Quantify the Maximum Limit Value of the Framework Ti Content in TS-1*

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The substitution of Si^{4+} by Ti^{4+} in titanosilicates is always limited, originally, Taramasso et al. prepared TS-1 with more than ≈2wt% titanium in the lattice. Both XANES and XPS allow to titrate framework tetrahedral Ti and extra-framework TiO_2 anatase species. There was no detectable extra-framework Ti up to 1.5wt% Ti, above 1.5%. A limit of ca.1.8% of Ti incorporation into the framework of the S-1silicalite has been calculated by titration using Raman spectroscopy or using voltametric measurments, XRD and Rietveld calculation of the unit cell expansion led to higher limit of ca.2.5%. Higher level of incorporation of as much as ca.6 and 8% were claimed. Therefore, the maximum of Ti incorporation is still a controversial matter that prompted us to develop a new technique to quantify them.

Ultraviolet diffuse reflectance spectroscopy (DRUV) was one of the first spectral techniques used for the determination of the valence and coordination states of titanium in titanium silicalites. The presence of the ~212 nm band in the spectrum is accepted as evidence of isolated Ti(IV) in the framework position ,whereas the appearance of the band about 330 nm is an indication of extra-framework titanium – containing species . Moreover, this spectroscopy is more sensitive to extra-framework titanium than Raman spectroscopy. So now we develop a new method to quantify the limit value of the framework Ti content in Titanium Silicalites TS-1. This method combines UV-vis spectroscopy characteristic for Ti species with element analysis. First, a series of samples TS-1 were synthesized with different SiO_2/TiO_2 ratio, and these calcined samples were characterized using UV-Vis spectra, no band about 330nm and ~280-400 nm in UV-Vis spectra indicated that Ti content in the sample TS-1 synthesized all is the framework titanium. Secondly, Ti content of these samples described above were determined by the element analysis, thus the maximum Ti content of the sample without extra-framework is the limit value of the framework Ti content in Titanium silicalite TS-1. The limit value of TS-2, Ti-β etc. is also determined by this method.

According to this method described above, a limit of ca. 1.68 mol% of Ti incorporated into the framework of the S-1 silicalite has been calculated in this paper.

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