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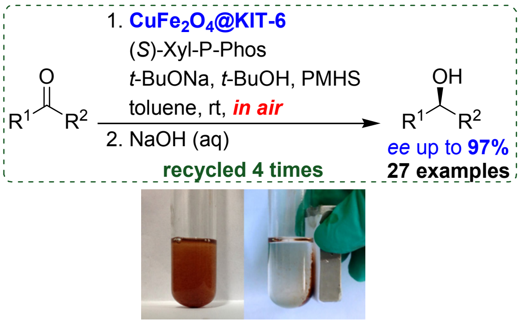
Asymmetric hydrosilylation of ketones catalyzed by magnetically recoverable superparamagnetic $CuFe_2O_4$ nanoparticles supported on mesoporous silica KIT-6 proceeded in air with up to 97% *ee*.



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PAPER

Mesoporous silica KIT-6 supported superparamagnetic $CuFe_2O_4$ nanoparticles for catalytic asymmetric hydrosilylation of ketones in air

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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 $CuFe_2O_4$ nanoparticles supported on mesoporous silica KIT-6 and non-racemic dipyridylphosphine ligand, stoichiometric hydride donor polymethylhydrosiloxane (PMHS) as well as certain amounts of additives. The magnetically separable catalysts could be efficiently reused for 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 scope of chiral alcohols, has attracted growing interests 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[9i,10] and nickel[11] have been developed in the past two decades and applied in the relevant hydrosilylation reactions with moderate to excellent enantioselectivities.

Previous studies on metal-catalyzed asymmetric hydrosilylations mainly focused on the 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 are successfully applied in the asymmetric reduction of aryl alkyl ketones with good reaction activities and enantioselectivities.[14] The 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 the 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 MNPs-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. $CuFe_2O_4$ nanoparticles have been demonstrated to possess high catalytic activities in several organic reactions such as coupling[16] and asymmetric hydrosilylation of ketones.[17] In 2009, Kantam et al. described $CuFe_2O_4$ nanoparticles obtainable by 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 the nanosized particles with high exposure of active sites are featured for catalytic reactions, and the bulk-sized supports are benefit for the separation and recycling manipulation. Particularly, 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 endeavors have been devoted to the development of

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† Electronic Supplementary Information (ESI) available: [spectral, analytical data for all chiral products are available in Supporting Information]. See DOI: 10.1039/b000000x/

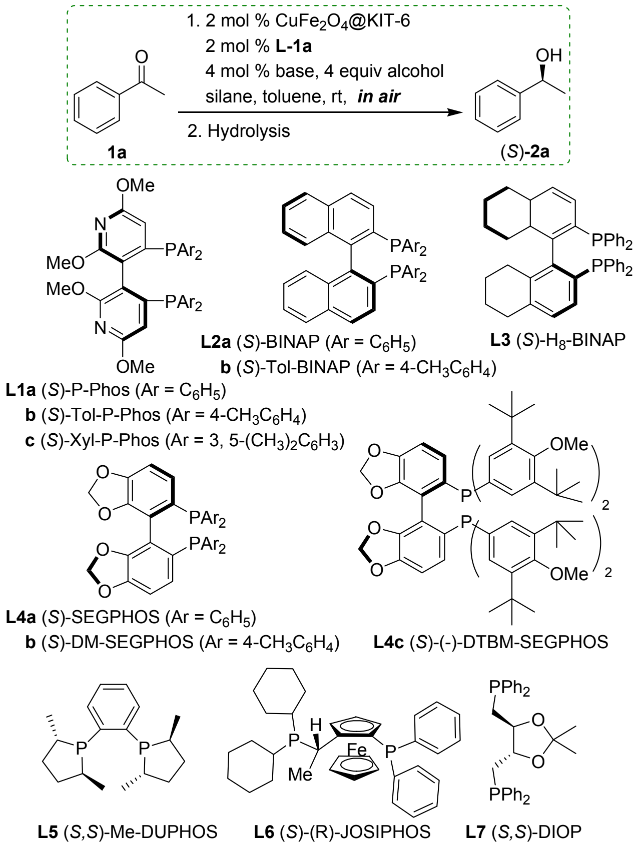
novel and efficacious mesoporous supported nanoparticles for green asymmetric catalytic reactions.[18]

More recently, we successfully synthesized a magnetic catalytic material $CuFe_2O_4$@KIT-6, which was composed by homogeneously dispersed $CuFe_2O_4$ nanoparticles supported on a mesoporous silica KIT-6 matrix.[19] Preliminary investigation on the catalytic performance of the obtained $CuFe_2O_4$@KIT-6 indicated that it was efficient for the enantioselective hydrosilylation of acetophenone to furnish the desired alcohol product in 93% yield and 93% *ee* at room temperature under air atmosphere, which is much better than the homogeneous catalyst systems under identical conditions. Moreover, the copper ferrite nanoparticles could be magnetically recycled and reused, which exhibited good practical potential and prompted us to further broaden its application scope. Hereby, we adopted the synthesized $CuFe_2O_4$@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 of good to excellent optically purities. The $CuFe_2O_4$@KIT-6 catalyst could be recycled for reuse at least for 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 $CuFe_2O_4$@KIT-6 catalyst have been well preserved after the reaction.

Results and discussion

In the beginning, we investigated the ability of chiral dipyridylphosphine 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 catalyst precursor $CuFe_2O_4$@KIT-6, which was prepared according to the previous procedure,[19] 2 mol % of **L1a**, and 1.2 equivalent of hydride donor $PhSiH_3$, 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 unchanged (entry 2 vs entry 1). Similar with 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).

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

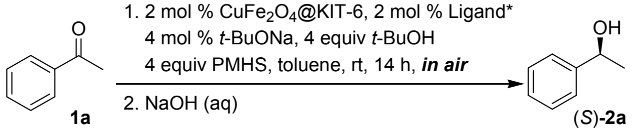


Entry	Silane	Equiv	Alcohol	Base	Conv [%][b]	*ee* [%][c]
1	$PhSiH_3$	1.2	–	–	99	84
2	PMHS	4	–	–	42	82
3	PMHS	4	*t*-BuOH	*t*-BuONa	>99	79

[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 Supporting Information).

Next, a series of chiral ligands were examined in the reduction of acetophenone and the results indicated that ligands had 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*)-H_8-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, 8, 9, 10 and 11). (*S*)-Xyl-P-Phos (**L1c**) was beneficial to both the higher optical yield (91% *ee*) and reaction rate (entry 2). For instance, when **1a** was submitted to a given set of conditions [2 mol % of (*S*)-Xyl-P-Phos, 2 mol % of $CuFe_2O_4$@KIT-6, 4 equiv of PMHS as the reductant, 4 mol % *t*-BuONa and 4 equiv *t*-BuOH as the additives], the reaction proceeded smoothly at room temperature in air and afforded (*S*)-**2a** neatly bearing 91% of enantiopurity within 14 h (entry 2). Moreover, the enantioselectivity of reaction under nitrogen was lower than that obtainable in air (entries 12 vs 2). At this stage, what is the role of the air for the increased enantioselectivity remains elusive. It appears that air played an intriguing role in the formation of the active catalyst precursor in the catalytic cycle. Studies aimed at investigating mechanistic features relevant to aforementioned factors are underway in our laboratory.

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



1a (*S*)-**2a**

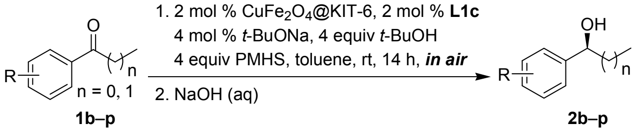
Entry	Ligand	Conv [%][b]	*ee* [%][c]
1	**L1b**	>99	74
2	**L1c**	>99	91
3	**L2a**	>99	75
4	**L2b**	>99	77
5	**L3**	65	59
6	**L4a**	>99	78
7	**L4b**	>99	87
8	**L4c**	32	70
9	**L5**	12	4
10	**L6**	38	1
11	**L7**	>99	8
12[d]	**L1c**	>99	86

[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 Supporting Information). [d] The reaction was carried out under N_2. The *ee* value is the average of 3 runs.

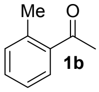
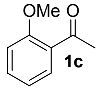
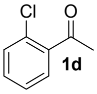
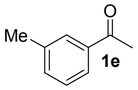
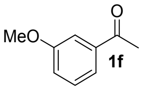
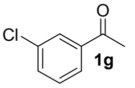
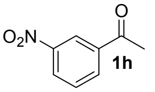
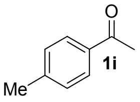
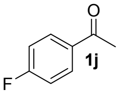
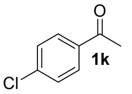
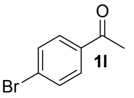
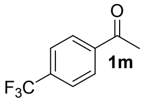
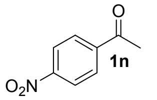
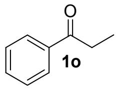
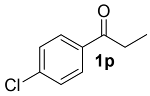
Having established the optimized conditions, we set out to evaluate the general utility of the present heterogeneous catalyst system for the enantioselective reduction of a wide spectrum of aryl alkyl ketones **1b**−**1p** at room temperature under air atmosphere, and the representative results were 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 dramatic effects 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, the *ortho*-substitution on the phenyl group of acetophenone resulted in the diminution in stereoselectivities (72−87% *ee*, entries 1–3), possibly owing to 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 the otherweise 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 structral elements in some natural products and medicinal chemistry (Figure 1). For instance, product **2h** is a valuable intermdeiate for the synthesis of a β_3-adrenergic receptor

Table 3 Asymmetric hydrosilylation of aryl alkyl ketones in air.[a]



1b–p **2b–p**

Entry	Substrate	Yield [%][b]	*ee* [%][c]
1	 **1b**	96	79
2	 **1c**	97	75
3	 **1d**	96	87
4	 **1e**	98	90
5	 **1f**	96	96
6	 **1g**	98	**97**
7[d]	 **1h**	93	91
8	 **1i**	96	92
9	 **1j**	97	89
10	 **1k**	98	94
11	 **1l**	97	96
12[d]	 **1m**	97	91
13	 **1n**	98	91
14	 **1o**	95	87
15	 **1p**	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 Supporting Information). [d] Reaction temperature = 0 °C

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-350634[27] 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 the access to the key optically active precursor **2m**.

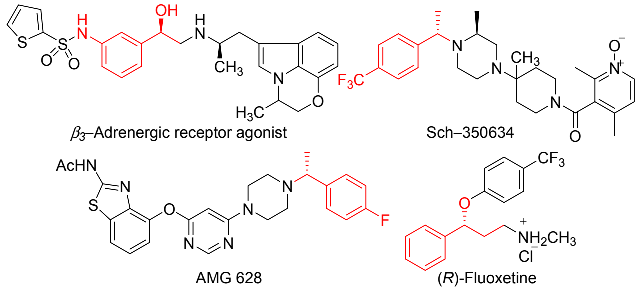
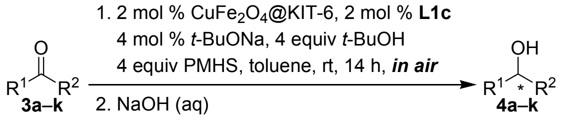
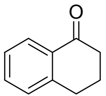
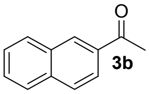
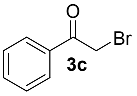
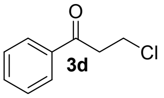
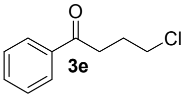
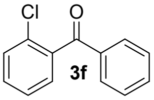
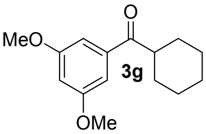
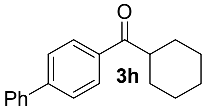
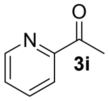
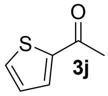
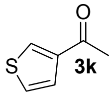


Figure 1 Representative examples of biologically active compounds derived from chiral alcohols.

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, 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 CuFe$_2$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 CuFe$_2$O$_4$@KIT-6 as the catalyst precursor, the enantioselective hydrosilylation 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 (Figure 1) is often prescribed for the treatment of psychiatric disorder or some metabolic problems, the synthesis of which demands 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 completed after 14 hours to afford corresponding *γ*-chloro alcohol**4d** in 88% *ee*. Additionally, the chiral dipyridylphosphine ligated heterogeneous catalyst also worked efficiently for some ketonic substrates bearing 2-pyridyl, 2-thienyl, or 3-thienyl moiety, redering moderate to good enantioselectivities (entries 9–11, 64–87% *ee*) under optimized conditions.

Table 4 Asymmetric hydrosilylation of other representative simple ketones in air.[a]



Entry	Substrate	Yield [%][b]	*ee* [%][c]
1	 **3a**	98	60
2	 **3b**	97	**96**
3[d]	 **3c**	96	91
4[d]	 **3d**	90	88
5[d]	 **3e**	90	87
6	 **3f**	95	58
7[d]	 **3g**	94	95
8[d]	 **3h**	96	90
9	 **3i**	96	64
10[d,e]	 **3j**	60	87
11[d,e]	 **3k**	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 Supporting Information). [d] Reaction temperature = 0 °C. [e] Reaction time = 36 h.

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 CuFe$_2$O$_4$@KIT-6 catalyst were both negligible, indicating that it's a superparamagnetic material, which can be attribute to the small particle size of CuFe$_2$O$_4$.[19] This superparamagnetic property along with the microsized KIT-6 matrix facilitated the separation of the catalyst from reaction solutions upon reaction completion either by magnetic recovery or by filtration.

Finally, the recyclability of the CuFe$_2$O$_4$@KIT-6 catalyst was examined using **1l** as the model substrate. As Figure 2 illustrated, upon 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, cool down under nitrogen flow and used directly for the next cycle without further purification. The catalyst was reused for four cycles and the catalytic results were listed in Table 5. The yield retained in all the four cycles, while the enantioselectivity slightly decreased from 94% to 88%.

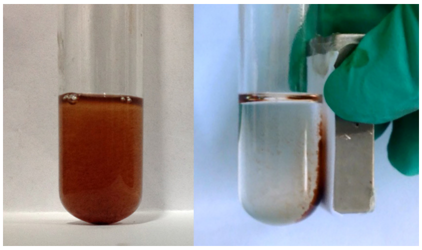
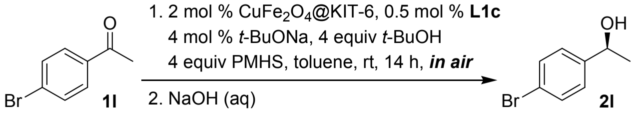


Figure 2 Magnetic separation behavior of $CuFe_2O_4$@KIT-6 catalyst.

Table 5 Reusability of $CuFe_2O_4$@KIT-6 catalyst for the asymmetric hydrosilylation of 1-(4-bromophenyl)ethanone in air [a]



Run	1	2	3	4	5
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 Supporting Information).

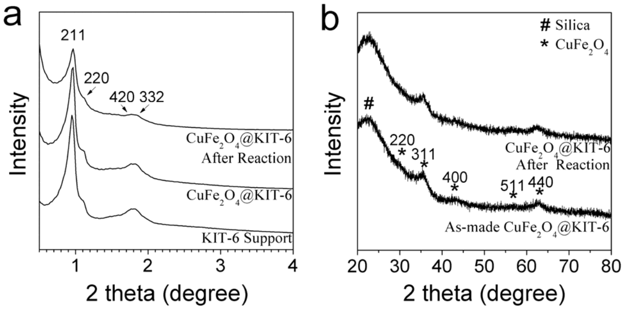


Figure 3 (a) Small and (b) wide angle XRD patterns of the $CuFe_2O_4$@KIT-6 material before and after the catalysis reaction.

Small angle XRD pattern (Figure 3a) of the recycled $CuFe_2O_4$@KIT-6 exhibited several intense diffraction peaks (Figure 3a) in the 2 theta value range between 0.5 and 3.0º, similar with those of as-made $CuFe_2O_4$@KIT-6 and mesoporous silica support KIT-6. This result clearly demonstrated the stability of mesoporous silica support during the $CuFe_2O_4$ loading process and the catalytic reaction. No detectable difference can be found between the wide angle XRD patterns of the as-made $CuFe_2O_4$@KIT-6 and the recycle sample (Figure 3b). Both of them revealed the presence of nanocrystalline pure phase $CuFe_2O_4$ with similar crystal size. This means that no phase change happened and the crystal size kept stable during the catalytic process, indicating that the $CuFe_2O_4$ nanoparticle is stable, as reported by Kantam before.[17]

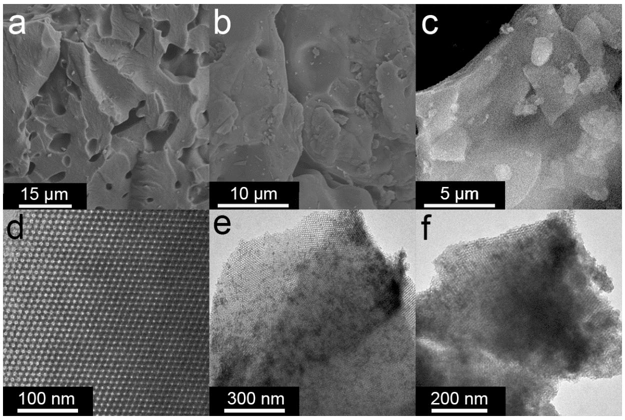


Figure 4 (a, b, c) SEM and (d, e, f) TEM images of (a, d) mesoporous silica KIT-6 support, (b, e) as-made $CuFe_2O_4$@KIT-6, and (c, f) $CuFe_2O_4$@KIT-6 after catalytic reaction.

SEM observation (Figure 4a, b, c) found that the recycled $CuFe_2O_4$@KIT-6 sample only showed negligible change in its particle morphology during the reaction, further confirming the stability of the mesoporous silica support. TEM image of the as-made $CuFe_2O_4$@KIT-6 (Figure 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 agree 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 (Figure 4f). All these results clearly proved that the surface morphology and the mesostructure regularity of the KIT-6 support, the crystal phase and particle size of the $CuFe_2O_4$ nanoparticles were almost unchanged after the catalytic reaction. In another words, all these results supported the good stability and reusability of the present $CuFe_2O_4$@KIT-6 catalyst system.

Nitrogen sorption analysis indicated that the specific surface area decreased from 706 to 593 m^2/g, and the pore volume decreased from 1.1 to 0.95 cm^3/g after the mesoporous KIT-6 support was loaded with $CuFe_2O_4$ nanoparticles (Figure S1a, b). After the catalytic reaction, the specific surface area and the pore volume further significantly decreased to 319 m^2/g and 0.72 cm^3/g, respectively (Figure S1c). Since XRD, SEM and TEM observations all confirmed the stability of our sample, it should not be caused by the collapse of mesostructure. Careful investigation revealed that this decrease of mesoprosity ought to be attributed to the adsorption of 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 $CuFe_2O_4$@KIT-6 sample after catalytic reaction by the weight drop steps from 300 to 750^{o}C (Figure S2). This result indicated that the organic chiral dipyridylphosphine ligand molecules were strongly bind to the CuFe$_2$O$_4$ nanoparticles via coordinate bond, making it can hardly be washed away by organic solvents.

Conclusion

In conclusion, well-dispersed superparamagnetic CuFe$_2$O$_4$ nanoparticles supported on mesoporous silica KIT-6 have been synthesized and successfully applied as metal center 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 amount of a commercially available and air-stable chiral dipyridylphosphine (*S*)-Xyl-P-Phos as ligand, as well as 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 CuFe$_2$O$_4$@KIT-6 catalyst could be recycled by either filtration or magenetic seperation, and it could be reused at least for four times without lossing its activity and enantioselectivity. In light of the reusability, air-stability, mild reaction conditions, good enatioselectivities and wide substrate scope, the present heterogeneous catalyst system is therefore of good potential for practical applications.

Experimental Section

General

Mesoporous silica KIT-6 and the supported CuFe$_2$O$_4$@KIT-6 catalyst were prepared and characterized according to our previous precedure.[19] The CuFe$_2$O$_4$ loading amount is 12% and the calcination temperature is 600 ^{o} 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, H$_8$-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 previous reported procedure.[29] All solvents were purified and dried according to standard methods prior to use. Phenylsilane, ketone substrates, and other reagents were purchased from Aldrich, Alfa Aesar or Acros organics and used as received without further purification unless otherwise stated.

^{1}H NMR and ^{13}C 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 performed on a Bruker TENSOR27 and only noteworthy absorptions (in cm^{-1}) are listed. Conversions were determined by ^{1}H 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 Kα radiation source on a Bruker D8 diffractometer. Scanning electron microscope images were collected on 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.

General procedure for the catalytic asymmetric hydrosilylation reaction in air (Table 5, entry 1, 1-(4-bromophenyl)ethanone, 1l): The synthesized CuFe$_2$O$_4$@KIT-6 with 12% loading amount was used in the catalytic reaction. CuFe$_2$O$_4$@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 μL, 7.2 mmol) was added under vigorous stirring and the mixture was again allowed to stir for 30 min. A solution of 1-(4-bromophenyl)ethanone (**1l**, 358 mg, 1.8 mmol) and *t*-BuOH (680 μL, 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 vacum to yield the crude product. The conversion and the enantiomeric excess of the product (*S*)-1-(4-Bromophenyl)ethanol (**2l**) were determined by NMR and GC (Capillary GC, Chirasil-DEX CB column; 25 m × 0.25 mm, carrier gas, N$_2$) analysis. The pure product was isolated (347 mg, 96% yield) by column chromatography (ethyl acetate:petroleum ether = 1:4).

Reuse of the catalysts: The CuFe$_2$O$_4$@KIT-6 catalyst was magnetically separated from above reaction mixture, washed with toluene (2 × 10 mL) and acetone (2 × 10 mL), dried under vacuum at 120 °C overnight, cool down under nitrogen flow. The catalytic ability of the recovered CuFe$_2$O$_4$ was tested by performing the asymmetric hydrosilylation reaction on the next recycle according to the above procedure.

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