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Mesoporous silica KIT-6 supported superparamagnetic CuFe₂O₄ nanoparticles for catalytic asymmetric hydrosilylation of ketones in air†

Min Li, Bin Li, Hong-Feng Xia, Danru Ye, Jing Wu* and Yifeng Shi*

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A diverse range of prochiral ketones were reduced in air with high yields and good-to-excellent enantioselectivities (up to 97% ee) in the presence of a heterogeneous catalyst system, which was *in situ* formed from catalytic amounts of superparamagnetic CuFe₂O₄ nanoparticles supported on mesoporous silica KIT-6 and non-racemic dipyridylphosphine ligand, the stoichiometric hydride donor polymethylhydrosiloxane (PMHS) as well as certain amounts of additives. The magnetically separable catalysts could be efficiently reused 4 times without apparent loss of both the activity and enantioselectivity.

Introduction

It is a significant objective in organic synthesis research to develop efficient methods for the production of enantiomerically enriched secondary alcohols, which constitute valuable intermediates for the preparation of structurally interesting and biologically active compounds.¹ The non-precious transition metal-catalyzed asymmetric hydrosilylation of prochiral ketones as a desirable approach, leading to a broad range of chiral alcohols, has attracted growing interest because of its mild reaction conditions, economic benefits, and operational simplicity.² Thus, a variety of efficient chiral transition metal catalysts, especially those based on titanium,³ zinc,⁴ tin,⁵ copper,^{6,7} iron,^{8,9} cobalt^{9,10} and nickel,¹¹ have been developed in the past two decades and applied in relevant hydrosilylation reactions with moderate to excellent enantioselectivities.

Previous studies on metal-catalyzed asymmetric hydrosilylations mainly focused on homogeneous catalysis, while industry favours the heterogeneous catalytic process due to its easy operation, simple workup, minimization of metal traces in the product, and regenerability.¹² In 2006, Lipshutz reported a copper-in-charcoal material as a catalyst precursor. When ligated by catalytic amounts of a non-racemic diphosphine ligand, the generated chiral heterogeneous catalyst allowed for the enantioselective hydrosilylation of a selection of functional groups to afford corresponding products in high yields and

with excellent ee values.¹³ In the presence of catalytic amounts of enantiomeric BINAP as the chiral ligand and the stoichiometric polymethylhydrosiloxane (PMHS) as the hydride source, Kantam and co-workers developed a series of heterogeneous catalyst precursors such as nanocrystalline copper(II) oxide and copper-aluminium hydrotalcite, which have been successfully applied in the asymmetric reduction of aryl alkyl ketones with good reaction activities and enantioselectivities.¹⁴ Nanosized particle catalysts can be separated from the reaction mixture by filtration or sedimentation.

Functionalized magnetic nanoparticles (MNPs) with good stability are of great interest for application in catalysis, especially in liquid phase catalytic reactions.¹⁵ Generally, compared to the homogeneous catalyst system, similar or even higher activity and selectivity can be achieved by employing MNP-based catalysts. Furthermore, the magnetic property makes the separation and recovery of catalysts in a liquid-phase reaction mixture much easier than those by centrifugation or cross flow filtration. CuFe₂O₄ nanoparticles have been demonstrated to possess high catalytic activities in several organic reactions such as coupling¹⁶ and asymmetric hydrosilylation of ketones.¹⁷ In 2009, Kantam *et al.* described CuFe₂O₄ nanoparticles obtainable by the coprecipitation method for the enantioselective hydrosilylation of several prochiral aryl alkyl ketones at room temperature using (*S*)-BINAP as the chiral ligand and PMHS as the stoichiometric reductant in good to excellent ee values. The copper ferrite nanoparticles could be magnetically recycled and reused two times without distinct decreases in ee values.¹⁷

Mesoporous supported nanoparticles are widely used in heterogeneous catalysis because nanosized particles with high exposure of active sites are featured for catalytic reactions, and

College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, P. R. China. E-mail: jingwubc@hznu.edu.cn, yfshi@hznu.edu.cn

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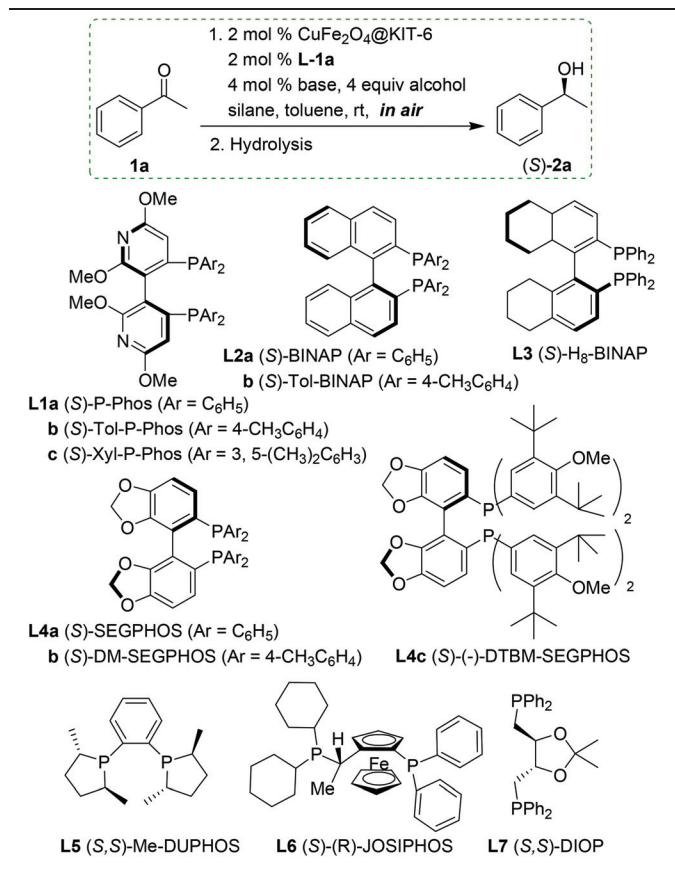
the bulk-sized supports are beneficial for the separation and recycling manipulation. In particular, the chiral microenvironments of active centers could be adjusted by both the tunable nanosized pore space and an additional nano confinement effect, which led to pronounced enhancements in enantioselectivities of some asymmetric reactions. Hence, considerable endeavor has been devoted to the development of novel and efficacious mesoporous supported nanoparticles for green asymmetric catalytic reactions.¹⁸

More recently, we successfully synthesized a magnetic catalytic material CuFe₂O₄@KIT-6, which was composed of homogeneously dispersed CuFe₂O₄ nanoparticles supported on a mesoporous silica KIT-6 matrix.¹⁹ Preliminary investigation on the catalytic performance of the obtained CuFe₂O₄@KIT-6 indicated that it was efficient for the enantioselective hydrosilylation of acetophenone to yield the desired alcohol product in 93% yield and 93% ee at room temperature under air atmosphere, which shows that it is much better than the homogeneous catalyst systems under identical conditions. Moreover, the copper ferrite nanoparticles could be magnetically recycled and reused, which indicated its good practical potential and prompted us to further broaden its application scope. Here, we adopted the synthesized CuFe₂O₄@KIT-6 material as a catalyst precursor for the asymmetric hydrosilylation of a wide range of prochiral ketones. The corresponding chiral secondary alcohols were produced in air with high yields and were of good to excellent optical purities. The CuFe₂O₄@KIT-6 catalyst could be recycled for reuse at least four times without losing both the activity and selectivity. XRD, TEM and nitrogen sorption analyses all confirmed that the mesostructure, crystal phase and porosity of the CuFe₂O₄@KIT-6 catalyst have been well preserved after the reaction.

Results and discussion

In the beginning, we investigated the ability of the chiral dipyrrolylphosphine ligand P-Phos (Table 1, **L1a**),²⁰ which was previously demonstrated to be highly efficient in the non-precious metal-catalyzed asymmetric hydrosilylation of a diverse assortment of prochiral ketones^{7f,10b,11,21} as well as conjugate reduction of β -dehydroamino acid derivatives,²² to promote the hydrosilylation of the model substrate acetophenone **1a**. As shown in entry 1 of Table 1, in the presence of 2 mol% of the catalyst precursor CuFe₂O₄@KIT-6, which was prepared according to the previously reported procedure,¹⁹ 2 mol% of **L1a** and 1.2 equivalents of the hydride donor PhSiH₃, the reaction in toluene was completed at room temperature in air after 14 h to afford (*S*)-**2a** in 84% ee. PMHS as a by-product of the organosilicon industry has been well known for its cost efficiency, non-toxicity and air stability. It is therefore a desirable hydride resource for economical, practical and environmentally benign reduction processes.²³ As illustrated in entry 2, in the case of PMHS as the stoichiometric reductant, only 42% conversion was obtained although the enantioselectivity remained almost

Table 1 Effects of silane and additives on the asymmetric hydrosilylation of acetophenone **1a**^a



| Entry | Silane | Equiv. | Alcohol | Base | Conv ^b [%] | ee ^c [%] |
|-------|--------------------|--------|----------------|-----------------|-----------------------|---------------------|
| 1 | PhSiH ₃ | 1.2 | — | — | 99 | 84 |
| 2 | PMHS | 4 | — | — | 42 | 82 |
| 3 | PMHS | 4 | <i>t</i> -BuOH | <i>t</i> -BuONa | >99 | 79 |

^a Reaction conditions: 0.30 mmol substrate, substrate concentration = 0.20 M in toluene. ^b The conversions were determined by NMR and GC analysis. ^c The ee values were determined by chiral GC analysis. The absolute configuration was determined by comparing the retention times with known data (see the ESI).

unchanged (entry 2 vs. entry 1). Similar to previous findings,²⁴ the introduction of certain amounts of *t*-BuONa and sterically encumbered alcohol *t*-BuOH to the catalyst system allowed for the complete transformation of **1a** to the desired alcohol in 79% ee (entry 3).

Next, a series of chiral ligands were examined in the reduction of acetophenone and the results indicated that ligands had a pronounced influence on the reaction activities and enantioselectivities (Table 2). Among the screened chiral diphosphine ligands, high conversions and moderate to good ee values were attained by utilizing (*S*)-Tol-P-Phos (**L1b**), (*S*)-BINAP (**L2a**), (*S*)-Tol-BINAP (**L2b**), (*S*)-SEGPHOS (**L4a**) or (*S*)-DM-SEGPHOS (**L4b**, entries 1, 3, 4, 6 and 7). However, (*S*)-H₈-BINAP (**L3**), (*S*)-DTBM-SEGPHOS (**L4c**), (*S,S*)-Me-Duphos (**L5**), (*S*)-(*R*)-Josiphos (**L6**) or (*S,S*)-DIOP (**L7**) exhibited either poor activities or low selectivities (entries 5 and 8–11). (*S*)-Xyl-

Table 2 Effects of ligands on the asymmetric hydrosilylation of acetophenone **1a**^a

| Entry | Ligand | Conv ^b [%] | ee ^c [%] |
|-----------------|------------|-----------------------|---------------------|
| 1 | L1b | >99 | 74 |
| 2 | L1c | >99 | 91 |
| 3 | L2a | >99 | 75 |
| 4 | L2b | >99 | 77 |
| 5 | L3 | 65 | 59 |
| 6 | L4a | >99 | 78 |
| 7 | L4b | >99 | 87 |
| 8 | L4c | 32 | 70 |
| 9 | L5 | 12 | 4 |
| 10 | L6 | 38 | 1 |
| 11 | L7 | >99 | 8 |
| 12 ^d | L1c | >99 | 86 |

^a Reaction conditions: 0.30 mmol substrate, substrate concentration = 0.20 M in toluene. ^b The conversions were determined by NMR and GC analysis. ^c The ee values were determined by chiral GC analysis. The absolute configuration was determined by comparing the retention times with known data (see the ESI). ^d The reaction was carried out under N₂. The ee value is the average of 3 runs.

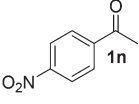
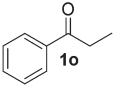
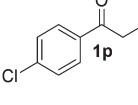
P-Phos (**L1c**) was beneficial for achieving both the higher optical yield (91% ee) and reaction rate (entry 2). For instance, when **1a** was subjected to a given set of conditions [2 mol% of (S)-Xyl-P-Phos, 2 mol% of CuFe₂O₄@KIT-6, 4 equiv. of PMHS as the reductant, 4 mol% of *t*-BuONa and 4 equiv. of *t*-BuOH as the additives], the reaction proceeded smoothly at room temperature in air and afforded (S)-**2a** neatly bearing 91% enantiopurity within 14 h (entry 2). Moreover, the enantioselectivity of the reaction under nitrogen was lower than that obtainable in air (entry 12 vs. 2). At this stage, what is the role of the air in the increased enantioselectivity remains elusive. It appears that air plays an intriguing role in the formation of the active catalyst precursor in the catalytic cycle. Studies aimed at investigating the mechanistic features relevant to the aforementioned factors are underway in our laboratory.

Having established the optimized conditions, we set out to evaluate the general utility of the present heterogeneous catalyst system for the enantioselective reduction of a wide spectrum of aryl alkyl ketones **1b–1p** at room temperature under air atmosphere, and the representative results are summarized in Table 3. Complete reductions of most substrates were realized in 14 h and the positioning of the substituents on the phenyl ring of acetophenone had a dramatic effect on the enantioselectivities. Aryl methyl ketone substrates possessing a *meta*- or *para*-substituted electron-rich or electron-deficient aryl group all underwent facile hydrosilylation in air, affording the desired alcohols neatly of consistently high enantiopurities (89–97% ee, entries 4–13), whereas *ortho*-substitution on the phenyl group of acetophenone resulted in the diminution of stereoselectivities (72–87% ee, entries 1–3), possibly owing to

Table 3 Asymmetric hydrosilylation of aryl alkyl ketones in air^a

| Entry | Substrate | Yield ^b [%] | ee ^c [%] |
|-----------------|-----------|------------------------|---------------------|
| 1 | | 96 | 79 |
| 2 | | 97 | 75 |
| 3 | | 96 | 87 |
| 4 | | 98 | 90 |
| 5 | | 96 | 96 |
| 6 | | 98 | 97 |
| 7 ^d | | 93 | 91 |
| 8 | | 96 | 92 |
| 9 | | 97 | 89 |
| 10 | | 98 | 94 |
| 11 | | 97 | 96 |
| 12 ^d | | 97 | 91 |

Table 3 (Contd.)

| Entry | Substrate | Yield ^b [%] | ee ^c [%] |
|-------|---|------------------------|---------------------|
| 13 |  | 98 | 91 |
| 14 |  | 95 | 87 |
| 15 |  | 95 | 87 |

^a Reaction conditions: 0.30 mmol substrate, substrate concentration = 0.20 M in toluene. ^b Isolated yield. ^c The ee values were determined by chiral GC and HPLC analysis. The absolute configuration was determined by comparing the retention times with known data (see the ESI). ^d Reaction temperature = 0 °C.

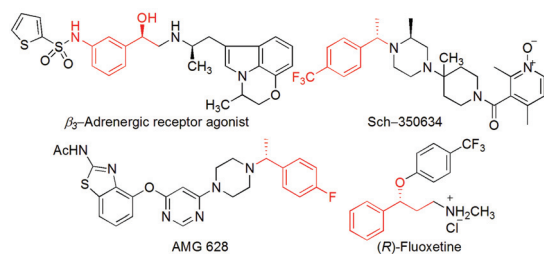


Fig. 1 Representative examples of biologically active compounds derived from chiral alcohols.

the bulky substituents at the *ortho*-position, which blocked the approach of the carbonyl group to the metal center. Changing the methyl group of acetophenone to an ethyl group diminished the optical yields to 87% under otherwise identical reaction conditions (entry 15 vs. entry 10, entry 14 of Table 3 vs. entry 2 of Table 2).

Among the obtained optically enriched alcohol products listed in Table 3, several of them, such as **2h**, **2j** and **2m**, are key structural elements in some natural products and medicinal chemistry (Fig. 1). For instance, product **2h** is a valuable intermediate for the synthesis of a β_3 -adrenergic receptor agonist,²⁵ used for the treatment of obesity, noninsulin dependent diabetes mellitus and frequent urination, while optically active **2j** could be transformed to a vanilloid receptor-1 antagonist AMG 628.²⁶ In addition, Sch-350634²⁷ could inhibit the replication of HIV-1 *via* blockade of its entry into cells and could therefore act as a potential new target for antiviral therapy. An efficient route to Sch-350634 relied on access to the key optically active precursor **2m**.

Given the good performance of the present heterogeneous catalyst system in the asymmetric hydrosilylation of a series of aryl alkyl ketones, we were interested in further broadening its applicability. Thus, as indicated in Table 4, a variety of other ketonic substrates **3a–3k**, including α -, β -, or γ -halo substituted alkyl aryl ketones, and diaryl, aryl cycloalkyl as well as alkyl heteroaryl ketones, have been selected to produce some valuable pharmaceutical and agricultural chemical intermediates. For example, in the presence of 2 mol% each of $\text{CuFe}_2\text{O}_4@$ -KIT-6 and **L4c**, 2-acetonaphthone (**3b**) and cyclohexyl aryl ketones (**3g**, **3h**) were converted into the expected (*S*)-alcohol products quantitatively in 90–96% ee (entries 2, 7 and 8). Owing to the existence of the halogen that can readily act as a good leaving group, enantiomerically enriched halo alcohols constitute especially significant building blocks for the construction of a number of structurally versatile and biologically active compounds, such as chiral diols, epoxides, amino alcohols, and azido alcohols. By utilizing $\text{CuFe}_2\text{O}_4@$ -KIT-6 as the catalyst precursor, the enantioselective hydrosilylations of α -, β - or γ -halo substituted alkyl aryl ketones all proceeded well in air at 0 °C to obtain full conversions and 87–91% ee values (entries 3–5). (*R*)-Fluoxetine (Fig. 1) is often prescribed for the treatment of psychiatric disorders or some metabolic problems, and the synthesis of it requires a γ -halo-substituted alcohol intermediate such as **4d**.²⁸ As shown in entry 5, when β -chloropropiophenone **3d** was subjected to a given set of reaction conditions, the reaction was complete after 14 hours to afford the corresponding γ -chloro alcohol **4d** in 88% ee. Additionally, the chiral dipyriddyphosphine ligated heterogeneous catalyst also worked efficiently for some ketonic substrates bearing the 2-pyridyl, 2-thienyl, or 3-thienyl moiety, rendering moderate to good enantioselectivities (entries 9–11, 64–87% ee) under optimized conditions.

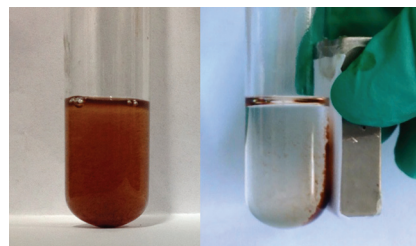
In comparison with homogeneous catalysts, an important feature of heterogeneous catalysts is the easy separation and recyclability. The magnetic behavior analysis showed that the coercivity and the remanence of our synthesized $\text{CuFe}_2\text{O}_4@$ -KIT-6 catalyst were both negligible, indicating that it is a superparamagnetic material, which can be attributed to the small particle size of CuFe_2O_4 .¹⁹ This superparamagnetic property along with the microsized KIT-6 matrix facilitated separation of the catalyst from reaction solutions upon reaction completion either by magnetic recovery or by filtration.

Finally, the recyclability of the $\text{CuFe}_2\text{O}_4@$ -KIT-6 catalyst was examined using **11** as the model substrate. As Fig. 2 illustrates, upon the finishing of each cycle, mesoporous silica KIT-6 supported superparamagnetic CuFe_2O_4 nanoparticles were separated out by applying an external permanent magnetic field, and the catalyst was then washed with toluene and acetone, dried under vacuum at 120 °C overnight, cooled down under a nitrogen flow and used directly for the next cycle without further purification. The catalyst was reused for four cycles and the catalytic results are listed in Table 5. The yield was retained in all the four cycles, while the enantioselectivity slightly decreased from 94% to 88%.

Table 4 Asymmetric hydrosilylation of other representative simple ketones in air^a

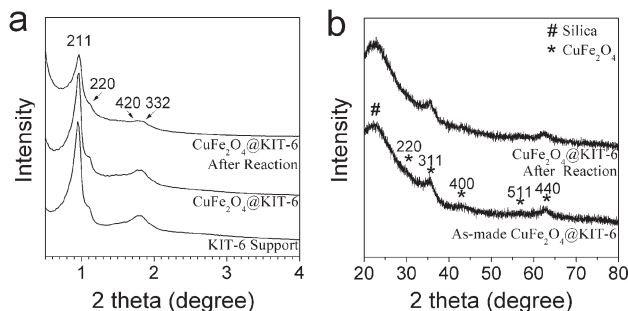
| Entry | Substrate | Yield ^b [%] | ee ^c [%] |
|--|-----------|------------------------|---------------------|
| 1. 2 mol % CuFe ₂ O ₄ @KIT-6, 2 mol % L1c 4 mol % <i>t</i> -BuONa, 4 equiv <i>t</i> -BuOH 4 equiv PMHS, toluene, rt, 14 h, <i>in air</i> 2. NaOH (aq) | | | |
| | | | |
| 1 | | 98 | 60 |
| 2 | | 97 | 96 |
| 3 ^d | | 96 | 91 |
| 4 ^d | | 90 | 88 |
| 5 ^d | | 90 | 87 |
| 6 | | 95 | 58 |
| 7 ^d | | 94 | 95 |
| 8 ^d | | 96 | 90 |
| 9 | | 96 | 64 |
| 10 ^{d,e} | | 60 | 87 |
| 11 ^{d,e} | | 90 | 80 |

^a Reaction conditions: 0.30 mmol substrate, substrate concentration = 0.20 M in toluene. ^b Isolated yields. ^c The ee values were determined by chiral GC and HPLC analysis. The absolute configuration was determined by comparing the retention times with known data (see the ESI). ^d Reaction temperature = 0 °C. ^e Reaction time = 36 h.

**Fig. 2** Magnetic separation behavior of the CuFe₂O₄@KIT-6 catalyst.**Table 5** Reusability of the CuFe₂O₄@KIT-6 catalyst for the asymmetric hydrosilylation of 1-(4-bromophenyl)ethanone in air^a

| Run | 1 | 2 | 3 | 4 | 5 |
|--|----|----|----|----|----|
| 1. 2 mol % CuFe ₂ O ₄ @KIT-6, 0.5 mol % L1c 4 mol % <i>t</i> -BuONa, 4 equiv <i>t</i> -BuOH 4 equiv PMHS, toluene, rt, 14 h, <i>in air</i> 2. NaOH (aq) | | | | | |
| | | | | | |
| Yield ^b [%] | 98 | 97 | 96 | 97 | 76 |
| ee ^c [%] | 94 | 93 | 90 | 88 | 82 |

^a Reaction conditions: 1.8 mmol substrate, substrate concentration = 0.30 M in toluene. ^b Isolated yields. ^c The ee values were determined by chiral GC analysis. The absolute configuration was determined by comparing the retention times with known data (see the ESI).

**Fig. 3** (a) Small and (b) wide angle XRD patterns of the CuFe₂O₄@KIT-6 material before and after the catalysis reaction.

Small angle XRD patterns (Fig. 3a) of the recycled CuFe₂O₄@KIT-6 exhibited several intense diffraction peaks (Fig. 3a) in the 2 theta value range between 0.5 and 3.0°, similar to those of as-made CuFe₂O₄@KIT-6 and the mesoporous silica support KIT-6. This result clearly demonstrated the stability of the mesoporous silica support during the CuFe₂O₄ loading process and the catalytic reaction. No detectable difference can be found between the wide angle XRD patterns of the as-made CuFe₂O₄@KIT-6 and the recycle sample (Fig. 3b). Both of them revealed the presence of nanocrystalline pure phase CuFe₂O₄ with a similar crystal size. This means that no phase change took place and the crystal size remained stable during the catalytic process, indicating that

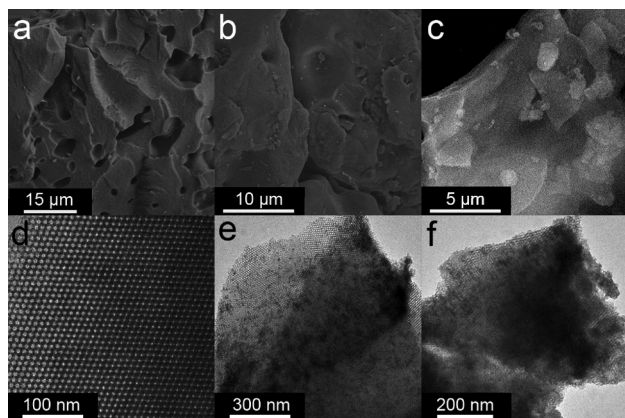


Fig. 4 (a, b, c) SEM and (d, e, f) TEM images of (a, d) mesoporous silica KIT-6 support, (b, e) as-made $\text{CuFe}_2\text{O}_4@KIT-6$, and (c, f) $\text{CuFe}_2\text{O}_4@KIT-6$ after catalytic reaction.

the CuFe_2O_4 nanoparticle is stable, as was reported by Kantam before.¹⁷

SEM observations (Fig. 4a–c) found that the recycled $\text{CuFe}_2\text{O}_4@KIT-6$ sample only showed negligible change in its particle morphology during the reaction, further confirming the stability of the mesoporous silica support. A TEM image of the as-made $\text{CuFe}_2\text{O}_4@KIT-6$ (Fig. 4e) clearly showed that nanosized CuFe_2O_4 particles were homogeneously distributed within the ordered mesoporous silica support before the catalytic reaction. The mean particle size was less than 10 nm, in agreement with the crystal size value estimated from the wide angle XRD pattern. After the catalytic reaction, the guest CuFe_2O_4 species still possessed a homogeneously distributed nanosized particle morphology (Fig. 4f). All these results clearly proved that the surface morphology and the mesostructure regularity of the KIT-6 support, the crystal phase and the particle size of the CuFe_2O_4 nanoparticles were almost unchanged after the catalytic reaction. In other words, all these results supported the good stability and reusability of the present $\text{CuFe}_2\text{O}_4@KIT-6$ catalyst system.

Nitrogen sorption analysis indicated that the specific surface area decreased from 706 to 593 $\text{m}^2 \text{g}^{-1}$, and the pore volume decreased from 1.1 to 0.95 $\text{cm}^3 \text{g}^{-1}$ after the mesoporous KIT-6 support was loaded with CuFe_2O_4 nanoparticles (Fig. S1a, b†). After the catalytic reaction, the specific surface area and the pore volume further significantly decreased to 319 $\text{m}^2 \text{g}^{-1}$ and 0.72 $\text{cm}^3 \text{g}^{-1}$, respectively (Fig. S1c†). Since XRD, SEM and TEM observations all confirmed the stability of our sample, it should not be attributed to the collapse of the mesostructure. Careful investigation revealed that this decrease of mesoporosity ought to be attributed to the adsorption of the organic chiral dipyridylphosphine ligand within the mesopore tunnel of the KIT-6 support. TGA analysis showed that more than 8 wt% organic species were recorded for the recycled $\text{CuFe}_2\text{O}_4@KIT-6$ sample after catalytic reaction by weight drop steps from 300 to 750 °C (Fig. S2†). This result indicated that the organic chiral dipyridylphosphine ligand molecules were strongly bound to the CuFe_2O_4 nanoparticles

via coordinate bonds, making them difficult to be washed away by organic solvents.

Conclusion

In conclusion, well-dispersed superparamagnetic CuFe_2O_4 nanoparticles supported on mesoporous silica KIT-6 have been synthesized and successfully applied as metal centers to catalyze the enantioselective hydrosilylation of a diverse range of prochiral ketones in air. In the presence of certain amounts of *t*-BuONa and *t*-BuOH as additives, catalytic amounts of a commercially available and air-stable chiral dipyridylphosphine (*S*)-Xyl-P-Phos as the ligand, and the stoichiometric desirable hydride source PMHS, a vast array of optically active alcohols were obtained in air with high yields and good to excellent enantioselectivities (up to 97%). The $\text{CuFe}_2\text{O}_4@KIT-6$ catalyst could be recycled by either filtration or magnetic separation, and it could be reused at least four times without losing its activity and enantioselectivity. In light of the reusability, air-stability, mild reaction conditions, good enantioselectivities and wide substrate scope, the present heterogeneous catalyst system therefore has good potential for practical applications.

Experimental section

General

Mesoporous silica KIT-6 and the supported $\text{CuFe}_2\text{O}_4@KIT-6$ catalyst were prepared and characterized according to our previously reported procedure.¹⁹ The CuFe_2O_4 loading amount is 12% and the calcination temperature is 600 °C. Other experimental parameters and the detailed synthesis procedure can be found in the literature report.¹⁹ Optically pure P-Phos, Xyl-P-Phos, BINAP, Tol-BINAP, H₈-BINAP, SEGPHOS, DM-SEGPHOS, DTBM-SEGPHOS, (*S*)-(*R*)-Josiphos, (*S,S*)-DIOP and (*S,S*)-Me-Duphos were purchased from Strem or Aldrich. (*S*)-Tol-P-Phos was prepared according to a previously reported procedure.²⁹ Prior to use, all solvents were purified and dried according to standard methods. Phenylsilane, ketone substrates, and other reagents were purchased from Aldrich, Alfa Aesar or Acros Organics and were used as received without further purification unless otherwise stated.

¹H NMR and ¹³C NMR spectra were recorded in CDCl_3 on a Bruker Advance spectrophotometer (400 or 500 MHz) at room temperature. Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. IR absorption spectra (FT = diffuse reflectance spectroscopy) were recorded on a Bruker TENSOR27 and only noteworthy absorptions (in cm^{-1}) are listed. Conversions were determined by ¹H NMR and gas chromatographic analyses. Enantiomeric excesses of the asymmetric hydrosilylation products were determined by chiral GC or HPLC. GC analyses were conducted on an Agilent 7820A or a Fuli 9790 with an FID detector. HPLC analyses were performed using an Agilent 1200 with a UV detector. Optical

rotations were measured on a Perkin-Elmer Model 341 polarimeter in a 10 cm cell. X-ray diffraction patterns were recorded with a Cu K α radiation source on a Bruker D8 diffractometer. Scanning electron microscope images were collected on an FEI XL40 instrument. Transmission electron microscopy images were collected on a Hitachi HT7700. Nitrogen sorption isotherms were measured at 77 K on a Quadrasorb SI apparatus. The samples were degassed at 150 °C overnight before the measurements. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated from the adsorption branch of the isotherms using the BJH method. Thermogravimetric analysis was carried out on a NETZSCH STA 409PC apparatus under an air flow at a rate of 40 mL min⁻¹.

General procedure for the catalytic asymmetric hydrosilylation reaction in air (Table 5, entry 1, 1-(4-bromophenyl)ethanone, **1I).** The synthesized CuFe₂O₄@KIT-6 with 12% loading amount was used in the catalytic reaction. CuFe₂O₄@KIT-6 (72 mg, 3.6 × 10⁻² mmol), (*S*)-Xyl-P-Phos (**L1C**, 7.0 mg, 9 × 10⁻³ mmol) and *t*-BuONa (6.9 mg, 7.2 × 10⁻² mmol) were weighed under air and placed in a 25 mL round-bottomed flask equipped with a magnetic stirring bar. Toluene (3.0 mL) was added and the mixture was stirred at room temperature for 2 h. To the solution, PMHS (480 μ L, 7.2 mmol) was added under vigorous stirring and the mixture was again stirred for 30 min. A solution of 1-(4-bromophenyl)ethanone (**1I**, 358 mg, 1.8 mmol) and *t*-BuOH (680 μ L, 7.2 mmol) in toluene (2 mL) was added and the flask was stoppered. The reaction was monitored by TLC. Upon completion, the reaction mixture was magnetically concentrated with the aid of a magnet to separate the catalyst. The recovered catalyst was washed with ether (6 × 3 mL). The combined organic layer was treated with 1 mol L⁻¹ NaOH (3 mL) and the mixture was stirred vigorously for 3 h. The organic product was extracted with ethyl acetate (3 × 10 mL). The combined extract was washed with water, dried with anhydrous sodium sulfate, filtered through a plug of silica and concentrated in a vacuum to yield the crude product. The conversion and the enantiomeric excess of the product (*S*)-1-(4-Bromophenyl)ethanol (**2I**) were determined by NMR and GC (Capillary GC, Chirasil-DEX CB column; 25 m × 0.25 mm, carrier gas, N₂) analysis. The pure product was isolated (347 mg, 96% yield) by column chromatography (ethyl acetate–petroleum ether = 1 : 4).

Reuse of the catalysts. The CuFe₂O₄@KIT-6 catalyst was magnetically separated from the above reaction mixture, washed with toluene (2 × 10 mL) and acetone (2 × 10 mL), dried under vacuum at 120 °C overnight, and cooled down under a nitrogen flow. The catalytic ability of the recovered CuFe₂O₄ was tested by performing the asymmetric hydrosilylation reaction on the next recycle according to the above procedure.

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