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ARTICLE TYPE

Amine functionalized MCM-41: an efficient heterogeneous recyclable catalyst for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones from carbon dioxide and 2-aminobenzonitriles in water

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A simple covalently linked amine functionalized MCM-41 were investigated as a highly efficient, heterogeneous and recyclable mesoporous catalytic protocol for the synthesis of a wide variety of quinazoline-2,4(1*H*,3*H*)-diones derivatives from 2-aminobenzonitriles and carbon dioxide in aqueous reaction medium. This catalytic system represents a heterogeneous and environmentally benign protocol. The effect of various reaction parameters, such as influences of solvent, temperature, CO₂ pressure and time for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones were studied. The developed protocol can be applicable for the synthesis of most important key intermediate 6,7-dimethoxyquinazoline-2,4(1*H*,3*H*)-dione and several biologically active derivatives such as Prazosin, Bunazosin and Doxazosin. Besides this, the developed catalyst could be reused for five consecutive recycles without any significant loss in its catalytic activity. The catalyst amine functionalized MCM-41 were characterized by various characterization technique such as FT-IR, TGA/DTA, XRD, Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM), and solid state ²⁹Si CP MAS NMR analysis.

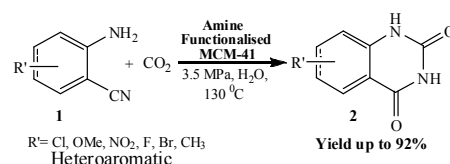
Introduction

Chemical fixation of carbon dioxide (CO₂) into valuable organic molecules is one of the most important and challenging subjects in synthetic organic chemistry from last two decades, owing to its economic and environmental benefits.¹ CO₂ as an abundant, nontoxic, easily available, and typical renewable C1 building block as well an important “greenhouse gas” has been drawing much more attention in the field of green chemistry and a sustainable society.² Now a days, CO₂ is used as a feedstock for the synthesis of variety of valuable organic compounds like dimethyl carbonate,³ cyclic carbonates,⁴ urethanes,⁵ polycarbonates,⁶ formic acids,⁷ *N,N'*-disubstituted ureas,⁸ and 5-aryl-2-oxazolidinones.⁹

Quinazoline-2,4(1*H*,3*H*)-diones are an important heterocyclic compounds in the pharmaceutical industries and biotechnology. They are also useful building blocks for the production of an active pharmaceutical intermediate, anti-diabetes agents, anti-hypertensive, anti-alpha adrenergic receptor and other biologically important compounds such as FK 366 (Zearestat), KF 31327 molecules, Prazosin (Minipress®), Bunazosin

(Detantol®) and Doxazosin (Cardenalin®).¹⁰

Traditionally, these quinazoline-2,4(1*H*,3*H*)-diones are synthesized *via* reaction of an anthranilic acid with urea,¹¹ anthranilic acid with potassium cyanate or chlorosulfonyl isocyanate,¹² anthranilamide with phosgene,¹³ aromatic amino nitriles with diethylformamide,¹⁴ methyl anthranilate with various iso(thio)cyanates,¹⁵ and 2-nitrobenzamide with CO.¹⁶ However, most of the existing methodologies have disadvantages such as requirement of some specialized and/or toxic reagents like phosgene and CO, required drastic reaction conditions, generate a stoichiometric amount of chemical waste. Considering these issues, few efforts were made to replace toxic reagents using incorporation of CO₂ into quinazoline-2,4(1*H*,3*H*)-diones derivatives. The development of green protocol by replacing toxic reagents for synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO₂ is still desired.¹⁷



Scheme 1 Synthesis of various quinazoline-2,4(1*H*,3*H*)-diones from substituted 2-aminobenzonitriles and carbon dioxide in aqueous medium.

The literature reveals that, quinazoline-2,4(1*H*,3*H*)-diones are synthesized by reacting 2-aminobenzonitrile with carbon dioxide using various catalytic protocols like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),¹⁸ Cs₂CO₃,^{17a} 1-butyl-3-

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methylimidazolium hydroxide [(Bmim)OH],^{17b} MgO/ZrO₂,^{17c} 1,1,3,3-tetramethylguanidine (TMG),¹⁹ *N*-methyl-tetrahydropyrimidine or poly(amidine),²⁰ monomeric tungstate TBA₂[WO₄]²¹ and [Bmim]Ac.²² Recently, Han and co-workers reported the synthesis of quinazoline-2,4(1*H*,3*H*)-diones by reacting 2-aminobenzonitrile with carbon dioxide using water as a solvent having drawback of higher reaction pressure, temperature, and longer reaction time.²³ Hence, by considering the economical value of the title reaction still there is a need to develop simple protocol which could minimize the number of waste streams and unit operations.

Recently, we observed that amine functionalized MCM-41 as a highly active catalysts for the activation of CO₂ due to its high surface area, tunable pore diameters, good mesoporous structural ordering, larger BET surface area, high porosities and a narrow pore size distribution,²⁴ and which was employed for the synthesis of selective carbamate derivatives.^{25–26} We visualized that the presence of amino as a functional groups on the catalyst MCM-41 have a great potential to accelerate the rate of reaction in forward direction by transforming CO₂ and 2-aminobenzonitriles into quinazoline-2,4(1*H*,3*H*)-diones derivatives. In the light of our ongoing efforts to widen new methods, we herein report an amine functionalized MCM-41 as well-organized, green, stable, recyclable and commercially feasible catalytic route for efficient synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO₂ and 2-aminobenzonitriles using water as a solvent under mild reaction conditions (Scheme 1).

Results and discussion

Catalyst characterization

The FT-IR absorption spectra of various amine functionalized MCM-41 catalysts are shown in Fig. S1 (see supporting information). The characteristic band at 1080–1250 cm⁻¹ is due to the Si–O stretching frequency in Si–O–Si structure of the catalyst. At 1620–1650 cm⁻¹ is the absorption band for H–O–H bending vibration of water. The spectrum has broad band around 3100–3600 cm⁻¹ due to the adsorbed water molecules. The presence of N–H bending vibration at 750 cm⁻¹ and –NH₂ symmetric bending vibration at 1532 cm⁻¹, indicate that the successful grafting of –NH₂ on the surface of the catalysts.

The organic content of the surface modified catalysts estimated by thermal gravimetric analysis are shown in Fig. S2 (see supporting information). Amine functionalized silica showed a higher mass loss signifying AEPTMS was functionalized on the surface of silica. The loss observed at 100 °C for desorption of water molecules, at 250 °C for the breakdown of amine and the removal of surfactant at 500 °C respectively.

The high angle powder X-ray diffraction (HA-XRD) pattern of the different amine loaded catalysts (14.6, 12.8, 10.2, 4.2 and 2.8 wt%) shown in Fig. S3(A) (see supporting information). The sample showed a distinctive mesoporous structures and packed in spherical symmetry with sharp peak of organic –NH₂ functional group of MCM-41 confirmed from TEM analysis. The prominent peak at 2θ ranging from 15° to 30° which was the same as the parent MCM-41. Hence, it shows very high dispersion of amine in a non-crystalline form on the surface of MCM-41.

Small angle X-ray diffraction (SA-XRD) pattern of standard MCM-41(a) and 14.6% AEPTMS@MCM-41(b) samples are shown in Fig. S3(B). The samples illustrate a typical mesoporous

structure of standard MCM-41 with three sharp peaks corresponding (100), (110) and (200) planes respectively. After AEPTMS loading, the intensity of the peak is somewhat reduced and peak position is to some extent shifted towards right but this material retained its mesoporosity like MCM-41.^{24a}

The morphology and particle size of the 14.6 wt% of triamine modified silica materials (AEPTMS) studied using SEM technique is shown in Fig. S4. The highest (14.6 wt%) of AEPTMS loaded on mesoporous silica it became spherical morphology and also the particles are well order arranged. It is also depends upon the concentration of the organic group. From lower wt% to higher wt% of organic amine group loaded on mesoporous silica, its morphology has been changed from kidney-bean-shaped like structure to spherical shaped.

The TEM of the 14.6 wt% AEPTMS modified MCM-41 is shown in Fig. S5 (see supporting information). From the figures, it is observed that hydrophobic organo-alkoxysilanes showed well organized mesopores packed in the hexagonal matrix and also confirmed that AEPTMS with the higher degree of functionalization as compared to lower 2.8 wt% of AEPTMS on the support surface.²⁷

Solid state ²⁹Si CP MAS NMR spectra provided the information of co-ordination environments of silicon elements in 14.6 wt% AEPTMS@MCM-41 materials shown in Fig. S6. In this spectra, the five individual peaks observed corresponding to Q⁴ [Si(OSi)₄], Q³ [Si(OSi)₃OH], Q² [Si(OSi)₂(OH)₂], T³ [RSi(OSi)₃] and T² [RSi(OSi)₂OH] at 112.02 ppm, 102.75 ppm, 94 ppm, 69.74 ppm and 57.49 ppm. The three peaks match to siloxane species of Q bands. Later, the presence of T² and T³ were also the confirmation to prove the amine group is on the silica skeleton. Hence, we confirmed the successful covalent grafting of amino (AEPTMS) group throughout Si–O–M linkage. In ²⁹Si NMR, the Tⁿ value increases from lower to higher wt%. So it is confirmed that higher degree of functionalization exists.²⁷

Catalytic activity of amine functionalized MCM-41 catalysts

We have prepared covalently linked five different wt% of amines loaded on the MCM-41 mesoporous catalysts such as 14.6, 12.8, 10.2, 4.2 and 2.8 wt% respectively, and its catalytic activities were studied for quinazoline-2,4(1*H*,3*H*)-diones synthesis, the typical results obtained are shown in Fig. 1.

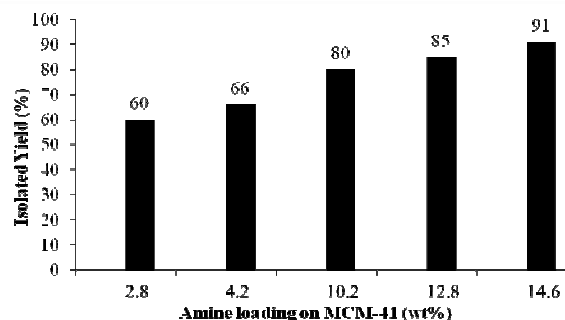


Fig. 1 Various loading of amine wt% on MCM-41^a

^aReaction conditions: 2-aminobenzonitrile (2 mmol), catalyst amine functionalized MCM-41 (12 wt% with respect to **1a**), water (5 mL), CO₂ pressure (3.5 MPa), temperature (130 °C), time (18 h).

The experiments were carried out in the absence of catalyst maintaining other reaction parameters unvarying, the desired product was not achieved (Table 1, entry 1), and indicating that amine functionalized MCM-41 was only responsible for the

respective transformation. Conversely, we observed that 14.6 wt% amine functionalized MCM-41 catalyst is the best to give up to 91% isolated yield (Fig. 1).

In order to optimize the reaction conditions, initial studies were conducted using amine functionalized MCM-41 (14.6 wt% amine loaded) as a choice of catalyst for synthesis of quinazoline-2,4(1*H*,3*H*)-diones from 2-aminobenzonitrile and CO₂ as a best representative model reaction. Various reaction parameters such as catalyst screening, catalyst loading, solvent, temperature, pressure and time were studied.

The reaction using various catalytic concentrations of amine functionalized MCM-41 (14.6 wt% amine loaded) was carried out and typical results are shown in Table 1 (entries 2–5). It was observed that the yield of **2a** was almost constant for 15 wt% and 12 wt% of the catalyst concentration (Table 1, entries 2–3). However, lowering the catalyst concentration provided less yield of **2a** (Table 1, entry 4–5). Thus, amine functionalized MCM-41 (14.6 wt% amine loaded) as the choice of catalyst was employed for further screening for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones.

Table 1 Effect of concentration of catalyst on the synthesis of quinazoline-2,4(1*H*,3*H*)-dione from 2-aminobenzonitrile and CO₂^a

Entry	Concentration of catalyst (wt%)	Yield (%) ^b
1	00	0
2	15	91
3	12	91
4	10	80
5	5	65

^aReaction conditions: 2-aminobenzonitrile (2 mmol), amine functionalized MCM-41 (14.6 wt% amine loaded) as a catalyst, water (5 mL), CO₂ pressure (3.5 MPa), 18 h at 130 °C. ^bIsolated Yield.

The solvents play an essential role in the reactivity and selectivity performance, thus, the choice of proper solvent is necessary. We observed that the reaction did not work under solvent free condition (Table 2, entry 1). Later, the various organic solvents were screened for this reaction. In ethanol and non-polar solvents like toluene, THF were found to be ineffective under the present reaction condition (Table 2, entries 2–4), whereas, highly polar solvent like DMF and water were found to give excellent (85%–91%) yield of **2a** (Table 2, entries 5–6). Interestingly, the reaction proceeded smoothly in water and providing an excellent yield (91%) of **2a**, which was comparably higher yield than other reported in literatures.¹⁹ In order to isolate the product from the reaction mixture we have chosen the DMF over the DMSO.

We have investigated the influence of temperature on the yield of **2a** by using the amine functionalized catalyst (14.6 wt% amine loaded) at 3.5 MPa CO₂ pressure ranging from 80 °C to 140 °C with a reaction time of 18 h (Fig. 2a). It was shown that the temperature had a significant role on the yield of the product (**2a**). As the temperature increases, the yield of **2a** was also increased from 45% to 91%. It was observed that at 120 °C the yield of desired product was quite low. With increasing the temperature to 130 °C, the desired product was obtained in 91% yield within 18 h. while further increasing the temperature to 140 °C, the yield remained constant even time increases to 24 h. Hence by evaluating above results, the good yield obtained was found to be at the optimal temperature 130 °C.

Table 2 Influences of solvent on the synthesis of quinazoline-2,4(1*H*,3*H*)-diones^a

Entry	Solvent	Yield (%) ^b
1	Neat	0
2	Toluene	0
3	Ethanol	0
4	THF	0
5	Water	91
6	DMF	85

^aReaction conditions: 2-aminobenzonitrile (2 mmol), catalyst (14.6 wt% amine loaded) amine functionalized MCM-41 (12 wt%), solvent (5 mL), CO₂ pressure (3.5 MPa), 18 h at 130 °C. ^bIsolated Yield.

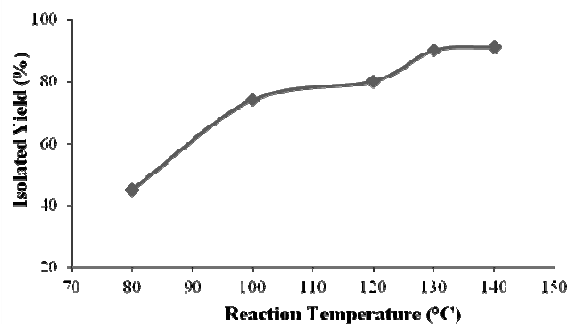


Fig. (a) The effect of reaction temperature (°C).

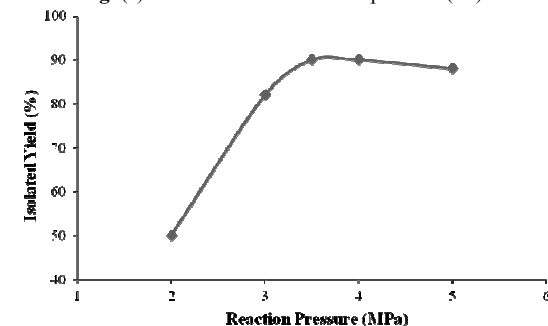


Fig. (b) The effect of reaction pressure (MPa).

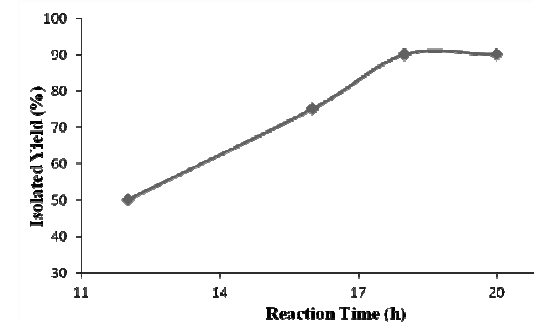


Fig. (c) The effect of reaction time (h).

Fig. 2 The influence of reaction parameters on the isolated yield of quinazoline-2,4(1*H*,3*H*)-dione (**2a**)^a

^aReaction conditions: (a) 2-aminobenzonitrile (2 mmol), catalyst (14.6 wt% amine loaded) amine functionalized MCM-41 (12 wt%), water (5 mL), CO₂ pressure (3.5 MPa) 18 h; (b) 2-aminobenzonitrile (2 mmol), catalyst (14.6 wt% amine loaded) amine functionalized MCM-41 (12 wt%), water (5 mL), 130 °C, 18 h; (c) 2-aminobenzonitrile (2 mmol), catalyst (14.6 wt% amine loaded) amine functionalized MCM-41 (12 wt%), water (5 mL), CO₂ pressure (3.5 MPa), 130 °C.


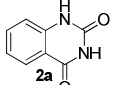
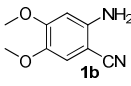
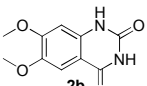
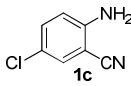
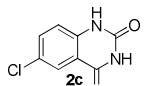

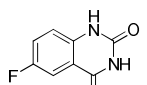

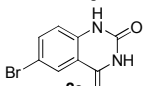
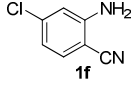
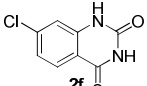

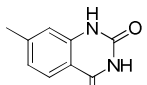

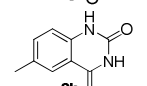

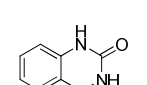
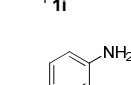
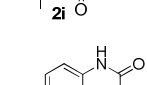
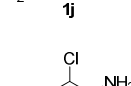
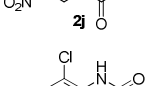

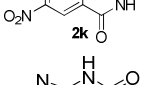

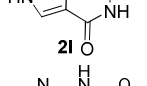
The effect of CO₂ pressure on the yield was examined at 130 °C and in 18 hours shown in Fig. 2b. The yield of **2a** increased significantly with increasing pressure from 2 to 3.5 MPa but above increasing the pressure from 4 to 5 MPa, the yield was decreased (Fig. 2b). Higher yield of **2a** was obtained at pressure of 3.5 MPa. Fig. 2c indicated that with the increase of time, the yield of **2a** was also increased up to 91% in time of 18 h and was not changed with increasing the time to 20 h, indicating the completion of the reaction in 18 h.

To examine the utility and generality of this approach, we have performed the reaction under the optimized reaction conditions for the synthesis of a wide variety of quinazoline-2,4(1*H*,3*H*)-diones (**2a–m**) from structurally diverse 2-aminobenzonitriles (**1a–m**) and CO₂ (Table 3, entries 1–13). 2-aminobenzonitrile (**1a**) reacted with CO₂ providing 91% yield of quinazoline-2,4(1*H*,3*H*)-dione (**2a**) under given reaction conditions (Table 3, entry 1). The presence of electron-donating groups had slight influence on the reaction, the 2-Amino-4,5-dimethoxybenzonitrile (**1b**) was effectively reacted with CO₂ affording excellent yield up to 92% of 6,7-dimethoxyquinazoline-2,4(1*H*,3*H*)-dione (**2b**) (Table 3, entry 2) which is a key intermediate in Prazosin (Minipress), Bunazosin (Detantol), IAAP and Doxazosin (Cardenalin) synthesis.

Further, to confirm the effectiveness and generality of the present catalytic system which we extended to various 5-halogen-substituted 2-aminobenzonitriles (**1c–e**), efficiently converted into corresponding quinazoline-2,4(1*H*,3*H*)-diones (**2c–e**) in excellent yields (Table 3, entries 3–5). However, 2-amino-4-chlorobenzonitrile (**1f**) was providing only 81% yield of 7-chloroquinazoline-2,4(1*H*,3*H*)-dione (**2f**) due to the electron-withdrawing effect of Cl group under the present experimental condition (Table 3, entry 6). In addition, reactions more efficiently proceeded in the presence of methyl group at 4 and 5 position of 2-aminobenzonitriles (**1g–h**) provided corresponding quinazoline-2,4(1*H*,3*H*)-diones (**2g–h**) with excellent yields 84%–89% respectively (Table 3, entries 7–8). But the 6-methyl-2-aminobenzonitriles (**1i**) gave (**2i**) somewhat lower yield (72%) of desired product, which is due to the steric effect of methyl group (Table 3, entry 9).

Notably, inactive 5-nitro-2-aminobenzonitrile (**1j**) and 3-chloro-5-nitro-2-aminobenzonitrile (**1k**) substrates in the literature^{18b,19} were also selectively converted into the corresponding 6-nitro-quinazoline-2,4(1*H*,3*H*)-dione (**2j**, 64%) and 8-chloro-6-nitroquinazoline-2,4(1*H*,3*H*)-dione (**2k**, 70%) with slight increase the reaction temperature to 150 °C respectively (Table 3, entries 10–11). Mizuno *et al.* reported that DBU was unable to convert **1j** to **2j** due to its low basicity and gave complex mixture instead of expected product.^{18b} Recently, He *et al.* reported that using TMG as a catalyst, 3-chloro-5-nitro-2-aminobenzonitrile (**1k**) failed to convert 8-chloro-6-nitroquinazoline-2,4(1*H*,3*H*)-dione (**2k**) even at higher reaction temperature.¹⁹ Moreover, we have also applied this catalytic protocol to check the effectiveness of catalyst for five and six member *N*-heterocyclic carbonitriles. It was observed that 3-aminopyrazole-4-carbonitrile (**1l**) reacts with CO₂ affording 60% yield of 2*H*-pyrazolo[3,4-*d*]pyrimidine-4,6(5*H*,7*H*)-dione (**2l**) (Table 3, entry 12), whereas 4-aminopyrimidine-5-carbonitrile (**1m**) did not provide the product (**2m**) in present reaction

Table 3 Synthesis of various quinazoline-2,4(1*H*,3*H*)-diones (**2a–m**)^a

Entry	Substrate	Product	Yield (%) ^b
1			91
2			92
3			88
4			82
5			92
6			81
7			84
8			89
9			72
10			64
11 ^c			70
12			60
13 ^d			No reaction

^aReaction conditions: Substrate (2 mmol), catalyst (14.6 wt% amine loaded) amine functionalized MCM-41 (12 wt%), water (5 mL), CO₂ pressure (3.5 MPa), temperature (130 °C), time (18 h). ^bIsolated Yield. ^cTemperature 150 °C. ^dTemperature 150 °C and time 24 h.

condition even with increasing the reaction temperature (Table 3, entry 13).

In order to craft the developed catalytic system, one of the most important criterions for heterogeneous catalysis is reusability. Hence, the recyclability of the (14.6% amine loaded) amine functionalized MCM-41 catalyst was also studied for the

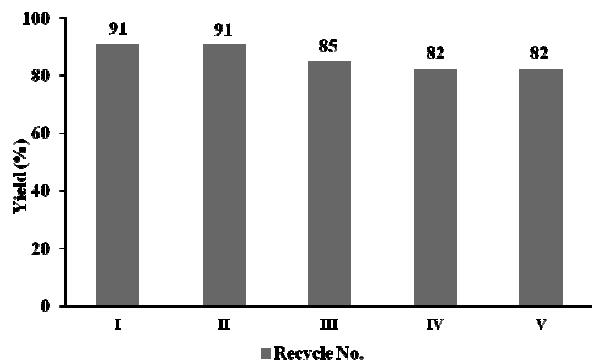
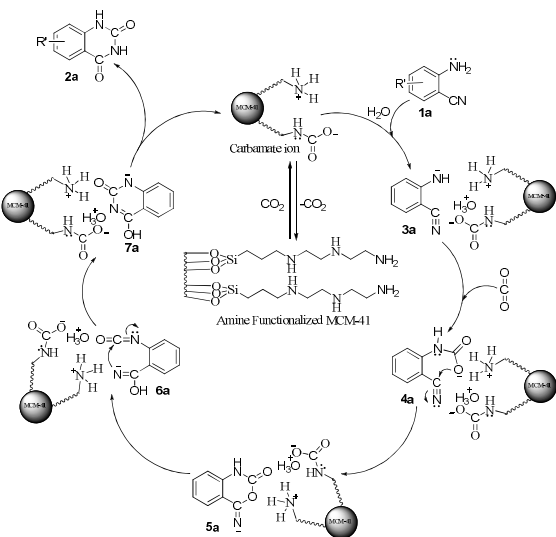


Fig. 3 Recyclability study of 14.6% amine functionalized MCM-41 catalyst.

synthesis of quinazoline-2,4(1*H*,3*H*)-diones derivatives from 2-aminobenzonitriles and CO₂ under the optimized reaction conditions and the results are shown in Fig. 3. The catalyst was found to be effective up to five consecutive recycles without any significant loss in its catalytic activity.

A proposed plausible reaction mechanism for the reaction of 2-aminobenzonitrile with carbon dioxide (CO₂), catalyzed by amine functionalized MCM-41 for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones (**2a**) is shown in Scheme 2. Ren et al. have shown that the 2-aminobenzonitrile can easily react with CO₂ only in presence of catalytic environment of base.^{28d} It is well known that carbon dioxide can form carbonic acid (H₂CO₃) in water, which is more active than CO₂.²⁸ In our case, the presence of both the catalytic environment of base and H₂O as a solvent which should significantly affects the yield of product. As per our previous report the generation of carbamate ion from CO₂ and amine functionalized catalyst forwarded the reaction towards the product (**2a**).^{9d} During the reaction path, *in situ* formation of amide intermediate (**3a**), which can be produced by the reaction of 2-aminobenzonitrile (**1a**) with carbamate anion of amine functionalized MCM-41. The carbamate ion abstract the proton of amino group of 2-aminobenzonitrile and activate the more nucleophilic amide towards the formation of carbamate ester (**4a**). After that, intermediate (**5a**) is formed *via* an intramolecular nucleophilic cyclization of (**4a**). Consequently, the rearrangement



Scheme 2 The plausible reaction mechanism for the reaction of 2-aminobenzonitrile and CO₂

of (**5a**) forming the isocyanate intermediate (**6a**), which provides **7a**. Finally, stabilization of **7a** offered the final product (**2a**). In the whole catalytic cycle, the formation of isocyanate intermediate (**6a**) assisted by the *ortho*-cyano group emerged to be more importance.^{18b}

Conclusions

In summary, we have developed a highly efficient, green, economical and recyclable catalytic protocol using amine functionalized MCM-41 as a catalyst for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones from 2-aminobenzonitrile and CO₂ in water. After reaction the catalyst could be easily recovered, and reused for five times without considerable decrease in catalytic activity. This developed protocol was efficient with respect to different electron-rich, electron-deficient group on aminobenzonitriles. The five membered *N*-heterocyclic carbonitrile was also providing good to excellent yield of the desired product.

Experimental section

All chemicals were procured from firms of repute. The various amine functionalized MCM-41 catalysts were prepared according to the procedure reported in previous literature with some modification.^{9d}

Recyclability study

The recyclability of the (14.6% amine loaded) amine functionalized MCM-41 catalyst was also studied for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones derivatives from 2-aminobenzonitriles and CO₂ under the optimized reaction conditions. After completion of the reaction, the residual mixture was poured into 10 × 15 mL water. Then removal of aqueous layer by centrifugation, the residual mixture washed with ethanol followed by *tert*-butyl methyl ether. The product was separated through dimethylformamide. The catalyst was washed with distilled water and absolute ethanol, dried under vacuum and then reused for successive recycles. The catalyst was found to be effective up to five consecutive recycles without any significant loss in its catalytic activity, indicating high activity and stability of the developed catalyst is shown in Fig. 3.

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Graphical Abstract

Amine functionalized MCM-41: an efficient heterogeneous recyclable catalyst for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones from carbon dioxide and 2-aminobenzonitriles in water

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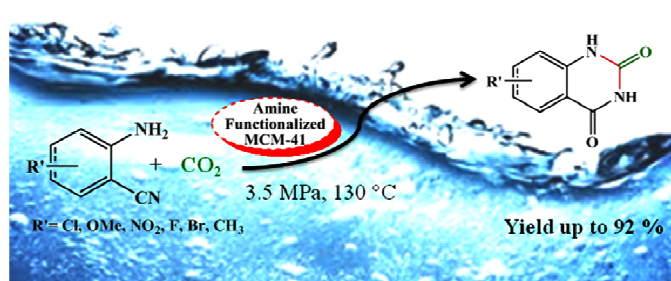
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A simple covalently linked amine functionalized MCM-41 were investigated as an efficient, heterogeneous catalyst for the synthesis of variety of quinazoline-2,4(1*H*,3*H*)-diones derivatives from 2-aminobenzonitriles and carbon dioxide in aqueous medium.