JOURNAL OF CATALYSIS **101,** 90–102 (1986)

Methanol Synthesis Mechanism over Zirconium Dioxide

NANCY B. JACKSON AND JOHN G. EKERDT

Department of Chemical Engineering, University of Texas, Austin, Texas 78712

Received November 19, 1985; revised April 18, 1986

The source and role of oxygen in the formation of carbonates, formate, methoxide, and methanol were studied over zirconium dioxide at 1 atm. Temperature-programmed and steady-state reaction techniques and ^{18}O-labeled reactants were used. Water was required to produce methanol; however, none of the oxygen from water was incorporated into the methanol. The data indicated that carbonate species formed from carbon dioxide and a water-based hydroxyl group whereas formate formed between CO and a different hydroxyl group, which may be a bridging hydroxyl group. The labeling studies are consistent with a formate-to-methoxide mechanism for methanol synthesis and suggest the nature of the active surface sites for this mechanism. © 1986 Academic Press, Inc.

I. INTRODUCTION

A previous report from our laboratory (*1*) reported that methanol was synthesized over ZrO_2 in the presence of $CO/H_2/H_2O$ and that methane was synthesized in the presence of CO/H_2. A mechanism was proposed in which a methoxide species was the common intermediate to methane and methanol, and in which the methoxide was either hydrolyzed or hydrogenated to methanol or methane, respectively. Additional studies (*2, 3*) have suggested that CO interacts with the ZrO_2 surface to form a formate and that the formate is hydrogenated to the methoxide.

Methanol synthesis mechanisms have been discussed in recent reviews (*4–6*). Three mechanisms have been proposed over metal oxides. The formate-to-methoxide mechanism is the only mechanism of the three that involves interaction of CO with lattice oxygen and with the potential for incorporation of lattice oxygen into methanol (*4, 6, 7*). The other two mechanisms, formyl-to-enol (H_2COH) (*4, 5*) and adsorbed formaldehyde (*4*), proceed without cleavage of the C–O bond of carbon monoxide. A series of ^{18}O-labeling experiments was carried out over ZrO_2 to determine whether the Zr–OCH_3 or the ZrO–CH_3 bond was being hydrolyzed and if lattice oxygen was incorporated into methanol. The incorporation of lattice oxygen would support earlier publications (*1–3*) that, on the basis of different techniques, had reasoned that the formate to methoxide route was followed over ZrO_2.

II. METHODS

The experimental apparatus is represented schematically in Fig. 1. The ZrO_2 was placed in a quartz tube. Water was added to the reactant stream by allowing the mixed-reactant gases to bubble through a saturator before entering the reactor. The saturator was designed to operate with approximately 1 ml of water and was maintained at room temperature for the experiments reported here.

The reactor effluent was monitored continuously using a UTI 100C quadrupole mass spectrometer and at discrete points in time by actuating an 8-loop gas sampling valve. Gas samples were subsequently analyzed on a Varian 2440 gas chromatograph equipped with a 1.83 m × 3.2 mm o.d. column of 0.2% Carbowax on 60/80 mesh Carbopak C.

Each series of temperature-programmed desorption (TPD) studies was started with a fresh 2-g charge of ZrO_2. The following steps were taken to produce methanol in a TPD experiment: (1) The ZrO_2 was treated

0021-9517/86 $3.00

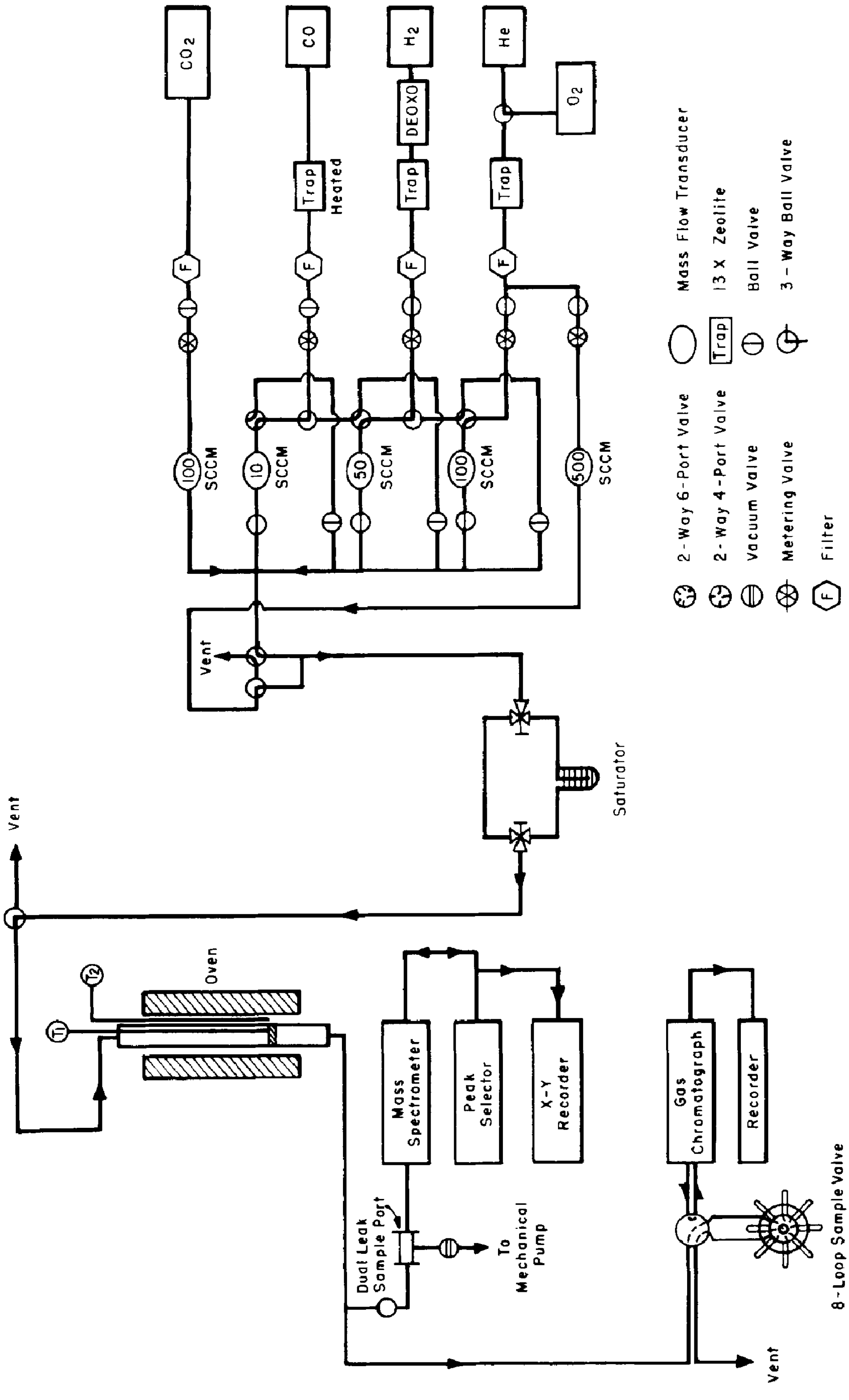


FIG. 1. Schematic of the experimental apparatus.

at 600°C for 10 min in flowing oxygen (30 cm^3/min), and after it was cooled to room temperature, the reactor was flushed with helium (30 cm^3/min) for 10–15 min. (2) The catalyst was exposed to a helium–water vapor stream at 25°C for 10 min. (3) The temperature was ramped linearly (ca. 1°/sec) from 25 to 600°C in a flowing stream of 1/1 H_2/CO (30 cm^3/min total). (4) The reactor was cooled to 25°C in 1/1 H_2/CO (30 cm^3/min) in no less than 20 min. (5) The temperature of the reactor was ramped linearly from 25 to 600°C in a flowing stream (30 cm^3/min) of 49/49/2 $H_2/CO/H_2O$. (6) The reactant stream was diverted past the saturator and the 1/1 H_2/CO stream was allowed to flow over the catalyst at 600°C for approximately 1 min before cooling to 25°C in no less than 20 min. The cycle was repeated by beginning with step 5.

The procedures for a steady-state experiment were similar to the initial procedures for a TPD experiment: (1) A fresh charge of ZrO_2 (approximately 2 g) was oxygen-treated at 600°C, cooled, and flushed with helium. (2) The temperature was ramped linearly from 25 to 600°C in a flowing stream of 1/1 H_2/CO and then cooled back to 25°C in about 10 min in the flowing stream. (3) A 1/1 H_2/CO mixture (30 cm^3/min) was directed through the water-filled saturator and the temperature was raised to the operating temperature. Reactor effluent was collected in the sample loops and was analyzed periodically during the experiment.

Blank activity of the reactor and the stainless steel-sheathed thermocouple, which touched the ZrO_2, was established. The thermocouple was withdrawn for most experiments.

Catalyst preparation. The ZrO_2 was made by slowly dissolving $ZrCl_4$ in distilled water. The resulting solution had a slight pinkish tinge and a pH of 2. Concentrated NH_4OH was added under constant stirring until the pH of the solution was just above 10.0. The white hydrous ZrO_2 was vacuum filtered and distilled water was slowly dripped through the hydrous ZrO_2 until the filtrate had a pH of 7. The hydrous zirconia was subsequently frozen in liquid nitrogen, dried for 20–24 hr at 120°C in zero air (air containing less than 1 ppm total organic carbon and less then 3 ppm water), and calcined for 4 hr at 600°C in zero air.

The X-Ray diffraction pattern was characteristic of monoclinic ZrO_2. Only a small peak was observed at 31°, the characteristic angle for tetragonal ZrO_2 (*8*). The N_2 BET area ranged from 30 to 36 m^2/g.

Hydrous zirconia has been found to be a good ion exchanger (*9*). Hydroxyl groups can be displaced by anions and, additionally, anions have been found to be trapped within the hydrated zirconia and may be later incorporated into the crystal. Bulk chlorine analysis by Galbraith Laboratories, Inc. showed a batch of monoclinic ZrO_2 made from $ZrCl_4$ having 50 ppm chlorine present. If the chlorine was distributed evenly throughout the zirconia, the surface would have a Zr/Cl mole ratio of 5750/1. Using the monoclinic lattice constants given in Ref. (*10*), a ratio of 600/1 would be calculated if all the chlorine atoms were on the surface.

Materials. The hydrogen used was chromatographic grade with a minimum purity of 99.98 mol%. It was sent through a Matheson oxygen-removing purifier before use. The carbon monoxide was purchased from Matheson and was 99.99 mol% pure. The CO was sent through a molecular sieve trap that was kept at 150°C or above. The helium flowed through a molecular sieve trap for water removal before use. The carbon dioxide was of ultrahigh purity, 99.6%. The oxygen was 99.6% pure and was used without further purification.

The $H_2{}^{18}O$ was purchased from Cambridge Isotope Labs (98% isotopically pure) and Isotec Inc. (97% isotopically pure). The $C^{18}O$, also purchased from Isotec Inc., had an isotopic purity of 95%.

III. RESULTS

The experimental results of this study are divided into two parts. The first is the

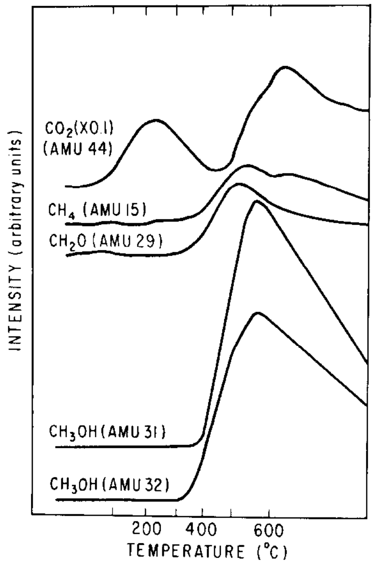


FIG. 2. Mass signals characteristic of the indicated molecules during the TPD experiment identified as step 5 under Methods.

results of the temperature-programmed desorption studies. The second covers the synthesis gas reactions run under steady-state conditions.

1. Temperature-Programmed Desorption Studies

Methanol may be generated during temperature-programmed heating in flowing CO/H_2 when water vapor is present in the reactant stream. In order to produce methanol in a TPD reaction over zirconia, all six steps outlined under Methods must be followed.

The result of step 5, a methanol-producing TPD, is shown in Fig. 2. As can be seen from Fig. 2, methanol desorbed at an average temperature of 580°C and methane at an average of 600°C. These desorption temperatures remained relatively constant for all catalyst batches and all sample sizes. At about 500°C, AMU 29 shows a small peak and, presumably, this was formaldehyde (*11*). Carbon dioxide desorbed at two different temperatures, 200–250°C (occasionally as high as 300°C) for the low temperature CO_2 ($LTCO_2$) and 580–620°C for the high temperature CO_2 ($HTCO_2$). Occasionally, it appeared that a small CO_2 peak at about 570–580°C was being hidden by the $HTCO_2$ peak.

This TPD process may be repeated at least nine times on the same charge of catalyst as long as the catalyst is not exposed to air and as long as steps 5 and 6 are repeated as specified above. The preadsorption of H_2/CO in the cooling cycle was critical to the formation of methanol. The longer the H_2/CO cooling cycle lasted, the greater the methanol AMU 31 and 32 peaks were. If cooling was done in flowing He, whether or not water was included in the reactant stream, methanol was not produced, but methane was, and the low temperature CO_2 failed to form.

The above-described work was based on methanol formation over an Alfa-Ventron monoclinic ZrO_2 powder with a 5.8 m^2/g BET area (*1*). The methanol peak in the previous study (*1*) was observed at 125°C under conditions similar to those reported under Methods. The amount of 30–36 m^2/g ZrO_2 placed in the quartz tube was varied to determine if the large differences in temperatures between this study (580–620°C) and the earlier study were associated with extensive readsorption. Methanol was consistently formed at 580–620°C. The temperature difference cannot be associated with residual chlorine because 25 m^2/g monoclinic ZrO_2 prepared from zirconyl nitrate also produced methanol at ca. 580°C (*12*). An explanation for the large differences in the temperatures at which methanol desorption was observed for these two samples was not established in this work.

If H_2O was added to H_2/CO in the cooling (or H_2/CO preadsorption) cycle, then methanol was not found in the subsequent TPD step. Methane was evolved at 600°C, and both the high and low temperature carbon dioxide peaks were seen. The AMU 29 peak was not seen.

Another essential step in generating

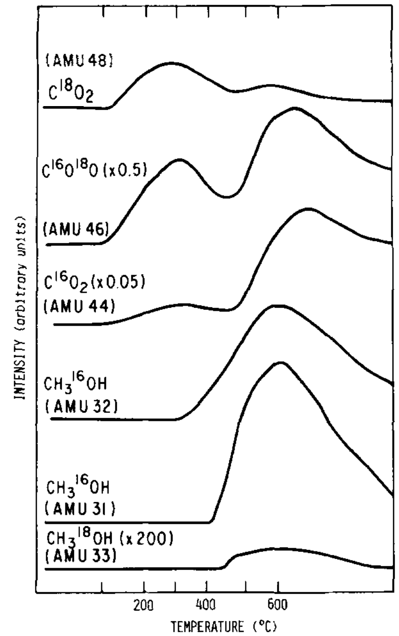


FIG. 3. Mass signals characteristic of the indicated molecules during a methanol-generating TPD experiment using $H_2/C^{16}O/H_2{}^{18}O$.

methanol in the temperature-programmed desorption studies was the preadsorption of water before the catalyst was exposed to H_2/CO as described in step 2. When this step was eliminated, methanol was either nonexistent or substantially diminished.

Methanol was also formed on zirconia when the oxygen pretreatment in step 1 was followed by a 10-min exposure to H_2 at 600°C. Exposing ZrO_2 to H_2 at high temperatures has been seen to increase the water on the surface (*12*).

If water was not present in the H_2/CO reactant stream in step 5, methane, not methanol, formed and desorbed as its characteristic temperature of 600°C. Both the low and high temperature CO_2 peaks were greatly decreased, but the decrease was more significant in the $HTCO_2$ peak.

In order to understand the role of water in the methanol formation mechanism better, the standard methanol-generating TPD experiment was repeated using $H_2{}^{18}O$, $C^{16}O$, and H_2. The results are shown in Fig. 3. Less than 1% of the methanol that formed incorporated oxygen from the water to make $CH_3{}^{18}OH$. This experiment was repeated many times, and twice the cycle was repeated 8–10 times on the same catalyst. The ratio of $CH_3{}^{18}OH/CH_3{}^{16}OH$ never increased to more than what is shown in Fig. 3. In fact, quite often the amount of $CH_3{}^{18}OH$ was less. Although not shown, methane was also formed and desorbed at 600°C. Also, $C^{18}O$ began desorbing at 550°C and continued at a constant level at temperatures greater than 550°C. Three different AMUs were monitored corresponding to the carbon dioxides incorporating various amounts of labeled oxygen. The low temperature CO_2 contained proportionally more of the labeled oxygen from $H_2{}^{18}O$ than the high temperature CO_2. Table 1 lists the percentages of oxygen-labeled carbon dioxide from a typical $H_2/C^{16}O/H_2{}^{18}O$ TPD experiment.

The standard methanol-generating TPD experiment was also run using $H_2/C^{18}O/H_2{}^{16}O$ and the TPD is shown in Fig. 4. Due to the cost of $C^{18}O$, only two methanol-producing cycles were run on the same catalyst. Sixty-four percent of the methanol produced in the two runs contained oxy-

TABLE 1

CO_2 Isotope Distributions during Temperature-Programmed Heating

	Peak area (%)	
	Low temperature peak	High temperature peak
I. TPD in $H_2/C^{16}O/H_2{}^{18}O$[a]		
$C^{16}O_2$ (AMU 44)	60	87
$C^{16}O^{18}O$ (AMU 46)	34	10
$C^{18}O_2$ (AMU 48)	6	3
II. TPD in $H_2/C^{18}O/H_2{}^{16}O$		
$C^{16}O_2$ (AMU 44)	8	11
$C^{16}O^{18}O$ (AMU 46)	38	43
$C^{18}O_2$ (AMU 48)	54	46

[a] The amount of labeled CO_2 desorbing increased during the first several runs and then leveled out. The numbers are taken from a typical TPD experimental after the constant level had been reached.

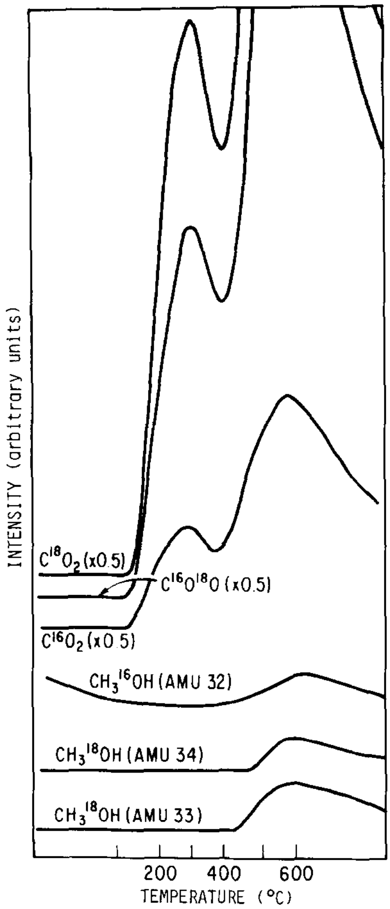


FIG. 4. Mass signals characteristic of the indicated molecules during a methanol-generating TPD experiment using $H_2/C^{18}O/H_2{}^{16}O$.

gen-18. The methanol was 68% $CH_3{}^{18}OH$ in the first cycle and 59% $CH_3{}^{18}OH$ in the second. The percentage of isotopic carbon dioxide desorbed at both the low and high temperatures during the second run is reported in Table 1.

An experiment was performed that involved adsorbing methanol onto oxygen-treated zirconia. Desorbing preadsorbed methanol into flowing He or H_2 gave two methanol peaks, one at 250°C and one at 480°C. With either H_2 or He as the flushing gas, the higher temperature methanol peak was slightly larger than the lower temperature peak. Desorption of preadsorbed methanol into flowing He or H_2 saturated with H_2O also gave two methanol peaks. However, the low temperature peak was almost twice as large as the high temperature peak when water was present in the flushing stream. When preadsorbed methanol was desorbed into $He/H_2{}^{18}O$, 3% of the methanol desorbed contained oxygen-18. Table 2 compares this result with the amount of methanol incorporating oxygen-18 made in the $H_2/C^{18}O/H_2{}^{16}O$ and $H_2/C^{16}O/H_2{}^{18}O$ TPD experiments.

Two different temperature-programmed desorption experiments were conducted using carbon dioxide. In the first, CO_2 was used instead of H_2O in step 5 (see Methods). Methane was formed and methanol was not formed. In the second, CO_2 was used instead of CO in steps 3–6. Neither methane nor methanol was generated when CO_2 was the sole carbon source. A large off-scale peak for AMU 32, probably oxygen, was produced during step 3 when water was not present and during step 5 when water was present.

2. *Steady-State Experiments*

Methanol may be generated over zirconia in flowing H_2/CO if water vapor is present and steps 1–3 described under Methods for a steady-state experiment are followed. A plot of the rate of methanol produced following CO/H_2 preadsorption versus time at 290°C is shown in Fig. 5. No appreciable amount of methane was found at this temperature. The rate of methanol formation decreased rapidly with time. Regeneration

TABLE 2

Methanol Isotope Distributions during Temperature-Programmed Heating

	$CH_3{}^{16}OH$ (%)	$CH_3{}^{18}OH$ (%)
$H_2/C^{18}O/H_2{}^{16}O$[a] TPD	36	64
$H_2/C^{16}O/H_2{}^{18}O$ TPD	97	3
Preadsorbed $CH_3{}^{16}OH$ subjected to $He/H_2{}^{18}O$ TPD	97	3

[a] The $C^{18}O$ was 95% isotopically pure.

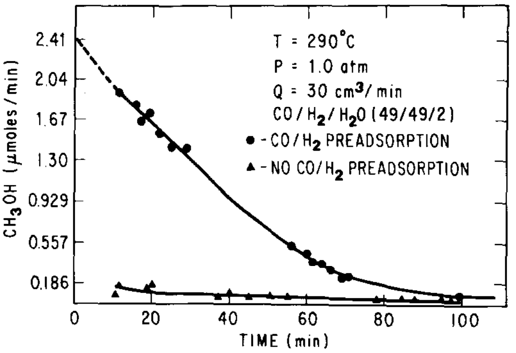


FIG. 5. Rate of methanol formation versus time in flowing $CO/H_2/H_2O$ at 290°C.

was tried following a steady-state experiment by oxidizing the ZrO_2 at 600°C and subsequently cooling to 25°C in H_2/CO. The regenerated ZrO_2 (not shown) was approximately one-fourth as active as the fresh ZrO_2.

Steady-state experiments were also performed without the preadsorption of H_2/CO as described in step 2. The rate versus time results are shown in Fig. 5. The rate of methanol formation remained more constant and was much lower when H_2/CO was not preadsorbed.

It appeared that the methanol precursor formed on the available sites during cooling in H_2/CO and these precursors were titrated off with a $H_2/CO/H_2O$ stream. Three different catalyst pretreatments were made on the same batch of catalyst, and the amount of methanol titrated off the surface at 290°C was measured. The results are presented in Table 3. Oxygen treatment at 600°C for 10 min had the same effect as treatment in helium at 700°C for 3 hr. However, high temperature oxygen treatment followed by a 10-min exposure to hydrogen at 600°C had the effect of quadrupling the amount of methanol formed.

Since methanol was not made without water being present in the reactant stream, the percentage of water was increased from 2 to 12% to see whether this would increase the rate of methanol formed. The rate of methanol formation following H_2/CO preadsorption was decreased rather than increased with the increased partial pressure of water. The amount of methanol made with 12% water was a factor of 4 smaller than the amount made with 2% water.

Since methane and methanol are believed to come from the same precursor, methoxide (*1*, *13*), an attempt was made to see whether methane could be generated catalytically over zirconia at higher temperatures. The system was cooled in flowing H_2/CO from 600°C and then raised to 480°C in H_2/CO. The rate of methane formation may be seen in Fig. 6. Methane was formed and the rate at which it formed decreased rapidly with time similar to methanol formation at 290°C with H_2/CO preadsorbed on the catalyst.

Methane was also synthesized at 480 and 570°C without preadsorption of H_2/CO. Figure 7 presents the observations at 570°C. Both methane and methanol were produced at 570°C. The rate of formation at 570°C did not show the rapid decay evidenced at lower temperatures.

IV. DISCUSSION

Oxygen-18 Labeling Studies

The source of oxygen in the methanol product was investigated using ^{18}O-labeled CO and H_2O. Because water was required to form methanol, three possible sources existed: (1) carbon monoxide, (2) water, and (3) lattice oxygen of zirconia. The term lattice oxygen must include adsorbed oxygen ions and lattice oxygen anions because

TABLE 3

Methanol Yields at 290°C following Various Pretreatments

Pretreatment	Molecules MeOH formed/cm²[a]
O_2 600°C 10 min	6.6×10^{13}
He 700°C 3 hr	6.8×10^{13}
O_2 600°C 10 min followed by H_2 600°C 10 min	27.6×10^{13}

[a] Integrated yield over the first 112 min.

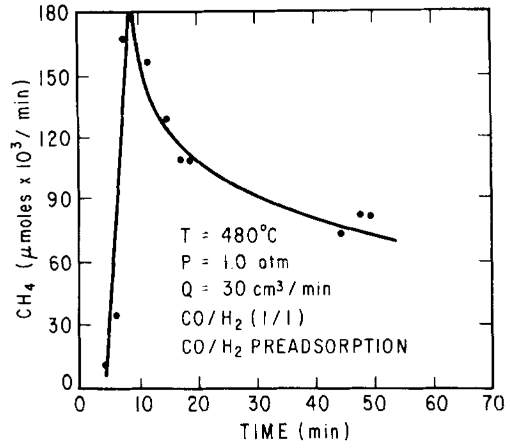


FIG. 6. Rate of methane formation versus time in flowing CO/H_2 at 480°C following CO/H_2 preadsorption.

no attempt was made to discriminate between them in this study. The $H_2/C^{16}O/H_2{}^{18}O$ TPD study (Table 2) revealed that there was negligible direct incorporation of oxygen from water during the formation of methanol. The $H_2/C^{18}O/H_2{}^{16}O$ TPD study produced a mixture of [^{16}O] and [^{18}O]methanol. Since the ^{16}O did not come from water, the interaction of CO with ZrO_2 must proceed through intermediates that permit C–O bond scission and incorporation of lattice oxygen into the methanol precursor.

The manner in which CO interacts with the ZrO_2 surface has been proposed in previous studies (*2*, *3*). The methanol and methane precursor was reasoned to be a methoxide species (*1*) that formed via a formate species. The labeling studies are consistent with this mechanism and provide additional insight into formate formation as well as other oxygen-containing surface species. These points are discussed below.

Two carbon dioxide peaks were consistently generated in the TPD experiments. Previous studies identified the $LTCO_2$ peak as coming from carbonate/bicarbonate species and the $HTCO_2$ peak as coming from a formate (*2*, *14*). The isotope distributions for these peaks (Table 1) suggest that the surface species are formed by different routes.

The $C^{16}O/H_2{}^{18}O$ study results permit one to group the source of oxygen in the CO_2 either as CO and lattice oxygen or as water. Similarly the $C^{18}O/H_2{}^{16}O$ study groups the source of oxygen either as CO or as lattice oxygen and water. For example, the $C^{16}O/H_2{}^{18}O$ study revealed that 23% of the total number of oxygen atoms in the $LTCO_2$ peak were from water. (Out of 100 CO_2 molecules, 34 ^{18}O atoms came from $C^{16}O^{18}O$ and 12 ^{18}O atoms came from $C^{18}O_2$, $(34 + 12)/200 = 0.23$.) Likewise, 77% of the oxygen atoms in the $LTCO_2$ peak for this experiment came from CO and the lattice.

The results of the $C^{16}O/H_2{}^{18}O$ and $C^{18}O/H_2{}^{16}O$ studies can be combined with a total oxygen balance. (The fractions of oxygen from CO, lattice oxygen, and water must sum to unity.) The three resulting equations were solved for the fraction of each oxygen source in the CO_2. The results are listed in Table 4. The values listed in Table 4 should not be taken as absolute for several reasons: (1) The $C^{18}O$ was only 95% isotopically pure, (2) the peak areas assigned to $LTCO_2$ and $HTCO_2$ (Table 1) from Figs. 3 and 4 have some uncertainty associated with them because the CO_2 peaks were not well resolved, and (3) an internal standard was not present in the feed gas to check that the catalyst was exposed to the identical feed conditions for each experiment.

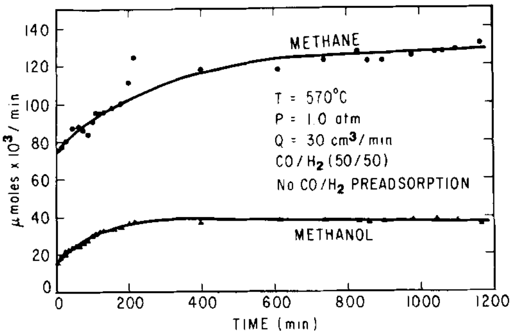


FIG. 7. Rates of methane and methanol formation vs time in flowing CO/H_2 at 570°C without CO/H_2 preadsorption.

TABLE 4

Calculated Oxygen Source for CO_2

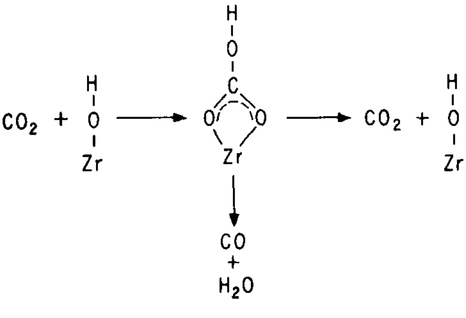
	Low temperature peak (at.%)	High temperature peak (at.%)
Carbon monoxide	73	67
Lattice oxygen	4	25
Water	23	8

Both CO_2 peaks incorporate approximately the same amount of CO oxygen. The balance of the oxygen in the CO_2 peaks appears to come from different sources, water for the $LTCO_2$ and lattice oxygen for the $HTCO_2$. Some of the CO oxygen that was incorporated into the CO_2 may be associated with the oxygen left behind during the formation of CH_4. The amount of methane formed (see Fig. 2) is insufficient to account for the amount of CO oxygen in excess of 50% that was calculated to incorporate into CO_2. The discrepancy in the oxygen balance may be associated with the reasons listed above. The oxygen balance does strongly suggest that, in addition to CO, $LTCO_2$ incorporated a different source of oxygen than $HTCO_2$.

The $LTCO_2$ never formed when the catalyst was cooled in He between CO/H_2 cycles. The surface species producing this CO_2 must be formed from something made at higher temperatures that was present over the catalyst during the cooling cycle. Carbon dioxide desorbed at high temperatures and was present in the system whenever CO was also present at high temperatures. Infrared studies have shown CO_2 to interact with zirconia to form primarily surface bicarbonates and carbonates. Carbon monoxide adsorbed on catalyst made in this study showed adsorption of primarily the formate species in the IR with only a small bicarbonate peak (*15*).

Since this $LTCO_2$ derived the balance of its oxygen from water, it is proposed that a bicarbonate forms over zirconia by a CO_2 molecule interacting with a water-based hydroxyl group. This mechanism of bicarbonate formation is more probable than direct oxidation of the formate by water to the bicarbonate because CO_2 must form before the $LTCO_2$ is seen. Formate has been seen in the IR after exposure to CO at temperatures as low as 225°C (desorption temperature of $LTCO_2$); but the presence of water in the CO/H_2 reactant stream at this temperature did not lead to $LTCO_2$ desorption unless H_2/CO was preadsorbed and substantial amounts of CO_2 had a chance to form. This interaction of CO_2 with a water-based hydroxyl group is further supported by the observation that the amount of oxygen in the $LTCO_2$ from water increased during the first several runs and then evened out to a constant level.

From the evidence gathered in this study, it would be difficult to distinguish between the bicarbonate and carbonate since both desorbed from the surface as CO or CO_2. Since the species creating the $LTCO_2$ came from a CO_2 and a hydroxyl group, the bicarbonate was the likely species to be formed and desorbed as the $LTCO_2$ as shown in Scheme I. However, the species formed from CO_2 interaction with the hydroxyl could have been immediately oxidized to a carbonate. It is more likely that the low temperature CO_2 was a bicarbonate and, when oxidized, was a carbonate that desorbed at temperatures close to 600°C as the third CO_2 peak that was obscured by the $HTCO_2$.



SCHEME I

At about the same temperature at which carbon dioxide first began to desorb, carbon monoxide appeared with an oxygen exchanged from water. This CO oxygen exchange reaction could come from the bicarbonate forming and immediately desorbing as carbon monoxide at the higher temperatures (Scheme I).

Evidence indicates that the formate is made from CO and a surface hydroxyl group (*3*). However, the CO_2 from formate incorporates very little oxygen from water. This would imply that if formate does come from a CO molecule and a surface hydroxyl, then the oxygen of this hydroxyl group does not come from water. The source of oxygen in the CO_2 from the bicarbonate indicates that the CO_2 interacts with a water-based hydroxyl group. Therefore, this implies the hydroxyl groups in these two reactions are different. Two hydroxyl groups, terminal and bridged, are seen on the surface of zirconia and it seems likely that the terminal hydroxyl, which is known to be the less stable hydroxyl group (*16*), is the one that exchanges oxygen with water. If this is the case, the bicarbonate forms from the interaction of CO_2 with a terminal, water-based hydroxyl group and, therefore, the formate forms from a bridged hydroxyl.

The Active Site for CO Conversion

Preadsorption of CO/H_2 from 600 to 25°C was necessary to generate significant amounts of methanol during the TPD and steady-state experiments, suggesting that the methanol precursor formed during preadsorption. The length of the cooling cycle was directly proportional to height of the methanol TPD peak for cooling times between 20 and 30 min. Beyond a 30-min cooling time, the increase in the methanol peak was small compared to the additional cooling time. Therefore, the amount of methanol formed may give an indication of the number of active sites at which methoxide, the immediate precursor to methanol, formed.

Table 3 lists the methanol yields during steady-state experiments. Oxygen and helium pretreatment produced equivalent amounts of methanol, whereas hydrogen pretreatment appeared to increase the number of sites by a factor of four. Hydrogen reacts with ZrO_2 to make water on the surface (*12, 13*). The formation of water should involve a partial reduction of the zirconia surface creating oxygen vacancies. We propose a mechanism in the next section that involves CO interacting with an oxygen anion vacancy. Part of the enhancement observed for H_2 pretreatment may be due to the expected increase in anion vacancies. Hydrogen may also act to increase the concentration of bridged-hydroxyl groups. These hydroxyl groups may be involved in formate formation and its reduction to the methoxide.

The temperature reached during pretreatment, 600°C, and during the initial temperature ramping in H_2/CO was sufficient to cause water to desorb before CO/H_2 was preadsorbed. Water desorption was observed to begin at 450°C during ramping in flowing H_2/CO. The surface contained molecular water and hydroxyl groups following any of the pretreatment procedures. Attempts to quantify changes in the amounts of linear and bridged hydroxyls and adsorbed water following the different pretreatments or heating to 600°C in H_2/CO using infrared spectroscopy were unsuccessful. The infrared bands were poorly resolved and were not sufficiently reproducible to provide meaningful spectra. It seems reasonable to assume that the surface was not saturated with molecular water and was partially dehydroxylated prior to preadsorption of H_2/CO from 600 to 25°C.

When water was introduced along with CO and H_2 during preadsorption, methanol was not made. It appears that water occupied the active site for methoxide formation and/or prevented the formation of the methoxide species. Water displaces methoxide from the surface during the formation of methanol. Water is known to adsorb dissociatively on the Zr cations (*17*) producing both linear and bridged hydroxyl groups (*18*). The sites at which methoxide forms may also be sites at which water adsorbs dissociatively.

Water did not appear to prevent the formate from forming; it was the methoxide formation which appeared inhibited, in part, by water. In fact, water seemed to play a role in surface formate production. The $HTCO_2$, which came from the formate (*2*), decreased when water was removed from the reactant stream during TPD experiments. Also, the amount of oxygen from water in the $HTCO_2$ increased when H_2O was present in the H_2/CO preadsorption stream. The zirconia surface needed to be exposed to water following oxygen treatment in order for methanol to form in the TPD experiments. This may indicate the need for hydroxyl groups in CO hydrogenation on ZrO_2. Without the water pretreatment, the population of hydroxyl groups, following exposure to H_2/CO at 600°C, may have been too low for the methoxide to form.

During steady-state experiments increasing the water vapor in the reactant stream above a certain point decreased the amount of methanol titrated from zirconia during a steady-state reaction. Since most of the methanol precursor was presumed to be formed during the H_2/CO preadsorption step, the excess water may have, in this case, played the role of an oxidizing agent, decreasing the amount of methoxide on the surface.

Mechanism for CO Conversion to Methanol

The formate and methoxide species appeared to have the same oxygen origin, CO and lattice oxygen. This observation suggests a connection between the formate and methoxide species on the surface. Such a connection is important because while formate is observed (using infrared spectroscopy) to form from CO (*15*) we have been unable to reduce this formate species to the methoxide in an infrared cell using an atmosphere of H_2 and temperatures as high as 500°C (*12*). A possible reason could be that the surface needs to be kept saturated with formate species for a measurable amount of methoxide species to form via formate hydrogenation. The steady-state experiments at 480°C revealed methane could be synthesized for periods up to 2 hr, suggesting that under a constant pressure of CO/H_2 the methoxide species forms below 500°C.

Water was required to make methanol in the TPD studies. Water presumably formed during the surface reduction which must occur to complete the catalytic cycle during methane synthesis over a metal oxide. This would have provided the source of water for the experiment listed in Fig. 7.

Even though it appeared water was responsible for breaking the oxygen–zirconium bond of the methoxide, a water-based hydroxyl group did not remain on the surface and interact with CO to make a formate or a methoxide. This could have been due, in part, to the need to maintain the reactor at 600°C for approximately 1–2 min in flowing H_2/CO following a temperature-programmed heating cycle in $H_2/CO/H_2O$. This may have provided ample time for the water-based hydroxyl groups to desorb. Water-based hydroxyl groups may also be lost through their proposed reaction with CO_2.

A proposed mechanism for CO reduction over ZrO_2 is presented in Fig. 8. The formate-to-methoxide mechanism is consistent with previous studies over ZrO_2 (*1–3*) and accounts for the experimental results reported here. Carbon monoxide reacts with a zirconium cation that has an adjacent oxygen vacancy and a bridged-hydroxyl group attached to it. The hydroxyl hydrogen reacts with CO (*3*) to form a formate. The formate is reduced to the methoxide via the oxymethylene. The sites where the hydrogens, participating in the reduction, originate are unknown. Evidence for the oxymethylene has been discussed previously (*3*); we can offer no additional arguments for or against its role in the reduction

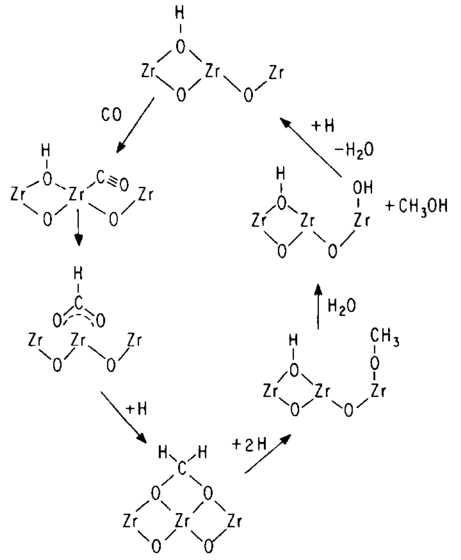
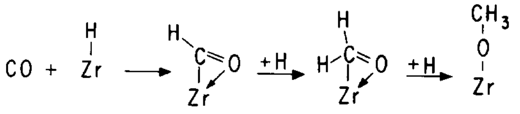


FIG. 8. Proposed methanol synthesis mechanism over ZrO_2.

process. The reduction of the oxymethylene to a methoxide could lead to the second oxygen of the formate forming a bridged oxygen or the bridged-hydroxyl group that is shown. Water exchanges with the methoxide leaving behind a hydroxyl group that must eventually desorb to regenerate the active site.

Other mechanisms could be considered. A dizirconium homogeneous complex has been shown to hydrogenate CO to the methoxide (*19*). The intermediate involved a zirconium atom bonded to both the carbon and oxygen of a formyl, in a type of three-sided cyclic resonance structure. Since the formate has never been satisfactorily shown to convert directly to the methoxide (*1*, *3*, *12*), this type of formyl structure may occur on the ZrO_2 surface and lead to the methoxide, as shown in Scheme II, rather than the formate-to-methoxide route proposed in Fig. 8. This formyl mechanism does not directly account for the large amount of lattice oxygen found in methanol (Table 2), since, in this mechanism, the C–O bond is never broken. Any inclusion of lattice oxygen in the methoxide could come from CO produced by the CO–lattice-oxygen exchange reaction of the formate. However, the data in Table 2 for $H_2/C^{18}O/H_2{}^{16}O$ were obtained in a large excess of $C^{18}O$. The formyl mechanism would require that the overwhelming majority of the methanol be $CH_3{}^{18}OH$. We feel our data are better accounted for with the formate-to-methoxide mechanism; the formyl-to-methoxide scheme was presented because it cannot be ruled out on the basis of our data.



SCHEME II

V. CONCLUSIONS

(1) Oxygen that went into forming methanol came from either CO or the ZrO_2 lattice, but not from water.

(2) Carbonate/bicarbonate was proposed to form over ZrO_2 by CO_2 interaction with a water-based hydroxyl group.

(3) Formate and methanol showed similar sources of oxygen; most came from CO or the lattice.

(4) Carbonate/bicarbonate and formate formation was proposed to involve the reaction of different hydroxyl groups, terminal and bridged, respectively.

(5) The data support a formate-to-methoxide mechanism.

ACKNOWLEDGMENTS

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE–AS05–80ER10720.

REFERENCES

1. He, M-Y., and Ekerdt, J. G., *J. Catal.* **90,** 17 (1984).
2. He, M-Y., and Ekerdt, J. G., *J. Catal.* **87,** 238 (1984).
3. He, M-Y., and Ekerdt, J. G., *J. Catal.* **87,** 381 (1984).
4. Klier, K., "Advances in Catalysis," Vol. 31, p. 243. Academic Press, New York, 1982.

5. Kung, H. H., *Catal. Rev.* **22,** 235 (1980).
6. Denise, B., Sneeden, R. P. A., and Hamon, C., *J. Mol. Catal.* **17,** 359 (1982).
7. Sapienza, R. S., Sansone, M. J., Spaulding, L. D., and Lynch, J. F., *in* "Fundamental Research in Homogeneous Catalysis" (M. Tsutsui, Ed.), Vol. 3, Plenum, New York, 1979.
8. Davis, B. H., Ganesan, P., *Ind. Eng. Chem. Prod. Res. Dev.* **18,** 191 (1979).
9. Clearfield, A., Nancollas, G. H., and Blessing, R. H., *in* "Ion Exchange and Solvent Extraction" (J. A. Marinsky and Y. Marcus, Eds.), Vol. 5, p. 92. Dekker, New York, 1973.
10. McCullough, J. D., and Trueblood, K. N., *Acta Crystallogr.* **12,** 507 (1959).
11. Onishi, T., Abe, H., Maruya, K., and Domen, K., *J. Chem. Soc. Chem. Commun.*, 617 (1985).
12. Silver, R. G., The University of Texas at Austin, unpublished results.
13. Abe, H., Maruya, K., Domen, K., and Onishi, T., *Chem. Lett.*, 1875 (11) (1984).
14. He, M-Y., White, J. M., and Ekerdt, J. G., *J. Mol. Catal.* **30,** 415 (1985).
15. Ekerdt, J. G., Formate and methoxide intermediates in CO and CO_2 hydrogenation over metal oxides, *in* "Second China–U.S.–Japan Symposium on Heterogeneous Catalysis, Berkely, Calif., 1985.
16. Yamaguchi, T., Nakano, Y., and Tanabe, K., *Bull. Chem. Soc. Japan* **51,** 2482 (1978).
17. Agron, P. A., Fuller, E. L., Jr., and Holmes, H. F., *J. Colloid Interface Sci.* **52,** 553 (1975).
18. Tret'yakov, N. E., Pozdnyakov, D. V., Oranskaya, O. M., and Filimonov, V. N., Russ. *J. Phys. Chem.* **44,** 596 (1970).
19. Manriquez, J. M., McAlister, D. R., Sanner, R. D., and Bercaw, J. E., *J. Amer. Chem. Soc.* **100,** 276 (1978).