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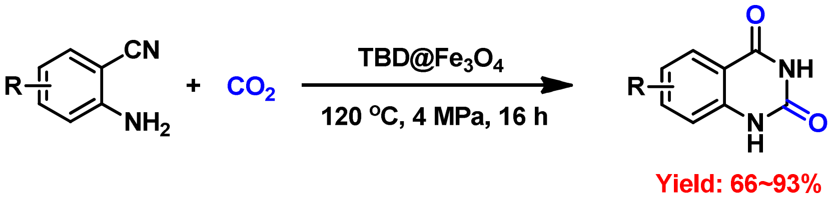
Graphical Abstract

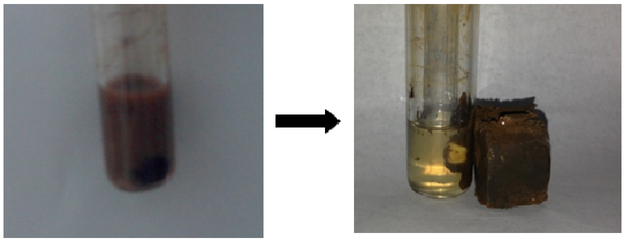
Magnetic catalysts for chemical fixation of carbon dioxide to quinazoline-2,4(1H,3H)-diones

Ya-Nan Zhao, Bing Yu, Zhen-Zhen Yang, and Liang-Nian He*

TBD-functionalized Fe_3O_4 was proved to be an efficient and recyclable magnetic heterogeneous catalyst for chemical fixation of CO_2 with 2-aminobenzonitriles under mild conditions.



Magnetic recycle:



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Magnetic base catalysts for chemical fixation of carbon dioxide to quinazoline-2,4(1*H*,3*H*)-diones

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Organic superbase-functionalized magnetic Fe_3O_4 was investigated to catalyze the fixation of CO_2 with 2-aminobenzonitriles, resulting in the synthesis of quinazoline-2,4(1*H*,3*H*)-diones. After optimization of various reaction parameters such as reaction time, solvent, temperature and CO_2 pressure, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) functionalized Fe_3O_4 was proved to be an efficient and recyclable magnetic heterogeneous catalyst for the synthesis of various quinazoline-2,4(1*H*,3*H*)-diones in reasonable yields (66%-93%), and could be recovered using an external magnetic field.

Introduction

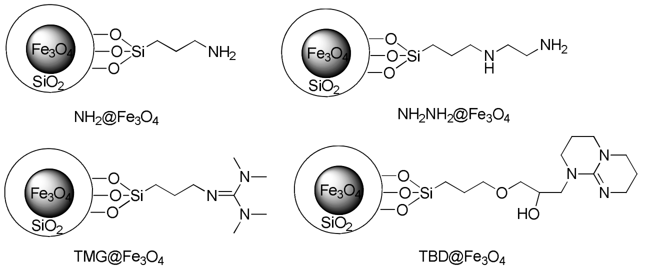
Being non-toxic, naturally abundant and economical feedstock, CO_2 can be regarded as an easily available renewable C_1 building block in organic synthesis.[1] In the last decades, several catalytic processes involving epoxides, aziridines, propargylic amines and propargylic alcohols for CO_2 fixation have emerged.[2]

Quinazoline-2,4(1*H*,3*H*)-diones have been widely used in the biological and pharmaceutical industry.[3] Various synthetic routes have been reported to obtain quinazoline-2,4(1*H*,3*H*)-diones, especially the reactions of anthranilic acid with urea,[4] anthranilamide with phosgene,[5] anthranilic acid with potassium cyanate[6] and chlorosulfonyl isocyanate.[7] Recently, alternative methods, such as microwave-assisted synthesis[8] or metal involved methods[9] were developed to avoid the use of high toxic reagents and alleviate harsh reaction conditions. However, the cyanate reagent is still required in those process. Notably, quinazoline-2,4(1*H*,3*H*)-diones can also be obtained from the reaction of 2-aminobenzonitriles and CO_2, which presents greener procedures circumventing the use of hazardous C_1 resource.

In 2000, Mizuno and co-workers[10] reported the stoichiometric amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) mediated atom-efficient synthesis of quinazoline-2,4(1*H*,3*H*)-diones from 2-aminobenzonitriles and CO_2. To date, kinds of base catalysts have been developed for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO_2 and 2-aminobenzonitriles, such as homogeneous catalysts including DBU,[11] 1,1,3,3-tetramethylguanidine (TMG),[12] $TBA_2[WO_4]$ (TBA = tetra-*n*-butylammonium),[13] ionic liquids (i.e. [Bmim][OH], [Bmim][Ac], [HDBU][TFE]),[14] and heterogeneous catalysts, for example MgO/ZrO_2,[15] Cs_2CO_3,[16] amidine moiety supported polymer[17] and amine functionalized MCM-41.[18] In particular, Han *et al* recently performed the reaction in aqueous media without any additional catalyst.[19] However, those existed catalytic systems have several limitations in most cases including higher pressure of CO_2, or limitation in catalyst reusability. Consequently, development of efficient and recyclable catalysts are still highly desirable and valuable.

Compared to homogeneous catalysts, heterogeneous catalysts are easy to handle and facilely recovered from the resultants.[20] Thus, designing alternative types of sustainable heterogeneous catalysis in the synthesis of chemicals and pharmaceuticals is gaining increasing importance.[21] On the other hand, magnetite is an ideal support, which is easy to prepare, separate and functionalize, as well as low toxic and inexpensive.[22] These attractive features have made magnetic Fe_3O_4 (magnetite) a promising catalyst support alternative to porous and mesoporous materials. Recently, the direct use of magnetic Fe_3O_4 as a magnetically reusable catalyst has been successfully developed for a variety of fundamental reactions.[23]

As our continuous interest in chemical fixation of CO_2, we developed organic superbase-functionalized Fe_3O_4 (base@Fe_3O_4, Scheme 1) for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones using CO_2 as a sustainable synthon. Notably, TBD@Fe_3O_4 displayed high catalytic activity in toluene. More importantly, the catalyst can be recovered by magnetic separation and reused for four times.



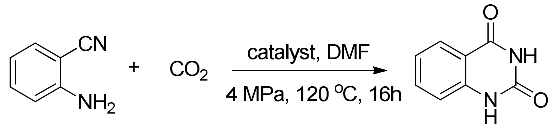
Scheme 1 The magnetic catalysts used in this study

Results and discussion

In the preliminary study, the reaction of 2-aminobenzontrile with CO_2 for the preparation of quinazoline-2,4(1*H*,3*H*)-dione was chosen as the model reaction to evaluate the different magnetic catalysts. A series of magnetic catalysts were prepared according to the published procedures[23b] (see Experiment section). The base content in these magnetic catalysts determined by element analysis, e.g. TBD in TBD@Fe_3O_4 was found to be 4.7 wt% (see Supporting Information).

The synthesis of quinazoline-2,4(1*H*,3*H*)-dione was carried out in the presence of a series of base-functionalized magnetic Fe_3O_4 under identical reaction conditions. As seen from Table 1, about 64% yield of the desired quinazoline-2,4(1*H*,3*H*)-dione was obtained in the presence of 10 mol% of TBD@Fe_3O_4 magnetic catalyst (entry 1). And the catalytic efficiency decreased with the trend of : TBD@Fe_3O_4 > TMG@Fe_3O_4 > NH_2NH_2@Fe_3O_4 > NH_2@Fe_3O_4, which is probably relative to the basicity (entries 1-4). Then, the influence of catalyst loading was also investigated (entries 5 and 6). 10 mol% of TBD@Fe_3O_4 showed higher catalytic performance than 5 mol% of TBD@Fe_3O_4 (entry 1 *vs* 5). Further increasing the amount of catalyst gave no promotion for catalytic activity (entry 1 *vs* 6). TBD@Fe_3O_4 (10 mol%) showed the highest catalytic activity among the catalysts screening, and accordingly TBD@Fe_3O_4 was chosen as the optimal catalyst for further investigation. Importantly, Fe_3O_4 was found to be inactive (entry 7). Using TBD as catalyst under identical conditions gave the product with similar yield as TBD@Fe_3O_4 (entry 1 v*s* 8), suggesting that the reaction is catalyzed by the basic moieties.

Table 1 Synthesis of quinazoline-2,4(1*H*,3*H*)-diones by various base@Fe_3O_4[a]

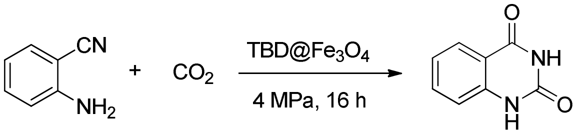


Entry	Catalysts	Catalysts loading /mol%	Isolated Yield/%
1	TBD@Fe_3O_4	10	64
2	TMG@Fe_3O_4	10	35
3	NH_2NH_2@Fe_3O_4	10	18
4	NH_2@ Fe_3O_4	10	11
5	TBD@Fe_3O_4	5	45
6	TBD@Fe_3O_4	20	66
7	Fe_3O_4	10	0
8	TBD	10	66

[a]Reaction conditions: 2-aminobenzonitrile (0.5 mmol, 0.0591 g), catalyst (10 mol%), DMF (1 mL), CO_2 (4 MPa), 140 °C, 16 h.

As listed in Table 2, the effects of various solvents and temperature on reaction of CO_2 with 2-aminobenzonitrile were investigated. Among solvents investigation, toluene was demonstrated to be the most efficient solvent. The reactions in N,N-dimethylformamide (DMF), methanol, and toluene at 140 °C gave quinazoline-2,4(1*H*,3*H*)-dione in 64%, 58%, 60% yield, respectively (entries 1-3). Whereas, dimethyl sulfoxide (DMSO) was an ineffective solvent (entry 4). Decreasing the temperature to 120 °C, the yield was dropped in most solvents except toluene (entries 5-7). The isolated yield was drop to 26%, possibly due to the loss of base at higher temperature in polar solvent. On the other hand, better solubility of the catalyst and substrates than products in toluene which could be beneficial to further promote the balance to the right. Whereas, there was a sharp decrease of the yield at 100 °C using toluene as solvent, which may be attributed to the inadequate reaction energy (entry 8). These results revealed that the appropriate reaction temperature would be 120 °C using toluene as solvent.

Table 2 The influence of solvents and reaction temperature[a]

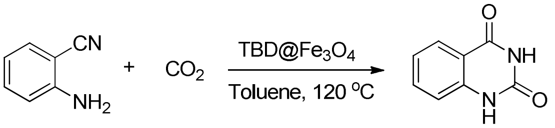


Entry	Solvent	T/°C	Isolated Yield/%
1	DMF	140	64
2	Methanol	140	58
3	Toluene	140	60
4	DMSO	140	13
5	DMF	120	26
6	Methanol	120	37
7	Toluene	120	66
8	Toluene	100	13

[a]Reaction conditions: 2-aminobenzonitrile (0.5 mmol, 0.0591 g), catalyst (10 mol%, 0.1468 g), solvent (1 mL), CO_2 (4 MPa), 16 h.

Next, the amount of toluene and other reaction parameters were examined. As summarized in Table 3, 1.0 mL of toluene as solvent gave a better yield (entries 1 *vs* 2). On the other hand, catalytic activity was sensitive to CO_2 pressure (entries 1, 3 and 4). Increasing CO_2 pressure up to 6 MPa, the isolated yield decreased to 63%. However, a lower yield of 38% was obtained by decreasing the pressure of CO_2 to 2 MPa. Hence, 4 MPa of CO_2 was the suitable pressure. In addition, only a slight improvement was achieved through prolonging the reaction time to 24 h (entry 1 *vs* 5).

Table 3 Optimization of the reaction condtions[a]



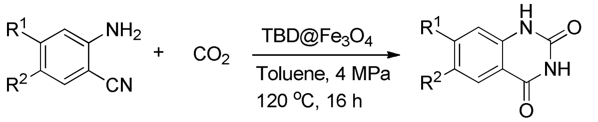
Entry	Pressure /MPa	Time /h	Isolated Yield/%
1	4	16	66
2[b]	4	16	58
3	6	16	63
4	2	16	38
5	4	24	70
6[c]	4	16	63
7[d]	4	16	59
8[e]	4	16	43

[a] Reaction conditions: 2-aminobenzonitrile (0.5 mmol, 0.0591 g), catalyst (10 mol%, 0.1468 g), toluene (1 mL);
[b] 0.5 mL of toluene was used;
[c] The catalyst was recovered for the second run;
[d] The catalyst was recovered for the third run;
[e] The catalyst was recovered for the fourth run;

In addition, the stability and reusability of this catalyst was also examined. When TBD@Fe_3O_4 was recovered from the reaction mixture using a magnet, and reused under the identical conditions, we obtained the expected product in 63% yield. However, in the fourth run, there is a slight decrease in the catalytic activity (entries 7-9, Table 3).

Having established the optimal conditions, we then converted a variety of commercially available 2-aminobenzionitriles with electron-donating and electron-withdrawing group and CO_2 into the corresponding quinazolidine-2,4(1*H*,3*H*)-diones to further explore the scope of this protocol. Various quinazolidine-2,4(1*H*,3*H*)-diones were formed in good to excellent isolated yields (entries 1-6, Table 4), employing TBD-functionalized magnetic Fe_3O_4 as catalyst. The substrate with electron-donating group *i.e.* 2-amino-4,5-dimethoxybenzonitrile gave 77% yield of 6,7-dimethoxyquinazoline-2,4(1*H*,3*H*)-dione, which is a key intermediate for preparation of prazosin, iodoazidoaryl prazosin (IAAP), and doxazosin (entry 2).[24] 4-Halogen substituted 2-aminobenzonitrile showed less reactivity compared with 5-halogen substituted substrate (entry 3 *vs* 4-6), possibly owing to electron withdrawing effect on the basicity. In addition, 5-halogen substituted 2-aminobenzonitriles were converted into the corresponding quinazoline-2,4(1*H*,3*H*)-diones in excellent yields in the following order : Cl > F > Br (entries 4-6).

Table 4 Synthesis of various quinalidine-2,4(1*H*,3*H*)-diones[a]



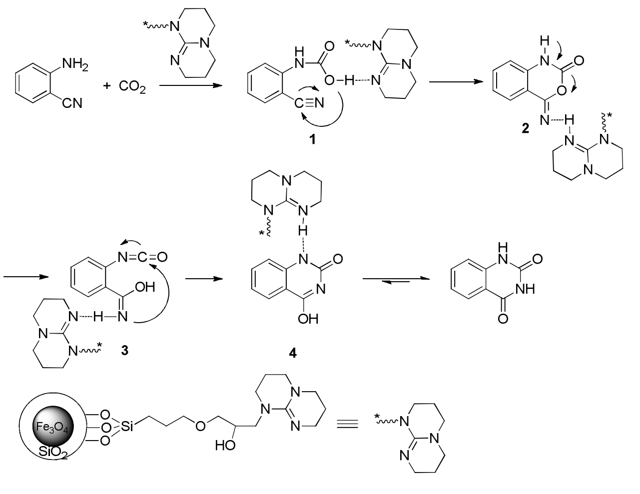
Entry	R^1	R^2	Isolated yield/%
1	H	H	66
2	OMe	OMe	77
3	Cl	H	68
4	H	Cl	93
5	H	Br	80
6	H	F	90

[a]Reaction conditions: substrate (0.5 mmol), catalyst (10 mol%, 0.1468 g) Toluene (1 mL), 120 °C, CO_2 (4 MPa), 16 h;

On the basis of previous studies[11-17] and experimental results, a plausible mechanism for the TBD@Fe_3O_4-catalyzed reaction of 2-aminobenzonitrile and CO_2 was proposed as depicted in Scheme 2. Firstly, the carbamate intermediate **1** is formed through base-promoted carbonylation of 2-aminobenzonitrile with CO_2. Then, **2** is given by intramolecular nucleophilic cyclization of **1**, followed by rearrangement to afford the isocyanate species **3**. Through an intramolecular cyclization of **3**, **4** could be generated. Finally, the target product quinazolidine-2,4(1*H*,3*H*)-dione is formed by means of isomerization involving proton transfer.

Conclusion

In summary, TBD@Fe_3O_4 was developed as an efficient magnetic heterogeneous catalyst for the synthesis of various quinazoline-2,4(1*H*,3*H*)-diones by chemical fixation of CO_2 with 2-aminobenzonitriles. The catalyst used here is stable, easily synthesized with ease of separation by external magnetic field. The protocol was efficient for various electron-rich, electron-deficient 2-aminobenzonitriles, providing good to excellent yields of the desired quinazoline-2,4(1*H*,3*H*)-diones.



Scheme 2 The possible reaction pathway

Experimental

Materials

Various derivatives of 2-aminobenzonitrile, iron chloride hexahydrate and iron(II) chloride tetrahydrate were purchased from Sigma–Aldrich. The other organic and inorganic compounds from Tianjin Guangfu Fine Chemical Research Institute were used without further purification except for the solvents, which were distilled by the known method prior to use.

Methods

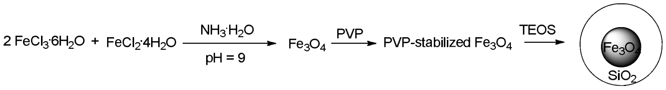
^1H NMR spectra was recorded at Bruker 400 spectrometer in d_6-DMSO and d_6-DMSO (2.50 ppm) was used as internal reference, ^{13}C NMR was record at 100.6 MHz in d_6-DMSO and d_6-DMSO (39.5 ppm) was used as internal reference. Element analysis was measured on vario EL CUBE. ESI-MS spectra were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. Melting points were measured on an X_4 apparatus and uncorrected. Infrared (IR) spectra were recorded on Bruker Tensor27 FT-IR spectrophotometer with KBr pellets. Transmission Electron Microscope (TEM) was recorded on Jem-2100f.

Typical procedure for the reaction of CO_2 and 2-aminobenzonitrile

In a typical experiment, to a 25 mL autoclave reactor was charged with 2-aminobenzonitrile (0.5 mmol, 0.059 g), the catalyst (10 mol%), and toluene (1 mL). A certain amount of CO_2 was introduced into the autoclave and the mixture was heated to 120 °C. Then CO_2 pressure was adjusted to 4 MPa and the reaction was run under stirring for 16 h. When the reaction finished, the reactor was cooled in ice-water and CO_2 was ejected slowly. After treated with DMF, the residue was evaporated in vacuum to yield crude product and the catalyst was recovered by magnetism. The crude product was washed with *t*-BuOMe and dried at 80 ^oC under vacuum. The product was further identified by NMR and ESI-MS (See Supplementary Information) being consistent with those reported in the literature.

Preparation of organic superbase-functionalized magnetic catalysts:

Synthesis of PVP-stabilized magnetite nanoparticles



Firstly, the magnetic (Fe_3O_4) particles were prepared in co-precipitation according to the procedure reported before.[25,23b] The mixture of $FeCl_3$•$6H_2O$ (22.0 g, 81.4 mmol) and $FeCl_2$•$4H_2O$ in deionized water (120 mL) was heated to 85 ^oC under nitrogen, and pH value was adjusted to 9 by concentrated NH_3•H_2O. Then, the mixture was washed to 7 by deionized water after four hours. The black precipitate was collected by a permanent magnetic field beside the reaction flask and the upper solution was separated. The sediment was dispersed in deionized water (100 mL), following the addition of 8.8 mL aqueous PVP (Polyvinylpyrrolidone) (25.6 g/L). After stirring for 1 day at room temperature, the PVP-stabilized magnetic particles were separated by a permanent magnetic field just as previous step. The magnetic precipitated particles was rinsed by EtOH for twice and dried in vacuum.

The synthesis of SiO_2-coated magnetite nanoparticles[26]

To a stirred mixture of PVP stabilized magnetic particles (2 g) in 400 mL EtOH, NH_3•H_2O (12 mL) and Tetraethyl orthosilicate (TEOS) (4.0 mL) was added successively. The resulting suspension was stirred for 24 h and then the black magnetic precipitate was separated with a permanent magnetic field. After washed with EtOH three times, the black product was dried and stored in vacuum. The content of N is less than 0.3 % determined by elemental analysis. The TEM shows that the magnetic Fe_3O_4 (< 20 nm particle size (TEM)) was wrapped with SiO_2 successfully (Figure 1).

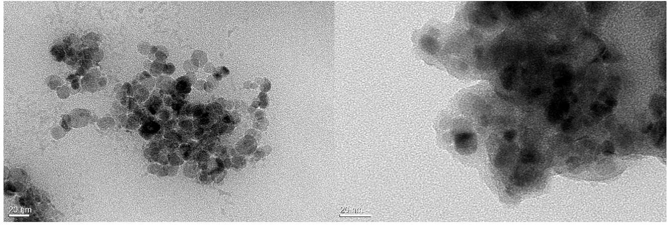
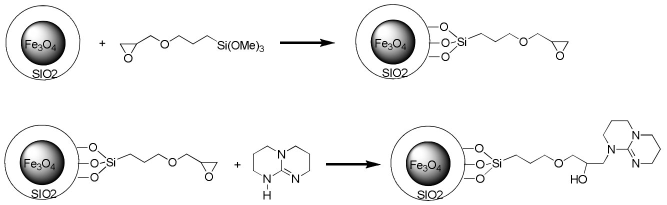


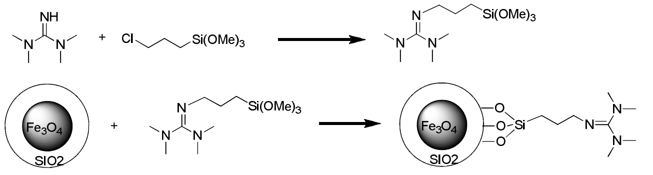
Figure 1 TEM image of (left) Fe_3O_4 and SiO_2 coated Fe_3O_4 (right) (All the samples were prepared in H_2O)

Synthesis of TBD-functionalized Fe_3O_4 (TBD@Fe_3O_4)[27]



To a suspension of SiO_2-coated magnetite particles (5 g) in toluene (60 mL), 3-glycidyloxypropyltrimethoxysilane (10 mmol, 2.36 g) was added. The mixture was refluxed for 2 d at 110 ^oC and then cooled down to room temperature. The magnetic product was sedimented by magnetic field and washed with EtOH for three times. The obtained particle was dried in vacuum for 8 h at 80 ^oC. Then, the precipitate was dispersed in toluene (60 mL) and TBD (10 mmol, 1.39 g) was added. After refluxing at 110 ^oC for 2 days, the product was separated by magnetic field and rinsed three times with EtOH. At last, the obtained particles were dried in vacuum for 8 h at 80 ^oC. The catalyst loading was determined to be 0.3405 mmol/g according to elemental analysis. IR spectrum (KBr, cm^{-1}): 3388, 3208, 1628, 1095.

Synthesis of TMG-functionalized Fe_3O_4 (TMG@Fe_3O_4)



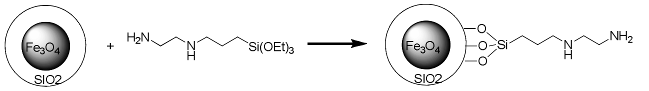
Preparation of 1,1,3,3-tetramethyl-2-(3-trimethoxysilylpropyl)-guanidine [28]

To a round-bottom flask was added TMG (17.39 g, 0.151 mol) and xylene (1.8 mL) under nitrogen. The system was heated up to 120 ^oC and maintained at this temperature for 2 h. Then (3-chloropropyl)trimethoxysilane (14.93 g, 0.076 mol) was added dropwise over 2 h. After heating at 120 ^oC for 7 h under nitrogen, the resulting mixture was cooled down to room temperature. Then 1,1,3,3-tetramethyl-2-(3- trimethoxy silylpropyl)-guanidine was obtained after distilling the filtrated liquid under reduced pressure.

Preparation of TMG@Fe_3O_4 [23a]

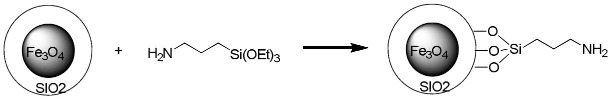
To a suspension of SiO_2-coated magnetite particles (0.32 g) in toluene (100 mL), 1,1,3,3-tetramethyl-2-(3-trimethoxy silylpropyl)-guanidine (5 mL) was added. The mixture was stirred for 24 h at room temperature. the TMG@Fe_3O_4 was isolated by using permanent magnet and rinsed with 30 mL EtOH for six times. The product was dried in vacuum for 8 h at 80 ^oC. The catalyst loading was determined to be 0.1833 mmol/g by elemental analysis. IR spectrum (KBr, cm^{-1}): 3179, 2984, 2951, 1611, 1090.

Synthesis of NH_2NH_2@Fe_3O_4[23a]



To a suspension of SiO_2-coated magnetite particles (0.32 g) in toluene (100 mL), N-[3-(Trimethoxysilyl) propyl] ethylene diamine (5 mL) was added. The mixture was stirred for 24 h at room temperature. the NH_2NH_2@Fe_3O_4 was collected using magnetic decantation and rinsed with 30 mL EtOH for six times. The product was dried in vacuum for 8 h at 80 ^oC. The loading of the catalyst was determined to be 0.899 mmol/g by elemental analysis. IR spectrum (KBr, cm^{-1}): 3389, 2921, 2848, 1622, 1092

Synthesis of $NH_2@Fe_3O_4$[23a]



To a suspension of SiO_2-coated magnetite particles (0.32 g) in toluene (100 mL), 3-Aminopropyltriethoxy-silane (5 mL) was added. The mixture was stirred for 24 h at room temperature. $NH_2@Fe_3O_4$ was collected using magnetic decantation and rinsed with 30 ml EtOH for six times. The product was dried in vacuum for 8 h at 80 ^oC. The catalyst loading was determined to be 0.600 mmol/g by elemental analysis. IR spectrum (KBr, cm^{-1}): 3382, 2973, 2890, 1630, 1071

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Notes and references

[a] State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, People’s Republic of China
Electronic Supplementary Information (ESI) available: Characterization products and copies of the NMR spectra. See DOI: 10.1039/b000000x/

1. For reviews on carbon dioxide transformation, see: a) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107,** 2365; b) M. Aresta and A. Dibenedetto, *Dalton Trans*., 2007, 2975; c) I. Omae, *Catal. Today*, 2006, **115**, 33; d) Z. Z. Yang, L. N. He, J. Gao, A. H. Liu and B. Yu, *Energy Environ. Sci.*, 2012, **5**, 6602.
2. S. Hayao, H. J. Havera, W. G. Strycker, T. J. Leipzig, R. A. Kulp and H. E. Hartzler, *J. Med. Chem.*, 1965, **8**, 807.
3. a) R. K. Russell, J. B. Press, R. A. Rampulla, J. J. McNally, R. Falotico, J. A. Keiser, D. A. Bright and A. Tobia, *J. Med. Chem.*, 1988, **31**, 1786; b) J. D. Prugh, G. D. Hartman, P. J. Mallorga, B. M. McKeever, S. R. Michelson, M. A. Murcko, H. Schwam, R. L. Smith, J. M. Sondey, *J. Med. Chem.*, 1991, **34**, 180; c) E. Mounetou, J. Legault, J. Lacroix, and R. Gaudreault, *J. Med. Chem.*, 2001, **44**, 694; d) G. Pastor, C. Blanchard, C. Montginoul, E. Torreilles, L. Giral, A. Texier, *Bull. Soc. Chim. Fr.*, 1975, 1331.
4. M. Michman, S. Patai, Y. Wiesel, *Org. Prep. Proced. Int.*, 1978, **10**, 13.
5. N. A. Lange and F. E. Sheibley, *Org. Synth.*, 1943, **2**, 79.
6. H. Vorbrtlggen and K. Krolikiewicz, *Tetrahedron*, 1994, **50**, 6549.
7. F. Nikpour and T. Paibast, *Chem. Lett.*, 2005, **34**, 1438.
8. L. Gouilleux, J. A. Fehrentz, F. Winternitz and J. Martinez, *Tetrahedron Lett*. 1996, **37**, 7031.
9. H. P. Choo, M. Kim, S. K. Lee, S. W. Kim and I. K. Chung, *Bioorg. Med. Chem. Lett*. 2002, **10**, 517.
10. T. Mizuno, N. Okamoto, T. Ito and T. Miyata, *Tetrahedron Lett.*, 2000, **41**, 1051.
11. a) T. Mizuno and Y. Ishino, *Tetrahedron,* 2002, **58**, 3155; b) T. Mizuno, T. Iwai and Y. Ishino, *Tetrahedron Lett.*, 2004, **45**, 7073; c) T. Mizuno, N. Okamoto, T. Ito and T. Miyata, *Heteroatom Chem.*, 2000, **11**, 428; d) T. Mizuno, M. Mihara, T. Nakai and T. Iwai, *Synthesis,* 2007, **16**, 2524.
12. J. Gao, L. N. He, C. X. Miao, S. Chanfreau, *Tetrahedron*, 2010, **66**, 4063.
13. a) T. Kimura, K. Kamata and N. Mizuno, *Angew. Chem. Int. Ed*, 2012, **51**, 6700; b) T. Kimura, H. Sunaba, K. Kamata and N. Mizuno, *Inorg. Chem.*, 2012, **51**, 13001.
14. For selective examples promoted by ionic liquid, see: a) Y. P. Patil, P. J. Tambade, K. M. Deshmukh and B. M. Bhanage, *Catal. Today*, 2009, **148**, 355; b) W. Lu, J. Ma, J. Hu, J. Song, Z. Zhang, G. Yang and B. Han, *Green Chem.*, 2014, **16**, 221; c) Y. Zhao, B. Yu, Z. Yang, H. Zhang, L. Hao, X. Gao and Z. Liu, *Angew. Chem. Int. Ed.*, 2014, **53**, 5922.
15. Y. P. Patil, P. J. Tambade, K. D. Parghi, R. V. Jayaram and B. M. Bhanage, *Catal. Lett.*, 2009, **133**, 201.
16. Y. P. Patil, P. J. Tambade, S. R. Jagtapa and B. M. Bhanagea, *Green Chem. Lett. Rev.*, 2008, **1**, 127.
17. D. Nagai, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 653.
18. D. B. Nalea, S. Ranab, K. Paridab and B. M. Bhanagea, *Catal. Sci. Technol.*, 2014, **4**, 1608.
19. J. Ma, B. X. Han, J. Song, J. Hu, W. Lu, D. Yang, Z. Zhang, T. Jiang and M. Hou, *Green Chem.*, 2013, **15**, 1485.
20. For reviews on heterogeneous catalysis, see: a) A. Corma, *J. Catal.*, 2003, **216**, 298; b) M. B. Gawande, R. K. Pandey and R. V. Jayaram, *Catal. Sci. Technol*., 2012, **2**, 1113; c) M. J. Climent, A. Corma and S. Iborra, *Chem. Rev.*, 2010, **111**, 1072, and references therein.
21. a) B. M. Trost, *Science*, 1991, **254**, 1471; b) P. T. Anastas and J. C. Warner, Green Chemistry: Theory and Practice; Oxford University Press: Oxford, 1998; c) J. F. Jenck, F. Agterberg and M. J Droescher, *Green Chem.,* 2004, **6**, 544.
22. a) S. Sun and H. Zeng, *J. Am. Chem. Soc*. 2002, **124**, 8204; b) S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst, R. N. Muller, *Chem. Rev.* 2008, **108**, 2064.
23. a) T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores and C. Li, *Org. lett.*, 2011, **13**, 442; b) X. Zheng, S. Luo, L. Zhang and J. P. Cheng, *Green Chem.*, 2009, **11**, 455; c) S. E. García-Garrido, J. Francos, V. Cadierno, J. M. Basset and V. Polshettiwar, *ChemSusChem*, 2011, **4**, 104; d) K. V. S. Ranganath, J. Kloesges, A. H. Schäfer and F. Glorius, *Angew. Chem. Int. Ed.*, 2010, **49**, 7786.
24. a) P. A. Zunszain, C. Federico, M. Sechi, S. Al-Damluji and C. R. Ganellin, *Bioorg. Med. Chem.*, 2005, **13**, 3681; b) M. B. Andrus, S. N. Mettath, and C. Song, *J. Org. Chem.*, 2002, **67**, 8284; c) S. F. Campbell, M. J. Davey, J. D. Hardstone, B. N. Lewis and M. J. Palmer, *J. Med. Chem.* 1987, **30**, 49.
25. a) A. Bee, R. Massart, S. Neveu, *J. Magn. Magn. Mater.*, 1995, **149**, 6; b)T. J. Yoon, J. S. Kim, B. G. Kim, K. N. Yu, M. H. Cho and J. K. Lee, *Angew. Chem. Int. Ed.*, 2005, **44**, 1068; c) S. Luo, X. Zheng and J. P. Cheng, *Chem. Commun.*, 2008, 5719.
26. M. Shokouhimehr, Y. Piao, J. Kim, Y. Jang and T. Hyeon, *Angew. Chem. Int. Ed.*, 2007, **46**, 7039.
27. M. L. Kantam and P. Sreekanth, *Catal. Lett.*, 2001, **77**, 241.

28. a) H. Q. Yang, Z. C. Ma, Y. Qing, G. Y. Xie, J. Gao, L. Zhang, J. H. Gao and L. Du, *Appl. Catal. A: Gen.*, 2010, **382**, 312; b) H. Yang, B. X. Han, Z. Ma, R. Wang, J. Liu and X. Ji, *Green Chem.* 2010, **12**, 441.