Supramolecular self-assembling in mesostructured materials through charge tuning in the inorganic phase

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Supramolecular self-assembling of organic CTA+ micelles and inorganic $[VO(H_2O)PO_4]_n^{q-}$ 2D-anions for the isolation of hexagonal mesostructured materials can be reached by charge tuning in the inorganic phase through the adjustment of the vanadium mean oxidation state.

When researchers of the Mobil company reported the discovery of new mesoporous silica based materials denoted MCM-41,[1] the scientific community imagination was newly stimulated and a large amount of related work was published in a very short time.[2] Originally, the synthesis of mesoporous silica materials was related to a liquid-crystal templating mechanism in which surfactant micelles act as supramolecular templates. However, for low surfactant concentrations another model based on the cooperative organisation of inorganic and organic molecular species has been developed. In that case, the most important point in the synthesis of a mesostructured solid is charge density matching at the organic–inorganic interface.[3]

Although much work has been reported on the influence that variation of surfactant characteristics has in the isolation of mesoporous materials,[4] very little has been done regarding the inorganic counterpart. In contrast with silica based materials, other metal oxides show, in general, shorter progression of their hydrolysis and condensation reactions and hence strong limiting problems related with charge matching at the interface appear. In this sense we present here, to the best of our knowledge for the first time, the possibility of controlling the formation of mesostructured solids by tuning the charge density at the inorganic phase through the adjustment of the metal oxidation state in a mixed-valence system.

We have succeeded in the preparation of mesostructured mixed-valence oxovanadium phosphates with different $V^{IV}:V^V$ content (ICMUV-2 materials) using CTAB (cetyltrimethylammonium bromide) as a surfactant directing agent in water. A constant $V:H_3PO_4:CTAB:H_2O$ molar ratio of $1:5:0.1:150$ was always used in the starting reactants and the $V^{IV}:V^V$ content was adjusted in a continuous way by adding variable amounts of H_2O_2.

Owing to the complexity of the $V–H_3PO_4–CTAB–H_2O$ system our approach has been based on the independent consideration of the organic and inorganic species present in the mother-liquor. Regarding the organic subsystem, we have used low surfactant concentration to favour a cooperative mechanism in which the charge density matching at the interface must be the leading force to the supramolecular organisation for the preparation of ICMUV-2 solids.

In relation to the inorganic moieties, we have carried out our synthesis at very low pH value since under this condition the oxovanadium cations are present as isolated aqua cations[5] and, in the presence of oxophosphorus anions ($H_2PO_4^-$ at the working pH), should lead to successive hydrolysis and condensation reactions which would lead to the formation of the $[VO(H_2O)PO_4]_n^{q-}$ two-dimensional anions.[6] Supramolecular assembling between organic and inorganic species into a mesostructured solid will take place when the charge density of the inorganic moieties matches with that of CTA+ micelles. We have calculated an approximate charge density at the rod-like micelles surface of $q = +0.014$ e $Å^{-2}$ presuming a hexagonal close packing of surfactant head groups at the micelle surface and using the micelle diameter (37.5 Å) and the van der Waals radius of the head groups (4.5 Å).[7] From this value and taking into account the bond topology of the $[VO(H_2O)PO_4]_n^{q-}$ moieties,[6] the $V^{IV}:V^V$ molar ratio which matches the surfactant micelles charge should be $0.54:0.46$. According to this simple calculation we have experimentally found that it is only possible to obtain hexagonal mesostructured solids when the $V^{IV}:V^V$ molar ratio lies between $0.20:0.80$ (sample 1) and $0.61:0.39$ (sample 4), the most crystalline solids being those for which the $V^{IV}:V^V$ molar ratio has a value around unity ($0.54:0.46$; sample 3) (see Fig. 1). The existence of a $V^{IV}:V^V$ range in which charge density matching must somehow occur, is consistent with the ability of the micelle to change its molecular packing and in this way to accommodate its charge density at the surface to the inorganic phase charge. Hence, the highest crystallinity must correspond to the solid with the most ordered micelles, *i.e.* that with close packing of surfactant head groups at the surface. Also, the $V^{IV}:V^V$ matching range can be extended to a greater degree below the best calculated value of 0.54 than above since the micelle can easily adopt a looser packing but not a closer one.

In a typical sample preparation, an aqueous suspension (50 ml) containing V metal (0.226 g, 4.44 mmol), V_2O_5 (1.617 g,
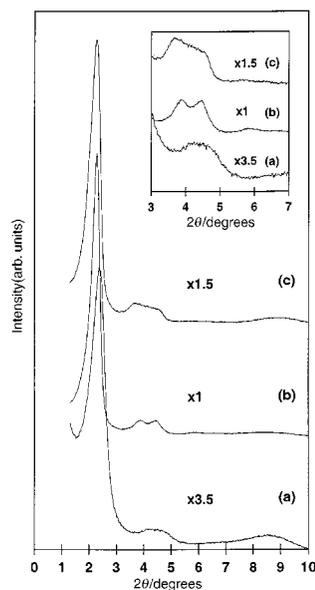
Fig. 1 X-Ray powder diffraction patterns of ICMUV-2 materials having different $V^{IV}:V^V$ molar ratios and CTA+ content; (a) sample 1, (b) sample 3, (c) sample 4

Table 1 Selected synthetic and compositional parameters for ICMUV-2 solids: $[CTA]_x[(V^{IV}O)_y(V^VO)_{1-y}PO_4]\cdot zH_2O$

Sample	V^{IV} in solution %	y	x	z
1	35	0.20	0.20	2.01
2	55	0.33	0.33	1.41
3	60	0.54	0.53	1.01
4	85	0.61	0.60	0.65

8.88 mmol) and 7.6 ml of 85% H_3PO_4 was refluxed until complete dissolution. Amounts of V metal and V_2O_5 were adjusted in order to obtain a V^{IV} starting solution and the $V^{IV}:V^V$ ratio in the solution was then adjusted by controlled addition of H_2O_2. Subsequently, a 10 ml aqueous solution of CTAB (0.81 g) was added. After stirring for 1 h at room temperature the ICMUV-2 solid was isolated by filtration. Although ICMUV-2 solids can be prepared with slightly higher CTAB concentration (up to $CTAB:H_2O = 0.3:150$) the surfactant concentration used here allows us to obtain the most ordered solids. Table 1 summarises the main synthesis variables and compositional data of selected ICMUV-2 materials. Vanadium oxidation states in the solids were determined by atomic absorption and a redox titration procedure. All the samples were analyzed and characterized by X-ray powder diffraction (Seifert 3000TT diffractometer using Cu-Kα radiation in steps of $0.02°$ (2θ) for 10 s per step) and TEM on a Philips CM10 instrument operated at 120 kV. Fig. 1 shows the XRD patterns of selected ICMUV-2 materials. Although differences in crystallinity can be observed among solids with different composition, all of them present a similar regular hexagonal array according to TEM analysis and Fig. 2 shows a representative TEM image.

Previously to this work, it was reported the preparation of solids in the V–O–P system which consisted of mixtures of amorphous vanadium and phosphorus oxides[8,9] with a $V:P = 2:1$ molar ratio rather than a genuine vanadyl phosphate. However, in order to obtain an adequate $(VO)_2P_2O_7$ catalyst precursor it is necessary to maintain a $V:P = 1$ molar ratio.[10] In our experiences neither vanadium(V) starting solutions (zero global charged ($[VOPO_4]_n^0$) species, $S^+X^-I^0$ mechanism) nor vanadium(IV) ones ($[VOPO_4]_n^-$ species, S^+I^- mechanism) allowed us to synthesize any kind of solid, only when we reached the necessary charge density matching at the organic-inorganic interface by adjustment of the $V^{IV}:V^V$ molar ratio were mesostructured solids obtained. Hence, instead of ran-
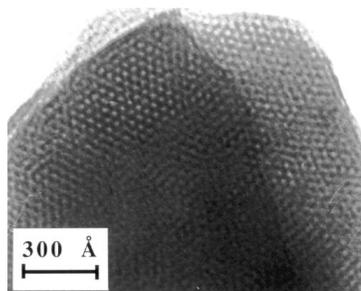
Fig. 2 Representative TEM micrograph of the mesostructured ICMUV-2 materials corresponding to sample 3

domly varying the charge density at the organic phase employed up to now, our approach has allowed us not only a wider range of charge variation when comparing with possible variations offered by changing surfactant characteristics, but a continuous modulation of the charge density at the inorganic phase from $q = 0$ to $q = -1$ per vanadium atom.

The approach reported here suggests that it should be possible to design synthetic strategies for the preparation of hexagonal mesostructured/mesoporous materials for inorganic systems in which different accessible oxidation states are possible for the metallic centre by the simple adjustment of the charge at the inorganic framework.

Notes and References

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