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# Long chain alkyl amine templated synthesis of a mesostructured lamellar vanadium phosphate phase

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***n*-Hexadecylamine (HDA) has been used as a template to synthesize a mesolamellar vanadium phosphate (VPO) phase. FTIR studies indicate covalent interaction of the amine head with the vanadyl groups of the VPO matrix, in contrast to the other reported syntheses of mesostructured VPO phases which involve ionic interaction between a cationic surfactant and the inorganic matrix. XRD, TEM and solid state $^{13}$C MAS NMR studies show that the incorporated HDA induces the formation of a mesolamellar phase with a basal spacing of 44.5 Å. On ageing however, a restructuring of the incorporated HDA is observed resulting in a curvature of the inorganic layers and a decrease of the basal spacing to 38.04 Å.**

One of the major areas of research in the quest for new catalytic materials is the synthesis of new open structures with pores in the mesoporous range as well as lamellar phases of mesoscopic dimensions.[1] To this end, the synthesis by researchers[2] at Mobil in 1992 of mesostructured silicates (M41S) using long chain surfactants as supramolecular templates opened new horizons in this area, and this templating method has now been applied to a number of non-silica based materials as well. In this context, some attempts have been recently made to induce mesostructure formation in layered vanadium phosphates which are catalytically very important as commercial catalysts for the selective oxidation of butane to maleic anhydride and also as strong potential catalysts for the oxidation of other light alkanes.[3] So far, all the reported syntheses of mesostructured vanadium phosphates have involved $S^+I^-$ type charge density matching at the organic–inorganic interface between a cationic surfactant ($S^+$), cetyl trimethylammonium bromide/chloride/hydroxide and a negatively charged soluble vanadium phosphate precursor ($I^-$).[4,5] There has also been a recent report[6] of the synthesis of a lamellar oxovanadium(v) phosphate through an $S^+X^-I^0$ mechanism using a long chain amine as the templating agent. In the present work we report, what we believe to be the first example of the synthesis of a mesoscopic vanadium phosphate by covalent templating with the surfactant rather than through ionic interaction.

The HDA (HDA = *n*-hexadecylamine) templated materials prepared here were synthesized from a reaction mixture of the following molar composition, $V_2O_5:H_3PO_4:NH_2OH.HCl:HDA:H_2O = 1:2:2:0.5:669$. In a typical synthesis, $V_2O_5$ (0.909 g, 0.005 mol) powder was stirred in 30 ml of an aqueous solution of $NH_2OH{\cdot}HCl$ (0.695 g, 0.01 mol) in the presence of 1.153 g of 85% phosphoric acid (0.01 mol) at 80 °C for 1 h to obtain a blue solution. A homogeneous dispersion of the HDA (0.603 g, 0.0025 mol) in 30 ml water was added to the blue solution resulting in immediate precipitation of a sky blue solid. The solid was separated from the reaction mixture after stirring for 1 h at 80 °C and was thoroughly washed with boiling water followed by acetone to remove any unreacted HDA and the resulting material was designated as **A-1**. In another experiment the precipitated solid was separated from the mother-liquor after 24 h of stirring at 80 °C while maintaining all other reaction conditions the same as in the case of **A-1**. This material is denoted **A-2**.

The average vanadium oxidation state determined through redox titrations was found to be +4.0 in both **A-1** and **A-2**. The chemical composition of **A-1** and **A-2** were found from elemental analysis to be $(C_{16}H_{33}NH_2)_{0.88}VP_{0.78}O_{3.94}{\cdot}2.8H_2O$ and $(C_{16}H_{33}NH_2)_{0.64}VP_{0.6}O_{3.5}{\cdot}2H_2O$, respectively. It is evident that on ageing, the V : P ratio had increased indicating dissolution of phosphorus, as has been reported[5] in another synthesis of mesostructured vanadium phosphates.

The XRD pattern of **A-1** (Fig. 1) showed a strong diffraction peak at $d$ = 44.5 Å and two other peaks of weaker intensity at $d$ = 22.2 and 14.8 Å, respectively. The strong peak can be assigned to the (001) reflection and the other two to the (002) and (003) reflections of a mesolamellar phase with a basal spacing of 44.5 Å. Interestingly, in the case of **A-2**, the basal spacing decreased to 38.04 Å and only one other diffraction peak with a $d$ value of 18.9 Å and assignable to the (002) reflection was observed. This indicated restructuring of the incorporated HDA molecules on ageing.

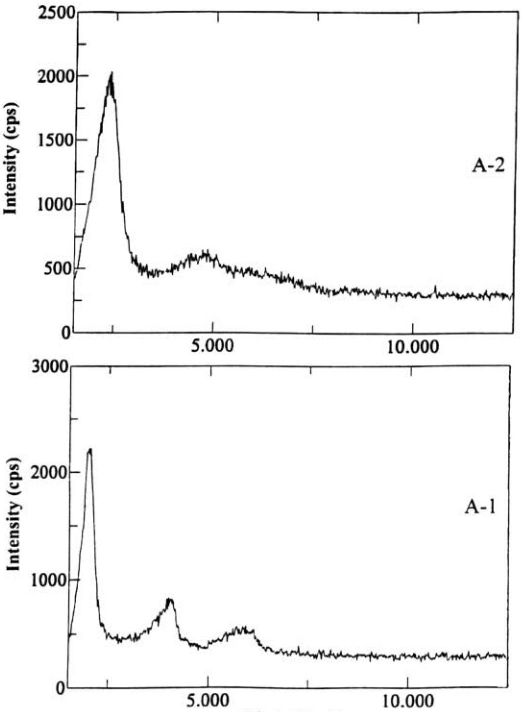

**Fig. 1** XRD patterns of HDA templated mesostructured vanadium phosphates **A-1** (1 h) and **A-2** (24 h).

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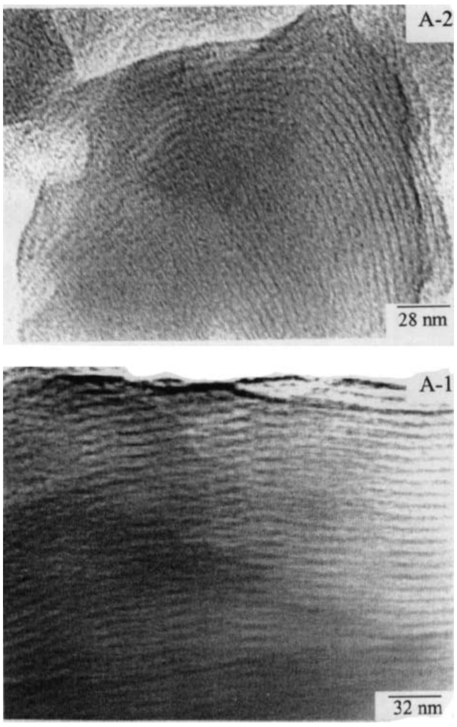

**Fig. 2** TEM images of samples **A-1** and **A-2** (accelerating voltage = 200 kV).

A transmission electron microscopy (TEM) image of **A-1** (Fig. 2) shows a parallel stacking of layers with an interlayer spacing of 44.1 Å which corresponds well with the basal spacing of 44.5 Å obtained from XRD data. In the case of **A-2**, a considerable degree of curvature in the layer structure has been introduced, with a concomitant decrease in the layer spacing to 38.08 Å (38.04 Å from XRD data).

The $^{13}C$ NMR spectra (Fig. 3) of pure HDA (**P-1**) and **A-1** show a resonance at 32.2 ppm. It is reported that resonances in the range 30–33 ppm are due to alkyl chains, with a peak at ~33 ppm being a characteristic $^{13}C$ chemical shift for the interior methylene carbons in an *all trans* conformation and a resonance at 30 ppm being due to equilibrium populations of *trans* and *gauche* conformations.[7] It is evident therefore that in **A-1** the HDA molecules are oriented in an ordered *all-trans* conformation as is also the case in pure HDA. The increased width of the peak in the spectrum of **A-1** compared to that of pure HDA is due to the decreased mobility of the HDA molecules constrained between the layers of the VPO solid. On the other hand, for **A-2**, the upfield shift of the methylene resonance to 30.1 ppm indicates the presence of both *gauche* and *trans* conformations.

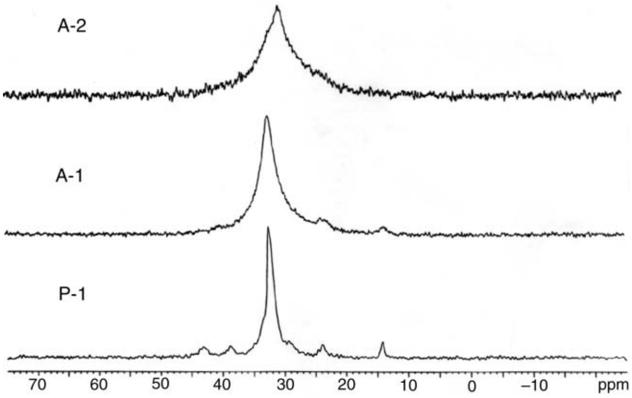

**Fig. 3** Solid state $^{13}C$ CP-MAS NMR spectra of HDA (**P-1**) and HDA templated vanadium phosphates **A-1** and **A-2**.

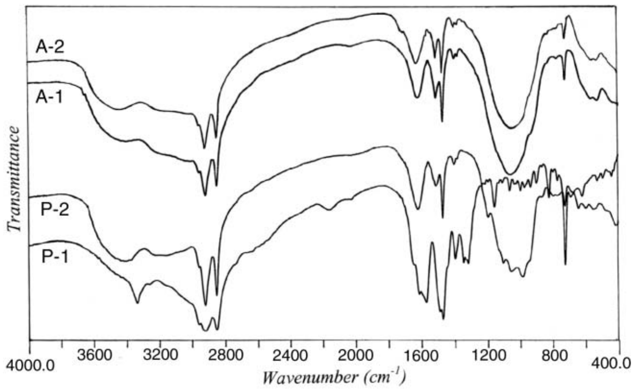

**Fig. 4** FTIR spectra of solid HDA (**P-1**), HDA intercalated $VOHPO_4{\cdot}0.5H_2O$ (**P-2**) and HDA templated mesostructured vanadium phosphates (**A-1** and **A-2**).

The infrared spectra (Fig. 4) of **A-1** and **A-2** show broad bands centered at 3222 and 3203 $cm^{-1}$, respectively, which is in the region of $NH_2$ stretching vibrations. The spectrum of solid HDA (**P-1**) shows a strong band at 3335 $cm^{-1}$ and a weaker one at 3260 $cm^{-1}$ due to the asymmetric and symmetric stretching of the $NH_2$ group.[8] The substantial shift of the $NH_2$ stretching frequencies in **A-1** and **A-2** with respect to that of HDA therefore indicates strong interaction of the $NH_2$ groups of the incorporated HDA molecules with the inorganic matrix. Similar shifts in $NH_2$ stretching frequency have been observed in aliphatic amine intercalated $VOPO_4{\cdot}2H_2O$ where the amine head groups are anchored on distorted vanadium octahedra.[9] In addition, the $NH_2$ deformation band which occurs at 1613 $cm^{-1}$ in HDA is shifted to higher wavenumbers to 1619 and 1625 $cm^{-1}$ for **A-1** and **A-2**, respectively. Also, the infrared spectra of both **A-1** and **A-2** do not show any strong absorption bands at 3200 and 2800 $cm^{-1}$ due to the asymmetric and symmetric stretching of $NH_3^+$ type species,[8] or bands at 1580 and 1540 $cm^{-1}$, characteristic of the bending mode of protonated alkyl amines,[10] indicating that the amine molecules incorporated into **A-1** and **A-2** are not present in a protonated form. The strong interaction of the amine head group of HDA with the inorganic matrix in **A-1** and **A-2** is also reflected in the $\nu(V^{4+}{=}O)$ stretch. We have observed in the course of a parallel study on the intercalation of different amines into various VPO phases that on intercalation of HDA into $VOHPO_4{\cdot}0.5H_2O$ a shoulder appears at 940 $cm^{-1}$ which can be assigned to the $\nu(V{=}O)$ stretch of vanadyl groups bound to HDA through coordinate covalent bond formation. The spectrum of this phase denoted **P-2** is shown in Fig. 4 for comparison. Such a large red shift of 36 $cm^{-1}$ of the $\nu(V{=}O)$ of the parent $VOHPO_4{\cdot}0.5H_2O$ which appears at 976 $cm^{-1}$ has also been reported in alkyl amine intercalated vanadyl organophosphonates where the alkyl amines remain strongly bound to the V–P–O lattice by forming V–N bonds[11,12] and in pyridine and methylamine complexes of $VO(acac)_2$.[13] The presence of shoulders at 936 and 940 $cm^{-1}$ in **A-1** and **A-2**, respectively, thus indicates strong anchoring of the HDA molecules on the V–P–O matrix thus providing strong evidence for the covalent interaction of the unprotonated amine surfactant with the inorganic matrix. The broad feature in the 800–1200 $cm^{-1}$ region in **A-1** and **A-2** indicates the amorphous nature of the inorganic wall.

It is evident therefore that it is possible to organize soluble vanadium phosphate precursors into mesolamellar V–P–O phases by using a long chain amine such as HDA as the template. The strong interaction of the incorporated HDA molecules in the free amine form, with the VPO matrix, provides compelling evidence in favour of a ligand templating mechanism of mesostructure formation. A more detailed study is in progress.

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