Chemistry Research Journal, 2017, 2(2):133-138

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Ammonia capture by pure and Co(II), Mn(II), Cr(III) and Al(III) modified vanadyl phosphates

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Abstract In the present work is reported the synthesis and characterization (by infrared spectroscopy, X-ray diffractometry. X-rayfluorescence and SEM microscopy) of the vanadylphospahtes: $VOPO_4.2H_2O$, $VOHPO_4.0.5H_2O$, $CoVOPO_4.2H_2O$, $MnVOPO_4.3H_2O$, $CrVOPO_4.2H_2O$ and $AlVOPO_4.2H_2O$. The prepared matrices had their adsorption capacities towards ammonia tested. The obtained adsorption capacities (mg/g) are as follows: 112.1, 96.6, 125.1, 200.4, 145.1 and 216.8, respectively.

Keywords Ammonia, Adsorption, Vanadyl phosphate, Transition metals

Introduction

Vanadium pentoxide, V_2O_5, has been used as precursor material in the synthesis of vanadyl phosphate, $VOPO_4.2H_2O$ [1-7]. This compound is one of the catalysts used in the oxidation of organic molecules [1].

In $VOPO_4.2H_2O$, a central vanadium atom is connected to six oxygen atoms, giving a regular octahedral structure. The organization of the structure for man open lattice which can accommodate positive ions and/or organic molecules [1-7].

Because of the oxidative properties of $VOPO_4.2H_2O$, 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 [1-7].

The vanadyl phosphate is a lamellar compound and therefore able to accommodate in their nanostructure molecules of small dimensions. In the literature [1-7] is reported that changes in the structure and chemical composition of this new molecule enhance chemical, physical and morphological vanadyl phosphate properties.

Furthermore, vanadyl phosphate has been employed to gas capture, such as NO [6] and H_2S [7].

In the present the vanadyl phospahtes $VOPO_4.2H_2O$, $VOHPO_4.0.5H_2O$, $CoVOPO_4.2H_2O$, $MnVOPO_4.3H_2O$, $CrVOPO_4.2H_2O$ and $AlVOPO_4.2H_2O$ are prepared and employed to gaseous the ammonia capture.

Experimental

The compound $VOPO_4.2H_2O$ was prepared according to the methodology described elsewhere [6-11]: 12.5 gof vanadium pentoxide, V_2O_5 (Aldrich), 111g of$H_3PO_4$85% (Vetec), 288 mL of distilled water and 1.5 mL of HNO_3 65 % (Vetec) were mixed under reflux (130 ºC) for16 hours. After this period, a yellows solid was obtained and filtered off, washed with acetone and dried under vacuum at room temperature.

Vanadyl hydrogen phosphate ($VOHPO_4.0.5H_2O$) was prepared by mixing 4 g of $VOPO_4.2H_2O$ with 60 mL of 1-butanol under reflux (24 h). The obtained light blue solid was filtered off, washed (20 mL of cold water) and dried under under vacuum at room temperature.

The cobalt doped vanadyl phosphate was prepared as follows: stoichiometric amounts of V_2O_5 and $Co(NO_3)_2.6H_2O$ 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. Analogous routes were employed to prepare $MnVOPO_4.3H_2O$, $CrVOPO_4.2H_2O$ and $AlVOPO_4.2H_2O$.

The ammonia adsorption experiments were performed, to all matrices, as follows: 20.0 mg of the solid matrix, suspended in distilled water was submitted to a flux of ammonia under atmosphere pressure for 30 minutes. After this, the matrix was filtered off and dried under vacuum.

The NH elemental analysis was performed in a Perkin Elmer apparatus, model 2400, series 2.

The FT-IR spectra (4000-400 cm^{-1}) were obtained in KBr discs, on a Perkin Elmer equipment, model Spectrum 65.

The X-ray diffraction patterns were obtained in a Rigaku diffractometer model MiniflexII, with a scan rate of5^o/min (applied voltage of15kV; current of 15 mA, using Cudetector).

EDS analysis were performed in a TM3000 Hitachi equipment.

X-ray fluorescence analysis was performed in a Shimadzu EDX-720 equipment.

The SEM images were obtained using a microscopePhillipsmodelXL30-ESEM.

Results and Discussion

The FT-IR spectrum for $VOPO_4.2H_2O$ is shown in Figure 1. The main band are located at 3580, 1626, 1093, 946 and 685 cm^{-1}, due to the υ(OH), δ(OH), υ_{as}(P-O), υ(V-O) and δ(V-OH) or (P-OH) vibration modes, respectively, as has been previously assigned [1-7].

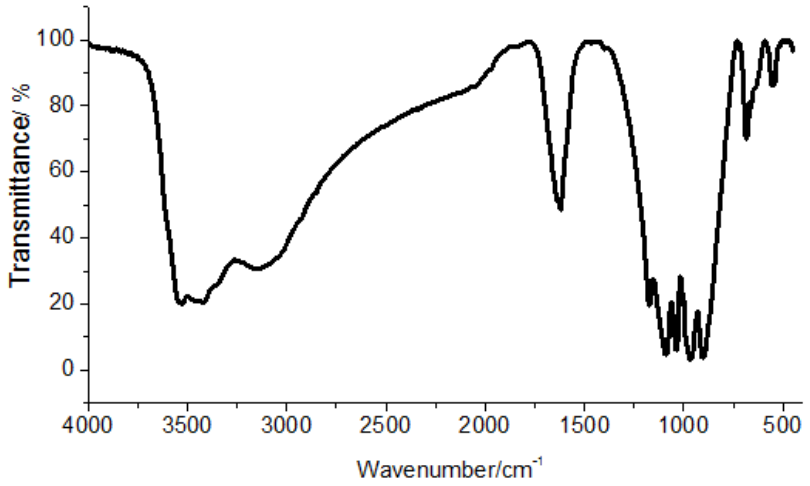

Figure 1: FT-IR spectrum for$VOPO_4.2H_2O$

To the matrix $VOHPO_4.0.5H_2O$, whose FT-IR spectrum is shown in Figure 2, the mains infrared bands are located at 3399 cm^{-1}, 1632 cm^{-1} and 506 cm^{-1} (stretching modes of free water molecules into the lattice); 1190, 981, 638 and 113 cm^{-1} (stretching modes of the PO_4^{3-} group); 1047 cm^{-1} (stretching of the $VO^{2+/3+}$ group); , 638 cm^{-1} (PO_4^{3-} stretching +O-V-O deformation) and 538 cm^{-1} (symmetric stretching of the $(VOPO_4)_\infty$ lattice.

The main infrared band to the metal doped vanadyl phosphate matrices are summarized in Table 1. As illustrative example, the FT-IR spectrum to $AlVOPO_4.2H_2O$ is shown in Figure 3.

Table 1: Main infrared bands to metal doped vanadyl phosphates.

$MnVOPO_4.2H_2O$		$AlVOPO_4.2H_2O$		$CoVOPO_4.2H_2O$		$CrVOPO_4.2H_2O$		Assignment
$\lambda(cm^{-1})$	%T	$\lambda(cm^{-1})$	%T	$\lambda(cm^{-1})$	%T	$\lambda(cm^{-1})$	%T	
3464	97	3443	88	3407	66	3436	59	$\nu(H_2O)$
3213	82	3232	71	3102	55	3210	48	$\nu(H_2O)$
1636	79	1632	56	1621	40	1629	33	$\nu(H_2O)$
1466	1,4	1455	4,5	1458	1	1451	1	$\nu_{ass}(MO_4)$
1385	8,3	1400	7,3	1393	3	1397	8,3	$\nu_{ass}(MO_4)$
1197	72	1124	78	1164	59	1182	30	$\nu(PO_4)$
1080	92	-	-	1076	79	1096	68	$\nu(PO_4)$
1044	90	-	-	-	-	-	-	$\nu(V=O)$
946	94	947	96	946	81	957	79	$\nu(PO_4)+$ $_{\delta}(O\text{-}V\text{-}O)$
677	38	682	33	684	29	678	25	$\nu_{lattice}$ $(VOPO_4)_{\infty}$
552	14	571	8	576	7,5	560	4,3	$\nu(H_2O)$

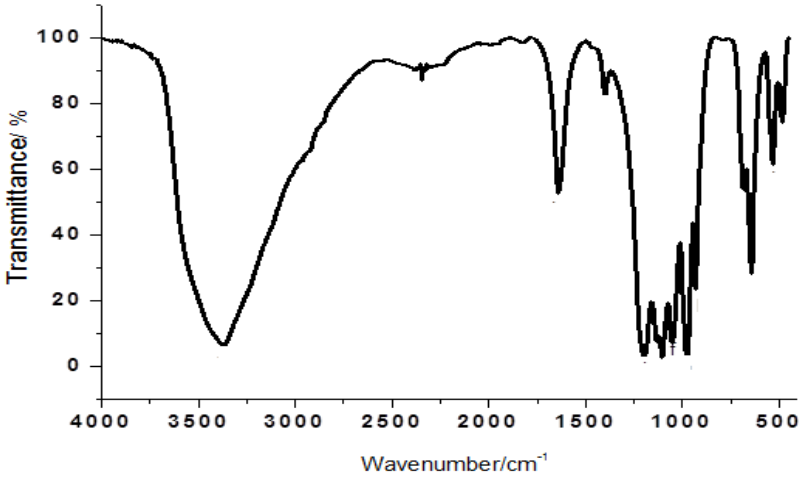

Figure 2: FT-IR spectrum for$VOHPO_4.0.5H_2O$

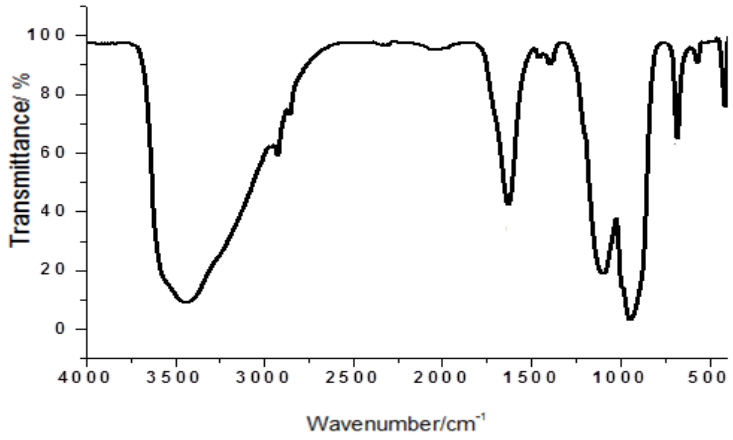

Figure 3: FT-IR spectrum for$AlVOPO_4.2H_2O$

The X-ray diffraction pattern to $VOPO_4.2H_2O$ and $VOHPO_4.0.5H_2O$ are in agreement with those previously reported [1-7]. It was verified that the metal doped $VOPO_4.2H_2O$ exhibits the same structure exhibited by the pure

vanadyl phosphate (there is no changes in the 001, 002 and 003 interlayer distances. As illustrative example, the X-ray diffraction pattern to is shown in Figure 4.

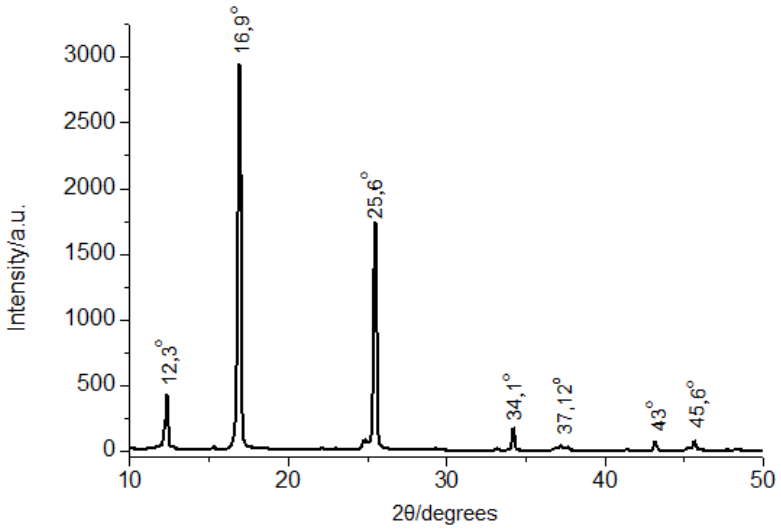

Figure 4: X-ray diffraction pattern for cobalt-doped vanadyl phosphate.

The chemical composition of the prepared matrices, as obtained by X-ray fluorescence are shown in Table 2.

Table 2: Chemical composition of the prepared matrices, as obtained by X-Ray fluorescence

Matrix	**Chemical composition (as oxides)**		
$VOPO_4.2H_2O$	82.02% V_2O_5	17.98% P_2O_5	
$VOHPO_4.0{,}5H_2O$	93.15% V_2O_5	6.85% P_2O_5	
$CoVOPO_4.2H_2O$	93.36% V_2O_5	6.56% P_2O_5	0.08% Co_2O_3
$AlVOPO_4.2H_2O$	89.34% V_2O_5	10.05% P_2O_5	0.62% Al_2O_3
$CrVOPO_4.2H_2O$	85.30% V_2O_5	6.24% P_2O_5	8.46% Cr_2O_3
$MnVOPO_4.2H_2O$	67.38% V_2O_5	15.92% P_2O_5	16.70% MnO

The adsorption capacities (mg/g) towards ammonia (as calculated based on the elemental analysis results), of the prepared matrices $VOPO_4.2H_2O$, $VOHPO_4.0{,}5H_2O$, $CoVOPO_4.2H_2O$, $MnVOPO_4.3H_2O$, $CrVOPO_4.2H_2O$ and $AlVOPO_4.2H_2O$ are as follows: 112.1, 96.6, 125.1, 200.4, 145.1 and 216.8, respectively.

These values are much higher than the previous obtained ones (from 0.6 to 1.8 mg NH_3/g at 40 °C; from 0.2 to 0.7 mg NH_3/g at 80 °C and from 0.15 to 0.35 mg NH_3/g at 120 °C) to the gaseous [8] or aqueous solution (17.19 mg/g) [9] ammonia adsorption on activated carbon.

Adsorption of ammonia (as measured volumetrically) on activated alumina at temperatures of (273, 298, and 323) K and gas pressures up to 108 kPa exhibits the following values: (3.13, 2.53, and 1.89) mmol·g−1 at (273, 298, and 323) K, respectively [11]. So, an adsorption capacity well below those reported in the present work. Furthermore, using bamboo charcoal [11] an adsorption capacity (mg NH_3/g) in aqueous solution, for a series of treated and not treated samples, always lower than 10.0mg/g was measured.

As can be verified, even when incorporated to the vanadyl phosphate matrix (Table 2) aluminium can double the ammonia adsorption capacity (compared with the undopedvanadyl phosphate). At a first looking, the higher charge (+3) of aluminium could be pointed out as the reason for such remarkable result. However, the Cr (III) matrix exhibits an adsorption capacity lower than the Mn(II) matrix. Such facts, that is, a +3 cation (Cr) doped matrix exhibiting a lower adsorption capacity than a +32 cation doped (Mn) one, al well as the fact that Mn(II) doped matrix exhibits the higher adsorption capacity, must be found in Table 2 data. As can be verified, the manganese matrix is the one with the higher doping cation content.

Both, the insertion of metal cations and the reaction with ammonia are able to affect the microstructure of the vanadyl phosphate, as shown in Figure 5.

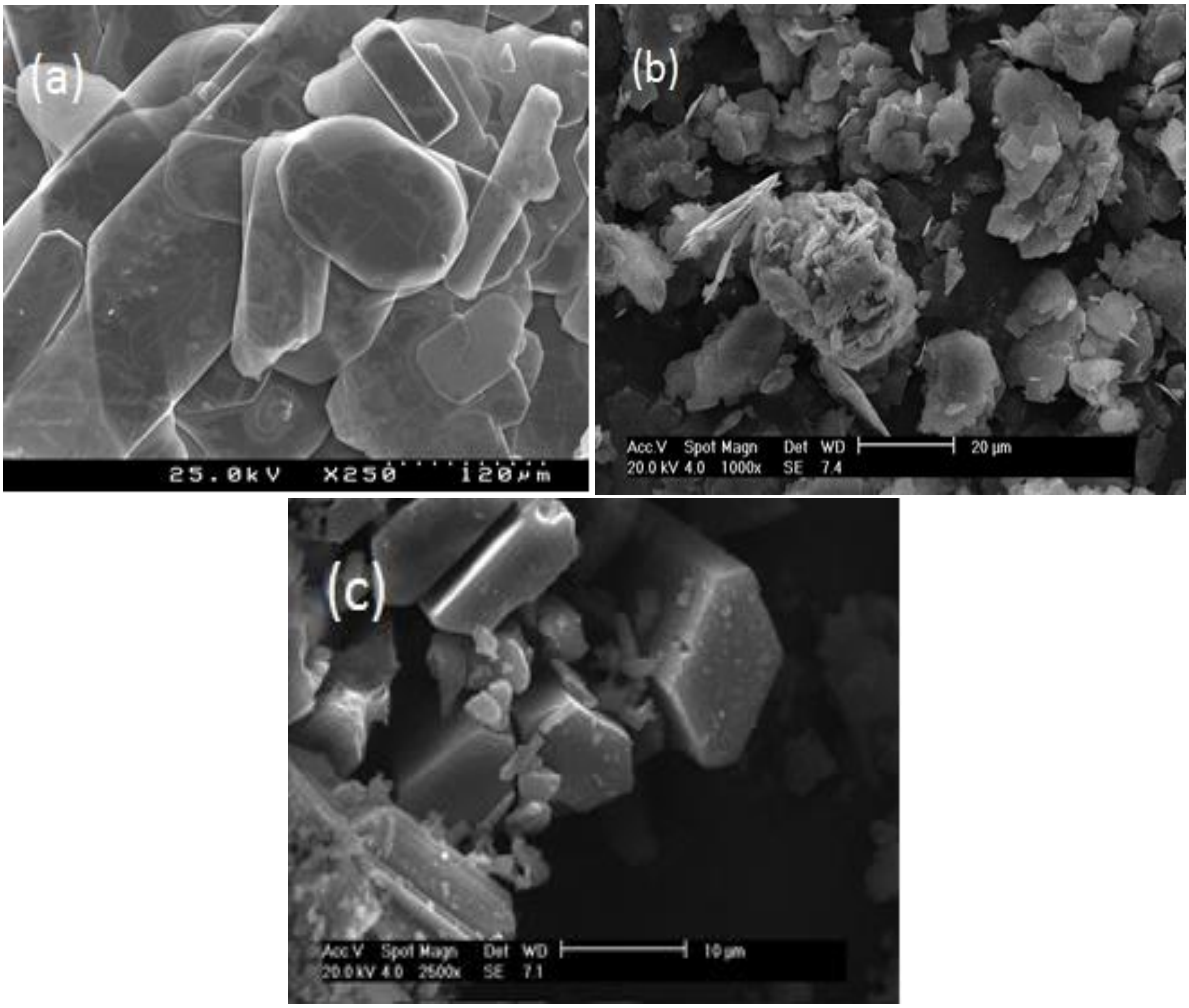

Figure 5: SEM images for: (a) $VOPO_4.2H_2O$ (b) $MnVOPO_4.2H_2O$ and (c) $VOPO_4.2H_2O$ after 30 minutes of reaction with NH_3

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