Noble Gas Uptake

 How to cite:
 Angew. Chem. Int. Ed. 2021, 60, 5250–5256

 International Edition:
 doi.org/10.1002/anie.202015019

 German Edition:
 doi.org/10.1002/ange.202015019

Kinetic Barriers and Microscopic Mechanisms of Noble Gas Adsorption by Nanoporous γ -Mg(BH₄)₂ Obtained by Means of Sub-Second X-Ray Diffraction

Iurii Dovgaliuk,* Irena Senkovska, Xiao Li, Vadim Dyadkin, Yaroslav Filinchuk,* and Dmitry Chernyshov*

Abstract: Gas adsorption by porous frameworks sometimes results in structure "breathing", "pores opening/closing", "negative gas adsorption", and other phenomena. Timedependent diffraction can address both kinetics of the guest uptake and structural response of the host framework. Using sub-second in situ powder X-ray diffraction, three intracrystalline diffusion scenarios have been evaluated from the isothermal kinetics of Ar, Kr, and Xe adsorption by nanoporous γ -Mg(BH₄)₂. These scenarios are dictated by two possible simultaneous transport mechanisms: diffusion through the intra- (i) and interchannel apertures (ii) of γ -Mg(BH₄)₂ crystal structure. The contribution of (i) and (ii) changes depending on the kinetic diameter of the noble gas molecule and temperature regime. The lowest single activation barrier for the smallest Ar suggests equal diffusion of the atoms trough both pathways. Contrary, for the medium sized Kr we resolve the contributions of two parallel transport mechanisms, which tentatively can be attributed to the smaller barrier of the migration paths via the channel like pores and the higher barrier for the diffusion via narrow aperture between these channels. The largest Xe atoms diffuse only along 1D channels and show the highest single activation barrier.

Crystalline porous materials such as metal–organic frameworks, covalent organic frameworks, and zeolites are one of the most blossoming fields in chemistry and material sci-

[*]	 Dr. I. Dovgaliuk, Dr. V. Dyadkin, Dr. D. Chernyshov Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility 38000 Grenoble (France) E-mail: iurii.dovgaliuk@mail.chimie.ens.fr dmitry.chernyshov@esrf.fr
	Dr. I. Dovgaliuk Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, CNRS, PSL Université 75005 Paris (France)
	Dr. I. Senkovska Inorganic Chemistry I, Technische Universität Dresden Bergstrasse 66, 01069 Dresden (Germany) X. Li, Prof. Y. Filinchuk Institute of Condensed Matter and Nanosciences, Université catholique de Louvain Place L. Pasteur. 1348 Louvain-la-Neuve (Belgium)
	E-mail: yaroslav.filinchuk@uclouvain.be
D	Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202015019.

ence^[1-3] due to their regular porosity and great potential for selective adsorption, separation and storage of guest molecules of interest.^[4] In the last decades more and more attention has been paid to flexibility of the crystalline porous materials, seriously affecting guest adsorption/desorption and a mechanical response of the material to perturbation of external conditions. It is also a key feature in several fascinating adsorption-driven phenomena, such as "breathing",^[5-7] "gate opening/closing",^[8,9] (photo)switching^[10,11] and negative gas adsorption (NGA).^[11] Notably, structural flexibility of the host is often provoked by adsorption and thus the kinetics of the guest uptake and of the framework transformation are coupled. So, the monitoring of dynamics in such materials play a key role for the materials science and for further materials development. To enable such investigations, a wide range of advanced in situ characterization methods were explored in recent years, including diffraction, scattering, vibrational and NMR spectroscopies.^[12,13] Thanks to the crystallinity, the in situ X-ray, electron, and neutron diffraction methods became indispensable techniques for understanding the mechanisms of gas adsorption or separation in porous crystalline materials, and present a new possibility to crystallographically evaluate the population of individual adsorption sites, to study the cooperativity and to visualize the isotherms of individual pores in materials with hieratical porosity.[12,14,15]

A common Scheme for the structural characterization of a dynamic process, such as adsorption and desorption, assumes crystal structure determination at few different static states representing different stages of adsorption process,^[16] frequently augmented by macroscopic evaluation of thermodynamics and kinetics as well as by theoretical calculations.^[17] However, the time resolved tracking of guest molecules inside the porous framework upon adsorption has not been reported before. This work addresses a possibility to implement a sub-second X-ray powder diffraction for determination of kinetic barriers and visualization of the possible microscopic gas adsorption mechanisms simultaneously, from a single experiment. This approach has a potential to resolve site-specific kinetics of guest uptake, that is not accessible to microscopic methods.

As an object for the time-dependent study, we selected a microporous γ -Mg(BH₄)₂, a representative of metal borohydrides which attract much attention as multifunctional materials.^[18] This framework has tubular-like pores with ca. 7 Å in size, that is between one and two kinetic diameters of Kr and Xe atoms (3.6–7.2 Å for Kr and 3.95–7.9 Å for Xe),

Angewandte

al Edition Chemie

showing a significant non-isothermal kinetics upon Kr adsorption,^[19,20] therefore interesting for potential separation of these gases.^[21–23] In particular, the selective capture of Xe and Kr from the radioactive products generated from nuclear fission is highly needed.^[24–26]

The light elements of γ -Mg(BH₄)₂ host structure enhance the X-ray contrast for the guest atoms such as Ar, Kr or Xe significantly, because of sufficient difference between low scattering (form) factors of Mg (Z = 12), B (Z = 4) and H (Z=1) and comparable or higher scattering (form) factors of noble gas molecules (e.g. for Kr at $2\theta = 0^{\circ}$, it equals to the atomic number Z = 36). For this reason the noble gas atoms can be easily localized in the structure close to the center of the pore, while the light B and H atoms contribute little to the total scattering. The additional fluorescence signal of Kr atoms can be observed as an increase of all background points, which originates from the Kr K-edge X-ray absorption (14.3256 keV or 0.8655 Å),^[27] achievable in our experimental conditions with higher energy (15900 keV or 0.77936 Å), see Figure 1. Such combination of the host and guest responsiveness makes this compound ideal candidate for in situ investigations by X-rays.

The Kr adsorption experiments were performed at 170, 180, 190 and 200 K, in which the sample was exposed to 0.5 bar Kr and four diffraction patterns were collected per second for 2500 seconds. The in situ data show significant changes in the peak intensities in the XRD patterns of γ -Mg(BH₄)₂ with the Kr adsorption time (see Figure 1 for 170 K). The variation of the background is related to the increase of Kr fluorescence due its progressive adsorption by the framework,^[18] which we used as an independent measure of Kr adsorption kinetics.

Sequential Rietveld refinement to the multitude of diffraction patterns confirms the two-phase model, used in our previous variable-temperature experiment,^[20] see Figures S1 and S2, and Table S1. Kr atoms in the phase (2), having smaller unit cell parameter, are closer to the center of the pore cavities, as compared to the dominant phase (1).

However, a small amount of the secondary phase (2) present in the mixture, a strong peaks' overlap for the two phases, and the limitation of the X-ray powder diffraction to locate hydrogen atoms do not allow to capture structural differences associated with the smaller unit cell volume for the phase (2). We think that the two phases differ by the orientation of the $[BH_4]^-$ groups, a detail that is hardly seen in an X-ray experiment. The two phases have therefore been treated as isostructural with only slight difference in unit cell dimensions and location of Kr atoms.

In the phase (1) $Mg(BH_4)_2 x Kr$, the guest atoms are located in the 1D channels running along the body diagonal of the cubic unit cell, at the crystallographic position 32e(x, x, x). Secondary $Mg(BH_4)_2 y Kr$ phase (2) can be represented as a special case of phase (1), where the Kr atoms adopt the crystallographic position 16b with (1/8, 1/8, 1/8) coordinates right in the middle of the pore, see Figure 2.

The total Kr uptake for kinetic analysis was extracted using the Kr occupancies in each phase and their refined weight fractions. In the first approximation, Kr adsorption on γ -Mg(BH₄)₂ can be considered as an addition reaction, where Mg(BH₄)₂· q_e Kr adduct is forming (q_e is the total amount of Kr adsorbed at equilibrium for a given temperature and pressure). In an attempt to describe the transformation from empty γ -Mg(BH₄)₂ to Mg(BH₄)₂· q_e Kr, the time-dependent occupancy of Kr (q_t) was derived from the Johnson-Mehl-Avrami-Kolmogorov (JMAK) relation,^[28,29] widely used to describe kinetics of different chemical reactions:^[30]

$$q_{t} = q_{\min} + (q_{e} - q_{\min})[1 - \exp(-(kt)^{n})]$$
(1)

The Equation (1) is a fractional order kinetic model, where q_{\min} is amount of preoccupied Kr positions before data collection, q_e is an equilibrium value that sets the maximum for a given thermodynamic conditions, k is Avrami kinetic constant, n is an order of reaction (expected to be $0.5 \le n \le 1$ for a diffusion controlled case),^[30] t is the time elapsed from the beginning of the process. This relation is widely used to describe adsorption kinetics of various gases/vapors on activated carbons and is known as Linear driving force (LDF) model, if n = 1.^[31] The LDF model is consistent with



Figure 1. Time-dependent powder diffraction from γ -Mg(BH₄)₂ loaded with Kr gas (*p*(Kr) = 0.5 bar, T=170 K, λ = 0.77936 Å). The significant change of the intensities of Bragg peaks and of the fluorescent background correlate with the amount of the adsorbed gas.



Figure 2. Fragments of the crystal structures representing the phases (1) and (2) of γ -Mg(BH₄)₂ loaded with Kr. The minor phase (2) has smaller cell parameter and is modelled by occupation of the middle of the pore (coordinates 1/8, 1/8, 1/8) by Kr atoms. The pores are organized into channels running perpendicular to the plane of the Figure.

Angew. Chem. Int. Ed. 2021, 60, 5250-5256

© 2020 Wiley-VCH GmbH

Communications

a single rate constant (k), relaxation time, and barrier for diffusion into a periodic porous structure.^[32]

However, the least square fit of the data collected between 170 and 200 K with Equation (1) has shown the need of one additional term to model pore depopulation likely due to radiation damage, at least for the data collected at 200 K. Therefore, the Equation (1) was modified as follows:

$$q_{t} = q_{\min} + (q_{e} - q_{\min})[A(1 - \exp(-(k_{1}t)^{n})) - (1 - A)\exp(k_{2}t)]$$
(2)

Here A stands for the non-degraded part of the sample, and the decay constant k_2 maps the rate of sample degradation.

The corresponding Sharp–Hancock plots form the Equation (1) and the obtained Arrhenius plot of the rate constant from equations (1) and (2) versus T^{-1} result in unexpected behavior. They show partially anti-Arrhenius slope suggesting higher adsorption rates at lower temperatures (190–170 K), while the rate at 200 K is an outlier of the general trend (Figures S3 and S4). The anti-Arrhenius behavior is quite rare and usually can be observed during significant structural transitions in the kinetic process of guest uptake,^[33–35] while the outlier point indicate a possible need of a different model for the kinetic process.

One of the possible kinetic models, enabling to coherently describe the data is the one assuming two barriers:^[32]

$$q_{t} = q_{\min} + (q_{e} - q_{\min})[A(1 - \exp(-k_{1}t)) + (1 - A)(1 - \exp(-k_{2}t))]$$
(3)

Similarly to the Equation (2), the double exponent Equation (3) can be modified for the sample degradation at higher temperatures, via inclusion of additional parameters: A_1 (part of the adsorbed Kr limited by a rate constant k_1), A_2 (part of the adsorbed Kr limited by a rate constant k_2) and k_3 maps the rate of the sample degradation:

$$q_{t} = q_{\min} + (q_{e} - q_{\min})[A_{1}(1 - \exp(-k_{1}t)) + A_{2}(1 - \exp(-k_{2}t)) - (1 - A_{1} - A_{2})(\exp(k_{3}t))]$$
(4)

Indeed, the resulting Equation (4) successfully describes the experimental data for all investigated temperatures and the fitted q_e confirms the Kr content obtained from isobaric experiments, see Figure 3. On the other hand, Equation (3) works equally well for the data below 200 K due to the smaller effect of the radiation damage. The Equation (4) applied to the Kr fluorescence background shows rates that are very similar to those fitted from Kr occupancies, see Figure 4 and Figure S5. Kr fluorescence is an independent probe to the adsorption kinetics, free of the Rietveld refinement of thousands of powder diffraction patterns and of the related assumptions. However, it is giving access only to the kinetics of the adsorption without the underlying microscopic (structural) picture, and is limited to guests showing strong fluorescent signal, such as Kr. These independent measures suggest that Kr uptake is taking place in the crystalline part of the sample only.



Figure 3. Comparison of calculated Kr content from the isobaric variable-temperature experiments^[20] and kinetic data obtained using Equation (4). The fitted values of q_e fall in the middle of the kinetic hysteresis loops, and thus give even better estimate of the equilibrium Kr content than the quasi-equilibrium variable-temperature experiments.

Kr adsorption isotherms were also measured volumetrically at 170, 180, 190 and 200 K up to 1 bar (Figure S6). The adsorption rate analysis was performed at 0.5 bar equilibrium Kr pressure using LDF approximation. The obtained mass transfer coefficients follow the same trend as from the in situ X-ray data (Table S1), proving the reliability of the proposed approach.

The Kr adsorption isotherms were fitted using Langmuir model (Figures S7 and S8) and the derived equilibrium constants were used to extract the thermodynamic parameters from the van't Hoff plot (Figure S9). The resulting values of ΔH of 18.4(7) kJmol⁻¹ of adsorbed Kr and ΔS of 140-(4)Jmol⁻¹K⁻¹ are close to the initial estimates of $\Delta H = 21-24$ kJmol⁻¹ and $\Delta S = 103-113$ Jmol⁻¹K⁻¹ made from non-isothermal diffraction data.^[18]

In contrast to the equations (1) and (2), Arrhenius plots derived from the rate constants fitted by equations (3) and (4) demonstrate the ordinary behavior, see Figure 5 a. Linear fits to the Arrhenius plots yield kinetic barriers that are nearly equal for kinetic models (3) and (4). According to the Equation (4) applied to Kr occupancies, the radiation damage at 200 K affects about 0.05 part of the sample with the rate k_3 approximately 20 and 230 times lower than k_1 and k_2 , respectively, see Tables S2–S4. The parametrization of Equation (4) below 200 K gives similar result for 190 K and much lower values for 180 K and 170 K indicating a suppression of the radiation damage at low temperatures. We therefore neglected the radiation damage contribution and used double exponent Equation (3) for the data collected below 200 K.

The Arrhenius plots obtained from Kr occupancies and fluorescence background yield the first kinetic barrier of 8(1) and the second one of 13(2) kJ mol⁻¹. Analysis of the temperature evolution of the pre-exponential factors suggests a dominant contribution of the smaller kinetic barrier above 175–188 K, see Figure 5b and Figure S10. Such a behavior indicates two parallel adsorption mechanisms with different

5252 www.angewandte.org



Figure 4. The experimental, calculated, and difference kinetic curves for Kr adsorption at 200 K (top) as well as comparison of the experimental kinetics and fits obtained using Equations (3) and (4) (bottom). Left: Kr occupancies obtained using Rietveld method (each point is an independent refinement of the Kr occupancies in phases (1) and (2)); Right: measured Kr fluorescence background and corresponding fit obtained using Equations (3) and (4).

contributions, which change within investigated temperature intervals.

Based on structural consideration, we propose two simultaneous Kr diffusion mechanisms in γ -Mg(BH₄)₂ that agree with this observation. The lower barrier represents Kr diffusion along the quasi 1D channels of the nanoporous y- $Mg(BH_4)_2$, similarly to previously determined gas diffusion along 1D channels in microporous structures (e.g. Xe diffusion in TCF-1 with 7.1 kJ mol⁻¹ activation energy),^[36] while the higher diffusion barrier is more common for the guest-promoting rotary motions in tight channels of some crystal structures.^[37–39] In particular, the origin of the higher kinetic barrier of Kr adsorption in γ -Mg(BH₄)₂ can be related to the rotational motions of the [BH₄]⁻ groups in the structure. Notably, previously reported activation energy for $[BH_4]^-$ reorientations around 2-fold (C_2) axis in β -Mg(BH₄)₂ polymorph has a very similar value of 13.3 kJ mol^{-1.[40]} [BH₄]⁻ rotations near the 2-fold axis may therefore be considered as a predominant structural mechanism associated with the higher barrier of Kr diffusion. The barriers for $[BH_4]^$ orientational jumps in γ -Mg(BH₄)₂ are significantly higher and include at least two motions.^[41,42]

Taking into account these considerations together with the crystal structure of γ -Mg(BH₄)₂, we propose two concerted mechanisms for Kr adsorption: the first is caused by Kr diffusion along 1D channels running in c direction and it dominates at high temperatures (>175 K), while at low temperatures (<175 K) the second mechanism, namely the diffusion through the windows between channels, governs the kinetics, see Figure 5d. The first kinetic mechanism involves a larger (≈ 5.8 Å) aperture of the channels, which does not affect the diffusion of Kr (kinetic diameter of 3.6 Å) to such extent as a smaller interchannel aperture with ≈ 5.0 Å in size. According to contact surface analysis made with Mercury using 0.7 Å grid spacing,^[43] the smaller aperture is suitable for a diffusion of the guest molecules with a kinetic diameter smaller than 3.4 Å. Thus, rotational motions of $[BH_4]^-$ around 2-fold (C_2) axis of Mg-BH₄-Mg bonds with an activation barrier of 13 kJ mol⁻¹ can support the diffusion of Kr molecules (kinetic diameter 3.6 Å) via a pedal-wheel mechanism, see Figure 5d.

The characterization of the size and shape of γ -Mg(BH₄)₂ by scanning electron microscopy (SEM) reveals the presence of two types of Mg(BH₄)₂ particles (see Figure S11). One type







Figure 5. a) The representation of quasi 1D channels with the corresponding pore cavities of empty γ -Mg(BH₄)₂ and their filling by Kr molecules. The formed Mg(BH₄)₂ (x, y)Kr are presented along the [-1 1 1] crystallographic direction. b) The Arrhenius plots of kinetic rates calculated from the Equations (3) and (4) and partial contributions (c) of each exponential component both for the calculated Kr occupancies using Rietveld refinement of powder patterns and the fluorescence background. The corresponding temperature-dependent mechanisms (b and d) of the limiting Kr kinetic rates are shown as a smooth transformation from red to blue: via diffusion along the 1D channels with large pore apertures above 175–188 K (red) and diffusion between these 1D channels, promoted by the rotation of [BH₄]⁻ groups located in the small apertures below 175–188 K (blue).

of these particles belongs to the porous γ -Mg(BH₄)₂ and another one apparently is the amorphous polymorph of Mg(BH₄)₂, suggested by the Refs. [41,44] and our volumetric data. This makes impossible to get the correlations between particle size of γ -Mg(BH₄)₂ and Kr uptake time and requires additional studies for the conditions of its shape/size and yield control. In order to link microscopic diffusion mechanisms with the crystal structure of γ -Mg(BH₄)₂ and the size of the guest molecules, we additionally performed the kinetic analysis for the smaller Ar (kinetic diameter σ =3.4 Å) and the larger Xe (σ =3.95 Å) atoms, see Figure 6. Contrary to the Kr, they both follow a single barrier resistance with expect-

5254 www.angewandte.org

© 2020 Wiley-VCH GmbH

<u>GDCh</u>

Communications



Figure 6. The Arrhenius plots of Ar, Kr and Xe adsorption kinetics and the schemes of corresponding microscopic diffusion mechanisms. Ar and Xe follow a single exponent adsorption behaviour, while Kr has a double exponent parallel kinetics, denoted as the first and the second kinetic barriers. The smooth transition from the domination of interchannel to the intrachannel activation barrier upon Kr adsorption by γ -Mg(BH₄)₂ is presented by gradient change of colour from blue to red (temperature). Colour code: Ar—purple, B—olive, H—grey, Kr—orange, Mg—red, Xe—violet.

edly lower activation energy for Ar $(5.4(3) \text{ kJ mol}^{-1})$ and the higher one for Xe atoms $(9.5(6) \text{ kJ mol}^{-1})$, see Figures 6, S12 and Table S5. This suggest that Ar atoms diffuse easily along 1D channels as well as between them within the investigated temperature range. On the other hand, larger Kr atoms (3.8 Å) have higher activation barrier along 1D channels $(8(1) \text{ kJ mol}^{-1})$ as well as through the interchannel aperture, where its size is matching the penetration limit. The diffusion along the latter is likely hindered by the dynamic rotation of the [BH₄]⁻ groups between Mg atoms, resulting in higher activation barrier (13(2) kJ mol⁻¹). The largest Xe atoms ($\sigma =$ 3.95 Å) apparently do not diffuse through the interchannel apertures at all due to large size. In such case, the obtained intrachannel activation barriers increase in accordance with their larger kinetic diameters in a series Ar < Kr < Xe, being common upon adsorption by other porous materials, see Figure S13.^[45,46]

The understanding of adsorption mechanisms and their corresponding energetic characteristics is of high importance for predictions of the adsorption selectivity. Particularly, the evaluation of structure- and guest-defined activation barriers in dynamic materials may explain such phenomena as selectivity of adsorption-induced phase transitions.^[47] The latter enables to use the same porous framework for

separation of various guests, depending on temperature regime. In our case the potential separation of Kr over Xe by γ -Mg(BH₄)₂ will be limited by the rotational motions of [BH₄]⁻ groups below 175–188 K and by the guest diffusivity along 1D channels above this temperature range. The similar kinetic characterization of the Xe adsorption in γ -Mg(BH₄)₂ should demonstrate the preferable high temperature (>188 K) range for Xe over Kr kinetic selectivity, providing that its hindered interchannel diffusivity is confirmed experimentally.

In line with the previously presented capability to resolve individual site-specific guest uptake characteristics, like thermodynamics^[14] and/or adsorption isotherms,^[14, 19, 20] this work also shows a promising potential of sub-second X-ray powder diffraction to monitor kinetics of guest adsorption for multi-adsorption site frameworks, as this information is completely inaccessible by classical bulk (volumetric, gravimetric, calorimetric) methods. Despite the fact, that sequential Rietveld analysis of thousands of diffraction patterns remains challenging, in the near future it can be combined with other computational methods, like Principal Component Analysis (PCA),^[48] which will open much room for its implementation in numerous kinetic studies.

Acknowledgements

This work was supported by the Académie Universitaire Louvain (AUL, Belgium) under Grant ADi/DB/1058.2011 and FNRS (CC 1.5169.12, PDR T.0169.13, EQP U.N038.13).

Conflict of interest

The authors declare no conflict of interest.

Keywords: crystal structure · kinetics · nanoporous frameworks · selectivity · synchrotron X-ray diffraction

- [1] G. Férey, Chem. Soc. Rev. 2008, 37, 191-214.
- [2] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, Acc. Chem. Res. 2001, 34, 319–330.
- [3] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* 2013, 341, 1230444.
- [4] K. Adil, Y. Belmabkhout, R. S. Pillai, A. Cadiau, P. M. Bhatt, A. H. Assen, G. Maurin, M. Eddaoudi, *Chem. Soc. Rev.* 2017, 46, 3402–3430.
- [5] C. Serre, C. Mellot-Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk, G. Férey, *Science* 2007, 315, 1828–1832.
- [6] C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër, G. Férey, J. Am. Chem. Soc. 2002, 124, 13519–13526.
- [7] R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, Angew. Chem. Int. Ed. 2003, 42, 428–431; Angew. Chem. 2003, 115, 444–447.
- [8] D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons, T. Düren, J. Am. Chem. Soc. 2011, 133, 8900-8902.
- [9] J. W. Brown, B. L. Henderson, M. D. Kiesz, A. C. Whalley, W. Morris, S. Grunder, H. Deng, H. Furukawa, J. I. Zink, J. F. Stoddart, et al., *Chem. Sci.* 2013, *4*, 2858–2864.
- [10] S. Castellanos, F. Kapteijn, J. Gascon, CrystEngComm 2016, 18, 4006–4012.
- [11] S. Krause, V. Bon, I. Senkovska, U. Stoeck, D. Wallacher, D. M. Többens, S. Zander, R. S. Pillai, G. Maurin, F. X. Coudert, et al., *Nature* 2016, *532*, 348–352.
- [12] S. Krause, J. D. Evans, V. Bon, I. Senkovska, P. Iacomi, F. Kolbe, S. Ehrling, E. Troschke, J. Getzschmann, D. M. Többens, et al., *Nat. Commun.* 2019, 10, 3632.
- [13] D. B. Ravnsbœk, L. H. Sørensen, Y. Filinchuk, F. Besenbacher, T. R. Jensen, Angew. Chem. Int. Ed. 2012, 51, 3582–3586; Angew. Chem. 2012, 124, 3642–3646.
- [14] I. Dovgaliuk, F. Nouar, C. Serre, Y. Filinchuk, D. Chernyshov, *Chem. Eur. J.* 2017, 23, 17714–17720.
- [15] H. S. Cho, J. Yang, X. Gong, Y. B. Zhang, K. Momma, B. M. Weckhuysen, H. Deng, J. K. Kang, O. M. Yaghi, O. Terasaki, *Nat. Chem.* **2019**, *11*, 562–570.
- [16] J. P. Zhang, P. Q. Liao, H. L. Zhou, R. B. Lin, X. M. Chen, *Chem. Soc. Rev.* 2014, 43, 5789–5814.
- [17] L. Sarkisov, R. L. Martin, M. Haranczyk, B. Smit, J. Am. Chem. Soc. 2014, 136, 2228–2231.
- [18] M. Paskevicius, L. H. Jepsen, P. Schouwink, R. Černý, D. B. Ravnsbæk, Y. Filinchuk, M. Dornheim, F. Besenbacher, T. R. Jensen, *Chem. Soc. Rev.* 2017, 46, 1565-1634.
- [19] Y. Filinchuk, B. Richter, T. R. Jensen, V. Dmitriev, D. Chernyshov, H. Hagemann, *Angew. Chem. Int. Ed.* **2011**, *50*, 11162– 11166; *Angew. Chem.* **2011**, *123*, 11358–11362.
- [20] I. Dovgaliuk, V. Dyadkin, M. Vander Donckt, Y. Filinchuk, D. Chernyshov, ACS Appl. Mater. Interfaces 2020, 12, 7710–7716.

- [21] J. J. Perry, S. L. Teich-Mcgoldrick, S. T. Meek, J. A. Greathouse, M. Haranczyk, M. D. Allendorf, *J. Phys. Chem. C* 2014, *118*, 11685–11698.
- [22] B. J. Sikora, C. E. Wilmer, M. L. Greenfield, R. Q. Snurr, *Chem. Sci.* 2012, *3*, 2217–2223.
- [23] M. Witman, S. Ling, S. Jawahery, P. G. Boyd, M. Haranczyk, B. Slater, B. Smit, J. Am. Chem. Soc. 2017, 139, 5547–5557.
- [24] F. Kerry, Industrial Gas Handbook: Gas Separation and Purification, CRC, Boca Raton, 2006.
- [25] J. Liu, P. K. Thallapally, D. Strachan, *Langmuir* 2012, 28, 11584– 11589.
- [26] L. Chen, P.S. Reiss, S. Y. Chong, D. Holden, K. E. Jelfs, T. Hasell, M. A. Little, A. Kewley, M. E. Briggs, A. Stephenson, et al., *Nat. Mater.* 2014, *13*, 954–960.
- [27] J. A. Bearden, A. F. Burr, Rev. Mod. Phys. 1967, 39, 125-142.
- [28] A. N. Kolmogorov, Bull. Acad. Sci. USSR Math. Ser. 1937, 1, 355–359.
- [29] M. Avrami, J. Chem. Phys. 1939, 7, 1103-1112.
- [30] R. Serna-Guerrero, A. Sayari, Chem. Eng. J. 2010, 161, 182-190.
- [31] E. Glueckauf, Trans. Faraday Soc. 1955, 51, 1540-1551.
- [32] A. J. Fletcher, E. J. Cussen, D. Bradshaw, M. J. Rosseinsky, K. M. Thomas, J. Am. Chem. Soc. 2004, 126, 9750–9759.
- [33] A. Kondo, N. Kojima, H. Kajiro, H. Noguchi, Y. Hattori, F. Okino, K. Maeda, T. Ohba, K. Kaneko, H. Kanoh, *J. Phys. Chem. C* 2012, *116*, 4157–4162.
- [34] M. R. Caira, T. le Roex, L. R. Nassimbeni, E. Weber, Cryst. Growth Des. 2006, 6, 127-131.
- [35] L. J. Barbour, M. R. Caira, L. R. Nassimbeni, J. Chem. Soc. Perkin Trans. 2 1993, 2321–2322.
- [36] I. Bassanetti, S. Bracco, A. Comotti, M. Negroni, C. Bezuidenhout, S. Canossa, P. P. Mazzeo, L. Marchió, P. Sozzani, *J. Mater. Chem. A* 2018, 6, 14231–14239.
- [37] A. Comotti, S. Bracco, P. Sozzani, Acc. Chem. Res. 2016, 49, 1701–1710.
- [38] A. Comotti, S. Bracco, A. Yamamoto, M. Beretta, T. Hirukawa, N. Tohnai, M. Miyata, P. Sozzani, J. Am. Chem. Soc. 2014, 136, 618–621.
- [39] A. Comotti, S. Bracco, P. Valsesia, M. Beretta, P. Sozzani, Angew. Chem. Int. Ed. 2010, 49, 1760–1764; Angew. Chem. 2010, 122, 1804–1808.
- [40] A. V. Soloninin, O. A. Babanova, A. V. Skripov, H. Hagemann, B. Richter, T. R. Jensen, Y. Filinchuk, J. Phys. Chem. C 2012, 116, 4913–4920.
- [41] V. Ban, A. V. Soloninin, A. V. Skripov, J. Hadermann, A. Abakumov, Y. Filinchuk, J. Phys. Chem. C 2014, 118, 23402– 23408.
- [42] M. Eagles, B. Sun, B. Richter, T. R. Jensen, Y. Filinchuk, M. S. Conradi, J. Phys. Chem. C 2012, 116, 13033-13037.
- [43] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. Van De Streek, P. A. Wood, J. Appl. Crystallogr. 2008, 41, 466– 470.
- [44] N. P. Stadie, E. Callini, P. Mauron, A. Borgschulte, A. Züttel, J. Visualized Exp. 2015, 95, 7–9.
- [45] Handbook of Zeolite Science and Technology (Eds.: S. M. Auerbach, K. A. Carrado, P. K. Dutta, Marcel Dekker, New York, 2003.
- [46] Y. Liu, J. Liu, J. Hu, BMC Chem. Eng. 2019, 1-7.
- [47] C. A. Fernandez, J. Liu, P. K. Thallapally, M. Strachan, J. Am. Chem. Soc. 2012, 134, 9046–9049.
- [48] D. Chernyshov, I. Dovgaliuk, V. Dyadkin, W. van Beek, *Crystals* 2020, 10, 581.

Manuscript received: November 10, 2020

- Accepted manuscript online: November 16, 2020
- Version of record online: January 19, 2021

