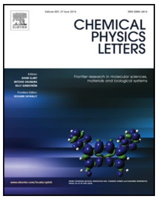
Chemical Physics Letters 616–617 (2014) 115–119

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett



New insight into the structure of dispersed titania by combining normal-mode analysis with experiment

David Nitsche, Christian Hess*

Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Alarich-Weiss-Str. 8, 64287 Darmstadt, Germany

ARTICLE INFO

Article history:
Received 6 August 2014
In final form 17 October 2014
Available online 23 October 2014

ABSTRACT

Normal-mode analysis has been combined with experiment to gain new insight into the vibrational structure of dispersed titania. For the calculations, double- and tri-grafted hydroxylated titania species have been adapted to a model silica support based on polyhedral oligomeric silsesquioxane (POSS). The choice of hydroxylated models was validated by IR detection of the O—H stretching band of dispersed titania (0.7 Ti/nm^2). UV resonance Raman experiments have identified three titania-related vibrational features within the spectral region 900–1100 cm^{-1} due to Ti—O—Si interphase, Ti—O—Si in-phase and out-of-phase stretching vibrations. This behaviour is fully consistent with the results obtained by the normal-mode analysis.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Titanium oxide is an extensively studied material and important component of many practical applications [1], such as titania silicalite-1 (TS-1) catalysts for low-temperature selective oxidation reactions using aqueous H_2O_2 as oxidant [2–4], solar cells [5] and sensors [6]. More recently, silica-supported (dispersed) titania has been shown to be an interesting material for photocatalytic reduction of CO_2 with H_2O [7]. Further performance improvement of such titanium-containing materials will be facilitated by a detailed understanding of the active site structure(s).

Previous studies have addressed the structure of silica-supported titania both experimentally [8–14] and theoretically [14,8,15]. From these studies it can be concluded that, at low content, Ti atoms are predominantly present in tetrahedral coordination, whereas with higher Ti content increasing crosslinking (Ti—O—Ti) and changes in the coordination gain importance. As reported in the literature for SBA-15 supported titania, at low loadings (0.5 Ti/nm^2) predominantly isolated TiO_4 species are present [13]. At higher loadings (*e.g.* 1.3 Ti/nm^2) increasing formation of Ti—O—Ti bridges without the formation of TiO_2 bulk is observed. Also, there has been no indication of the formation of terminating Ti=O groups as occurs for other transition metal oxides, for instance vanadia [16]. Rather, dispersed titania surface species containing hydroxyl groups such as $Ti(OH)_n(OSi)_{3-n}$ have been proposed. Previous theoretical studies performed with density functional theory (DFT) have significantly contributed to the current understanding of the electronic structure of dispersed titania [14,8,15]. To this end, models based on polyhedral oligomeric silsesquioxane (POSS) have been shown to provide a good description of the electronic structure of the silica support. In the present study, titania-modified POSS models were used to calculate the vibrational structure of silica-supported titania using a normal-mode analysis. To the best of our knowledge, such an approach has not been applied to dispersed titania before. Consistent with the literature, isolated titanium species were adapted to POSS to describe the titania surface site. For comparison with the calculations, UV Raman, UV–vis, and FT-IR spectroscopy have been used to characterize the structure of silica SBA-15-supported titania (Ti density: 0.7 Ti/nm^2). Raman experiments have been performed at an UV excitation wavelength to allow for selective resonance enhancement [9,17].

In this communication, we present a combined approach based on normal-mode analysis and *in situ* spectroscopy to gain new insights into the structure of dispersed titania. Our results provide experimental evidence for the presence of hydroxylated titania surface species and demonstrate that the silica support significantly influences the vibrational characteristics of the titania species. Thus, combining spectroscopic experiments with theoretical calculations may reveal new information about the vibrational structure and provide a more detailed understanding of dispersed transition metal oxide species.

---

* Corresponding author.
E-mail address: hess@pc.chemie.tu-darmstadt.de (C. Hess).

http://dx.doi.org/10.1016/j.cplett.2014.10.042
0009-2614/© 2014 Elsevier B.V. All rights reserved.

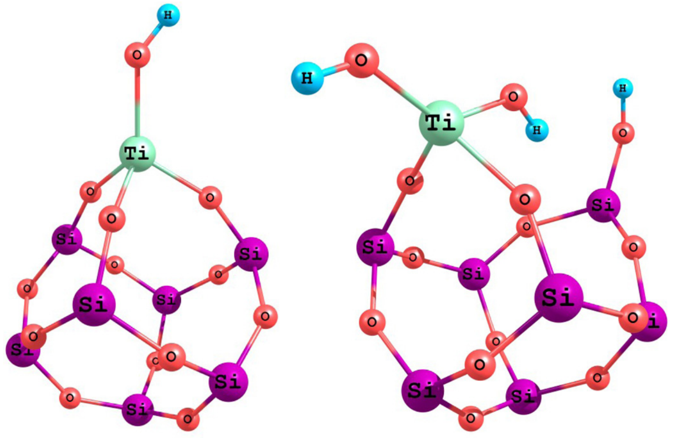


Figure 1. (Left) Model for monomeric titania species on silica with three anchoring Ti—O—Si bonds (Model A). (Right) Model for mono monomeric titania species on silica with two Ti—O—Si bonds (Model B).

2. Simulations

The simulation of the silica-supported titania models have been performed using Vibratz V2.3 (Shape Software), which calculates the Raman frequencies based on a normal mode analysis [18,19]. To validate the suitability of the method we performed reference calculations on anatase TiO_2. The calculated eigenvalues of the normal mode analysis agree with the experimental results of anatase TiO_2 within $\leq 5\,cm^{-1}$ [20]. Previous studies have already proved [19] that the adaptation of the surface site to a silica support is crucial for the correct assignment of their eigenvalues. Therefore, a complex model, consisting of a modified polyhedral oligomeric silsesquioxane (POSS, Si_8O_{12}) and a titania surface site (tri-grafted [Model A] and double-grafted [Model B]) has been applied to the calculations. Here, two different monomeric titania models have been chosen to investigate the impact of the silica support and a variation of Ti—OH groups to the normal modes of the surface site. Please note that the hydrogen-atoms within the POSS molecule have been eliminated since their contribution to the displacement of the inner coordinates is insignificant. In the present study, the influence of strain and stress has not been considered owing to its complexity. However, we are aware of the fact that strain and stress may affect the spectral position of the Raman features.

The model for the tri-grafted monomeric titania species (Model A) was generated by replacing one silicon edge atom of the POSS molecule by Ti—OH, resulting in a titanium surface site anchored to the silica support. The double-grafted monomeric titania model (Model B) consists of two terminating hydroxyl groups, in which one anchoring Ti—O—Si bond has been replaced by a hydroxyl group. Both models are depicted schematically in Figure 1.

Table 1 summarizes the force constants used for the normal-mode analysis. The value for the Si—O bonds was refined to 4.14 mdyn/Å, starting from the value of 4.5 dyn/Å for amorphous silica [21,22] and using the in-phase Si—O—Si vibration of the cubic POSS molecule as a reference vibration. The force constant for the Si—O bond of the anchoring Ti—O—Si bond was refined to 4.56 mdyn/Å, using the out-of-phase vibration of the corresponding Ti—O—Si vibration. The Ti—O bond of the anchoring Ti—O—Si bond was refined to 4.4 mdyn/Å using the out-of-phase Ti—O—Si vibration, whereas the force constant $f(\text{Ti—O})_{\text{Ti–O–H}}$ was determined as 4.63 mdyn/Å using the Ti—OH stretch vibration of the titania surface site. For the simulation of the titania species no point group was assigned since here only the Raman frequencies are of interest and their eigenvalues do not depend on the molecular symmetry.

3. Experimental

Silica-supported titania with a loading density of $0.7\,Ti/nm^2$ was prepared according to an incipient wetness impregnation procedure described previously [23,24]. The BET surface area ($609\,m^2/g$) and the pore diameter (7.0 nm) were determined based on nitrogen adsorption/desorption isotherms on a Quantachrome NOVA 3000e at 77 K.

In situ UV Raman experiments were performed on a multi-wavelength Raman setup, consisting of a tunable Ti-sapphire laser (Indigo-S, Coherent), a triple Raman spectrometer (Princeton Instruments) and a confocal microscope (BX-51, Olympus) using 217.5 nm excitation [17]. The laser power was adjusted to 1 mW at the sample position. The spectral resolution of the spectrometer is $0.6\,cm^{-1}$. The *in situ* cell consists of a stainless steel body and sapphire glass window and was placed on a motorized *X*–*Y*-stage in order to avoid laser-induced sample degradation.

Data analysis of the UV Raman data included baseline correction, manual cosmic ray removal, and a peak fit analysis using Lorentzian functions. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Bruker Vertex 70 spectrometer equipped with a liquid-nitrogen (LN)-cooled mercury cadmium telluride (MCT) detector, a Praying Mantis diffuse reflection accessory and a high temperature *in situ* cell (Harrick). All UV–vis, Raman and IR experiments were performed under dehydrated conditions. Prior to data collection, samples were heated at 773 K for 1 h under controlled atmosphere (80/20% O_2/N_2) and then cooled to room temperature.

4. Results and discussion

4.1. Normal mode analysis

The use of normal-mode analysis allows detailed insight into the vibrational structure of silica-supported titania species. This includes the effect of the silica support and the hydroxyl groups on the Raman frequencies. Table 2 summarizes the results of the calculations for both models. The eigenvalues of the normal-mode analysis are denoted as in-phase Ti—O—Si, out-of-phase Ti—O—Si, interphase Ti—O—Si and Ti—OH stretching vibrations. Please note that the calculations yield eigenvalues in the spectral region $<800\,cm^{-1}$. However, the present analysis focuses on the spectral region where pure stretching vibrations are expected.

The eigenvalues calculated on the basis of models A and B are labelled according to the direction of the oscillating atoms and their corresponding force constants. As presented in Table 2, the two models show eigenvalues at 940 and $951\,cm^{-1}$, respectively, denoted as interphase Ti—O—Si vibration. These vibrations clearly originate from a momentum transfer from the silica support to the surface site, as the main contribution for that vibration results from $f(\text{Si—O})_{\text{Si–O–Si}}$ (Model A: 94%; Model B: 94%). Besides, there is a significant blue shift of about $11\,cm^{-1}$ for the interphase Ti—O—Si with decreasing adaptation to the silica support, indicating the influence of the support material on the spectral position of the eigenmodes. These results are in good agreement with previous UV Raman data and DFT calculations, where the feature at $960\,cm^{-1}$ has been assigned to an asymmetric stretching mode of the Ti—O—Si bridge [8,23–29]. The two interphase modes at $940/951\,cm^{-1}$ and $1036/1035\,cm^{-1}$ differ by the degree to which the force constant $f(\text{Si—O})_{\text{Ti–O–Si}}$ contributes to these modes. As shown in Table 2, in case of the mode at $940/951\,cm^{-1}$ there is no such contribution, whereas in case of the $1036/1035\,cm^{-1}$ mode there is a small contribution of 6/9%, respectively.

The normal-mode analysis identifies the Ti—OH stretching vibration within the spectral window of $800–900\,cm^{-1}$ (Model A:

Download English Version:

https://daneshyari.com/en/article/5380257

Download Persian Version:

https://daneshyari.com/article/5380257

Daneshyari.com