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Structural archetypes in nickel(II) hybrid vanadates. Towards a directed hydrothermal synthesis

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ABSTRACT

In the present work, we relate the modifications of the initial synthesis parameters (pH value, stoichiometry and concentration) with the different structural archetypes obtained in the {Ni/Bpy/VO} and {Ni/Bpe/VO} systems (4,4′-bipyridine (Bpy), 1,2-di(4-pyridyl) ethylene (Bpe)). The vanadium coordination is partially controlled by the hydrothermal synthesis conditions, and the final crystal structures depend on the synergetic interaction between the metal-organic subnets and the vanadium oxide subunits.

1. Introduction

The construction of new hybrid vanadates through the rational combination of organic ligands (spacers), metal nodes and $\{V_xO_y\}$ oxoanion, has become an area of great interest recently due to their structural diversity [1,2]. In that respect, the hydrothermal synthesis is a powerful technique that exploits the self-assembly of the initial building blocks [3]. In the case of hybrid nickel(II) vanadates, the initial pH value modify drastically the polymeric state of the $\{V_xO_y\}$ subunits, giving rise to various crystal structures in the same {Metal/Ligand/VO} system [4,5]. Therefore, this paper presents the comparison between the hydrothermal synthesis conditions, and the final crystal structures, in the {Ni/Bpy/VO} and {Ni/Bpe/VO} systems.

2. Experimental

The starting reagents were purchased from Aldrich. The hydrothermal reactions were carried out in polytetrafluoroethylene-lined stainless steel containers (50 ml) under autogenous pressure. The pH value of the initial mixtures was adjusted with a 0.1 M HNO_3 solution, and measured with a Crison 2002 pHmeter. The final products were washed with water and acetone, and characterized by X-ray powder diffraction. The powder patterns were recorded in 2θ steps of 0.02° in the range $5 \leq 2\theta \leq 69°$, counting for 1 s per step, with a Philips Analytical PW1710 (CuKα) diffractometer. *{Ni/Bpy/VO} system*: time of reaction: 5 days. Temperature: 170 °C. Initial stoichiometry and reagents: 1:1:1, $Ni(NO_3)_2{\cdot}6H_2O$, $NaVO_3$, Bpy (4,4′-bipyridine). Filling factor: 60% (30 ml H_2O). The pH value was adjusted in the range between 7.0 and 2.5, approximately each 0.5 interval. The concentration was progressively increased between 0.26 and 1.21 mmol. *{Ni/Bpe/VO} system*: time of reaction: 3 days. Temperature: 120 °C. Reagents: $Ni(NO_3)_2{\cdot}6H_2O$, $NaVO_3$, Bpe 1,2-di(4-pyridyl) ethylene. Filling factor 60% (30 ml H_2O). The pH value was adjusted in the range between 6.5 and 3.5, approximately each 0.5 interval.

3. Results and discussion

The Fig. 1 summarizes the most significant characteristics of the obtained crystal structures, pointing the $\{V_xO_y\}$ subunits and the metal-organic moieties. The modification of the hydrothermal synthesis conditions gives rise to three different phases in the {Ni/Bpy/VO} system; (**1**) $[\{Ni_2(H_2O)_2(Bpy)_3\}(V_4O_{12})]{\cdot}2.5H_2O]$ (Fig. 1 (a.i)) previously reported by Yang et al. [6], (**2**) $[\{Ni_8(Bpy)_{16}\}(V_{24}O_{68})]{\cdot}0.5H_2O$ (Fig. 1 (a.ii)) and (**3**) $[\{Ni_6(H_2O)_{10}(Bpy)_6\}(V_{18}O_{51})]{\cdot}0.5H_2O$ (Fig. 1 (a.iii)), and other two in the {Ni/Bpe/VO} system, (**4**) $\{Ni(Bpe)\}(VO_3)_2$ [7] (Fig. 1 (b.i)), (**5**) $[\{Ni(H_2O)_2(Bpe)\}(V_4O_{11})]{\cdot}0.5H_2O$ [8] (Fig. 1 (b.ii)).

The compounds (**1**) and (**2**) possess four coordinated vanadium forming $\{V_5O_{15}\}$ cycles and $\{VO_3\}$ metavanadate chains, respectively. The phase (**3**) shows four and five coordinated vanadium

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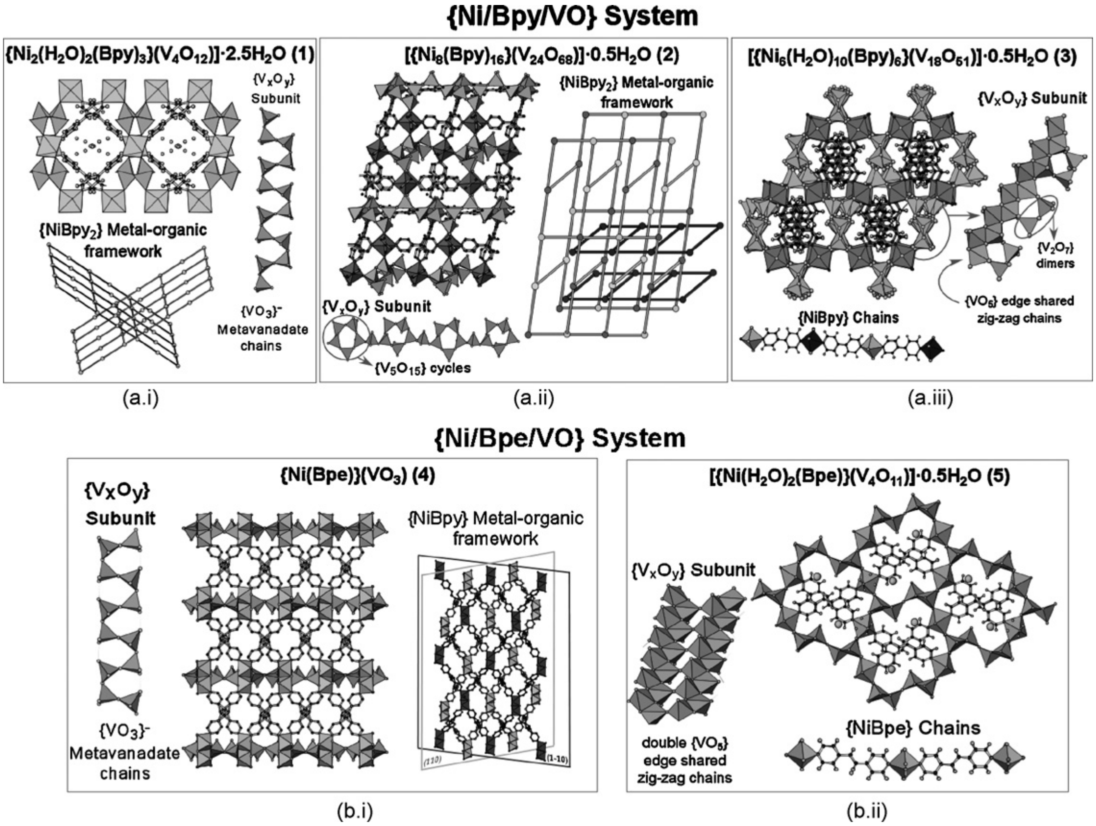

Fig. 1. (a.i), (a.ii) and (a.iii) Crystal structures and related vanadium oxide subunits and metal organic frameworks of the nickel(II) hybrid vanadates synthesized in the {Ni/Bpy/VO} system. (b.i) and (b.ii) Crystal structures and related vanadium oxide subunits and metal organic frameworks of the nickel(II) hybrid vanadates synthesized in the {Ni/Bpe/VO} system.

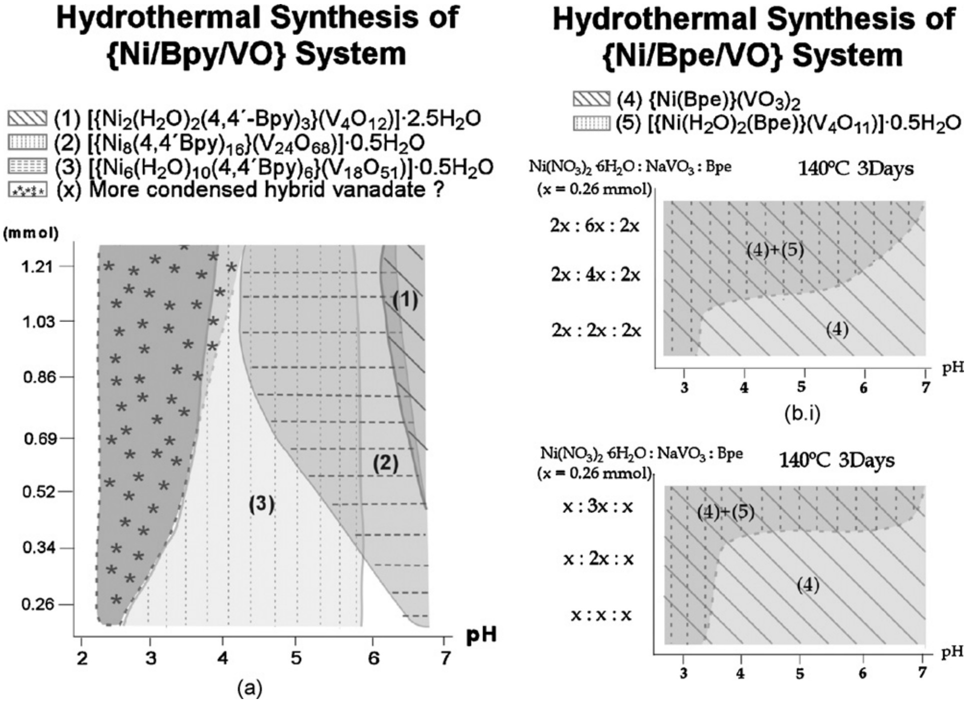

Fig. 2. (a) Stability fields obtained after the X-ray powder diffraction analysis in the {Ni/Bpy/VO} system. (b) Stability fields obtained after the X-ray powder diffraction analysis in the {Ni/Bpe/VO} system. ((b.i) higher concentration, (b.ii) lower concentration).

giving rise to zig-zag chains of edge shared [VO_5] polyhedra, corner linked to {V_2O_7} dimmers. With respect to the metal-organic moieties, the phases (**1**) and (**2**) exhibit complex interpenetrated frameworks, while the compound (**3**) shows simpler metal organic chains. All of them possess 3D architectures with 3D inorganic frameworks (Fig. 1(a)).

The crystal structure of (**4**) is constructed from inorganic layers pillared by the organic ligand. The vanadium is four coordinated and give rise to {VO_3} metavanadate chains. The connectivity between the metal centres and the ligand generates interpenetrated metal-organic layers. The phase (**5**) exhibit five coordinated vanadium forming double zig-zag chains of edge shared [VO_5] polyhedra. In the same way that the phase (**3**), the compound (**5**) possess Ni-ligand metal organic chains, and a very similar inorganic framework (Fig. 1(b)).

3.1. Hydrothermal synthesis, {Ni/Bpy/VO} system

The X-ray powder diffraction analysis reveals the four stability fields of the Fig. 2(a). The initial and final pH values are approximately the same. The compound (**1**) is stable at nearly neutral pH values and higher concentrations. At lower pH values the phase (**2**) began to crystallize and is strongly overlapped with the phase (**3**) between 6 and 4.5 pH values at high-medium concentrations. At lower pH values a red compound (x) is obtained after the reaction time; unfortunately this one has a very low crystallinity, and all attempts to obtain single crystals have been unsuccessful.

A comparison between the crystal structures of the different phases reveals an increase of the polymerization of the {V_xO_y} subunits related to the decrease of the pH value. Moreover, the compounds obtained at higher pH values have more complex metal-organic moieties, and less condensed architectures.

The strong overlapping of the stability fields of (**2**) and (**3**) could be explained by a sequential crystallization process. This way, at high concentration and acidic conditions the phase (**3**) begin to crystallize. This one has five coordinated vanadium and Ni:V:Bpy molar ratio of 1:3:1. The progressive crystallization of (**3**) lowered the vanadium concentration in solution three times faster than the Ni and Bpy, favouring the four coordinated species in solution, like the {V_5O_{15}} cycles, and hence the crystallization of (**2**).

3.2. Hydrothermal synthesis, {Ni/Bpe/VO} system

The X-ray powder diffraction analysis reveals that the phase (**4**) crystallizes in all the studied conditions, but acidic pH values or a higher molar ratios of vanadium in the initial stoichiometry favours the precipitation of the compound (**5**) with the (**4**) one (Fig. 2 (b.i)). We have to take into account that a slight increase of the pH value (0.5) is observed after the reaction. The decreasing of the concentration (Figure 2 (b.ii)) displaces the stability field of the compound (**5**) to lower pH values and to higher vanadium rates in the initial stoichiometry.

The overlapping of the stability fields of (**4**) and (**5**) can be explained by a sequential crystallization process. The phase (**5**) began to crystallize at acidic conditions or higher vanadium ratios in the initial stoichiometry. This compound possess 1:4 molar ratio of Ni:V in it's formula. The progressive crystallization of (**5**) lower the vanadium concentration in solution fourth time faster than the nickel or the Bpe, and finally allows the precipitation of (**4**), with four coordinated vanadium, and less condensed crystal structure.

4. Conclusions

The study of the hydrothermal synthetic conditions in the {Ni/Bpy/VO} and {Ni/Bpe/VO} system allows to establish some general trends with respect to the obtained final architecture. In that respect, a lower pH values promote an increase in the {V_xO_y} polymerization giving rise to more condensed three dimensional inorganic frameworks stabilized with metal–ligand chains. In the case of less condensate {V_xO_y} subunits, favoured by neutral or slightly acidic pH values and lower concentrations, the crystal structures present more complex metal-organic moieties and less condensate inorganic architectures.

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