

Methanol Chemistry on Cu and Oxygen-Covered Cu Nanoclusters Supported on TiO₂(110)

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Received: June 5, 2004; In Final Form: September 9, 2004

The thermal decomposition of methanol has been studied on TiO₂(110) as well as on Cu and oxygen-covered Cu nanoclusters supported on TiO₂(110) using temperature programmed desorption (TPD). The sizes of the Cu clusters were characterized by scanning tunneling microscopy (STM). Methanol chemistry on the vacuum-annealed, reduced TiO₂ surface itself produces ethylene as the main desorption product. Reoxidation of the TiO₂ surface quenches the production of ethylene but also results in a new formaldehyde desorption peak at 870 K. The reactivity of methanol on small Cu nanoclusters (40.2 ± 7.0 Å diameter, 12.7 ± 2.4 Å height) is minimal, but trace amounts of formaldehyde, CO₂, methane and H₂ are detected in TPD experiments, demonstrating that the Cu nanoclusters are more active than bulk single-crystal Cu surfaces. On oxygen-covered Cu nanoclusters, methanol reaction produces formaldehyde and CO₂ as the major gaseous products as well as H₂, water, and methane. The yields of formaldehyde and CO₂ increase as the Cu coverage is increased from 2 to 12 ML, indicating that these products are formed from reaction associated with the Cu surface. Lattice oxygen from the titania surface participates in methanol reaction because reoxidation of the titania surface with ¹⁸O₂ prior Cu deposition results in the evolution of H₂¹⁸O, C¹⁶O¹⁸O, and C¹⁸O₂ in TPD experiments. No cluster size effects were observed for methanol chemistry on the pure Cu and oxygen-covered Cu clusters.

Introduction

Understanding chemistry occurring on the surfaces of oxide-supported metal clusters provides critical information for the design and development of superior heterogeneous catalysts. Although the industrial catalysts typically consist of metal clusters dispersed on oxide supports, these catalytic systems are frequently too complicated for a complete understanding of the surface chemistry on the molecular level. Consequently, metal nanoclusters supported on single-crystal oxide surfaces have been used as simple models for investigating catalytically important chemical reactions on nanocluster surfaces. The surface chemistry occurring in these systems has been studied under ultrahigh vacuum conditions ($P \sim 1 \times 10^{-10}$ Torr) so that chemical reactions on well-defined and well-characterized surfaces can be investigated in a highly controlled environment.

In the catalysis literature, it has been shown that the surface chemistry of oxide-supported metal nanoclusters can be distinctly different from chemistry on the corresponding bulk materials.^{1–3} It is also possible to change the activity of the metal clusters by changing their sizes, as Haruta and co-workers demonstrated for Au on titania catalysts.^{4–7} The catalytic activity of Au particles is believed to arise from interaction with the titania support, and the Au–titania perimeter around the supported clusters is proposed to be the active site.^{4,6,7} There are a number of other studies in the recent catalysis literature that illustrate cluster size-dependent reactivity, such as the catalytic reduction of NO_x with C₃H₆ over Pt,⁸ propene oxidation over Ag,⁹ and hydrodechlorination of chlorobenzene over Ni.¹⁰

In this work, we have investigated the reaction of methanol on pure Cu and oxygen-covered Cu clusters deposited on a

single-crystal rutile TiO₂(110) surface as a model system for understanding the commercial Cu catalysts, which are industrially important materials for the conversion of methanol to formaldehyde.^{11,12} TiO₂(110) was chosen as the support because the structure of this surface is well-studied, thermally stable and can be made sufficiently conductive for electron spectroscopy and diffraction studies by heating in vacuo; this heating process removes oxygen from the crystal, resulting in an n-type semiconductor. Furthermore, titania is a support on which cluster-size dependent activity has been observed for Au by Haruta and co-workers, and the support surface is believed to play a major role in the unusually high catalytic activity of Au on titania. Titania is also known to be a particularly good support for Cu catalysts used in the reduction of NO.¹³

Methanol oxidation is a good probe reaction for investigating the activity of the supported Cu clusters because methanol adsorption and reaction on single crystal Cu surfaces has been widely studied and is well understood. Previous investigations of methanol reaction on clean single-crystal Cu surfaces reported little or no reactivity. On Cu(111), the surface was completely inert to methanol decomposition, and only the desorption of molecularly adsorbed methanol was observed in temperature programmed desorption (TPD) experiments.¹⁴ The Cu(110) surface is believed to be slightly more reactive; although methanol can dissociate to methoxide around 270 K, no reaction products were observed, and only methanol desorption between 140 and 400 K was detected.¹⁵ Another study confirmed that the clean Cu(110) surface was unreactive toward methanol,^{16,17} but a recent high-resolution XPS investigation reported molecular formaldehyde as a minor surface species in addition to methanol and methoxide.¹⁸

The reactivity of methanol is greatly enhanced on oxygen-covered Cu because O–H bond scission is facilitated by adsorbed oxygen.^{14,15,19} For methanol reaction on O–Cu(111),

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formaldehyde and water were the major products with CO₂ as a minor product.¹⁴ Formaldehyde was believed to form via a methoxide intermediate whereas CO₂ was produced via a formate intermediate. Surface formate was identified by infrared spectroscopy during methanol reaction on O–Cu(100).²⁰ The activity of the surface toward methanol reaction reached a maximum at an intermediate oxygen coverage. This dependence on oxygen coverage for both Cu(110)¹⁷ and Cu(111)¹⁴ can be explained by the fact that the active sites require metallic Cu sites in proximity to an oxygen atom, which promotes methoxide formation. STM studies showed that methoxide was formed at the edges of oxygen islands rather than within the islands.^{17,21} For methanol decomposition on O–Cu(110), water and formaldehyde were also the major gaseous products, but in some cases CO₂ was observed.^{15,19} Studies have shown that the selectivity of formaldehyde production over CO₂ is highly sensitive to the structure of the methoxide–oxygen overlayer.²² To produce surface formate, methoxide decomposition must occur in the presence of atomic oxygen, and this is a condition that is favored by coadsorption or adsorption at higher temperatures.

There are a few cases in which cluster-size effects have been observed for Cu catalysts. For example, Cu catalysts supported on alumina-based mixed oxides are used for CO removal in methanol steam re-formed gas, and smaller Cu clusters were observed to have the highest catalytic activity.²³ The reduction of NO over Cu clusters on titania also showed that particles of a specific size had the greatest activity.²⁴ For nanometer-sized Cu clusters on mesoporous Al supports, smaller clusters promoted selective hydrogenation of the carbonyl group in cinnamaldehyde, in contrast to hydrogenation of the C=C bond observed on larger Cu clusters.²⁵

The studies presented here focus on TPD experiments for methanol reaction on TiO₂-supported Cu nanoclusters, which are characterized by STM. Small (40.2 ± 7.9 Å diameter, 12.7 ± 2.4 Å height) Cu clusters as well as 12 monolayer (ML) Cu films are found to be relatively inactive for methanol chemistry although both are more active than single-crystal Cu surfaces. On oxygen-covered Cu clusters, formaldehyde, CO₂, water, and H₂ are the main reaction products, and their yields increase with increasing Cu coverage. Isotopic labeling experiments with ¹⁸O₂ demonstrate that lattice oxygen from TiO₂ is incorporated into CO₂ and H₂O desorption products. The Cu clusters are annealed to 800 K to produce large cluster sizes (68.8 ± 8.3 Å diameter, 25.8 ± 3.9 Å height) before exposure to methanol and oxygen. For both the Cu and oxygen-covered Cu clusters, methanol reaction is not sensitive to cluster size; the same desorption products and temperatures are observed on the small clusters, large clusters, and 12 ML Cu film.

Experimental Section

All TPD and Auger experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 1.2×10^{-10} Torr, which was maintained with a Varian 500 L/s ion pump and Varian 300 L/s turbomolecular pump. The chamber was equipped with a Hiden HAL 301/3F quadrupole mass spectrometer for TPD studies, an Omicron cylindrical mirror analyzer for Auger electron spectroscopy, Omicron Spectaleed three-grid optics for low energy electron diffraction (LEED), and a Specs IQE 11/35 ion source for sputter cleaning. STM experiments were conducted using a variable-temperature Omicron STM (VT-25) in a separate UHV chamber, which is described in more detail elsewhere.^{26–28}

In the TPD chamber, the rutile TiO₂ (110) crystal (Commercial Crystal Laboratories, Inc.) was mounted on a 0.25 mm

Ta (ESPI, 99.98%) backplate closely cut to the dimensions of the 1 cm² crystal and was held in place with 0.127 mm tantalum foil strips wrapped over the side edges of the crystal. The sample can be cooled to ~100 K by thermal contact with a liquid nitrogen reservoir and heated to 1200 K by electron bombardment from a thoriated tungsten filament positioned 1 mm behind the backplate. The sample temperature was monitored using a Type C thermocouple spot-welded to the backplate. The crystal was cleaned by Ar⁺ bombardment (500 eV, 4.0 μA current to the crystal) for 20 min, followed by annealing at 1050 K for three 5 min cycles. Crystal cleanliness and structure were confirmed by Auger spectroscopy, and the crystal exhibited a (1×1) LEED pattern after sputtering and annealing.

The quadrupole mass spectrometer used for TPD experiments was enclosed in a 7.6 cm diameter stainless steel shroud capped by a gold-plated moveable flag with a 4 mm diameter round aperture cut in the flag. To minimize contributions from desorption from the sample holder during TPD experiments, the crystal was positioned directly in front of the aperture and 1 mm from the flag. The crystal was also biased at –100 V to prevent electron induced desorption or reaction from the mass spectrometer filament. A linear temperature ramp of 1 K/s was generated using an in-house LabView program interfaced with the power supply (Kepco ABC 10-10DM) that provided current to the heater filament. The thermocouple signal was passed through a signal conditioner (Analog Devices 5B401-2) that removed the bias voltage and amplified the signal by a factor of 100.

Copper was evaporated from a homemade source using a copper pellet (Aldrich 99.9999%) wrapped in tungsten wire (0.25 mm, Alfa Aesar 99.95%), which was enclosed within a tantalum foil shroud. The Cu coverage was calibrated using a quartz crystal microbalance (Inficon), and coverages in monolayers (ML) are defined with respect to the packing of the Cu(111) surface (1.77×10^{15} atoms/cm²). Methanol (Fisher Scientific, 99.9%, HPLC grade) was purified by three freeze–pump–thaw cycles before each experiment and was dosed via a stainless steel directed dosing tube with the crystal positioned 2 mm away from the end of the tube. The oxygen gas (Matheson, 99.9%) was used as received. Before each experiment, the crystal was sputtered and annealed at room temperature and then cooled to 100 K. For experiments on oxygen-covered Cu clusters, Cu was dosed at room temperature (300 K) at 0.5 ML/min, followed by exposure to oxygen via directed dosing at 300 K for 2 min at a chamber pressure of 5.0×10^{-9} Torr. The crystal was then allowed to cool to 100 K before exposure to methanol via directed dosing for 6 s at a chamber pressure of 1.0×10^{-9} Torr.

The TPD data were collected using the multiple ion detection mode of the Hiden software. Up to 12 masses were monitored as well as the temperature using a 45 ms dwell time and 6 ms settle time. Before each TPD experiment, the surface was subjected to a saturation exposure of methanol at liquid nitrogen temperature (<100 K) and then flashed to 200 K to remove methanol multilayers. To confirm the absence of any additional products, wide mass scans from 0 to 100 amu were conducted while adsorbed methanol was heated to 950 K on the following surfaces: TiO₂, reoxidized TiO₂, 2 ML Cu clusters on TiO₂, and oxygen-covered 2 ML Cu clusters on TiO₂. In all cases, no masses were detected other than the cracking fragments associated with the assigned products. Heating the TiO₂, oxygen-treated TiO₂ and Cu clusters in front of the mass spectrometer without any methanol dosing established that there was no

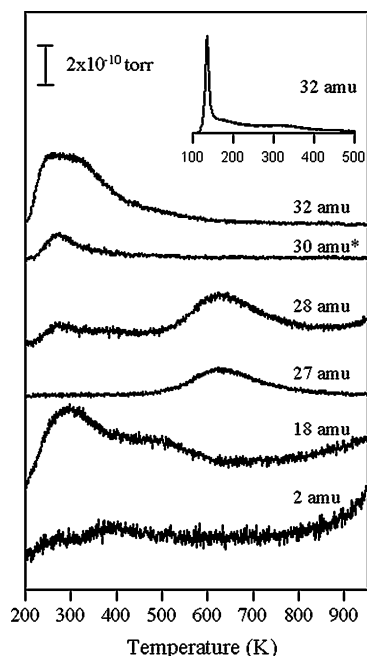


Figure 1. Temperature programmed desorption data for a saturation exposure of methanol adsorbed on vacuum annealed $\text{TiO}_2(110)$ at 100 K and heated at 1 K/s to 950 K. The surface was first heated to 200 K to desorb methanol multilayers before data collection. The inset shows methanol desorption data for the identical experiment in which the surface was *not* heated to 200 K before data collection.

desorption from the sample holder or from potential surface contaminants.

Results

TPD studies of methanol on the vacuum annealed $\text{TiO}_2(110)$ surface show that titania itself is active for methanol decomposition (Figure 1). The primary desorption products are water (18 amu), which has a main peak at 300 K and a smaller shoulder at 500 K, and ethylene (27, 28 amu) at 630 K; the ratios for the 25:26:27:28 amu signals at 630 K correspond to the cracking ratio for ethylene reported in the NIST database. Furthermore, methanol desorption (32 amu) between 200 and 400 K is detected. The inset to Figure 1 shows methanol multilayer desorption at 140 K for a surface that was not flashed to 200 K before TPD, and the broad peak centered at 300 K is also observed in this experiment. Trace amounts of H_2 (2 amu) are produced between 300 and 500 K, and a small 30 amu desorption peak at 270 K is attributed to formaldehyde, on the basis of the ratios of the 28, 29, and 30 amu signals. These signals were first corrected for contribution from methanol cracking, which was determined from the 28:29:30:31:32 amu ratios measured by the mass spectrometer when methanol was leaked into the chamber. No methane (16 amu) or CO_2 (44 amu) desorption is observed, and the 31:32 amu ratio is correct for methanol.

The TiO_2 surface could be made less active toward methanol decomposition by reoxidizing the surface after sputtering and annealing. Specifically, the surface was exposed to oxygen at 5×10^{-7} Torr for 15 min at 900 K. The TPD data shown in Figure 2a indicate that reoxidation of the TiO_2 surface suppresses the production of ethylene at 630 K, but a high temperature 30 amu signal attributed to formaldehyde appears at 870 K and is accompanied by methanol desorption at the same temperature. Formaldehyde production at 270 K is not observed. The only other desorption products detected are water (18 amu) in a peak centered at 350 K and traces of H_2 (2 amu) between 300 and

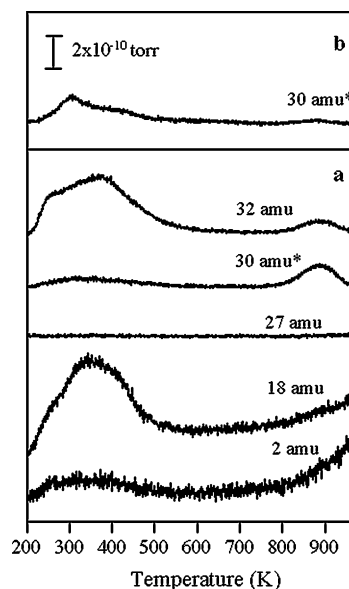


Figure 2. Temperature programmed desorption data for a saturation exposure of methanol adsorbed at 100 K and heated at 1 K/s to 980 K on $\text{TiO}_2(110)$ reoxidized by heating at 900 K for (a) 15 min at an oxygen pressure of 5×10^{-7} Torr (standard reoxidation procedure) and (b) three 15 min cycles at 1×10^{-7} Torr. The 30 amu signals (*) have been corrected for the cracking contribution of methanol, and the surface were heated to 200 K to desorb methanol multilayers before data collection.

400 K. The ratios of the O(KLL):Ti(LMM) Auger peaks are 1.55 for unoxidized titania and 1.66 for the reoxidized surface. The intensity of the 870 K formaldehyde desorption peak is more sensitive to the amount of surface oxygen than the O:Ti Auger ratio, with greater oxygen content diminishing the intensity of the 870 K peak. In general, higher oxygen pressures of 3×10^{-7} to 5×10^{-7} Torr during reoxidation did not increase the O:Ti Auger ratio or decrease the high temperature formaldehyde peak in the TPD spectrum, whereas multiple oxidation cycles of 15 min each decreased the 870 K peak but did not affect the O:Ti Auger ratio. For example, methanol TPD on titania reoxidized at an oxygen pressure of 1×10^{-7} Torr and 900 K for three 15 min cycles results in the complete disappearance of the high temperature formaldehyde peak and the reappearance of the 270 K peak (Figure 2b). Heating the surface to 700 K after reoxidation also removes enough surface oxygen to affect the intensity of the high temperature formaldehyde peak.

The 2 ML Cu clusters deposited on $\text{TiO}_2(110)$ show some activity for methanol decomposition, unlike the inert single-crystal Cu surfaces. STM images of the 2 ML Cu clusters (Figure 3a) indicate that the average size of the Cu clusters is 40.2 ± 7.0 Å in diameter and 12.7 ± 2.4 Å in height, based on measurements for 30 clusters. Although Cu clusters on TiO_2 are known to sinter upon annealing,^{26,29} the STM images in Figure 3b,c illustrate that when the Cu clusters are heated at 2 K/s to 500 and 700 K, there is little change in cluster size. The TPD data in Figure 4a for methanol reaction on the 2 ML Cu clusters demonstrate that the main desorption species include water (18 amu) with peaks at 270 and 400 K, and methanol (32 amu) with a main desorption feature at 270 K and shoulder at 350 K. The production of water suggests that O–H bonds in methanol are broken, and methanol desorption occurs after recombination of methoxide and surface hydrogen. The desorption of formaldehyde (30 amu) is observed in broad peaks centered at 270, 500, and 680 K. The 30 amu signal has been corrected for the cracking contribution of methanol; although

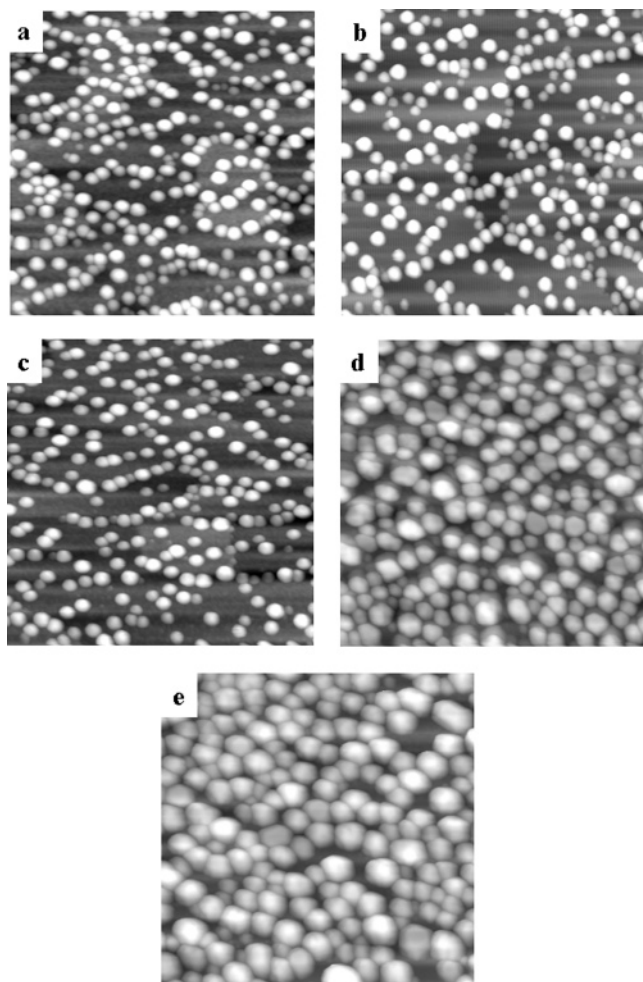


Figure 3. Scanning tunneling microscopy images ($1000 \text{ \AA} \times 1000 \text{ \AA}$) of Cu deposited on $\text{TiO}_2(110)$ at room temperature and at 0.5 ML/min for the (a) 2 ML Cu clusters, (b) 2 ML Cu clusters heated to 500 K, (c) 2 ML Cu clusters heated to 700 K, (d) 12 ML Cu film, and (e) 12 ML Cu film heated to 700 K. Images were collected at a $+1.8 \text{ eV}$ sample bias and 0.15 nA tunneling current.

the 30:32 amu ratio in methanol is relatively low (0.204), methanol cracking has a noticeable contribution to the overall peak shape because the total 30 amu signal is much smaller than the 32 amu signal from methanol. Trace amounts of H_2 (2 amu), methanol (16 amu), and CO_2 (44 amu) are also detected.

Methanol reaction on Cu clusters corresponding to higher coverages (4, 8, 12 ML) is nearly identical to that on the 2 ML clusters, illustrating that methanol chemistry is insensitive to Cu coverage. For comparison, the TPD spectrum for methanol reaction on 12 ML of Cu is shown in Figure 4b. An STM image of the 12 ML Cu film (Figure 3d) shows that the surface consists of Cu clusters ranging from ~ 50 – 100 \AA in diameter and 12 – 23 \AA in height. Even at this high coverage, the Cu film does not completely cover the TiO_2 surface, and Cu clusters appear to grow on top of existing clusters instead of covering exposed regions of TiO_2 . After heating the Cu film to 700 K at a rate of 2 K/s , the clusters coalesce into larger islands with more regular shapes that are as large as 125 \AA in diameter and 35 \AA in height. As the coverage is increased from 2 to 12 ML, the only differences in the TPD spectra are that the higher temperature 30 amu peaks at 500 and 680 K disappear, and the 32 amu shoulder at 380 K is diminished (data not shown). The 350 K shoulder for methanol desorption appears to be associated with methanol adsorption on the titania surface because its intensity decreases with increasing Cu coverage. Similarly, the broad 680

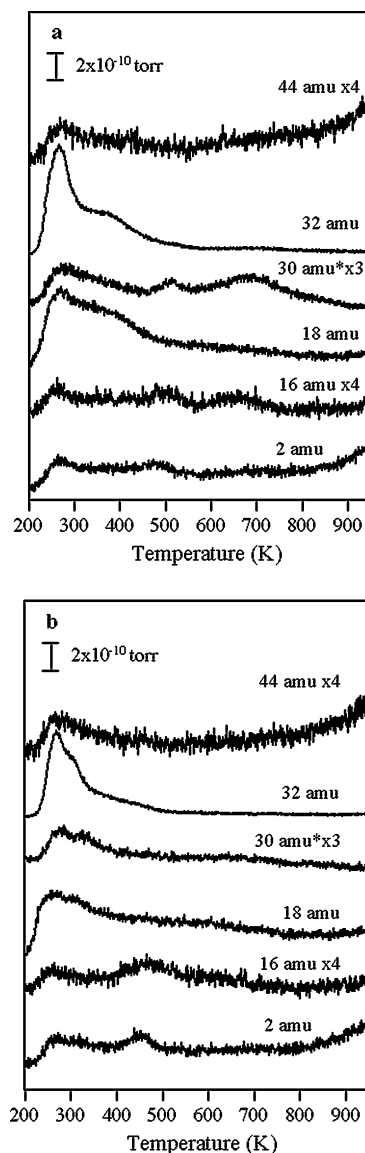


Figure 4. Temperature programmed desorption data for a saturation exposure of methanol adsorbed at 100 K on the (a) 2 ML Cu clusters and (b) 12 ML Cu film, deposited on the reoxidized $\text{TiO}_2(110)$ surface and heated at 1 K/s to 980 K. The surface was first heated to 200 K to desorb methanol multilayers before data collection. The 30 amu signals (*) have been corrected for the cracking contribution of methanol.

K formaldehyde peak is most likely associated with reaction on oxygen-covered titania. There are no significant changes in the 2, 16, or 44 amu signals with increasing Cu coverage. The 500 K formaldehyde desorption peak is still present on the 4 ML Cu clusters but is completely absent on 8 and 12 ML clusters. As discussed in the next section, the 500 K formaldehyde peak is associated with methanol reaction on oxygen-covered Cu surfaces, and for the lower Cu coverages, diffusion of oxygen from the titania surface to the Cu surfaces may be responsible for the production of formaldehyde. However, when the oxygen content of the titania surface was intentionally increased by reoxidation at higher oxygen pressures for multiple cycles, reaction of methanol on the 2 ML Cu clusters did not produce more formaldehyde at 500 K.

Methanol activity on oxygen-covered Cu clusters is much higher than on the unoxidized clusters and is similar to that reported for methanol reaction on oxidized single-crystal Cu surfaces. As shown in Figure 5, methanol reaction on the oxygen-covered 2 ML Cu clusters produces H_2 (2 amu) at 495

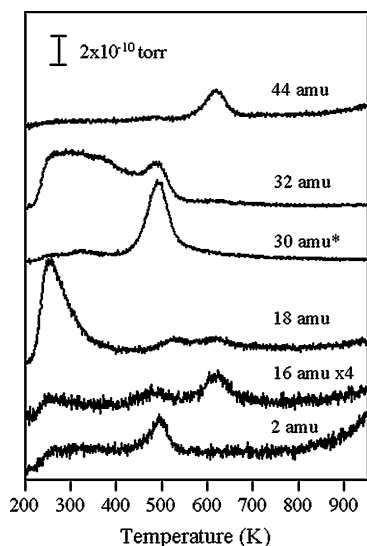


Figure 5. Temperature programmed desorption data for a saturation exposure of methanol adsorbed at 100 K on oxygen-covered 2 ML Cu clusters deposited on reoxidized $\text{TiO}_2(110)$. Saturation exposure of methanol was carried out at 100 K, and oxidation of the Cu clusters was carried out at room temperature. The surface was first heated to 200 K to desorb methanol multilayers before data collection, and the temperature ramp was 1 K/s. The 30 amu signals (*) have been corrected for the cracking contribution of methanol.

K, formaldehyde (30 amu) at 490 K, and CO_2 (44 amu) at 620 K. Based on the integrated peak areas, the 28:30 amu and 29:30 amu ratios are within 10–20% of the ratios reported for formaldehyde in the NIST database of mass spectra. Water (18 amu) is also formed with a major peak at 255 K and two smaller features at 530 and 620 K. Methanol desorption occurs in a broad feature between 230 and 400 K as well as in a sharper peak at 485 K. The 31:32 signal ratio confirms that the 32 amu peak is from methanol only. A small amount of methane (16 amu) is also detected at 620 K. Other products such as ethylene (27 amu), acetic acid (60 amu), ethanol (45 amu), and formate (46 amu) are not observed. As the Cu coverage is increased to 12 ML (Figure 6), the yields of formaldehyde, CO_2 , and H_2 increase, indicating that these products are associated with methanol reaction on the oxygen-covered Cu surface. The sharp methanol peak at 485 K and the high temperature water peaks also grow with increasing Cu coverage. There is little change in the signal intensities between reaction on 8 and 12 ML of Cu. The two high temperature 18 amu peaks become more distinct with increasing Cu coverage because the production of water at higher temperature is associated with the decomposition of methanol into formaldehyde and CO_2 on oxygen-covered Cu. Both of these reactions liberate hydrogen atoms that can combine with surface oxygen to produce water. Notably, the deposition of 2 ML of Cu suppresses the high temperature desorption of methanol and formaldehyde, which are observed on the reoxidized TiO_2 surface itself.

STM studies of the 2 ML Cu clusters before (Figure 3a) and after exposure to oxygen (data not shown) indicate that oxygen does not induce major changes in cluster size. Previous studies involving the oxidation of Cu clusters supported on TiO_2 reported that oxygen exposure resulted in the disappearance of three-dimensional (3D) Cu clusters from the STM images, and this behavior was attributed to oxygen-induced dissociation of 3D clusters into 2D islands.^{30,31} For the oxygen exposures used in this work, only subtle changes in the Cu clusters are observed; specifically, the density of 3D clusters (height > 2 Å) decreases by ~20% after oxygen exposure, and smaller 2D clusters appear.

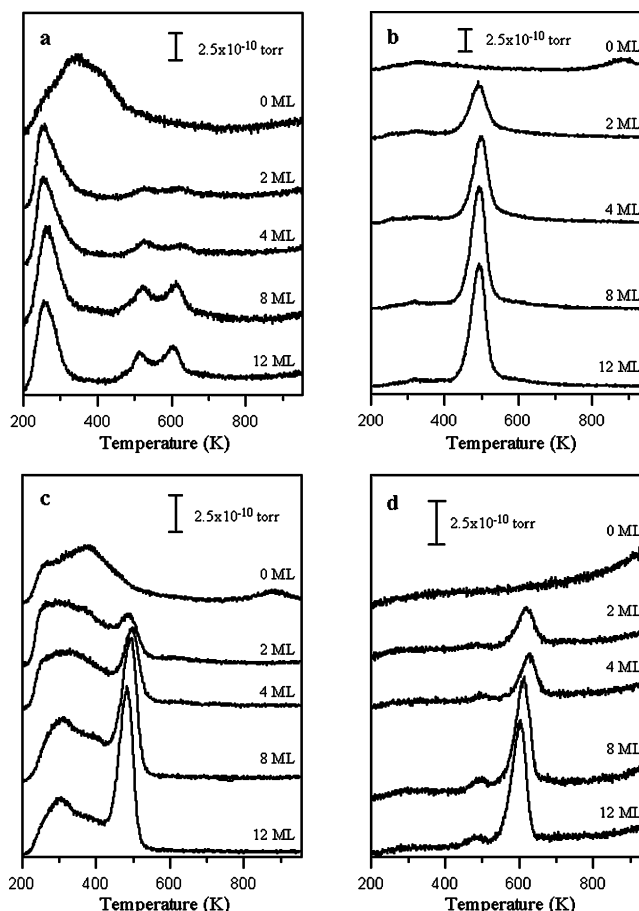


Figure 6. Temperature programmed desorption data for a saturation exposure of methanol adsorbed on oxygen-covered Cu clusters deposited on reoxidized $\text{TiO}_2(110)$ for Cu coverages of 0–12 ML: (a) 18 amu; (b) 30 amu corrected for the cracking contribution of methanol; (c) 32 amu; (d) 44 amu. Methanol multilayers were removed from the surface by heating to 200 K before collecting the TPD data with a linear temperature ramp of 1 K/s.

Isotopic labeling experiments with $^{18}\text{O}_2$ demonstrate that lattice oxygen from the titania support participates in methanol reaction. Incorporation of ^{18}O in the titania lattice was achieved by exposure of the surface to $^{18}\text{O}_2$ at 900 K for 15 min at a pressure of 5×10^{-7} Torr following the usual sputtering and annealing treatment. Methanol reaction on this reoxidized surface produces H_2^{18}O (20 amu) in addition to H_2^{16}O (18 amu), indicating that the formation of water involves the combination of a hydroxyl hydrogen from methanol and oxygen from the titania surface. Methanol reaction on the oxidized and unoxidized 2 ML Cu clusters deposited on ^{18}O -enriched titania also produces H_2^{18}O but no $\text{CH}_3^{18}\text{OH}$ or HCH^{18}O , which would result from C–O bond scission and exchange of ^{16}O and ^{18}O atoms. Furthermore, reaction on the oxygen ^{16}O -covered 2 ML Cu clusters (Figure 7a) produces $\text{C}^{18}\text{O}^{16}\text{O}$ (46 amu) and C^{18}O_2 (48 amu) in addition to C^{16}O_2 (44 amu), indicating that C–O scission and oxygen exchange with the titania lattice occurs at 620 K. In a complementary experiment, the titania surface was reoxidized with $^{16}\text{O}_2$, 2 ML Cu clusters were deposited, the clusters were exposed to $^{18}\text{O}_2$, and the surface was then exposed to methanol. The resulting TPD spectrum (Figure 7b) shows that $\text{C}^{18}\text{O}^{16}\text{O}$, C^{18}O_2 , and C^{16}O_2 are produced as well as H_2^{18}O and H_2^{16}O ; again, ^{18}O was not incorporated into methanol or formaldehyde. In both experiments shown in Figure 7, the yields for C^{16}O_2 and $\text{C}^{16}\text{O}^{18}\text{O}$ were approximately the same whereas the C^{18}O_2 yield was decreased by a factor of 2. When the titania surface was reoxidized with $^{18}\text{O}_2$ before Cu deposition, most

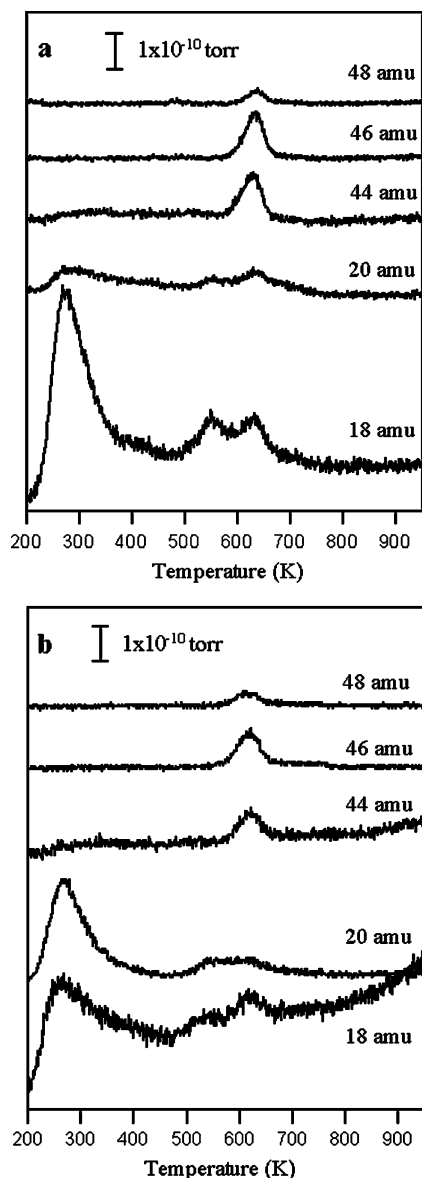


Figure 7. Temperature programmed desorption data for methanol adsorption on oxygen-covered 2 ML Cu clusters deposited on reoxidized $\text{TiO}_2(110)$ for the surface: (a) reoxidized with $^{18}\text{O}_2$ and then exposed to $^{16}\text{O}_2$ after Cu deposition; (b) reoxidized with $^{16}\text{O}_2$ and then exposed to $^{18}\text{O}_2$ after Cu deposition. Only signals corresponding to water and carbon dioxide are shown here. Saturation exposure to methanol was carried out at 100 K, and methanol multilayers were removed from the surface by heating to 200 K before collecting the TPD data with a linear temperature ramp of 1 K/s.

of the water desorption at 255 K occurs as H_2^{16}O rather than H_2^{18}O . However, exposure of the Cu clusters directly to $^{18}\text{O}_2$ results in significant H_2^{18}O desorption at 255 K. Therefore, the majority of low temperature water production occurs on the surface of the 2 ML Cu clusters, and lattice oxygen does not migrate onto the Cu clusters at 255 K.

Methanol chemistry on both the Cu and oxygen-covered Cu clusters is insensitive to cluster size. Large clusters were formed by room-temperature deposition of 4 ML of Cu followed by annealing to 800 K for 2 min. As shown in the STM images in Figure 8, the average cluster size increased from 43.8 ± 6.5 Å in diameter and 16.7 ± 3.5 Å in height to 68.8 ± 8.3 and 25.8 ± 3.9 Å, respectively. The Cu(MNN):Ti(LMM) Auger ratio is decreased by 40% after annealing. For the 4 ML Cu clusters annealed to 800 K, methanol activity is identical to that on the unannealed clusters (Figure 9a); this result is not surprising given

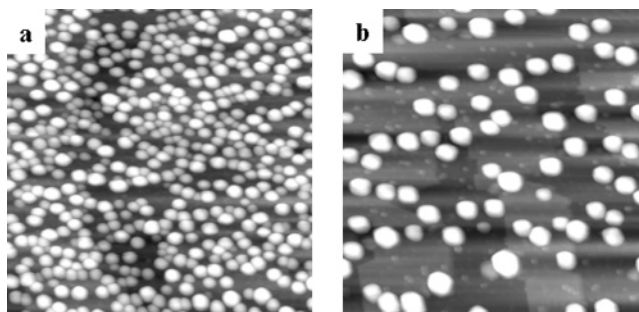


Figure 8. Scanning tunneling microscopy images ($1000 \text{ Å} \times 1000 \text{ Å}$) of Cu deposited on $\text{TiO}_2(110)$ at room temperature and at 0.5 ML/min for (a) 4 ML Cu clusters and (b) 4 ML Cu clusters heated to 800 K for 2 min.

that there is little activity on the pure Cu clusters. For methanol reaction on Cu clusters deposited on the vacuum annealed (unoxidized) TiO_2 surface and annealed to 800 K, ethylene desorption at 680 K is detected from reaction on exposed TiO_2 . As expected, more ethylene is produced on annealed 5.5 ML clusters compared to 12 ML clusters because the lower Cu coverage leaves more of the titania surface exposed after annealing due to cluster sintering. For methanol reaction on the oxygen-covered 4 ML Cu clusters, annealing to 800 K for 2 min before oxygen exposure also has no effect on the resulting methanol TPD experiment (Figure 9b). The same products, desorption temperatures, and peak intensities are observed as compared that with the smaller, unannealed Cu clusters. Although the Cu clusters are known to sinter and decrease the available surface area after annealing, the formaldehyde or CO_2 yields are approximately the same for the annealed vs unannealed clusters.

Discussion

Our TPD studies of methanol reaction on the highly reduced, vacuum annealed $\text{TiO}_2(110)$ surface shows that water and ethylene are the main desorption products whereas small amounts of H_2 and formaldehyde are also produced. A number of studies involving methanol adsorption on TiO_2 have demonstrated that the main surface intermediate is methoxide, which is formed from O–H bond scission in methanol.^{32–37} Farfan-Arribas and Madix also investigated methanol chemistry on $\text{TiO}_2(110)$ surfaces on which oxygen vacancy defects were introduced by electron bombardment.³² These defective TiO_2 surfaces were active for methanol reaction, but methane rather than ethylene was the main desorption product. However, on the surface with the greatest defect concentration, a small amount of ethylene was produced at 500 K and was attributed to reaction occurring between methoxide groups on adjacent defect sites. The formation of methane occurred via the methoxide intermediate, which undergoes C–O bond breaking to produce a methyl species that hydrogenates to methane. Defects in our TiO_2 surface are produced by annealing, which can introduce structural changes in the surface as well as oxygen vacancies, and therefore our surfaces may be slightly different from those used in the Madix study.

Earlier work by Henderson et al.^{33,36} reported only methanol desorption from $\text{TiO}_2(110)$, and therefore our $\text{TiO}_2(110)$ surface is apparently more defective than the surface in Henderson's studies. Henderson's surface was estimated to have ~8% oxygen vacancy sites, and although some methanol is believed to dissociate into methoxide, irreversible decomposition of methoxide was not observed.³³ In general, the number of defects in the TiO_2 surface has been found to significantly influence the

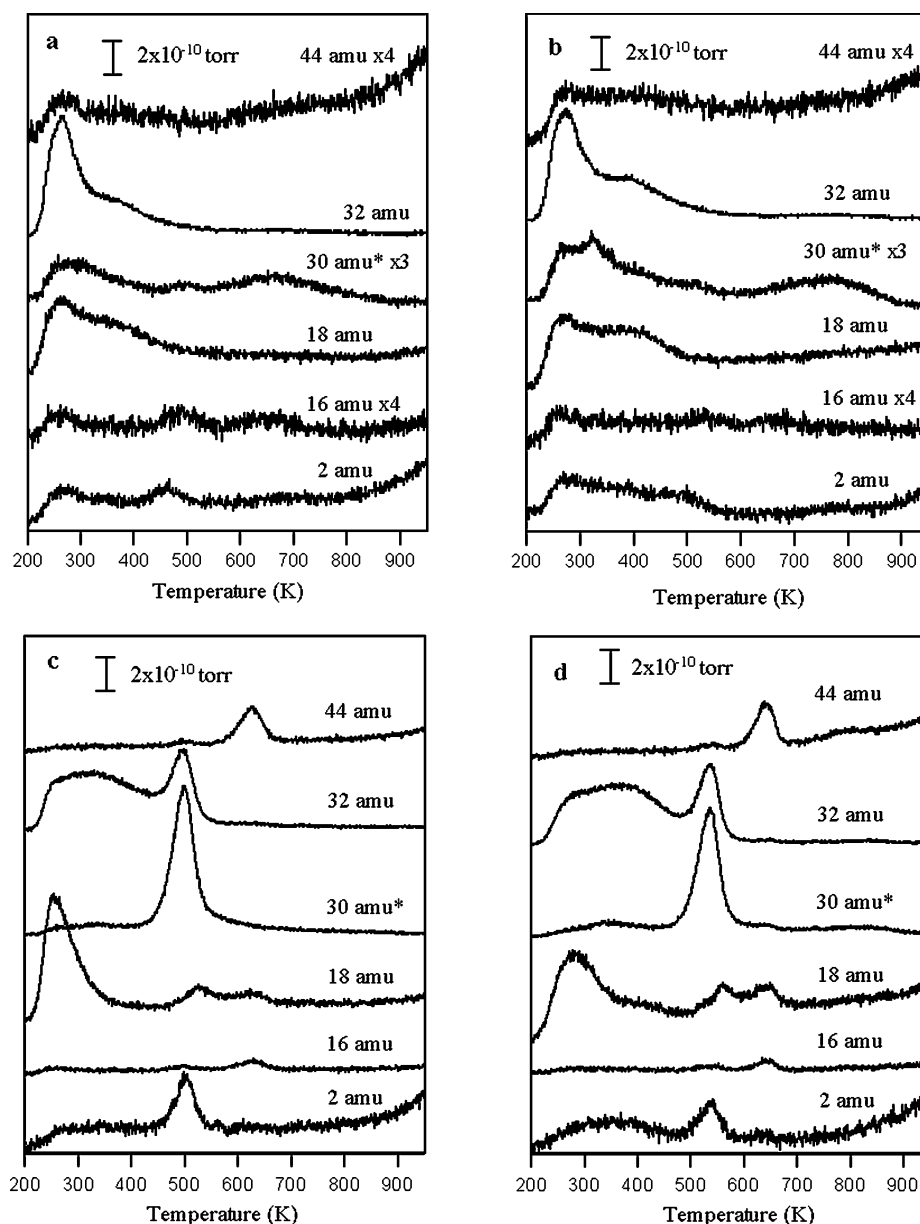


Figure 9. Temperature programmed desorption data for methanol adsorbed on the following clusters deposited on reoxidized TiO_2 : (a) 4 ML Cu clusters; (b) 4 ML Cu clusters annealed to 800 K for 2 min; (c) oxygen-covered 4 ML Cu clusters; (d) 4 ML Cu clusters annealed to 800 K for 2 min and exposed to O_2 . Saturation exposure of methanol was carried out at 100 K, and reoxidation occurred at room temperature. Methanol multilayers were removed from the surface by heating to 200 K before collecting the TPD data with a linear temperature ramp of 1 K/s. The 30 amu signals (*) have been corrected for the cracking contribution of methanol.

adsorption and decomposition of alcohols.^{32,38,39} A greater number of oxygen vacancies, which can be produced by extensive annealing in UHV, Ar^+ sputtering or electron bombardment, increases alcohol adsorption and reactivity. Our TPD studies have also shown that a near stoichiometric surface, which has undergone only a few cycles of sputtering and annealing, is inert toward methanol reaction, and ethylene production is not observed until the crystal has been subjected to many sputter-anneal cycles. Furthermore, the structure of the TiO_2 surface plays a role in determining methanol chemistry. On $\text{TiO}_2(001)$, the thermal decomposition of methanol produced methane, CO, and water,³⁷ and formaldehyde and methane desorption were also observed in some cases.³⁵ On anatase $\text{TiO}_2(101)$, only methanol desorption was observed, and X-ray photoelectron experiments did not show evidence for O–H bond scission;³⁴ the lack of reactivity on the anatase surface was attributed to the fact that oxygen vacancies are not as easily formed in the anatase surface compared to rutile TiO_2 .

When the TiO_2 surface is reoxidized at 900 K to eliminate oxygen vacancy defects, ethylene production is quenched, and high temperature formaldehyde and methanol desorption peaks appear at 870 K. X-ray photoelectron spectroscopy data for the $\text{Ti}(2p)$ region (data not shown) illustrate that the vacuum-annealed surface contains Ti^{3+} , which appears as a small high binding energy shoulder around 457 eV; after oxidation at high temperature, the shoulder from Ti^{3+} disappears, indicating that the surface is oxidized back to Ti^{4+} . These results suggest that ethylene formation is associated with Ti^{3+} sites because the elimination of these sites suppresses the production of ethylene. Notably, the Ti^{3+} shoulder for our vacuum annealed crystal was less pronounced compared to the crystal subjected to the lowest electron bombardment exposure in the Madix study.³² The production of formaldehyde and methanol at temperatures above 600 K has been observed on other oxidized titania surfaces^{32,33,37} and is attributed to the disproportionation of two methoxide groups, explaining the lack of hydrogen or water desorption at

the same temperature. This also suggests that surface oxygen stabilizes the methoxide intermediate at higher temperatures by inhibiting the recombination of methoxide and hydroxyl groups.³² Farfan-Arribas and Madix reported that oxygen dosed on the defective TiO₂ surfaces after methanol exposure shifted the selectivity from methane to formaldehyde production because in the absence of surface oxygen, decomposition of methanol to methane provides surface oxygen atoms to heal oxygen vacancies.³² In our experiments, the high temperature desorption peaks are extremely sensitive to the extent of surface reoxidation. Greater oxidation initially shifts the desorption peaks to higher temperature, but on the most highly oxidized surfaces, the high temperature peaks disappear while formaldehyde desorption at lower temperature (300 K) is observed. This behavior is not surprising given that the reactivity of oxygen on TiO₂ is a complex process that can depend on the oxidation temperature as well as the extent of bulk reduction of the crystal.^{40–43} Consequently, a number of different oxygen species can exist on the titania surface.³³ The deposition of Cu clusters on the surface suppressed the high temperature formaldehyde production but did not suppress the production of ethylene, suggesting that the surface sites responsible for formaldehyde and ethylene production are different and that Cu selectively binds to the former.

In comparison with the single-crystal Cu(111) and Cu(110) surfaces, the Cu clusters and 12 ML film are more active for methanol reaction. On the Cu surfaces deposited at room temperature, TPD experiments show that trace amounts of H₂, H₂O, HCHO, and CO₂ are formed although methanol is still the major desorption species. This suggests that the Cu clusters and film contain more active sites, presumably due to the greater number of defects; studies of Pd clusters deposited on oxide surfaces demonstrated that the surfaces of the clusters contain a high density of step and edge defects compared to Pd(111).^{44–48} Defects on the surface of the Cu clusters are expected to facilitate formation of the methoxide intermediate via O–H scission. In fact, O–H bond scission has also been reported to be more facile on the more open Cu(110) surface compared to the close-packed Cu(111) surface.^{15,19}

The TiO₂ surface plays a role in methanol chemistry on the Cu clusters, given that H₂¹⁸O is produced from a titania surface that has been reoxidized with ¹⁸O₂ prior to deposition of the Cu clusters. Because methanol decomposition to formaldehyde is facilitated by oxygen on the Cu surfaces, the lack of formaldehyde production indicates that there is not significant oxygen diffusion from the titania substrate to the Cu clusters. There is, however, a small formaldehyde peak at 500 K on the 2–4 ML Cu clusters but not on the clusters deposited at higher Cu coverages, suggesting that some oxygen migration to the Cu surface may occur only when a significant fraction of the titania surface is still exposed. When the 2 ML Cu clusters are deposited on the highly oxidized TiO₂ surface, increased formaldehyde production is not observed, which indicates that increasing the concentration of surface oxygen at this level does not promote diffusion of oxygen onto the Cu clusters.

Lattice oxygen from the titania support also participates in methanol chemistry on the oxygen-covered Cu clusters. Reoxidation of the surface with ¹⁸O₂ before Cu deposition results in the evolution of C¹⁸O₂ and C¹⁸O¹⁶O from methanol reaction, indicating that the C–O bond breaking occurs and that ~20% of the CO₂ production occurs via the recombination of surface carbon and oxygen atoms. Furthermore, H₂¹⁸O is also evolved at 250, 510, and 600 K. The lower temperature desorption peak is ascribed to hydrogen from the breaking of O–H bonds in

methanol, whereas the higher temperature peaks are attributed to hydrogen liberated by the decomposition of methoxide to formaldehyde or CO₂. Similar to methanol reaction on the TiO₂ surface reoxidized with ¹⁸O₂, H₂¹⁸O desorption is observed at 250 K and is assigned to the adsorption of hydroxyl hydrogen on lattice oxygen. The desorption of H₂¹⁸O at 510 and 600 K on the oxygen-covered 2 ML Cu clusters indicates that either lattice oxygen from the titania surface migrates onto the Cu clusters to combine with surface hydrogen atoms or that the hydrogen atoms migrate onto the titania surface, where they combine with lattice oxygen. There are a number of cases in the literature in which the oxide support participates in reactions on metal clusters on oxide surfaces. For example, our recent study of dimethyl methylphosphonate chemistry on TiO₂-supported Ni clusters demonstrated that carbon on the surface of the Ni clusters was oxidized by lattice oxygen from titania to produce CO.⁴³ A study by Bowker and co-workers reported that when O₂ dissociated on the surface of Pd particles on TiO₂, the oxygen atoms spilled over to the titania surface and promoted the growth of new titania islands.^{49,50} Henderson's study of formic acid on titania showed incorporation of ¹⁸O from the titania lattice into the formate surface intermediate, which decomposed into CO, formaldehyde, and water.⁵¹

The products formed on oxygen-covered Cu clusters and 12 ML film are the same as those on oxygen-covered single-crystal Cu surfaces such as Cu(110)^{15,17–19,22} and Cu(111).¹⁴ The presence of surface oxygen on the Cu clusters increases the activity for methanol oxidation to formaldehyde and CO₂ by facilitating O–H bond scission in methanol. The methoxide intermediate then decomposes to formaldehyde, H₂O, and H₂ as well as trace amounts of CH₄. CO₂ production at higher temperature is believed to occur via a formate intermediate.^{14,18–20} The product yields of formaldehyde, CO₂, water, and H₂ increase with increasing Cu coverage, illustrating that these products are formed from reaction on Cu; the trace amounts of methane do not increase with Cu coverage. After the Cu coverage reaches 8 ML, further Cu deposition has little effect, indicating that the surface area and morphology do not change significantly for higher coverages, and the reactivity at 8 ML is the same as that of a Cu film. In contrast to reaction on the single-crystal Cu surfaces, CO₂ desorption is accompanied by the production of water rather than H₂, presumably due to the fact that at temperatures above 600 K, the hydrogen atoms are mobile enough to migrate onto the TiO₂ surface, where they combine with lattice oxygen to produce water. A sharp methanol desorption peak occurs concomitantly with formaldehyde production at ~490 K, and both products are believed to originate from a surface methoxide intermediate that is stabilized in the presence of surface oxygen. The surface methoxy intermediate can either lose a hydrogen to produce formaldehyde or pick up a hydrogen to form the methanol, and on oxygen-covered Cu(110), formaldehyde production is also accompanied by methanol desorption.^{15,19} Notably, STM studies show that the small (2 ML) Cu clusters do not increase in size during TPD heating to 700 K, and all of the major reaction products desorb below 700 K. The 12 ML Cu clusters, which cover most of the TiO₂ surface, agglomerate into larger clusters after TPD heating to 700 K, but despite the change in surface morphology, the reactivity of the 12 ML surface is much like bulk Cu surfaces.

The reaction of methanol on pure Cu clusters is insensitive to cluster size. Cu clusters 68.8 ± 8.3 Å in diameter and 25.8 ± 3.9 Å in height are produced by annealing 4 ML of Cu to 800 K for 2 min. The larger Cu clusters have reactivity identical to that of the small, unannealed 4 ML Cu clusters that are 43.8

± 6.5 Å in diameter and 16.7 ± 3.5 Å in height. Oxygen-covered Cu clusters heated to 800 K for 2 min also have identical reactivity to the smaller, unannealed clusters. These results are not unexpected, given that methanol oxidation on Cu is not known to be a structure sensitive reaction. Furthermore, Cu atoms diffuse on Cu surfaces at room temperature,^{52,53} and the surface structure of the Cu clusters may be dynamic. Consequently, Cu clusters would not exhibit cluster size effects due to unique surface structures on clusters of different sizes. Preliminary scanning tunneling spectroscopy experiments on the large and small Cu clusters indicate that there are no obvious differences in the electronic properties for clusters of different sizes. Unlike the Au clusters on TiO₂,^{6,7,54} Cu clusters do not exhibit quantum size effects. Annealing causes aggregation of the Cu clusters into larger islands, and a calculation of the Cu surface areas based on integration of the STM images in Figure 8⁴³ show that the Cu surface area decrease by approximately 50% after annealing. However, the product yields from methanol TPD on the annealed vs unannealed clusters are roughly the same although the formaldehyde and H₂ yields are slightly lower on the annealed clusters. This suggests that methanol chemistry is not highly sensitive to the Cu surface area, or that the 4 ML clusters sinter and lose surface area after heating to 500–700 K, which is the temperature range corresponding to formaldehyde and CO₂ production. The morphology of the 2 ML clusters is not substantially altered after heating to 700 K, but significant cluster sintering occurs for higher coverages of Cu (12 ML).

The 490 K desorption temperature for formaldehyde in our experiments is higher than the 330–370 K reported for oxygen-covered Cu(110).^{15,17,22} It is possible that formaldehyde production simply occurs at a higher temperature on the surfaces of the Cu clusters. However, a major source of discrepancy could be inaccuracy in our thermocouple readings because there is a temperature gradient between the TiO₂ crystal and the Ta backplate to which the thermocouple is spot-welded. The difference between the measured and true temperature of the crystal is estimated to be at least: 30 K at 250 K, 45 K at 500 K, and 60 K at 600 K. These estimates are based on the desorption temperatures for methanol on oxygen-covered Cu clusters for multiple TiO₂ crystals and a comparison with desorption temperatures for H₂O on TiO₂ reported by Henderson et al. for a thermocouple glued directly to the titania crystal.^{55–57} Although the absolute temperatures are higher than the true values, the temperatures reported in this work are completely self-consistent.

Summary

Temperature programmed desorption studies of methanol chemistry were conducted on Cu and oxygen-covered Cu clusters deposited on TiO₂(110). Reaction on the oxygen-covered Cu clusters produces formaldehyde, CO₂, H₂O, and H₂ as the main products, and methanol chemistry is the same on clusters of different sizes as well as on a Cu film that completely covers the surface. Isotopic labeling experiments demonstrate that lattice oxygen is incorporated into the CO₂ and water desorption products. The unoxidized Cu clusters are far less active for methanol chemistry, but these clusters produce trace amounts of H₂, formaldehyde, H₂O, and CO₂ from methanol reaction, in contrast to the inert single-crystal Cu surfaces. Notably, methanol reaction on the vacuum annealed TiO₂ surface produces significant amounts of ethylene, H₂O, and formaldehyde. Although reoxidation of the TiO₂ surface suppresses ethylene production, the desorption of formaldehyde and methanol is observed at high temperatures.

Acknowledgment. We gratefully acknowledge financial support from the Department of Energy-EPSCoR, Office of Basic Energy Science (DE-FG02-01ER45892) and from the National Science Foundation through a CAREER Award (CHE 0133926). We also thank the Army Research Office for financial support through a DURIP grant (DAAD19-01-1-0325).

References and Notes

- (1) Santra, A. K.; Goodman, D. W. *J. Phys.-Condens. Mater.* **2003**, *15*, R31.
- (2) Prevot, G.; Meerson, O.; Piccolo, L.; Henry, C. R. *J. Phys.-Condens. Mater.* **2002**, *14*, 4251.
- (3) Bell, A. T. *Science* **2003**, *299*, 1688.
- (4) Haruta, M. *Catal. Today* **1997**, *36*, 153.
- (5) Hayashi, T.; Tanaka, K.; Haruta, M. *J. Catal.* **1998**, *178*, 566.
- (6) Haruta, M.; Date, M. *Appl. Catal. A* **2001**, *222*, 427.
- (7) Haruta, M. *Cattech* **2002**, *6*, 102.
- (8) Garcia-Cortes, J. M.; Perez-Ramirez, J.; Illan-Gomez, M. J.; Salinas-Martinez de Lecea, C. *Catal. Commun.* **2003**, *4*, 165.
- (9) Zemichael, F. W.; Palermo, A.; Tikhov, M. S.; Lambert, R. M. *Catal. Lett.* **2002**, *80*, 93.
- (10) Keane, M. A.; Park, C.; Menini, C. *Catal. Lett.* **2003**, *88*, 89.
- (11) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980.
- (12) Thomas, C. L. *Catalytic Processes and Proven Catalysis*; Academic Press: New York, 1970.
- (13) Aritani, H.; Tanaka, T.; Akasaka, N.; Funabiki, T.; Yoshida, S.; Gotoh, H.; Okamoto, Y. *J. Catal.* **1997**, *168*, 412.
- (14) Russell, J. N.; Gates, S. M.; Yates, J. T. *Surf. Sci.* **1985**, *163*, 516.
- (15) Bowker, M.; Madix, R. J. *Surf. Sci.* **1980**, *95*, 190.
- (16) Sexton, B. A.; Hughes, A. E.; Avery, N. R. *Surf. Sci.* **1985**, *155*, 366.
- (17) Francis, S. M.; Leibsle, F. M.; Haq, S.; Xiang, N.; Bowker, M. *Surf. Sci.* **1994**, *315*, 284.
- (18) Ammon, C.; Bayer, A.; Held, G.; Richter, B.; Schmidt, T.; Steinruck, H. P. *Surf. Sci.* **2002**, *507*, 845.
- (19) Wachs, I. E.; Madix, R. J. *J. Catal.* **1978**, *53*, 208.
- (20) Mudalige, K.; Trenary, M. *Surf. Sci.* **2002**, *504*, 208.
- (21) Leibsle, F. M.; Francis, S. M.; Davis, R.; Xiang, N.; Haq, S.; Bowker, M. *Phys. Rev. Lett.* **1994**, *72*, 2569.
- (22) Davies, P. R.; Mariotti, G. G. *J. Phys. Chem.* **1996**, *100*, 19975.
- (23) Sekizawa, K.; Yano, S.; Eguchi, K.; Arai, H. *Appl. Catal. A* **1998**, *169*, 291.
- (24) Aritani, H.; Akasaka, N.; Tanaka, T.; Funabiki, T.; Yoshida, S.; Gotoh, H.; Okamoto, Y. *J. of the Chem. Soc.-Faraday Trans.* **1996**, *92*, 2625.
- (25) Valange, S.; Gabelica, Z.; Derouault, A.; Barrault, J. *Stud. Surf. Sci. Catal.* **2000**, 3477.
- (26) Zhou, J.; Chen, D. A. *Surf. Sci.* **2003**, *527*, 183.
- (27) Zhou, J.; Varazo, K.; Reddic, J. E.; Myrick, M. L.; Chen, D. A. *Anal. Chim. Acta* **2003**, *496*, 289.
- (28) Illingworth, A.; Zhou, J.; Ozturk, O.; Chen, D. A. *J. Vac. Sci. Technol. B* **2004**, *22* (5), 2552.
- (29) Chen, D. A.; Bartelt, M. C.; McCarty, K. F.; Hwang, R. Q. *Surf. Sci.* **2000**, *450*, 78.
- (30) Zhou, J.; Ma, S.; Kang, Y. C.; Chen, D. A. *Surf. Sci.* **2004**, *562*, 113.
- (31) Zhou, J.; Kang, Y. C.; Chen, D. A. *J. Phys. Chem. B* **2003**, *107*, 6664.
- (32) Farfan-Arribas, E.; Madix, R. J. *Surf. Sci.* **2003**, *544*, 241.
- (33) Henderson, M. A.; Otero-Tapia, S.; Castro, M. E. *Faraday Discuss.* **2000**, *114*, 313.
- (34) Herman, G. S.; Dohnalek, Z.; Ruzyski, N.; Diebold, U. *J. Phys. Chem. B* **2003**, *107*, 2788.
- (35) Roman, E.; Bustillo, F. J.; de Segovia, J. L. *Vacuum* **1990**, *41*, 40.
- (36) Henderson, M. A.; Otero-Tapia, S.; Castro, M. E. *Surf. Sci.* **1998**, *412*, 252.
- (37) Kim, K. S.; Barteau, M. *Surf. Sci.* **1989**, *223*, 13.
- (38) Farfan-Arribas, E.; Madix, R. J. *J. Phys. Chem. B* **2002**, *106*, 10680.
- (39) Wang, L.-Q.; Ferris, K. F.; Winokur, J. P.; Shultz, A. N.; Baer, D. R.; Engelhard, M. H. *J. Vac. Sci. Technol. A* **1998**, *16*, 3034.
- (40) Li, M.; Hebenstreit, W.; Diebold, U.; Henderson, M.; Jennison, D. R. *Faraday Discuss.* **1999**, *114*, 245.
- (41) Henderson, M. A.; Epling, W. S.; Perkins, C. L.; Peden, C. H. F.; Diebold, U. *J. Phys. Chem. B* **1999**, *103*, 5328.
- (42) Li, M.; Hebenstreit, W.; Diebold, U. *Surf. Sci.* **1998**, *414*, L951.
- (43) Zhou, J.; Ma, S.; Kang, Y. C.; Chen, D. A. *J. Phys. Chem. B* **2004**, *108*, 11633–11644.

- (44) Yudanov, I. V.; Sahnoun, R.; Neyman, K. M.; Rosch, N.; Hoffmann, J.; Schauer mann, S.; Johanek, V.; Unterhalt, H.; Rupprechter, G.; Libuda, J.; Freund, H. J. *J. Phys. Chem. B* **2003**, *107*, 255.
- (45) Cunningham, D. A. H.; Vogel, W.; Sanchez, R. M. T.; Tanaka, K.; Haruta, M. *J. Catal.* **1999**, *183*, 24.
- (46) Rupprechter, G.; Unterhalt, H.; Morkel, M.; Galletto, P.; Hu, L. J.; Freund, H. J. *Surf. Sci.* **2002**, *502*, 109.
- (47) Schauer mann, S.; Hoffmann, J.; Johanek, V.; Hartmann, J.; Libuda, J.; Freund, H. J. *Catal. Lett.* **2002**, *84*, 209.
- (48) Stroschio, J. A.; Pierce, D. T. *Phys. Rev. B* **1994**, *49*, 8522.
- (49) Bennett, R. A.; Stone, P.; Bowker, M. *Faraday Discuss.* **2000**, *114*, 267.
- (50) Bowker, M.; Smith, R. D.; Bennett, R. A. *Surf. Sci.* **2001**, *478*, L309.
- (51) Henderson, M. A. *J. Phys. Chem.* **1995**, *99*, 15253.
- (52) Matsumoto, T.; Bennett, R. A.; Stone, P.; Yamada, T.; Domen, K.; Bowker, M. *Surf. Sci.* **2001**, *471*, 225.
- (53) Besenbacher, F.; Norskov, J. K. *Prog. Surf. Sci.* **1993**, *44*, 67.
- (54) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.
- (55) Henderson, M. A. *Surf. Sci.* **1994**, *319*, 315.
- (56) Henderson, M. A.; Epling, W. S.; Peden, C. H. F.; Perkins, C. L. *J. Phys. Chem. B* **2003**, *107*, 534.
- (57) Henderson, M. A. *Langmuir* **1996**, *12*, 5093.