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BRIEF COMMUNICATIONS

A Raman Spectral Study of Hydrated Vanadium Sulfate (VSO_5) Phases*

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Raman spectra were measured for various hydrated VSO_5 materials. Spectral differences were noted and interpreted for α-VSO_5, $VSO_5 \cdot H_2O$ possessing vanadium atoms bonded to H_2O molecules in the interlayers, and other hydrated phases which involve broken V–O–S linkages.

Introduction

α-ABO_5-type materials where A = V, Mo, or Nb and B = P, S, or Mo have potential applications as catalysts (*1*, *2*). Such materials possess interlamellar spaces where sorption and catalytic reaction of compounds can occur. α-VSO_5 is the most susceptible of this series to hydration. Several studies have investigated the structural changes that occur during its hydration using techniques such as X-ray diffraction (*3*–*5*). This study will report on the Raman spectral/structural changes that occur during heat treatment of hydrated VSO_5 and its rehydration.

Experimental

Commercial $VSO_5 \cdot xH_2O$ ($x \approx 5$) which was obtained from Alpha products was first dried at 165°C for 12 h to form $VSO_5 \cdot H_2O$ and then treated at 260°C for 4 h in a tube furnace into which dry nitrogen flowed. Finally, it was heated at 330°C for 1 h to improve the crystallinity of the anhydrous α-VSO_5 phase. Anhydrous powders were also allowed to rehydrate for various lengths of time in an air atmosphere. Powders were sealed at various stages of treatment in capillary tubes for spectral measurement. Raman spectra were measured with a Spex Model 1401 spectrometer and a CRL Model CR3 argon ion laser using 90° optics and both the blue and green laser lines.

Analysis of the X-ray powder diffraction pattern of commercial $VSO_5 \cdot xH_2O$ indicated that $VSO_5 \cdot 5H_2O$ was the dominant phase in the powder. Also, the powder of anhydrous α-VSO_5 that was generated from $VSO_5 \cdot xH_2O$ was characterized by its X-ray powder diffraction pattern. Only X-ray peaks associated with α-VSO_5 were observed in the latter pattern. However, the relative intensities of the X-ray peaks varied from those calculated theoretically, sug-

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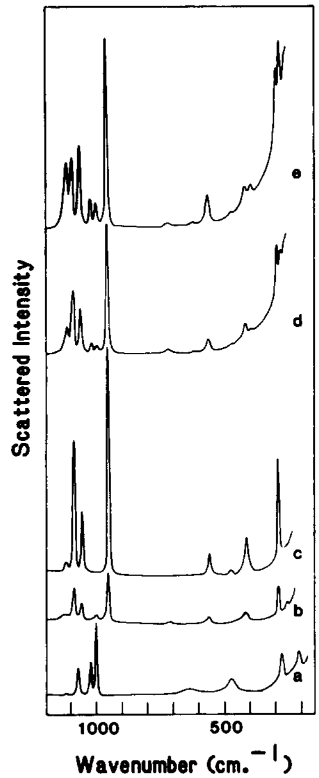

FIG. 1. Raman spectra for various hydrated and anhydrous VSO_5 phases: (a) Commercial grade $VSO_5 \cdot xH_2O$, (b) $VSO_5 \cdot H_2O$, (c) α-VSO_5, (d) α-VSO_5 rehydrated for 1 day, and (e) α-VSO_5 rehydrated for 6 days.

TABLE I

BAND LOCATIONS (cm^{-1}) AND EMPIRICAL ASSIGNMENTS FOR VARIOUS HYDRATED AND ANHYDROUS VSO_5 PHASES

Commercial $VSO_5 \cdot xH_2O$	$VSO_5 \cdot H_2O$	α-VSO_5[a]	Assignment
1118	1118	1118	ν_{asym} (S—O)
1071	1087	1087	
1023	1054	1054	ν_{sym} (S—O)
1000	998		ν(V═O)
	951	951	
640	708		ν(V—O)
	557	557	ν(V—O) and δ(O—S—O) and δ(O—V—O)
473	464	474	
	411	411	δ(O—V—O) and δ(O—S—O)
275	287	287	
208	253		

[a] Band assignments for α-VSO_5 from Ref. (7).

gesting selective orientation effects. This suggestion was consistent with the observation of only platelets in the scanning electron micrograph of α-VSO_5. Wet chemical analysis indicated that the weight percentage of V_2O_4 in α-VSO_5 was 50.5% while the calculated percentage was 50.9%. Trace emission spectrographic analysis indicated that the trace element impurity contents were below 0.1 wt.%. Finally, X-ray powder diffraction analysis indicated that $VSO_5 \cdot H_2O$ was generated when $VSO_5 \cdot xH_2O$ was heat treated at 165°C.

Result and Discussion

Figure 1 illustrates the Raman spectra obtained for VSO_5-containing materials after different stages of dehydration or rehydration. Structural interpretations of the observed spectra are consistent with the recent model suggested by Tachez and Theobald (*6*) concerning the nature of the oxygen atoms bonding to the vanadium atoms in the various anhydrous and hydrated VSO_5 phases. Emphasis will be placed upon the interpretation of the V–O and S–O stretching vibrations. The locations and assignments of the various Raman bands for the investigated hydrate materials are collected in Table I.

Spectra (b) and (c) are associated with $VSO_5 \cdot H_2O$ and α-VSO_5, respectively. The Raman spectra of both phases are characterized by a very strong band at 951 cm^{-1}. This band has been assigned for α-VSO_5 using normal coordinate analysis to the stretching mode of the short V═O bond (*7*). The corresponding Raman band for $VSO_5 \cdot xH_2O$ (where $x \approx 5$) occurs at 1000 cm^{-1}. Tachez and Theobald (*6*) found that the V═O bonds in $VSO_5 \cdot xH_2O$ phases were $x > 1$ are shorter than the corresponding bonds in α-VSO_5. The decrease of these bond lengths accounts for the shift of the V═O stretching mode to higher wavenumber for $VSO_5 \cdot xH_2O$. Corresponding bands are observed in their infrared spectra. A very weak Raman band may still be noted in spectrum (b) at ca. 1000 cm^{-1}. This band can be assigned to the very strong band for the starting material (commercial $VSO_5 \cdot xH_2O$) which is still present at low concentrations.

Normal coordinate analysis for α-VSO_5 indicates that the bands between 460 and 710 cm^{-1} in both the Raman and infrared spectra involve mainly stretching motions of the equatorial V–O bonds (*7*). The shifting of these bands or the appearance of new bands in this region of the vibrational spectra occur upon formation of hydrate phases. These spectral changes occur due to changes in VO_6-site symmetry, V–O bonding or vibrational coupling either from the replacement of elongated V–O bonds between layers by V–O bonds involving water molecules in the layers or from the breakage of V–O–S linkages by hydration (*6*).

Force constant analysis for α-VSO_5 indicates that bands in the region 1020–1120 cm^{-1} are due to modes involving mainly the stretching motions of SO_4 tetrahedra (*7*). The locations and relatives intensities of bands observed in this spectral region for α-VSO_5 and $VSO_5 \cdot H_2O$ are similar. This spectral observation is consistent with Tachez and Theobald's expectation (*6*) that the V–O–S linkages in the layer network are intact for both phases. In contrast, the corresponding bands for $VSO_5 \cdot xH_2O$ are significantly shifted. Tachez and Theobald (*6*) have noted that water molecules in multihydrated VSO_5-containing phases attached the V–O–S linkages, generating SO_4 units with nonbridging oxygen atoms. The structural arrangement of such SO_4 units are significantly different from those in the earlier mentioned phases, causing different spectral patterns.

Bands below 425 cm^{-1} in the Raman spectra can be associated with mainly O–S–O and O–V–O bending motions, many of which should be coupled (*7*). The most noticeable differences between the spectrum of α-VSO_5 and those of the hydrated phases in this region are the splitting of the bands at 411 and 287 cm^{-1}. Again, this splitting is a result of the structural changes for the SO_4 and VO_5 units with hydration.

The Raman spectra of α-VSO_5 rehydrated for different periods of time are consistent with those observed for the various VSO_5 hydrate phases. The most intense band occurred at 951 cm^{-1} indicating that α-VSO_5 and/or $VSO \cdot H_2O$ are the major phases present. The band at 708 cm^{-1} may also be associated with $VSO_5 \cdot H_2O$. The weak band at 992 cm^{-1} indicates layered VSO_5 networks with V–O–S linkages broken by hydration. Changes in the relative intensities of the S–O stretching modes also indicate increased breakage of V–O–S linkages with increased periods of hydration.

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