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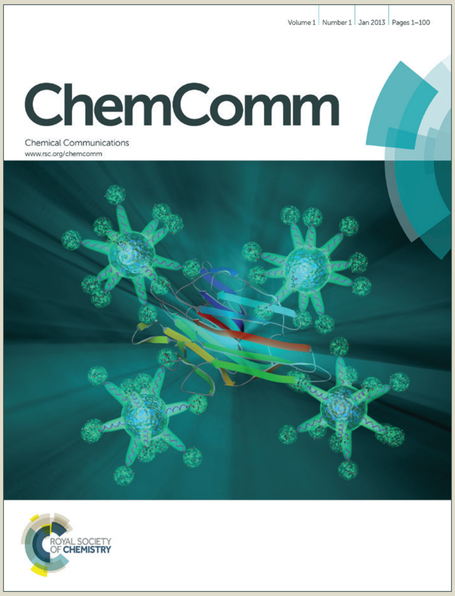

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ARTICLE TYPE

Facile Fabrication of Magnetically Recyclable Metal-Organic Framework Nanocomposites for Highly Efficient and Selective Catalytic Oxidation of Benzylic C-H Bonds**

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HKUST-1@Fe_3O_4 chemically bonded core-shell nanoparticles have been prepared by growing HKUST-1 thin layers joined by carboxyl groups onto Fe_3O_4 nanospheres. These magnetic core-shell MOF nanostructures show exceptional catalytic activity for the oxidation of benzylic C-H bonds and they can be recovered by magnetic separation and reused without losing any activity.

The oxidation of C-H bonds is one of the most important and fundamental reactions. Highly efficient catalysis of this transformation remains a challenge and great efforts had been made in exploring new catalysts.[1] The oxidation of benzylic C-H bonds, for instance, is a powerful tool to generate high value chemical feedstock from less expensive raw materials such as alkyl aromatics. In this regard, the means to convert benzylic hydrocarbons into valuable compounds have received considerable attention in recent years.[2] Despite of the high conversion rate, many benzylic C-H bonds oxidation reactions reported to date rely on homogeneous catalysts and thus recyclability and reusability of these specially-designed catalysts can be problematic.[3] Immobilization of the molecular catalysts or developing heterogeneous catalytic systems from scratch has proved to be two valuable strategies to solve this problem.[4]

Metal-organic frameworks (MOFs) are a class of porous polymeric materials consisting of metal ions or metal clusters covalently joined by organic links.[5] By virtue of their structural tunability, well-defined channels and rich functionalities, MOFs had found their way in potential applications including gas storage, separation, sensing, molecular recognition and heterogeneous catalysis.[6] However, only few MOFs have shown catalytic activity in the oxidation of benzylic C-H bonds with unsatisfactory conversion rate and/or selectivity, needless to say that no rational design has been reported on highly efficient C-H activation using MOF-based heterogeneous catalysts with proven recyclability.[7]

One of the methods to design easily recyclable catalysts is to introduce magnetism and test reusability by magnetic separation in between cycles.[8] Beyond directly incorporating magnetic components in MOF building units, forming composites using simple yet catalytically active MOF nanostructures that are anchored on the surface of magnetic nanoparticles could serve as a simple alternative route for this purpose.

Recently core-shell structured nanocomposites have attracted increasing attention due to their novel properties and potential applications that cannot be achieved solely with single component.[9] We thus decided to directly grow MOF nanolayers onto Fe_3O_4 nanospheres that are grafted with carboxylic functional groups. The chemical bonding of copper ions and carboxyl oxygen can help to tightly hold the active MOF layers and maintain the intactness of the nanocomposites through catalytic cycles.

Herein, we report a facile yet powerful strategy to synthesize HKUST-1@Fe_3O_4 core-shell nanoparticles (50 to 100 nm) by assembling HKUST-1 thin layers bonded through carboxyl groups onto Fe_3O_4 nanospheres. We also successfully employed the magnetic HKUST-1@Fe_3O_4 core-shell nanocomposites as highly efficient catalyst for the oxidation of benzylic hydrocarbons up to 99% conv. 99% sel.. Furthermore, these MOF core-shell nanocomposites can be easily recovered *via* simple magnetic separation and reused without losing activity through multiple reaction cycles. This may serve as a start in designing MOF catalysts for continuous magnetic fluid bed.

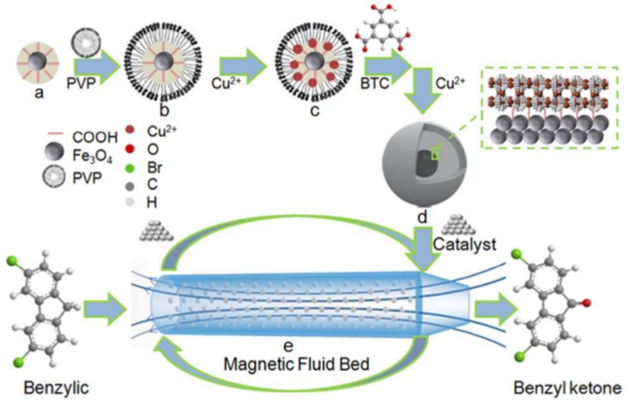


Fig. 1 The schematic representation of the synthetic route of HKUST-1@Fe_3O_4 and its potential applications in magnetic fluid bed.

The synthetic procedures of HKUST-1@Fe_3O_4 core-shell nanocomposites are summarized schematically in Fig. 1. Firstly, the carboxyl functionalized Fe_3O_4 cores with a diameter about 20 nm (ESI†, Fig. S1) is capped with polyvinylpyrrolidone (PVP), which acts as stabilizer agent and thus allows the magnetic cores to uniformly disperse in a mixed solution of DMF/C_2H_5OH/H_2O. Then copper ions are added and directly coordinate with carboxyl groups anchored to the surface of Fe_3O_4 nanospheres. Finally, the nanoparticles are encapsulated by a HKUST-1 shell *via* in-situ generation of HKUST-1 frameworks along with the introduction of trimesic acid and additional $Cu(OAc)_2$ into the mixture.

Scanning electron microscopy (SEM) (Fig. 2a) and high-resolution transmission electron microscopy (HR-TEM) investigations (Fig. 2b-c) show that the obtained HKUST-1@Fe_3O_4 nanoparticles have a spherical morphology with dimensions ranging from 50 to 100 nm. The nano-scaled composites are confirmed as core-shell structures by TEM. The rough interface between core and shell is clearly observed due to the different electron penetrability for the Fe_3O_4 and HKUST-1 components (Fig. 2b-c). Energy dispersive X-ray spectroscopy (ESI†, Fig. S2) and elemental mapping (Fig. 2e) indicate the presence of Fe and Cu ions in the composites. Analysis of the shells by TEM illustrates that the spacing between the adjacent planes measures at 0.21 nm (Fig. 2d). This value is consistent with the spacing of (044) spacing planes of HKUST-1, revealing that the shells with thickness of 5-18 nm in the composites are indeed HKUST-1.[10] It is validated by the analysis in selected-area electron diffraction of the shell that exhibits clear crystalline spot ring of crystalline HKUST-1 (ESI†, Fig. S3). Powder X-ray diffraction (PXRD) patterns for the core-shell composites unambiguously indicate the formation of the HKUST-1 phase and the retaining of Fe_3O_4 phase (ESI†, Fig. S4).

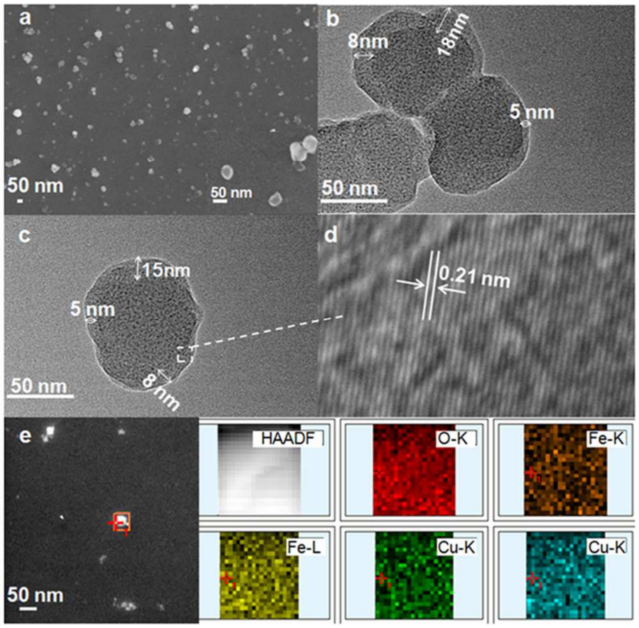


Fig. 2 a) SEM image of HKUST-1@Fe_3O_4. b) and c) TEM images of HKUST-1@ Fe_3O_4. d) HRTEM image of the circled site from c, the distance of the adjacent planes is 0.21 nm. e) EDS mapping images of HKUST-1@Fe_3O_4.

Fourier transform infrared (FT-IR) spectra further demonstrate the formation of HKUST-1@Fe_3O_4 nanocomposites. As shown in Fig. 3, the FT-IR spectrum of HKUST-1@Fe_3O_4 displays characteristic bands of HKUST-1. The peaks at 667, 729 and 765 cm^{-1} are attributed to the deformation modes of C-C-C in the benzene ring; the peaks at 1059, 1109 and 1165 cm^{-1} are associated with the C-O-C bending vibration of the ethylenedioxy moiety; the peaks at 1374, 1446 and 1566 cm^{-1} are assigned to the C-H stretching of the benzene ring. Concomitant with the encapsulation of Fe_3O_4 by HKUST-1 shell, the 1616, 1646 and 1674 cm^{-1} transmission bands can be ascribed to C=O stretching in various structural environments. Compared with Fe_3O_4, $Fe_3O_4/Cu(NO_3)_2 \cdot 3H_2O$ and HKUST-1, C=O stretching vibrations in the composites are obviously shifted, suggesting that HKUST-1 has been coated on the surface of the Fe_3O_4 core through coordination interactions.

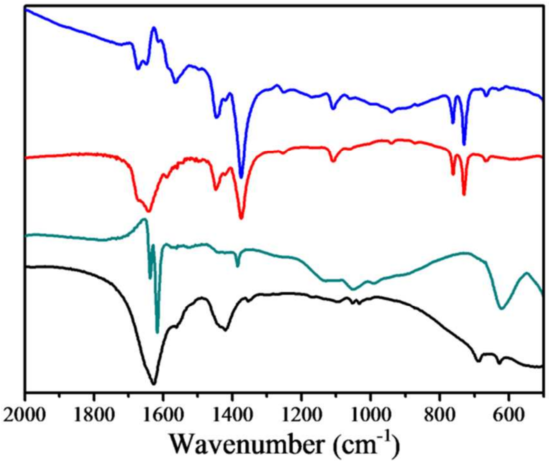


Fig. 3 IR spectra of Fe_3O_4 (black), $Fe_3O_4/Cu(NO_3)_2 \cdot 3H_2O$ (cyan), HKUST-1 (red) and HKUST-1@Fe_3O_4 (blue).

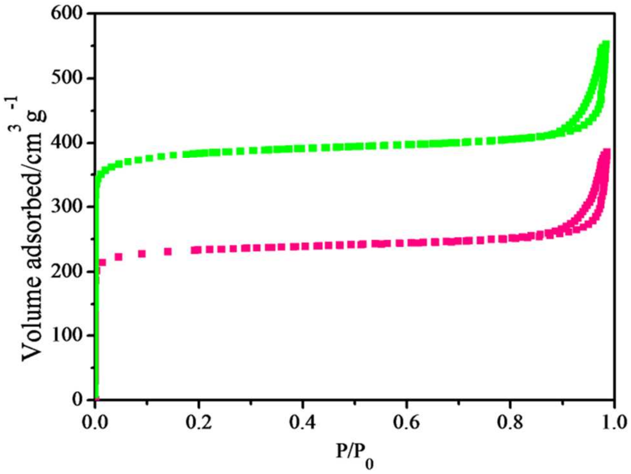


Fig. 4 Nitrogen sorption isotherms of HKUST-1 (green) and HKUST-1@Fe_3O_4 (pink).

In order to identify the chemical composition of the HKUST-1@Fe_3O_4, N_2 sorption isotherm measurement and elemental analysis were performed. From the adsorption isotherms (Fig. 4a), the Brunauer-Emmett-Teller (BET) surface areas of 10, 1220 and 738 m^2g^{-1} are achieved for Fe_3O_4, HKUST-1and HKUST-1@Fe_3O_4 (pore size distributions display in ESI†, Fig.S5), respectively. On the basis of the contributions of each component to the total surface area of HKUST-1@Fe_3O_4, the mass percentage of HKUST-1 is approximately evaluated to be 60.50% of the composites. The formula of HKUST-1@Fe_3O_4 is thus calculated to be $Cu_3Fe_{5.2}C_{18}O_{18.9}H_{12}$ (Fe_3O_4:HKUST-1 = 1.73).

Elemental analysis reveals the composites are constituted of 19.34% Cu and 28.63% Fe (ESI†, S6), which is in agreement with the values Cu, 18.98% and Fe, 28.78% derived from the formula based on adsorption analyses when taking the deviation into account.

Given the fact that the oxidation of benzylic C-H bonds is one of the key transformations in organic synthesis and nano-scaled HKUST-1@Fe_3O_4 encompasses numerous potential catalytic centers, we decided to evaluate the catalytic activity of the composites in the context of the oxidation reaction (Fig. 5). The reactions were performed using *tert*-butyl hydroperoxide (TBHP) as the oxidant. The transformation of diphenylmethane to benzophenone was selected as a model reaction. Heating a mixture of diphenylmethane (0.250 mmol) and TBHP (0.625 mmol) in benzonitrile at 80ºC for 14h in the presence of HKUST-1@Fe_3O_4 (25 mg) led to the formation of benzophenone in 94.7% conversion with 95.2% selectivity.

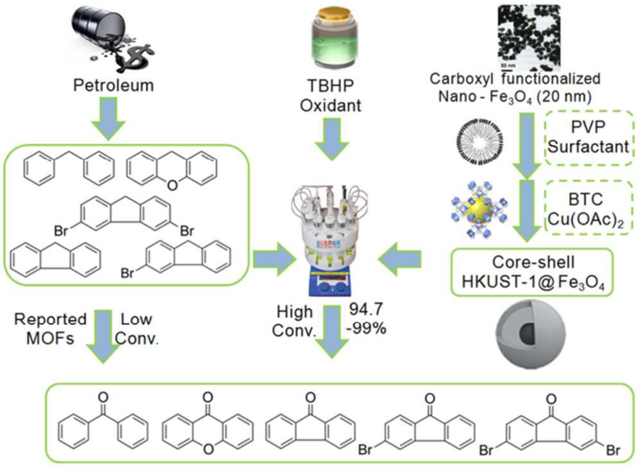
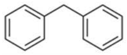
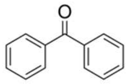
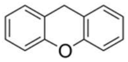
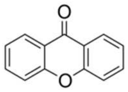
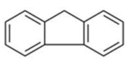
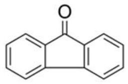
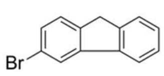
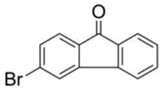
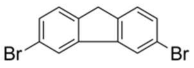
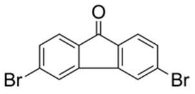


Fig. 5 Schematic diagram of the oxidation of benzylic hydrocarbons by using HKUST-1@Fe_3O_4 as catalyst.

Utilizing the optimized reaction conditions, the reaction scope by employing a variety of benzylic C-H compounds was subsequently explored. The corresponding ketones with aryl side chain groups were successfully synthesized from corresponding benzylic C-H compounds in great conversion rate (94.7-99%) and exceptional selectivity (95.2-99%) by using HKUST-1@Fe_3O_4 as the catalyst (Table 1). These preliminary results exhibit that HKUST-1@Fe_3O_4 can facilitate the oxidation of benzylic C-H bonds and serve as highly efficient and selective catalyst. And indeed, yield of HKUST-1@Fe_3O_4 outperforms many effective heterogeneous catalysts reported to date, *i.e.* nano-sized coordination cages $[Cu_4L_4]_4X$ (L= 1,3,5-tris(1-benzylbenzimidazol-2-yl)benzene, X= ClO_4, OTs, OTf),[11] NHPI/Cu@PILC[12] and even noble Pd@N-doped carbon,[13] etc.

Control catalytic experiments of the catalytic oxidation of diphenylmethane were performed on Fe_3O_4 and HKUST-1 under the same reaction conditions. The conversions were 56.4% and 86.5% when using Fe_3O_4 and HKUST-1, respectively. Based on the above findings, we could confirm that the Fe_3O_4 does not only act as a magnetic component for separation, but also participates in the catalysis.[14] The control experiments show that the catalytic C-H activation can be obviously enhanced when the core-shell nanostructures of HKUST-1@Fe_3O_4 are used. This may suggest the synergy effect in the bi-component nanocomposites of HKUST-1@Fe_3O_4 when catalyzing the oxidation of C-H bonds.

Table 1 The oxidation of benzylic hydrocarbons catalyzed by HKUST-1@Fe_3O_4[a]

Entry	Substrates	Products	Conv.(%)	Sele.(%)[b]
1			94.7	95.2
2			>99	>99
3			>99	>99
4			>99	98.3
5			>99	97.1

[a] Reaction conditions: Benzyl hydrocarbons (0.250 mmol), HKUST-1@Fe_3O_4 (25 mg), benzonitrile (0.5 mL), TBHP (0.625 mmol), 80ºC. [b] Selectivity to ketones.

Recyclability is an important and essential feature for any catalyst to be considered in large-scale catalytic reactions. A big advantage of HKUST-1@Fe_3O_4 composites is their saturation magnetization is still high enough for efficient separation using existing magnetic technology (ESI†, Fig. S7), which enables it to be potentially used in magnetic fluid bed for continuous industrial catalysis. As a proof-of-concept, the reusability of HKUST-1@Fe_3O_4 was thus tested.

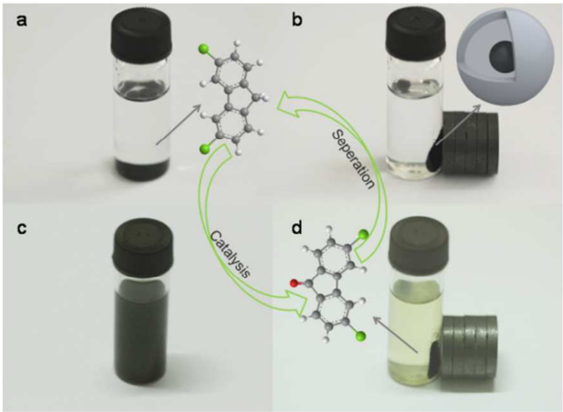


Fig. 6 Procedure of the recycling of magnetic HKUST-1@Fe_3O_4 catalyst in the oxidation of benzylic hydrocarbons.

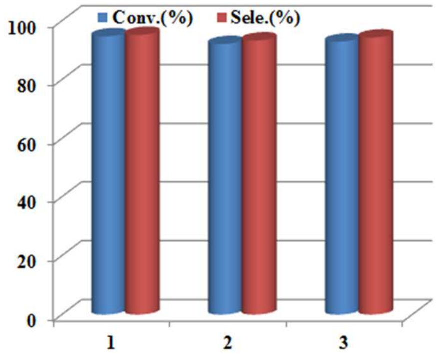


Fig. 7 Conversions and selectivities of HKUST-1@Fe_3O_4 in recycle experiments. Reaction conditions: diphenylmethane (0.250 mmol); catalyst (25 mg); 80 ºC; TBHP (0.625 mmol), 14 h.

As shown in Fig. 6, after completion of the oxidation reaction, the magnetic catalyst can easily be separated from the reaction mixture with an external magnet. The recovered catalyst was re-activated by washing with DMF four times (reclaimed with the same external magnet after each rinse) and further reused directly in a subsequent oxidation of benzylic C-H bonds reaction. The catalytic activity did not decrease after three catalytic cycles (Fig. 7) and the PXRD patterns of the recovered HKUST-1@Fe_3O_4 samples are identical to those of the freshly prepared HKUST-1@Fe_3O_4 (ESI†, Fig. S8). Atomic absorption analysis of the liquid phase after separation of the catalyst by an external magnet showed that there were no leaching of the copper and iron ions from the catalyst to the reaction mixture (ESI†, S9).

Conclusions

In summary, we successfully synthesized a chemically-bonded, nano-sized and magnetic HKUST-1@Fe_3O_4 composites. This material maintains highly active metal sites and can successfully catalyze the oxidation of benzylic C-H bonds with excellent conversion and selectivity. Moreover, this new MOF catalytic system can be easily recovered *via* magnetic separation and reused in several catalytic iterations without losing its structural integrity and catalytic activity. This opens great perspectives in terms of catalytic industrial processand sheds light on developing strategies aimed at rendering MOFs with new functionalities.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental Section; Synthesis, characterization, catalytic cycles details and additional figures and tables. See DOI:10.1039/b000000x/

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