Data Article

In situ X-ray absorption spectroscopy data during formation of active Pt- and Pd-sites in functionalized UiO-67 metal-organic frameworks

Aram L. Bugaev a,*, Alina A. Skorynina a, Elizaveta G. Kamysheva a, Kirill A. Lomachenko b, Alexander A. Guda a, Alexander V. Soldatov a, Carlo Lamberti a, c

a The Smart Materials Research Institute, Southern Federal University, Sladkova 178/24, 344090, Rostov-on-Don, Russia
b European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS 40220, 38043 Grenoble Cedex 9, France
c Department of Physics and CrisDi Interdepartmental Centre, University of Turin, Via P. Giuria 1, 10125 Turin, Italy

Article info

Article history:
Received 26 March 2019
Received in revised form 9 July 2019
Accepted 10 July 2019
Available online 17 July 2019

Keywords:
EXAFS
XANES
MOFs
Nanoparticles

Abstract

We report a series of Pd K-edge and Pt L3-edge X-ray absorption spectra (XAS) collected in situ during thermal treatment of functionalized UiO-67-Pd and UiO-67-Pt metal-organic frameworks in inert and reducing atmospheres. We present raw synchrotron data from three subsequent experiments at different beamlines, normalized XAS spectra and $k^2$-weighted oscillatory $\chi(k)$ functions extracted from one of the datasets. Pd K-edge spectra were collected for the samples in 5% H2/He, 3% H2/He and pure He in the temperature range from room temperature (RT) to 450 °C. Pt L3-edge were collected for the samples in 3% H2/He, 10% H2/He and pure He in the temperature range from RT to 300 °C. All spectra are reported together with the used atmosphere and temperature. For the analysis of all reported datasets, please see “Evolution of Pt and Pd species in functionalized UiO-67 metal-organic frameworks”.

DOI of original article: https://doi.org/10.1016/j.cattod.2019.03.054.

* Corresponding author.
E-mail address: abugaev@sfedu.ru (A.L. Bugaev).
Fourier-analysis of Pd K-edge is reported in “Formation and growth of Pd nanoparticles in UiO-67 MOF by in situ EXAFS”. © 2019 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Data

The dataset contains 77 Pt L3-edge XAS spectra and 72 Pd K-edge XAS spectra collected during thermal treatment of UiO-67 samples functionalized by Pt [1] and Pd [1,2], respectively, in inert (He) and reducing (H2/He) atmospheres with different H2/He content. The raw data is presented in the form of unnormalized X-ray absorption coefficient $\mu(E)$ (see files with extension *.mu in the Supporting materials) together with the normalized ones (see Figs. 1–6 and files with extension *.norm in the Supporting materials). For 10 extended X-ray absorption fine structure (EXAFS) spectra collected at Pd K-edge, extracted $k^2$-weighted oscillatory $\chi(k)$ functions are also reported in Fig. 6b and file “11_Pd_5H2_ramp.chik2” of the Supporting materials. The experimental conditions under which the spectra were collected are reported in Tables 1 and 2 for Pt L3-edge and, respectively, Pd K-edge data.

2. Experimental design, materials, and methods

**Samples.** The sample are metal-organic frameworks of UiO-67 type. by palladium and platinum was achieved via substitution of 10% standard bpdc linkers by MCl2bpymdc (M = Pd, Pt) ones using the pre-made linker synthesis (PMLS) approach [3]. The synthesis procedure have been described in more detail in our previous works for both Pd [4] and Pt [5,6].
Pt $L_3$-edge XAS spectra for UiO-67-Pt samples (Figs. 1–3) were collected at BM01B beamline [7] (now moved to BM31 port) of ESRF. The sample powder was loaded inside a 1.5 mm capillary and fixed by the quartz wool from both sizes. The mass of the samples was varied from 2.4 to 2.8 mg in the three subsequent experiments with different treatment procedures. The capillary was glued inside a metal holder, which was then connected to a remotely controlled gas line, equipped with Bronkhorst mass flow controllers. Below the sample, there was a gas blower mounted, calibrated using a thermocouple. The sample was heated from room temperature (RT) to 300 °C with the ramp of 5 °C/min. The total flux of the gas through the capillary was adjusted to 1.4 mL/min, which was checked by the mass flow meter. Three different gas mixtures were sent: pure He (Figs. 1), 3% H$_2$/He (Figs. 2), and 10% H$_2$/He (Fig. 3). XAS spectra were collected continuously during the ramp and after reaching 300 °C. The photon energy was scanned from 11.35 to 12.42 keV by Si(111) double crystal monochromator operated in continuous scanning mode. In such mode, one full spectrum was collected in 4 minutes. The
rejection of higher harmonics was achieved by detuning of the second crystal until 60% of the maximal intensity (when both crystals are perfectly tuned) was observed.

**Pd K-edge XAS spectra** for UiO-67-Pd samples (Figs. 4–5) were collected at BM31 beamline [7] ESRF, using a similar setup as described above for Pt L3-edge. The mass of the sample inside the capillaries was around 5 mg. The samples were sieved before loading into the capillaries and the fraction below 100 μm was removed. The total flux of 50 mL/min was applied. Two different gas mixtures were sent: pure He (Figs. 4), 3% H2/He (Fig. 5). The samples were first heated stepwise until no spectral changes were observed and were then kept at 300 and 215 °C in inert and reducing flux, respectively, and the spectra were measured continuously. The photon energy was scanned from 24.0 to 25.4 keV using Si(111) double crystal monochromator operated in continuous scanning mode. In such mode, one full spectrum was collected in 11 minutes. The rejection of higher harmonics was achieved by detuning of the second crystal until 80% of the maximal intensity (when both crystals are perfectly tuned) was observed.

**Fig. 3.** Normalized Pt L3-edge XANES spectra collected for UiO-67 functionalized by Pt during activation in 10% H2/He (part a) from RT (black) to 300 °C (red), and subsequently collected (4 minutes per spectrum) at 300 °C (part b, from bottom to top).

**Fig. 4.** Normalized Pd K-edge XANES spectra collected for UiO-67 functionalized by Pd during activation in He (part a) from RT (black) to 300 °C (red), and subsequently collected (11 minutes per spectrum) at 300 °C (part b, from bottom to top).
Additional measurements were performed at BM23 beamline of ESRF using the sample in a pelletized form to optimize the absorption step and collect also high-quality EXAFS data (Fig. 6). A pelletized sample was held in a microtomo cell [8] and was activated in a flow of 5% H2/He (50 mL/min). A double-crystal fixed-exit Si(111) monochromator was employed. Harmonic rejection was done by two flat Pt-coated mirrors positioned at 2 mrad angle. The spectra were collected in the energy range from 24.1 to 25.1 eV, which correspond to \( k_{\text{max}} \) of about 14 Å. The energy step in the pre-edge region was set to 5 eV with acquisition time of 1 s per point. In XANES region, 1 eV step was used with 1 s/point. In the EXAFS region, the step of 0.04 Å\(^{-1}\) in the \( k \)-space was used, with the time per point increasing linearly from 1 to 4 s.

All spectra were collected in transmission mode, and Pt and Pd foils were measured simultaneously with third ionization chamber for energy calibration. Demeter software [9] was used to normalize the data and to obtain oscillatory \( \chi(k) \) functions reported in Fig. 6a. The capillary setups used at BM01B and BM31 also allowed quasi-simultaneous collection of X-ray diffraction as described elsewhere [10–13].
### Table 1
Experimental conditions applied during Pt L₃-edge spectra collection and their correspondence with the column in *.mu and *.norm files. T is the temperature in °C registered in the beginning of each spectrum acquired during the ramp. t is the time in minutes, the sample had spent at 300 °C before the beginning of the corresponding spectrum. The first and second columns in each file correspond to energy in eV and absorption spectrum of the reference Pt foil, respectively.

| Conditions Column | He 3% H₂/He | 10% H₂/He |
|-------------------|-------------|-----------|
|                   | T, °C       | t, min    | T, °C       | t, min    |
| 3                 | 20          | 0         | 22          | 0         |
| 4                 | 22          | 4         | 40          | 4         |
| 5                 | 40          | 8         | 77          | 8         |
| 6                 | 58          | 12        | 58          | 12        |
| 7                 | 77          | 16        | 95          | 16        |
| 8                 | 95          | 20        | 113         | 113       |
| 9                 | 113         | 24        | 131         | 131       |
| 10                | 131         | 28        | 149         | 149       |
| 11                | 149         | 32        | 167         | 167       |
| 12                | 167         | 36        | 185         | 185       |
| 13                | 185         | 40        | 203         | 203       |
| 14                | 203         | 44        | 221         | 221       |
| 15                | 221         | 48        | 239         | 239       |
| 16                | 239         | 52        | 257         | 257       |
| 17                | 257         | 54        | 274         | 274       |
| 18                | 274         | 52        | 293         | 293       |
| 19                | 293         |           |             |           |

### Table 2
Experimental conditions applied during Pd K-edge spectra collection and their correspondence with the column in *.mu and *.norm files. T is the temperature at which the spectra were °C registered. t is the time in minutes, the sample had spent at 300 and 215 °C in He and 3% H₂/He, respectively, before the beginning of the corresponding spectrum. The first and second columns in each file correspond to energy in eV and absorption spectrum of the reference Pd foil, respectively.

| Conditions Column | He | 3% H₂/He |
|-------------------|----|----------|
|                   | T, °C | t, min | T, °C | t, min |
| 3                 | 46   | 0       | 46   | 0     |
| 4                 | 89   | 11      | 89   | 11    |
| 5                 | 131  | 22      | 131  | 22    |
| 6                 | 174  | 33      | 174  | 33    |
| 7                 | 217  | 44      | 217  | 44    |
| 8                 | 260  | 55      | 260  | 55    |
| 9                 | 66   |         | 66   |       |
| 10                | 77   |         | 77   |       |
| 11                | 88   |         | 88   |       |
| 12                | 99   |         | 99   |       |
| 13                | 110  |         | 110  |       |
| 14                | 121  |         | 121  |       |
| 15                | 132  |         | 132  |       |
| 16                | 143  |         | 143  |       |
| 17                | 154  |         | 154  |       |
| 18                | 165  |         | 165  |       |
| 19                | 176  |         | 176  |       |
| 20                | 187  |         | 187  |       |
| 21                | 198  |         | 198  |       |
| 22                | 209  |         | 209  |       |
| 23                | 220  |         | 220  |       |
| 24                | 231  |         | 231  |       |
| 25                |       |         |       |       |
| 26                |       |         |       |       |
| 27                |       |         |       |       |
| 28                |       |         |       |       |
| 29                |       |         |       |       |
| 30                |       |         |       |       |
| 31                |       |         |       |       |
| 32                |       |         |       |       |
Acknowledgments

Authors acknowledge Russian Science Foundation project No. 18-73-00189 for funding this research.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dib.2019.104280.

References

[1] A.L. Bugaev, A.A. Skorynina, L. Braglia, K.A. Lomachenko, A.A. Guda, A. Lazzarini, S. Bordiga, U. Olsbye, K.P. Lillerud, A.V. Soldatov, C. Lamberti, Evolution of Pt and Pd species in functionalized UiO-67 metal-organic frameworks, Catal. Today, https://doi.org/10.1016/j.cattod.2019.03.054 (in press).
[2] E.G. Kamyshova, A.A. Skorynina, A.L. Bugaev, C. Lamberti, A.V. Soldatov, Formation and growth of Pd nanoparticles in UiO-67 MOF by in situ EXAFS, Radiat. Phys. Chem., https://doi.org/10.1016/j.radphyschem.2019.02.003 (in press).
[3] S. Øien, G. Agostini, S. Svelle, E. Borfecchia, K.A. Lomachenko, L. Mino, E. Gallo, S. Bordiga, U. Olsbye, K.P. Lillerud, C. Lamberti, Probing reactive platinum sites in UiO-67 zirconium metal–organic frameworks, Chem. Mater. 27 (2015) 1042–1056.
[4] A.L. Bugaev, A.A. Guda, K.A. Lomachenko, E.G. Kamyshova, M.A. Soldatov, G. Kaur, S. Øien-Odegaard, L. Braglia, A. Lazzarini, M. Manzoli, S. Bordiga, U. Olsbye, K.P. Lillerud, A.V. Soldatov, C. Lamberti, Operando study of palladium nanoparticles inside UiO-67 MOF for catalytic hydrogenation of hydrocarbons, Faraday Discuss 208 (2018) 287–306.
[5] L. Braglia, E. Borfecchia, K.A. Lomachenko, A.L. Bugaev, A.A. Guda, A.V. Soldatov, B.T.L. Bleken, S. Øien-Odegaard, U. Olsbye, K.P. Lillerud, S. Bordiga, G. Agostini, M. Manzoli, C. Lamberti, Tuning Pt and Cu sites population inside functionalized UiO-67 MOF by controlling activation conditions, Faraday Discuss 201 (2017) 277–298.
[6] L. Braglia, E. Borfecchia, A. Martini, A.L. Bugaev, A.V. Soldatov, S. Øien-Odegaard, B.T. Lonstad-Bleken, U. Olsbye, K.P. Lillerud, K.A. Lomachenko, G. Agostini, M. Manzoli, C. Lamberti, The duality of UiO-67-Pt MOFs: connecting treatment conditions and encapsulated Pt species by operando XAS, Phys. Chem. Chem. Phys. 19 (2017) 27489–27507.
[7] W. van Beek, O.V. Salanova, G. Wiker, H. Emerich, SNBL, a dedicated beamline for combined in situ X-ray diffraction, X-ray absorption and Raman scattering experiments, Phase Transitions 84 (2011) 726–732.
[8] D. Bellet, B. Gorges, A. Dallery, F. Bernard, E. Pereiro, J. Baruchel, A 1300 K furnace for in situ X-ray microtomography, J. Appl. Crystallogr. 36 (2003) 366–367.
[9] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, J. Synchrotron Radiat. 12 (2005) 537–541.
[10] A.L. Bugaev, A.A. Guda, K.A. Lomachenko, A. Lazzarini, V.V. Srbionyan, J.G. Vitillo, A. Piovano, E. Groppo, L.A. Bugaev, A.V. Soldatov, V.P. Dmitriev, R. Pellegrini, J.A. van Bokhoven, C. Lamberti, Hydride phase formation in carbon supported palladium hydride nanoparticles by in situ EXAFS and XRD, J. Phys. Conf. Ser. 712 (2016), 012032.
[11] A.L. Bugaev, A.A. Guda, K.A. Lomachenko, V.V. Shapovalov, A. Lazzarini, J.G. Vitillo, L.A. Bugaev, E. Groppo, R. Pellegrini, A.V. Soldatov, J.A. van Bokhoven, C. Lamberti, Core–shell structure of palladium hydride nanoparticles revealed by combined X-ray absorption spectroscopy and X-ray diffraction, J. Phys. Chem. C 121 (2017) 18202–18213.
[12] A.L. Bugaev, O.A. Usoltsev, A. Lazzarini, K.A. Lomachenko, A.A. Guda, R. Pellegrini, M. Carosso, J.G. Vitillo, E. Groppo, J. van Bokhoven, A.V. Soldatov, C. Lamberti, Time-resolved operando studies of carbon supported Pd nanoparticles under hydrogenation reactions by X-ray diffraction and absorption, Faraday Discuss 208 (2018) 187–205.
[13] A.A. Skorynina, A.A. Tereshchenko, O.A. Usoltsev, A.L. Bugaev, K.A. Lomachenko, A.A. Guda, E. Groppo, R. Pellegrini, C. Lamberti, A. Soldatov, Time-dependent carbide phase formation in palladium nanoparticles, Radiat. Phys. Chem., https://doi.org/10.1016/j.radphyschem.2018.11.033 (in press).