Raman spectroscopic studies of the thermal decomposition mechanism of ammonium metavanadate

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Thermal decomposition of NH_4VO_3 under N_2 and $NH_3 + H_2O$ has been studied on a molecular level by *in situ* Raman spectroscopy in the temperature range 150–400 °C. Under N_2, the decomposition mechanism leading to formation of V_2O_5 has been observed to proceed *via* two intermediates: *viz.* an amorphous, transitional $(NH_4)_2V_4O_{11}$ and $NH_4V_3O_8$. Under NH_3+H_2O, a slightly different decomposition pathway, rationalized in terms of stability of intermediates, leading to the formation of V_2O_3 has been observed. The identification of Raman-inactive V_2O_3 is further supported by the formation of V_2O_4 and V_2O_5, along with monomeric vanadyl species, through oxidation of V_2O_3 at 400 °C.

Vanadium pentoxides have attracted serious attention due to their applications in selective oxidation of hydrocarbons, selective catalytic reduction of nitrogen oxides and oxidation of sulfur dioxide.[1–3] Thermal decomposition of NH_4VO_3 in air, involving formation of $NH_4V_3O_8$ around 190–250 °C, is the most popular method to prepare vanadium pentoxide.[4–10] In addition to $NH_4V_3O_8$, several other intermediates such as $NH_4V_3O_8\cdot 0.5H_2O$,[5] $(NH_4)_2V_4O_{11}$,[6,10] discrete $NH_4V_3O_8$[8] and $V_2O_5\cdot H_2O$[9] have been proposed by different researchers using thermal analysis and X-ray powder diffraction, whereas *in situ* IR emission spectroscopic study has suggested direct transformation of NH_4VO_3 into V_2O_5.[11] In the presence of NH_3, however, a completely different decomposition mechanism and final products are obtained. Von Sacken and Dahn[6] have studied the effect of different atmospheres on these reactions by thermogravimetry and evolved gas analysis (EGA) and concluded that NH_3 plays a critical role in determining the stoichiometry of the final products above 250 °C. Lampe-Onnerud and Thomas have studied the effect of rates of heating and release of NH_3+H_2O by DSC, X-ray diffraction and EGA, and concluded that V_2O_5, V_3O_7 and V_6O_{13} can be obtained as final products through formation of the intermediates $NH_4V_3O_8\cdot 0.5H_2O$ and $V_3O_7\cdot H_2O$.[5] Although thermal decomposition studies of NH_4VO_3 have been extensive, a universally acknowledged mechanism, especially at a molecular level, is still lacking. In the last two decades, Raman spectroscopy has been demonstrated to be a powerful technique for characterization of a wide range of vanadium-related compounds.[12–17] Therefore, thermal decomposition of NH_4VO_3 is investigated in this study under either flowing N_2 or in the presence of NH_3+H_2O by *in situ* Raman spectroscopy. A comparison of these two different reaction pathways provides information at the molecular level, pertaining to the identification and structure of both stable as well as transitional intermediates in the bulk as well as on the surface. As part of a research program aimed at development of vanadium-based SCR catalyst, studies on the synthetic and mechanistic chemistry of novel vanadium oxides using structure-directing templates under hydrothermal condition are in progress.

Experimental

Reagent-grade NH_4VO_3 was purchased from Aldrich and 99.9% N_2 was purchased from Lian Hua Gas (Taiwan). These chemicals were used without any further purification. Each sample was subjected to a heating rate of 10 °C min^{-1} by a Linkam THMS 600 heating cell up to the designated temperatures either under flowing N_2 with a flow rate of 200 cm^3 min^{-1} or by closing the outlet of the cell to prevent release of NH_3+H_2O. The Raman spectrometer used in this study was a Renishaw system 2000 micro-Raman spectrometer. A 25 mW HeNe laser, operating at 632 nm, formed the excitation source. A 5 µm exit slit offered resolution better than ±1 cm^{-1}. All Raman spectra were recorded *in situ* at designated temperatures. Thermogravimetry was performed on a Du Pont Model 2200 at a heating rate of 10 °C min^{-1} in N_2 atmosphere with a flow rate of 60 cm^3 min^{-1}.

Results and Discussion

The results of TG–DTG on NH_4VO_3 are presented in Fig. 1.[6,7] Two major mass losses appear in the temperature ranges 160–210 and 260–300 °C; while no significant mass loss was observed in the temperature range 210–250 °C. Additionally, a decrease in rate of mass loss is noticed at *ca.* 195 °C by DTG,[6] corresponding to 88.7% of the initial mass. When the temperature is raised above 300 °C, desorption of volatile components (ammonia and water) is complete and no more mass loss is observed. Fig. 2 shows the *in situ* Raman spectra of NH_4VO_3, heated to 150, 165, 180 and 190 °C under flowing N_2, recorded *in situ* during heating. At 150 °C, a strong band at 927 cm^{-1}, medium and weak bands at 260, 320, 378, 495, 645 and 895 cm^{-1} are observed [Fig. 2(*a*)]. This spectrum is no different than that of NH_4VO_3 at room temperature, which is comprised

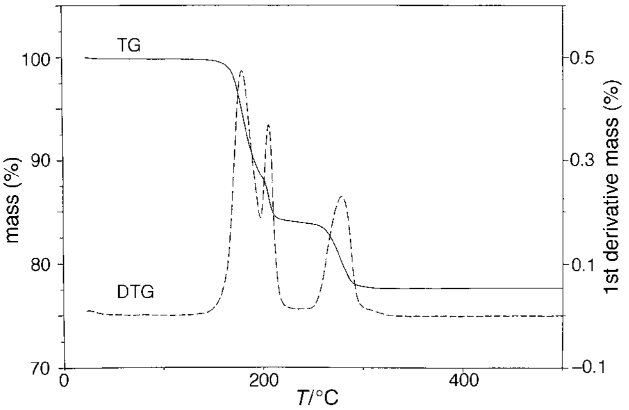


Fig. 1 Thermogravimetric analysis of NH_4VO_3 under an N_2 atmosphere

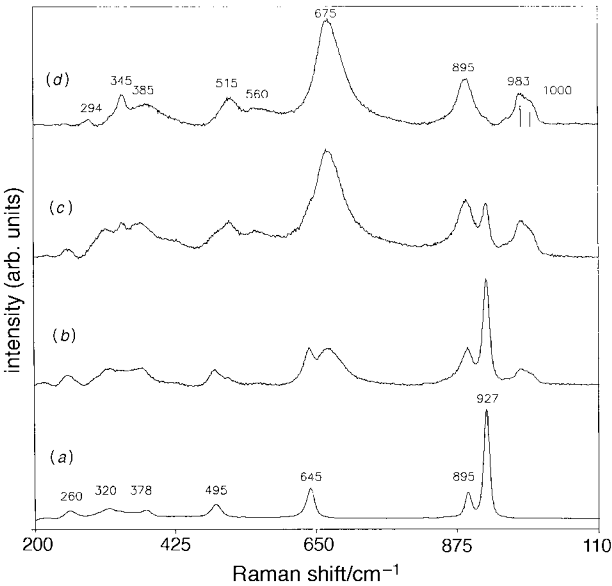


Fig. 2 *In situ* Raman spectra of NH_4VO_3 at (*a*) 150 °C, (*b*) 165 °C, (*c*) 180 °C and (*d*) 190 °C, during heating under an N_2 atmosphere

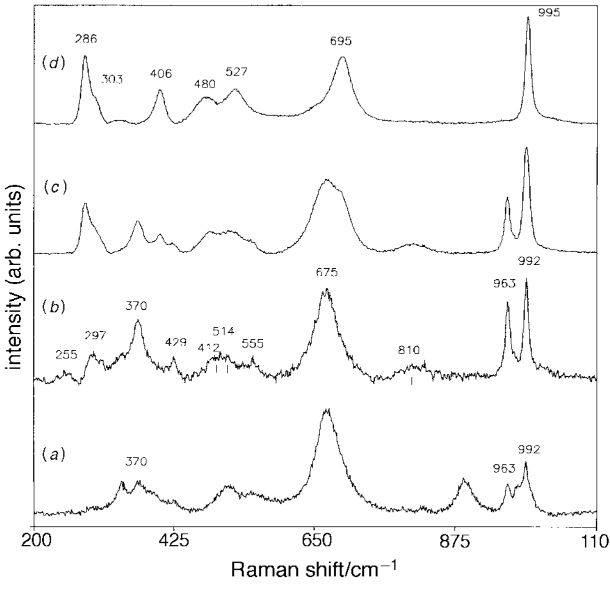


Fig. 3 *In situ* Raman spectra of NH_4VO_3 at (*a*) 195 °C, (*b*) 220 °C (*c*) 275 °C and (*d*) 325 °C, during heating under an N_2 atmosphere

of tetrahedral basic units connected to form a chain-like structure.[18] At 190 °C, a strong band at 675 cm^{-1}, medium and weak bands at 294, 345, 385, 515, 560 and 895 cm^{-1} as well as a broad band containing two unresolved components at 983 and 1000 cm^{-1} is observed [Fig. 2(*d*)]. The Raman spectra in Fig. 2(*b*) (165 °C) and (*c*) (180 °C), consist of a combination of various bands in Fig. 2(*a*) and (*d*), with different ratios. Fig. 3 shows the Raman spectra of NH_4VO_3 at 195, 220, 275 and 325 °C under flowing N_2. At 195 °C, in addition to the bands in Fig. 2(*d*), new bands of medium intensity at 370, 963 and 992 cm^{-1} are observed [Fig. 3(*a*)]. At 220 °C, strong bands at 675, 963 and 992 cm^{-1} and medium and weak bands at 255, 297, 370, 429, 412, 514, 555 and 810 cm^{-1} can be observed [Fig. 3(*b*)] whereas at 325 °C, a strong band at 995 cm^{-1} and medium and weak bands at 286, 303, 406, 480, 527 and 695 cm^{-1} can be observed [Fig. 3(*d*)]. All these bands are associated with crystalline V_2O_5.[13] At 275 °C [Fig. 3(*c*)], a combination of the bands in Fig. 3(*b*) and (*d*) can be seen. From the above Raman results, two discrete vanadate intermediates, characterized by the spectra in Fig. 2(*d*) and 3(*b*), respectively, can be identified. However, the understanding of the properties of these intermediates differs dramatically in the literature owing to their contrasting stabilities.[19–22] A consensus on composition has been reached for $NH_4V_3O_8$ [Fig. 3(*b*)],[19–22] whereas a variety of compositions, such as $NH_4V_3O_8 \cdot 0.5H_2O$,[5] $(NH_4)_2V_4O_{11}$,[6,10] discrete $NH_4V_3O_8$[8] and $V_2O_5 \cdot H_2O$[9] have been proposed for the intermediate around 190 °C [Fig. 2(*d*)]. Structural studies by X-ray,[19] NMR,[20] IR[21] and Raman[22] on a series of MV_3O_8 (M = K, Cs, Li, Rb, NH_4), prepared in the form of aqueous solutions under acidic conditions, have been reported. These compounds are comprised of chain-like vanadium–oxygen polyhedra, that are formed by edge-sharing distorted VO_6 octahedra and VO_5 square-pyramids connected by cations to form a sheet-like structure.[19] According to the reported Raman spectra of vanadium oxides,[12–15] frequencies of V—O vibrations can be divided into V—O stretching (800–1100 cm^{-1}), V—O—V stretching (400–800 cm^{-1}), V—O bending and the lattice modes (below 400 cm^{-1}). Amongst these vibrations, critical structural information, pertaining to geometry and bond distance, can usually be obtained from the analysis of the features of V—O stretching.[13–15] The reported Raman spectrum of $NH_4V_3O_8$, prepared in acidic aqueous solution,[22] displays an identical spectrum to that in Fig. 3(*b*). The bands at 963 and 992 cm^{-1} are assigned to V=O stretching of distorted octahedra and distorted square pyramids, respectively, while the strong band at 675 cm^{-1} is due to the coordination of vanadium atoms with three oxygen atoms.[22] The bands at 983 and 1000 cm^{-1} in Fig. 2(*d*) can be assigned to V=O stretching modes of the distorted octahedra[13,15] whereas the unresolved feature reflects the distribution of bond lengths over a wide range, which can be attributed to the amorphous nature of the sample.[13,15] The band at 895 cm^{-1} can be assigned to a weakened V=O stretching mode, probably due to hydrogen-bonding caused by ammonium ions.[16,23] The bands at 514, 555 and 675 cm^{-1} can be assigned to V—O—V stretching modes, while other bands in the frequency range below 400 cm^{-1} can be assigned to V—O, V—O—V and N—H bending modes.[13–17] The overwhelming intensity of the band at 675 cm^{-1}, characteristic of coordination of vanadium atoms with three oxygen atoms,[22] confirms the existence of a more expanded framework[7] than the chain-like structure of NH_4VO_3, consisting of tetrahedral building units.[18] Although some structural information can be obtained from the spectrum in Fig. 2(*d*), none of the reported Raman spectra for a wide range of vanadates show a close resemblance to this spectrum, thus precluding the exact determination of the structure of the corresponding compound. On the other hand, the intermediate $(NH_4)_2V_4O_{11}$[6,10] shows a stoichiometry close to the results of thermal analysis, *viz.* 88.9% (calc.) *vs.* 88.7% (exptl.) of initial mass. However, no discussion on the structure of this intermediate was presented. The Raman spectra reported for the hydrated vanadium pentoxide systems[23] show that $V_2O_5 \cdot 0.6H_2O$ exhibits strong bands at 890 and 707 cm^{-1}, and medium and weak bands at 1020, 985, 670, 515, 485, 395, 350, 325, 280 and 265 cm^{-1}. However, since a significant amount of ammonium ions is still present, formation of $V_2O_5 \cdot 0.6H_2O$ appears unlikely. On the other hand, although the $V_{10}O_{28}{}^{6-}$ ion has been proposed to be critical to generate $NH_4V_3O_8$ in acidic aqueous solution,[19] its Raman spectrum[13,15] shows dramatic differences from that in Fig. 2(*d*). Moreover, there is also some discrepancy in the stoichiometry calculated from thermal analysis. Therefore, $(NH_4)_6V_{10}O_{28}$ is not considered to explain the spectrum in Fig. 2(*d*). In order to further investigate its properties, isolation of this intermediate was attempted by cooling to 25 °C under ambient conditions. Fig. 4 shows the Raman spectrum of the cooled intermediate which, in addition to a better signal-to-noise ratio, consists of $NH_4V_3O_8$ and NH_4VO_3 (asterisked). This behavior not only confirms its transitional nature as reflected in the thermogravimetric result, but also can be used to reject other proposed

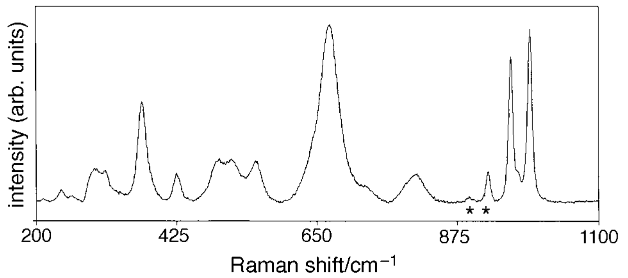
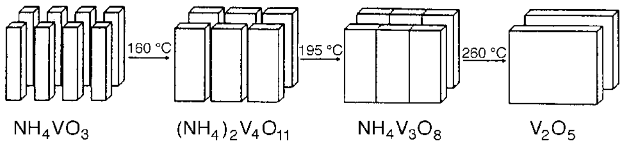


Fig. 4 Raman spectrum of NH_4VO_3 heated to 190 °C under an N_2 atmosphere, and subsequently cooled to room temperature under ambient conditions

intermediates such as $NH_4V_3O_8 \cdot 0.5H_2O$[5] and $V_2O_5 \cdot H_2O$,[9] since the former can not generate NH_4VO_3 and the latter can not generate $NH_4V_3O_8$ upon cooling. Moreover, the molar ratio between NH_4VO_3 and $NH_4V_3O_8$ of the cooled intermediate can be estimated by comparing the area ratio of their designated peaks, *e.g.*, the 927 cm^{-1} peak *vs.* the 810 cm^{-1} peak, with area ratios obtained from reference mixtures of known composition.[24] The molar ratio between NH_4VO_3 and $NH_4V_3O_8$ of the cooled intermediate (Fig. 4) is determined to be 0.94 ± 0.10, which supports the stoichiometry proposed for the intermediate since $(NH_4)_2V_4O_{11} = NH_4V_3O_8 + NH_4VO_3$. The deviation from unity may be linked to either the formation of Raman-inactive species upon cooling or the quantitative limitation of Raman spectroscopy.[12] Thus, a composition of $(NH_4)_2V_4O_{11}$, with an amorphous structure consisting of edge-sharing distorted VO_6 octahedra or VO_5 square pyramids, is proposed to be responsible for the Raman spectrum in Fig. 2(*d*). However, the exact structure of this compound is as yet, undetermined. When the temperature is raised to 275 °C, bands due to V_2O_5 begin to appear in the presence of $NH_4V_3O_8$, and transformation to a single phase of crystalline V_2O_5 is observed at 325 °C.

It is important to note here that, upon comparison with previous studies, some of the differences between the present and other reported results can be explained in terms of the lack of sensitivity of Raman spectroscopy towards certain product compounds such as amorphous vanadium pentoxides.[17] However, since an excess of N_2 is intentionally introduced into the heating cell, formation of V_3O_7, $V_3O_7 \cdot H_2O$ and V_6O_{13}[5] which has been observed in other studies under different conditions, appears to be minimized throughout the decomposition process.

Several interesting features can be noted from the above spectra. First, the conversion of NH_4VO_3 to V_2O_5 can be characterized by framework rearrangement and formation of $(NH_4)_2V_4O_{11}$ and $NH_4V_3O_8$, brought about by the modification of coordination of vanadium atoms as a consequence of release of NH_3 and H_2O. Accordingly, the thermal evolution pathway can be summarized as shown in Scheme 1. It should be noted that while both $(NH_4)_2V_4O_{11}$ and $NH_4V_3O_8$ consist of a more expanded framework[7] rather than a chain-like structure, only $NH_4V_3O_8$ exhibits a layer-like structure facilitated by cross-linking ammonium ions,[16] which however do not function similarly in $(NH_4)_2V_4O_{11}$, as evidenced by its transitional and amorphous nature. Secondly, the presence of various oxovanadate species such as H_3VO_4,[25] $[VO(H_2O)_6]^{2+}$ [26] and (V_3O_8)[8] has been proposed in zeolite poisoning, thermal decomposition of a vanadium-containing heteropolyacid ($H_3PW_{11}VO_{40} \cdot 14H_2O$) and NH_4VO_3 at elevated temperatures. In contrast, no discrete vanadate species, exhibiting reasonable stability and acidity (*i.e.* $H_2VO_4^-$),[15,27] such as $H_nV_{10}O_{28}^{n-6}$, $H_nV_2O_7^{n-4}$, VO_2^+ or H_2VO_4 are observed in the present study. Third, a direct transition from NH_4VO_3 to V_2O_5 has been observed by IR spectroscopy,[11] the capability of which towards identification of vanadates is limited by the broadness of the characteristic vibrational bands within a narrow range of frequencies.[12,28] On the other hand, there have been a number of reports recently upon ($V_{3n}O_{8n}^{n-}$)-related novel compounds synthesized by structure-directing surfactants,[29,30] for example, a mesoporous structure is assigned to $C_{20.1}H_{48.0}N_{1.0}V_{2.9}O_{11.4}$[29] {$[C_{16}H_{33}N(CH_3)_3]$-$V_3O_8 \cdot 3H_2O$[30]} whereas a layered structure is assigned to $[C_{12}H_{25}N(CH_3)_3]_4V_{12}O_{32} \cdot 6H_2O$;[30] while their coordination geometries remain unclear. Amongst various characterization techniques, IR spectroscopy has been employed as a major probe to obtain molecular details pertaining to their structural and mechanistic properties.[29,30] IR spectroscopy, however, does not provide complete understanding of these properties. In contrast, a detailed and clear specification for various vanadate compounds can be established by complementary Raman spectroscopy, which will be published elsewhere.



Scheme 1

Fig. 5 shows the Raman spectra of NH_4VO_3 at 150, 220, 280 and 350 °C, heated in a closed cell, thus maximizing the effects of releasing gases, *viz.* NH_3 and H_2O. At 150 °C, Fig. 5(*a*) displays an identical spectrum to that in Fig. 2(*a*), whereas a spectrum predominantly comprising $NH_4V_3O_8$ bands with a trace of bands of NH_4VO_3, is obtained when the temperature is raised to 220 °C [Fig. 5(*b*)]. At 280 °C, a spectrum characteristic of $NH_4V_3O_8$ is observed [Fig. 5(*c*)]; upon further heating, intensities of the bands associated with $NH_4V_3O_8$ diminish gradually and these bands become almost invisible at around 350 °C [Fig. 5(*d*)]. Notably, no difference can be observed between the spectra at 150 °C, heated in the presence of NH_3 and H_2O [Fig. 5(*a*)], and N_2 atmosphere [Fig. 2(*a*)]. This can be attributed to the fact that release of NH_3 and H_2O has not been initiated at this temperature. At 220 °C, instead of only $NH_4V_3O_8$, a mixture of $NH_4V_3O_8$ and NH_4VO_3 is observed, which suggests suppression of decomposition of NH_4VO_3 and formation of the transitional $(NH_4)_2V_4O_{11}$ owing to the presence of NH_3 and H_2O. At 350 °C, suppression of decomposition of $NH_4V_3O_8$ can be observed as compared to that in flowing N_2, which is complete around 260 °C. The inability to observe

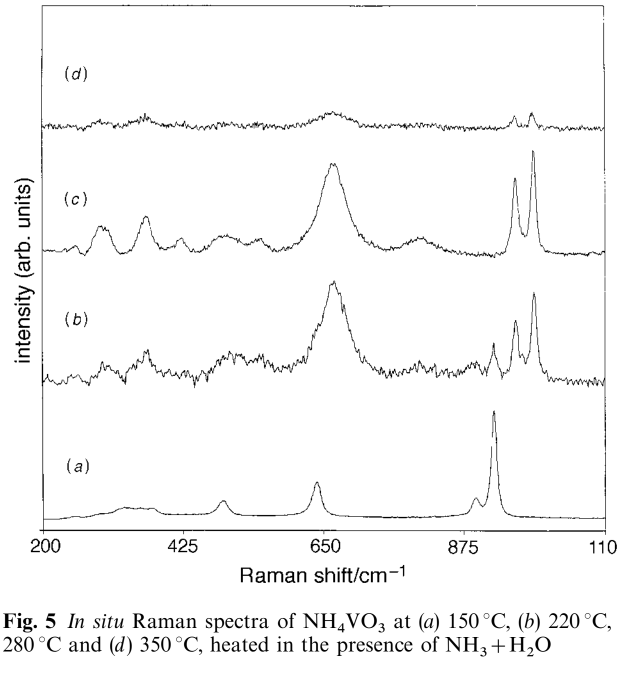


Fig. 5 *In situ* Raman spectra of NH_4VO_3 at (*a*) 150 °C, (*b*) 220 °C, (*c*) 280 °C and (*d*) 350 °C, heated in the presence of $NH_3 + H_2O$

other bands, despite dramatic decreases in the intensities of bands corresponding to $NH_4V_3O_8$ at 350 °C [Fig. 5(*d*)], suggests the formation of Raman-inactive product compounds whose composition can not be specified. In contrast, an intermediate $V_3O_7 \cdot H_2O$ has been identified by XRD, while crystallization of amorphous vanadium pentoxide has been proposed based on the DSC results, in the presence of NH_3 and H_2O in the temperature range 200–400 °C.[5] Thus, the spectra in Fig. 5 suggest that a slightly different decomposition pathway occurs under the influence of NH_3 and H_2O, which can be rationalized in terms of stability of the intermediates as well as sensitivity of the present characterization technique (Raman spectroscopy) towards these intermediates.

Fig. 6(*a*) presents the Raman spectra of NH_4VO_3 at 400 °C, heated in the presence of releasing gases, *viz.* NH_3 and H_2O, which do not give any Raman spectrum. In order to determine the compositions and structure of the species giving the spectrum in Fig. 6(*a*), air was intentionally introduced at 400 °C, aimed at oxidizing vanadium suboxide which may possibly exist.[31–35] After 3 min, a clear spectrum exhibiting strong bands at 270, 530 and 695 cm^{-1}, medium and weak bands at 295, 408, 430, 995 and 1040 cm^{-1} [Fig. 6(*b*)] was obtained. After 6 min, a slightly modified spectrum exhibiting strong bands at 270, 286, 530, 695 and 995 cm^{-1}, and weak bands at 303, 406, 430 and 480 cm^{-1} was observed [Fig. 6(*c*)]. Upon longer exposure to air, a spectrum corresponding to crystalline V_2O_5 was obtained [Fig. 6(*d*)].

Formation of V_2O_3 by thermal decomposition of NH_4VO_3, as evidenced by XRD, has been reported by Von Sacken and Dahn in the presence of an excess of NH_3,[6] whereas formation of a single phase, V_6O_{13}, has been reported by Lampe-Onnerud and Thomas[5] in a closed cell. Previous studies on adsorption of NH_3 on V_2O_5 at 400 °C have concluded that the formation of V_2O_4 occurs through the stoichiometry: $3V_2O_5 + 2NH_3 \rightarrow 3V_2O_4 + N_2 + 3H_2O$.[31] Whereas in the presence of an excess of NH_3, a wide range of intermediate adsorbates as well as further reduction of vanadium to the +3 oxidation state have been discussed.[34–36] Therefore, the spectrum in Fig. 6(*a*) may be attributed to formation of Raman-inactive V_2O_3 on the surface instead of V_2O_4,[10] which would exhibit characteristic Raman bands at 295, 408, 430, 530 and 695 cm^{-1}.[37] Analysis of Fig. 6(*b*)–(*d*) indicates that a correlation between various bands can be established by noting their dependence on the degree of oxidation by air. Based on this observation as well as the characteristic frequencies of the various reported vanadium oxide systems,[37–44] the spectra in Fig. 6(*b*) and (*c*) can be associated with a mixture of three components: *viz.* vanadyl (270 and 1040 cm^{-1}),[38,44] V_2O_4 (295, 408, 430, 530 and 695 cm^{-1}) and V_2O_5 (286, 303, 406 480, 527, 695 and 995 cm^{-1}), whereas a single phase of crystalline V_2O_5 is ascribed to the spectrum in Fig. 6(*d*). Identification of surface-bound monomeric vanadyl species, containing one terminal V=O bond and three bridging V—O—M (M = Al, Ti, Zr, Nb and Si) bonds, have been established based on a single sharp band, attributed to V=O stretching, in the range 1020–1040 cm^{-1}.[39–41] In contrast, vanadium oxide supported on SiO_2 by wet impregnation shows bands at 266, 521, 706, 1014 and 1033 cm^{-1}, whereas bands at 521, 706 and 1014 cm^{-1} disappear and bands at 492 and 787 cm^{-1} emerge upon heating, caused by increasing the laser power.[44] These bands can be explained in terms of V=O groups of square-pyramidal moieties within the extended layers[42–44] which transform into small clusters owing to laser-induced spreading.[44] In comparison with Fig. 6(*b*), not only the difference in thermal behaviors of these bands but also a dramatic difference in the ratio between bands at 521 and 706 cm^{-1} can be noted. Therefore, the bands at 295, 408, 430, 530 and 695 cm^{-1} in Fig. 6(*b*) are attributed to V_2O_4, which is further supported by good agreement with the Raman spectrum of single phase V_2O_4.[37] The oxidation stoichiometry, as indicated by the spectra in Fig. 6, can be explained as follows. Initially, a mixture of predominantly V_2O_4 with trace amounts of V_2O_5 is formed upon oxidation of V_2O_3, while vanadyl appears to be only a transitional surface species [Fig. 6(*b*)]. Upon further oxidation, V_2O_5 gradually becomes dominant at the expense of V_2O_4 and vanadyl [Fig. 6(*c*)], and finally a single phase of V_2O_5 is obtained [Fig. 6(*d*)]. Since vanadyl appears to coexist with V_2O_4, it might be responsible for facilitating oxidation of V_2O_4. However, the exact role of vanadyl can not be specified by the present characterization technique. More detailed investigations in this direction are underway.

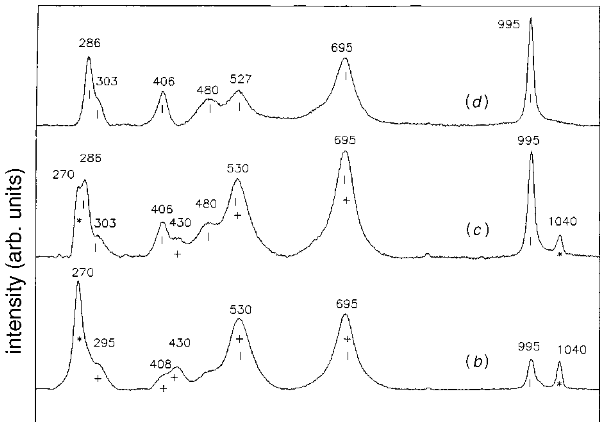


Fig. 6 *In situ* Raman spectra of NH_4VO_3 (*a*) at 400 °C heated in the presence of $NH_3 + H_2O$; after subsequent introduction of air for (*b*) 3 min, (*c*) 6 min and (*d*) 12 min; (*) vanadyl, (+) V_2O_4, (|) V_2O_5

Conclusion

Thermal decomposition of NH_4VO_3 under N_2 and an $NH_3 + H_2O$ atmosphere has been studied by *in situ* Raman spectroscopy in the temperature range 150–400 °C. Identification of both stable as well as transitional intermediate bulk and surface species that form in the decomposition process has been carried out and their structures have been examined in detail. The present study provides not only complementary information on decomposition of NH_4VO_3 at a molecular level, but also sheds new light on the structural and mechanistic properties of vanadates and vanadium oxides.

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References

1 D. J. Hucknall, *Selective Oxidation of Hydrocarbons*, Academic Press, London, 1974.
2 H. Bosch and F. Janssen, *Catal. Today*, 1988, **2**, 369.
3 P. Mars and J. G. H. Massen, *J. Catal.*, 1968, **10**, 1.
4 M. Taniguchi and T. R. Ingraham, *Can. J. Chem.*, 1964, **42**, 2467.
5 C. Lampe-Onnerud and J. O. Thomas, *J. Mater. Chem.*, 1995, **5**, 1075.
6 U. Von Sacken and J. R. Dahn, *J. Power Sources*, 1989, **26**, 461.
7 A. Shimizu, T. Watanabe and M. Inagaki, *J. Mater. Chem.*, 1994, **4**, 1475.
8 M. E. Brown, L. Glasser and B. V. Stewart, *J. Therm. Anal.*, 1975, **7**, 125.
9 S. A. Selim, Ch. A. Philp and R. Ch. Mikhail, *Thermochim. Acta*, 1980, **36**, 287.

10 M. E. Brown, L. Glasser and B. V. Stewart, *J. Therm. Anal.*, 1974, **6**, 529.

11 C. Li, H. Zhang, K. Wang, Y. Miao and Q. Xin, *Appl. Spectrosc.*, 1993, **47**, 56.

12 J. M. Stencel, *Raman Spectroscopy For Catalysis*, Van Nostrand Reinhold, New York, 1990.

13 F. D. Hardcastle and I. E. Wach, *J. Phys. Chem.*, 1991, **95**, 5031.

14 J. Twu and P. K. Dutta, *J. Phys. Chem.*, 1989, **93**, 7863.

15 J. Twu and P. K. Dutta, *J. Catal.*, 1990, **124**, 503.

16 A. M. Heyns and M. W. Venter, *Z. Naturforsch., Teil B,* 1987, **42**, 843.

17 J. Haber, T. Machej, E. M. Serwicka and I. E. Wachs, *Catal. Lett.*, 1995, **32**, 101.

18 S. Onodera and Y. Ikegami, *Inorg. Chem.*, 1980, **19**, 615.

19 H. T. Evan, Jr. and S. Block, *Inorg. Chem.*, 1996, **5**, 1808.

20 J. Skibsted, N. C. Nielsen, H. Bildsoe and H. J. Jakobsen, *J. Am. Chem. Soc.*, 1993, **115**, 7351.

21 A. D. Kelmers, *J. Inorg. Nucl. Chem.*, 1961, **21**, 45.

22 L. V. Kristallov, O. V. Koryakova, L. A. Perelyaeva and M. P. Tsvetkova, *Russ. J. Inorg. Chem.*, 1987, **32**, 1073.

23 L. Abello, E. Husson, Y. Repelin and G. Lucazeau, *J. Solid State Chem.*, 1985, **56**, 379.

24 J. P. Baltrus, L. E. Makovsky, J. M. Stencel and D. M. Hercules, *Anal. Chem.*, 1985, **57**, 2500.

25 R. F. Wormsbecher, A. W. Peters and J. M. Maselli, *J. Catal.*, 1985, **96**, 363.

26 M. Fournier, C. Feumi-Jantou, C. Rabia, G. Herve and S. Launay, *J. Mater. Chem.*, 1992, **2**, 971.

27 J. J. Cruywagen, J. Bernard, B. Heyns and A. N. Westra, *Inorg. Chem.*, 1996, **35**, 1556.

28 L. D. Frederickson, Jr., *Anal. Chem.*, 1963, **35**, 819.

29 V. Luca, D. J. Maclachlan, J. M. Hook and R. Withers, *Chem. Mater.*, 1995, **7**, 2220.

30 G. G. Janauer, A. Dobley, J. Guo, P. Zavalij and M. S. Whittingham, *Chem. Mater.*, 1996, **8**, 2096.

31 F. J. J. G. Janssen, F. M. G. van den Kerkhof, H. Boasch and J. R. H. Ross, *J. Phys. Chem.*, 1987, **91**, 6633.

32 S. T. Oyama, G. T. Went, K. B. Lewis, A. T. Bell and G. A. Somorjai, *J. Phys. Chem.*, 1989, **93**, 6786.

33 G. T. Went, L. J. Leu, S. J. Lombardo and A. T. Bell, *J. Phys. Chem.*, 1992, **96**, 2235.

34 R. B. Bjorklund, L. A. H. Andersson, C. U. I. Odenbrand, L. Sjoqvist and A. Lund, *J. Phys. Chem.*, 1992, **96**, 10953.

35 W. S. Went and J. A. Reimer, *J. Am. Chem. Soc.*, 1992, **114**, 5768.

36 K. V. Narayana, A. Venugopal, K. S. Rama Rao, V. Venkat Rao, S. Khaja Masthan and P. Kanta Rao, *Appl. Catal. A*, 1997, **150**, 269.

37 I. E. Wachs and S. S. Chan, *Appl. Surf. Sci.*, 1984, **20**, 181.

38 F. A. Miller and L. R. Cousins, *J. Chem. Phys.*, 1957, **26**, 329.

39 N. Das, H. Eckert, H. Hu, I. E. Wachs, J. F. Walzer and F. J. Feher, *J. Phys. Chem.*, 1993, **97**, 8240.

40 G. T. Went, S. T. Oyama and A. T. Bell, *J. Phys. Chem.*, 1990, **94**, 4240.

41 I. E. Wachs, G. Deo, M. A. Vuurman, H. Hu, D. S. Kim and J.-M. Jehng, *J. Mol. Catal.*, 1993, **82**, 443.

42 M. Schraml-Marth, A. Wokaun and A. Baiker, *Fresenius' J. Anal. Chem.*, 1991, **341**, 87.

43 K. Inumaru, M. Misono and T. Okuhara, *Appl. Catal. A*, 1997, **149**, 133.

44 U. Scharf, M. Schrami-Marth, A. Wokaun and A. Baiker, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3299.

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