

Enhancement of Catalytic Activity in Epoxide Hydration by Increasing the Concentration of Cobalt(III)/Salen in Porous Polymer Catalysts

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The rational design of catalytic materials from the reaction characteristics is expected to be a useful strategy to create highly efficient catalysts. Herein, according to a well-established reaction pathway of epoxide hydration catalyzed a dual-molecular system of Co^{3+} /salen in which a high concentration of active sites is favorable to enhance the activity, we provide an alternative way to prepare a highly efficient heterogeneous catalyst with a high concentration of Co^{3+} /salen from the polymerization of vinyl-functionalized salen monomers followed by

Introduction

The design of catalytic materials from reaction characteristics is of great help for the preparation of efficient catalysts.^[1–7] The cooperative activation of reagents by two or more catalytically active sites is recognized to be a common feature in organic transformations.^[8-14] Typically, epoxide hydration catalyzed by Co³⁺/salen complex involves the dual activation of the epoxide and water, respectively, and a high concentration of Co³⁺/salen is favorable for the enhancement of activities.^[15-18] Notably, soluble Co³⁺/salen complexes are dispersed homogeneously in the catalytic system, and the concentration of Co³⁺/salen species is low. In contrast, insoluble Co³⁺/salen catalysts are expected to provide a promising platform to create a confined space in which the active species could be enriched.^[19-21] For example, Cui et al.^[22] and Yang et al.^[23,24] designed Co³⁺/salen species in metal-organic frameworks (MOFs) and ordered mesoporous silica materials rationally, respectively. These insoluble catalysts have high concentrations of Co³⁺/salen species in the confined space and show superior catalytic performances in the hydration of epoxides. Despite this encouraging progress,

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the loading of Co^{3+} species (Co^{3+}/POL -salen). Co^{3+}/POL -salen has a hierarchical porosity and an extraordinary hydrothermal stability. Importantly, catalytic tests in epoxide hydration demonstrate that Co^{3+}/POL -salen affords excellent high activities, which are even better than those of the homogeneous version. This phenomenon is related to the very high concentration of $Co^{3+}/salen$ in the catalyst. In addition, this catalyst can be recycled readily because of its excellent hydrothermal stability.

the relatively low hydrothermal stability of MOFs^[25–27] and ordered mesoporous silica materials^[28,29] still represents a limitation for long-term practical applications, in particular to the presence of water as a reactant. Therefore, it is strongly desirable to search for hydrothermally stable heterogeneous catalysts with a high Co³⁺/salen concentration.

Porous organic polymers (POPs) are an emerging class of porous materials that have attracted much attention because of their excellent hydrothermal and chemical stability, designable pore walls, and high surface areas.^[30–46] If the POPs are constructed by salen-functionalized ligand themselves, the resultant materials should have an extremely high concentration of salen moieties.^[47–50] After the introduction of Co³⁺ species, a very high density of Co³⁺/salen species could be obtained in the sample.

In this contribution, to demonstrate the "proof-of-concept", a hierarchically porous salen-functionalized polymer (POL-salen) was fabricated successfully from the polymerization of vinyl-functionalized salen monomers. POL-salen has an extraordinary hydrothermal stability, hierarchical porosity, large surface areas, flexible frameworks, and a high concentration of salen species (1.56 mmol g⁻¹). After metalation with Co species, the obtained Co³⁺/POL-salen heterogeneous catalyst exhibits high activities in the hydration of epoxides to monoalkylene glycols under mild reaction conditions and outperforms the homogeneous counterpart. The superior catalytic performance of the catalyst is strongly related to the high concentration of Co³⁺/salen in the confined pores of the Co³⁺/POL-salen catalyst, which promotes the cooperative activation of water and epoxide.



Results and Discussion

Synthesis and characterization of Co³⁺/POL-salen

POL-salen was synthesized from the polymerization of vinylfunctionalized salen monomer (Scheme 1, Scheme S1) in the presence of 1-methyl-2-pyrrolidinone (NMP) solvent at 100 °C for 24 h. After washing with CH_2Cl_2 and drying at 50 °C under vacuum, a yellow solid (POL-salen) in a higher than 99.0% yield was obtained.

The morphology of the POL-salen was examined by SEM and TEM (Figure 1 A and B). POL-salen displays rather rough surfaces and appears as aggregates of much smaller particles on the order of tens of nanometers in size. The powder X-ray diffraction (PXRD) pattern (Figure S1) shows a very broad peak at $2\theta = 10-30^{\circ}$, which indicates the amorphous nature of POL-



Scheme 1. Synthesis of POL-salen polymer from the vinyl-functionalized salen monomer.

salen. The ¹³C magic-angle spinning (MAS) NMR spectrum of POL-salen (Figure 1 C) shows a peak at $\delta = 40.3$ ppm assigned to the polymerized vinyl groups in addition to the peaks attributed to the characteristic structure of the salen ligand (Figure S2).^[47] These results suggest that the structure of the salen ligand is well maintained during the polymerization process. N_2 sorption isotherms of POL-salen collected at -196 °C show a steep step at $P/P_0 < 0.01$ and a hysteresis loop at $0.1 < P/P_0 <$ 0.98 with a sharp N₂ uptake at a high relative pressure (Figure 1D), which suggests the coexistence of micro-, meso-, and macroporsity in the framework.^[51,52] Correspondingly, pore sizes of the sample are mainly distributed at 0.65-1.5, 2.7-50, and over 50 nm (Figure S3), as calculated by the nonlocal density functional theory method (NLDFT). The BET surface area and total pore volume of POL-salen are estimated at 540 m²g⁻¹ and 0.74 cm³g⁻¹, respectively. The hieratical porosity is expected to improve the efficiency of transport processes as well as the accessibility of active sites.[53-55]

The introduction of Co³⁺ species into POL-salen was performed by the treatment of POL-salen with Co(OAc)₂·4H₂O in a mixed solvent of CH₂Cl₂ and MeOH under a N₂ atmosphere to obtain Co²⁺/POL-salen that was followed by the oxidation of the metaled POL-salen in open air in the presence of acetic acid to obtain Co³⁺/POL-salen. The Co species only exist as molecular species coordinated to salen and do not form aggregates or nanoparticles because of the presence of a large amount of acetic acid and air, which is also supported by TEM (Figure S5). In addition, compared with POL-salen, Co²⁺/POLsalen shows a new peak at approximately λ =430 nm in the UV/Vis spectrum, which can be assigned to d– π^* of the Co²⁺/ salen complex. After oxidation, the resultant sample gives peaks at λ =411 and 692 nm, which are characteristic of Co³⁺/



Figure 1. A) SEM image, B) TEM image, C) ¹³C MAS NMR spectrum, and D) N₂ sorption isotherms of POL-salen.

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salen species (Figure S6).^[54] Similar changes were also observed in homogeneous Co³⁺/salen, developed by Jacobsen et al. (Scheme S2, Figure S7).^[15] These results confirm that the Co species in POL-salen is in the 3+ oxidation state. In addition, the color of POL-salen changed from yellow to dark red after the introduction of Co²⁺ species and then became dark brown after oxidation. These color changes are associated with the characteristic colors of Co²⁺/salen and Co³⁺/salen species in good agreement with those reported previously.^[56] These results demonstrate that Co3+ species are coordinated successfully with salen ligands in POL-salen. Inductively coupled plasma optical emission spectroscopy (ICP-OES) revealed a Co loading of 68.4 mg g^{-1} (1.16 mmol g⁻¹), which suggests that pprox 88% of the salen ligands in POL-salen were coordinated with Co species. Notably, the Co³⁺/POL-salen catalyst still possesses a BET surface area of 512 m²g⁻¹ and a total pore volume of $0.58 \text{ cm}^3 \text{g}^{-1}$ (Figure 2 A). Excitingly, even after hydrothermal treatment for 48 h at 100 °C, Co3+/POL-salen maintained its surface area (519 $m^2 g^{-1}$; Figure 2B, Figure S8). However, the uptake at a high relative pressure is reduced, which might be related to the partial aggregation of the polymer. ICP analysis of the sample shows that the Co species in the catalyst are stable during the hydrothermal treatment because Co species are undetectable (< 10 ppb) in the filtrate. This catalyst feature is very helpful for their long-term application in the hydration of epoxides.



Figure 2. N_2 sorption isotherms of Co^3+/POL-salen a) before and b) after treatment in boiling water for 48 h.

Evaluation of catalytic performance

The production of monoalkylene glycols from the hydration of epoxides has received much attention because they are important raw materials for the manufacture of polyester resins, antifreezes, cosmetics, and medicines.^[57,58] Currently, the biggest challenge encountered in industry is that a large excess of water (10-25 moles of water per mole of alkylene oxide) is required to realize a high selectivity of monoalkylene glycol by suppressing the side reactions of unreacted epoxides with the formed monoalkylene glycol. As a result, a large amount of water has to be distilled to enable the recovery of the monoalkylene glycols from the reaction mixture, which in turn involves the consumption of a huge amount of energy. This process is environmentally unfriendly.^[59-63] Co³⁺/salen-catalyzed epoxide hydration is considered to be a promising alternative route toward monoalkylene glycols because it could be operated at a relatively low molar ratio of water to alkylene oxide (as low as 2.0) and mild reaction temperatures (such as room temperature). Nevertheless, for practical applications, heterogeneous catalysis is more attractive because of the simple and complete separation of the product from the catalyst.^[64-68]

The potential of the Co³⁺/POL-salen catalyst for epoxide hydration was evaluated using propylene oxide (PO) as a model substrate. Hydration reactions were performed at room temperature with a molar ratio of H₂O/PO of 2:1 and 0.2 mol% of catalyst based on Co species. Catalytic data for the hydration of PO over various catalysts are presented in Table 1. Notably,

Table 1. Hydration of PO over various catalysts. ^[a]					
Entry	Catalyst	Conversion [%]	Selectivity [%]		
1	Co ³⁺ /POL-salen	98.1	> 99.0		
2 ^[b]	H-ZSM-5	2.3	87.9		
3	Amberlyst-15	5.6	75.3		
4	H_2SO_4	42.1	76.1		
5	Co ³⁺ /salen	86.2	> 99.0		
6 ^[c]	Co ³⁺ /POL-salen	91.6	> 99.0		
7 ^[c]	Co ³⁺ /salen	71.5	> 99.0		
8 ^[d]	Co ³⁺ /POL-salen	89.5	> 99.0		
9 ^[e]	Co ³⁺ /POL-salen	97.6	> 99.0		

[a] Reaction conditions: PO (0.725 g, 12.5 mmol), H₂O (0.45 g, 25 mmol), catalyst (0.2 mol% based on Co species), S/C=500, RT, 10 h; [b] 0.1 g catalyst was used, Si/Al=20; [c] catalyst (0.05 mol%), S/C=2000, 40 h; [d] recycled five times of Co³⁺/POL-salen catalyst (0.05 mol%, S/C=2000); [e] after treatment in boiling water for 48 h and regenerated similarly to that in the recycling tests.

Co³⁺/POL-salen gives a conversion of PO as high as 98.1% with a selectivity for 1,2-propanediol of over 99.0% (entry 1 in Table 1). This activity and selectivity are even comparable with those of the heterogeneous catalyst with high Co³⁺/salen concentration in the mesocages of FDU-12, one of the best heterogeneous catalysts for epoxide hydration.^[22-24] In contrast, conventional solid acid catalysts H-ZSM-5 and Amberlyst-15 afford very low activities (2.3 and 5.6%, entries 2 and 3 in Table 1); the conventional liquid acid catalyst of H₂SO₄ shows a PO conversion of 42.1% and 1,2-propanediol selectivity of 76.1% (entry 4 in Table 1).

In particular, the heterogeneous Co^{3+}/POL -salen catalyst is more active than the homogeneous $Co^{3+}/salen$ catalyst (con-



version of 98.1 vs. 86.2%, entries 1 and 5 in Table 1). The differences in terms of the activity between Co^{3+}/POL -salen and $Co^{3+}/salen$ become greater as the catalyst amount decreases in the catalytic system. For example, if the catalyst amount is reduced to 0.05 mol%, Co^{3+}/POL -salen still gives a PO conversion of 91.6%, whereas the soluble $Co^{3+}/salen$ complex affords a conversion of only 71.5% (Figure S9, entries 6 and 7 in Table 1).

Generally, homogeneous catalysts exhibit higher catalytic activities than the corresponding heterogeneous catalysts because the active sites in the homogeneous catalysts are fully accessible to the reactants. However, here the catalytic tests show that the heterogeneous Co^{3+}/POL -salen catalyst has a much better catalytic performance than the homogeneous version with the same number of active sites, which should be related directly to the unique features of Co^{3+}/POL -salen, such as the porosity and high concentration of $Co^{3+}/salen$. It has been reported that the proposed mechanism of the $Co^{3+}/salen$ salen-catalyzed hydration of epoxides was through a dual-molecular ($Co^{3+}/salen$) cooperative activation pathway (Figure 3).



Figure 3. Proposed cooperative activation reaction pathway on dual $Co^{3+}/$ salen species.

In this case, the high concentration of Co³⁺/salen is favorable for the cooperative activation of dual Co³⁺/salen groups. For the Co³⁺/POL-salen catalyst, densely populated Co³⁺/salen species benefit their synergistic cooperation in catalysis. As a result, the rate of the formation of product is improved significantly. In comparison, the Co³⁺ species in the homogeneous catalytic system is highly separated, and the interaction between the water and epoxide activated by the Co³⁺/salen species is relatively difficult. Notably, if the ratio of substrate to catalyst (S/C) is increased, the concentration of active sites in the homogeneous Co³⁺/salen system is further diluted, in contrast, for Co³⁺/POL-salen, the Co³⁺ species only confined in the catalyst and the local density of Co³⁺ species in the catalyst remains almost the same regardless of the change in the S/C ratio. Consequently, the heterogeneous catalyst shows a much higher activity than the homogeneous counterpart, especially at a high S/C ratio.

To further access the importance of the local concentration of active species in the Co^{3+}/POL -salen catalyst, we have synthesized a series of catalysts with an adjustable concentration of $Co^{3+}/salen$ species by the copolymerization of vinyl-functionalized salen monomers with divinybenzene (DVB) at various mass ratios (PDVB-x-salen, x is the mass fraction of salen in the polymer). After the metalation of PDVB-x-salen polymers with Co^{3+} species, the resultant catalysts were tested in the hydration of PO, and the catalytic activities demonstrated that the PO conversion increases almost linearly with the mass fraction of salen ligand in the polymer catalysts (Figure 4). As the textural parameters, such as surface area, are very similar and active sites are the same in these catalysts (Figure S10, Table S2), the major difference in them is the continuity of the active sites in the polymer catalysts with various amounts of DVB molecules. Presumably, the continuity of the active sites might affect their local concentration. Therefore, it is reasonable to propose that a high local concentration of the active sites in the Co^{3+}/POL -salen catalyst is indeed an important factor to maximize the cooperative activation of water and epoxide species over $Co^{3+}/salen$ species, which is further supported by the kinetic tests (Figure S11) and is consistent previous studies.^[8-14]



Figure 4. Influence of the mass fraction of salen in the polymer ($Co^{3+}/PDVB$ x-salen, x = 1 stands for Co^{3+}/POL -salen) on the catalytic performance (the selectivity of the reaction is high than 99.0%). Reaction conditions: PO (25 mmol), H₂O (50 mmol), RT, substrate to catalyst ratio of 2000, 40 h.

The stability of the catalytic system is of great importance for practical applications. To evaluate the recyclability, $Co^{3+}/$ POL-salen was recovered after each reaction by simple centrifugation and regenerated under aerobic and acidic conditions. The catalytic activity and selectivity were well maintained to give a PO conversion of 89.5% (fresh catalyst affords a conversion of 91.6%) with a selectivity of 1,2-propanediol above 99.0% after five cycles (Table S3), which demonstrates the excellent recyclability of the Co^{3+}/POL -salen catalyst. In addition, after hydrothermal treatment in boiling water for 48 h, the sample still shows a high conversion (97.6%) and excellent selectivity (>99%, entry 9 in Table 1). These results indicate the excellent hydrothermal stability of the catalyst, which is very helpful for its industrial application.

Similarly, epichlorohydrin, 1,2-epoxyhexane, and 1,2-epoxyethylbenzene were employed as the substrate for epoxide hydration over Co^{3+}/POL -salen. Interestingly, the heterogeneous Co^{3+}/POL -salen catalyst still exhibits a much higher activity than the homogeneous $Co^{3+}/salen$ catalyst (Figure 5, Table S4). These results confirm the high efficiency of the Co^{3+}/POL -salen catalyst for epoxide hydration.



Figure 5. Catalytic performance of Co³⁺/POL-salen (orange) and homogeneous Co³⁺/salen (green) for the hydration of various epoxides. Reaction conditions: epoxide (12.5 mmol), H₂O (25 mmol), 40 °C for A) epichlorohydrin, S/C = 500, 8 h, B) 1,2-epoxyhexane, S/C = 500, 16 h, and C) 1,2-epoxyethylbenzene, S/C = 250, 60 h.

Conclusions

We have demonstrated a successful rational design of a highly efficient heterogeneous catalyst based on the reaction mechanism, as exemplified by Co3+/salen-catalyzed epoxide hydration. An efficient heterogeneous catalyst that has an extremely high concentration of Co³⁺/salen has been synthesized from the polymerization of vinyl-functionalized salen ligand monomer followed by the introduction of Co³⁺ species (Co³⁺/POLsalen). Interestingly, in comparison with that of the homogeneous Co³⁺/salen catalytic system, a significant rate acceleration was observed for Co³⁺/POL-salen in epoxide hydration. The high concentration of the Co³⁺/salen confined in the heterogeneous catalyst is responsible for the extraordinary activities of Co³⁺/POL-salen. In addition, the excellent hydrothermal stability of the catalyst is helpful for the long-term industrial applications in epoxide hydration. This approach to prepare porous organic ligand materials offers a good opportunity to design heterogeneous catalysts rationally and efficiently in the future.

Experimental Section

Chemicals and materials

Solvents were purified according to standard laboratory methods. For example, THF was distilled over sodium/benzophenone, and toluene was distilled over calcium hydride. Azobisisobutyronitrile (AIBN), DVB, and ethylbenzene were obtained from Tianjin Guangfu Chemical Reagent. SnCl₄, 4-vinylphenylboronic acid, paraformal-dehyde, Co(OAc)₂·4H₂O, 3-*tert*-butylphenol, 1,2-cyclohexanediamine, and tributylamine were purchased from Aladdin Company, Co. Ltd and were used directly without further purification.

Synthesis of POL-salen

POL-salen was synthesized by polymerization. Typically, vinyl-functionalized salen monomer (0.5 g) was dissolved in NMP (5.0 mL), and AIBN (20 mg) was added. The mixture was transferred into an autoclave at 100 °C and maintained for 24 h. After extraction with CH_2Cl_2 , a yellow solid with a yield higher than 99.0% was obtained.

Synthesis of Co²⁺/POL-salen

Co²⁺/POL-salen was synthesized by the addition of a solution of Co(OAc)₂·4H₂O (0.22 g) in MeOH (20 mL) to POL-salen (0.5 g), which was preswelled in CH₂Cl₂ (20 mL) with stirring under N₂ at RT. After 12 h, the polymer was collected by filtration, rinsed sequentially with MeOH and CH₂Cl₂, and then dried under vacuum to yield the product as a dark red powder.

Synthesis of Co³⁺/POL-salen

Co²⁺/POL-salen (0.5 g) was added to a 9:1 PhMe/AcOH solution (20 mL). The mixture was stirred in air at RT for 3 h. The polymer was collected by filtration, rinsed with CH_2Cl_2 , and dried under vacuum to yield the product as a dark brown powder.

Procedure for the hydration of epoxides

Typically, Co^{3+}/POL -salen (10.8 mg) was added into a 10 mL glass tube followed by the addition of PO (1.45 g, 25 mmol) and water (0.9 g, 50 mmol). After the mixture was stirred at RT for 40 h, the reaction was diluted with MeOH, and the catalyst was removed from the system by centrifugation or by passing through a short silica gel column. The solution was analyzed by GC (GC-1690 Kexiao Co., with a flame ionization detector) with a flexible quartz capillary column coated with FFAB.

Recycling of Co³⁺/POL-salen

After the reaction, the solid catalyst was separated by centrifugation and washed thoroughly with CH_2Cl_2 and MeOH. The catalyst was regenerated by treating it with AcOH/PhMe (1:9 v/v, 5.0 mL) under air for 3 h. The catalyst was isolated, dried under vacuum, and used in the next cycle.

Characterization methods

 $\rm N_2$ sorption isotherms at 77 K were measured by using Micromeritics ASAP 2020M and Tristar systems. The samples were outgassed for 10 h at 100 °C before the measurements. ICP-OES was measured by using a PerkinElmer plasma OES8000. ¹H NMR spectra were recorded by using a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from TMS at $\delta=0$ ppm, and J values are given in Hz. ¹³C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS) solid-state NMR spectra were recorded by using a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4 mm ZrO₂ rotor. UV/ Vis spectra were recorded by using a Hitachi SU 1510. TEM was performed by using a Hitachi HT-7700.

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- [1] W.-Y. Gao, M. Chrzanowski, S. Ma, Chem. Soc. Rev. 2014, 43, 5841-5866.
- [2] Z.-A. Qiao, P. Zhang, S.-H. Chai, M. Chi, G. M. Veith, N. C. Gallego, M. Kidder, S. Dai, J. Am. Chem. Soc. 2014, 136, 11260–11263.
- [3] D. Wang, R. Cai, S. Sharma, J. Jirak, S. K. Thummanapelli, N. G. Akhmedov, H. Zhang, X. Liu, J. L. Petersen, X. Shi, J. Am. Chem. Soc. 2012, 134, 9012–9019.
- [4] R. G. Konsler, J. Karl, E. N. Jacobsen, J. Am. Chem. Soc. 1998, 120, 10780-10781.
- [5] H. Steinhagen, G. Helmchen, Angew. Chem. Int. Ed. Engl. 1996, 35, 2339–2342; Angew. Chem. 1996, 108, 2489–2492.
- [6] Y. Wang, G. Ye, H. Chen, X. Hu, Z. Niu, S. Ma, J. Mater. Chem. A 2015, 3, 15292-15298.
- [7] D. S. Su, S. Perathoner, G. Centi, Chem. Rev. 2013, 113, 5782-5816.
- [8] M. Sawamura, Y. Ito, Chem. Rev. **1992**, 92, 857–871.
- [9] M. Shibasaki, N. Yoshikawa, Chem. Rev. 2002, 102, 2187-2210.
- [10] H. Peng, N. G. Akhmedov, Y.-F. Liang, N. Jiao, X. Shi, J. Am. Chem. Soc. 2015, 137, 8912–8915.
- [11] C. Baleizão, H. Garcia, Chem. Rev. 2006, 106, 3987-4043.
- [12] R. Cai, M. Lu, E. Y. Aguilera, Y. Xi, N. G. Akhmedov, J. L. Petersen, H. Chen, X. Shi, Angew. Chem. Int. Ed. 2015, 54, 8772–8776; Angew. Chem. 2015, 127, 8896–8900.
- [13] B. M. Trost, V. S. C. Yeh, Angew. Chem. Int. Ed. 2002, 41, 861–863; Angew. Chem. 2002, 114, 889–891.
- [14] J.-A. Ma, D. Cahard, Angew. Chem. Int. Ed. 2004, 43, 4566-4583; Angew. Chem. 2004, 116, 4666-4683.
- [15] M. Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* 1997, 277, 936–938.
- [16] B. M. Rossbach, K. Leopold, R. Weberskirch, Angew. Chem. Int. Ed. 2006, 45, 1309-1312; Angew. Chem. 2006, 118, 1331-1335.
- [17] X. Zheng, C. W. Jones, M. Weck, J. Am. Chem. Soc. 2007, 129, 1105– 1112.
- [18] R. Breinbauer, E. N. Jacobsen, Angew. Chem. Int. Ed. 2000, 39, 3604– 3607; Angew. Chem. 2000, 112, 3750–3753.
- [19] K. Venkatasubbaiah, Y. Feng, T. Arrowood, P. Nickias, C. W. Jones, Chem-CatChem 2013, 5, 201–209.
- [20] S. Bai, B. Li, J. Peng, X. Zhang, Q. Yang, C. Li, Chem. Sci. 2012, 3, 2864– 2867.
- [21] M. Shakeri, R. J. M. K. Gebbink, P. E. de Jongh, K. P. de Jong, Angew. Chem. Int. Ed. 2013, 52, 10854–10857; Angew. Chem. 2013, 125, 11054– 11057.
- [22] C. Zhu, G. Yuan, X. Chen, Z. Yang, Y. Cui, J. Am. Chem. Soc. 2012, 134, 8058-8061.
- [23] H. Q. Yang, L. Zhang, L. Zhong, Q. Yang, C. Li, Angew. Chem. Int. Ed. 2007, 46, 6861–6865; Angew. Chem. 2007, 119, 6985–6989.
- [24] B. Li, S. Bai, X. Wang, M. Zhong, Q. Yang, C. Li, Angew. Chem. Int. Ed. 2012, 51, 11517–11521; Angew. Chem. 2012, 124, 11685–11689.
- [25] W. Zhang, Y. Hu, J. Ge, H.-L. Jiang, S.-H. Yu, J. Am. Chem. Soc. 2014, 136, 16978–16981.
- [26] K. K. Tanabe, S. M. Cohen, Chem. Soc. Rev. 2011, 40, 498-519.
- [27] J. B. DeCoste, G. W. Peterson, Chem. Rev. 2014, 114, 5695-5727.
- [28] F.-S. Xiao, Y. Han, X. Meng, M. Yang, S. Wu, J. Am. Chem. Soc. 2002, 124, 888–889.
- [29] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548–552.
- [30] C. E. Chan-Thaw, A. Villa, P. Katekomol, D. S. Su, A. Thomas, L. Prati, Nano Lett. 2010, 10, 537–541.
- [31] S. Fischer, J. Schmidt, P. Strauch, A. Thomas, Angew. Chem. Int. Ed. 2013, 52, 12174–12178; Angew. Chem. 2013, 125, 12396–12400.
- [32] M. Rose, ChemCatChem 2014, 6, 1166-1182.
- [33] L. Wang, J. Zhang, J. Sun, L. Zhu, H. Zhang, F. Liu, D. Zheng, X. Meng, X. Shi, F.-S. Xiao, ChemCatChem 2013, 5, 1606–1613.
- [34] P. Zhang, Z. Weng, J. Guo, C. Wang, *Chem. Mater.* 2011, *23*, 5243–5249.
 [35] Z. Ma, J. Yu, S. Dai, *Adv. Mater.* 2010, *22*, 261–285.

- [36] S. De, A. Balu, J. C. van der Waal, R. Luque, ChemCatChem 2015, 7, 1608–1629.
- [37] Z.-A. Qiao, S.-H. Chai, K. Nelson, Z. Bi, J. Chen, S. M. Mahurin, X. Zhu, S. Dai, *Nat. Commun.* **2014**, *5*, 3705.
- [38] B. Li, Y. Zhang, R. Krishna, K. Yao, Y. Han, Z. Wu, D. Ma, Z. Shi, T. Pham, B. Space, J. Liu, P. K. Thallapally, J. Liu, M. Chrzanowski, S. Ma, J. Am. Chem. Soc. 2014, 136, 8654–8660.
- [39] Y. Zhang, B. Li, S. Ma, Chem. Commun. 2014, 50, 8507-8510.
- [40] P. Kaur, J. T. Hupp, S. T. Nguyen, ACS Catal. 2011, 1, 819-835.
- [41] Y. Zhang, S. N. Riduan, Chem. Soc. Rev. 2012, 41, 2083 2094.
- [42] E. B. Anderson, M. R. Buchmeiser, *ChemCatChem* **2012**, *4*, 30–44.
- [43] Q. Zhao, P. Zhang, M. Antonietti, J. Yuan, J. Am. Chem. Soc. 2012, 134, 11852–11855.
- [44] K. K. Tanabe, M. S. Ferrandon, N. A. Siladke, S. J. Kraft, G. Zhang, J. Niklas, O. G. Poluektov, S. J. Lopykinski, E. E. Bunel, T. R. Krause, J. T. Miller, A. S. Hock, S. T. Nguyen, *Angew. Chem. Int. Ed.* **2014**, *53*, 12055–12058; *Angew. Chem.* **2014**, *126*, 12251–12254.
- [45] Q. Fang, S. Gu, J. Zheng, Z. Zhuang, S. Qiu, Y. Yan, Angew. Chem. Int. Ed. 2014, 53, 2878–2882; Angew. Chem. 2014, 126, 2922–2926.
- [46] Q. Fang, Z. Zhuang, S. Gu, R. B. Kaspar, J. Zheng, J. Wang, S. Qiu, Y. Yan, Nat. Commun. 2014, 5, 4503.
- [47] Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng, F.-S. Xiao, J. Am. Chem. Soc. 2015, 137, 5204–5209.
- [48] Q. Sun, M. Jiang, Z. Shen, Y. Jin, S. Pan, L. Wang, X. Meng, W. Chen, Y. Ding, J. Li, F.-S. Xiao, Chem. Commun. 2014, 50, 11844–11847.
- [49] Y. Huangfu, Q. Sun, S. Pan, X. Meng, F.-S. Xiao, ACS Catal. 2015, 5, 1556–1559.
- [50] Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, W.-Q. Deng, Nat. Commun. 2013, 4, 1960.
- [51] K. S. W. Sing, Pure Appl. Chem. 1987, 57, 603-619.
- [52] J. Rouquerol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. M. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing, K. K. Unger, *Pure Appl. Chem.* **1994**, *66*, 1739–1758.
- [53] B.-L. Su, C. Sanchez, X.-Y. Yang, *Hierarchically Structured Porous Materials from Nanoscience to Catalysis, Separation, Optics, Energy, and Life Science*, Wiley-VCH, Weinheim, **2012**.
- [54] W. Xuan, C. Zhu, Y. Liu, Y. Cui, Chem. Soc. Rev. 2012, 41, 1677-1695.
- [55] P. Zhang, H. Zhu, and S. Dai, ChemCatChem 2015, DOI: 10.1002/ cctc.201500368.
- [56] X. Zheng, C. W. Jones, M. Weck, Chem. Eur. J. 2006, 12, 576-583.
- [57] R. E. Kirk, D. F. Othmer in *Encyclopedia of Chemical Technology* (Ed.: A. Seidel), Wiley, New York, **2005**, pp. 644–660.
- [58] K. Weissermel, H. J. Arpe, Industrial Organic Chemistry, Wiley-VCH, Weinheim, 1993.
- [59] J. W. Van Hal, J. S. Ledford, X. Zhang, Catal. Today 2007, 123, 310-315.
- [60] D. F. Othmer, M. S. Thakar, Ind. Eng. Chem. 1958, 50, 1235–1244.
- [61] V. F. Shvets, R. A. Kozlovskiy, I. A. Kozlovskiy, M. G. Makarov, J. P. Suchkov, A. V. Koustov, Org. Process Res. Dev. 2005, 9, 768–773.
- [62] Y. C. Li, S. R. Yan, L. P. Qian, W. M. Yang, Z. K. Xie, Q. L. Chen, B. Yue, H. Y. He, J. Catal. 2006, 241, 173–179.
- [63] Y. C. Li, S. R. Yan, B. Yue, W. M. Yang, Z. K. Xie, Q. L. Chen, H. Y. He, Appl. Catal. A 2004, 272, 305–310.
- [64] B. C. Gates, Catalytic Chemistry, Wiley, New York, 1992.
- [65] F. Zhang, X. Yang, F. Zhu, J. Huang, W. He, W. Wang, H. Li, Chem. Sci. 2012, 3, 476–484.
- [66] D. E. De Vos, M. Dams, B. F. Sels, P. Jacobs, Chem. Rev. 2002, 102, 3615– 3640.
- [67] K. G. M. Laurier, F. Vermoortele, R. Ameloot, D. E. De Vos, J. Hofkens, M. B. J. Roeffaers, J. Am. Chem. Soc. 2013, 135, 14488-14491.
- [68] F. Vermoortele, M. Vandichel, B. V. de Voorde, R. Ameloot, M. Waroquier,
 V. Van Speybroeck, D. E. De Vos, *Angew. Chem. Int. Ed.* 2012, *51*, 4887–4890; *Angew. Chem.* 2012, *124*, 4971–4974.

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