In situ characterization of porous VPO catalysts with fibrous structure: identifying the redox behavior of active sites

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Two VPO materials with fibrilar morphology have been prepared. One is a VPO carbon-supported material (VCF200) with fibrous morphology and a very high surface area, stable under oxidizing conditions up to 350ºC. The other material is a bulk mixed VPO oxide (VPO500) with fibrous structure obtained after optimizing the calcination of the supported material. This material presents a very high surface area although it is a bulk oxide material (more than 60 m2/g). The redox behavior of both samples was monitored under *in situ* Raman under oxidation/reduction cycles.

For the supported sample, it is detected the pyrophosphate phase $(VO)_2P_2O_7$, which has been described as the active phase, in the dehydrated sample. The results show that this phase, identified by a Raman peak near 930 cm^{-1}, is quite stable, since such band does not disappear under oxidation/reduction cycles. The results show that under reduction conditions, in consecutive cycles, and always around 125ºC, additional Raman bands appear near 1089 and 1090, characteristic of α_{II} $VOPO_4$ phase. The VPO phases that are present in the bulk catalyst are different, but also show a reversible behavior under redox cycles. Under reducing conditions, a Raman band near 980 cm^{-1}, that is identified with the β VPO phase is detected, whereas under oxidation conditions some segregation to VOx oxides occur, although such segregation is reversible and the VPO phase forms again under reducing conditions.

Thus, these results demonstrate that the active VPO phases of these samples are quite stable, and that the structure of the catalysts is reversible under several redox cycles, which make it suitable as catalyst.

Figure: In situ Raman spectra under redox cycles conditions for VCF200 sample