

Ni/Pd@MIL-101: Synergistic Catalysis with Cavity-Conform Ni/Pd Nanoparticles**

Justus Hermannsdörfer, Martin Friedrich, Nobuyoshi Miyajima, Rodrigo Q. Albuquerque, Stephan Kümmel, and Rhett Kempe*

Porous coordination polymers (PCP)^[1] or metal–organic frameworks (MOF)^[2] are currently being intensively investigated, for example regarding gas storage,^[3] separation,^[4] sensing,^[5] and as catalysts.^[6] In view of catalytic applications, PCP/MOFs are well-suited to stabilize very small metal nanoparticles (MNP) without blocking their surface by strongly binding ligands. The cavities and windows of the PCP/MOFs can regulate particle size and simultaneously guarantee access to the catalytically active sites of the MNP. In comparison to loading by solution infiltration,^[7] solid grinding,^[8] microwave irradiation,^[9] and surface grafting,^[10] the MOCVD method (metal–organic chemical vapor deposition) developed by Fischer and co-workers is of advantage especially in terms of control and high metal loadings (> 5 wt %).^[11] The host structures MOF-5,^[2] MOF-177,^[26] and MIL-101^[27] have mainly been used for loading with different MNPs (Fe,^[12–15] Co,^[15,16] Cu,^[12,13,17] Zn,^[12,13,17,18] Sn,^[12] Pt,^[12,14] Au,^[12,19] Pd,^[12–14,20–23] Ru,^[14,24] and Ni).^[25] The significantly higher stability of MIL-101 to hydrolysis in comparison to MOF-5 and MOF-177 makes it attractive for the synthesis of robust catalyst systems.^[22,23] Debatable (independent from the loading method used) is the question as to whether the generated MNPs are localized inside the PCP/MOF cavities or not. Frequently, MNPs larger than the cavities and particles localized on the outer surface of the PCP/MOF crystallite were observed. Recently, we could show that one can synthesize MIL-101 cavity-conform PdNPs by applying the MOCVD method using the precursor [(C₅H₅)Pd(C₃H₅)] followed by reduction with H₂ at room temperature (Figure 1, left).^[23] If the reduction is carried out at 70 °C, significantly smaller PdNPs were generated. Their diameter seems to be determined by the window sizes and not so much

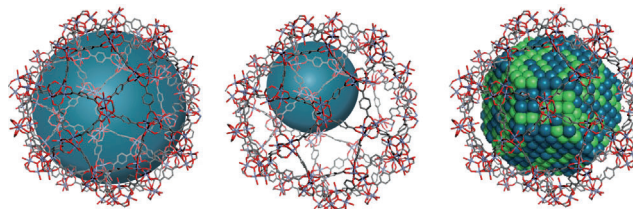


Figure 1. Size-selective cavity loading of MIL-101 (left: cavity-conform; center: undersized cavity loading; right: introduction of a second metal).

by the cavity sizes (Figure 1, center).^[23] This observation allows to conclude that the remaining space can be used to load a second metal. Thus, bimetallic NPs in the sub-nanometer range (< 10 nm) are accessible (Figure 1, right). This is interesting for catalytic applications for a number of reasons. Very small NPs have a very large surface-to-volume ratio. The dilution of costly noble metals by inexpensive metals such as Ni is economical. Bimetallic NP catalysts can show synergistic effects regarding activity and/or selectivity as (for instance) observed for Au/Pt NPs supported on spherical polyelectrolyte brushes.^[28]

We report herein on the generation of cavity-conform Ni/Pd NPs of different composition and their synergism in the catalytic hydrogenation of dialkyl ketones. The synthesis of bimetallic NPs in PCP/MOF by MOCVD has not been significantly investigated.^[14] Catalytic synergy effects of cavity-conform bimetallic MNPs stored in PCP/MOF cavities are not known. PCP/MOFs were used as support (localization of the MNP also at the outer surface of the PCP/MOF crystallites and/or regarding the size, not cavity-conformity) for bimetallic Au/Pd and Ag/Au NPs and catalytic synergism could be observed.^[29,30] The optimal synthesis of the Ni/Pd@MIL-101 catalysts was firstly investigated with respect to two loading versions, namely successively and simultaneously. The successive loading seems attractive, as the undersized PdNPs offer enough room to form cavity-conform bimetallic particles. Admittedly, the PdNPs could function as agglomeration sites and initiate excessive particle growth. The simultaneous loading becomes difficult owing to the different reduction behavior of the two precursors. A 1:1 loading with Pd and Ni precursors, [(C₅H₅)Pd(C₃H₅)] and [(C₅H₅)₂Ni], leads to (after reduction) NPs that are mainly in the size range of the MIL-101 cavities for both variants (Supporting Information, Figure S1). For successive loading, comparably more oversized particles were generated. PXRD (powder X-ray diffraction) shows two separated Ni and Pd 111 peaks for

[*] J. Hermannsdörfer, M. Friedrich, Prof. Dr. R. Kempe
Lehrstuhl Anorganische Chemie II, Universität Bayreuth,
95440 Bayreuth (Germany)
E-mail: kempe@uni-bayreuth.de

Dr. N. Miyajima
Bayerisches Geoinstitut, Universität Bayreuth,
95440 Bayreuth (Germany)

Prof. Dr. R. Q. Albuquerque, Prof. Dr. S. Kümmel
Theoretische Physik IV, Universität Bayreuth,
95440 Bayreuth (Germany)

Prof. Dr. R. Q. Albuquerque
Institute of Chemistry of São Carlos, University of São Paulo,
13560-970 São Carlos (Brazil)

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the successive loading (Supporting Information, Figure S2), with the Ni peak being considerably weaker. In contrast, the simultaneous loading shows a single broad 111 peak, indicating bimetallic NPs. The synthesis of the $\text{Pd}_x\text{Ni}_y\text{@MIL-101}$ catalyst systems with an exact adjustment of the Pd to Ni ratio by substitution of Pd by Ni in 20 weight percent steps (Supporting Information, Figure S3) was therefore carried out by applying the simultaneous loading. First, the reduction was carried out at 70 °C and 50 bar H_2 pressure for 20 h (1. generation).^[23] TEM (transmission electron microscopy) confirm NPs from 2 to 3 nm (Supporting Information, Figure S4–S6) for the systems with high Pd content ($\text{Pd} > \text{Ni}$). Additionally, the formation of large particles at the outer surface of the MIL-101 crystals (Supporting Information, Figure S7) is observed at high Ni content. Pure Ni@MIL-101 follows this tendency and leads to NPs that are clearly over the size of the MIL-101 cavities. Owing to an increasing particle size with increasing Ni content, the reduction conditions were optimized. Cavity-conform bimetallic NPs could be generated by increasing the temperature and reducing the pressure (second generation; Figure 2).

PXRD and IR spectroscopy investigations confirm the stability of the support under the relatively harsh reduction conditions (Supporting Information, Figure S11, S12, S14). Elemental analysis shows an average metal loading of 18 wt %, which matches with the calculated metal content (Supporting Information, Figure S15). Even a small amount of Pd changes the reduction behavior of $[(\text{C}_5\text{H}_5)_2\text{Ni}]$ and prevents the formation of larger Ni particles. HR TEM EDS measurements of $\text{Pd}_4\text{Ni}_1\text{@MIL-101}$ and $\text{Pd}_3\text{Ni}_2\text{@MIL-101}$ indicate bimetallic particles. EDS investigations of the whole sample and a few of the single particles show identical Ni:Pd ratios (Figure 3). In combination with the catalytic activity and the calculations carried out (see below), the formation of bimetallic Ni/Pd NPs can be concluded. In comparison to pure MIL-101, N_2 physisorption shows a lowered surface for the loaded systems, which results from a higher sample weight and the occupation of pores by MNP (Supporting Information, Table S2). Interestingly, pure Pd@MIL-101 and pure Ni@MIL-101 show a larger specific surface than the mixed systems. This might be explained by the localization of some MNPs on the outer surface for Ni@MIL-101 and the formation of undersized MNPs in case of Pd@MIL-101.

The $\text{Pd}_x\text{Ni}_y\text{@MIL-101}$ catalyst systems were investigated in different hydrogenation reactions. For the reduction of phenol and cyclic ketones (Figure 4) and dialkyl ketones (Table 1), a clearly pronounced synergistic effect is observed. The mixed Ni/Pd catalysts are definitely more active than the pure Pd or Ni catalysts. Generally, the hydrogenation of dialkyl ketones is difficult to accomplish by heterogeneous catalysts.^[31] Aryl alkyl ketones are hydrogenated without problems by these catalysts.^[23] Neither 3-heptanone nor cyclohexanone are reduced by the Ni@MIL-101 catalyst under the conditions used. Pd@MIL-101 also has clearly lower conversions, which are comparable to that of Pd on activated carbon (Pd/C). In contrast, the combination of both metals in the bimetallic $\text{Pd}_x\text{Ni}_y\text{@MIL-101}$ catalyst systems shows high conversions also at 25 °C (Table 1, entry 1).

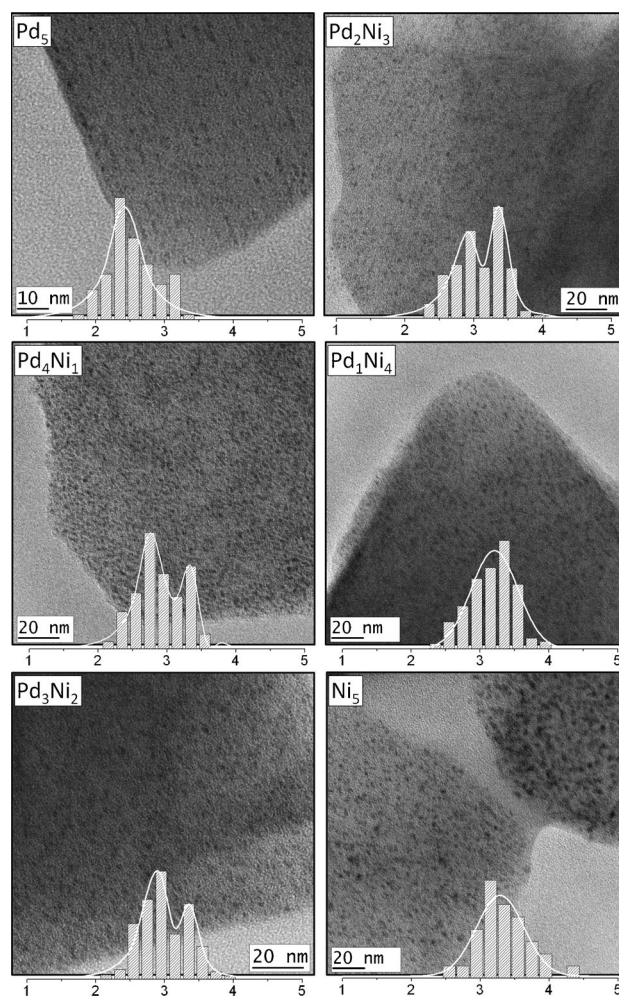


Figure 2. TEM investigations of the $\text{Pd}_x\text{Ni}_y\text{@MIL-101}$ catalyst systems using the optimized reduction conditions (second generation). With increasing Ni content, the reduction temperature is increased and the pressure is reduced (Pd_5 , Pd_4Ni_1 , Pd_3Ni_2 = 70 °C/50 bar; Pd_2Ni_3 = 70 °C/5 bar; Pd_1Ni_4 , Ni_5 = 90 °C/5 bar). The reduction time was 20 h. The averaged metal loading is 18 wt %. The substitution of Pd by Ni was carried out in 20 wt % steps.

Table 1 shows the results of the reduction of 3-heptanone under different conditions. The use of a mixture of pure Pd@MIL-101 and pure Ni@MIL-101 in a 3:2 ratio (entries 4, 5, and 11) shows a clearly lower catalytic activity than the corresponding catalyst $\text{Pd}_3\text{Ni}_2\text{@MIL-101}$ and as $\text{Pd}_4\text{Ni}_1\text{@MIL-101}$ (entries 7 and 8). The conversions of a corresponding mixture of Pd/C and Ni powder (Merck) (entries 6 and 12) are lower. The lower conversions (under analogous conditions) of the mixture of pure Pd@MIL-101 and Ni@MIL-101 catalyst in comparison to the bimetallic cavity-conform $\text{Pd}_x\text{Ni}_y\text{@MIL-101}$ catalyst systems indicate a synergistic catalysis effect that is based on bimetallic particles. A comparison between successive and simultaneous loading (entries 8 and 9) shows that the successive loading leads to catalytically less active Ni/Pd NP structures. Experiments with first-generation $\text{Pd}_x\text{Ni}_y\text{@MIL-101}$ (15–17) also yielded lower conversions than that of the second generation. The adjustment of the reduction conditions towards cavity-conform NPs has a positive influence on the activity as well.

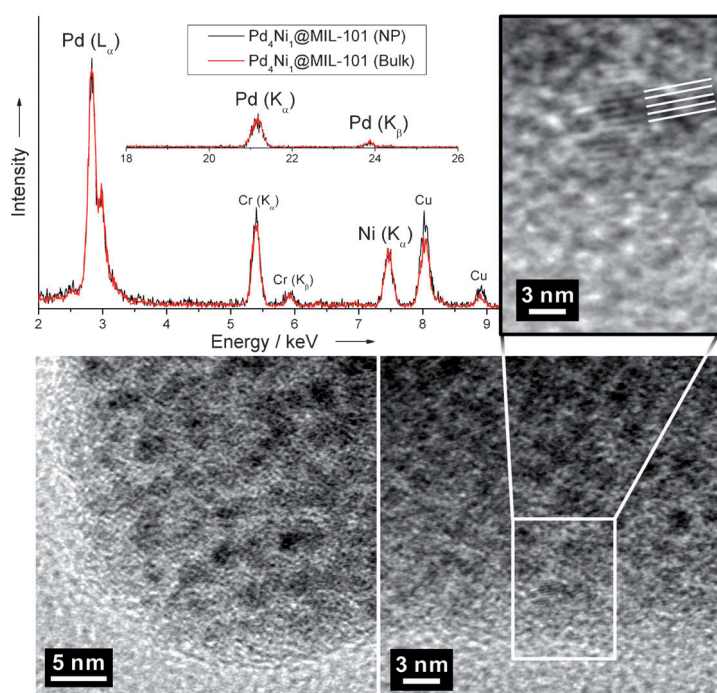


Figure 3. HR TEM EDS analysis of $\text{Pd}_4\text{Ni}_3\text{@MIL-101}$. The Ni/Pd ratio is identical if the bulk sample is considered and if single particles are analyzed. The d-spacing (fringes) of the Ni/Pd NP observed by TEM (for example, for $\text{Pd}_3\text{Ni}_2\text{@MIL-101}$ [111] 2.19(5) Å) matches with the expected value and the PXRD data (Supporting Information, Figure S14).

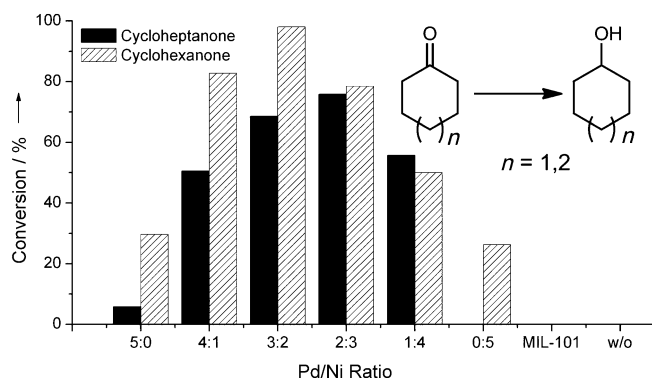


Figure 4. Reduction of cyclohexanone (0.18 mg Pd (0.52×10^{-3} mol%), 350 μL , 60°C, 24 h) and cycloheptanone (0.36 mg Pd (0.8×10^{-3} mol-%), 500 μL , 60°C, 48 h) at 20 bar H_2 ; w/o = without catalyst.

The hypothesis of the formation of bimetallic Ni/Pd NPs is also supported by molecular dynamics (MD) calculations. NPs with 1289 atoms (which means a number of atoms that allows a closed octahedron to be formed in the experimentally relevant size range of 3.5 nm) were constructed in three different ways: as Ni-core/Pd-shell NPs, as Ni-shell/Pd-core NPs, and as NPs with a random distribution of the atoms. 3:2 was chosen as the Pd to Ni ratio in accordance with the ratio at which experimentally high conversions were observed. All of the structures were first heated to 1400 K and afterwards slowly tempered to generate energetically favorable struc-

tures. Two examples are shown in Figure 5. The left structure (a) is the energetically most favorable structure that we found by tempering. It is characterized by a strong mixing of the Ni and Pd atoms and a correspondingly corrugated surface. The right structure (b) was formed by tempering of a Ni-core/Pd-shell particle. Ni atoms have migrated towards the surface during tempering and the particle no longer has a core-shell structure. Its surface is still rich in Pd and has an energy that is about 120 eV (2%) higher than that of particle (a). If the Pd/Ni ratio is changed to 3:5, a truncated octahedron with a perfect Ni core of 805 atoms and a closed Pd shell with 484 atoms can be constructed. These “magic” numbers of atoms should make core-shell NP energetically more favorable. The energy differences between a core-shell particle and randomly mixed NPs become smaller, but tempering again leads to mixed bimetallic NPs as energetically preferred structures. Thus, the MD simulations support the existence of bimetallic Ni/Pd NPs. Ni/Pd NPs are different in comparison to (for instance) Au/Pt or Au/Pd NPs, which were also used in catalysis. For these, NPs having an Au shell were predicted to be the energetically more stable on the basis of empirical potentials and DFT calculations.^[32]

The differences in size of the Ni and the Pd atoms could be a reason for the mixing of the atoms in the Ni/Pd NPs.^[32b] Thus, well-fitted surface boundaries are difficult to create. The resulting corrugated structure could enable the observed synergistic catalysis effects.

According to the phase diagram, Ni and Pd are miscible in the relevant temperature range.^[33]

Table 1: Catalytic results of the reduction of 3-heptanone with $\text{Pd}_x\text{Ni}_y\text{@MIL-101}$.^[a]

$\text{CH}_3\text{CH}_2\text{CH}_2\text{C(=O)CH}_2\text{CH}_2\text{CH}_3 \xrightarrow[20 \text{ bar } \text{Pd}_x\text{Ni}_y]{\text{H}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH(OH)CH}_2\text{CH}_2\text{CH}_3$					
Entry	System	T [°C]	t [h]	Conversion [%]	Pd/ketone [mol% $\times 10^{-3}$]
1	Pd_3Ni_2	25	27	50	2.88
2	Pd_3Ni_2	35	20	80	2.88
3	Pd_3Ni_2	60	20	75	1.44
4	$\text{Pd}_5 + \text{Ni}_5$	35	20	14	2.88
5	$\text{Pd}_5 + \text{Ni}_5$	35	40	25	2.88
6	$\text{Pd/C} + \text{Ni pwd}$	35	20	12	2.88
7	Pd_3Ni_2	35	20	80	2.88
8	Pd_4Ni_1	35	20	72	2.88
9	Pd_3Ni_2 (sB)	35	20	22	2.88
10	Pd_5	35	20	1	4.75
11	$\text{Pd}_5 + \text{Ni}_5$	60	20	10	1.85
12	$\text{Pd/C} + \text{Ni pwd}$	60	20	8	1.85
13	Pd_3Ni_2	60	20	60	1.13
14	Pd_4Ni_1	60	20	52	1.13
15	Pd_3Ni_2 (G1)	60	20	12	1.13
16	Pd_4Ni_1 (G1)	60	20	5	1.13
17	Ni_5 (G1)	60	20	0	1.13

[a] T = temperature; sL = successive loading; $\text{Pd}_5 + \text{Ni}_5 = \text{Pd}_5\text{@MIL-101} + \text{Ni}_5\text{@MIL-101}$; Pd/C = Pd on activated carbon (5 wt% Pd); Ni pwd = nickel powder (Merck); G1 = first generation.

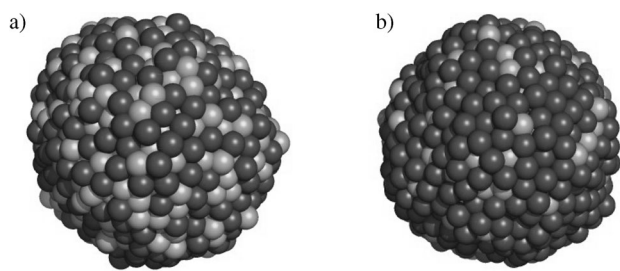


Figure 5. Structures of bimetallic Ni/Pd NPs based on MD simulations. a) A bimetallic mixed structure of low energy for Pd₇₇₅Ni₅₁₄. b) A structure of higher energy that was simulated starting from a Ni-core/Pd-shell particle and that already shows Ni atoms (gray) on the surface.

Reusability tests were carried out for the synergistically interesting Pd₃Ni₂@MIL-101 system (hydrogenation of 3-heptanone). After each catalytic experiment, the catalyst was centrifuged, the reaction mixture was decanted off, and the catalyst was washed with THF. The catalyst was again separated from THF by decanting and dried at 10^{−3} bar and 30 °C for 2 h. Reusability studies at 60 °C and 35 °C show no significant decrease in the conversion in 7 or 10 catalytic cycles, respectively (Supporting Information, Figures S24, S25). PXRD investigations confirm the stability of the MIL-101 support (Supporting Information, Figure S26). TEM investigations show no increase in the particle size after multiple use in catalysis (Supporting Information, Figure S27). Similarly, ICP-OES analyses show stable Ni/Pd, Pd/Cr and Ni/Cr ratios (Supporting Information, Table S4). The specific surface does not change even after multiple cycles (Supporting Information, Table S2).

In summary, we introduce a bimetallic synergistically acting catalyst system. By MOCVD, the sublimable metal-organic precursors [(C₅H₅)Pd(C₃H₅)] and [(C₅H₅)₂Ni] can be loaded quantitatively and in different mixtures into the porous host structure of MIL-101. Cavity-conform Ni/Pd NPs of different composition were generated by an optimized reduction of the loaded precursors by H₂. The so-formed catalysts are active in the hydrogenation of dialkyl ketones. High catalytic efficiency is only observed if both metals operate synergistically and are nearly atomically dispersed. The bimetallic Ni/Pd NP catalysts are reusable. The MIL-101 support combines ideally stability and good access of the educts to the catalytically active sites. The synthesis of such bare (bi)metallic NPs, which are tunable regarding their size, is generally of great interest.^[34]

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- [1] a) B. F. Abrahams, B. F. Hoskins, D. M. Michail, R. Robson, *Nature* **1994**, 369, 727–729; b) B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1989**, 111, 5962–5964.
- [2] H. Li, M. Eddaoudi, M. O’Keeffe, O. M. Yaghi, *Nature* **1999**, 402, 276–279.
- [3] M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, *Chem. Rev.* **2012**, 112, 782–835.
- [4] J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, 112, 869–932.
- [5] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, 112, 1105–1125.
- [6] a) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, 112, 1196–1231; b) A. Dhakshinamoorthy, H. Garcia, *Chem. Soc. Rev.* **2012**, 41, 5262–5284.
- [7] a) M. Sabo, A. Henschel, H. Froede, E. Klemm, S. Kaskel, *J. Mater. Chem.* **2007**, 17, 3827–3832; b) N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin, O. A. Kholdeeva, *J. Catal.* **2008**, 257, 315–323; c) H. Liu, Y. Liu, Y. Li, Z. Tang, H. Jiang, *J. Phys. Chem. C* **2010**, 114, 13362–13369; d) Y. Pana, B. Yuana, Y. Li, D. He, *Chem. Commun.* **2010**, 46, 2280–2282; e) A. Henschel, K. Gedrich, R. Kraehnert, S. Kaskel, *Chem. Commun.* **2008**, 4192–4194.
- [8] T. Ishida, M. Nagaoka, T. Akita, M. Haruta, *Chem. Eur. J.* **2008**, 14, 8456–8460.
- [9] M. S. El-Shall, V. Abdelsayed, A. El Rahman, S. Khder, H. M. A. Hassan, H. M. El-Kaderi, T. E. Reich, *J. Mater. Chem.* **2009**, 19, 7625–7631.
- [10] Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem.* **2008**, 120, 4212–4216; *Angew. Chem. Int. Ed.* **2008**, 47, 4144–4148.
- [11] a) S. Hermes, M.-K. Schröter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R. W. Fischer, R. A. Fischer, *Angew. Chem.* **2005**, 117, 6394–6397; *Angew. Chem. Int. Ed.* **2005**, 44, 6237–6241; b) M. Meilikhov, K. Yusenko, D. Esken, S. Turner, G. V. Tendeloo, R. A. Fischer, *Eur. J. Inorg. Chem.* **2010**, 3701–3714.
- [12] S. Hermes, F. Schröder, S. Amirjalayer, R. Schmid, R. A. Fischer, *J. Mater. Chem.* **2006**, 16, 2464–2472.
- [13] M. Müller, O. Lebedev, R. A. Fischer, *J. Mater. Chem.* **2008**, 18, 5274–5281.
- [14] F. Schröder, S. Henke, X. Zhang, R. A. Fischer, *Eur. J. Inorg. Chem.* **2009**, 3131–3140.
- [15] M. Meilikhov, K. Yusenko, R. A. Fischer, *Dalton Trans.* **2010**, 39, 10990–10999.
- [16] M. Meilikhov, K. Yusenko, A. Torrisi, B. Jee, C. Mellot-Draznieks, A. Pöpl, R. A. Fischer, *Angew. Chem.* **2010**, 122, 6348–6351; *Angew. Chem. Int. Ed.* **2010**, 49, 6212–6215.
- [17] M. Müller, S. Hermes, K. Kähler, M. W. E. van den Berg, M. Muhler, R. A. Fischer, *Chem. Mater.* **2008**, 20, 4576–4587.
- [18] D. Esken, H. Noei, Y. Wang, C. Wiktor, S. Turner, G. V. Tendeloo, R. A. Fischer, *J. Mater. Chem.* **2011**, 21, 5907–5915.
- [19] a) D. Esken, S. Turner, O. I. Lebedev, G. Van Tendeloo, R. A. Fischer, *Chem. Mater.* **2010**, 22, 6393–6401; b) M. Mueller, S. Turner, O. I. Lebedev, Y. Wang, G. van Tendeloo, R. A. Fischer, *Eur. J. Inorg. Chem.* **2011**, 1876–1887.
- [20] a) S. Hermes, D. Zacher, A. Baunemann, C. Wöll, R. A. Fischer, *Chem. Mater.* **2007**, 19, 2168–2173; b) D. Esken, X. Zhang, O. I. Lebedev, F. Schröder, R. A. Fischer, *J. Mater. Chem.* **2009**, 19, 1314–1319.
- [21] S. Turner, O. I. Lebedev, F. Schröder, D. Esken, R. A. Fischer, G. Van Tendeloo, *Chem. Mater.* **2008**, 20, 5622–5627.
- [22] S. Proch, J. Herrmannsdörfer, R. Kempe, C. Kern, A. Jess, L. Seyfarth, J. Senker, *Chem. Eur. J.* **2008**, 14, 8204–8212.
- [23] J. Herrmannsdörfer, R. Kempe, *Chem. Eur. J.* **2011**, 17, 8071–8077.

- [24] F. Schroeder, D. Esken, M. Cokoja, M. W. E. van den Berg, O. I. Lebedev, G. van Tendeloo, B. Walaszek, G. Buntkowsky, H. H. Limbach, B. Chaudret, R. A. Fischer, *J. Am. Chem. Soc.* **2008**, *130*, 6119–6130.
- [25] a) Y. K. Park, S. B. Choi, H. J. Nam, D. Y. Jung, H. C. Ahn, K. Choi, H. Furukawa, J. Kim, *Chem. Commun.* **2010**, *46*, 3086–3088; b) P.-Z. Li, K. Aranishi, Q. Xu, *Chem. Commun.* **2012**, *48*, 3173–3175.
- [26] H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M. O’Keeffe, O. M. Yaghi, *Nature* **2004**, *427*, 523–527.
- [27] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *306*, 2040–2042.
- [28] M. Schrinner, S. Proch, Y. Mei, R. Kempe, N. Miyajima, M. Ballauff, *Adv. Mater.* **2008**, *20*, 1928–1933.
- [29] X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita, Q. Xu, *J. Am. Chem. Soc.* **2011**, *133*, 11822–11825.
- [30] H.-L. Jiang, T. Akita, T. Ishida, M. Haruta, Q. Xu, *J. Am. Chem. Soc.* **2011**, *133*, 1304–1306.
- [31] M. J. Jacinto, R. Landers, L. M. Rossi, *Catal. Commun.* **2009**, *10*, 1971–1974.
- [32] a) D. T. Tran, R. L. Johnston, *Proc. R. Soc. London Ser. A* **2011**, *467*, 2004–2019; b) R. Ferrando, J. Jellinek, R. L. Johnston, *Chem. Rev.* **2008**, *108*, 845–910; c) H. B. Liu, U. Pal, J. A. Ascencio, *J. Phys. Chem. C* **2008**, *112*, 19173–19177; d) L. Leppert, S. Kümmel, *Phys. Chem. C* **2011**, *115*, 6694–6702; e) J. Kaiser, L. Leppert, H. Welz, F. Polzer, S. Wunder, N. Wanderka, M. Albrecht, T. Lunkenbein, J. Breu, S. Kümmel, Y. Lu, M. Ballauff, *Phys. Chem. Chem. Phys.* **2012**, *14*, 6487–6495.
- [33] M. Hansen, K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, **1958**.
- [34] a) C. Vollmer, C. Janiak, *Coord. Chem. Rev.* **2011**, *255*, 2039–2057; b) S. F. L. Mertens, C. Vollmer, A. Held, M. H. Aguirre, M. Walter, C. Janiak, T. Wandlowski, *Angew. Chem.* **2011**, *123*, 9909–9912; *Angew. Chem. Int. Ed.* **2011**, *50*, 9735–9738.