EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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.

ESRF	**Experiment title: Characterization of the adsorption sites of noble gases in CPO-27 Metal-Organic Frameworks using high-resolution X-ray powder diffraction**	**Experiment number**: ch3878
Beamline: ID31	**Date of experiment**: from: 22.11.2013 to: 25.11.2013	**Date of report**: 08.01.2014
Shifts: 9	**Local contact(s)**: Christina DRATHEN	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Robert E. Dinnebier, Max Planck Institute for Solid State Research, Stuttgart, Germany
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Report:

The structure of CPO-27-Ni determined for the low loading of Xe and Kr confirms that the open 5-coordinated metal ion sites are the strongest adsorption sites. The Ni-Xe distance is 3.01(2) Å and the Ni-Kr distance is 3.03(3) Å for highest loading (1000 mbar). The second adsorption site for Xe is at 4.10(3) Å from the carboxilate oxygen group and at 4.23(3) Å from the oxygen atoms from benzene ring (170^{o}C, 1000 mbar). The second adsorption site for Kr is at 4.02(3) Å from the carboxilate oxygen group and 4.10(3) Å from the oxygen atoms from benzene ring (130^{o}C, 1000 mbar), and it has approximately half of occupancy factor of the first adsorption site at measured temperatures and high applied pressures. It appears almost simultaneously with the first adsorption site. The third adsorption site for both Xe and Kr is located in the center of the channels and represents unbounded noble gas atoms. With increasing pressure, the amount of unbounded adsorbed Xe becomes close to 1 atom per unit cell (1/18 Xe atom per Ni atom). The amount of adsorbed unbonded Kr is close to 2 atoms per unit cell at 130^{o}C, and drops to ca. 0.3 atoms per unit cell at 250^{o}C. The maximal amount of adsorbed Xe corresponds to 0.75 Xe atom per Ni atom at 170^{o}C, 1000 mbar, and ca. 0.65 Xe atoms per Ni atom at 250^{o}C, 1000 mbar (ca. 0.6 Xe atoms per Ni atom at 250^{o}C, 500 mbar), but saturation of Xe adsorption is not reached at 250^{o}C, 1000 mbar and amount of adsorbed Xe can be increased on increasing pressure. The maximal amount of adsorbed Kr corresponds to ca. 1.0 Kr atoms per Ni atom at 130^{o}C, 0.95 Kr atoms per Ni atom at 170^{o}C, and 0.45 Kr atoms per Ni atom at 250^{o}C.

The experimental results for CPO-27 showed that the open metal sites are the major binding sites for Xe and Kr gases. On the other site, recent report of noble gas adsorption in HKUST-1 (Hulvey *et al.*, J. Phys. Chem. C 2013, 117, 20116−20126) did not show any interaction of noble atoms with open Cu^{2+} metal sites. Thus, noble gas adsorption behavior depends not only from the presence of the open metal sites, but also from the pore's topology – the small pockets in HKUST-1 provides strong geometrical confinement of noble

gas atoms. The uniform channels of CPO-27 do not imply geometrical restrictions on noble gas adsorption, and easily polarizable sites along the channels are the main adsorption sites.