



	Experiment title: Strong metal-support interactions in Pt/TiO ₂ catalysts: Elucidating mechanisms, structures and kinetics using combined, time resolved high energy XRD/PDF and DRIFTS/MS	Experiment number: CH-5670
Beamline: ID15A	Date of experiment: from: 29/06/2021 to: 05/07/2021	Date of report: 13.09.2021
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Report:

The phenomenon of strong metal support interactions (SMSI) in catalysis has been long known. This phenomenon manifests as a gross reduction in the capacity of metal nanoparticles (e.g. Pt) anchored upon reducible oxides, such as TiO₂, to adsorb gases after high temperature treatment. The most widely accepted mechanism, as this is what is observed in electron microscopy, is “direct encapsulation”, wherein a partial reduction of the support around the Pt metal/oxide interface occurs first. This is followed by encapsulation of the metal nanoparticle by an oxidic shell.

During the present experiments, we investigated this phenomena studying two different Pt/TiO₂ catalysts. One catalyst with the anatase and the other with the rutile crystal structure. By employing time resolved high-resolution powder X-ray diffraction (HR-PXRD) and high-angle pair distribution function (PDF) measurements, we captured the response of the catalyst structure to a change in the gas atmosphere.

We covered a temperature range from room temperatures up to 700 °C (in 100 °C steps) and performed different experiments with alternating gas atmospheres (Ar → H₂ → Ar → O₂) as well as switches from Ar to only one of the two gases (H₂ or O₂). The big amount of condition space that we covered in the series of experiments gives us the confidence that we will be able to construct a condition-structure map of the catalysts, which will contain structural understanding to level of detail not described before.

Our initial analysis of the data (Figure 1+2) suggests that there are severe structural changes occurring and that the behaviour is strongly dependent on the underlying structure of the TiO₂. Figure 1 depicts the Pt(111) reflection at 400 °C evolving with time while the gas atmosphere was changed. It can be found that the Pt reflection of the rutile catalysts responds to larger degree than the anatase catalyst. Yet, in both samples changes are visible and especially changes in the background are observed. Using the PDF data, we hope to also decipher the contribution of amorphous phases to the structure.

As the temperature was increased the observed reversible and irreversible changes within the catalyst's structure became much more pronounced. As can be seen in Figure 2, when the same gas switches were carried out at 700 °C. The platinum reflection underwent much more substantial transformations. For the anatase catalyst under hydrogen the platinum reflection weakens strongly in intensity while the reflection also shifts to higher angles which hints at a contraction of the Pt unit cell. For rutile, a similar shift of the reflection can be seen, however the peak is not decreasing in intensity. This preliminary analysis reveals that there are substantially different mechanisms at work which involve the Pt and TiO₂ phase.

The successfully acquired data is currently analyzed.

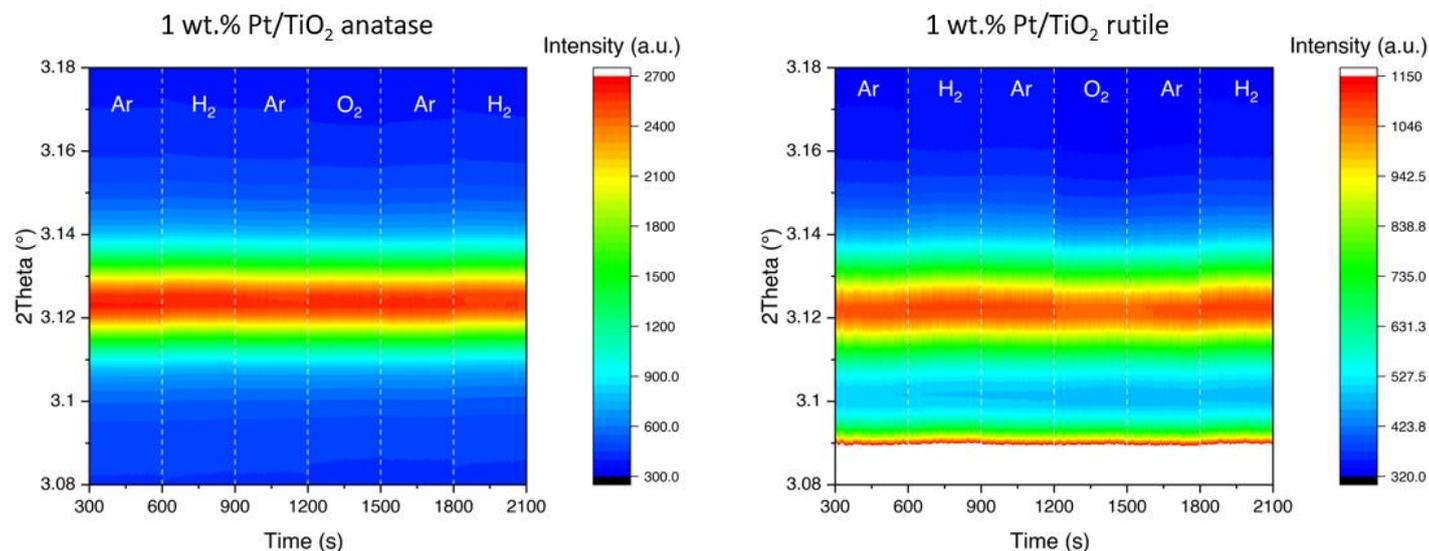


Figure 1: Contour plots of the Pt(111) reflection region at 400 °C of the acquired high-resolution diffraction patterns during dynamic switches between Ar, H₂, and O₂ (as indicated) of the two tested catalysts of Pt/TiO₂ with either anatase or rutile structure.

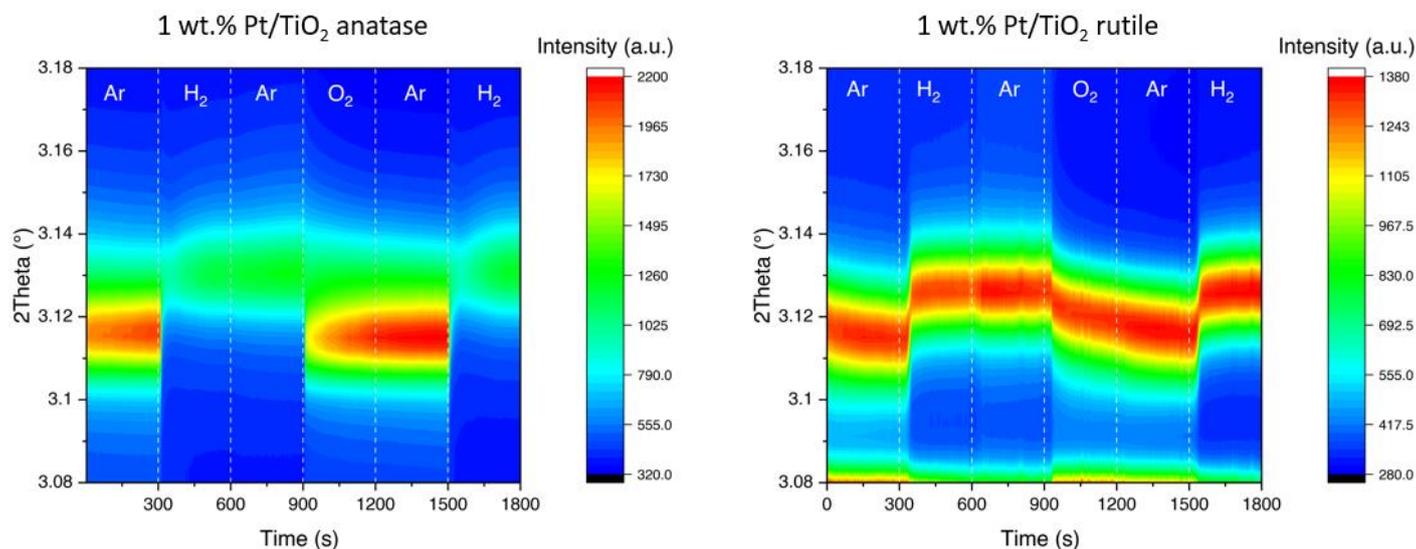


Figure 2: Contour plots of the Pt(111) reflection region at 700 °C of the acquired high-resolution diffraction patterns during dynamic switches between Ar, H₂, and O₂ (as indicated) of the two tested catalysts of Pt/TiO₂ with either anatase or rutile structure.