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Kinetic study of template removal of MCM-41 derived from rice husk ash

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Abstract Molecular sieves MCM-41 were synthesized from rice husk ash (RHA) as alternative sources of silica, called RHA MCM-41. The material was synthesized by a hydrothermal method from a gel with the molar composition 1.00 CTMABr:4.00 SiO_2:1.00 Na_2O:200.00 H_2O at 100 °C for 120 h with pH correction. The cetyltrimethylammonium bromide (CTMABr) was used as a structure template. The material was characterized by X-ray powder diffraction, FTIR, TG/DTG, and surface area determination by the BET method. The kinetics models proposed by Ozawa, Flynn–Wall, and Vyazovkin were used to determine the apparent activation energy for $CTMA^+$ species decomposition from the pores of MCM-41 material. The results were compared with those obtained from the MCM-41 synthesized with silica gel. The synthesized material had specific surface area, size, and pore volume as specified by mesoporous materials developed from conventional sources of silica.

Keywords MCM-41 · Hydrothermal synthesis · Rice husk ash · Kinetic

Introduction

MCM-41 molecular sieves developed by researchers at *Mobil Oil Corporation* have attracted great interest since their discovery in 1992. Their physical properties, such as high specific surface area, controllable diameter, and pore volume, allow them to be applied as adsorbents, catalyst supports, and heterogeneous catalysts in various branches of the chemical industry.

The synthesis of MCM-41 is performed in aqueous alkaline conditions, basically using different sources of silica and structure template. The gel prepared with these reagents in different molar ratios of template/silicon is subjected to hydrothermal treatment, then washed and dried at room temperature. The removal of the template occurs through calcination. The best condition for calcination is of fundamental importance for obtaining a high-quality material free of organic template species with good preservation of the ordered silica structure. The variables in a typical calcination process are time, temperature, heating rate, catalyst mass, and calcination's atmosphere [1].

The synthesis conditions can be changed to obtain materials with different properties. Factors affecting the final product are molar ratio template/silica, concentration and carbon chain length of the template, temperature, pH, and nature of the silica [2, 3]. As a silica source, typically, sodium silicate, TEOS (tertaetilortosilicato), TMA-silicate (tetramethylammonium silicate), and amorphous silica are

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used. However, a disadvantage of these silicon precursors is the price, resulting in a higher production cost.

Researchers are investigating different sources of silica to produce the mesoporous silicates, particularly MCM-41. Jang [4] synthesized mesoporous MCM-41, MCM-48, and SBA-15 using rice husk ash (RHA) as the silica source. RHA was obtained by heat-treating the rice husk at 700 °C for 24 h. Sodium silicate solution was extracted by refluxing RHA (93 % SiO_2) in 2 M NaOH in H_2O at 70 °C for 24 h. Wittayakun et al. [5] synthesized AlMCM-41 with RHA, which was washed and dried at 100 °C overnight, refluxed with 3 M HCl for 6 h, filtered and washed again with water until the filtrate was neutral, and dried at 100 °C overnight before the pyrolysis in a furnace at 550 °C for 6 h to remove the hydrocarbon and volatile organic compounds. This silica source was used in the synthesis of MCM-41 with a molar composition of $4SiO_2$:1 CTMABr:0.29 H_2SO_4:400 H_2O. The mesoporous materials obtained by these silica extraction methods showed good proprieties such as high specific surface area.

RHA is the most voluminous by-product of the rice industry. The high silica content makes this residue a valuable raw material that can be used in various industry sectors. A few zeolitic materials, such as ZSM-5 [6–8], ETS-10 [9], MCM-48 [4, 10], zeolite beta [11], and mordenite [12], synthesized from RHA have been reported. Its use as a replacement of silica, conventionally used in the production of zeolites, catalyst supports, and the production of silicates among other products, reduces the process toxicity and increases its economy because it is a natural material which has a low cost. There are many methods of extraction of silica from natural sources. Many authors have suggested that acid treatment prior to heat treatment is a suitable method for extraction of natural silica [5, 13, 14].

The present study aims to synthesize the mesoporous molecular sieve MCM-41 using the RHA as a natural silica source, obtaining the global kinetic parameters of decomposition of the surfactant $CTMA^+$ in the pores of MCM-41 synthesized by model “Free Kinetics”, and compare results obtained with material synthesized with conventional silica.

Experimental

Silica extraction

The rice husk was washed with deionized water heated to 60 °C, under stirring for 20 min. This material was dried at 80 °C for 16 h, then comminuted in knives mill (TECNAL TE 631) to increase the surface area, and calcined in a muffle furnace (TECNAL 3000) at 600 °C, 10 °C min^{-1} for 2 h. The material obtained was used as the silica source for the production of RHA MCM-41.

Synthesis of MCM-41

The MCM-41 was obtained through the hydrothermal method using RHA as sources of silica, cetyltrimethylammonium bromide (CTMABr) as the structure template, sodium silicate, and distilled water. The MCM-41 was synthesized by stirring an aqueous solution containing the silica source and sodium silicate at a controlled temperature of 60 °C. After 2 h of agitation, a solution containing the CTMABr was added to the mixture at room temperature. The system was stirred for 1 h. The reactive gel, with molar composition 1.0 CTAMBr:4.0 SiO_2:1.0 Na_2O:200 H_2O resulting from this process, was put into a Teflon vial, inserted into a stainless steel autoclave, and heated in an oven at 100 °C for 120 h. The pH correction was performed every 24 h, adjusted to a range between 9 and 10 with a 30 % solution of acetic acid, until it stabilized. Sodium acetate was added to complete the stabilization of the silica at molar ratio director/salt 3 when pH stabilizes, and the system was reinserted in the oven for 48 h at 100 °C.

Characterization

A chemical analysis of the silicon precursor was performed by X-ray energy dispersive fluorescence (EDX) in a Shimadzu EDX-820 model. The FTIR spectra were obtained in a Fourier Transform of Bio-Raid Excalibur Series (model FTS 3000 MX) spectrophotometer, in KBr disks. The X-ray powder diffraction (XRD) analyses were conducted on a Shimadzu XRD-6000 diffractometer, using Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å, 30 kV, 30 mA). The samples were scanned in the 2θ range of 1°–10° with the step time of $2^\circ\ min^{-1}$ and the step of 0.02°. The BET surface area of the samples was determined by nitrogen adsorption at 77 K using Quantachrome NOVA 2000 instrument. Before the nitrogen measurement, samples were degassed at 300 °C in helium for 3 h. The wall thickness (W) of MCM-41 was obtained by the difference between the lattice parameter a_0 and the pore diameter. Thermogravimetric (TG) analysis was performed on a Shimadzu TG/DTA-60H equipment under dynamic nitrogen atmosphere 50 mL min^{-1}, heated at 30–800 °C.

Kinetic methods

The determination of global kinetic parameters via TG is based on methods proposed by Ozawa [15], Flynn–Wall [16], and Vyazovkin and Wight [17], which are models of “Free Kinetics,” which involves measuring the temperature corresponding to fixed values of conversion, α, from experiments at different heating rates, β, and plotting ln (α) against $1/T$ giving straights lines with slopes $-E_a/R$ [18]. The model, Free Kinetic, allows evaluating both simple and complex reactions kinetics, and was used to monitor the optimal time and temperature to remove the template [17]. The velocity of template decomposition $CTMA^+$ in RHA MCM-41 depends on the parameters conversion (α), temperature (T), and time of reaction (t). In each process, the reaction velocity is given as a function of conversion $f(\alpha)$ and can be determined from experimental TG data [19]. The models proposed require at least three dynamic curves with different and constant heating rates (β); in this work it was assumed as 5, 10, and 20 °C min^{-1} with temperature between 30 and 800 °C. The mass of the samples was approximately 3 mg and the carrier gas was N_2 with a flow of 50 mL min^{-1}. These models were used to determine the apparent activation energy (Eq. 1) and conversion (α) as a function of temperature.

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \tag{1}$$

Results and discussion

The chemical composition of RHA is a function of the soil where it is planted, the types and amounts of fertilizer applied, the climatic conditions, and the kind of rice. The results of the chemical analysis of RHA showed that by a simple extraction method without chemical treatment, it was possible to obtain high-purity silica (96 %).

The infrared absorption spectra of the precursor material (RHA) and the RHA MCM-41 are shown in Fig. 1. In the region of 1,082 cm^{-1} there is an intense band, related to the asymmetrical stretching of Si–O–Si, and at 798 cm^{-1} a band of lower intensity, related to the symmetric stretching of that bond (Si–O–Si), is observed. The band appearing at 3,498 cm^{-1} is related to the vibrations of axial deformation of the hydroxyl group of Si–OH [20]. These bands are also present in the RHA MCM-41 and in the silica source RHA spectra, proving the influence of this silica source in the material structure formation. The infrared spectra of RHA MCM-41 present bands between 400 and 1,400 cm^{-1}, which are fundamental vibration characteristics of the structure of MCM-41 [14, 21]. The bands appearing at 2,936 and 2,854 cm^{-1} in the spectra of non-calcined RHA MCM-41 are related to the asymmetric and symmetric axial strain, respectively, of the methylene group (CH_2) present in CTMABr, the structure template of MCM-41. It is also possible to observe the presence of bond $-CH_2Br$, a band of medium intensity in the range of 1,230 cm^{-1} (Fig. 1) [20].

The results of the XRD of RHA MCM-41 (Fig. 2) show similar characteristics to the standard XRD pattern of mesoporous materials, as three peaks at 2θ reflection = 2.12, 3.71, and 4.27. The most intense peak ($2\theta = 2.12$) was attributed to the line of the reflection plane (100), and the two others of lower intensities ($2\theta = 3.71$ and 4.27) were attributed to the reflections on the planes (110) and (200), characteristic of mesoporous hexagonal structure, as described by *Mobil Oil Research and Development Co* researchers [22], confirming that the removal of the structure template did not affect the MCM-41 structure. The XRD patterns of materials obtained from alternative sources of silica follow the same pattern of the MCM-41 synthesized with silica gel [21].

The synthesized materials have a specific surface area, size, and pore volume as specified of mesoporous materials developed from conventional sources of silica (TEOS, TMA-silicate, silica gel); however, the method of silica extraction used in this work is presented in a simpler and faster way than that discussed in the literature [4, 5, 13, 14]. Table 1 shows the results of the textural properties as pore diameter, pore volume, specific surface area, and wall thickness of the synthesized material.

The kinetic decomposition of $CTMA^+$ species from the pores of the material RHA MCM-41 was obtained from the TG curves (Fig. 3) at different heating rates (5, 10, and 20 °C min^{-1}). Three typical mass losses were observed: (i) In the temperature range of 30–100 °C due to physically adsorbed water, (ii) 100–310 °C due to the first stage of decomposition of the surfactant, and (iii) 310–600 °C due to the decomposition of the residual surfactant and condensation of adjacent silanol groups resulting in siloxane bonds [21, 23]. For step (ii), Ozawa, Flynn–Wall, and Vyazovkin models were used to determine the activation energy involved in the decomposition of the $CTMA^+$

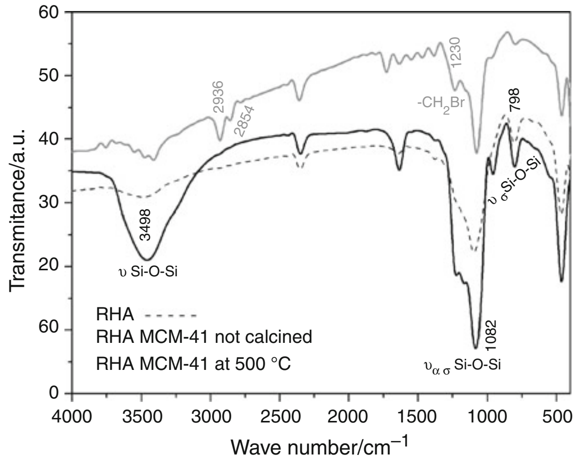

Fig. 1 FTIR *spectra* of RHA silica source and the MCM-41 synthesized

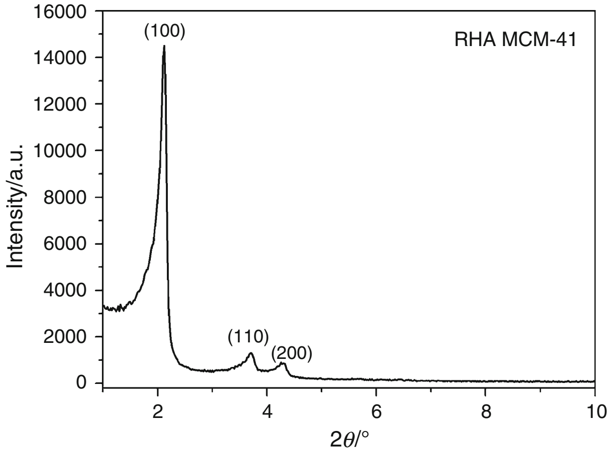

Fig. 2 XRD pattern of RHA MCM-41 calcined at 500 °C

Table 1 Textural properties of the RHA MCM-41 obtained by BET analysis

Pore diameter/nm	Pore volume/cm^3 g^{-1}	S_{BET}/m^2 g^{-1}	W/nm
3.35	0.63	757	1.47

species. Figure 4 shows the conversion curves as a function of temperature, obtained by Eq. 2:

$$\alpha = \frac{(m_0 - m_t)}{(m_0 - m_f)} \qquad (2)$$

where α is the conversion, m_0 is the initial mass of the sample, m_f is the mass of the sample at the end of the stage being studied, and m_t is the mass of the sample that varies with time (t) or temperature (T).

To calculate the apparent activation energy by the Ozawa and Flynn–Wall method, the logarithm of the heating rate (log β) versus the inverse of the conversion temperature ($1/T\alpha$) was plotted for the three heating rates.

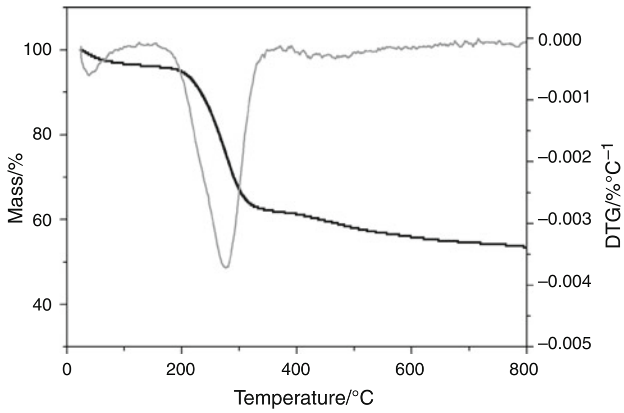

Fig. 3 TG/DTG *curves* of the uncalcined RHA MCM-41 material at heating hate of 10 °C min^{-1}

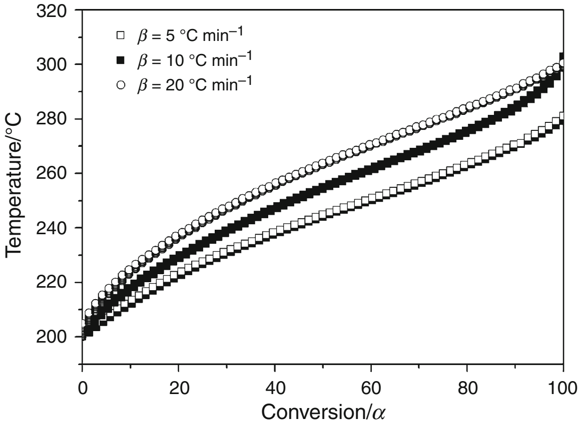

Fig. 4 Conversion *curves* as a function of temperature of RHA MCM-41

Straight lines were achieved, Figs. 5 and 6; the slope of each line corresponds to $-E_a/R$ ($R = 8.314$ J mol^{-1} K^{-1}). For the Vyazovkin method for each conversion, ln β/T_α^2 was graphed as a function of *1*/$T\alpha$, also resulting in a series of straight lines represented in Fig. 7 with the slope $-E_a/R$ [24].

It can be noted from the results shown in Table 2 that the activation energy values are very close, suggesting that the Ozawa, Flynn–Wall, and Vyazovkin methods are suitable for the determination of apparent activation energy of decomposition of CTMA$^+$ from RHA MCM-41.

During the synthesis of MCM-41 with a cationic surfactant (CTMA$^+$), the hydrophilic part of template, which has positive charge, interacts with the surface of the pore of mesoporous silica material via coulomb forces. The apparent activation energy involved in the removal process of organic species located within the pores of molecular

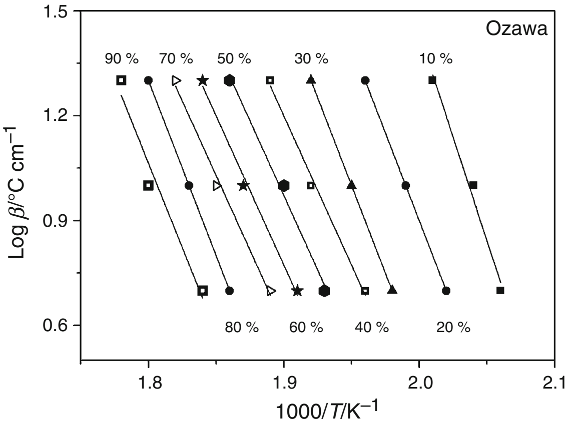

Fig. 5 Logarithm of the heating rate as a function of the inverse of the temperature for various conversion levels of the thermal decomposition stage of CTMA$^+$ in RHA MCM-41 by Ozawa method

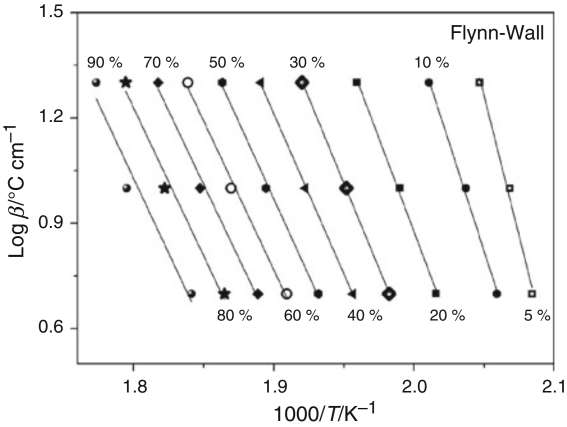

Fig. 6 Logarithm of the heating rate as a function of the inverse of the temperature for various conversion levels of the thermal decomposition stage of CTMA$^+$ in RHA MCM-41 by Flynn–Wall method

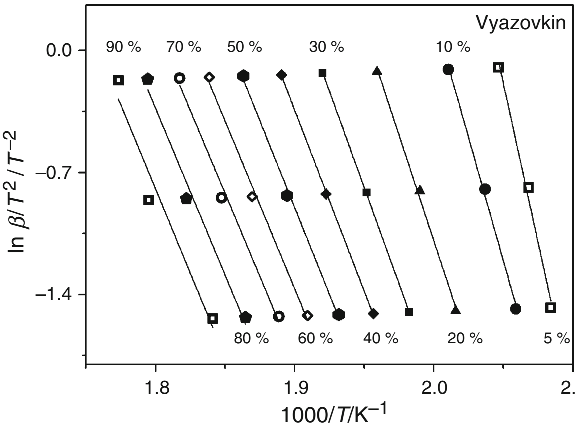

Fig. 7 *Curves* for determination of the apparent activation energy using the Vyazovkin kinetic method for decomposition of CTMA$^+$ in RHA MCM-41

Table 2 Activation energies for the 10–90 % conversions for the RHA MCM-41 obtained by the Ozawa, Vyazovkin, and Flynn–Wall methods

Conversion/ %	Ozawa E_a/ kJ mol^{-1}	Flynn–Wall E_a/ kJ mol^{-1}	Vyazovkin E_a/ kJ mol^{-1}
10	224	225	235
20	200	193	201
30	177	177	184
40	163	166	173
50	155	159	165
60	154	154	160
70	156	153	158
80	165	154	159
90	169	155	161
$E_{a\ \mathrm{average}}$	173.7 ± 23	170.7 ± 24	177.3 ± 26

sieve provides the magnitude of the interactions between the template and silica.

In this study, the apparent activation energy involved in the process of removing the CTMA$^+$ of MCM-41, in the range of 10–90 % of conversion by Vyazovkin model, has value slightly larger (177 ± 26 kJ mol^{-1}) than that found for the same material synthesized from the conventional source of silica, found by Souza et al. [21]. This can be associated with increased interaction of CTMA$^+$ with the silica wall because there are more reactive functional groups present on the surface causing structural shrinkage and reducing the sizes of the mesoporous diameters, which makes difficult the removal of residual surfactant.

Conclusions

The molecular sieve obtained from RHA as an alternative source of silica has similar properties to those synthesized materials with conventional silica, without requiring chemical treatment of RHA. The RHA, of a negligible cost, can be a promising replacement for the high cost silica. The FTIR and XRD data demonstrated that the highly pure MCM-41 was successfully synthesized from RHA. It was found that for the removal of the organic phase in the molecular sieve in this study had higher values for activation energy than the same material synthesized from the conventional source of silica. This can be associated with increased interaction of CTMA$^+$ with the silica wall because there are more reactive functional groups.

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