

Optimum calcination temperature in the synthesis of a N-C-S co-doped TiO₂ photocatalyst, as monitored by neutron diffraction

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Abstract. Calcination of a co-doped (N-C-S) TiO₂ photocatalyst has been done following the whole process by neutron diffraction (instrument D1B of the ILL) with the objective of study the transition between two crystalline phases: anatase and rutile in order to find the optimum temperature leading to the coexistence of both for this catalyst whose band gap has been shifted to give activity in the visible part of the electromagnetic spectrum. This coexistence is important as it has been established that these catalyst are more efficient than those having only one individual phase. At this respect, it is very important to find the optimum temperature at which synthesis has to be done. In this research it was established that at the heating ramp of 17°C/5 min, the coexistence of both crystalline phases took place within a narrow margin of temperatures between 610°C and 690°C. At higher temperatures only rutile can be identified as the crystalline phase of the TiO₂.

1. Introduction

The discovery of the photosplitting of water in semiconductor-based photoelectrochemical cells by Fujishima and Honda in the earlier 1970 [1] was the origin of a flourishing interest in photocatalysis, initially focused on energy production from water and light and later also on degradation of environmental pollutants in water and air. The crystalline phases of TiO₂ most frequently used in photocatalytic applications are anatase and rutile, with band gaps of 3.26 and 3.05 eV respectively [2], that correspond to absorption of wavelengths in the near-ultraviolet region. This fact cause impediment for the photocatalytic degradation of contaminants under conditions with poor illumination or lack of UV light, for example indoor environments and road tunnels. To enhance the advantage of present and common light sources, the development of visible light active TiO₂ can be of considerable interest.



The red-shift in absorption to visible light of photocatalytic materials can be induced by the incorporation of foreign elements in the semiconductor material. Previously employed methods are impregnation of the surface [3-4], integration of the foreign atoms in substitutional or interstitial positions of the semiconductor crystal structure by either ion implantation [5] or chemical synthesis [4]. This produces changes inside the electronic band structure by formation of intermediate states inside the forbidden gap or by deformation of the band itself. Co-doped titanium active photocatalyst have received much attention during the last decades for its promising impact on environmental protection, and it is known that the microstructure of the photocatalytic materials has a critical role on the photocatalytic activity [6] being the mixture anatase-rutile more active than both phases by itself. The synthesis and the preparation of photocatalytic active titanium dioxide have an important influence on the microstructure but also the calcination procedure plays a significant role, when increasing the temperature the transformation of anatase to rutile is enhanced [7,8]. Therefore it is important to find in each case, the calcination temperature that leads to the formation of the two phases in an optimum way.

In this work, an N-C-S- co-doped photocatalyst synthesized by the authors [9] have been monitored by neutron diffraction under controlled calcination, following the transition between anatase and rutile trying to find the range of coexistence for this catalyst.

2. Experimental

TiO₂ based photocatalysts were synthesized following the method described in [10], with some modifications. Titanium isopropoxide was used as precursor and thiourea ((NH₂)₂CS) was used to introduce dopants into the crystal network of TiO₂, provided that it contains the three species.

The synthesis was as follows: pure thiourea (53.6 g) was dissolved during continuous stirring in 700 ml ethanol, heated to 65°C. Titanium isopropoxide (50 g) was then added slowly and let to stir during 1 h. The solution was concentrated under reduced pressure resulting in the formation of white slurry that was left to dry in room temperature for 2 days to obtain a white powder.

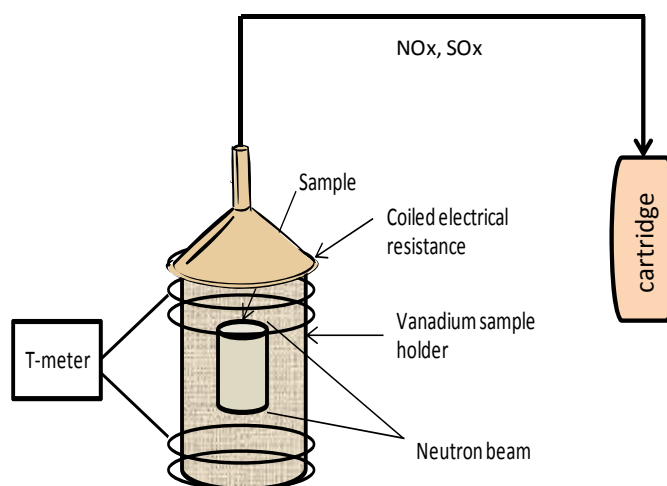


Figure 1. Experimental set up.

Samples were calcinated at the CRG-two-axis diffractometer D1B place in the Institut Laue-Langevin in Grenoble (France), being monitored on site by taking continuous diffraction patterns of the process. A schematic representation of the experimental device can be seen in Fig. 1.

A coiled electrical resistance, connected to a temperature programmer and to a data logger was used to heat the sample. It was opened resulting in a gap in its structure in order to avoid overlapping

of their peaks in the spectrum acquisition. During the experiment they were kept inside of a vanadium sample holder with a high of 10 cm, an external diameter of 8.5 cm and an internal diameter of 4.8 cm. It was also tested a sample holder made of ceramic; however, it was discarded because the neutron diffraction spectrum of the catalyst was highly influenced by the composition of the ceramic. The sample was connected to a cartridge of activated charcoal in order to capture the SO_x and NO_x gasses being resulting from the calcinations. This is the reason why a conventional furnace was not used, to be able to safely recover the gasses. Heating followed a temperature ramp: 17°C/5 min, until 820°C.

D1B diffractometer was chosen because of its high efficiency position sensitive detector (PSD) which makes it suitable for real time experiments and for very small samples. The vertical distribution of neutron beam during the experiment was wide enough to cover the whole sample. The wavelength of the experiment was 2,52Å.

3. Results and discussion

Several peaks were identified during the different steps of the experiment; some of them were due to the presence of the vanadium sample holder, others correspond to the different crystalline phases of the titanium dioxide. In Figure 2 an example of diffraction patterns at different temperatures in the region between values of 2 theta of 60 and 74 (in order to avoid overlapping) are presented. As can be seen in Fig. 2 at the beginning of the experiment (T=25°C) there are no peaks in the region of interest. During the experiment the shape of the diffraction patterns varies and a small peak can be seen growing when the temperature reaches 450°C at 2 theta value between 66 and 67. This peak can be an indicative of the formation of anatase.

The transition between both crystalline phases can be established when the temperature reaches 653°C. In the pattern depicted in Fig. 2 it can be seen a remaining peak corresponding to anatase and two new peaks corresponding to the formation of rutile (2 theta = 67.2 and 71). At the end of the experiment (T = 820°C) there is no anatase in the sample and another peak corresponding to rutile appears (2 theta = 69.3). It is also represented the evolution of the diffraction pattern when cooling noting that the most intense rutile peaks remain without presence of anatase.

According to the results obtained it can be said that there is a coexistence of both crystalline phases in a very small range of temperature, between 610°C and 690°C. This coexistence disappears when heating.

Figure 3 represents the projection in two dimensions of the experiment since the beginning till the end of the experiment in function of the temperature in °C where, marked as a shaded band, it can be seen the narrow margin of coexistence of both crystalline phases, between 610°C and 690°C.

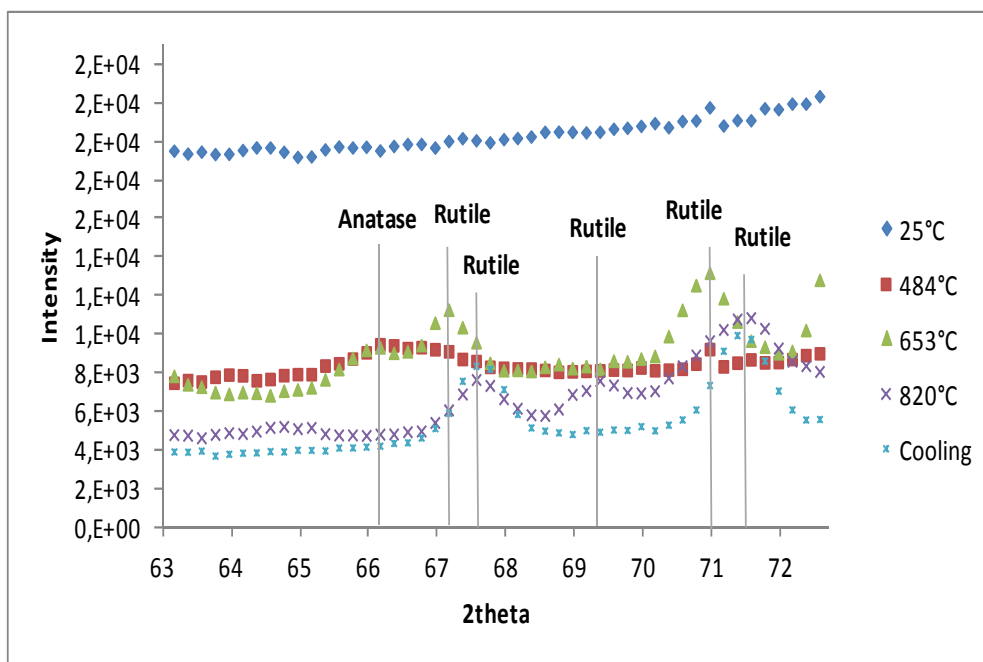


Figure 2. Diffraction patterns at different temperatures.

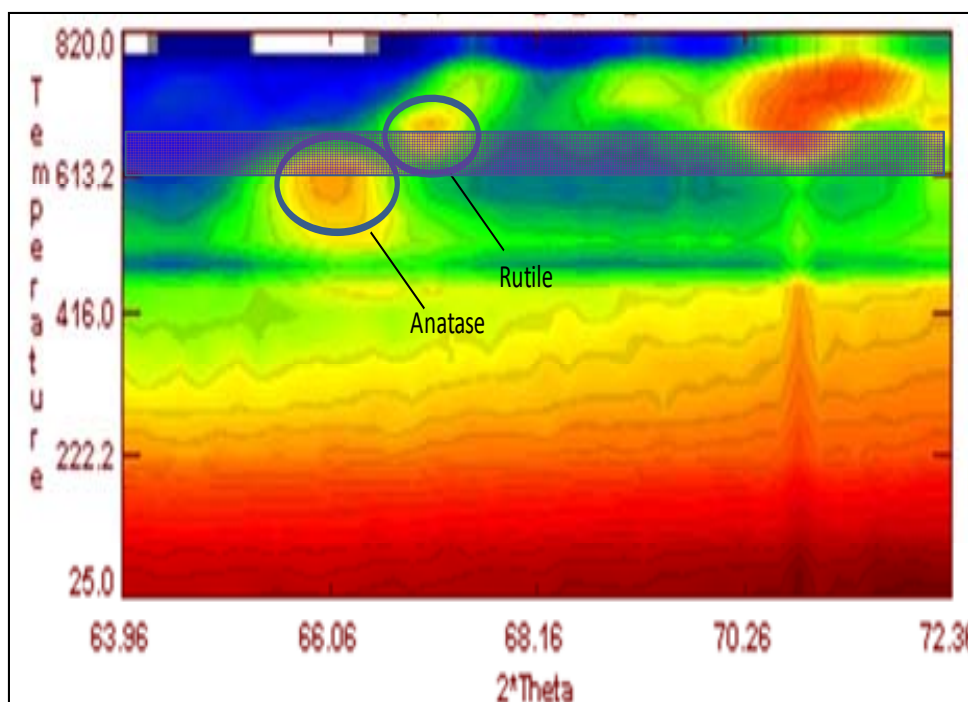


Figure 3. Contour plot of the experiment. The range of coexistence of anatase and rutile has been marked as a shaded band.

4. Conclusions

In this research the evolution of the phase transition anatase \rightarrow rutile in a co-doped N-S-C titanium active photocatalyst was followed by means of neutron diffraction. At the heating ramp of 17°C/5 min, the coexistence of both crystalline phases was established within the margin of temperatures between 610°C and 690°C, disappearing when heating and remaining only the crystalline phase rutile.

Acknowledgements

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