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Journal of Solid State Chemistry 171 (2003) 371–374

JOURNAL OF SOLID STATE CHEMISTRY

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Synthesis, characterization and catalytic application of cerium-modified MCM-41

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Received 28 April 2002; received in revised form 15 August 2002; accepted 27 August 2002

Abstract

The nanostructured CeMCM-41 material was synthesized by the hydrothermal method, using cethyltrimethylammonium bromide as template. The sample was characterized by X-ray diffraction, energy-disperse X-ray, thermogravimetry, nitrogen adsorption isotherm and pore size distribution. The specific surface area of CeMCM-41 was equivalent to 850 $m^2 g^{-1}$, with the pore width and mesopore volume of 3.8 nm and 0.8 $cm^3 g^{-1}$, respectively. To evaluate the catalytic performance of the CeMCM-41, a mass of ca. 0.1 g was heated from room temperature up to 723 K at heating hate of 10°C min^{-1} using oxygen flowing at 50 ml min^{-1}. The CeMCM-41 was tested as catalyst for *n*-heptane oxidation, in a fixed-bed continuous-flow reactor, at 723 K and F/W ratio (molar flow of reactant per mass of catalyst) of 0.4–0.6 g h mol^{-1}. The obtained products were analyzed in a gas chromatograph coupled to a mass spectrometer. The GC-MS analysis revealed that the main oxidation products obtained were typically CO and CO_2, with 12% of hydrocarbon conversion.

Keywords: pH adjustment; CeMCM-41; *n*-Heptane oxidation; Catalytic cracking; LGP

1. Introduction

The discovery of the mesoporous M41S materials opened new perspectives in the catalysis and adsorption fields [1,2]. The quality of these materials can be improved by incorporation of heteroatoms such as titanium [3,4], boron [5,6], vanadium [7], gallium [8], and recently lanthanides (mainly La and Ce) [9,10]. The presence of silanol groups on the surface of these mesoporous materials allows for bonding of organic and inorganic ligands [11].

The unique properties of lanthanide-based materials, e.g., lanthanide-silicates and lanthanide-doped silicas, can be related to the special properties of the $4f^n$ orbitals. Among lanthanide oxides, only Ce, Pr and Tb form dioxides, which crystallize in one simple structure with M^{4+} ions showing octahedral coordination [12]. For instance, cerium dioxide exhibits an 8:4 cation:anion coordination [13]. Its characteristic feature is the ability to undergo oxidation–reduction cycles in a reversible way [14]. It was shown that the presence of Ce and La additives in mesoporous silicas, e.g., MCM-41, improves their thermal and hydrothermal stability.

Lanthanide-containing porous materials have found many applications in various fields [15,16]. Cerium oxide has been employed as a catalyst or as a structural promoter for supported metal oxide catalysts [17]. The promotion ability of cerium is attributed to its capability to form crystalline oxides with lattice defects, which may act as active sites [18]. In addition, the presence of cerium oxide in the catalyst improves its thermal stability and mechanical resistance [19]. In this current work, cerium-modified MCM-41 mesoporous molecular sieve was synthesized resulting ordered mesoporous material. Its surface and structural properties were extensively studied by nitrogen adsorption and high-resolution thermogravimetry.

2. Experimental

The chemicals used to synthesize CeMCM-41 were fumed silica M-5 (Cab-O-Sil) from Cabot Co. (Tuscola,

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doi:10.1016/S0022-4596(02)00215-3

IL), heptahydrated cerium chloride, sodium hydroxide, cethyltrimethylammonium bromide (CTMABr) from Aldrich Chemical Co. (Milwauke, WI), and distilled water. The reactants were mixed in order to obtain gels of the following molar composition: 0.08 CeO_2:4 SiO_2:1 Na_2O:1 $C_{16}H_{33}(CH_3)_3NBr$:200 H_2O. The pure silica MCM-41 sample was synthesized using sodium silicate and CTMABr solutions. The fumed silica was added to 1 M sodium hydroxide solution and continuously stirred at 70°C until a clear solution was obtained. Subsequently, the surfactant solution was added at room temperature, and then aged for 1 h, to obtain a homogeneous gel. For the CeMCM-41 material, the required amount of heptahydrated cerium chloride was added to the gel, and then aged for one more hour. The reaction mixtures were hydrothermally treated under autogeneous pressure at 100°C for 4 days. The adjustment of pH to 10 was done after first day. For the sample, a small amount of sodium acetate (salt/surfactant molar ratio equal to 3) was added to the mixtures [20]. The resulting products were filtered, washed with deionized water and dried at 100°C in static air. Their calcination was carried out at 550°C for 2 h under nitrogen and then for an additional period of 4 h under dry air atmosphere. The calcination temperature was reached at a heating rate of 2.5°C min^{-1}.

Thermogravimetric measurements for uncalcined samples were carried out in flowing nitrogen on a high-resolution TGA 2950 thermogravimetric analyzer from TA Instruments, Inc. (New Castle, DE) in the temperature range up to 1000°C with maximum heating rate of 5°C min^{-1} and nitrogen flow rate of 60 ml min^{-1}. Thermogravimetry was also used to study the acid properties of calcined materials, which, in prior measurements, were exposed to *n*-butylamine vapor [21]. Nitrogen adsorption measurements were carried out at −196°C on a volumetric adsorption analyzer ASAP 2010 model from Micromeritics (Norcross, GA).

The catalytic performance of CeMCM-41 and MCM-41 was evaluated in a fixed-bed continuous-flow reactor. The catalytic tests were accomplished by starting of 100 mg of catalyst at 450°C and a W/F ratio of 0.4–0.5 g h mol^{-1} using air oxidant atmosphere as carrier and *n*-heptane as source of hydrocarbon. The obtained products were analyzed in a CG-17A gas chromatograph coupled in a QP5000 mass spectrometer (Shimadzu).

3. Results and discussion

EDX analysis showed that the synthesized CeMCM-41 material presents a Si/Ce atomic ratio of ca. 75. Thermogravimetric analysis (TGA) of both pure silica MCM-41 and CeMCM-41 provides information about the weight loss steps corresponding to physically adsorbed water, surfactant thermodesorption and/or decomposition, and silanol condensation (Fig. 1). As can be seen from this figure, the presence of cerium in MCM-41 does not have a substantial influence on the sample weight change. Both TGA curves show analogous behavior, which is characteristic for uncalcinated MCM-41-type materials. Their calcination at 550°C leads to removal of physically adsorbed water, thermodesorption and/or decomposition of template, as well as condensation of silanols. In the case of CeMCM-41, the calcination process can also lead to the formation of acid sites as a result of decomposition of hydrated cerium species [9]: $Ce(H_2O)^{4+} \rightarrow CeOH^{3+} + H^+$. Probably, protons may interact with oxygen attached to silicon and form Brönsted-type acid sites of the following type: $SiOH\text{-}H^+$, while the $CeOH^{3+}$ cations present on the surface can act as Lewis-type acid sites.

The evaluation of the acid properties of calcined materials was based on the assumption that *n*-butylamine molecules interact with all acid sites, and the total acidity of the sample studied can be determined from the maximum amount adsorbed. The thermogravimetric curves for *n*-butylamine thermodesorption, which were used to evaluate the amount of medium and strong acid sites for both samples are shown in Fig. 2. Thermodesorption of *n*-butylamine from CeMCM-41 exhibits three distinct ranges: (i) desorption of physically adsorbed amine bellow 230°C; (ii) desorption of *n*-butylamine from medium acid sites at 230–410°C (0.25 mmol g^{-1}), and (iii) its desorption from strong acid sites at 410–590°C (0.21 mmol g^{-1}). However, only one weight loss was observed for pure silica MCM-41 due to thermodesorption of physically adsorbed amine, indicating negligible acidity of this material.

Nitrogen adsorption isotherms were measured on both samples to evaluate their structural and surface

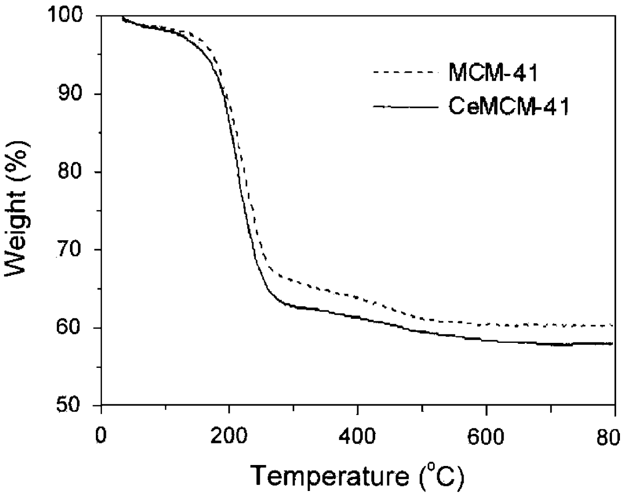

Fig. 1. TGA curves for uncalcined MCM-41 and CeMCM-41 samples.

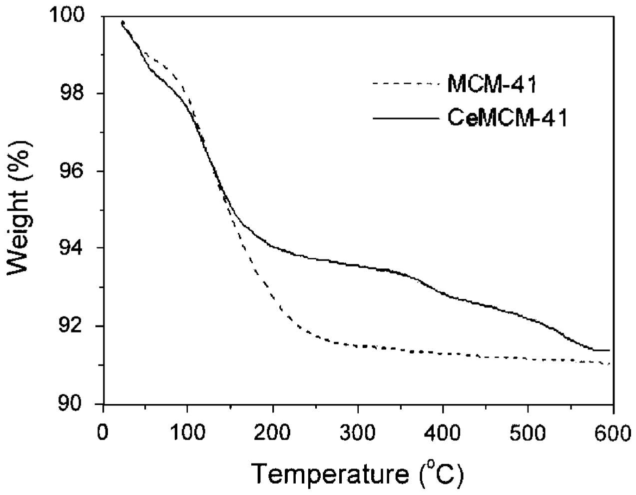

Fig. 2. TGA curves for *n*-butylamine (nBA) adsorbed on MCM-41 and CeMCM-41 materials.

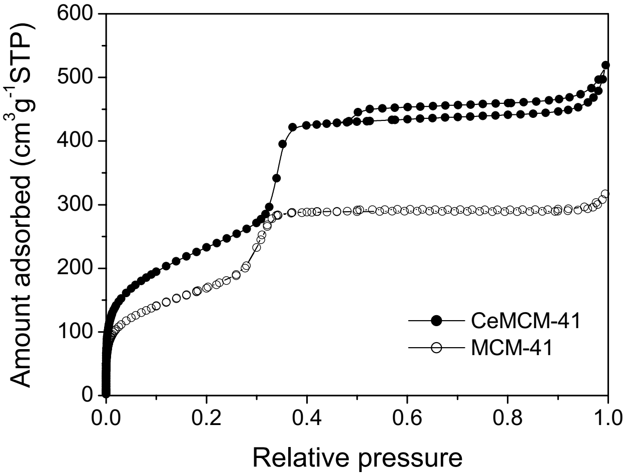

Fig. 3. Nitrogen-adsorption isotherms for the MCM-41 and CeMCM-41 samples.

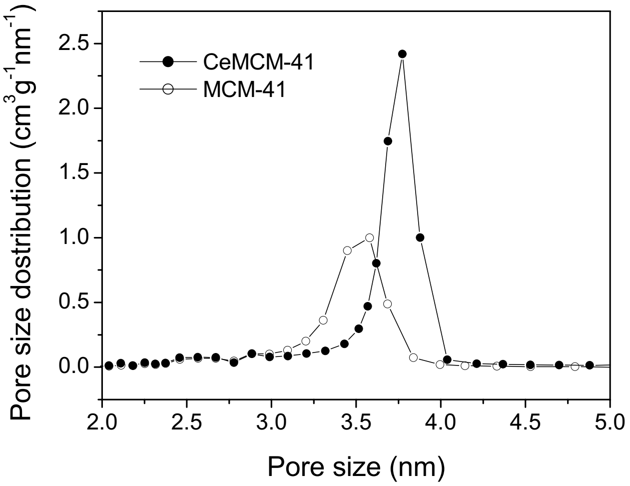

Fig. 4. Pore size distributions for the MCM-41 and CeMCM-41 samples.

properties (Fig. 3). The specific surface area was determined according to the standard Brunauer–Emmett–Teller (BET) method [22] in the relative pressure range 0.04–0.2. The total pore volume was evaluated from the amount adsorbed at a relative pressure of about 0.99. Pore size distributions were calculated according to the Barrett–Joyner–Halenda (BJH) algorithm [23].

The obtained materials exhibit the shape characteristics for nanostructured materials with uniform mesopores [24]. The step in the relative pressure range between 0.3 and 0.4 reflects nitrogen condensation in primary mesopores. For CeMCM-41 this step is sharper than that for pure silica MCM-41, which can be an indication of improving the material quality by cerium incorporation. At relative pressures greater than 0.4, an increase in the amount adsorbed on the CeMCM-41 sample is observed due to the existence of secondary (larger) mesopores, for which a type H4 hysteresis loop is observed [25]. The hysteresis loop for MCM-41 is narrow and resembles more type H1, which is characteristic for agglomerates of fairly uniform particles [25]. As can be seen in Fig. 4, the distribution of primary mesopores for CeMCM-41 is narrower than that for the corresponding MCM-41 sample. The low-pressure region of adsorption isotherms was analyzed to compare the surface properties of the CeMCM-41 and MCM-41 samples. The values of the BET surface area, the volume of primary mesopores and the pore widths corresponding to the maximum of the pore size distributions for the samples studied are given in Table 1.

Concerning the catalytic properties of the materials, the GC-MS analysis showed that the main products of *n*-heptane reaction over CeMCM-41 were CO (incomplete oxidation) and CO_2 (complete oxidation) with conversion ranging of 4 from 12% at an F/W value of 0.4–0.6, respectively (Table 2). Other products as ethane, propane and butane were obtained via catalytic cracking reactions. These reactions occur due to existence of acid sites with several forces and natures in the surface of the CeMCM-41. A gradual increase in the *n*-heptane conversion with decrease in the F/W ratio at 450°C was observed. The catalytic tests were also realized using the pure MCM-41. In this case, the catalytic activity to the *h*-heptane conversion (Fig. 5a) in comparison with CeMCM-41 material is not observed (Fig. 5b).

4. Conclusions

The CeMCM-41 material studied had much higher quality than the corresponding MCM-41 sample synthesized under the same conditions. While both materials exhibited analogous adsorption properties

Table 1
Adsorption parameters for the MCM-41 and CeMCM-41 samples

Sample	S_{BET} ($m^2 g^{-1}$)	V_t ($cm^3 g^{-1}$)	w (nm)
MCM-41	610	0.48	3.56
CeMCM-41	850	0.78	3.77

S_{BET}–BET specific surface area; V_t–single-point total pore volume; w—pore width at the maximum of the pore size distribution calculated using the BJH method with the corrected form of the Kelvin equation [24].

Table 2
Degree of conversion and selectivity of *n*-heptane oxidation over CeMCM-41 as a function of F/W ratio

F/W ($mol\,g^{-1}\,h^{-1}$)	% Conversion	% CO_2	% CO	% Ethane	% Propane	% Butane
0.04	51.4	15.6	28.4	2.1	35.8	18.1
0.05	42.5	22.9	25.4	1.2	31.9	18.5
0.06	17.1	24.1	29.5	—	46.36	—

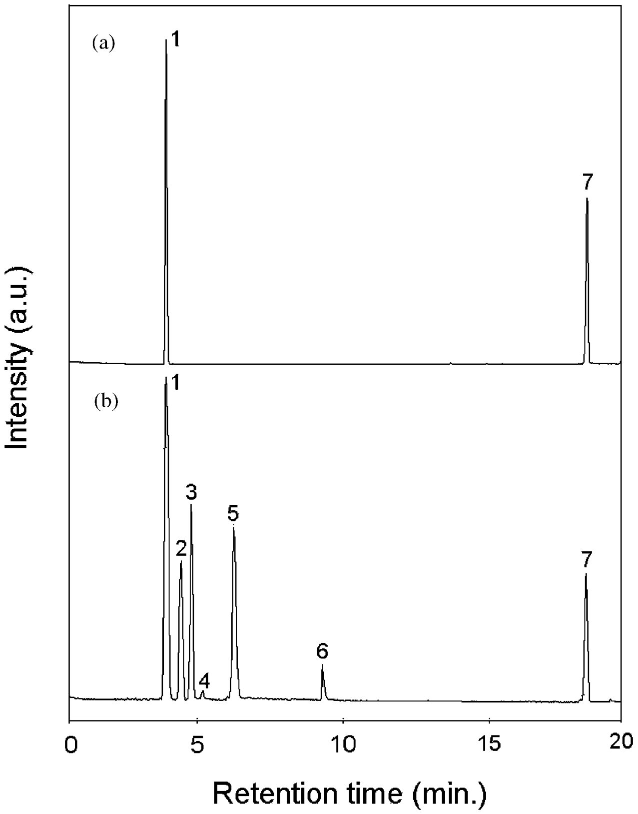

Fig. 5. Typical chromatograms of the *n*-heptane reaction over MCM-41 (a) and CeMCM-41 (b) materials at 450°C, where: 1 = air, 2 = carbon dioxide, 3 = carbon monoxide, 4 = ethane, 5 = propane, 6 = butane and 7 = heptane.

with respect to nitrogen, their interaction with *n*-butylamine was different. Thermogravimetric analysis of *n*-butylamine thermodesorption showed that CeMCM-41 possessed medium and strong acid sites in contrast to the pure silica MCM-41, the acidity of which was negligible. Thus, incorporation of cerium to MCM-41 seems to improve its hydrothermal stability and enhance the adsorption and catalytic properties for acid and oxidation reactions.

Acknowledgments

The authors would like to acknowledge the support from the *Conselho Nacional de Desenvolvimento Cientifico e Tecnologico* (CNPq Process 300291/93-0, Brazil), and the PRH-14 from *Agência Nacional do Petróleo* (ANP, Brazil).

References

[1] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[2] C.T. Kresge, M.E. Leonowicz, J.S. Beck, J.C. Vartuli, W.J. Roth, Nature 359 (1992) 710.
[3] A. Corma, M.T. Navarro, J.P. Pariente, J. Chem. Soc. Chem. Commun. 2 (1994).
[4] M. Kruk, M. Jaroniec, A. Sayari, Microporous Mater. 9 (1997) 173.
[5] A. Sayari, C. Danumah, I.L. Moudrakovski, Chem. Mater. 7 (1995) 813.
[6] A. Sayari, I.L. Moudrakovski, C. Danumah, C.I. Ratcliffe, J.A. Ripmeester, K.F. Preston, J. Phys. Chem. 99 (1995) 16373.
[7] J.S. Reddy, A. Sayari, J. Chem. Soc. Chem. Commun. 21 (1995) 2231.
[8] C.F. Cheng, H. He, W. Zhou, J. Klinowski, J.A.S. Goncalves, L.F. Gladden, J. Phys. Chem. 100 (1996) 390.
[9] A.S. Araujo, M. Jaroniec, J. Colloid Interface Sci. 218 (1999) 462.
[10] S.C. Laha, P. Mukherjee, S.R. Sainkar, R. Kumar, J. Catal. 207 (2002) 213.
[11] C.P. Jaroniec, M. Kruk, M. Jaroniec, A. Sayari, J. Phys. Chem. B. 102 (1998) 5503.
[12] A.F. Wells, Structural Inorganic Chemistry, 5th Edition, Clarendon Press, Oxford, 1984, p. 540.
[13] L. Smart, E. Moore, Solid State Chemistry: An Introduction, Chapman & Hall, London, 1992, p. 32.
[14] A. Tschope, R. Birringer, Nanostruct. Mater. 9 (1977) 591.
[15] G.A.M. Hussein, J. Anal. Appl. Pyrol. 37 (1996) 111.
[16] G.A.M. Hussein, J. Phys. Chem. 98 (1994) 9657.
[17] A. Trovarelli, Catal. Rev. 38 (1996) 439.
[18] T. Miki, T. Ogawa, M. Haneda, N. Nakuda, A. Ueno, S. Tateishi, S. Matsuura, J. Chem. Phys. 94 (1990) 6464.
[19] J.C. Jiang, G.W. Graham, R.W. McCabe, J. Schwank, Catal. Lett. 53 (1998) 37.
[20] R. Ryoo, J.M. Kim, Chem. Commun. (1995) 711.
[21] A.S. Araujo, V.J. Fernandes Jr., G.J.T. Fernandes, J. Therm. Anal. 49 (1997) 567.
[22] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.
[23] E.P. Barrett, L.J. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.
[24] M. Kruk, M. Jaroniec, A. Sayari, Langmuir 13 (1997) 6267.
[25] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1992.