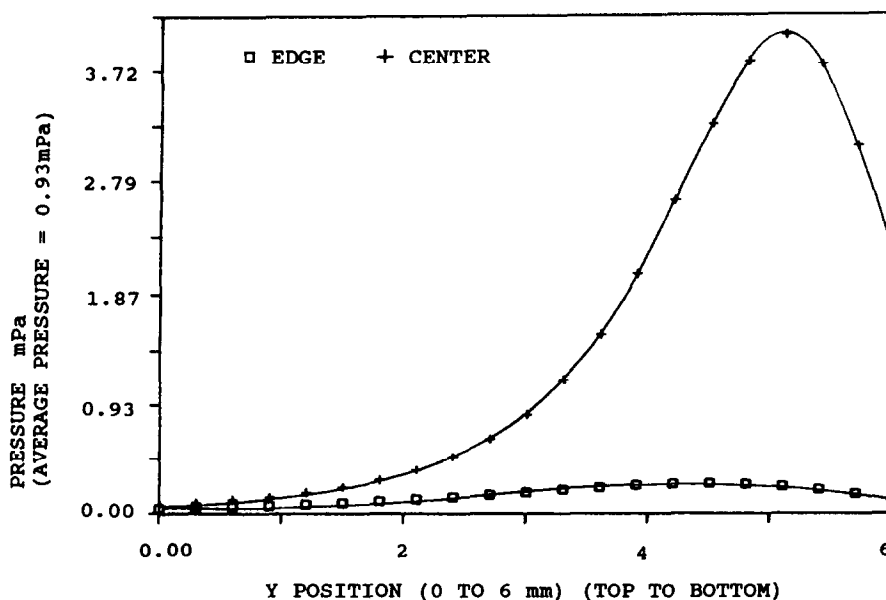

FIG. 2. The calculated distribution of methanol pressure across the surface for an average pressure of 0.93 mPa.
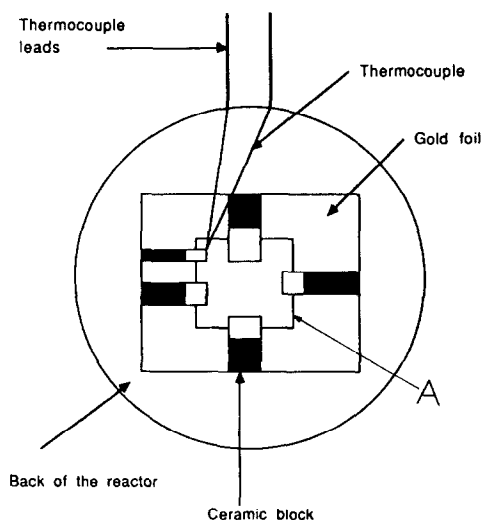
FIG. 3. Schematic drawing of the sample holder in the near-atmospheric pressure reactor. The ZnO sample (A) was held in place by four gold prongs of the gold foil that was mounted on a ceramic block.

foil also reduced the heating of the ceramic block by the incident light. The temperature of the ZnO sample was measured with a 0.037-cm-diameter chromel–alumel thermocouple, the head of which was flattened to maximize the contact area between the thermocouple and the surface. The thermocouple head was shielded from the incident light with a small piece of gold foil to prevent heating of the thermocouple by the light. The samples were heated by focusing light onto them that was emitted from a 1000-W quartz halogen lamp placed outside the reactor. A UV filter was placed in the light path to prevent light of energy higher than 3 eV from reaching the samples in order to avoid any photochemical reactions. This device could heat the sample to any of the desired temperatures within 2 min.

Procedure. After the surface to be studied was ordered and cleaned in the ultrahigh vacuum chamber, it was removed from the chamber and mounted into the batch reactor within 30 min. The surface was then cleaned by the following oxygen treatment. First the reactor was filled with 66 Pa O_2 and the ZnO sample was heated to

250°C for 2 min. Afterwards the reactor was evacuated, then refilled with O_2, and the sample temperature was raised to 270°C for 2 min. This cycle was repeated as the temperature was raised to 290°, 310°, 330°, and 350°C. Finally, after the reactor was evacuated, the temperature was raised to 400°C for 30 min before it was lowered to 250°C. A desired pressure of methanol vapor was then introduced into the reactor, and the surface was heated to the desired temperature to begin the experiments. Before each subsequent experiment, the sample was cleaned by this oxygen treatment. It was determined separately by repeating the procedure in the ultrahigh vacuum chamber that this oxygen treatment was sufficient to clean a carbon-contaminated surface that had been exposed to methanol or air.

At the end of the reaction, the reaction mixture was removed from the reactor and analyzed by gas chromatography. Two columns were used: a 5-m Porapak T column to separate CO, CO_2, HCHO, and CH_3OH, and a 1-m molecular sieve column to separate CO from air that might have leaked into the system.

In the gas chromatographic analyses, although the gas compositions could be obtained quite accurately, the absolute concentrations could be determined only to 2% accuracy because of the limited reproducibility in injecting the same volume of gas into the gas chromatograph. Thus the conversions were calculated from the compositions of the mixtures and not from the decreases in the concentrations of methanol. From control experiments in which mixtures of known compositions were introduced into the reactor, it was found that the detection limits were 0.2% for CO_2, 0.3% for HCHO, and 1.0% for H_2O. H_2 was not analyzed, but its presence could be detected in the gas chromatograms.

RESULTS

I. Low-Pressure Experiments

General observations. In all of the experiments, CH_2O, H_2O, CO_2, and Zn were the

only products whose signals were significantly above background. The background pressure of Zn was very low and its signal could be accurately measured. On the other hand, the uncertainties in the CO_2 and H_2O signals were high because of their high background pressures. The background pressure of CH_3OH was also quite high and increased at higher CH_3OH fluxes, and it affected the accuracies of the measurements of CO and HCHO. The problem was particularly severe for CO because CH_2O also cracked into mass 28. Thus the uncertainty of the data for CO was very high. Within these large uncertainties, no CO was detected (see Appendix I for further discussion).

It was found that the indirect flux of H_2 was 90% of the direct flux. This high background made it quite impossible to obtain accurate measurements of rates of formation of H_2.

The rates of product formation on the Zn-polar (0001) surface did not depend on the recent temperature history of the surface, but the rates on the O-polar (000$\bar{1}$) and the stepped nonpolar (50$\bar{5}$1) surfaces were often higher when the sample temperature was lowered from 375°C than when the temperature was raised to 325 or 350°C. The rates were higher when the sample was cooled to 325 or 350°C in 20 of the 22 measurements on the O-polar surface, and in 30 of the 40 measurements on the (50$\bar{5}$1) surface. It appeared that these surfaces became activated after reaching 375°C. In view of this, the data reported for these two surfaces were those obtained when the sample temperature was lowered from 375°C.

Pressure dependence of reaction rates. The dependence of the rates on pressure was found to be quite similar at 325, 350, and 375°C (*15*). Since more data were taken at 350°C than at the other temperatures, only the results at this temperature will be presented.

Figures 4a–4d show the data for CH_2O, Zn, H_2O, and CO_2. Below about 6 mPa of methanol, the rates increased rapidly with increasing pressure. The maximum rates were reached at about 27 mPa.

Among the three surfaces studied, the Zn-polar surface was found to be the most active for the formation of all products. The activities of the O-polar and the (50$\bar{5}$1) surfaces were at least five times lower than those of the Zn-polar surface, and the (50$\bar{5}$1) surface might be marginally more active than the O-polar surface.

Temperature dependence. The temperature dependence of the rates of production of the various products was investigated at three average surface pressures of methanol: 0.93, 11.7, and 42.6 mPa. The data for 0.93 and 11.7 mPa are shown in Figs. 5a–5d and 6a–6d, respectively. The data for 42.6 mPa were very similar to those for 11.7 mPa. Since the background was lower and the conversions were higher at 0.93 mPa, the experiments at the lowest pressures were studied more extensively, whereas for the two higher pressures, measurements were made at only four temperatures, 300, 325, 350, and 375°C. In addition, experiments at temperatures above 375°C were run only on the Zn-polar surface.

The uncertainties of the data in each of the experiments were not very large, but the reproducibility from one experiment to another was relatively poor (see discussions in Appendix II). Thus the relative rates at different temperatures were found to be substantially more reproducible than the absolute rates. The data shown in Figs. 5 and 6 were obtained in several different temperature variation experiments.

As shown in the figures, the activities of the Zn-polar surface were much higher than those of the O-polar and the (50$\bar{5}$1) surfaces. On the Zn-polar surface, the rates increased exponentially with increasing temperature up to about 375°C. Above 375°C, the rate increased more slowly. The Arrhenius plots for the Zn-polar surface at 0.93 mPa methanol are shown in Fig. 7 and the activation energies are reported in Table 1. Because of the low activities of the O-polar and the (50$\bar{5}$1) surfaces, no attempts

TABLE 1

Activation Energies for the Formation of Various Products on the Zn-Polar Surface of ZnO at Low Pressures

	Activation energy (kJ/mole)			
	0.93 mPa	375–425°C	11.7 mPa	42.6 mPa
Product	250–375°C	375–425°C	250–375°C	250–375°C
H_2O	95 ± 19	53 ± 11	171 ± 59	306 ± 73
CH_2O	91 ± 10	19 ± 2	112 ± 64	161 ± 16
CO_2	154 ± 34	43 ± 9	207 ± 46	331 ± 65
Zn	97 ± 17	58 ± 10	175 ± 60	216 ± 18

were made to calculate activation energies from those data.

Surface conditions after reactions. Graphitic carbon was found by AES to have deposited on all three ZnO surfaces during an experiment. Although the amount was smaller than that found after a reaction study, carbon deposit was also detected after a ZnO surface was exposed to the methanol flux at room temperature for 2 h. Estimating from the AES peak intensities, the surface could have been completely covered by carbon at the time the experiment was finished. Since the data for the Zn-polar surface were reproducible at the beginning and at the end of an experiment, the accumulation of carbon must have reached a steady state when the data were obtained. The situations for the O-polar and the (50$\overline{5}$1) surface were less clear since their rates depended on whether the sample was heated or cooled to a certain temperature. Nonetheless the rates reported here were steady-state rates.

Once an equivalent of one monolayer of carbon was deposited on the surface, AES did not detect any additional build up of carbon. Heating of the sample to 400°C for several hours did not remove the carbon.

When the sample was removed from the vacuum chamber, a dark surface layer was visually observed on all three surfaces studied. The dark surface layer could be a combination of carbon deposits as well as metallic Zn. Interestingly, Auger analyses of the sample immediately before removal from the chamber showed Zn, O, and C.

II. Near-Atmospheric Pressure Experiments

Activities of the reactor and the O-polar surface. The activity of the reactor was studied at 270°C at three pressures—2.7, 5.3, and 13.3 kPa—and at 2.7 kPa at three temperatures—260, 270, and 300°C. In these experiments, the ZnO sample was replaced either by a gold-plated ceramic piece or by a gold-plated Zn-polar surface. The reactor was found to possess some activities for methanol decomposition. CO was found to be the major carbon product. Small amounts of CO_2 (less than 5% of CO) were also detected. However, no formaldehyde was detected. The amount of CO formed as a function of time is shown in Fig. 8 for 5.3 kPa and 270°C. Curves for the other conditions were similar (*16*).

When the experiments were conducted using the O-polar surface instead of the gold-plated samples, the rate of formation of CO was found to be essentially the same under all of the conditions studied. Some sample data are shown in Fig. 8, curve a. Estimating from the uncertainties of these data, it was concluded that the rate of formation of CO on the O-polar surface at 270°C and 5.3 kPa was less than 1.7 × 10^{12} molecules/cm^2 s. From similar data obtained under other conditions, the maximum activities of this surface could be estimated. These values are shown in Table 2.

TABLE 2

The Estimated Maximum Activity for CO Formation on the O-Polar Surface of ZnO at Near-Atmospheric Pressure

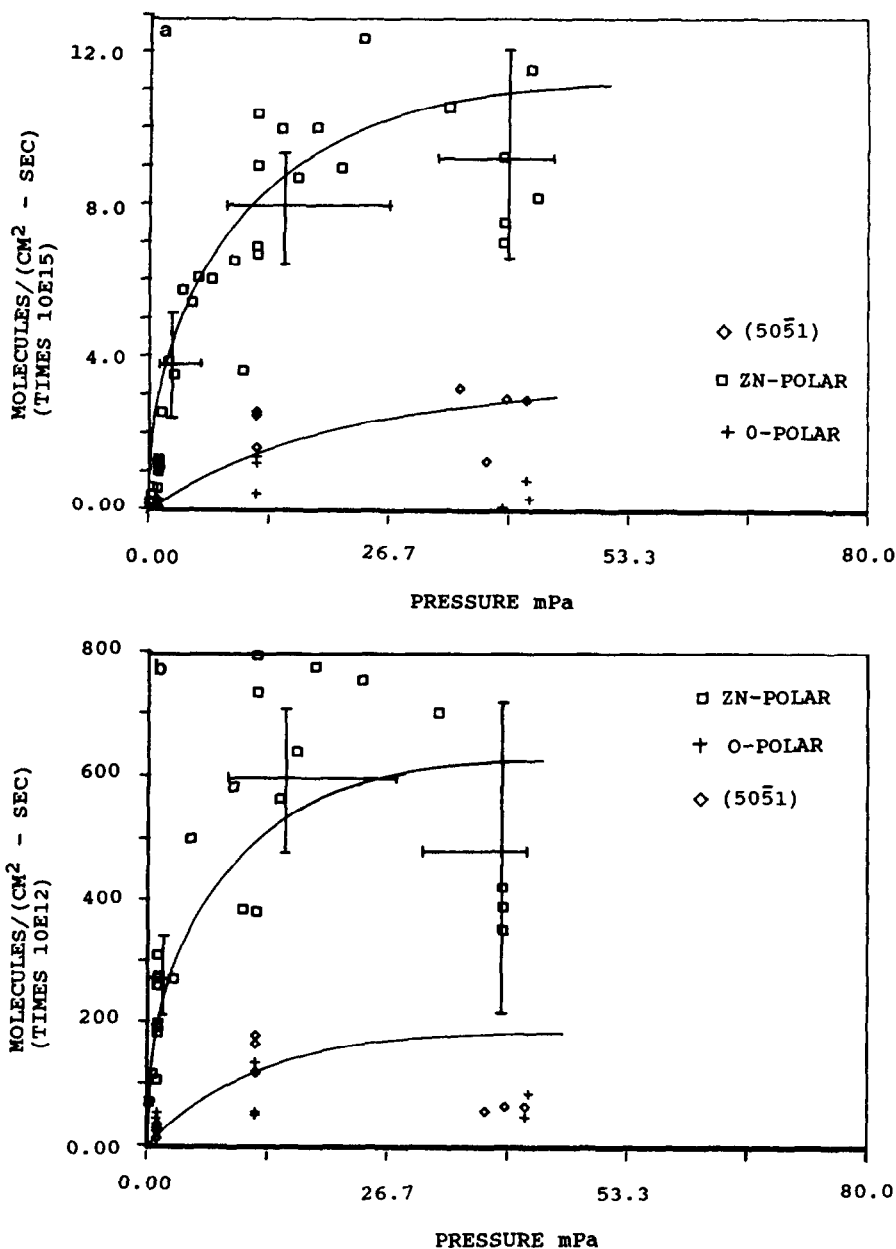| Temp (°C)	Methanol pressure (kPa)	Max. rate (±11%), 10^{12} molecule/cm^2 s
260	2.7	1.2
270	2.7	1.9
	5.3	1.8
	13.3	2.3
280	2.7	3.0
290	2.7	6.0
300	2.7	7.2

FIG. 4. The rates of product formation at different pressures at 350°C. (a) CH_2O; (b) Zn; (c) H_2O; and (d) CO_2. The filled and open symbols are used for clarity.

Zn-polar surface. The activity of the Zn-polar surface was studied between 1.3 and 13.3 kPa of methanol and 250 and 300°C. In this temperature range, the results were reproducible and independent of the sequence of the experiment. Above 300°C, the activities of the sample and of the reac-

tor increased with time. An inspection of the crystal afterwards found that the gold coating at the back and the side of the crystal had cracked.

At 300°C and below, the major carbon-containing product was CO. Small amounts of CO_2 were occasionally detected, but
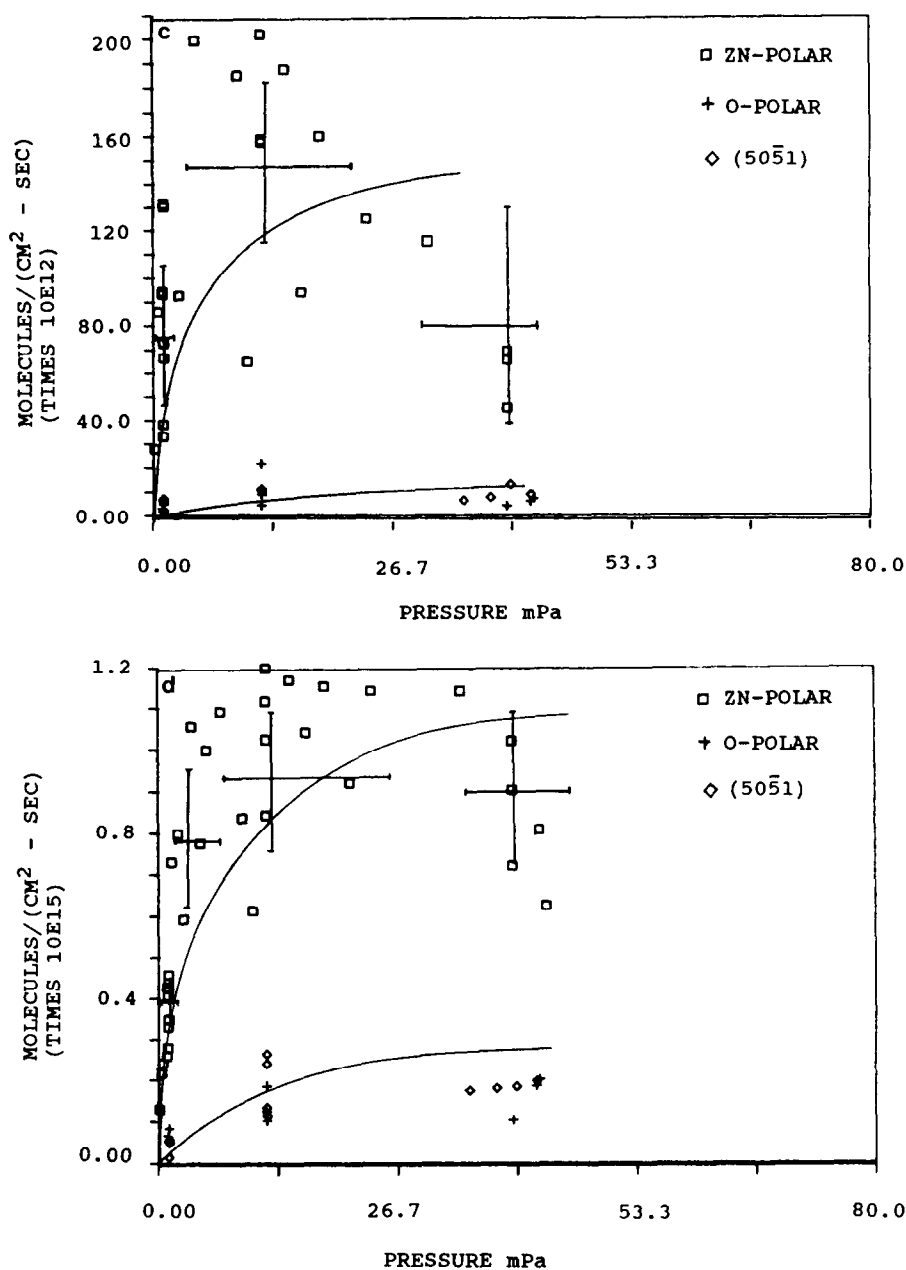
FIG. 4—Continued

these amounts were not reproducible and were very small. H_2 was also a product. No formaldehyde or water was detected.

The rates of formation of CO were higher than the rates due to the activity of the background. The differences between these two sets of rates were used to calculate the activity of the Zn-polar surface. Figure 8, curve b shows the formation of CO on the Zn-polar surface at 2.6 kPa and 270°C after correcting for the background activity of the reactor. The rate of CO formation was calculated from the slope of this plot. The rates at various pressures and temperatures
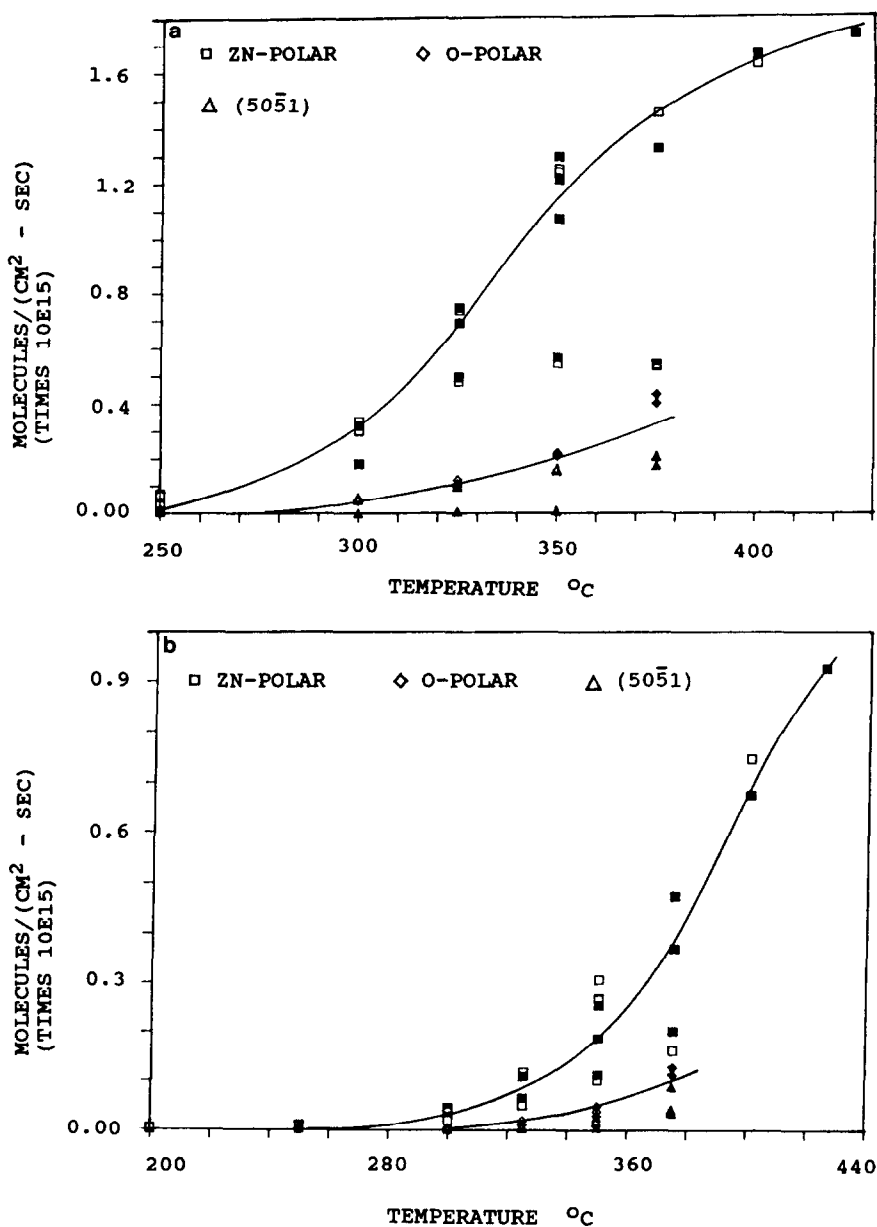
FIG. 5. The rates of product formation at different temperatures at 0.93 mPa. (a) CH_2O; (b) Zn; (c) H_2O; and (d) CO_2.

are summarized in Table 3. Within experimental uncertainties, the rates of methanol consumption determined from the decrease in the methanol concentration in the reaction mixture were the same as the rates of CO production.

Figure 9 shows the Arrhenius plot using the data in Table 3. The activation energy was found to be 138 ± 8 kJ/mole. From the data in Table 3, the reaction was found to be zeroth order in methanol.

Conditions of the Zn-polar surface. The conditions of the Zn-polar surface after the oxygen pretreatment and after being used
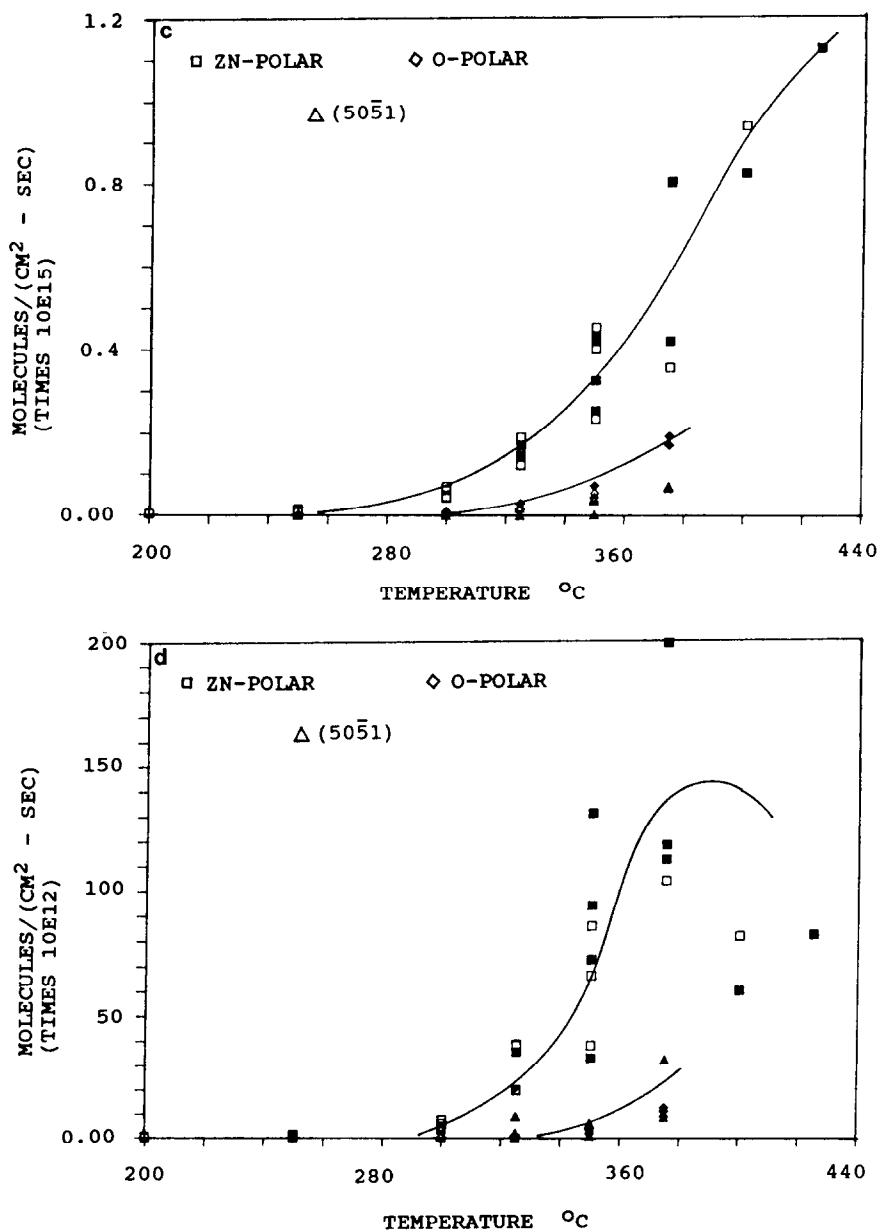
FIG. 5—*Continued*

in a reaction study were investigated using TPDe of methanol. A fresh surface that had been cleaned and ordered by ion sputtering and annealing showed some activities to decompose methanol in a manner similar to that described in previous reports (8–11). CO, CO_2, and HCHO were the observed carbon-containing decomposition products.

With the sample left in the UHV chamber, the surface was subjected to the same oxygen pretreatment as the one used for reaction studies. Then five consecutive TPDe experiments were performed. The surface was inactive in the first run and no decomposition products were detected. The decomposition activity began to develop in
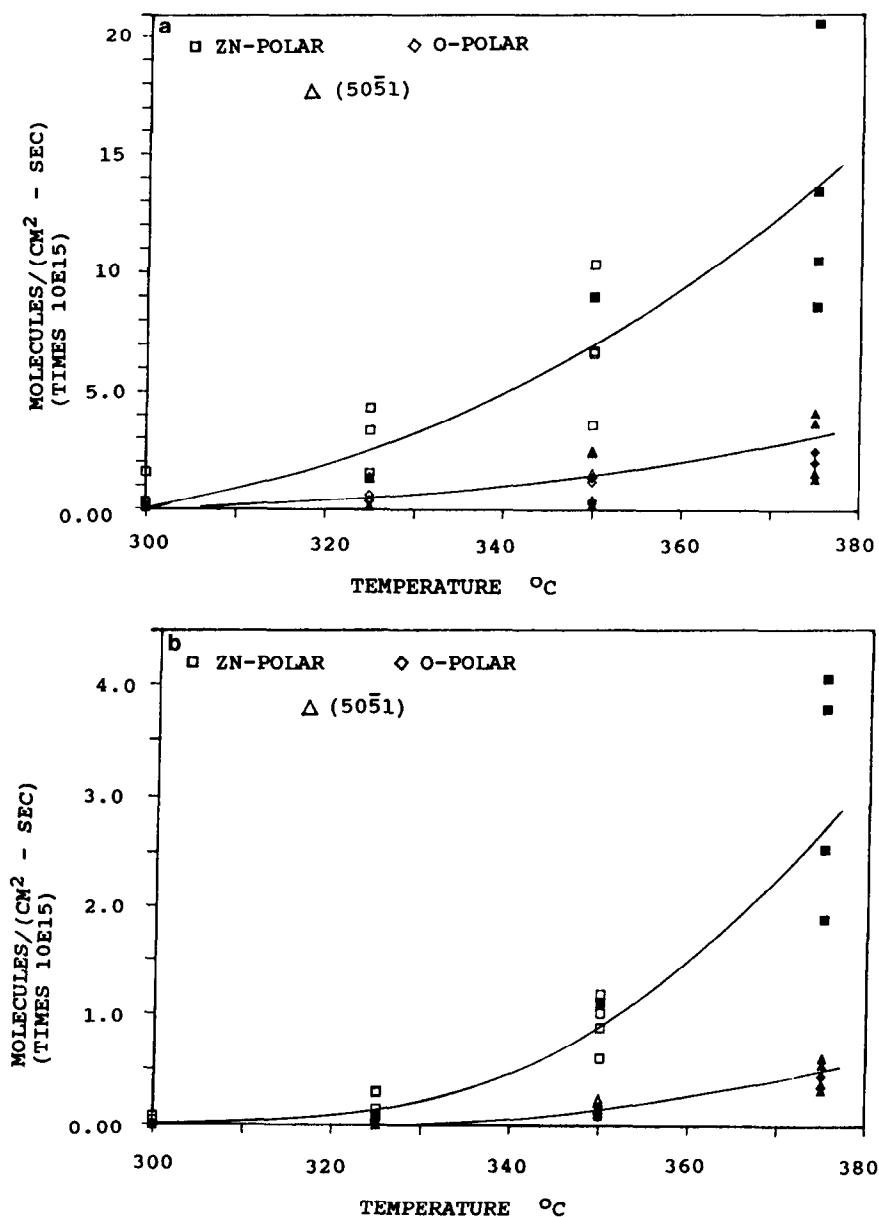
FIG. 6. The rates of product formation at different temperatures at 11.7 mPa. (a) CH_2O; (b) Zn; (c) H_2O; and (d) CO_2.

the second run and continued to increase in subsequent runs. The activity in the fifth run was only about 20% of the value before the oxygen pretreatment.

Stepped nonpolar (50$\bar{5}$1) surface. Only a few experiments were performed on the stepped nonpolar surface to test if it was active or inactive. Decomposition rates

above the background were observed. The major products were CO and H_2; small amounts of CO_2 were sometimes observed. In this regard the results were very similar to the Zn-polar surface. The rates of CO formation are shown in Table 3. Because fewer data points were obtained, the uncertainties in the rates were higher.
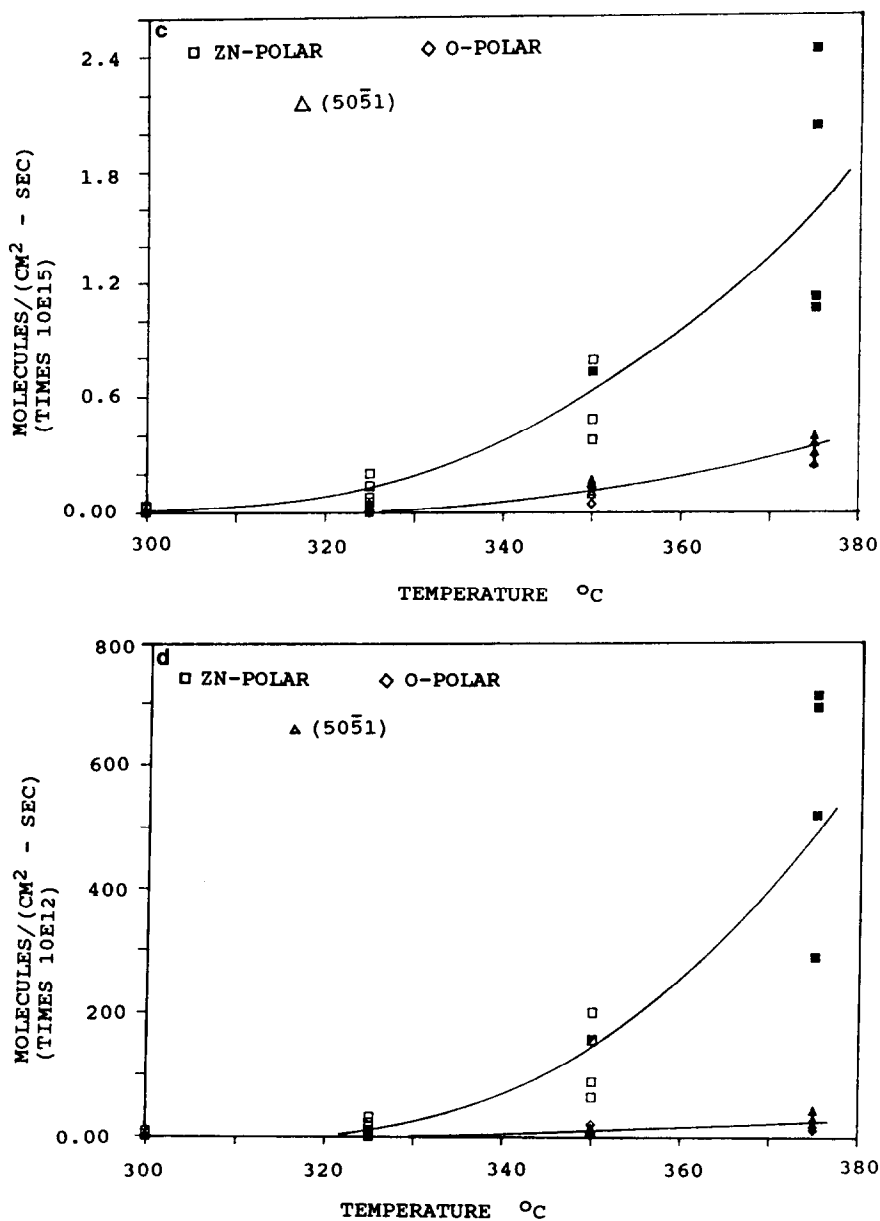
FIG. 6—*Continued*

DISCUSSION

The results in this study can be summarized as follows: (i) The activity for methanol decomposition is different for different ZnO surfaces, and the differences depend on the pressure. At near-atmospheric pressures, a Zn-polar or a stepped nonpolar surface is much more active than an O-polar surface. At low pressures, a Zn-polar surface is also more active than an O-polar surface, but a stepped nonpolar surface becomes almost as inactive as an O-polar surface. (ii) The product distribution is a strong function of pressure. The principal carbon product is HCHO at low pressures versus CO at near-atmospheric pressures. (iii) On a Zn-polar surface, the reaction rate
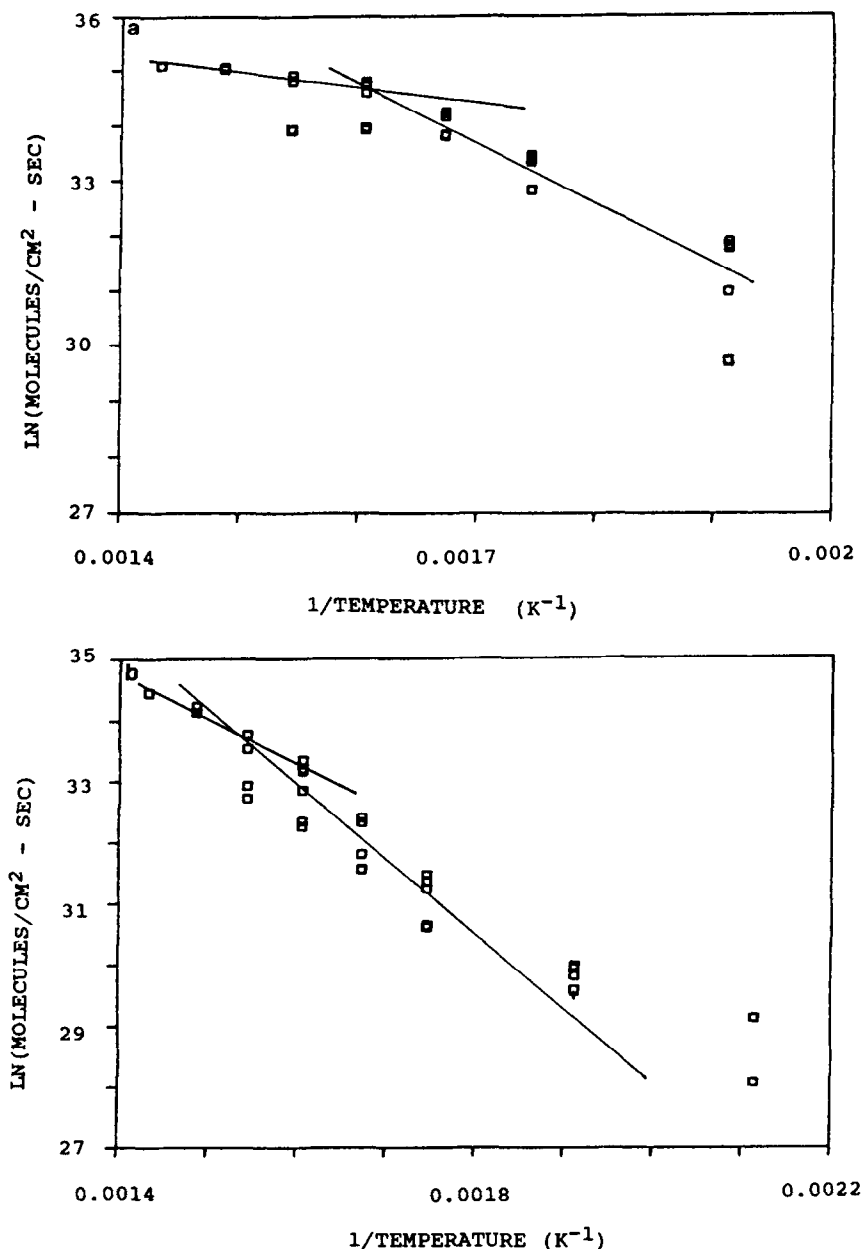
FIG. 7. Arrhenius plots for the formation of various products at 0.93 mPa. (a) CH_2O; (b) Zn; (c) H_2O; and (d) CO_2.

increases with increasing methanol pressure up to almost 26 mPa beyond which the reaction is zeroth order. (iv) In the zeroth order region on a Zn-polar surface, the activation energy is 138 to 161 kJ/mole and is lower at lower pressures. (v) The steady state of a Zn-polar surface during catalytic methanol decomposition is probably not the same as that of the surface after an oxygen treatment or sputtering and annealing *in vacuo*. Since the data obtained on the Zn-polar surface are the most accurate and abundant, and this face is the most active, we shall first discuss the results on this surface
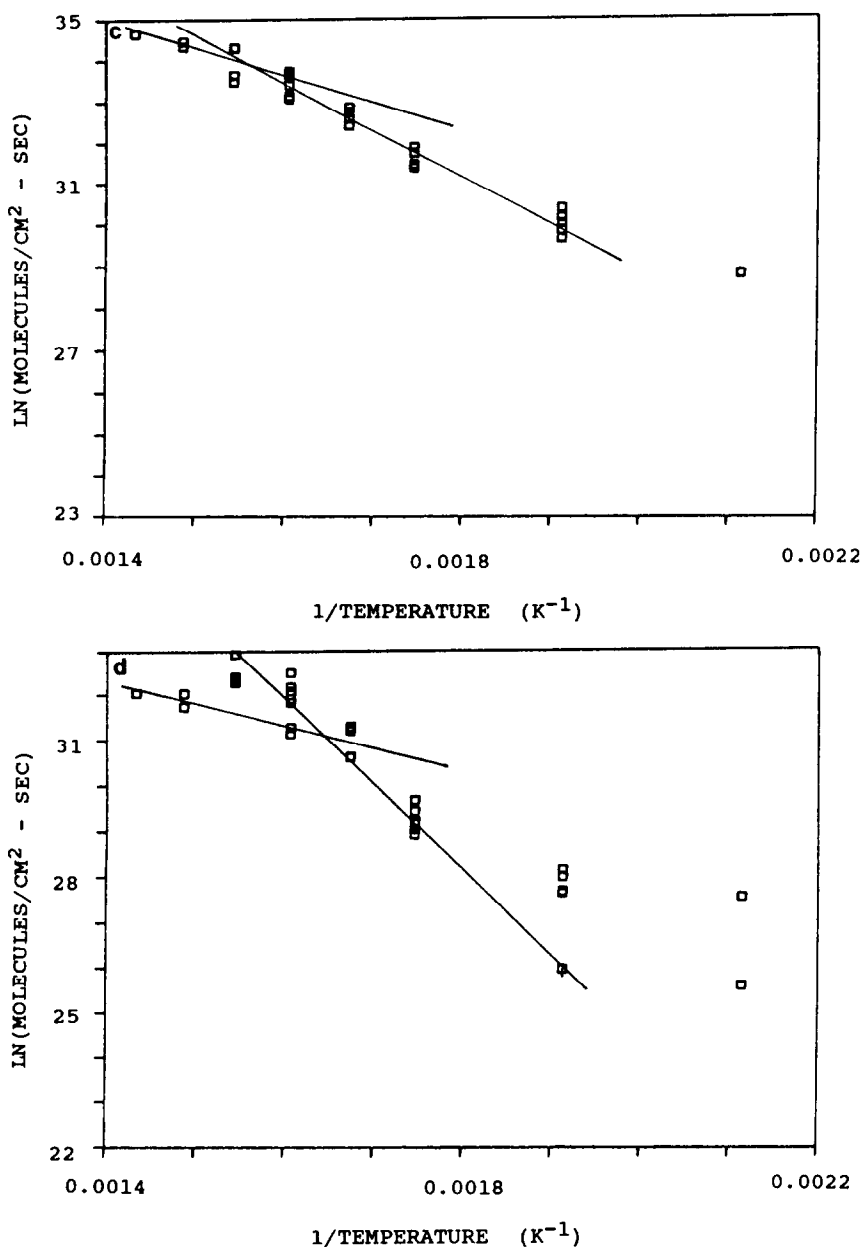
FIG. 7—Continued

before making comparisons among different faces.

1. Reactions on the Zn-polar surface

General discussion. It is important in single-crystal studies to establish that the reactions are catalytic. For the experiments under near-atmospheric pressures of methanol, it can be calculated that the turnover number on the Zn-polar surface is at least 10^2 using the data shown in Table 3 and assuming that every surface Zn–O pair is an active site and that the density of the Zn–O pairs is $1.1 \times 10^{15}/cm$. Thus these results represent the catalytic behavior of

TABLE 3

Rates of CO Formation on Single-Crystal ZnO
Surfaces at Near-Atmospheric Pressures

Surface	P (kPa)	Temp (°C)	CO formation rate (±22%), 10^{12} molecules/cm² s
Zn-polar	2.7	250	3.6
		260	7.7
		270	11.7
		280	21
		290	25
		300	61
Zn-polar	1.3	270	14.2
	2.7		11.7
	5.3		11.4
	10.6		14.9
	13.3		11.1
(50$\bar{5}$1)	2.7	260	4.3
		280	26

FIG. 9. The Arrhenius plot of the CO formation rate on a Zn-polar surface at 2.7 kPa.

this surface. The same argument applies to the stepped nonpolar surface.

In addition, each data point in Figs. 8 and 9, and in similar figures for other conditions (16) represents an individual experiment. The linearity in these figures suggests that
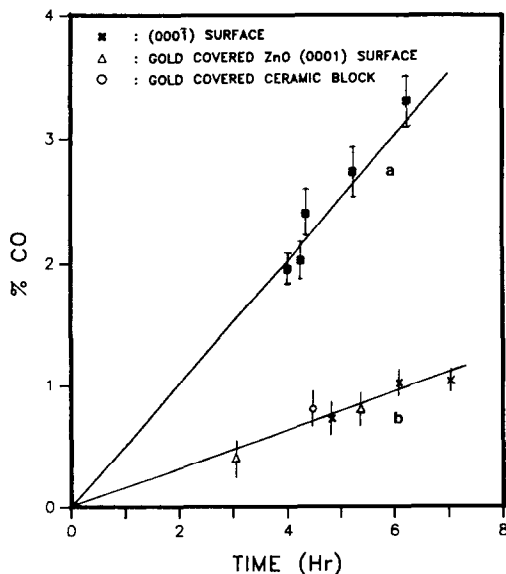

FIG. 8. The concentration of CO in the reaction mixture as a function of reaction time at (curve a) 2.6 kPa of methanol and 270°C, using a Zn-polar surface, and at (curve b) 5.3 kPa and 270°C, using either a gold-plated Zn-polar surface, a gold-plated ceramic block, or a (000$\bar{1}$) surface.
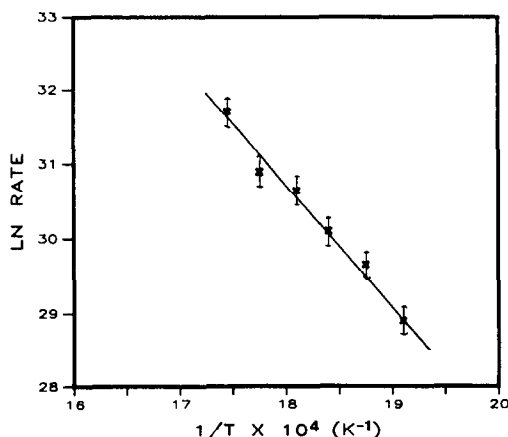
the data are reproducible and that the surfaces do not deactivate with time of reaction.

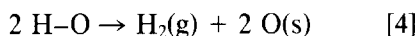In the low-pressure experiments, the rate of CH_2O production on the Zn-polar surface is about 10×10^{15} molecules/cm² s at the high-pressure limit and 375°C. Assuming again that every Zn–O pair is an active site, a turnover number for a 10-h experiment for the production of CH_2O would be of the order of 10^6. However, during reaction, the surface is continuously reduced and Zn atoms are desorbed from the surface. In the zeroth-order region, the rate of Zn desorption is about 1×10^{15} atoms/cm² s, or 10 times smaller than the rate of CH_2O production. Thus it can be concluded that the majority of the reaction occurred catalytically because the rate of surface erosion is much smaller than the rate of methanol decomposition. In addition, since the majority of the surface is covered with a carbonaceous layer, the number of exposed active sites must be quite small; that is, the number of exposed active sites should be much less than the number of Zn–O pairs used in the calculation and the turnover number should be much greater than 10^6. These sites must be catalytic.

Reaction mechanism. The products observed are CO and H_2 in the near-atmo-

spheric pressure experiments and CH_2O, H_2O, Zn, and CO_2 in the low-pressure experiments. In the latter case, CH_2O is the major product and CO, if present, is a minor product. H_2, although unidentified because of large uncertainties, must be a product also to account for the reaction stoichiometry.

All of these products have been observed in TPDe studies on single-crystal ZnO surfaces (8–13). It has been proposed that methanol decomposes in two separate pathways on the Zn-polar surface. The first involves the dehydrogenation of methanol to formaldehyde:
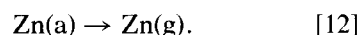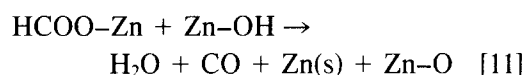Scheme I, dehydrogenation pathway:

$$CH_3OH(g) + Zn{-}O \rightleftharpoons$$
$$CH_3O{-}Zn + H{-}O \quad [1]$$

$$CH_3O{-}Zn + O(s) \rightarrow$$
$$CH_2O{-}Zn + H{-}O \quad [2]$$

$$CH_2O{-}Zn \rightarrow CH_2O(g) + Zn(s) \quad [3]$$

$$2\,H{-}O \rightarrow H_2(g) + 2\,O(s) \quad [4]$$
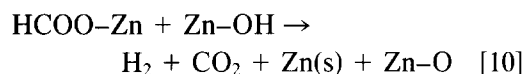
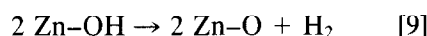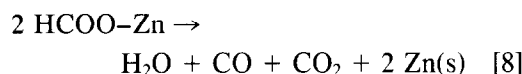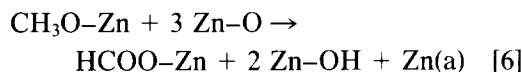$$CH_2O{-}Zn \rightarrow CO(g) + H_2(g) + Zn(s), \quad [5]$$
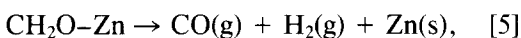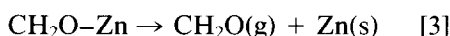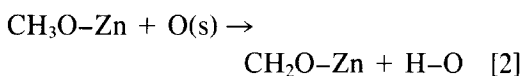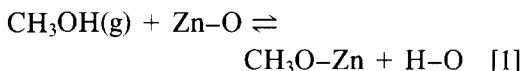
where O(s) and Zn(s) represent surface oxide and Zn ions. In this scheme, methanol is adsorbed dissociatively to form an adsorbed methoxy and a hydroxyl. This step may or may not be reversible. The adsorbed methoxy breaks a C–H bond to form an adsorbed formaldehyde. The formaldehyde and the hydrogen then desorb. The formaldehyde may also further decompose to CO and H_2. This scheme is supported by two observations from the literature. Adsorbed methoxy has been detected by both infrared spectroscopy (19, 20) and XPS (13), and $CH_3^{18}OH$ has been observed to decompose only to $CH_2^{18}O$ (no $CH_2^{16}O$ was detected (10)).

The other products CO_2, H_2O, and Zn are produced by an oxidation pathway (Scheme II) (8–11, 13, 21, 22). ZnO oxidizes the adsorbed methoxy to a formate. The formate then decomposes to CO, CO_2, H_2, and H_2O. The formation of the formate

reduces the surface layer of ZnO to Zn, which then desorbs from the surface:
Scheme II, oxidation pathway:

$$CH_3O{-}Zn + 3\,Zn{-}O \rightarrow$$
$$HCOO{-}Zn + 2\,Zn{-}OH + Zn(a) \quad [6]$$

$$2\,HCOO{-}Zn \rightarrow H_2 + 2\,CO_2 + 2\,Zn(s) \quad [7]$$

$$2\,HCOO{-}Zn \rightarrow$$
$$H_2O + CO + CO_2 + 2\,Zn(s) \quad [8]$$

$$2\,Zn{-}OH \rightarrow 2\,Zn{-}O + H_2 \quad [9]$$

$$HCOO{-}Zn + Zn{-}OH \rightarrow$$
$$H_2 + CO_2 + Zn(s) + Zn{-}O \quad [10]$$

$$HCOO{-}Zn + Zn{-}OH \rightarrow$$
$$H_2O + CO + Zn(s) + Zn{-}O \quad [11]$$

$$Zn(a) \rightarrow Zn(g). \quad [12]$$

The existence of this pathway has been confirmed by TPDe experiments, IR, and XPS. During TPDe of methanol, formaldehyde, or formic acid, very similar peaks of decomposition products of CO, CO_2, H_2O, and H_2 have been observed. Using IR spectroscopy or XPS, a surface formate formed from adsorbed methanol has been detected. It has been further shown in TPDe experiments that the products of the oxidation pathway desorb at temperatures 30 to 50°C higher than do the products of the dehydrogenation pathway. Similarly, a steady-state reaction study has also shown that the decomposition of methanol to formaldehyde occurs at a lower temperature than the formation of CO_2 (23).

The lattice oxygen has been shown to participate in the oxidation pathway in a TPDe experiment using ^{18}O-labeled methanol. Contrary to the dehydrogenation pathway which produces exclusively ^{18}O-labeled formaldehyde, the oxidation pathway produces mainly ^{16}O-labeled CO_2, H_2O, and CO (10).

In the oxidation pathway, the ZnO surface is reduced. The resulting metallic Zn desorbs from the surface, generating fresh ZnO active sites. This phenomenon has been observed during TPDe of methanol on

ZnO single-crystal surfaces (10, 13) and during steady-state decomposition of CH_3OH on powder ZnO samples (23, 24). If the suggestion that the ZnO surface is "regenerated" by Zn desorption is true, then one would expect that the ratio of steady-state production rates of $(H_2O + CO_2)/Zn$ would be unity in the low-pressure experiments. Values of this ratio are shown in Tables 4 and 5. Within the large uncertainties, they are close to unity and are much smaller than the ratios of CH_2O/Zn.

We believe that H_2 is also a major product in the low-pressure experiments since H_2O alone could not account for the hydrogen atoms released from methanol during the formation of CH_2O and CO_2 (Tables 4 and 5). In fact, the production rate of H_2 has to be substantially larger than that of H_2O in order to balance the H atoms in the reaction.

It is interesting that CO and H_2 are the major products in the near-atmospheric pressure experiments, which agrees with all the published studies on the catalytic de-

composition of methanol on ZnO at close to atmospheric pressures (24–27). Only small amounts of other products such as CH_2O and CO_2 have been observed. This contrasts sharply with the observation that CH_2O is the major product in the low-pressure experiments. There are two possible reasons for this discrepancy. The first reason is that at the low pressures, desorbed CH_2O would not be able to readsorb and would further decompose to CO and H_2. On the other hand, at the higher pressures, there is probably a stagnant boundary layer at the surface through which desorbed CH_2O has to diffuse to enter the bulk gas phase. The presence of this stagnant layer would increase the probability of readsorption and thus further reaction of CH_2O.

The second reason is that the ZnO surface may be more reduced at higher pressures. It has been shown that the desorption of metallic Zn in a TPDe experiment could be suppressed by 10^{-4} Pa of O_2 (10). It has also been observed that a more reduced ZnO surface produces a higher ratio

TABLE 4

Rates of Product Formation Relative to the Rates of CH_2O and Zn Formation at 350°C

Product formed	Zn-polar surface rate relative to		(50$\bar{5}$1) surface rate relative to		O-polar surface rate relative to	
	CH_2O	Zn	CH_2O	Zn	CH_2O	Zn
Surface pressure = 0.93 mPa						
H_2O	20 ± 3	62 ± 11	15 ± 12	54 ± 44	18 ± 4	67 ± 24
CH_2O	100	303 ± 40	100	371 ± 330	100	369 ± 96
CO_2	7 ± 2	21 ± 7	4 ± 3	14 ± 12	1 ± 1	5 ± 3
Zn	33 ± 4	100	27 ± 24	100	27 ± 7	100
Surface pressure = 11.7 mPa						
H_2O	8 ± 2	65 ± 17	9 ± 7	79 ± 33	18 ± 15	59 ± 43
CH_2O	100	832 ± 200	100	853 ± 648	100	330 ± 210
CO_2	2 ± 1	16 ± 5	1 ± 1	7 ± 3	3 ± 3	9 ± 8
Zn	12 ± 3	100	12 ± 9	100	30 ± 19	100
Surface pressure = 42.6 mPa						
H_2O	5 ± 3	52 ± 28	2 ± 1	25 ± 17	12 ± 18	28 ± 28
CH_2O	100	1040 ± 350	100	1470 ± 510	100	224 ± 250
CO_2	1 ± 1	8 ± 5	1 ± 1	13 ± 15	2 ± 2	4 ± 2
Zn	10 ± 3	100	7 ± 2	100	45 ± 51	100

TABLE 5

Rates of Product Formation Relative to the Rates of CH_2O and Zn Formation at 375°C

Product formed	Zn-polar surface rate relative to		$(50\bar{5}1)$ surface rate relative to		O-polar surface rate relative to	
	CH_2O	Zn	CH_2O	Zn	CH_2O	Zn
Surface pressure = 0.93 mPa						
H_2O	32 ± 21	54 ± 32	29 ± 3	66 ± 6	20 ± 3	55 ± 6
CH_2O	100	167 ± 95	100	227 ± 23	100	278 ± 27
CO_2	12 ± 7	21 ± 11	3 ± 1	7 ± 1	5 ± 1	15 ± 3
Zn	60 ± 34	100	44 ± 4	100	36 ± 3	100
Surface pressure = 11.7 mPa						
H_2O	35 ± 17	54 ± 53	12 ± 3	67 ± 20	12 ± 7	71 ± 27
CH_2O	100	446 ± 279	100	553 ± 168	100	569 ± 348
CO_2	4 ± 3	20 ± 11	1 ± 1	4 ± 1	1 ± 1	8 ± 3
Zn	21 ± 13	100	18 ± 5	100	18 ± 11	100
Surface pressure = 42.6 mPa						
H_2O	8 ± 2	48 ± 13	13 ± 6	52 ± 33	5 ± 2	43 ± 13
CH_2O	100	574 ± 133	100	394 ± 178	100	929 ± 137
CO_2	2 ± 1	10 ± 3	1 ± 1	3 ± 1	0.00	5 ± 1
Zn	17 ± 4	100	25 ± 11	100	11 ± 2	100

of CO/CH_2O than a less reduced surface (9). If the rate of surface reduction is higher or if the desorption of Zn is suppressed by a high-pressure of methanol, then the surface would contain a higher density of metallic Zn and produce more CO and less CH_2O than at low pressures. Although our data do not discriminate between the two explanations, we believe that this latter effect is more plausible. In fact, the TPDe experiments performed to study the conditions of the Zn-polar surface described earlier suggest that the decomposition of methanol activates a surface that has become inactive after the oxygen pretreatment for the near-atmospheric experiments. This activation phenomenon, together with the fact that Zn atoms desorb from a surface during methanol decomposition (10), suggest that at steady state, the ZnO surface contains a significant density of defect that could be the active sites, as has been shown in previous TPDe experiments (8).

In addition to the different production rates of CO and HCHO at different pres-sures, the rate of H_2O production is also higher at low pressures than at high pres-sures. This indicates that the oxidation pathway of the decomposition reaction, which involves the decomposition of a sur-face formate, is less prominent at high pres-sures than at low pressures. This is consis-tent with the presence of a more reduced surface at higher pressures and thus a lower rate of formation of surface formate.

Pressure dependence. The dependence of the rates on pressure presented in Fig. 4 shows that the rates first increase with pres-sure and then decrease at pressures higher than 27 mPa. The decrease is more appar-ent for H_2O and CO_2 than for CH_2O or Zn. As is explained in Appendix III, these de-creases (with the possible exception of CO_2) are most likely due to over-correction of the data for background contributions. Therefore the actual pressure dependence is such that below about 26 mPa, the rate increases with increasing methanol pres-sure; above 26 mPa, the rate is independent of pressure. This is consistent with the

near-atmospheric pressure results in Table 3 that the rate is zeroth order in the pressure range between 1.3 and 13 kPa. A zeroth-order dependence on methanol pressure has also been found on ZnO powders in the range 1.3 to 4.6 kPa (24) and at pressures close to atmospheric (25, 28, 29). Interestingly, one study reported a negative-order dependence for the rate of formation of CO and CO_2 at methanol pressures between 3 to 130 Pa, and a positive-order dependence for the rate of H_2 production (23).

The dependence of the rate of formation of CH_2O on pressure can be explained by Scheme I. If step [1] is irreversible and the breaking of the C–H bond (step [2]) is the slow step (the step whose rate constant is much smaller than the others), then the areal rate can be expressed as

$$\text{rate} = k_1 k_2 P / (k_2 + k_1 P), \qquad [13]$$

where k_1 and k_2 are the rate constant for reactions [1] and [2], respectively, and P is the pressure of methanol. This rate expression predicts a transition from a first-order rate dependent at low methanol pressures to a zeroth-order dependence at high pressures.

A similar pressure dependence is obtained if step [1] is reversible. If we further assume that the desorption of formaldehyde and H_2 in steps [3] and [4] are rapid such that the surface concentrations of CH_2O–Zn and O–H are small, then the areal rate of formation of formaldehyde can be expressed as

$$\text{rate} = k_2 K_1 P / (1 + K_1 P), \qquad [14]$$

where K_1 is the equilibrium constant for reaction [1]. This expression predicts a pressure dependence of the rate similar to that in Eq. [13].

Methanol is known to adsorb reversibly on ZnO. In the temperature-programmed decomposition studies, some of the methanol desorbs from ZnO without decomposing (8–13, 21). However, methanol also adsorbs irreversibly and dissociatively at room temperature, and the resulting sur-

face methoxy species can be detected by infrared spectroscopy (19, 20) and XPS (13). In view of the possibility that at steady state during reaction only a small fraction of the surface remains clean and is active, it is not clear how applicable these literature results are to the situation under reaction conditions, since the techniques used in these studies only detect species that are present in high densities on the surface. At present we tend to favor irreversible adsorption of methanol. In addition, as will be discussed later, it is also possible that surface defects are the active sites whose concentration may depend on the pressure of methanol. Then the values of k_1, k_2, and K_1 in Eqs. [13] and [14] will be functions of pressure.

Temperature dependence. The turnover rates of the various products are shown as a function of temperature for all three surfaces in Figs. 5 and 6 and in Tables 2 and 3. The corresponding Arrhenius plots for the Zn-polar surface are shown in Figs. 7 and 9. The rates increase exponentially with increasing temperature below about 375°C. Above 375°C the rate of increase is slower. The activation energies for the Zn-polar surface at low pressures are shown in Table 1. Because of the high uncertainties in the data, the activation energies for the other two surfaces are not shown.

The value for CH_2O production at 43 mPa of methanol is 161 kJ/mole. It is comparable to the value of 138 kJ/mole obtained for the primary reaction of CO formation at 2.6 kPa on the same Zn-polar single-crystal surface. The activation energies reported in the literature are summarized in Table 6. These values vary widely. Below about 330°C the range of the reported values is from 127 to 255 kJ/mole. The values in this study fall within the range.

The values at low pressures shown in Table 1 show three interesting trends: the activation energies increase when the pressure is increased; they are lower at temperatures above 375°C than below 375°C (at least for

TABLE 6

Summary of Activation Energy Values Published in
the Literature

Activation energy (kJ/mol)	Temperature range (°C)	Method	Ref.
156	230–372	Pressure[a]	Dandy (24)
146	295–330	CO[b]	Dohse (25)
92	330–376	CO	Dohse
225 ± 8	312–330	Pressure	Fuderer (32)
115 ± 3	330–356	Pressure	Fuderer
191	298–330	CO	Uchida (31)
67	330–425	CO	Uchida
247	260–337	Conversions[c]	Morelli (28)
121	337–370	Conversions	Morelli
127	288–315	CO + CO$_2$[d]	Tawarah (23)
42.5	315–340	CO + CO$_2$	Tawarah

[a] Rates measured by pressure increase in the system.
[b] Rates measured by the formation of CO. The activation energies for total product formation were the same.
[c] Rates measured by the conversions of CH$_3$OH.
[d] Rates measured by the formation of CO + CO$_2$.

the data at 0.93 mPa); and below 375°C, the activation energy for the formation of CO$_2$ is higher than those for the other products, whereas the value for formaldehyde above 375°C is lower than for the other products.

The increase in activation energy when the pressure is increased is predicted by the rate expressions [13] and [14]. Examining expression [13], the rate at the low-pressure (first-order) limit is given by rate $= k_1P$, and the apparent activation energy is E_1. The rate at the high-pressure (zeroth-order) limit is given by rate $= k_2$, and the apparent activation energy is E_2. Since it has been shown that dissociative adsorption of methanol occurs even at room temperature but the decomposition to formaldehyde does not, it is reasonable to assume that $E_1 < E_2$, which would result in an increase in activation energy when the pressure of methanol is increased.

Likewise, from rate expression [14], the rate at the low-pressure limit is given by rate $= k_2K_1P$, and the apparent activation energy is $E_2 + H$, where H is the heat of adsorption of methanol. The rate at the high-pressure limit is given by rate $= k_2$, and the apparent activation energy is E_2. Since the heat of adsorption of methanol on

ZnO is negative (30), the apparent activation energy should be lower at low pressures than at high pressures.

Although these arguments explain the data qualitatively, they do not take into account the possible changes in the surface conditions with pressure and particularly with temperature. If indeed the surface is partly reduced at the steady state, it is reasonable to assume that the degree of reduction depends on temperature and pressure. This would affect the apparent activation energies.

A smaller activation energy at high temperatures than that at low temperatures has also been reported by other workers (Table 6). Several explanations have been proposed in the literature. Dohse has suggested that methanol decomposes sequentially, first into formaldehyde and then into CO. At low temperatures the step with the higher activation energy is the rate-limiting step, and at high temperatures the step with the lower activation energy is the rate-limiting step (25). In the study by Uchida and Ogino, it was found that the temperature at which the activation energy of the methanol decomposition reaction changed was the same as the temperature at which the activation energy of the conductivity of the ZnO powder in H$_2$ changed (31). This might indicate a change in the extent of reduction of the ZnO surface. Tawarah and Hansen explained the change in the activation energy of the reaction with the proposal that methanol decomposition occurred only when there was a vacant active site adjacent to an adsorbed methoxy species. The higher activation energy at low temperatures was due to the fact that the surface was nearly fully saturated and some CH$_3$OH needed to be desorbed before decomposition could take place (23). The negative-order dependence they observed for the production of CO + CO$_2$ could also be explained by a requirement of two adjacent sites.

Neither Dohse's nor Tawarah's model could explain our data. Dohse's explana-

tion would apply to the formation of CO as a subsequent reaction of formaldehyde. However, the major product in our low-pressure study is formaldehyde, the formation of which shows the same change in activation energy as those of the other products. Since we did not observe a negative order in the rates, Tawarah's explanation would not apply here.

The effect of pore diffusion is another common explanation for a lower activation energy at higher temperatures than at lower temperatures. Since our single-crystal samples do not have pores, a pore diffusional effect is not applicable.

Our results cannot be readily explained using Schemes I or II, which would predict no changes in the activation energy in the region of first-order kinetics.

If the schemes are correct, this change in activation energies with temperature may reflect a change in the temperature dependence of the concentration of surface active sites, perhaps because of a change in surface defect concentration as proposed by Uchida and Ogino (31) and/or in surface carbon coverage. Unfortunately, there are no data to evaluate this possibility.

Turnover frequencies (TOF). Assuming that each surface Zn ion is an active site, the turnover frequency for the Zn-polar surface in the zeroth-order region at low pressure is about 10 s^{-1} (10×10^{15} molecules/cm^2 s) at 350°C. At near-atmospheric pressure, it is 6×10^{-2} s^{-1} (6×10^{13} molecules/cm^2 s) at 300°C or 0.6 s^{-1} (6×10^{14} molecules/cm^2 s) at 350°C (using an activation energy of 138 kJ/mole). These two values are reasonably close considering the very different pressures and the very different experimental techniques used. This close agreement lends strong support to the validity of the measurements reported in this paper.

However, from the rate data on powder ZnO and the surface areas published by other workers, we calculated widely different TOF's. Morelli *et al.* reported a value of 1.5×10^{13} molecules/cm^2 s at 320°C (28,

29), Uchida and Ogino reported 1×10^{14} at 425°C (31), Dandy reported 6×10^{12} at 375°C (24), and Tawarah and Hansen reported 6×10^{11} at 340°C (23). It is tempting to attribute the wide variation to the structure sensitivity of this reaction.

2. Comparison among Different Surfaces

Figures 4a–4d show that at low pressures the catalytic activities of the stepped nonpolar (50$\bar{5}$1) or the O-polar (000$\bar{1}$) surface are much lower than the Zn-polar (0001) surface. This trend is the same as that observed during the low-pressure catalytic decomposition of 2-propanol (5, 6), as well as during the temperature-programmed decomposition of methanol (9, 13). Such a trend has been used by some investigators to explain their results on powder ZnO (22, 23).

On the other hand, the stepped nonpolar is about as active as the Zn-polar surface at near-atmospheric pressures (Table 3), and they are both much more active than the O-polar surface.

To explain these results, we make use of the assumption that the active sites are surface defects produced by reduction of the surface. The Zn-polar surface is the most easily reduced. Thus it is the most active. The stepped nonpolar surface is less reducible and is less active than the Zn-polar surface at low methanol pressures. However, at high pressures of methanol, the surface is sufficiently reduced to be as active as the Zn-polar surface. The O-polar surface is reduced with difficulty and is thus the least active.

It is also possible that the adsorption of methanol on the nonpolar surface is weaker than that on the Zn-polar surface. Thus a much higher pressure of methanol is required to result in a saturation coverage of methanol and the corresponding high catalytic activity on this surface.

If indeed the active sites are surface defects, why is the Zn-polar surface more easily reduced than the nonpolar surface? We conjecture that the presence of coor-

dinatively unsaturated (cus) O ions on the nonpolar surface help prevent the surface from being reduced because these O ions are more easily protonated and participate with greater difficulty in the oxidation of surface methoxy species to surface formate. The Zn-polar surface does not have any (ideally) O cus ions, but it does have coordinatively saturated surface O ions. These O ions participate more readily in the oxidation of surface methoxy to formate. The result is that it is more difficult to reduce the Zn ions in the nonpolar surface to Zn atoms. Another possibility is that methanol adsorbs less strongly on the nonpolar surface than on the Zn-polar surface because of their different electronic structures. This results in a low surface coverage of methanol on the nonpolar surface and a low activity.

The product distributions on the three surfaces are similar: at near-atmospheric pressures, CO and H_2 are the products detected; at low pressures, CH_2O is the major product, but CO_2, H_2O, Zn, and H_2 are also produced. However, for the $(50\bar{5}1)$ and the $(000\bar{1})$ surfaces, it is possible that CO and H_2 are actually the major products which have gone undetected because of the high background pressures of these gases. Indeed during the TPDe of methanol, CH_2O is not a product formed on these two surfaces (9). However, the higher rate of CH_2O production than of H_2O production observed here suggests that the surface behaves differently during steady-state catalytic reactions than during TPDe reactions.

From the data, it is not possible to evaluate the effect of surface carbon. Other experiments need to be conducted to elucidate this point.

CONCLUSION

It has been shown that catalytic decomposition of methanol takes place on single-crystal surfaces of ZnO. Between 0.93 and about 43 mPa of methanol and up to 425°C, a Zn-polar surface is much more active than a stepped nonpolar $(50\bar{5}1)$ or an O-polar

$(000\bar{1})$ surface. Between 2.7 and 13.3 kPa, the Zn-polar and the $(50\bar{5}1)$ surfaces are about equally active and are much more active than the O-polar surface. Thus the decomposition of methanol on ZnO is structure sensitive. The rate of decomposition of methanol increases with increasing pressure up to about 27 mPa. Above this pressure the rate is zeroth order in methanol. The turnover frequencies and the activation energies found on the Zn-polar surface at low and near-atmospheric pressures are comparable.

The major product at low pressures is formaldehyde. CO_2, H_2O, and Zn are also detected. H_2 is also a product but it is not detected because of the high background of this gas in the system. Although CO could be formed, it could not be the major product on the Zn-polar surface. However, at near-atmospheric pressures, CO and H_2 are the major products, which agrees with previous work using ZnO powders at similar pressures. The difference in the products at different pressures is attributed to two factors: the presence of a boundary layer in the near-atmospheric pressure studies that facilitates readsorption and further reactions of formaldehyde, and the different degrees of surface reduction at different pressures. The active sites on the Zn-polar surface are proposed to be surface defects generated by the reduction of the surface during reaction.

APPENDIX 1: MAXIMUM POSSIBLE RATE OF CO FORMATION

An estimate of the maximum possible rate of CO formation was made using some limiting and probably unreasonably conservative assumptions about the fragmentation of CH_3OH, CH_2O, and CO_2 into $m/e = 28$. If we assumed that the $m/e = 28$ peak was due only to CO and fragmentation from methanol (whereas in reality, both CH_2O and CO_2 also fragmented significantly into this peak) and that the mass spectrometer sensitivities of CO and CH_2O were the same (whereas the spectrometer was about

2.86 times more sensitive to CO than CH_2O), the rate of CO production was calculated to be only about 0.58 times the rate of CH_2O production. Thus CH_2O was undoubtedly the major product in these measurements.

APPENDIX II: ESTIMATION OF UNCERTAINTIES IN THE DATA

Whether the rates of reaction could be accurately determined and whether the ZnO surfaces behaved as catalysts were of great concern throughout this study. The reproducibility of the data has been an important criterion. As can be seen in Figs. 4a–4d, the variation from one measurement to another could be as large as a factor of 2.

In these figures, an error bar along the y-axis represented a 95% confidence limit in the reproducibility estimated from a group of data points collected under similar conditions, whereas an error bar along the x-axis represented the pressure range of the same group of data points.

The magnitudes of the various sources of errors in the data can be discussed with respect to whether they would affect the reproducibility or the accuracy of the data. The noise imparted by the mass spectrometer and the uncertainties in the measured flow rates of methanol through the doser tube were small, less than the width of the data point in Fig. 4. During an experiment, the sample holder and the ZnO sample were frequently rotated away from and back to the mass spectrometer to measure in an alternate sequence the direct and the indirect fluxes at the reaction temperature. An error of 1° off the optimal position of the sample with respect to the mass spectrometer was found to lead to a 10% decrease in the MS intensity. However, the maximum error in repositioning should be less than 0.5° or 3% in the MS intensity.

The temperature of the ZnO surface measured by the thermocouple could only be set to ±2°C. Because there were temperature variations across the surface, it was possible that different temperature varia-

tions from one experiment to another could affect the reproducibility. The effect induced by a temperature variation was estimated using the data on Zn production, which had the smallest contributions from the background. Assuming an activation energy of Zn production of 150 kJ/mole, such a temperature variation at 350°C would result in a rate variation of ±10%. Although this did not totally account for the 33% spread in the rates shown in Fig. 4b, it did contribute significantly.

Using the methanol signal, the day-to-day variations in the sensitivity of the mass spectrometer were estimated to be ±14% when the sample was at room temperature. Thus this contribution to the lack of reproducibility of the data was also substantial. Finally, judging from the data, the change in the activities of the surface from one experiment to another was not expected to be large in view of the other contributions discussed.

APPENDIX III: DECREASE IN RATES AT PRESSURES HIGHER THAN 27 mPa

The decrease in rates is attributed to over-correction of the data for background contributions in the low-pressure experiments. For example, the rates for water were calculated from the difference in MS intensities of the direct flux and the indirect flux measured at reaction temperature minus the same difference measured at room temperature when no reaction occurred. However, if the room temperature corrections were not applied, the rates were not lower at the higher pressures. The room temperature correction for H_2O was large and increased with increasing methanol flux due to both the displacement of water from the chamber walls by methanol and the presence of water impurity in the methanol. We believe that this large correction is the reason that water appeared to show a lower rate at high pressures (Fig. 4c).

Two other possibilities for this effect could be excluded. One possibility is the effect due to collision of molecules at high

pressures. However, at 43 mPa, the mean free path of methanol is 18 cm, which is much longer than the distance between the sample surface and the ionizer of the mass spectrometer, thereby eliminating this possibility. The linear relationship between the direct flux MS intensity at room temperature and the methanol pressure (Fig. 1) supports this conclusion. The second possibility is that the impinging methanol molecules collide with the adsorbed species causing the desorbing species to desorb in angles that do not follow the cosine law of desorption. This effect should be larger for the lighter product molecules such as H_2O and CH_2O than for the heavier ones such as Zn and CO_2. However, such a dependence on the molecular weight was not observed.

REFERENCES

1. Taylor, H., *Proc. R. Soc. London A* **108**, 105 (1925).
2. Somorjai, G. A., "Chemistry in Two-Dimension: Surfaces." Cornell Univ. Press, Ithaca, NY, 1981.
3. Salmeron, M., Gale, R., and Somorjai, G. A., *J. Chem. Phys.* **72**, 2807 (1979).
4. Engel, T., and Ertl, G., *J. Chem. Phys.* **69**, 1267 (1978).
5. Berlowitz, P., and Kung, H., *J. Amer. Chem. Soc.* **108**, 3532 (1986).
6. Vest, M., Berlowitz, P., and Kung, H., in "Catalysis 1987" (J. Ward, Ed.), p. 577. Elsevier Science Publishing Co., Amsterdam/New York, 1988.
7. Djega-Mariadassou, G., and Davignon, L., *J. Chem. Soc. Faraday Trans. 1* **78**, 2447 (1982).
8. Cheng, W. H., and Kung, H., *Surf. Sci.* **122**, 21 (1982).
9. Akhter, S., Cheng, W. H., Lui, K., and Kung, H. H., *J. Catal.* **85**, 437 (1984).
10. Lui, K., Akhter, S., Vest, M., and Kung, H., *J. Phys. Chem.* **90**, 3183 (1986).
11. Akhter, S., Lui, K., and Kung, H. H., *J. Phys. Chem.* **89**, 1958 (1985).
12. Zwicker, G., Jacobi, K., and Cunningham, J., *Int. J. Mass Spectrom. Ion Processes* **60**, 213 (1984).
13. Vohs, J., and Barteau, M., *Surf. Sci.* **176**, 91 (1986).
14. Berlowitz, P., Ph.D. thesis, Northwestern University, 1986.
15. Vest, M., Ph.D. thesis, Northwestern University, 1989.
16. Lui, K., Ph.D. thesis, Northwestern University, 1989.
17. Christmann, K., Schober, O., and Ertl, G., *J. Chem. Phys.* **60**, 4719 (1974).
18. Netzer, F. P., and Medley, T. E., *J. Chem. Phys.* **76**, 710 (1982).
19. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **66**, 756 (1970).
20. Noto, Y., Fukuda, K., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **63**, 3081 (1967).
21. Chan, L., and Griffin, G., *Surf. Sci.* **155**, 400 (1985).
22. Bowker, M., Houghton, H., and Waugh, K., *J. Chem. Soc. Faraday Trans. 1* **77**, 3023 (1981).
23. Tawarah, K., and Hansen, R., *J. Catal.* **87**, 305 (1984).
24. Dandy, A., *J. Chem. Soc.*, 5956 (1963).
25. Dohse, H., *Z. Phys. Chem. B* **8**, 159 (1930).
26. Huffman, J., and Dodge, B., *Ind. Eng. Chem.* **21**, 1056 (1929).
27. Smith, D., and Hauk, C., *J. Phys. Chem.* **32**, 415 (1928).
28. Morelli, F., Giorgini, M., Guerrini, R., and Tartarelli, R., *J. Catal.* **27**, 471 (1972).
29. Morelli, F., Giorgini, M., and Tartarelli, R., *J. Catal.* **26**, 106 (1972).
30. Nagao, M., and Morimoto, T., *J. Phys. Chem.* **84**, 2054 (1984).
31. Uchida, H., and Ogino, Y., *Bull. Chem. Soc. Japan* **29**, 587 (1956).
32. Fuderer-Luctic, P., and Sviben, I., *J. Catal.* **4**, 109 (1965).