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Heterogeneous silica-supported copper catalyst for the ultrasound-mediated rapid reaction between dimedone, formaldehyde, and amines at room temperature

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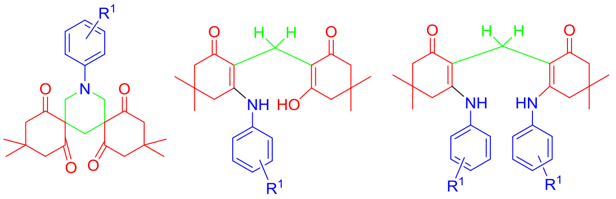
Abstract A copper-incorporated mesoporous silica catalyst was synthesized and characterized by N_2 adsorption analysis, HRTEM, EDX-elemental analysis, and XRD studies. The silica material possesses mesopores of dimension 3–5 nm. Incorporation of copper within the silica network produces enhanced surface acidity in comparison to pure silica, which is reflected in the sonication-assisted rapid reaction between dimedone, formaldehyde, and amines. Sonication-mediated room temperature synthesis was proved to be more convenient and rapid than ordinary stirring. A standard leaching experiment proved that the reaction was heterogeneous with this recyclable catalyst.

Graphical abstract



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Keywords Ultrasound-assisted synthesis · Heterogeneous catalyst · Mesoporous silica-supported copper catalyst · Multicomponent synthesis

Introduction

The collective accomplishment of making multiple bonds in a one-pot synthesis operation is well known as multicomponent reaction (MCR), which promotes a sustainable synthesis approach to molecule and drug discovery processes [1]. An important reaction in the realm of multicomponent syntheses is the three-component condensation of aromatic amines with dimedone and formaldehyde in the presence of a catalyst leading to the formation of 3,5-dispirosubstituted piperidines. Spiro-fused piperidine compounds have attracted particular attention as synthesis targets due to their miscellaneous important activities as pharmacophores in several biologically active compounds, mainly alkaloids, which are responsible for a number of unique activities, including anti-hypertensive, anticonvulsant, and anti-inflammatory activities [1–6].

Again in recent years, the concept of “green chemistry” has been well accepted to meet the fundamental scientific challenges of protecting the environment while simultaneously achieving commercial feasibility [7]. One of the thrust areas of sustainable synthesis is to explore alternative reaction conditions. The development in the last few years of synthesis protocols employing ultrasound irradiation has led to an important change in organic reactions and has permitted the activation of poorly reactive substrates [8]. Ultrasonic (US) waves are propagated via alternating compressions and rarefactions cycles, induced in the transmitting liquid, with the expansion cycles exerting negative pressure on the liquid [9]. If this applied negative pressure is strong enough to collapse the intermolecular van der Waals force of the liquid, small cavities or gas-filled micro-bubbles are formed. These cavities absorb energy from US waves and grow to reach a stage where it can no longer absorb energy efficiently and implodes [10–14]. These rapid and violent implosions generate short-lived regions with very high local temperature and pressure. This cavitationally induced phenomenon is known to activate reactant molecules entering into cavity and consequently converts them into reactive intermediates.

The use of heterogeneous catalysts has received tremendous attention as alternatives in alleviating the limitations of homogeneous catalysts [1]. Thus, the search for an inexpensive, readily available, and convenient catalyst is desirable. Solid catalysts provide numerous opportunities for recovering and recycling catalysts from a reaction mixture [1]. Among the various heterogeneous catalysts, mesoporous silica-supported catalysts are of particular advantage because of combination of interesting properties, such as a high surface area with a robust yet flexible structure and a wide range of compositional variations [15, 16]. When such ultrasound-assisted synthesis is coupled with heterogeneous catalysis, it fulfills most of the criteria of sustainable synthesis.

Results and discussion

It has been noticed that silica and some of the support materials like alumina, zinc oxide, zirconia, etc. exhibit significant surface acidity in copper-based catalysts [17–24]. In recent past, the acidity of a mesoporous silica-supported copper catalyst has been utilized in the Biginelli reaction, Mannich reaction, different multicomponent reactions, and catalytic transformations of benzyl alcohol, etc. [17, 25–27]. In the present context, we exploited the surface acidity of Cu/SiO_2 in the synthesis of 3,5-dispirosubstituted piperidines using silica-supported copper as catalyst under ultrasound irradiation (Scheme 1). So far only three reports on the synthesis of various 3,5-dispirosubstituted piperidines are available [1, 7, 28]. Moreover, at the outset of our studies, there was no literature precedent for the direct application of a heterogeneous reusable catalyst in combination with ultrasound for the synthesis of 3,5-dispirosubstituted piperidines.

The catalyst was prepared by co-condensation of tetraethyl orthosilicate (TEOS) and $Cu(OAc)_2$ in basic medium followed by calcinations at 550 °C. It was characterized by N_2 adsorption analysis, HRTEM, EDX-elemental analysis, and XRD studies.

Characterization of catalyst

Nitrogen adsorption analysis

The N_2 adsorption/desorption isotherms and corresponding pore size distribution of the silica-supported copper catalyst is shown in Fig. 1. The isotherm is a typical type IV isotherm with the presence of a hysteresis loop (H_2 type), which indicates the presence of mesopores in the material (panel a). The BET surface area calculated from this isotherm is 4.78×10^4 cm^2 g^{-1}. The pore volume estimated for this sample is 0.3819 cm^3 g^{-1}. Corresponding pore size distribution was estimated by the non-local density functional theory (NLDFT) model is shown in panel b (Fig. 1). Estimated pore dimension for the sample is found to be ca. 5.7 nm.

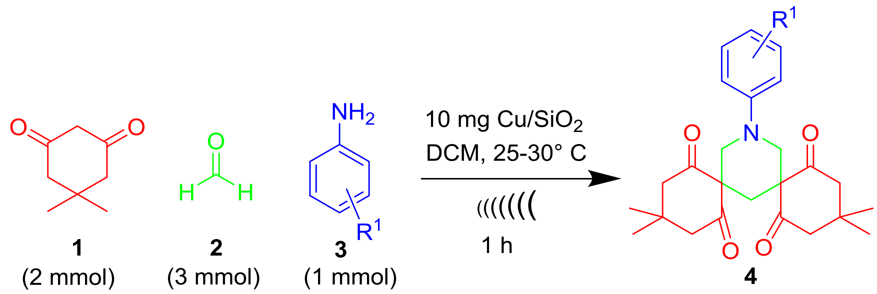
HRTEM images of Cu incorporated silica

Representative HRTEM images of material are shown in Fig. 2 (panel a–c). From the representative TEM images, it is clear that there are pores in the dimension of 3–5 nm present throughout the specimen grid. These data match well with the pore dimension obtained from N_2 sorption data.

Elemental analysis

The chemical characterization for the material was carried out by EDX analysis. It revealed that three elements O, Si,

Scheme 1



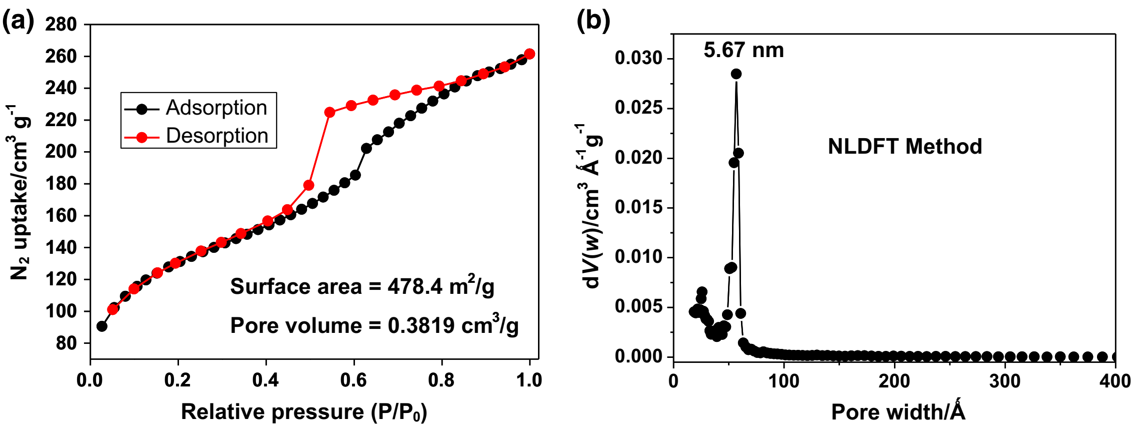


Fig. 1 N_2 adsorption isotherm and pore size distribution of Cu/SiO_2. Adsorption points are marked by *filled circle,* whereas those for desorption are marked by *empty circles*

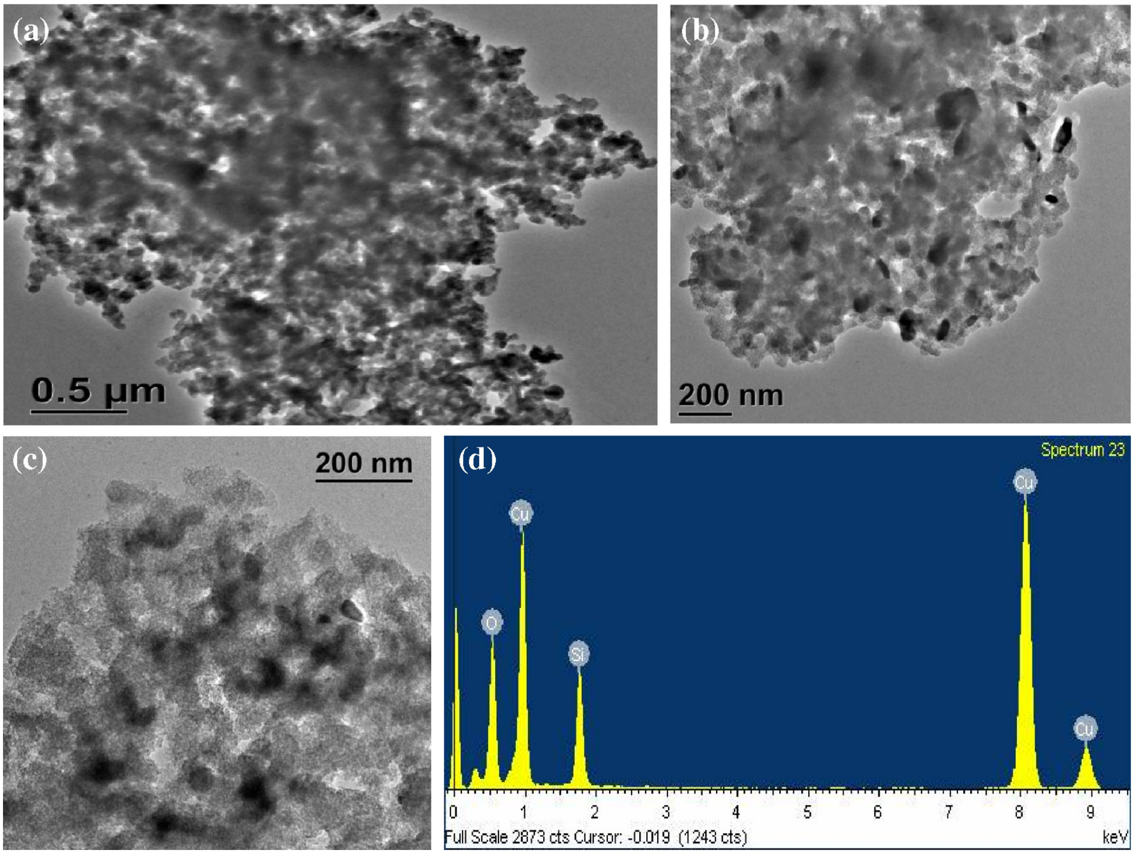


Fig. 2 **a–c** HRTEM images of Cu/SiO_2 catalyst, and **d** EDX spectrum of Cu/SiO_2 catalyst

and Cu are present in the material (Fig. 2, panel d). EDX chemical analysis confirmed that the expected copper-incorporated mesoporous silica has successfully developed in this study.

Powder XRD pattern

The formation of copper oxide within the silica matrix was confirmed from the wide-angle powder XRD pattern of Cu/SiO_2 sample (Fig. 3). Several diffraction peaks can be

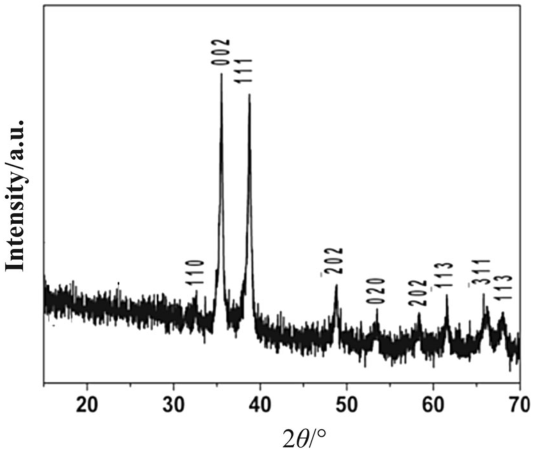


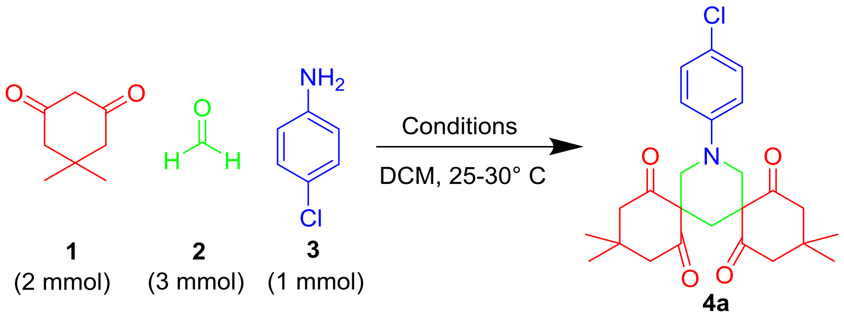
Fig. 3 Powder XRD pattern of Cu/SiO_2

indexed to the diffraction planes (110), (002), (111), ($\bar{2}02$), (020), (202), ($\bar{1}13$), ($\bar{3}11$), and (113) for CuO in the monoclinic phase [29].

Synthesis application of the catalyst

Multicomponent reactions enable simultaneous cyclization and functionalization making it possible to efficiently prepare diverse derivatives bearing a variety of functionalities. However, this type of multicomponent tandem cyclization requires several reaction components having multiple reaction sites; an unregulated reaction readily forms a complex mixture of undesired products. The challenge is to conduct an MCR in such a way that the reaction yields only the main product and not the side-products. In order to optimize the reaction condition (Table 1), a series of experiments were conducted under ultrasonic irradiation and ordinary stirring conditions, taking the reaction of dimedone (2 mmol), 4-chloroaniline (1 mmol), and formaldehyde (3 mmol) as a model reaction. Different homogeneous acids like HCl, H_2SO_4, $HClO_4$, TfOH, PTS, HPF_6, HBF_4, and AcOH were tested (Table 1). Ordinary to moderate conversions were achieved with these homogeneous acids. However, they

Table 1 Optimization reaction conditions



Entry	Catalyst	Conventional heating		Ultrasound irradiation	
		Time/min	Yield/%[a]	Time/min	Yield/%[a]
1	HCl	60	33	60	39
2	H_2SO_4	60	30	60	36
3	$HClO_4$	60	30	60	35
4	TfOH	60	35	60	41
5	PTS	60	36	60	43
6	AcOH	60	34	60	41
7	TiO_2	60	37	60	78
8	SiO_2	60	39	60	81
9	$ZnTiO_3$	60	36	60	77
10	Cu/SiO_2	60	43	60	91
11	Cu/SiO_2	600	81	600	91

Reaction conditions: dimedone (2 mmol), 4-chloroaniline (1 mmol), formaldehyde (3 mmol), different catalysts (0.1 mmol for homogeneous catalysts and 10 mg for heterogeneous catalysts), dichloromethane (4 cm^3), different times, room temperature (25–30 °C)

[a] Isolated yields

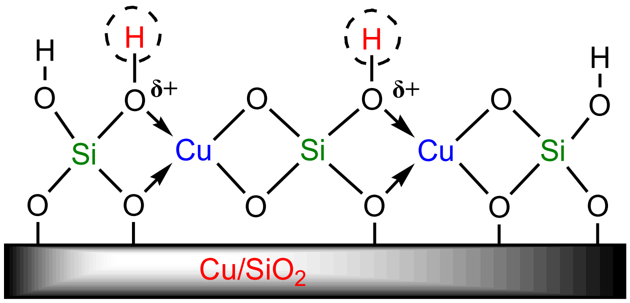


Fig. 4 Diagram explaining enhanced surface acidity of copper-incorporated silica

required repeated work-up, neutralization of strong acids, and extensive chromatographic purification. Ultimately, the isolated yields were not satisfactory (Table 1, entries 1–6). Compared to these homogeneous catalysts, heterogeneous acid catalysts like TiO_2, SiO_2, and $ZnTiO_3$ nanopowder afforded better isolated yields of **4** (Table 1, entries 7–9). However, a maximum yield of **4** was obtained with heterogeneous copper-incorporated silica catalyst (Table 1, entry 10). This is because of the fact that introduction of copper within the silica network produces enhanced surface acidity in comparison to pure silica. The significant surface acidity of Cu/SiO_2 catalyst originates from the combination of the Lewis acidic property of Cu^{2+} ion and Brønsted acidity of silica silanol. The silanol oxygens coordinate with copper ion in the network and the hydrogen of silanol becomes labile and easily comes out as proton. In Fig. 4 the labile hydrogens are marked in red color.

Again, the yield of the spiro-piperidine **4** in the Cu/SiO_2 catalyzed synthesis was always greater under ultrasound irradiation than for ordinary stirring (Table 1). Under ordinary stirring condition, without the use of ultrasonication, moderate to good yields of spiro-piperidines **4** were only obtained after 10–12 h time (Table 1, entry 11). In contrast, a much higher yield of **4** was obtained within only 60 min at room temperature under ultrasound condition. Thus, the best yield, cleanest reaction, and most facile work-up were achieved under ultrasonic irradiation at room temperature, employing 10 mg of Cu/SiO_2 as the right choice of catalyst (entry 10).

The higher activity of the heterogeneous Cu/SiO_2 catalyst under sonochemical conditions can be explained on the basis of higher adsorption and mass transfer of organic molecules on the surface of catalyst, caused by shockwave and microjets formed [30, 31]. Symmetrical cavitation and collapse of bubbles in the liquid medium are very common; however, if cavitation bubbles are formed at or near a solid surface, the dynamics of cavity collapse change drastically. Close to a solid boundary, cavity collapse is asymmetric and creates high-speed jets of liquid. These jets hit the surface with tremendous force. This process can produce newly exposed highly reactive catalyst surfaces and increase the mass transfer to the catalyst surface [32, 33]. Therefore, the shock waves and high-speed jets may probably enhance the rate of the reaction under sonic condition.

Plausible mechanism

A mechanism portraying the probable sequence of steps for the synthesis of spiro-piperidine is shown in Scheme 2. The spirocyclization may take place as a domino sequence of Knoevenagel, Michael, and double Mannich reactions. A literature survey [34, 35] revealed that dimedone is not only a Knoevenagel reagent but it also adds easily to

Scheme 2

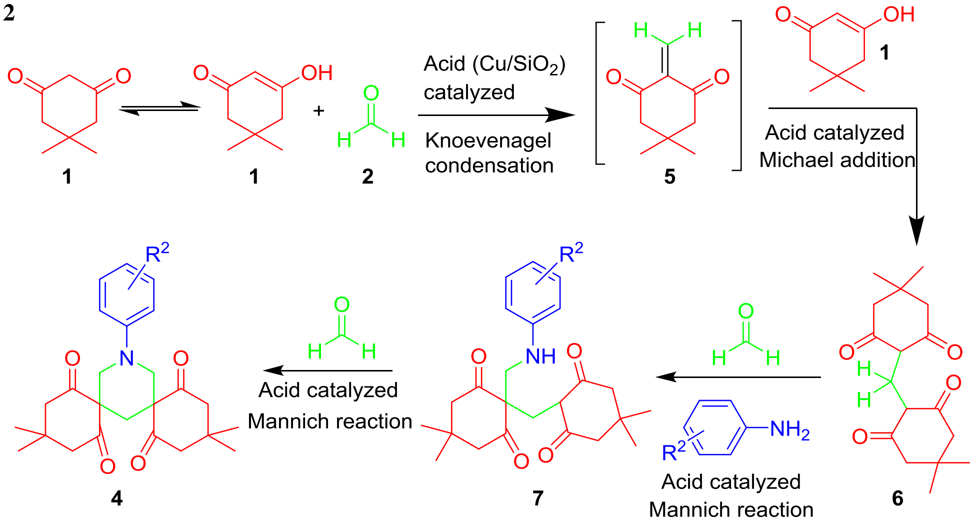
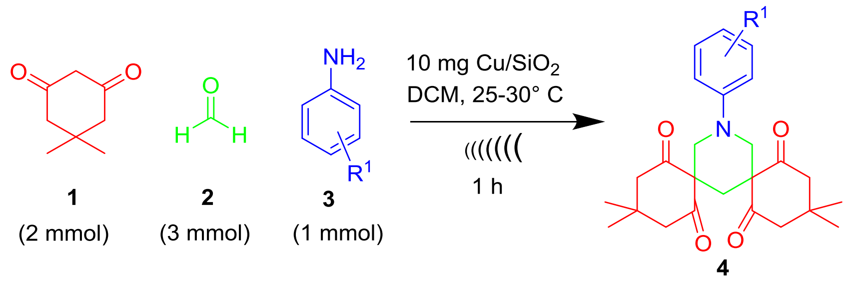


Table 2 Cu/SiO_2 catalyzed multicomponent synthesis of dispirosubstituted piperidines



Entry	Product	R^1	Yield/%[a]	References
1	**4a**	4-Cl	91	[1]
2	**4b**	3,4-Me_2	94	[1]
3	**4c**	H	92	[2]
4	**4d**	4-Me	93	[2]
5	**4e**	3-Me	90	[28]
6	**4f**	4-OMe	89	[2]
7	**4g**	4-Br	88	[2]

Reaction conditions: dimedone (2 mmol), amines (1 mmol), formaldehyde (3 mmol), Cu/SiO_2 catalyst (10 mg), dichloromethane (4 cm^3), 60 min ultrasound irradiation at room temperature (25–30 °C)

[a] Isolated yields

electron-poor alkenes in the Michael addition fashion leading to the dimedone–formaldehyde adducts **6** (Scheme 2). The well-known dimedone–formaldehyde adducts then undergo two consecutive Mannich reactions with aromatic amine and formaldehyde to produce the dispirosubstituted piperidine. Again **6** was also formed by the reaction of dimedone (2 mmol) and HCHO (1 mmol) at room temperature in presence of Cu/SiO_2 catalyst in 20 min. This compound **6** when reacted with aromatic amine afforded the final product **4**. Therefore, intermediacy of **6** in this transformation is proved. Isolation of intermediate **6** and its structure determination by NMR spectroscopy proves the mechanism conclusively. Here, Cu/SiO_2 having enhanced surface acidity catalyzes all the steps.

Substrate scope

The attenuated acidity of the Cu/SiO_2 was found to be crucial for cyclization but insufficient to affect the acid-sensitive moieties because methoxy-substituted aryl amines as well as heteroaromatic amines reacted very efficiently with no side reactions (Table 2). For precursors **3** bearing either electron-donating or electron-withdrawing substituents on the aromatic ring, the reactions all proceeded very smoothly to provide the corresponding spiro-piperidines **4**. Therefore, the present Cu/SiO_2 catalyzed protocol has a general applicability accommodating a variety of substitution patterns. It is pertinent to mention that the product structure was unambiguously proved by X-ray single crystal analysis of the two distinct compounds **4a** (CCDC 1015248) and **4g** (CCDC 1015247) (Fig. 5).

After successful formation of spiro-piperidines **4**, to delineate this approach, the scope and generality of this catalyst were next extended in the reaction between enaminoketones **8**, formaldehyde, and dimedone to yield **9** (Table 3).

Moreover, the synthesis of compound **10** was also explored using this catalyst to further extend the generality of this protocol (Table 4). The structure of **10** was unambiguously assigned by X-ray single crystal analysis (Fig. 6).

Recycling and leaching experiment

The reusability of the Cu/SiO_2 catalyst in the spiro-piperidine **4** formation reaction was examined taking the reaction forming **4a** as model reaction. Nearly quantitatively catalyst (up to 98 %) could be recovered from each run. In a test of six cycles, the catalyst could be reused without significant loss of catalytic activity. The kinetics of the fresh catalyst was evaluated as shown in Fig. 7. The yield did not further increase substantially after 1 h. Also we performed the kinetic study with the recycled catalyst for the next consecutive five runs. The results of kinetic plots suggested that the catalyst retained good efficiency

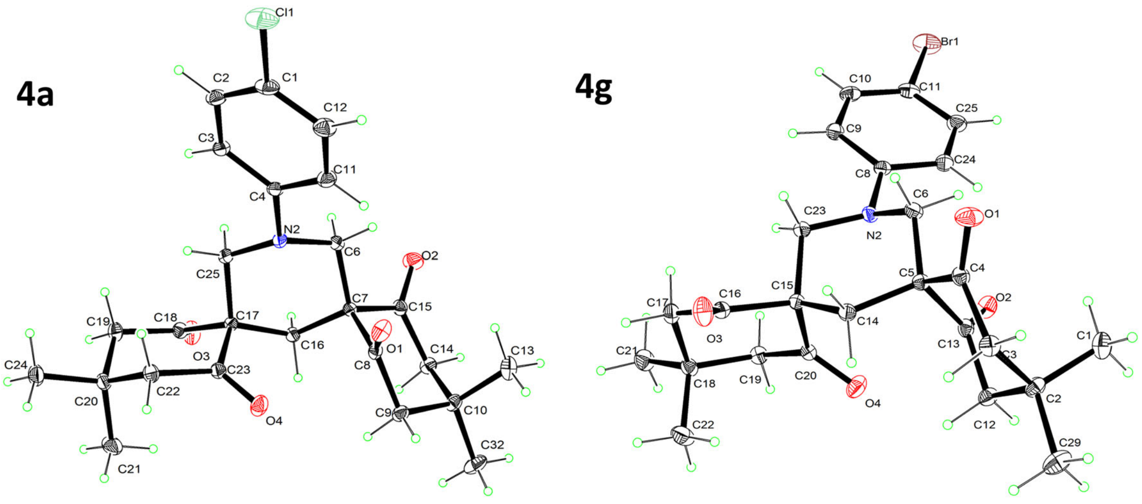
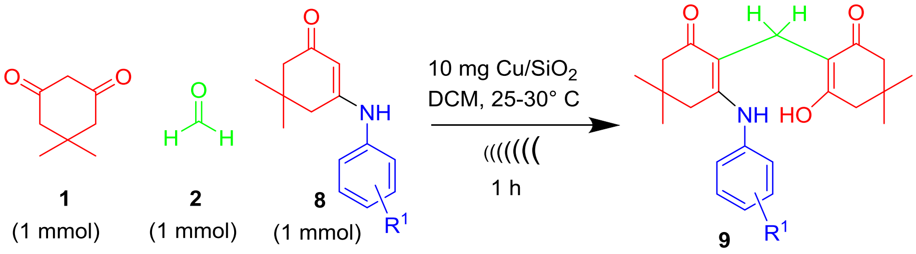


Fig. 5 X-ray single crystal structures of **4a** (CCDC 1015248) and **4g** (CCDC 1015247)

Table 3 Cu/SiO_2 catalyzed multicomponent synthesis of compound **9**



Entry	Product	R^1	Yield/%[a]	References
1	**9a**	4-Me	90	[35]
2	**9b**	4-OMe	92	[35]
3	**9c**	4-Br	91	–

Reaction conditions: dimedone (1 mmol), formaldehyde (1 mmol), enaminoketones (1 mmol), Cu/SiO_2 catalysts (10 mg), dichloromethane (4 cm^3), 60 min ultrasound irradiation at room temperature (25–30 °C)

[a] Isolated yields

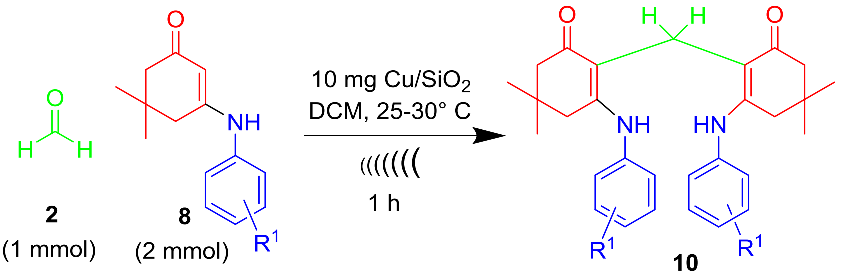
after recycling. The recovered catalyst after six runs had no obvious change in the structure referring to the HRTEM images in comparison with the fresh one (figure given in Supplementary material). These results revealed that the catalyst was very stable.

To confirm the heterogeneous nature of catalyst and catalytic activity bound to the solid phase, a standard leaching experiment was conducted [36]. A mixture of dimedone, 4-chloroaniline, and HCHO in DCM was allowed to react for 30 min under sonication in the presence of Cu/SiO_2 to afford the corresponding spiro-piperidine **4a**. After this 30 min period, the reaction mixture was filtered. The filtered reaction mixture was then sonicated without a catalyst for the next 1 h; no further formation of the corresponding product was observed, indicating that no homogeneous catalyst was involved. XPS analysis of the filtrate showed that copper was not leached in the solution.

Conclusion

In conclusion, as part of the continuing exploration of combined use of ultrasound/heterogeneous catalyst for the green organic reactions, this method has great prospects of applications in organic syntheses, pharmacy, and industrial processes. Simplicity of the procedure, rapid reaction, and reusability of the catalyst makes it convenient for parallel synthesis.

Table 4 Cu/SiO$_2$ catalyzed multicomponent synthesis of compound **10**



Entry	Product	R^1	Yield/%^{a}
1	**10a**	4-Me	84
2	**10b**	4-Br	85

Reaction conditions: formaldehyde (1 mmol), enaminoketones (2 mmol), Cu/SiO$_2$ catalysts (10 mg), dichloromethane (4 cm^3), 60 min ultrasound irradiation at room temperature (25–30 °C)

[a] Isolated yields

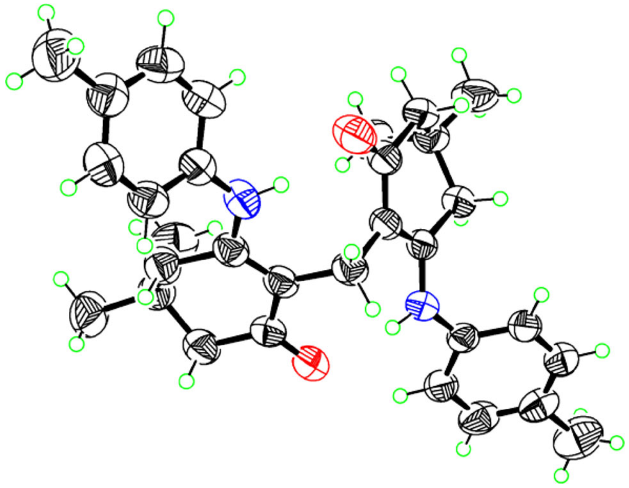


Fig. 6 X-ray single crystal structure of **10a** (CCDC 1035549)

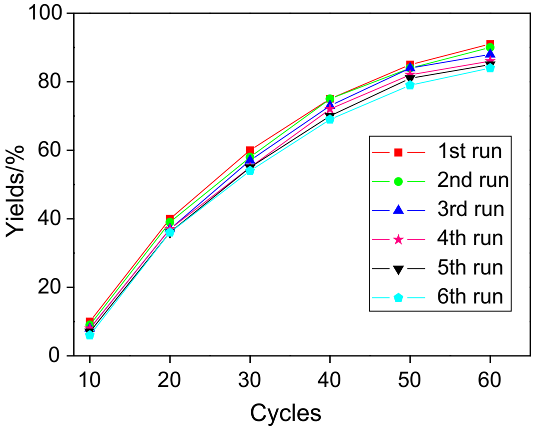


Fig. 7 Kinetic plot demonstrating the recycling efficiency of the catalyst

Experimental

The ^{1}H and ^{13}C NMR spectra were carried out on Bruker-Avance Digital 300 MHz instrument in CDCl$_3$ with TMS as internal reference. CHN analysis was performed using a Perkin-Elmer 2400 Series II CHN analyzer, their results were found to be in good agreement (±0.3 %) with the calculated values. Melting points were determined on an electrical melting point apparatus with an open capillary. Sonication was carried out in TAKASHI ultrasonic cleaning bath (Model no. UD200SH). Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb 1C at 77 K. Prior to gas adsorption, all the samples were degassed for 2 h at 353 K. XPS analysis was performed on the Omicron-Nanotech operated at 15 kV and 20 mA using a monochromatic AlK$_\alpha$ as X-ray source. X-ray diffraction patterns of the powder sample were obtained with a Seifert P3000 diffractometer using Cu Kα ($\lambda = 0.15406$ nm) radiation. Transmission electron microscopic images were recorded on a JEOL 2010 TEM operated at 200 kV in the Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India. All known compounds were characterized by IR, NMR, CHN. Spectral data and copy of ^{1}H and ^{13}C NMR spectra of representative compounds are given in supporting information.

Preparation of copper-incorporated mesoporous silica

In a 1 dm^3 open beaker fitted with a magnetic stirrer, 390 cm^3 water and 400 cm^3 MeOH were mixed. Then 3.52 g CTAB was added at 30–35 °C and stirred for 30 min. After a clear solution was obtained, tetraethylorthosilicate (TEOS) was added drop wise from a dropping funnel under stirring. Next, 71.3 mg $Cu(OAc)_2$ was added and the stirring was continued for another 5 min. Then 10 cm^3 0.4 N NaOH solution was added drop wise for 1 h. The stirring was continued for the next 8 h at room temperature and then aged overnight (12–14 h) at room temperature. It was filtered and washed thoroughly with deionized water and dried at 35–40 °C for 5 days. The dry powder was calcined at 550 °C for 6–8 h under static air.

General synthesis of the dispirosubstituted piperidines derivatives 4

A mixture of 0.14 g dimedone (**1**, 1 mmol), 0.09 g formaldehyde (**2**, 3 mmol), and 1 mmol amine **3** in dichloromethane was heated under reflux for a few minutes just to dissolve the starting materials. Then 10 mg of the silica-supported copper catalyst was added and the mixture was subjected to ultrasound irradiation for 60 min at room temperature (25–30 °C). The progress of the reaction was monitored by TLC (10 % EtOAc/90 % petroleum ether). After the completion of the reaction, the reaction mixture was diluted with dichloromethane and filtered to separate the product as filtrate from the catalyst (as residue). The solvent was dried in a rotary evaporator and the product was purified by silica gel column chromatography using EtOAc/petroleum ether as eluent.

General synthesis of the compounds 9

A mixture of 0.14 g dimedone (**1**, 1 mmol), 0.06 g formaldehyde (**2**, 1 mmol), and enaminoketones **8** in 5 cm^3 dichloromethane was heated under reflux for a few minutes just to dissolve the starting materials. Then 10 mg of the silica-supported copper catalyst was added and the mixture was subjected to ultrasound irradiation for 60 min at room temperature (25–30 °C). The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with dichloromethane and filtered. The solvent was evaporated in a rotary evaporator and the product was purified by silica gel column chromatography using EtOAc/petroleum ether as eluent.

2-[[2-(4-Bromophenylamino)-4,4-dimethyl-6-oxocyclohex-1-enyl]methyl]-3-hydroxy-5,5-dimethylcyclohex-2-enone (**9c**, $C_{23}H_{28}BrNO_3$)
White solid, m.p.: 196–198 °C (EtOAc); IR (KBr): $\bar{\nu} = 2956, 2924, 1634, 1584, 1511, 1488, 1444, 1401, 1391, 1363, 1324, 1282, 1211, 1154, 1082, 944\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 12.79$ (1H, s, OH), 10.53 (1H, s, NH), 7.48 (2H, d, $J = 8.7$ Hz, ArH), 7.03 (2H, d, $J = 8.7$ Hz, ArH), 3.34–3.29 (2H, m, CH_2), 2.53–2.19 (8H, m, 4 × CH_2), 1.05 (9H, br s, 3 × CH_3), 0.98 (3H, s, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.9$, 197.7, 189.5, 177.2, 162.1, 138.1, 132.3, 125.6, 118.4, 113.3, 111.0, 50.1, 49.0, 46.0, 43.5, 40.4, 33.0, 31.8, 29.1, 28.7, 27.3, 17.4, 15.9 ppm.

General synthesis of the compounds 10

A mixture of 0.03 g formaldehyde (**2**, 1 mmol) and enaminoketones **8** in 5 cm^3 dichloromethane was heated under reflux for a few minutes just to dissolve the starting materials. Then 10 mg of the silica-supported copper catalyst was added and the mixture was subjected to ultrasound irradiation for 60 min at room temperature (25–30 °C). The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with dichloromethane and filtered. The solvent was removed in a rotary evaporator and the product was purified by silica gel column chromatography using EtOAc/petroleum ether as eluent.

2-[[2-(p-Tolylamino)-4,4-dimethyl-6-oxocyclohex-1-enyl]-methyl]-3-(p-tolylamino)-5,5-dimethylcyclohex-2-enone (**10a**, $C_{31}H_{38}N_2O_2$)
White solid, m.p.: 192–194 °C (EtOAc); IR (KBr): $\bar{\nu} = 2922, 1638, 1581, 1512, 1481, 1442, 1392, 1361, 1322, 1281, 1154, 1082\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.68$ (2H, s, NH), 7.15 (4H, d, $J = 8.1$ Hz, ArH), 7.03 (4H, d, $J = 8.1$ Hz, ArH), 3.54 (2H, s, CH_2), 2.35–2.28 (14H, m, 4 × CH_2 and 2 × CH_3), 0.98 (12H, s, 4 × CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.8$, 162.1, 136.9, 134.7, 129.6, 124.6, 109.7, 50.0, 40.9, 32.6, 28.1, 20.9, 17.8 ppm.

2-[[2-(4-Bromophenylamino)-4,4-dimethyl-6-oxocyclohex-1-enyl]methyl]-3-(4-bromophenylamino)-5,5-dimethylcyclohex-2-enone (**10b**, $C_{29}H_{32}Br_2N_2O_2$)
White solid, m.p.: 222–224 °C (EtOAc); IR (KBr): $\bar{\nu} = 2926, 1634, 1582, 1510, 1481, 1452, 1382, 1361, 1281, 1152, 1088\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 10.60$ (2H, s, NH), 7.36 (4H, d, $J = 8.7$ Hz, ArH), 6.99 (4H, d, $J = 8.7$ Hz, ArH), 3.59 (2H, s, CH_2), 2.40 (4H, s, 2 × CH_2), 2.30 (4H, s, 2 × CH_2), 1.00 (12H, s,

4 × CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 196.0$, 162.4, 150.1, 132.0, 120.2, 113.7, 110.0, 50.1, 41.0, 32.8, 28.4, 21.0 ppm.

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