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High-throughput screening: speeding up porous materials discovery†

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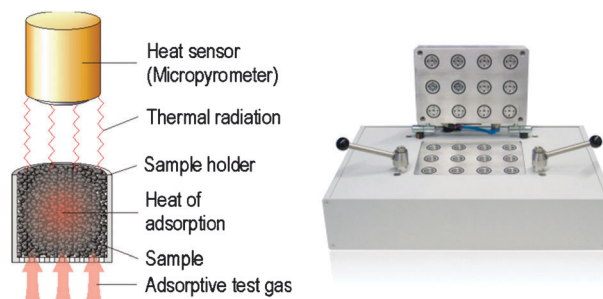
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A new tool (Infrasorb-12) for the screening of porosity is described, identifying high surface area materials in a very short time with high accuracy. Further, an example for the application of the tool in the discovery of new cobalt-based metal–organic frameworks is given.

The discovery of novel porous materials is an essential element in the development of materials for energy and gas storage, emission reduction and carbon dioxide separation, as well as targeted drug delivery. Tremendous progress was achieved in the area of zeolites^{1,2} and, recently, metal–organic frameworks (MOFs)^{3,4} and covalent materials^{3,5} reached new records in terms of porosity and gas capture ability. Carbide-derived carbons (CDCs)⁶ have shown unprecedented performance in supercapacitors and a plethora of novel acronyms such as EOFs,^{5,7} PAEs,⁸ PIMs,⁹ HCPs¹⁰ and others^{11,12} reflects the activity in this field. High-throughput screening is nowadays an established tool for the discovery of novel materials^{13–15} and catalyst screening.^{15,16} Some automated synthesis techniques are commercially available. The discovery of novel zeolites^{17,18} and more recently also MOFs^{19,20} focuses on automated X-ray powder diffraction and the identification of new phases. However, structural analysis from powder patterns is still a bottle neck in the discovery of new materials and slight changes in synthesis conditions can lead to non-porous phases or interpenetrated networks.

Since porosity and gas storage ability is the key target in the development of porous materials, our interest was to develop an instrument that allows a rapid screening of porosity. In the following we describe a new tool (Infrasorb-12)²¹ that can identify high surface area materials out of 12 samples in less than 5 minutes and we give an example for the application of Infrasorb during the discovery of new cobalt-based MOFs



Scheme 1 Measurement principle (left) and Infrasorb-12 device (right).

DUT-27, DUT-28 (DUT = Dresden University of Technology), and MOF-39(Co).

Infrasorb-12 is based on infrared detection of heat, generated during gas adsorption (Scheme 1). The use of *n*-butane allows us to perform the measurement at room temperature and on small sample amounts because of a relatively high heat of adsorption,²² however a general access for *n*-butane (kinetic diameter 4.3 Å) to the pore system is required.

The investigated materials were transferred to the sample cells and purged with an inert gas (N₂). The heat radiation signal is recorded after a defined flux of *n*-butane is dosed to the samples and the sensor output is correlated to temperature values according to the sensor specification. After data processing (see experimental sections and ESI†), an integration is performed to determine the heat of adsorption. For the validation of the parallelization, a 12-port measurement with an activated carbon reference was performed showing a small standard deviation of only 3.4% (Fig. S2 (ESI†), absolute value: 2.4).

Furthermore, using reference materials with a well defined *n*-butane index, a linear correlation between the integrated heat signal and *n*-butane capacity was observed (Fig. 1 and Table S1 (ESI†)). The latter directly reflects the accessible specific pore volume for the light alkane and is not limited to *n*-butane (see ESI†, Fig. S3). A satisfying linear correlation was also observed between the specific surface area determined from nitrogen adsorption measurements at 77 K and the integrated signal (quality factor: R^2 0.9847, see Fig. 2). Due to the dependence of the adsorption enthalpy on the probe used, a calibration should be performed for each specific class of materials, in order to increase the accuracy of the surface area determination.

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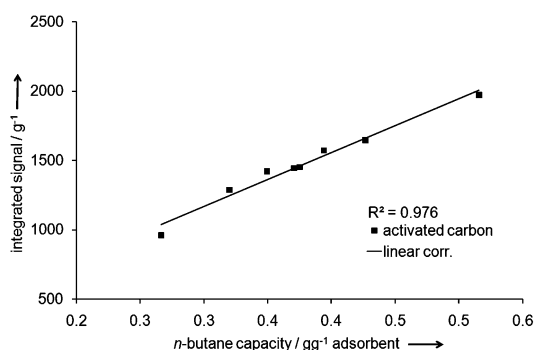


Fig. 1 Correlation of integrated signal to gravimetrically determined *n*-butane capacity.

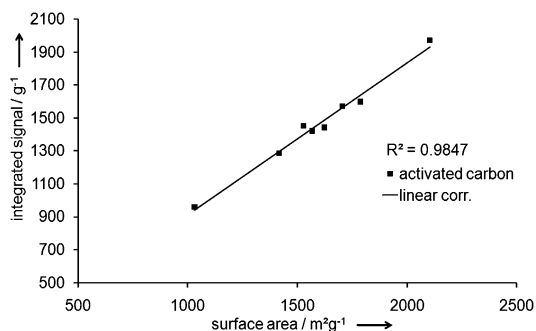


Fig. 2 Correlation of integrated signal to single-point BET-surface area.

The practical applicability for different classes of reference materials was proven by screening different commercial adsorbents (Sorbonorit 3, ZEOCat ZP-2, Basolite C300 (HKUST-1), Basolite A100 (MIL-53) and Basolite Z1200 (ZIF-8), see also ESI†, Fig. S5). All materials (activated carbon, MOFs, zeolite) were measured simultaneously (Fig. S4, ESI†) showing an asymmetric peak shape in the heat signals and a good correlation to gravimetrically determined *n*-butane capacity with a quality factor of $R^2 = 0.9765$ (Fig. S6, ESI†) which is essential for high-throughput testing. Also the applicability of Infrisorb-12 to flexible MOFs was shown on the example of DUT-8(Ni)²³ (Fig. S7, ESI†).

The Infrisorb-12 system was successfully applied during the discovery of new porous MOFs consisting of Co and the BTB (BTB = benzene-1,3,5-tribenzoate) linker. The BTB was successfully used for synthesis of high porous MOFs, using Zn (MOF-177, MOF-39),^{24,25} Cu (MOF-14),²⁶ Ni (DUT-9)⁴ and others. However, no work about Co based BTB MOFs is reported until now.

Different matrices for the synthesis parameter ranges were screened. For this work a synthesis matrix of 12 samples with variation of synthesis temperature and cobalt source was used (Scheme S1, ESI†). Subsequently, the reaction products were dried simultaneously using supercritical CO₂ and afterwards screened using the Infrisorb-12 system. The results for selected samples, later identified as single phase products, are given in Fig. 3 and Table S4 (ESI†). Ports 9 and 10 indicate distinct hits in the discovery while the other samples are more or less non-porous. Subsequently, using X-ray powder diffraction, samples in ports 3, 4/8/12, and 9/10 were identified as crystalline material and

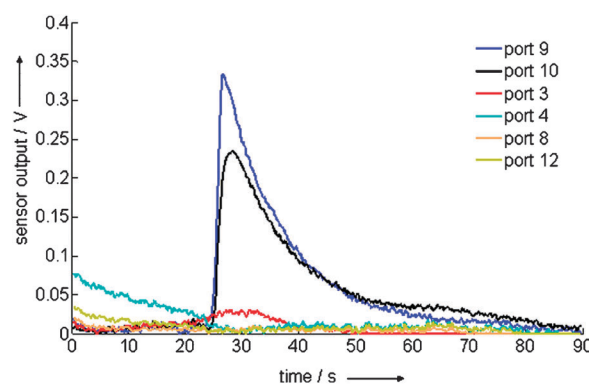


Fig. 3 Sensor output during the heat of adsorption measurement on Co/BTB (ports 3, 4, 8–10, 12).

positions 9/10 and positions 4/8/12 showed identical phases, respectively. The lower synthesis temperature for the substance in port 9 (90 °C) results in a slightly higher porosity in comparison to port 10 (100 °C). For full structure determination, single crystals were analyzed and three new MOFs were identified namely DUT-27 (port 3), MOF-39(Co) (port 4/8/12) and DUT-28 (port 9/10).[‡]

DUT-27 has a layered structure and crystallizes in the space group $C2/c$ and the composition can be described as $\text{Co}_2(\text{BTB})\text{NO}_3(\text{DEF})_3(\text{H}_2\text{O})_2$ (DEF = *N,N*-diethylformamide). A dinuclear cobalt unit (Fig. 4a) acts as SBU and is connected by three carboxylates of three BTB linkers. Two carboxylic groups adopt a bidentate bridging coordination mode and the third group has a tridentate bridging-chelating mode. The co-ligands (NO_3^- and three DEF molecules) complete the cobalt coordination sphere. However, the structure is dense as expected (Fig. 4b).

The compound from reaction vessel 4 (named MOF-39(Co)) crystallizes in the $Pnma$ space group and is isomorphous to MOF-39(Zn)²⁵ and the mixed metal MOF-39(Zn/Co).²⁷ Here, the SBU is a three-nuclear cluster with mirror symmetry consisting of two CoO_4 tetrahedrons and a CoO_6 octahedron (Fig. 4a). They are connected by six carboxylic groups forming a 3D framework. Four carboxylates adopt a bidentate bridging coordination mode and two other coordinate in a monodentate fashion. MOF-39(Co) consists of two equivalent interwoven nets of primitive cubic topology (Fig. 4c).

Single-crystal X-ray studies revealed that the DUT-28 ($\text{Co}_{22}(\text{BTB})_{12}(\text{NO}_3)_8(\text{DEF})_x(\text{H}_2\text{O})_y$) adopts the space group $C2/m$ at room temperature (RT) and consists of $\text{Co}_2(\text{COO})_3$ “paddle-wheel” clusters and $\text{Co}_3(\text{COO})_6$ cluster (Fig. 4a). The clusters are linked together through BTB-ligands to generate a 3D cationic framework (Fig. 4d). The non-coordinating counterions (NO_3^-) could not be located by single-crystal X-ray analysis and were identified by IR-spectroscopic measurements (Fig. S16 and Table S5, ESI†). This framework has a complex system of cavities and channels that are periodically distributed throughout the structure. The free accessible volume calculated using PLATON amounts to 81.8% of the unit cell. Interestingly, the structure shows a strong temperature induced transformation, which could be discovered during the single crystal data collection at 100 K. At low temperature, the space group is changing to $C2/c$ (DUT-28(LT)) and a cell volume decrease of 9% is observed (see ESI†).

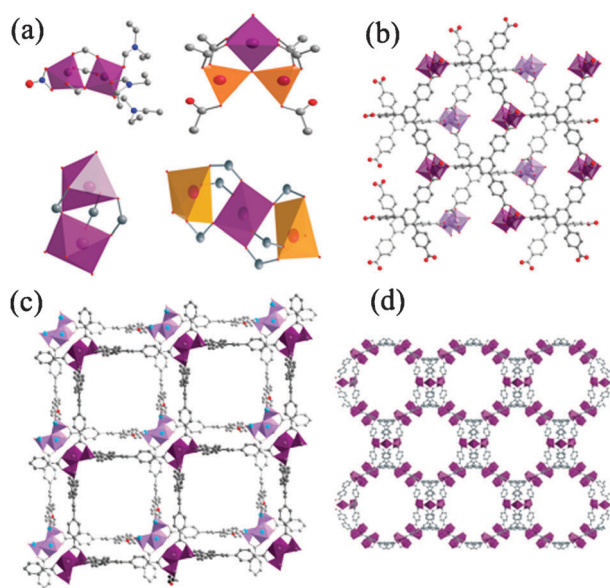


Fig. 4 (a) Clusters existing in the structures of Co/BTB: top left—DUT-27; top right—MOF-39(Co), bottom—DUT-28; (b) view of the two layers of DUT-27 along c ; (c) view of the interpenetrated network of MOF-39(Co) along a ; (d) view of the structure of DUT-28(RT) along c . For further structure figures see ESI.†

The nitrogen physisorption at 77 K confirm exactly the results of the Infrisorb-12: DUT-27 and MOF-39(Co) are not porous while DUT-28 shows a moderate surface area of $450 \text{ m}^2 \text{ g}^{-1}$ (Fig. S17, ESI†). Thus, the fast screening results are confirmed and it can be demonstrated that even the discovery of new MOFs with a moderate surface area is feasible.

Summarizing, we have developed a new instrument for very high speed and accurate detection of porosity. The instrument is based on an optical detection of the adsorption heat and shows good applicability to reference materials. For the first time, the Infrisorb-12 was successfully applied for the testing of porosity of MOFs during the discovery process. Three new MOFs were identified (DUT-27, MOF-39(Co), DUT-28) as highly connected nets containing multinuclear cobalt clusters with open metal sites suitable for catalytic applications or separation.

In our view, the Infrisorb-12 development will speed up the discovery of new porous materials significantly and thus broaden the wide range of materials suitable for gas storage, selective adsorption, catalysis, and life science applications.

Notes and references

† Test setup: a single port of Infrisorb-12 has a vertical height and a diameter of 5 mm each. Sensors are focused on the sample and connected to a voltage source Keithley SourceMeter and a data acquisition module Keithley K-USB 3102. All samples were purged with nitrogen and afterwards exposed to n -butane (100%) with a flow of 20 ml min^{-1} per port. Prior to the integration, a linear baseline correction and further data treatment was performed. Crystal data: DUT-27: $\text{C}_{42}\text{H}_{48}\text{Co}_3\text{N}_3\text{O}_{12}$, $M_r = 963.65$, monoclinic, $C2/c$, $a = 27.853(6) \text{ \AA}$, $b = 16.823(3) \text{ \AA}$, $c = 20.998(4) \text{ \AA}$, $\beta = 116.28(3)^\circ$, $V = 8822(3) \text{ \AA}^3$, $Z = 8$, $\rho = 1.451 \text{ g cm}^{-3}$, $\lambda = 0.88561 \text{ \AA}$, $T = 293 \text{ K}$, $\theta_{\text{max}} = 36.83^\circ$, reflections collected/unique 5540/5227, $R_{\text{int}} = 0.038$, $R_1 = 0.0677$, $wR_2 = 0.1800$; MOF-39(Co): $\text{C}_{54}\text{H}_{30}\text{Co}_3\text{O}_{14}$, $M_r = 1079.57$, orthorhombic, $Pnma$, $a = 17.448(3) \text{ \AA}$, $b = 24.994(6) \text{ \AA}$, $c = 22.250(4) \text{ \AA}$, $V = 9703(4) \text{ \AA}^3$, $Z = 4$, $\rho = 0.739 \text{ g cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $T = 20^\circ \text{ C}$, $\theta_{\text{max}} = 26.0^\circ$, reflections collected/unique 71 153/3936, $R_{\text{int}} = 0.0386$, $R_1 = 0.1031$, $wR_2 = 0.2127$; DUT-28(RT): $\text{C}_{162}\text{H}_{90}\text{Co}_{11}\text{O}_{60}$, $M_r = 3644.58$, monoclinic, $C2/m$,

$a = 32.997(7) \text{ \AA}$, $b = 39.073(8) \text{ \AA}$, $c = 27.640(6) \text{ \AA}$, $\beta = 123.71(3)^\circ$, $V = 29642(10) \text{ \AA}^3$, $Z = 2$, $\rho = 0.408 \text{ g cm}^{-3}$, $\lambda = 0.88561 \text{ \AA}$, $T = 293 \text{ K}$, $\theta_{\text{max}} = 29.12^\circ$, reflections collected/unique 79 642/13 965, $R_{\text{int}} = 0.03$, $R_1 = 0.0905$, $wR_2 = 0.2749$; DUT-28(LT): $\text{C}_{162}\text{H}_{90}\text{Co}_{11}\text{O}_{60}$, $M_r = 3644.58$, monoclinic, $C2/c$, $a = 45.386(9) \text{ \AA}$, $b = 35.904(7) \text{ \AA}$, $c = 33.184(7) \text{ \AA}$, $\beta = 94.91(3)^\circ$, $V = 53876(19) \text{ \AA}^3$, $Z = 8$, $\rho = 0.449 \text{ g cm}^{-3}$, $\lambda = 0.88561 \text{ \AA}$, $T = 100 \text{ K}$, $\theta_{\text{max}} = 25.50^\circ$, reflections collected/unique 99 640/18 857, $R_{\text{int}} = 0.0935$, $R_1 = 0.0763$, $wR_2 = 0.2133$. CCDC 801199–801202 contain the supplementary crystallographic data for this communication.

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