Scientific paper

Efficient Synthesis of 2-Amino-4*H*-benzo[*b*]pyrans via Copper-periodic Mesoporous Organosilica Nanocomposites Catalyst in Aqueous Media

Roghaye Ramazannejad lori[1], Zahra Fahimeh alsadat Mortazavi[2,*], Vajihe Nejadshafiee[3,†], Asadollah Hassankhani[4,‡]

[1] *Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran.*

[2] *Department of Chemical Engineering, Sirjan University of Technology, Sirjan, Iran.*

[3] *Central Lab, Vali-e-Asr University, Rafsanjan, Iran, 77176.*

[4] *Associate Professor in Organic Chemistry Department of Materials Science and Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology Kerman, Iran.*

**,†&‡ Corresponding author: E-mail: vajihenejadshafiee@yahoo.com, zahrafsmrtz@gmail.com & ahassankhani@gmail.com*

Received: 09-08-2024

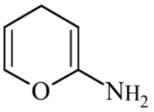
Abstract

In this study, the efficient method was introduced for the preparation of copper-periodic mesoporous organosilica nanocomposites (Cu@MOS NCs) as a high performance heterogeneous nanocatalyst. Then the nanocomposite was characterized with various methods such as X-ray diffraction (XRD), BET analysis, SEM and EDS microscopy and thermogravimetric analysis (TGA). The Cu@MOS NC as nanocatalyst was applied for one-pot three component reactions of aromatic aldehydes, 1,3-Cyclohexanedione and malononitrile for the effective and green synthesis of 2-amino-4*H*-benzo[*b*]pyran derivatives in high yields, with operational simplicity, environmental friendliness, wide applicability and reusability and easy recovery of the catalyst.

Keywords: 2-amino-4H-benzo[b]pyran, catalyst, nanocomposites, organosilica.

1. Introduction

O-Heterocycles are an important class of organic compounds with a wide variety as most of them are biologically active molecules.[1] 2-Amino-4*H*-pyran (Scheme 1) derivatives found in the typical six-membered *O*-heterocycles, which exhibit interesting antiallergic, anti-coagulant, anticancer and antibacterial activities.[2] And also these compounds were reported in the treatment of some diseases such as schizophrenia, Alzheimer, and mycolonous.[2–5] Furthermore, 2-amino-4*H*-pyrans exhibited good photoactive properties.[6,7] Due to their biological and synthetic values, a number of methods have been developed for the preparation of 2-amino-4*H*-pyrans.



Scheme 1. 2-Amino-4*H*-pyran

In recent years, periodic mesoporous organosilicas (MOSs) were introduced as mesoporous materials containing these heteroelements with the organic-inorganic framework, that provides these materials with variety of physical properties, such as highly ordered pore systems, very large specific surface areas (up to 2000 $m^2 \cdot g^{-1}$), and pore size (approximately 2 to 50 nm).[8] Moreover, metal loading in the silica matrix can affect the overall acid strength, ion-exchange capacity, and catalytic performances extensively.[9] The MOS composites have received considerable interest for a broad range of applications, such as catalysis,[10–12] adsorbent,[13,14] gas separation,[15,16] drug delivery system,[17,18] and some biological uses.[19,20] In continuation of our previous research, a nanocomposite based on incorporation of copper (Cu^{2+}) into periodic mesoporous organosilica (Cu@MOS NCs) was prepared and used as a catalyst in various organic reactions.[21–23] Herein, we report the synthesis of the 4*H*-benzo[*b*]pyran derivatives via three component reaction in the presence of effective Cu@MOS NCs catalyst.

2. Experimental Section

All chemicals were purchased from commercial suppliers such as Fluka, Aldrich and Merck chemical companies.

2. 1. Preparation of the Catalyst

The copper heterogeneous catalyst was prepared by loading copper metal onto mesoporous organosilica nanocomposites (Cu@MOS NCs). The MSO structure was synthesized in sol-gel process and under hydrothermal condition via three steps: (i) to prepare the copper complex: melamine derivate (ligand, 1 mmol) and copper acetate monohydrate (1 mmol) in *N*,*N*-dimethylformamide solvent (15 mL) under reflux for 3 h. The solid was filtered, washed with ethanol and dried for 12 h in a vacuum oven. (ii) For the synthesis of copper complex-organosilica: copper complex (1.3 mmol) was dissolved in dry ethanol (60 mL), then 3-chloropropyltrimethoxysilane (2.6 mmol) and NaH (1 mmol) as a base was added to the mixture and also, ascorbic acid (1 mmol) for the reduction of the Cu(II) to Cu(I) was added. The reaction mixture was stirred and heated for 14 h under N_2 atmosphere. The solid was washed with ether (2 × 30 mL) and dried in a vacuum oven overnight at 40 °C. (iii) To prepare Cu@MOS NCs: the CTAB as surfactant (2.74 mmol) was dissolved in distilled water (47 mL). Then ammonia (25%, 11 mL) was added to the mixture and stirred for 30 min to obtain a clear solution. The organometallic-silica copper complex (0.52 mmol) and TEOS (10 mmol) were added to the above solution and refluxed for 24 h. After this time, the solid was filtered and washed with DI water, and dried in a vacuum oven for 10 h at 40 °C. The CTAB compound was removed with HCl solution (0.05 M) at 50 °C for 10 h (50 mL of 0.05 M ethanolic HCl for 1 g of solid material).

2. 2. General Procedure for Three Component Reaction on Cu@MOS NCs Catalyst

The three component reaction of aldehyde (1 mmol), dimedone (1 mmol) and malononitrile (1 mmol) was carried out with Cu@MOS NCs (5 mol %) in H_2O:ethanol (2:1, 10 mL) as solvent. The reaction was carried out at 50 °C and monitored by the TLC until total conversion of the starting materials. After completion of the reaction, to separate the catalyst, the obtained solid was dissolved in hot ethanol. Subsequently, the whole mixture was directly passed through a filter funnel and the catalyst remained on the filter paper, and the solvent was removed in vacuum to give the corresponding 2-amino-4*H*-pyran derivative **4**.

2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4a). White solid, m.p. 214–217 °C. IR (KBr) ν_{max} 84, 1039, 1213, 1367, 1594, 1655, 2192, 2962, 3320 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05 (s, 3H), 1.14 (s, 3H), 2.12 (d, 1H, J = 16.0 Hz), 2.22 (d, 1H, J = 16.0 Hz) 2.19–2.25 (m, 2H), 4.62 (s, 1H), 7.20 (s, 2H), 7.27 (d, 2H, J = 8.0 Hz), 7.20 (d, 2H, J = 8.0 Hz).

2-Amino-4-(2,4-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4b). White solid, m.p. 118–120 °C. IR (KBr) ν_{max} 563, 862, 1045, 1216, 1367, 1609, 1685, 2192, 2966, 3360 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.00 (s, 3H), 1.06 (s, 3H), 2.11 (d, 1H, J = 16.0 Hz), 2.27 (d, 1H, J = 16.0 Hz), 2.47–2.61 (m, 2H), 4.70 (s, 1H), 7.15 (s, 2H), 7.25 (d, 1H, J = 8.4 Hz), 7.39 (d, 1H, J = 8.4 Hz), 7.56 (s, 1H)

2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4c). White solid, m.p. 176–178 °C. IR (KBr) ν_{max} 865, 1039, 1215, 1366, 1522, 1656, 2192, 2964, 3322 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.02 (s, 3H), 1.06 (s, 3H), 2.26 (s, 2H), 2.48–2.52 (m, 2H), 4.55 (s, 1H), 6.04 (s, 2H), 7.46–8.06 (m, 4H).[24]

2-Amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4d). White solid, m.p. 204–206 °C. IR (KBr) ν_{max} 841, 1152, 1307, 1594, 1655, 2192, 2962, 3321 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.95 (s, 3H), 1.04 (s, 3H), 2.11 (d, 1H, J = 16.0 Hz), 2.27 (d, 1H, J = 16.0 Hz), 2.50 (s, 2H), 4.41 (s, 1H), 7.20 (s, 2H), 7.64 (m, 2H), 7.97 (s, 1H), 8.07 (d,1H, J = 7.7 Hz).

2-Amino-4-(3,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4e). White solid, m.p. 207–208 °C. IR (KBr) ν_{max} 841, 1039, 1367, 1594, 1655, 2192, 2962, 3321 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.96 (s, 2H), 6.87–6.85 (d, 1H, J = 8.4 Hz), 6.69–6.68 (d, 1H, J = 2.0 Hz), 6.66–6.64 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.0 Hz), 4.12 (s, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.52–2.49 (m, 2H), 2.28–2.08 (m, 2H), 1.03 (s, 3H), 0.97 (s, 3H).[25]

2-Amino-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4g). White solid, m.p. 224–225 °C. IR (KBr) ν_{max} 829, 1007, 1486, 1680, 2194, 3253, 3333 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.96–2.00 (m, 2H), 2.20–2.36 (m, 2H), 2.50–2.70 (m, 2H), 4.22 (s, 1H), 7.08 (s, 2H), 7.21 (d, 2H, J = 12 Hz), 7.35 (d, 2H, J = 12 Hz).

2-Amino-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4h). White solid, m.p. 235–237 °C. IR (KBr) ν_{max} 617, 1092, 1355, 1257, 2195, 3203, 3316 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.90–2.20 (m, 2H), 2.20–2.40 (m, 2H), 2.59–2.69 (m, 2H), 4.37 (s, 1H), 7.19 (s, 2H), 7.46 (d, 2H, J = 16 Hz), 8.17 (d, 2H, J = 16 Hz).

2-Amino-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4i). White solid, m.p. 201–

203 °C. IR (KBr) ν_{max} 617, 1001, 1355, 1527, 1658, 2195, 3203 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.85–2.10 (m, 2H), 2.20–2.40 (m, 2H), 2.65–2.72 (m, 2H), 4.42 (s, 1H), 7.20 (s, 2H), 7.60–7.70 (m, 2H), 7.99–8.01 (m, 2H).

2-Amino-4-(3,4-dimethoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4j). White solid, m.p. 203–204 °C. IR (KBr) ν_{max} 598, 825, 1088, 1204, 1402, 1583, 1657, 2222, 3138 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.96 (s, 2H), 6.86–6.84 (d, 1H, J = 8.4 Hz), 6.72 (s, 1H), 6.65–6.63 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.0 Hz), 4.14 (s, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.65–2.58 (m, 2H), 2.31–2.26 (m, 2H), 1.98–1.87 (m, 2H).[25]

3. Result and Discussion

Over time, scientists have investigated various catalytic techniques to effectively and selectively synthesize 1,3-dicarbonyl compounds, aldehydes, and malononitriles, which play a pivotal role in organic chemistry as essential precursors for the synthesis of diverse pharmaceuticals, agrochemicals, and functional materials. Examples of these catalysts are: (a) Cu(II) oxymetasilicate (0.1–0.5 mol%),[26] (b) hexamethylenetetramine,[27] (c) L-valine,[28] (d) Mg(II)-based MOFs,[29] (e) KF-Al$_2$O$_3$,[30] (f) NbCl$_5$,[31] (g) SiO$_2$NPs,[32] (h) ionic liquids like [2-aemim][PF$_6$],[33] and (i) Fe$_3$O$_4$/PEO/SO$_3$H nanocatalyst.[34] Every approach possesses its own set of benefits and drawbacks. Nevertheless, due to the extensive array of biological properties exhibited by tetrahydrobenzo[*b*]pyran derivatives, we are interested in investigating the catalytic potential of the copper-periodic mesoporous organosilica nanocomposites (Cu@MOS NCs) for the synthesis of these products. The catalyst not only offers easy separation from the reaction medium and convenient recovery but also exhibits high efficiency and short reaction times. The Cu@MOS NCs catalyst was prepared based on the report in the literature (Scheme 2).[22] In this research, a nanocomposite of Cu@MOS NC was prepared by treating organometallic-silica copper complex with TEOS and CTAB as a structural directing surfactant under basic conditions in distilled water (Scheme 2).

3. 1. Characterization of Cu@MOS NCs Catalyst

The BET isotherm and BJH pore size distribution analysis is very important for mesoporous structures, so these data for Cu@MOS NC are shown in Figure 1. The isotherm showed type IV patterns with H3 hysteresis loops, which is a characteristic of mesoporous solids.[35] The specific surface area, pore diameter and total pore volume were 462.40 m^2·g^{-1}, 3.98 nm and 0.5 cm^3·g^{-1}, respectively (Figure 1).

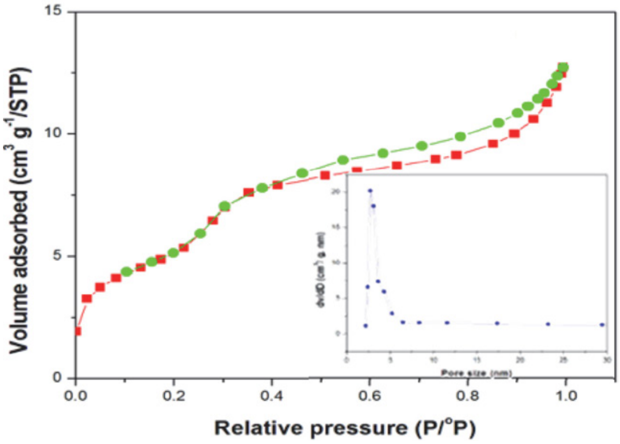
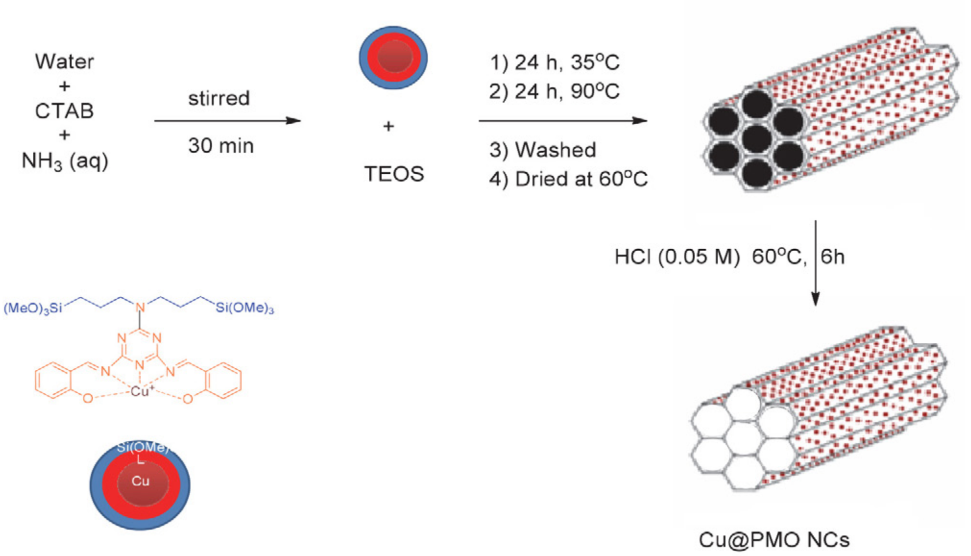


Figure 1. BET and BJH curve of Cu@MOS NC.



Scheme 2. Preparation of Cu@MOS NC.

TGA of Cu@MOS NCs is shown in Figure 2. According to the thermogram, 3–4 % weight loss within a temperature range of around 100–300 °C was observed, due to the loss of adsorbed water molecules. Furthermore, it shows that a degradation process occurs between 300–483 °C and the weight loss is about 11–12%. This is due to the breakdown of copper imprinted periodic mesoporous organosilica nanocomposite groups imprinted to the MOS.

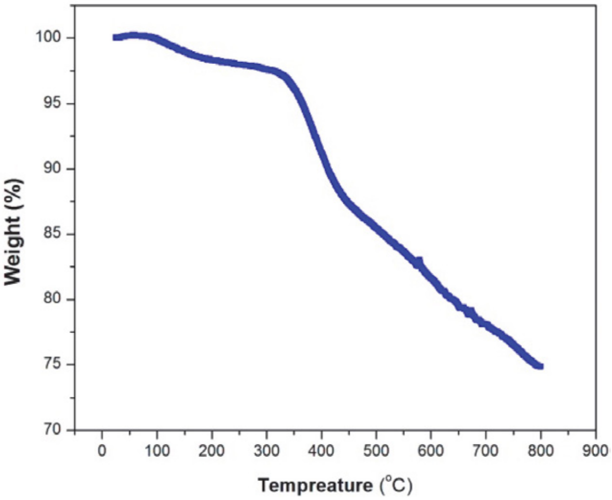


Figure 2. TGA thermograms of Cu@MOS NCs.

Figure 3a shows the SEM image of the Cu@MOS NCs which contain many short rods. Moreover, this surface morphology of the catalyst is indicative of the presence of a well-ordered mesostructure with hexagonal lattice arrangements.

For Cu@MOS NCs, the obtained results by EDS were as follows: C, 18.42; N, 7.09; Cu, 3.43; Si, 24.73; O, 49.34% (Figure 3b). The EDS analysis confirmed the presence of copper complex on MOS.

The well-ordered mesostructural arrangement of the Cu@MOS NCs hybrid was confirmed by low angle XRD. Figure 4 shows the low angle XRD patterns of Cu@MOS NCs. The three reflection peaks corresponding to 2θ = 0.5–5° of 1.05°, 1.9° and 2.3° were indexed to the (100), (110) and (200) reflections, respectively, which are clearly indicative of the presence of a well-ordered mesostructure of the materials with hexagonal lattice arrangements.

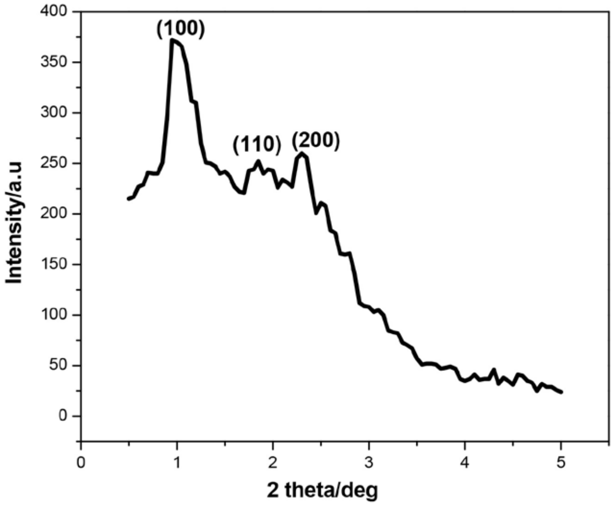


Figure 4. XRD spectrum of Cu@MOS NCs.

The FT-IR spectra of Cu@MOS NCs exhibited a broad band in the hydroxyl region at 3367 cm^{-1}. The C=N stretching vibration frequency of Cu@MOS NCs was observed at 1561 cm^{-1}. The vibration bands at 2853 and 2923 cm^{-1} were assigned to the C–H stretching vibrations of propyl and methyl groups, respectively. The vibration peak at 1474 cm^{-1} was characteristic of N–C vibrations of the aromatic functional groups related to the Cu@MOS NCs. The band in the range 1000–1100 cm^{-1} was assigned to

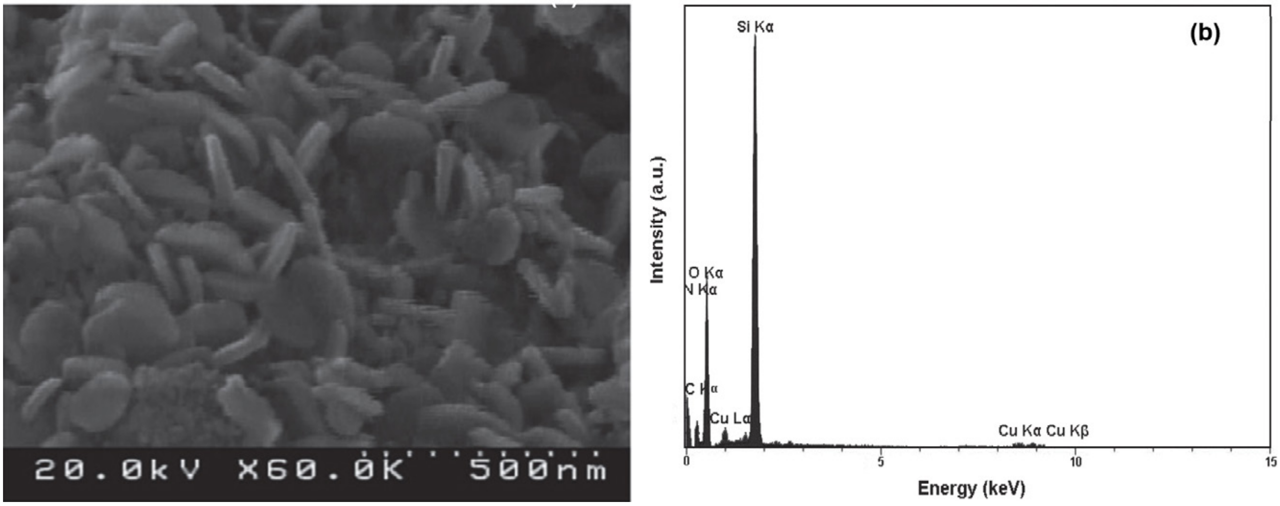


Figure 3. (a) FE-SEM image of Cu@MOS NCs, (b) EDS pattern of Cu@MOS NCs.

Si–O–Si groups and the band at 961 cm^{-1} was attributed to Si–OH groups (Figure 5c).

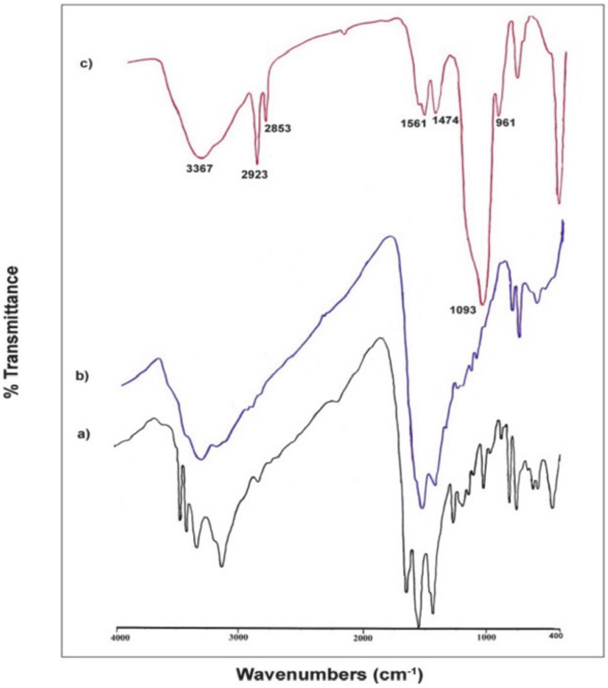


Figure 5. FT-IR spectra of (a) ligand, (b) copper-complex and (c) Cu@MOS NCs.

The synthesis of the 2-amino-4*H*-benzo[*b*]pyran derivatives via one-pot three component reaction from corresponding aromatic aldehyde (1 mmol), dimedone (1 mmol) and malononitrile (1 mmol) in the presence of Cu@MOS NCs (5 mol%) was reported (Scheme 3).

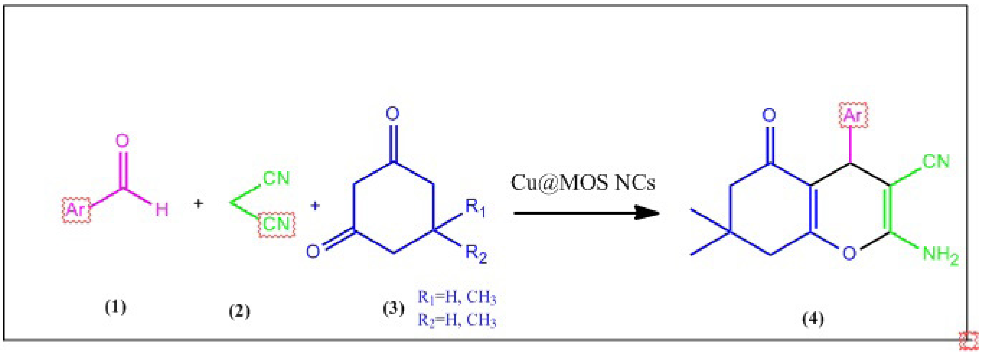
In order to optimize the reaction conditions, the reaction was carried out at different temperatures and with various solvents. Initially, we chose 2,4-dichlorobenzaldehyde, dimedone and maloninitrile as model substrates to optimize the reaction conditions. As shown in Table 1, the effect of temperature on the reaction efficiency was found to be insignificant and it was observed that the reaction without solvent and catalyst had a low yield. When the reaction was carried out in the presence of H_2O/EtOH as a solvent, at ambient temperature and without catalyst, it did not have a good efficiency (10%). Furthermore, we observed that, even when the reaction was conducted solely in the presence of H_2O as a solvent and the catalyst at a temperature of 50 °C, a satisfactory yield was not achieved (47%). The best result obtained is related to the solvent H_2O/EtOH with a ratio of 2:1 at a temperature of 50 °C and in the presence of a catalyst (Table 1).

Table 1. The Optimized reaction conditions for the synthesis of 2-amino-4*H*-benzo[*b*]pyrans.

Entry	Solvent	*T* (°C)	time (min)	yield (%)	cat (mol%)
1	H_2O	r.t	12	53	5
2	H_2O	r.t	30	49	–
3	H_2O	50	17	47	5
4	EtOH	r.t	120	19	5
5	EtOH	r.t	24 h	–	–
6	EtOH	50	150	16	5
7	H_2O/EtOH	r.t	8	83	5
8	H_2O/EtOH	r.t	16	10	–
9	H_2O/EtOH	50	5	94	5

The reaction of various aromatic aldehydes **1** with malononitrile **2** and some β-diketone molecules **3** in H_2O/EtOH as green solvent under Cu@MOS NCs catalyst led to the formation of 2-amino-4*H*-benzo[*b*]pyran **4** (Scheme 3). The catalyst showed high activity in terms of high yields and short reaction times, and also it was recovered and reused up to four cycles of the reaction. This reaction was carried out under the condition of green chemistry as only water and ethanol were used as solvents at room temperature and the product was easily isolated by simple filtration.

The data presented in Table 2 clearly indicate that aromatic aldehydes containing electron-withdrawing groups, such as nitro groups, as well as electron-donating groups, halogens, and hydroxyl groups, have exhibited remarkable reactivity in the presence of this catalyst. Consequently, these reactions have led to the formation of the products with high yields.



Scheme 3. Synthesis of 4*H*-benzo[*b*]pyran from aromatic aldehyde, 1,3-Cyclohexanedione and malononitrile under Cu@MOS NCs catalyst.

Table 2. Catalytic Synthesis of 2- amino-4*H*-benzo[*b*]pyran derivatives.

Entry	Ar	R_1	R_2	time (min)	yield[a] (%)	M.p. (°C)
4a	4-Cl-C_6H_4	CH_3	CH_3	10	90	214–217
4b	2,4-Cl_2-C_6H_3	CH_3	CH_3	5	94	118–120
4c	4-NO_2-C_6H_4	CH_3	CH_3	9	95	176–180
4d	3-NO_2-C_6H_4	CH_3	CH_3	45	94	204–207
4e	3,4-$(OCH_3)_2$-C_6H_3	CH_3	CH_3	50	90	207–208
4f	3-OMe-4-OH-C_6H_3	CH_3	CH_3	40	87	208–210
4g	4-Cl-C_6H_4	H	H	30	83	224–225
4h	4-NO_2-C_6H_4	H	H	60	90	235–237
4i	3-NO_2-C_6H_4	H	H	75	96	201–203
4j	3,4-$(OCH_3)_2$-C_6H_3	H	H	90	88	203–204

[a] Isolated yield of pure product

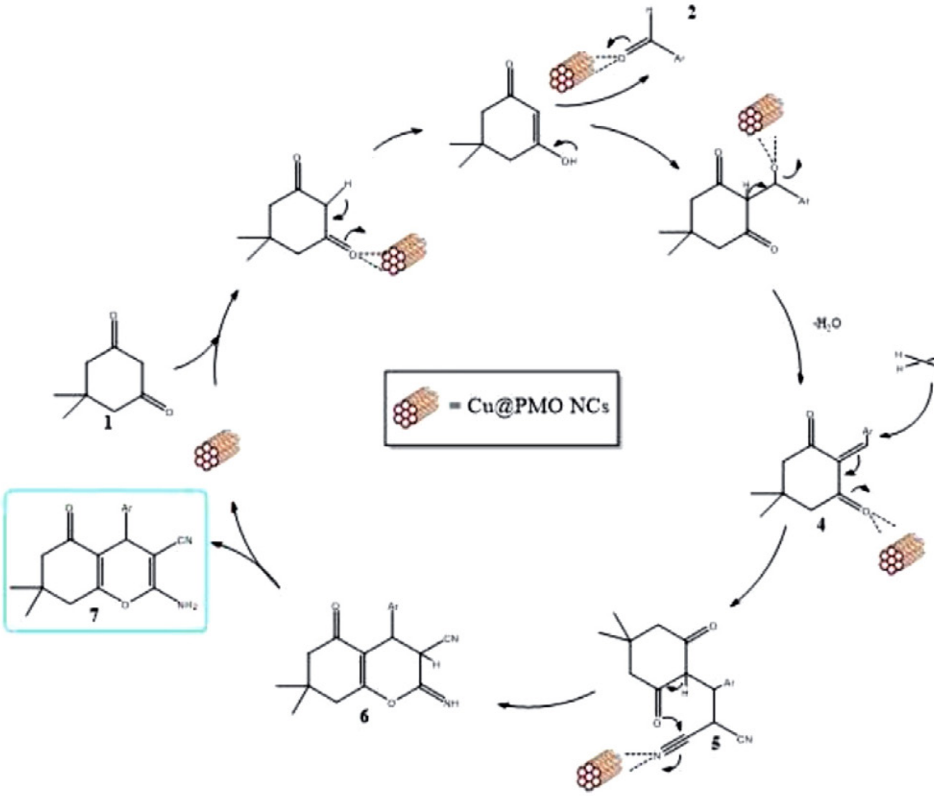
All the products were characterized by recording their melting points and comparing them with the corresponding values from the literature, as well as analyzing their IR and ^1H NMR spectra. The IR spectra exhibited absorption bands due to the carbonyl groups at 1520–1680 cm^{-1} (section 3 of the Supporting Information).

The proposed mechanism of 2-amino-3-cyano-4*H*-benzo[*b*]pyrans formation is given in Scheme 4.

As shown in Scheme 4, the Cu@MOS NCs nanocatalyst enhances the electrophilicity of the carbonyl groups in dimedone (**1**) and aldehyde **2** through a strong interaction. Molecule **4** is the result of a Lewis acid-catalyzed Knoevenagel condensation between the aldehyde and dimedone. Subsequently, this molecule undergoes an attack by malononitrile as a Michael acceptor, leading to an intramolecular cyclization. The cyclization process leads to the formation of intermediate **6**, and the final product **7** obtained via tautomerism of the intermediate **6**.

3. 2. Recycling of the Catalyst

One of the main aims of this work was to develop an easy way of recovery and recycling of the heterogeneous catalyst. The catalyst was easily and completely separated



Scheme 4. Proposed reaction mechanism for the formation of 2-amino-3-cyano-*4H*-benzo *[b]* pyran.

from the reaction mixture by simple filtration, washed with double distilled water and dried at 60 °C in an oven for 3 h, and the recovered catalyst was charged for the further run. The corresponding results indicate that this simple separation method could be repeated for 5 consecutive runs and the recovered catalyst showed remarkably constant catalytic activity in all the 5 cycles (Figure 6).

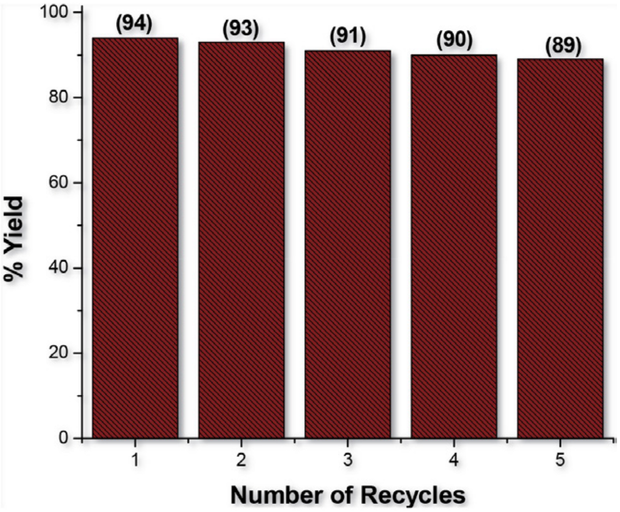


Figure 6. Recycling of the Cu@MOS NCs catalyst.

4. Conclusion

In conclusion we have developed a highly efficient method for synthesizing 2-amino-4*H*-benzo[*b*]pyran derivatives using copper-periodic mesoporous organosilica nanocomposite as a nanocatalyst. The yields achieved with this catalyst are impressive, ranging from good to excellent. The strength of our approach lies in its simplicity, as we have streamlined the reaction process and made it more accessible and user-friendly. Furthermore, our method allows for the recovery of the catalyst without any loss of reactivity, improving cost-effectiveness and promoting sustainability by reducing waste.

Acknowledgment

We express our sincere gratitude from the Research Committee of Graduate University of Advanced Technology in Kerman and Sirjan University of Technology for their financial support perfect assistances.

5. References

1 J. M. V. Lauridsen, R. R. Kragh, J. W. Lee. *Synthesis*. **2022**, 329-490. **DOI:**10.1016/B978-0-12-818655-8.00005-6

2 G. Brahmachari, B. Banerjee, *ACS Sustain. Chem. Eng.* **2013**, *2*, 411–422. **DOI:**10.1021/sc400312n

3 D. Kumar, V. B. Reddy, S. Sharad, U. Dube, S. Kapur, *Eur. J. Med. Chem.* **2009**, *44*, 3805–3809. **DOI:**10.1016/j.ejmech.2009.04.017

4 U. R. Pratap, D. V. Jawale, P. D. Netankar, R. A. Mane, *Tetrahedron Lett.* **2011**, *52*, 5817–5819. **DOI:**10.1016/j.tetlet.2011.08.135

5 C. Chen, M. Lu, Z. Liu, J. Wan, Z. Tu, T. Zhang, M. Yan, *Open J. Med. Chem.* **2103**, *3*, 128–135.

6 D. Armesto, W. M. Horspool, N. Martin, A. Ramos, C. Seoane, *J. Org. Chem.* **1989**, *54*, 3069–3072. **DOI:**10.1021/jo00274a021

7 D. Armesto, W. M. Horspool, N. Martin, A. Ramos, C. Seoane, *J. Chem. Soc.* **1987**, *16*, 1231–1232. **DOI:**10.1039/c39870001231

8 M. F. V. Rebbin, M. Jakubowski, S. Potz, *Micropor. Mesopor. Mater.* **2004**, *72*, 99–105. **DOI:**10.1016/j.micromeso.2004.04.018

9 S. Samanta, S. Giri, P. U. Sastry, N. K. Mal, A. Manna, A. Bhaumik, *Ind. Eng. Chem. Res.* **2003**, *42*, 3012–3018. **DOI:**10.1021/ie020905g

10 Y. Jiang, K. Lin, Y. Zhang, J. Liu, G. Li, J. Sun, X. Xu, *Appl. Catal. A: General* **2012**, *445–446*, 172–179. **DOI:**10.1016/j.apcata.2012.08.016

11 F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 3216–3251. **DOI:**10.1002/anie.200503075

12 B. Karimi, D. Enders, *Org. Lett.* **2006**, *8*, 1237–1240. **DOI:**10.1021/ol060129z

13 S.Houa, Y. Tang, T. Zhu, Z. H. Huang, Y.Liu, Y.Sun, X. Li, F. Shen, *J. Hazard. Mater.* **2022**, *436*, 129–208. **DOI:**10.1016/j.jhazmat.2022.129208

14 T. L. Chew, A. L. Ahmad, S. Bhatia, *Adv. Colloid Interface Sci.* **2010**, *153*, 43–57. **DOI:**10.1016/j.cis.2009.12.001

15 Y.Songa, P.Huang, H.Li, R.Li, W.Zhan, Y.Du, M.Ma, J. L. Tian, Z. D. Du, *Sci. Total Environ.* **2022**, *833*, 154858. **DOI:**10.1016/j.scitotenv.2022.154858

16 B. Zhang, X. Liu, H. Wang, K. Li, T. Tatsumi, J. Wang, *Mater. Lett.* **2022**, *321*, 132422. **DOI:**10.1016/j.matlet.2022.132422

17 H. Ahmed, S. S. Gomte, V. Prathyush, A. Prabakaran, M. Agrawal, A. Alexander, *Int. J. Drug Deliv. Technol.* **2022**, *30*, 103729. **DOI:**10.1016/j.jddst.2022.103729

18 V. Nejadsha, H. Naeimi, B. Goliaei, B. Bigdeli, A. Sadighi, *Mater. Sci. Eng. C.* **2019**, *99*, 805–815. **DOI:**10.1016/j.msec.2019.02.017

19 S. Alharthi, Z. M. Ziora, T. Janjua, A. Popat, P. M. Moyle, *Pharmaceutics.* **2022**, *14*, 986. **DOI:**10.3390/pharmaceutics14050986

20 D. Zhao, Y. Wan, W. Zhou: Ordered Mesoporous Materials, John Wiley & Sons, **2012**. **DOI:**10.1002/9783527647866

21 H. Naeimi, V. Nejadshafiee, S. Masoum, *Appl. Organometal. Chem.* **2015**, *29*, 314–321. **DOI:**10.1002/aoc.3293

22 H. Naeimi, V. Nejadshafiee, M. R. Islami, *Bull. Chem. Soc. Jpn.* **2016**, *89*, 212–219. **DOI:**10.1246/bcsj.20150291

23 H. Naeimi, V. Nejadshafiee, S. Masoum, *RSC Adv.* **2015**, *5*, 15006–15016. **DOI:**10.1039/C4RA17229A

24 S. Rathod, B. Arbad, M. Lande, *Chin. J. Catal.* **2010**, *31*, 631–636. **DOI:**10.1016/S1872-2067(09)60078-4

25 J. Xu, W. Li, H. Zheng, Y. Lai, P. Zhang, *Tetrahedron* **2011**, *67*, 9582–9587. **DOI:**10.1016/j.tet.2011.09.137

26 J. M. V. Lauridsen, R. R. Kragh, J.-W. Lee, *Compr. Heterocycl. Chem. IV*, **2022**, *7*, 329–490. **DOI:**10.1016/B978-0-12-818655-8.00005-6

27 M. Habibi, A. Habibi, S. H. Nasab, D. H, S. M. Mahdavi, *J. Heterocycl. Chem.* **2017**, *54*, 1880–1886. **DOI:**10.1002/jhet.2781

28 J. Tiwari, S. Singh, M. Saquib, F. Tufail, A. K. Sharma, S. Singh, J. Singh, *Synth. Commun.* **2018**, *48*, 188–196. **DOI:**10.1080/00397911.2017.1393087

29 K. K. Gangu, S. Maddila, S. B. Mukkamala, S. B. Jonnalagadda, *Ind. Eng. Chem. Res.* **2017**, *56*, 2917–2924. **DOI:**10.1021/acs.iecr.6b04795

30 I. Kharbangar, M. R. Rohman, H. Mecadon, B. Myrboh, *Int. J. Org. Chem.* **2012**, *2*, 282–286. **DOI:**10.4236/ijoc.2012.23038

31 M. S. Siqueira, L. C. Silva-Filho, *Tetrahedron Lett.* **2016**, *57*, 5050–5052. **DOI:**10.1016/j.tetlet.2016.10.008

32 S. Banerjee, A. Horn, H. Khatri, G. Sered, *Tetrahedron Lett.* **2011**, *52*, 1878–1881. **DOI:**10.1016/j.tetlet.2011.02.031

33 J. Safaei-Ghomi, R. Teymuri, H. Shahbazi-Alavi, *Chin. Chem. Lett.* **2013**, *24*, 921–925. **DOI:**10.1016/j.cclet.2013.06.021

34 A. Maleki, M. Azizi, Z. Emdadi, *Green Chem. Lett. Rev.* **2018**, *11*, 573–582. **DOI:**10.1080/17518253.2018.1547795

35 G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, *Catal. Today.* **1998**, *41,* 207–211. **DOI:**10.1016/S0920-5861(98)00050-9

Povzetek

V tej študiji predstavljamo učinkovito metodo priprave bakrovih periodičnih mezoporoznih organosilikatnih nanokompozitov (Cu@MOS NC) kot visokozmogljivih nanokatalizatorjev. Nanokompozit smo karakterizirali z različnimi metodami, vključno z rentgensko difrakcijo (XRD), BET analizo, SEM in EDS mikroskopijo ter s termogravimetrično analizo (TGA). Cu@MOS NC nanokatalizator smo uporabili pri trikomponentni reakciji med aromatskimi aldehidi, dimedonom in malononitrilom, ki predstavlja učinkovito in zeleno sintezo 2-amino-4*H*-benzo[*b*]piranskih derivatov z visokimi izkoristki. Sinteza je s stališča izvedbe enostavna, okolju prijazna, ima široko uporabnost, katalizator pa se lahko enostavno reciklira in večkrat uporabi.