

# Synthesis of orthorhombic sulfur by hydrogen sulfide reaction with cobalt-doped lamellar vanadyl phosphate

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**Abstract:** In the present work, cobalt-doped vanadyl phosphate is synthesized and used to prepare orthorhombic sulfur by reaction with hydrogen sulfide. The obtained X-ray fluorescence results for the cobalt doped matrix are as follows: 93.36 %  $V_2O_5$ ; 6.56%  $P_2O_5$  and 0,08%  $Co_2O_3$ . The maximum  $H_2S$  adsorption capacity was measured as 44.3 mg of  $H_2S$  per gram of matrix. The interlayer distance (as measured by X-ray diffraction data) in the cobalt-doped matrix is 0.52 nm. It is verified by SEM images that orthorhombic sulfur crystals are formed.

**Keywords:** vanadyl phosphate, nanostructures, surface properties, chemisorptions.

## 1. INTRODUCTION

Hydrogen sulfide is an important air and water pollutant, and large amounts of it are produced as a by-product in industrial chemical processes. Being soluble in water and organic solvents,  $H_2S$  acts as a strong corrosive agent towards metals. Hence, there is a lot of interest to obtain chemical or physical routes and procedures able to capture this compound from air or water.

Vanadium pentoxide,  $V_2O_5$ , has been used as precursor material in the synthesis of vanadyl phosphate,  $VOPO_4 \cdot 2H_2O$  [1-12]. This compound is one of the catalysts used in the oxidation of organic molecules [3].

In  $VOPO_4 \cdot 2H_2O$ , a central vanadium atom is connected to six oxygen atoms, giving a regular octahedral structure [4-12]. The organization of the structures form an open lattice which can accommodate positive ions and/or organic molecules [1-12].

Because of the oxidative properties of  $VOPO_4 \cdot 2H_2O$ , when neutral molecules enter the lamellar structure, they undergo oxidation by transferring one or more electrons to the host species. The chemical species,  $V^{5+}$ , is the promoter of such oxidative processes, especially for organic molecules [4-12].

The vanadyl phosphate is a lamellar compound and therefore able to accommodate in their nanostructure molecules of small

dimensions. It is reported in the literature [4-12] that changes in the structure and chemical composition of this new molecule enhance chemical, physical and morphological vanadyl phosphate properties. Furthermore, it was shown that the insertion of metal cations such as  $Mn^{2+}$ ,  $Li^+$ ,  $K^+$ ,  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Ga^{3+}$  and organic molecules such as aniline, can cause changes in its nanostructure, and form various compounds with several catalytic applications [1-12].

In the present work, cobalt doped vanadyl phosphate is employed to capture hydrogen sulfide. It is verified that the capture occurs with reaction and the consequent sulfur oxidation, forming orthorhombic sulfur crystals with an average size of 15  $\mu m$ .

## 2. EXPERIMENTAL

The cobalt doped vanadyl phosphate was prepared as follows: stoichiometric amounts of  $V_2O_5$  and  $Co(NO_3)_2 \cdot 6H_2O$  were dissolved into 1:1 phosphoric acid and distilled water. After this, the mixture was refluxed for 24 h and the obtained green powder was filtered off, washed with a 1:1 distilled water-acetone mixture and then dried under vacuum at room temperature.

The reaction with  $H_2S$  was promoted as follows: 20 mg of the green powder was suspended in 10  $cm^3$  of distilled water and then a flux (10  $cm^3/min$ ) of  $H_2S$  was passed through the suspension for 30 minutes. After this, the powder was filtered off and dried under vacuum at room temperature.

The FT-IR spectra were obtained in a PerkinElmer apparatus, model Spectrum 65 in KBr discs (4000 to 400  $cm^{-1}$ ). The X-ray diffraction patterns were obtained in a Rigaku diffractometer model Miniflex II, with a scan rate of 5°/min, angle equal to 0.05 with the step, the applied voltage of 15 kV and current 15 mA, using Cu detector. EDS analysis were performed in a TM3000 Hitachi equipment. X-ray fluorescence analysis were performed in a Shimadzu EDX-720 equipment. The SEM images were obtained using a microscope Phillips model XL30-ESEM. The quantum chemical calculations were performed using Spartan Pro.

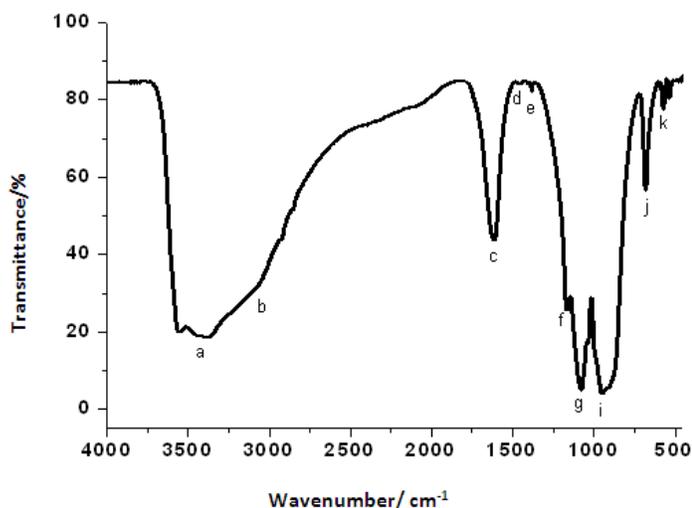
### 3. RESULTS AND DISCUSSION

The obtained X-ray fluorescence results obtained to the cobalt doped matrix are as follows: 93.36 %  $V_2O_5$ ; 6.56%  $P_2O_5$  and 0,08%  $Co_2O_3$ .

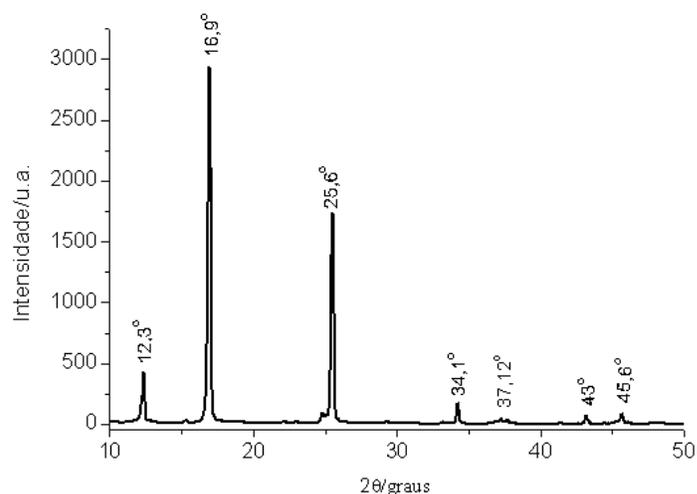
The maximum  $H_2S$  adsorption capacity was measure as 44.3 mg of  $H_2S$  per gram of matrix. It is worth noting that such adsorption capacity is well above those verified for 13X and 5A zeolites [13],  $Zn^{2+}$  and  $Fe^{3+}$  pillarized montmorillonite [14], and it is comparable to those measured for  $Cu^{2+}$  pillarized montmorillonite [14].

The FTIR spectrum is shown in Figure 1. The signed band in  $cm^{-1}$  are as follows: a = 3407,  $\nu(H_2O)$ ; b = 3102,  $\nu(H_2O)$ ; c = 1621,  $\nu(H_2O)$ ; d = 1458,  $\nu_{ass}(CoO_4)$ ; e = 1393,  $\nu_{ass}(CoO_4)$ ; f = 1164,  $\nu(PO_4)$ ; g = 1076,  $\nu(PO_4)$ ; i = 946,  $\nu(PO_4) + \delta(O-V-O)$ ; j = 684,  $\nu$  lattice ( $VOPO_4$ )<sub>∞</sub>; k = 576,  $\nu(H_2O)$ . It is worth noting that the strong band at  $1038\text{ cm}^{-1}$  associated with  $\nu(V=O)$  vibration mode that is present in the pure vanadyl phosphate [6-11] ( $VOPO_4 \cdot 2H_2O$ ) it is absent in the cobalt-doped matrix. The profile of the absorption bands due to the  $VOPO_4$  lattice vibration around  $1100\text{ cm}^{-1}$  was retained after reaction, providing evidence that an intercalation compound and not merely a salt of V-P-O species was produced [6-12]. This conclusion, based on infrared, is supported by the X-ray diffraction patterns.

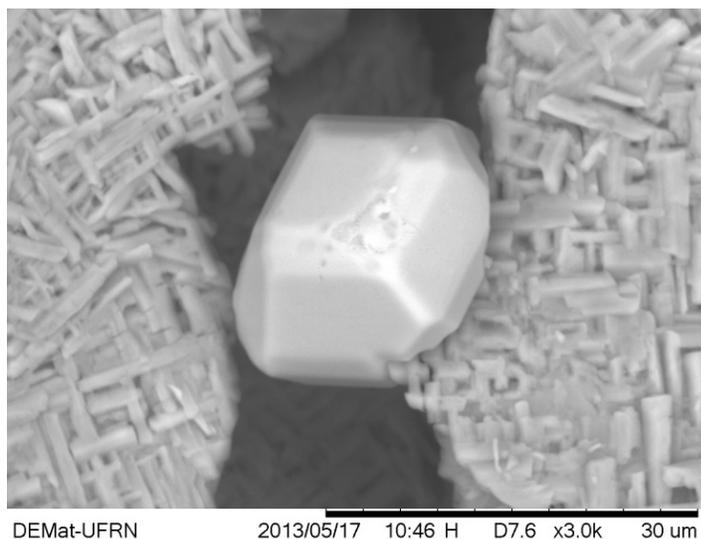
The X-Ray diffraction pattern obtained for the cobalt doped matrix is shown in Figure 2. The diffraction peaks at 16.9 and 34.1 degrees are associated with the 001 and 002 diffraction pales of this doped matrix. For comparison, the 001 diffraction peak is located at 12.3 degrees in  $VOPO_4 \cdot 2H_2O$ . So, a reduction of the interlayer space from 0.72 nm (pure vanadyl phosphate) to 0.52 nm (cobalt-doped vanadyl phosphate) can be pointed out. Taking into account that the calculated volume for  $H_2S$  molecule is  $3.96\text{ nm}^3$  it can be concluded that a suitable interlayer distance (more narrow nanometric channels through which the hydrogen sulfide molecules will enter and react) is obtained when the doping process is performed [6].



**Figure 1.** FTIR spectrum for cobalt-doped vanadyl phosphate.



**Figure 2:** X-ray diffraction pattern for cobalt-doped vanadyl phosphate.



**Figure 3:** SEM image (3000 X) for cobalt-doped vanadyl phosphate after  $H_2S$  exposure for 30 minutes.

The SEM image obtained to the  $H_2S$  exposed matrix is shown in Figure 3. As can be verified, an orthorhombic sulfur crystal is inserted into the cobalt-doped vanadyl phosphare crystals population, showing that the hydrogen sulfide capture involves sulfur formation. The EDS analysis results for the crystal shown in Figure 3 are: O, 87%; Co, 1.43%; P, 3.279%, V, and S, 95.204%.

### 4. CONCLUSION

Based on the obtained results it can be concluded that cobalt-doped vanadyl phosphate can be successfully employed as host species in order to prepare orthorhombic sulfur from hydrogen sulfide.

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