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FULL PAPER

Oxidative amidation of benzyl alcohol, benzaldhyde, benzoic acid styrene and phenyl acetylene catalyzed by ordered mesoporous HKUST-1-Cu: Effect of surface area on oxidative amidation reaction

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HKUST-1-Cu synthesized in the presence and absence of P-123 trough solvotermal method. After characterization using some different microscopic and spectroscopic techniques such as XRD, FT-IR, SEM, ICP, BET and TEM its catalytic activity was investigated in the oxidative coupling of benzyl alcohol, benzaldhyde, benzoic acid, styrene and phenyl acetylene with N,N-dialkylformamides for the preparation of N,N-dimethylformamides. Different derivatives of tertiary amides were synthesized in moderate to good yields in the presence of just ~0.28 mol% of this catalytic system. Reusability of the synthesized catalysts was examined and catalysts were reusable for 8 times without significant decrease in optimized conditions.

KEYWORDS
heterogeneous catalysis, HKUST-1, ordered mesoporous HKUST-1, oxidative amidation

1 | INTRODUCTION

In recent best studies, Amide functional groups in medicinal compounds are one of the most significant functional groups in chemistry world, because it has key role for instance as a linker for amino acid conversion to protein.[1] Generally amides have synthesized in two steps; at the first step carboxylic group transform to more reactive functional group likewise acyl chloride and second step contain reaction between these product and amine compounds.[2] The creation of stoichiometric values of waste, low atom economy and the use of toxic reagents are the results of these processes. For solving these problems, new methods have been replaced with them such as metal-free methods (like organo-catalysts) and boron reagents. Nevertheless, it faces with low atomic efficiency and difficult products separation.[3] Amide synthesis methods catalyzed with metals have been drawn attention. In addition, direct amidation are the best solution for synthesizing amides through oxidative coupling via various precursors. Utilization simple and low cost reagent has included both aspect of eco-friendly and step economically of reactions that cause to convert to efficient methods for amidation. Since, direct amidation of aldehydes and alcohol with amines,[4] carboxylic acids, azoles and alcohol with formamides[5] and methyl arens with different source of amines[6] have been reported. There are most attractive due to the achieving best efficiency from homogenous catalysts than heterogeneous ones.[4h, 7] But using homogenous catalyst have accompanied with increasing toxicity and the cost of metals. Hence, these methods have been applied for researching more than industrial. For achieving more efficiency, usage of heterogeneous or homo-heterogonous catalysts (fixing them on organic or inorganic supports in liquid phase) has been developed.[8,9] According to the green chemistry, new development synthesis methods for making new linkers are very important in organic chemistry and also all of them have been done with heterogeneous catalysts. Accordingly, amplification of methods based on heterogonous catalysts is more attractive in industrial applications.[9]

Metal organic frameworks (MOFs) are classes of mesoporous compounds which have been shown good abilities as heterogonous catalysts. As we can know MOFs have been illustrated essentially catalytic properties because of their organic- inorganic and polymeric structures. Therefore, Catalysts based on MOFs can synthesis by post-synthesis and assembling. In contrast, the number of Catalysts based on MOFs are less than number of MOFs have made.[10,11] Among of them, the most significant things are open metal sites. Notably, the most important applications of these structures are catalysts,[12] adsorption/separation,[13] storage[14] and sensing.[15] Following our last works about oxidative amidation methods, we addresses synthesis of N, N-dimethyle amides via oxidative coupling of benzyl alcohol, benzaldhyde, benzoic acid styrene and phenyl acetylene catalyzed and N, N- dialkyl foramides under moderate conditions and using ordered mesoporous HKUST-1 as a catalysts.

2 | EXPERIMENTAL SECTION

2.1 | General

All materials were purchased from *Merck* Company and used with no more purification. The reaction was precisely monitored by analytical thin layer chromatography (TLC) using ethyl acetate and n-hexane as eluents. Due to needs to achieving final pure and isolated target molecules, a scaled-up thin layer chromatography was Merck 0.2 mm of silica gel 60F-254 Al-plates. Spectral analysis performed with aid of Infrared spectra (IR) on a Shimadzu FT-IR-8400S spectrometer and in following for definite characterization of all first-made products with ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra recorded on Bruker DRX-500 Avance spectrometers with $CHCl_3$ and DMSO as solvent at ambient temperature (relative to TMS as internal standard). Primary results for reaction progress were obtained by Gas Chromatography (GC) (Yonglin 6100; BP-5; 30 m × 0.25 × mm × 0.25 μm) with toluene as general solvent for injection and nitrogen as inert carrier gas. All yields referred to the isolated products. The mentioned catalyst EDX spectra were recorded on an Oxford Instrumental® and also SEM images were obtained on *Zeiss-Sigma VP 500*. Transmission electron microscopy (TEM) measurements were carried out at 120 kV (Philips, model CM120).

2.2 | Preparation of the HKUST-1

Porous HKUST-1 MOF was prepared using a hydrothermal method based on the reported procedures.[16] In a typical experiment, 6 mmmol (1.4 g) of copper nitrate trihydrate and 3.36 mmol (0.71 g) of trimisic acid (benzene-1,3,5-tricarboxylic acid or H_3BTC) were dissolved in 40 ml of DMF at room temperature. The mixture was stirred magnetically completely for 2 h. The reaction mixture was kept at 80 °C overnight without stirring. The solid was filtered off and washed thoroughly with hot EtOH/DMF. The resultant blue solid (denoted as HK) was dried in air at 110 °C overnight.

2.3 | Preparation of the ordered mesoporous HKUST-1

In a typical experiment, 2.0 g of Pluronic P123 (Aldrich, average Mw ≅ 5800), was dissolved in 40 ml of DMF at room temperature. The mixture was stirred magnetically dissolving the surfactant completely and subsequently sonicated for 15 mins. Then, 6 mmmol (1.4 g) of copper nitrate trihydrate and 3.36 mmol (0.71 g) of trimisic acid (benzene-1,3,5-tricarboxylic acid or H_3BTC) were added frequently and the mixture was stirred at 35 °C for 10 hr. Then, for aging process, the reaction mixture was kept at 80 °C overnight without stirring. The solid was filtered off and washed thoroughly with hot EtOH/DMF using a soxhelet apparatus for 36 hr to remove the surfactant molecules. The resultant blue solid (denoted as OMHK) was dried in air at 110 °C overnight.[17]

2.4 | General procedure for the oxidative amidation of benzyl alcohol, benzaldhyde, benzoic acid styrene and phenyl acetylene with N,N-dialkylformamide

The oxidative amidation reaction was carried out in a two necked round bottom flask with a condenser at air atmosphere. In a typical experiment, a mixture of substrate (1 mmol and 0.5 mL about toluene) and catalyst (20 mg, ~0.28 mol%) in N,N-dialkylformamide (2.0 ml) was placed in reactor at room temperature. Then, TBHP (70 wt % in H_2O, 1.5 equiv.) was slowly added to the reaction mixture over a 5 min period, and the mixturewas placed in an oil bath with magnetic stirring at 80 °C in an open atmosphere. After completion as judged by TLC, the reaction mixture was cooled to room temperature, extracted with ethyl acetate, and washed with saturated $NaHCO_3$ solution, water, and brine solution, respectively. The organic layer was collected and dried over Na_2SO_4.

The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the pure product. The products were characterized by IR, NMR analysis, and mass spectrum. The spectral data of known compounds were compared with those reported in the literature.

3 | RESULTS AND DISCUSSIONS

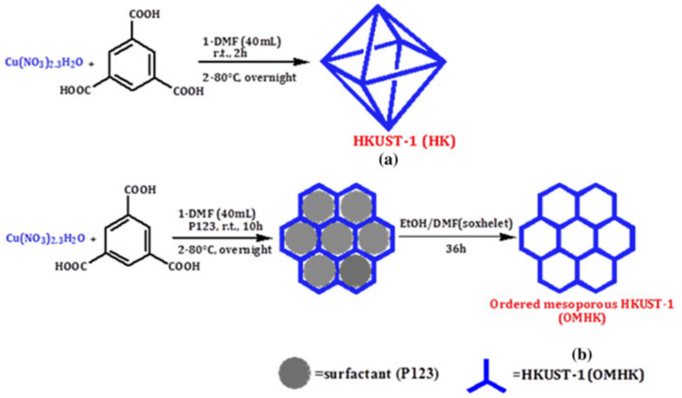
As shown in Scheme 1, HKUST-1 was prepared in three steps. At first, a solution of Cu $(NO_3)_2.3H_2O$ and trimisic acid (benzene-1,3,5-tricarboxylic acid or H_3BTC) in DMF was prepared by the mixing precursors for 2 hr. On the other hand, the reaction mixture was kept at solvotermal conditions without stirring. (Scheme 1). The blue solid filtered off and washed using a soxhelet apparatus to remove the unreacted molecules (or surfactant molecules about OMHK). The final structure of the catalyst was obtained via the drying of B. (for details see experimental section).

3.1 | Characterization of HKUST-1 and ordered mesoporous HKUST-1

After Preparation, some different microscopic and spectroscopic techniques such as XRD, FT-IR, SEM, ICP, BET and TEM were used to confirm the structure of the catalyst.

3.1.1 | FT-IR spectroscopy

The formation of HKUST-1 was further confirmed by the FT-IR spectroscopy (Figure 1). The broad band observed at 2500–3300 cm^{-1} region in benzene tricarboxylic acid is due to O–H stretching in carboxylic group, which is shifted to 3100–3600 cm^{-1} region in the complex indicating the presence of loosely bound water molecules in $[Cu_3(BTC)_2]$. The presence of located EtOH was confirmed by the stretching vibrations that appeared at about 2923 cm^{-1} (C–H stretching vibrations) in the FT-IR spectrum. In particular, the IR absorption bands in the 1700–1500 cm^{-1} and 1500–



SCHEME 1 Schematic synthesis of HKUST-1 (HK) and ordered mesoporous HKUST-1 (OMHK)

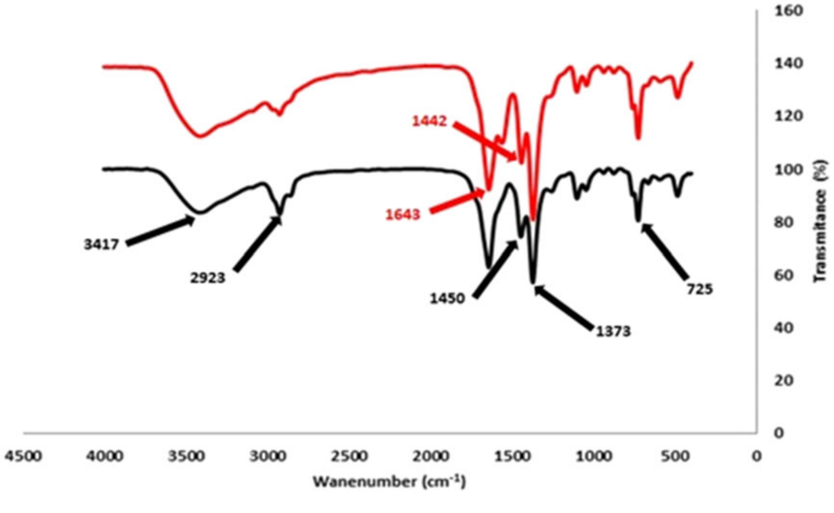


FIGURE 1 FT-IR spectra of HK (Black), OMHK (red)

1300 cm^{-1} range are due to $\upsilon_{asym}(C–O_2)$ and $\upsilon_{sym}(C–O_2)$ stretching mode, respectively; The band observed around 1715 cm^{-1} can be significantly assigned to acidic C=O stretching vibration present in the ligand BTC, which after complexation with Cu^{2+} is shifted to 1643 cm^{-1} suggesting that deprotonation has happened. This clearly indicates that the carboxylate ion participates in the complex formation. Moreover, the characteristic vibration at 725 cm^{-1} may be attributed to Cu–O stretching vibration, in which the oxygen atom is coordinated with Cu. Moreover, the absence of DMF absorption bands for the HKUST-1 synthesized in DMF showed that $[Cu_3(BTC)_2]$ DMF is exchanged with EtOH trough soxhelet apparatus so no observed; IR bands around 1450 cm^{-1} are due to a combination of benzene ring stretching and deformation modes; whereas, IR absorption bands around 700 cm^{-1} are due to υ (C– H) bending mode.

3.1.2 | Thermogravimetric/differential thermal analyses (TGA/DTA)

As shown in Figure 2, the thermogravimetric profile of synthesized OMHK is consistent with prominent weight-loss steps. It followed that a fully hydrated molecular sieve contains up to 12 wt. % water and other guest molecules. At the initial period the weight loss is due to the evaporation of water or guest molecules. OMHK MOF molecular formula was assumed as $Cu_3(BTC)_2(H_2O)_3.xH_2O$ and number of crystal water (x) was about 3.0. After that the sample was not shown any significant weight change up to 250 °C and then gradually started to lose the weight. This result confirmed the stability of the framework at higher temperature and there were almost no impurities on the structure. Complete decomposition started at about 320 to 400 °C to A sudden weight change (around 45 wt.%) was observed at 295 °C due to a complete transformation into CO_2 and Cu_2O or metal Cu.[18]

3.1.3 | Scanning Electron microscopy (SEM) analysis

As illustrated in Figure 3, the particle morphology was studied by scanning electron microscopy (SEM) and the identification of HK (a) and OMHK (b) before and after (d) reaction was based on the analysis of SEM images (Figure 3). It has been confirmed from the FE-SEM that there are no other phases present except the blocks of the produced MOF. Thus, we may conclude that our synthesized samples were almost free from the unreacted chemicals. It also shows that the HK-1 AND OMHK particles have octahedral shape with average diameters of approximately 15–20 μm and after 5 cycle this morphology is stable.

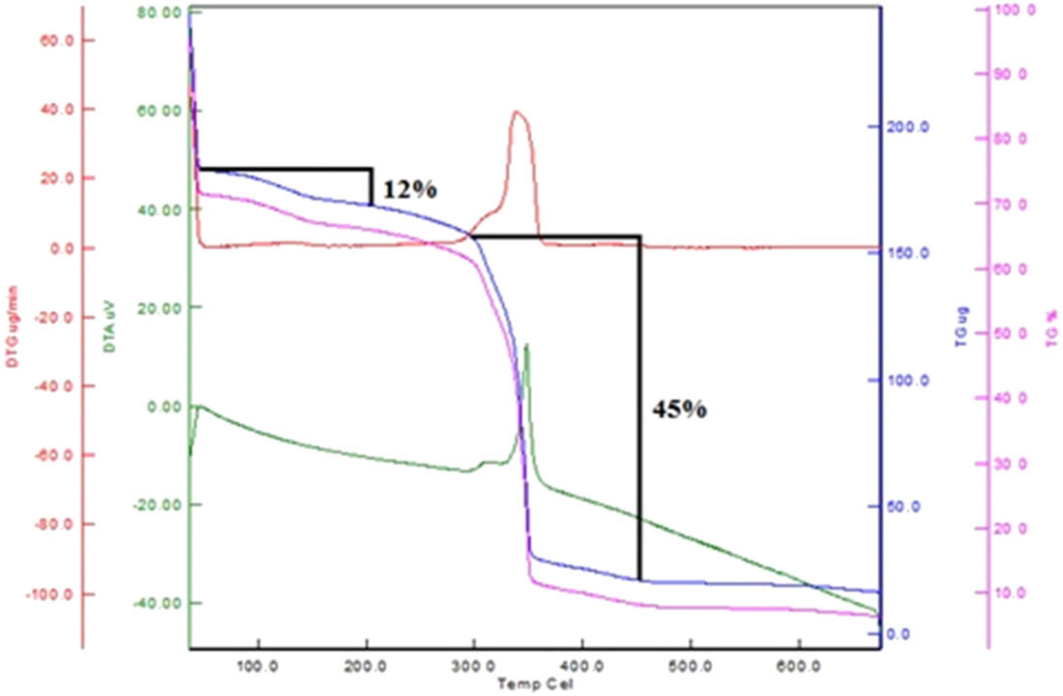


FIGURE 2 Thermogravimetric and differential thermogravimetric analysis of the catalyst

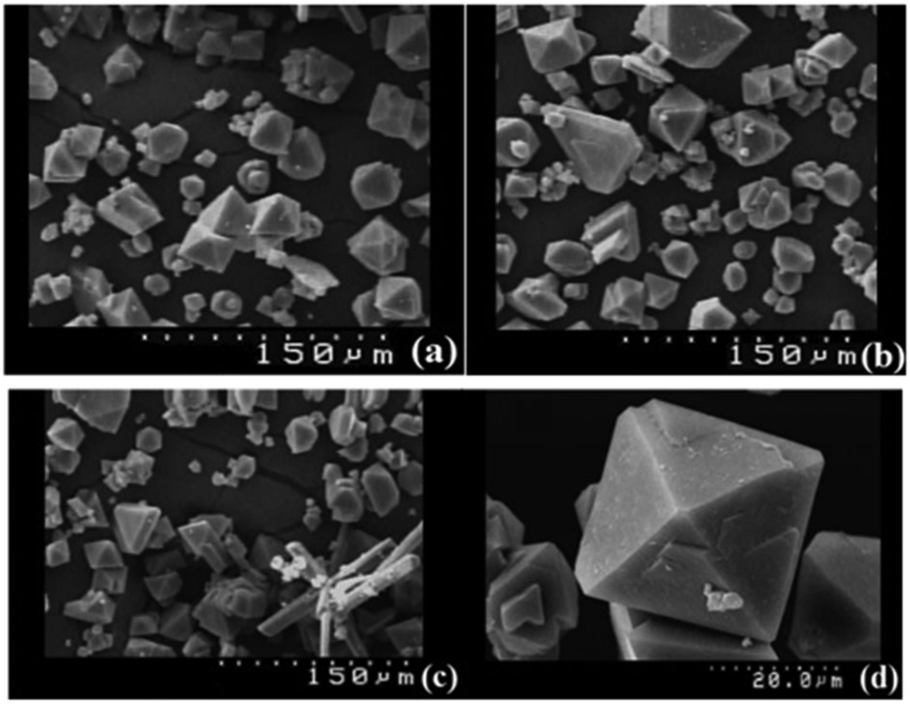


FIGURE 3 SEM Analysis of the HK before (a) and after (b) and OMHK before (c) and after reaction (d)

3.1.4 | Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) confirmed the ordered mesochannels in the OMHK, with octahedral morphology and a pore size range of ~15 nm (Figure 4).

3.1.5 | X-ray powder diffraction (XRD) patterns

The phase purity of bulk products were confirmed by powder X-Ray analysis (Figure 3) and fitted with the simulated pattern from the single X-Ray data (CCDC number 2300380 or 112954). The diffraction peaks of HK and OMHK solvotermal synthesized samples are well consistent with available literature and the simulated pattern published by Chui et al,[13] calculated using single crystal data are comparable (with three main peaks, 2θ = 11.01, 13.53 and 15.59). Difrractogram of the $[Cu_3(BTC)_2]$ resulted at presence of surfactant (OMHK, red diagram) lower crystallinity indicated from the peaks that not really sharp (Figure 5). Moreover, the sharper peaks in the range area of 2θ from 18 to 26° assumed represent the peak of the coordinated and or uncoordinated solvent in the compound. However, these kinds of peaks do not imply the

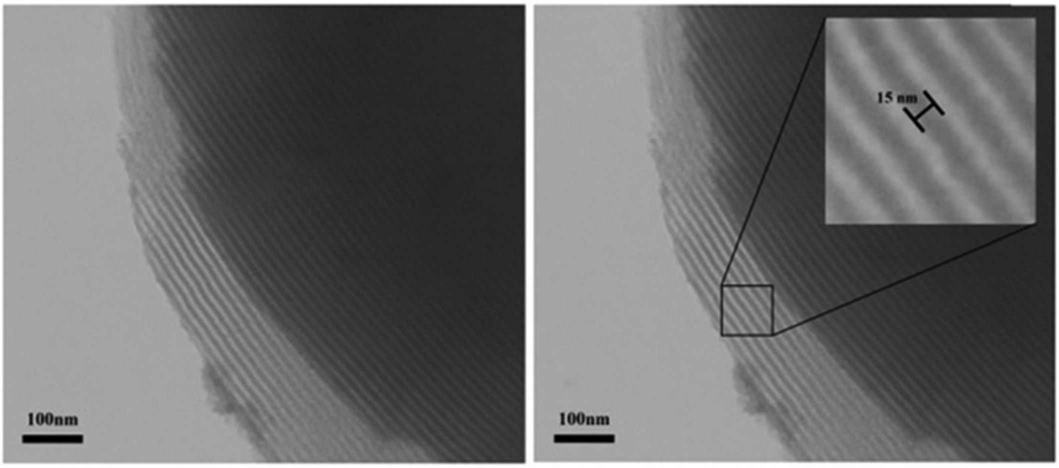


FIGURE 4 TEM micrographs of OMHK

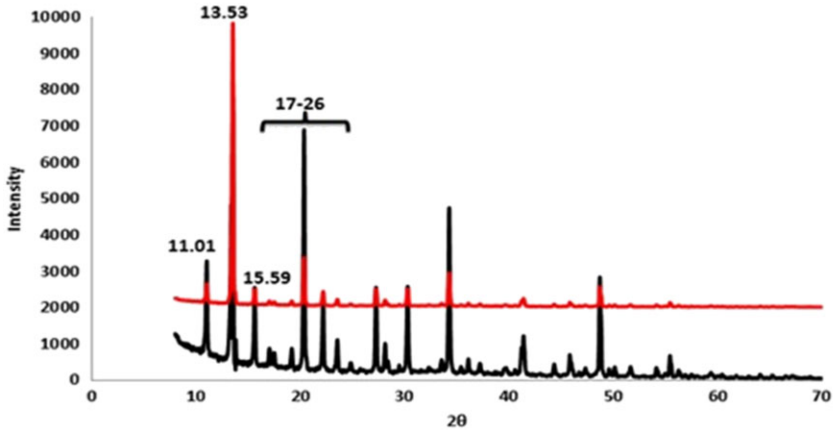


FIGURE 5 XRD pattern of HK (Black) and OMHK (red)

significant impurities and found also in some referred literatures. Therefore synthesized [Cu3(BTC)2] under this experimental condition exhibits the crystalline structure of [Cu3(BTC)2] in which twelve carboxylate oxygen atom from two BTC molecules and each of the three Cu^{2+} ions forms [Cu3(BTC)2] like structure with paddle-wheel units of fcc lattice.[19]

3.1.6 | Brunauer–Emmett–teller (BET) analysis

The specific surface area was measured using the BET method and the pore size distribution was calculated using the classical Barrett–Joyner–Halenda model. As shown in Figure 6, the adsorption desorption curves for

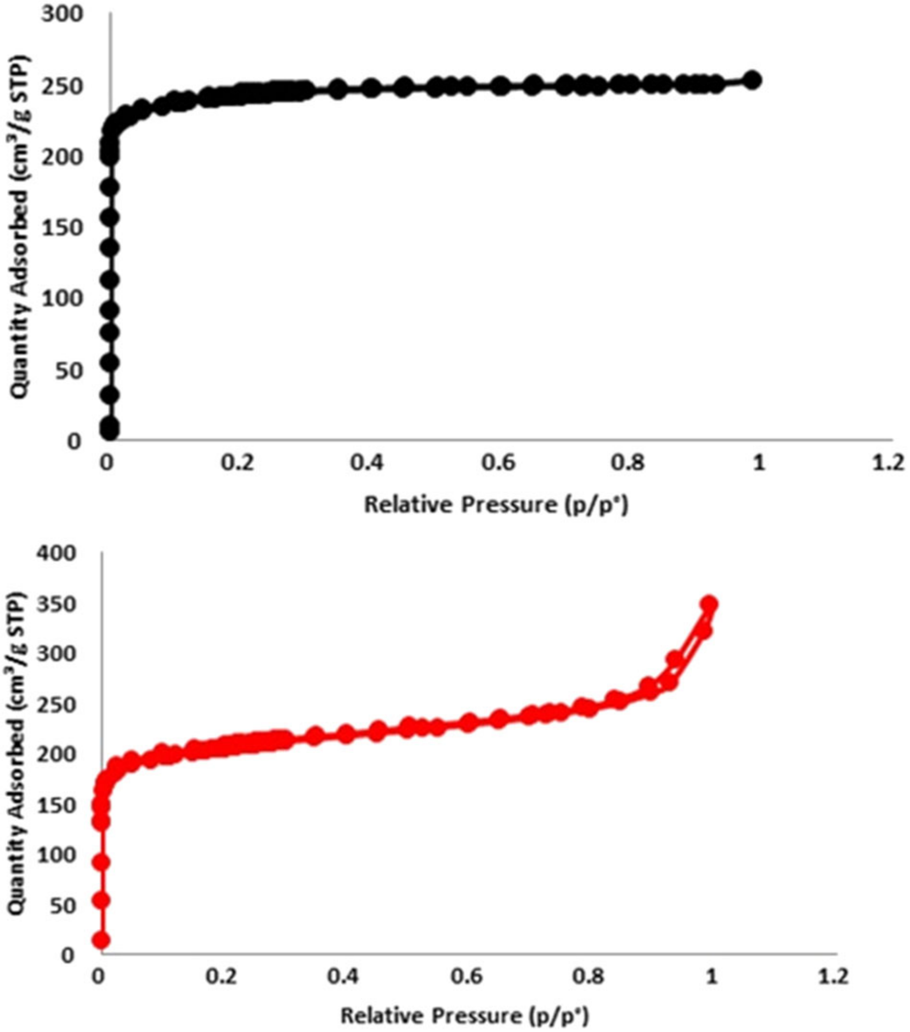


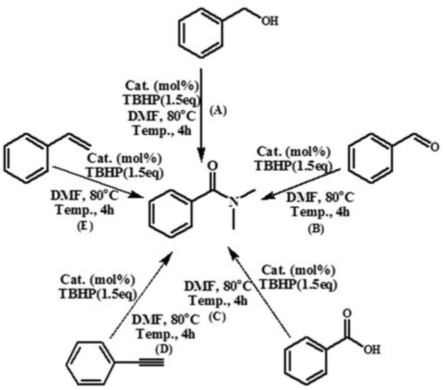
FIGURE 6 N_2 adsorption–desorption isotherms of HK (black) and OMHK (red)

the composites displayed the type IV adsorption–desorption isotherms, which is the typical characteristics of mesoporous materials. And the BET specific surface area is calculated 582 and 1271m^2/g for HK and OMHK respectively. The composites also showed the narrow pore size distribution, and the pore size is 1.63 and 2.52 nm for HK and OMHK respectively (Figure 7).

3.2 | Application of HK and OMHK for the oxidative amidation reaction

3.2.1 | General survey to investigate the best primary condition of reactions

After characterization of the catalyst structure, its catalytic activity was studied in coupling reaction between different substrates (benzyl alcohol, benzaldhyde, styrene and phenyl acetylene) and N,N-dialkyl formamides. The reactions between substrates and N,N-dimethyl formamide were performed as the model reactions to find the optimum conditions (Scheme 2).



SCHEME 2 Model reactions for oxidative amidation of different substrates (reaction A, B,C, D, E for benzyl alcohol, benzaldhyde, styrene and phenyl acetylene respectively)

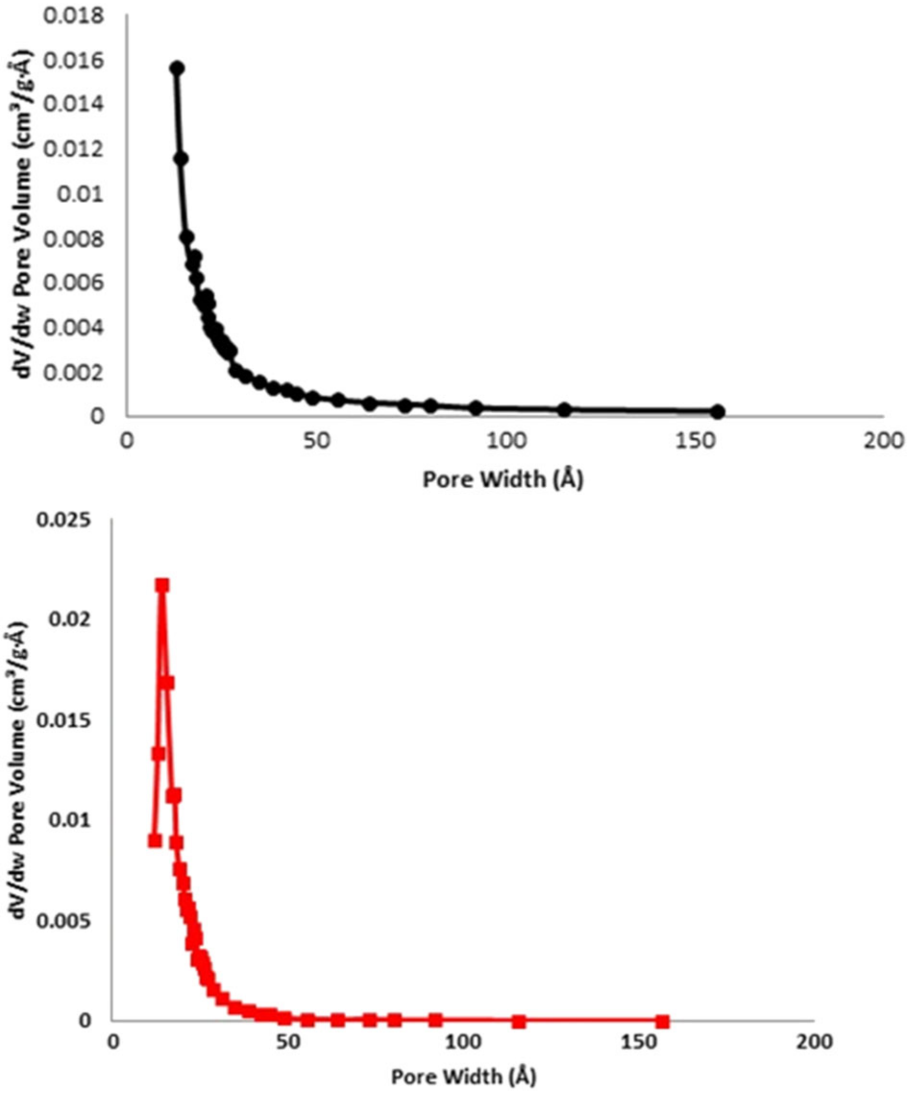


FIGURE 7 BJH desorption dV/dD Pore Volume plot

The first reaction was implemented under the following conditions: substrates (benzyl alcohol, benzaldhyde, styrene and phenyl acetylene, 1 mmol), N,N-dimethylformamide (2 ml), aqueous tert-butyl hydroperoxide (TBHP) as the oxidant (1.5 equiv), catalyst (10 mg, ~0.28 mol% of Cu), under Ar atmosphere at room temperature for 4 hr. Under these conditions, the corresponding product was achieved with 9(7), 5(5), 10(6), 8(5), 5(3) % yield respectively (Yields in parentheses are corresponded to reactions in the presence of HK) (Figure 8).

Owing to the improved efficacy, the effect of parameters such as amount of the catalyst, different oxidants, time of the reactions and different temperatures were investigated and the results are as follows: The amount of catalyst was initially optimized and it was found that 40 mg of HK and OMHK (for all of the reactions of A, B, C, D, E) were sufficient to promote these reactions and OMHK was better than HK (Figure 9).

Apart from TBHP, oxidative effect of other various oxidants such as mCPBA, H_2O_2, UHP and NaOCl in different equivalents was probed but none was as effective as TBHP (Figure 10). In the absence of the catalyst and oxidant, no product was formed (Figure 11).

By increasing the temperature to 80 °C, the product yield significantly rose and higher temperature had little impact on the reaction efficiency (Figure 12).

About reaction D and E increasing the temperature had negative effect (Figure 12).

To evaluate the catalytic activity in the synthesis of other amides by this method, various substrates used and reacted with dialkylformamides (Table 1). Under the standard reaction conditions, at the first time different derivatives (include of EDG and EWG functional groups) of benzyl alcohol, benzaldhyde, benzoic acid, styrene and phenyl acetylene were converted to the corresponding amides in acceptable yields (Table 2).

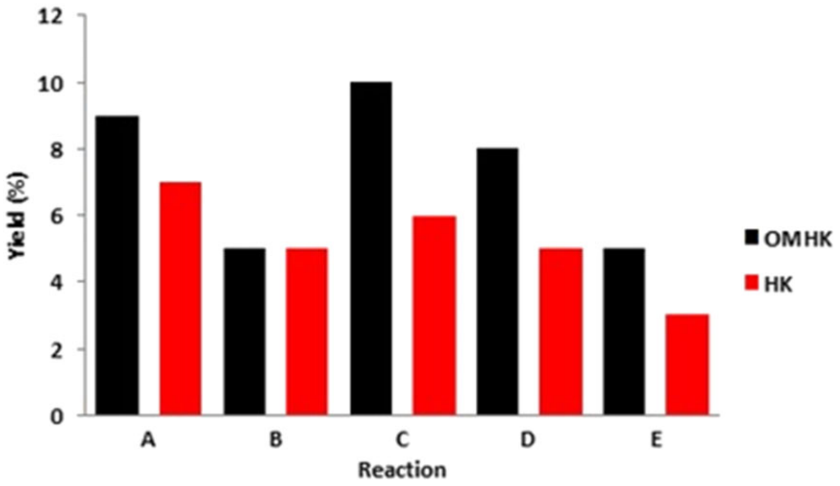


FIGURE 8 Yields of model reactions (reactions was run with 10 mg catalyst, substrates (benzyl alcohol, benzaldhyde, benzoic acid, styrene and phenyl acetylene, 1 mmol), DMF (2 ml), TBHP (1.5 equiv.), 8 hr at room temperature under Ar atmosphere. Yield determined by GC-FID spectroscopy with an internal standard)

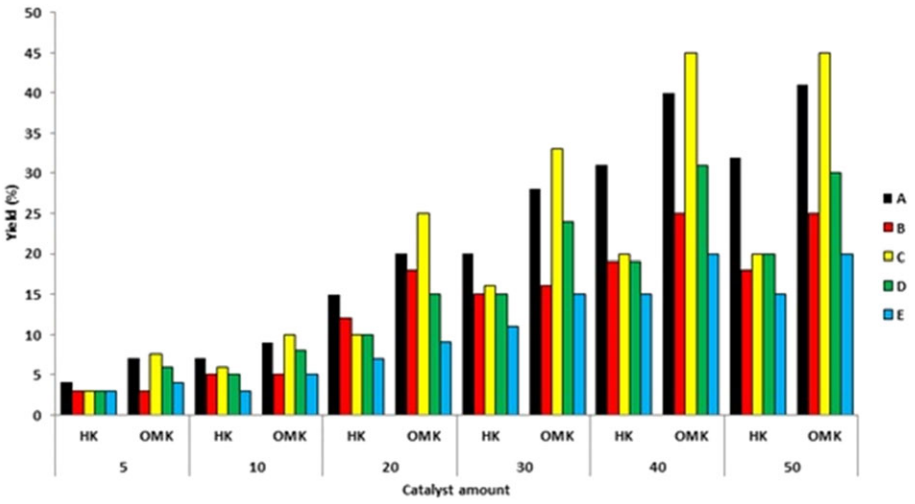


FIGURE 9 Checking the effect of catalysts amount on reaction yield (reactions was run with different mass of catalyst, substrates (benzyl alcohol, benzaldhyde, benzoic acid, styrene and phenyl acetylene, 1 mmol), DMF (2 ml), TBHP (1.5 equiv.), 8 hr at room temperature under Ar atmosphere. Yield determined by GC-FID spectroscopy with an internal standard)

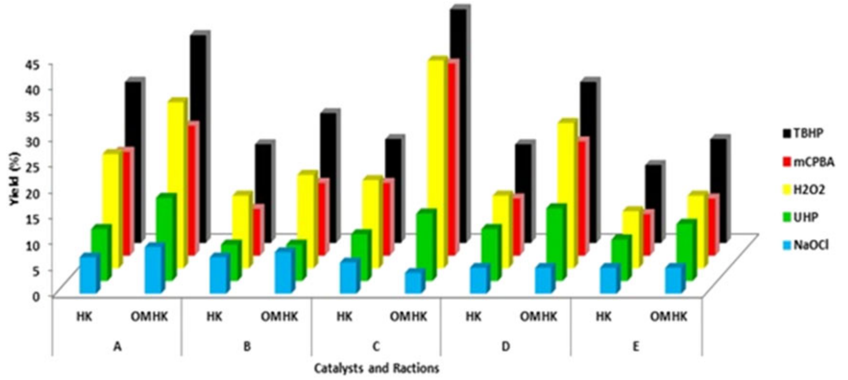


FIGURE 10 Checking the effect of oxidant on reaction yield (reactions was run with different 40 mg of catalysts, substrates (benzyl alcohol, benzaldhyde, benzoic acid, styrene and phenyl acetylene, 1 mmol), DMF (2 ml), oxidant (1.5 equiv.), 8 hr at room temperature under Ar atmosphere. Yield determined by GC-FID spectroscopy with an internal standard)

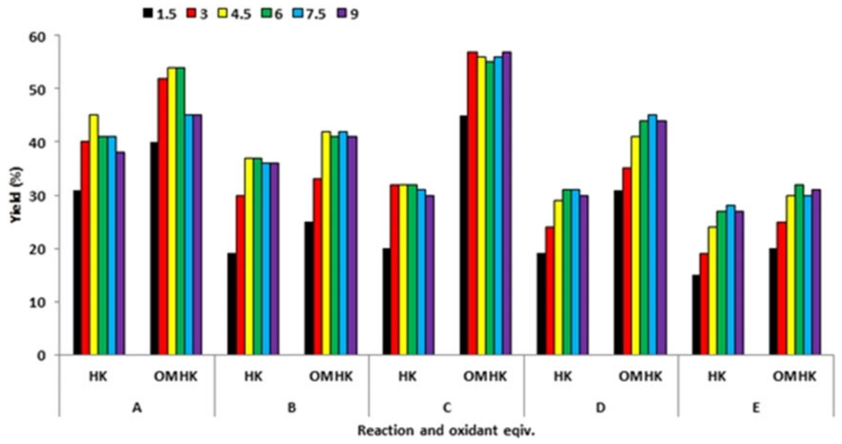


FIGURE 11 Checking the effect of amount of oxidant on reaction yield (reactions were run with 40 mg of catalysts, substrates (benzyl alcohol, benzaldhyde, benzoic acid, styrene and phenyl acetylene, 1 mmol), DMF (2 ml), different equivalents (1.5, 3, 4.5, 6, 7.5, 9) of TBHP as oxidant (1.5 equiv.), 8 hr at room temperature under Ar atmosphere. Yield determined by GC-FID spectroscopy with an internal standard)

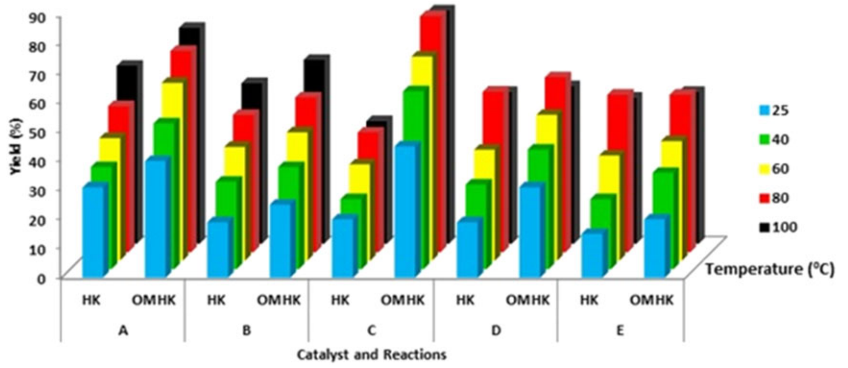
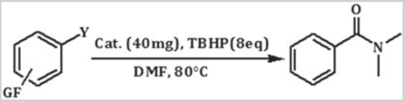
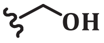
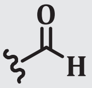
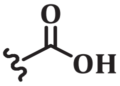
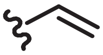


FIGURE 12 Checking the effect of temperature on reaction yield (reaction was run with 40 mg catalyst, substrates (benzyl alcohol, benzaldhyde, benzoic acid, styrene and phenyl acetylene, 1 mmol), DMF (2 ml), TBHP (8 equiv.), 8 hr at different temperatures under Ar atmosphere. Yield determined by GC-FID spectroscopy with an internal standard)

In this study, two methods for the synthesis of HKUST-1 have been used. According to the characterizations of the prepared structures, one of the methods is HKUST-1 and in another method, ordered mesoporous HKUST-1. These two structures are different in surface area and interaction between substrates and catalysts. In ordered mesoporous structures, the type of interaction of the substrates with the structure increases due to the presence of regular honeycomb structure that results from the use of surfactants and the formation of structures around surfactants. These pores actually act like nano-reactors and the reactions inside these nano-reactors are performed with high efficiency. In this reaction, the copper ions in the catalyst with electron transfer (based on the mechanisms proposed in related reports[20]) to the oxidant (which is herein to be known TBHP) causes the formation of radical active species and eventually, by binding radical species together, the product, the final one is created. These electron transfer reactions between copper and oxidizing species as well as substrates are carried out at the catalyst surface. Therefore, the higher the contact surface of the catalyst with the species, the efficiency increases. By changing the structure from HKUST-1 to ordered mesoporous

TABLE 1 Preparation of various amides in the presence of HK[a]

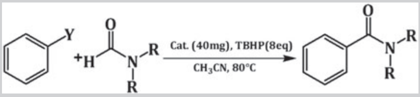


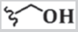
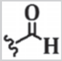
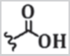
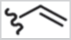
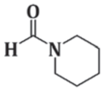
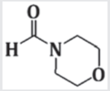
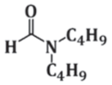
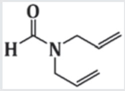
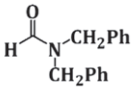
Y	FG	Yield (%)[b]
	H (1a)	74
	p-OMe (2a)	46
	p-Cl (3a)	59
	p-NO2 (4a)	65
	H (1a)	63
	p-OMe (2a)	40
	p-Cl (3a)	55
	p-NO2 (4a)	63
	H (1a)	80
	p-OMe (2a)	50
	p-Cl (3a)	65
	p-NO2 (4a)	70
	H (1a)	54
	p-OMe (2a)	37
	p-Cl (3a)	47
	p-NO2 (4a)	55
	H (1a)	52
	p-OMe (2a)	30
	p-Cl (3a)	40
	p-NO2 (4a)	51

[a] Reaction conditions: Substrate (1 mmol), DMF (2 ml), TBHP (8 equiv.), Catalyst (40 mg, ~0.28 mol%), at 80 °C under Ar. atmosphere.

[b] The yields refer to the isolated pure products.

TABLE 2 Preparation of various amides in the presence of HK and OMHK[a]



					
	11a (62%)[b] (61%)[c]	11b (45%) (44%)	11c (65%) (65%)	11d (33%) (35%)	11e (30%) (30%)
	12a (61%) (60%)	12b (45%) (44%)	12c (61%) (63%)	12d (33%) (35%)	12e (30%) (31%)
	13a (20%) (28%)	13b (15%) (19%)	13c (23%) (35%)	13d (N.D.)[d] (10%)	13e (N.D.) (10%)
	14a (31%) (40%)	14b (21%) (30%)	14c (40%) (51%)	14d (10%) (22%)	14e (10%) (19%)
	15a (20%) (38%)	15b (15%) (28%)	15c (61%) (46%)	15d (N.D.) (12%)	15e (N.D.) (10%)

[a] Reaction conditions: Substrate (1 mmol), DMF (2 ml), TBHP (8 equiv.), Catalyst (40 mg, ~0.28 mol%), at 80 °C under Ar. atmosphere.

[b] The yields refer to the isolated pure products.

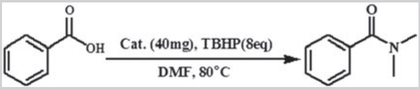
[c] The yields refer to the isolated pure products by HK and OMHK respectively.

[d] Not detected.

HKUST-1, due to the presence of honeycomb cavities resulting from the use of surfactants (as seen clearly in TEM images), the available catalyst surface, and more specifically, the copper ion, is increased to produce radical active species. As shown in Table 1, the derivatives of benzyl alcohol, benzaldhyde, benzoic acid styrene and phenyl acetylene, which differ only electronically and have different functional groups, have been investigated and compared with each other. From the yield of the reactions, the existence of EWGs (electron withdrawing groups) on substrates causes the reaction to be carried out with higher efficiency. Given the mechanism of these reactions, it is evident that the EWGs (electron withdrawing groups) cause radical stability, and thus the field will be conducive to the reaction. Instead, the presence of EWGs (electron withdrawing groups) has made the conditions unfavorable for the formation of radical species, and this clearly manifests itself in the efficiency of the reactions.

On the other hand, as mentioned above, these honeycomb cavities act like a nano-reactors, which increases the catalytic efficiency. Additionally, in the HKUST-1 structure, the pores have a spatial extent and there is no possibility of reacting to some substrates. To investigate the effects of size of molecules and the effect of synthesized catalysts using surfactant (honeycomb structure), different derivatives of dimethylformamide

TABLE 3 Preparation of various amides in the presence of HK and OMHK[a]



Cat.	Yield (%)[b]
1	**80**
2	**81**
3	**84**
4	**85**
5	**88**

[a] Reaction conditions: benzoic acid (1 mmol), DMF (2 ml), TBHP (8 equiv.), Catalyst (40 mg, ~0.28 mol%), at 80 °C under Ar. atmosphere.

[b] The yields refer to the isolated pure products.

Catalysts 1, 2, 3, 4, 5 are OMHK-H_2O, OMHK-CH_3CN-72 (72 hr immersion in CH_3CN, without heating and vacuum), OMHK-24 (24 h immersion in CH_3CN, after heating and vacuum), OMHK-48 (48 hr immersion in CH_3CN, after heating and vacuum), OMHK-72 (72 h immersion in CH_3CN, after heating and vacuum) respectively.

were investigated. To compare these derivatives, benzyl alcohol, benzaldehyde, benzoic acid, and phenyl acetylene has been used without functional groups to prevent electron effects.

As the results of the reactions show (Table 2), when small derivatives are used, there is no significant difference in the structure of HKUST-1 and ordered mesoporous HKUST-1, while in the case of larger derivatives, difference is clearly visible.

Regarding the mechanisms reported in the references, the reaction of oxidative amidation on benzoic acid is associated with better efficiency for both catalysts due to the less probability of producing different products. Due to the fact that other substrates were first converted to benzoic acid during the process (reported according to the proposed mechanisms) and then reacted with DMF, there was a likelihood of the production of side products in this direction, thus reducing the reaction efficiency.

To investigate the effects of the metal center of the synthesized structure, the structure with the coordinated water molecules (host solvent) was first immersed in the acetonitrile (guest solvent) for 24, 48 and 72 hrs, and then

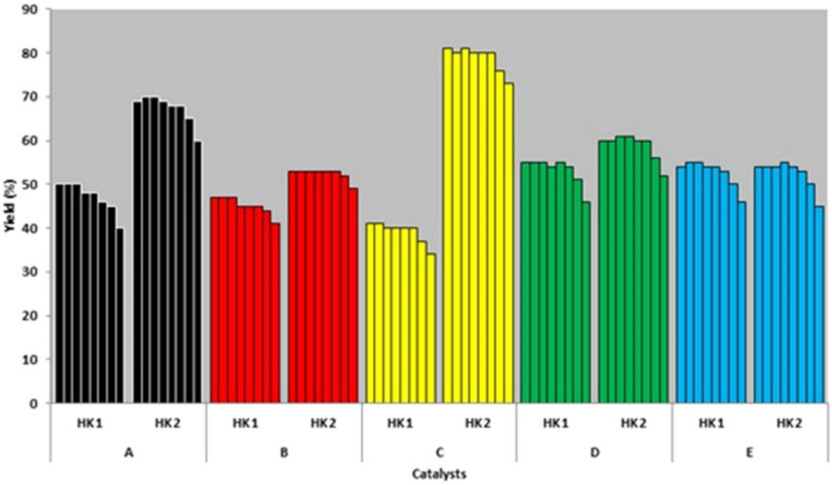


FIGURE 13 Catalyst reusability (reaction was run Substrate (1 mmol), DMF (2 ml), TBHP (8 equiv.), Catalyst (40 mg, ~0.28 mol%), 8 h at 80 °C under Ar atmosphere. Yield determined by GC-FID spectroscopy with an internal standard)

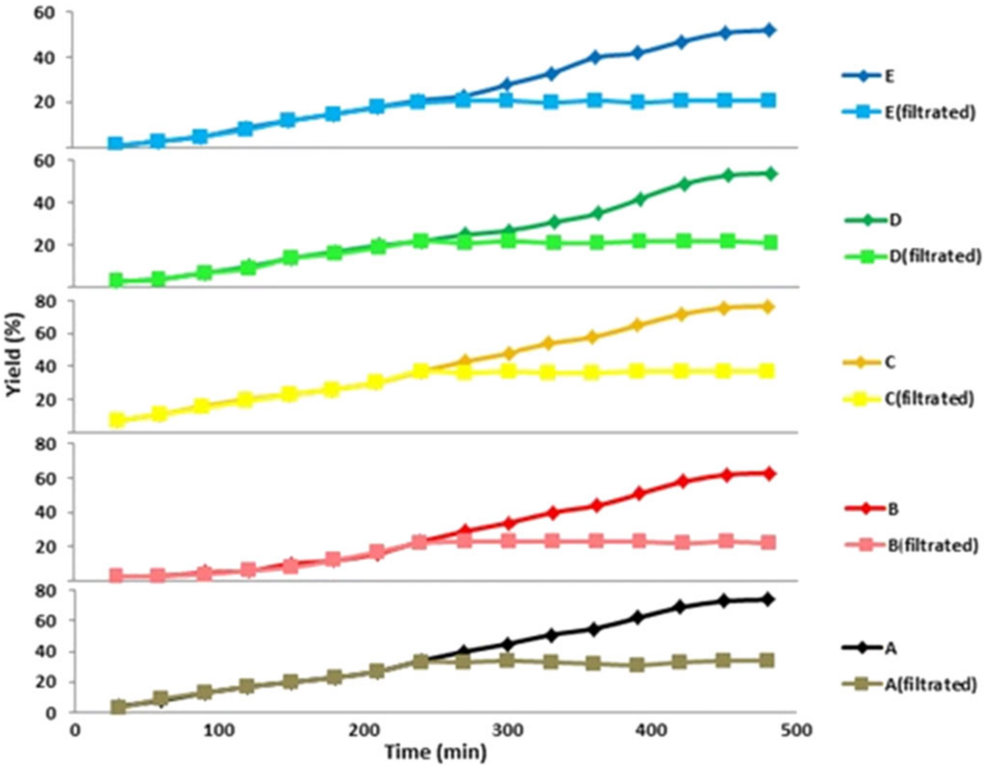
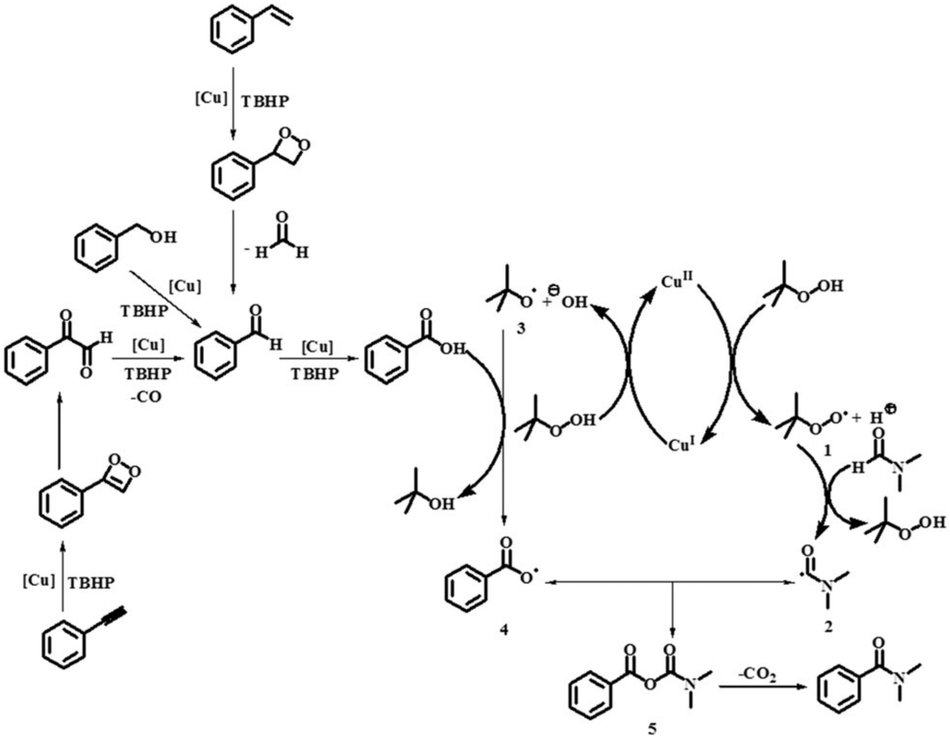


FIGURE 14 Leaching test for catalytic oxidation based on OMHK



SCHEME 3 Plausible mechanism for the oxidative amidation of benzyl alcohol, benzaldhyde, benzoic acid styrene and phenyl acetylene in the presence of Cu (II)-TBHP

the structure was immersed in a temperature of 80 °C for 24 hrs, until the acetonitrile molecule coordinate to the metal (guest solvent) removed. Then, for comparison, the oxidation reaction was studied using two structures. As can be seen, using two structures, there is no significant difference in the efficiency of the reaction. Of course, the slight increase in reaction efficiency by using an open metal site structure could be due to its ability to coordination using substrate and increase its electron transfer capability (Table 3). The results of the reactions using the structures show that, with increasing time for immersion of the catalyst in acetonitrile, the amount of solvent that has been replaced is increased and the size of the open metal sites is increasing, thereby increasing the efficiency of the reactions.

All the products were characterized by recording their melting points (in some cases), and from their IR, ^{1}H-NMR and ^{13}C-NMR spectra.

Reusability of the catalysts was evaluated in the synthesis of *N*,*N*-dimethylbenzamide (Figure 13). After completing the reaction; the catalyst was removed by centrifuging, washed with ethanol and dried for reuse. HK and OMHK were recycled 8 times in the oxidative amidation reaction without significant loss of its activity.

In order to gain insight into the heterogeneous nature of catalyst, a leaching test was carried out. As indicated in Figure 14, no further reaction took place without catalyst after initiation of the oxidative amidation reaction at 240 min. This finding indicates that no leaching of the catalytically active sites occurs and that HK and OMHK exhibit a typical heterogeneous catalyst nature.

Although there is no precise mechanism for this transformation, according to previous reports,[20] the proposed mechanism is shown in Scheme 3. First, the substrates (benzyl alcohol, benzaldehyde and phenyl acetylene) are oxidized to benzoic acid by Cu (II)/TBHP. Then in the presence of copper (II), TBHP produces radical 1 which immediately reacts with DMF and radical 2 is formed. The copper (I) generated at this step of the reaction converts TBHP to radical 3 and the copper (II) is again formed and recycled. Then radical 4 is achieved via abstraction of H from acid by radical 3. Coupling radical 2 with radical 3 followed by the extrusion of CO_2 will form the final product.

4 | CONCLUSIONS

In summary, we have developed a novel protocol for the one-pot oxidative amidation of benzyl alcohol, benzaldhyde, benzoic acid styrene and phenyl acetylene with N,N-dialkylformamides. ~0.28 mol% of catalyst was used for the preparation of different derivatives of amides in moderate to good yields. Porosity of this catalyst has crucial important effect on selectivity and yield of reaction. The ordered mesoporous nanocatalyst was stable and could be reused in 8 successive runs with no significant loss of activity.

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