SYNTHESIS AND CHARACTERIZATION OF MCM-41 CONTAINING CeO$_2$

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SUMMARY

MCM-41 and cerium containing MCM-41 mesoporous materials were obtained by hydrothermal method under atmospheric pressure (the molar ratio SiO$_2$/CeO$_2$= x, x = 160, 80, 40, 20). The characteristics of all samples were investigated by ThermoGravimetric - Differential Thermal Analysis (TG-DTA), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Energy-Dispersive X-ray spectrometry (EDX) and nitrogen adsorption-desorption isotherms. The results indicated that: particles are sphere, uniform and pore size is about 50 nm; the pore systems are hexagonal structure, ordered arrangement; the samples have high surface area (> 600 m^2/g) with narrow pore size distribution curve. Results of EDX showed that the SiO$_2$/CeO$_2$ molar ratios of samples were very similar to the molar ratios in gel.

I - INTRODUCTION

Porous materials, which have high surface area, high thermal and hydrothermal stability, are widely used in many fields: catalyst for oil refining, petrochemistry and chemical synthesis; adsorbents…[1, 2]. Since 1930, microporous materials, especially zeolites, have attracted strong attention as solid acids, base and redox-catalysts. However, zeolites present limitations when large molecules are involved. In 1992, researchers at Mobil Research and Development Corporation synthesized a type of mesoporous materials designated M41S. These of materials have highly ordered hexagonal array of unidimensional pores with a very narrow pore size distribution [3, 4]. They are interesting materials.

In this paper, we report the results of studies concerning syntheses of MCM-41 and cerium containing MCM-41 mesoporous materials by hydrothermal method in which sodium silicate and cetyltrimethylammonium bromide were used as source of SiO$_2$ and template, respectively. The characteristics of materials were determined by physical method (XRD, SEM, TEM, EDX, nitrogen adsorption isotherm).

II - EXPERIMENTAL.

1. Syntheses of MCM-41 and cerium containing MCM-41

Synthesis of MCM-41: 30.2 g solution of sodium silicate and 30ml distillation water were taken to a flask. The solution was heated at 80ºC with medium stir for 1 hour (solution A). Solution B, which included 5 g CTAB and 15 ml water, was heated at 70ºC with vigorous stir for 2 hours. After that, two solutions were cooled naturally to room temperature.

Step 1: Solution A was dropped slowly into solution B with violent stir. After that, the stir was continued for 1 hour at room temperature.

Step 2: The gel was taken in a 300 ml flask and refluxed with vigorous stir for 24 hours at 100ºC and atmospheric pressure.

Step 3: The flask was cooled to room temperature, pH of the solution was adjusted to 11 by CH_3COOH 30% solution or NH_3 25% solution. After that, the solution was refluxed for 24 hours at 100°C with vigorous stir.

Step 2 and step 3 were repeated three times. The obtained materials were centrifugalized and washed with distillation water (8 - 10 times) until pH of washed water achieved ~7. The product was dried at 120°C in 24 hours and then calcined at 550°C in 10 hours in the presence of air.

Synthesis of cerium containing MCM-41 (Ce-MCM-41): The above process was repeated with slight modification: After complete addition solution A into solution B, solution that contain calculated amount of $Ce(SO_4)_2$ was added.

2. Characterization

- Thermogravimetric-Differential Thermal Analyses (TG-DTA) were carried out on DSC-SDT2960 TA (USA) under a flow of 2 l/h at a heating rate of 10°C/min to 800°C.

- All X-Ray Diffraction patterns were recorded on Bruker D5005 (Germany) with CuKα radiation between 1 and 10^0 (step: 0.005, steptime: 1s).

- Transmission Electron Macrographs (TEM) were obtained in JEOL JEM-1010 Electron Microscope (Japan) with 80 kV acceleration voltage.

- Scanning Electron Micrographs (SEM) were obtained in JEOL JEM-5410LV Scanning Microscope (Japan).

- The metal contents of samples were determined by EDX analyses with module of EDS ISIS 300 (Oxford, England) attached to JEOL JEM 5410LV Scanning Microscope.

- The specific surface area and pore size distribution were determined by BET method from Nitrogen adsorption-desorption isotherms at 77K using Micromeritics ASAP-2010 (Micromeritics, USA).

III - RESULTS AND DISCUSSION

1. Thermal Analysis

Thermogravimetric-Differential Thermal analyses of MCM-41 and Ce-MCM-41 were carried out under the same experimental conditions. The patterns are very similar. The curves of TG-DTA are shown in Fig. 1.

Total mass losses are about 39% including three steps. In the first step (50 - 120°C), the mass loss is about 4.2 - 4.8% due to desorption of physisorbed water held in the pores. In the second step (150 - 400°C), the mass loss is about 28 - 30% including two small steps which overlap each other: 1) decomposition of templates and oxidation of eliminated gases (according to exothermal peak on DTA curve); 2) remove of coke formed in the above step by the decomposition of templates. In the last step (400 - 500°C), the mass loss is about 5 - 7% due to the loss of water formed by the condensation of silanol groups. The TG-DTA curves show that almost all the template, including the water formed due to condensation of silanol groups, is lost completely from the pore system at 550°C.

2. The results of EDX and XRD

All the samples of MCM-41 and Ce-MCM-41 were analyzed EDX (Energy-Dispersive X-ray spectrometer) for determining elemental composition and the SiO_2/CeO_2 molar ratios of sample (table 1).

The results in table 1 indicate that most of cerium were incorporated into the framework position or walls of silica network of MCM-41.

All samples were recorded XRD. From 1 to 6° on the patterns, four peaks (d_{100}, d_{110}, d_{200}, d_{210}) which are characteristics of MCM-41 structure (hexagonal lattice symmetry) appear (Figs. 2a, 2b). When content of CeO_2 increases, value of d_{100} increases lightly due to size of Ce^{4+} is larger than size of Si^{4+} in the network.

However, reflection from 10 - 50° showed that the pore walls are SiO_2 amorphous (have no peak on the XRD pattern, Fig. 2c).

Using data obtained from XRD, we can calculate the distance between two centres of pores by below formula [5]:

$$a_0 = \frac{2d_{100}}{\sqrt{3}}$$

Table 2 indicates values of distance d_{hkl} and   distance between two centre of pores a_0.
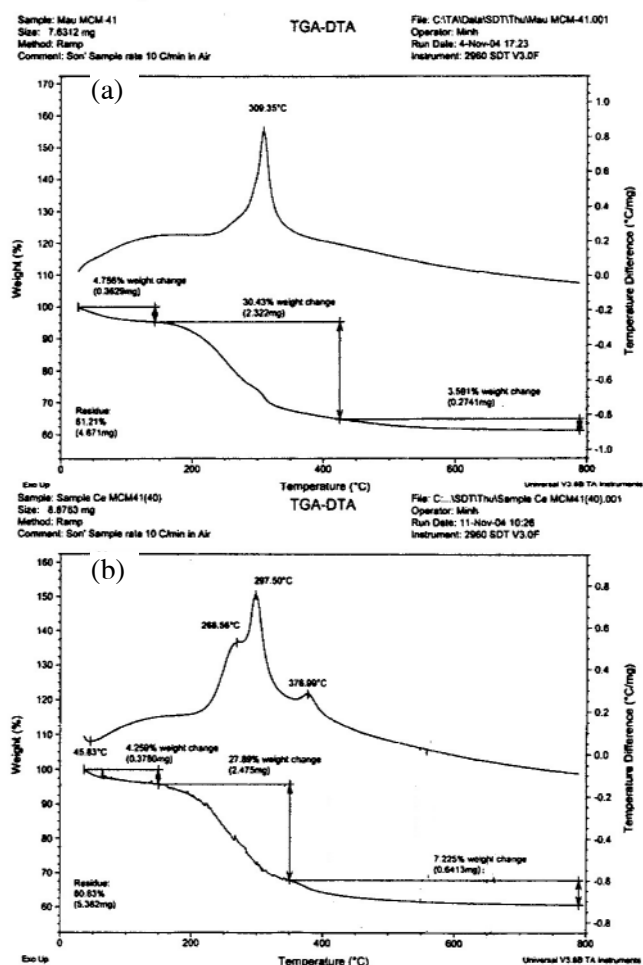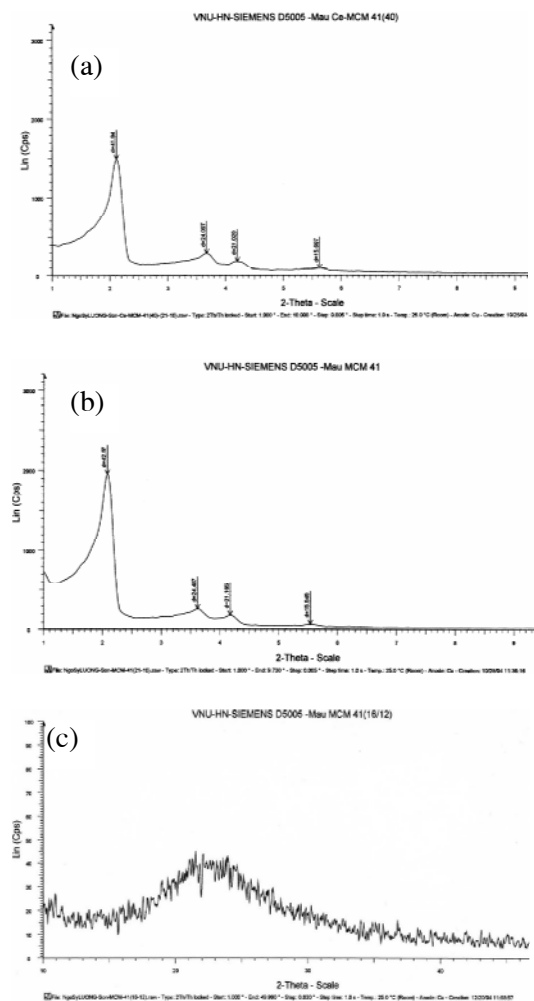

Figure 1: TG-DTA curves of MCM-41 (a)
and Ce-MCM-41 (b)

Figure 2: XRD patterns of MCM-41 (a),
Ce-MCM-41 (40) (b) and XRD pattern with
$2\theta = 10 - 50^o$ (c)

Table 1: Results of elemental analysis of Ce-MCM-41 samples

Sample	% Element of Si	% Element of Ce	Ratio of $(Si/Ce)_{sam}$ [a]	Ratio of $(Si/Ce)_{gel}$ [b]
Ce-MCM-41 (160)	99.33	0.67	148.3	160
Ce-MCM-41 (80)	98.74	1.26	78.4	80
Ce-MCM-41 (40)	97.55	2.45	39.8	40
Ce-MCM-41 (20)	95.25	4.75	20.1	20

(a) SiO_2/CeO_2 molar ratios of samples obtained from EDX method; (b) SiO_2/CeO_2 molar ratios in gel.

Table 2: Distances d_{hkl} and a_0 of MCM-41 and Ce-MCM-41 samples

Samples	d_{100}, Å	d_{110}, Å	d_{200}, Å	d_{210}, Å	a_0, Å
Si-MCM-41	42.57	24.44	21.17	15.95	**49.2**
Ce-MCM-41 (160)	41.79	24.05	20.94	15.65	**48.3**
Ce-MCM-41 (80)	42.32	24.21	21.05	15.70	**48.9**
Ce-MCM-41 (40)	41.94	24.10	21.03	15.70	**48.4**
Ce-MCM-41 (20)	41.95	24.12	20.91	15.80	**48.4**

3. SEM and TEM

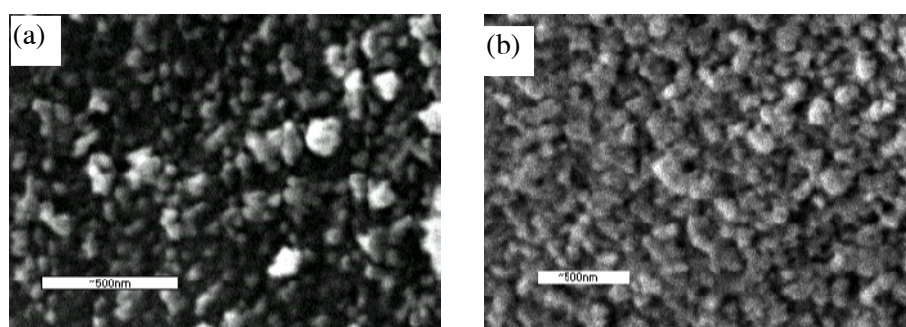The SEM micrographs of MCM-41 and Ce-MCM-41 samples are shown in Fig. 3.

Figure 3: Scanning Electron Micrographs of MCM-41 (a) and Ce-MCM-41 (b)

These micrographs showed that particle morphology is sphere and uniform. The particle size is about 40 - 60 nm.
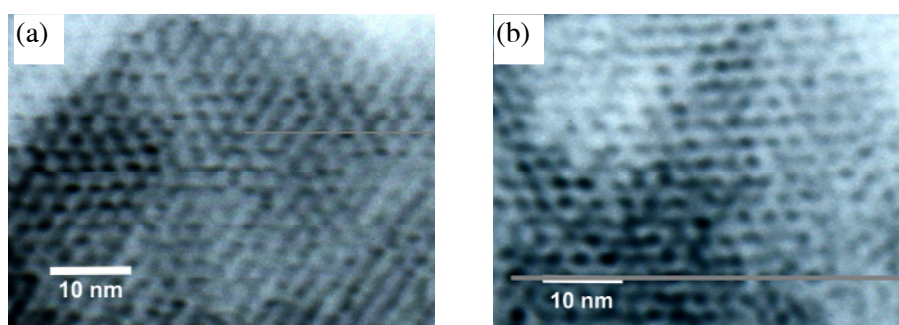

Figure 4: Transmission Electron Micrographs of MCM-41 (a) and Ce-MCM-41 (b)

Transmission Electron Micrographs revealed that arrangement of pores is ordered; pore structure is hexagonal; pore size is about 3 nm; thickness of pore wall is about 1 nm.

3. N_2 adsorption - desorption isotherm

All the samples showed that isotherms of type IV have inflection around $P/P_0 = 0.3 - 0.4$. This is a characteristic of MCM-41, ordered mesoporous materials.

These curves indicate the uniformity of the narrow pore size distribution. The specific BET surface area and average pore diameters are

calculated from a N_2 adsorption isotherm using BJH model. All results are shown in table 3.
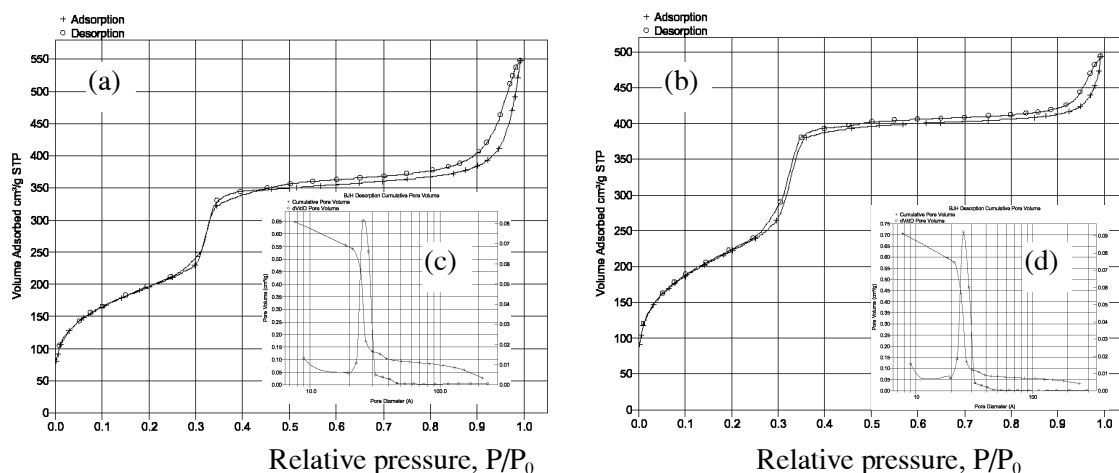

Figure 5: N_2 adsorption - desorption isotherm of MCM-41 (a) and Ce-MCM-41 (40) (b)
Pore size distribution curves of MCM-41 (c) and Ce-MCM-41 (40) (d)

Table 3: Nitrogen sorption pore diameter, BET surface area, distance between two pore a_0, wall thickness of MCM-41 and Ce-MCM-41 samples

Sample	S_{BET}, m^2/g	Pore diameter d_0, Å	Wall thickness, Å
Si-MCM-41	743.89	41.1	8.1
Ce-MCM-41 (160)	743.75	44.0	4.3
Ce-MCM-41 (80)	646.48	35.0	13.9
Ce-MCM-41 (40)	813.68	37.1	11.3
Ce-MCM-41 (20)	707.14	33.4	15.0

Wall thickness = a_0 - d_0 *(The values of a_0 are indicated in table 2).*

IV - CONCLUSIONS

MCM-41 and Ce-MCM-41 mesoporous materials were prepared by hydrothermal method using sodium silicate and CTAB as sources of SiO_2 and structure direction, respectively. The SEM micrographs indicate that particles are sphere and uniform and pore size is about 50 nm. The pore systems, which are hexagonal structure with ordered arrangement, are showed by XRD and TEM. All the samples have high BET surface area (> 600 m^2/g) with narrow pore size distribution (pore size is about 3 nm). Results of EDX show that the SiO_2/CeO_2 molar ratios of samples were very similar to the molar ratios in gel.

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