

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

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Organic superbase-functionalized magnetic Fe₃O₄ was investigated to catalyze the fixation of CO₂ 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 CO₂ pressure, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)-functionalized Fe₃O₄ was proven 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 it could be recovered using an external magnetic field.

Introduction

Being non-toxic, naturally abundant and an economical feed-stock, CO₂ can be regarded as an easily available renewable C₁ building block in organic synthesis.¹ In the last few decades, several catalytic processes for CO₂ fixation, involving epoxides, aziridines, propargylic amines and propargylic alcohols, have emerged.²

Quinazoline-2,4(1*H*,3*H*)-diones have been widely used in the biological and pharmaceutical industries.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 cyanate⁶ and chlorosulfonyl isocyanate.⁷ Recently, alternative methods, such as microwave-assisted synthesis⁸ or methods involving metals⁹ have been developed to avoid the use of highly toxic reagents and to alleviate harsh reaction conditions. However, the cyanate reagent is still required in these processes. Notably, quinazoline-2,4(1*H*,3*H*)-diones can also be obtained from the reaction of 2-aminobenzonitriles and CO₂, which involves greener procedures circumventing the use of the hazardous C₁ resource.

In 2000, Mizuno and co-workers¹⁰ reported stoichiometric amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) from the mediated atom-efficient synthesis of quinazoline-2,4(1*H*,3*H*)-diones from 2-aminobenzonitriles and CO₂. To date, a number of base catalysts have been developed for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO₂ and 2-aminobenzonitriles, such as homogeneous catalysts, including DBU,¹¹ 1,1,3,3-tetramethylguanidine (TMG),¹² TBA₂[WO₄] (TBA = tetra-*n*-butylammonium),¹³ ionic liquids (*i.e.* [Bmim][OH],

[Bmim][Ac], [HDBU][TFE]),¹⁴ and heterogeneous catalysts such as MgO/ZrO₂,¹⁵ Cs₂CO₃,¹⁶ amidine moiety supported polymer¹⁷ and amine functionalized MCM-41.¹⁸ In particular, Han *et al.* recently performed the reaction in aqueous media without any additional catalyst.¹⁹ However, these catalytic systems have several limitations in most cases, including higher pressure of CO₂, or a limitation in catalyst reusability. Consequently, the development of efficient and recyclable catalysts is still highly desirable and valuable.

Compared to homogeneous catalysts, heterogeneous catalysts are easy to handle and can be readily recovered from the resultant reaction products.²⁰ Thus, the design of 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; moreover, it is inexpensive and has low toxicity.²² These attractive features have made magnetic Fe₃O₄ (magnetite) a promising catalyst support alternative to porous and mesoporous materials. Recently, the direct use of magnetic Fe₃O₄ as a magnetically reusable catalyst has been successfully developed for a variety of fundamental reactions.²³

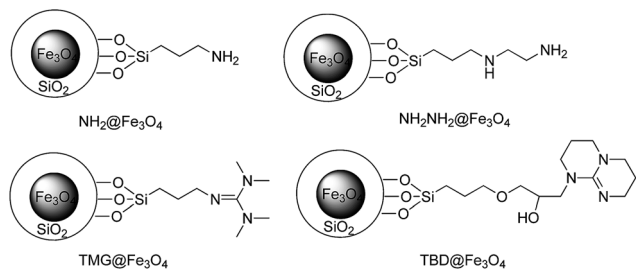
As part of our continuous interest in the chemical fixation of CO₂, we developed organic superbase-functionalized Fe₃O₄ (base@Fe₃O₄, Scheme 1) for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones using CO₂ as a sustainable synthon. Notably, TBD@Fe₃O₄ displayed a high catalytic activity in toluene. More importantly, the catalyst can be recovered by magnetic separation and reused up to four times.

Results and discussion

In the preliminary study, the reaction of 2-aminobenzonitrile with CO₂ 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

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Scheme 1 The magnetic catalysts used in this study.

according to the published procedures^{23b} (see Experimental section). The base content in these magnetic catalysts was determined by elemental analysis, *e.g.* TBD in TBD@Fe₃O₄ was found to be 4.7 wt% (see ESI†).

The synthesis of quinazoline-2,4(1*H*,3*H*)-dione was carried out in the presence of a series of base-functionalized magnetic Fe₃O₄ 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@Fe₃O₄ magnetic catalyst (entry 1). The decrease in the catalytic efficiency shows the following trend: TBD@Fe₃O₄ > TMG@Fe₃O₄ > NH₂NH₂@Fe₃O₄ > NH₂@Fe₃O₄, which is probably relative to their basicity (entries 1–4). Then, the influence of the catalyst loading was also investigated (entries 5 and 6). 10 mol% of TBD@Fe₃O₄ showed a higher catalytic performance than 5 mol% of TBD@Fe₃O₄ (entry 1 *vs.* 5). Furthermore, increasing the amount of catalyst gave no promotion of catalytic activity (entry 1 *vs.* 6). TBD@Fe₃O₄ (10 mol%) showed the highest catalytic activity among the catalysts screened, and accordingly TBD@Fe₃O₄ was chosen as the optimal catalyst for further investigation. Importantly, Fe₃O₄ was found to be inactive (entry 7). Using TBD as a catalyst under identical conditions afforded the product with a similar yield as TBD@Fe₃O₄ (entry 1 *vs.* 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@Fe₃O₄^a

Entry	Catalyst	Catalyst loading/mol%	Isolated yield/%
1	TBD@Fe ₃ O ₄	10	64
2	TMG@Fe ₃ O ₄	10	35
3	NH ₂ NH ₂ @Fe ₃ O ₄	10	18
4	NH ₂ @Fe ₃ O ₄	10	11
5	TBD@Fe ₃ O ₄	5	45
6	TBD@Fe ₃ O ₄	20	66
7	Fe ₃ O ₄	10	0
8	TBD	10	66

^a Reaction conditions: 2-aminobenzonitrile (0.5 mmol, 0.0591 g), catalyst (10 mol%), DMF (1 mL), CO₂ (4 MPa), 140 °C, 16 h.

Table 2 The influence of solvents and reaction temperature^a

Entry	Solvent	<i>T</i> /°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), CO₂ (4 MPa), 16 h.

As listed in Table 2, the effects of various solvents and temperatures on the reaction of CO₂ with 2-aminobenzonitrile were investigated. Among the solvents investigated, toluene was demonstrated to be the most efficient solvent. The reactions in *N,N*-dimethylformamide (DMF), methanol, and toluene at 140 °C afforded quinazoline-2,4(1*H*,3*H*)-dione in 64%, 58%, and 60% yield, respectively (entries 1–3), whereas dimethyl sulfoxide (DMSO) was an ineffective solvent (entry 4). When the temperature was decreased to 120 °C, the yield reduced in most solvents except toluene (entries 5–7). The isolated yield reduced to 26%, possibly due to the loss of base at the higher temperature in the polar solvent. On the other hand, a better solubility of the catalyst and substrates than the products in toluene could be beneficial to further promote the balance to the right hand side of the equation. However, 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 most appropriate reaction temperature would be 120 °C using toluene as solvent.

Next, the amount of toluene and other reaction parameters were examined. As summarized in Table 3, 1.0 mL of toluene as solvent afforded a better yield (entries 1 *vs.* 2). On the other hand, catalytic activity was sensitive to CO₂ pressure (entries 1, 3 and 4). Raising the CO₂ pressure up to 6 MPa, the isolated yield decreased to 63%. However, a lower yield of 38% was obtained by decreasing the pressure of CO₂ to 2 MPa. Hence, 4 MPa of CO₂ appeared the most suitable pressure. In addition, only a slight improvement was achieved through prolonging the reaction time to 24 h (entry 1 *vs.* 5).

In addition, the stability and reusability of this catalyst was also examined. When TBD@Fe₃O₄ was recovered from the reaction mixture using a magnet, and reused under identical conditions, we obtained the expected product in a 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-aminobenzonitriles

Table 3 Optimization of the reaction conditions^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

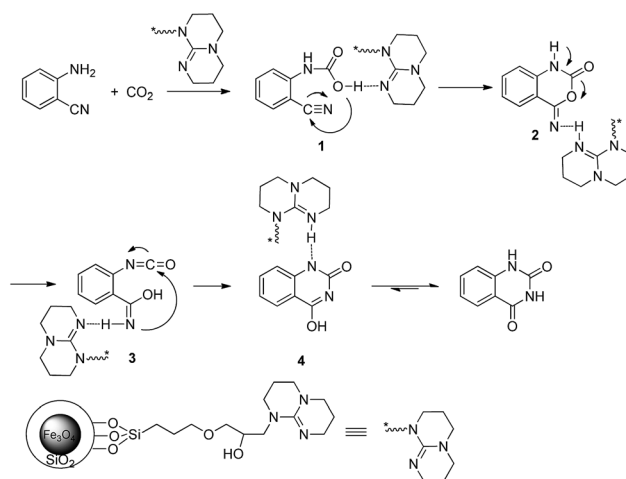
^a Reaction conditions: 2-aminobenzonitrile (0.5 mmol, 0.0591 g), catalyst (10 mol%, 0.1468 g), toluene (1 mL). ^b 0.5 mL of toluene was used. ^c The catalyst was recovered for the second run. ^d The catalyst was recovered for the third run. ^e The catalyst was recovered for the fourth run.

with electron-donating and electron-withdrawing groups and CO₂ 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 with good to excellent isolated yields (entries 1–6, Table 4) employing TBD-functionalized magnetic Fe₃O₄ as catalyst. The substrate with the electron-donating group, *i.e.* 2-amino-4,5-dimethoxybenzonitrile, afforded 6,7-dimethoxyquinazoline-2,4(1*H*,3*H*)-dione, which is a key intermediate for the preparation of prazosin, iodoazidoaryl prazosin (IAAP), and doxazosin (entry 2), in 77% yield.²⁴ 4-Halogen substituted 2-aminobenzonitrile showed less reactivity compared to the 5-halogen substituted substrate (entry 3 *vs.* 4–6), possibly because of the 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 quinazolidine-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, CO₂ (4 MPa), 16 h.



Scheme 2 The possible reaction pathway.

On the basis of previous studies^{11–17} and experimental results, a plausible mechanism for the TBD@Fe₃O₄-catalyzed reaction of 2-aminobenzonitrile and CO₂ was proposed, as depicted in Scheme 2. Firstly, the carbamate intermediate **1** is formed through the base-promoted carbonylation of 2-aminobenzonitrile with CO₂. Then, **2** is obtained by the 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@Fe₃O₄ was developed as an efficient magnetic heterogeneous catalyst for the synthesis of various quinazoline-2,4(1*H*,3*H*)-diones by the chemical fixation of CO₂ with 2-aminobenzonitriles. The catalyst used here is stable, easily synthesized and readily separated by an 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.

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 were recorded on a Bruker 400 spectrometer in *d*₆-DMSO, with *d*₆-DMSO (2.50 ppm) used as the internal reference; a ¹³C NMR was recorded at 100.6 MHz in *d*₆-DMSO, with *d*₆-DMSO (39.5 ppm) used as the internal reference. Elemental

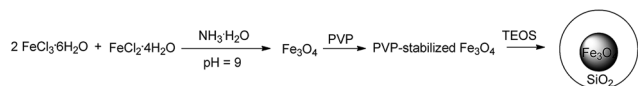
analyses were measured on a vario EL CUBE. ESI-MS spectra were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. Melting points were measured on an X₄ apparatus and uncorrected. Infrared (IR) spectra were recorded on a Bruker Tensor27 FT-IR spectrophotometer with KBr pellets. The Transmission Electron Microscope (TEM) was recorded on a Jem-2100f.

Typical procedure for the reaction of CO₂ and 2-aminobenzonitrile

In a typical experiment, 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 CO₂ was introduced into the autoclave and the mixture was heated to 120 °C. Then the CO₂ pressure was adjusted to 4 MPa, and the reaction was continued with stirring for 16 h. When the reaction completed, the reactor was cooled in ice-water and CO₂ was ejected slowly. After treatment with DMF, the residue was evaporated in a vacuum to obtain the crude product and the catalyst was recovered by magnetism. The crude product was washed with *t*-BuOMe and dried at 80 °C under vacuum. The product structure was identified by NMR and ESI-MS (see ESI†) being consistent with those reported in the literature.

Preparation of organic superbase-functionalized magnetic catalysts

Synthesis of PVP-stabilized magnetite nanoparticles.



Firstly, the magnetic (Fe₃O₄) particles were prepared in co-precipitation according to the procedure reported before.^{25,23b} The mixture of FeCl₃·6H₂O (22.0 g, 81.4 mmol) and FeCl₂·4H₂O in deionized water (120 mL) was heated to 85 °C under nitrogen, and the pH value was adjusted to 9 by adding concentrated NH₃·H₂O. Then, the mixture was washed to pH = 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) after the addition of 8.8 mL aqueous PVP (polyvinylpyrrolidone) (25.6 g L⁻¹). Similar to the previous step, after stirring for 1 day at room temperature, the PVP-stabilized magnetic particles were separated by a permanent magnetic field. The magnetic precipitated particles were rinsed by EtOH twice and dried in vacuum.

The synthesis of SiO₂-coated magnetite nanoparticles.²⁶ To a stirred mixture of PVP stabilized magnetic particles (2 g) in 400 mL EtOH, NH₃·H₂O (12 mL) and tetraethyl orthosilicate (TEOS) (4.0 mL) were added successively. The resultant suspension was stirred for 24 h, and then the black magnetic precipitate was separated by a permanent magnetic field. After being washed with EtOH three times, the black product was dried and stored in a vacuum. The content of N is less than 0.3%, as determined by elemental analysis. The TEM shows that the magnetic Fe₃O₄

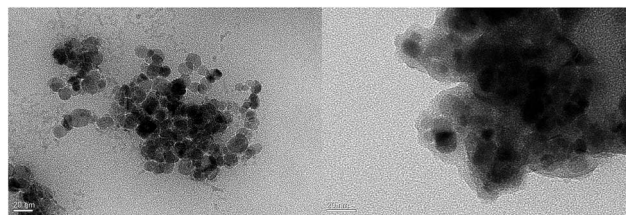
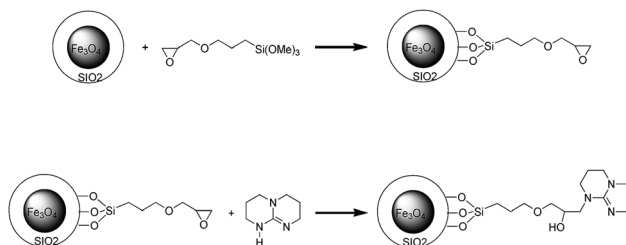


Fig. 1 TEM image of (left) Fe₃O₄ and SiO₂ coated Fe₃O₄ (right) (all the samples were prepared in H₂O).

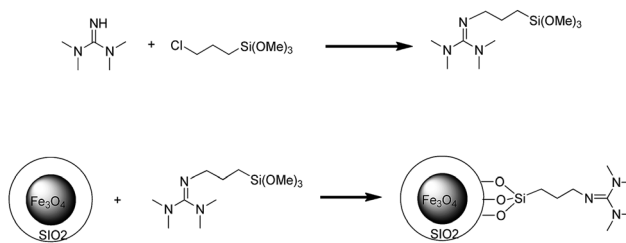
(<20 nm particle size (TEM)) was wrapped with SiO₂ successfully (Fig. 1).

Synthesis of TBD-functionalized Fe₃O₄ (TBD@Fe₃O₄).²⁷



To a suspension of SiO₂-coated magnetite particles (5 g) in toluene (60 mL), 3-glycidyloxypropyltrimethoxysilane (10 mmol, 2.36 g) was added. The mixture was refluxed for 2 days at 110 °C, and then cooled to room temperature. The magnetic product was sedimented by a magnetic field and washed with EtOH three times. The obtained particle was dried under vacuum for 8 h at 80 °C. Then, the precipitate was dispersed in toluene (60 mL), and TBD (10 mmol, 1.39 g) was added. After refluxing at 110 °C for 2 days, the product was separated by magnetic field and rinsed three times with EtOH. Finally, the obtained particles were dried in vacuum for 8 h at 80 °C. The catalyst loading was determined to be 0.3405 mmol g⁻¹ according to elemental analysis. IR spectrum (KBr, cm⁻¹): 3388, 3208, 1628, 1095.

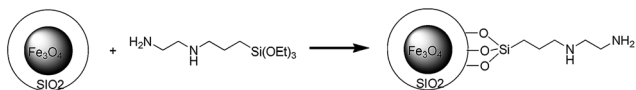
Synthesis of TMG-functionalized Fe₃O₄ (TMG@Fe₃O₄).



Preparation of 1,1,3,3-tetramethyl-2-(3-trimethoxysilylpropyl)guanidine.²⁸ To a round-bottomed flask, TMG (17.39 g, 0.151 mol) and xylene (1.8 mL) was added under nitrogen atmosphere. The system was heated up to 120 °C 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 °C for 7 h under nitrogen, the resultant mixture was cooled to room temperature. Then, 1,1,3,3-tetramethyl-2-(3-trimethoxysilylpropyl)guanidine was obtained after distilling the filtrated liquid under reduced pressure.

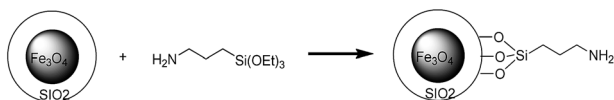
Preparation of TMG@Fe₃O₄.^{23a} To a suspension of SiO₂-coated magnetite particles (0.32 g) in toluene (100 mL), 1,1,3,3-tetra-methyl-2-(3-trimethoxy silylpropyl)-guanidine (5 mL) was added. The mixture was stirred for 24 h at room temperature. TMG@Fe₃O₄ was isolated by using a permanent magnet and rinsed with 30 mL EtOH six times. The product was dried in vacuum for 8 h at 80 °C. The catalyst loading was determined to be 0.1833 mmol g⁻¹ by elemental analysis. IR spectrum (KBr, cm⁻¹): 3179, 2984, 2951, 1611, 1090.

Synthesis of NH₂NH₂@Fe₃O₄.^{23a}



To a suspension of SiO₂-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. NH₂NH₂@Fe₃O₄ was collected using magnetic decantation and rinsed with 30 mL EtOH six times. The product was dried in vacuum for 8 h at 80 °C. The loading of the catalyst was determined to be 0.899 mmol g⁻¹ by elemental analysis. IR spectrum (KBr, cm⁻¹): 3389, 2921, 2848, 1622, 1092.

Synthesis of NH₂@Fe₃O₄.^{23a}



To a suspension of SiO₂-coated magnetite particles (0.32 g) in toluene (100 mL), 3-aminopropyltriethoxysilane (5 mL) was added. The mixture was stirred for 24 h at room temperature. NH₂@Fe₃O₄ was collected using magnetic decantation and rinsed with 30 mL EtOH six times. The product was dried in vacuum for 8 h at 80 °C. The catalyst loading was determined to be 0.600 mmol g⁻¹ by elemental analysis. IR spectrum (KBr, cm⁻¹): 3382, 2973, 2890, 1630, 1071.

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