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Synthesis and characterization of Fe-Ce-MCM-48 from silatrane precursor via sol–gel process

Hussaya Maneesuwan, Rujirat Longloilert, Thanyalak Chaisuwan, Sujitra Wongkasemjit *

The Petroleum and Petrochemical College and Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand

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ABSTRACT

A series of Fe (0.01 mol) and Ce (0.01 to 0.09 mol) incorporated into MCM-48 framework was successfully synthesized by sol–gel method using cetyltrimethylammonium bromide (CTAB) as a structural directing agent; and silatrane, $FeCl_3$, and cerium glycolate as silica, iron, and cerium sources, respectively. X-ray diffraction (XRD) patterns showed well-defined order cubic mesoporous structures while N_2 adsorption/desorption measurements indicated that the synthesized bimetallic materials had a BET surface area of up to 1225 m^2/g, large mesopores (3.1 nm), mean pore volume, and diameters of 0.83 cm^2/g and 2.89 nm, respectively. X-ray fluorescence (XRF) revealed the total metal content of the final product. UV–visible absorption spectra confirmed that both iron (Fe^{3+}) and cerium (Ce^{4+}) species highly dispersed in the framework. Scanning electron microscopy (SEM) showed the truncated octahedron morphology of Fe-Ce-MCM-48.

1. Introduction

The mesoporous materials discovered by Mobil group are known as the M41S family [1]. These materials can overcome the limitations of microporous materials unable to allow large reactants to penetrate inside the pores. The main members of the M41S family are hexagonal MCM-41, cubic MCM-48, and unstable lamellar MCM-50 mesostructures. Among them, MCM-48 is the most attractive material, owing to its three-dimensional, interconnected channels, providing more advantages—including fast diffusion and resistance to pore blocking of coming molecules—over the one-dimensional pores of MCM-41. Moreover, due to its long-range order, large surface area, and narrow pore size distribution, MCM-48 has been used as an adsorbent, catalyst, and catalyst support, sensor, as well as an inorganic template for the synthesis of advanced nanostructure [2–5]. However, the pure silica MCM-48 lacks catalytic active sites, and thus, many researchers have attempted to incorporate heteroatoms (such as Fe, Ce, Cr, V, Ti, etc. [6–8]) into the mesoporous framework to enhance its redox properties. MCM-48, supporting two or more metal atoms, is very attractive since one metal can modify the structural and redox properties of the other. Consequently, bimetallic catalysts usually improve catalytic activity, selectivity, and stability of the monometallic catalysts. Many reports have shown that Fe-containing materials have a high activity in phenol hydroxylation [6,9] and cerium enhances hydrothermal stability [7,10]. Generally, in

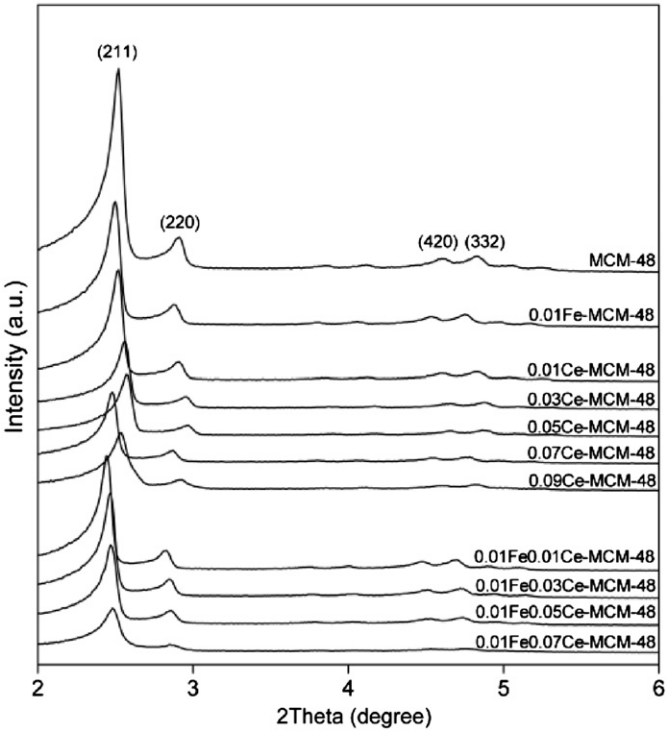

Fig. 1. XRD patterns of MCM-48, Fe-MCM-48, Ce-MCM-48 and Fe-Ce-MCM-48.

* Corresponding author. Tel.: +66 2 218 4133; fax: +66 2 215 4459.
E-mail address: dsujitra@chula.ac.th (S. Wongkasemjit).

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catalytic reactions, the catalyst is exposed to high temperatures or boiling water; therefore, the loss of hydrothermal stability could be a serious barrier for application. Simultaneous incorporation of these two metals on to MCM-48 might enhance both its phenol hydroxylation and hydrothermal properties. In this study, Fe-Ce-MCM-48 loading different iron and cerium contents was hydrothermally synthesized via sol–gel method and characterized using XRD, XRF, N_2 adsorption/desorption, DRUV, and SEM.

2. Experimental

Materials: Fumed silica (99.8%, SiO_2), cerium (IV) hydroxide ($Ce(OH)_4$), and iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) from Sigma-Aldrich, USA; hexadecyltrimethyl ammonium bromide (CTAB) from Fluka, Denmark; triethylenetetramine (TETA) from Facai, Thailand; ethylene glycol (EG) from J.T. Baker, USA; triethanolamine (TEA) from QREC, Asia; and acetronitrile and sodium hydroxide (NaOH) from Labscan, Asia, were used without purification.

Synthesis of xFe-yCe-MCM-48: Bimetallic MCM-48 materials were synthesized using Wongkasemjit's method [11]. A desired amount of $FeCl_3 \cdot 6H_2O$ was dissolved in water. The solution was stirred continuously while adding 2 M NaOH. The mixture was then slightly heated at 50 °C while adding CTAB, followed by dissolving silatrane precursor, which was synthesized according to the method described elsewhere [12]. A required amount of cerium glycolate, prepared according to the method in Ref. [13], was added and stirred for 1 h. The molar ratio composition of the gel was $1.0SiO_2$:0.3CTAB:0.5NaOH:$62.0H_2O$:*x*Fe:*y*Ce, where $0.01 \le x,\ y \le 0.09$. The mixture was autoclaved for 16 h in a

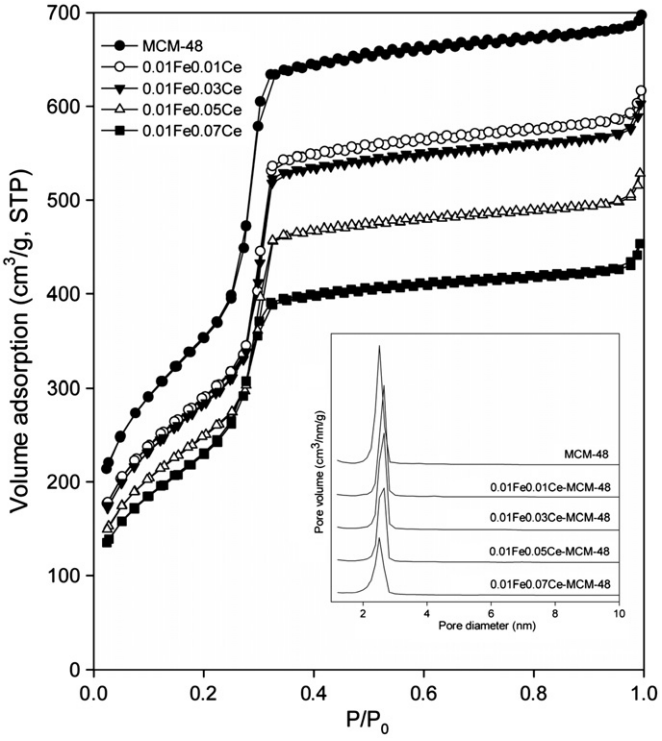

Fig. 2. N_2 adsorption/desorption isotherms of MCM-48 and Fe-Ce-MCM-48.

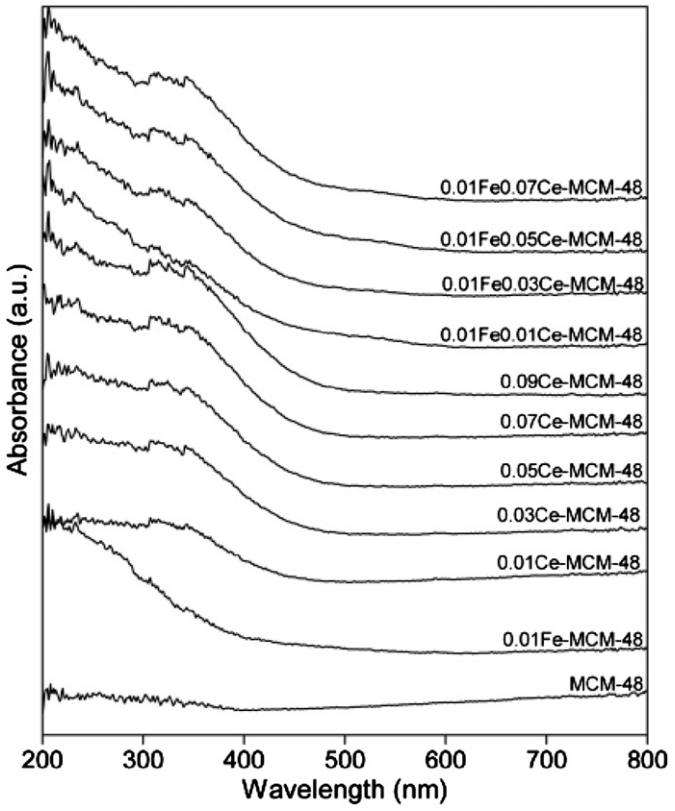

Fig. 3. DRUV–vis spectra of MCM-48, Fe-MCM-48, Ce-MCM-48 and Fe-Ce-MCM-48.

Table 1
Textural properties of MCM-48 and metal modified MCM-48.

Sample	Fe/Si*(mole ratio)		Ce/Si*(mole ratio)		BET surface area (m^2/g)	pore volume (cm^2/g)	pore diameter (nm)	a_0[a] (nm)	d_{211} (nm)	wall thickness[b] (nm)
	Gel	Product	Gel	Product						
MCM-48	0	0	0	0	1673	1.07	2.56	8.57	3.50	1.46
0.01Fe-MCM-48	0.01	0.004	0	0	1295	0.98	3.04	8.65	3.53	1.28
0.01Ce-MCM-48	0	0	0.01	0.004	1469	0.91	2.47	8.57	3.50	1.54
0.03Ce-MCM-48	0	0	0.03	0.010	1318	0.82	2.49	8.45	3.45	1.49
0.05Ce-MCM-48	0	0	0.05	0.018	1213	0.76	2.52	8.40	3.43	1.46
0.07Ce-MCM-48	0	0	0.07	0.028	1128	0.76	2.68	8.72	3.56	1.50
0.09Ce-MCM-48	0	0	0.09	0.030	1131	0.74	2.63	8.52	3.48	1.44
0.01Fe-0.01Ce-MCM-48	0.01	0.005	0.01	0.005	1214	0.93	3.07	8.87	3.62	1.33
0.01Fe-0.03Ce-MCM-48	0.01	0.005	0.03	0.014	1225	0.91	2.97	8.77	3.58	1.35
0.01Fe-0.05Ce-MCM-48	0.01	0.004	0.05	0.020	1080	0.80	2.95	8.74	3.57	1.35
0.01Fe-0.07Ce-MCM-48	0.01	0.005	0.07	0.033	1070	0.68	2.55	8.72	3.56	1.55

[a] $a_0 = d_{211}(6)^{1/2}$.
[b] Wall thickness = $a_0/3.0919$ − pore diameter/2.
* Data were obtained from XRF.