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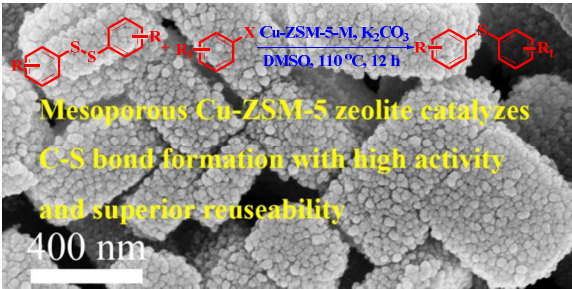


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High Activity and Stability in the Cross-Coupling of Aryl Halides with Disulfides over Cu-doped Hierarchically Porous Zeolite ZSM-5

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A Cu-doped zeolite ZSM-5 (Cu-ZSM-5-M) with micro-meso-macroporous structure was directly synthesized, and it exhibits excellent catalytic activity and good recyclability in cross-coupling of aryl halides with diphenyl disulfides. This feature should be attributed to the structural characteristics of meso-macroporosity and homogeneous dispersion of active Cu^{δ+} ($\delta < 2$) species in the Cu-ZSM-5-M.

The carbon-sulfur bond formation is one of the significant organic transformations.¹ For instance, diaryl thioethers are important structural motifs in a wide range of molecules with numerous applications,² which can be synthesized from cross-coupling of aryl halides with sulfides catalyzed by transition-metal such as palladium,³ nickel,⁴ copper,⁵ and iron⁶ as well as ligated metal complexes.^{4,7} Despite these homogeneous transition-metal catalysts have been extensively investigated, and present high activity, the industrial applications of these catalysts are still remain challenging because of their drawbacks including high cost, difficult separation and regeneration. Although, a number of solid materials such as carbons,⁸ polymers,⁹ metal organic frameworks,¹⁰ covalent organic frameworks,¹¹ and mesoporous silica¹² have been employed as supports for preparing heterogeneous metal catalysts, the applications of these solid catalysts for organic synthesis are still limited due to their relatively low stability or metal leaching tolerance. From a practical point of view, following basic but important issues should be taken into account in order to design and synthesize heterogeneous metal catalysts for organic synthesis chemistry.

- (1) The catalyst must show high thermal stability, which is important for the regeneration of deactivated catalyst by calcination.
- (2) Suitable pores structure that can enhance the fast diffusion of the bulk substrates and products.
- (3) Good chemical stability and Metal leaching tolerance as well as mechanical stability in organic solvents under reaction conditions.
- (4) Very importantly, how to utilize the properties of the support for preparation of functionalized metal catalyst with high activity?

It is well known that aluminosilicate zeolites are crystalline porous materials with good thermal, chemical and mechanical stability, which are widely used in the industry as support of metal catalysts.¹³ Especially, the negatively charged framework of zeolites

can interact with their assembled metal species, resulting in decoration of the electronic property on metal species, which may improve the catalytic performance of their assembled metals.¹⁴ Furthermore, the mesoporous introduced into the zeolite crystals could benefit the mass transfer of the bulk substrates and products, and improve their catalytic performance.¹⁵ Therefore, based on the characteristics of zeolite framework and the catalytic properties of the transition-metals, it should be possible to design and synthesis of highly active and stable metal catalysts, in which the metal species are confined in the mesoporous zeolite framework for organic transformations.

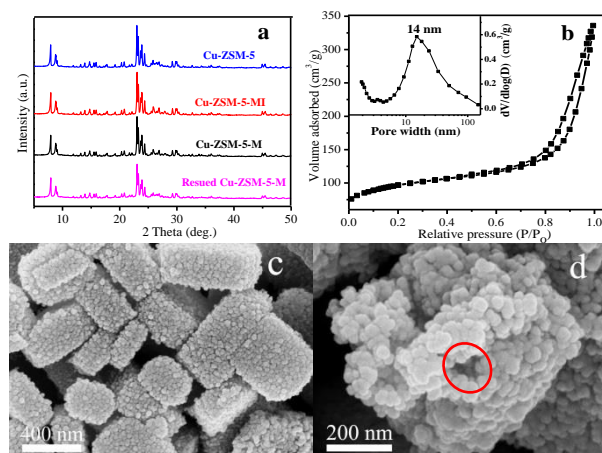


Fig. 1 (a) XRD patterns of Cu-ZSM-5-M, Cu-ZSM-5-MI, Cu-ZSM-5 and reused Cu-ZSM-5-M samples, (b) N₂ adsorption isotherm of the Cu-ZSM-5-M sample (inset: pore size distribution of the Cu-ZSM-5-M), (c) low resolution SEM image and (d) high resolution SEM image of Cu-ZSM-5-M sample.

Herein, we report a facile method to synthesize Cu-doped zeolite ZSM-5 (Cu-ZSM-5-M) with micro-meso-macroporous structure by using silane of N,N-dimethyl-N-octadecyl-N-(3-triethoxysilylpropyl) ammonium bromide as a mesoscale template (ESI[†]), which exhibits much higher activity and superior reusability in the cross-coupling of aryl halides with diphenyl disulfides, compared with Cu-doped micropore ZSM-5 (Cu-ZSM-5) and mesoporous zeolite ZSM-5

supported Cu catalyst (Cu-ZSM-5-MI) that was prepared by impregnation method. This feature may be attributed to the fact that the Cu^{2+} in the synthesis gel could be confined in zeolite framework during the crystallization process, resulting in the highly active $\text{Cu}^{\delta+}$ ($\delta < 2$) species. In addition, the meso-macroporosity in the Cu-ZSM-5-M catalyst benefits the mass transfer and therefore improves its catalytic performance. This catalyst design concept provides a new strategy for developing high efficient heterogeneous metal catalysts, which will be potential for their wide applications for organic transformations in industry.

Fig. 1a showed the XRD patterns of various samples, which exhibit a series of peaks at 7.9, 8.8, 23.1, 23.9 and 24.4°, associated with MFI structure could be clearly observed in Cu-ZSM-5-M, Cu-ZSM-5 and Cu-ZSM-5-MI samples, indicating highly crystalline degree in these samples. The inductively coupled plasma (ICP) analysis show that the Cu content in the Cu-ZSM-5-M and Cu-ZSM-5 is 1.3 and 1.4 wt. %, respectively, which suggests that the Cu element has been successfully introduced into the zeolite. The nitrogen sorption isotherm of the Cu-ZSM-5-M exhibits a hysteresis loop at a relative pressure of 0.70-0.95, which is typically assigned to the presence of mesostructure (Fig. 1b). Correspondingly, the pore-size diameter is centred at 14 nm (insert, Fig. 1b). Sample textural parameters are presented in Table S1. The SEM images reveal the Cu-ZSM-5-M sample with a particle size of 400-600 nm. It seems that the particle is composed by the aggregation of the nanoparticles with mainly size of 20-40 nm (Fig. 1c,d). In this manner, the mesopores and macropores (marked circle, Fig. 1d) could be formed in aggregates. However, the TEM image of the thin-sectioned sample clearly shows that the Cu-ZSM-5-M particle presents a core-shell structure, in which the core is covered by nanoparticle layers with thickness of about 60 nm (Fig. S1a, ESI†). Additionally, the high resolution TEM image represents the mesopore cavities within the crystal (bright areas in Fig. S1b, ESI†). The mesopores diameters in the crystal are ranged from 8 to 12 nm determined by TEM, in agreement with the pore size distribution derived from N_2 sorption experiment. Furthermore, the nanoparticles on the surface of the core also show crystal structure (Fig. S1c, ESI†). Combination of the SEM and TEM results, Cu-ZSM-5-M exhibits micro-meso-macroporous structure, which could facilitate the mass transfer. It is worth noting that the Cu particles are not observed in the TEM images, while the ICP analysis shows that the Cu content in the Cu-ZSM-5-M sample is 1.3 wt.%. These results indicate that the Cu species could be highly dispersed in Cu-ZSM-5-M. As a comparison, the Cu nanoparticles with size of 1-1.5 nm could be observed in the Cu-ZSM-5-MI sample (Fig. S1d, ESI†).

To further investigate the location of Cu species in the Cu-ZSM-5-M catalyst, the additional TEM and the X-ray energy dispersive spectroscopy (EDS) analysis of a thin-sectioned Cu-ZSM-5-M and Cu-ZSM-5 samples were performed, as shown in Fig. S2-S6. The TEM images show that the Cu-ZSM-5 sample only contains micropores, and that no Cu particles can be observed (Fig. S2a and b, ESI†). However, the EDS element mapping of the selected zone confirms the presence of Cu element (Fig. S3, ESI†). For the Cu-ZSM-5-M sample, no Cu particles can be observed in the selected zone (Fig. S4a and b, ESI†). Similarly, the Cu element is detected by the EDS element mapping in the selected zone. In addition, after destruction of the zeolite framework by the electron beam in the selected zone, small nanoparticles (1-2 nm) are observed (Fig. S6, ESI†). The very small nanoparticles should be attributed to the aggregation of the copper species in the micro-mesopores. These phenomena indicate that the micropore and mesopore in the Cu-ZSM-5-M sample should contain high dispersed Cu species.

To study the state of Cu species in the Cu-ZSM-5-M catalyst, the X-ray photoelectron spectroscopy (XPS) and UV-vis diffuse

reflectance spectroscopy (UV-vis DRS) analysis were performed. From the Fig. 2a, the binding energy of $\text{Cu}2\text{p}_{3/2}$ for the Cu-ZSM-5-MI sample is 933.6 eV, which is well-ascribed to Cu^{2+} .^{16a} In contrast, this value is 933.0 eV for the Cu-ZSM-5-M. Possibly, the electron transfer from negatively charged framework of zeolites to the copper species occurred due to the strong interaction between zeolite framework and copper species in the Cu-ZSM-5-M,^{14c} resulting in formation of $\text{Cu}^{\delta+}$ ($\delta < 2$) species in comparison with Cu^{2+} in the Cu-ZSM-5-MI catalyst. Fig. 2b shows the UV-vis DR spectra of the Cu-ZSM-5-M and Cu-ZSM-5-MI samples. The Cu-ZSM-5-M catalyst displays one absorption band at 200-260 nm, which could be assigned to the charge-transfer in the O-to-metal related to the Cu^+ or Cu^{2+} ions stabilized in the zeolite framework,^{16a,b,c} The absorption band in the 250 nm is attributed to Cu^+ .^{16d} Compared with Cu-ZSM-5-M, the Cu-ZSM-5-MI catalyst displays one absorption band centred at 210 nm, and a broad shoulder band at 280-320 nm. The broad band at 280-320 nm is ascribed to Cu^{2+} .^{16d} Combination of XPS and UV-vis results, Cu species in the Cu-ZSM-5-M are mainly present in the form of $\text{Cu}^{\delta+}$ ($\delta < 2$) ions.

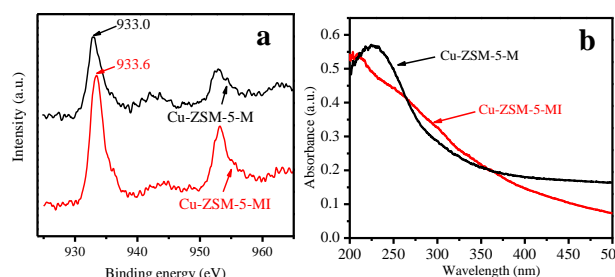


Fig. 2 (a) XPS and (b) UV-vis DR spectra of Cu-ZSM-5-M and Cu-ZSM-5-MI catalysts, respectively.

The cross-coupling of aryl halides with diaryl disulfides to synthesize diaryl thioether compounds was firstly studied by choosing iodobenzene and diphenyl disulfide as the model substrates to investigate our tentative idea (Table 1). To our delight, the high desired product yield (100%) of diphenyl thioether is obtained over Cu-ZSM-5-M catalyst (entry 1). The micropore Cu-ZSM-5 and Cu-ZSM-5-MI catalysts give yields of 61 and 76 % (entries 2,3), much lower than that of Cu-ZSM-5-M. It should be noted that the product is indeed formed over the metal salt of $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}(\text{OAc})_2$ catalysts with good yields (entries 4,5).

Table 1 Synthesis of diaryl thioethers over series catalysts under different conditions.^a

Entry	Catalyst	Yield (%)
1	Cu-MZS-5-M	100 (95) ^b
2	Cu-ZSM-5	61 (55)
3	Cu-ZSM-5-MI	76 (72)
4 ^c	$\text{Cu}(\text{NO}_3)_2$	94 (90)
5 ^c	$\text{Cu}(\text{OAc})_2$	95 (90)

^a Reaction conditions: diphenyl disulfide (0.2 mmol), iodobenzene (0.6 mmol), Cu-ZSM-5-M (30 mg), base (3 equiv), DMDS 2 mL, 12 h. Yields were analyzed by GC-FID. ^b The value in parenthesis is isolated yield. ^c The Cu content equivalent equal to that of 30 mg Cu-ZSM-5-M.

Encouraged by the promising results, we further studied series of substrates in this Cu-ZSM-5-M-catalyzed cross-coupling of aryl halides with disulfides (Table 2). First, the

scope of the various aryl halide substrates was investigated. Delightfully, the Cu-ZSM-5-M catalyst tolerates various functional groups, both electron-rich (entries 2,3), electron-deficient (entry 4) aryl iodides, as well as the more sterically hindered ortho-substituted one (entry 5), afforded good yields for the target products. Notably, the substrate of 1-iodonaphthalene with large molecular dimension is also suitable for this transformation and gives excellent yield (97%), indicating that the Cu-ZSM-5-M catalyst shows superior catalytic performance. Very interestingly, although the activation of carbon-chlorine (C-Cl) and carbon-bromine (C-Br) bonds are much more difficult than carbon-iodine (C-I) bond,¹⁷ both of the p-nitrochlorobenzene and p-nitrobromobenzene are successfully applied to this transformation in gratifying yields (entries 7,8). In addition, we further applied the Cu-ZSM-5-M catalyst to examine the substrate scope of diaryl disulfides. Diaryl disulfides containing methoxyl and bromo substituents are underwent in good yields (entries 9,10). Although, the nitro group weakened the nucleophilicity of the -S-S- bond, it still results in a moderate yield of 67% (entry 11). Interestingly, when the difurfuryldisulfide was chosen as a substrate, an excellent yield is obtained (90%, entry 12).

Table 2 The cross-coupling reaction between aryl halides and disulfides.^a

$\text{R-S-S-R} + \text{R}_1\text{-C}_6\text{H}_4\text{-X} \xrightarrow[\text{DMSO, 110 } ^\circ\text{C, 12 h}]{\text{Cu-ZSM-5-M, K}_2\text{CO}_3} \text{R-S-C}_6\text{H}_4\text{-R}_1$				
Entry	Aryl halide	Disulfide	Product	Yield (%)
1				100
2				97
3				94
4				99
5				96
6				97
7				84
8				95
9				98
10				100
11				67
12				90

^a Reaction conditions: diphenyl disulfide (0.2 mmol), aryl halide (0.6 mmol), Cu-ZSM-5-M (30 mg), K₂CO₃ (3 equiv), DMSO 2 mL, 12 h. The yields were obtained by GC analysis.

The superior catalytic performance of the Cu-ZSM-5-M catalyst should be attributed to its unique structural characteristics of the meso-macroporosity and homogeneous dispersion of active Cu^{δ+} (δ<2) species. Because of the large size of the reaction substrate and products, the cross-coupling reaction mainly occurs on the external surface and mesopores in catalysts. The Cu-ZSM-5-M shows meso-macropore surface area of 168 m²/g, while Cu-ZSM-5 shows external surface area only 67 m²/g (Table S1, ESI†). So, it is reasonable that the Cu-ZSM-5-M catalyst shows much higher catalytic activity than Cu-ZSM-5 (entries 1,2, Table 1). This result indicates that the meso-macroporous in the Cu-ZSM-5-M catalyst benefits the mass transfer and improves its catalytic performance.

On the other hand, Cu-ZSM-5-M and Cu-ZSM-5-MI catalysts have the similar meso-macropore area (168 and 164 m²/g) and mesoporous volume (0.45 and 0.46 m³/g) as shown in Table S1, and the Cu-ZSM-5-MI catalyst has a relatively higher metal loading (1.8 wt.%) than Cu-ZSM-5-M (1.3 wt.%), but the product yield over Cu-ZSM-5-M catalyst (100%) is much higher than that of over Cu-ZSM-5-MI catalyst (76%, Table 1). This phenomenon should be assigned to the difference in electronic property of the active Cu species between the Cu-ZSM-5-M and Cu-ZSM-5-MI catalysts. It has been reported that the catalytic activity of the metal catalyst such as copper,¹⁸ palladium,¹⁹ nickel,²⁰ and cobalt²¹ can be improved through decoration of their electronic properties by addition of electron-rich ligands. In our case, the Cu²⁺ in the synthesis gel could be confined in the zeolite Cu-ZSM-5-M during the crystallization process, and strongly interacted with negatively charged framework, resulting in highly active Cu^{δ+} (δ<2) species.

The reusable ability of Cu-ZSM-5-M and Cu-ZSM-5-MI catalysts in the cross-coupling reaction was also investigated. The yield of the product decreased from 100 and 77% (Run 1) to 84 and 45% (Run 8, Table S2, ESI†) for Cu-ZSM-5-M and Cu-ZSM-5-MI catalysts, respectively. Importantly, when the deactivated catalysts were calcined at 500 °C in air for 4 h, the activity was recovered to 93 and 50% (Run 9) for Cu-ZSM-5-M and Cu-ZSM-5-MI catalysts, respectively. These results demonstrate that the Cu-ZSM-5-M catalyst has a good reusability, which is one of the key features in the practical application in industry. The ICP analysis show that the Cu content in the reused Cu-ZSM-5-M and Cu-ZSM-5-MI catalysts is 1.2 and 0.8 wt.%, while in the as synthesized Cu-ZSM-5-M and Cu-ZSM-5-MI is 1.3 and 1.8 wt.%. Clearly, the metal leaching has not occurred for the Cu-ZSM-5-M catalyst during reaction process. Furthermore, the Si/Al ratio for reused and fresh Cu-ZSM-5-M is 33 and 32, respectively. Obviously, Cu-ZSM-5-M possesses good chemical stability, which is very important for industrial applications in the future. Additionally, the intensity of the XRD diffraction peaks for the reused Cu-ZSM-5-M is similar to the fresh catalyst (Fig. 1a), and the textual structure of the reused Cu-ZSM-5-M has no change (Fig. S7 and Table S1), which demonstrates that the Cu-ZSM-5-M catalyst have good mechanical stability.

In summary, the Cu-ZSM-5-M with micro-meso-macroporous structure was synthesized by using mesoscale surfactant as a template, which was investigated for catalyzing synthesis of diaryl thioethers through cross-coupling of aryl halides with disulfides. A variety of functional groups on both the aryl halide and disulphide substrates are well tolerated. Compared with micropore Cu-ZSM-5 and Cu-ZSM-5-MI catalysts, the Cu-ZSM-5-M catalyst shows high activity and excellent reusability in the cross-coupling reaction. This is attributed to the fact that the highly dispersed Cu^{δ+} (δ<2)

confined in framework present high activity, and the meso-macroporosity in the Cu-ZSM-5-M catalyst facilitates the mass transfer and therefore improves its catalytic performance.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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