Short Communication

Normal mode analysis of silica-supported vanadium oxide catalysts: Comparison of theory with experiment

David Nitsche, Christian Hess *

Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Petersenstr. 20, 64287 Darmstadt, Germany

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ABSTRACT

The vibrational structure of silica-supported vanadium oxide species has been studied by normal mode analysis using polyhedral oligomeric silsesquioxanes (POSSs) to describe the silica support. The analysis reveals that the vanadium oxide-related vibrational bands are characterized by significant contributions of several force constants. Their discussion in terms of single bond-unit designators is therefore not adequate. The consideration of the silica support is shown to be of importance for the vibrational spectrum. The theoretical results are fully consistent with experimental data for a silica-supported vanadium oxide catalyst with a vanadium coverage of 0.7 atoms/nm^2.

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1. Introduction

Silica-supported vanadium oxide is active and selective in a variety of oxidation reactions, such as the selective oxidation of methane to formaldehyde, the oxidative dehydrogenation of alkanes, or the selective photo-oxidation of alcohols [1–7]. Knowledge-based improvement of catalysts strongly relies on meaningful structure–activity relationships. Therefore, a detailed understanding of the molecular structure of the active surface site(s) is essential. While dispersed vanadium oxide species are considered the active species in these catalysts, the detailed vanadium oxide structure has been a matter of debate. In the literature, several structural models for dehydrated silica-supported (dispersed) vanadium oxide have been proposed: (i) trigrafted $OV(O-Si)_3$, (ii) hydroxylated species $OV(OH)_n(O-Si)_{3-n}$ with one or two $V-O-Si$ linkages replaced by OH groups, and (iii) dimeric/oligomeric species (see for example Refs. [8–16,1] and references therein).

Previous theoretical investigations using density functional theory (DFT) have greatly contributed to the current understanding of the structure of silica-supported vanadium oxide by analyzing the models proposed on the basis of spectroscopic experiments [10–12]. To this end, however, the description of the amorphous silica support constitutes a formidable task. In the past, molecular and embedded cluster models for vanadium oxide on silica have been developed. Polyhydral oligomeric silsesquioxanes (POSSs) such as the cubic POSS $H_8Si_8O_{12}$

(see Fig.1) have been shown to be convenient finite-size models mimicking the silica electronic structure well [17]. To generate, for example, a model for a monomeric trigrafted vanadium oxide species on silica, one Si–H group of $H_8Si_8O_{12}$ is replaced by a V=O group. In contrast to DFT, normal mode analysis has not been applied to silica-supported vanadium oxide. Previously, the vanadyl site has been modeled by an $OV(O-Si)_3$ molecule [18].

In this communication we apply a normal mode analysis to silica-supported vanadium oxide catalysts using cubic POSS to model the silica support. We compare the results with experimental Raman and IR data for a silica SBA-15-supported vanadium oxide catalyst. While the focus of the present study is on supported vanadium oxide, our results also give important insights for other commonly studied supported transition metal oxides of, for example, Cr, Ti, or Mo.

2. Simulations

The normal mode analysis has been performed using Vibratz V2.3 (Shape Software), which calculates the eigenvalues of the differential equation of the models of interest based on the Wilson **G** matrix. Thereby, those inner coordinates are denoted as eigenvalues, which contribute most to the displacement of the atoms [19]. To model the silica support cubic polyhedral oligomeric silsesquioxane ($H_8Si_8O_{12}$) was used as shown in Fig. 1.

A model for a monomeric trigrafted vanadium oxide species on silica was generated by replacing one Si–H group of $H_8Si_8O_{12}$ by V=O, resulting in a surface species anchored to the support by three Si–O–V bonds (Model A). The second model employed (Model B) describes a
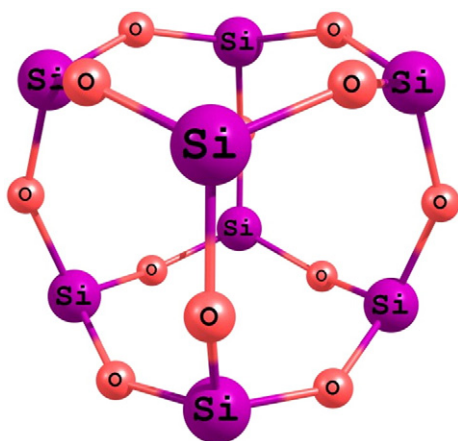
Fig. 1. Cubic polyhedral oligomeric silsesquioxane (POSS).

Table 1
Summary of force constants used for the normal mode analysis. Units are given in mdyn/Å (1 mdyn/Å = 100 N/m).

	f(V=O)	f(V−O)	f(Si−O)$_{Si−O−Si}$	f(Si−O)$_{V−O−Si}$	f(O−H)
Before refinement	7.6	3	4.5	4.5	7.3
After refinement	7.56	4.6	4.14	4.18	7.3

monohydroxylated surface species, in which one bond to the support has been replaced by a hydroxyl group, resulting in two anchoring Si−O−V bonds. Models A and B are shown schematically on the left and right of Fig. 2, respectively.

Table 1 summarizes the force constants used for the normal mode analysis. Starting from a previous estimate for the Si−O force constant in amorphous silica of f(Si−O) = 4.5 mdyn/Å [20,21], the value of the corresponding Si−O bond in POSS was refined to 4.14 mdyn/Å using the in-phase Si−O−Si vibration of the cubic POSS molecule. The force constant of the anchoring Si−;O bond was refined to 4.18 mdyn/Å using the out-of-phase vibration of the surface site. The force constant for the hydroxy group in Model B was adopted from reference [22]. The starting value for the force constant of the V=O group was determined experimentally as f(V=O) = 7.6 mdyn/Å based on the 2070 cm^{-1} overtone of the corresponding vanadyl stretch vibration at 1037 cm^{-1} (see discussion below). The force constants for the metal–oxygen bonds f(V−O) were obtained by starting from the well-studied small molecules VOCl₃, VOBr₃, and VOF₃ [23,24] and refinement with the out-of-phase vibration of Model A. For the analysis of the vanadium oxide species, no point groups could be assigned to the models owing to their complexity. However, applying the force field to the models still yields correct values for the Raman frequencies. Our preliminary investigations have indicated that angle/torsion/interaction force constants are not as influential for the complex molecules discussed

here as compared to small molecules such as VOCl₃. Furthermore, values for these force constants are difficult to evaluate due to the lack of comparative data and would make the calculations more vulnerable to calculative errors. The models employed do not consider the effect of strain/stress on the structure. Please note that the sum over all contributions is not necessarily 100% since the analysis software presents only the bands with the largest contributions. Therefore, those values not available were marked as 'n.a.' (see Table 2). For simplicity, the H atoms have been eliminated in the calculations, as their contribution to the vanadium oxide-related Raman frequencies can be neglected.

3. Experimental

Silica SBA-15-supported vanadium oxide with a loading density of 0.7 V/nm^2 was prepared according to a grafting/ion-exchange procedure described previously [25,26]. Based on nitrogen adsorption/desorption isotherms (Quantachrome), the specific surface area and the pore diameter were determined as 618 m^2/g (multipoint BET) and 5.3 nm (BJH), respectively.

For Raman experiments a multi-wavelength *in situ* Raman spectroscopic setup based on a tunable laser source (Coherent Indigo) and a triple spectrometer (Princeton Instruments) was employed, as described in detail elsewhere [27]. For excitation, UV radiation at 217.5 nm was used. The laser power at the sample position was reduced to ~1 mW. The spectral resolution of the spectrometer was <0.6 cm^{-1}. The *in situ* cell consisted of a stainless steel body and a sapphire glass window and was placed on a motorized X–Y stage. To avoid laser-induced changes the sample was translated during signal collection. Prior to experiments, the sample was dehydrated by treatment in 20% O₂/N₂ flow (20/80 mL/min) for 1 h at 773 K and then cooled to room temperature. Data analysis included a baseline correction and a least-squares-fit analysis using Lorentzian functions.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed on a Vertex 70 FT-IR spectrometer
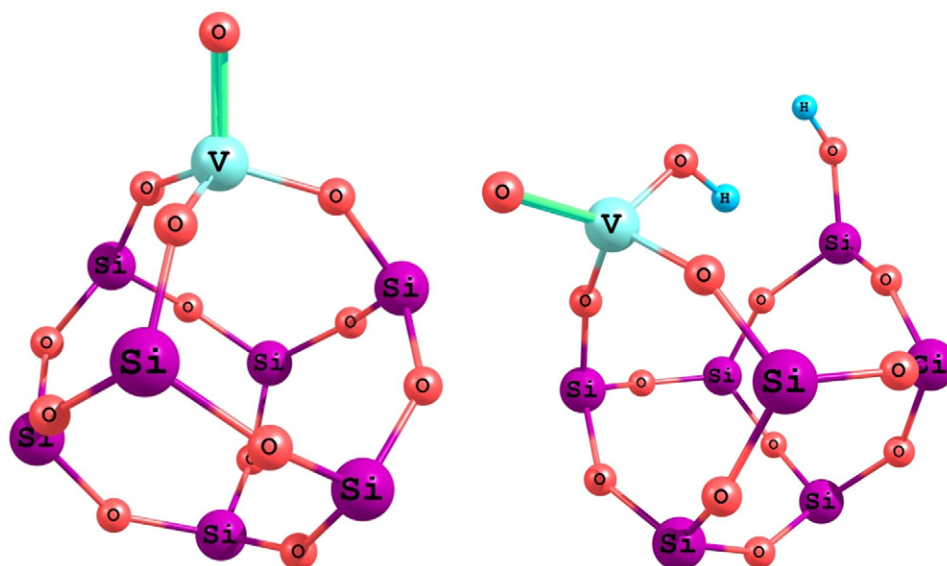

Fig. 2. Left. Model for unhydroxylated monomeric vanadium oxide species on silica (Model A). Right. Model for monohydroxylated monomeric vanadium oxide species on silica (Model B).