



	Experiment title: Study of the effect of Mn on PtMn/C catalyst in aqueous phase reforming of ethylene glycol	Experiment number: A31-1-193
Beamline: BM31	Date of experiment: from: 08 Feb 2023 to: 13 Feb 2023	Date of report: 10 Oct 2023
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Report:

Aqueous phase reforming (APR) is a process proposed by Dumesic and co-workers to produce H₂ from biomass-derived waste streams at relatively mild reaction conditions [1]. These hydrothermal conditions favor the production of H₂ with low concentrations of CO but promote side reactions such as methanation and Fisher-Tropsch synthesis, compromising the overall H₂ yield [2]. Additionally, the stability of the catalyst is affected during APR, with metal leaching, sintering and coke deposition as the main deactivation mechanisms [3].

Carbon materials possess good hydrothermal stability compared to metal oxides, are resistant to acidic and basic media, and the physical properties can be tailored, such as surface functionalization and heteroatom doping, to tune the electronic properties of the active phases and favor the catalytic activity [4]. It has been previously reported [5] that an enhancement in the catalytic activity in Pt-based catalysts supported on nitrogen-doped carbon nanofibers is attributed to metal-support interactions that decrease the electron density of Pt, promoting H₂ formation. Hence, a way to modify the Pt active phase to increase the activity while maintaining the H₂ selectivity can be related to metal-support interactions.

This study chose typical carbon dopants such as oxygen, nitrogen, sulfur, phosphorous, and boron based on their properties that can bring acidic or basic functional groups to the carbon surface. Hence, doped carbon nanofibers (CNF-HT, N-CNF, S-CNF, P-CNF, B-CNF) were used as catalyst support with Pt as the metal phase during APR of ethylene glycol to identify the platinum oxidation state and species formed during the reaction. Due to the large percentage of Mn leaching (95%), it was decided to study only the monometallic catalyst based on platinum. Hence, this study aims to correlate the electronic state of the catalyst with the catalytic activity.

Experimental Method:

In-situ XAS-XRD experiments were conducted at BM31 of the Swiss-Norwegian beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF). The catalyst samples, which were within the 120-200 μm sieve fraction, were inserted into a quartz capillary tube with a 2.0 mm internal diameter and a 0.02 mm wall thickness. At both ends of the 1 cm long catalyst bed, quartz wool plugs and segments of Kapton polyamide tubing (provided by MicroLumen) were added to secure the catalyst in position throughout the reaction. The capillary reactor was mounted in a custom stage and exposed to X-rays while the capillary temperature was regulated using a hot air blower (Figure 1 (a)). X-ray absorption spectra were collected at the Pt L_3 edge (11.564 keV) using transmission mode for the data acquisition.

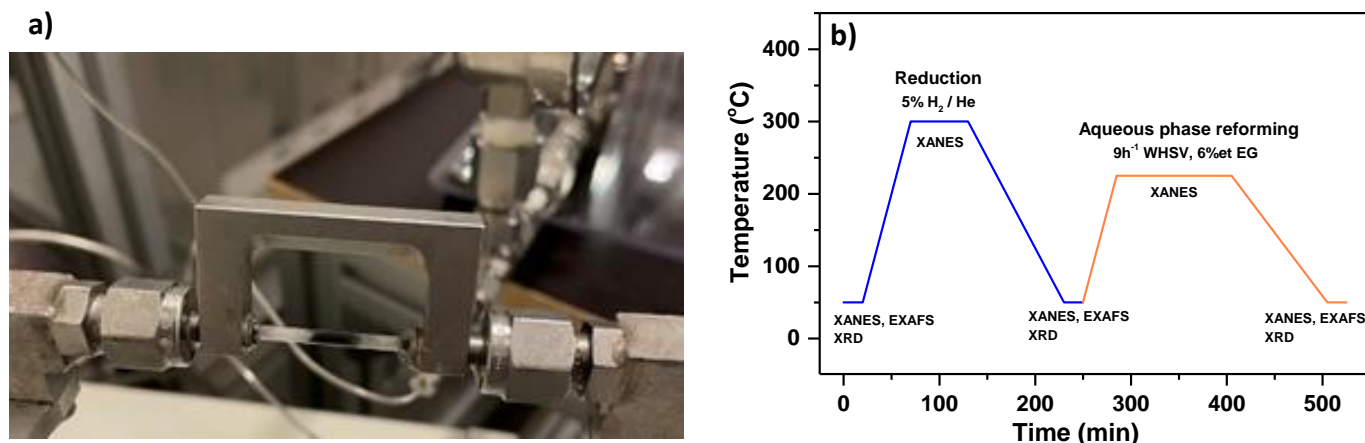


Figure 1. a) Capillary used for the in-situ studies. b) Experimental procedure followed for the in-situ studies, reduction at 300°C in 10% H₂/He and aqueous phase reforming of ethylene glycol at 225°C and 30 bars for 4 hours.

The experimental procedure followed for each samples is presented in Figure 1 (b). In short, after a reduction step (10% H₂/He - 5°C/min ramp, 300°C 1h), the catalysts is exposed to 6% w/w EG in H₂O at 30 bars. The reaction is studied at 225°C while monitoring the outlet gases via an online micro-GC and a mass spectrometer.

Results:

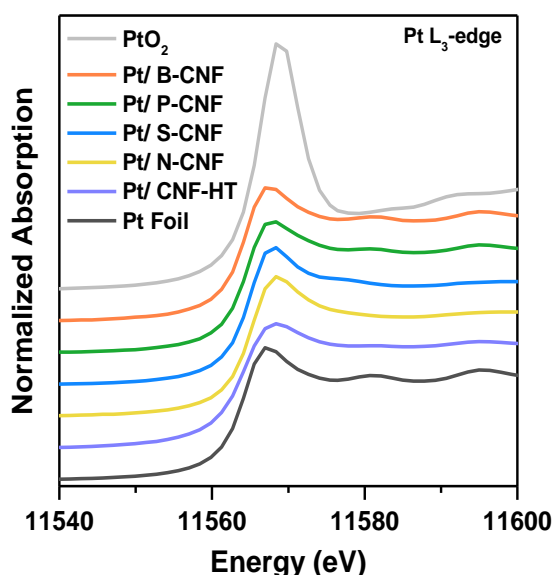


Figure 2. XANES spectra at the Pt L_3 -edge of reduced Pt/X-CNF catalysts in comparison to Pt foil and PtO₂ references

The Pt L_3 XANES spectra shown in Figure 2 for the Pt/X-CNF catalysts reveal that the catalysts are in a reduced state after being exposed H₂ flow at high temperatures, 300°C. Distinct changes in the intensities and profile of the spectra, in comparison to Pt foil, are observed and can be attributed to variations in the chemical environment of the absorbing atom (Pt).

Multivariate curve resolution with alternating least squares method (MCR-ALS) was conducted on the XAS spectra collected during aqueous phase reforming of ethylene glycol (Figure 3). This study revealed the contributions of different species in the catalyst of the doped-carbons with the various heteroatoms. Platinum species were directly coordinated with the heteroatoms in the carbon supports containing S, P and N presenting contributions of PtS, PPt and PtN. While in the catalyst supported on B-CNF, no contributions of Pt-B could be detected, observing only contributions from Pt-O and Pt-Pt, which could be attributed to oxidized boron species in the carbon surface interacting with the platinum nanoparticles.

It is important to approach the nitrogen contribution results with caution, as the limitations of XAS make it difficult to differentiate between Pt-C, Pt-N, and Pt-O due to their similar scattering amplitudes of C, N, and O. Therefore, a careful interpretation of the

results is necessary to avoid any misinterpretation. Further analysis of the data, in conjunction with other characterization techniques, is being conducted to establish a successful correlation between the catalyst structure and the observed differences in catalytic activity.

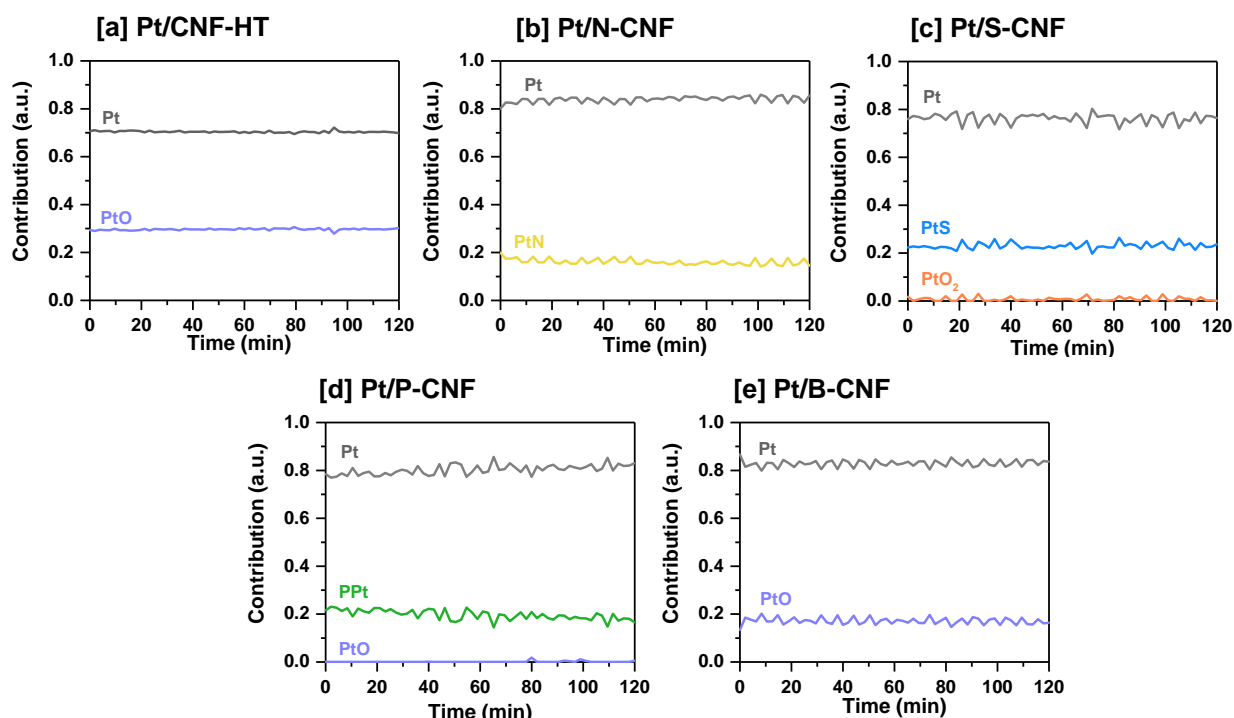


Figure 3. MCR-ALS results from the normalized XANES spectra at the Pt L3-edge acquired during APR of ethylene glycol including the contribution of the species according to standards [6]. [a] Pt/CNF-HT [b] Pt/N-CNF [c] Pt/S-CNF [d] Pt/P-CNF [e] Pt/B-CNF.

References

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