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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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## Cu(II)-Impregnated Sulfated MCM-41: An Efficient and Convenient Protocol for the Synthesis of 1,3-benzodioxoles

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An efficient synthesis of 1,3-benzodioxoles was achieved from catechol with different aldehydes and ketones using Cu(II) impregnated sulfated MCM-41 as an efficient and reusable catalyst.

Keywords 1,3-benzodioxoles, catechol, heterogeneous catalysis, metal impregnated MCM-41

#### INTRODUCTION

The design of highly active heterogeneous catalyst is considered crucial in the successful operation of the chemical industry. Most of the bulk chemical and petrochemical processes could not be operated commercially without a heterogeneous catalyst. Recently, there has been an increased awareness that heterogeneous catalysts could significantly improve a large number of fine chemical processes.

The 1,3-benzodioxoles are well-known heterocyclic units in the realm of natural and synthetic organic chemistry due to their existence as inhibitors of mono-oxygenase enzymes,<sup>[1]</sup> pesticide intermediates,<sup>[2–4]</sup> herbicides,<sup>[5]</sup> antioxidants,<sup>[6]</sup> and antimicrobials and medicines.<sup>[7–8]</sup> In other words, the formation of 1,3benzodioxole derivatives serves as the method for the protection of catechol as well as carbonyl compounds.<sup>[9]</sup>

1,3-benzodioxoles with various substituents at 2-position have received much more attention, as this ring system is an integral part of many natural products, such as sesamol and piperine.<sup>[10]</sup> Therefore, their synthesis assumed great importance in both biological chemistry and organic synthesis. The commonly used catalysts for the synthesis of 1,3-benzodioxoles are phosphorus pentoxide,<sup>[11]</sup> trimethylsilyl chloride,<sup>[12]</sup> phosphorus trichloride,<sup>[13]</sup> super acids,<sup>[14]</sup> montmorillonite KSF or K-10,<sup>[15]</sup> and p-toluenesulfonic acid.<sup>[16]</sup> Most of these catalysts are not environment-friendly, they cause corrosion, and also leads to tedious work-up processes with prolonged reaction times. Moreover, catalysts like trimethylsilyl chloride and phosphorus trichloride are poisonous, expensive, and unstable. Also, most of the catalysts could not be recycled due to the difficulty in purification. Consequently, there is a genuine need for an efficient catalytic procedure for these reactions, and in the present study the interest was focused on modified MCM-41 mesoporous solids.

Recently, MCM-41 of uniform hexagonal pores with pore diameter ranging between 2-10 nm is most studied. The high surface area and highly ordered uniform pores in nanometer range make it a potential catalyst for conversions of bulky molecules in the manufacture of fine chemicals and pharmaceuticals. In spite of having large pore dimensions, the acidity of these materials is much weaker than that of the microporous zeolites. In order to overcome this drawback, a great effort was focused on introducing strong acid sites on the mesoporous materials, and one such method reported is to sulfate the MCM-41 using H<sub>2</sub>SO<sub>4</sub>, thereby increasing both the Lewis and Bronsted acidic sites.<sup>[17]</sup> Coupled with sulfation, modification of these mesoporous materials by impregnation of transition metals like Cu will also enhance the acidity. However, there are no examples of the use of the metal impregnated SO<sup>4-</sup>/MCM-41 for the preparation of 1,3-benzodioxoles. In view of the emerging importance of the use of heterogeneous solid acids as reusable catalysts in organic synthesis, herein we wish to disclose a mild and efficient protocol for the synthesis of 1,3-benzodioxoles using a Cu(II)-SO<sup>4-</sup>/MCM-41 as a novel heterogeneous catalyst (Scheme 1).



#### **RESULTS AND DISCUSSION**

The Cu(II)-sulfated MCM-41 catalyst is found to be an efficient catalyst for a wide range of carbonyls employed for the condensation with catechol, and the water formed among

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TABLE 1 Synthesis of 1,3-benzodioxoles catalyzed by Cu(II) -SO<sup>4-</sup>/MCM-41



 TABLE 1

 Synthesis of 1,3-benzodioxoles catalyzed by Cu(II) 

 SO<sup>4–</sup>/MCM-41 (Continued)

Entry	Carbonyl compound	Product	Time (h)	% Yield
13	Ph Ph OH	OH OH Ph	4.0	06.0
14	Ph	C Ph Ph	5.0	15.0

<sup>a</sup>Benzene is used as a solvent.

the process could readily be removed by azeotropic distillation with hydrocarbons as solvent using Dean-stark apparatus. It is observed that catechol, irrespective of the presence of electronwithdrawing or -releasing groups that are present in the carbonyl compounds, were condensed well to form 1,3-benzodioxoles, whereas the role of steric effect seems to be maximum as revealed by the decrease in the yield of the products in the cases of carbonyls like benzoin, having bulkier groups in the  $\alpha$  position. This method proved to be compatible with many functional groups like halo, hydroxyl, nitro, and alkoxy.

In all cases, the reactions proceeded efficiently under heterogeneous conditions and the results are listed in Table 1. All of the products were characterized by <sup>1</sup>H, <sup>13</sup>C NMR, IR, and mass spectral analysis and also by comparison with literature.<sup>[15]</sup> This method is effective for the preparation of 1,3-benzodioxoles from both aldehyde as well as ketones. The catalyst was easily separated by simple filtration and reused after drying with slight decrease in activity in the successive runs. For instance, the reaction of catechol and cyclohexanone afforded spiro[benzo[d][1,3]dioxole-2,1'-cyclohexane] in 95%, 89%, 85%, and 80% yields over four cycles. This procedure provides an easy access to the preparation of substituted 1,3benzodioxoles with a wide range of substitution patterns.

Cu(II)-sulfated MCM-41 worked better than an ordinary MCM-41 (only 20% conversion) for protection of catechol, and this may be due to the structure that retains more acidic sites after treatment with 0.25N H<sub>2</sub>SO<sub>4</sub>. For almost all the aliphatic acyclic ketone compounds (Entries 2–3), the yields were around 80%, but decreased in the case of acetone. This could be due to the high miscibility with water, which makes the removal of water from the reaction system difficult (Entry 1).

In this work the performance of several solid acid catalysts was evaluated for the synthesis of 1,3-benzodioxoles. The efficacies of different catalysts are given in Table 2.

In all the cases, 10 mol% of catalyst was used in the condensation of catechol (10 mmol) with cyclohexanone (10 mmol) to its corresponding 1,3-benzodioxoles in Dean-stark conditions. When Cu(II)-sulfated MCM-41 showed the highest catalytic

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TABLE 2 Effect of catalyst on Ketalization of cyclohexanone with catechol

Entry	Catalyst	Time(h)	Yield %
1	MCM-41 <sup>a</sup>	6.0	_
2	Sulfated MCM-41	5.0	12
3	Cu(II)-sulfated MCM-41	1.0	98
4	Ni(II)-MCM-41	4.0	20
5	Fe(III)-MCM-41	1.0	90
6	Co(II)-MCM-41	5.0	15
7	Montmorillonite K-10	2.7	93 <sup>15</sup>
8	HY-Zeolite	6.0	81 <sup>18</sup>

<sup>a</sup>The reactions are carried out with untreated MCM-41.

activity for the reaction with the conversion over 98% within 1 h, while the similar catalysts with Ni(II) and Co(II) were not so efficient with the conversion below 20% even after 4 h. Even though the Fe(III)-MCM-41 gave a preferable result with the conversion around 90%, it is having difficulties of catalyst instability and product separation. No reaction was observed over ZSM-5, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>; HX was found to be slightly active, whereas NaX was also inactive.

In conclusion, we have developed a highly convenient method for the synthesis of 1,3-benzodioxoles using Cu(II)-sulfated MCM-41 as catalyst. The yields of the products produced are very high compared to earlier methods with a shorter reaction time. The great advantage of the present method is that the catalyst is easily prepared and can easily be recovered and reused.

#### Preparation of Metal-impregnated Sulfated MCM-41

The sulfated MCM-41 catalyst was prepared and characterized by the procedure reported in literature.<sup>[17]</sup> The metal impregnated sulfated MCM-41 were prepared by slowly adding the MCM-41 (1.0 g) to dilute solutions of  $Cu(NO_3)_2$  (1 M, 12.5 mL), Fe(NO<sub>3</sub>)<sub>3</sub> (1 M, 12.5 mL), Co(NO<sub>3</sub>)<sub>2</sub>(1 M, 12.5 mL) and Ni(NO<sub>3</sub>)<sub>2</sub>(1 M, 12.5 mL), respectively, in acetone and stirring for a period of 24 h. After impregnation, suspensions were filtered and the resultant solids were dried and activated at 400°C for 2 h in an electric furnace to obtain a catalyst.

#### Synthesis of 1,3-benzodioxoles

A mixture of carbonyl compound (10 mmol), catechol (10 mmol), 10 mL of toluene/benzene, and the catalyst (10 mol%) were mixed in a two-necked round bottom flask equipped with thermometer, and a Dean-Stark apparatus was used to remove the water continuously from the reaction mixture. The mixture was refluxed with stirring for the specified periods. TLC was used to monitor the progress of the reaction. After completion of the reaction, the reaction mixture was filtered, washed with H<sub>2</sub>O (10 mL) and dried over (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent followed by recrystallization from diethyl ether gave the desired product. The spectral data (<sup>1</sup>H NMR and IR) of the compounds were in agreement with that reported in literature.<sup>[15]</sup>

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