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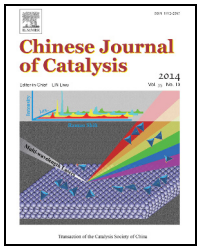

Review

Multi-wavelength Raman spectroscopy study of supported vanadia catalysts: Structure identification and quantification

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ABSTRACT

Revealing the structure of supported metal oxide catalysts is a prerequisite for establishing the structure-catalysis relationship. Among a variety of characterization techniques, multi-wavelength Raman spectroscopy, combining resonance Raman and non-resonance Raman with different excitation wavelengths, has recently emerged as a particularly powerful tool in not only identifying but also quantifying the structure of supported metal oxide clusters. In this review, we make use of two supported vanadia systems, VO_x/SiO_2 and VO_x/CeO_2, as examples to showcase how one can employ this technique to investigate the heterogeneous structure of active oxide clusters and to understand the complex interaction between the oxide clusters and the support. The qualitative and quantitative structural information gained from the multi-wavelength Raman spectroscopy can be utilized to provide fundamental insights for designing more efficient supported metal oxide catalysts.

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1. Introduction

Raman spectroscopy has long been used as a powerful tool for characterizing the molecular structure of catalytic materials under various conditions [1–4]. In recent years, multi-wavelength (MW) Raman spectroscopy studies of heterogeneous catalysts have added additional dimensions to this technique by providing the capability of probing the structure and heterogeneity of catalytically relevant sites [5–20]. Specifically, the heterogeneously distributed catalytic phases (sites) with characteristic electron absorption can be selectively resonance enhanced in Raman spectroscopy by using appropriate laser excitation whose energy matches or approaches that of the maximum of the electronic absorption band. So the different catalytic phases (sites) could be individually probed by tuning the laser excitations (multi-wavelength excitation). The working mechanism of MW Raman spectroscopy is schematically depicted in Fig. 1. Taking supported vanadia (VO_x) catalysts as an example, excitations by both UV and visible lasers of a dehydrated VO_x/Al_2O_3 sample lead to the selective distinction between monovanadate and polyvanadate species on the surface of alumina [6,21]. Furthermore, three types of monovanadate structures have been identified on the Al_2O_3 surface as three different vanadyl stretching bands were observed on a low loaded VO_x/Al_2O_3 sample when excited by different UV laser wavelengths [7]. Even within one type of VO_x species, the different bonds (V=O, V–O–V, V–O–support, etc.) may have different electronic absorption through charge transfer from oxygen

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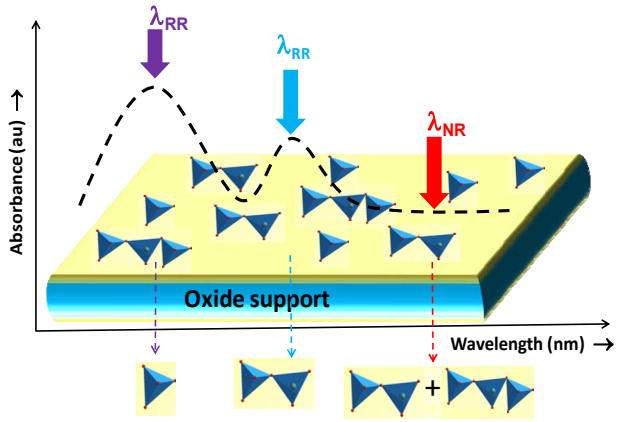

Fig. 1. Illustration of the working principle of multi-wavelength Raman spectroscopy of supported metal oxide. λ_{RR} and λ_{NR} refer to excitations resulting in resonance and non-resonance Raman, respectively.

to vanadium [8]. Excitation of Raman spectra within the absorption region will produce resonance-enhanced spectra from the specific local V–O bonding with absorptions at/near the excitation wavelength. Therefore, through measurement of the Raman spectra at several wavelengths, more detailed structural information can be obtained not only on the various VO_x species in the distribution but also the local V–O bondings in a specific VO_x species. Furthermore, resonance Raman (RR), often inducing overtone and combination modes, can also potentially shed light on the anharmonic potential of the ground state and on the nature of excited states relevant to photocatalysis of the catalytic materials. In light of these advantages, MW Raman has currently seen to play an increasing role in characterizing the complex structure of heterogeneous catalysts.

Supported vanadia catalysts represent an important class of heterogeneous catalysts widely used in variety of redox reactions [22–26]. These catalytic reactions usually occur at some specific active sites related to vanadia clusters on the surface. Thus, a key step for understanding the structure-catalysis relationship is to obtain knowledge of the molecular structure of vanadia species anchored on the support surface. In this work, we present our recent Raman studies of the structure of VO_x/SiO_2 [27] and VO_x/CeO_2 [28–30] catalysts as two illustrative examples for the power of the MW Raman technique. It is shown that combination of RR with non-resonance Raman, i.e., MW Raman spectroscopy, is able to provide not only qualitative information on the structure of different surface VO_x species but also quantitative information on the distribution of these VO_x species as a function of vanadium loading for VO_x/SiO_2 system. The observation of overtone and combination bands of surface VO_x on silica helps the assignment of the fundamental modes of VO_x species. The reduction behavior of the different VO_x species on silica has been distinguished by the MW Raman spectroscopy. In the case of VO_x/CeO_2, MW Raman is demonstrated to be able to reveal not only the structure of surface vanadia species *via* non-resonance Raman but also the nature of the interaction between vanadia and ceria support by monitoring the defect sites evolution of ceria *via* RR. The transformation of surface vanadia species into $CeVO_4$ upon thermal treatment is also found affected by the support property (surface lattice oxygen reactivity and defect sites) through a MW Raman investigation.

2. Case study I: SiO_2-supported vanadia catalysts

2.1. Introduction

The structural identification of VO_x/SiO_2 has been the subject of many spectroscopic studies including Raman, infrared, UV-vis-NIR, EXAFS, NMR, and EPR [1,3,24,25,31–40]. It is generally agreed that vanadium oxide is present on the dehydrated silica surface in two different forms, i.e., as monomeric VO_4 species at low loadings (typical < 2 VO_x/nm^2) and as mixture of monomer and V_2O_5 crystals at high loadings (> 2 VO_x/nm^2) [38]. It has been long accepted that a pyramidal model ($O{=}V{-}(O{-}Si)_3$) is the only structure for dehydrated VO_x/SiO_2 at low VO_x loading (< 2 V/nm^2) [31,41] and thus VO_x/SiO_2 has been considered as an example of a nearly single-site heterogeneous catalyst.

Recently, there has been renewed experimental [39,40,42–51] and theoretical [42,49,50,52–56] interest in what precisely the geometrical molecular structure of surface vanadia on silica is under dehydrated condition. This is because the pyramidal model cannot satisfactorily explain all the experimental data collected over the years especially the uncertainties about specific spectral assignments in the vibrational spectra as illustrated in studies by Magg et al. [42], Gijzeman and co-workers [43–45], and Moisii et al. [46,47]. It has been realized that there is strong vibrational coupling between the vanadia species and the silica support [42], which makes the vibrational spectra of vanadia/silica more complex and difficult to interpret. Especially controversial is the assignment of the vibrational band at around 915 cm^{-1} which was assigned to V–O–V [40,57], V–O–support mode [6,36,42,48,49,52–56], O–O mode [43,44,58], or V=O mode [46]. Controversies also exist on the assignment of the Raman bands above 1000 cm^{-1} where the vanadyl stretch and silica modes are close in vibrational energy and thus strongly coupled together [42,46]. Based on the different assignments, three structures have been suggested for monomeric VO_4 species anchored at the silica surface under dehydrated conditions, namely, pyramidal, bi-grafted species (two V–O–Si, one V=O and one V–OH), and the so-called umbrella structure (one V–O–Si, one V=O and a perturbed oxygen molecular bonded to V). A recent study by Wachs and coworker [59] demonstrates definitively with Raman and UV-Vis spectroscopy that the surface vanadia umbrella-like structure is not present for both hydrated and dehydrated supported vanadia catalysts *via* comparing with the vibrational spectrum of $K[VO(O_2)(heida)]$ where the umbrella structure is present. Up to date, both experimental and theoretical work have concluded that the traditionally accepted pyramidal model is the most likely structure for stable VO_x species under highly dehydrated condition. However, even the exclusive presence of monomeric vanadia species on silica surface was challenged recently by Schlogl and co-workers [60,61] via comparing the theoretical and experimental NEXAFS spectra of a silica SBA-15 supported

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