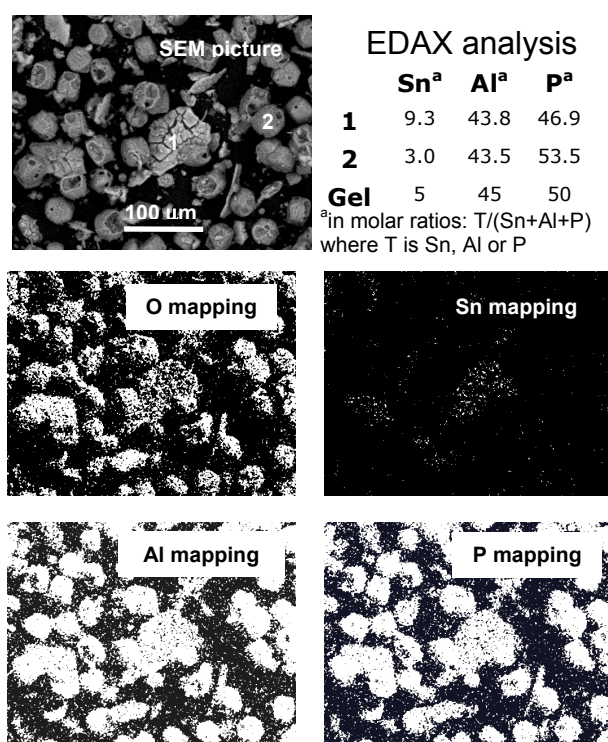


### SEM-EDAX mapping of Sn(IV)APO-5 samples

In order to look for some differences in composition between both kinds of particles constituting the Sn(IV)APO-5 sample (made clear in the main text and Figure 2), a region of the sample Sn(IV)<sub>0.1</sub>APO-5 was studied by mapping-EDAX of the four inorganic elements constituting the framework. The results are shown in Figure S2. Whereas phosphorous, aluminum and oxygen atoms can be found homogeneously distributed in any single particle of the studied region, tin is predominantly found in the shapeless particles, presumably not crystalline. Supporting the mapping results, elemental analysis of the different points in this sample certifies that shapeless particles are at ca. three times more concentrated in Sn than spherical particles. As an example, the elemental analysis results of two particular points (one per each kind of particle) of the SEM picture from Figure 3 are also shown in a Table within Figure 3. Furthermore, chemical analysis confirms that even the particles attributed to crystalline AFI material contain Sn in some extent. On the contrary, similar elemental analysis of the different particles forming the sample Sn(II)<sub>0.1</sub>APO-5 (not shown) confirmed a homogeneous distribution of all elements, including tin, along the particles, and global element contents quite close to those of the starting gel.



**Fig. S1** SEM pictures of the sample Sn(IV)<sub>0.1</sub>APO-5 and the corresponding EDAX mapping pictures of oxygen, phosphorous, aluminium and tin. The table indicates the composition of the points marked by numbers in the SEM picture.

### Clarifying the assignment of the UV-vis bands

The UV-vis band at ca. 225-235 nm appearing in the spectra of Sn(II)APO-5 has not been unequivocally assigned but a couple of possibilities has been pointed out in the main text of this article. To try to clarify those possibilities, Figure S2 shows an enlargement of the UV region (195-265 nm) of the selected samples. The spectra have been moved out along Y-axis to avoid overlappings.

As suggested in the main text, the band whose maximum absorption is near or even below 200 nm is undoubtedly attributed to tetrahedral Sn(II). This band has a shoulder centered at ca. 230 nm, whose origin could be due to:

1. Charge transference from  $O^{2-}$  to  $Al^{3+}$ . Supporting this assignment, Figure S2 also contains the UV region of the spectrum of the  $AlPO_4-5$  sample. This charge transference band has been found in  $AlPO_4-5$  prepared with other structure-directing agents (SDAs) [1,3]. In the case of our  $AlPO_4-5$  sample, it consists on a broad band centered at ca. 220 nm, although its position and shape can be modified either by the incorporation of heteroatoms in the AFI framework, as it has been made clear by comparing UV-vis spectra of  $AlPO_4-5$  to its homologue SAPO-5 [1,2], or by changing the nature of SDA [1]. It could justify the small shift of the band between the spectra of  $AlPO_4-5$  and Sn(II)APO-5. In our opinion, the reason why this band is not more often commented in bibliography is because it appears in a region far away from that of interest when transition metals is the heteroatom [3] whereas it overlaps with the bands of interest in the case of TiAPOs or Sn(IV)APOs.
2. Tetrahedral Sn(IV). Although Sn(II) is relatively stable tin oxidation state, Sn(IV) is

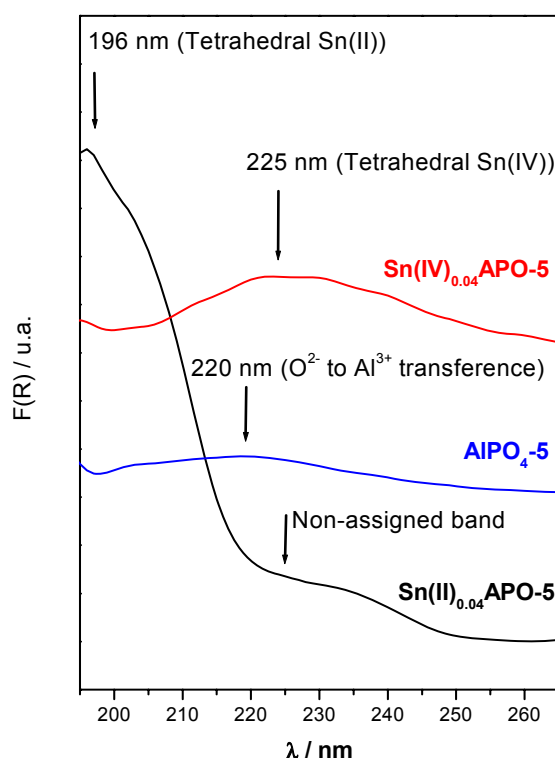


Fig. S2 195-265 nm UV region of  $Sn(II)_{0.04}APO-5$ ,  $Sn(IV)_{0.04}APO-5$  and  $AlPO_4-5$ .

the most stable one in aqueous solution [4]. The added source is Sn(II) but the gel is treated at 170 °C for almost one day. Under these conditions, it is reasonable to think in a possible partial oxidation of Sn(II) to Sn(IV). Figure S2 contains the UV-vis of the sample Sn(IV)<sub>0.04</sub>APO-5, possessing a wide band centered at ca. 225 nm, which has been attributed to tetrahedral Sn(IV), in good agreement with the literature [5]. The comparison of the spectra of Sn(II)APO-5 and Sn(IV)APO-5 supports the partial oxidation of tin in Sn(II)APO-5 sample.

Because none of both possibilities can be ruled out and both are consistent, a unique and unequivocal assignment of the shoulder at ca. 225-235 nm of the spectrum of the Sn(IV)APO-5 samples is uncertain.

### ICP analyses of Sn-contained samples

Table S1 shows the chemical composition of the SnAPO-5 as determined by ICP analyses. General speaking, the samples prepared from gels containing Sn(II) are richer in tin than the samples prepared from gels containing Sn(IV). Indeed, Sn(II)APO-5 are Sn-richer than the Sn(II)-gels whereas Sn(IV)APO-5 samples are Sn-poorer than their gel precursors. It is in good agreement with the efficiency of tin incorporation as a function of the oxidation state of the tin source, widely discussed in the main text.

On the other hand, general speaking, Sn(II) mainly substitutes Al(III) into the AlPO<sub>4</sub> framework, whereas Sn(IV) tends to be incorporated in the P(V) sites, in good agreement with the experiment design. The systematic Al excess of the Sn(IV)APO-5 samples agrees the detection of unreacted Al (5- and 6- coordinated Al) by <sup>27</sup>Al MAS NMR:

**Table S1** Chemical composition of the SnAPO-5 samples, expressed as Sn<sub>x</sub>Al<sub>y</sub>P<sub>z</sub>O<sub>4</sub>

Sample	Sn (x)	Al (y)	P (z)
AlPO <sub>4</sub> -5	0.000	1.015	0.985
Sn(II) <sub>0.04</sub> APO-5	0.046	0.943	1.011
Sn(IV) <sub>0.04</sub> APO-5	0.031	1.097	0.872
Sn(II) <sub>0.1</sub> APO-5	0.124	0.926	0.950
Sn(IV) <sub>0.04</sub> APO-5	0.066	1.030	0.904
Sn(II) <sub>0.2</sub> APO-5	0.269	0.801	0.930

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