

Synthesis of ZIF-8 and ZIF-67 by Steam-Assisted Conversion and an Investigation of Their Tribological Behaviors**

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Zeolitic imidazolate frameworks (ZIFs) are a new subclass of porous metal–organic frameworks (MOFs) which frequently have expanded zeolite topologies.^[1–8] Most interestingly, some guest-free ZIFs have the large surface area and pore volume of classical MOFs; at the same time, they also have the high chemical and thermal stability of conventional zeolites.^[4] Because of these combined and desirable features, ZIFs show great potential for many applications, especially for gas storage and separations.^[5,9–12]

ZIF-8 ($\text{Zn}(\text{mim})_2$, mim = 2-methylimidazolate) and ZIF-67 ($\text{Co}(\text{mim})_2$) are the most representative ZIF materials with a zeolite sod topology. The expanded sod framework exhibits intriguing features: a large sod cage (11.6 Å) is accessible through a narrow six-ring pore (3.4 Å). Moreover, ZIF-8 has a high thermal stability (550 °C in N_2) and large surface area (BET: 1630 $\text{m}^2 \text{g}^{-1}$).^[4] These features have made ZIF-8 the most established ZIF material and it has found a variety of impressive applications.^[9,11,13–15]

Thermally and chemically stable ZIF-8 and ZIF-67 have generally been synthesized by using DMF as an organic solvent that ultimately fills the pore space.^[4] However, the guest molecule DMF is actually larger than the aperture of the sod cage, and could not be directly released. Their extensive applications require that the synthesis and activation of ZIF-8 and ZIF-67 samples are facile and environmentally friendly. Therefore, solvent-free (melting) synthesis (possible because of the low melting point of mim: m.p. 144 °C) or hydrothermal synthesis, have significant potential for the development of effective and environmentally benign routes to ZIF-8 and ZIF-67.

Actually, in the absence of the organic solvent DMF, a eutectic mixture is formed upon heating a mixture of $\text{Zn}(\text{OAc})_2$ and mim below the melting point of mim (Supporting Information, Figure S1). The eutectic mixture was then kept for 24 h either at 120 °C or 150 °C. However, the powder X-ray diffraction (PXRD) analysis of the unwashed products showed that this solvent-free (melting) synthesis had not

lead to any detectable ZIF phase (Supporting Information, Figure S2). Moreover, the unwashed products were found to be soluble upon washing with water, further indicating that the required crystallization had not occurred.

We attempted a hydrothermal synthesis of ZIF-8 and ZIF-67. However, only two new compounds with the dense dia framework (referred to as dia(Zn): $\text{Zn}(\text{mim})_2$ and dia(Co): $\text{Co}(\text{mim})_2$) were formed from $\text{Zn}(\text{OAc})_2$ or $\text{Co}(\text{OAc})_2$ with excess mim (Figure 1, left). The structure of dia(Zn) was determined by single-crystal X-ray diffraction. Each Zn^{II} ion is coordinated by four N atoms from bridging 2-methylimidazolate groups. A view along the *b*-axis of the monoclinic cell reveals 1D channel with chairlike hexagonal apertures, which intersect with other regular channels to form an infinite 3D framework that resembles the dia topology (Supporting Information, Figure S3). The dia(Co) analogue was identified as being isostructural to dia(Zn) on the basis of the PXRD pattern (Supporting Information, Figure S4). The porosities of dia(Zn) and dia(Co) could not be established by N_2 uptake owing to the small pore size (Supporting Information, Figure S7). The calculated density of dia(Zn) (1.58 g cm^{-3}) is higher than that of other ZIFs (e.g. ZIF-8, 0.95 g cm^{-3}), confirming, the two new compounds with the dia framework are quite dense.

These results inspired us to devise a new path to exploit the structure-directing effect of H_2O to prepare open and porous ZIF-8 and ZIF-67. A path (denoted as dry-gel conversion) that has been exploited in our laboratory, is the transformation of aluminosilicate gels into zeolites by contact with a vapor of volatile amines.^[16] A similar method (denoted as steam-assisted conversion) for transforming a gel to a zeolite in H_2O vapor has also been developed (Figure 1, right).^[17] Compared to most conventional hydro-solvothermal synthesis or solid-state transport synthesis, the difference in this method is due to the high concentration of the

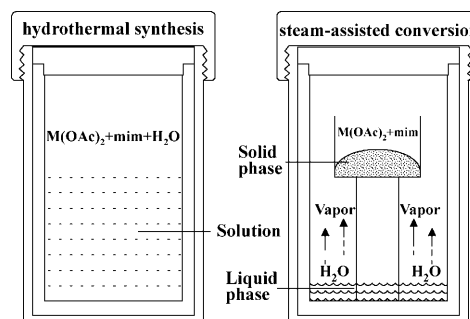


Figure 1. Schematic diagram of the reaction vessels for ZIFs synthesis. Left: hydrothermal synthesis (HTS), and right: the steam-assisted conversion (SAC) method; M = Zn, Co.

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solid phase present and the apparent separation of the solid and liquid phase.

By applying this synthetic method, we succeeded in obtaining the porous material ZIF-8 and ZIF-67 by replacing the organic DMF with H_2O . The solid phase contained the hydrated metal salt (usually $\text{Zn}(\text{OAc})_2$ or $\text{Co}(\text{OAc})_2$) and excess mim. The liquid phase was H_2O (Figure 1, right). To date, there is a limited number of reports on porous MOFs prepared under hydrothermal conditions.^[18] Herein we report the first example of the preparation of porous ZIFs by using H_2O as medium without other additives. Furthermore, the dry-gel conversion or steam-assisted conversion can be easily extended to study the synthesis of other MOF or ZIF materials.

The relative intensity and peak positions of the PXRD pattern are in agreement with previous reports,^[4] confirming the formation of pure crystalline ZIF-8 and ZIF-67 (Supporting Information, Figure S9). The thermogravimetric analysis (TGA) of ZIF-8 or ZIF-67 obtained by steam-assisted conversion, shows that the H_2O guest molecule was removed much more easily from the narrow six-ring pore of the sod cage than organic DMF (Supporting Information, Figure S11). The N_2 sorption properties of ZIF-8 and ZIF-67 were also investigated. They were found to exhibit type I isotherms, indicating their microporous nature (Supporting Information, Figure S15). The BET surface areas were measured as $1470 \text{ m}^2 \text{ g}^{-1}$ and $1319 \text{ m}^2 \text{ g}^{-1}$ for ZIF-8 and ZIF-67, respectively, with micropore volumes of $0.69 \text{ cm}^3 \text{ g}^{-1}$ and $0.61 \text{ cm}^3 \text{ g}^{-1}$, respectively.

To understand the crystallization process in the steam-assisted synthesis of ZIF-8, the PXRD patterns of the unwashed products obtained after different reaction times at 120°C are shown in Supporting Information Figure S16. After 10 min, no ZIF crystallization can be evidenced. Based on the differential scanning calorimetry (DSC) data we assume that the eutectic mixture is quickly formed. Upon cooling the mixture to room temperature, the product appeared as a eutectic mixture embedded in the excess mim. When the reaction time was extended beyond 1 h, weak diffraction peaks characteristic of ZIF-8 began to appear in the PXRD pattern, implying reorganization between the eutectic mixtures and excess mim has occurred under the influence of H_2O steam. When the steam treatment was increased from 1 h through to 24 h, the diffraction peaks of ZIF-8 gradually became sharper, indicating that the crystallinity of ZIF-8 increased with increasing reaction time. Note that the excess mim is present within the forming crystals, so the characteristic mim PXRD peaks remain throughout the reaction time.

Several researchers have reported on the nucleation and crystal-growth mechanism of zeolite crystals formed by hydrothermal or solvothermal synthesis. At the two extremes of the proposed mechanism for zeolite synthesis are: 1) the solution-mediated transport mechanism, and 2) the solid-phase transformation mechanism.^[19] The solution-mediated transport mechanism involves dissolution of the reagents in the solution phase and subsequent transport of the dissolved species by solution-mediated diffusion to the nucleation sites where crystal growth takes place.^[19] Metal salts ($\text{Zn}(\text{OAc})_2$ or

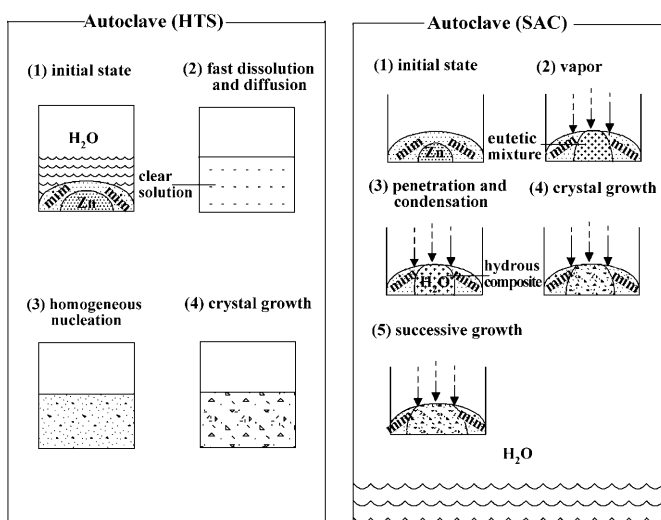


Figure 2. Formation processes of ZIFs. Left: hydrothermal synthesis; and right: steam-assisted conversion. See text for details.

$\text{Co}(\text{OAc})_2$) and mim could dissolve readily in the H_2O or DMF used for hydrothermal or solvothermal synthesis, and so the solution-mediated transformation is most probable (Figure 2, left) using these methods.

The above PXRD data suggest the following sequence of events in the steam-assisted synthesis of ZIF-8 (Figure 2, right). From the properties of pure water, it is estimated that the autogenous pressure (1.9848 atm) inside the Teflon-lined autoclaves at 120°C would be sufficient to make H_2O steam fill it. Simultaneously, transformation (solid phase) may proceed through the intermediate formation of a eutectic mixture embedded in the excess of mim. Once H_2O steam is formed, it can penetrate into the surface of eutectic mixtures and excess mim. The small amount of penetrating H_2O molecules will interact with some of the eutectic mixture and excess mim through sorption and condensation, resulting in the formation and densification of hydrous composites (H_2O -Zn-mim). It is apparent that such composites will contain adsorbed and condensed water, so that they present a “solution-like” phase in which the same chemistry can occur as that in bulk solution; however, there may be differences due to mass-transport limitations and concentration gradients.^[19] The condensed composites dynamically rearrange to a sod structure (ZIF-8). The ZIF-8 crystallization begins in the interior of hydrous composites, and successive growth may occur through the pressure and concentration gradient caused by the transport of water and excess mim, setting up a vapor–liquid equilibrium with H_2O that is present in the steam. So this process cannot be viewed as a pure solid–solid mechanism either, since sorption and condensation of water also plays an important role during the transformation.^[19] At any time, there will be a composite of ZIF-8 crystals and excess mim.

The earlier reports by Morris et al.^[20] and also by Tian et al.,^[21] described the advantageous effect of small amounts of water added to eutectic mixture systems in the ionothermal synthesis of zeolite. Therefore, the question is whether ZIF-8 or ZIF-67 could be prepared by adding small amounts of water directly to the eutectic mixture in the ionothermal regime? Thus, parallel experiments (ionothermal/eutectic

mixture conditions and steam-assisted conversion conditions) have been performed for comparison. Neither in the eutectic mixture ($\text{Zn}(\text{OAc})_2/\text{Co}(\text{OAc})_2\text{-mim}$) regime nor by steam-assisted conversion conditions, under low levels of water (0.05–0.1 mL) was any product obtained after 24 h of heating at 120°C. In the case of eutectic mixture regime, with intermediate amounts of water added (0.3–2.0 mL) ZIF-8 or a mixture of ZIF-67 and small unidentified phase was dominate product, with even more water (4.0 mL) dense dia(Zn) or dia(Co) was the main product (Supporting Information, Figure S17 and Figure S18). It is suggested that a small amount water is advantageous for the ionothermal synthesis of zeolites and too much water is detrimental to the formation of zeolites, leading to dense phases being formed.^[20,21] In contrast, ZIF-8 or ZIF-67 was found across all levels of water content by the steam-assisted conversion method. Similar experiments were also carried out at 150°C (Supporting Information, Figure S19 and Figure S20). The data shown indicate that phase region is broad for crystallization of ZIF-8 or ZIF-67 by steam-assisted conversion. Thus, controlling the crystallization of ZIF-8 or ZIF-67 by adding different amounts of water to the eutectic mixture was not straightforward. And the steam-assisted conversion is a reliable way to the crystallization of ZIF-8 and ZIF-67 by the transport of water content to the eutectic mixture under the autogenous pressure.

Very recently, Cheetham et al.^[22] reported that ZIFs display good mechanical behaviors, such as elastic moduli and hardness properties. Notably, it is important to recognize that the mechanical properties of ZIF-8 are superior to those of metal–organic frameworks (e.g. MOF-5), and comparable with those of pure organic polymers. Classical organic polymers, such as polytetrafluoroethylene (PTFE), have been used as lubricant additives since the early 1940s.^[23] From the practical standpoint, ZIFs are expected to operate under mechanical stresses and substantial pressures.^[22] Thus, it was of interest to ascertain whether they might exhibit good tribological behavior as additives in liquid lubricants. Thus the tribological properties, such as the anti-wear capacity and load-carrying capacity, of these materials have been investigated.

Table 1 shows the wear scar diameter (WSD) and the maximum non-seizure load (P_B) value of base oil (100 SN, paraffinic neutral oil) containing different additives. For comparison, the data for the oil treated with polytetrafluoroethylene (PTFE) were also measured under identical conditions. The WSD is used to evaluate the anti-wear property of a lubricant. It can be seen that the anti-wear property of the oil was improved by the addition of the tested samples. With ZIF-8 and ZIF-67, the WSD were 0.32 and 0.30 mm, respectively. The WSD was reduced by 45% with ZIF-8 and by 48% with ZIF-67 based on the pure oil. The observed wear scar areas and wear degrees in scanning electron microscope (SEM) images (Supporting Information, Figure S22) also show that a steel ball lubricated with pure oil was damaged more seriously in comparison to those lubricated with oil containing additives.

The P_B value is an important index to evaluate the load-carrying capacity of a lubricant. It can be seen that ZIF-8 and ZIF-67 as additives can considerably improve a lubricant's

Table 1: The WSD and P_B value in oil and oil + additives.

Lubricant	WSD [mm]	P_B [N]
Pure oil	0.58	470
Oil + 1.0 wt% ZIF-8	0.32	549
Oil + 1.0 wt% ZIF-67	0.30	549
Oil + 1.0 wt% PTFE	0.32	510

P_B value as compared to pure oil. The P_B values were increased by 16.8% after adding ZIF-8 or ZIF-67 to the oil. Note that the anti-wear property of the base oil was improved by adding ZIFs or PTFE; however, the load-carrying capacity of the base oil containing ZIFs (549 N) was superior to that containing PTFE (510 N). These results show that both of the ZIF materials exhibit excellent tribological properties when used as additives in liquid lubricants, in comparison to the typical lubrication additive PTFE. Further tribological tests of other ZIF materials are currently under investigation.

In summary, ZIF-8 and ZIF-67 with the sod framework have been synthesized by replacing the organic solvent, such as DMF, with H_2O through a steam-assisted conversion method. These materials are not accessible through conventional hydrothermal or solvent-free (melting) synthesis. The work provides the first example of water possibly having a structure-directing effect on the synthesis of an open and porous ZIF material. It could be possible to use the dry-gel conversion or steam-assisted conversion as a new approach to the preparation of porous ZIFs as well as MOFs. Moreover, ZIF-8 and ZIF-67, used as additives in liquid lubricants, show excellent anti-wear and load-carrying abilities. We expect that such materials have potential industrial application as lubricant additives.

Experimental Section

Steam-assisted conversion method: A typical procedure for the preparation of ZIF-8: $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.11 g, 0.5 mmol) and 2-methylimidazole (0.41 g, 5 mmol) were placed in a small Teflon cup, which was supported by a Teflon holder. Each cup and holder was placed in a Teflon-lined stainless steel autoclave. H_2O (2.0 mL) was added to the bottom of the autoclave. The crystallization was then carried out at 120°C for 24 h. After cooling the autoclave to room temperature, the solid products were separated by filtration and washed with distilled water (yield: 0.07 g). The procedure for obtaining ZIF-67 was similar to that for ZIF-8, except that $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was used instead of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (yield: 0.06 g).

The detailed synthesis procedures by solvent-free (melting) synthesis method and hydrothermal method are included in the Supporting Information. The experimental characterization techniques, including PXRD, SEM, DSC, TGA, and FTIR methods are described in detail in the Supporting Information. CCDC 783838 (dia(Zn)) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Tribological behaviors: Samples of ZIF-8, ZIF-67, PTFE as additives in base oil were investigated using a four-ball machine. The balls (diameter 12.7 mm) used in the test were made of GCr15 bearing steel (SAE52100 steel) with an HRc of 59–61. The base oil employed in this work was mineral oil (100 SN), which has a viscosity of $16.27 \text{ mm}^2 \text{ s}^{-1}$ at 40°C, a viscosity index of 68, and a flash point of 196°C. Noted that the samples of ZIF-8 and ZIF-67 were carefully

milled prior to use until an edge length of about several hundred nanometers was obtained (Supporting Information, Figure S21). The anti-wear properties (wear scar diameter, WSD) of the samples as additives in base oil were evaluated with a four-ball tester operated at a rotating speed of 1200 revolutions min⁻¹ (rpm) and room temperature of 25 °C. The test duration was 60 min and the load applied was 147 N. At the end of each test, WSD on the three stationary balls were measured by means of a digital-reading optical microscope to an accuracy of 0.01 mm in the directions parallel and perpendicular to the sliding motion. The load-carrying capacity (maximum non-seizure load, P_B) of the samples was determined according to the China National Standard method GB/T3142-90, which is similar to ASTM D2783. For each sample, three identical tests were performed so as to minimize data scattering. The average WSD of the three identical tests was calculated as the WSD in this work. The morphologies of the worn surfaces (scars) of the ball were examined by means of SEM (Supporting Information, Figure S22).

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- [1] a) R. Lehnert, F. Z. Seel, *Z. Anorg. Allg. Chem.* **1980**, *464*, 187–194; b) M. Sturm, F. Bromdl, D. Engel, W. Hoppe, *Acta Crystallogr. Sect. B* **1975**, *31*, 2369–2378.
- [2] a) Y. Q. Tian, C. X. Cai, Y. Ji, X. Z. You, S. M. Peng, G. H. Lee, *Angew. Chem.* **2002**, *114*, 1442–1444; *Angew. Chem. Int. Ed.* **2002**, *41*, 1384–1386; b) Y. Q. Tian, Y. M. Zhao, Z. X. Chen, G. N. Zhang, L. H. Weng, D. Y. Zhao, *Chem. Eur. J.* **2007**, *13*, 4146–4154; c) Y. Q. Tian, S. Y. Yao, D. Gu, K. H. Cui, D. W. Guo, G. Zhang, Z. X. Chen, D. Y. Zhao, *Chem. Eur. J.* **2010**, *16*, 1137–1141.
- [3] X. C. Huang, Y. Y. Lin, J. P. Zhang, X. M. Chen, *Angew. Chem.* **2006**, *118*, 1587–1589; *Angew. Chem. Int. Ed.* **2006**, *45*, 1557–1559.
- [4] a) K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186–10191; b) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939–943.
- [5] a) H. Hayashi, A. P. Côté, H. Furukawa, M. O’Keeffe, O. M. Yaghi, *Nat. Mater.* **2007**, *6*, 501–506; b) B. Wang, A. P. Côté, H. Furukawa, M. O’Keeffe, O. M. Yaghi, *Nature* **2008**, *453*, 207–211; c) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 3875–3877; d) A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O’Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2010**, *43*, 58–67.
- [6] a) T. Wu, X. Bu, R. Liu, Z. E. Lin, J. Zhang, P. Feng, *Chem. Eur. J.* **2008**, *14*, 7771–7773; b) T. Wu, X. Bu, J. Zhang, P. Feng, *Chem. Mater.* **2008**, *20*, 7377–7382; c) J. Zhang, T. Wu, C. Zhou, S. Chen, P. Feng, X. Bu, *Angew. Chem.* **2009**, *121*, 2580–2583; *Angew. Chem. Int. Ed.* **2009**, *48*, 2542–2545; d) T. Wu, J. Zhang, C. Zhou, L. Wang, X. Bu, P. Feng, *J. Am. Chem. Soc.* **2009**, *131*, 6111–6113.
- [7] a) G. A. V. Martins, P. J. Byrne, P. Allan, S. J. Teat, A. M. Z. Slawin, Y. Li, R. E. Morris, *Dalton Trans.* **2010**, *39*, 1758–1762; b) S. M. Chen, J. Zhang, P. Y. Feng, X. H. Bu, *Dalton Trans.* **2010**, *39*, 697–699.
- [8] a) Y. L. Liu, V. C. Kravtsov, R. Larsen, M. Eddaoudi, *Chem. Commun.* **2006**, 1488–1490; b) Y. L. Liu, V. C. Kravtsov, M. Eddaoudi, *Angew. Chem.* **2008**, *120*, 8574–8577; *Angew. Chem. Int. Ed.* **2008**, *47*, 8446–8449; c) D. F. Sava, V. Kravtsov, F. Nouar, J. Eckert, J. F. Eubank, F. Nouar, M. Eddaoudi, *J. Am. Chem. Soc.* **2009**, *131*, 10394–10396; d) M. H. Alkordi, J. A. Brant, L. Wojtas, V. C. Kravtsov, A. J. Cairns, M. Eddaoudi, *J. Am. Chem. Soc.* **2009**, *131*, 17753–17755.
- [9] a) W. Zhou, H. Wu, M. R. Hartman, T. Yildirim, *J. Phys. Chem. C* **2007**, *111*, 16131–16137; b) H. Wu, W. Zhou, T. Yildirim, *J. Am. Chem. Soc.* **2009**, *131*, 4995–5000; c) H. Wu, W. Zhou, T. Yildirim, *J. Phys. Chem. C* **2009**, *113*, 3029–3035.
- [10] J. Pérez-Pellitero, H. Amrouche, F. R. Siperstein, G. Pirngruber, C. Nieto-Draghi, G. Chaplais, A. Simon-Masseron, D. Bazer-Bachi, D. Peralta, N. Bats, *Chem. Eur. J.* **2010**, *16*, 1560–1571.
- [11] a) H. Bux, F. Y. Liang, Y. S. Li, J. Cravillon, M. Wiebcke, J. Caro, *J. Am. Chem. Soc.* **2009**, *131*, 16000–16001; b) K. H. Li, D. H. Olson, J. Seidel, T. J. Emge, H. W. Gong, H. P. Zeng, J. Li, *J. Am. Chem. Soc.* **2009**, *131*, 10368–10369; c) S. R. Venna, M. A. Carreon, *J. Am. Chem. Soc.* **2010**, *132*, 76–78; d) S. Basu, M. Maes, A. Cano-Odena, L. Alaerts, D. E. De Vos, I. F. J. Vankelecom, *J. Membr. Sci.* **2009**, *344*, 190–198; e) R. Krishna, J. M. van Baten, *J. Membr. Sci.* **2010**, *360*, 323–333; f) M. J. C. Ordoñez, K. J. Balkus, Jr., J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2010**, *361*, 28–37.
- [12] a) Y. S. Li, F. Y. Liang, H. Bux, A. Feldhoff, W. S. Yang, J. Caro, *Angew. Chem.* **2010**, *122*, 558–561; *Angew. Chem. Int. Ed.* **2010**, *49*, 548–551; b) Y. S. Li, F. Y. Liang, H. Bux, W. S. Yang, J. Caro, *J. Membr. Sci.* **2010**, *354*, 48–54; c) A. S. Huang, H. Bux, F. Steinbach, J. Caro, *Angew. Chem.* **2010**, *122*, 5078–5081; *Angew. Chem. Int. Ed.* **2010**, *49*, 4958–4961; d) Y. Y. Liu, E. P. Hu, E. A. Khan, Z. P. Lai, *J. Membr. Sci.* **2010**, *353*, 36–40.
- [13] a) C. Chizallet, N. Bats, *J. Phys. Chem. Lett.* **2010**, *1*, 349–353; b) G. Lu, J. T. Hupp, *J. Am. Chem. Soc.* **2010**, *132*, 7832–7833.
- [14] a) K. W. Chapman, G. J. Halder, P. J. Chupas, *J. Am. Chem. Soc.* **2009**, *131*, 17546–17547; b) E. C. Spencer, R. J. Angel, N. L. Ross, B. E. Hanson, J. A. K. Howard, *J. Am. Chem. Soc.* **2009**, *131*, 4022–4026; c) J. Cravillon, S. Münzer, Lohmeier, S. J. Feldhoff, A. Feldhoff, K. Huber, M. Wiebcke, *Chem. Mater.* **2009**, *21*, 1410–1412; d) S. A. Moggach, T. D. Bennett, A. K. Cheetham, *Angew. Chem.* **2009**, *121*, 7221–7223; *Angew. Chem. Int. Ed.* **2009**, *48*, 7087–7089; e) S. K. Nune, P. K. Thallapally, A. Dohnalkova, C. M. Wang, J. Liu, G. J. Exarhos, *Chem. Commun.* **2010**, *46*, 4878–4880.
- [15] H. L. Jiang, B. Liu, T. Akita, M. Haruta, H. Sakurai, Q. Xu, *J. Am. Chem. Soc.* **2009**, *131*, 11302–11303.
- [16] W. Y. Xu, J. X. Dong, J. P. Li, J. Q. Li, F. Wu, *J. Chem. Soc. Chem. Commun.* **1990**, 755–756.
- [17] M. Matsukata, M. Ogura, T. Osaki, P. R. H. Rao, M. Nomura, E. Kikuchi, *Top. Catal.* **1999**, *9*, 77–92.
- [18] S. T. Zheng, T. Wu, J. Zhang, M. Chow, R. A. Nieto, P. Y. Feng, X. H. Bu, *Angew. Chem.* **2010**, *122*, 5490–5494; *Angew. Chem. Int. Ed.* **2010**, *49*, 5362–5366.
- [19] C. S. Cundy, P. A. Cox, *Microporous Mesoporous Mater.* **2005**, *82*, 1–78.
- [20] a) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* **2004**, *430*, 1012–1016; b) E. R. Parnham, R. E. Morris, *Acc. Chem. Res.* **2007**, *40*, 1005–1013; c) D. S. Wragg, A. M. Z. Slawin, R. E. Morris, *Solid State Sci.* **2009**, *11*, 411–416; d) R. E. Morris, *Chem. Commun.* **2009**, 2990–2998.
- [21] H. J. Ma, Z. J. Tian, R. S. Xu, B. C. Wang, Y. Wei, L. Wang, Y. P. Xu, W. P. Zhang, L. W. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 8120–8121.
- [22] J. C. Tan, T. D. Bennett, A. K. Cheetham, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 9938–9943.
- [23] G. Mariani, *Lubricant Additives: Chemistry and Applications* (Ed.: L. R. Rudnick), Taylor & Francis Group–CRC Press, Boca Raton, **2009**, chap. 6, pp. 173–194.