In situ characterization of Xe and Kr adsorption sites in Covalent Organic Frameworks using high-resolution X-ray powder diffraction and combination of Rietveld and MEM (Maximum Entropy method)

*O.V. Magdysyuk, F. Adams, R.E. Dinnebier**

Max Planck institute for Solid State Research, Heisenbergstr, 1, 70565 Stuttgart, Germany

We examined the temperature-dependent uptake of Xe and Kr by CPO-27 with abundant open metal sites along uniform channels.

Rietveld refinements of CPO-27-Ni and CPO-27-Mg loaded with Kr and Xe revealed that the preferable adsorption positions for Kr are similar to those of Xe in the corresponding MOF with only slight differences in the refined positions.

The crystal structure of CPO-27-Ni determined for low loading of Xe and Kr confirms that the open 5-coordinated metal ion sites are the strongest adsorption sites with a Ni-Xe distance of 3.01(2) Å and a Ni-Kr distance of 3.03(3) Å at 1000 mbar. The second adsorption site for Xe is located at a distance of 4.10(3) Å from the carboxilate oxygen and at 4.23(3) Å from the oxygen atoms of the benzene ring (170K, 1000 mbar). The second adsorption site for Kr is located at a distance of 4.02(3) Å from the carboxilate oxygen and 4.10(3) Å from the oxygen atoms of the organic linker (130K, 1000 mbar), having approximately half the occupancy of the first adsorption site at all measured temperatures. The second adsorption site 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.

Unexpected Xe and Kr adsorption behavior was found for CPO-27-Mg. In this case the second binding site near the oxygen atoms is almost simultaneously occupied with the first binding site near the open metal ion and has a similar value of the occupancy factor. The Mg-Xe distance is 3.14(2) Å at 170K (500 mbar), and the Mg-Kr distance is 3.23(3) Å at 130K (1000 mbar). The second adsorption site for Xe is at a distance of 4.10(3) Å from the carboxilate oxygen group and at a distance of 4.23(3) Å from the oxygen atoms of the benzene ring (170K, 500 mbar). The second adsorption site for Kr is at 3.92(3) Å from the carboxilate oxygen group and 3.96(3) Å from the oxygen atoms of the benzene ring (130K, 1000 mbar). The third adsorption site for both, Xe and Kr, is located in the center of the channel, and its occupancy is highest at lowest temperatures and is decreasing with increasing temperature. At 250K the third adsorption site is unoccupied since the first and the second strong adsorption sites are not fully occupied at this temperature.

Thus, CPO-27-Mg shows weaker binding to both Xe and Ke atoms than CPO-27-Ni, presumably due to the larger polarizability of the Ni atom in comparison to the Mg atom.

The experimental results for CPO-27 revealed that the open metal sites are the major (in the case of Ni^{2+}) or one of two major (in the case of Mg^{2+}) binding sites for Xe and Kr gases.

References

[1] O.V. Magdysyuk *et al.*, In preparation, will be submitted to Phys. Chem C.