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 situreactor system (Protochips AtmosphereTM) 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 um 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 F m -3 m(225)) and presence of TiO under H₂, whereas under oxidizing condition smaller oxidized particles (PtO₂ with space group of P a-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].



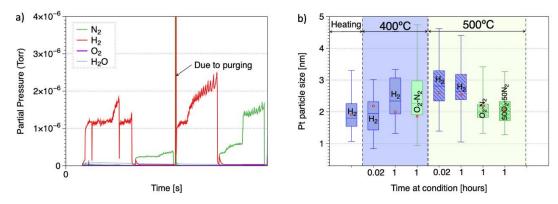


Figure 1. a) Partial pressure vs. time acquired during in situ STEM reaction of Pt/TiO2 on the outlet side of the TEM holder. b) Pt particle size measurements at different exposure condition

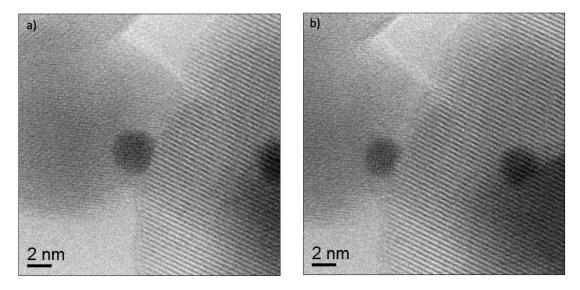


Figure 2. BF-STEM images of Pt/TiO2 catalyst acquired under series of reaction conditions at 500°C at ~750 Torr after 1h under flowing H2 (a) and under flowing 1%O2-99%N2 (b).

References

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