Loading of g-C$_3$N$_4$ on Core-Shell Magnetic Mesoporous Silica Nanospheres as a Solid Base Catalyst for the Green Synthesis of some Chromene Derivatives under Different Conditions

Shekofeh Neamani and Leila Moradi* 

Using heterogeneous basic catalysts has a great importance in chemical reactions because of their advantages (such as easy separation and thermal stability at harsh conditions) over homogeneous catalysts. In this study, magnetic mesoporous silica nanoparticles (mSiO$_2$) containing graphitic carbon nitride layers (mSiO$_2$/g-C$_3$N$_x$(x)) were fabricated through a facile process (x signifies the amount of melamine applied during synthesis). Graphitic carbon nitride layers were decorated on mSiO$_2$ by calcination of immobilized melamine (as graphitic carbon nitride precursor) on mSiO$_2$ in the last step of catalyst synthesis. The structure of the prepared catalysts was confirmed using XRD, BET, FESEM, EDX, elemental mapping and TEM methods. The catalytic efficiency of the so-obtained solid base composite was investigated for the synthesis of some dihydroxyanochromenes and spiro-dihydroxyanochromenes under thermal and microwave conditions. Using mSiO$_2$/g-C$_3$N$_x$(x) led to high yields under green conditions and in short reaction times and without a decrease in catalytic activity after four consecutive cycles.

Introduction

Nowadays, improving the utilization of catalysts in the synthesis of organic compounds has become an important topic. Chemical reactions developed by the base catalysis are great processes for many of fine chemical productions. In this respect, aldol and Knoevenagel condensations are of the most important carbon-carbon bond establishment reactions.$^{[1,2]}$ Basic catalysts comprise both homogeneous and heterogeneous base catalysts. Heterogeneous catalysts were applied to defeat the problems affected by homogeneous ones. The possibility of reusing these catalysts over and over again makes them suitable in chemical reactions. Also, using such catalysts makes the corresponding reactions more environmentally friendly.$^{[3,5]}$ The activity of base catalysts depends on their number of basic sites.$^{[6]}$ Basic sites at the catalyst surfaces can include functional groups anchored to their surface, edges and also structural defects. Recently, it has been demonstrated that structural defects in heterogeneous catalysts play a considerable role in their catalytic properties.$^{[10,11]}$ Defects, for catalysts, means deviations of the real crystal structure relative to the ideal lattice structure. The study of defects in catalyst supports activity became a significant topic in the catalyst field. Defects in heterogeneous catalysts have diverse types owing to the different crystalline structures of catalysts. For instance, several defect sorts which include edges, vacancies, and pentagon defects can exist in carbon-based catalysts, influencing catalytic activity.$^{[10–13]}$

Carbon nitrides are a group of polymeric materials that mainly contain carbon and nitrogen atoms. Carbon nitride layers, due to having attractive surface features and active basic sites, have been found excellent candidates for use in various catalysis fields.$^{[14–17]}$

Generally, graphitic carbon nitrides (g-C$_3$N$_x$) are obtained from the thermal polymerization of nitrogen-containing precursors at high temperatures. Studies have shown that incomplete polymerization during the formation of g-C$_3$N$_x$ layers leads to structural defects in the overall g-C$_3$N$_x$ structures, which result in increasing the number of edges and defects in the final g-C$_3$N$_x$ structure. Increasing the g-C$_3$N$_x$ structural defects can then bring about improved basic properties and activity of the final structure of g-C$_3$N$_x$ layers.$^{[18,19]}$

Heating is one of the main methods developed by scientists to destroy the regular structure of g-C$_3$N$_x$. Indeed, at high temperatures, the strong covalent bonds between carbon and nitrogen in tri-s-triazine units do not change, but hydrogen bonds between graphite carbon nitride plates are gradually weakened, which leads to a change in angle and the rotation of the corresponding plates. In consequence, irregular short units with basic features forms are obtained.$^{[15,16,20]}$ It is necessary to mention that applying of g-C$_3$N$_x$ as a catalyst in catalytic process has some restrictions and problems. One of them is the low specific surface area of g-C$_3$N$_x$ which is due to its high agglomeration property. In fact, once the layers of g-C$_3$N$_x$ form, they assemble on top of each other and aggregations occur.
that result in poor catalytic activity.\cite{23,24} Thus, restricting the formation of long layers of g-C\(_3\)N\(_4\) can cause to break them to the short chains which cater numerous structural defects and high specific surface area on its layers.\cite{25,26} In this regard, mesoporous silica nanoparticles (NPs), due to their properties such as high surface areas (more than 700 m\(^2\) g\(^{-1}\)), high chemical and thermal stability, appropriate particle size (2 to 10 nm), specific morphology and controllable porosity, are a useful option for catalyst support.\cite{23,27} By using mesoporous silica as a support for the formation of g-C\(_3\)N\(_4\) layers in their pores, incomplete polymerization occurs, causing an increase in the number of structural defects, edges and basic features. Furthermore, loading of g-C\(_3\)N\(_4\) in the pores of magnetic mesoporous silica NPs can make them easy to separate from the reaction medium.

In this contribution, this method was thus successfully used to prepare an efficient basic heterogeneous catalyst. The obtained catalyst was employed in the preparation of some dihydropyranochromene and spiro-dihydropyranochromene derivatives through the environmentally friendly method in green solvents (Scheme 1) which are desirable from the point of green chemistry.\cite{30}

Due to special properties of chromene derivatives such as anti-HIV, anti-tuberculosis, antioxidants anti-cancer, antiseptic and anti-inflammatory (in the field of medicinal chemistry), they have attracted much attention in recent years.\cite{31,32} Furthermore, the interest in chromenes bearing an additional nitrile functionality arises from their potential application in the treatment of human inflammatory TNFa-mediated diseases, such as rheumatoid and psoriatic arthritis, and in cancer therapy.\cite{33,34} Thus, new methods for the preparation of these compounds are of interest in organic and pharmaceutical syntheses.

Results and Discussion

Catalyst Characterization

The procedure applied for the synthesis of mSiO\(_2\)/g-C\(_3\)N\(_4\) composite is presented in Scheme 2. After preparation of magnetic mesoporous silica nanoparticles (mSiO\(_2\)) (according to our previous work\cite{25}), acidic solution of melamine as a precursor of g-C\(_3\)N\(_4\) was added to the synthesized mSiO\(_2\) NPs. Therefore, most of the melamine molecules stuck into the channel pores and on the surfaces of mSiO\(_2\) NPs. Then, calcination of the obtained solids at 550 °C caused incomplete structure formation of the g-C\(_3\)N\(_4\) layers inside the channel pores and on the surface of the mSiO\(_2\) NPs.

Different amounts of melamine, namely 0.05, 0.1 and 0.15 g, were used to prepare the mSiO\(_2\)/g-C\(_3\)N\(_4\)(0.05), mSiO\(_2\)/g-C\(_3\)N\(_4\)(0.1) and mSiO\(_2\)/g-C\(_3\)N\(_4\)(0.15) composites, respectively. In the following, the structure of mSiO\(_2\)/g-C\(_3\)N\(_4\)(0.1) as the high performance catalyst was studied. Figure 1 shows FESEM images of mSiO\(_2\) and of the mSiO\(_2\)/g-C\(_3\)N\(_4\)(0.1) composite. As can be seen in Figure 1 (a, b), mSiO\(_2\) NPs have spherical morphology. Against, in the synthesized catalysts (Figure 1c, d), due to formation of graphitic carbon nitride layers in channels as well as on the surfaces of mSiO\(_2\) NPs, more cumulative structures are observed.

The elemental mapping analysis of mSiO\(_2\)/g-C\(_3\)N\(_4\)(0.1) is shown in Figure 2. As can be seen, next to the presence of Si, O, and Fe from mSiO\(_2\), the presence of nitrogen and carbon atoms (from g-C\(_3\)N\(_4\)) with good dispersion on the mSiO\(_2\) surfaces was well proved.

To study the phase and crystalline structure of the mSiO\(_2\)/g-C\(_3\)N\(_4\)(0.1), powder X-ray diffraction (XRD) patterns of mSiO\(_2\) and mSiO\(_2\)/g-C\(_3\)N\(_4\)(0.1) were compared (Figure 3).
In the diffractogram of mSiO$_2$ (Figure 3a), a broad peak in the region of 20 = 21–28° indicates the amorphous structure of silica. In the diffractogram of mSiO$_2$/g-C$_3$N$_4$(0.1), graphitic carbon nitride has two clear peaks at 13.1 and 27.4° which are related to the (100) and (002) planes of the carbon nitride structure, respectively.$^{[14,15]}$ These peaks show repetitive tri-s-triazine structures and accumulations of aromatic carbon plates in the graphitic carbon nitride. According to the literature,$^{[14]}$ these peaks, in the absence of long carbon chains of graphitic carbon nitride, begin to weaken and widen, which in fact indicates the amorphous structure for graphite carbon nitride. The presence of a peak at around 27.4° for all of three synthesized catalysts confirms the formation of carbon nitride plates in amorphous forms. Other peaks in the X-ray diffraction spectrum in all samples are associated to the presence of Fe$_2$O$_3$ NPs as well as to Fe$_3$O$_4$ NPs which are formed by surface oxidation of Fe$_2$O$_3$ NPs in the furnace.$^{[40]}$

Nitrogen gas adsorption and desorption isotherms as well as BJH-plots for mSiO$_2$ and mSiO$_2$/g-C$_3$N$_4$(0.1) are shown in Figure 4. Obtained information from BET analysis of these samples is presented in Table 1. The obtained data show that mSiO$_2$ and mSiO$_2$/g-C$_3$N$_4$(0.1) have a specific surface area of 361 and 168 m$^2$g$^{-1}$, respectively. The decrease in surface area of the prepared catalyst compared to mSiO$_2$ is due to the filling of pores and also due to covering of the silica NP surface by the g-C$_3$N$_4$ layers. The increase of average pore diameter is due to the porous structure of g-C$_3$N$_4$ attached to the mSiO$_2$ NPs.

Figure 5 shows the TEM images of mSiO$_2$/g-C$_3$N$_4$(0.1). As can be seen, silica NPs containing Fe$_2$O$_3$ NPs have been successfully formed. Also, layers of g-C$_3$N$_4$ on the surface and into the channel pores of mSiO$_2$ were well dispersed.

**Catalytic Performance for the Synthesis of Chromone Derivatives**

In order to optimize the reaction conditions in the presence of the catalyst, the reaction of 4-hydroxycoumarin, 4-nitrobenzaldehyde and malononitrile was selected as the model reaction. Then (as shown in Table 2), the efficiency of synthesized catalysts with some homogeneous catalysts in different solvents were compared for this model reaction (Entries 1–7). The results show that, for the model reaction, mSiO$_2$/g-C$_3$N$_4$(0.1) in 10 mL ethanol under reflux conditions had the highest efficiency (about 84%) compared to other homogeneous catalysts. In the following, the effect of water as a co-solvent for ethanol was investigated (Entries 8–11). According to the obtained results, a volume ratio of water to ethanol (3:7) showed the best performance (Entry 11). Also, increasing the temperature from 80 to 90°C has not obvious effect on the efficiency of reaction (Entries 11, 12). Finally, the basic activity of prepared catalysts containing different amounts of graphitic carbon nitride was investigated (Entries 11, 14, 15). As is clear, by increasing the amount of melamine as a precursor of g-C$_3$N$_4$, the catalytic activity of synthesized catalyst was increased. It is, however, assumed that the accumulation of g-C$_3$N$_4$ layers in mSiO$_2$/g-C$_3$N$_4$(0.15) rather than for mSiO$_2$/g-C$_3$N$_4$(0.1) caused a decrease in basic sites concentration and thus a decline in the catalytic activity of the catalyst. Consequently, 15 mg of catalyst (mSiO$_2$/g-C$_3$N$_4$(0.1)) in H$_2$O/Ethanol (3:7) at 80°C was identified the optimum reaction conditions.

| Table 1. Obtained results from BET analysis. |
|---------------------------------------------|
| Sample          | BET surface area (m$^2$g$^{-1}$) | Total pore volume (cm$^3$g$^{-1}$) | Average pore diameter [nm] |
| mSiO$_2$       | 361                          | 0.37                      | 4.1                      |
| mSiO$_2$/g-C$_3$N$_4$(0.1) | 168                          | 0.34                      | 8.1                      |

In this table, BET surface area, total pore volume, and average pore diameter are calculated from the adsorption and desorption isotherms and BJH-plots.
In the following, mSiO$_2$/g-C$_3$N$_4$ (0.1) as the best catalyst was used to prepare some chromene derivatives (Table 3). In this way, some pyrano- and spiro-pyranochromenes were prepared through the multi-component reaction of 4-hydroxycoumarin, malononitrile and benzaldehyde (isatin) in 10 mL of water and ethanol with a volume ratio of 3:7 in the presence of 15 mg mSiO$_2$/g-C$_3$N$_4$(0.1) as the solid base catalyst. The reaction was performed under thermal and also microwave conditions (Scheme 1). Products were obtained in high to excellent yields and their structure was investigated by FTIR spectroscopy as well as by $^1$H NMR and $^{13}$C NMR analysis. The achieved results are presented in Table 3.

As shown in Table 3, different derivatives of benzaldehyde and isatin were used in the reaction to investigate the effect of electron-donating and -withdrawing groups on the reaction efficiency. As can be seen, the presence of electron-withdrawing groups on the phenyl ring of benzaldehyde and isatin structures increases the efficiency of reaction, and the presence of electron-donating groups on the benzaldehyde structure reduces the reaction efficiency both under thermal and micro-

**Table 2.** Optimization of solvent, temperature and catalyst.$^{[a]}$

| Entry | Solvent           | Catalyst (Loading) | Temperature     | Yield [%] |
|-------|-------------------|--------------------|-----------------|-----------|
| 1     | EIOH              | –                  | Reflux          | 0         |
| 2     | EIOH              | Et$_3$N (10 mol%)  | Reflux          | 68        |
| 3     | EIOH              | L-Prolin (10 mol%) | Reflux          | 62        |
| 4     | EIOH              | (NH$_4$)$_2$HPO$_4$ (10 mol%) | Reflux | 55 |
| 5     | CHCl$_3$         | Et$_3$N (10 mol%)  | Reflux          | 61        |
| 6     | CH$_3$CN         | Et$_3$N (10 mol%)  | Reflux          | 65        |
| 7     | EIOH              | mSiO$_2$/g-C$_3$N$_4$(0.1) (15 mg) | Reflux | 84 |
| 8     | H$_2$O/Ethanol (9:1) | mSiO$_2$/g-C$_3$N$_4$(0.1) (15 mg) | Reflux (80°C) | 88 |
| 9     | H$_2$O/Ethanol (7:3) | mSiO$_2$/g-C$_3$N$_4$(0.1) (15 mg) | Reflux (80°C) | 91 |
| 10    | H$_2$O/Ethanol (5:5) | mSiO$_2$/g-C$_3$N$_4$(0.1) (15 mg) | Reflux (80°C) | 89 |
| 11    | H$_2$O/Ethanol (3:7) | mSiO$_2$/g-C$_3$N$_4$(0.1) (15 mg) | Reflux (80°C) | 93 |
| 12    | H$_2$O/Ethanol (3:7) | mSiO$_2$/g-C$_3$N$_4$(0.1) (15 mg) | Reflux (90°C) | 91 |
| 13    | H$_2$O/Ethanol (3:7) | mSiO$_2$/g-C$_3$N$_4$(0.1) (10 mg) | Reflux (80°C) | 86 |
| 14    | H$_2$O/Ethanol (3:7) | mSiO$_2$/g-C$_3$N$_4$(0.05) (15 mg) | Reflux (80°C) | 20 |
| 15    | H$_2$O/Ethanol (3:7) | mSiO$_2$/g-C$_3$N$_4$(0.15) (15 mg) | Reflux (80°C) | 82 |

[a] Reaction conditions: carbonyl (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol) in 10 mL solvent at reflux for 8 h.
Table 3. Investigation of mSiO$_2$/g-C$_3$N$_4$(0.1) for the synthesis of pyrano and spiropyranochromenes.$^{15}$

| MW Time [min] / Yield [%] | Thermal Time [h] / Yield [%] | Product | Aldehyde/Isatin | Entry |
|--------------------------|-------------------------------|---------|----------------|-------|
| 10/95                    | 4/93                          | ![Chemical Structure](image1) | CHO    | 1     |
| 8/88                     | 5/87                          | ![Chemical Structure](image2) | CHO    | 2     |
| 12/79                    | 6/81                          | ![Chemical Structure](image3) | CHO    | 3     |
| 8/94                     | 4/92                          | ![Chemical Structure](image4) | CHO    | 4     |
| 15/81                    | 7/85                          | ![Chemical Structure](image5) | CHO    | 5     |
| 13/80                    | 7/80                          | ![Chemical Structure](image6) | CHO    | 6     |
| 10/87                    | 7/89                          | ![Chemical Structure](image7) | CHO    | 7     |
| 16/84                    | 8/86                          | ![Chemical Structure](image8) | CHO    | 8     |
wave conditions. Furthermore, using the microwave method, all of performed reactions were done in shorter times in comparison to thermal conditions.

**Reaction Mechanism**

For the preparation of dihydropyranochromenes derivatives, 4-hydroxycoumarin, malononitrile, benzaldehyde and for the preparation of spiro-dihydropyranochromene, 4-hydroxycoumarin, malononitrile and isatin in the presence of mSiO$_2$/g-C$_3$N$_4$(0.1) catalyst were reacted under both thermal and microwave conditions. Based on similar work done for the mentioned multi-component reaction, the following mechanism is presented in Scheme 3.\textsuperscript{[27]} At first, the solid base catalyst captures the proton of active methylene of malononitrile for a Knoevenagel condensation with benzaldehyde (or isatin) to form the intermediate (I). After that, a Michael addition by nucleophilic attack of 4-hydroxycoumarin to intermediate (I) produces the intermediate (II) and then an intramolecular cyclization causes the formation of intermediate (III). Finally, a tautomerization in (III) produces the desired product (IV).

Table 3. continued

| MW Time [min] / Yield [%] | Thermal Time [h] / Yield [%] | Product | Aldehyde/Isatin | Entry |
|--------------------------|-----------------------------|---------|-----------------|-------|
| 11/87                    | 9/88                        | ![Image](image1) | ![Image](image2) | 9     |
| 9/89                     | 9/89                        | ![Image](image3) | ![Image](image4) | 10    |
| 8/94                     | 8/92                        | ![Image](image5) | ![Image](image6) | 11    |
| 8/91                     | 8/90                        | ![Image](image7) | ![Image](image8) | 12    |

[a] Reaction conditions: benzaldehyde (isatin) (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol) in 10 mL EtOH/H$_2$O (7:3) and 15 mg mSiO$_2$/g-C$_3$N$_4$(0.1) at 80°C (thermal conditions) / 600 W (microwave conditions).

Ensuring the capability of reusing heterogeneous base catalysts for repeated cycles is a significant challenge in their design and use. The ease of separation and reusing them is a very important feature. Therefore, the prepared magnetic...
mSiO$_2$g-C$_3$N$_4$(0.1) was separated from the reaction medium by a magnet and was washed several times with water and ethanol. Then, after drying, it was used again in the same reaction. The results showed that, after four cycles, there was no significant change in the efficiency of catalyst and the yield of product (Figure 6).

A study on the activity of prepared catalyst compare to the other reported works has been done and results were collected in Table 4. As can be seen, mSiO$_2$g-C$_3$N$_4$(0.1) shows considerable efficiency both with respect to reaction time and yield of product when compare to others (Entry 6, 10).

### Conclusion

In the present study, magnetic mesoporous silica NPs containing graphitic carbon nitride layers (mSiO$_2$g-C$_3$N$_4$) were fabricated using different amounts of melamine (as a precursor of graphitic carbon nitride). In the prepared catalysts, amorphous structure of g-C$_3$N$_4$ trapped in the holes of mesoporous silica NPs (consisting of numerical basic sites), revealed them to be an appropriate choice for catalytic reactions. The synthesized catalysts were used successfully to prepare some dihydropyranochromene and spiro-dihydropyranochromene derivatives. The mSiO$_2$g-C$_3$N$_4$(0.1) catalyst was found to display the best efficiency for the synthesis of dihydropyranochromene and spirodihydropyranochromene under both heating and microwave conditions in the green solvents. Also, the catalyst showed proper reusability in the repeatable cycles.

### Experimental Section

#### Materials and Apparatuses

Hydrochloric acid solution (37%), potassium permanganate (KMnO$_4$), tetraethyl orthosilicate (TEOS), cetrimonium bromide (CTAB), FeCl$_3$·4H$_2$O and FeCl$_2$·6H$_2$O, melamine and all solvents were purchased from Sigma-Aldrich. 4-Hydroxycoumarine, benzenediahyde derivatives, Isatin derivatives, malononitrile and ammonia solution (25%), as well as the commercial thin-layer chromatography (TLC) plates (silica gel 60 F254) were purchased from Merck. Chemicals were used directly without any further purification.

To study the crystalline structure of the obtained composites, X-ray diffraction patterns were measured using a Philips X’pert MPD diffractometer with a copper target working at the current of 100 mA and a voltage of 45 kV, with Cu–K$_x$ radiation ($\lambda = 0.154056$ nm) an a 20 = 10–70’’ scanning range at the speed of 0.05’’/min. The N$_2$ adsorption/desorption analysis (BET) was done to control the specific surface area of the synthesis catalyst composites by using an automated gas adsorption analyzer (Tristar 3000, Micromeritics) at −196°C. The surface morphology of the attained catalysts was investigated by a Mira3-XMU field emission scanning electron microscope (FESEM) instrument with the scanning electron electrode at 15 kV. The morphology of synthesized catalysts was studied by TEM technique by a PhilipsCM 120, Netherlands, microscope with an accelerating voltage of 150 kV.

#### Table 4. A comparison between the efficiency of mSiO$_2$g-C$_3$N$_4$(0.1) and other reported works for the synthesis of chromene derivatives.[a]

| Entry | Reaction conditions | Yield (%) | Ref. |
|-------|---------------------|-----------|------|
| 1     | Sodium citrate in ethanol/water at 20°C, 10 min | 95 | [41] |
| 2     | Tetrabutylammonium bromide on water at 80°C, for 0.25 h | 85 | [42] |
| 3     | Aq. buffer (pH 4.5) at 40°C, 15 h | 85 | [43] |
| 4     | Acetonitrile at 50°C, 3 h | 72 | [44] |
| 5     | DMAP, 150°C, 0.33 h; microwave irradiation; mSiO$_2$g-C$_3$N$_4$, U.S., r.t., 10 min | 95 | This work |
| 7     | PTSA In water for 6 h, Reflux | 85 | [46] |
| 8     | Carbon sheets with sulfuric acid, thanol, 80°C, 5 h | 86 | [47] |
| 9     | magnetic nano-sized copper ferrite, H$_2$O/EtOH, 95°C, 85 min. | 90 | [48] |
| 10    | mSiO$_2$g-C$_3$N$_4$, U.S., r.t., 8 min | 94 | This work |

[a] Entries 1 to 6: reaction conditions for the preparation of product “a”; entries 7 to 10: reaction conditions for the synthesis of product “k”.

#### Synthesis of Magnetic Fe$_3$O$_4$ Nanoparticles

Conforming our prior work,[23] 0.085 g FeCl$_3$·4H$_2$O and 0.2 g FeCl$_2$·6H$_2$O (the molar ratio of Fe$^{3+}$/Fe$^{2+}$ being equal to 1.75) were added into 50 mL of deionized water at 85°C. Next, ammonia solution (0.6 mL) was added to the mixture and stirred under an inert nitrogen atmosphere at 85°C for 30 min. Finally, the prepared magnetic NPs were separated with an external magnetic field, washed with DI water and ethanol and dried at room temperature.

#### Synthesis of Magnetic Mesoporous Silica Nanoparticles (mSiO$_2$)

The preparation of mSiO$_2$ nanoparticles was done according to our previous work,[23] 0.1 g of the synthesized magnetic NPs and 0.7 g CTAB were added into 160 mL of deionized water and the mixture was sonicated for 10 min in a bath sonicator. Then, the obtained mixture was added to 220 mL of ethanol containing 1.2 mL of the...
NH₄ solution (25%). Next, TEOS solution (0.4 mL TEOS in 10 mL ethanol) was added dropwise to the above mixture under stirring. The so-obtained mixture was stirred for 12 h at room temperature. The collected magnetic NPs were separated by an external magnetic field and washed several times with ethanol. Resulted solid was calcinated at 550°C for 6 h to obtain mSiO₄.

Synthesis of Magnetic Mesoporous Silica NPs Containing Graphitic Carbon Nitride Layers (mSiO₄/g-C₃N₄)

For the synthesis of magnetic mesoporous silica nanoparticles containing graphitic carbon nitride layers, the different amounts of melamine (including 0.05, 0.1 and 0.15 g) in acidic solution (melamine dissolved in 20 mL water and 2 mL hydrochloric acid) were added to 0.1 g of the prepared mSiO₄ NPs. The resultant mixture was sonicated and then stirred at 50°C to evaporate the solvent. In the following, the obtained solid was put in a furnace at 550°C for 4 h at a ramp rate of 5°C/min. Fabricated catalysts were labeled as mSiO₄/g-C₃N₄(x), with x defined as the amount of applied melamine as the precursor of graphitic carbon nitride layers. In this regard, mSiO₄/g-C₃N₄(0.05), mSiO₄/g-C₃N₄(0.1) and mSiO₄/g-C₃N₄(0.15) were prepared.

Catalyst Performance for the Synthesis of Chromene Derivatives under Thermal and Microwave Conditions

To synthesis of pyrano[2,3-c]chromene and spiro-pyrano[2,3-c]chromene derivatives, equimolar amounts of 4-hydroxycoumarin, malononitrile and benzaldehyde or isatin (for spiro products) in the presence of 15 mg of synthesized catalyst in a mixture of DI water and ethanol (as an environmentally friendly solvent; 10 mL of 3:7 volume ratio, respectively) at 80°C were reacted under reflux conditions. The progress of the reaction was monitored by TLC. After the end of the reaction, the catalyst was separated by an external magnetic field. The obtained solid product was filtered and washed with water and ethanol to remove unreacted substrates. The identity of the so-obtained products was completely confirmed by FTIR, ¹H NMR and ¹³C NMR spectra information consistent in comparison with authentic samples.[27, 46-51]

For the synthesis of chromene derivatives under microwave conditions, equimolar amounts of 4-hydroxycoumarin, malononitrile and benzaldehyde or isatin (for spiro products) in the presence of 15 mg of prepared catalyst in 10 mL of green solvent (3:7 volume ratio of H₂O/EOH) was reacted under microwave irradiation with a power of 600 W for an appropriate time. The progress of reaction was monitored by TLC. The separation of reaction products was carried as previously described for the thermal condition procedure.

Acknowledgements

We are grateful to the University of Kashan for supporting this work by grant number 1073180.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: basic catalyst · dihydropyranochromenes · graphitic carbon nitride · magnetic mesoporous silica nanoparticles · spiro-dihydropyranochromenes

[1] F. Su, M. Antonietti, X. Wang, Catal. Sci. Technol. 2012, 2, 1005–1009.
[2] K. Ebitani, K. Motokura, K. Mori, T. Mizugaki, K. Kaneda, J. Org. Chem. 2006, 71, 5440–5447.
[3] S. Neamani, L. Moradi, M. Sun, Appl. Surf. Sci. 2020, 504, 144466–144477.
[4] S. Ernst, M. Hartmann, S. Sauerbeck, T. Bongers, Appl. Catal. A 2000, 269, 117–123.
[5] S. H. Y. S. Abdullah, N. H. M. Hanapi, A. Azid, R. Umar, H. Juahir, H. Khatooon, A. Endut, Renewable Sustainable Energy Rev. 2017, 70, 1040–1051.
[6] L. Zhu, X. Q. Liu, H. L. Jiang, L. B. Sun, Chem. Rev. 2017, 117, 8129–8176.
[7] L. Jia, A. Shahzeydi, M. Ghiauci, M. Sun, J. Environ. Chem. Eng. 2021, 9, 105086–105095.
[8] L. Moradi, M. Zare, Green Chem. Lett. Rev. 2018, 11, 197–208.
[9] H. Alshammari, M. Alhumaimess, M. H. Alotaibi, A. S. Alshammari, J. King Saud Univ. Sci. 2017, 29, 561–566.
[10] C. Xie, D. Yan, H. L. Su, D. Wu, C. Chen, Y. Wang, Y. Zou, R. Chen, S. Wang, ACS Catal. 2020, 10, 11082–11098.
[11] J. Maier, Angew. Chem. Int. Ed. 1993, 32, 313–335; Angew. Chem. 1993, 105, 335–354.
[12] J. Jia, C. Qian, Y. Dong, Y. F. Li, H. Wang, M. Ghousoun, K. T. Butler, A. Walsh, G. A. Ozin, Chem. Soc. Rev. 2017, 46, 4631–4644.
[13] J. Zhu, Y. Huang, W. Mei, C. Zhao, C. Zhang, J. Zhang, I. S. Aminiu, S. Mu, Angew. Chem. Int. Ed. 2019, 58, 3859–3864; Angew. Chem. 2019, 131, 3899–3904.
[14] A. Shahzeydi, M. Ghiauci, H. Farrokhpour, A. Shavhar, M. Sun, M. Saraji, Chem. Eng. J. 2019, 370, 1310–1321.
[15] J. Zhu, P. Xiao, H. Li, S. A. C. Carabineiro, ACS Appl. Mater. Interfaces 2016, 8, 16444–16465.
[16] Z. Huang, F. Li, B. Chen, T. Lu, Y. Yuan, G. Yuan, Appl. Catal. B 2013, 136, 7159–7329.
[17] S. N. Rizi, A. Shahzeydi, M. Ghiauci, L. Zhang, J. Environ. Chem. Eng. 2020, 8, 104219–104231.
[18] W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, Chem. Rev. 2016, 116, 7159–7329.
[19] Y. Kang, Y. Yang, L. C. Yin, X. Kang, G. Liu, H. M. Cheng, Adv. Mater. 2015, 27, 4572–4577.
[20] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J. O. Müller, R. Schlögl, J. M. Carlsson, J. Mater. Chem. 2018, 18, 4893–4908.
[21] S. Neamani, L. Moradi, M. Sun, J. Environ. Chem. Eng. 2015, 3, 197–208.
[22] F. Su, M. Antonietti, X. Wang, J. Mater. Chem. A. 2020, 8, 14081–14092.
[23] B. C. Raju, R. N. Rao, P. Suman, P. Yogeeswari, D. Sriram, T. B. Shaik, S. V. Sambasivara, RSC Adv. 2020, 10, 100577–100599.
[24] K. Sugino, N. Oya, N. Yoshie, M. Ogura, J. Am. Chem. Soc. 2011, 133, 20030–20032.
[25] A. Shahzeydi, M. Ghiauci, L. Jia, A. Jomaei, M. Panjepour, Appl. Surf. Sci. 2019, 485, 194–203.
[26] S. Neamani, L. Moradi, ChemistrySelect 2020, 5, 7439–7446.
[27] J. M. Khurana, B. Nand, P. Saluja, Tetrahedron 2010, 66, 5637–5641.
[28] C. S. Konkay, D. B. Fick, S. X. Cai, N. C. Lan, J. F. W. Keana, PCT Int. Appl. WO Patent 0075123, Chem. Abstr. 2001, 134, 29313a.
[29] Y. K. Al-Majedy, A. A. H. Kadhum, A. A. Al-Amiery, A. B. Mohamad, Syst. Rev. Pharm. 2017, 8, 62–70.
[30] B. C. Raju, R. N. Rao, P. Suman, P. Yogeesswari, D. Sriram, T. B. Shaik, S. V. Kalivendi, Bioorg. Med. Chem. Lett. 2011, 21, 2855–2859.
[31] P. Gebhardt, K. Dornbnder, F. A. Gollmick, U. Gräfe, A. Härtl, H. Göris, B. Schlegel, C. Hertweck, Bioorg. Med. Chem. Lett. 2007, 17, 2558–2560.
[32] N. Noroozi Pehay, G. Rezanajade Bardajee, E. Kashani, M. Mohammadi, H. Batmani, Res. Chem. Intermed. 2020, 46, 347–367.
[33] K. Ogajhi Aghbash, N. Noroozi Pehay, H. Batmani, Appl. Organomet. Chem. 2019, 33, e5287.
[34] K. Ogajhi Aghbash, N. Noroozi Pehay, E. Şahin, Res. Chem. Intermed. 2019, 45, 2079–2094.
[35] K. Ojaghi Aghbash, N. Noroozi Pesyan, G. Marandi, N. Dege, E. Sahin, *Res. Chem. Intermed.* 2019, 45, 4543–4554.

[36] J. Skommer, D. Wlodkowic, M. Matteo, M. Eray, J. Pelkonen, *Leukemia Res.* 2006, 30, 322–331.

[37] W. Kemnitzer, S. Kasibhatla, S. Jiang, H. Zhang, J. Zhao, S. Jia, C. Crogan-Grundy, R. Denis, N. Barriaux, L. Vaillancourt, S. Charron, J. Dodd, G. Attardo, D. Labrecque, S. Lamotte, H. Gourdeau, B. Tseng, J. Drewe, S. X. Cai, *Bioorg. Med. Chem. Lett.* 2005, 15, 4745–4751.

[38] W. Kemnitzer, J. Drewe, S. Jiang, H. Zhang, Y. Wang, J. Zhao, S. Jia, J. Herich, D. Labrecque, R. Storer, K. Meeroivitch, D. Bouffard, R. Rej, R. Denis, C. Blais, S. Lamotte, G. Attardo, H. Gourdeau, B. Tseng, S. Kasibhatla, S. X. Cai, *J. Med. Chem.* 2004, 47, 6299–6310.

[39] H. Gourdeau, L. Leblond, B. Hamelin, C. Desputeau, K. Dong, I. Kianicka, D. Custeau, C. Bourdeau, L. Geerts, S. X. Cai, J. Drewe, D. Labrecque, S. Kasibhatla, B. Tseng, *Mol. Cancer Ther.* 2004, 3, 1375–1384.

[40] S. Neamani, L. Moradi, M. Sun, *Appl. Surf. Sci.* 2014, 309, 144466–144477.

[41] A. Thongn, P. T. Phamnang, A. Dutta, R. Nongkshirt, *Synth. Commun.* 2022, 52, 43–62.

[42] R. Sarma, M. M. Sarmah, K. C. Lekhok, D. Prajapati, *Synlett* 2010, 19, 2847–2852.

[43] M. Mogharabi-Manzari, M. H. Ghahremani, T. Sedaghat, F. Shayan, M. A. Faramarzi, *Eur. J. Org. Chem.* 2019, 2019, 1741–1747.

[44] A. Montagut-Romans, M. Boulven, M. Lemaire, F. Popowycz, *RSC Adv.* 2016, 6, 4540–4544.

[45] K. Ramandeep, N. Fatima, S. Sahil, M. Samir, G. Manish Kumar, B. Preet Mohinder Singh, N. Kunal, *Med. Chem. Res.* 2015, 24, 3334–3349.

[46] R. Gahremanzadeh, T. Amanpour, A. Bazgir, *J. Heterocycl. Chem.* 2009, 46, 1266–1270.

[47] B. Maheshwar Rao, G. Niranjan Reddy, T. Vijaikumar Reddy, B. L. A. Prabhavathi Devi, R. B. N. Prasad, J. S. Yadav, B. V. Subba Reddy, *Tetrahedron Lett.* 2013, 54, 2466–2471.

[48] M. Baghernejad, S. Khodabakhshi, S. Tajik, *New J. Chem.* 2016, 40, 2704–2709.

[49] H. R. Safaei, M. Shekouhy, S. Rahmanpur, A. Shririnfeshan, *Green Chem.* 2012, 14, 1696–04.

[50] A. Hasaninejad, N. Golzar, M. Beyrati, A. Zare, M. M. Doroodmand, *J. Mol. Catal. A* 2013, 372, 137–50.

[51] S. Riyaz, A. Indrasena, P. Dubey, *Indian J. Chem.* 2014, 53B, 1442–1447.

Manuscript received: February 22, 2022
Revised manuscript received: May 1, 2022