



Syntheses Benzimidazol Using $Fe_3O_4@Cu-Ce-MCM-41$ Catalyst

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Abstract: In this thesis, benzimidazole derivatives have been synthesized from the reaction of various aldehydes with orthophenyene diamine using catalytic amounts of $Fe_3O_4@Cu-Ce-MCM-41$ in ethanol under reflux condition. $Fe_3O_4@Cu-Ce-MCM-41$ catalysts were synthesized with different molar ratios of Si/Ce and Si/Cu and characterized by SEM, XRD, FT-IR techniques. The catalyst with molar ratio of Si/Ce=90 and Si/Cu=30 in ethanol under reflux conditions showed the best catalytic activity in above mentioned reaction and the benzimidazoles were synthesized with high yields. Reusability of both catalysts were considered in reactions and the results showed that the $Fe_3O_4@Cu-Ce-MCM-41$ catalyst have reaction reusability with no decrease in its activity also, the $Fe_3O_4@Cu-Ce-MCM-41$ catalyst after calcination has reusability with low decrease in this activity.

Keywords: Mesoporous, Cu-Ce-MCM-41, Magnetic, Cerium, Copera, Benzimidazoles

INTRODUCTION

Historically, the first benzimidazole was prepared in 1872 by Hoebrecker (327), who obtained 2,5(or 2,6) dimethylbenzimidazole (Wright, 1951). Benzimidazoles have been used in many fields and are very essential for human kind (Prashant et al., 2016).

Compounds which have benzimidazole as a structural motif have been widely used in medicinal chemistry and drug development, and researchers are actively seeking new uses and applications of this heterocycle (Alasmay et al., 2015).

According to the IUPAC (International Union of Pure and Applied Chemistry), the catalyst materials can be classified into three categories based on their pore sizes: microporous (less than 2 nm), mesoporous (between 2 and 50 nm), and macroporous (more than 50 nm). One of the most famous mesoporous molecular sieves, M41S, has attracted much more attention (Se Ho Park et al., 2007). Since the discovery of MCM-41 by Mobil scientists, (Igor et al., 2006).

attention after the discovery of new family of molecular sieve called mesoporous silica materials have attracted special M41S, MCM-41, MCM-48 and SBA-15 are the most common mesoporous silica materials with the pore size ranging from 2 -10 nm and 2D-hexagonal and 3D-cubic structural characteristics (Asad Mehmood et al., 2017). One approach that achieves this goal is the templating method. In a typical procedure, mesoporous silica is filled with a carbon precursor (e.g. sucrose), which is subsequently carbonized through a series of high temperature processes. The template is then removed using

hydrofluoric acid or caustic soda (Se Ho Park et al., 2007) silica and contains a considerable amount of silanol groups. In order to improve the catalytic properties of MCM-41, many researches have been carried out the incorporation of various transition metals (Al, Co, Zn, Mn, Ce, etc.) into the framework of the MCM-41 (Budarin et al., 2009). and their oxides have been introduced into the silica matrix to obtain modified-mesoporous materials with appreciate catalytic properties (Lan et al., 2013). The wet impregnated Al-MCM-41 with iron salts was found to be the most effective catalyst in the sulfurisation of methanol when compared with purely siliceous MCM-41 (Esther et al., 2009). Copper is an efficient, cheap and non-toxic ingredient in many heterogeneous and homogeneous catalysts (Abdollahi-Alibeik et al., 2015). In addition to this, copper-modified mesoporous silica shows favorable activity and recoverability in the catalyzed transformations (Mohan et al., 2016). Cerium based MCM-41 are used in various types of organic transformation reaction (Lan et al., 2013). In addition, in a preliminary investigation, we found that ceria doped silica as catalyst support shows a rather stable catalytic activity in the methane decomposition reaction (Guevara et al., 2010). But no such research has been done on Fe₃O₄, ceria and copper impregnated and incorporated Fe₃O₄@Cu-Ce-MCM-41.

Experimental

Materials

The cetyltrimethylammonium bromide (CTAB), tetraethylorthoxysilicane (TEOS), EtOH, cerium nitrate hexahydrate (Ce(NO₃)₃). Copper nitrate Cu(NO₃)₂.6H₂O, ammonia 25 wt%, ferric nitrate (Fe(NO₃)₃9H₂O), aldehydes and *o*-phenylenediamine. All the chemicals are of AR grade and purchased from Merck Germany.

The synthesis mcm-41 carry Cu and Ce metal oxides with magnetic core by a hydrothermal method

In the model synthesis method, Chloride iron II 4 water (2 mg, 10 mmol) and iron chloride III 6 water, (5.30 mg, 20 mmol) was dissolved in 30 ml of water. The solution is under argon gas for up to 60 degrees Celsius 30 minutes by magnetic stirrer. Then 25% ammonia (35 ml) was added dropwise and the mixture was stirred for 30 minutes. The precipitate was separated by external magnet and washed with water and finally deposited at 80 ° C for 2 hours allowed to dry in the oven. then Weighed Fe₃O₄ (1 mg, 0.143 mg) sediment and dispersed in 90 ml of deionized water under ultrasonic conditions and reached a temperature of 70 ° C. Salt Sterile Ammonium Bromide (CTAB) (0.3 mg / 46.0 g) was added and then drops dropped over half an hour, tetraethyl carosilicate (TEOS) (12 mm, 2.5 milliliters). Acetate copper (0.333mL, 0.21g) was added immediately and nitric acid (0.11µL, 481.0g) was slowly added to the solution and stirred for 70 minutes at 70 ° C with magnetic stirrer. Then the heat was discontinued and, with increasing profit (1 mol, 2.5 g), the pH was adjusted to 10.5-10.5, and finally the reaction mixture was stirred for 10 hours with a magnetic stirrer and then Was placed inside the autoclave for 8 hours. The resulting mixture was calcined in an electric oven at 550 ° C for 4 hours after drying in an electric oven for 2 hours at 100 ° C.

The synthesis benzimidazoles

The synthesis benzimidazoles mixture of 1,2-phenyldiamine (1 mmol, 108 mg), aldehyde (1 mM), Fe₃O₄ @ CU-Ce-MCM-41 (50 mg), 1 ml ethanol solvent and reflux temperature for 5 to 40 minutes, Magnetized by a magnetic stirrer. The reaction progress was followed by TLC (solvent 6: 3, n-hexane: EtoAc). After the reaction was complete, the resulting mixture was separated from the catalyst by centrifugation and dissolved in ethanol (10 mL). Then a mixture of water and ice (30 ml) was added. The resulting precipitate was collected by filter paper and washed with water

Physical and spectroscopic information of synthesis compounds

MP: 290°C (Lit. {86} 291-292 °c), IR (KBR):ν(cm⁻¹) 1590, 1444 (C=C aromatic), 1662(C=N), 1611(N-H), 650 (CH)

Results and Discussions

Identify and characterize the structural properties of Fe₃O₄ @ Cu-Ce-MCM-41

In order to detect the $\text{Fe}_3\text{O}_4 @ \text{Cu-Ce-MCM-41}$ mesoporous structure and to verify the presence of $\text{Fe}_3\text{O}_4 @ \text{Cu-Ce}$ in the hexagonal form in the substrates, its XRD spectrum was studied (Fig. 1a).

To determine the functional groups, the synthesized samples were performed using FT-IR method.

Transmission electron microscopy (TEM) for unique measurements of space spatial data, morphological details such as the shape, size, and order of the particles of the surface of a sample, the composition information (the information and composition of the object from which it was made and their actual value), Crystallographic information (arrangement of atoms in a crystal) and internal analyzes (depletion, layering problems, etc.).

The morphology and particle size were examined by SEM electron microscope with the aid of the HITACHI S-4160 machine.

The XRD and MCM-41 FT-IR and $\text{Fe}_3\text{O}_4 @ \text{Cu-Ce-MCM-41}$ and TEM and SEM designs are shown.

The low-angle XRD spectrum shows a peak of Cu-MCM-41 of Cu-MCM-41, 1/84 of 1.45. The presence of $\text{Fe}_3\text{O}_4 @ \text{Cu-Ce}$ in hexagonal cavities MCM-41 affects the width and severity of the peaks, so that the increase of $\text{Fe}_3\text{O}_4 @ \text{Cu-Ce}$ on the substrate (causes widespreading and weakening of the peaks). These changes signify a slight collapse of the hexagonal structure order due to the entry of $\text{Fe}_3\text{O}_4 @ \text{Cu-Ce}$ in the MCM-41 cavities.

Low Crystal XRD Spectrum (a) Cu-MCM-41 and Cu-Ce-MCM-41

The FT-IR spectrum, $\text{Fe}_3\text{O}_4 @ \text{Cu-Ce-MCM-41}$ catalyst with ratios of 3: 2 CU / Ce and 2: 1 CU / Ce and 3: 1 CU / Ce is shown in Fig. 3-4

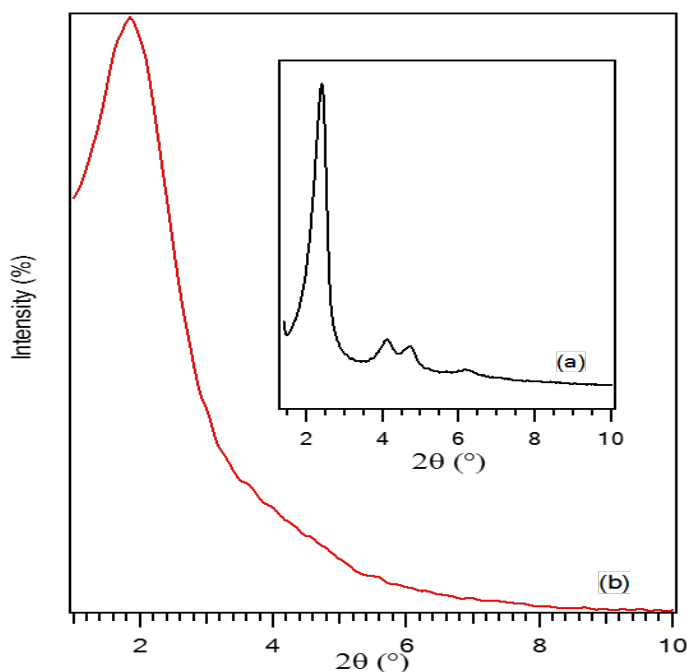


Figure 1: The XRD Spectrum (a) Cu-MCM-41 and Cu-Ce-MCM-41.

Spacing 4-4 peaks at Figure 2-3-The XRD spectrum with low angles (a) Cu-MCM-41 and (b) Cu-Ce-MCM-41 450 and 1020 cm and 1068 cm, 1076 cm and 1087 cm, 1700 cm, 1720 cm and 3500 cm, represent the peaks of Si-O, Ce-O and Cu-O bands.

The overlap of peaks at 1080 cm and 3500 cm areas has led to an increase in their intensity and expansion in the $\text{Fe}_3\text{O}_4 @ \text{Cu-Ce-MCM-41}$ catalyst.

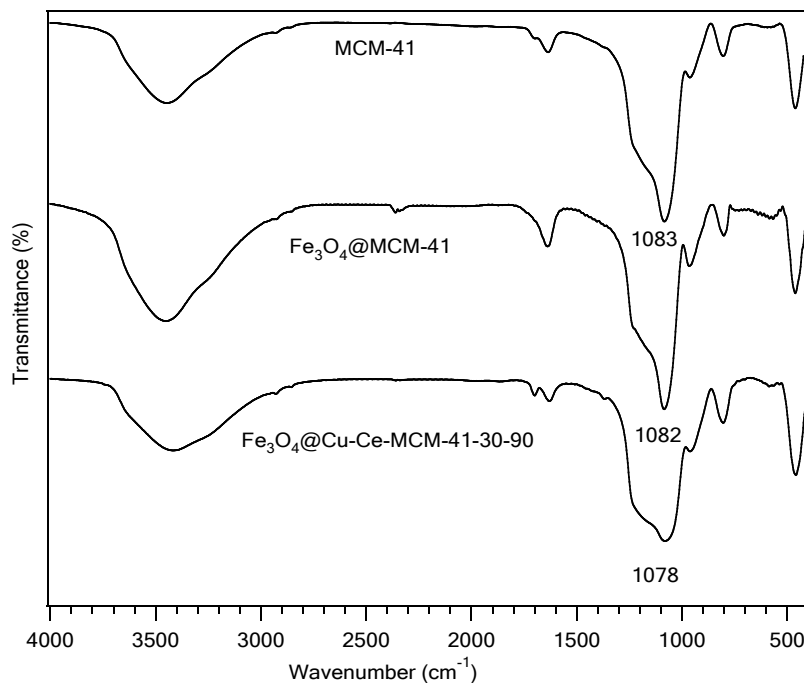


Figure 2. FT-IR Spectrum with Cu-Ce-MCM-41 Fe₃O₄ @ and @ MCM-41 Fe₃O₄ and MCM-41

The SEM image of the MCM-41 substrate is shown in Figure 3-5. Particles of MCM-41 with dimensions less than 100 nm are specified in the image.

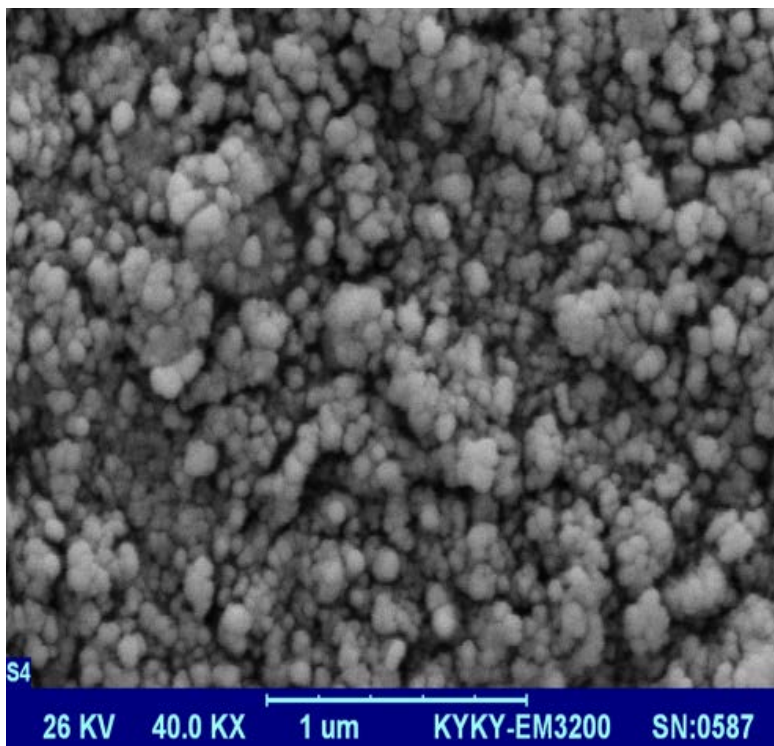
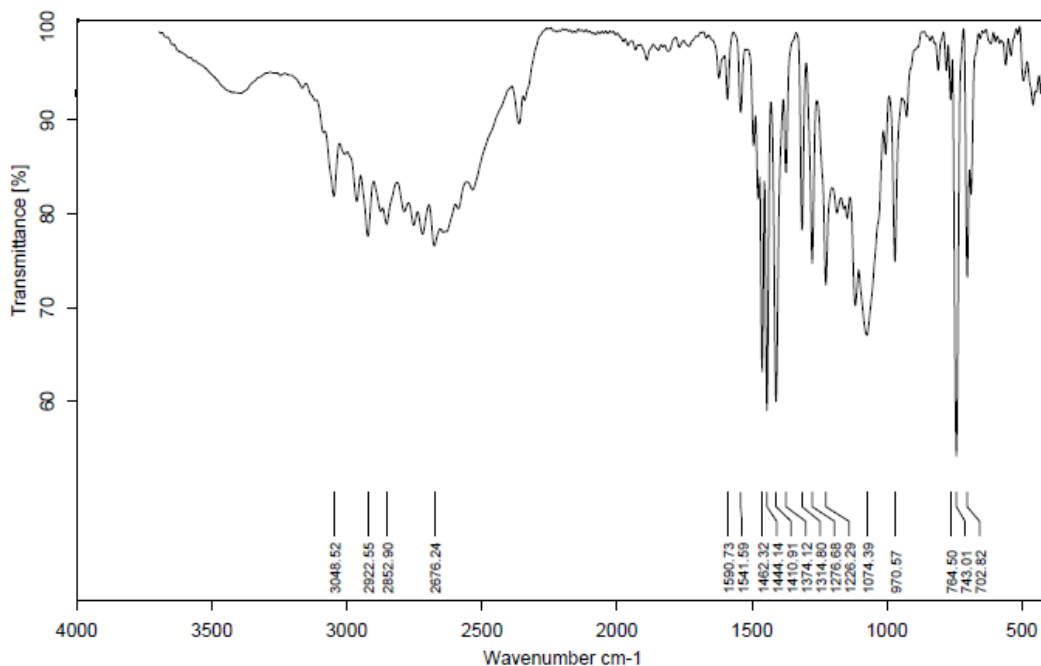
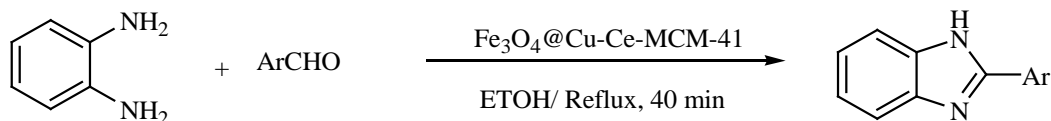


Figure 3. SEM Nano Substrate MCM-41

In order to investigate the efficiency of Fe₃O₄@Cu-Ce-MCM-41 catalyst for the synthesis of benzimidazoles from the reaction of orthophilic amine with aldehydes in the presence of a Fe₃O₄@Cu-Ce-MCM-41 catalyst, benzaldehyde reaction with orthophenylenediamine was selected as the reaction of the model



Spectrum (1): FT-IR (KBr) 2-Phenyl-Benzimidazole

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