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Synthesis, characterization, and photocatalytic activity of MCM-41 and MCM-48 impregnated with CeO₂ nanoparticles

Hamid Reza Pouretedal^{1*} and Mina Ahmadi²

Abstract

MCM-41/CeO₂ and MCM-48/CeO₂ were synthesized by direct and indirect methods in solvent media and by grinding method in a solvent-free media. The materials prepared by grinding method are characterized by X-ray diffraction, infrared spectrum analysis, and N₂ adsorption and desorption. Surface areas and pore size of MCM-48/CeO₂ were obtained with values of 680.9 m²·g⁻¹ and 1.64 nm, respectively, by BET method. The results showed that CeO₂ nanoparticles were introduced into MCM-41 and MCM-48, and there was formation of CeO₂ crystallites as secondary phase in the extra framework of MCM-41 and MCM-48. MCM-41/CeO₂ and MCM-48/CeO₂ materials are used as photocatalysts in degradation of Congo red as a dye pollutant. The MCM-41/CeO₂ and MCM-48/CeO₂ prepared by grinding method showed the higher photoreactivity with 97.6 % and 93.1 %, respectively, of degradation of Congo red. The higher photoreactivity is due to the complete incorporation of cerium ions in mesoporous material of MCMs in a solvent-free media.

Keywords: Photocatalytic, MCM-41, MCM-48, CeO₂, Congo red

Background

Ordered mesoporous materials such as MCM-41, MCM-48, and SBAs have been the subject of intensive research in the field of heterogeneous catalysis owing to their high surface area, uniform pores, and relatively high thermal stability [1]. These materials containing various transition metals are used as heterogeneous catalysts for many organic compound reactions [2,3]. Pure silica mesoporous material has only a few crystal defects and low reaction activity. Because of these disadvantages, researchers attempt to introduce some nanoparticles into this mesoporous material. The successful usages of the transition and rare earth metals in the catalysts are mainly the promoters; in oxides or in the microporous material, some attention have been paid to the combination of the transition and rare earth metals with the mesoporous materials in which the transition and rare earth metals are used as the active components of catalyst [2-4].

Cerium oxide is one of the most reactive rare earth metal oxides, which has been extensively studied and employed in various applications including fast ion conductors, oxygen storage capacitors, catalysts, UV blockers, polishing materials, and electrolytes for solid oxide fuel cells [5]. CeO₂ or CeO₂-based materials have also been found to be very important in environmental protection. In particular, supported CeO₂ and CeO₂-based mixed oxides are effective catalysts for the oxidation of different hydrocarbons and for the removal of organics from polluted water from different sources [6].

In this study, the impregnation synthesis of MCM-41/CeO₂ and MCM-48/CeO₂ was done using direct and indirect solvothermal and grinding (without solvent) methods. The mesoporous materials of MCM-41 and MCM-48 were synthesized hydrothermally at ambient temperature conditions. A comparative study in structural properties of MCM-41/CeO₂ and MCM-48/CeO₂ materials was evaluated. The performance of these substrates toward the photocatalytic degradation of Congo red in aqueous solution was studied.

* Correspondence: HR_POURETEDAL@mut-es.ac.ir

¹Faculty of Applied Chemistry, Malek-Ashtar University of Technology, Shahin-Shahr 83145-115, Iran

Full list of author information is available at the end of the article

Methods

Synthesis of MCM-41 and MCM-48

All of the materials purchased are of highest purity. All solutions were prepared with double distilled water. MCM-41 was synthesized by dispersion of sodium silicate (2.5 g) in deionized water (18.24 ml) [7]. The surfactant cetyltrimethylammonium bromide (CTAB) was added after stirring the components. The reaction mixture was stirred for 45 min at room temperature. During the vigorous stirring, an adequate amount of 25 % solution of tetramethylammonium hydroxide was added, and the pH was adjusted at 10 to 11. The mixture was stirred at room temperature for 24 h, then introduced into a Teflon-lined autoclave, and kept at a temperature of 100 °C for 3 days. The powder was recovered by filtration, was subsequently washed with acidic water-ethanol solution, and then dried in a vacuum oven. The obtained solid was calcined at 500 °C for 4 h.

Sodium hydroxide and tetraethyl orthosilicate (TEOS) were added to the CTAB solution in the synthesis of MCM-48. The molar composition of the obtained gel is 1 M TEOS:0.25 M Na₂O:0.65 M CTAB:0.62 M H₂O [8]. The solution was stirred for about 1 h, then transferred into a polypropylene bottle, and heated up to 100 °C for 3 days. The product was filtered, washed with water, and dried in air at ambient temperature. The dried product was finally calcined at 550 °C for 6 h.

Synthesis of MCM-41/CeO₂ and MCM-48/CeO₂ by indirect method

Some polyethylene glycol as dispersant agent was added to the solution of (NH₄)₂Ce(NO₃)₆ (0.2134 g), and then 0.1 g of synthesized MCM-41 and/or MCM-48 material was added into the cerium solution. After heating the solution till 40 °C under stirring and adjusting the pH to 7 to 8, ammonium nitrate solution was quickly added, and then the mixed solution was thoroughly stirred for 30 min. After aging for 12 h, the colloid was filtered, washed, and dried in a vacuum oven at 60 °C for 10 h. The synthesized sample was calcined at 600 °C for 5 h in air stream with a heating rate of 10 °C/min [9]. Cooling it naturally with ambient temperature, MCM-41/CeO₂ (40 wt.%) and MCM-48/CeO₂ (40 wt.%) were gained.

Synthesis of MCM-41/CeO₂ and MCM-48/CeO₂ by direct method

MCM-41/CeO₂ and MCM-48/CeO₂ were prepared using a modified Stöber's synthesis at room temperature. The weight percent of CeO₂ in prepared materials is 40 %. In a typical synthesis, 12.5 g of hexadecyltrimethylammonium bromide and the required amount (0.2134 g) of ammonium cerium nitrate are taken in a polypropylene bottle. Water and ethanol were added to the obtained mixture, which was stirred well until the dissolution of the metal precursor was completed. To this solution, NH₃ was added followed

by 1.8 ml of TEOS. The precipitate obtained was filtered and washed with deionized water extensively. The solid was dried at 80 °C overnight in static air. The dried powder was ground finely and calcined in static air at 550 °C to remove the surfactant molecules for 6 h [10].

Synthesis of MCM-41/CeO₂ and MCM-48/CeO₂ by grinding method

In this method, 0.2134 g of (NH₄)₂Ce(NO₃)₆ and 0.1 g of synthesized MCM-41 and/or MCM-48 were placed in a mortar and ground drastically at room temperature. The obtained solid was calcined at 550 °C in air for 3 to 4 h to remove the surfactant molecules [11]. MCM-41/CeO₂ (40 wt.%) and MCM-48/CeO₂ (40 wt.%) were obtained.

Photocatalytic activity of prepared photocatalysts

Photocatalytic degradation of Congo red (CR) was studied at 25 °C and pH = 7 to 8 in the presence of prepared catalysts. The degradation was carried out in a Pyrex photoreactor that has a high pressure mercury lamp of 70 W with maximum irradiation at a wavelength of 332 nm. The degradation was performed at suitable time intervals at room temperature while the samples were stirred continuously. The photoreactor was filled with 25 ml of 10 mg/l CR and 0.7 g/l catalysts. The degradation efficiency (%D) was calculated using initial concentration (C₀) and residual concentration (C_t) of CR by spectrophotometric method at λ of 510 nm (%D = [(C₀ - C_t)/C₀] × 100). The kinetic rate constant of degradation (k_{obs}) was calculated using the model of Langmuir-Hinshelwood's kinetic expression (ln (C₀/C_t) = k_{obs}t) [12].

Results and discussion

Characterization of MCM-41/CeO₂ and MCM-48/CeO₂

The characterization of MCM-41, MCM-48, MCM-41/CeO₂, and MCM-48/CeO₂ prepared by grinding method are performed using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and Brunauer, Emmett, and Teller (BET) N₂ adsorption-desorption isotherm. The XRD patterns of MCM-41 and MCM-41/CeO₂ samples and MCM-48 and MCM-48/CeO₂ samples are shown, respectively, in Figures 1 and 2. The hexagonal and cubic ordered structured of MCM-41 and MCM-48, respectively, are confirmed by the XRD patterns [9].

In Figure 1a, in the small-angle XRD patterns of the prepared material MCM-41, an intense diffraction peak (100), together with an additional peak (110), and a very weak peak (200) were observed. It can be seen that peak (200) is not strong enough and also that the diffraction peaks move to the high angle, and the peaks become weaker when the CeO₂ particles are doped into MCM-41. The increase of CeO₂ particles in the framework of MCM-41 is due to reduction of the tunnel size of the substrate [9-11]. The XRD patterns of MCM-41 and MCM-41/CeO₂ (wide angle) are

Figure 1 Small-angle (a) and wide-angle (b) XRD patterns of samples (1) MCM-41 and (2) MCM-41/CeO₂.

Figure 2 Small-angle (a) and wide-angle (b) XRD patterns of samples (1) MCM-48 and (2) MCM-48/CeO₂.

shown in Figure 1b. The main substance of MCM-41 is amorphous silica as evident in one diffusion peak observed in the pattern of MCM-41. However, the peak of amorphous silica became weaker, and the peaks of CeO_2 appeared when the CeO_2 nanoparticles are introduced into MCM-41 [9]. The peaks with 2θ values of 28.3, 33.2, 47.5 and 56.4 correspond to the (111), (200), (220), and (311) planes [13].

In the small-angle XRD patterns of MCM-48, the most intense diffraction peak (211) appears at $2\theta = 2.9^\circ$ (Figure 2a), while low intense diffraction peaks are seen at $2\theta = 3^\circ$ to 6° . With cerium doping and a gradual loss of long-range ordering of MCM-48, the intensity of the diffraction peak of MCM-48/ CeO_2 decreases at a small angle. The diffraction peaks of CeO_2 in the wide-angle XRD pattern have appeared obviously which show the content of CeO_2 in the channel (or in the extra framework) of the sample [14].

The FT-IR spectra of MCM-41 and MCM-41/ CeO_2 are shown in Figure 3. In the spectra of MCM-41, the stretching vibrating absorption peaks of the O-H band in the surfaced hydroxyl and in the planar water is seen at 3440 cm^{-1} . The symmetry and asymmetry flexural vibrating peaks of Si-O-Si at 1,080, 812, and 464 cm^{-1} , respectively, are related to the framework of silicon [9]. As seen, there are some differences of the intensities of the peaks in the FT-IR spectra of MCM-41 and MCM-41/ CeO_2 , which resulted from the doping of CeO_2 . A strong absorption peak at $1,632\text{ cm}^{-1}$ is observed in the spectra of MCM-41/ CeO_2 , and it indicates the formation of Ce-O-Ce [9].

Figure 4 shows the FT-IR absorption spectra of the MCM-48 and MCM-48/ CeO_2 samples. The absorption bands of asymmetric vibration of Si-O-Si of the silica framework appear at 1,200 and $1,080\text{ cm}^{-1}$. The stretching vibration peak of silica is at 815 cm^{-1} . The vibration band at $1,080\text{ cm}^{-1}$ are shifted 4 to 9 cm^{-1} for the MCM-48/ CeO_2 sample compared with the spectrum

Figure 3 FT-IR spectra of (a) MCM-41 and (b) MCM-41/ CeO_2 .

Figure 4 FT-IR spectra of (a) MCM-48 and (b) MCM-48/ CeO_2 .

of MCM-48. This shift is due to the incorporation of Ce into the framework of MCM-48 [14].

The N_2 adsorption and desorption isotherms of the MCM-48/ CeO_2 sample is shown in Figure 5, and the corresponding pore size distribution curve is shown in Figure 6. It is shown that these isotherms have the typical characteristics of the mesoporous material isotherm and are of the type IV according to the IUPAC classification [14]. The BET surface areas, average pore size calculated by the BJH model, and the pore volume of MCM-48 [14] and MCM-48/ CeO_2 samples are presented in Table 1.

Photocatalytic degradation of Congo red

The control experiment indicates that CR was not degraded completely when irradiated with UV in the absence of a catalyst; only 24.7 % was degraded after 120 min. The primary factor of photocatalytic degradation is the adsorption of CR onto the catalyst surface via the interaction of surface hydroxyl groups, particularly onto high-surface area support, i.e., MCM-41 and MCM-48 [15]. In other words, the adsorption of anionic dye on oxide surface is favored, leading to an increase of the dye concentration on the surface and the facilitation of photocatalytic degradation of the dye being investigated [16,17]. The presence of transition metal cations such as cerium doped on the mesoporous materials, such as MCM-41 and MCM-48, may prevent the recombination between the photogenerated holes and electrons or elongate the time of charge separation because it acts as an electron acceptor center [18,19]. One can assumed that the hydroxyl groups on the surface of prepared catalysts act as an electron donor for photogenerated H^+ , forming active hydroxyl radicals ($\text{OH}^{\cdot+}$) which attack the CR.

Table 2 shows the performances of MCM-41/ CeO_2 and MCM-48/ CeO_2 (prepared by different methods) and nanoparticles of CeO_2 as photocatalysts for the photocatalytic degradation of CR in 120 min. The k_{obs} values are also

Figure 5 Nitrogen adsorption and desorption isotherms of MCM-48/CeO₂.

collected in Table 2. Among the prepared catalysts, the mesoporous MCM-41/CeO₂ and MCM-48/CeO₂ that were synthesized by grinding method show the most photocatalytic activity with 97.6 % and 91.3 % photodegradation of CR, respectively. Apparently, the most cerium ions are doped in mesoporous materials by grinding method, and the weight percentage of CeO₂ in MCM/CeO₂ is near 40 % which is in accordance to what was mentioned in the 'Methods' section. However, a lot of cerium ions have been lost in the preparation of MCM/CeO₂ by direct and indirect methods in a solvent medium.

The amount of CR degraded on the surface of the different catalysts showed the order of sequence: MCM-41/CeO₂ > MCM-48/CeO₂ > CeO₂, which can be directly related to the surface area that is available for adsorption. As for CeO₂ nanoparticles, they show 51.9 % of degradation. However, good photodegradation is obtained over the MCMs/CeO₂ catalyst. The enhanced photocatalytic activity over the composite MCMs/CeO₂ is reflecting the beneficial adsorption properties of MCM-41 and MCM-48. Thus, it is clear that the presence of cerium in MCM-41/CeO₂ and MCM-48/CeO₂ plays a role in the catalytic reaction, that is to say, the

Figure 6 Pore size distribution curves of MCM-48/CeO₂.

Table 1 Textural properties of MCM-48 and MCM-48/CeO₂ samples

Sample	Surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Pore size (nm)
MCM-48	895.0	0.850	2.23
MCM-48/CeO ₂	680.9	0.398	1.64

Ce ions that dispersed highly in MCM/CeO₂ are the active sites. The enhancements of CR degradation may be due to the high dispersion of CeO₂ in the amorphous wall of MCM-41 and MCM-48 and the increase of the bandgap between the conduction band and valance band of CeO₂ in MCMs. In addition, due to the wide bandgap of MCM-41/CeO₂ and MCM-48/CeO₂, the lifetime of photogenerated holes and electrons of the MCMs/CeO₂ is longer than that of CeO₂ nanoparticles [20-22].

The higher activity of MCM-41/CeO₂ may be due to the hexagonal ordered structured compared to MCM-48 with cubic ordered structured [21,22]. The hexagonal ordered structured of MCM-41 due to the higher dispersion of cerium on this sample.

Conclusions

The grinding method can be used to prepare cerium-doped MCM-41 and MCM-48 mesoporous materials. Using this method, certain cerium cations can be incorporated into the framework of MCM-41 and MCM-48. After CeO₂ particles are being doped into substrates of MCM-41 and MCM-48, the surface area of the material was reduced, and the pore volume also decreased. The prepared MCM-41/CeO₂ and MCM-48/CeO₂ show the photoreactivity in CR degradation. The hexagonal structure of MCM-41 has a larger surface area and has active sites. Also, there are CeO₂ nanoparticles in the secondary phase in the extra framework of mesoporous materials. Thus, the MCM-41/CeO₂ catalyst exhibits the higher reactivity in comparison with MCM-48/CeO₂.

Table 2 CR degradation in 120 min and k_{obs} of photocatalytic process over CeO₂, MCM-41/CeO₂, and MCM-48/CeO₂

Catalysts	%D	$k_{obs} \times 10^{-3}$ (min ⁻¹)
Without photocatalyst	24.7	1.9
CeO ₂	51.9	6.0
MCM-41/CeO ₂ , direct method	44.2	5.0
MCM-48/CeO ₂ , direct method	37.6	3.7
MCM-41/CeO ₂ , indirect method	52.7	6.0
MCM-48/CeO ₂ , indirect method	46.7	5.4
MCM-41/CeO ₂ , grinding method	97.6	36.0
MCM-48/CeO ₂ , grinding method	91.3	22.7

Competing interests

The authors declare that they have no competing interest.

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Author details

¹Faculty of Applied Chemistry, Malek-Ashtar University of Technology, Shahin-Shahr 83145-115, Iran. ²Department of Chemistry, Islamic Azad University, Shahreza Branch, Shahreza, Iran.

Authors' contribution

Both authors participated in the experiments, read and approved the final manuscript.

Authors' information

HRP is an associate professor of Chemistry, and MA is an M.Sc. student of Chemistry.

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