MOF colloquium

Selected coordination chemistry topics (what are coordination compounds with knowledge of relevant examples, coordination bonding compared to other bonding types, *18 electron rule, crystal field splitting, ligand field strength and spectrochemical series*). Definition of MOFs/PCPs (PCP = porous coordination polymers). *Reticular chemistry (isoreticular series, e.g. IRMOFs) topology of the underlying nets (square planar, diamond, honeycomb, primitive cubic nets as the most typical)*. Typical metals and ligands used (classification, typical ligand geometries, mixed ligand MOFs). Important (archetypal) MOF types; *list up to five example of MOFs of general importance(MOF-5, HKUST-1, ZIF-8, MOF-74, MIL-53, MIL-100 and -101, MIL-88, $Zn_2(dabco)(BDC)_2$ type pillared MOFs, UiO-66)*. **Draw and explain the structure of the MOF, targeted in the laboratory work**. HSAB principle; predictive analysis context of thermodynamic stability (chemical and thermal; also compared with other porous materials), kinetic stability (*e.g.* chromium MOFs, *reasons*). Interpenetration (topological and structural phenomenon). Activation of MOFs (direct, via exchange and supercritical CO_2 drying). Porosity characteristics of MOFs (surface areas and possible limits, pore sizes). General methods of MOFs's syntheses *(nanoparticulated MOFs)*. Notion about tuneability of MOFs *(ligand-side functionalization, postsynthetic exchange)*. Structural flexibility of MOFs *(MIL-53, MIL-88)*. Potential applications of MOFs (explanation of the principles at least for gas storage and separation, catalysis, sensorics; comparative advantages and disadvantages of MOFs).

Analytical colloquium

Vibrational spectroscopy (IR, Raman)

Principles of vibrational spectroscopy, instrumentation (transmission mode *vs* ATR, sample preparation; wavelength scan *vs* FTIR). Harmonic oscillator model and parameters influencing the bands. Selection rules. *Number and types of vibrations (distinction by symmetry, e.g. symmetric and asymmetric stretching, wagging, twisting, scissoring, rocking etc.). Normal vibration analysis (general understanding only).* Units, spectral range. Characteristic vibrations, fingerprint region. Analysis of a typical IR-spectrum of a MOF (aromatic and aliphatic C-H, X-H (X = O, N), -C(O)X groups, C-C stretches in aromatics, coordination bonding).

The use of IR spectroscopy in MOF chemistry (particularly in the context of activation, adsorption, active sites).

Powder X-ray diffractometry (PXRD)

Diffractometer (geometry, *source of X-rays, Kα1, Kα2, K_β bands; monochromation*). *Miller indices*. Bragg equation (with derivation). *Systematic absences*. Powder diffraction pattern as a function of crystal structure, specimen's morphology, sample geometry (e.g. sample shift, *roughness, X-ray adsorption*) and instrumental factors *(incl. X-ray fluorescence)*. Information, which could be extracted from PXRD data *(incl. general understanding of Rietveld refinement)*. Influence of particle size *(Scherer equation)* and preferred orientation.

Analysis of an experimental PXRD and peculiarities of MOFs (influence of semi-amorphosity, guest molecules, framework flexibility on the pattern).

Thermogravimetric analysis (TGA)

Thermogravimetric analyser. Information, which could be extracted from TGA. *Differential scanning calorimetry (DSC).*

Practical TGA example on example of a MOF (in N_2 and O_2), decomposition pathways, determination of composition.

Gas adsorption

Classification of porous materials (micro-, meso-, macroporous materials; examples). Physisorption vs chemisorption. Types of gas adsorption isotherms (IUPAC classification). Explanation of hysteresis (ink-flask pores and kinetic reasons). Adsorption models (Langmuir, with derivation; BET with understanding of derivation principles; *a notion about other models e.g. Dubinin's*). Conditions of applicability of BET criteria *(incl. $n(P_0-P)$ growing with P/P_0)*. Applicability of BET model for MOFs. *Heat of adsorption (notion about the Clausius–Clapeyron equation).*

Gas adsorption analyser, principle. A typical gas adsorption isotherm for a MOF. Determination of the BET-based surface area on a linearized graph.