# Product Selectivity during CH<sub>3</sub>OH Decomposition on TiO<sub>2</sub> Powders

E. A. Taylor<sup>†</sup> and G. L. Griffin<sup>\*‡</sup>

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455 (Received: June 18, 1987)

We show that the product selectivity during the temperature-programmed decomposition of CH<sub>1</sub>OH on TiO<sub>2</sub> is a strong function of the initial CH<sub>3</sub>OH coverage. For low coverages, the dissociated CH<sub>3</sub>OH protons react with residual HO<sub>(a)</sub> groups on the TiO<sub>2</sub> surface, leading to the desorption of  $H_2O$  and leaving behind isolated  $CH_3O_{(a)}$  groups that are stable to 673 K. For higher coverages a range of additional products is observed, including recombined CH<sub>3</sub>OH, CH<sub>3</sub>OCH<sub>3</sub>, and CH<sub>2</sub>O below 673 K and CO, CO<sub>2</sub>, and CH<sub>4</sub> at higher temperature. We propose a model in which the decomposition selectivity is determined by the coverage of neighboring HO<sub>(a)</sub>, CH<sub>3</sub>O<sub>(a)</sub>, and O<sup>2-</sup><sub>(a)</sub> species. In the case of HO<sub>(a)</sub> species, evidence suggests that surface diffusion of protons from non-nearest-neighbor sites also affects the decomposition selectivity. The product selectivity is compared with that observed when CH<sub>3</sub>OH decomposes on ZnO, and differences are discussed in terms of the relative strengths of HO<sub>(a)</sub> and CH<sub>3</sub>O<sub>(a)</sub> bonds on the two surfaces.

## Introduction

The decomposition of adsorbed alkoxide species on TiO<sub>2</sub> surfaces is perhaps the most important elementary step in the chemical vapor deposition of TiO<sub>2</sub> films with alkoxide precursors.<sup>1-3</sup> Knowledge of alkoxide reactions on TiO<sub>2</sub> is also relevant to the design of selective oxidation catalysts using TiO<sub>2</sub> supports<sup>4,5</sup> and olefin polymerization catalysts using supported titanium alkoxides.6 Fundamental decomposition studies also improve our general understanding of the principles of chemical bonding and reactions at oxide surfaces.

As the simplest alcohol, the decomposition of CH<sub>3</sub>OH provides a logical starting point for developing an understanding of alkoxide reactions on TiO<sub>2</sub>. Infrared spectroscopy has provided evidence that CH<sub>3</sub>OH adsorbs on TiO<sub>2</sub> in at least two forms which are distinguished by different vibrational frequencies.<sup>7-10</sup> Bands at 2850 and 2950 cm<sup>-1</sup> are assigned to the symmetric and asymmetric C-H stretching frequencies of the molecularly adsorbed state,  $CH_3OH_{(a)}$ , while bands at 2830 and 2930 cm<sup>-1</sup> are assigned to the dissociated state,  $CH_3O_{(a)}$ . Both states are irreversibly adsorbed at 273 K, but the molecular state either desorbs or converts to the dissociated form when the temperature is increased to 473 K.<sup>9</sup> The C-H stretching frequencies of the dissociated state are slightly different from those of  $CH_3O_{(a)}$  on ZnO, which are observed at 2936 and 2918 cm<sup>-1.11</sup> Thus, the identity of the cation to which a CH<sub>3</sub>O<sub>(a)</sub> group is bound appears to have a minor effect on its C-H vibrational frequencies.

In contrast, the decomposition behavior of CH<sub>3</sub>O<sub>(a)</sub> groups on TiO<sub>2</sub> is dramatically different from the behavior observed on ZnO. The first study of the temperature-programmed decomposition of CH<sub>3</sub>OH adsorbed on TiO<sub>2</sub> was reported by Carrizosa et al.<sup>8</sup> Below 673 K the main products were H<sub>2</sub>O, CH<sub>3</sub>OH, and CH<sub>3</sub>- $OCH_3$ , while at higher temperature smaller amounts of CO, CO<sub>2</sub>,  $H_2$ ,  $CH_4$ , and  $C_2H_6$  were also observed. In contrast, the only products observed during CH<sub>3</sub>OH decomposition on porous ZnO are  $H_2$ , CO, and CO<sub>2</sub>, and the decomposition is completed below 600 K.12

The factors which determine these differences in selectivity are fundamental to our understanding of molecular transformations on oxide surfaces. Our earlier studies of CH<sub>3</sub>OH decomposition on ZnO<sup>11,12</sup> have shown that the combination of temperatureprogrammed desorption and IR spectroscopy provides a powerful tool for monitoring the behavior of adsorbed species in the course of their decomposition. Therefore, we decided to perform a similar study of the  $\dot{C}H_3OH/TiO_2$  system. The present study will emphasize the coverage dependence of the product selectivity during CH<sub>3</sub>OH decomposition. Using these results, we propose a model

\* Author to whom correspondence should be addressed.

which correlates the decomposition selectivity with the coverage of neighboring adsorbate species. We will also compare these results with our earlier studies of the CH<sub>3</sub>OH/ZnO system, to gain further insight about the bonding of oxygen-containing species on these surfaces.

#### **Experimental Section**

All of the experiments are performed using a sample cell which permits us to simultaneously record IR spectra and TPD product fluxes.<sup>11</sup> The acquistion and analysis of the product desorption spectra have been enhanced by the addition of a computer-controlled signal acquisition system (IBM-PC plus Metrabyte DASCON-1 expansion board), which allows the desorption yields of up to 10 products to be monitored during a single experiment. Infrared spectra are recorded on an FTIR spectrometer (Nicolet 60-SX).

The sample material is Degussa P-25 TiO<sub>2</sub> powder, which has a measured BET surface area of 47 m<sup>2</sup>/g and a phase composition of 60% anatase and 40% rutile.<sup>13</sup> A 50-mg sample is deposited from an aqueous suspension as a thin layer on the reflecting surface of the IR/TPD cell (reflecting area  $2 \text{ cm}^2$ ). The subsequent pretreatment steps include heating the sample under vacuum to 723 K (the upper temperature limit of the cell) to partially dehydroxylate the surface and then admitting and evacuating three successive cycles of 4 Torr of O2 at 673 K to remove carbonaceous residues.

Three groups of experiments were performed. The first is a series using different initial coverages of CH<sub>3</sub>OH. Measured amounts of CH<sub>3</sub>OH vapor are admitted to the cell at the beginning of each experiment; for the coverages studied here, all of the CH<sub>3</sub>OH admitted is adsorbed within a few minutes. The TPD warm-up is done with a heating rate of 0.3 K/s, and the products which escape from the porous sample are analyzed with the quadrupole mass spectrometer. At the end of each TPD warm-up, the sample is reoxidized to remove unreacted CH<sub>3</sub>O<sub>(a)</sub> groups before beginning the next experiment (see below).

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<sup>&</sup>lt;sup>†</sup> Present address: AMOCO Chemical Company, Naperville, IL. <sup>‡</sup>Present address: Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803.

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Figure 1. Infrared spectra of CH<sub>3</sub>OH adsorbed on oxidized TiO<sub>2</sub> at 300 K (lower curve) and 423 K (upper curve). Coverage is 28  $\mu$ mol/g in both cases.

The second group of experiments is performed with a constant initial  $CH_3OH$  exposure but without reoxidizing the sample at the end of each experiment. This tests the effect of the unreacted  $CH_3O_{(a)}$  groups on the selectivity of subsequent decomposition experiments. The final experiments measure the photoinduced  $CH_3OH$  decomposition and compare the selectivity and extent of the photoinduced reaction with the results of the conventional TPD experiments.

### Results

Infrared Spectra of Adsorbed  $CH_3OH$ . To confirm the existence of two vibrationally distinguishable  $CH_3OH$  adsorption states, we first recorded the IR spectrum of  $CH_3OH$  adsorbed at 300 K. This spectrum is shown in the lower curve of Figure 1. Both pairs of C-H stretching peaks are observed with comparable intensity (i.e., the  $CH_3OH_{(a)}$  bands at 2952 and 2852 cm<sup>-1</sup> and the  $CH_3O_{(a)}$  bands at 2930 and 2830 cm<sup>-1</sup>).

In contrast, the upper curve in Figure 1 shows the spectrum obtained when the same amount of  $CH_3OH$  is adsorbed at 423 K. The total intensity of the C-H stretching bands appears about the same in the two spectra, but the intensity in the upper curve is primarily concentrated in the  $CH_3O_{(a)}$  peaks at 2930 and 2830 cm<sup>-1</sup>. These results show that a kinetic barrier exists which inhibits the conversion of  $CH_3OH_{(a)}$  into  $CH_3O_{(a)}$  and that this barrier can be partially overcome by increasing the adsorption temperature. Even at 423 K, however, there is still some intensity in the  $CH_3OH_{(a)}$  bands.

The amount of CH<sub>3</sub>OH adsorbed in the experiments shown in Figure 1 corresponds to a coverage of 28  $\mu$ mol/g. This is equivalent to a surface concentration of 0.36 CH<sub>3</sub>OH molecule/nm<sup>2</sup>, based on the BET area of the TiO<sub>2</sub>. This is well below the monolayer concentration, which is estimated to be 3.6 molecules CH<sub>3</sub>OH molecules/nm<sup>2</sup>.<sup>10,14</sup> However, it is comparable to the concentration of residual HO<sub>(a)</sub> groups on the surface of TiO<sub>2</sub> outgassed at 673 K.<sup>14</sup>

The IR spectra for a series of different initial CH<sub>3</sub>OH coverages adsorbed at 423 K are shown in Figure 2. At this elevated temperature, the IR intensity for all coverages is located mainly in the CH<sub>3</sub>O<sub>(a)</sub> bands at 2930 and 2830 cm<sup>-1</sup>, although there is some intensity in the CH<sub>3</sub>OH<sub>(a)</sub> bands at 2950 and 2850 cm<sup>-1</sup>.

The spectra in Figure 2 also show the effect of increasing CH<sub>3</sub>OH coverage on the vibrational structure of the residual HO<sub>(a)</sub> groups in the isolated O–H stretching region ( $3800-3600 \text{ cm}^{-1}$ ). The presence of several bands in this region prior to CH<sub>3</sub>OH adsorption confirms the presence of these residual groups, even after the outgassing and oxidation cycles at 673 K. The overall appearance of these bands is in agreement with earlier spectra reported for HO<sub>(a)</sub> groups on outgassed P-25 TiO<sub>2</sub>.<sup>15</sup> As increasing amounts of CH<sub>3</sub>OH are adsorbed, the intensity of these isolated HO<sub>(a)</sub> bands decreases, and in their place a broad band



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Figure 2. Infrared spectra of  $CH_3OH$  adsorbed on  $TiO_2$  at 423 K, as a function of initial coverage.



Figure 3. Infrared spectra recorded during temperature-programmed decomposition of CH<sub>3</sub>OH adsorbed on TiO<sub>2</sub>. Initial coverage is 80  $\mu$ mol/g.

develops in the hydrogen-bonded O-H stretching region  $(3500-3100 \text{ cm}^{-1})$ . This proves that the residual HO<sub>(a)</sub> groups and the CH<sub>3</sub>OH adsorption sites are homogeneously mixed on a molecular length scale and suggests that the residual HO<sub>(a)</sub> groups have become hydrogen bonded to the oxygen atoms of adsorbed CH<sub>3</sub>OH<sub>(a)</sub> or CH<sub>3</sub>O<sub>(a)</sub> species.

Figure 3 shows the IR spectra recorded during the TPD warm-up of a sample containing an initial CH<sub>3</sub>OH coverage of 80  $\mu$ mol/g. In the beginning of the warm-up (i.e., between 423 and 573 K), the major change is a decrease in the intensity of the hydrogen-bonded O-H region (3500-3100 cm<sup>-1</sup>). This decrease is *not* accompanied by a reappearance of the originally observed isolated OH bands in the region 3710-3650 cm<sup>-1</sup>. This shows that most of the residual HO<sub>(a)</sub> species have been removed from the surface during the first part of the TPD warm-up. (An exception is the significant intensity remaining in the band at 3730 cm<sup>-1</sup> which has previously been assigned to isolated OH groups at Si impurity sites in TiO<sub>2</sub> and thus might be expected to show unique behavior.<sup>10</sup>)

The bands in the C-H region do not begin to decrease significantly until the temperature reaches 573 K. The bands may become slightly narrower between 473 and 573 K, which suggests that the molecular  $CH_3O_{(a)}$  state may be desorbed or converted to  $CH_3O_{(a)}$  over this temperature range. Between 573 and 723 K, the intensity of the bands at 2930 and 2830 cm<sup>-1</sup> decreases by about two-thirds. As discussed below, it is significant that a substantial fraction of the adsorbed  $CH_3O_{(a)}$  species are stable to 723 K and appear to have taken the place of the residual  $HO_{(a)}$ groups that were present at the beginning of the TPD experiment.

Compared with our earlier results for CH<sub>3</sub>OH decomposition on ZnO, one other significant feature is the fact that very little intensity develops in the bands at 1560 and 1360 cm<sup>-1</sup> which are



Figure 4. Desorption spectra of  $H_2O$  evolved during TPD of  $CH_3OH$  adsorbed on TiO<sub>2</sub>, as a function of initial coverage.



Figure 5. Desorption spectra of  $CH_3OH$  evolved during TPD of  $CH_3OH$  adsorbed on TiO<sub>2</sub>, as a function of initial coverage.

assigned to surface  $HCOO_{(a)}$  species. In contrast, CH<sub>3</sub>OH decomposition on ZnO proceeds primarily via the  $HCOO_{(a)}$  intermediate, and the latter bands become quite pronounced at intermediate temperatures.<sup>11</sup> We also note that on ZnO all of the adsorbate bands are eliminated by 623 K, in contrast to the significant amount of CH<sub>3</sub>O<sub>(a)</sub> that remains on the TiO<sub>2</sub> surface.

Temperature-Programmed Decomposition Experiments. The product fluxes observed during the series of coverage-dependent TPD experiments are shown in Figures 4–7. Figure 4 shows the  $H_2O$  yields for initial CH<sub>3</sub>OH coverages of 0, 10, 15, 20, 40, and 80  $\mu$ mol/g. The control experiment (lowest curve) shows that even without adsorbed CH<sub>3</sub>OH, the residual HO<sub>(a)</sub> groups can react to desorb as H<sub>2</sub>O, beginning at about 573 K. However, the fact that H<sub>2</sub>O desorption occurs at this temperature even though the sample was evacuated at 723 K before starting the experiment began suggests that the H<sub>2</sub>O desorption process does not obey simple first- or second-order kinetics between neighboring HO<sub>(a)</sub> groups. Instead, we propose that desorption may become limited by the surface diffusion of protons between HO<sub>(a)</sub> groups that are separated by more than one lattice spacing.

When CH<sub>3</sub>OH is adsorbed in increasing amounts, the desorption of H<sub>2</sub>O begins at progressively lower temperatures, and the H<sub>2</sub>O desorption curve develops a resolvable maximum which shifts to lower temperature with increasing CH<sub>3</sub>OH coverage (i.e., from 648 to 523 K for coverages between 10 and 80  $\mu$ mol/g). The width of the curves is larger than would be expected for an ideal first- or second-order desorption process, which prevents us from assigning a meaningful value for the activation energy for the H<sub>2</sub>O desorption kinetics. The width may be caused by surface heterogeneity and/or repulsive interactions between reacting species, or it may be due to the effects of the surface diffusion step suggested above.

Figure 5 shows the  $CH_3OH$  yields for the same set of experiments. The behavior can be separated into two coverage regimes.



Figure 6. Desorption spectra of  $CH_3OCH_3$  evolved during TPD of  $CH_3OH$  adsorbed on TiO<sub>2</sub>, as a function of initial coverage.



Figure 7. Desorption spectra of  $CH_2O$  evolved during TPD of  $CH_3OH$  adsorbed on TiO<sub>2</sub>, as a function of initial coverage.

For initial CH<sub>3</sub>OH coverages less than 40  $\mu$ mol/g, there is no significant desorption of molecular CH<sub>3</sub>OH. This is consistent with the IR spectra in Figure 3, which showed that a fraction of the initially adsorbed CH<sub>3</sub>O<sub>(a)</sub> is stable through 723 K. However, the fact that the desorption of H<sub>2</sub>O showed an enhancement at all initial CH<sub>3</sub>OH coverages confirms that the dissociated CH<sub>3</sub>OH protons are able to react with the residual HO<sub>(a)</sub> groups, leading to H<sub>2</sub>O desorption. The fact that the majority of these CH<sub>3</sub>OH molecules are already dissociated upon adsorption at 423 K shows that the H<sub>2</sub>O desorption product (cf. Figure 4) is *not* the result of a condensation reaction between HO<sub>(a)</sub> groups and molecularly adsorbed CH<sub>3</sub>OH<sub>(a)</sub> species.

For initial CH<sub>3</sub>OH coverages greater than 40  $\mu$ mol/g, molecular CH<sub>3</sub>OH desorbs in a broad peak with a coverage-dependent maximum. The shape and coverage dependence of this peak are similar to the behavior of the H<sub>2</sub>O desorption peak, which suggests that the desorption kinetics are similar, i.e., that CH<sub>3</sub>OH is desorbing via a recombinative process and that surface heterogeneity, repulsive interactions, and/or surface diffusion of protons may be affecting the desorption kinetics. Comparison with the IR spectra in Figure 3 shows that dissociated CH<sub>3</sub>O<sub>(a)</sub> species are disappearing as CH<sub>3</sub>OH desorption product is produced by recombination of CH<sub>3</sub>O<sub>(a)</sub> and HO<sub>(a)</sub> protons.

In Figure 6 we show the desorption curves of CH<sub>3</sub>OCH<sub>3</sub>. Again we see that significant yields are not observed for initial CH<sub>3</sub>OH coverages less than 40  $\mu$ mol/g. For higher initial coverages, CH<sub>3</sub>OCH<sub>3</sub> desorbs in a relatively narrow peak, with a peak temperature that is much less strongly dependent on the initial CH<sub>3</sub>OH coverage than for the case of H<sub>2</sub>O and CH<sub>3</sub>OH desorption. The onset of CH<sub>3</sub>OCH<sub>3</sub> evolution also occurs at a higher temperature than either H<sub>2</sub>O or CH<sub>3</sub>OH. Both observations suggest that the type of reaction involved in the rate-determining step for CH<sub>3</sub>OCH<sub>3</sub> desorption is fundamentally different from that for H<sub>2</sub>O and CH<sub>3</sub>OH desorption.

The desorption curves for the  $CH_2O$  product are shown in Figure 7. It is likely that the observed fluxes are lower than the actual rate of  $CH_2O$  formation, because the reactive  $CH_2O$ product is likely to readsorb and react to produce secondary products at other sites in the porous sample. This secondary reaction may account for the  $HCOO_{(a)}$  vibrational bands observed in the IR spectra at the end of the warm-up (cf. Figure 3). Despite these readsorption effects,  $CH_2O$  desorption is observed even at the lowest initial  $CH_3OH$  coverage. This is in contrast to the coverage dependence of the  $CH_3OH$  and  $CH_3OCH_3$  yields but is similar to the behavior of the  $H_2O$  yields.

We also observed monotonically increasing yields of CO, CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>2</sub> during the last part of each warm-up. The onset of CO desorption occurred at 523 K, while the onset of CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>2</sub> occurred simultaneously at 623 K.

Behavior of Stable  $CH_3O_{(a)}$  Groups. The residual  $CH_3O_{(a)}$  species that remain on the surface at the end of the TPD warm-up could only be removed at 673 K by admitting  $O_2$  into the cell. This step presumably oxidizes the residual  $CH_3O_{(a)}$  species to CO or  $CO_2$  and leaves residual  $OH_{(a)}$  species in their place. We also tested the effect of admitting  $O_2$  to the sample at lower temperature and found that this did not remove the residual  $CH_3O_{(a)}$  species; i.e., high-temperature oxidation is necessary to remove these species.

To test how the results in Figures 4-7 might be influenced by the presence of the residual  $CH_3O_{(a)}$  groups, we performed a sequence of repetitive TPD experiments *without* reoxidizing the sample at the end of each warm-up. Each repetition was performed with an initial CH<sub>3</sub>OH dosage of 40  $\mu$ mol/g, the amount needed to fill the high-stability sites on a clean surface (cf. Figure 5).

The behavior of the successive TPD scans showed that the effect of the residual  $CH_3O_{(a)}$  species is essentially cumulative. The desorption curves for the first experiment in the sequence are identical with those shown in Figures 4–7 for an initial  $CH_3OH$ coverage of 40  $\mu$ mol/g. After two or three repeated experiments, the curves for  $CH_3OH$ ,  $CH_2O$ , and  $CH_3OCH_3$  converge to resemble the results in Figures 5–7 for an initial  $CH_3OH$  coverage of 80  $\mu$ mol/g (i.e., the coverage for which about half of the adsorbed  $CH_3OH$  would react and half would remain on the surface in the high-stability sites).

Photoinduced CH<sub>3</sub>OH Decomposition. Finally, we measured the photoinduced product desorption fluxes upon exposing the sample to UV radiation following the CH<sub>3</sub>OH adsorption step. The observed products, in order of decreasing yield, included H<sub>2</sub>O, CO, H<sub>2</sub>, CH<sub>3</sub>OH, CH<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub>. The only product seen in the TPD experiments which was not also observed in the photodesorption experiments is CH<sub>3</sub>OCH<sub>3</sub>. Earlier steady-state kinetic measurements of photoassisted CH<sub>3</sub>OH oxidation also showed that the formation of CH<sub>3</sub>OCH<sub>3</sub> is not a photoassisted process.<sup>13</sup>

The evolution of the photodesorption flux with time was similar for all products. When the light was turned on, the initial rise in the product fluxes was instantaneous, compared to the response time of TPD apparatus. All of the fluxes subsequently decayed to 50% of their initial value within 3-5 min. Further decay took place over much longer times. This behavior suggests that the arrival of photogenerated carriers at the TiO<sub>2</sub> surface is the single rate-limiting process for the formation of all photodesorbed products and that this arrival rate decays as the barrier for charge migration to the surface increases due to changes in the potential distribution across the depletion layer (i.e., due to accumulation of uncompensated surface charge).

A more significant result is that the amount of photodesorbed products was small, compared to the yields observed during the TPD experiments with equal initial CH<sub>3</sub>OH coverages. This was easily confirmed by performing a TPD warm-up after completing each photodesorption experiment. We observed decreases in product yields of the order of 5%, relative to the amounts observed during a TPD experiment without preceding exposure to UV light. Thus, the stoichiometric yield of the photodesorption experiments corresponds to only a small fraction of the initial  $CH_3OH$  coverage. This in turn shows that the time-dependent decay in the photodesorption flux noted above is *not* due to the decrease in reactant coverage but instead represents a real decrease in photoefficiency of the process (e.g., as expected if bulk-surface charge transfer occurs to perturb the potential profile across the depletion layer).

During the photodesorption experiments we also observed that the sample changes color from white to blue, which is indicative of the formation of Ti(3+) cations in the bulk phase. We also observed a decrease in the optical transmission of the sample when recording an IR spectrum after the photodesorption experiment. Both observations indicate that the sample is reduced by exposure to UV radiation in the presence of adsorbed CH<sub>3</sub>OH. We confirmed that it is necessary to have preadsorbed CH<sub>3</sub>OH for reduction to occur by performing a control experiment without preadsorbed CH<sub>3</sub>OH. No color change was observed, which confirms that a reducing agent is necessary to accomplish the color change.

We also measured the extent of catalyst reduction by admitting measured amounts of  $O_2$  to the cell until the sample returned to its original white color. In this manner we determined that less than 2  $\mu$ mol/g of  $O_2$  is required to reoxidize the sample. This is much smaller than the initial amount of CH<sub>3</sub>OH on the surface (i.e., coverages up to 100  $\mu$ mol/g were studied in the photodesorption experiments) and further confirms that only a small amount of the surface CH<sub>3</sub>OH species is converted during the photodesorption experiments.

#### Discussion

In contrast to its behavior on ZnO, the decomposition of  $CH_3OH$  on  $TiO_2$  involves a complex reaction network which gives rise to several different gas-phase products. With the exception of  $CH_3OCH_3$ , which is observed only during the TPD experiments, all of these products can be produced either by increasing the sample temperature or by exposing the sample to UV light. All products appear to originate from  $CH_3O_{(a)}$  species with similar IR bands, i.e., the C-H stretching modes at 2930 and 2830 cm<sup>-1</sup>. The parameter which has the greatest effect on product selectivity is the initial  $CH_3OH$  coverage. This coverage dependence could originate from surface heterogeneity, repulsive interactions between adsorbates, and/or the statistics of surface coverage. In the latter two cases, surface diffusion of adsorbate partners prior to their bimolecular reaction may also influence the apparent kinetics.

Comparison of Decomposition on  $TiO_2$  vs ZnO. The CH<sub>3</sub>O<sub>(a)</sub> species adsorbed on ZnO are stable with respect to recombinative desorption and eventually decompose entirely via  $HCOO_{(a)}$  intermediates to produce H<sub>2</sub>, CO, and CO<sub>2</sub>. In contrast, CH<sub>3</sub>O<sub>(a)</sub> species on TiO<sub>2</sub> can undergo several reactions (e.g., recombinative desorption to yield CH<sub>3</sub>OH, condensation to yield H<sub>2</sub>O and CH<sub>3</sub>OCH<sub>3</sub>, oxidation to yield CH<sub>2</sub>O) or no reaction at all up to 723 K.

With the exception of the last observation, this behavior suggests that the metal-oxygen bond which binds the alkoxide group to the surface is stronger on ZnO than on TiO<sub>2</sub>. Possible causes for this difference include the difference in the coordination number of Zn and Ti cations on their respective oxide surfaces and/or the participation of d-electron orbitals in the metal-oxygen bond in the case of adsorption on TiO<sub>2</sub>. The former explanation would imply that it is harder to dissociate the Zn-OCH<sub>3</sub> bond at a 3-fold coordinated surface Zn cation than the corresponding Ti-OCH<sub>3</sub> bond at a 4- or 5-fold coordinated surface Ti cation. The latter explanation implies that the charge redistribution process that is required to dissociate the cation-oxygen bond is easier at a surface Ti cation, because of the larger number and spatial distribution of atomic orbitals that are available to participate in the reaction.

To account for the fact that a significant fraction of the  $CH_3O_{(a)}$ species on TiO<sub>2</sub> are stable to 673 K while  $CH_3O_{(a)}$  groups on ZnO decompose completely to  $HCOO_{(a)}$  species well below this temperature and also to account for the number of products observed during  $CH_3O_{(a)}$  decomposition on TiO<sub>2</sub>, we propose that the decomposition selectivity on the latter material is strongly influenced by the occupancy of neighboring surface sites. To illustrate this, four elementary bimolecular surface reactions are considered: If an  $HO_{(a)}$  group is near the  $CH_3O_{(a)}$  group, then proton

transfer takes place leading to  $CH_3O_{(a)}$  group, then proton

$$HO_{(a)} + CH_3O_{(a)} \rightarrow O_{(a)} + CH_3OH_{(g)}$$
(1)

If the HO<sub>(a)</sub> group is near a second HO<sub>(a)</sub> group, then an alternate proton-transfer reaction leads to H<sub>2</sub>O desorption:

$$HO_{(a)} + HO_{(a)} \rightarrow O_{(a)} + H_2O_{(g)}$$
(2)

If two  $CH_3O_{(a)}$  groups occupy neighboring sites, then methyl transfer occurs at a slightly higher temperature, leading to  $CH_3OCH_3$  desorption:

$$CH_3O_{(a)} + CH_3O_{(a)} \rightarrow O_{(a)} + CH_3OCH_{3(g)}$$
 (3)

If a  $CH_3O_{(a)}$  group has a neighboring  $O_{(a)}$  anion with no proton, then an oxidative H abstraction occurs, leading to  $CH_2O$  desorption:

$$CH_{3}O_{(a)} + O_{(a)} \rightarrow HO_{(a)} + CH_{2}O_{(g)} + 2e^{-}$$
 (4)

If none of the neighboring species listed above are present, then the  $CH_3O_{(a)}$  remains unreacted on the surface.

Reactions 1–3 can account for the large amounts of  $H_2O$ , CH<sub>3</sub>OH, and CH<sub>3</sub>OCH<sub>3</sub> that are observed during the TPD experiments. The fact that the desorption peaks for H<sub>2</sub>O and CH<sub>3</sub>OH are broad and coverage dependent suggests that the surface diffusion of protons occurs rapidly enough that HO<sub>(a)</sub> species at non-nearest-neighbor sites can contribute to the apparent desorption kinetics. In contrast, surface diffusion of methyl groups is expected to be negligibly slow, so that only the reaction of neighboring CH<sub>3</sub>O<sub>(a)</sub> groups can contribute to CH<sub>3</sub>OCH<sub>3</sub> desorption. This would explain why the CH<sub>3</sub>OCH<sub>3</sub> peak is narrow and does not shift greatly with coverage.

Reaction 4 is the only one of the four steps which occurs on ZnO. Moreover, in the case of ZnO the  $CH_2O$  product is immediately readsorbed and converted to a  $HCOO_{(a)}$  species. The fact that both reactions go to completion on ZnO below 600 K implies that the necessary  $O_{(a)}$  anions are always present on the ZnO surface. This is consistent with the fact that  $H_2$  instead of  $H_2O$  is observed during  $CH_3OH$  decomposition on ZnO; i.e., the  $O_{(a)}$  anions are not removed from the ZnO surface under these conditions.

For TiO<sub>2</sub> it appears that the surface sites surrounding the  $CH_3O_{(a)}$  group can become depleted of the necessary  $O_{(a)}$  anions, so that the  $CH_3O_{(a)}$  group may remain on the surface to much higher temperatures. This is consistent with the fact that  $H_2O$  instead of  $H_2$  is observed during  $CH_3OH$  decomposition on TiO<sub>2</sub>.

The loss of  $O_{(a)}$  anions can also explain why CH<sub>2</sub>O is able to diffuse out of the porous TiO<sub>2</sub> sample and reach the product detector, since  $O_{(a)}$  is assumed necessary to adsorb CH<sub>2</sub>O and convert it to HCOO<sub>(a)</sub>. Finally, the comparative behavior of the two materials suggests that the Zn–OH bonds are stronger than Ti–OH bonds, which parallels our earlier conclusion about the relative strength of Zn–OCH<sub>3</sub> and Ti–OCH<sub>3</sub> bonds.

We note that the removal of  $O_{(a)}$  anions from the TiO<sub>2</sub> surface by reactions 1 and 2 does not reduce the catalyst (i.e., no charge transfer is involved). In contrast, the formation of CH<sub>2</sub>O in reaction 4 releases two electrons, formally reducing the catalyst. However, no color change was ever observed during any of the TPD experiments. This is in contrast to the behavior during the photoinduced decomposition experiments where a blue color change occurred as the catalyst was reduced (see above). We interpret this to mean that the bulk to surface charge-transfer step which activates the photoinduced surface reactions at lower temperatures is not an essential step in the reactions at the higher temperatures characteristic of the TPD experiment. Instead, we propose that the electrons released by reaction 4 remain localized on the surface, presumably by reducing surface Ti(4+) cations to a lower oxidation state.

### Summary

The decomposition of CH<sub>3</sub>OH on TiO<sub>2</sub> yields several products and is strongly coverage dependent, in marked contrast to the decomposition of CH<sub>3</sub>OH on ZnO. The coverage dependence of the product selectivity can be attributed to the coverage statistics of neighboring adsorbates which serve as reaction partners. These include  $CH_3O_{(a)}$ ,  $HO_{(a)}$ , and  $O_{(a)}$  species. The bond between a surface cation and an adsorbate oxygen atom is much more easily broken on  $TiO_2$  than on ZnO, either because the Ti(IV) cation has a higher maximum coordination number and is thus better disposed to dissociate the bond to one of its oxygen neighbors or because the Ti(3d)-O(2p) orbital overlap allows easier charge redistribution during the dissociation step. The desorption of oxygen-containing products can be effected at room temperature by photoinduced charge transfer from the bulk to surface region, thereby creating bulk Ti(3+) sites. At higher temperatures, the thermally induced reactions occur without this bulk to surface charge-transfer step, presumably by the formation of surface Ti(3+) cations.

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