



Experiment title: Structural investigation Of location of Ti(IV) sites in Ti-Silicalite framework and of Si vacancies in defective silicalites

Experiment number: CH257

Beamline:
BM16

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12

Local contact(s):
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Names and affiliations of applicants (* indicates experimentalists):

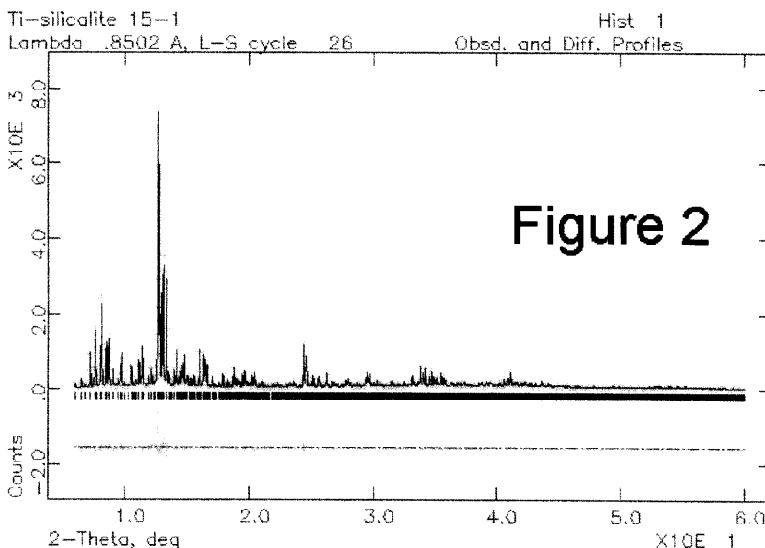
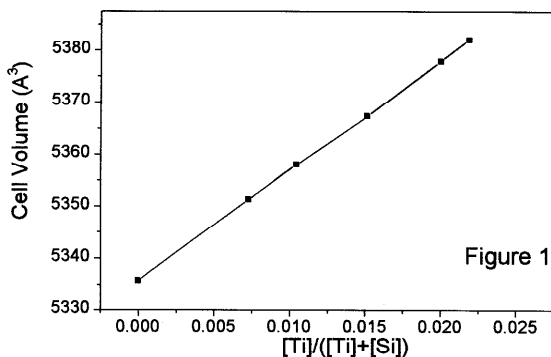
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Report: Ti-silicalite is a zeolitic material that exhibits unique catalytic properties, particularly in selective oxidation reactions employing H_2O_2 as the oxidant (1). Many efforts have been made in the past decade in order to characterize the material and in particular the nature of the catalytic site as well as the role played by Ti atoms dispersed in the zeolitic matrix (2-5). It is now generally accepted that Ti atoms can be incorporated in the framework as Ti (IV), substituting Si atoms and so occupying tetrahedral positions (2-5). The isolated Ti (IV) species are supposed to have a relatively high propensity to expand their coordination sphere (up to six) upon adsorption of molecules, such as the reagent species in the catalytic reaction (3-5).

The XRD measurements of Millini *et al.* (2) have evidenced that, for well manufactured Ti-silicalites, the unit cell volume increases linearly with the Ti loading of the sample: measurements of that work were performed on hydrated samples. This means that all Ti centers coordinate up to 2 water molecules (3-5) with a direct consequence on the cell parameters. In this experiment we have measured a set of Ti-silicalite samples with Ti content ranging from 0 (reference silicalite) to 0.022 ($[Ti]/([Ti]+[Si])$) in carefully dehydrated conditions, following the same experimental procedure already successfully adopted during experiment **CH-107** (6). As proof of the Ti insertion (substitutional to Si in MFI framework), in Fig.1 we report the variation of the cell volume vs. the Ti loading under dehydrated conditions: the linearity of these data are remarkable and is to be compared with the results of Millini *et al.* (2) obtained on hydrated samples.

A second important result is that our experimental data confirm the theoretical calculations of Jentys and Catlow, who claimed (7) that all the T sites in MFI framework are **equivalent**, from an energetical point of view, for Ti insertion. In fact, the Rietveld refinement (Fig. 2) doesn't observe any preferential Ti site.



References

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