UvA-DARE (Digital Academic Repository)

Homochiral metal-organic frameworks as heterogeneous catalysts

Gheorghe, A.; Tepaske, M.A.; Tanase, S.

DOI

[10.1039/c8qi00063h](https://doi.org/10.1039/c8qi00063h)

Publication date

2018

Document Version

Final published version

Published in

Inorganic Chemistry Frontiers

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Gheorghe, A., Tepaske, M. A., & Tanase, S. (2018). Homochiral metal-organic frameworks as heterogeneous catalysts. *Inorganic Chemistry Frontiers*, 5(7), 1512-1523.
<https://doi.org/10.1039/c8qi00063h>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

REVIEW

View Article Online

View Journal | View Issue

Cite this: *Inorg. Chem. Front.*, 2018, **5**, 1512

Homochiral metal–organic frameworks as heterogeneous catalysts

Andreea Gheorghe, Martijn A. Tepaske and Stefania Tanase *

Homochiral metal–organic frameworks (HMOFs) are attractive materials for asymmetric catalysis because they possess high surface area and uniform active sites. A variety of catalytic applications reported so far indicate that HMOFs catalyse a range of transformations, including cyanosilylation, aldol condensation and hydrogenation reactions. Besides contribution to fundamental knowledge, it is also important to evaluate the relevance of organic transformations catalysed by HMOFs and how existing achievements compare with already established enantioselective catalysts. This mini-review gives an overview of the structural design and the catalytic performance of HMOFs and it focuses on the relevance of the chemical reactions tested. It aims at combining the existing demand for heterogeneous asymmetric catalysts with the current knowledge on HMOFs. This is important for the MOF community since it highlights relevant broad scope asymmetric catalytic transformations performed in industry and the insight gained from the catalytic reactions carried out using HMOFs as catalysts. We hope that this work will motivate researchers to rationally design HMOFs with a goal to unveil reaction mechanisms and the interactions between the HMOFs and the reaction molecules for industrially relevant catalytic reactions.

Received 23rd January 2018,

Accepted 3rd April 2018

DOI: 10.1039/c8qi00063h

rsc.li/frontiers-inorganic

Introduction

Chiral molecules are used in different industrial areas, such as pharma,¹ agro-chemistry,² fine-chemicals,³ or liquid crystals.⁴ In the pharmaceutical industry, 56% of the drugs produced are chiral, out of which 88% are commercialised as racemates.¹ This is contrary to the way nature “does it”, where most of the molecules in living systems, including amino

acids, proteins, and nucleic acids are homochiral.² It is well known that biological receptors often bind to a single enantiomer while the other can have harmful or undesirable effects. This gives rise to an increased demand for enantiopure chemicals. Therefore, different strategies have been developed so far to supply the desired enantiomer. The main directions exploited cover chemical transformation of chiral pool precursors,⁵ resolution of racemates,⁶ and enantioselective synthesis.^{2,7}

The chiral pool approach can lead directly to the enantiomer of choice, by converting readily-available homochiral precursors from the chiral pool.⁸ This strategy has the advantage

Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands. E-mail: s.grecea@uva.nl

Andreea Gheorghe

Andreea Gheorghe obtained a BSc in Chemistry (2013) and a MSc in Materials Chemistry (2015), both from the University of Bucharest. She is currently pursuing a PhD in chemistry under Dr Stefania Tanase's guidance. Her research is focused on the rational design of homochiral metal–organic frameworks for enantioselective catalysis.

Martijn A. Tepaske

Martijn Tepaske obtained his BSc degree in 2015 from the Vrije Universiteit Amsterdam under the guidance of Dr Eelco Ruijter doing research in Synthetic and Bio-Organic Chemistry. He is currently undertaking his major MSc research project under the supervision of Dr Stefania Tanase, working on the designed synthesis of homochiral metal–organic frameworks via chiral induction.

of producing the desired enantiopure or enantioenriched product in only one step, but it is limited to available chiral building blocks from nature. Resolution or deracemisation is a two-step strategy that can be coupled with the existing production processes, where firstly the racemic mixture of the target molecule is prepared, followed by the resolution to the desired enantiomer. The main drawback of this approach is in the significant amounts of waste being produced, with possible financial and environmental implications.⁴ Extensive research into racemisation methods have managed the recycling of the undesired enantiomer, making resolution the economically preferred route (e.g. synthesis of (S)-naproxen).^{4,9,10}

The synthesis of enantiopure compounds *via* asymmetric synthesis is a one-step method which has the advantage of each molecule of a chiral catalyst, which is continuously regenerated, producing many molecules of the chiral product.^{11,12} This is, in fact, how nature produces enantiomerically pure compounds, using chirality transfer from enzyme catalysts.¹³ Blaser¹⁴ has classified the asymmetric catalysts into three main types: homogeneous metal complexes, heterogeneous metallic catalysts with chiral functionalities and chiral soluble organic bases and acids, also known as organocatalysts. The first commercialised asymmetric catalysis application was developed in the early seventies at Monsanto.¹⁵ It produces the (S)-dihydroxyphenylalanine (L-DOPA) drug with 97.5% ee using a Rh diphosphine complex as a catalyst, Rh/(DiPAMP).¹⁶ Despite extensive research, only a few production processes

have been developed until now.¹⁷ In most of the cases, the catalyst is a homogeneous metal complex which contains a chiral ligand and it has high selectivity and activity.¹² Although the lengthy synthesis of chiral ligands is currently overcome due to large commercially available libraries, they can still have a high cost. Some metals used to synthesise homogeneous catalysts are also expensive.¹⁸ Some difficulties in the application can arise from differences between the substrates to be transformed and the model ones. Thus, specific functionalities on the substrate or the modifications of the catalyst are needed for the reaction to occur.¹⁹

Another class of applied asymmetric catalysts consists of achiral heterogeneous catalysts modified with enantiopure organic molecules. Representative examples are the cinchona modified Pt/Al₂O₃ catalyst²⁰ which is used for the asymmetric hydrogenation of α -keto esters or the (R,R)-tartaric acid RANEY® Ni/NaBr²¹ system utilised in β -functionalised ketone asymmetric hydrogenations.^{4,22,23} Although this class of catalysts is cheap and easy to synthesise, there are very few examples, with narrow substrate scope and challenging to optimise because of difficulties in unravelling the reaction mechanisms.¹⁰ Therefore, not many processes could be scale-up.⁴

Organocatalysts form a particular class of asymmetric catalysts. They are small organic molecules able to catalyse organic reactions in the homogeneous phase with very high enantioselectivity.²⁴ Their advantages include high tolerance to humidity and air, easy availability and low cost as well as no contamination of products with metal traces. Generally, they are difficult to recover and they also require high loadings.^{25,26} The use of selective and stable heterogeneous catalysts would enable easy recovery from the reaction medium and the reuse in consecutive cycles, which in turn can result in low cost applications.

Nowadays, a plethora of homochiral MOFs (HMOFs) have been reported as catalysts for asymmetric transformations. HMOFs have well defined, single-crystalline solid structures, high concentration of catalytic sites, more uniform and accessible catalytic centers, and enhanced catalytic activity due to the lack of multimolecular catalyst deactivation pathways.^{18,27} Indeed, some HMOFs containing specifically designed chiral linkers show both a high catalyst density with single-site catalysis and promising activities in asymmetric reactions.^{28–33} The application of HMOFs in asymmetric transformations can provide a fundamental understanding of the reaction mechanisms. It also allows studying of the confinement effects on the catalytic activity. The main advantage of using HMOFs as catalysts in asymmetric reactions is the easy separation of the catalyst, which reduces product contamination that is highly regulated in the pharmaceutical industry.³⁴

Several reviews have covered the designed synthesis of MOFs and their activity as heterogeneous catalysts in various organic reactions.^{35–39} In the first part of this review, we focus on the synthetic strategies developed to prepare HMOFs, highlighting the main advantages and disadvantages. This includes the availability of precursors, reaction conditions and the stability of the chiral framework upon solvent removal. The

Stefania Tanase

Stefania Tanase received her BSc in Chemistry and Physics in 1996 from the University of Bucharest and an MSc in Advanced Inorganic Synthesis in 1997 from the Polytechnic University of Bucharest in Romania. She obtained her PhD in Inorganic Chemistry in 2002 from the University of Bucharest for which she received a Young Investigator Award. She was a postdoc (2001–2004) and an independent VENI research

fellow (2005–2008) at the University of Leiden in The Netherlands. In 2009, she joined the University of Amsterdam as a senior researcher and since 2011 she has been working as Assistant Professor in Heterogeneous Catalysis and Sustainable Chemistry, leading the Inorganic Materials group. Tanase's research focuses on the development of synthetic methodologies for the preparation of inorganic and hybrid inorganic–organic materials with applications in molecular separation, magnetism, molecular sensing, catalysis and as proton conductive membranes for fuel cells. She has co-authored over 75 publications and two book chapters.

second part discusses industrially relevant asymmetric organic transformations carried out with HMOFs. It covers the performance of the catalytic HMOFs, the basis on which the catalysts were developed and the achievements in specific organic reactions, including the product yield, enantioselectivity and catalytic activity as compared to their homogeneous analogues.

Strategies for synthesizing HMOFs for asymmetric catalysis

Designed synthesis of MOFs has developed remarkably since the first report on the highly porous MOF-5 in 1999.⁴⁰ The classical description of MOFs is a 3D porous coordination network of metal ions or clusters joined through organic linkers.

The general synthesis employs the solvothermal reaction between metal salts and specifically chosen organic linkers. Here, the main goal is to establish the synthesis conditions which facilitate the formation of well-defined building blocks without decomposition of the organic linker. Based on this knowledge, Yaghi *et al.*⁴¹ developed a reticular synthesis strategy which uses secondary building units (SBUs) as molecular polygons or polyhedra to construct MOFs. MOFs built from the SBUs have several advantages, including a higher surface area and increased pore size as well as enhanced robustness. This is due to the greater relative size and higher stability of the SBUs which contain multiple metal ions bridged in a cluster by multiple coordinating organic linkers. Considering the approaches discussed above, a straightforward route to obtain HMOFs would be to combine specific metal ions and chiral organic linkers or to use an auxiliary chiral linker that forms chiral SBUs which can be connected further by achiral linkers. Indeed, many commercially available enantiopure organic linkers were used in combination with various metal ions for the synthesis of HMOFs. It includes amino acids (*e.g.* L-tyrosine, L-histidine, L-tryptophan and L-glutamic acid),⁴² diacids (*e.g.* D-(+)-camphoric acid, tartaric acid and malic acid)⁴³ and enantiopure carbohydrates (*e.g.* sugars).^{44,45} Kim *et al.*³¹ reported the first chiral porous framework, $[\text{Zn}_3(\mu_3\text{-O})](\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_5\text{H})_6 \cdot 2\text{H}_2\text{O} \cdot 12\text{H}_2\text{O}$ (known as L-POST-1/D-POST-1), which is constructed from trinuclear oxo-bridged $[\text{Zn}_3(\mu_3\text{-O})]^{4+}$ clusters (SBUs) acting as nodes and an enantiopure tartaric acid derivative acting as an organic linker (Fig. 1 and 2, left). There are six linkers per node with two distinct binding modes. One half binds through the carboxyl endings and the other half uses both carboxyl and pyridyl groups to form a 2D layered structure with large chiral channels (~ 13.4 Å) across the *c* axis (Fig. 1). Because two of the pyridyl units exposed in the HMOF channels are in a protonated form, a cation exchange with alkali metal ions (*e.g.* Na^+ , K^+ , and Rb^+) was possible without framework disruption.³¹ The framework collapses upon removing the guest solvent molecules, but its crystallinity is regained by exposure to either ethanol or water. Although the enantioselective transesterification of racemic 2,4-dinitrophenyl acetate in the presence of D-POST-1 leads to

Fig. 1 View along the *c* axis of the 3D framework D-POST-1 showing the large chiral 1D channels.²⁶

Fig. 2 Direct synthesis of HMOFs using chiral organic linkers and $[\text{Zn}_3(\mu_3\text{-O})]^{4+}$ (left) or $[\text{Zn}_4(\mu_4\text{-O})]^{6+}$ (right) as SBUs.^{31,46}

only *ca.* 8% ee, it represents the first example of enantioselective catalysis with a HMOF. The main advantage of L-POST-1/D-POST-1 is the possibility of tuning the charge of the framework (from negative to positive) or the pore size by *N*-alkylation of the pyridyl group with different chain length alkyls.³¹

Several attempts to synthesise HMOFs using other cheap and abundant chiral linkers have failed mainly due to the flexibility of the organic linkers. Therefore, Lin *et al.*⁴⁶ proposed using rigid chiral linkers, *e.g.* functionalised 1,1'-bi-2-naphthol (BINOL), to render more robust frameworks. These types of linkers give rise to fourfold interpenetrated 3D frameworks which are built from $[\text{Zn}_4(\mu_4\text{-O})]^{6+}$ clusters and BINOL derivatives (Fig. 2, right).⁴⁶ Despite the tendency of $[\text{Zn}_4(\mu_4\text{-O})]^{6+}$ to form interpenetrated network frameworks, many HMOFs built from BINOL derivatives were synthesized and showed excellent activity in a wide range of organic transformations.^{27,47–49} Fig. 2 illustrates that the direct synthesis of HMOFs is possible by assembling $[\text{Zn}_3(\mu_3\text{-O})]^{4+}$ or $[\text{Zn}_4(\mu_4\text{-O})]^{6+}$ SBUs in the presence of multidentate chiral linkers. However, this strategy is limited to only a few chiral organic linkers and no systematic

studies on development of reticular synthesis have been undertaken so far.

Rosseinsky *et al.*^{50,51} proposed the use of an auxiliary chiral linker to induce asymmetric crystallization in a porous solid. Enantiopure 1,2-propanediol was used as a chiral co-linker to assemble a HMOF from 1,3,5-benzenetricarboxylic acid (H_3BTC) and $M(NO_3)_2 \cdot 6H_2O$ ($M^{2+} = Ni, Co$).⁵⁰ The enantiomerically pure 1,2-propanediol chelates to the metal center, and therefore the stereochemistry of the metal enables control of the absolute helicity of the growing polymeric structure and determination of the type of interpenetration.⁵⁰ In terms of asymmetric catalytic applications, these materials rely only on the Lewis acidity of the metal centres and the asymmetric induction of the auxiliary linkers, thereby having a limited tuning of the confined space.

Synthesis of robust HMOFs for catalytic applications implies the use of rigid and homochiral linkers which have predefined functionality and connectivity. This is mostly achieved by post-synthetic modification (PSM) which indeed afforded the incorporation of highly active catalysts, such as organocatalysts or metal complexes in metal-organic frameworks. The PSM facilitates chemical transformations on either an achiral parent MOF or a HMOF without changing the overall network structure.^{52–54} Several reviews have already discussed these PSM approaches in detail.^{55–59} Based on the nature of the new bond formed, the PSM of HMOFs consists of covalent or coordinative modifications. The first HMOF catalyst, D-POST was modified post-synthetically without framework disruption by covalent *N*-alkylation of the pyridyl group with different alkyl chains.³¹ An achiral framework can be turned into a chiral analogue by covalent binding of a chiral moiety. This strategy affords various modifications on the linker, irrespective of the framework synthesis conditions. Farrusseng and Canivet *et al.*⁶⁰ successfully modified achiral parent MOFs, *e.g.* Al-MIL-101-NH₂, MIL-68-NH₂ and Zr-Uio-66-NH₂ with amino acids or peptides *via* amide coupling to the 2-aminoterephthalate linker.⁶⁰ Although no racemisation of chiral centers was observed in this case after the post-synthetic deprotection by microwave treatment, the thermal deprotection can lead to a certain degree of racemisation or even loss of stereoinformation.^{61,65} A derivative of proline was used by Kim *et al.*⁵³ to prepare an achiral framework by coordinating the chiral organocatalyst to the open sites of MIL-101. Most MOFs prepared by the PSM retain structural integrity, but isolated examples of structure disruption have been reported.⁶²

Tuning the spatial environment around the active site of HMOFs to create pore homogeneity is highly relevant for catalytic transformations. An effective approach to preserve pore homogeneity is to build-up multicomponent MOFs by using a combination of two or three topologically distinct linkers.⁶³ Because the linkers can be discriminated during the framework assembly, they become positioned in unique lattice sites. Recently, Telfer *et al.*⁶⁴ embedded a catalytic unit in a pore of the MUF-77 framework and then tuned its environment by introducing different functional groups into the surrounding

linkers. Prolinyl groups, which are well-known as organo-catalysts, were selected and covalently bound to either 1,4-benzenedicarboxylate (bdc) or 4,4'-biphenyldicarboxylate (bpdc) linkers using amide coupling reactions. The two distinct ditopic linkers and a tritopic truxene 5,5',10,10',15,15'-hexamethyltruxene-2,7,12-tricarboxylic acid (H_3hmtt) were combined with $Zn(NO_3)_2 \cdot 4H_2O$ to form $[Zn_4O(bdc-Pro)_{1/2}(bpdc)_{1/2}(hmtt)_{4/3}]$ (Fig. 3) and $[Zn_4O(bdc)_{1/2}(bpdc-Pro)_{1/2}(hmtt)_{4/3}]$.⁶⁴ Systematic engineering of the pore structure was achieved by incorporating modulator groups on the framework linkers. It is important to note that this type of structure crystallises only when the prolinyl group on the linkers is protected.⁶⁴

Because of the limited availability and high cost of enantiopure linkers, it is desirable to synthesise HMOFs from achiral building blocks by means of chiral induction. For this, not only generation of chirality but also enantiomeric bias to favour one handedness are needed.⁶⁶ Therefore, recent synthetic strategies for building chiral MOFs have explored induction of chirality *via* various means, *e.g.* chiral additives, chiral templates or chiral solvents.^{67,68} Zhang *et al.*⁶⁹ successfully synthesized a HMOF with a zeolitic topology by using a chiral lactic acid derivative, (*R*)-5-(1-carboxyethoxy)isophthalic acid ((*R*)- H_3CIA) as a template in the reaction of the achiral 1,4-di(1*H*-imidazol-1-yl)benzene (DIB) ligand with Zn^{2+} ions. This is a 3D interpenetrated framework, $C_{24}H_{20}N_8O_2Zn_2$, with 1D channels of *ca.* 3.3 nm (Fig. 4), which accommodates the guest (*R*)- CIA^{3-} ions. Using (*S*)- H_3CIA instead of (*R*)- H_3CIA did not result in a HMOF with opposite handedness. In fact, (*R*)- H_3CIA not only behaves as a chiral template in the crystallization of the HMOF but also contributes to the formation of the crystal-line phase.⁶⁹ Because this is a template-based synthesis, the template removal should be the final synthetic step. However, this is not discussed yet.⁶⁹

Recently, Zaworotko *et al.*⁷⁰ reported the synthesis of a chiral polymorph of the well-known MOF-5 (also known as

Fig. 3 View down axis of $[Zn_4O(bdc-Pro)_{1/2}(bpdc)_{1/2}(hmtt)_{4/3}]$. For simplicity, the Pro unit is represented by a black sphere and it is covalently bound to the bdc linker.⁶⁴

Fig. 4 View of the twofold interpenetrated $C_{24}H_{20}N_8O_2Zn_2$ framework (anion guest molecules are not depicted in this representation).⁶⁹

IRMOF-1).⁷⁰ This was accomplished by addition of the chiral L- or D-proline additives and the achiral solvent *N*-methyl-2-pyrrolidone (NMP) to the conventional solvothermal synthesis of MOF-5.⁷⁰ Single-crystal XRD analysis showed that the framework crystallizes in the cubic chiral space group $P2_13$ and appears to be a distorted structure of MOF-5, namely CMOF-5 (Fig. 5). Solvent exchange of CMOF-5 caused a reversal to its achiral analogue and using NMP as a solvent caused the formation of a racemic conglomerate. Even though the chiral induction by adsorption of chiral guests was reported previously,⁷¹ its occurrence upon adsorption of achiral molecules has not been reported yet. It seems that the use of NMP as a solvent is the key for stabilising CMOF-5. Evans *et al.*⁷² studied the microscopic mechanism of the chiral induction of NMP by employing multiscale molecular simulations. The intrinsic stability of CMOF-5 was analysed using quantum chemistry calculations at the density functional theory (DFT) level, which are thoroughly used to probe the stability of crystalline materials.⁷² The DFT energy minimization calculations, in the absence of NMP, demonstrated that both CMOF-5 structures relax back to the achiral MOF-5 framework.⁷² This suggests that CMOF-5 is not stable upon guest evacuation. Similar to the evacuated CMOF-5, the chiral composite loaded with DMF also relaxes back to the achiral MOF-5. In contrast to DMF, NMP positions are closer to the phenyl ligand because these are larger molecules and unable to converge closer to the $Zn_4(\mu_4-O)$ cluster. Moreover, NMP is in close contact (~ 4 Å) with adjacent molecules and therefore leads to stronger guest-guest

Fig. 5 View of the pore geometries of the achiral MOF-5 (left) and the Δ enantiomer of CMOF-5 (right).^{40,70}

interactions than DMF. Therefore, NMP mediates *bridging* of neighbouring aromatic rings, thus generating the internal shearing stress responsible for chiral induction in CMOF-5 by twisting the linker.⁷²

Synthesis of HMOFs by using structure directing chiral solvents such as ionic liquids with chiral and enantiomerically pure anions is scarce.^{73,74} Morris *et al.*⁷³ reported the synthesis of a chiral MOF, namely $[C_4mim]_2[Ni(hbtc)_2(H_2O)_2]$ MOF (SIMOF-1), using 1-butyl 3-methylimidazolium L-aspartate ($[C_4mim][L-aspartate]$). This is an example in which the chiral anion is not included in the structure of the material, but it directs the chirality of the MOF towards one enantiomer.⁷⁵ It was also possible to control the configuration of the MOF by changing the chirality of the chiral ionic liquid solvent. If the synthesis is performed with $[C_4mim][D-aspartate]$, the opposite handedness of the MOF is obtained.⁷³ Instead of using chiral solvents, Bu *et al.*⁶⁷ has explored chiral alkaloids as chiral additives. The additives were added into the solvothermal reaction of thiophene-2,5-dicarboxylic acid (H_2thb) and In (NO_3) $\cdot xH_2O$ leading to chiral porous solids. The donor atoms of (+)-cinchonine or (–)-cinchonidine chelate to the In^{3+} sites and control the chirality of the MOFs.⁷³

The main difference between chiral templating and other methods is the presence of the chiral component in the final material. Therefore, the difficulty in induction remains in the removal of the chiral agent, without disrupting the framework's chirality. Templating is also a challenging strategy since it requires chirality transfer to the framework.

Asymmetric organic transformations relevant for industrial applications

The quest for enantiopure chemicals along with the advantages of enantioselective catalysts has led to production processes of chiral building blocks (*e.g.* carboxylic acids, amines, alcohols, and epoxides),⁷⁶ novel biologically active pharmaceuticals (*e.g.* Crixivan)⁷⁷ and commodity chemicals (*e.g.* menthol).⁷⁸ Nevertheless, the majority of commercial processes are hydrogenations of various unsaturated functions, such as $C=C$, $C=O$ and $C=N$ bonds.^{79–82} This is most likely due to its broad scope application, and also due to extensive research conducted for this reaction.^{4,81,83} In terms of substrate scope, they are followed by the epoxidation and the dihydroxylation of the $C=C$ bonds as well as various addition reactions.^{84–86}

So far, asymmetric catalysis with HMOFs has been reported for various organic transformations: hydrogenation,⁸⁷ aldol,⁸⁸ cyanosilylation,⁸⁸ diethylzinc addition,⁵⁴ epoxidation,²⁹ transesterification,³¹ addition of a Grignard reagent⁸⁹ and ring opening.⁴⁷ The motivation behind using HMOFs for asymmetric catalysis is closely related to the highly tunable size⁹⁰ and functionality³¹ of MOF pores and the ability to confine the chiral active sites.⁵³ Naturally, the goal is to apply HMOFs in industrial processes, however research in this field is not mature and it requires detailed mechanistic studies before

finding optimum catalytic parameters towards highly enantioselective reactions. Therefore, this section focuses on progress in designing HMOFs which catalyse asymmetric reactions that are relevant for industrial application.

Asymmetric hydrogenation reactions that generate chiral centers with specific enantiomeric configurations are being intensively studied.⁸¹ State-of-the-art asymmetric hydrogenations of various olefins, including enamides, enol acetates, allylic alcohols, itaconates *etc.*, can lead to ee values between 80–99%.⁸³ The preferred and most common industrial catalyst types are Ru²⁺ or Rh⁺ complexes with atropisomeric diphosphines,^{91,92} or Ir⁺ complexes with bisoxazolidines.⁹³ Based on the excellent performance of the mentioned complexes, Lin *et al.*^{87,88} prepared very efficient homochiral porous catalysts for asymmetric hydrogenation using bridging chiral linkers with coordinated Ru²⁺ ions. These catalysts were used in the heterogeneous asymmetric hydrogenation of aromatic ketones⁹⁴ (Fig. 6) or β -ketoesters⁹⁵ (Fig. 7) affording quantitative conversions and up to 97% ee.

Recycling and reusing 1-acetophenone using [Zr{Ru(C₅₈H₄₆N₂O₆P₄Cl₂)}]·4H₂O with bis(phosphonic acid) at the 6,6' position was possible for 6 runs without loss of activity or ee.⁹⁴ It was also possible to use [Zr{Ru(C₅₀H₄₄N₂O₈P₄Cl₂)}]·2MeOH with bis(phosphonic acid) at the 6,6' position for the asymmetric hydrogenation of methyl acetoacetate for 4 cycles with complete conversions and ~94% ee.⁹⁴ Surprisingly, there was no correlation between the catalytic activity and the surface area of the materials. Moreover, the materials are amorphous, making it difficult to determine their exact structure and study interactions between the framework and substrate. They are however the first examples of rational design of heterogeneous asymmetric catalysts.

The BINAP based Zr-MOF, Zr₆(OH)₄O₄(C₆₂H₄₀P₂O₄)₆·126DMF·156H₂O was successfully synthesized (Fig. 8) using a post-synthetic modification method.⁸⁷ Its metalation with Rh⁺ or Ru²⁺ phosphine complexes gave materials with different metal loadings, *e.g.* 33% Rh⁺ or 50% Ru²⁺. The Rh⁺ derivative

Fig. 6 The asymmetric hydrogenation of aromatic ketones using 0.1 mol% [Zr{Ru(C₅₈H₄₆N₂O₆P₄Cl₂)}]·4H₂O with bis(phosphonic acid) at the 4,4' or 6,6' position; Ar = Ph, 2-naphthyl, 4'-^tBu-Ph, 4'-MeO-Ph, 4'-Cl-Ph, 4'-Me-Ph, 1-naphthyl; R = Me, Et, *cyclo*-Pr.⁹⁴

Fig. 7 The asymmetric hydrogenation of β -keto esters catalysed by phosphine-based MOFs: (a) 0.1 mol% [Zr{Ru(C₅₀H₄₄N₂O₈P₄Cl₂)}]·2MeOH with bis(phosphonic acid) at the 4,4' or 6,6' position; R₁ = CH₃, C₂H₅, Ph; R₂ = CH₃, C₂H₅, ^tPr, O^tBu, 60 °C, 700/1400 psi H₂⁹⁵ and (b) 0.5 mol% Zr₆(OH)₄O₄(C₆₂H₄₀P₂O₄)₆·126DMF·156H₂O, RT, 40 bar H₂; R₁ = Me, Et, Me; R₂ = Me, Et, ^tBu.⁸⁷

Fig. 8 View of the 3D structure of the parent Zr-MOF of the first phosphine based Zr–Ru–MOF, Zr₆(OH)₄O₄(C₆₂H₄₀P₂O₄)₆·126DMF·156H₂O.⁸⁷

has a high catalytic activity in addition reactions,⁸⁷ while the Ru²⁺ functionalized MOF catalyses the asymmetric hydrogenation of different β -keto esters (Fig. 7) with up to 97% ee and the asymmetric hydrogenation of substituted alkenes with up to 91% ee. Quantitative yields were obtained for both catalytic applications and the ee was almost the same as the one observed with the homogeneous analogues (99% ee). This example showed that incorporating the catalyst within a matrix is ultimately non-beneficial, and the conventional homogeneous system is still the preferred one. Furthermore, the leaching of Ru²⁺ during the catalytic reaction clearly indicates that further catalyst optimisation is required.

The asymmetric hydrogenation of olefins by a Rh⁺ chiral catalyst with achiral MOFs as additives was attempted by van Bokhoven *et al.*⁹⁶ leading to the adsorption of the complex within the framework. Addition of UMCM-1-NH₂ to the reaction mixture of the asymmetric hydrogenation of dimethyl itaconate with (*S,S*)-[Rh(C₁₄H₂₈P₂)(C₈H₁₂)]CF₃SO₃ resulted in 92% complex adsorbed within the MOF pores. As compared to the homogeneous system, this new chiral catalytic system shows a slight increase in enantioselectivity from 92 to 94% ee and doubled the conversion (21%) (Fig. 9). Recycling of the catalyst was possible but with significant loss of activity.⁹⁶

The asymmetric hydrogenation processes can have a broad, medium or narrow substrate scope depending on the diversity of substrates to transform.¹⁷ Asymmetric oxidations however have a narrow substrate scope and pertain to niche appli-

Fig. 9 The asymmetric hydrogenation of dimethyl itaconate using 0.33 mol% (*S,S*)-[Rh(C₁₄H₂₈P₂)(C₈H₁₂)]CF₃SO₃ and 14 mg of UMCM-NH₂.⁹⁶

cations.¹⁷ Industrially relevant oxidation processes include the dihydroxylation⁹⁷ and the epoxidation of C=C bonds,⁸⁴ the oxidation of sulphides⁹⁸ and the aminohydroxylation of C=C bonds.⁹⁹ Unlike asymmetric hydrogenations, where homogeneous metal complexes are the predominant catalysts employed, the oxidation reactions have already been tested using different types of catalysts: enzymes,¹⁰⁰ whole cells¹⁰¹ and homogeneous metal complexes.⁸⁴

The asymmetric epoxidation of olefins is an important organic transformation that leads to highly reactive chiral epoxides, the key intermediates for the synthesis of value-added compounds.⁷⁶ Early research¹⁰² indicated that manganese complexes of chiral Schiff bases are effective catalysts for this reaction. This work led to the Merck/ChiRex process for synthesising *cis* aminoindanol, an intermediate for indinavir synthesis (HIV protease inhibitor).⁴ Indene epoxidation is performed with a Mn-salen complex with a *N*-pyridine oxide co-catalyst, Mn/SALEN/P₃NO.¹⁰³ The critical issues of this process are ligand stability, deactivation of the manganese complex through the formation of dimeric species and pH control.^{17,28,83,104} Therefore, studies focused on immobilizing the active catalytic site in the confined space of a MOF would prevent the catalyst deactivation through the dimerisation process.

The first successful Mn-salen based MOF, Zn₂(C₁₄H₈O₄)₂[Mn(C₃₈H₄₂N₄O₂Cl)]·10DMF·8H₂O, for the asymmetric epoxidation of olefins was achieved using Mn-salen-derived bipyridine bridging ligands in combination with 4,4-biphenyldicarboxylic acid linkers and Zn²⁺ ions (Fig. 11).²⁹ The catalyst could be recycled and reused three times, with the ee values decreasing only in the third cycle. Notably, immobilising the salen group into the MOF structure increased the stability of the catalyst from a few minutes to a few hours. Accessibility of the active sites was possible due to the diagonal displacement of the network and the catalyst was efficient in the epoxidation of 2,2-dimethyl-2*H*-chromene (Fig. 10), with 71% yield and 82% ee, slightly lower than the homogeneous analogue (88% ee).²⁹ This was attributed to the electron-withdrawing effect of the Zn-coordinated pyridinic terminations of the salen-derived ligand.²⁹ Later on, studies performed by Snurr *et al.*¹⁰⁵ showed that the steric environment created by the MOF influenced the enantioselectivity of the catalyst.

Lin *et al.*²⁷ synthesised a family of isorecticular HMOFs with Mn-salen-type bridging ligands by using solvent molecules of

Fig. 11 View along the *a* axis of Zn₂(C₁₄H₈O₄)₂[Mn(C₃₈H₄₂N₄O₂Cl)]·10DMF·8H₂O.²⁹

different steric bulk to control the framework interpenetration. The size of the open channels in these MOFs were systematically tuned by introducing spacers of different lengths. The N₂ adsorption measurements indicated negligible surface areas, caused by the breathing effect of the large open channels.²⁷ By testing the uptake of dyes, the differences between the structures could be observed.²⁷ The catalysts prepared were tested for the epoxidation of 2,2-dimethyl-2*H*-chromene. By correlating the catalytic conversion to the channel size of the MOF, it was shown that diffusion is a limiting factor, especially for the interpenetrated structures.²⁷ With increasing channel size, the reaction rates of the HMOF catalysts were even higher than the reaction rate of the homogeneous Mn-salen complex, Mn(C₄₆H₄₆N₂O₂Cl). Moreover, the epoxidation of several chromene derivatives led to higher yields for the epoxidation products than those observed for the homogeneous analogues (Fig. 8 and Table 1). The negative impact of the Mn-salen MOF interpenetration was also discussed by Snurr *et al.*¹⁰⁵ in terms of the steric interactions between the substrates and the MOF host as well as the flexibility of the salen units.¹⁰⁵ Similar Mn-salen chiral MOFs were also used as catalysts in sequential asymmetric epoxidation/ring opening reactions.^{30,32}

An alternative approach to designing enantioselective catalysts for alkene epoxidation is the entrapment of a Mn³⁺ complex within the MIL-101.²⁸ By encapsulating the Mn-salen complex in the MIL-101 pores, no steric hindrance occurs at the active site. Therefore, the enantioselective epoxidation of dihydronaphthalene with Mn-salen@MIL-101 gives similar enantioselectivity as the homogeneous catalyst, but with lower turnover number.²⁸ The catalyst is stable and maintains its activity over four cycles.²⁸ The catalytic results obtained with the catalysts tested in the olefin epoxidation reactions have shown that by controlling specific parameters, such as

Fig. 10 The asymmetric epoxidation of derived chromene with 2-(*t*-Bu-sulfonyl)iodobenzene using 0.01 mol% Zn₂(C₁₄H₈O₄)₂[Mn(C₃₈H₄₂N₄O₂Cl)]·10DMF·8H₂O, R = H;²⁹ 0.1 mol% catalyst and R = H, CN, NO₂, CH₃O, CH₃.²⁷

Table 1 The asymmetric epoxidation of alkenes (Fig. 13) catalyzed by HMOFs²⁷

R	Catalyst	C ^a (%)	ee ^b (%)
H	Zn ₄ O[Mn(C ₄₆ H ₄₆ N ₂ O ₂ Cl)] ₃ ·38DMF·11EtOH ⁺	82	92
H	Zn ₄ O[Mn(C ₃₄ H ₃₈ N ₂ O ₂ Cl)] ₃ ·37DEF·23EtOH·4H ₂ O	87	85
H	Mn(C ₃₆ H ₄₄ N ₂ O ₂ Cl)	90	92
CN	Zn ₄ O[Mn(C ₄₆ H ₄₆ N ₂ O ₂ Cl)] ₃ ·38DMF·11EtOH ⁺	60	79
CN	Zn ₄ O[Mn(C ₃₄ H ₃₈ N ₂ O ₂ Cl)] ₃ ·37DEF·23EtOH·4H ₂ O	79	83
CN	Mn(C ₃₆ H ₄₄ N ₂ O ₂ Cl)	82	88
NO ₂	Zn ₄ O[Mn(C ₃₄ H ₃₈ N ₂ O ₂ Cl)] ₃ ·37DEF·23EtOH·4H ₂ O	93	81
NO ₂	Mn(C ₃₆ H ₄₄ N ₂ O ₂ Cl)	97	88
CH ₃ O	Zn ₄ O[Mn(C ₃₄ H ₃₈ N ₂ O ₂ Cl)] ₃ ·37DEF·23EtOH·4H ₂ O	89	77
CH ₃ O	Mn(C ₃₆ H ₄₄ N ₂ O ₂ Cl)	80	87
CH ₃	Zn ₄ O[Mn(C ₃₄ H ₃₈ N ₂ O ₂ Cl)] ₃ ·37DEF·23EtOH·4H ₂ O	79	75
CH ₃	Mn(C ₃₆ H ₄₄ N ₂ O ₂ Cl)	81	88

^a Conversion. ^b Enantiomeric excess.

diffusion or steric environments, it is possible to improve the performance of the salen complex by immobilisation.

Chiral 1,2-diols are industrially manufactured *via* a two-step process of olefin epoxidation and a subsequent epoxide hydrolysis.¹⁰⁶ However, the asymmetric dihydroxylation of prochiral olefins is a more atom-efficient pathway.¹⁰⁶ The preferred catalysts used in industry are osmium complexes with cinchona alkaloid ligands in combination with oxidants.^{83,106} The oxidant, K₃Fe(CN)₆–K₂CO₃, is the main drawback associated with the scaling up of the process because it generates significant amounts of waste.^{83,97}

A recent example of HMOF as a catalyst for the olefin asymmetric dihydroxylation highlights the importance of synergistic catalysis, where the active guest species perform cooperatively near chiral linker functionalities. Duan *et al.*¹⁰⁷ prepared a chiral MOF with an encapsulated [BW₁₂O₄₀]^{5–} oxidation catalyst.¹⁰⁷ This was formed in the self-assembly reaction of Ni₂H [BW₁₂O₄₀], 4,4'-bipyridine (bpy) and L-BCIP (L-*tert*-butoxycarbonyl-2-imidazole-1-pyrrolidine). During HMOF synthesis, the Boc protecting group of L-BCIP is removed, and the pyrrolidine N atoms are protonated.¹⁰⁷ Ultimately, the Ni-PYI1 (C₃₈H₅₂BN₁₁NiO₄₂W₁₂) 3D framework (Fig. 12) crystallizes with the chiral PYI1 organocatalyst and the [BW₁₂O₄₀]^{5–} polyoxometalate (POM) aligned inside the channels and linked *via* hydrogen bonding.¹⁰⁷ The amphipathic properties of the HMOF induced by the organic linkers and the POM anions proved advantageous for the miscibility of the aqueous oxidizing agent and the reactants.

The asymmetric dihydroxylation of various aryl olefins (Fig. 13) to their corresponding chiral diols using Ni-PYI1 was performed with good conversions (~76%) and high enantioselectivities (>95% ee). Testing bulky 3,5-di-*t*-Bu-4'-vinylbiphenyl led to less than 10% conversion, since this molecule was larger than the channels of the catalyst.¹⁰⁷ By changing the pH of the HMOF synthesis, an achiral material was prepared that does not contain the chiral organocatalyst, C₅₀H_{45.50}BCl_{0.50}N₁₀Ni₂O₄₂W₁₂ (Ni-BPY). The asymmetric dihydroxylation of styrene in the presence of Ni-BPY resulted in a moderate yield (60%) but no enantioselectivity was observed. A comparison of the catalytic activities of Ni-PYI1 and Ni-BPY shows that the

Fig. 12 Crystal structure of Ni-PYI1 (C₃₈H₅₂BN₁₁NiO₄₂W₁₂) along the *a* axis with polyoxometalate [BW₁₂O₄₀]^{5–} anions embedded and the chiral organocatalytic L-PYI1 moiety coordinated to the Ni²⁺ ions.¹⁰⁷

Fig. 13 Asymmetric dihydroxylation of aryl olefins with 0.7 mol% Ni-PYI1, 15% H₂O₂; R = H, Cl, 3,5-di-*t*-Bu.¹⁰⁷

synergistic interactions between the chiral PYI and the POM have an influence on catalysis.¹⁰⁷ It is important to mention that the crystallinity of Ni-PYI1 was maintained even after 3 runs.¹⁰⁷

Oxidation of aromatic or hetero-aromatic sulphides using Ti/TART catalysts lead to good enantioselectivity, but usually with very low TONs and TOFs. One industrial application is the large-scale production of esomeprazole (anti-ulcer drug) using a Ti complex. The critical issues are over-oxidation to sulfone, high catalyst loading, substrate purity, chemical yield

and ee.^{16,83} So far, a few HMOFs have been reported as catalysts for the asymmetric oxidation of aromatic sulphides.^{108–111}

The addition reactions generate one or more chiral centers, and therefore can provide chiral centers unavailable *via* hydrogenation.¹⁰⁴ One of the first industrial processes involves the addition of a primary carbon functionality to a C=C bond to form a stereoisomeric cyclopropane moiety.¹¹² This cyclopropanation between isobutene and ethyl diazoacetate for the preparation of a Cilastatin intermediate is catalysed by the Sumitomo copper complex at 40 °C with 92% ee.¹¹² The only known critical issue with this process involves the preparation and handling of diazo compounds.^{16,83} A few chiral metal-organic frameworks for asymmetric cyclopropanation reactions of terminal olefins are reported.^{33,113} Lin *et al.*³³ reported HMOFs with different pore sizes which are built from Zn₄(μ₄-O) clusters joined by Ru³⁺-salen linkers.³³ These catalysts were active in the cyclopropanation of several olefins, but only upon reduction of Ru³⁺ to Ru²⁺. A similar trend was also observed for another series of Ru³⁺-salen containing MOFs.³²

Addition reactions with a broad substrate scope are (hetero) Diels Alder, Michael additions, aldol and ene reactions and several C=O and C=N additions.⁸³ They can be catalysed by homogeneous metal complexes such as Ln/BINOL,¹¹⁴ Ag/BIAR,¹¹⁵ Cu/OXAZ,¹¹⁶ and also by small chiral molecules, *e.g.* organocatalysts.¹¹⁷ The possible drawbacks of homogeneous complexes are clear at this stage, so we will focus further on a strategy that uses organocatalytic pendant molecules within the HMOF cavity.

In the first part of this review we discussed the chiral [Zn₄O(bdc-Pro)_{1/2}(bpdc)_{1/2}(hmtt)_{4/3}] framework with covalently attached prolanyl (Fig. 3).⁶⁴ This HMOF is able to catalyse the aldol reaction between acetone and 4-nitrobenzaldehyde with a –4% ee.⁶⁴ An improvement up to –25% ee can be obtained by replacing the H₂bpdc ditopic linker with other ditopic coordinating linkers. This is called a modulating effect since variations in the HMOF cavity influence the enantiomeric excess of the aldol reaction. Moreover, certain alkyl modulators on the tritopic linkers even create an enantiomeric bias on the aldol product. Another important effect demonstrated in this work is the stereochemical reversal in an asymmetric aldol reaction upon heterogenisation of a homogeneous catalyst: Me₂bdc-Pro catalyst gives the *R* enantiomer with 8% ee, while [Zn₄O(bdc-Pro)_{1/2}(bpdc)_{1/2}(hmtt)_{4/3}] favors the formation of the *S* enantiomer (–4% ee).⁶⁴ The crystallinity and morphology of the catalyst as a function of the reaction conditions (20% water) were analysed by powder X-ray diffraction studies and optical microscopy.⁶⁴ The mechanism is proposed to be similar to the homogeneous catalysts,⁶⁴ but the confinement effect and the possible non-covalent interactions between the pore wall and reaction intermediates need further studies.

Conclusions

The extensive research in designing and testing HMOFs for asymmetric catalysis is sustained by the highly tunable nature

of these materials. Currently, the main focus is on the fundamental understanding of the reaction mechanisms and unravelling the optimum catalyst form and/or reaction parameters. Accomplishing systematic and accessible chiral catalytic centers in porous solids is the main challenge when designing a HMOF for catalysis. This requires appropriate choice of chiral organic linkers and metal salts that assemble periodically while maintaining appropriate pore channels. The accessibility of the active sites, which is dependent on the shape and size of the channels in the HMOFs, is decisive for the activity and selectivity of the catalyst. A vast majority of the catalytic studies using HMOFs indicates that pores of nanometre size are favourable to access the catalytic sites and achieve strong interactions between the substrates and the chiral environment of the voids. Different synthetic strategies toward HMOFs have been successful up to now. Synthesis of HMOFs *via* the rational design of chiral linkers is a suitable approach for studying the performance of the catalytic system as it allows fine tuning of the environment, and of the active site. It is only limited to the synthetic abilities of chemists. Other reasonable possibility is the embedding of specific moieties in the framework by post-synthetic modifications. The most successful approaches so far include the incorporation of molecular catalysts such as homogeneous catalysts and organocatalytic moieties within the MOF pores. A simple incorporation of a salen catalyst within a MOF structure has proven to provide valuable information on how immobilisation can improve its stability. It is noteworthy to mention that biocatalysts are also employed in the production of chiral molecules,^{3,118,119} with difficulties and advantages much like chemocatalysts.¹⁰¹ Synthesis of biomimetic HMOFs has indeed started to develop over the past few years.^{120–123}

The benefit of using HMOFs for asymmetric catalysis is due to a combination of single-site catalysis and facile recycle and reuse, with no metal contamination at the end of the reaction. Although several HMOFs have been proven to catalyze various asymmetric organic reactions, the challenge remaining is not only to design efficient catalysts but also catalysts for a broad scope of catalytic applications. Considering the performance of asymmetric catalysts used currently in industry, it is highly unlikely that HMOFs will be implemented in the immediate future. Currently, it is of utmost importance to focus on the synthesis and application of these materials towards a fundamental understanding of the framework stability and its interactions with various substrates during the catalytic reaction. More studies, both experimental and theoretical, are needed to understand the diffusion of the reactants through the MOF pores. Understanding the transfer of reactants and products to and from the active sites is an important aspect in porous catalysts, especially because surface catalysis can occur as well. Importantly, in depth mechanistic studies have not been reported so far, although they are the key to understanding the interactions between various substrates and MOF pores, as these interactions play an important role in the stability of different intermediates.

In conclusion, HMOF synthesis and their catalytic applications are mainly driven by the synthetic facility of MOFs and

less on the necessity for a particular framework. Most of the examples reported are proofs-of-concept and not necessarily focused on understanding the catalytic processes that already exist and have specific drawbacks.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is funded by the Netherlands Organisation for Scientific Research (NWO) through a TOP-Punt grant and it is part of the Research Priority Area Sustainable Chemistry of the University of Amsterdam, <http://suschem.uva.nl>.

Notes and references

- 1 L. A. Nguyen, H. He and C. Pham-Huy, *Int. J. Biomed. Sci. IJBS*, 2006, **2**, 85–100.
- 2 R. A. Sheldon, *Chirotechnology: Industrial Synthesis of Optically Active Compounds*, CRC Press, 1993.
- 3 A. J. J. Straathof, S. Panke and A. Schmid, *Curr. Opin. Biotechnol.*, 2002, **13**, 548–556.
- 4 H.-J. Federsel, *Nat. Rev. Drug Discovery*, 2005, **4**, 685–697.
- 5 F.-Z. Li, S. Li, P.-P. Zhang, Z.-H. Huang, W.-B. Zhang, J. Gong and Z. Yang, *Chem. Commun.*, 2016, **52**, 12426–12429.
- 6 T. Vries, H. Wynberg, E. van Echten, J. Koek, W. ten Hoeve, R. M. Kellogg, Q. B. Broxterman, A. Minnaard, B. Kaptein, S. van der Sluis, *et al.*, *Angew. Chem., Int. Ed.*, 1998, **37**, 2349–2354.
- 7 R. A. Sheldon, *Drug Inf. J.*, 1990, **24**, 129–139.
- 8 Z. G. Brill, M. L. Condakes, C. P. Ting and T. J. Maimone, *Chem. Rev.*, 2017, **117**, 11753–11795.
- 9 L. K. Thalén and J.-E. Bäckvall, *Beilstein J. Org. Chem.*, 2010, **6**, 823–829.
- 10 O. Verho and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 2015, **137**, 3996–4009.
- 11 P. O. Lagaditis, P. E. Sues, J. F. Sonnenberg, K. Y. Wan, A. J. Lough and R. H. Morris, *J. Am. Chem. Soc.*, 2014, **136**, 1367–1380.
- 12 S. Akutagawa, *Top. Catal.*, 1997, **4**, 271–274.
- 13 N. Nandi, *Chirality in Biological Nanospaces: Reactions in Active Sites*, CRC Press, 2011.
- 14 H.-U. Blaser, *Chem. Commun.*, 2003, 293–296.
- 15 J. H. Jones, *Platinum Met. Rev.*, 2000, **44**, 94–105.
- 16 H. U. Blaser, F. Spindler and M. Studer, *Appl. Catal., A*, 2001, **221**, 119–143.
- 17 H.-U. Blaser, *Rend. Lincei*, 2007, **18**, 281–304.
- 18 A. R. Silva, *Curr. Org. Chem.*, 2014, **18**, 1226–1241.
- 19 B. Cornils, W. A. Herrmann, M. Beller and R. Paciello, *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Four Volumes*, John Wiley & Sons, 2018.
- 20 X. Li, N. Dummer, R. Jenkins, R. P. K. Wells, P. B. Wells, D. J. Willock, S. H. Taylor, P. Johnston and G. J. Hutchings, *Catal. Lett.*, 2004, **96**, 147–151.
- 21 K. Ito, T. Harada and A. Tai, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3367–3368.
- 22 D. Ager, *Handbook of Chiral Chemicals*, CRC Press, 2nd edn, 2005.
- 23 M. Heitbaum, F. Glorius and I. Escher, *Angew. Chem., Int. Ed.*, 2006, **45**, 4732–4762.
- 24 D. W. C. MacMillan, *Nature*, 2008, **455**, 304–308.
- 25 O. Mahé, J.-F. Brière and I. Dez, *Eur. J. Org. Chem.*, 2015, 2559–2578.
- 26 C. Nájera, J. M. Sansano and M. Yus, *J. Braz. Chem. Soc.*, 2010, **21**, 377–412.
- 27 F. Song, C. Wang, J. M. Falkowski, L. Ma and W. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 15390–15398.
- 28 T. Bogaerts, A. van Yperen-De Deyne, Y.-Y. Liu, F. Lynen, V. V. Speybroeck and P. V. D. Voort, *Chem. Commun.*, 2013, **49**, 8021–8023.
- 29 S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, *Chem. Commun.*, 2006, 2563–2565.
- 30 F. Song, T. Zhang, C. Wang and W. Lin, *Proc. Math. Phys. Eng. Sci.*, 2012, **468**, 2035–2052.
- 31 J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982–986.
- 32 F. Song, C. Wang and W. Lin, *Chem. Commun.*, 2011, **47**, 8256–8258.
- 33 J. M. Falkowski, S. Liu, C. Wang and W. Lin, *Chem. Commun.*, 2012, **48**, 6508–6510.
- 34 *Metal Organic Frameworks as Heterogeneous Catalysts*, ed. F. Llabres i Xamena and J. Gascon, The Royal Society of Chemistry, 2013.
- 35 A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606–4655.
- 36 D. Farrusseng, S. Aguado and C. Pinel, *Angew. Chem., Int. Ed.*, 2009, **48**, 7502–7513.
- 37 J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011–6061.
- 38 S. Ou and C.-D. Wu, *Inorg. Chem. Front.*, 2014, **1**, 721–734.
- 39 L. Zhu, X.-Q. Liu, H.-L. Jiang and L.-B. Sun, *Chem. Rev.*, 2017, **117**, 8129–8176.
- 40 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276–279.
- 41 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.
- 42 J.-H. Zhang, R.-Y. Nong, S.-M. Xie, B.-J. Wang, P. Ai and L.-M. Yuan, *Electrophoresis*, 2017, **38**, 2513–2520.
- 43 C. Kutzscher, P. Müller, S. Raschke and S. Kaskel, in *Chem. Met. Framew.*, ed. S. Kaskel, Wiley-VCH Verlag GmbH & Co. KGaA, 2016, pp. 387–419.
- 44 R. A. Smaldone, R. S. Forgan, H. Furukawa, J. J. Gassensmith, A. M. Z. Slawin, O. M. Yaghi and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2010, **49**, 8630–8634.

- 45 R. S. Forgan, R. A. Smaldone, J. J. Gassensmith, H. Furukawa, D. B. Cordes, Q. Li, C. E. Wilmer, Y. Y. Botros, R. Q. Snurr, A. M. Z. Slawin, *et al.*, *J. Am. Chem. Soc.*, 2012, **134**, 406–417.
- 46 B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath and W. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 72–75.
- 47 K. Tanaka, S. Oda and M. Shiro, *Chem. Commun.*, 2008, 820–822.
- 48 M. Zheng, Y. Liu, C. Wang, S. Liu and W. Lin, *Chem. Sci.*, 2012, **3**, 2623–2627.
- 49 C. Abney, J. M. Falkowski, L. Ma and W. Lin, *Nat. Chem.*, 2010, **2**, 838.
- 50 C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158–5168.
- 51 D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2004, **126**, 6106–6114.
- 52 S. J. Garibay, Z. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, 2009, **48**, 7341–7349.
- 53 M. Banerjee, S. Das, M. Yoon, H. J. Choi, M. H. Hyun, S. M. Park, G. Seo and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 7524–7525.
- 54 C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940–8941.
- 55 A. D. Burrows, *CrystEngComm*, 2011, **13**, 3623–3642.
- 56 S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970–1000.
- 57 Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315–1329.
- 58 K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498–519.
- 59 S. M. Cohen, *Chem. Sci.*, 2010, **1**, 32–36.
- 60 J. Bonnefoy, A. Legrand, E. A. Quadrelli, J. Canivet and D. Farrusseng, *J. Am. Chem. Soc.*, 2015, **137**, 9409–9416.
- 61 C. Kutzscher, H. C. Hoffmann, S. Krause, U. Stoeck, I. Senkovska, E. Brunner and S. Kaskel, *Inorg. Chem.*, 2015, **54**, 1003–1009.
- 62 S. Barman, A. Remhof, R. Koitz, M. Iannuzzi, O. Blacque, Y. Yan, T. Fox, J. Hutter, A. Züttel and H. Berke, *Chem. – Eur. J.*, 2017, **23**, 8823–8828.
- 63 S. J. Lee, C. Doussot, A. Baux, L. Liu, G. B. Jameson, C. Richardson, J. J. Pak, F. Trouselet, F.-X. Coudert and S. G. Telfer, *Chem. Mater.*, 2016, **28**, 368–375.
- 64 L. Liu, T.-Y. Zhou and S. G. Telfer, *J. Am. Chem. Soc.*, 2017, **139**, 13936–13943.
- 65 D. J. Lun, G. I. N. Waterhouse and S. G. Telfer, *J. Am. Chem. Soc.*, 2011, **133**, 5806–5809.
- 66 R. E. Morris and X. Bu, *Nat. Chem.*, 2010, **2**, 353–361.
- 67 J. Zhang, S. Chen, T. Wu, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2008, **130**, 12882–12883.
- 68 K. K. Bisht and E. Suresh, *J. Am. Chem. Soc.*, 2013, **135**, 15690–15693.
- 69 Z.-X. Xu, Y.-L. Ma and J. Zhang, *Chem. Commun.*, 2016, **52**, 1923–1925.
- 70 S.-Y. Zhang, D. Li, D. Guo, H. Zhang, W. Shi, P. Cheng, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2015, **137**, 15406–15409.
- 71 J. Zhang, S. Chen, R. A. Nieto, T. Wu, P. Feng and X. Bu, *Angew. Chem., Int. Ed.*, 2010, **49**, 1267–1270.
- 72 J. D. Evans and F.-X. Coudert, *J. Am. Chem. Soc.*, 2016, **138**, 6131–6134.
- 73 Z. Lin, A. M. Z. Slawin and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880–4881.
- 74 Q.-Y. Liu, W.-L. Xiong, C.-M. Liu, Y.-L. Wang, J.-J. Wei, Z.-J. Xiahou and L.-H. Xiong, *Inorg. Chem.*, 2013, **52**, 6773–6775.
- 75 T. P. Vaid, S. P. Kelley and R. D. Rogers, *IUCrJ*, 2017, **4**, 380–392.
- 76 M. Breuer, K. Ditrich, T. Habicher, B. Hauer, M. Kessler, R. Stürmer and T. Zelinski, *Angew. Chem., Int. Ed.*, 2004, **43**, 788–824.
- 77 P. J. Reider, *Chim. Int. J. Chem.*, 1997, **51**, 306–308.
- 78 J. T. Mohr, M. R. Krout and B. M. Stoltz, *Nature*, 2008, **455**, 323–332.
- 79 M. J. Burk, F. Bienewald, M. Harris and A. Zanotti-Gerosa, *Angew. Chem., Int. Ed.*, 1998, **37**, 1931–1933.
- 80 H. Kumobayashi, *Recl. Trav. Chim. Pays-Bas*, 1996, **115**, 201–210.
- 81 N. B. Johnson, I. C. Lennon, P. H. Moran and J. A. Ramsden, *Acc. Chem. Res.*, 2007, **40**, 1291–1299.
- 82 C. J. Cobley, E. Foucher, J.-P. Lecouvé, I. C. Lennon, J. A. Ramsden and G. Thomlinot, *Tetrahedron: Asymmetry*, 2003, **14**, 3431–3433.
- 83 H.-U. Blaser, B. Pugin and F. Spindler, *J. Mol. Catal. A: Chem.*, 2005, **231**, 1–20.
- 84 T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc.*, 1980, **102**, 5974–5976.
- 85 G. P. Chiusoli and P. M. Maitlis, *Metal-Catalysis in Industrial Organic Processes*, Royal Society of Chemistry, 2008.
- 86 K. Hoi-Lun, C. Sorato, Y. Ogino, C. Hou and K. Barry Sharpless, *Tetrahedron Lett.*, 1990, **31**, 2999–3002.
- 87 J. M. Falkowski, T. Sawano, T. Zhang, G. Tsun, Y. Chen, J. V. Lockard and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 5213–5216.
- 88 D. Dang, P. Wu, C. He, Z. Xie and C. Duan, *J. Am. Chem. Soc.*, 2010, **132**, 14321–14323.
- 89 M. Wang, M.-H. Xie, C.-D. Wu and Y.-G. Wang, *Chem. Commun.*, 2009, 2396–2398.
- 90 H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, *et al.*, *Science*, 2012, **336**, 1018–1023.
- 91 H. Takaya, T. Ohta, N. Sayo, H. Kumobayashi, S. Akutagawa, S. Inoue, I. Kasahara and R. Noyori, *J. Am. Chem. Soc.*, 1987, **109**, 1596–1597.
- 92 B. D. Vineyard, W. S. Knowles and M. J. Sabacky, *J. Mol. Catal.*, 1983, **19**, 159–169.
- 93 S. Bell, B. Wüstenberg, S. Kaiser, F. Menges, T. Netscher and A. Pfalz, *Science*, 2006, **311**, 642–644.
- 94 A. Hu, H. L. Ngo and W. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 11490–11491.
- 95 A. Hu, H. L. Ngo and W. Lin, *Angew. Chem.*, 2003, **115**, 6182–6185.

- 96 B. Vilhanová, M. Ranocchiari and J. A. van Bokhoven, *ChemCatChem*, 2016, **8**, 308–312.
- 97 L. Ahrgren and L. Sutin, *Org. Process Res. Dev.*, 1997, **1**, 425–427.
- 98 M. Seenivasaperumal, H.-J. Federsel and K. J. Szabó, *Adv. Synth. Amp Catal.*, 2009, **351**, 903–919.
- 99 N. S. Barta, D. R. Sidler, K. B. Somerville, S. A. Weissman, R. D. Larsen and P. J. Reider, *Org. Lett.*, 2000, **2**, 2821–2824.
- 100 A. Rioz-Martínez, G. de Gonzalo, D. E. T. Pazmiño, M. W. Fraaije and V. Gotor, *Eur. J. Org. Chem.*, 2010, 6409–6416.
- 101 H. U. Blaser and E. Schmidt, *Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions*, John Wiley & Sons, 2007.
- 102 W. Zhang, J. L. Loebach, S. R. Wilson and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1990, **112**, 2801–2803.
- 103 D. L. Hughes, G. B. Smith, J. Liu, G. C. Dezeny, C. H. Senanayake, R. D. Larsen, T. R. Verhoeven and P. J. Reider, *J. Org. Chem.*, 1997, **62**, 2222–2229.
- 104 C. A. Busacca, D. R. Fandrick, J. J. Song and C. H. Senanayake, *Adv. Synth. Catal.*, 2011, **353**, 1825–1864.
- 105 G. A. E. Oxford, D. Dubbeldam, L. J. Broadbelt and R. Q. Snurr, *J. Mol. Catal. A: Chem.*, 2011, **334**, 89–97.
- 106 J.-E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010.
- 107 Q. Han, C. He, M. Zhao, B. Qi, J. Niu and C. Duan, *J. Am. Chem. Soc.*, 2013, **135**, 10186–10189.
- 108 Z. Yang, C. Zhu, Z. Li, Y. Liu, G. Liu and Y. Cui, *Chem. Commun.*, 2014, **50**, 8775–8778.
- 109 C. Zhu, X. Chen, Z. Yang, X. Du, Y. Liu and Y. Cui, *Chem. Commun.*, 2013, **49**, 7120–7122.
- 110 W. Xuan, C. Ye, M. Zhang, Z. Chen and Y. Cui, *Chem. Sci.*, 2013, **4**, 3154–3159.
- 111 K. Tanaka, K. Kubo, K. Iida, K. Otani, T. Murase, D. Yanamoto and M. Shiro, *Asian J. Org. Chem.*, 2013, **2**, 1055–1060.
- 112 A. J. DelMonte, E. D. Dowdy and D. J. Watson, in *Organomet. Process Chem*, Springer, Berlin, Heidelberg, 2004, pp. 97–122.
- 113 J. M. Falkowski, C. Wang, S. Liu and W. Lin, *Angew. Chem.*, 2011, **123**, 8833–8837.
- 114 M. Shibasaki and N. Yoshikawa, *Chem. Rev.*, 2002, **102**, 2187–2210.
- 115 T. F. Knöpfel, P. Aschwanden, T. Ichikawa, T. Watanabe and E. M. Carreira, *Angew. Chem.*, 2004, **116**, 6097–6099.
- 116 J. S. Johnson and D. A. Evans, *Acc. Chem. Res.*, 2000, **33**, 325–335.
- 117 B. List, R. A. Lerner and C. F. Barbas, *J. Am. Chem. Soc.*, 2000, **122**, 2395–2396.
- 118 K. M. Koeller and C.-H. Wong, *Enzymes for chemical synthesis*, 2001, DOI: 10.1038/35051706 can be found at <https://www.nature.com/articles/35051706>.
- 119 P. K. Robinson, *Essays Biochem.*, 2015, **59**, 1–41.
- 120 I. Nath, J. Chakraborty and F. Verpoort, *Chem. Soc. Rev.*, 2016, **45**, 4127–4170.
- 121 Y. Chen and S. Ma, *Dalton Trans.*, 2016, **45**, 9744–9753.
- 122 M. Zhao, S. Ou and C.-D. Wu, *Acc. Chem. Res.*, 2014, **47**, 1199–1207.
- 123 Z.-Y. Gu, J. Park, A. Raiff, Z. Wei and H.-C. Zhou, *ChemCatChem*, 2014, **6**, 67–75.