

Batch Reaction of Methanol and Oxygen over TiO₂ at 400°C: Observing Surface Species by Infrared Spectroscopy, and Gas Species by Mass Spectroscopy

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Received July 5, 1983; revised January 10, 1984

Batch reactions of methanol-oxygen mixtures have been studied over TiO₂ at 400°C. Analysis of the combined infrared and mass spectroscopic results suggests the following reaction mechanism: chemisorption of methanol to form surface methoxy; hydrogen abstraction from surface methoxy to give surface hydroxyl and gas-phase formaldehyde; formaldehyde chemisorption to give surface formate; and surface formate decomposition by dehydrogenation giving H₂ and CO₂, and by dehydration giving H₂O and CO. Kinetic isotope effects present in reactant consumption, product formation, and surface species evolution support assignments of the rate-limiting step in the reaction sequence to hydrogen abstraction from the surface methoxy.

INTRODUCTION

Much work has been done identifying infrared active surface species on various metal oxides at temperatures such that reaction did not occur during the experiment (1). However, relatively little infrared work has been done at high temperatures where significant reaction was expected to occur (1). Methanol oxidation to formaldehyde is known (2) to occur on a number of metal oxides, including TiO₂. However, little is known about the reaction mechanism (3-5) because intermediates have not been observed under actual reaction conditions. Herein we present infrared and mass spectroscopic analyses of reacting methanol-oxygen mixtures over oxidized rutile TiO₂ powders at 400°C.

EXPERIMENTAL

Rutile powder used for this work was prepared by flame hydrolysis of titanium tetrachloride. The starting material for this work was the same as that used in a study of the adsorptive properties of rutile at low temperatures (70-100°C) (6). Further details regarding sample preparation techniques can be found in Ref. (7).

The infrared cell and gas mixing manifold (volumes 500 and 250 cm³, respectively) were part of a metal vacuum system pumped with a 30 liter/s ion pump together with a turbomolecular pump which also served as the backing pump for an Extranuclear Laboratories Model Spectrel mass spectrometer. After introducing a new sample into the infrared cell and before changing to a different isotopic methanol species, the entire system was baked at 300°C. This usually resulted in a marked increase in overall optical density of the sample, indicating that reduction had occurred. The original sample transparency was readily restored by heating at 400°C in 10 Torr (1 Torr = 133 N m⁻²) oxygen. This was our standard oxidation procedure prior to all experiments. Following this preliminary oxidation, the sample cell was evacuated and a methanol-oxygen mixture was expanded from the mixing manifold into the infrared cell. Various isotopically labeled methanol species were studied: CH₃OH (Fisher); and CH₃OD(-d₁), CD₃OH(-d₃), and CD₃OD(-d₄), all obtained from Stohler. The isotopic purities of the methanol (-d₁, -d₃, -d₄) isotopes were >99 atom%.

After introducing the methanol–oxygen mixture into the infrared cell, mass spectra were taken periodically at a partial pressure in the mass spectrometer ionizer region of about 10^{-7} Torr obtained by sampling through a variable leak valve into the infrared cell. Interferograms were obtained with a Nicolet 7001P interferometer and processed with a PDP 11/55 minicomputer to give 4-cm^{-1} spectra. Spectra obtained during the reaction were corrected to eliminate gas-phase features by using as a background the spectrum obtained with the heated sample moved out of the infrared beam. Difference spectra were obtained by subtracting from the sample spectrum a reference spectrum which was the spectrum of the oxidized sample taken immediately before introducing the reactants. The difference spectra thus show the net changes taking place in the sample including its surface (further details may be obtained from Refs. (6, 7)), but not including the gas phase in the infrared cell.

Figure 1 shows infrared spectral changes taking place upon exposing a 10-mg pellet (1 cm diameter) of TiO_2 to a methanol ($-d_0$)/oxygen mixture at 400°C . The sample reference spectrum which was subtracted

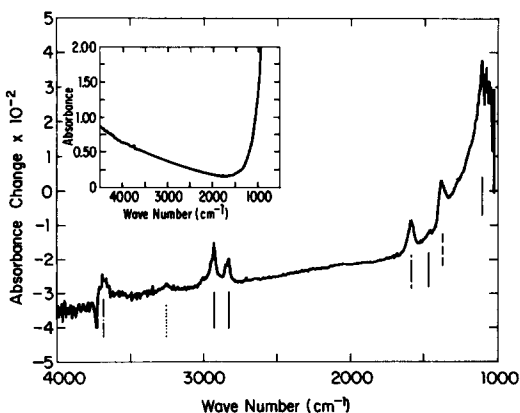


FIG. 1. Infrared difference spectrum showing surface species created when a TiO_2 sample at 400°C is contacted with a methanol–oxygen mixture. The band origins are (—), methoxy; (---), formate; (-.-), surface hydroxyl; and (· · ·), lattice hydroxyl. Inset: ir spectrum of sample at 400°C before reaction.

to give the difference spectrum is shown in the inset to Fig. 1. The 3737-cm^{-1} band in the reference spectrum arises from a surface hydroxyl associated with silica impurity (7–9), which is not removed under our oxidation conditions.

From Fig. 1 and Ref. (6) the assignments of the major bands are readily determined as follows:

Surface methoxy: Bands at 2931, 2831, 1450, 1390, and 1365 cm^{-1} assigned to methyl antisymmetric stretch, methyl symmetric stretch, methyl deformation, and CO stretch, respectively.

Surface formate: Bands at 1590, 1390, and 1365 cm^{-1} assigned to carboxyl antisymmetric stretch, C–H deformation, and carboxyl symmetric stretch, respectively.

Titania surface hydroxyl: Band at 3690 cm^{-1} .

Silica surface hydroxyl: Band at 3737 cm^{-1} .

Titania bulk hydroxyl: Weak band at 3260 cm^{-1} .

The weak lattice hydroxyl band at 3260 cm^{-1} has not been previously observed following adsorption of organic molecules at temperatures below 100°C . This band appeared when the methanol–oxygen mixture was admitted to the ir cell, and its intensity did not change during any of the experiments. Subsequent evacuation removed this band immediately, in contrast with the behavior of the other bands which remained for varying periods of time. However, this band has been extensively studied in conjunction with hydrogen diffusion in TiO_2 single crystals (10), and has been assigned to a “bulk” hydroxyl ion OH^- in which the oxygen occupies a regular oxygen lattice site and the O–H bond is perpendicular to the c -axis. Since its concentration did not change during any of the experiments, nothing more will be said about it. Substituting methanol ($-d_4$) for $-d_0$ shifted the methoxy bands to 2220, 2068, 1130, and 1184 cm^{-1} , respectively; the formate bands to 1560 and 1355 cm^{-1} , respectively, and the surface silica, surface titania, and

“bulk” titania hydroxyls to 2750, 2716, and 2417 cm⁻¹, respectively. Methanol ($-d_1$ and $-d_3$) gave various combinations of the bands for methanol ($-d_0$ and $-d_4$), as expected.

The relative concentrations of surface methoxy and formate were estimated from the intensities of the 2931- and 1590-cm⁻¹ bands and their deuterated analogs, respectively. Similarly, the relative hydroxyl concentrations were estimated from the intensities of their respective bands.

Products observed by mass spectroscopy during the methanol oxidation were water, formaldehyde, carbon dioxide, carbon monoxide, and hydrogen, and sometimes small amounts of dimethyl ether. Fragmentation patterns, obtained separately for all reactants and products, were used for the gas phase analysis, e.g., contributions from methanol ($-d_0$) had to be subtracted from observed mass peaks at 32 and 30 AMU to obtain accurate relative concentration of oxygen and formaldehyde, respectively. CO analysis was particularly difficult since both formaldehyde and methanol ($-d_0$) contributed to the peak at 28 AMU. Similar considerations apply for the substituted methanols used in this work. The mass spectrometer was tuned for constant mass peak width (for a detailed description of the theory and operation of quadrupole mass spectrometers, see Ref. (11)). This resulted in a sensitivity decrease approximately proportional to $\exp(0.09m)$ for masses, m , greater than 15 AMU. After correcting for both mass spectrometer sensitivity and ionizer efficiency (12), for presentation the concentrations were adjusted to approximately equal the sum of the major bands observed for each reactant and product.

It should be emphasized that even though these experiments were carried out at pressures such that gas diffusion effects were negligible (Ref. (13)), “wall retention” effects were not negligible, due to different “sticking” probabilities for different gases. Thus, formaldehyde and water take considerably longer to reach the mass spectrom-

eter ionizer than do carbon monoxide, carbon dioxide, and hydrogen. Also, products could be irreversibly absorbed on the infrared-cell walls (which had a total area comparable to that of the sample surface) thereby making an accurate mass balance impossible, even with a calibrated mass spectrometer. Nevertheless, relative gas concentrations should be accurate.

RESULTS AND DISCUSSION

A batch reactor experiment was carried out in which a 2-Torr methanol-oxygen mixture (1:1) was introduced into the infrared cell containing 10 mg TiO₂ at 400°C. Figure 2 shows the relative concentrations of (a) surface species, (b) reactants, and (c) products as a function of time after introducing the methanol-oxygen mixture. Only carbon dioxide is shown in Fig. 2c, but hydrogen, carbon monoxide, and carbon dioxide all had the same time dependence. The ratio of CO₂ to CO was about 1.4:1 throughout the reaction. The lines through the data points shown in Fig. 2a are included only as a visual aid.

Figure 3 shows the analogous results for a methanol ($-d_4$)-oxygen (1:1) mixture with the same TiO₂ sample at 400°C. The ratio of CO₂ and CO was about 1.6:1 throughout the reaction.

Figure 4 shows the relative concentrations of surface species for a methanol ($-d_1$)-oxygen mixture (1:1) with the same TiO₂ sample at 400°C. For this reaction the observed products were H₂O, HDO, D₂O, CH₂O, CO₂, H₂, HD, CO, and traces of dimethyl ether ($-d_0$) which were too small to measure. No evidence was found for D₂, CD₂O, or CHDO. The time dependence of the reactant concentrations was similar to that shown in Fig. 2b. The ratio of H₂ to HD was about 2:1 throughout the reaction time studied. However, the relative concentrations of D₂O, HDO, and H₂O changed from about 2:4:1 during the first 10 min of reaction to 1:4:2 during the last 100 min of reaction.

When a methanol ($-d_3$)-oxygen mixture

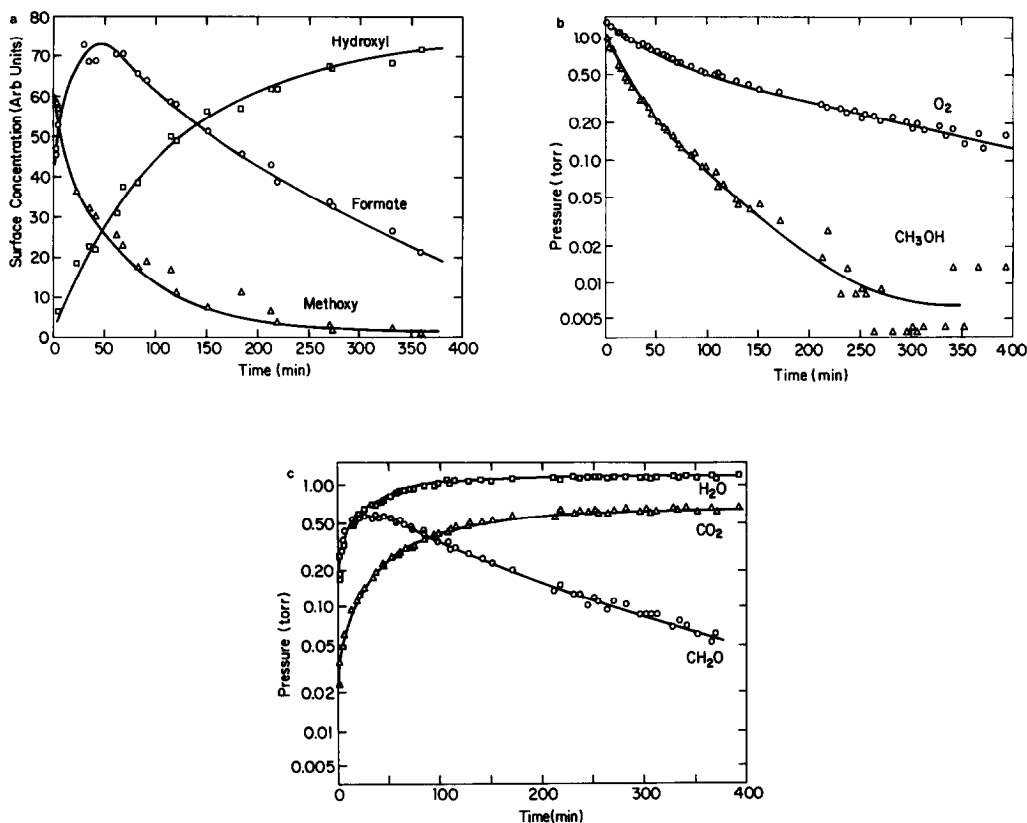
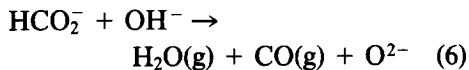
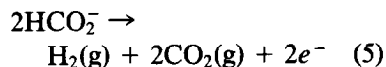
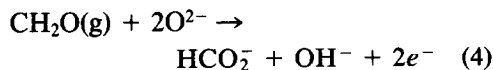
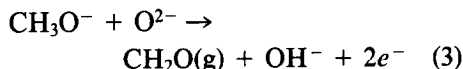
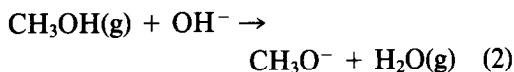
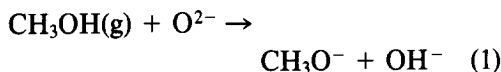


FIG. 2. Concentrations of (a) surface species, (b) reactants and (c) products as a function of time after introducing CH₃OH-O₂ into the infrared cell containing TiO₂ at 400°C.

(1 : 1) was reacted on the same TiO₂ sample at 400°C, the observed products were H₂O, HDO, D₂O, CD₂O, CO₂, HD, D₂, CO, and traces of dimethyl ether (*-d*₆). A small constant amount of H₂ evolved throughout the reaction which may have been an artifact. No CH₂O or CHDO was observed. Relative amounts of H₂O, HDO, and D₂O were difficult to deconvolute because of interference from the methyl (*-d*₃) peak at 18 AMU. However, at the end of the reaction the principle water products were HDO and D₂O in the ratio 3 : 1. The ratio of HD to D₂ was about 2.5 : 1 throughout the reaction.

The infrared data in Figs. 2a and 3a taken alone suggest a surface reaction involving the sequential intermediates methoxy → formate → hydroxyl. However, including the mass spectrometric data suggest a substantially different overall reaction picture

which can be described by



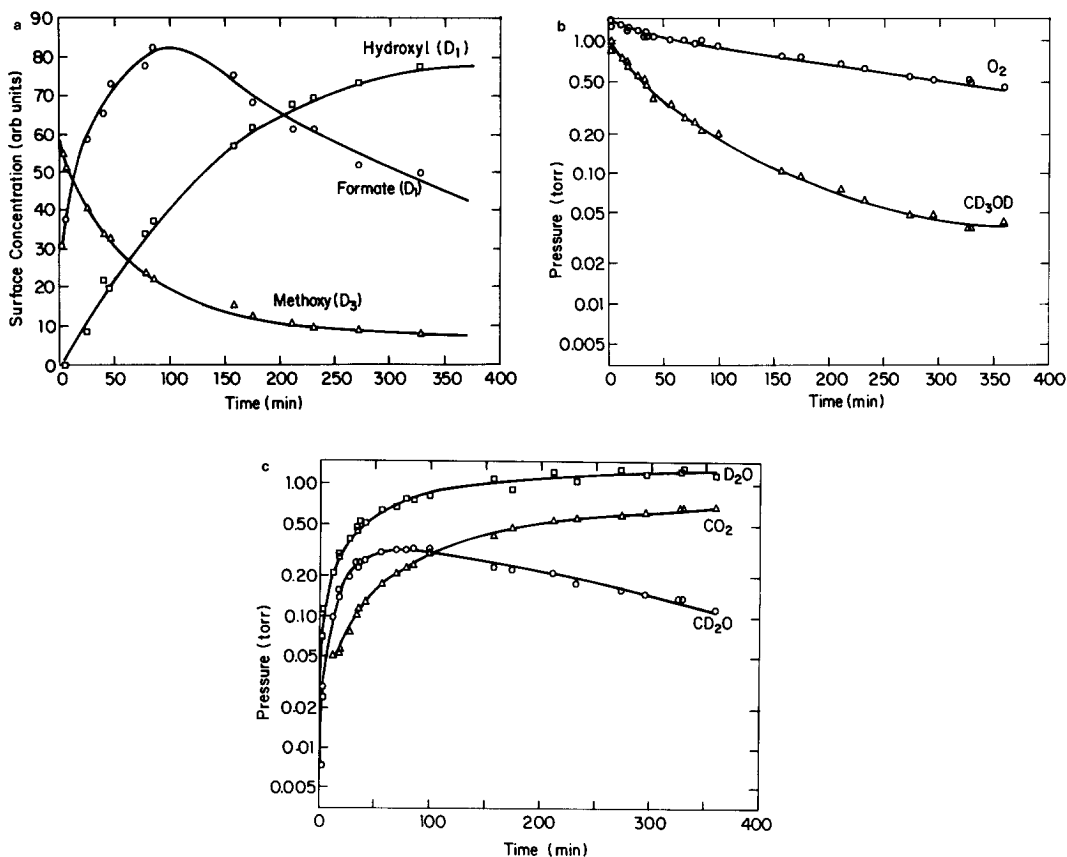


FIG. 3. Concentrations of (a) surface species, (b) reactants, and (c) products as a function of time after introducing CD₃OD–O₂ into the infrared cell containing TiO₂ at 400°C.

Note that in reactions (1)–(8) all gas phase quantities are indicated by (g). Other species are on the surface. These surface spe-

cies are presented as negative ions for convenience in keeping track of the electrons. The actual situation is undoubtedly more complex. Bonding to the surface is probably more covalent than ionic, and the indicated surface species are contained in sites involving Ti(IV) or Ti(III) ions.

Further discussion of the processes (1)–(8) is divided in the following sections into methoxy formation (reactions (1) and (2)), formaldehyde and formate formation (reactions (3) and (4)), formate decomposition (reactions (5) and (6)), and surface reoxidation (reaction (7)).

Methoxy Formation

Methanol chemisorption can occur via both dissociation (reaction (1)) to form surface methoxy plus free hydroxyl, or by hy-

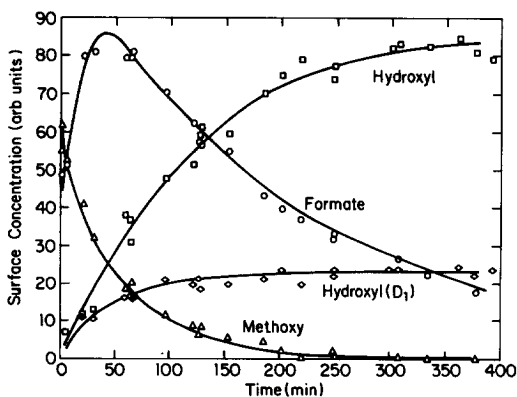


FIG. 4. Concentrations of surface species as a function of time after introducing CH₃OD–O₂ into the infrared cell containing TiO₂ at 400°C.

droxyl displacement (reaction (2)) to form surface methoxy plus water which is released to the gas phase. Reactions (1) and (2) have both been observed with rutile for $T < 100^\circ\text{C}$ (6). For methanol exposure conditions leading to low surface methoxy coverage, reaction (1) dominates; whereas at higher pressures and longer exposure times reaction (2) dominates. The only difference noted here is that at 400°C the water in reaction (2) is released from the surface whereas at 100°C it is not. We conclude for the present case that, although hydroxyl formation due to reaction (1) occurs, because of reaction (2) no significant surface hydroxyl concentration can exist until the gas-phase methanol is used-up. The importance of reaction (2) in removing surface hydroxyls also accounts for the approximate inverse relationship between surface hydroxyl and surface methoxy concentrations, and in addition, partially explains the release of large quantities of water early in the reaction.

Formaldehyde and Formate Formation

Reaction (3) appears to be the rate-limiting step in the conversion of methanol to formaldehyde over TiO_2 . Previous work (6) with rutile at temperatures below 100°C indicates that formaldehyde adsorbs on TiO_2 to form a symmetrical surface formate with the same frequencies observed in this work. Figure 2 shows that buildup of gas-phase formaldehyde precedes the buildup of surface formate concentration. When CD_3OD is used (Fig. 3), buildup of CD_2O is slower thus suggesting that breaking of the C-H bond in reaction (3) is rate-limiting. Formaldehyde build up is also slower with CD_3OH but not with CH_3OD .

Formate Decomposition

Previous work with the catalytic decomposition of formic acid on TiO_2 (14) has shown that surface formate decomposes by both dehydrogenation (reaction (5)) and dehydration (reaction (6)) for $T > 300^\circ\text{C}$. The dehydration reaction is thought to be a two-

step process consisting of (i) elimination of CO with formation of a hydroxyl; and (ii) condensation of two surface hydroxyls to form water. The latter is assumed to be the rate-limiting step (14). In the absence of oxygen, formate decomposition by dehydration is the dominant mechanism (14, 15). However, as suggested in Ref. (16), the dehydrogenation reaction should be much stronger if oxygen is present during the decomposition. This appears to be the case here since CO_2 and CO evolution are of comparable magnitude.

H_2 , CO, and CO_2 gas-phase concentrations all had the same time dependence in this work although only CO_2 is shown in Figs. 2c and 3c. Evidently both dehydrogenation (reaction (5)) and dehydration (reaction (6)) are occurring as formate decomposition pathways in this system. Figures 2 and 3 show that CO_2 , H_2 , and CO are evolved more slowly when CD_3OD is substituted for CH_3OH . A similar result is obtained with CD_3OH but not CH_3OD . These isotope effects are consistent with the view that surface formate decomposition follows the rate-limiting step in the methanol-oxygen reaction sequence.

Surface Reoxidation

In this work we saw no indication of overall sample reduction. This would be accompanied by a marked increase in the optical density of the sample. Since sample reduction occurs in reactions (3)–(5), sample reoxidation (reaction (7)) occurs continuously during the methanol oxidation. Figures 2 and 3 show that oxygen is consumed much more slowly when CD_3OD is substituted for CH_3OH . A similar result is obtained with CD_3OH but not with CH_3OD . These isotope effects show that reoxidation of the TiO_2 surface follows the rate-limiting steps. In the absence of oxygen, formate decomposition via the dehydrogenation reaction results in a reduced TiO_2 sample (15). Sample reduction is not observed in our experiments presumably because the reoxidation (reaction (7)) takes place rap-

idly. Nevertheless, reoxidation following the dehydrogenation reaction accounts for the continued oxygen consumption at long times when the only remaining reaction is surface formate decomposition.

Hydroxyl Condensation

As has already been pointed out, hydroxyl condensation is thought to be the rate-limiting step (14) in the decomposition of surface formate by dehydration (reaction (6)). Although reaction (8) undoubtedly occurs, distinguishing the water released by this mechanism from that released by reaction (2) (which occurs throughout the experiment) is virtually impossible without additional work at higher temperatures and/or longer experimental times.

SUMMARY AND CONCLUSIONS

In this work, we have studied methanol oxidation to formaldehyde on the rutile form of TiO₂ at 400°C, directly observing concentrations of surface intermediates during the reaction by using infrared spectroscopy. Concentrations of gas-phase intermediates and products were followed using mass spectrometry. Analysis of the combined spectroscopic results suggests a detailed mechanism for the overall reaction demonstrating the power and utility of combining these spectroscopic techniques.

The suggested mechanism involves initial chemisorption of methanol to form surface methoxy. Hydrogen abstraction from surface methoxy to give surface hydroxyl and gas-phase formaldehyde is the rate-limiting step for the overall reaction. Formaldehyde then chemisorbs to form a surface formate. The surface formate subsequently decomposes by dehydrogenation giving H₂ and CO₂, and by dehydration giving H₂O and

CO. No sample reduction is observed indicating that reoxidation takes place rapidly. Kinetic isotope effects present in reactant consumption, product formation, and surface species evolution support assignments of the rate-limiting steps. No evidence was found for physisorbed formaldehyde.

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