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Intercalation of dipeptides during $V_2O_5.nH_2O$ xerogel condensation

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Abstract

(dipeptide)$_x$$V_2O_5.1.0H_2O$ ($0.27 < x < 0.37$) precipitates have been synthesized by adding dipeptides (Val-Gln, Ala-Gln, Gly Gln, Gly Glu and Ala-Gly) to a metavanadate solution acidified using a proton exchange resin. As evidenced by X-ray diffraction, these vanadium oxides exhibit the layered structure of the $V_2O_5.1.8H_2O$ xerogels in which dipeptides are intercalated between the layers. These precipitates result from the assembly of ribbon like particles into a sponge like morphology as evidenced by scanning electron microscopy. The vanadium oxide phases were also characterized by ^{51}V MAS NMR while ^{13}C CP MAS NMR allowed to investigate the dipeptide preservation during the synthesis.

Keywords: A. oxides; B. sol-gel growth; D. nuclear magnetic resonance (NMR)

1. Introduction

The entrapment of biomolecules or bioactive molecules in an inorganic matrix appears as a very promising approach for drug delivery applications, as well as for the design of biosensors and bioreactors [1,2]. Many studies have been performed on 3D porous materials but layered inorganic matrices may also be useful for such application due to the flexibility of intercalation/deintercalation process [3]. Various layered materials such as clay minerals [4,5], lamellar double hydroxides [6–9] (LDH), metal phosphates [10–12] and metal hexathiohypodiphosphate [13,14] (MPS_3) have been demonstrated to be suitable host for numerous amino acids [4,8], peptides [7], polysaccharides [15], enzymes [12], drugs [16], nucleosides and even DNA [9]. The protection of the biomolecules and their controlled release are not the only foreseen applications of those materials: bioorganic species may be used for their catalytic properties, their ability to build chiral pillaring or to delaminate the layered host.

Among intercalation compounds, $V_2O_5.1.8H_2O$ xerogels and cation intercalated xerogels $M_{0.3}V_2O_5.1.5H_2O$ ($M = Li^+$, Na^+) have been extensively studied for their electrochemical properties [17–19]. These hydrated vanadium oxides are found as stacked ribbon-like particles about 20 nm wide, 2 nm thick and 1 μm long [20]. They consist of V_2O_5 bilayers whose interlayer space is occupied by water molecules ($V_2O_5.1.5H_2O$) and cations ($M_{0.3}V_2O_5.1.5H_2O$). A wide range of molecular species including metal cations, transition metal complexes, polymers were incorporated in the interlayer space of V_2O_5 xerogels [21,22]. The intercalation of glucose oxidase enzymes in V_2O_5 gels for glucose biosensing has also been reported [23]. Apart from their biological activity, another interesting feature of biomolecular systems is that they often exhibit self-organization properties that can be used to template the growth of an inorganic network.

The introduction of a biomolecule during the V_2O_5 synthesis may modify the pH and the ionic strength of the solution like a simple inorganic base or salt. More specifically, the different chemical functions of the organic species may induce some reduction of the vanadium (V) species or bind them through complex formation. We previously reported the effect of adding a base or a salt to the vanadium oxide precursors that condense into $V_2O_5.nH_2O$ gels [24]. The introduction of foreign species that change chemical parameters such as pH and ionic strength modified the growth process of the $V_2O_5.nH_2O$ gels and poorly ordered $Na_{0.3}V_2O_5.nH_2O$ precipitates and crystalline NaV_3O_8 $1.5H_2O$ were obtained [24]. This work represents the next step, where we extended the study to five dipeptides (Val-Gln, Ala-Gln, Gly-Gln, Gly-Glu and Ala-Gly.) whose complexing functions may interact with vanadium precursors through electrostatic interactions, covalent, hydrogen and van der Waals bonds. Actually, covalent links between dipeptides and polyoxovanadate species inside complexes at pH 7 were clearly evidenced by different NMR experiments [25]. The dipeptide-vanadium oxide compounds were characterized by X-ray diffraction, scanning electron microscopy (SEM), ^{51}V and ^{13}C MAS NMR spectroscopies.

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2. Experimental procedure

The dipeptides L-H_2N-Alanine-Glycine-OH (L-Ala-Gly), H_2N-Alanine-Glutamine-OH (Ala-Gln), H_2N-Valine-Glutamine-OH (Val-Gln), H_2N-Glycine-Glutamine-OH (Gly-Gln) and H_2N-Glycine-Acide Glutamique-OH (Gly-Glu) were purchased from Sigma and used without any purification. Their structure is presented in Fig. 1. Vanadium oxides have been prepared via the acidification of an aqueous solution of sodium metavanadate $NaVO_3$ (Sigma, $>99\%$, 0.5 mol.L^{-1}, pH $=8$) according to a procedure currently used for the synthesis of vanadium oxide gels [26]. Acidification of a 0.5 mol.L^{-1} metavanadate solution, with an initial pH close to 8, was performed using a proton exchange resin (DOWEX 50WX 4–100 mesh). A clear yellow solution (pH ~ 1) was obtained after full proton exchange that progressively turns into a red $V_2O_5.nH_2O$ gel after about 12 h. The pH slightly increases up to 1.5 during the formation of the solid network [27]. In order to study the role of dipeptides on the formation of the vanadium oxide network, different amount of solid dipeptides were added to the yellow acid solution of V(V) precursors (10 mL). The concentration of dipeptide in the vanadate solution was 100 mmol.L^{-1} except for Ala-Gln whose concentration was varied between 25 and 150 mmol.L^{-1}. The initial pH of the solution (pH_i) before condensation increased from 1.4 to 2.2 when the concentration of Ala-Gln varied from 25 to 150 mmol.L^{-1}. In some experiments, the initial pH (pH_i) of the solution after dipeptide addition was adjusted to 1.0 by adding few drops of chlorhydric acid (2.0 mol.L^{-1}). The solutions were then left for ageing 24 hours at room temperature in a closed vessel. A dark red to black precipitate rather than a gel was obtained after a few hours. It was separated from the supernatant solution by filtration, rinsed twice with 20 mL of deionised water and left to dry at room temperature for 24 h. The final pH (pH_f) of the supernatant solution was measured: pH_i between 1.4 and 2.2 increased to a final value of 3 while pre-adjusted $pH_i \sim 1.0$ increased slightly to 1.5. The amount of solid phase increased when the initial pH of the solution decreased. The post-intercalation process of dipeptides in a preformed vanadium oxide film was also tried but it failed since the dipeptides present in the solution rapidly reduced the film up to its destruction.

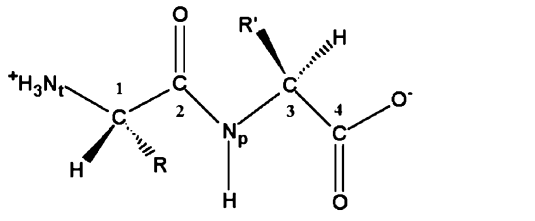

Fig. 1. Schematic structure of the dipeptides Val-Gln, Ala-Gln, Ala-Gly, Gly Gln and Gly Glu.

The nature and the relative amount of the vanadium (V) species present in the supernatant solutions were determined using ^{51}V NMR spectroscopy in solution. ^{51}V NMR spectra were recorded at 78.9 MHz on a Bruker AC 300 spectrometer. The chemical shifts were referenced to $VOCl_3$ ($\delta = 0$ ppm). A spectral width of 30 kHz, a pulse width of 11 μs ($\theta \sim 90°$), with an accumulation time of 0.13 s and no relaxation delay, were used. An accumulation of 2000 transients was usually performed on 5 mm NMR tubes. The relative amount of remaining dipeptides in the supernatant solutions was determined using ^1H NMR spectroscopy in solution. ^1H NMR spectra were recorded at 300 MHz on a Bruker AC 300 spectrometer.

X-ray diffraction (XRD) patterns were recorded at room temperature with a θ–2θ diffraction mode and a Bragg-Brentano geometry on a Philips PW1830 diffractometer (CuK_α $\lambda = 1.542$ Å, in the 3–53° 2θ range). Thermogravimetric analyses (TGA) were performed on a TA SDT 2960 apparatus. Solids were heated up to 600 °C with a heating rate of 5 °C.min^{-1} in an oxygen atmosphere. The relative amount of V(IV) in solids was measured by a spectroscopic UV-Visible method. 10 mg of solid were dissolved in 2.0 mL of a 3 mol.L^{-1} hydrochloric acid solution. The concentration of VO^{2+} (V(IV)) ions in this solution was measured at 760 nm ($\varepsilon = 16.4$ mol^{-1} L cm^{-1}), that of VO_2^+ (V(V)) ions in this solution was measured at 400 nm ($\varepsilon = 11.5$ mol^{-1} L cm^{-1}). Errors on the amount of V(IV) determined were close to 1%. Scanning electronic microscopy (SEM) micrographs of gold-coated samples were recorded on a Stereoscan 120-Cambridge apparatus using a secondary electron detector.

Solid state ^{51}V MAS NMR and ^{13}C CP MAS NMR spectra were recorded on a Bruker Avance 300 spectrometer using a 4 mm MQ-MAS probe. For ^{51}V MAS NMR spectra, solid samples were spun at 10 and 14 kHz using 4 mm ZrO_2 rotors. ^{51}V MAS NMR spectra were recorded at 79.0 MHz with a Hahn echo sequence (π/2-τ-π-τ-acquisition) with a synchronized τ (with rotor frequency) and a 16 phases pulse program. The following acquisition parameters were used: spectral width 2 MHz, pulse width 0.7 μs with a 0.5 s recycle time. Very short pulse length and wide spectral windows were used in order to ensure that all the spinning sidebands are observed with their right intensity. An accumulation of 14000 transients was usually performed on each sample. Isotropic chemical shifts are referenced to pure $VOCl_3$ using a solution of 0.1 mol.L^{-1} NH_4VO_3 ($\delta_{iso} = -578$ ppm) as secondary reference. For ^{13}C MAS NMR experiments, solid samples were spun at 14 kHz using 4 mm ZrO_2 rotors. The ^{13}C CP MAS NMR spectra were recorded at 75.47 MHz with a contact time of 1 ms and a recycle delay between pulses of 5 s. TMS was used as a reference for ^{13}C chemical shifts. All the ^{13}C NMR experiments were performed with high-power decoupling.

3. Results and discussion

The synthesis process of a $V_2O_5.nH_2O$ gel is usually based on the acidification of a metavanadate solution by a proton-exchange