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Self-supported chiral catalysts for heterogeneous enantioselective reactions*

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Abstract: The development of a new strategy to immobilize the homogeneous chiral catalysts for enantioselective reactions is highly desirable in order to overcome some drawbacks of conventional approaches. In this lecture, a conceptually new strategy for heterogenization of homogeneous chiral catalysts (i.e., "self-supporting" approach) is presented. The concept focuses on the use of homochiral metal-organic coordination polymers generated by self-assembly of chiral multitopic ligands with metal ions as the heterogeneous catalysts, and thus obviating the need of any exogenous support. The application of this "self-supporting" strategy has been exemplified in heterogeneous catalysis of asymmetric carbonyl-ene, sulfoxidation, and epoxidation, as well as asymmetric hydrogenation reactions.

Keywords: asymmetric catalysis; immobilization; enantioselective; heterogeneous; self-supporting.

INTRODUCTION

Asymmetric catalysis of organic reactions to provide enantiomerically enriched products is of central importance to modern synthetic and pharmaceutical chemistry [1]. Although homogeneous asymmetric catalysis has the advantages of high enantioselectivity and catalytic activity in various asymmetric transformations under mild reaction conditions, the high catalyst loadings (usually 1-10 mol %) and the difficulties associated with the recovery and reuse of expensive chiral catalysts severely hampered their practical applications. In addition, the metal contaminants sometimes may leach from the homogeneous catalysts into the products, which is particularly unacceptable for pharmaceutical production. As one of the most promising solutions to these problems, immobilization of homogeneous chiral catalysts for asymmetric catalysis has attracted a great deal of interest recently [2]. Various approaches have been developed for this purpose, including the use of inorganic materials, organic polymers, dendrimers, or membranes as supports, as well as performing reactions in ionic liquid and other biphasic systems [3]. In the conventional immobilization of homogeneous catalysts with organic polymers [4], the chiral ligands or the catalytically active units are usually anchored randomly onto irregular polymers (mode 1, Scheme 1), or incorporated into the main chain of the polymers (mode 2, Scheme 1). Whereas these strategies have yielded impressive successes [5], the polymeric ligands must be prepared before the active metallic species are uploaded, and their syntheses are usually nontrivial. In the present article, we present a new strategy, i.e., a "self-supporting" approach [6], for the immobilization of homogeneous catalysts through assembly of chiral multitopic ligands and metal ions without the use of any support (Scheme 2).

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Mode 1. Pendent ligands by anchoring on a polymer -- by polymer reaction



Mode 2. Ligand on the backbone -- by copolymerization



Scheme 2

Scheme 1

While numerous coordination polymers have been developed over the past two decades [7], only sporadic successful applications in the catalytic transformations can be found in the literature [7b,8], even fewer for catalytic enantioselective reactions [9]. An inherent reason for this limitation might be attributed to the fact that most coordination polymers prepared thus far have the coordinatively saturated metal centers, which precludes their involvement in catalytic transformation [7b]. In order to overcome this difficulty, one has to design the coordination polymers with catalytically active sites. As shown in Scheme 2, the metal centers in the homochiral metal-organic assembly play the dual roles as both the structural binders and the catalytically active centers, it is essential that they should be capable of simultaneously bonding with at least two ligand moieties (same or different), and still having vacant or labile sites available for substrate and/or reagent coordination polymers can be expected by judicious choice of the bridged chiral ligand and metal species [6]. The applications of this strategy will be exemplified in heterogeneous asymmetric carbonyl-ene, sulfoxidation, and epoxidation, as well as asymmetric hydrogenation reactions.

RESULTS AND DISCUSSION

Self-supported heterogeneous titanium catalysts for enantioselective carbonyl-ene and sulfoxidation reactions

Titanium complexes of 1,1'-bi-2-naphthol (BINOL) represents one of the most important types of chiral Lewis acids with widespread applications in asymmetric catalysis [10]. Sasai [11a] and our group [11b,12] independently reported the heterogenization of chiral titanium catalysts by in situ assembly of bridged multitopic BINOL ligands with Ti(O*i*Pr)₄ (Scheme 3), and the assembled heterogeneous catalysts were found to show excellent enantioselectivity (up to 98 % ee) in carbonyl-ene reaction of α -methylstyrene with ethyl glyoxylate. Consistent with the activities exhibited by the discrete Ti-Binolate catalysts for the same reaction under the homogeneous conditions, the ratio of the BINOL units to $Ti(OiPr)_4$ employed in the preparation of the coordination polymers was found to be critical for their catalytic activity [11a,b,12]. The heterogeneous catalyst **2c** obtained by employing a 2:1 molar ratio of BINOL units to $Ti(OiPr)_4$ is obviously more active and enantioselective than the catalyst **3c** prepared with a 1:1 molar ratio of BINOL units to $Ti(OiPr)_4$. The spacers between two BINOL units of the ligands in the assembled catalysts showed significant impact on the catalytic activity and enantioselectivity of the carbonyl-ene reaction. This fact suggests that a minor change of the linker moieties in the ligands may alter the supramolecular structures of the assemblies. The introduction of electron-withdrawing substituents to the backbone of BINOL, such as ligand **1d**, resulted in the improvement of the catalytic activity due to the increase of Lewis acidity of Ti(IV) complexes, affording the product in very high yield (99 %) with excellent enantioselectivity (98 % ee) [12]. It was found that catalyst **2d** could be used for five cycles in the carbonyl-ene reaction with gradually deteriorated activity (from 87 to 70 % yield) and enantioselectivity (from 97 to 70 % ee), presumably caused by the partial decomposition of the assemblies during the catalysis [12].



Scheme 3

The heterogenized Kagan–Uemura-type [13] catalysts **4a–c** for asymmetric sulfoxidation of sulfides were prepared in a similar manner, i.e., by the reaction of bridged BINOL ligands **1a–c** with Ti(*Oi*Pr)₄ (1:1 molar ratio) followed by addition of H₂O (40 equiv relative to ligand). Catalysts **4a–c** were found to be completely insoluble in CCl₄ [12]. The heterogeneous enantioselective oxidation of a variety of aryl alkyl sulfides was then investigated using catalysts **4a–c** with CMHP as the oxidant. The oxidation of both para- or meta-substituted phenyl methyl sulfides **8a–e** afforded chiral sulfoxides **9a–e** with very high enantioselectivities (from 75 to >99 % ee) in moderate yields (ca. 40 %). The heterogeneous nature of the above catalyst systems was confirmed by the inductively coupled plasma (ICP) spectroscopic analyses of the liquid phase after filtration of the insoluble catalysts, indicating that no detectable Ti (<0.1 ppm) was leached into organic solution. The facile recovery and remarkable stability of this type of heterogeneous catalysts was exemplified by the sulfoxidation of thioanisole (**8a**) using catalyst **4a**, which has been reused for eight cycles that covered a period of more than one month without any loss of enantioselectivity (99.0–>99.9 % ee) or obvious deterioration of activity (38–33 % yield).

Heterogenization of Shibasaki's BINOL/La(III) catalyst for enantioselective epoxidation of α , β -unsaturated ketones

As shown in Scheme 4, four types of multitopic ligands (**10a–i**) containing different bridging linkers, including linear (**10a–d**), angular (**10e–g**), trigonal-planar (**10h**), and tetrahedral (**10i**) spacers, were designed to investigate the impact of spatial arrangement of chiral (*S*)-BINOL units, on the catalytic properties of their assemblies with lanthanum ion [14]. The heterogeneous catalysts (**11a–i**) were prepared by dropwise addition of a tetrahydrofuran (THF) solution of the corresponding multitopic ligand (**10a–i**) and triphenylphosphine oxide to a solution of La($OiPr_{13}$ under argon atmosphere. The application of the heterogenized catalysts **11a–i** in the epoxidation [15] of chalcone **12a** demonstrated that the influence of the spacer geometry on the enantioselectivity of the catalysis was dramatic (83–97 % ee). Given the modular nature of the multitopic ligands, it can be expected that both the reactivity and enantioselectivity may be fine-tuned by judicious choice of the spacer part of the ligands.



Scheme 4

Under the optimized reaction conditions, the enantioselective epoxidation of several α , β -unsaturated ketones **12a-h** was then performed in the presence of catalyst **11a** with CMHP as oxidant. The reactions proceeded efficiently to give corresponding epoxides in excellent yields (91–99 %) and high enantioselectivities (85–97 % ee). Moreover, catalyst **11a** could be recycled and reused for at least six cycles without significant loss of enantioselectivity (96–93 % ee) and activity (99–83 % yield). The lanthanum leaching in each run during the recycle of the catalyst was determined to be less than 0.4 ppm by ICP. The heterogeneous nature of the above catalyst system was further confirmed by the fact that the supernatant of **11a** in THF did not exhibit any catalytic activity for the epoxidation under the same experimental conditions.

Self-supported MonoPhos/Rh(I) catalysts for enantioselective hydrogenations

It is widely accepted that in Rh-catalyzed enantioselective hydrogenation of olefin derivatives using monodentate phosphorus ligands, the catalytically active species has a composition of 2:1 molar ratio of monodentate ligands to Rh(I) metallic ion [16]. Based on this mechanistic consideration, the homochiral metal-ligand coordination polymers could be conveniently constructed by the reaction of the corresponding multitopic phosphorus ligands with Rh(I) precursor. The reaction of linker-bridged Feringa's MonoPhos ligands (14a–c) with the catalyst precursor [Rh(cod)]BF₄ in dichloromethane/toluene mixed solvent resulted in the immediate formation of orange solids which

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were insoluble in toluene [17]. These self-supported Rh(I) catalysts (15a-c) were subsequently applied in the asymmetric hydrogenation of some representative substrates, including β -aryl or alkyl substituted dehydro- α -amino acid (16a-c) and enamide (16d) derivatives, affording a variety of amino acid (17a-c) and secondary amine (17d) derivatives with high yields and excellent enantioselectivities (Scheme 5), which are comparable to the cases of homogeneous catalysis at the same level of catalyst loading. Particularly, the self-supported catalysts demonstrated remarkably improved enantioselectivity (95-97 % ee) in the hydrogenation of enamide derivative in comparison with the cases using MonoPhos/Rh homogeneous catalyst (88 % ee). The heterogeneous nature of the catalysis was also confirmed by the inactivity of the supernatants of these self-supported catalysts for the hydrogenation. The ICP spectroscopic analysis indicated that no detectable rhodium was leached into the solution phase and the concentration of phosphor in solution was less than 3 ppm for each round of hydrogenation, which further confirmed the heterogeneous nature of the present catalytic systems. The catalysts could be readily recycled and reused for at least seven runs without significant loss of activity and enantioselectivity (95–89 % ee) [17]. Very recently, Wong and coworkers also designed a nice ditopic chiral "linear" monodentate phosphoramidite ligand bearing a biphenylene backbone for generation of self-assembled oligomeric or polymeric Rh catalyst. The solid catalyst demonstrated excellent enantioselectivities (97–99 % ee) in the hydrogenation of a variety of dehydro- α -amino acid derivatives [18].





We further envisaged the use of chiral ligands possessing hydrogen-bonding (HB) donor-acceptor moieties for the construction of multitopic ligands through complementary or self-complementary HB recognition motifs. In combination with current self-supporting strategies, such ligand assemblies are expected to spontaneously form immobilized catalytic systems in the presence of catalytically active metal species. Accordingly, ureido-4[1H]-ureidopyrimidone (UP), a commonly used HB self-complementary unit [19], and MonoPhos [16b] were integrated into one molecule (18) which, in principle, can form ditopic ligand through self-complementary HB interaction in a suitable solvent (Scheme 6) [20]. Based on the "orthogonal" nature of noncovalent interactions (HB and metal-to-ligand coordination), $[Rh(cod)_2]BF_4$ salt was then reacted with 18 in CH₂Cl₂ solution, resulting in the immediate precipitation of a yellow solid 19 in quantitative yield. This supramolecular metal-organic polymer is insoluble in less polar organic solvents such as toluene, thus providing an excellent opportunity for conducting heterogeneous asymmetric reactions. As shown in Scheme 6, asymmetric hydrogenation of dehydro- α -amino acid derivatives (16a-b, 16e-f) and the enamide (16d) catalyzed by 19 proceeded smoothly with complete conversion within a standard 20 h. The products (17a-b, 17e-f) were obtained in excellent enantiomeric excesses (91–96 %) (ee) [20]. The reusability of the present catalyst system was exemplified in the hydrogenation of 16b. The hydrogenation proceeds with near quantitative con-



Scheme 6

version and almost constant enantioselectivity (96–92 % ee) for at least 10 cycles. However, the catalyst reactivity declined with consecutive hydrogenations as shown by the lower turnover frequency (TOF) value for each run. Preliminary studies suggest that the absence of a hydrogen atmosphere during product/catalyst separation results in partial catalyst decomposition.

The heterogeneous nature of the catalyst was confirmed by the fact that the supernatant of **19** does not result in further hydrogenation of **16b** under otherwise identical experimental conditions. Furthermore, ICP spectroscopic analyses of both filtrated organic solution and isolated product (**17b**) could not detect any metal leaching within the detection limit of the instrument (1 ppm).

Programmed assembly of two different ligands with metallic ions: Self-supported Noyori-type catalysts for heterogeneous asymmetric hydrogenation of ketones

As mentioned above, the heterogenization of the chiral catalysts using self-supporting strategy by homo-combination of multitopic chiral ligands with metallic ions is straightforward. On the other hand, the assembly of polymeric or oligomeric homochiral catalyst by hetero-combination of two different multitopic chiral ligands (L_1 and L_2) with metal ions (M) is a very challenging task, since a complex multispecies system (e.g., ML_1L_1 , ML_2L_2 , ML_1L_2 , etc.) would be easily envisioned when the three reacting components were mixed together. Thus, specific formation of a hetero-ligand combination complex (ML_1L_2) would require that the structural and coordination information stored in the ligands and metallic ion, respectively, to be sufficiently strong to dictate their coordinating organization and thus direct the assembly process in a programmed way. In this respect, the iteratively occurring structural feature of Noyori's catalyst [21], [RuCl₂{(*R*)-BINAP}{(*R*,*R*)-DPEN}] (BINAP: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; DPEN: 1,2-diphenylethylenediamine), can provide an excellent opportunity for generation of self-supported catalysts by the programmed assembly [22] of ML_1L_2 type of coordination polymers.

As shown in Scheme 7, both bridged BINAP 20 and diamine 21 were designed to possess a 1,4-phenylene or a 1,4-phenylene-bis-methoxy linkers, which were assembled at 6-position of the corresponding 1,1'-binaphthyl backbone or at 4'-position of (*S*,*S*)-DPEN derivative, respectively, in order to avoid the intramolecular interaction of two chiral units. The self-supported catalysts (22a-b) were prepared by reacting bridged BINAP ligands (20a-b) with $[(C_6H_6)RuCl_2]_2$ in DMF at 100 °C, followed by the treatment of the resulting reddish brown solution with 1 equiv of bridged DPEN 21 at room temperature. The application of the self-supported catalysts 22 in the catalysis of the asymmetric hydrogenation of acetophenone (23a) indicated that catalyst 22b was highly efficient and enantioselective, affording 1-phenylethanol in quantitative yield with 97.4 % ee, which is slightly higher than those



Scheme 7

obtained with its homogeneous counterparts (95.5–96.4 %) [22]. Moreover, the catalyst loading for **22b** can be further reduced to 0.01 mol % without significant deterioration of the yield or enantioselectivity. The TOF under this circumstance is calculated to be ~500 h⁻¹, illustrating the high activity of the assembled solid catalyst. The supernatant of catalyst **22b** in 2-propanol did not show any catalytic activity in the hydrogenation of acetophenone, indicating the heterogeneous nature of catalysis. Furthermore, the catalysis with **22b** was extended to the hydrogenation of a series of aromatic ketones (**23a–h**), affording the corresponding secondary alcohols (**24a–h**) with excellent enantioselectivities (94–97 % ee). The self-supported catalyst **22b** could be reused for seven cycles of hydrogenation without obvious loss of enantioselectivities and catalytic activities [22].

This approach has been also extended to the generation of self-supported Noyori-type catalysts **25** through hetero-coordination of *achiral* bridged diphosphine and chiral bridged diamine ligands with Ru(II) metallic ions (Scheme 8) [23]. The immobilized catalyst demonstrates good enantioselectivity (up to 87 % ee) and activity in the heterogeneous catalysis of the hydrogenation of aromatic ketones and could be recycled four times without obvious loss of selectivity and activity.

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Scheme 8

CONCLUSION AND OUTLOOK

In summary, a conceptually new strategy (i.e., "self-supporting" approach) has been developed for the immobilization of homogeneous catalysts through self-assembly of chiral multitopic ligands and metal ions without the use of any support. The application of this strategy has been exemplified in heterogeneous catalysis of asymmetric carbonyl-ene, sulfoxidation, and epoxidation, as well as in asymmetric hydrogenation reactions. In addition to the simple recovery and convenient recycle commonly associated with heterogeneous catalysts, such kinds of homochiral metal-organic coordination polymers may also exhibit advantages of facile preparation, robust chiral structures, and excellent enantioselectivities. These remarkable features coupled with the versatile methods for rational design and synthesis of the multitopic chiral ligand, suggest a considerable scope of application of this "self-supporting" strategy in the development of new, efficient, and practical catalysts for the heterogeneous asymmetric catalysis. We hope that the present strategy might provide an approach to bridging the gap between homogeneous and heterogeneous asymmetric catalysis.

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