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Methanol Formation on Zirconium Dioxide

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The adsorption and reaction of CO, CO_2, H_2, CH_3OH, HCOOH, H_2CO, and $HCOOCH_3$ were studied over oxygen-treated ZrO_2. Temperature-programmed techniques were used in the presence of a flowing gas which always contained H_2. Infrared spectroscopy was used to examine the species formed upon H_2CO adsorption; oxymethylene, $H_2CO_2^-$, is proposed to form. Methanol formed at two temperatures, ca. 125 and 600°C. The mechanisms for formation are discussed; low-temperature methanol formed by hydrolysis of methoxide and high-temperature methanol formed by hydrogenolysis of a methyl formate-like surface species. © 1984 Academic Press, Inc.

I. INTRODUCTION

Methanol synthesis is an important industrial process which is predominantly conducted over metal oxide catalysts. Metal oxides are effective for methanol formation because they activate CO (or CO_2) and catalyze its hydrogenation without cleavage of the C–O sigma bond. The reaction mechanisms have been reviewed recently (*1–3*); three synthesis mechanisms are proposed over metal oxides. These synthesis mechanisms can be categorized according to the key intermediates involved; they are (1) the hydroxycarbene (HCOH)-enol (H_2COH) mechanism, (2) the formate ($HCOO^-$)-methoxide (CH_3O^-) mechanism, and (3) the adsorbed formaldehyde (H_2CO) mechanism.

Zirconium dioxide is an effective catalyst for the isosynthesis process (*4, 5*) in which CO is hydrogenated to branched alkanes with the major product being isobutane. Studies at 35 atm have suggested that C_4 products are formed by the reaction of a C_1 and a C_3 species; the chemical nature of these species was not revealed (*6*) and is currently under investigation. The isosynthesis process also produces oxygenated products, methanol and dimethyl ether, which were shown to be intermediate products (*4*).

The catalytic chemistry of the H_2/CO/CO_2/ZrO_2 system at 1 atm has been under investigation by the authors (*7–9*); these studies have been directed toward identifying the C_1 surface species which form over ZrO_2 and toward determining how these species form. Carbonate, bicarbonate, formate, and methoxide form over ZrO_2. Bicarbonate was hydrogenated to formate and the formate was reversibly hydrogenated to the methoxide (*8*). This hydrogenation behavior suggests that these C_1 surface species are possible intermediates for CO or CO_2 hydrogenation to hydrocarbon and oxygenated products. This paper examines the processes by which methanol forms as well as some C_2 species which form over ZrO_2.

II. METHODS

The details of the experimental apparatus and procedures are presented elsewhere (*7, 8*). The temperature-programmed desorption/temperature-programmed decomposition (TPD/TPDE) experiments were conducted at 1 atm using 2 g of ZrO_2 (1- to 3-μm powder with a 5.8-m^2/g BET area (Alfa-Ventron)). Fresh ZrO_2 was conditioned in flowing O_2 at 620°C for 0.5 hr and cooled to 25°C in flowing He. (The surface

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remains hydroxylated as long as the temperature is less than 750°C (*10*).) Following pretreatment, the ZrO_2 was exposed to the gas to be adsorbed as the temperature was increased to 620°C and reduced back to 25°C. The adsorption of vapors (H_2O, D_2O, HCOOH, CH_3OH, and $HCOOCH_3$) was accomplished by bubbling He (30 ml/min) through the liquid and passing the He/vapor mixture over the ZrO_2; the liquid and quartz reactor were maintained at 25°C. Formaldehyde was generated by decomposing paraformaldehyde at 80°C and directing the formaldehyde/He mixture over 25°C ZrO_2. The TPD/TPDE step involved heating the ZrO_2 at 1°C/sec in the presence of a carrier and/or reacting gas while monitoring the reactor effluent with a mass spectrometer.

The infrared (ir) measurements were recorded with the ZrO_2 wafer at 25°C. The ZrO_2 wafer was conditioned at 500°C in O_2 overnight and evacuated to 9.7×10^{-4} Torr and cooled under vacuum to 25°C prior to adsorbing any gas.

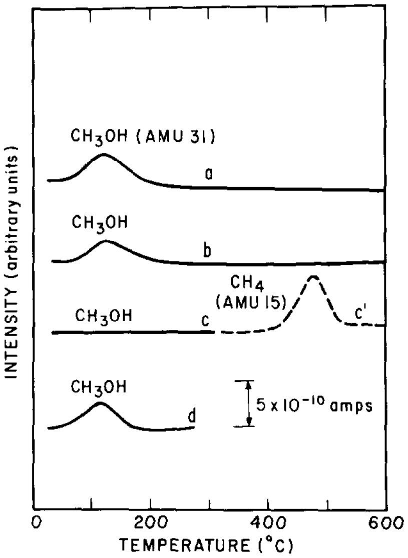


FIG. 1. Methanol formation over ZrO_2 at 100–200°C where (a) represents the methanol signal during temperature-programmed heating of H_2O-treated ZrO_2 in H_2/CO (1/1, 30 ml/min); (b) represents the methanol signal during temperature-programmed heating of ZrO_2 in $H_2/H_2O/CO$; (c) represents the methanol signal during temperature-programmed heating of ZrO_2 in H_2/CO; (c') represents the methane signal for experiment c; and, (d) represents the methanol signal upon reconnection of H_2O and repeating experiment b.

III. RESULTS

1. Methanol Formation at Low Temperature

Methanol was catalytically synthesized at low temperature (ca. 125°C) during temperature-programmed heating in H_2/CO when water was either preadsorbed at 25°C or present in the H_2/CO mixture. (Hydrogen was bubbled through 25°C water and mixed with CO.) The results shown in Fig. 1 represent a sequence of experiments over the same charge of ZrO_2. Oxygen-treated ZrO_2 was exposed to water vapor at 25°C for 0.25 hr prior to recording curve a. For b–d the ZrO_2 was cooled to 25°C in H_2/CO prior to initiating the temperature-programmed process. Temperature-programmed heating in the absence of water (Figs. 1c and c') resulted in a methane signal at 480°C.

2. Methanol Formation at High Temperature

Methanol was generated in a noncatalytic reaction in a variety of experiments (see below) provided a fresh charge of ZrO_2 was not exposed to H_2 in the absence of CO or CO_2 at temperatures in excess of 500°C following oxygen treatment. Figure 2, which is representative of the TPD/TPDE spectra, demonstrates that methanol was generated at 600°C during temperature-programmed heating in 1/1 H_2/CO_2. Methanol was also observed ca. 600°C during temperature-programmed heating in 1/1 H_2/CO, and following preadsorption of CO or CO_2 with subsequent heating in H_2. Approximately (within a factor of 2.5) equal amounts of methanol were detected for preadsorbed CO, and for flowing H_2/CO and H_2/CO_2. Preadsorbed CO_2 resulted in the largest methanol signal; 5 times larger than that

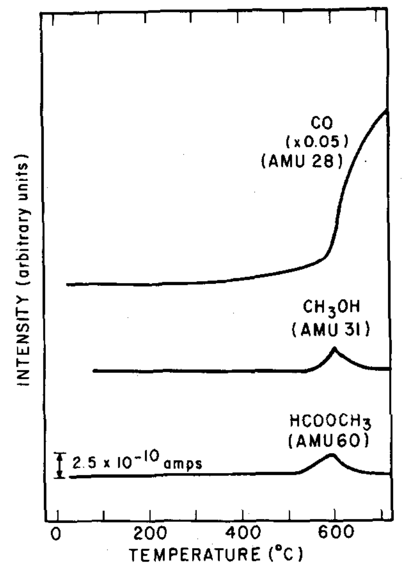


FIG. 2. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen-treated ZrO_2, without preadsorption into H_2/CO_2.

shown in Fig. 2 and 9 times larger than that observed for preadsorbed CO.

Multiple products appeared during the TPD/TPDE experiments listed above. A signal of atomic mass unit (AMU) 60, which was assigned to methyl formate, was detected in parallel with CH_3OH during heating in H_2/CO_2 and H_2/CO. Temperature-programmed heating in H_2/CO resulted in a signal for AMU 45 at 540–580°C. This signal could be assigned to either ethanol or dimethyl ether; the complicated fracturing pattern resulting from the simultaneous appearance of methanol and methyl formate prevented us from making an assignment for AMU 45. Methane formed ca. 460–500°C following preadsorption of CO or CO_2, consistent with a previous study (*7*).

The temperature-programmed process in flowing $H_2/H_2O/CO_2$ resulted in a spectrum similar to that presented in Fig. 2. A signal for AMU 45 was also detected at 580°C. No methanol was formed at a low temperature in this experiment.

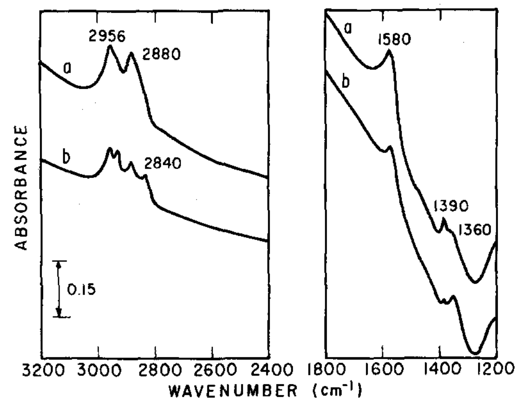


FIG. 3. Infrared spectra recorded after the adsorption of H_2CO and (a) evacuation at 150°C; (b) exposure of the evacuated surface to H_2 at 350°C.

3. Adsorption and Hydrogenation of H_2CO, CH_3OH, HCOOH, and $HCOOCH_3$

The adsorption of H_2CO and reduction of the resulting species were investigated by FTIR. Figure 3a was recorded after evacuation at 150°C for 0.25 hr. The peaks at 2880, 1580, 1390, and 1360 cm^{-1} are assigned to formate (*8*) which formed upon oxidation of formaldehyde or formaldehyde-induced species over ZrO_2. A strong absorbance band at 2956 cm^{-1} and a weak absorbance band at 2928 cm^{-1} were also present following evacuation. Hydrogenation of the surface species in spectrum 3a at 350°C, 300 Torr H_2 followed by evacuation produced spectrum 3b. The formate bands at 2880, 1580, and 1390 cm^{-1} and the band at 2956 cm^{-1} were attenuated. The band at 2928 cm^{-1} became more apparent and a new band appeared at 2840 cm^{-1}.

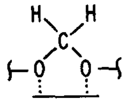
A series of TPD/TPDE experiments was performed in which H_2CO, CH_3OH, HCOOH, and $HCOOCH_3$ were adsorbed on oxygen-treated ZrO_2. Multiple products formed at different temperatures during TPD/TPDE in H_2; in all cases methanol was generated at temperatures ranging from 540 to 610°C. Methane was observed at 510°C during the TPD/TPDE of H_2CO induced surface species into H_2. Methyl formate was also adsorbed and subjected to TPD/TPDE into He. In this case a methyl formate signal was observed at 560°C and no methanol was detected.

IV. DISCUSSION

1. Surface Reactions during CO and CO_2 Hydrogenation

Previous studies have shown that CO, CO_2, H_2/CO, and H_2/CO_2 interact over ZrO_2 to generate carbonate, bicarbonate, formate, and methoxide species (*7, 8*). The H_2CO studies were performed to determine if oxymethylene, $H_2CO_2^-$, formed and if it could be oxidized to formate or reduced to methoxide. The FTIR spectrum established that formaldehyde adsorption resulted in formate and a species other than methoxide. This additional species is interpreted to be oxymethylene; justification for this assignment is provided below.

Busca and Lorenzelli (*11*) observed infrared C–H stretching bands at 2950–2920 cm^{-1}, and a band at 1430 cm^{-1} following adsorption of H_2CO on α-Fe_2O_3 which they assigned to polyers of formaldehyde (shown below as **I**). The oxymethylene species is expected to have the structure represented by **II** (3)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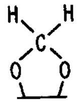

II

which should have C–H stretching bands in the region of 2950 cm^{-1}. The spectrum in Fig. 3a shows absorbance bands at 2956 and 2928 cm^{-1} and possibly a weak band at 2840 cm^{-1}. The methoxide species on ZrO_2 has C–H stretching bands at 2950 and 2840 cm^{-1}; the absorbance intensity ratio 2950 cm^{-1}/2840 cm^{-1} is 1.2–1.4 (*8*). The intensity of the 2956-cm^{-1} band in Fig. 3a is such that 1/1.2 of this intensity should be well resolved for the corresponding methoxide band at 2840 cm^{-1}. The lack of a well-resolved band at 2840 cm^{-1} strongly suggests that oxymethylene was present following H_2CO adsorption. Exposure of the species present in spectrum 3a to H_2 at 350°C resulted in the attenuation of the formate bands and the appearance of a well-resolved band at 2840 cm^{-1} (Fig. 3b). This is consistent with our proposed mechanism (*7, 8*) in which formate is reduced to methoxide via oxymethylene over ZrO_2 and is consistent with proposed mechanisms over Cu/Zn (*3*).

The infrared results of Fig. 3 indicate that more than one species may give rise to absorbance bands in the region of 2960–2930 cm^{-1}. This suggests that the assignment of bands in this region to a surface species be supported by the simultaneous appearance of additional characteristic bands (e.g., 2950 and 2840 cm^{-1} for methoxide). In the previous infrared study (*8*) we reported that formate and methoxide formed from CO/H_2 and CO_2/H_2 and that the formate could be converted into methoxide. The methoxide's presence was based on the appearance of a weak band at ca. 2950 cm^{-1}; a formate band at 2880 cm^{-1} was always present and we pointed out it may have obscured the 2840-cm^{-1} band. The current results suggest that oxymethylene may also have contributed to the 2950-cm^{-1} absorbance intensities in Ref. (*8*) when the 2840-cm^{-1} band was not well resolved. This does not change the conclusions of those experiments because either methoxide or oxymethylene demonstrate that formate is reduced over ZrO_2.

The H_2CO results support the hydrogenation scheme which is presented in Fig. 4. Previous studies have demonstrated that reactants in the top row form the indicated surface species (second row) and that these surface species decompose during TPD/TPDE to the products indicated in the third row (*7, 8*). Methane was observed at 510°C during TPD/TPDE of preadsorbed H_2CO which signified that some of the H_2CO-induced species were reduced to methoxide during TPD/TPDE in H_2. The appearance of formate stretching bands along with oxymethylene bands following H_2CO adsorption demonstrated the reversibility of the interconversion in that the oxymethylene

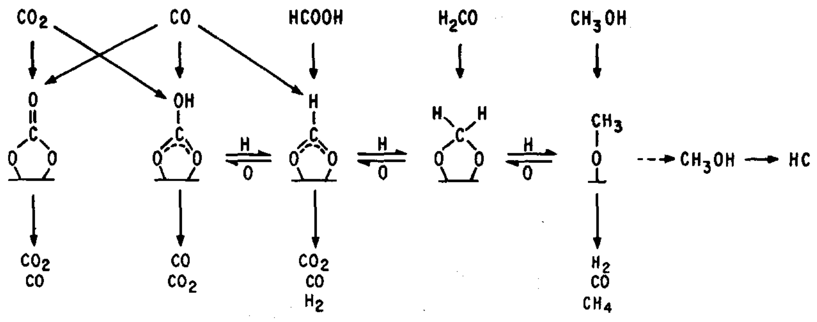
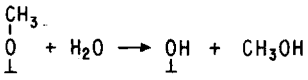


FIG. 4. Proposed surface chemistry of CO and CO_2 hydrogenation over ZrO_2.

was oxidized. The source of oxygen was not revealed and may have been lattice oxygen or molecular H_2CO. Oxymethylene oxidation has been reported (*12, 13*) and is supported by previous infrared observations in which methoxide was oxidized to formate and reduced back to methoxide (*8*).

2. *Methanol Formation at Low Temperature*

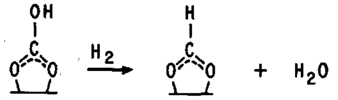
Water proved pivotal in CH_3OH formation at low temperature. The results in Fig. 1 demonstrated that CH_3OH was catalytically generated at ca. 125°C when H_2O was present in the H_2/CO flushing gas and additional studies (not shown) demonstrate that CH_4 is catalytically generated ca. 480°C in the absence of H_2O. These TPD/TPDE experiments were conducted over a ZrO_2 surface which had been cooled from 620 to 25°C in H_2/CO; this provides ample opportunity for the species shown on the second row of Fig. 4 to form (*7*). Methoxide is the TPD/TPDE precursor to CH_4. Methane was not detected at any temperature between 25 and 620°C during TPD/TPDE in $H_2/H_2O/CO$. These results suggest that low-temperature methanol formed by the reaction of H_2O with methoxide



$$\underset{\perp}{\overset{CH_3}{O}} + H_2O \longrightarrow \underset{\perp}{OH} + CH_3OH \qquad (1)$$

Klier (*1*) examined the thermodynamic barriers for the proposed methanol synthesis mechanisms and indicated that removal of methoxide by hydrolysis proceeded with a lower thermodynamic barrier than removal by hydrogenation. This supports the reaction shown above and may explain why water facilitates methanol formation.

The mixture of $H_2/H_2O/CO_2$ did not interact with ZrO_2 to form the low-temperature CH_3OH product; CH_3OH was observed at 580°C. This may have resulted from the initial species which form between CO and CO_2 and the ZrO_2 surface, formate and bicarbonate, respectively (*8*). Formate reduction to methoxide is required before methanol can be generated by hydrolysis with water. Bicarbonate reduction to formate, which was demonstrated (*8*), may evolve water as shown below



(2)

in which case formate formation could be inhibited in the presence of gas phase water.

3. *Methanol Formation at High Temperature*

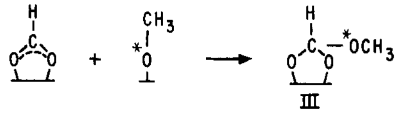
The high-temperature methanol peak appeared ca. 580–610°C and could be generated by preadsorbing CO_2 or CO over the temperature range 25–620–25°C and heating in H_2, by temperature-programmed heating of oxygen-treated ZrO_2 in H_2/CO_2 or H_2/CO, and by adsorbing H_2CO,

CH_3OH, HCOOH, or $HCOOCH_3$ and heating in flowing H_2. The C_1 surface species shown in the second row of Fig. 4 are not thought to be the immediate precursors to high-temperature methanol. Methoxide is hydrogenated to methane ca. 460–510°C (*7*). Methyl formate-induced surface species resulted in CH_3OH during TPD/TPDE in H_2 and $HCOOCH_3$ during TPD/TPDE in He. Methanol formation during $HCOOCH_3$ decomposition has been demonstrated over other metal oxides (*14*). We propose that a C_2 species containing the C–O–C group of methyl formate forms over ZrO_2 and undergoes hydrogenolysis to methanol; this C_2 species is proposed to form via bimolecular interaction of the C_1 surface species shown in Fig. 4.

The Gibbs free energies (*15*) of formation of methanol from CO or CO_2 and H_2 are sufficiently positive at ca. 600°C that direct synthesis is unlikely at 1 atm. Methyl formate formation from CO/H_2 is favored at temperatures below 125°C and is unfavored from CO_2/H_2. However, CO_2-induced bicarbonate converts to formate (*8*) which then follows the hydrogenation path of CO suggesting that a methyl formate-like structure may form from either CO or CO_2. Methyl formate decomposition into methanol and CO or CO_2 exhibits large negative free energies at 600°C. If an adsorbed methyl formate-like structure forms and if its thermochemistry trends parallel methyl formate, it may be possible to form the adsorbed structure and have it decompose to methanol during TPD/TPDE in H_2.

Klier (*1*) has pointed out that methyl formate may form directly from the interaction of C_1 surface intermediates during methanol synthesis. Possible C_1 species over ZrO_2 include formate, oxymethylene, and methoxide. Figure 3a established that formate formed at or below 150°C from H_2CO and coexisted with oxymethylene; a previous study (*8*) established that methoxide to formate conversion can occur at 25°C and that bicarbonate to formate and formate to methoxide and/or oxymethylene conversion occurs at or below 150°C. These observations demonstrate that formate and either/both oxymethylene or/and methoxide were present for the studies reported here.

Muetterties and Stein (*16*) discussed carbon–oxygen bond forming reactions in their review paper and suggest that nucleophilic attack on the carbon of metal carbonyls and metal formyls by CH_3O^- gives rise to a methyl formate-like structure. We found no evidence that formyl formed over ZrO_2 and molecular CO was weakly bonded (desorbing between 40 and 60°C). A reaction over ZrO_2 is proposed below which involves nucleophilic attack of methoxide on the formate carbon.



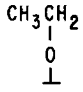
(3)

Reaction product **III** may rearrange further or could be the species which underwent hydrogenolysis to methanol. Deuterium labeling experiments were performed to identify the methanol precursor but C–H/C–D and O–H/O–D exchange made the results inconclusive.

The reactions giving rise to high-temperature CH_3OH and C_2 products, $HCOOCH_3$, and AMU 45, were stoichiometric and could only be carried out over oxygen-treated ZrO_2. This suggests that the nature of the oxide surface controls the secondary and possibly primary reactions; the surface properties are currently under investigation. A possible cause for the oxygen treatment effect could be that surface O^{2-} or O^- are required to facilitate the nucleophilic attack of CH_3O^- on $HCOO^-$, on which are possibly based all the secondary reactions.

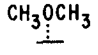
4. C_2 Surface Intermediates

Methanol formation at high temperature was proposed to occur via a methyl formate-like intermediate. The TPD/TPDE process of oxygen-treated ZrO_2 in flowing H_2/CO gave rise to an AMU signal of 45 which could be either ethanol or dimethyl ether. In either case, secondary reactions of C_1 intermediates are suspected and could give rise to the formation of



$$\begin{array}{c} CH_3CH_2 \\ | \\ O \\ \perp \end{array}$$

or



$$\underset{\perp}{CH_3\dot{O}CH_3}$$

The possible existence of these C_2 intermediates provides mechanistic clues for chain growth and the formation of oxygenated compounds which are possible precursors to hydrocarbons during isosynthesis (*4*).

V. CONCLUSIONS

1. The TPD/TPDE reaction of $H_2/H_2O/CO$ over ZrO_2 forms methanol catalytically at temperatures ca. 125°C via the hydrolysis of surface methoxide.

2. TPD/TPDE of preadsorbed CO_2 or CO on oxygen-treated ZrO_2 into H_2, or TPD/TPDE of oxygen-treated ZrO_2 into H_2/CO or H_2/CO_2 resulted in methanol at 580–610°C. This was proposed to involve hydrogenolysis of a methyl formate-like surface species which formed via nucleophilic attack of the carbon of $HCOO^-$ by CH_3O^-.

3. Infrared evidence was presented which suggested that $H_2CO_2^-$ formed over ZrO_2 from H_2CO.

ACKNOWLEDGMENTS

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