Shape-dependence of the thermal and photochemical reactions of methanol on nanocrystalline anatase TiO$_2$

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ABSTRACT

Structure-activity relationships and the influence of particle size and shape on the partial- and photo-oxidation of methanol on nanocrystalline anatase TiO$_2$ were investigated using temperature-programmed desorption. The study employed two distinct nanoparticle morphologies: truncated bipyramids exposing primarily {101} facets, and flatter platelets exposing primarily {001} surfaces, whose nominal sizes ranged from 10 to 25 nm. The platelets were found to be more active for thermally-driven reactions, such as coupling of methoxide groups to produce dimethyl ether, and deoxygenation to produce methane. A dependence of the reactivity of {001} facets for the coupling of methoxide groups to produce dimethyl ether on facet size was also observed. In contrast to the thermally-driven reactions, the bipyramidal nanoparticles were observed to be more active for a range of photochemical reactions, including oxidation and coupling to produce methyl formate, and photo-decomposition of surface methoxide species. This study also shows how well-defined nanocrystals can be used to help bridge the materials gap between studies of single crystal model catalysts and their high surface area industrial analogs.

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1. Introduction

Surface science studies of well-defined, single-crystal, model catalysts have made many important contributions to our understanding of the reactivity of a range of catalytic materials. Indeed, this approach has been invaluable in elucidating structure-activity relationships, and the identification of specific active sites, reaction pathways, and the structure of adsorbed intermediates [1–4]. While this approach has been very successful, it still has its limitations since single crystals often do not contain the range of sites that occur in the analogous high surface area catalysts that are used in industrial practice. Recently studies have started to appear in the literature in which an effort has been made to bridge this so called "materials gap" [5–12]. One promising approach to achieving this goal is the use of thin films of well-defined nanocrystals as model catalysts. This approach has the advantage that the exposed crystal planes are still well-defined which can allow comparisons to be made to the single crystal literature, if available, while at the same time providing for a wider range of sites, such as those at edges and corners, whose concentration can be systematically controlled by varying the crystallite size and shape. Using well-defined nanocrystals may in many cases also allow one to systematically study the reactivity of individual exposed crystal planes for materials for which single crystals are not readily available, which is the case for many metal oxides.

A recent study by the Overbury group at Oak Ridge National Laboratory of the catalytic activity of ceria nanocrystals (octahedra, cubes, and nanowires) provides a good example of this type of study [5]. In this work it was found that ceria nanowires had higher activity than the octahedral nanocrystals for the conversion of acetaldehyde to both decomposition and coupling products in a flow reactor. Furthermore, the wires and cubes were more selective for C—C bond scission to produce C$_1$ products, while octahedra were more selective for aldol condensation. This was attributed, in part to the cerium cations with lower coordination numbers and a higher defect density on the surface of the nanowires and cubes.

We have also recently used this approach to study structure-activity relationships for both catalytic and photocatalytic reactions on anatase TiO$_2$ (A-TiO$_2$) using methanol as a prototypical oxygenate reactant [13]. This study made use of size-selected, A-TiO$_2$ nanocrystals with a truncated bipyramidal shape that were cast into thin films on oxidized silicon wafers. As shown in Fig. 1, these A-TiO$_2$ crystals expose the {101} family of crystal planes on the sides of the pyramids and are capped by {001} planes. Temperature-programmed desorption (TPD) studies of the thermal and photo-oxidation of methanol were used to probe how the crystallite size affected reactivity. As will be discussed in more detail below, we observed that in the absence of UV
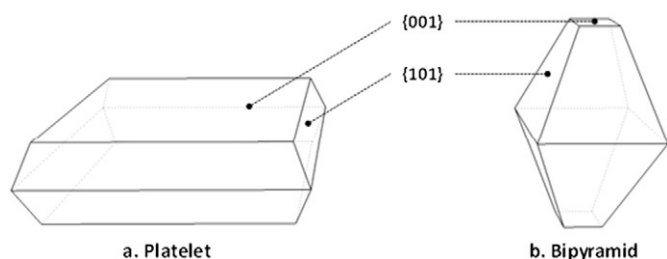
Fig. 1. Schematic showing the shape and exposed crystal planes of the (a) platelet and (b) bipyramidal anatase nanocrystals. Both forms present exclusively {101} and {001} surfaces, but the {001} surfaces account for a larger fraction of the platelet nanocrystals.

illumination the nanocrystals were active for the coupling of adsorbed methoxide groups to produce dimethyl ether which occurred primarily on undercoordinated Ti cation sites located on the {001} planes. UV illumination caused methyl formate to also be produced which appeared to occur on sites located on the {101} planes. The relative yield of this photochemical product was also found to be dependent on the crystallite size.

In the work reported here we have extended our previous study to include the reactions and photoreactions of methanol over TiO_2 nanocrystals that have the platelet geometry shown in Fig. 1. Note that this shape is just a more truncated version of the bipyramids that were used in our previous study, but due to the different aspect ratio the area of the {001} planes relative to the {101} planes is much higher in the platelets compared to the bipyramids.

2. Materials and methods

A detailed description of the synthesis of the TiO_2 nanocrystals can be found in Gordon et al. [14]. Briefly, a stock solution of TiF_4 and $TiCl_4$ was added to a cosurfactant (either oleylamine or 1-octadecanol) and heated to 563 K. After seed crystal formation, additional stock solution was delivered via a syringe pump. Nanocrystal size was controlled by varying the amounts of added stock solution. The nanocrystal shape was determined by the relative surface energies of the {101} and {001} facets. The {001} surface is stabilized in the presence of HF generated during hydrolysis of the TiF_4 precursor. Thus oleylamine, which moderates the amount of HF, favors the growth of the {101} surfaces and leads to a bipyramidal shape, while 1-octadecanol promotes a higher fraction of exposed {001} surfaces, leading to a flatter, platelet shape (see Fig. 1). In the current study three different sizes of platelet nanocrystals were used which had lateral dimensions of 14 nm, 18 nm, and 22 nm as determined by electron microscopy. (These values have an accuracy of ± 3 nm). We also compare to data obtained previously for bipyramidal nanocrystals which had long axes of 10 nm, 18 nm, and 25 nm [13]. To allow the use of traditional surface science analytical techniques, the nanocrystals were suspended in hexane and then spin-cast onto oxidized, single crystal Si substrates to produce thin films.

Transmission electron microscopy (TEM) was used to characterize the as-synthesized nanocrystals. For these experiments the nanocrystals were dispersed onto a 300 mesh C-coated Cu TEM grid and images were collected using a JEOL JEM1400 TEM operating at 120 kV. The thin film samples were also characterized by scanning electron microscopy (SEM) using a JEOL 7500F HRSEM. For these experiments the samples were not coated but a conducting tape was applied near the edge of the substrate to reduce sample charging. Images were collected in secondary electron imaging mode with a 5 kV beam.

Reactivity experiments were conducted in an ultra-high vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr. The chamber was equipped with a quadrupole mass spectrometer (Stanford Research Systems) which was used for temperature programmed desorption (TPD) experiments, and a dual-anode X-ray source (VG Microtech) and a hemispherical electron energy analyzer (Leybold-Heraeus)

which were used for X-ray photoelectron spectroscopy (XPS). The thin film samples were cut into pieces approximately 8 mm × 6 mm and mounted in Ta foil holders which were spot welded to an electrical feedthrough on the UHV chamber. Each sample was heated resistively by passing electrical current through the Ta foil and cooled by conduction from a liquid nitrogen reservoir in contact with the electrical feedthrough. The sample temperature was monitored by a type-K thermocouple which was fixed to the back of the Si substrate using ceramic adhesive (Aremco).

HPLC-grade methanol (Fisher Scientific) was used as the reactant and was subjected to multiple freeze-pump-thaw cycles before use. The methanol was stored in a glass vial and was admitted to the chamber through a variable leak valve (Varian) and directed onto the sample by a dosing needle positioned near the surface of the sample. The sample was held at 160 K during methanol dosing. The sample temperature was ramped upwards at 3 K s^{-1} during TPD experiments. Oxygen (Matheson, 99.997%) was used for sample cleaning and was admitted to the chamber in the same fashion as the methanol.

To study photochemical reactions the samples were illuminated with monochromatic UV light (365 nm) from a UV LED source (Prizmatix). This light was admitted into the chamber via a fiber optic cable and the sample was positioned in front of the end of this cable during UV illumination. The photon flux at the surface of the sample was 10^{15} cm^{-2} s^{-1} as determined by a photodiode detector (Thorlabs). The samples were held at 160 K during illumination to prevent desorption of surface species.

In order to allow quantitative comparison of the product yields from different thin film samples, desorption peak areas were scaled to account for mass spectrometer sensitivity factors and for exposed surface area. The latter was estimated using methanol TPD data as a function of methanol coverage to determine the point at which condensed methanol multilayers first form. The following masses were monitored during TPD experiments: 16 (CH_4), 18 (H_2O), 30 (CH_2O), 31 (CH_3OH), 45 (CH_3OCH_3), and 60 ($HCOOCH_3$).

3. Results

3.1. Catalyst characterization

TEM micrographs of one size of each of the platelet and bipyramidal A-TiO_2 nanocrystals are displayed in Fig. 2a and b, respectively. In these images the bipyramidal crystallites are laying on one of the {101} planes while the platelets are situated with the {001} surfaces parallel to the image plane. SEM images of spin-cast films of each crystallite morphology are displayed in Fig. 2c and d. These images were obtained after the samples were annealed in UHV at 800 K. The crystallites in the films have a random orientation and the image of the platelet film (Fig. 2d) shows that the crystallites in this particular sample have a thickness of ~4 nm. These images also show that in both instances the nanocrystals completely cover the substrate to a depth of at least several particles and that heating to 800 K does not result in any appreciable sintering of the particles.

XPS analysis of freshly-prepared bipyramidal and platelet thin film samples showed that the surfaces of the nanocrystals were covered with both fluorine and carbon. The fluorine results from the use of TiF_4 as one of the precursors during synthesis. Chlorine was not detected via XPS. It was found, however, that both of the F and C impurities could be removed by annealing in 10^{-8} Torr of oxygen at 750 K. Ti(2p) XP spectra obtained after this treatment were indicative of Ti^{+4}. Representative XP spectra are provided in the Supplemental information.

3.2. Thermal reactions

Representative TPD results for the platelet nanocrystals are given in Fig. 3a. This dataset was obtained from a thin film of the 14 nm nanocrystals dosed with 2.5 L (1 L = 10^{-6} Torr·s) of methanol (CH_3OH), an exposure that was found to be sufficient to saturate the