



An Atomic-Scale View of Transition Metal Oxide Catalysis

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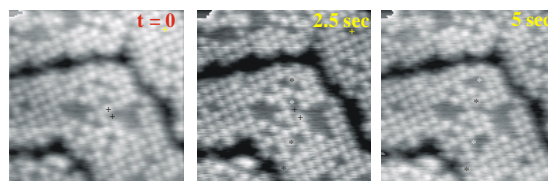


Introduction

Transition metal oxides are widely used as heterogeneous catalysts in the chemical and energy industries. As partial oxidation catalysts, oxides are used to convert hydrocarbon feedstocks into more valuable oxygenates. Improvements in activity and selectivity offer the promise of using less expensive feedstocks more efficiently, thus reducing waste generation and making better use of scarce resources. Oxides are also used to selectively reduce NO emitted from power plants where more active and selective catalysts can potentially reduce power generation costs while simultaneously reducing pollution. It has been well-established that the activity of oxide catalysts depends strongly on the environment surrounding the adsorption site, though the details of the relationship between structure and catalytic properties have been elusive. Since rational catalyst design hinges on a detailed understanding of how local structure determines the preferred catalytic pathway, we have been using scanning tunneling and non-contact atomic force microscopies (STM and NC-AFM) along with macroscopic techniques to determine where molecules adsorb on oxide surfaces and their chemical pathway once they adsorb.

Dynamics of WO₃ Surfaces

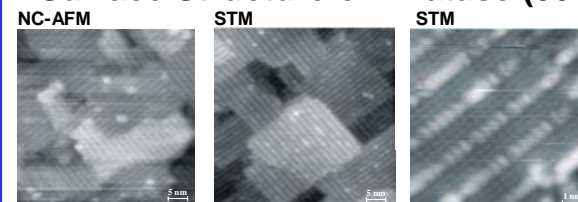
STM Movie Frames



+ Mark change between first and second images.
* Mark change between second and third images.

By recording STM movies, dynamical events can be followed in real time at the atomic level. The movie frames show the c(2x2) WO₃(001) surface at 300 K. Each of the white spots corresponds to an oxygen atom; in this case there are gray patches where oxygen atoms are missing. The sequence of frames shows that even at just 300 K, the oxygen atoms change location with time or diffuse. Thus the usual picture of a metal-oxygen bond in an oxide as a strong, localized bond is not entirely appropriate.

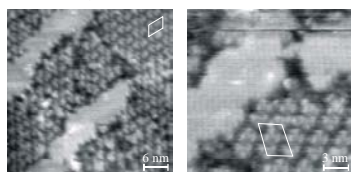
Surface Structure of Anatase (001)



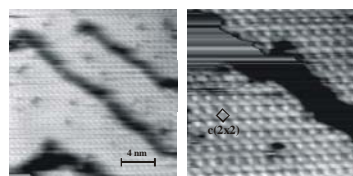
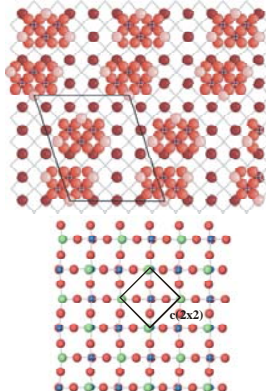
The anatase polymorph of TiO₂ is often used in catalysis both as the active phase and as a support for other transition metal oxides. In the latter case, anatase supported oxides are uniquely active and selective for certain reactions. There had been little known about the nature of anatase surfaces because of the lack of availability of crystals suitable for study. Therefore, we grew single crystal thin films and characterized their surface structure and chemistry. The above images reveal a quadrupling of the bulk unit cell along one direction to create a (4x1) surface reconstruction which accounts for the characteristic striped appearance of the STM and NC-AFM images.

Surface Structures of WO₃(001)

STM Images



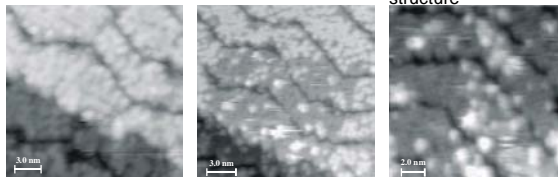
Models



Tungsten oxide is a prototypical transition metal oxide catalyst. The pictures show that its surface structure, and hence chemistry, varies widely depending on reaction conditions. Under reducing conditions (top) an ordered array of WO₃ clusters form on the surface while oxidation (bottom) produces a c(2x2) surface with every other surface oxygen (green) missing exposing W⁶⁺ (blue).

Reaction of Alcohols on WO₃(001)

Adsorb 1-propanol Remove molecules Image underlying structure



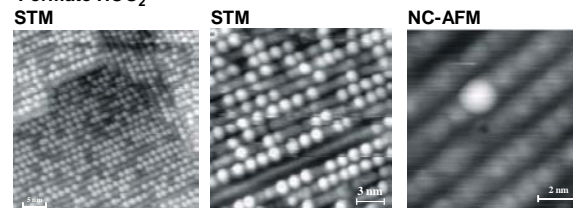
After exposure to alcohols the surface becomes randomly covered by featureless white balls, these are alkoxide groups formed by deprotonating the alcohols. By moving the STM tip close to the surface the alkoxides can be swept aside to reveal the structure of the underlying surface, in this case c(2x2). By looking at the registry of the alkoxides with respect to the surface lattice, it is determined that the molecules bond to the exposed W⁶⁺ cations. Complementary results indicate that molecules adsorbed here only undergo dehydration reactions to form alkenes. Further, this reaction is limited by the rate of breaking the C-O bond.

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Carboxylate Chemistry on Anatase

Formate HCO₂⁻



Carboxylates, such as formate, are known to attach to exposed metal cations. The bright spots in the images are the formate groups and these are only seen centered on top of the bright rows formed by the (4x1) reconstruction, thus there must be Ti atoms centered along these rows. Further, the spacing of the molecules indicates that each formate is bridge bound to two Ti atoms. This configuration eliminates several structural models proposed for the reconstruction. We also find that molecules adsorbed on these sites are held very strongly, only leaving the surface after dissociation followed by oxidation at high temperatures. This is very different from what happens on the rutile polymorph where formate dehydrates to CO and water at modest temperatures. Thus the reconstruction creates sites on the anatase surface with unique reactivity.