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Additional Information

# Quasi-HKUST as Tandem Catalyst for Direct Imine Formation under Green Approach

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**Abstract:**

Copper based metal-organic framework (Cu$_3$(BTC)$_2$(H$_2$O)$_3$]$_n$·nH$_2$OMeOH (HKUST) has been submitted to ~~under controlled conditions to~~ thermolysis under air atmosphere at different temperatures ranging from 100 to 300 °C. This treatment produces the partial removal of ligands~~,~~ ~~as well as~~, the generation of structural defects and additional porosity in a controlled way. ~~The resulting defective materials,~~The resulting defective materials denoted according to the literature as *quasi* MOFs, were subsequently employed as heterogeneous ~~tandem~~ catalysts in the one pot synthesis of N-benzylideneaniline from aniline and benzyl alcohol in open air as terminal oxidant at 70 °C under base- and dehydrating agent-free conditions. The Q-HKUST catalysts calcined at 240 °C ~~and 260 °C~~ (QH-240 ~~and QH-260, respectively~~) was the most efficient in the series, ~~can efficiently~~ promot~~e~~ing imine synthesis~~, in particular QH-240 within 1h by forming water as the only by-product~~. Data from Knoevenagel condensation of malononitrile shows that in QH-240 the distances of Cu ions in HKUST cavities are preserved, increasing the Knoevenagel activity, but a strong rearrangement takes place at 300 ºC or above. The unsaturated copper active sites with simultaneous presence of micro- and mesopores in QH-240 ~~tandem catalyst~~ are responsible for this excellent catalytic performance. The effective parameters on catalytic activity of QH-240 including deligandation temperature, the amount of catalyst, the ratio of reactants, and reaction temperature as well as the stability and recyclability of the catalyst were also investigated. The possible mechanism used by QH-240 follows alcohol aerobic oxidation and subsequent anaerobic condensation of aldehyde intermediate with aniline.

**Keywords:** ~~Tandem catalysis,~~ Quasi metal-organic frameworks, Partial deligandation, Pore engineering, Tandem catalysis, Imine formation.

**INTRODUCTION**

Synthesis of chemical compounds by tandem catalysts conducts a multistep reaction in a one pot with greater efficiency, reduced by-product and waste formations, ultimately increasing efficiency and safety.[1] However, the number of available tandem catalysts with the ability to simultaneously catalyze two or more different processes is still limited.[2] In addition, large amounts of expensive reagents or activators are required in the tandem process, which often complicates workup and decreases the cost-effectiveness for the synthesis.[3] Therefore, the development of multifunctional catalysts with the ability to perform efficiently reactions simultaneously and sequentially remains a challenge.

Imines with the rich chemistry of reactive C=N bonds play a key role both as crucial intermediates in the synthesis of chemicals and pharmaceutical compounds due to their diverse reactivity, including reduction, addition, condensation as well as in multicomponent reactions.[4, 5] Several traditional methods for the imine synthesis are reported in the literature.[6] However, over the past decade more attention has been paid to the direct synthesis of imines in one pot process starting from alcohols and amines, leading to savings in energy consumption and diminution of wastes as well as work up simplification.[7] Three green methods have been largely employed for imine synthesis due to easy access of the corresponding starting materials and also to the use of air or $O_2$ as a terminal oxidant, instead of environmentally harmful chemical oxidants.[8] Among them, the cross coupling of alcohols with amines is one of the most convenient approaches for imine preparation. The most important features of this tandem process are: water

production as the only by-product of the reaction and synthesis of different symmetric and asymmetric imines using various starting materials.[7, 9]

Metal-organic frameworks (MOFs) are a class of porous crystalline material~~compound~~s containing metal ions or clusters coordinated to rigid organic ligands, defining an open structure with a large proportion of ~~with potential~~ void space~~s~~. In some cases, the pores in a framework are filled with guest molecules (often solvents) that can be removed without damaging the structure of the material~~could be omitted~~. Porosity and regular structure~~These features~~ of MOFs are of interest for application in gas storage, gas separation, gas purification, catalysis, and renewable energy processes~~supercapacitors~~.[1, 10, 11] Since their catalytic active sites are located in metal nodes, linkers and/or in the pores, appropriate strategies are needed to ~~achieve~~ increase the density of these active sites.[12] So far, three methods have been prop~~os~~~~esent~~ed to access the active catalytic sites. Pore engineering is ~~an obligatory way~~mandatory to ~~obtain suitable~~allow substrate and reagent diffusion to the catalytic active MOFs, while activ~~modul~~ating their ~~catalytic~~ compartments[13] ~~producing~~ generating coordinatively unsaturated metal active sites ~~via deletion~~by removal of the adsorbe~~coordinat~~ed solvent or guest molecules.[14, 15] Recently, much attention has been paid to partial linker removal ("*deligandation process*") to create additional Lewis acid centers.[16, 17] The MOF treated material has been~~which~~ named as ~~the~~ "quasi MOFs" (Q-MOFs). They correspond to~~,~~ intermediate ~~structures~~ materials between metal oxides and perfectly crystalline MOFs with features and advantages of both.[18] It is worth noting that *defective MOFs* refer to the existence of defects or vacancies of either linkers or metal nodes in the framework of MOFs. ~~. That is a MOF with certain defects in its framework~~ while ~~the~~ quasi MOFs are transition ~~state structure~~material~~s~~ between MOFs and metal oxides. Q-MOFs ~~which~~ are obtained by partial deligandation at relatively low temperatures.[19]

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Herein, ~~for the first time,~~ the superior activity of ~~we present an effective approach to achieve~~ a ~~proper tandem~~ Q-MOF as tandem catalyst ~~in~~ for direct coupling of alcohol and amine for one pot imine synthesis ~~of imine~~ reported ~~based on the Cu MOF (HKUST)~~ under base- and dehydrating agent-free conditions. The Q-MOFs under study are based on the partial deligandation of Cu-MOF (HKUST), resulting in ~~Our strategy is based on producing a heterogeneous tandem catalyst using pore engineering, in which the framework of HKUST consists of~~ an extra ~~high~~ density of open active copper sites ~~that can prepare an abundance of reactive centres~~ with simultaneous pore engineering with a distribution of both micro- and mesopores after partial deligandation treatment ~~in the sightly network of Q-MOF~~. ~~Our plan~~The objective is the ~~was to~~ development of a direct, green, and easy tandem catalyst~~method~~ for one pot synthesis of imine with air as ~~a cheap and readily available~~ oxidant under solvent-free and mild conditions.

Previously, other~~Some~~ copper based catalysts have been applied for imine synthesis.[4, 20-25] including a~~while~~ few MOFs with and/or without co-catalysts ~~have been studied as catalysts in this field.~~[26-29] [26-29] However, up to now, the potential of *quasi* MOF engineering has not been applied to ~~the best of our knowledge, there is no previous report on the use of quasi MOFs in the catalytic~~ synthesis of imines under mild and green conditions. Herein, ~~we describe~~it is described how controlled ~~partial~~ thermolysis ~~process~~ can produce a quasi HKUST- copper 1,3,5-benzenetricarboxylate (BTC) MOF- as catalyst for one pot imine synthesis by cross coupling of alcohols with amines. The remarkable catalytic activity found for the optimal Q-H compared to HKUST precursor derives from the increased density of ~~that contain~~ coordinatively unsaturated Lewis acid sites. ~~and~~ simultaneously the generation ~~distribution~~ of additional micro- and meso-pores in the materials ~~. The Q-HKUST has been prepared via partial deligandation in air at different temperatures ranging from 100 to 300 °C with a heating rate of 5 °C min⁻¹ to eliminate organic linkers for modifying the interactions between Cu nodes and desired~~

and thermodynamic propeties parameters for the one-pot imine synthesis were also investigated. The catalytic activity of HKUST precursor was also investigated. Our findings show predict that Q-HKUST can construct possesses a porous structure and with strong interactions between the guest and acid and basic sites caused by thermolysis, which that cannot be obtained are not present in the related parent MOF and the final metal oxide.

## EXPERIMENTAL SECTION

**Materials and CharacterizationPhysical Techniques.**

All reagents and materials for the synthesis, reactions and analysis were commercially available from Aldrich and Merck Company and used as received. IR spectra were recorded using Thermo Nicolet IR 100 FT-IR spectrophotometer. PL-STA 1500 apparatus was used for measurement of thermal behavior using a heatingwith the rate of 10 °C min$^{-1}$ underin a static nitrogen atmosphere of nitrogen. Powder X-ray diffraction (PXRD) measurements were performed using a Philips X'pert diffractometer with monochromated Cu-K$_\alpha$ radiation. Sorption studies were performed using the TriStar II 3020 surface area analyzer from Micrometrics Instrument Corporation and BELSORP-mini II from LMS Instruments Co., Ltd.÷ N$_2$ adsorption were carried out at 77 K. All samples were activated at 120 °C for 14 h under vacuum. The morphologies of the samples were characterized with a field emission scanning electron microscope (FE-SEM) TESCAN MIRAIII (Czech). The pore-size distributions were calculated from the adsorption branch of the nitrogen isotherms according to the BJH method. Particle morphologies were characterized with a field emission scanning electron microscope (FE-SEM) TESCAN MIRAIII (Czech). ^{1}H NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer. Thermoprogrammed desorptions and reductions were performed in a TPD-TPR 2900 system equipped with a thermal conductivity detector (TCD). First, a desired amount of the catalyst was pretreated at 150 °C in He stream with gas rate of 20 mL min$^{-1}$ for 1 h, then cooled down up to 40 °C, and subsequently exposed to

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ammonia (4 vol.% in He, 20 mL min$^{-1}$) for 1 h~~one hour~~. Then, the ammonia that did not bind to the catalyst was removed by ~~purification with~~ 20 mL min$^{-1}$ of He flow ~~within~~ for 30 min. Subseqeuntl~~Eventual~~ly, the desorption was performed by raising the temperature from 40 to 750 °C at a heating rate of 10 °C min$^{-1}$ in He stream (20 mL min$^{-1}$).

## Synthesis of [Cu$_3$(BTC)$_2$(H$_2$O)$_3$]$_n$·nH$_2$O.MeOH (HKUST)

In a typical ~~experiment~~ preparation, powder sample of HKUST was obtained by mixing BTC (b~~B~~enzene-1,3,5-tricarboxylic acid, 2.1 g, 10 mmol) and Cu(OAc)$_2$.-H$_2$O (3.21 g, 16 mmol) in 400 ml H$_2$O:EtOH (50:50) in a round bottom flask heated at 110 °C with an oil bath for 4 h. The resulting powder was isolated by centrifugation, washed four times with ethanol and water ~~4 times~~ and dried in air for characterization. Yield: 3.185 g (91 % based on BTC). IR data (KBr pellet, v/cm$^{-1}$): 485(w), 733(m), 756(m), 1108(w), 1374(s), 1463(s), 1557(s), 1615(s), 1656(s), 1702(m) and 3417(w-br) (Figure S1).

Partial~~The~~ deligandation of HKUST was carried out by thermal treatment in air at~~with~~ a heating rate of 5 -°C min$^{-1}$ between 100 and 300 °C for a period from~~of~~ 30 min to 2 h to achieve Q-HKUST, denoted by QH-x, where "H" and "x" stand for HKUST and the deligandation temperature ~~of deligandation~~, respectively.

### Catalytic activity evaluation of the samples

The performance of tandem Q–H-x~~KUST~~ catalysts for the one-pot synthesis of imine from benzyl alcohol and aniline under solvent-–free and mild conditions was evaluated by adding -~~Desired amounts of Q-HKUST~~ catalyst ~~were successively added to~~ 5 ml benzyl alcohol (0.5 mmol) and 5 ml aniline (0.5 mmol) to the desired amount of QH-x in a 25 ml reaction vessel equipped with a magnetic stirrer at room temperature. Then, resulting reaction mixture was introduced in a

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preheated oil bath at 60 °C under open air for a given time. The course of the reaction was analyzed by ~~After that, some of the reaction mixture was withdrawn by~~taking with a syringe a reaction aliquot that was~~and~~ analyzed by gas chromatography and a flame ionization detector (GC-FID (Echrom GC A90)). The conversion and yields were also determined~~obtained~~ by GC based on the ratio of alcohol to imine as follows:[6]

Conversion (%) based on substrate = [1− ((concentration of substrate left after reaction) × (initial concentration of substrate) $^{-1}$)] ×100 (1)

After the completion~~, of~~ the reaction mixture was monitored by TLC and GC~~.~~, ~~T~~the catalyst was separated via filtration and washed several times with ethanol and deionized water (1:1) and dried at 100 °C under vacuum to~~for~~ remov~~eal of~~ volatile organic impurities. Then, the catalyst~~and then~~ was ~~applied~~used in the next catalytic runs at the same reaction conditions. Finally, the desired N-benzylidenaniline product was ~~detected~~characterized by H- NMR spectroscopy ~~analysis~~.

**RESULTS AND DISCUSSION**

HKUST was synthesized by solvothermal reaction between copper(II) acetate and BTC ligand. This MOF includes a three-dimensional interconnected framework with square-shaped pores (9 Å × 9 Å) constructed by linking binuclear paddlewheel Cu(II) units via BTC ligands. At the metal nodes, each Cu(II) atom exhibits a pseudo-octahedral coordination geometry e~~E~~ach six coordinate Cu(II) metal center is bound to four oxygen atoms from four BTC ligands along with a Cu-Cu bond~~interaction~~ (2.628 Å) and one $H_2O$ molecule along the Cu-Cu axis. A model of HKUST structure is presented in ~~(~~Figure 1~~)~~. As shown in this Figure, binuclear paddlewheel Cu(II) units are connected together via BTC ligand ~~and form a three-dimensional interconnected framework with square-shaped pores of 9 Å × 9 Å. In the metal nodes, pseudo-octahedral coordination~~
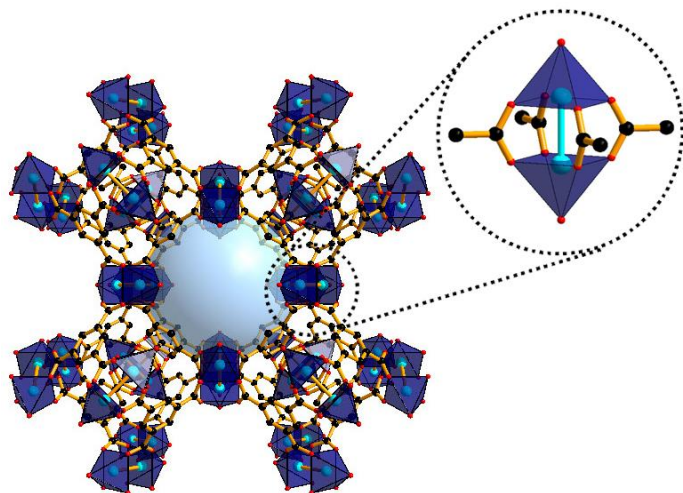
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**Figure 1.** Single-crystal X-ray structure of HKUST. Color code: O, red; C, black; and Cu, blue. Reproduced with permission from ref. #.

Based on the TGA evaluation (Figure S2), thermal treatment ~~strategy was chosen for partial deligandation~~ of HKUST should produce partial deligandation, opening~~to tune the~~ pores and creat~~e~~ing unsaturated inorganic nodes. ~~For this reason~~On one hand,~~,~~ HKUST was activated at 120 °C for 14 h (labeled as HKUST) to remove H₂O/EtOH guest molecules from cavities and H₂O bonded molecules. On the other hand, aimed at the generation of structural defects in a controlled way by thermal treatment~~Also~~, the MOF was heated at 200, 240, 260 °C for 30 min and 300 °C for 2 h, denoted as QH-200, QH-240, QH-260 and QH-300, respectively ~~for deligandation of the framework~~. Scheme 1 summarizes the expected effects of the thermal treatment.

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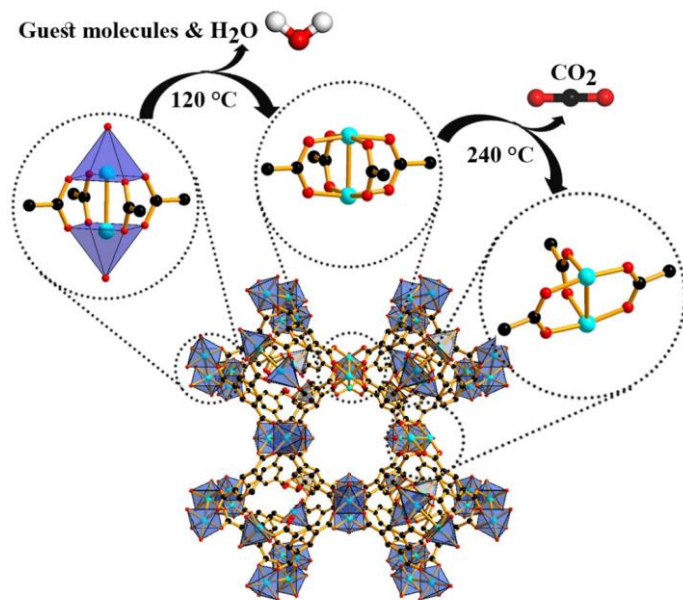
**Scheme 1.** Schematic representation for creation of unsaturated copper centers upon controlled thermal treatment.

ParticleThe morphologyies of HKUST and Q-HKUST samples wasere determined by FE-SEM. The images show that the HKUST sample is comprised of loose agglomeration of cuboidal nanoparticles attached to cube and upon increasing the temperature treatment temperature fusion of the individual cuboidal particles into larger agglomerates becomes more apparenttion were observed (Figure S3).

The temperature dependent PXRD of HKUST demonstrates that the crystal structure is stable up to 240 °C with a decrease in the intensity and a slight broadening of the diffractions around 5° – 10°-. which can imply a decrease in the crystallinity of the material as consequence of the primaryeliminary deligandation stages of HKUST. When the temperature rises up to 260 °C the characteristic peaks observed for HKUSTsignificantly decrease and disappear showing high

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degree of deligandation and production of Cu$_2$O/CuO (JCPDS No. 05-0667 and 48-1548). The transformation of HKUST into CuO ~~and it~~ is complete~~ly converted to CuO~~ at 300 °C, implying the complete decomposition of HKUST (Figure 2).
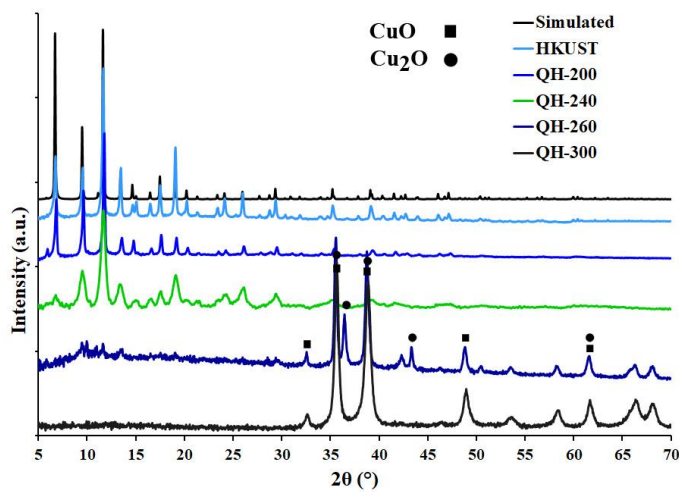


 **Figure 2** PXRD patterns of HKUST and QH-x samples.

Changes in t~~T~~he por~~oe characteristie~~sity associated to the thermal treatment were~~ere~~ examined by N$_2$ isotherm collected at 77 K (Figure 3). The data show types I, (I, IV), IV and V isotherms for HKUST, QH-200, QH-240 and QH-260 with BET specific surface areas of 1182, 913, 160 and 5.6 m$^2$·g$^{-1}$, respectively (Table S1). As consequence of~~In~~ the thermal ~~decomposed~~ ~~samples~~treatment, appearance~~creation~~ of a pronounced hysteresis in the adsorption isotherms indicate the ~~presence~~ generation of large cavities. Also, the pore size distribution exhibit a considerable increase in mesopores ~~of the frameworks~~ after deligandation for QH-240 (Figure 3 and Table S1). The simultaneous observation~~existence~~ of micro- and mesopores ~~together~~ in QH-240 can be attributed to the creation of defects or vacant sites by partial deligandation ~~and~~ ~~development of a quasi MOF~~. As a result, a homogeneous distribution of unsaturated metal ~~active~~

seites in both micro- and mesopores could be reflected in anan efficiently enhancement of the catalytic performance, as it was in fact observeds.
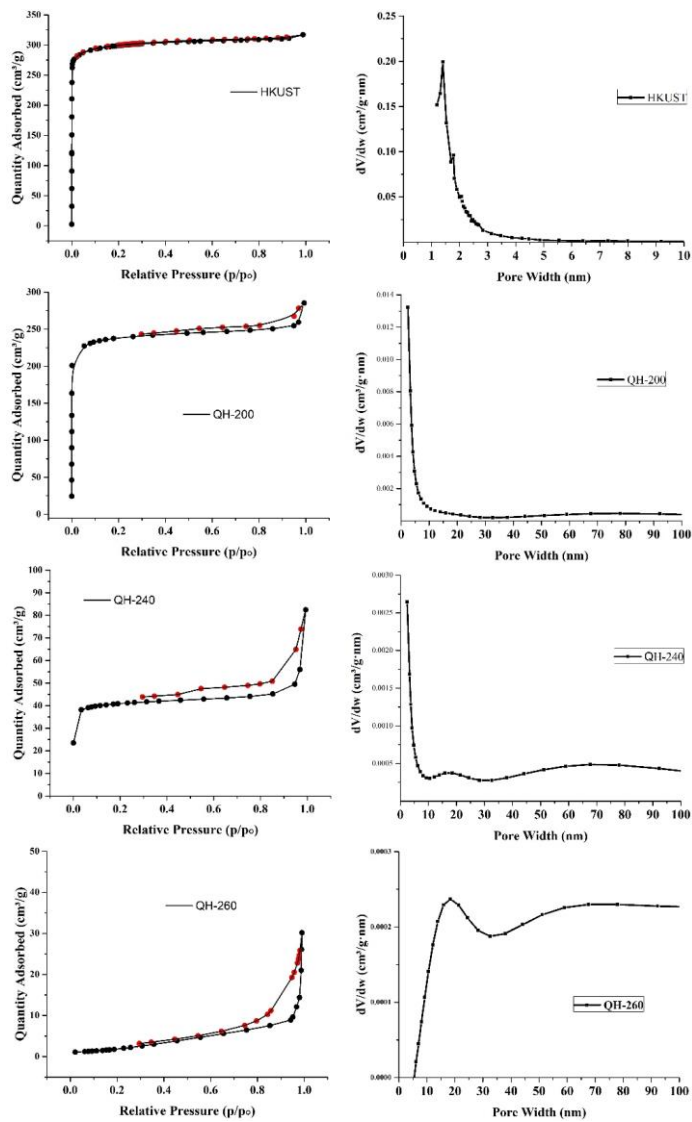
**Figure 3.** N$_2$ isotherm at 77 K and 1 bar and pore size distribution for HKUST, QH-200, QH-240 and QH-260.

**The tandem catalytic performance of Q-HKUST samples**

The one pot synthesis of imines ~~using~~ by cross coupling of alcohols and amines is a~~catalyzed by a tandem catalyst is very notable and interesting because there is a distinction between the~~ two steps ~~of the cross coupling~~ reaction that ~~. So, achieving both reaction conditions~~ involves aerobic oxidation of alcohols to aldehydes followed by~~and the~~n anaerobic condensation ~~step in one pot which is practically complex and difficult~~. Herein, the tandem reaction was performed using~~catalytic management of~~ the set of ~~various~~ QH-x to evaluate the effect of deligandation in the catalytic performance~~quasi HKUST-1 MOFs (Q-HKUST) was evaluated in direct s~~. The synthesis of N-benzylideneaniline from aniline and benzyl alcohol was selected as model reaction~~substrates~~. To reach the best imine conversion, the reaction conditions ~~for the mentioned oxidative coupling process~~ were also optimized.

**Effect of deligandation temperature on t~~he~~andem catalytic performance**

The effects of deligandation temperature on t~~he~~andem catalytic ~~behaviors~~ activity of ~~different quasi~~ HKUST and QH-x~~, i.e. QH-200, QH-240, QH-260, and QH-300~~ in the N–benzylidenaniline imine formation ~~of N–Benzylidenaniline from its related alcohol and amine with~~ under solvent free conditions at the~~under~~ open air and ~~at~~ 70 °C were investigated (Figure S4 and Table 1). No imine was formed when the catalytic conversion was carried out under vacuum and without any catalyst at 70 °C, confirming that a proper catalyst and air as oxidant are required in the~~to~~ formation of the imine product. In contrast,~~While~~ in presence of QH-x as catalysts, the expected N-benzylideneaniline is produced at a specific ~~time~~ rate depending on the deligandation temperature

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of the QH-x catalyst. The conversion percentage increases within a shorter time by increasing the deligandation temperature in the range of 240-260 °C, while it decreases afterwards. The catalytic conversion over QH-240 catalyst reaches 99.5 % within 4 h, which is 3.5 times greater than that measured for HKUST-1 parent. This observation can be explained by considering the changes in both pore structure and density of coordinatively unsaturated active copper sites. So, the synergistic effects of the uniform and extended distribution of active copper sites across the framework and avoidance of particle agglomeration along with the simultaneous existence of both micro- and mesopores are responsible for the evolution of the catalytic activity observed for QH-x as a function of the thermal treatment. These results are strong evidence showing that controlled generation of structural defects, including higher coordination sites and pore engineering can be effective and practical to enhance the catalytic activity of HKUST for the imine formation from benzyl alcohol and aniline.

According to this initial screening, QH-240 sample was selected as the best tandem catalyst and it was subsequently used in further catalytic studies.

**Table 1.** Effect of deligandation temperature on the catalytic activity of various quasi HKUST MOFs in the N-benzylidenaniline formation.

| Catalyst | Time (h) | Yield (%) |
|---|---|---|
| No catalyst | 24 | - |
| HKUST | 16 | 32 |
| QH-200 | 12 | 95 |
| *QH-200 | 24 | trace |
| QH-240 | 4 | 99.5 |
| *QH-240 | 24 | trace |

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| | | |
|---|---|---|
| **QH-260** | 6 | 98 |
| **\*\*QH-300** | 18 | 48.5 |

Experimental conditions: Catalyst mass =2.5 mg, benzylalcohol and aniline = 5 ml (0.5 mmol), T = 70°C under open air. * the reaction under vacuum; ** CuO

The amount and types of acidic sites in ~~HKUST~~ parent HKUST and QH-240 catalysts were ~~also~~ measured by $NH_3$-TPD (Figure~~s~~ 5 and Table 2). Two $NH_3$ desorbed peaks of HKUSU appeared at 170 °C and 303 °C which correspond~~is related~~ to low and medium acidity strength, respectively. In the case of QH-240, these peaks appeared at 172 °C and 313 °C. TPD results demonstrated that QH-240 catalyst ad~~b~~sorbed a much higher~~more~~ amount of ammonia compared with its parent (HKUST). In other words, deligandation of HKUST at 240 °C leads to an increase in total acidity of about 2.2 times, most of which is related to the increase in medium acid sites. Th~~us~~erefore, the higher acidity of QH-240 is a factor that contributes to ~~catalyst exhibits~~the higher catalytic ~~conversion~~ activity for the one pot imine formation.

**Table 2.** Density~~The amounts~~ of acidic sites in HKUST-1 and QH-240 catalysts according to $NH_3$-TPD experiments.

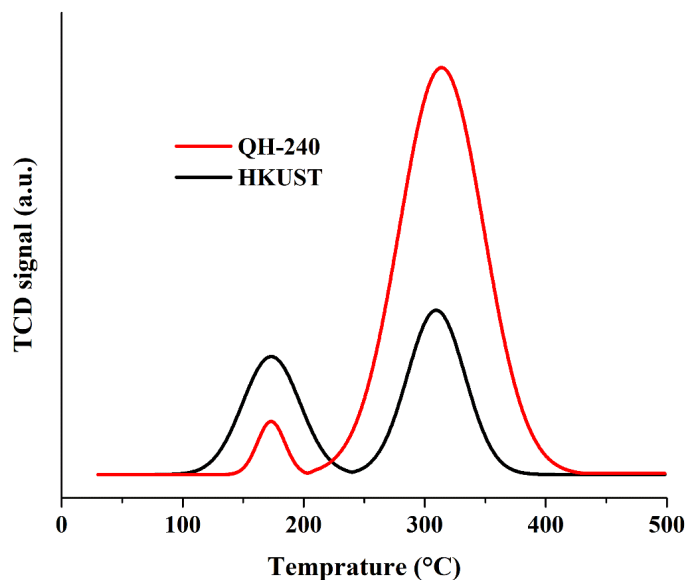| Catalyst | weak acid | | Strong acid | | Total acidity (mmolg$^{-1}$) |
|---|---|---|---|---|---|
| | Peak position (°C) | Value (mmolg$^{-1}$) | Peak position (°C) | Value (mmolg$^{-1}$) | |
| HKUST | 170 | 9.1 | 309 | 12.6 | 21.7 |
| QH-240 | 172 | 1.7 | 313 | 46.8 | 48.5 |

**Figure 4** Temperature-programmed desorption of NH$_3$ from HKUST and QH-240 catalysts.

**Effect of QH-240 catalyst dosage**

Various amounts of QH-240 catalyst were ~~applied~~ used in the~~for~~ N-benzylideneaniline synthesis ~~from cross coupling of the related alcohol and amine by green approach~~ under ~~mild and~~ solvent free conditions ~~involving open air~~by aerobic oxygen as terminal oxidizing reagent at 70 °C (Table 2). As expected, upon~~with~~ increasing the catalyst amount ~~of catalyst~~ up to 3 mg, the ~~efficiency~~ conversions increased within less time. Beyond this amount no significant changes in activity were observed ~~and after that it remained almost constant~~. The maximum conversion was observed over 3.0 mg of QH-240 catalyst for 4 h. Thus, 3.0 mg is chosen as the desired amount of QH-240 catalyst in all experiments.

To prove that ~~understand the tandem catalytic nature of~~ QH-240 is acting as heterogeneous catalysts in the tandem imine formation, the catalyst was filtered from the reaction solution after 2

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h and the remaining solution was transferred to a new vial. The reaction mixture in the absence of solid ~~and the reaction was continued heated at 70°C for 4 hours under the same initial conditions. No~~ ~~more addition conversion was observed reaction took place in the absence~~ after filtration of the catalyst ~~after~~ for 2 h, thus confirming that catalysis takes place on the solid and that any possible leachate species in the solution is not contributing to ~~indicating the impressive effect of the catalyst on~~ imine ~~production~~ formation (Figure S5).

**Table 2**. ~~Effect~~ Influence of QH-240 ~~amount~~ dosage ~~as a tandem catalyst~~ on N-benzylideneaniline synthesis.

| Entry | Catalyst dosage (mg) | Conversion* (%) | Time (h) | Yield* (%) |
|-------|----------------------|-----------------|----------|------------|
| 1 | 0 | - | 36 | - |
| 2 | 1.5 | 68 | 5 | 65 |
| 3 | 2 | 85 | 4 | 84 |
| 4 | 2.5 | 99.5 | 4 | 99.1 |
| 5 | 3 | 99.6 | 3 | 99.0 |
| 6 | 3.5 | 99.2 | 3 | 99.1 |

Experimental conditions: [benzyl alcohol] = 0.5 mmol and [aniline] = 0.52 mmol at 70 °C under open air. * Determined by GC.

**Effect of the alcohol to amine ~~amounts~~ ratio**

The catalytic conversion of tandem QH-240 catalyst for benzyl imine formation using different amounts of benzyl alcohol and aniline was evaluated (Table 3). The maximum catalytic performance was observed in the higher amine to alcohol molar ratio ~~of amine to alcohol~~. In case of 1:1.25 molar ratio of alcohol to amine, the catalytic conversion increased up to 98.5 % within

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a shorter period of 1 h and the conversion time increased to about 2 h for an alcohol:amine molar ratio of 1:1.5 ~~with almost the same catalytic activity afterwards~~. The reason for these results ~~may~~ could be due to the good balance in the competition of the two reagents and intermediates for ~~blockage of~~ the active ~~catalyst surface~~sites with increasing reagent concentration ~~of the reagents~~. Therefore, the optimal alcohol to amine molar ratio ~~of~~ of 1:1.25 ~~alcohol to amine~~ was chosen ~~as 1:1.25~~ for further experimental reactions.

**Table 3.** Effect of the alcohol to amine ratio for imine formation catalyzed by QH-2~~4~~50.

| Entry | Benzyl alcohol (mmol) | Aniline (mmol) | Time (h) | Alcohol to Amine | Conversion (%) |
|---|---|---|---|---|---|
| 1 | 0.3 | 0.3 | 6 | 1:1.17 | 72 |
| 2 | 0.35 | 0.3 | 6 | 1.17:1 | 68.3 |
| 3 | 0.35 | 0.35 | 6 | 1:1 | 65.2 |
| 4 | 0.5 | 0.52 | 3 | 1:1.04 | 99.6 |
| 5 | 1 | 1.2 | 2 | 1 : 1.2 | 99.3 |
| 6 | 2 | 2.5 | 1 | 1:1.25 | 98.5 |
| 7 | 2 | 3 | 2 | 1: 1.5 | 99.1 |

Experimental conditions: mass of catalyst = 3 mg, T= 70 °C under open air.

**Effect of the temperature on ~~tandem synthesis of~~ benzyl imine synthesis**

The catalytic efficiency over QH-240 for N-benzylideneaniline production from benzyl alcohol and aniline at various temperatures was, then, investigated (Figure S6 and Table 4). Upon increasing temperature from 25 °C to 80 °C, the conversion rate increased ~~increased within a shorter period of time~~. Interestingly, the ~~catalytic~~ almost full conversion ~~and its related time remained almost constant~~was achieved in 1 h reaction time in the temperature range of 60-80 °C in presence of QH-240 tandem catalyst (inset of Figure S6). Thus, a convenient reaction~~the proper~~

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temperature for imine formation over QH-240 ~~quasi MOF~~ was ~~set at~~ 60 °C. Th<u>e conditions required for N-benzylideneaniline formation and the results achieved using</u>~~erefore,~~ QH-240 ~~tandem catalyst is able to~~ compar<u>e</u>~~te~~ <u>favorably with</u> <u>those of</u> other ~~reported~~ catalysts <u>reported in the literature to promote the tandem reaction of benzyl alcohol and aniline.</u> ~~used for N-benzylideneaniline formation (Table 5 summarizes conditions and activity data of some reported catalysts for the tandem reaction)~~.

**Table 4**. <u>Influence of t</u>~~T~~he temperature ~~effect~~ on imine formation catalyzed by QH-240.

| Temperature ( °C) | Time (h) | Conversion (%) |
|---|---|---|
| 25 | 6 | 10 |
| 40 | 3 | 52 |
| 60 | 1 | 99 |
| 70 | 1 | 98.5 |
| 80 | 1 | 99 |

Experimental conditions: $m_{cat}$ = 3 mg, [benzyl alcohol] = 2 mmol and [aniline] = 2.5 mmol under open air.

**Table 5.** Compari<u>son of</u>~~ng~~ the <u>catalytic activity of</u> QH-240 ~~tandem catalyst~~ with <u>that of</u> other catalysts <u>reported in the literature</u> for the oxidative ~~cross~~ coupling of ~~N-benzylideneaniline from~~ benzyl alcohol and aniline <u>to form N-benzylideneaniline</u>.

| Catalyst | Solvent | Oxidant | Temperature (°C) | Time (h) | Conversion (%) | Ref. |
|---|---|---|---|---|---|---|
| 9-azabicyclo [3.3.1] nonan- N – oxyl/KOH | toluene | air | 80 | 4 | 92 | [30] |
| MOF-1/KOH | - | air | 100 | 12 | 89 | [27] |

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| | | | | | | |
|---|---|---|---|---|---|---|
| **Pd(OAc) 2 /NEt 3/TEMPO** | - | air | R.T | 72 | 75 | 31 |
| **CuI-TEMPO** | $CH_3CN$ | air | R.T | 12 | 74 | 4 |
| **Pd−Au@Mn(II)-MOF/KOH** | toluene | air | 110 | 30 | 99 | 26 |
| **Quasi HKUST (QH-240)** | - | Open air | 60 | 1 | 99 | This study |

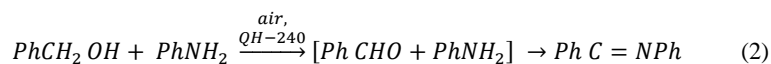TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxyl.

### Reusability of QH-240 catalyst

The reusability of QH-240 tandem catalyst for direct synthesis of benzylideneaniline was evaluated for four catalytic cycles determining the imine conversion rate for each run. The conversion rate remained relatively unchanged in the four catalytic cycles as observed in Figure S7a. In addition, the structure of the QH-240 after the fourth reuse remained unaltered as seen in its XRD pattern (Figure S7b), indicating the stability of the tandem catalyst. Thus, the available data indicate that the quasi HKUST MOF is stable and can be reused in the tandem catalytic formation of imine.

### Possible mechanism for imine formation over QH-240

The most reasonablepossible mechanism of N-benzylideneaniline formation during the one pot synthesis that is acceleratcatalyzed by QH-240 involves tandem catalyst can be described as the aerobic oxidation of benzyl alcohol and subsequent anaerobic condensation of the benzaldehyde as intermediate and aniline.[26, 27, 30] Both processes, aerobic benzyl alcohol oxidation and benzaldehyde condensation shouldthat be promoted byoccur simultaneously in presence of QH-240 tandem catalyst without the use need of a base under solvent-free conditions and open air as

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agent and also an oxidant ... Here, $Cu^{2+}$ ions ... Lewis acid sites. There several reports in the literature showing the general activity of HKUST promoting oxidation by molecular oxygen ... oxidation ... benzaldehyde.[33] In addition HKUST promotes condensation of carbonyl groups, including the Knoevenagel condensation commented below ... According to ... the mechanism for N-benzylideneaniline formation could be as follows:

$$PhCH_2\,OH + \; PhNH_2 \xrightarrow[\quad QH-240\quad]{air,} [Ph\,CHO + PhNH_2] \; \rightarrow Ph\,C = NPh \qquad (2)$$

QH-240 tandem catalyst generated from partial deligandation of HKUST at 240 °C combines a high density ~~with acceptable concentration~~ of copper active catalytic centers and a favorable reagent diffusion due to the combination of micro- and mesoporosity, the two factors being ~~is~~ responsible for the high catalytic activity observed ~~forming imine~~ in the~~a~~ one pot ~~process~~imine formation.

To further understand the local structure of QH-240, the Knoevenagel condensation of malononitrile and benzaldehyde was used as probe reaction. Theoretical calculations supported by catalytic data have shown that in the due to the special geometry with rigid linear N≡C-C-conformation, malononitrile is simultaneously activated in Knoevenagel condensation by two $Cu^{2+}$ ions of the same cavity belonging to different nodes geometrically positioned matching the malononitrile angle and distance. This special geometry of HKUST cavities explains its high catalytic activity for malononitrile Knoevenagel condensation. Thus, to learn more about QH-240 and the origin of its high activity in the tandem imine synthesis it was of interest to determine its relative activity respect to pristine HKUST and QH-250. The results are presented in Figure 5 that shows the temporal profiles of the Knovenagel product.
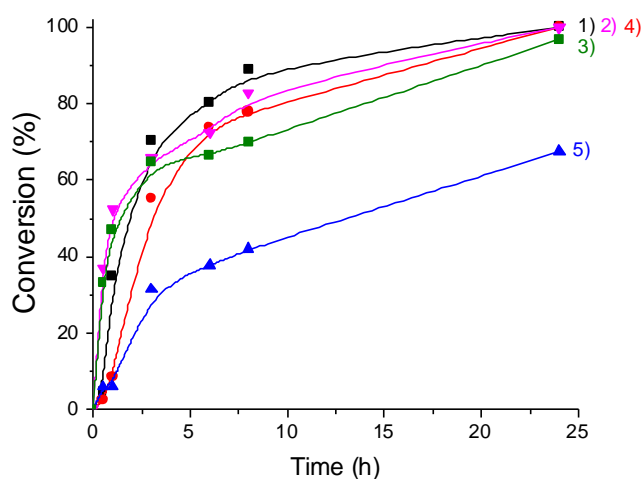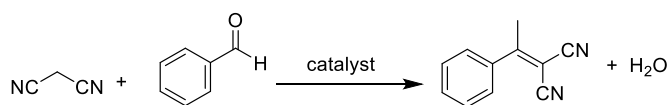
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Figure 5. Time-conversion plot for the Knoevenagel condensation of malononitrile with benzaldehyde: 1: HKUST, 2: QH-240, 3: QH-26300, and 4: QH-3400 and 5: QH-400. Reaction conditions: Malononitrile: 1.1 mmol, benzaldehyde 0.95 mmol, catalyst 10 mg, temperature 70 °C, ethyl acetate 10 ml.

Additionally, adsorption isotherms of malononitrile in ethyl acetate showed that while in pristine HKUST the amount of malononitrile adsorbed from ethyl acetate was 12 in 100 mg, the same adsorption in QH-300 and QH-400 was 6.4 and 2 mg, respectively. The higher malononitrile in

HKUST indicates a large collapse of the structure with a residual density of Cu····Cu pairs at the correct distance for malononitrile adsorption.

As it can be seen there, although β,β−dicyanostyrene was formed in all cases, the initial reaction rate of the parent HKUST was intermediate between those of QH-240 and QH-260. This observation indicates that in QH-240 the Cu···Cu distance in the cavities ~~are~~is preserved, and the catalytic activity for Knoevenagel condensation increased by the generation of defects, while in QH-260 the HKUST cavities should have started to ~~deform~~deform, and the density of Cu···Cu pairs decrease somewhat respect ~~ot~~to QH-240. Thus, the catalytic activity in Knoevenagel indicating the preservation of most of the HKUST cages in QH-240 agrees with the temperature dependent XRD and with the superior catalytic activity of QH-240 for the imine tandem reaction.

~~Reusability of QH-240 catalyst~~

## CONCLUSIONS

In this study, an efficient catalyst for the tandem ~~catalytic process~~oxidative coupling of benzyl alcohol and aniline has been presented ~~for N-benzylideneaniline synthesis from cross coupling of the related alcohol and amine~~by controlled defect generation in the HKUST structure by thermal treatment at 240 ºC at the open air. QH-240 is able to catalyze N-benzylideneaniline formation in the absence of soluble bases or promoters, at moderate temperatures and exhibiting catalytic and structural stability.~~over quasi copper-based metal organic framework catalysts (Q-HKUST) using green approach and mild conditions. The Q-HKUST catalysts have been successfully synthesized by controlled thermolysis treatments on HKUST MOF under air atmosphere at different temperatures ranging from 100 to 300 °C and can be readily performed for imine formation in the open air as terminal oxidant at 70 °C under base- and dehydrating agent-free conditions. The imine formation over quasi catalysts was investigated using various deligandation temperatures, catalyst~~

~~daghanhirsfunnahoimpurtaTlanhrathjafiraushagohodyHrainfellgnhbmptrAdkharindnpdllemunzhaidchhr~~ controlled defect generation is due to the synergistic effect~~s~~ of the uniform and extended distribution of coordinatively unsaturated ~~active~~ copper ~~catalytic~~ sites across the framework, ~~and~~ avoidance of particle agglomeration a~~long with~~nd the ~~simultaneous existence~~generation of micro- and mesopore~~s structures~~ (types I and IV) ~~are responsible for the excellent catalytic observations~~. This finding offers an economical and green approach for imine synthesis and highlights the great potential of ~~quasi MOFs~~quasi-MOFs as tandem catalysts in the synthesis of fine chemicals.

## AUTHOR INFORMATION

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**Notes**

The authors declare no competing financial interest.

**Supporting Information**

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