# Synthesis, Crystal Structure Redetermination and Vibrational Spectra of β-VOSO$_4$

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Dark bluish-green prismatic crystals of the compound β-VOSO$_4$, suitable for X-ray structure determination, have been obtained from solutions of V$_2$O$_5$ in molten K$_2$S$_2$O$_7$/Na$_2$S$_2$O$_7$ under sulfuric acid synthesis gas or flue gas atmospheres. Slow cooling from 480 to 420–440 °C gave a large crop of crystals of β-VOSO$_4$, and the crystal structure has been accurately redetermined. The compound crystallizes in the orthorhombic crystal system, space group Pnma (No. 62) with $a = 7.376(3)$, $b = 6.269$, $c = 7.082(3)$ Å and $Z = 4$. It contains distorted VO$_6$ octahedra linked together in a zigzag course parallel to the $a$-axis by sharing opposite corners in infinite chains along which adjacent VO$_6$ octahedra are also connected by a bridging sulfate group. The remaining two oxygen atoms of the sulfate groups link by corner sharing to upper and lower lying VO$_6$ octahedra along the $b$-axis, thus forming a three-dimensional network. Within the VO$_6$ octahedron a short V–O bond [1.598(2) Å], four in-plane (equatorial) bonds with intermediate lengths (1.994–1.998 Å) and a bond opposite to the short one with a length of 2.271(2) Å are found. The infrared and Raman spectra of the compound have been recorded and interpreted. The importance of β-VOSO$_4$ as deactivation product of working SO$_2$ oxidation catalyst model melts and industrial catalysts is discussed.

Recently, it has been established that the sudden drop of activity undergone by working V$_2$O$_5$-based SO$_2$ oxidation catalysts at temperatures below 420 °C is caused by precipitation of V$^{4+}$ (mainly) and V$^{3+}$ crystalline compounds.[1–3] In this respect, the study of the molten system V$_2$O$_5$/MHSO$_4$/M$_2$S$_2$O$_7$ (M = Na, K, Cs) in contact with SO$_2$/O$_2$/SO$_3$/N$_2$ at 400–600 °C, representing a realistic model of the working catalysts, has proven very useful. Thus the influence of process parameters such as type and amount of promoters, alkali-to-vanadium molar ratio and SO$_2$/SO$_3$ partial pressure ratio on catalyst activity are well recognized,[1,2] and a series of new compounds, i.e. K$_4$(VO)$_3$(SO$_4$)$_5$, KV(SO$_4$)$_2$, K$_3$(VO)$_2$(SO$_4$)$_4$, Na$_2$VO(SO$_4$)$_2$, Na$_3$(VO)$_2$(SO$_4$)$_4$, NaV(SO$_4$)$_2$, Na$_3$V(SO$_4$)$_3$, Cs$_2$(VO)$_2$(SO$_4$)$_3$ and CsV(SO$_4$)$_2$, have been identified as possible deactivation products and characterized by X-ray and spectroscopic methods.[4–12]

Lately, commercial sulfuric acid catalysts have also been used for SO$_2$ removal from flue gases emitted, e.g.,

from coal-fired power stations. During a preliminary investigation of the catalytic activity of sulfuric acid catalyst model melts under conditions of flue-gas desulfurization (i.e. using a 0.2% SO$_2$, 4% O$_2$, 7% H$_2$O, 14% CO$_2$ and 75% N$_2$ feed gas) a β-VOSO$_4$-like compound was identified as deactivation product. Furthermore, precipitation of the same compound, β-VOSO$_4$, has been shown to be the reason for the deactivation of commercial sulfuric acid catalysts at high conversion (i.e. using a 1% SO$_2$, 9% SO$_3$, 7% O$_2$ and 83% N$_2$ feed gas).[2]

VOSO$_4$ occurs in three modifications, as water-soluble tetragonal α-VOSO$_4$,[13,14] practically insoluble orthorhombic β-VOSO$_4$ (prisms)[15] and as γ-VOSO$_4$.[16] Among its hydrates VOSO$_4$·$x$H$_2$O, the physicochemical properties of which are available,[17] the only ones having been subject to single-crystal structure determination are VOSO$_4$·3H$_2$O[18] and VOSO$_4$·5H$_2$O.[19]

In view of the recognition of β-VOSO$_4$ as a deactivation product of on and sulfuric acid catalysts,[2] a new and more accurate single-crystal X-ray structure redetermination was considered necessary. In addition, the present work is also concerned with the spectroscopic characterization of β-VOSO$_4$.

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## Experimental

*Gas–molten-salt flow reactor.* A detailed description of the gas–molten-salt flow reactor system used has been presented earlier.[1] It includes a gas mixing unit equipped with mass flowmeters and a Pt-based preconverter whereby any desired $SO_2/O_2/SO_3/N_2$ gas mixture can be achieved. When flue gas was used, dry $SO_2$, $O_2$, $CO_2$ and $N_2$ were premixed in a steel bottle in a gas–addition vacuum line. Wetting of the gas to a 7% $H_2O$ level was done by bubbling the feed mixture through water flasks immersed in a 40°C thermostatted bath until saturation. A 0.2% $SO_2$, 4% $O_2$, 7% $H_2O$, 14% $CO_2$ and 75% $N_2$ composition, which is typical for flue gases not containing nitrogen oxides, could thus be achieved. The $SO_2$ concentration was monitored by *in-situ* UV spectrophotometry using a 100 mm path-length gas-flow cuvette or by on-line gas chromatography as earlier described.[1] The water vapor concentration could be checked by a Jenway 5075 humidity meter.

The reactor cell[1] possessed a sintered glass frit which supported the molten salt mixtures, allowing the gas to be bubbled through the melt, and was placed in a tiltable double-walled transparent quartz tube furnace.

*Synthesis of crystalline β-VOSO₄.* The compound was obtained from a $K_2S_2O_7$–$Na_2S_2O_7$–$V_2O_5$ molten mixture with a molar ratio $K/Na/V = 3/0.8/1$ corresponding to the composition of a widely used commercial sulfuric acid catalyst (VK 38, Haldor Topsøe, Denmark). $K_2S_2O_7$ and $Na_2S_2O_7$ were synthesized by thermal decomposition of $K_2S_2O_8$ (Merck, max 0.001% N) and $Na_2S_2O_8$ (Fluka, pro analysi) and stored in sealed ampoules as earlier described.[20] All handling of chemicals including the filling of the reactor cell took place in a nitrogen-filled glove box with a measured water vapor content of less than 5 ppm.

Approximately 2 ml of melt were contained in the reactor cell. During interaction of the 0.2% $SO_2$, 4% $O_2$, 7% $H_2O$, 14% $CO_2$ and 75% $N_2$ gas mixture with the melt, green and blue precipitates were formed as the temperature was gradually lowered from 480 to 420–400°C. The crystals were isolated by reversing the flow and filtering the melt. After cooling they could be flushed with water to dissolve the residual salts.

Crystals of the β-VOSO₄ were isolated by treating $K_2S_2O_7$–$V_2O_5$ (K/V = 3–5) or $Na_2S_2O_7$–$V_2O_5$ (Na/ V = 5) melts with a 1% $SO_2$, 9% $SO_3$, 7% $O_2$, 83% $N_2$ mixture in the reactor flow cell in the temperature range 480–360°C. Formation of crystals was observed around 420 and 440°C, respectively, while increasing amounts of precipitates were accumulated as temperature was lowered to 360°C. Furthermore, equilibrating a $V_2O_5$– $Na_2S_2O_7$ (Na/V = 10) molten mixture under 1.3 atm $SO_2$ and 0.1 atm $O_2$ in a sealed ampoule at 495°C and slow cooling to 475°C over a period of three days resulted also in the formation of β-VOSO₄ crystals. Dark bluish-green prismatic crystals of β-VOSO₄ were thus obtained, and crystals suitable for X-ray analysis were isolated under a polarization microscope.

*X-Ray investigation.* Intensity data were measured at 20°C on an Enraf-Nonius CAD-4F diffractometer using monochromated MoKα radiation and ω-scan technique. The cell dimensions were determined by least-squares refinement based on the settings of 25 high-order reflections. A total of 1062 reflections were corrected for Lorentz and polarization effects. Absorption correction was carried out by an empirical method, where the crystal shape is approximated by an ellipsoid, and the size (in units of $\mu m^{-1}$) and the orientations are treated as parameters.[21] The refinement of the parameters is based on ψ-scans on three reflections and their symmetry-related

*Table 1.* Crystal data for β-VOSO₄: R-values in parentheses are for observed reflections $F_o \geq 2\sigma(F_o)$.

| | |
|---|---|
| $M_w/g\ mol^{-1}$ | 163.00 |
| Crystal system | Orthorhombic |
| Space group | *Pnma* (No. 62) |
| $a/Å$ | 7.376(3) |
| $b/Å$ | 6.269(3) |
| $c/Å$ | 7.082(3) |
| $Z$ | 4 |
| $V/Å^3$ | 327.5(2) |
| $D_c/g\ cm^{-2}$ | 3.30 |
| $\mu(MoK\alpha)/cm^{-1}$ | 35.36 |
| Crystal size/mm | 0.23×0.10×0.065 |
| $\theta_{max}/°$ | 30 |
| Total number of reflections | 1062 |
| No. of unique reflections | 516 |
| R between symmetry related reflections | |
| $[\Sigma w(I - \langle I \rangle)^2/\Sigma wI^2]^{1/2}$ | 0.0161 |
| No. of parameters | 41 |
| Extinction parameter | 0.0378(18) |
| Weight function, $P1/3\ (F_o^2 + 2F_c^2)$ | $[\sigma^2(F_o^2) + (0.0138P)^2 + 0.4109P]^{-1}$ |
| $R_1\ \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$ | 0.0181(0.0148) |
| $R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$ | 0.0412(0.0404) |
| Residual charge density/e Å⁻³ | −0.48/0.43 |

*Table 2.* Fractional atomic coordinates and equivalent isotropic thermal parameters[a] for β-VOSO$_4$.

| Atom | Site symmetry | x | y | z | $U_{eq}$/Å$^2$ |
|------|---------------|---|---|---|----------------|
| V | m | 0.166 03(4) | 0.25 | 0.232 60(5) | 0.0056(1) |
| S | m | 0.877 16(6) | 0.25 | 0.868 08(7) | 0.0053(1) |
| O1 | m | 0.715 85(20) | 0.25 | 0.990 46(21) | 0.0107(3) |
| O2 | m | 0.044 46(21) | 0.25 | 0.980 55(22) | 0.0114(3) |
| O3 | m | 0.373 47(20) | 0.25 | 0.167 69(23) | 0.0105(3) |
| O4 | l | 0.125 01(15) | 0.563 21(17) | 0.256 29(15) | 0.0099(2) |

[a] $U_{eq} = 1/3\Sigma_{ij}U_{ij}a_i^*a_j^*a_ia_j$.

reflections, which amounts to 276 observations. The quantity minimized was $R = \Sigma w(I_{obs} - I_{corr}A)^2$, where $A$ is the absorption coefficient. The initial and final values of $(R/\Sigma wI_{obs}^2)^{1/2}$ were 0.0644 and 0.0243, respectively. The minimum and maximum transmission coefficients were 0.5983 and 0.6319. Positional and thermal parameters as well as an extinction parameter was refined by full-matrix least-squares methods based on $F^2$.[22] Crystal data and R-values are given in Table 1. The final structural parameters and bond distances and angles are listed in Tables 2 and 3. Lists of observed and calculated values of $F^2$ may be obtained from the authors.

*Infrared spectra.* IR spectra were recorded on a Perkin Elmer PC 16 FTIR spectrometer. The samples were ground in dry KBr and pressed into transparent discs.

*Raman spectra.* Raman spectra of polycrystalline β-VOSO$_4$ were excited with the 514.5 and 488.0 nm lines of a 4W Spectra Physics Ar$^+$ laser. The scattered light was collected at an angle of 90° (horizontal scattering plane) and analyzed with a Spex 1403 0.85 m double monochromator equipped with a $-20°$C-cooled RCA photomultiplier and EG&G/ORTEC photon counting and rate meter electronics.

## Results and discussion

*Description of the structure.* The structure is basically similar to that described earlier.[15] The distorted VO$_6$ octahedra are linked together in a zigzag course by sharing opposite vertices, thus forming infinite chains parallel to the $a$-axis. Along the chains, adjacent VO$_6$ octahedra are connected by a bridging sulfate group (V–O1–S–O2–V bridges) the remaining oxygen atoms of which link to upper and lower lying VO$_6$ octahedra along the $b$-axis (V–O4–S–O4–V bridges), thus forming a three-dimensional network. Bond lengths and angles for the VO$_6$ octahedra and the sulfate group are given in Table 3. Within the VO$_6$ octahedra, the vanadyl O3 is at a short distance [1.598(2) Å], the long axial oxygen opposite to it, i.e. O3', is at a long distance [2.271(2) Å], and the other four equatorial oxygens are at intermediate distances [1.994(1)–1.998(2) Å]. These values should be compared

to 1.59(3), 2.28(3) and 2.03(3) Å (average for the equatorial intermediate V–O distances) reported in Ref. 15. The O–V–O angles involving the vanadyl oxygen, O3, and the four equatorial oxygens range between 96 and 100°, whereas those involving the other axial oxygen, O3', and the four equatorial oxygens are below 83°. The O3–V–O3' angle involving the axial oxygens is 178.6° deviating slightly from the ideal angle of 180°, while the O–V–O angles involved in the equatorial plane are in the 87–90° range.

The V–O distances and O–V–O angles within the VO$_6$ octahedra are typical of those found for other vanadyl compounds[23] and for the known sulfates of vanadium (IV), namely α-VOSO$_4$,[13,14] VOSO$_4$·3H$_2$O,[18] VOSO$_4$·5H$_2$O,[19] K$_4$(VO)$_3$(SO$_4$)$_5$[4] and Na$_2$VO(SO$_4$)$_2$.[7] Table 4 summarizes the V–O distances (Å) and O–V–O angles (°) in compounds containing vanadyl and sulfate.

The bond lengths of 1.472, 1.469 and 1.465 Å found for the sulfate groups should be compared to the corresponding values of 1.449, 1.449 and 1.412 Å reported earlier.[15] Generally the bond distances and angles within the sulfate tetrahedra are close to the usual values of 1.474 Å and 109.47° (ideal angle) for the sulfate group.[24]

*Infrared and Raman spectra.* By considering that the crystal is composed of VO$^{2+}$ and SO$_4^{2-}$ ions one should expect to observe the free group vibrations of these units, i.e. the $\nu$(V = O) stretching mode at $985 \pm 50$ cm$^{-1}$,[23] and bands corresponding to the four fundamental ($\nu_1$–$\nu_4$) sul-

*Table 3.* Bond lengths (in Å) and angles (in °) for β-VOSO$_4$.

| | | | |
|---|---|---|---|
| V–O3 | 1.598(2) | V–O4 | 1.994(1)(2×) |
| V–O3' | 2.271(2) | S–O1 | 1.472(2) |
| V–O1 | 1.995(2) | S–O2 | 1.469(2) |
| V–O2 | 1.998(2) | S–O4 | 1.465(1)(2×) |
| | | | |
| O1–V–O2 | 163.94(6) | O3–V–O4 | 99.76(3)(2×) |
| O1–V–O3 | 96.11(8) | O3'–V–O4 | 80.19(3)(2×) |
| O1–V–O3' | 82.49(6) | O4–V–O4 | 160.01(7) |
| O1–V–O4 | 86.86(3)(2×) | O1–S–O2 | 111.09(10) |
| O2–V–O3 | 99.95(8) | O1–S–O4 | 110.19(6)(2×) |
| O2–V–O3' | 81.45(7) | O2–S–O4 | 109.58(6)(2×) |
| O2–V–O4 | 90.40(3)(2×) | O4–V–O4 | 106.09(10) |
| O3–V–O3' | 178.60(4) | | |

Symmetry operation for O3': $x - 1/2$, $1/2 - y$, $1/2 - z$.

Table 4. V–O distances (in Å) and O–V–O angles (in °) in compounds containing vanadyl and sulfate.

| | Space group | Z | V=O | V–O$_{plane}$ | V–O (trans to V=O) | O=V–O$_{trans}$ | O=V–O$_{plane}$ |
|---|---|---|---|---|---|---|---|
| α-VOSO$_4$[13] | P4/n | 2 | 1.63 | 2.04 | 2.47 | 180 | 88 |
| β-VOSO$_4$[15] | Pnma | 4 | 1.59 | 2.01–2.06 | 2.28 | 179.5 | 96.8–99.9 |
| β-VOSO$_4$[a] | Pnma | 4 | 1.598 | 1.994–1.998 | 2.271 | 178.6 | 96.11–99.76 |
| VOSO$_4$·3H$_2$O[18] | P2$_1$/c | 4 | 1.559 | 2.006–2.078 | 2.284 | 175.0 | 95.6–102.9 |
| VOSO$_4$·5H$_2$O[19] | P2$_1$/c | 4 | 1.591 | 1.983–2.048 | 2.223 | 174.2 | 93.8–100.7 |
| K$_4$(VO)$_3$(SO$_4$)$_5$[4] | P2$_1$/n | 4 | 1.580–1.588 | 2.023–2.058 | 2.216–2.230 | 170.1–177.6 | 94.9–101.0 |
| Na$_2$VO(SO$_4$)$_2$[7] | P2$_1$2$_1$2$_1$ | 4 | 1.595 | 2.016–2.068 | 2.215 | 178.17 | 94.60–99.88 |

[a] This work.

fate modes that span the following representation for a regular tetrahedral ($T_d$) configuration

$$\Gamma_{vib} = A_1 (v_1) + E (v_2) + 2 F_2 (v_3 + v_4)$$

and are well known[25] from Raman work on aqueous sulfate solutions: $v_1(A_1) \approx 980$ cm$^{-1}$, $v_2(E) \approx 450$ cm$^{-1}$, $v_3(F_2) \approx 1100$ cm$^{-1}$ and $v_4(F_2) \approx 615$ cm$^{-1}$. All modes are Raman-active, and only $F_2$ is IR allowed. However, coordination of the sulfate ion and interactions with other ions in the crystal lattice are expected to reduce the symmetry, and can thus, e.g., lift the degeneracies of the $v_2$, $v_3$ and $v_4$ modes and give rise to IR activity to the $v_1$ and $v_2$ modes.

Figure 1 shows the infrared spectrum of the dark bluish-green β-VOSO$_4$ obtained at room temperature from finely ground powder in a pressed KBr disc. Raman spectra obtained from a stationary polycrystalline β-VOSO$_4$ sample at room temperature are shown in Fig. 2. The observed bands and tentative assignments are listed in Table 5. As can be seen from the spectra in Figs. 1 and 2, many of the observed bands are common to both kinds of spectra. The presence in the IR and Raman spectra of a number of bands in the regions of 1000–1220, 580–670 and 400–500 cm$^{-1}$ indicates a lowering of the $T_d$ symmetry of the free SO$_4^{2-}$ in the β-VOSO$_4$ crystal, in ac-

cordance with the bond distances and angles found (Table 3). Previously, IR spectroscopy has been used for studying α-VOSO$_4$[14,26,27] and β-VOSO$_4$[28] and the data are included in Table 5 for comparison. The characteristic V = O stretching mode of β-VOSO$_4$ was found at 938 cm$^{-1}$ in the IR spectra in good agreement with the 945 cm$^{-1}$ value reported in Ref. 28, whereas values in the range 944–983 cm$^{-1}$ have been reported for α-VOSO$_4$ (Table 5). Other reports on IR work dealing with compounds containing vanadyl and sulfate involve K$_2$SO$_4$·2VOSO$_4$,[27] K$_2$O·V$_2$O$_4$·3SO$_3$,[29] K$_2$[V$_2$O$_2$(SO$_4$)$_3$] and K$_2$VO(SO$_4$)$_2$.[28] However, the only studies combining both IR and Raman spectroscopic characterization concern the K$_4$(VO)$_3$(SO$_4$)$_5$[4] and Na$_2$VO(SO$_4$)$_2$[7] compounds, where common bands to both IR and Raman (band-rich) spectra were also observed, as in the case of the present work. Indeed, this is to be expected from low-symmetry unit cells comprised of several and large formula units.

## Conclusions

The compound β-VOSO$_4$ has been isolated from V$_2$O$_5$/ K$_2$S$_2$O$_7$/Na$_2$S$_2$O$_7$ melts in contact with SO$_2$/SO$_3$/O$_2$/N$_2$ or SO$_2$/SO$_3$/O$_2$/H$_2$O/CO$_2$/N$_2$ gas atmospheres simulat-
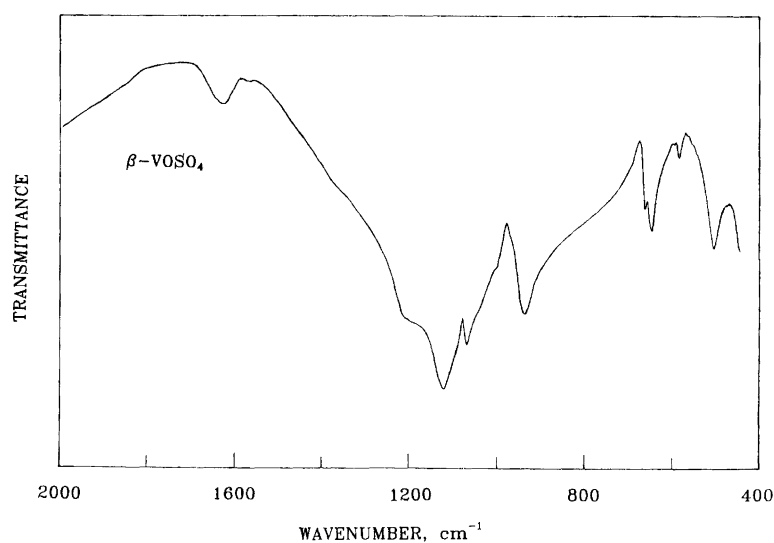


Fig. 1. Infrared spectrum of powdered β-VOSO$_4$ in a pressed KBr disc at room temperature (resolution ca. 5 cm$^{-1}$).
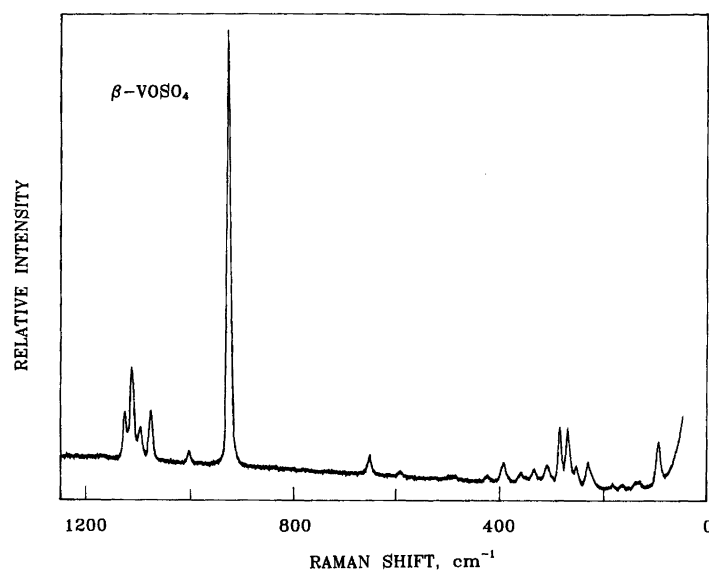
*Fig. 2.* Raman spectrum of polycrystalline $\beta$-VOSO$_4$ at room temperature. $\lambda_0 = 488.0$ nm; laser power, 80 mW; spectral slit width, 6 cm$^{-1}$.

ing various stages of important manufacturing (sulfuric acid production) and environmental protection (SO$_2$ removal from flue gas) processes. The crystal structure has

been accurately redetermined, and infrared and Raman characterization of polycrystalline samples has been performed.

*Table 5.* Infrared and Raman bands (in cm$^{-1}$) of $\beta$-VOSO$_4$ and $\alpha$-VOSO$_4$ and their tentative assignments.[a]

| $\beta$-VOSO$_4$ | | | | $\alpha$-VOSO$_4$ | | | |
|---|---|---|---|---|---|---|---|
| Raman (This work) | IR (This work) | Ref. 28 | Assgn. | IR Ref. 14 | Ref. 26 | Ref. 27 | Assgn. |
| | 1205 m,sh | 1205 | $v_3(SO_4^{2-})$ | 1199 | 1190 | 1195 | $v_3(SO_4^{2-})$ |
| 1125 s | 1122 s | 1130 | $v_3(SO_4^{2-})$ | 1113 | | 1120 | $v_3(SO_4^{2-})$ |
| 1112 s | | | $v_2(SO_4^{2-})$ | | | | |
| 1095 m | | 1095 | $v_3(SO_4^{2-})$ | | 1095 | 1078 | $v_3(SO_4^{2-})$ |
| 1075 s | 1068 m | 1070 | $v_3(SO_4^{2-})$ | | | | |
| 1002 m | 1000 w | 1010 | $v_1(SO_4^{2-})$ | | | 1008 | $v_1(SO_4^{2-})$ |
| 925 vs | 938 s | 945 | v(V=O) | 982 | 970 | 983 | v(V=O) |
| | | | | | | 944 | v(V=O) |
| | | | | | 720 | | |
| | | | | 695 | 690 | | $v_4(SO_4^{2-})$ |
| | 667 w | 670 | $v_4(SO_4^{2-})$ | | | | |
| 654 m | 650 m | 655 | $v_4(SO_4^{2-})$ | | | | |
| 596 w | 588 w | 590 | $v_4(SO_4^{2-})$ | 604 | | 608 | $v_4(SO_4^{2-})$ |
| 488 w | 508 m | 515 | v(V–O) | | | | |
| 425 w | | 440 | $v_2(SO_4^{2-})$ | 433 | | | $v_2(SO_4^{2-})$ |
| 395 m | | | $v_2(SO_4^{2-})$ | | | | |
| 361 w | | | $v_L$[b] | | | | |
| 335 w | | | $v_L$ | | | | |
| 311 w | | | $v_L$ | | | | |
| 285 s | | | $v_L$ | | | | |
| 269 s | | | $v_L$ | | | | |
| 253 w | | | $v_L$ | | | | |
| 231 m | | | $v_L$ | | | | |
| 184 w | | | $v_L$ | | | | |
| 167 w | | | $v_L$ | | | | |
| 136 w | | | $v_L$ | | | | |
| 96 s | | | $v_L$ | | | | |

[a] Abbreviations: s: strong. m: medium, w: weak, v: very, sh: shoulder. [b] External lattice mode.

The deactivation of $SO_2$ oxidation catalysts at low temperatures has been attributed to the precipitation of $V^{4+}$ (mainly) and $V^{3+}$ compounds.[1,2] $\beta$-$VOSO_4$ has been recognized as a deactivation product under laboratory conditions simulating (i) the last catalyst bed of industrial converters for sulfuric acid production[2] and (ii) the removal of $SO_2$ from flue gases among other compounds (work in progress).

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