

Growth and Catalytic Activity of WO₃ Clusters on TiO₂(110)*

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Abstract

Early transition metal oxides represent an important class of oxide catalysts. We combined atomically resolved imaging and ensemble averaged techniques to examine the adsorption, dissociation, and partial oxidation of alcohols on TiO₂(110) and (WO₃)₃/TiO₂(110) model catalysts. Model (WO₃)₃/TiO₂(110) systems were prepared using direct sublimation of WO₃ and characterized using high resolution Scanning Tunneling Microscopy, X-ray photoelectron spectroscopy and N₂ physisorption.

On clean TiO₂(110) the images obtained from the same area before and after adsorption show that both alcohols and H₂O adsorb preferentially on oxygen vacancies and that alcohol dissociation occurs via O-H bond scission. The dynamics of diffusion of protons created by water and alcohol dissociation on bridge-bonded oxygen (BBO) vacancies is examined as a function of adsorbate coverage.

The detailed molecular beam dosing and temperature-programmed desorption investigations of alcohol dehydration on TiO₂(110) reveal the presence of two distinct dehydration channels. We show that for the previously reported BBO vacancy-related high-temperature (500-650 K) dehydration channel, the alkene desorption temperature correlates with the induction effect of the alcohol alkyl-chain. A previously unobserved, low temperature channel (300-450 K) is attributed to a disproportionation reaction between two neighboring alkoxy groups (or alkoxy and alcohol) bound on Ti⁴⁺ rows. Based on the above observations, we propose detailed reaction steps involved in dehydration of alcohol molecules on TiO₂(110).

* This report reflects integrated day-by-day collaborative activities between PNNL and the University of Texas at Austin scientists supported by the DOE catalysis project entitled "Early transition metal oxides as catalysts: Crossing scales from clusters to single crystals to functioning materials". In particular, Zdenek Dohnalek and Bruce Kay at PNNL and J. M. White jointly appointed at UT-Austin and PNNL. Postdoctoral colleagues are Dr. Alexander Bondarchuk and Jooho Kim. Bondarchuk, stationed at PNNL, is supported by the University of Texas at Austin portion of the project while Dr. Jooho Kim, is supported by the PNNL portion of the project. Both are in residence at EMSL on the PNNL campus. While all participants are in steady collaboration, Bondarchuk focuses on scanning probe instrumentation while Kim focuses on molecular beam scattering and temperature programmed desorption.

Description of Results

The experiments were conducted in two ultra-high vacuum (UHV) chambers, one equipped with a variable-temperature scanning-tunneling/atomic-force microscope (VT STM) allowing for the determination of surface morphology with atomic or near atomic resolution, and the other equipped with molecular beam scattering and

temperature programmed desorption (TPD) capabilities required for adsorption/desorption dynamics and reaction kinetics measurements. Other instrumentation used for surface composition and order characterization such as Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), and X-ray Photoelectron Spectroscopy (XPS, second system only) is also present.

TiO₂(110) Substrate Characterization

The structure of the TiO₂(110) surface is schematically shown in the right side of Figure 1. The surface is composed of rows of bridge-bonded oxygen (BBO) and five-coordinated Ti⁴⁺ sites. Partial reduction of TiO₂ leads to oxygen deficiency in the bulk and the appearance of BBO vacancy sites as shown in the schematic. An atomically resolved STM image from TiO₂(110) is shown in the left part of Fig. 1. Based on the previous STM studies¹ and theoretical calculations² the bright and dark rows along the [001] direction correspond to the rows of Ti⁴⁺ ions and BBO sites, respectively. The bright spots on the dark rows are the oxygen vacancies in the BBO rows. These vacancies are a result of partial reduction of the TiO₂ sample due to annealing employed during the sample preparation.¹ In this particular image the concentration of BBO vacancies is estimated to be 7%. The vacancy concentration can be increased up to ~15% with further bulk reduction upon heating.

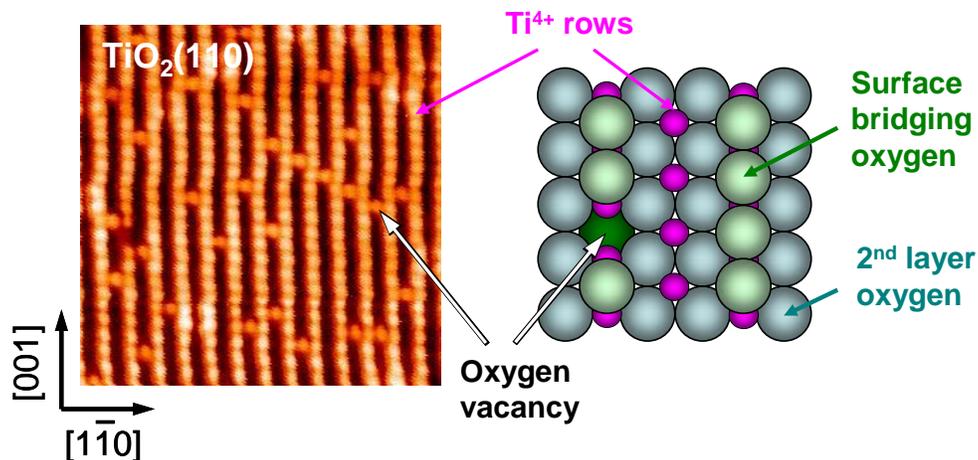


Figure 1. Left: The empty state STM image (10×10 nm²) of clean TiO₂(110)-(1×1) surface. Right: A schematic of TiO₂(110)-(1×1) surface with a BBO vacancy.

WO₃ Cluster Deposition on TiO₂(110)

Deposition of WO₃ was accomplished by direct evaporation of WO₃ vapor from an effusion cell. In related studies, thick WO₃ films (~1μm) were deposited using the same approach. Only W in the (6+) oxidation state was observed upon deposition at 300 K and upon subsequent thermal annealing to temperatures as high as 600 K. A set of XPS spectra for 1.8×10¹⁴ WO₃/cm² deposited on TiO₂(110) at 300 K, and subsequently annealed to 600K (Fig. 2) clearly shows the presence of W in the (6+) oxidation state. A spectrum from metallic W obtained by the annealing-induced (1200 K) reduction of a thick WO₃ film is also shown as a reference (Fig. 2c). The amount of deposited WO₃ is calibrated using a quartz crystal microbalance.

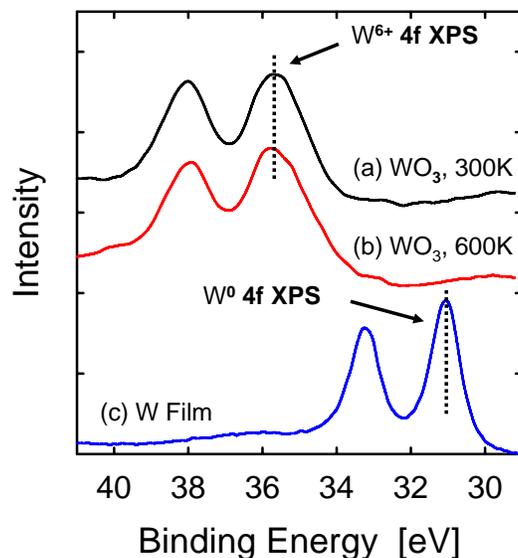


Figure 2. W 4f XPS spectra from (a) 1.8×10^{14} WO₃/cm² deposited at 300K, (b) 1.8×10^{14} WO₃/cm² deposited at 300K and annealed to 600K, (c) metallic W film.

Atomically resolved STM images corresponding to 3×10^{14} WO₃/cm² deposited on TiO₂(110) at 300K and after annealing to 600 K are shown in Fig. 3. The as-deposited WO₃ (Fig. 3a) appears as dark clustered features with fuzzy, poorly defined edges centered on the Ti⁴⁺ rows. The fuzzy nature of the WO₃ features suggests that the WO₃ is only weakly bound to the surface and is susceptible to STM tip induced effects. Annealing to 600K (Fig. 3b) leads to the appearance of bright, randomly distributed clusters also centered on Ti⁴⁺ rows. The dramatic difference in the appearance of the WO₃ clusters before and after annealing suggests that the clusters became more tightly bound to the substrate upon annealing.

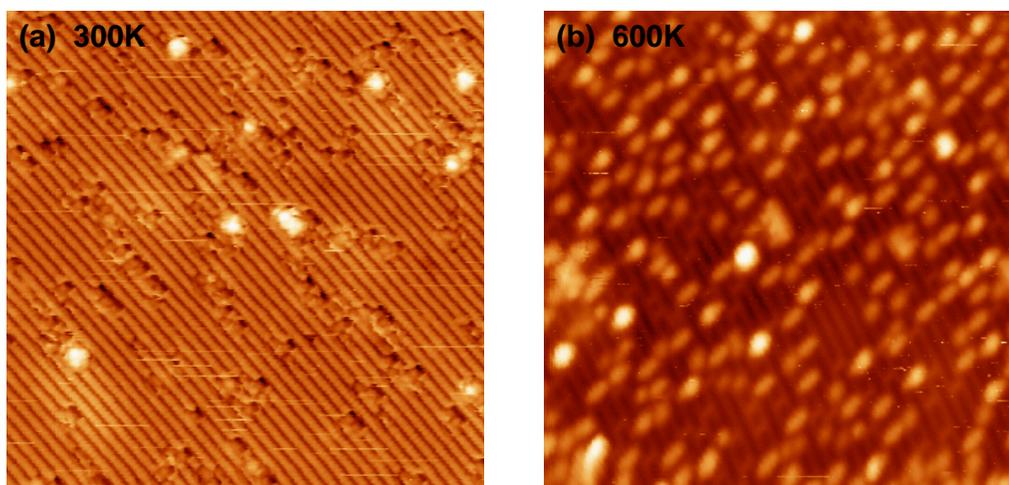


Figure 3. STM images (20×20 nm²) from (a) TiO₂(110) surface after 3×10^{13} WO₃/cm² deposition at 300K, and (b) after annealing at 600 K.

The amount of deposited WO_3 determined using a quartz crystal microbalance and the observed cluster coverage from the STM yields an upper bound of three W atoms in each cluster. And we have imaged these clusters using STM (Fig. 4).

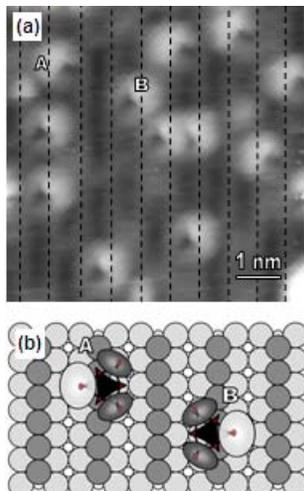


Figure 4. (a) Scanning tunneling microscope image of trimers of WO_3 dosed on $\text{TiO}_2(110)$, annealed to 600 K and recooled for imaging. Vertical dashed lines mark rows of Ti^{4+} cations. Bright circular regions with triangular dark cores mark positions of monodisperse $(\text{WO}_3)_3$ clusters. Note these are centered over the dark rows (bridge-bonded oxygen rows).

(b) Model of two WO_3 trimers. (A) is tilted to the left and (B) is tilted to the right. Ovals represent positions of W atoms in the proposed cyclic trimer. The plane of the three W atoms is not parallel to the support but one of the W atoms is further from the surface than the other two.

Catalytic Activity of Model $\text{WO}_3 / \text{TiO}_2(110)$ System

Our initial studies of the chemical activity of the WO_3 clusters on $\text{TiO}_2(110)$ focused on the partial oxidation of CH_3OH . The $\text{WO}_3/\text{TiO}_2(110)$ model catalyst used in these studies was prepared by WO_3 deposition at 300 K and subsequent annealing to 600 K as described above. The coverage dependent series of TPD spectra for CH_3OH adsorbed on clean $\text{TiO}_2(110)$, and on $\text{WO}_3/\text{TiO}_2(110)$ are shown in Fig. 5. For both systems, only molecular desorption of CH_3OH is observed. For 1 ML of CH_3OH adsorbed on clean $\text{TiO}_2(110)$ (Fig. 5a), the fraction of CH_3OH desorbing from Ti^{4+} (250-400K) and BBO (150-250 K) sites is approximately the same. This is very similar to H_2O desorption. For CH_3OH desorption from $\text{WO}_3/\text{TiO}_2(110)$ (Fig. 5b), a larger fraction of CH_3OH desorbs from oxygen terminated sites suggesting that the Ti^{4+} sites were covered by WO_3 . This is in agreement with the STM studies where WO_3 clusters are observed to bind to the Ti^{4+} rows.

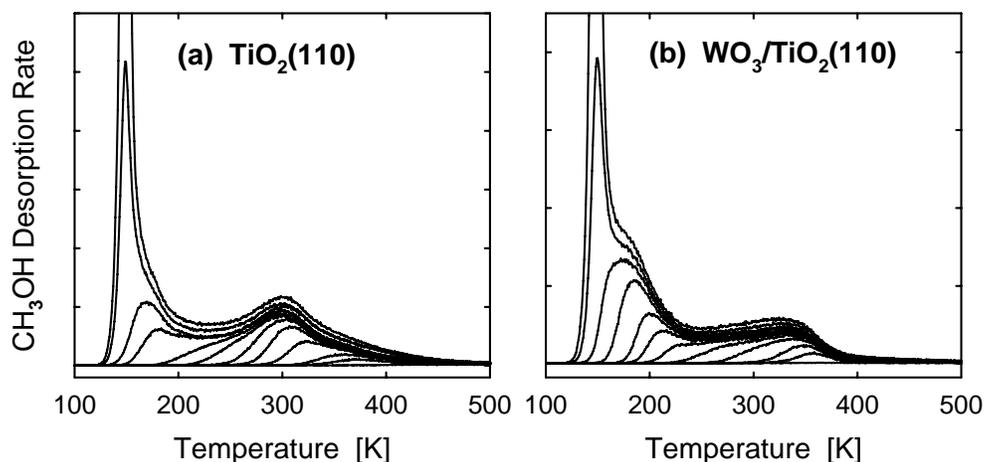


Figure 5. TPD spectra of CH₃OH from (a) TiO₂(110) and (b) WO₃/TiO₂(110) for a range of initial coverages, $\theta \leq 1.5\text{ML}$.

We have also explored the adsorption of formaldehyde as one of the potential products in the partial oxidation of CH₃OH. In this case a catalytic polymerization reaction resulting in the formation of trioxane (paraformaldehyde) was observed. Trioxane desorption is observed in TPD upon heating between 200 and 350 K (data not shown). We have explored the dependence of trioxane formation on H₂CO dose temperature and determined that the presence of formaldehyde multilayers is necessary for the trimerization reaction. Submonolayer amounts of formaldehyde on the WO₃/TiO₂(110) surface result only in the H₂CO monomer desorption. The trimerization yield was measured as a function of WO₃ coverage and formaldehyde exposure. Figure 6 shows that the yield increases linearly with the amount of deposited WO₃ but saturates at high formaldehyde doses. The linear dependence on WO₃ coverage, and the observation that the reaction can be repeated multiple times indicates WO₃ catalysis polymerization of H₂CO.

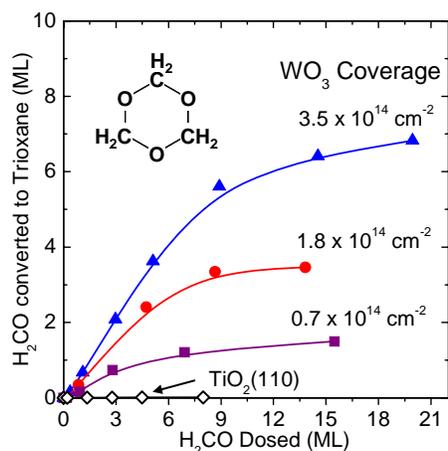


Figure 6. Trioxane formation yield on model WO₃/TiO₂(110) catalysts as a function of WO₃ coverage and H₂CO exposure.

Alcohol dehydration on $\text{TiO}_2(110)$.

As part of a series involving alcohol reactions on oxides, we have completed a study showing that empirical Taft parameter correlations often used to systematize organic reactions, can be extended to a heterogeneous system (Fig. 7). From these results, we conclude that the reaction transition state connecting the adsorbed reactant, alkoxide, and the gas phase product, alkene, is a structure involving concerted elongation of the C—O bond of the alkoxide and a C—H bond of the R group attached to the β -carbon.

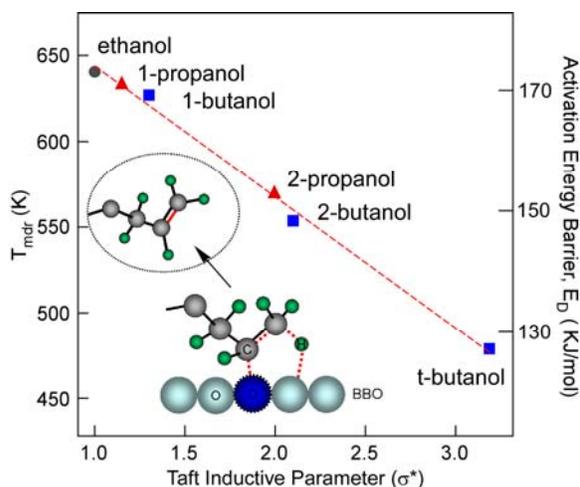


Figure 7. Temperature of maximum desorption rate, T_{mdr} , and activation energy for alkene formation, E_D , for high-temperature dehydration of alcohols adsorbed on $\text{TiO}_2(110)$ plotted against Taft inductive parameter (σ^*) of alcohol alkyl groups. The inset shows a schematic of the high-T dehydration of alkoxide bound to BBO_V . σ^* is scaled to set ethanol to 1.0.