

Conference Paper

Features of a Hybrid Mn(II)-Modified Mesoporous MCM-41 Material

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Abstract

The synthesis of hybrid Mn(II)-modified mesoporous MCM-41 material has been carried out. In this work, mesoporous MCM-41 was heated at 200°C for 3 hours and then modified through reacting with aniline and boron trifluoride at room temperature. The modified mesoporous MCM-41 was Hybridized with Mn(II) ion by a process reflux in acetonitrile solvent for 2 hours at 60°C. The obtained material was characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Atomic Absorption Spectroscopy (AAS). FTIR analysis showed that Mn(II) ion was incorporated into the modified mesoporous MCM-41. The morphology of Mn(II)-modified mesoporous MCM-41 was examined by SEM. From the SEM images it can be seen that the aggregates of MCM-41 break after being modified with the boron compound and manganese (II). Based on measurement of metal content by AAS, it was known that the value of metal loading is 67.60%. While for the leaching test, the hybrid material disappeared only 0.006% of Mn(II) ion which proved the stability of the interaction between Mn(II) ion and modified mesoporous MCM-41. Accordingly, this material is of the great interest for catalytic applications.

Keywords: manganese anchoring, MCM-41, functionalization, metal loading, metal leaching.

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1. Introduction

Mesoporous molecular sieves of type MCM-41 with a hexagonal packed array of channels and a narrow pore size distribution offer unique opportunities for the preparation of new nanostructure materials [1, 2]. The mesoporous silica materials have attracted much attention for their potential applications in the fields of catalysis, functional materials, and nanodevices [3–5]. Furthermore, the synthesis, characterization and applications of the mesoporous silica MCM-41 and their various modified forms are well-establish [6].

Although homogeneous catalytic processes are efficient for a wide variety of reactions, they have some disadvantages. The difficulty in separation of catalyst from the

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product has led to economical and environmental problems, which is also inconvenient in continuous production. To solve the problems, many attempts have been reported concerning immobilization of the homogeneous catalysis onto solid supports, combining their high activity and selectivity with the advantages of the heterogeneous catalysis [7–9].

MCM-41 materials have uniform channels, large pore size, high specific surface area and high thermal stability. In addition, the high concentration of silanol groups allows the development of different strategies to attach metal species [8–11].

The anchoring of $\text{Mn}(\text{acac})_2$ onto MCM-41 by using 3-amino-propyltrimethoxysilane (APTES) as a linking agent was used [8]. While, an organosilane (3-chloropropyltrimethoxysilane, CIPTS) and a diisocyanate (DIC-4) as another linking agents for the anchoring of Schiff base complexes onto MCM-41, as catalysts were tested in the limonene oxidation [9].

In this work, we report the incorporation of manganese onto the surface of modified mesoporous silica MCM-41 material. Modification of the mesoporous silica surface with aniline bearing amine group and boron trifluoride as a solid support for a heterogeneous catalyst was synthesized via post-synthesis grafting.

The catalyst material obtained by this method was tested in the metal content for loading of manganese and its stability for the leaching value.

2. Materials and Methods

2.1. Materials

The synthesis of hybrid Mn(II)-modified mesoporous MCM-41 sample was carried out by using MCM-41 as starting material which synthesized by the hydrothermal method in the previous work (the as-synthesized MCM-41 was extracted for removing the templating molecule, denoted as the extracted MCM-41). The chemicals used in this work are as follows: aniline, toluene, boron trifluoride, manganese(II) chloridehexahydrate ($\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$), acetonitrile. All chemicals were purchased from merck.

2.2. Methods

2.2.1. Catalyst preparation

Activation of the extracted mesoporous silica MCM-41

In this work, the mesoporous silica MCM-41 material synthesized in the previous work [10] was used for starting material. This mesoporous silica (3.5g) was activated prior to the functionalization step by heating at 200°C for 3 hours.

Introduction of aniline bearing amine functional group and boron trifluoride onto the mesoporous surface silica

Functional groups were attached to the mesoporous silica material by means of the post-synthesis grafting method [11]. In this procedure, modification of the mesoporous silica surface was performed in two steps. The first step, the activated mesoporous silica (3g) was reacted with a solution of 1.82 ml of aniline in 40.9 ml of toluene (>Si–OH: N (aniline) molar ratio of 1: 1.2). This mixture was stirred for 24 hours at room temperature. In the second step, the suspended silica-aniline was reacted with a 1.523 ml of boron trifluoride (>Si–OH: B (boron trifluoride) molar ratio of 1: 1.2). Afterwards, this mixture was stirred again for another 24 hours at room temperature. The solid product was filtered, washed with toluene for several times and dried in desiccator. Finally, the so obtained modified material, denoted as >Si–O–BF₃– +NH₃–Ar.

Metal anchoring

The mixture of the modified material (1.25g) in 10 ml of acetonitrile and anhydride MnCl₂ (1.13315 g) in 10 ml of acetonitrile was refluxed and stirred for 2 hours. After that, the obtained material was filtered and washed with acetonitrile for several times and then dried in desiccator. The final material will be further on named as hybrid Mn(II)-modified mesoporous silica MCM-41 (catalyst).

2.2.2. Catalyst characterization

Infrared spectra were recorded with a Perkin Elmer 1600 series spectrometer. The SEM images of samples were obtained using a SEM S-3400 Hitachi. While, the manganese loading and the manganese leaching of the catalyst were determined by Atomic Absorption Spectrometer (AAS) Youngin 8020 series instrument.

2.2.3. Metal loading experiment

The filtrate solution yielded from synthesis of the catalyst sample was tested in the metal content incorporated in the modified MCM-41. Manganese content was determined by AAS analysis for the loading value.

2.2.4. Leaching test

The leaching experiment was conducted as follows: catalyst sample (0.5046g) was added with 10 ml of acetonitrile, then refluxed and stirred for 24 hours at 60°C. The suspended was filtered to recover a solid and filtrate. Then, the filtrate solution was determined by AAS analysis for the leaching value.

3. Results and Discussion

3.1. Catalyst preparation

The manganese species was anchored on the modified MCM-41 support using aniline and boron trifluoride as a modifier. In this method, the MCM-41 as starting material was functionalized through a post-synthetic method, with aniline bearing amine group. Aniline as a Brønsted base reacts with silanol groups of silica surface. Aniline is protonated by Brønsted acid and become anilinium cation (ArNH_3^+) while boron trifluoride as a Lewis acid [8, 9, 12]. The modified mesoporous silica material denoted as $\text{>Si-O-BF}_3\text{-}^+\text{NH}_3\text{-Ar}$ was a solid support. Finally, the manganese metal was attached to the functionalized MCM-41 support. The solid product is a hybrid Mn(II)-modified mesoporous MCM-41 material as catalyst.

3.2. Catalyst characterization

3.2.1. Fourier transform infrared spectra (FTIR)

Fig. 1 (a), (b) and (c) show the spectra of the parent MCM-41, as well as Fig. 1 (d) and Fig. 1 (e) are the spectrum of the modified material and the spectrum of the catalyst (hybrid Mn(II)-modified MCM-4), respectively.

The spectra of all the unmodified parent MCM-41, Fig. 1 (a), (b) and (c), as well as the spectrum of the modified MCM-41, Fig. 1d, are dominated by strong bands characteristics of the support matrix, indicating that the support frame work remained unchanged.

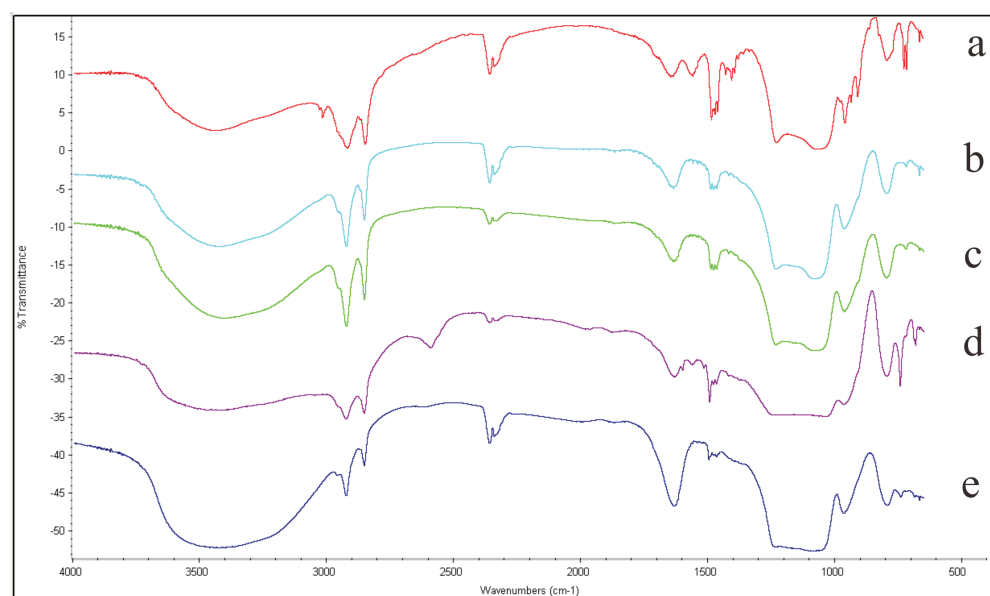


Figure 1: FTIR spectra of (a) as-synthesis silica MCM-41; (b) extracted MCM-41; (c) activated MCM-41; (d) modified MCM-41; (e) Mn(II)-Modified MCM-41.

These bands are due to the surface hydroxyl groups, in the range of $3770\text{--}3300\text{ cm}^{-1}$ attributed to the presence of the (O-H) stretching. While, lattice vibrations are in the range $1300\text{--}750\text{ cm}^{-1}$. Two strong bands are present at about 1085 cm^{-1} and 801 cm^{-1} , which can be assigned to $\nu_{\text{as}}(\text{Si-O-Si})$ and $\nu_{\text{s}}(\text{Si-O-Si})$, respectively. A band near 950 cm^{-1} is assigned to Si-O-H bending frequency. The band at about 970 cm^{-1} indicates the presence of surface silanol groups, $\nu(\text{Si-OH})$ vibrations [8, 9, 15–17].

After functionalizing MCM-41, Fig. 1(d), very weak new bands arise at $1526\text{--}1529\text{ cm}^{-1}$ assigned to a protonated aniline, NH_3^+ bending. Another two new bands also arise at 1478 cm^{-1} and 797 cm^{-1} probably due to the (C-N) aromatic stretching and vibration of ($-\text{NH}_2$) wagging of aniline, respectively. An additional new band at about 744 cm^{-1} is assignable to the characteristic vibration of (Si-O-B) [12]. It proved that MCM-41 surface was functionalized with the modifier of aniline and boron trifluoride, denoted as $>\text{Si-O-BF}_3^- + \text{NH}_3\text{-Ar}$. It is an indication that the modification of support material was achieved.

Interestingly, after the manganese anchoring, Fig. 1(e), that characteristic bands of aniline modifier practically disappear. In addition, no a new band is observed when compared with the modified MCM-41 vibrations. It suggests that feature of the hybrid Mn(II) onto the modified mesoporous silica MCM-41 occurs by an electrostatic interaction. The proposed interaction is denoted as $>\text{Si-O-BF}_3]_2\text{Mn}$.

3.2.2. Scanning electron microscopy (SEM)

The surface morphology and size of MCM-41 samples were investigated by SEM. The SEM micrographs of these MCM-41 materials are presented in Fig. 2(a), (b) and (c).

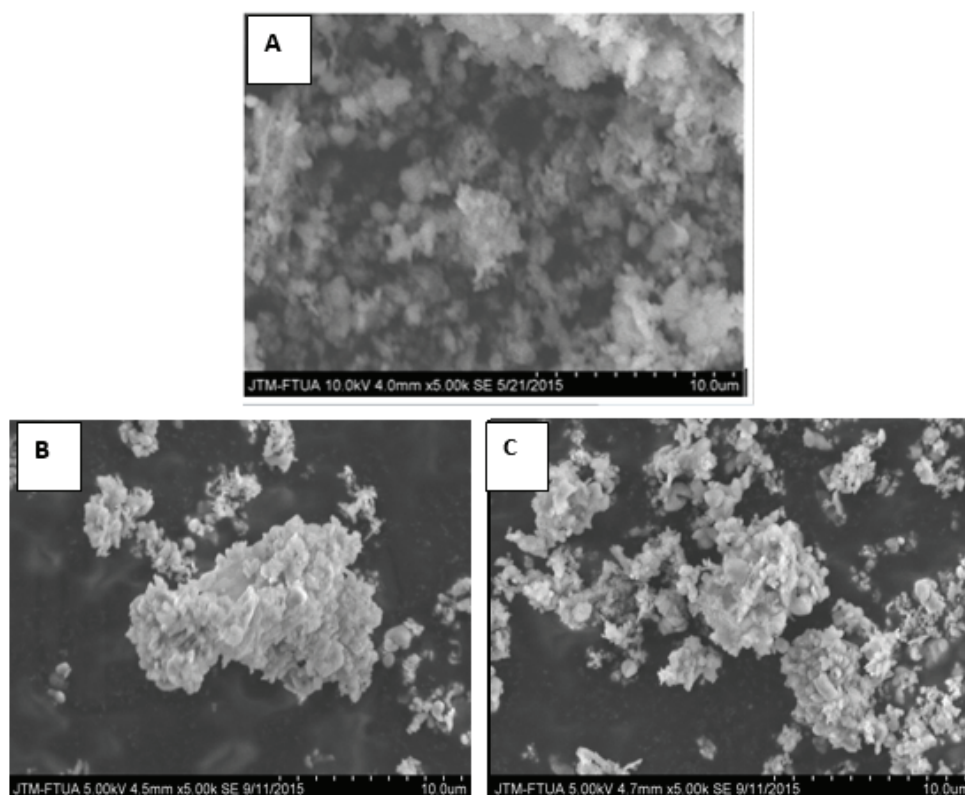


Figure 2: SEM micrographs of (a) MCM-41; (b) modified MCM-41; (c) Mn(II)-modified MCM-41.

It can be seen that the all solid samples have the same morphology corresponding to the aggregates which tend to form spherical edges. However, after modification with modifiers and anchoring manganese onto the MCM-41 surface led to aggregates size of samples become smaller. SEM micrographs in Fig. 2 (b) and (c) show the effect of modifiers and loading of manganese. The sizes of the hybrid Mn(II)-modified MCM-41 particles are smaller than the those in modified MCM-41. This is in agreement with previous reports [13, 18] for metal incorporated materials.

3.2.3. Atomic absorption spectroscopy (AAS) analyses

The bulk manganese content of catalyst sample as determined by AAS is summarized in Table.1.

TABLE 1: The values of metal loading and metal leaching as obtained by AAS analysis.

Heterogeneous Catalyst	Manganese loading (%)	Manganese leaching (%)
Hybrid Mn(II)-Modified MCM-41	67.60	0.006

The metal loading value of the prepared supported catalyst is 67.60 %. It is an indication that the manganese seems to be located in the inner porous structure of silica surface [8, 9]. While, the metal leaching value is 0.006%. The catalyst lost only 0.006% manganese metal. It confirms that interaction between the Mn(II) with support of the mesoporous silica is very stable and leaching proof [8, 9, 18].

4. Conclusions

The successful anchoring of manganese, bearing amine group in aniline and boron trifluoride, onto the modified MCM-41 surface, using post-synthesis method was achieved. Different characterization techniques such as FTIR, SEM, and AAS analysis showed evidences that the metal was attached to the modified MCM-41 surface by an electrostatic interaction. The total manganese amount in catalyst (hybrid of Mn(II)-modified mesoporous silica MCM-41) determined by AAS analysis exhibits that the metal loading value is 67.60%. It is an indication that the manganese anchoring carried out inside the functionalized porous silica system. In addition, the loss of only 0.006% manganese after leaching test proved that the catalyst seems to be very stable and leaching proof.

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