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Rapid synthesis of mesoporous SBA-15 molecular sieve by a microwave–hydrothermal process

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Ordered, hydrothermally stable mesoporous molecular sieve SBA-15 with hexagonal channel porosity has been synthesized for the first time under microwave–hydrothermal conditions from aged precursor gel within 15 min at 373 K; the crystallized product has been characterized using X-ray diffraction, nitrogen adsorption–desorption and transmission electron microscopy techniques.

Widespread applications of molecular sieves in the fields of separation and catalytic science have emphasised on the search for new structures with new framework compositions.[1] Thus, the last two decades have witnessed a rapid growth of molecular sieve science which has resulted in the discovery of an ordered, mesoporous molecular sieve family (designated as M41S)[2] for the first time. These materials, which can be synthesized with pore sizes from 15 to over 100 Å, are the potential candidates for a wide range of applications such as shape-selective catalysis and sorption of large organic molecules, guest–host chemistry and chromatographic separation. However, poor hydrothermal stability of these materials restricts their application potential. Thus, attempts are being made to improve their hydrothermal stability using various synthesis and post-synthesis routes. These attempts have resulted in the synthesis of the ordered, hydrothermally stable mesoporous molecular sieve SBA-15, which has been synthesized using a triblock organic copolymer as a template under hydrothermal conditions.[3] Here, we report, for the first time, a successful rapid synthesis of SBA-15 molecular sieve under microwave–hydrothermal (M–H) conditions within *ca.* 120 min. The term microwave–hydrothermal process was coined by Komarneni *et al.* in 1992 and this process has been used for the rapid synthesis of numerous ceramic oxides, hydroxylated phases, porous materials and metal powders.[4]

The microwave-assisted synthesis of molecular sieves is a relatively new area of research.[5] This method has been successfully applied for the synthesis of several types of zeolites namely zeolite A, Y, ZSM-5, MCM-41, metal substituted aluminophosphate and gallophosphate.[6–11] Microwave-assisted synthesis of molecular sieves offers many distinct advantages over conventional synthesis. They include rapid heating to crystallization temperature due to volumetric heating resulting in homogeneous nucleation, fast supersaturation by the rapid dissolution of precipitated gels and eventually a shorter crystallization time compared to conventional autoclave heating. Furthermore, it is energy efficient and economical.[4–11]

Microwave–hydrothermal synthesis of SBA-15 molecular sieve was performed using a MARS5 (CEM Corp., Matthews, NC, USA) microwave digestion system. This system operates at a maximum power of 1200 W and the power can be varied from 0 to 100% and is controlled by both pressure and temperature to a maximum of 350 psi and 513 K, respectively. A 2.45 GHz microwave frequency was used which is the same as that in domestic microwave ovens. The syntheses were carried out in double-walled digestion vessels which have an inner liner and cover made up of Teflon PFA and an outer strength vessel shell of Ultem polyetherimide. In a typical synthesis, 4 g of triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) ($EO_{20}PO_{70}EO_{20}$; M.W. 5800, Aldrich) was dispersed in 30 g of double distilled water. The resultant solution was mixed with 120 g of 2 M HCl (J. T. Baker) solution under stirring to obtain a homogeneous solution. Finally, 9.50 g tetraethylorthosilicate (TEOS, Aldrich) was added to the homogeneous solution with stirring to form a reactive gel. Thus obtained gel was allowed to crystallize under microwave–hydrothermal conditions at 373 K for the desired time. The crystallized product was filtered off, washed with warm distilled water, dried at 383 K and finally calcined at 813 K in air for 6 h. The calcined product was characterized by X-ray diffraction (X'pert system, Phillips, USA), nitrogen adsorption–desorption isotherm measurements at 77 K (Autosorb, AS-1, Quantachrome, USA) and transmission electron microscopy (JEM-2010, JEOL, Japan). To study the progress of crystallization under microwave–hydrothermal conditions, samples were prepared for 15, 30, 60, 90 and 120 min at 373 K and were characterized using X-ray diffraction and nitrogen adsorption–desorption methods. The standard SBA-15 sample was also prepared by following the reported synthesis preocedure[3b] and was used as a reference to estimate the purity of the samples obtained under microwave–hydrothermal conditions.

The specific surface area, S_{BET}, for crystallized samples was calculated by the standard BET method[12] for nitrogen adsorp-

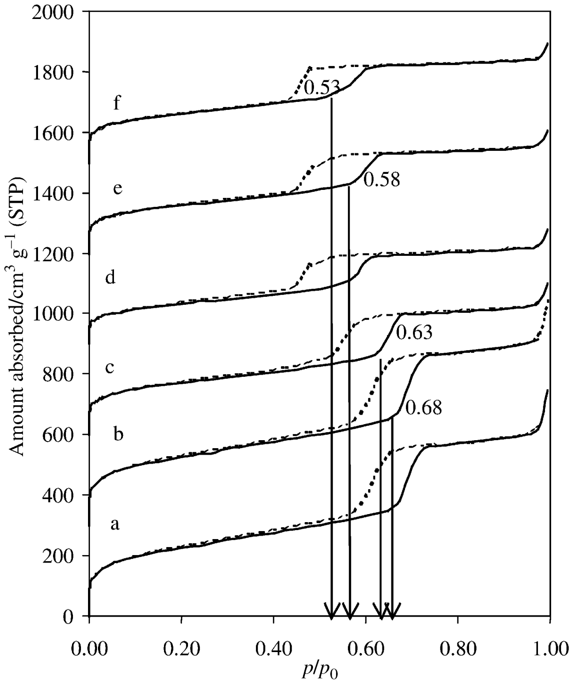

Fig. 1 Nitrogen adsorption (—)/desorption (······) isotherms for prepared samples: (a) reference, (b) 120 min, (c) 90 min, (d) 60 min, (e) 30 min and (f) 15 min; SBA-15 samples obtained under M–H conditions at 77 K. The adsorption–desorption isotherms for 15, 30, 60, 90 and 120 min samples are shifted by 1500, 1200, 900, 600 and 300 cm^3 (STP) g^{-1}, respectively.

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Table 1 Structural parameters for various samples (calcined) obtained at different time intervals

t/min	$a_0{}^a$/Å	S_{BET}/m^2 g^{-1}	S_{ex}/m^2 g^{-1}	V_{mesopore}/cm^{-} g^{-1}	V_{pore} (p/p_0 = 0.95)/cm^3 g^{-1}	p/p_0	W_{KJS}/Å
15	90.4	475.3	3.8	0.46	0.51	≈ 0.53	52.0
30	93.9	567.8	12.4	0.49	0.52	≈ 0.58	55.2
60	93.9	583.3	13.5	0.50	0.55	≈ 0.58	55.8
90	94.8	625.3	16.7	0.62	0.67	≈ 0.63	62.3
120	105.0	790.9	24.4	0.88	0.96	≈ 0.68	72.3
Reference^b	105.0	801.2	24.8	0.90	0.97	≈ 0.68	72.4

^{a} $a_o = 2d_{100}/\sqrt{3}$. ^{b} Reference sample was prepared by following the reported conventional synthesis route.[3b]

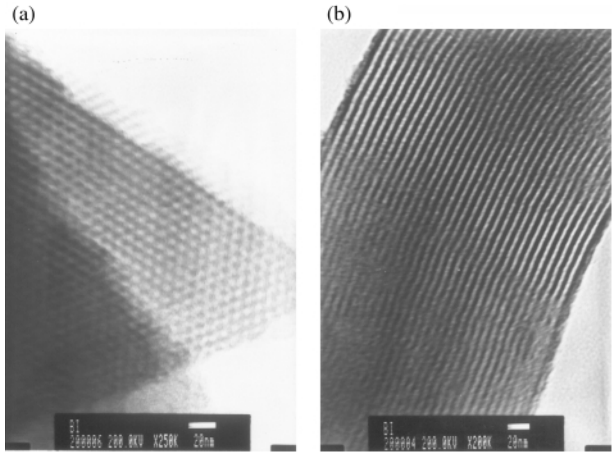

Fig. 2 Transmission electron micrographs with different orientations of a calcined hexagonal SBA-15 sample obtained at 120 min under M–H conditions.

tion data in a relative pressure range from 0.05 to 0.2. The calculation of pore size distribution (PSD) was performed by analyzing the adsorption data of the N_2 adsorption–desorption isotherm using the recently developed KJS (Kurk, Jaroniec, Sayari) approach.[13] The pore diameter corresponding to the maximum of PSD is denoted as W_{KJS}. The total pore volume was estimated from the amount adsorbed at a relative pressure of 0.95. The external surface area S_{ex}, and primary mesopore volume V_{p}, were estimated using the α_{s}-plot method, as described elsewhere.[14]

The X-ray diffraction patterns for SBA-15 samples obtained at various time intervals showed a well resolved pattern with a prominent peak at 2θ *ca.* 0.9° and two peaks at 2θ *ca.* 1.6 and 1.7° for all the crystallized samples which match well with the pattern reported for SBA-15.[3b]

Typical nitrogen adsorption–desorption isotherms for various samples are shown in Fig. 1. All the nitrogen adsorption–desorption isotherms are found to be of type IV in nature as per the IUPAC classification. The pore structure parameters for various SBA-15 samples calculated from the X-ray diffraction data and nitrogen adsorption–desorption isotherms are given in Table 1. Interestingly, the relative condensation pressure, which is a function of pore diameter, was found to increase with an increase in crystallization time which in turn reflected an increase in pore dimension and decrease in silica wall thickness for SBA-15 samples. These results are in good agreement with those reported under the conventional hydrothermal route[3b] and may be due to the rapid dehydration of EO blocks of the copolymer[15] at 373 K as a function of time under microwave–hydrothermal conditions. The condensation point for the 120 min sample was found to match with that of the reference sample (Fig. 1). Furthermore, a good agreement of pore structure parameters for the 120 min sample was observed with that of the reference sample. This indicates that the optimum reaction time for this synthesis is *ca.* 120 min at 373 K under microwave–hydrothermal conditions which is extremely short compared to the crystallization time required for conventional synthesis (*i.e.* 1–3 days). This observation is further reinforced by transmission electron microscopy (Fig. 2) which showed the ordered hexagonal pore structure with a one-dimensional channel structure of *ca.* 75 Å size, which is in close agreement with the value obtained from the KJS approach (Table 1), for a 120 min sample crystallized under M–H conditions.

In summary, the present study has established an extremely rapid synthesis method for SBA-15, which should also be applicable to other surfactants.

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