iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 14 **Issue:** II **Month of publication:** February 2026

DOI: https://doi.org/10.22214/ijraset.2026.77379

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.538
Volume 14 Issue II Feb 2026- Available at www.ijraset.com

Synthesis of MCM-41 Supported *L*-proline Copper (I) Complex and Its Catalytic Performance for the Coupling Reaction of p-Iodotoluene with Sodium Methanesulfinate

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Abstract: ***By sequentially condensing 3-chloropropyltrimethoxysilane and trimethylchlorosilane with MCM-41 in toluene, chloropropyl-functionalized MCM-41 (MCM-41-Cl) is obtained. L-proline sodium functionalized MCM-41 (MCM-41-L-Proline) is successfully prepared by condensation and immobilization of MCM-41-Cl with N-Boc-4-hydroxy-L-proline, followed by deprotection of Boc and acid-base neutralization reaction. The performance of MCM-41-L-Proline in catalyzing the coupling reaction of p-iodotoluene (PIT) with sodium methanesulfinate (CH_3SO_2Na) is investigated with the synergistic effect of CuI. The results indicate that, under optimized reaction conditions, the MCM-41-L-Proline/CuI catalytic system delivers a 48.5% yield of methylsulfonyl toluene (MST). Interestingly, FT-IR results indicate that MCM-41-L-Proline and CuI in situ formed the MCM-41-L-Proline Cu(I) complex during the coupling reaction. This catalyst demonstrates excellent catalytic stability and recyclability, maintaining its activity with no significant decline after six cycles.***
Keywords: ***MCM-41; N-Boc-L-hydroxyproline; copper; coupling reaction; recycling performance.***

I. INTRODUCTION

Sulfone compounds bear a distinctive sulfonyl functional group and exhibit diverse biological activities [1]. Due to their extensive applications in pharmaceuticals, agrochemicals, natural products, organic materials, and organic synthesis [2], they have emerged as a research hotspot in organic synthetic chemistry in recent years [1]. The primary synthetic methods for sulfonyl compounds include the oxidation of sulfides, Friedel-Crafts sulfonylation, and transition metal catalyzed coupling. The catalytic oxidation of sulfides represents the most direct approach, with commonly used oxidants including $KMnO_4$ [3], meta-chloroperoxybenzoic acid [4], O_2[5], and H_2O_2 [6]. This method features a straightforward reaction pathway, enabling the conversion of sulfides to corresponding sulfones through a single-step oxidation. However, selective oxidation of sulfides to sulfones remains challenging, particularly when substrates contain easily oxidizable functional groups, as side reactions are prone to occur. The Friedel-Crafts sulfonylation method employs sulfonyl chloride, sulfonic acid or sulfonate as the sulfonylation reagent. It reacts with halogenated hydrocarbons or aromatic hydrocarbons to synthesize sulfonyl compounds by electrophilic substitution reaction catalyzed by lewis acid or protonic acid. Traditional catalysts for Friedel-Crafts sulfonylation include $AlCl_3$ [7] and BF_3 [8]. In recent years, novel catalysts such as ionic liquids [9], ion exchange resins [10], and trifluoromethanesulfonic acid [11] have also been employed by researchers. This synthetic approach utilizes readily available and inexpensive starting materials, enables the construction of aryl sulfone structures in a single step reaction, and exhibits high reactivity toward electron-rich aromatic compounds. However, this method is susceptible to space steric hindrance and electronic effects of substituents, resulting in low regioselectivity on the aromatic ring. The transition metal catalyzed coupling method refers to the cross-coupling reaction of sulfinic acid salts with aryl halides or aryl boronic acids under the catalysis of transition metals such as Pd and Cu to form sulfone compounds. In 1995, Suzuki et al. [12] first reported the synthesis of unsymmetrical diaryl sulfones in high yields from aryl halides and sodium sulfonate under CuI catalysis. In 2018, Yue et al. [13] reported the cross-coupling reaction of sodium sulfinate with aryl, heteroaryl and halogenated vinyl compounds under the dual catalysis of nickel/photoredox at room temperature. This strategy provides a flexible and diverse approach for synthesizing various aromatic sulfones and exhibits excellent functional group tolerance. In 2005, Ma et al. [14] reported that aryl halides and sulfinic acid salts could undergo coupling reactions in a CuI/*L*-proline sodium salt system to synthesize various aryl sulfones.

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The incorporation of amino acid ligands into CuI systems enables efficient construction of asymmetric sulfones with excellent functional group compatibility and substrate scope, offering a novel approach for synthesizing heterocyclic and functionalized sulfones. However, such homogeneous catalytic systems still face challenges in catalyst separation, recovery, and recycling, limiting their industrial application.

To address this issue, developing highly efficient heterogeneous catalytic systems is particularly crucial, such as immobilizing catalytic active species onto solid carriers to construct heterogeneous catalysts at the molecular level [15]. In recent years, the preparation of supported organic Cu(I) complexes and their application in cross-coupling reactions have gained significant attention from researchers [16-20]. In 2008, Wang et al. [18] developed a novel silica-anchored proline-copper(I) organic-inorganic hybrid material. This catalyst delivered good to excellent yields in the cross-coupling reaction of terminal alkynes with aryl iodides and aryl bromides. In 2016, Cai et al. [19] synthesized the *L*-proline-functionalized MCM-41 immobilized copper(I) complex (MCM-41-*L*-proline-CuCl), which enabled the preparation of various N-arylsulfonamides with excellent yields in the heterogeneous Chan-Lam coupling reaction between sulfonyl azides and arylboronic acids. In 2017, Cai et al. [20] prepared an MCM-41-immobilized *L*-proline-copper(I) complex (MCM-41-*L*-proline-CuI), achieving efficient coupling of aryl iodides with acetamidine hydrochloride to yield various primary aromatic amines in good to excellent yields. As far as we know, although there have been some reports on the preparation of supported *L*-proline copper(I) complexes, studies on their application in catalyzing the coupling reaction between halogenated aromatics and CH_3SO_2Na are scarce.

In this study, chloropropyl functionalized MCM-41 (MCM-41-Cl) was prepared by using MCM-41 as heterogeneous carrier, 3-chloropropyltrimethoxysilane and trimethylchlorosilane as functional reagents. Furthermore, MCM-41-Cl was condensed and immobilized with N-Boc-4-hydroxy-*L*-proline, followed by deprotection of the Boc group, successfully yielding *L*-proline-functionalized MCM-41 (MCM-41-*L*-Proline). The catalytic performance of MCM-41-*L*-Proline in the cross-coupling reaction between Aryl iodide and CH_3SO_2Na is investigated under CuI synergism. The results indicate that the MCM-41-*L*-Proline CuI complex can be generated in situ during the reaction and can be reused for six cycles without deactivation.

II. EXPERIMENTAL

A. *Materials and Methods*

Cetyltrimethylammonium bromide (CTAB, 99%), tetraethyl orthosilicate (TEOS, 99%), 3-chloropropyltrimethoxysilane (CPTMS, 98%), trimethylchlorosilane (TMCS, 99%), *L*-Hydroxyproline (99%), di-tert-butyldicarbonate (Boc_2O, 98%), potassium hydrogen sulfate ($KHSO_4$, 99%), trifluoroacetic acid (TFA, 99%), p-iodotoluene (PIT, 98%), sodium methanesulfinate (CH_3SO_2Na, 90%) and CuI (99%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Methylsulfonyl toluene (MST, 99%) was purchased from Wuhan Qiangfeng Sciences Co., Ltd (Xiaogan, China). Sodium hydroxide (NaOH, AR) and dimethyl sulfoxide (DMSO, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tetrahydrofuran (THF, AR) was purchased from Tianjin Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). Ammonia solution (25%), ethanol, ethyl acetate, acetonitrile, xylene, dichloromethane, anhydrous sodium sulfate, tert-butanol, toluene, and other AR reagents were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China).

B. *Materials and Methods*

1) *Preparation and Functionalization of MCM-41:* The preparation of MCM-41 was carried out according to the reported procedure [21]. 9.0 g of CTAB was weighed and placed in a 1000 mL beaker, then dissolved by adding 384 mL of deionized water and sonicating. 31 mL of $NH_3 \cdot H_2O$ was added dropwise to the aforementioned CTAB aqueous solution. Then, 33.7 g of a mixture of ethanol and TEOS, in equal molar amounts, was prepared and added dropwise to the reaction mixture. After the addition was completed, the reaction mixture was stirred at room temperature for 6 h. The resulting mixture was filtered and washed, and dried at 383 K overnight. Finally, the obtained solid was ground and calcined at 813 K for 4 h (1 K/min) to obtain white powder MCM-41. The MCM-41 carrier was functionalized sequentially using CPTMS and TMCS [22]. First, 3.0 g of MCM-41, 90 mL of anhydrous toluene and 6.1 g of CPTMS were added to a 100 mL three-port flask in turn. Then, the mixture was heated to 373 K in a nitrogen atmosphere and stirred at this temperature for 24 h. After the reaction was completed, the mixture was cooled to room temperature, filtered with a sand core funnel and washed with methanol three times. Finally, the solid was vacuum-dried at 383 K for 5 h to yield CPTMS-functionalized MCM-41. Furthermore, 3.0 g of CPTMS-functionalized MCM-41, 90 mL of anhydrous toluene, and 9.8 g of TMCS were added to another three-neck flask. The mixture was stirred at room temperature under a nitrogen atmosphere for 24 hours. After the reaction, the mixture was processed using a similar method as described above, yielding a white solid powder labeled as MCM-41-Cl.

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2) *Synthesis and Immobilization of N-Boc-L-hydroxyproline:* The synthesis of N-Boc-*L*-hydroxyproline was modified based on the literature [23]. The typical procedure is as follows: First, 10.1 g of L-hydroxyproline was dissolved in an aqueous solution of tert-butanol (100 mL of tert-butanol and 84 mL of deionized water). Then, 35 mL 10% NaOH aqueous solution was added dropwise. After reacting at room temperature for 30 min, the mixed solution was placed in an ice-water bath. Then, the tert-butyl alcohol solution of Boc_2O (24.9 g Boc_2O dissolved in 40 mL tert-butyl alcohol) was added dropwise to the above solution. After dripping, the mixed solution was stirred at room temperature for 24 h. After the reaction was stopped, the mixture solution was concentrated by rotary evaporation to remove tert-butanol, and the remaining aqueous phase was extracted twice with ethyl acetate to remove impurities. Then, the pH of the above aqueous phase was adjusted to about 2 with 10% $KHSO_4$ solution. Then, the aqueous phase was extracted three times with ethyl acetate, and the organic phase was combined. Then, the combined organic phase was washed with deionized water and saturated salt water, and dried with anhydrous sodium sulfate. Then, the anhydrous sodium sulfate was removed by filtration, and the solvent is removed by rotary evaporation to obtain a colorless oil. Finally, the colorless oil was recrystallized by PE/EA mixed solution (1/1) to obtain N-Boc-*L*-hydroxyproline with a yield of 68.7%. The typical procedure for the immobilization of N-Boc-*L*-hydroxyproline is as follows: First, 1.000 g of MCM-41-Cl was dispersed in 30 mL of xylene and stirred at 413 K for 1 h under nitrogen protection. Then, 0.463 g N-Boc-*L*-hydroxyproline was added, and the stirring was continued for 14 h. After the reaction was completed, the mixture was filtered using a sand core funnel and wash three times sequentially with deionized water and methanol. The obtained solid was dried at 383 K for 5 h to obtain a white powder, labeled as MCM-41-Boc-*L*-Proline.
3) *Synthesis of MCM-41-L-Proline:* Typically, 1.0 g of MCM-41-Boc-*L*-Proline was dispersed in 5.0 mL of dichloromethane (DCM). Under an ice-water bath, 0.8 mL of TFA was added dropwise to the solution. Then, the mixture was continued to stir at room temperature for 8 h. After completion of the reaction, 10% aqueous ammonia was added to adjust the pH of the solution to 9-10. Then the mixture was then filtered and washed with water. Finally, the solid was dried under vacuum at 323 K for 8 h to obtain the Boc-deprotected MCM-41-Boc-*L*-Proline. Furthermore, 1.0 g of the Boc-deprotected MCM-41-Boc-*L*-Proline was dispersed in 12 mL of 0.1 mol/L NaOH solution (ethanol/water = 2/1, v/v), and the reaction was allowed to proceed at room temperature for 5 h. After the reaction, the mixture was filtered and washed sequentially with water and methanol three times. The solid was then dried under vacuum at 323 K for 8 h to obtain a white powder, which was denoted as MCM-41-*L*-Proline. The grafting density of MCM-41 was calculated to be 0.925 mmol/g based on the result of N elemental analysis.

C. Characterization

XRD patterns of the samples were recorded using a Panalytical Empyrea powder X-ray diffractometer (XRD) with a Cu-Kα radiation source, scanning at angles (2θ) from 0.5° to 10°. Samples were analyzed using a Nicolet 6700 Fourier Transform Infrared Spectrophotometer (FT-IR) with pure KBr as the background, measuring in the wavelength range of 400–4000 cm–1. The contents of C, H, and N elements in samples were determined using a Vario EL III fully automated elemental analyzer of German Elementar company.

D. Catalytic Activity and Cycle Application

1) *Coupling reaction of CH_3SO_2Na with PIT*: The catalytic performance of MCM-41-*L*-Proline in the presence of CuI was evaluated using the coupling reaction between CH_3SO_2Na and PIT as a probe reaction, with the specific reaction scheme shown in Scheme 1. A typical reaction procedure was as follows: First, PIT (0.446 g, 2.0 mmol), CH_3SO_2Na (0.272 g, 2.4 mmol), CuI (0.040 g, 0.3 mmol), and MCM-41-*L*-Proline (0.432 g, 0.4 mmol) were added to a 50 mL pressure tube in turn. Then the tube was evacuated and backfilled with nitrogen. Then, 5 mL of DMSO was added to the sealed tube through a syringe, and the reaction mixture was stirred in an oil bath at 383 K for 24 h. After the reaction, the mixture was cooled to room temperature. Then, it was centrifuged and washed with ethyl acetate to obtain the supernatant and solid. The solid was washed three times with ethyl acetate and water respectively, and the ethyl acetate phase was combined with the supernatant. The washed solid was dried overnight at 383 K to afford a light brown solid, labeled as MCM-41-*L*-Proline Cu(I). The combined organic phase was analyzed using a Shimadzu DGU-20As high-performance liquid chromatography (HPLC) instrument. The determination was performed on an Elite SinoChrom ODS-BP C18 column (250 mm × 4.6 mm, 5 μm) with detection wavelength at 223 nm. The mobile phase was acetonitrile/water solution with volume ratio of 50/50, the flow rate was 1.0 mL/min, and the injection volume was 60 μL. The MST content in the reaction supernatant was analyzed using the external standard method (single-point calibration). The MST yield was defined as the mass of MST in the supernatant divided by the theoretical mass of MST generated.

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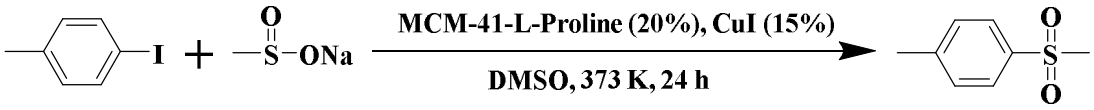

Scheme 1. MCM-41-*L*-Proline/CuI catalyzed coupling reaction of PIT with CH_3SO_2Na.

2) *Recycling Tests*: The cyclic experiment of the MCM-41-*L*-Proline Cu(I) catalyst was conducted in a 100 mL pressure-resistant tube. The reaction conditions for the first cyclic experiment were as follows: PIT (10.0 mmol), CH_3SO_2Na (120 mol%, 12 mmol), MCM-41-*L*-Proline (20 mol%, 2.0 mmol), DMSO 25 mL, reaction time 24 h, reaction temperature 373 K. The specific reaction procedure, product analysis, and catalyst recovery steps are identical to those described in Section 2.4.1. After the reaction, the recovered light brown solid was labeled as MCM-41-*L*-Proline Cu(I)R, where 'R' denotes the recovered catalyst. In each cyclic experiment, the dosages of PIT, CH_3SO_2Na, and DMSO were calculated based on the molar ratio of catalyst to PIT (20 mol%), the CH_3SO_2Na/PIT molar ratio, the PIT concentration in DMSO (0.4 mmol/mL), and the mass of the recovered catalyst from the previous run. Furthermore, the reaction temperature and time in each cyclic experiment were identical to those of the initial reaction. The MCM-41-*L*-Proline Cu(I) catalyst was recycled a total of seven times during the coupling reaction.

III. RESULTS AND DISCUSSION

A. Structural Characterizations

Figure 1 shows the small angle XRD patterns of samples. As shown in the figure, the MCM-41 carrier exhibits diffraction peaks at 2θ angles of 2.32°, 3.99°, and 4.52°, corresponding to the (100), (110), and (200) crystal planes of the hexagonal ordered mesoporous phase MCM-41, respectively. After loading *L*-hydroxyproline onto the sample, its diffraction pattern resembles that of the MCM-41 carrier, indicating the sample still possesses a hexagonal ordered mesoporous structure. However, the intensity of the diffraction peak at 2.32° in the MCM-41-*L*-Proline sample decreases, while the peaks at 3.99° and 4.52° become faint and diffuse. This phenomenon is attributed to the presence of organic groups within the mesoporous channels of MCM-41 [24]. The diffraction pattern of the sample recovered after the first coupling reaction resembles that of MCM-41-*L*-Proline, indicating the sample still has an ordered hexagonal arrangement of one-dimensional pore structure. The decrease in peak intensity at 2.32° is likely due to trace amounts of product present within the mesoporous channels. Compared to the sample recovered after the first coupling reaction, the peak intensity of the MCM-41-*L*-Proline Cu(I)R sample after seven cycles of reuse decreased, which is likely due to the accumulation of residual products within the carrier's pores after multiple uses. These results indicate that the mesoporous structure of the MCM-41-*L*-Proline Cu(I)R sample remains intact after repeated cycles of reuse.

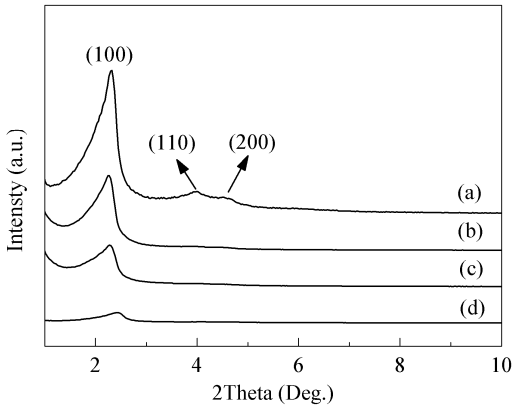

Figure 1. XRD pattern of samples: (a) MCM-41, (b) MCM-41-*L*-Proline, (c) MCM-41-*L*-Proline Cu(I)R after the first reaction, (d) MCM-41-*L*-Proline Cu(I)R after seven cycles of reuse.

Figure 2 shows the FT-IR spectra of samples. As seen in the figure, the MCM-41 sample exhibits distinct absorption peaks at 3423 and 1637 cm^{-1}, which are characteristic absorption peaks of the –OH group. Additionally, the absorption peaks observed at 1076, 800, and 460 cm^{-1} are characteristic absorption peaks of the Si–O–Si group [25]. After loading *L*-hydroxyproline onto MCM-41, new absorption peaks appear at 1419 cm^{-1} and 2933 cm^{-1}, which are attributed to the deformation vibration of CH_2 in NH–CH_2 group and the stretching vibration of CH, respectively [26].

The increased peak intensity at 1637 cm^{-1} indicates the presence of $–CO_2^-$group alongside –OH group in the sample. Additionally, the absorption peak at 3423 cm^{-1} shifted to 3469 cm^{-1}, which is attributed to the stretching vibration of N–H group [24]. These results indicate the presence of silylated *L*-Proline groups in the MCM-41-*L*-Proline sample. The infrared spectrum of the recovered sample after the first coupling reaction resembles that of MCM-41-*L*-Proline. However, the absorption peak at 3428 cm^{-1} shifted to 3434 cm^{-1}, indicating the coordination of –NH and $–CO_2^-$ with Cu metal [24]. This result indicates that *L*-proline copper(I) complexes were formed in situ during the coupling reaction between MCM-41-*L*-Proline and CuI. Compared to the sample recovered after the first coupling reaction, the infrared spectrum of the sample after seven cycles shows little change, indicating that the structure and composition of the sample remain virtually unchanged throughout the reaction process.

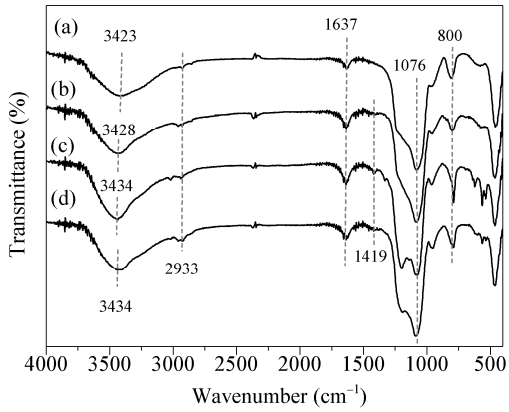

Figure 2. FT-IR spectra of samples: (a) MCM-41, (b) MCM-41-*L*-Proline, (c) MCM-41-*L*-Proline Cu(I)R after the first reaction, (d) MCM-41-*L*-Proline Cu(I)R after seven cycles of reuse.

B. Catalytic Activity

1) *Effect of reaction temperature*: A single-factor multilevel approach is employed to optimize the coupling reaction conditions. Figure 3 illustrates the effect of reaction temperature on the coupling reaction. As shown in Figure 3, the yield of MST increased with the increase of reaction temperature from 353 to 373 K. When the temperature is 373 K, the yield is up to 40.6%. Continue to increase the reaction temperature, the yield of MST is basically unchanged. Therefore, the appropriate temperature is 373 K.

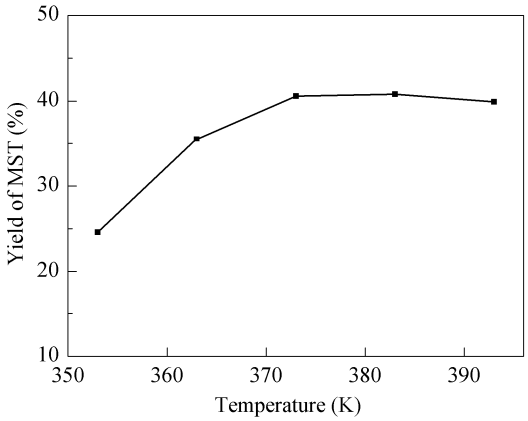

Figure 3. Effect of reaction temperature on the coupling reaction. Reaction conditions: PIT, 2 mmol; CH_3SO_2Na, 120 mol%; CuI, 10 mol%; MCM-41-*L*-Proline, 20 mol%; DMSO, 4 mL; under N_2 atmosphere, 24 h.

2) *Effect of CH_3SO_2Na/PIT molar ratio*: After optimizing the reaction temperature, the effect of CH_3SO_2Na/PIT molar ratio on the coupling reaction was further investigated. The results are shown in Figure 4. It can be seen that when the molar ratio of CH_3SO_2Na/PIT increased from 1.0 to 1.2, the yield of MST increased from 30.0 to 40.6%. When the molar ratio of CH_3SO_2Na/PIT continues to increase, the yield of MST does not change much. Therefore, the suitable molar ratio of CH_3SO_2Na/PIT is 1.2.

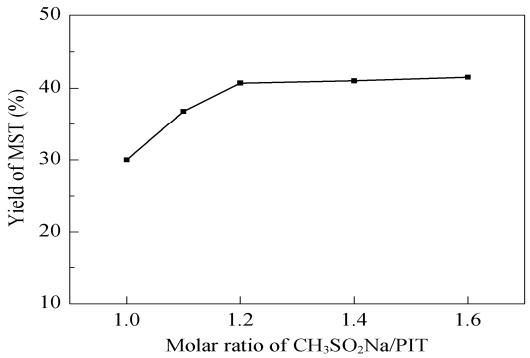

Figure 4. Effect of the molar ratio of CH_3SO_2Na to PIT on the coupling reaction. Reaction conditions: PIT, 2 mmol; CuI, 10 mol%; MCM-41-*L*-Proline, 20 mol%; DMSO, 4 mL; under N_2 atmosphere, 24 h; reaction temperature, 373 K.

3) *Effect of CuI dosage*: After optimizing the reaction temperature and the molar ratio of CH_3SO_2Na/PIT, the effect of CuI dosage on the coupling reaction was further investigated, and the results are shown in Figure 5. As illustrated in Figure 5, when the dosage of CuI is increased from 5 to 15 mol%, the yield of MST increased from 26.5 to 44.4%. However, further increasing the dosage of CuI led to a decrease in the product yield. Therefore, 15 mol% is determined to be the optimal dosage of CuI under the present reaction conditions.

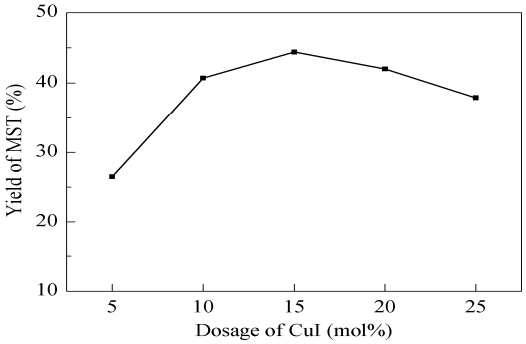

Figure 5. Effect of CuI dosage on the coupling reaction. Reaction conditions: PIT, 2 mmol; CH_3SO_2Na, 120 mol%; MCM-41-*L*-Proline, 20 mmol%; DMSO, 4 mL; under N_2 atmosphere: 24 h; reaction temperature, 373 K.

4) *Effect of MCM-41-L-Proline dosage*: After optimizing the reaction temperature, the CH_3SO_2Na/PIT molar ratio, and the CuI dosage, the effect of MCM-41-*L*-Proline dosage on the coupling reaction was further investigated. As can be seen from Figure 6, when the dosage of MCM-41-*L*-Proline increased from 10 to 20 mol%, the yield of MST increased from 24 to 44.4%. When the amount of MCM-41-*L*-Proline continued to increase to 25 mol%, the yield of MST remained basically unchanged. Further increasing the catalyst dosage, the yield of MST begins to decrease. Therefore, 20 mol% is determined to be the optimal MCM-41-*L*-Proline dosage under the present reaction conditions.

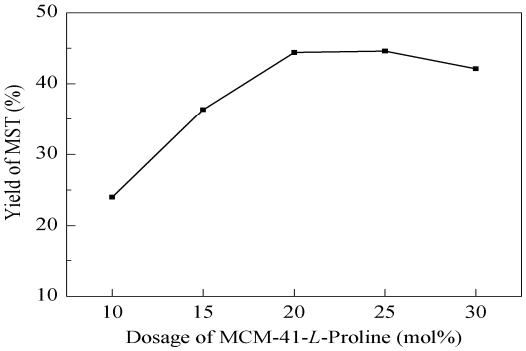

Figure 6. Effect of MCM-41-*L*-Proline dosage on the coupling reaction. Reaction conditions: PIT, 2 mmol; CH_3SO_2Na, 120 mol%; CuI, 15 mol%; DMSO, 4 mL; under N_2 atmosphere: 24 h; reaction temperature, 373 K.

5) *Effect of DMSO dosage*: On the basis of optimizing the reaction temperature, the molar ratio of CH_3SO_2Na/PIT, the dosage of CuI and the dosage of MCM-41-*L*-Proline, the effect of the dosage of DMSO on the coupling reaction was further investigated. As shown in Figure7, when the dosage of DMSO increased from 2.0 to 5.0 mL, the yield of MST gradually increased from 27.7 to 48.5%. When the dosage of DMSO continued to increase to 6.0 mL, the yield of MST decreased slightly. It can be seen that 5.0 mL is the appropriate dosage of DMSO.

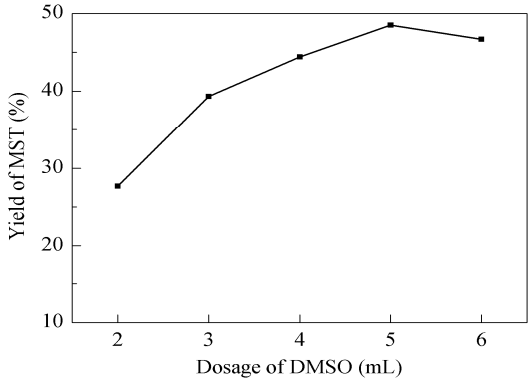

Figure 7. Effect of DMSO dosage on the coupling reaction. Reaction conditions: PIT, 2 mmol; CH_3SO_2Na, 120 mol%; CuI, 15 mol%; MCM-41-*L*-Proline, 20 mol%; under N_2 atmosphere: 24 h; reaction temperature, 373 K.

6) *Effect of reaction time*: On the basis of optimizing the reaction temperature, the molar ratio of CH_3SO_2Na/PIT, the dosage of CuI, the dosage of MCM-41-*L*-Proline and the dosage of DMSO, the reaction time was further optimized. The results are shown in Figure 8. It can be seen from the figure that the yield of MST gradually increases from 31.1% to 48.5% with the reaction time increasing from 6 to 24 h. Further prolonging the reaction time, the yield of MST does not change much. Therefore, the most suitable reaction time is 24 h.

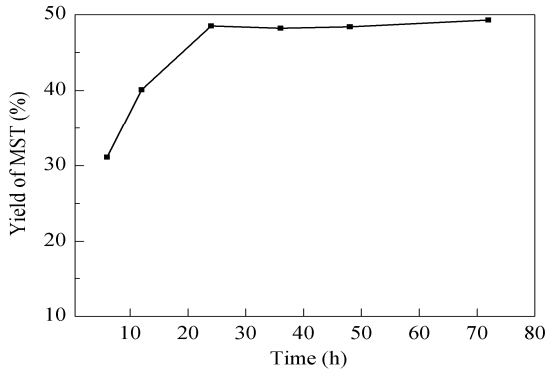

Figure 8. Effect of reaction time on the coupling reaction. Reaction conditions: PIT, 2 mmol; CH_3SO_2Na, 120 mol%; CuI, 15 mol%; MCM-41-*L*-Proline, 20 mol%; DMSO, 5 mL; reaction temperature: 373 K.

In summary, the optimal conditions for the coupling reaction of CH_3SO_2Na with PIT in the MCM-41-*L*-Proline/CuI catalytic system are as follows: PIT, 2 mmol; CH_3SO_2Na, 120 mol%; CuI, 15 mol%; CM-41-*L*-Proline, 20 mol%; DMSO, 5 mL; under N_2 atmosphere at 373 K for 24 h.

C. Recycling performance

To investigate the catalytic stability of MCM-41-*L*-Proline Cu(I), we conducted cycling experiments, the results of which are shown in Figure 9. As seen in the figure, the MST yield in the first cycle is 48.3%. After six cycles, the MST yield remains as high as 47.5%. As the number of cycles increases further, the MST yield begins to decrease. The results of the XRD analysis (Figure 1) indicate that the sample retains its hexagonal ordered mesoporous structure after seven cycles of use, demonstrating the excellent preservation of its pore structure. The FT-IR results (Figure 2) reveal that the infrared spectrum of the sample after seven cycles showed minimal changes compared to the MCM-41-*L*-Proline Cu(I) sample, suggesting that the structure and composition of the catalyst remain virtually unchanged throughout the reaction process. These results indicate that the MCM-41-*L*-Proline Cu(I) complex exhibits excellent catalytic stability and recycling performance.

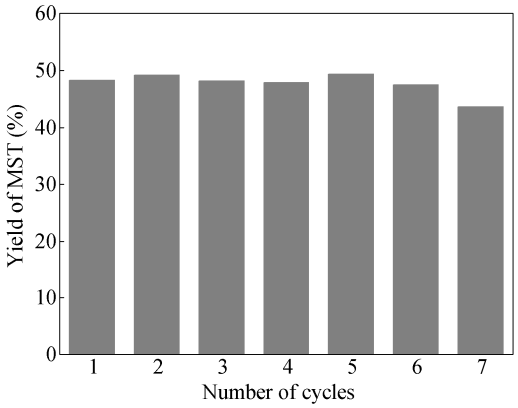

Figure 9: Recycling tests of MCM-41-*L*-Proline Cu(I)

IV. CONCLUSIONS

In summary, through a series of condensation reactions, L-hydroxyproline was successfully immobilized on MCM-41, and MCM-41-*L*-Proline was further obtained by acid-base neutralization reaction. The effects of reaction temperature, CH_3SO_2Na/PIT molar ratio, CuI dosage, DMSO dosage, MCM-41-*L*-Proline dosage and reaction time on the coupling reaction were investigated, and the suitable reaction conditions were obtained. Under optimized reaction conditions, the MCM-41-*L*-Proline/CuI catalytic system delivered a 48.5% yield of MST. FT-IR results indicate that MCM-41-*L*-Proline Cu(I) was prepared in situ between MCM-41-*L*-Proline and CuI during the coupling reaction. After six cycles, MCM-41-*L*-Proline Cu(I) still delivered a favorable yield of MST (47.5%) without deactivation. XRD and FT-IR results indicated that the mesoporous structure and composition of the MCM-41-*L*-Proline Cu(I) catalyst remained well-preserved after the recycling tests, indicating that the sample had good catalytic stability and recycling performance.

V. ACKNOWLEDGMENT

This work is supported by the National Natural Science Foundation of China (21303008) and Natural Science Foundation of Hubei Province of China (2012FFB00103).

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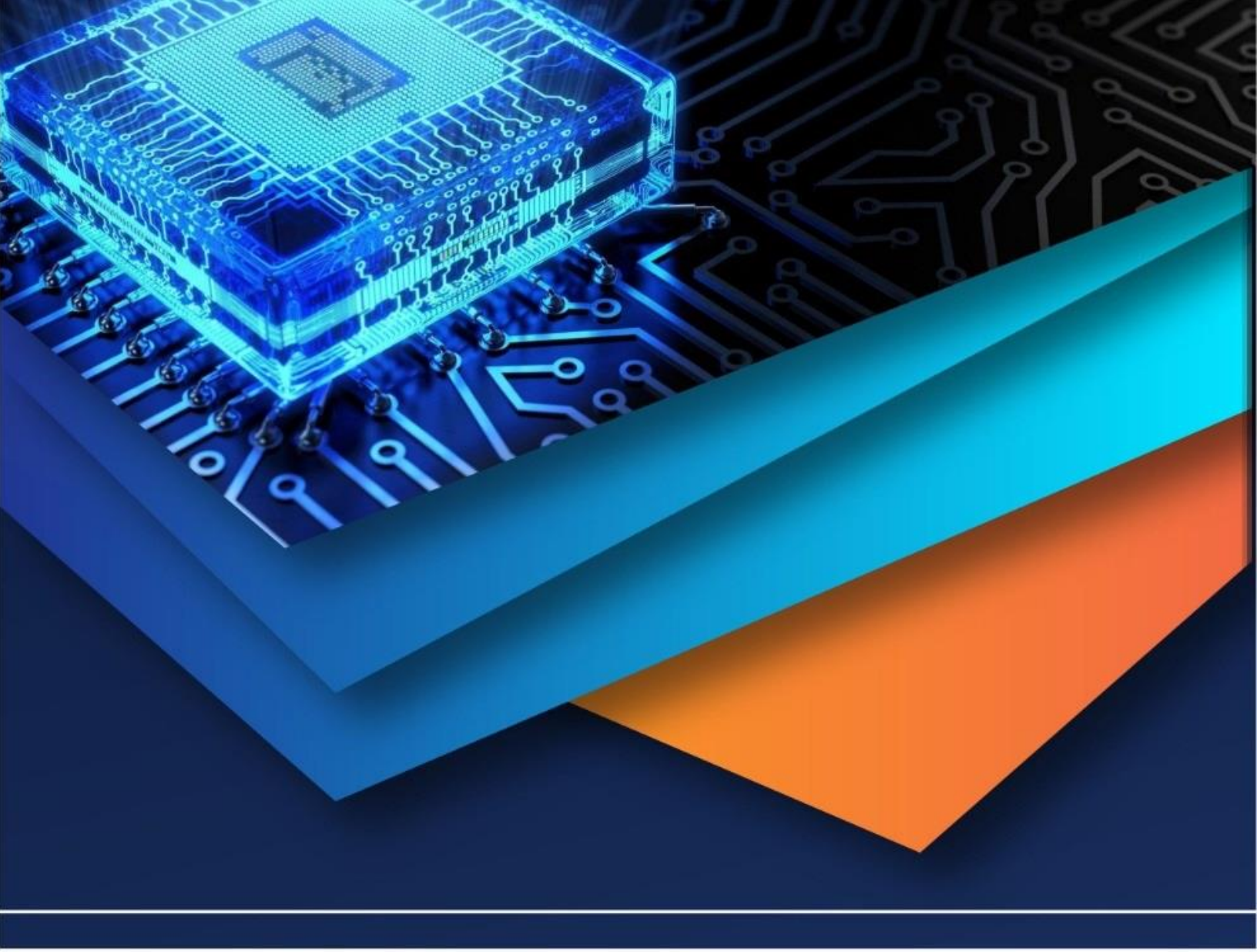

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