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Molecular Structures of Surface Vanadium Oxide Species on Titania Supports

In a recent publication in the *Journal of Catalysis* (*1*), a statement was attributed to me that I did not make in an earlier publication (*2*), and I would like to take this opportunity to comment on this statement as well as on other conclusions reached by Cristiani *et al.* from their Raman and infrared investigations regarding the molecular structures of surface vanadia species on titania supports. Cristiani *et al.* (*1*) state that "Wachs *et al.*, primarily from laser–Raman data, suggested the presence of tetrahedral dioxovanadium centers." The exact statement that was made by Wachs *et al.* (*2*) in the cited publication is "the coordination of the surface vanadia species cannot be assigned from the laser Raman data." The earlier publication, however, did go on to quote extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) measurements of Kozlowski *et al.* (*3*) which concluded that the surface vanadium oxide species possess two terminal and two bridging oxygen bonds. Thus, molecular structures of surface vanadia on titania were not derived from Raman vibrational data in the publication of Wachs *et al.* (*2*). In fact, I have always maintained that a complete structural analysis of surface metal oxide species on titania is not achievable solely with Raman spectroscopy (*2, 4–7*).

The molecular structures of surface vanadia species, as well as other surface metal oxide species (i.e., chromia, molybdena, tungsta, etc.) on titania cannot be determined solely by Raman spectroscopy because the strong titania Raman bands below 800 cm^{-1} prevent the detection of the additional Raman bands which are critical for a complete structural analysis (*2*). The only vanadia vibrations that can be observed in the vanadia–titania system are the stretching modes of terminal oxygen(s) which occur above 800 cm^{-1} (*8, 9*). Consequently, a complete structural assignment of the surface vanadia species cannot be made solely on information about the symmetric stretching mode since *distorted* tetrahedral and octahedral vanadia structures, monomeric as well as polymeric species, also produce vibrations in this region (*8–10*). This dilemma is not unique to Raman and is even more pronounced in infrared measurements of the vanadia–titania system (*1*). Raman spectroscopy, however, can be used to determine the nature of surface vanadia species on other oxide supports which are Raman inactive, such as γ-Al_2O_3, and allow collection of vanadia Raman bands down to approximately 100 cm^{-1} (*4, 10*). Unfortunately, the strong infrared absorptions of all oxide supports usually prevent accumulation of IR modes of surface vanadia species, as well as other surface metal oxides, in the low wavenumber region (*11*).

In spite of the above limitations, Cristiani *et al.* (*1*) have undertaken the assignment of the surface vanadia structures of vanadia–titania catalysts from Raman and infrared measurements. The hydrated surface vanadia species on the titania support were found to exhibit infrared bands at 990(s) and 940(m) cm^{-1} and Raman bands at 995(s), ~920(w) and ~850(w) cm^{-1}. The dehydrated surface vanadia species on the titania support were found to exhibit an infrared band at 1035(s) cm^{-1} and Raman bands at 1035(s), ~920(w), and ~850(w) cm^{-1}. The Raman and infrared bands at 1035 cm^{-1} of

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the dehydrated vanadate species were assigned to the symmetric vibration of surface monoxo vanadyl species with coordinate unsaturation, and the Raman and infrared bands at 990–995 cm^{-1} were assigned to the *same surface vanadia species* which is hydrated when the surface is wet. It was argued that the coincidence of the Raman and IR modes at 1035 cm^{-1} for the dehydrated vanadia–titania catalysts and 990–995 cm^{-1} for the hydrated vanadia titania catalysts is a consequence of the presence of only surface monoxo vanadia species because two bands separated by 10–30 cm^{-1} would be expected in the IR and Raman spectra with opposite relative intensity for surface dioxo vanadia species. The broad Raman bands centered at 920 and 850 cm^{-1} and the IR absorption at 940 cm^{-1} were assigned to the symmetric stretch of V_xO_y clusters. These symmetric vibrations, however, do not provide information about the coordination (tetrahedral or octahedral) or the molecular structures of the surface vanadia species on titania supports.

The limitations in determining the molecular structures of the surface vanadia species on titania solely from vibrational spectroscopies have recently been overcome by combining Raman spectroscopy studies with solid-state ^{51}V NMR investigations (*6, 7, 12–15*). The solid-state NMR experiments have been shown to readily discriminate between octahedral and tetrahedral vanadia coordination as well as between the number of oxo-vanadia bonds in tetrahedally coordinated vanadia (*6, 7*). These characterization studies revealed that the molecular structure of the surface vanadia species on titania is dependent on vanadia surface coverage and surface hydration. The system chosen for these investigations was vanadium oxide on a similar TiO_2 (Degussa P-25) as used by Cristiani *et al.* (*1*). The Raman studies demonstrated that a monolayer of surface vanadia species on this titania support, ~50 m^2/g, corresponds to ~6–7% V_2O_5/TiO_2. Under hydrated conditions and at low surface coverage a broad Raman band at ~940 cm^{-1} is present, and this band quickly shifts to ~990 cm^{-1} as the vanadia loading is increased (*12, 13*). The solid-state NMR experiments revealed that the 990-cm^{-1} Raman band originates from octahedrally coordinated surface vanadia species (*6, 7*). The Raman and NMR results corresponding to the 990-cm^{-1} band best match the distorted octahedral vanadia species present in decavanadate clusters. This conclusion is also consistent with infrared studies of decavanadates which give rise to one band in the 950 to 1000-cm^{-1} region (*16*). The structure of sodium decavanadate has been found to contain one short vanadium–oxygen bond, four intermediate vanadium–oxygen bonds, and one long vanadium–oxygen bond (*17*). The solid-state NMR experiments also revealed that the ~940-cm^{-1} Raman band primarily originates from tetrahedrally coordinated surface vanadia species (*6, 7*). The Raman and NMR results corresponding to the 940-cm^{-1} band best match the distorted tetrahedral vanadia species present in polymeric metavanadate compounds. Dehydration of the surface vanadia on oxide supports predominantly transforms the surface vanadia species to tetrahedral coordination and the Raman band shifts to 1020–1040 cm^{-1} (*7, 14, 15*). The Raman and NMR results corresponding to the 1020 to 1040-cm^{-1} band suggest a surface tetrahedral structure possessing one short terminal bond and three long bridging bonds.

Comparison of the combined Raman/NMR studies with the conclusions reached from the Raman/IR studies by Cristiani *et al.* reveals some significant differences. Cristiani *et al.* assigned the 1035- and 990- to 995-cm^{-1} bands to the *same surface species* which was coordinatively unsaturated and coordinatively saturated, respectively. The new NMR data clearly show that the 1035- and 990- to 995-cm^{-1} bands correspond to *different surface species* possessing tetrahedral and octahedral vanadia structures, respectively. Interestingly, both of these vanadia structures have only one short vanadium–oxygen bond and, thus, support the Raman/IR conclusions of Cristiani *et al.* that surface monoxo vanadia species are present on the titania support. Cristiani *et al.* also assigned the weak Raman/IR band in the 920- to 940-cm^{-1} region to V_xO_y clusters and the combined Raman/NMR data suggest that these bands are due to distorted tetrahedral surface species such as metavanadate. Thus, the combined Raman spectroscopy and solid-state ^{51}V NMR experiments have allowed the determination of the molecular structures of the surface vanadia species on titania and demonstrated the inherent limitations, due to the vibrational characteristics of the titania support, of only applying vibrational spectroscopies for the structural determination of the vanadia–titania system.

Cristiani *et al.* (*1*) also state that "the combined use of Raman and IR spectroscopies and the analysis of both wet and dry samples are required to discriminate between bulk vanadia and surface vanadyl absorptions." It is not necessary to perform *both* Raman and IR measurements to discriminate between the different types of vanadium oxide structures in vanadia–titania catalysts since either vibrational technique provides this information. Chan *et al.* (*14*) previously demonstrated that *in situ* Raman spectroscopy measurements readily discriminate between bulk metal oxide and surface metal oxide species for many different transition metal oxide systems. This discrimination is a consequence of the fact that the surface metal oxide species Raman bands sharpen and simultaneously shift in frequency upon the desorption of surface moisture and the crystalline metal oxide Raman bands do not change at all upon the desorption of surface moisture. Thus, for the vanadia–titania system the crystalline V_2O_5 Raman band always occurs at 994 cm^{-1} and the surface vanadium oxide species bands can occur between 800 and 995 cm^{-1} for a hydrated surface and are transformed to a sharp band at 1030–1035 cm^{-1} and a broad band at ~920 cm^{-1} for a dehydrated surface. Similarly for infrared spectroscopy measurements, the crystalline V_2O_5 IR absorption always occurs at 1020 cm^{-1} and the surface vanadium oxide species IR absorptions can occur between 800 and 995 cm^{-1} for a hydrated surface and are transformed to a sharp band at 1030–1035 cm^{-1} and a broad band at ~920 cm^{-1} for a dehydrated surface (*1*). For most situations, however, just a single vibrational measurement with Raman or infrared, hydrated or dehydrated, will usually suffice to discriminate between bulk vanadia and surface vanadium oxide species because of their different vibrational characteristics.

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ISRAEL E. WACHS

Zettlemoyer Center for Surface Studies
Department of Chemical Engineering
Lehigh University
Bethlehem, Pennsylvania 18015

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