Synthesis and application of SBA-15-supported CuO as an efficient catalyst for the oxidative C(sp²)-O coupling reaction

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Abstract. SBA-15-supported CuO was synthesized via wet impregnation of SBA-15 with copper (II) acetylacetonate followed by calcination in the static air. The BET surface area of the Cu-containing SBA-15 was approximately 600 m²/g, which significantly decreased in comparison with that of as-synthesized SBA-15 silica (1081 m²/g). The successful loading of copper with a 3.20 wt.% content was determined by ICP-OES analysis, consistent with theoretical composition. However, no Cu-based phases were detected on the PXRD results and TEM images for CuO/SBA-15 showed regular hexagonal meso channels remained, indicating that CuO species was well distributed in the SBA-15 framework via the applied synthetic procedure. Catalytic activity of SBA-15-supported CuO was investigated for the selective C(sp²)-O coupling reaction between salicylaldehyde and N,N-dimethylformamide (DMF) in the presence of di-tert butyl peroxide (DTBP) as an oxidant. Influence of the reaction conditions on the formation of desired product was studied including reaction time, temperature, reactant ratio, amount of catalyst and oxidant. The experimental results proved that the high activity of the prepared catalyst as the C(sp²)-O coupling product could be obtained in an excellent yield of 90% with only 3 mol% of SBA-15-supported CuO in the presence of 4 equivalents of DTBP at 120 °C in 2 hours.

1. Introduction
SBA-15 has been well-known as an ordered mesoporous silica material widely used with remarkable properties including pore size from 2 to 30 nm, simple synthesis conditions, high surface area (600 – 1000 m²/g), available pore volume, tunable mesopore size, high thermal and chemical stability, and facile functionalization. Notably, SBA-15 is an ideal support for the controllable immobilization of metals, oxides, and complexes towards many various applications such as wastewater treatment, biorefinery production, drug delivery, gas adsorption, photodegradation, gas-phase, and liquid-phase catalytic reaction [1-11]. To date, numerous synthetic SBA-15-supported metallic catalysts have been applied for a wide range of organic transformation with excellent activity and recyclability compared to other heterogeneous catalytic systems [11-13]. A stepwise manner of the direct oxidative conversion of methane to methanol was performed over CuO/SBA-15, in which the silica catalyst was activated in molecular oxygen at a high temperature (i.e. 550 °C) and subsequently interacted with methane at a lower temperature of 200 °C before an aqueous treatment to produce methanol [14]. Very recently, a novel Zr-based complex catalyst supported onto SBA-15 exhibited excellent catalytic performances for the multicomponent synthesis of a wide variety of the industrially important six-membered N-containing heterocyclic under green conditions [15].

The oxidative cross-coupling reactions catalyzed by transition metal are considered as one of the most beneficial approaches for the direct formation of carbon-carbon and carbon-heteroatom bonds.
without toxic and complicated intermediate steps [16, 17]. For instance, the \(-\text{C}(=\text{O})-\text{O}\) moiety which is very commonly present in a lot of pharmaceutical or natural products can be easily obtained via the oxidative coupling of a hydroxyl (-OH) group and an aldehyde (-CHO) one while the traditional two-step routes including oxidation of aldehyde and subsequent esterification require more time and cost but cannot be applied for all cases [17, 18]. In recent years, Cu, Co, Fe, and Ni catalysts considered as the promising alternatives to costly noble metal catalysts for coupling reactions have paid increasing attention due to economic advantages and comparable performances [19-27]. Among them, Cu sites was found to the most promising for the C(sp²)-O coupling with many Cu-containing catalytic systems previously reported. Chang et al. described the first oxidative C-O coupling reaction between the phenolic O-H and the formamidic C-H bonds in the presence of Cu(OAc)₂ as a homogenous catalyst and \textit{tert}-butyl hydroperoxide as an oxidant [28]. Phan et al. conducted this reaction using a novel heterogeneous catalytic system consisting of metal-organic framework Cu₂(BPDC)₂(BPY) which was obtained from expensive organic linkers and has a relatively low chemical stability [29]. Recently, CuFe₂O₄ nanoparticles have been applied to catalyze the direct coupling of phenol with \textit{N,N}-dialkylformamide, however, only a yield of 68% for the desired product was obtained in the presence of 5 mol% of CuFe₂O₄ [30].

Due to above-mentioned noteworthy and desirable characteristics supported SBA-15 materials for catalytic applications, we herein synthesized and used CuO/SBA-15 as a solid catalyst for the oxidative C(sp²)-O cross-coupling reaction between salicylaldehyde and \textit{N,N}-dimethylformamide. The high activity of CuO/SBA-15 is promising for expanding the catalytic application scope of this silica-based material to other oxidative coupling routes.

2. Experimental section

2.1. Synthesis of The Materials

Synthesis of SBA-15

SBA-15 was prepared according to the previous procedure [31]. Generally, P123 (EO₂₀PO₇₀EO₂₀, Mav = 5800, 2 g) was dissolved in a mixture of water (30 g) and a 2 M hydrochloric acid solution (60 g) at ~35 °C. After vigorous stirring for 1 h, tetraethyl orthosilicate (TEOS, 4.2 g) was added to the solution. The resulting mixture was stirred at the same temperature for 24 h before aging in a teflon-lined autoclave at 100 °C for another 24 h. The former white solid was then filtered, washed with water, dried at 110 °C for 12 h, and calcined in static air with a temperature ramp rate of 2 °C/min and kept at 500 °C for 4 h.

Synthesis of CuO/SBA-15

Cu (II) acetylacetonate (0.45 mmol) was added to a mixture of SBA-15 (0.975 g) and absolute ethanol (12 mL). After sonication at room temperature for 10 min, a slow evaporation of ethanol was performed at ~40 °C under vigorous stirring until a gel-like phase was obtained [14]. The sample was dried at 80 °C for 12 h for the removal of ethanol. The resulting powder was then calcinated in static air with a temperature ramp rate of 2 °C/min and kept at 550 °C for 4 h, yielding a green solid denoted as CuO/SBA-15. The Cu content of 3.2 wt.% in the as-synthesized CuO/SBA-15 sample was determined by inductively coupled plasma – optical emission spectrometry (ICP-OES) analysis.

Synthesis of CuO-SiO₂ mixed-oxide composite

For comparison purpose, a CuO-SiO₂ composite was synthesized via gel combustion. In detail, Cu(NO₃)₂·3H₂O (6.3 mmol) was dissolved in ethanol (40 mL) in a ceramic crucible. After addition of TEOS (83.2 mmol), the resulting solution was stirred for 30 min and subsequently slowly evaporated at 50 °C until a gel was obtained. The gel-containing crucible was heated in static air with a temperature ramp rate of 5 °C/min and kept at 550 °C for 6 h, yielding the black CuO-SiO₂ composite with the Cu content of 7.4 wt.% and the Brunauer–Emmett–Teller (BET) surface area of 340 m²/g.

2.2. Characterization of The Materials

Nitrogen physisorption measurements were carried out on Micromeritics ASAP 2020 volumetric adsorption analyzer system. Dried samples were activated at 150 °C under vacuum in 5 h before the
isothermal sorption at 77 K using high purity nitrogen. Surface areas were calculated by the Brunauer–Emmet–Teller (BET) model in the relative pressure range of 0.01 – 0.10 p/p°.

Powder X-ray diffraction (PXRD) patterns were obtained using a D8 Advance Diffractometer (Bruker AXS, Germany, Cu Kα radiation and a Ni filter). The measurements were performed in 20 range of 0.5 – 80° with an angular step size of 0.010s° and scanning rate of 0.63° per min.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo with the sample load of around 10 mg on an aluminia holder. The results were recorded in air within the temperature range of 30 – 850 °C and the ramping rate of 5 °C/min.

Transmission electron microscopy (TEM) images were recorded on a TECNAI G²20 S-TWIN electron microscope operated at 200 kV. For sample preparation, a drop of the material dispersed in ethanol was deposited onto a carbon-coated nickel grid via evaporation.

Energy-dispersive X-ray spectroscopy (EDX) images were recorded on a Hitachi-4000 scanning electron microscope (SEM) device equipped an EDX detector from Bruker. The samples were prepared on carbon pellets and then covered by thin gold layers.

2.3. Catalytic Studies

In a typical experiment, salicylaldehyde (24.4 mg, 0.2 mmol), N,N-dimethylformamide (DMF, 1 mL), CuO/SBA-15 (3 mol %) and di-tert-butylperoxide (DTBP, 116.8 mg, 0.8 mmol) were respectively added to a 4-mL pressurized vial. The reaction mixture was then vigorously stirred for 2 hours at 120 °C. The reaction mixture was cooled to room temperature and then added with a pre-determined amount of diphenyl ether (34.0 mg, 0.2 mmol). Consequently, an aliquot of the crude reaction mixture was withdrawn and quenched with brine (2 mL). The organic phase was extracted into ethyl acetate (2 mL), dried over anhydrous Na₂SO₄, filtered through a cotton layer, and analyzed by gas chromatography (GC) to determine the yield of the reaction using diphenyl ether as the internal standard.

GC analyses were performed on a Shimadzu GC 2010-Plus device equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The GC oven was initially held at 100 °C for 1 min then heated from 100 °C to 280 °C with a temperature ramp rate of 40 °C/min and further held at 280 °C for another 4.5 min before being cooled down to 100 °C. The inlet and detector temperature was kept constant at 280 °C.

2.4. Isolation and Identification of The Coupling Product

To isolate the product, the reaction was initially set up under the above-described conditions. After the reaction, the resulting mixture was diluted with ethyl acetate (30 mL). The organic phase was washed with brine (3 x 10 mL). The organic layer was subsequently dried over anhydrous Na₂SO₄, filtered through a cotton layer, and concentrated under a reduced pressure. The organic product was isolated by column chromatography, using silica gel (particle size 0.04–0.036 mm, 230-400 mesh, ASTM E.Merck) as a stationary phase and ethyl acetate/hexane mixture (1/3 volume ratio) as an eluent, affording a pale-yellow solid. The product structure was identified to be 2-formylphenyl dimethylcarbamate via gas chromatography-mass spectrometry (GC-MS), proton nuclear magnetic resonance (¹H-NMR), and carbon-13 nuclear magnetic resonance (¹³C-NMR) measurements.

MS spectra were collected on a Shimadzu GC-MS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis is as described: samples were held at 50 °C for 2 min then heated from 50 to 280 °C at 10 °C/min and finally held at 280 °C for 10 min. Inlet temperature was constantly set at 280 °C. The MS spectra were compared with references from the NIST library.

¹H-NMR and ¹³C-NMR spectra (Figures 1 and 2) were recorded in CDCl₃ solvent using residual solvent peak or tetramethylsilane as a reference on a Bruker AV 500 spectrometer.

¹H-NMR (500 MHz, CDCl₃) δ (ppm) 10.20 (s, 1H), 7.88 (dd, J = 7.7, 1.8 Hz, 1H), 7.67 – 7.56 (m, 1H), 7.34 (tt, J = 7.6, 0.8 Hz, 1H), 7.27 – 7.21 (m, 1H), 3.17 (s, 3H), 3.05 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ (ppm) 188.89, 154.24, 153.00, 135.18, 129.91, 128.50, 125.79, 123.67, 36.92, 36.63.
Figure 1. $^1$H-NMR spectrum of the isolated product.

Figure 2. $^{13}$C-NMR spectrum of the isolated product.

3. Results and Discussion

3.1. Catalyst Synthesis and Characterization
After synthesizing based on the typical procedure reported by Zhu et al., SBA-15 was impregnated with Cu(acac)$_2$ using ethanol as the dispersion phase [32]. Wet impregnation method is widely applied for supporting metallic sites onto silica materials due to its simplicity, efficiency, and easy controlling of metal loading. However, in some cases, the dispersion of metal species in the silica channels is limited due to size difference, metal-containing precursor decomposition and sintering issue. Indeed, at high temperature, e.g. in the calcination operation, individual metal oxide nanoparticles can rapidly sinter together to produce larger ones [14]. In this study, after the wet impregnation step, the Cu(acac)$_2$ precursor was dispersed into the mesopores of SBA-15. After calcination at 550 °C to remove organic substrates, formed CuO species were expected to be present in SBA-15 with good dispersion (Figure 3). The structural analyses were investigated to gain more insights into the copper species in the CuO/SBA-15 material.

**Figure 3.** Photographs of the materials including (a) SBA-15, (b) Cu(acac)$_2$, (c) SBA-15 impregnated with Cu(acac)$_2$ in ethanol, (d) SBA-15 impregnated with Cu(acac)$_2$ after the removal of ethanol, and (e) calcinated CuO/SBA-15.

**Figure 4.** TGA results of SBA-15 and the mixture before calcination.
Thermal behavior of SBA-15 impregnated with Cu(acac)$_2$ (Cu(acac)$_2$/SBA-15) was investigated by TGA in comparison with that of SBA-15, providing valuable information on the decomposition of Cu(acac)$_2$ in SBA-15 in the calcination step (Figure 4). For the SBA-15 material, the heating range from 25 to 150 °C exhibited a 20% weight loss, which could be related to the removal of absorbed water similar to the result found in the study of Kruk et al. on SBA-15 [33]. At the temperature higher than 200 °C, only a negligible mass decrease was detected, proving that SBA-15 had high thermal stability. In the case of Cu(acac)$_2$/SBA-15, which was not calcinated yet, the TGA result showed two main weight losses. Besides the mass drop due to the solvent removal mentioned above, the sample mass continued to significantly decrease for about 20% from 150 to 300 °C, which was attributed to the decomposition and combustion of organic substrates in copper (II) acetylacetonate in air, leading to formation of the gas products and copper oxide. From 550 °C, the change of mass was insignificant, confirming that the 550 °C temperature for calcination of Cu(acac)$_2$/SBA-15 was appropriate for a complete combustion. Indeed, the temperature range of 400 -550 °C was commonly applied to decompose the impregnated Cu-based precursors into copper(II) oxide for the synthesis of CuO/SBA-15 [34-38].

Morphology of the CuO/SBA-15 material was observed by TEM measurements. Similar to previous studies on the SBA-15 materials, regular hexagonal mesochannels of SBA-15 are observed for all samples, before and after Cu loading, indicating that the feature mesoporous silica structure was not affected by the impregnation procedure (Figure 5) [5, 10, 39]. Notably, EDX analysis indicated the appearance of Cu in the material with the content of 3.39 wt.%, which was close to the result obtained via ICP-OES analysis (Figure 6). However, no Cu-based nanoparticles were detected in the TEM images. These results suggested that Cu species were uniformly dispersed throughout the SBA framework. Le et al. previously reported that the homogeneous CuO phase was obtained with the Cu(acac)$_2$ precursor while the use of Cu(OAc)$_2$ for the impregnation led to the formation of large CuO nanoparticles in SBA-15.

![Figure 5. TEM images of SBA-15 and CuO/SBA-15.](image-url)
The PXRD pattern at low angles of the original SBA-15 showed three signature diffraction peaks at $2\theta = 0.92^\circ$, $1.55^\circ$, $1.82^\circ$ indexed as (100), (110), and (200) planes corresponding to the well-ordered two-dimensional hexagonal structure of SBA-15 [14]. The (100) diffraction peak was well observed in both materials, confirming that the porous structure of the SBA-15 pore was sustained after Cu loading. The decreased intensity of these low-angel peaks for Cu-containing samples can be attributed to the presence of Cu species in the SBA-15 channels (Figure 7). For wide-angle measurements, the broad peak at $2\theta = 24^\circ$ was assigned to amorphous phase of silica materials [10, 14, 39]. Besides, the wide-angle pattern of CuO/SBA-15 was familiar to the pure SBA-15 without additional peaks of Cu-based phases, indicating that the Cu species well-spread on the support (Figure 8). These results were consistent with the study on CuO/SBA-15 previously reported [14].

Figure 6. EDX spectrum of CuO/SBA-15.

Figure 7. Low-angle PXRD patterns of SBA-15 and CuO/SBA-15.
Figure 8. Wide-angle PXRD patterns of SBA-15 and CuO/SBA-15.

The nitrogen physisorption isotherms obtained for SBA-15 and CuO/SBA-15 were familiar to the earlier results for mesoporous silica materials (Figure 9). The adsorbed N$_2$ amount became significant at the relative pressure of 0.5-0.8, at which the adsorption mainly occurred in mesopores. Based on the isotherm data, pore size distribution was determined and shown in Figure 10. As expected, the pore width distribution for SBA-15 and CuO/SBA-15 focused at ~ 10 nm. Previous studies also reported the SBA-15 pore size in the range of 5-15 nm [5, 32, 33, 39, 40], depending on synthesis conditions and P123 polymer structure. Compared to the case of fresh SBA-15, the nitrogen volume adsorbed at such mesopores of CuO/SBA-15 significantly reduced, indicating the successful occupation of Cu species at these positions. As a result, the surface area of the material greatly decreased from 1081 to 600 m$^2$/g due to impregnation with Cu. However, the pore size was almost preserved after the Cu loading. It was obvious that the presence of Cu species in SBA-15 led to a considerable drop in the surface area but no change in the pore size. This phenomenon could be explained by the proposal that Cu species were filled in the cylindrical pores of SBA-15 along the length from the bottom rather than along the diameter of the pores. Such filling route decreased the total pore volume while the pore diameter was unchanged as reported in the literature [38, 41-44].
3.2. Catalytic Studies

In earlier studies, salicylaldehyde was proved to react with \( N,N \)-dimethylformamide to form 2-formylphenyl dimethylcarbamate as the main product [18, 45, 46] in the presence of a Cu-based catalyst under oxidizing conditions. Therefore, the as-synthesized CuO/SBA-15 material was applied as a solid catalyst for this oxidative C(sp\(^2\))-O cross-coupling reaction. The product obtained after the reaction was isolated by column chromatography and subsequently analyzed by GC/MS and NMR. Based on the results obtained from GC/MS and NMR measurements (Figures 1 and 2), it could be concluded that the reaction of salicylaldehyde with DMF catalyzed by CuO/SBA-15 yielded 2-formylphenyl dimethylcarbamate as the main product (Scheme 1). In next studies, the effect of the reaction conditions including reaction time, temperature, catalyst amount, oxidants, equivalents of oxidant, and amount of solvent on the yield of carbamate was intensively investigated.

The product was formed based on the selectively oxidative coupling between H-O- in salicylaldehyde and H-(C=O)- in DMF. Therefore, a -CHO group derived from salicylaldehyde still remained in the product structure, which was very sensitive to the oxidative phase. In this case, the product could be over-oxidized into other unwanted compounds. Therefore, the more reaction time is, the more the target product lost. Accordingly, the effect of reaction time on the formation of product should be first investigated. The reaction between salicylaldehyde (0.2 mmol) and \( N,N \)-dimethylformamide (1.5 mL) was carried out in the presence of CuO/SBA-15 (10 mol %) and DTBP (4 equivalents) at 120 °C in the time range from 10 min to 24 hours. As shown in Figure 11, the reaction proceeded readily in the first 2 hours and could afford a yield of 90% for the desired product.
Extending the reaction time from 2 hours to 4 hours is unnecessary because the yield of major product was not significantly improved. Importantly, after 4 hours of the reaction course, the product yield started decreasing. As a result, only a yield of 71% was obtained in the 24-hour reaction. This yield drop could be explained based on the above-mentioned fact that the aldehyde group in the product was indeed instable and can be further oxidized (Figure 11).

![Figure 11](image)

**Figure 11.** Effect of reaction time on the product yield.

In a reaction using a peroxide oxidant, the reaction temperature is an important factor because each peroxide substrate efficiently works at different temperature range. For instance, tert-butyl hydroperoxide (TBHP) should be used for the reaction at 80-100 °C while DTBP would become reactive at higher temperatures of 100-120 °C [46-49]. Therefore, in this study, the effect of the reaction temperature was explored via performing the reaction in 2 hours at different temperatures from room temperature (R.T) to 140 °C. In each experiment, DMF (1.5 mL) was allowed to react with salicylaldehyde (0.2 mmol) using 10 mol% of CuO/SBA-15 and 4 equivalents of DTBP. No product was detected in the reaction at the temperature below 60 °C. As expected, increasing the reaction temperature led to the product formation. In specific, at 100 °C, a moderate yield of 62% was achieved. Conducting the reaction at 120 °C gave the highest yield of 90%. Nevertheless, if the
reaction was carried out at 140 °C, a drop in the product yield to 64% was observed, which could be assigned to increasing reactivity of the aldehyde group in the product (Figure 12).

Another important factor that should be concerned on this reaction was the catalyst amount. The amount of catalyst was varied from 0 to 10 mol% at the reaction temperature of 120 °C. This reaction could not yield the major product in the absence of CuO/SBA-15. (Figure 13), verifying that the catalyst is indeed essential for the oxidative coupling between salicylaldehyde and DMF. Addition of the catalyst to the reaction phase led to a considerable formation of the product even at low catalyst concentration. Indeed, only with 1 mol% of catalyst used, a high yield of 84% was achieved in 2 hours. Using more catalyst amounts led to only a minor improvement in the formation of the main product. Importantly, these results demonstrated the great efficiency of the CuO/SBA-15 catalyst as compared to those previously reported under both homogeneous and heterogeneous catalysis conditions probably due to high dispersion of copper species inside the mesopore channel of SBA-15, at which the reactants and DTBP can easily access and get activated by the catalytic sites. Indeed, the coupling reaction of salicylaldehyde and DMF afforded a 81% isolated yield for the major product in the presence of 5 mol% of Cu(OAc)₂ [50]. Phan et al. applied 5 mol% of a Cu-MOF catalyst to obtain a yield of 70% in the same reaction [48]. Furthermore, 5 mol% of copper ferrite nanoparticles were required to form the corresponding product at a yield of 72% via catalyzing the C(sp²)-O coupling reaction of (2-hydroxyphenyl) benzothiazole with DMF [30].

It is obvious that a study on the oxidant amount is necessary to improve the reaction rate and control selectivity to the coupling product. In this work, no desired product was detected in the reaction without DTBP or using only 1 equivalent of DTBP, indicating that an excess amount of DTBP was required to activate DMF and yield the carbamate [30, 49-51]. As the DTBP amount was increased from 2 to 4 equivalents, the yield of 2-formylphenyl dimethylcarbamate was significantly improved from 33% to 90%. Nevertheless, the reaction gave a lower yield of 71% in the presence of 5 equivalents of DTBP. Such a yield drop could be rationalized upon the accelerated overoxidation of the sensitive aldehyde group in the carbamate under harsh conditions (Figure 14). In earlier studies on this coupling reaction, the used oxidant amount as in the range of 1.5 – 6 equivalents [46-49].
As above proved, the oxidant plays an essential role in the formation of the main product via an oxidative coupling manner [18, 30, 46–48, 50, 52]. It was therefore decided to investigate the impact of different oxidants on the coupling of salicylaldehyde with DMF including DTBP, TBHP in water, TBHP in decane, H2O2, K2S2O8, PhI(OAc)2, and dibenzoyl peroxide, respectively. The reaction was conducted using 3 mol% of CuO/SBA-15 and 4 equivalents of the oxidant at 120 °C for 2 hours. Inorganic oxidants, namely, H2O2 and K2S2O8, were found to be unsuitable for this coupling as the poor yields were recorded (2-15%). By contrast, using organic oxidants gave better yield results. PhI(OAc)2 or dibenzoyl peroxide allowed the carbamate to be produced in yields of ~ 20% while tert-butyl hydroperoxide-mediated reactions afforded 65% yields within 2 hours. Among the oxidants tested in this study, DTBP exhibited the highest efficiency for the formation of 2-formylphenyl dimethylcarbamate with an excellent yield of 90%. (Figure 15). In many oxidative coupling reactions,
peroxide-type oxidants were found to be appropriate to produce the desired product due to the facile and steady formation of highly reactive alkoxy radicals during the reaction course. Indeed, DTBP or TBHP could be decomposed into tert-butoxy radicals ((CH₃)₃CO·) at an elevated temperature in the presence of Cu species [28, 53-55]. This radical subsequently activated the aldehyde C(sp²)-H via abstracting the hydrogen atom to form a corresponding carbonyl radical for the coupling with the phenolic hydroxyl group.

To determine which site is responsible for this catalysis, different materials including CuO-SiO₂ composite (Cu content = 7.44 wt.%), as-synthesized SBA-15, and CuO/SBA-15 (Cu content = 3.39 wt.%) were respectively applied for the reaction between salicylaldehyde and DMF. Under identical conditions, no product was detected in the reaction using SBA-15 while the presence of Cu-containing materials led to the expected production of 2-formylphenyl dimethylcarbamate, proving that copper species was the only active site in CuO/SBA-15. The advantage of using CuO/SBA-15 was emphasized in comparison with Cu(OAc)₂ and the CuO-SiO₂ composite. The molecular catalyst the mixed-oxide composite afforded only a 58% yield while the CuO/SBA-15-mediated reaction was more favorable to produce the carbamate in a considerably higher yield of 90%, which was comparable with the homogeneous catalysis by Cu(OAc)₂. The high activity of CuO/SBA-15 can be attributed to the fact that active Cu species which was homogeneously dispersed were located at the mesopore channels of SBA-15 while the CuO-SiO₂ composite contained almost micropores with less accessibility for the reagents (Figure 16).

![Figure 16. Performance of different catalysts](image)

### 4. Conclusions

In this work, CuO/SBA-15 was facilely synthesized from SBA-15 and Cu(acac)₂ by wet impregnation and subsequent calcination. The mesoporous channels of SBA-15 remained unchanged after copper oxide species was incorporated into the framework. PXRD and TEM measurements confirmed that copper species were uniformly dispersed throughout the SBA-15 framework. This material was used as a solid catalyst for the oxidative cross-coupling reaction between salicylaldehyde and DMF in the presence of an oxidant. The catalytic studies showed that the 90% yield was achieved with 3 mol% of CuO/SBA-15 and equivalents of DTBP in 2 hours at 120 °C. Using 1 mol% of the catalyst could give a high yield of 84%, verifying the high activity of this Cu-containing silica material in the selective C(sp²)-O coupling in comparison with the catalytic systems previously reported. The next work will focus on expanding the substrate scope and recycling the catalyst to highlight its great benefits for this transformation.
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