Cyclocondensation of Anthranilamide with Aldehydes on Gallium-Containing MCM-22 Zeolite Materials

Preeti Sahu, Adarsh Sahu,* and Ayyamperumal Saktivel

ABSTRACT: A gallium-containing MCM-22 (Mobil Composition of Matter No. 22) zeolite material was prepared using a simple hydrothermal method. Fourier transform infrared spectroscopy analysis and powder X-ray diffraction provide evidence of the formation of a pure MCM-22 phase framework and an MWW (MCM-tWent-tWo) structure. Scanning electron microscopy images showed a uniform spherical shape, interpenetrating the platelet structure and a uniform particle size of approximately 6 μm. 7Ga nuclear magnetic resonance studies confirmed the presence of gallium in both the tetrahedral framework and the octahedral extra-framework environment. From the sorption studies, the presence of strong acidic sites and the microporous nature of the material were evident. The resultant Ga-MCM-22 material showed an excellent isolated yield of 95% in the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by cyclocondensation of anthranilamide with aldehydes in ethanol. The scope of the reaction was further explored by employing various cyclic, aromatic, and aliphatic aldehydes with anthranilamide. The results provide a very good yield (85–95%). A significant advantage of the developed protocol includes high yield, use of a green solvent, and easy removal of the catalyst through filtration within a short reaction time.

1. INTRODUCTION

Zeolites are well-defined microporous aluminosilicate materials with high crystallinity, which possess extensive applications as heterogeneous catalysts in petrochemical industries and refineries. A wide range of their applications is reported in the fine chemical industry, petroleum-petrochemical, pharmaceutical, and cosmetic industries owing to their tunable pore size and acid-base properties.1–9 Among the 240 zeolites recognized by the International Zeolite Association, the MCM-22 zeolite is one of the interesting zeolites, currently receiving significant attention in commercial applications due to its unique features, such as external pocket, thermal stability, large surface area, and adsorption capacity. Mobil Oil Co. researchers developed a crystalline porous material with the MWW (MCM-tWent-tWo) topology in 1991.6 Two independent pore systems form the internal structure of this medium pore opening-layered zeolite. The MCM-22 framework combined 10 membered rings (MRS) (4 Å × 5.9 Å), a two-dimensional interlayer sinusoidal channel, and 12 MR supercages (7.1 Å × 7.1 Å × 18.2 Å) connected by 10 MR apertures. An interesting feature of these deemed “cups” (supercages) is that half of them are present on the external surface of the crystals, and these cups are rich in acid sites available for large molecule transformations. MCM-22-based materials are explored as potential catalysts for various organic transformations, namely, selective aromatic alkylation, isomerization, and disproportionation. They also have potential for the transformation of paraffin to aromatics and olefins.9–19

The acidic sites and the strength of acidic sites on the zeolite framework can be tuned by introducing heteroatoms, which can transform its physicochemical properties and catalytic activity. The introduction of trivalent gallium into the framework of zeolite facilitates remarkable physicochemical and catalytic properties. The presence of trivalent gallium in the framework and nonframework zeolitic sites provides abundant surface medium-strong acid sites.20–27 The presence of heteroatoms in the extra-framework species and tetrahedral framework sites provides bifunctional active sites.20–27 In the MCM-22 case, isomorphous substitution other than trivalent aluminum species is interesting in tuning the physicochemical properties. Few reports are available on the gallium-exchanged MCM-22 zeolite. For example, Kumar et al. described Ga-MCM-22 zeolite synthesis, characterization, and its application for the aromatization of n-butane. Wang et al. explored propane dehydrogenation. The term gallosilicates refers to the absence of Al species although it is permissible to use the seeds for syntheses.24 Morrison and Rubin developed gallosilicate MCM-22, which showed high selectivity for toluene in synthesis.

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methylcyclohexane hydrogenation. Later, Kim et al. reported the synthesis and characterization of gallium containing MCM-22. Similarly, Fecteau et al. studied the physicochemical properties of synthesized Ga-MCM-22 and examined it for toluene disproportionation.

Gallium raised interest in isomorphous substitution during 1990, where UPO-BP introduced gallium in a pentasil catalyst, that is to say, ZSM-5 (Zeolite Socony Mobil-5) in a cycle process as a catalyst for producing aromatic compounds from short-chain hydrocarbons. Gallium-modified zeolites have achieved remarkable success in various catalytic processes. Some of them are biomass coconversion and dehydrogenation. The application of zeolites as catalysts for fine chemical production is explored at a limited level. In this regard, this study reports that 2,3-dihydroquinazolin-4(1H)-ones are an important class of heterocyclic compounds, which has been applied in agrochemicals and medicinal and organic chemistry. Consequently, the central structural motifs of biological interest coupled with another heterocyclic ring have exhibited therapeutic potential in different domains such as antileishmanial, anticancer, antimicrobial, and antituberculosis. Numerous methods have been reported for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones, which include the multicomponent reaction of isatoic anhydride, ammonium chloride, and aldehydes using indium chloride, condensation of 2-aminobenzamide with aldehydes using zirconium(IV) chloride (2 mol(M)%) in ethanol, and palladium-catalyzed cyclocarbonylation of o-iodoanilines.

Some of the reported methodologies produce good results. However, these reactions are limited because of their long reaction time, expensive catalyst, harsh reaction conditions, low yield of the product, and tedious workup conditions. Thus, it is crucial to develop simple, efficient, eco-friendly, inexpensive, and easy workup methodologies for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones. This study focuses on the synthesis of gallium that contains MCM-22 and investigates its cyclocondensation reaction of anthranilamide with aldehydes in ethanol. The goal is to report the efficient, quick, inexpensive, low catalyst loading, eco-friendly, greener synthesis of 2,3-dihydroquinazolin-4(1H)-ones. An important utility of the reaction is the ability of the compound to be isolated by filtration.

2. EXPERIMENTAL SECTION

2.1. Synthesis. The Ga-MCM-22 material was synthesized using an appropriate molar gel ratio of SiO₂:0.3 NaOH:0.6 HMIX: Ga₅O₇:y H₂O. Different synthetic conditions were applied for the synthesis by varying the concentrations of x and y, which is summarized in Table 1. For the synthesis of the catalysts, two steps are involved. The first step involves the synthesis of a mixture of NaOH (sodium hydroxide, Sisco Research Laboratories, SRL, India) solution (in Millipore water) and colloidal silica (SiO₂, Sigma-Aldrich, LUDOX HS-40, 40 wt %) under continuous stirring followed by the addition of gallium nitrate (Ga(NO₃)₃·xH₂O, Alfa Aesar, 99.9% metal basis) solution. The prepared gel was transferred to a stainless steel Teflon-lined autoclave and kept in a preheated (180 °C) oven for aging. Furthermore, the solution was cooled down and mixed with hexamethyldisiloxane (HMI, Alfa Aesar) and NaOH solution. Thereafter, the solution was transferred to the stainless steel Teflon-lined autoclave for 168 h and kept in a preheated oven at 155 °C. Furthermore, the prepared gel was cooled down to room temperature, filtered, washed with Millipore water, and dried at 80 °C overnight. Then the sample was calcined at 550 °C for 6 h under an air flow of 50—100 mL/min.

The calcined sample was exchanged with a 1 M solution of ammonium acetate to obtain protons from the catalyst. All the reagents used in the synthesis were purchased from commercial sources and used without further purification.

2.2. Characterization. The nature of the structural framework and structural building unit was analyzed by Fourier transform infrared (FTIR) spectroscopy in the range of 400—4000 cm⁻¹ with a PerkinElmer Spectrum using the KBr pellet technique. The powder X-ray diffraction (XRD) pattern was collected using a Rigaku MiniFlex 600 diffractometer with nickel-filtered Cu Kα radiation. Diffractionograms were recorded in a 2θ range from 5 to 45° with a step size of 0.02° and a scan rate of 2°/min. The morphology and size of the zeolites were characterized using an FEI Nova NanoSEM 450 scanning electron microscope operated at 5.00 kV. Thermogravimetric analysis (TGA) was performed using a PerkinElmer STA-6000 from room temperature up to 700 °C at a rate of 10 °C/min under a nitrogen environment. The Brunauer—Emmet—Teller (BET) surface area and N₂ adsorption—desorption of the calcined samples were determined using Quantachrome Instruments Autosorb-IQ volumetric adsorption analyzer. The samples were degassed at ~200 °C. The BET and t-plots micropore surface areas were calculated in a relative pressure (p/p₀) range of 0—0.1 over the adsorption branch of the isotherm. The Barrett—Joyner—Halenda (BJH) pore size distribution was obtained from the desorption branch of the isotherm. Other textural properties like pore volume were determined from the isotherm data. The acidity measurement was carried out using a BELCAT-M (Japan) temperature-programmed desorption (TPD) instrument equipped with a thermal conductivity detector. The sample was preheated in a quartz reactor at 500 °C for 30 min in a He flow. Ammonia was adsorbed at 100 °C for 30 min. Ammonia desorption was carried out at 100 °C for 15 min to remove any physisorbed ammonia. TPD of ammonia was performed from 50 to 700 °C at a heating rate 10 °C/min and a helium flow of 30 mL/min. The solid-state nuclear magnetic resonance (NMR) experiments were performed on a Bruker Avance III HD 400 MHz MAS spectrometer equipped with a 4 mm CP/MAS probe (high-resolution solid-state apparatus) and a superconducting magnet with a field of 9.4 T. The samples were recorded at a particular frequency packed in 4 mm zirconia rotors at a spinning speed of 7 kHz. The ²⁵Si NMR spectra were recorded at 79.5 MHz with a pulse duration of 3.5 µs with a delay of 10 s and 10 scans. The ⁷¹Ga NMR spectra were recorded at 122 MHz with a pulse duration of 3.5 µs with a delay of 1 s and 7150 scans.

| Sample no. | Gel ratio | Final gel temperature (K) | Final gel duration (H) |
|------------|-----------|--------------------------|------------------------|
| Ga-MCM-22 (A) | Si/Ga = 0.3, Na/Si = 0.6 | 428 | 240 |
| Ga-MCM-22 (B) | Si/Ga = 0.3, Na/Si = 0.6 | 428 | 240 |
| Ga-MCM-22 (C) | Si/Ga = 0.3, Na/Si = 0.6 | 428 | 168 |
1H NMR and 13C NMR experiments were conducted using a Bruker DX 500 MHz. The chemical shift was reported in parts per million relative to tetramethylsilane as an internal standard. The 1H NMR spectra were referenced with respect to the residual deuterated chloroform (CDCl3) and dimethyl sulfoxide or DMSO-d6 at 7.29 and 3.34 and 2.51 ppm. The coupling constants were reported in hertz (Hz). The 13C NMR spectrum pattern was fully decoupled and was referenced to the middle peak of the solvent at 77 (CDCl3) and 40 ppm spectrum pattern was fully decoupled and was referenced to Hz, 1H), 7.60 = 10 Hz, 1H), 6.90 (t, 1H), 6.6 (s, 3H);13C NMR (100 MHz, CDCl3): 164, 147, 138, 134, 130, 128, 126, 119, 114, 99, 69.

2.3.1. 1H and 13C NMR Spectra of the Synthesized Compounds. 2.3.1.1. 2-phenyl-2,3-dihydroquinazolin-4(1H)-one (1). Yield: 95% (white solid) mp 219 °C. 1H NMR (400 MHz, CDCl3) (ppm): 8.05 (s, 1H), 7.95 (d, J = 8 Hz, 1H), 7.60–7.56 (m, 1H), 7.44 (t, J = 5 Hz, 2H), 7.33 (t, J = 10 Hz, 1H), 6.90 (t, 1H), 6.6 (s, 3H); 13C NMR (100 MHz, CDCl3): 164, 147, 138, 134, 130, 128, 126, 119, 114, 99, 69.

2.3.1.2. 2-(4-hydroxyphenyl)quinazolin-4(3H)-one. 1H NMR (500 MHz, CDCl3) (ppm): 8.09 (s, 1H), 7.95 (d, J = 8 Hz, 1H), 7.59–7.56 (m, 1H), 7.45 (t, J = 8 Hz, 1H), 7.34 (t, J = 8 Hz, 1H), 7.23 (t, 1H), 6.90 (s, 1H), 6.68–6.66 (m, 1H), 6.00 (s, 1H), 5.90 (s, 1H).

2.3.1.3. 2-(4-diethylaminophenyl)-2,3-dihydroquinazolin-4(1H)-one. 1H NMR (500 MHz, CDCl3) (ppm): 8.09 (s, 1H), 7.39 (d, J = 8 Hz, 1H), 7.32 (d, J = 8 Hz, 1H), 7.20 (d, J = 8 Hz, 2H), 7.04 (m, 2H), 4.93 (s, 1H), 1.69–1.53 (m, 4H), 1.31–1.11 (m, 6H).

2.3.1.4. 2-(p-tolyl)-2,3-dihydroquinazolin-4(1H)-one. 1H NMR (500 MHz, CDCl3) (ppm): 8.04 (d, J = 8 Hz, 1H), 7.94 (t, J = 8 Hz, 2H), 7.44 (q, J = 8 Hz, 2H), 7.39 (t, J = 8 Hz, 1H), 6.90 (t, J = 8 Hz, 1H), 6.66 (d, J = 8 Hz, 1H), 6.00 (s, 1H), 5.90 (s, 1H), 5.83 (s, 1H).

2.3.1.5. 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one. 1H NMR (500 MHz, CDCl3) (ppm): 8.04 (d, J = 8 Hz, 1H), 7.93 (d, J = 8 Hz, 1H), 7.80 (s, 1H), 7.53 (d, J = 8 Hz, 1H), 7.40 (d, J = 8 Hz, 2H), 7.34 (t, J = 6 Hz, 1H), 6.91 (t, J = 8 Hz, 1H), 6.66 (d, J = 6 Hz, 1H), 5.88 (s, 1H), 5.83 (s, 1H).

2.3.1.6. 2-(1-hydroxycyclohexyl)-2,3-dihydroquinazolin-4(1H)-one. 1H NMR (400 MHz, DMSO-d6) (ppm): 8.36 (s, 1H), 7.62 (d, J = 8 Hz, 3H), 7.80 (d, J = 8 Hz, 2H), 4.93 (s, 2H), 1.90–1.86 (m, 2H), 1.72 (t, J = 8 Hz, 3H), 1.64 (t, J = 10 Hz, 1H), 1.48 (s, 1H), 1.40 (s, 1H), 1.26 (d, J = 10 Hz, 1H).

3. RESULTS AND DISCUSSION

As summarized in Table 1, the Ga-MCM-22 samples were prepared with different synthetic conditions. Among the several batches of samples prepared, the sample derived with a Si/Ga ratio of 30 and an H2O/Si ratio of 20 in 168 h at 428 K (Ga-MCM-22 (C)) showed characteristic doublet framework vibration and better crystallinity in the powder XRD spectra (Figures 1 and 2). Ga-MCM-22 (C) sample were used for the further characterization and study catalytic cyclocondensation of anthranilamide with aldehydes.

Figure 1 shows the FTIR spectra of as-synthesized, calcined Ga-MCM-22 samples. The vibrational bands at 1245 and 1080 cm⁻¹ are related to external and internal linkages of Si-O-Si (asymmetric stretching). The band at 790 cm⁻¹ is related to the Si-O-Si tetrahedral external linkage (symmetric stretching). The doublet between 600 and 500 cm⁻¹ is related to external linkages as secondary building units (double six-membered ring or D6R, referred to as a structural band of MWW characteristics. The band at 445 cm⁻¹ is related to internal tetrahedral (T-O bend) framework sites. The FTIR spectra of as-synthesized and calcined Ga-

![Figure 1](image1.png)

![Figure 2](image2.png)
MCM-22 showed all the vibrational bands similar to parent Al-MCM-22 as reported in the literature. However, a vibrational band shifted from 549 to 551 cm$^{-1}$ and 599 to 605 cm$^{-1}$. A shift was also observed for the framework vibrational bands that appeared around 1018 and 1071 cm$^{-1}$, at a lower frequency for Ga-MCM-22, which may be due to the presence of gallium.

Table 2. Textural Properties of MCM-22 and Ga-MCM-22

| s. no. | sample         | surface area (m$^2$/g) | pore volume (cm$^3$/g) |
|-------|----------------|------------------------|------------------------|
| 1     | commercial-MCM-22 | 487                    | 0.20                   | 0.36       |
| 2     | Ga-MCM-22 (30)  | 263                    | 0.197                  | 0.095      |

Figure 3. TGA thermogram of (a) MCM-22 and (b) Ga-MCM-22.

Figure 4. Scanning electron microscopy (SEM) images of the Ga-MCM-22 sample.

Figure 5. Nitrogen adsorption isotherm of the Ga-MCM-22 sample.
sample. The as-synthesized Ga-MCM-22 catalyst shows the formation of layered MCM-22 (P). The calcined material showed well-behaved peaks for the MWW characteristic reflection plane in the following positions: (100) at 6.8°, (101) at 7.7°, (102) at 9.7°, (220) at 24.7°, and (310) at 25.7°. The sharp and ordered peaks imply a well-crystallized Ga-MCM-22 crystal. Broadening of the Ga-MCM-22 X-ray reflections can be due to the large Ga³⁺ species present in the framework position reducing the particle size.

The TGA data of synthesized MCM-22 and Ga-MCM-22 are shown in Figure 3. The initial weight loss up to 180 °C is due to the desorption of water species formed by the condensation of the silanol group. The Ga-MCM-22 sample showed 3% loss in this region, whereas MCM-22 showed 2.5% loss. The template removal happens between 180 and 480 °C, and surface hydroxyl group condensation occurs between 480 and 650 °C. The total template weight loss observed for MCM-22 was 23.5%, and Ga-MCM-22 showed a 9% total template weight loss. Compared to conventional MCM-22, the much lower weight loss of the present Ga-MCM-22 may be due to the larger ionic size of the trivalent gallium ion in the framework and extra-framework positions, relative to the hydrophobic environment and less template accommodation on the surface of MCM-22. The SEM images of Ga-MCM-22 show the MWW zeolite platelet morphology, arranged in a spherical shape. The Ga-MCM-22 sample shows 6.2 μm with a flaky crystal structure (Figure 4). The SEM images support the absence of any segregated impurities, which agrees with the XRD studies.

Figure 5 shows the N₂ adsorption isotherm of the Ga-MCM-22 sample. The isotherm curves for the catalyst show a sharp uptake below 0.1 relative pressure (p/p₀), which are characterized by type-I isotherm, indicating the presence of a microporous structure with monolayer adsorption. The samples show the H4 type hysteresis loop generated by the narrow-slit type. Table 2 summarizes the textural properties of the samples. The BET surface area obtained for Ga-MCM-22 was 263 m²/g, less than that of the conventional MCM-22. The decrease in the surface area may be due to the bulky trivalent gallium species present in the framework and extra-framework sites, which block the channel and reduce the surface area. The Ga-MCM-22 sample shows a micropore volume of 0.095 cm³ g⁻¹, suggesting that gallium ions are distributed on the framework and extra-framework sites in the MCM-22 framework, which block the pores due to their large size.

The acidic properties of the materials were investigated by employing NH₃ TPD. Figure 6 shows the corresponding results. The Ga-MCM-22 sample shows two desorption peaks in the range of 100–600 °C. The broad peak in the lower temperature range (200–350 °C) indicates moderate Brønsted acidity. Desorption of ammonia causes this desorption peak from the acidic sites derived from the framework gallium species.

On the other hand, a desorption peak that appeared in a high-temperature range, corresponding to the ammonia bound to the strong acid sites (Lewis acid sites and Brønsted acidic sites), was produced by the trivalent gallium ions present in the extra-framework sites. The introduction of gallium enhances the acidic strength, as evident from Figure 6. The magic angle spinning (MAS) NMR spectroscopy was conducted to explore the incorporation of gallium into the framework and extra-framework sites. The °Si and °Ga MAS
NMR spectra of the calcined Ga-MCM-22 sample are shown in Figures 7 and 8, respectively. The $^{29}$Si MAS NMR spectrum shows a sharp peak at $-115$ ppm assigned to SiO$_4$ species (0 Ga) Q$^4$ and a weak shoulder at $-108$ due to Si (1 Ga) Q$^3$. The peaks assigned to the Q$^4$ and Q$^3$ sites observed in the spectra support the hypothesis that silicon species are present in highly crystalline environments.\textsuperscript{21,45,52}

The $^{71}$Ga MAS NMR spectrum of the calcined Ga-MCM-22 sample shows (Figure 8a) two peaks around +170 and 0 ppm. The peak at +170 ppm corresponds to tetrahedral Ga$^{3+}$ species in the MCM-22 framework. The peak near 0 ppm can be due to the presence of gallium species in the octahedral environment of the extra-framework site, corresponding to gallium oxide or gallium oxide-hydroxide species. The NMR result implies the incorporation of Ga species into the framework and the extra-framework surface of MCM-22.\textsuperscript{21,45,54} A comparison of the $^{71}$Ga MAS NMR spectrum of the Ga$_2$O$_3$ sample studied and the results is shown in Figure 8b. The pure Ga$_2$O$_3$ showed two doublet peaks centered around +196 and 13.8 ppm again to support the presence of gallium in fourfold and sixfold coordination sites.\textsuperscript{54} The bands at $-253$ and $-73$ ppm correspond to side bands. There is good correlation between Ga-MCM-22 and Ga$_2$O$_3$ species.\textsuperscript{54}

Inspired by the modified acidic properties of the zeolite Ga-MCM-22 sample, we explored its catalytic activity for synthesizing 2,3-dihydroquinazoline-4(1H)-ones. These reactions go well with the catalyst of Lewis acid. Initially, our reaction started with the addition of anthranilamide 1a and benzaldehyde 2a without any catalyst in ethanol with reflux (60 °C), and the progress of the reaction was monitored using a TLC. After 24 h, the reaction afforded 2,3-dihydroquinazoline-4(1H)-ones in a low yield (Table 3). Then, 1a with 2a was reacted in the presence of a catalytic amount of activated Ga-MCM-22 (10 M %) in ethanol with reflux for 2 h (Scheme 1). After the successful synthesis of 2,3-dihydroquinazoline-4(1H)-

| s. no. | catalyst loading | aldehyde | time (h) | yield (%) |
|-------|------------------|----------|----------|-----------|
| 1     | no catalyst, RT  | CHO      | 6        | nil       |
| 2     | no catalyst, reflux | CHO  | 6        | 15        |
| 3     | 5 M % Ga-MCM-22  | CHO      | 3        | 55        |
| 4     | 10 M % Ga-MCM-22 | CHO      | 3        | 90        |
| 5     | 15 M % Ga-MCM-22 | CHO      | 3        | 95        |
| 6     | 20 M % Ga-MCM-22 | CHO      | 3        | 95        |
| 7     | gallium nitrate  | CHO      | 6        | <10       |
| 8     | LiCO$_3$         | CHO      | 6        | trace     |
| 9     | anhy. Mg(ClO$_4$)$_2$ | CHO | 6        | 85%       |

Table 3. Condensation Reaction without a Catalyst and with Different Amounts of Catalyst

Scheme 1. Schematic Diagram for Condensation of Anthranilamide
one 3a, we explored the effect of Ga-MCM-22 at different catalytic concentrations in ethanol under reflux conditions. The outcome of this analysis is summarized in Table 3. The highest yield of 95% was achieved in the presence of 15 M % of the catalysts. A metal chloride acts by increasing the electrophilicity of the carbonyl groups. Thus, we screened the catalytic efficacy of anhydrous MgClO₄ along with gallium nitrate, gallium oxide, and Ga-MCM-22 (Table 3). The motive behind using gallium nitrate and gallium oxide is to compare the activity with the prepared catalyst. The gallium-containing MCM-22 possessing ample surface medium-strong acid sites has a high surface area. The tetrahedrally connected heteroatoms and the extra-framework cation together can provide Lewis and Bronsted active sites, which cooperate with the in-framework protonic acid site. A drastic increase in the rate of reaction was observed in the presence of a Ga-MCM-22 catalyst using benzaldehyde 2a and anthranilamide 1a under reflux conditions at 60 °C, furnishing 95% of the desired product (Table 3, entry 3). It is testified that using gallosilicate as a catalyst has improved the yield of the product by enhancing electrophilicity. Gallosilicate forms an ionic bond with the carbonyl oxygen, leading to an increase in electrophilicity of the carbonyl group. Encouraged by the success, we also evaluated the optimum catalyst loading. From the results reported in Table 3 (entries 3−5), it was clear that 15 M % catalyst loading was optimal.

| s.no. | aldehyde | product | yield |
|---|---|---|---|
| 1. | benzaldehyde | 2-phenyl-2,3-dihydroquinazolin-4(1H)-one | 95 |
| 2. | 4-hydroxybenzaldehyde | | 90 |
| 3. | 4-aminobenzaldehyde | | 85 |
| 4. | 4-formylacetophenone | 3,5-dimethylindole | 93 |
| 5. | 3-chlorobenzaldehyde | 2-aminonaphthalene | 90 |
| 6. | 3-formylbenzoic acid | 3-hydroxy-2-piperidone | 95 |
| 7. | formylacetone | 2-aminophenol | 92 |
Furthermore, the leaching experiment was followed by a hot filtration method to understand the catalyst’s stability. The reaction mixture was filtered out, and the catalyst was separated after 30 min of reaction. Subsequently, the reaction was further proceeded with the filtrate solution, which showed negligible conversion. This supports that there is no leaching of active species under the reaction conditions. Additionally, the catalyst activity almost remains intact with more than 85% yield even after 3 cycles.

The scope of the catalyst for the condensation of anthranilamide with various cyclic, aromatic, and aliphatic aldehydes was explored in the presence of ethanol at the reflux temperature (60 °C) for 3 h. As summarized in Table 4, the condensation reaction using anthranilamide, substituted aldehydes in the presence of Ga-MCM-22, and ethanol generated six products with a percentage yield in the range of 85–95%.

The formation of the product can be explained by a plausible mechanism, as shown in Scheme 2. It seems that enhancement of the electrophilicity of the carbonyl group in the aldehyde occurred using Ga-MCM-22. An intermediate (I) was formed by the reaction of 2-anthranilamide and the activated aldehyde. Afterward, intermediate (I) was formed by the reaction of 2-aminozenamide and the activated aldehyde. After intermediate (I) dehydration, an imine intermediate (II) was produced. However, a part of imine in this intermediate could be activated by metals. Then, intermediate (III) was prepared by an intramolecular nucleophilic attack of the amide nitrogen on the activated imine group. Then, the products were afforded by 1,5-proton transfer.

4. CONCLUSIONS

In summary, Ga-MCM-22 was prepared hydrothermally and characterized efficiently with the help of various characterization techniques. A well-crystalline MCM-22 framework was evident from powder XRD, FTIR, and SEM studies. The presence of moderate-to-strong acidic sites and a high surface area of Ga-MCM-22 were evident from sorption studies. The resultant Ga-MCM-22 proved to be a potential catalyst for the cyclocondensation of anthranilamide with various aldehydes for the synthesis of 2,3-dihydroquinazoline4(1H)-ones, where it showed the highest yield of 95%.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03704.

AUTHOR INFORMATION

Corresponding Authors
Adarsh Sahu — Department of Pharmaceutical Sciences, Dr. Harisingh Gour Central University, Sagar, Madhya Pradesh 470003, India; orcid.org/0000-0001-5190-8236; Email: adarshniper@gmail.com
Ayyamperumal Sakthivel — Inorganic Materials & Heterogeneous Catalysis Laboratory, Department of Chemistry, School of Physical Sciences Central University of Kerala, Kasaragod, Kerala 671320, India; orcid.org/0000-0003-2330-5192; Email: Sakthiveldu@gmail.com, sakthivelcuk@cukerala.ac.in

Author
Preeti Sahu — Inorganic Materials & Heterogeneous Catalysis Laboratory, Department of Chemistry, School of Physical Sciences Central University of Kerala, Kasaragod, Kerala 671320, India

Notes
The authors declare no competing financial interest.

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