

***Operando* S/TEM Reactions of Pt/TiO₂ Catalysts for Catalytic Fast Pyrolysis**

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Conversion of lignocellulosic biomass into the transportation fuel is an attractive concept [1]. Using *ex situ* Catalytic Fast Pyrolysis (CFP) improves to upgrade bio-oils via catalytic deoxygenation of the biomass pyrolysis vapors. Zeolites are often used in this technique as the catalyst; however, in order to reduce minimum fuel selling price and improve carbon yields, ongoing research emphasizes catalyst optimization [2]. By using bifunctional metal-acid catalysts and utilizing hydrogen, it is possible to improve carbon yields by minimizing the carbon-containing light gasses (since oxygen is removed as water) and by reducing coke formation. Current research and development activities focuses on Pt/TiO₂ catalysts as the most promising catalyst candidates for the hydrodeoxygenation process. The aim of this research is to determine the structure-function relationships of the Pt/TiO₂ catalyst and the role of Pt dispersions within the catalyst on performance, using *operando* scanning transmission electron microscopy (S/TEM).

Operando closed gas-cell *in situ* electron microscopy was used to study a reaction sequence applied to the lower-cost bifunctional 0.5 wt.% Pt/TiO₂ catalyst. In this study, an aberration-corrected JEOL 2200FS STEM/TEM instrument was used, which is equipped with a CEOS GmbH (Heidelberg, Ger) probe corrector and a MEMS-based closed-cell *in situ* reactor system (Protochips Atmosphere™) integrated with a residual gas analyzer (RGA) on the outlet side [3,4] to study materials behavior at the atomic level. Further, this arrangement allows to run *operando* experiments with quantitative measurements of gas composition and to confirm the environmental conditions during *in situ* STEM testing.

The catalyst was prepared via strong electrostatic adsorption to finely disperse Pt particles [2,5]. STEM analysis showed a uniform distribution of Pt particles (2.7±0.4nm) across the TiO₂ support. STEM, XRD and XPS confirmed the presence of metallic Pt, and TiO₂ support particles of about 20.1±4.4 nm size range. For the *in situ* STEM experiments, the fresh Pt/TiO₂ catalyst was crushed and sonicated in ethanol to obtain catalyst particle aggregates that when dispersed on a Protochips E-chip heater would easily fit within the nominal 5 μm gap between the heater and lower SiN window of the gas-cell [6]. The gas-cell was purged two times with nitrogen from 100 to 0.1 Torr to remove residual O₂, and then a final purging step of 100 to 0.01 Torr. The gas-cell was filled with 100% H₂ at 760 Torr and the catalyst was heated at 10°C/min. to 400°C under flowing H₂ and held for 1 hour. Then, the catalyst was exposed to 1% O₂-99N₂ for an additional hour. Afterwards, the temperature was increased under flowing H₂ and catalyst was again exposed for 1 hour first to H₂, and then to 1% O₂-99N₂, followed by an increased oxidizing condition (50% O₂-50N₂). The partial pressure was recorded (Fig. 1a) and particle size was measured for each condition (Fig. 1b). At 400°C the differences were marginal. However, exposure at 500°C showed formation of larger particles (identified as metallic Pt with a space group Fm-3m(225)) and presence of TiO under H₂, whereas under oxidizing condition smaller oxidized particles (PtO₂ with space group of Pa-3(205)) were found. Figure 2 shows an example of the catalyst after 1 hour at 500°C under H₂ (Fig. 2a) and 1% O₂-99N₂ (Fig. 2b). There was a change in the Pt particle size and character (metallic vs. oxide). These studies show the effect of the environment on structure and morphology of the catalytic species, using *operando* S/TEM capabilities to reliably perform a reaction sequence that enables research to accelerate catalyst development [7].

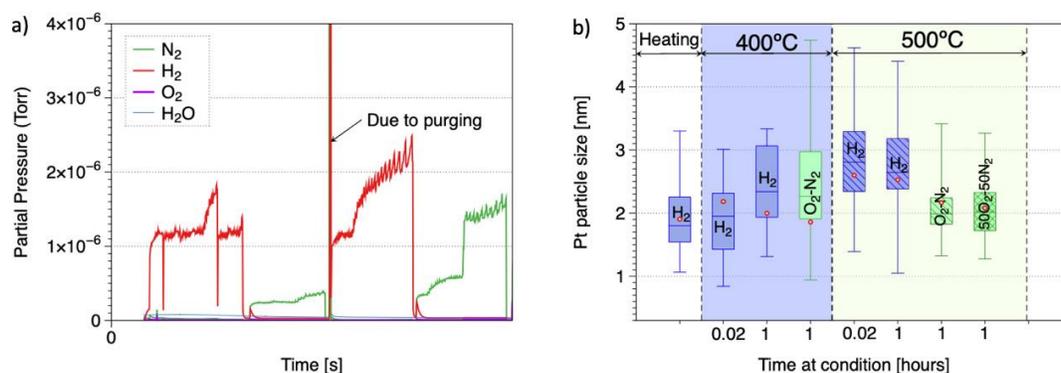


Figure 1. a) Partial pressure vs. time acquired during in situ STEM reaction of Pt/TiO₂ on the outlet side of the TEM holder. b) Pt particle size measurements at different exposure condition

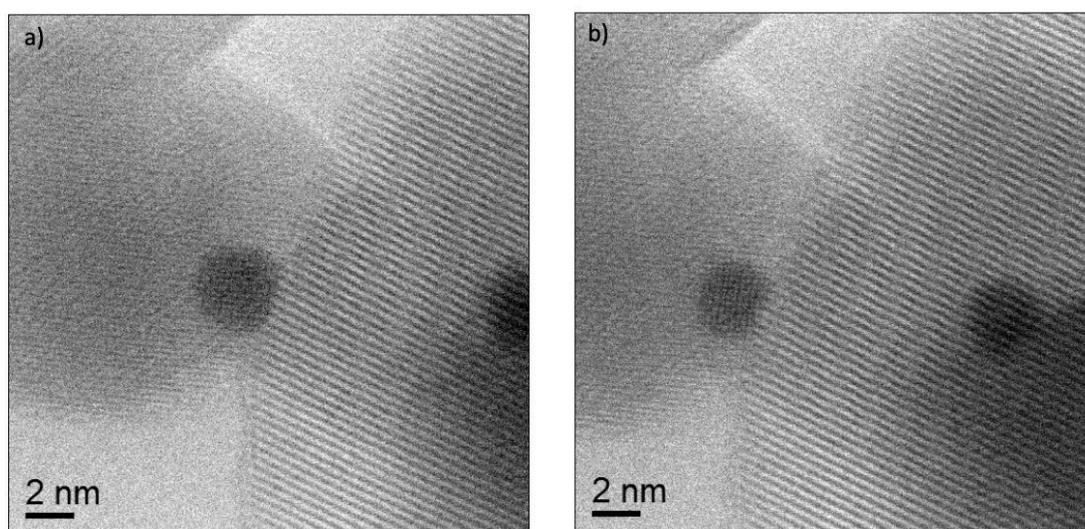


Figure 2. BF-STEM images of Pt/TiO₂ catalyst acquired under series of reaction conditions at 500°C at ~750 Torr after 1h under flowing H₂ (a) and under flowing 1% O₂-99% N₂ (b).

References

- [1] JC Serrano-Ruiz and J. A. Dumesic, *Energy Environ. Sci.* **4** (2011) p.83.
- [2] MB Griffin et al., *Energy Environ. Sci.* **11** (2018) p. 2904.
- [3] KA Unocic et al., *Microsc. Microanal.* **24** Suppl. 1 (2018), p. 286.
- [4] KA Unocic et al., *Microscopy and Microanalysis 2020 (accepted)*.
- [5] J. T. Miller et al., *J. Catal.*, 225 (2004) p.203.
- [6] KA Unocic et al., *Oxid. Metals* **88** (2017) p.495.
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