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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

Names and affiliations of applicants (* indicates experimentalists):

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Report:

During the beamtime we have investigated two sets of samples, metal-organic frameworks (MOFs) functionalized by palladium and supported alloyed PdZn nanoparticles, during the reaction of catalytic hydrogenation of carbon dioxide. The results for the latter samples was recently submitted (Ahoba-Sam, et al. Catal. Sci. Technol. Under Review), the abstract is shown below. For the MOF-based samples, all experimental data from the beamtime is analyzed and some additional laboratory work is required to complete the manuscript. The results obtained for this sample are summarized below.

Abstract of the submitted manuscript:

A challenge in converting CO_2 into hydrocarbons (HC) via methanol (MeOH) is the gap between the optimal temperature for each step (i.e. ≤ 250 °C for MeOH and ≥ 350 °C for HC). The focus of this study is to elucidate the cause of the limitations associated to oxygenate and hydrocarbon formation in combined PdZn and H-ZSM-5 catalysts at 250 to 350 °C. Starting with two different chemical states of Pd and Zn from two preparation approaches (physical mixture and surface organometallic chemistry grafting), operando X-ray absorption spectroscopy (XAS) and powder X-ray diffraction (XRD) studies revealed similar PdZn alloy active phase formed during pretreatment in flowing H_2/Inert at 400 °C. The physical mixture performed better than the grafted analogue, with up to 8.8 % yield to oxygenate (MeOH and dimethyl ether (DME)) at 300 °C, close to the estimated thermodynamic yield (9.0%). The space-time yield (STY) of oxygenates (MeOH and DME; MeOH+) increased from 250 to 300 °C, reaching 8.5 $\text{mol}_{(MeOH+)}/\text{kg}_{(PdZn)}.\text{h}$). The catalyst performance surpassed other reported yields in similar systems, which activity declined with temperature even below 300 °C. Operando XAS and XRD experiments further showed that the PdZn phase active for MeOH formation was maintained during testing in the 250-350 °C range. InfraRed (FT-IR) and XAS experiments revealed the poisoning of Brønsted acid sites in H-ZSM-5 by Zn(II) exchange, thereby rendering it inactive for hydrocarbon formation. Overall, to avoid biasing the hybrid catalyst performance, a careful and balanced choice of the compositional characteristics will be crucial in designing an improved multi-functional catalytic system for CO_2 valorisation

1. Description of the experimental procedure and data analysis.

XRPD and Pd K-edge XAS data were collected at the BM31 of the ESRF (Grenoble, France). The sample (ca. 10 mg) was loaded inside a 2.5 mm quartz glass capillary and fixed with quartz wool from both sides. A capillary was glued inside the sample holder connected to a remotely controlled gas line (See Figure S1). A gas blower was positioned below the sample to control the temperature. The samples were activated in situ by heating in a flow of 1.4 mL/min H_2 and 8.6 mL/min He from room temperature to 300 °C and left at this temperature for 30 min to allow the formation of nanoparticles. Then, the flow was switched to pure He to remove possible PdH_x phase. The activated material was cooled down to 240 °C, and exposed to a reaction mixture (7.5, 2.5, and 10 mL/min of H_2, CO_2, and He, respectively). The reaction was run at 240, 200, and 170 °C under total pressure of 1 and 8 bar, for 2 h under each of the above conditions. The resulting gas mixture after the sample was analyzed by online mass spectrometer (Pfeiffer OmniStar GSD 320).

Pd K-edge XAS were obtained in the transmission mode by continuous scanning of the double crystal Si(111) monochromator from 24.1 to 25.3 keV for steady state spectra and during reaction, and from 24.2 to 24.8 keV for measurements during activation. To reduce higher harmonics the monochromator was detuned to 80% of the maximal intensity. Palladium foil was measured simultaneously with each spectrum for energy calibration using a third ionization chamber.

XRPD was measured using 0.51067 Å radiation, selected by a Si(111) channel-cut monochromator. CMOS-Dexela 2D detector covered the 2θ region up to 35 °. The values of the photon wavelength, sample to detector distance and detectors tilts have been optimized by Rietveld refinement of NIST LaB_6 and Si samples and kept fixed in the refinement of the Pd/C samples. For better statistics 20 diffraction images and 20 dark images (without X-ray beam) with acquisition time of 5 second were collected at each experimental point.

Demeter software package [1] was used to process and analyze EXAFS spectra. Background subtraction, normalization and energy calibration were performed in Athena program using standard parameters. The first shell Fourier analysis of the EXAFS data was performed in Artemis program using Pd–Pd contribution with four variable parameters: ΔE_0, $R_{Pd–Pd}$, $\sigma^2_{Pd–Pd}$, $N_{Pd–Pd}$. The fit was performed in R-space in $1.0 – 3.0$ Å region for k^2-weighted data Fourier transformed in $3.0 – 10.0$ Å^{-1} Δk region ($2\Delta k\Delta R/\pi > 8$). The S_0^2 value was fixed at 0.77 as determined for Pd foil.

Analysis of experimental XANES spectra was performed using multivariate curve resolution (MCR) approach implemented in pyMCR 0.3.1 library. The whole dataset of normalized experimental spectra was represented by matrix D of size $m \times n$, where m is the number of spectra and n is the number of energy points. This matrix is decomposed as $D = CS^T + E$, where C with size $m \times k$ is the concentration profiles of k pure components from matrix S ($n \times k$), and E ($m \times n$) is the error matrix. The energy ranges were limited to $24.33 – 24.41$ keV. The optimal number of components was found from the principle component analysis (PCA) implemented in PyFitIt code.

Theoretical XANES spectra were calculated within a full potential finite difference method of FDMNES code. The computational sphere radius was chosen as 5.2 Å. The surfaces were represented by unit cell with 32 Pd atoms, adsorbed species (CO_2, CO, CH_3, H_2O, O and OH placed on top, bridge or hollow sites) and 13 Å of vacuum (See Figure S3). All geometries were initially optimized in VASP 5.3 code with PBE exchange-correlation potential using a 8x4x1 Monkhorst Pack grid with the plane-wave basis cutoff at 500 eV.

2D XRPD images were averaged in PyFAI code[2] to obtain $I(2\theta)$ patterns. Whole-pattern fitting by Pawley method was performed in Jana2006 code [3]. The used 2θ-range was from 3 to 30°. The initial structure was based on cubic cell of UiO-67 in *Fm-3m* symmetry with cell parameter $a = 26.8$ Å. The variable parameters included cell parameter (a), three parameters of Pseudo-Voight function and ten parameters of the background function.

2. Preliminary conclusions.

XAS and XRD data collected simultaneously under reaction condition provide significant insight on the structure of the catalyst during catalytic hydrogenation of carbon dioxide. EXAFS shows the increased interatomic distances (Figure 1) in palladium nanoparticles compared to metallic palladium which correlates with temperature changes and the partial hydrogen pressure indicating the formation of palladium hydride phase. At the same time XANES features (Figure 2) can be reproduced by considering CO adsorption on palladium particles, as one of the reaction intermediates. Finally, XRD shows that the MOF lattice is also dynamic during the reaction (Figure 3), which can be explained by diffusion of the reagents inside the pores of MOF.

3. Results of the data analysis

Figures 1-3 summarize the results of EXAFS, XANES and XRD analysis. In particular, each point in the figure 1 is the result of the Fourier-analysis of EXAFS spectra. For clarity, only the data for the most interesting samples/experimental procedures are shown in the figure 1.
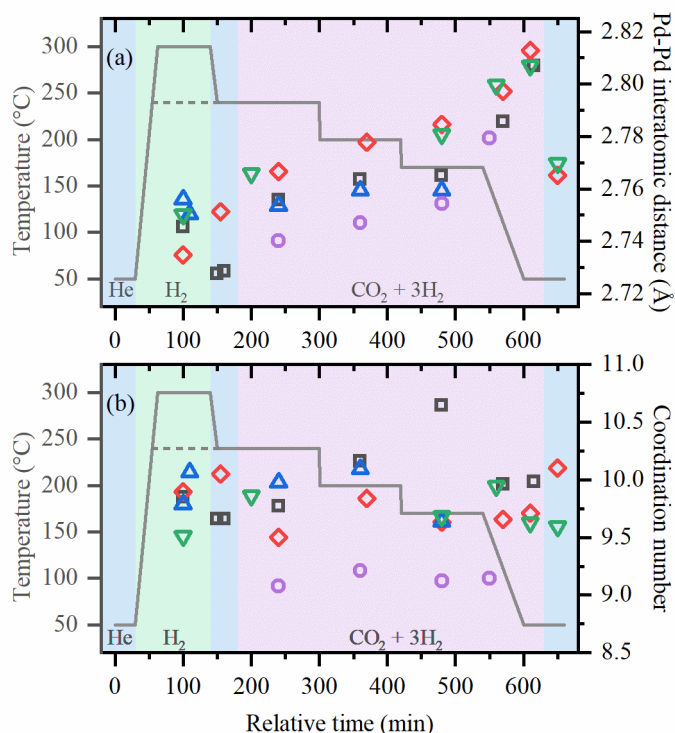

Figure 1. Pd–Pd interatomic distances (a) and coordination numbers (b) determined by Fourier-analysis of EXAFS data collected for the different samples (shown by differently colored and shaped scatters).
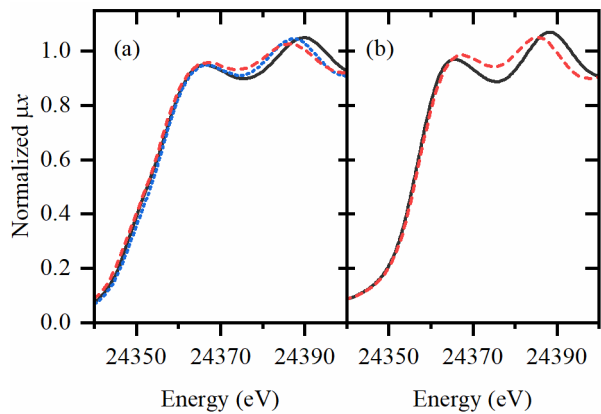
Figure 2. (a) XANES spectra extracted from the whole experimental dataset by MCR approach. and (b) theoretical spectra.
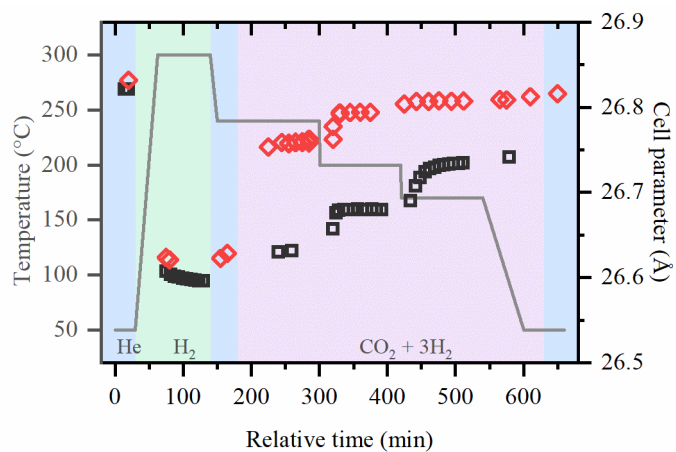

Figure 1. (a) Cell parameter of UiO-67 samples during activation in H_2 and reaction under 1 bar (black squares) and 8 bar (red diamonds) obtained by the refinement of XRD data.