

Unexpected Adsorption of Oxygen on TiO₂ Nanotube Arrays: Influence of Crystal Structure

S. Funk, B. Hokkanen, and U. Burghaus*

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

A. Ghicov and P. Schmuki

*University of Erlangen-Nuremberg Department of Materials Science,
Erlangen, Germany*

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ABSTRACT

We present kinetics data of O₂, *n*/iso-butane, CO₂, and CO adsorbed at ultrahigh vacuum conditions on TiO₂ nanotube (TiNTs) arrays produced by electrochemical anodization; amorphous and polycrystalline (anatase and mixed anatase/rutile) TiNTs have been studied addressing structure–activity relationships. Oxygen distinctly interacts with the TiNTs, whereas this process is not observed on fully oxidized TiO₂ single crystals. Both molecularly and atomically bonded oxygen have been observed. Variations in the binding energies of alkanes were also detected.

The combination of nanotechnology and surface science toward heterogeneous catalysis is a promising challenge for both industrial applications and fundamental research. Although much work has been done studying, for example, nanotubes for nanoelectronics, rather few studies have been conducted that bridge nanoscience and surface science for catalysis applications.¹ Most important for heterogeneous catalysis is an understanding of the adsorption kinetics of gas-phase species since this process is the first elementary step in all surface reactions.

Although a variety of materials,^{2–4} particularly TiO₂,^{5–8} have been used to synthesize nanotubes, we are not aware of any ultrahigh vacuum (UHV) surface science studies on nanotubes except carbon-based systems.^{9,10} However, a large variety of diverse applications for TiO₂ materials exist which could take advantage of the large surface to volume ratio of TiO₂ nanotubes (TiNTs). The most prominent example in heterogeneous catalysis is the Au–TiO₂ low-temperature CO oxidation catalysts.^{11,12} Besides the cleaning of exhaust pollution, the removal of CO from syngas is required for fuel cell applications, since trace amounts of CO can poison the surface of fuel cell electrodes.¹³ Furthermore, TiO₂ is important for PROX catalysts (preferential oxidation of CO in the presence of excess hydrogen)¹⁴ used in lean-burn gasoline engines, which have a higher energy consumption efficiency than gasoline-powered engines. Importantly, due to its unique photocatalytic properties, TiO₂ is the most

promising nanotube material in photocatalysis.^{7,15–17} Photocatalytic oxidation of, for example, chemical warfare agents and pesticides is a particularly attractive method¹⁸ because it is effective in remote locations. The effect of TiNTs is 2-fold: capture of toxic compounds (in the dark and over night) and photocatalytic decomposition (in the light, daytime). In all of these applications, the adsorption of oxygen is the first elementary reaction step which will, to a large extent, control the product formation rates.

Another issue that can be addressed uniquely when considering TiNTs is the long lasting question in surface science and catalysis whether different polymorphs of TiO₂ show different catalytic properties. Industrial powder catalysts consist of anatase/rutile mixtures, making it difficult to isolate the catalytically most active phase or phase combination. Although single-crystal rutile TiO₂ surfaces have been studied extensively,¹⁹ due to difficulties in obtaining large anatase TiO₂ single crystals, only a few surface science studies have been conducted on the anatase polymorph.²⁰ Thus, in addition to numerous technical applications, TiNTs are a perfect model system to correlate the structure with the catalytic activity.

In this letter, we focus on characterizing the adsorption kinetics of oxygen on amorphous and polycrystalline mixed anatase/rutile TiNTs which constitute the two extreme cases of TiNTs which can be synthesized. Distinctly different adsorption kinetics have been observed providing evidence for a structure–activity relationship (SAR) supporting catalyst improvement. In conjunction with oxygen adsorption,

* Corresponding author. E-mail: uwe.burghaus@nds.edu. Fax: 701.231.8831. Phone: 701.231.9742.

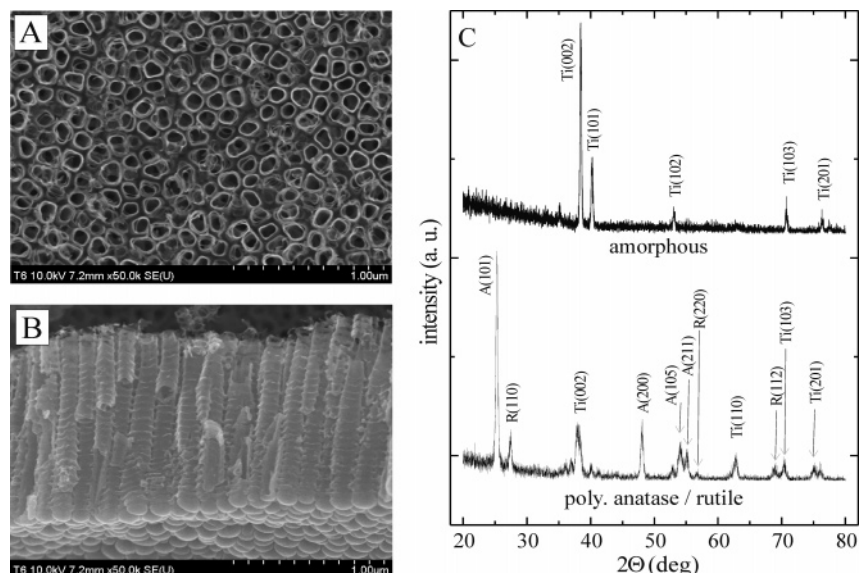


Figure 1. (A and B) SEM images of anodic TiO₂ nanotube layers formed in 1 M (NaH₂PO₄) + 0.5 wt % HF at 20 V for 2 h; top-view and cross-section and (C) XRD results of the TiNTs studied here.

we report briefly about the adsorption kinetics of a number of other probe molecules. Alkanes are important for the petroleum industry as building blocks to synthesize chemicals of greater value. CO₂ and CO are prototype adsorbates in surface chemistry model studies.

The TiO₂ nanotube arrays were grown electrochemically which leads initially to an amorphous structure that is converted to polycrystalline anatase TiO₂ nanotubes (porous annealed samples) upon annealing (723 K). At even higher annealing temperatures (950 K), a polycrystalline anatase/rutile mixture is obtained with typical crystallite sizes of ~ 20 Å.²¹ A scanning electron microscope (SEM) and X-ray diffraction system (XRD) was used for morphological characterization of the samples throughout the project (Figure 1). The chemical cleanliness of the TiNTs has been characterized with X-ray photoelectron spectroscopy.²² Thermal desorption experiments (TDS), a sample temperature ramping technique, have been conducted in an UHV system equipped with a shielded mass spectrometer. The TDS curves are smoothed, and an exponential background has been removed.

Figure 2 depicts TDS results for amorphous and polycrystalline (80%-anatase/20%-rutile; XRD estimate) TiNTs parametric in gas exposure, as indicated (in Langmuir, 1 L = 1 s exposure at 1×10^{-6} Torr). Flashing off the gas dosed at 95 K leads in the case of the amorphous system (Figure 2A) to a TDS peak position (~ 120 K) which is independent of exposure, consistent with standard coverage (surface particle density) independent first-order molecular adsorption/desorption kinetics. Importantly, oxygen does not adsorb on fully oxidized rutile TiO₂ single-crystal surfaces,²³ i.e., TiNTs show intrinsically a fundamentally different catalytic behavior than TiO₂ single-crystal model systems studied heretofore. Assuming a standard preexponential coefficient (1×10^{13} /s) results in a binding energy of 30.5 kJ/mol which is much smaller than the 108 kJ/mol (TDS peak at 400 K) determined for defected rutile TiO₂(110).²⁴ The large binding energy on TiO₂(110) is the result of surface defects indicating that the

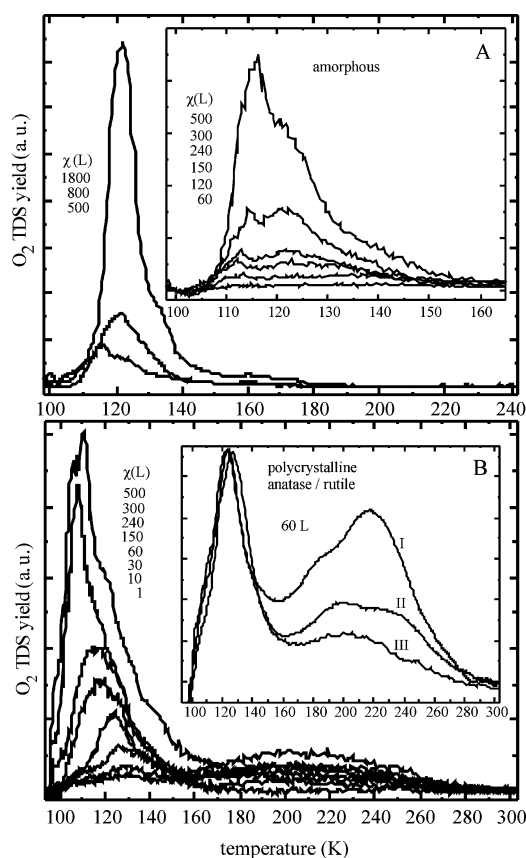


Figure 2. Adsorption of oxygen at low (95 K) sample temperatures. (A) TDS for amorphous TiNTs parametric in oxygen exposure. The inset shows TDS curves for small exposures. (B) TDS for polycrystalline 80%-anatase/20%-rutile TiNTs. The inset shows a series of adsorption/desorption cycles. (The curves have been normalized.)

amorphous TiNTs system is fairly homogeneous. No other TDS structures emerged at low adsorption temperatures on the amorphous TiNTs.

In the case of the polycrystalline TiNTs (Figure 2B), the low-temperature TDS peak shifts from 129 to 108 K with increasing exposure, indicating a deviation from first-order kinetics. Thus, TiNTs with an anatase crystal structure show distinct differences in the adsorption kinetics; that is, a kinetic SAR is present which promotes catalyst tailoring. Deviations from first-order kinetics have rarely been observed for molecular adsorption but could, in the case of metal catalysts,²⁵ be assigned to structural effects such as desorption starting along the rim of islands of the adsorbates.

Furthermore, TDS traces on the polycrystalline system provide evidence for a second adsorption pathway for oxygen. Dosing O₂ at 95 K and ramping the surface temperature results in another TDS feature at 160–300 K. Similar TDS curves have been observed for metal catalysts^{26,27} and indicate recombinative desorption (dissociative adsorption) of oxygen. This process is typically observed at larger sample temperatures due to larger binding energies of atomically bonded as compared with molecularly bonded species. Interestingly, this second adsorption pathway, observed only for the polycrystalline system, is controlled by the surface defect density. Repeating O₂ adsorption/desorption cycles leads to a quenching of this high-temperature adsorption pathway (inset Figure 2B). Adsorption of oxygen is known to “heal out” oxygen vacancy (defect) sites on rutile TiO₂(110) single crystals.^{23,28,29} Oxygen vacancy sites must also be present on the polycrystalline TiNTs additionally to more complex defects such as the grain boundaries of the crystallites. Thus, it is plausible to assume that oxygen molecules dissociate on these defect sites, as they do on TiO₂ single crystals, filling defect and adjacent pristine sites on the TiNTs. The oxygen atoms adsorbed on pristine sites can be flashed off resulting in the TDS peak observed at 160–300 K. The remaining oxygen atoms “heal out” the oxygen vacancy sites leading to a quenching of this adsorption pathway in subsequent adsorption/desorption cycles. Flashing cycles of the polycrystalline TiNTs in UHV to higher temperatures (550–600 K) restore this high-temperature adsorption pathway supporting our proposed mechanism.

Experiments where oxygen has been dosed on the TiNTs at higher temperatures have also been conducted. Interestingly, only for the amorphous system could measurable desorption rates be detected (Figure 3). Dosing O₂ at 150 K, cooling the sample to 95 K, and flashing the oxygen off leads to a symmetrical TDS peak at 200 K. (The start of the TDS trace already below 150 K is related to an O₂ background adsorption while the surface cooled down.) This type of kinetics is well-known for metal catalysts and is evidence for activated and dissociative oxygen adsorption.³⁰ The binding energy obtained by a Redhead analysis amounts to 50 kJ/mol (second-order preexponential 10²¹ cm²/(mol s)). It appears plausible that this adsorption pathway is not dominant for the polycrystalline system, where O₂ appears to dissociate at defect sites.

In addition to the kinetic SAR, the dynamics of oxygen adsorption³⁰ (gas-surface energy transfer processes) on the different TiNTs samples also show significant variations.

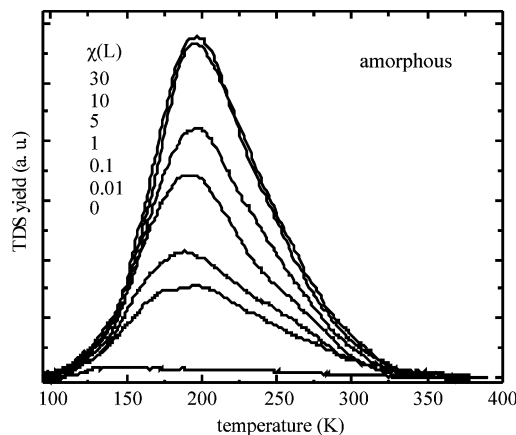


Figure 3. Adsorption of oxygen at higher (150 K) sample temperatures for the amorphous TiNTs.

According to the evolution of the total amount of adsorbed oxygen (quantified by the area of the TDS peaks) with oxygen exposure, the initial adsorption probability, S_0 , for O₂ is roughly larger by a factor of ~ 30 on the polycrystalline ($S_0 \sim 0.03$) system. For the dissociative adsorption of oxygen (Figure 3), S_0 is close to one.

With regard to heterogeneous catalysis, the amorphous system should be the better catalyst since oxygen adsorbed close to room temperature which will be important for applications such as the oxidation of toxic compounds. However, for low-temperature reactions, the larger adsorption probability of O₂ on the polycrystalline TiNTs will be pertinent. As compared with powder catalysts, TiNTs are of advantage in applications which require coated surfaces. Additionally, less expensive polycrystalline TiNTs (with control over the anatase/rutile composition) are a better model system for powder catalysts than single-crystal rutile TiO₂.

As a further screening of the reactivity, we collected data for iso/*n*-butane, CO₂, and CO adsorption. A kinetic SAR was also present for the alkanes with binding energies larger by 5 kJ/mol (TDS peak shift of ~ 20 K) on the mixed anatase/rutile system as compared with amorphous and pure polycrystalline anatase TiNTs. Desorption temperatures of 110–150 K (depending on the TiNTs system) and 100–120 K were present for CO₂ and CO, respectively, consistent with molecular physisorption.

In summary, this work demonstrates the first example of a (nanostructured) TiO₂-based system intrinsically active toward oxygen adsorption. The adsorption of oxygen (molecularly and atomically bonded) has so far only been reported on defected (reduced) TiO₂ single-crystal surfaces³¹ and TiO₂ powders.³² This opens up possibilities for fascinating applications since adsorption of oxygen is a prerequisite for a large variety of surface reactions. Furthermore, a clear structure activity relationship has been observed. Certainly further studies are required to understand the mechanistic details of the obviously rich and interesting kinetics/dynamics of oxygen adsorption on the novel TiNT system.

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Supporting Information Available: Experimental details and further data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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