



Experiment title: Operando XAS-XRD studies of bimetallic Pt-Mn/carbon nanofiber catalysts for aqueous phase reforming (APR)

Experiment number:
A31-1-166

Beamline: BM31	Date of experiment: from: 30 Nov 2021 to: 06 Dec 2021	Date of report: 10 Oct 2023
Shifts: 15	Local contact(s): Dragos constantin Stoian (email: dragos.stoian@esrf.fr) Wouter Van beek (email: wouter@esrf.fr)	<i>Received at ESRF:</i>
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Report:

Catalytic conversion of biomass via aqueous phase reforming (APR) has been demonstrated as a feasible hydrogen production process [1]. The reaction takes place at low operating temperatures (220- 250°C) and moderate pressures (20-50 bar) favouring the overall energy efficiency of the process. The high chemical functionality of the biomass used as a feedstock on the APR process leads to non-desired products that reduce the total yield and affect the catalyst stability [2]. The selectivity for H₂ production can be adjusted based on the active metal, catalyst support, feed composition, and process conditions.

Platinum-based catalysts are commonly used for APR, obtaining moderate activity and high hydrogen selectivity. Several groups have focused on modifying the catalyst to improve the catalytic activity without compromising hydrogen selectivity. Adding manganese to the platinum-based catalyst enhances the catalyst activity while maintaining high H₂ selectivity [3,4]. However, it has been observed that under APR reaction conditions, the catalyst may suffer deactivation caused by the sintering of the metal nanoparticles or metal oxidation that leads to metal leaching [5]. Therefore, in this study, we examine monometallic (Pt) and bimetallic (PtMn) catalysts supported on carbon nanofibers (CNF) to obtain information about their chemical state, local environment, and possible alterations under the APR reaction conditions.

Experimental method:

A sieved catalyst fraction (150-250 µm) was used for the operando XAS measurements at the BM31 beamline. A high-pressure cell with a gas/liquid dosage system was employed; designed at the Karlsruhe Institute of Technology (KIT) [6] for high-pressure applications (Fig. 1). The high-pressure cell is designed for simultaneous XAS and XRD measurements and is constructed of stainless steel with large solid angle openings.

The upper and bottom sides of the catalyst bed are fixed with 1.5 mm thick PF-60 Be foils (Materion, USA) sealed with graphite foils. The X-ray beam can pass through a 10 mm × 2 mm slit cut on the “outer” part of the cell, probe the catalyst bed and exit on the opposite side. The reactive gases are passed through the cell via a distributive inlet and outlet to ensure a homogeneous gas distribution in the catalyst bed. Up-flow configuration is used to assist the transport of the gas products, which is important for good signal of the spectra. The cell is heated by two 160 W heating cartridges (HORST, Germany). The temperature is controlled by an HT MC11 temperature regulator (HORST, Germany) and measured by a NiCr/Ni (type K) thermocouple mounted close to the reactor bed inside the stainless-steel body.

Initially, a reduction of the catalyst at 300°C in 5% H₂/He flow is conducted, followed by aqueous phase reforming of ethylene glycol for 4 hours on stream. The reaction products are monitored by an online MS and a μ GC. The reaction mixture (6% wt ethylene glycol-water) was introduced with an HPLC pump at 0.02 ml/min, and the entire system was pressurized to 30 bar and heated to 225°C. The electronic state of Pt and Mn in monometallic and bimetallic catalysts during catalyst activation and aqueous phase reforming was studied by measurements at Pt L₃ edge (11 564 eV) and Mn K edge (6539 eV) in transmission mode.

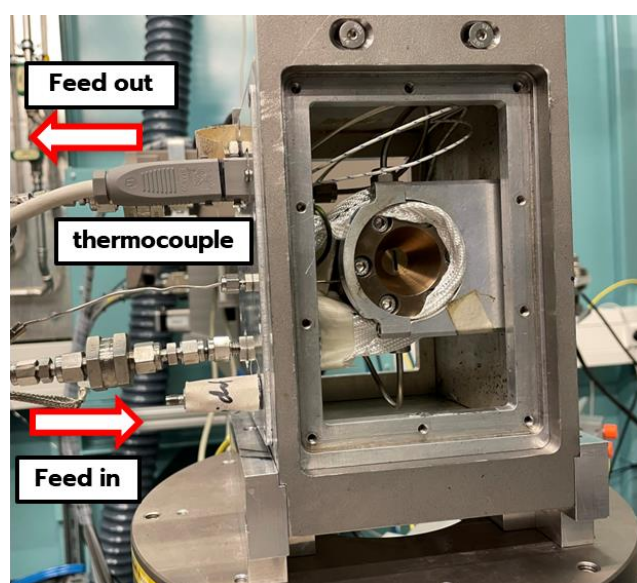
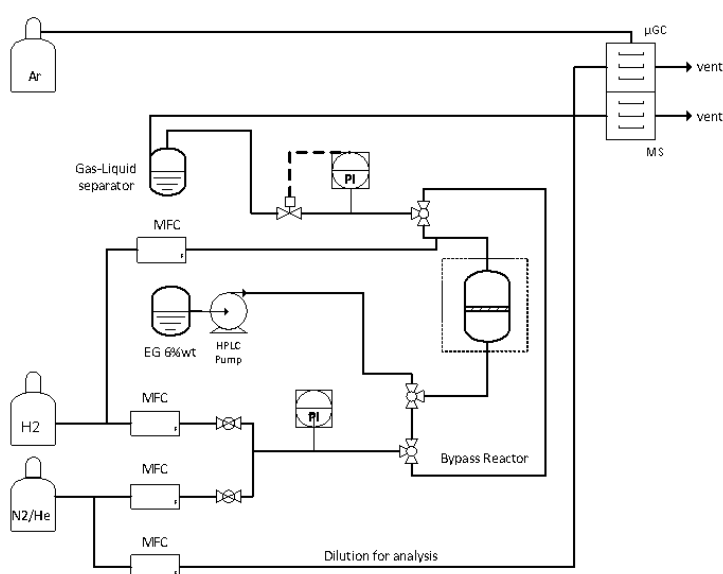


Figure 1. (left) Process flow diagram for the gas dosage system and the high-pressure operando cell. (Right) high pressure cell used to conduct the experiments.

Results:

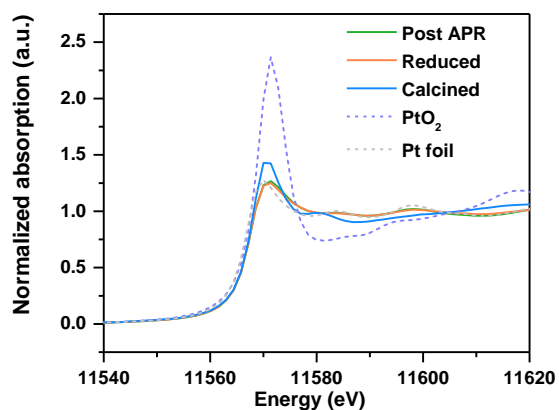


Figure 2. XANES spectra of PtMn/CNF-HT at Pt L_{III}-edge from the calcined catalyst, after the reduction procedure, after 4 hours of aqueous phase reforming of ethylene glycol at 225°C and 30 bars, PtO₂ and Pt-foil.

Analyzing closer the catalyst containing Pt and Mn supported in carbon nanofibers, Pt was identified in the calcined catalyst, the reduced catalyst, and the catalyst after 4 hours of aqueous phase reforming of 6% wt ethylene glycol. The XAS spectra acquired during catalyst activation in 5% H₂/He and under the reaction conditions indicate a predominantly reduced state of the noble metal component (Figure 2). At an initial examination, a stable form of Pt could be observed through the 4 hours of reaction, with no observable differences between the XAS spectra of the reduced and post-APR catalyst.

During the measurement of the Mn K-edge, it was found that there were traces of Fe in the catalyst attributed to the synthesis catalyst used in the growth of carbon nanofibers. Furthermore, the beryllium windows used to seal the high-pressure cell had a low amount of iron. As a result, the presence of Fe caused interference in the EXAFS

measurements conducted on the Mn K-edge. Thus, A combined analysis of Pt LIII edge and Mn K-edge was not performed; nonetheless, the EXAFS fitting in k-space ($3 < k < 12$) of the Pt LIII-edge was employed to determine the local environment of the Pt atoms comparing the reduced catalyst and the catalyst after the reaction, as presented in Figure 3. A slight increase in the Pt-Pt coordination number from 8.4 to 9.9 was observed, in agreement with the post-characterization of the catalyst by CO-chemisorption, following a decrease in dispersion. This trend indicates a slight level of sintering of the Pt nanoparticles during the reaction. A small coordination number is estimated for Pt-Mn after the reduction (0.78), and after aqueous phase reforming, it becomes almost negligible due to the considerable uncertainty of the value. Furthermore, after APR, the Pt-Pt bond distance closely approximates that of the Pt foil, varying from 2.69 Å after reduction to 2.76 Å after the reaction, suggesting a change in the local environment of Pt. This change was associated with Mn leaching during the process, observed as well by a decrease of the edge step on the Mn-K edge and verified subsequently by measures of metal loading of the fresh and used samples, estimating a 95% loss of Mn during the aqueous phase reforming of ethylene glycol.

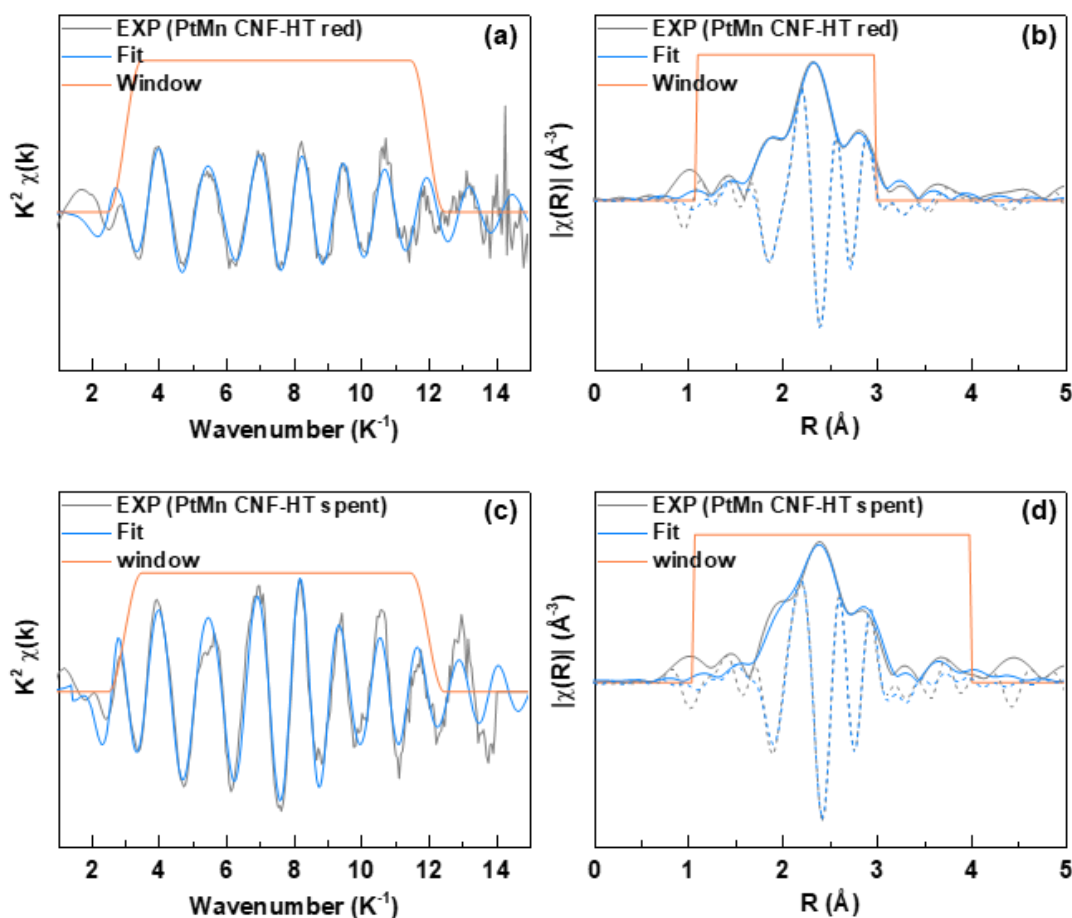


Figure 3. Pt L_{III}-edge EXAFS [a] Fit of the k^2 weighted EXAFS spectra and [b] corresponding Fourier transforms of PtMn/CNF-HT after catalyst reduction. [c] Fit of the k^2 weighted EXAFS spectra and [c] corresponding Fourier transforms of PtMn/CNF-HT after APR of ethylene glycol at 225°C and 30 bars (WHSV = 9h⁻¹)

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