Direct Synthesis of Titanium-Substituted Mesoporous SBA-15 Molecular Sieve under Microwave−Hydrothermal Conditions

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Titanium-substituted mesoporous SBA-15 molecular sieve has been successfully prepared at 373 K by direct synthesis under microwave−hydrothermal conditions within about 2 h. By means of X-ray diffraction, nitrogen adsorption, infrared, UV−vis diffuse reflectance, and Raman spectroscopies, a successful isomorphous substitution of titanium in the silica framework of SBA-15 samples with Si/Ti ratios of 20, 30, and 40 has been reported. The substitution of Ti for Si did not change the textural properties. The higher titanium loading leads to the formation of extraframework titanium species. These results show that microwave-assisted synthesis is an ideal approach to prepare Ti-substituted SBA-15, which is expected to be useful as a selective oxidation catalyst for reactions involving large molecules.

Introduction

The introduction of Ti-containing molecular sieves has added a new dimension to the applications of molecular sieves in oxidation catalysis.[1] Titanium silicate, TS-1, and TS-2 with MFI and MEL structures, respectively, were shown to be active for selective oxidation of a variety of organic compounds in the presence of hydrogen peroxide.[2,3] The use of Ti zeolites as oxidation catalysts was further expanded with a successful synthesis of a large pore Al/ Al-free Ti-β zeolite.[4−6] However, their applications were restricted to molecules smaller than 7 Å owing to the pore size limitation. In 1992, this barrier was overcome with the introduction of mesoporous molecular sieves (M41S) which have been synthesized using the surfactant templating approach.[7] This family mainly consists of three members, namely, MCM-41, MCM-48, and MCM-50. MCM-41 and related materials, which can be synthesized with pore sizes from 15 to over 100 Å,[8] are the potential candidates for wide range of applications such as shape-selective catalysis and sorption of large organic molecules, guest−host chemistry, and chromatographic separation.[9] Owing to these advantages, the first successful synthesis of Ti−MCM-41 was performed within 2 years of its discovery.[10] So far, numerous attempts have been made to prepare a Ti-containing MCM-41 mesoporous molecular sieve with various pore sizes to obtain an effective selective oxidation catalyst for large molecules such as cyclododecene.[11−13] However, poor hydrothermal stability of MCM-41 has so far restricted its application potential from a commercial point of view. Thus, attempts are being made to improve their hydrothermal stability using various synthesis and postsynthesis routes.

These efforts have resulted in a successful synthesis of hydrothermally stable SBA-15 silica molecular sieve with uniform hexagonal channels ranging from 50 to 300 Å.[14,15] This molecular sieve has been synthesized using a triblock organic copolymer as a template under hydrothermal conditions.[15] Owing to its structural characteristics, titanium-substituted SBA-15, if proven to be stable unlike Ti−MCM-41[16] in aqueous hydrogen peroxide, could serve as a versatile selective oxidation catalyst for many large molecules and hence could be an ideal candidate for fine chemicals and pharmaceutical industries. So far, to the best of authors' knowledge,

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successful attempts for the direct synthesis of Ti−SBA-15 have not been reported. Nevertheless, an attempt has been made to prepare Ti-substituted SBA-15 via a postsynthesis grafting route wherein all silica SBA-15 sample was exposed to titanium ion solution.[17] Such a procedure has been successfully applied to obtain Ti−MCM-41.[18] However, in the case of SBA-15, this procedure has led to a very low isomorphous substitution of titanium for silicon inside the framework (Si/Ti = 80).[17] Furthermore, another attempt to achieve a high degree of substitution (Si/Ti = 5, 10, 20) has resulted in the loss of textural properties, especially pore size, of the SBA-15 molecular sieve.[17] Therefore, efforts need to be focused on the synthesis of Ti−SBA-15 to achieve high substitution. Direct synthesis of Ti−SBA-15 through a conventional hydrothermal synthesis approach may not be a possible alternative as SBA-15 is synthesized in strong acidic media. To achieve this goal, we have concentrated our research efforts on a nonconventional route, namely, microwave-assisted−hydrothermal (M−H) synthesis. The term microwave−hydrothermal process was coined by Komarneni and colleagues[19] in 1992, and this process has been used for the rapid synthesis of numerous ceramic oxides, hydroxylated phases, and porous materials.[19−22]

The microwave-assisted synthesis of molecular sieves is a relatively new area of research.[23] It 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 those of conventional autoclave heating.[23] Furthermore, it is energy-efficient and economical.[23] 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.[23] It has also been successfully applied for the synthesis of mesostructured thiogermanates/germanium sulfides.[24] Recently, a rapid synthesis of titanium-substituted MCM-41 molecular sieve has also been reported using the microwave-assisted approach.[25]

In the present investigation, we report a successful direct synthesis of Ti−SBA-15 up to a bulk Si/Ti ratio of 20, under microwave−hydrothermal conditions. To the best of our knowledge, such a high level of Ti-substitution, without any loss in textural properties of SBA-15, has not been reported so far under conventional hydrothermal synthesis conditions. Thus, we believe, it is a significant step toward the preparation of SBA-15 based oxidation catalyst. The crystallized samples have been characterized with the help of X-ray diffraction, nitrogen adsorption, infrared, diffuse reflectance UV−vis, and Raman spectroscopies to distinguish the nature of titanium species inside the SBA-15 channel.

Experimental

Sample Preparation. Ti-substituted SBA-15 samples were prepared using tetraethyl orthosilicate, TEOS, (Aldrich) and titanium chloride, $TiCl_4$, (Aldrich) as silica and titanium sources, respectively.

A triblock polymer, poly(ethyleneoxide)−poly(propylene oxide)−poly(ethylene oxide), ($EO_{20}PO_{70}EO_{20}$; MW 5800, Aldrich) referred to hereafter as EO−PO−EO, was used as a structure-directing agent. Typically, 2 g of triblock EO−PO−EO was dispersed in 15 g of double-distilled water. The resultant solution was mixed with 60 g of a 2 M HCl (J. T. Baker) solution containing the requisite amount of titanium chloride under stirring to obtain a homogeneous solution. Finally, 4.25 g of tetraethyl orthosilicate (TEOS, Aldrich) was added to the homogeneous solution with stirring to form a reactive gel with a composition of 2 g of polymer: 0.020 mol SiO_2/x mol TiO_2/0.12 mol HCl/3.92 mol H_2O ($x = 0/0.004/0.002/0.001/0.00066/0.0005$; for Si/Ti = ∞, 5, 10, 20, 30, and 40 respectively). The gel thus obtained was subjected to microwave−hydrothermal conditions for crystallization under static conditions at 373 K for 2 h. Microwave−hydrothermal synthesis was performed using MARS5 (CEM Corp., Matthews, NC) microwave digestion system. This system operates at a maximum power of 1200 W, and power can be varied from 0 to 100% and is controlled by both pressure as well as 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. The crystallized product was filtered, washed with warm distilled water, dried at 383 K, and finally calcined at 813 K in air for 6 h.

Characterization. X-ray diffraction patterns were recorded using a Philips X'pert powder diffractometer system with Cu Kα radiation (40 kV, 40 mA) with a 0.02° step size and 1 s step time over the range $0.5° < 2\theta < 6°$. The samples were prepared as thin layers on aluminum sample holder.

The textural properties of the samples were evaluated using nitrogen adsorption/desorption measurements with an Autosorb-1 (Quantachrome) unit. Nitrogen adsorption/desorption isotherms were measured at 77 K after samples were degassed below 10^{-3} Torr at 473 K for 4 h. The BET specific surface area (S_{BET}) was estimated using adsorption data in a relative pressure range from 0.05 to 0.2. The external surface area, S_{ex}, and primary mesopore volume, V_p, were estimated using the α_s -plot method, as described elsewhere.[26,27] Amorphous nonporous silica ($S_{BET} = 7.0$ m^2/g, Thiokol) was used as a reference adsorbent. The calculation of mesopore size distribution (PSD) was performed by analyzing the adsorption data of N_2 isotherm using the recently developed KJS (Kruk−Jaroniec−Sayari) approach.[28] The pore diameter corresponding to the maximum of PSD is denoted as W_{KJS}. The total pore volume, V_t, was estimated from the amount adsorbed at a relative pressure of 0.95.

UV−vis diffuse reflectance spectra (DRUV) were measured with a Varian CARY 3E double-beam spectrophotometer. Powders were loaded in a quartz cell, and spectra were collected in the wavelength range from 190 to 600 nm against a siliceous SBA-15 standard.

IR spectra were recorded on a Nicolet Magna 560 FTIR spectrometer with 2 cm^{-1} resolutions using the KBr pellet technique. The pellets contained 1% finely powdered sample and were pressed at 4 ton/cm^2 under vacuum.

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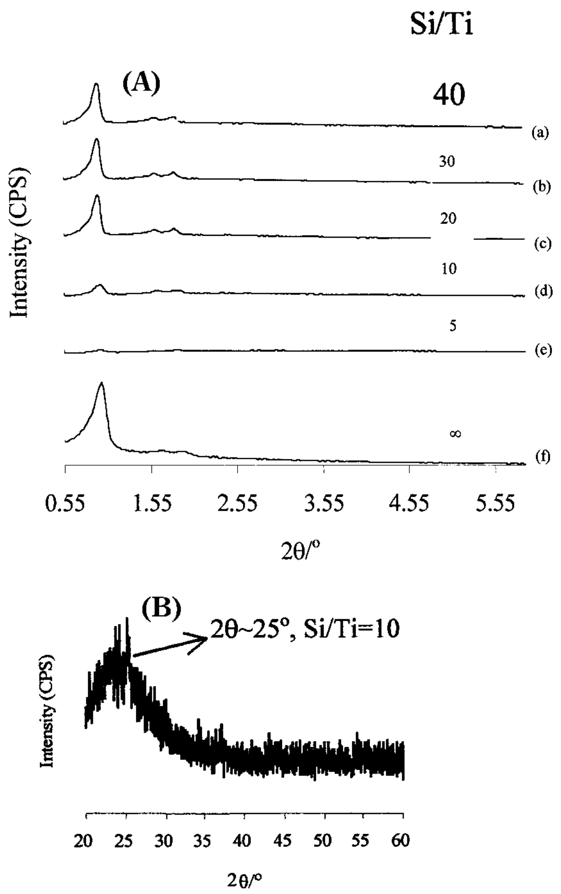

Figure 1. (A) X-ray diffraction pattern for the calcined Ti−SBA-15 samples with bulk Si/Ti ratios of (a) 40, (b) 30, (c) 20, (d) 10, (e) 5, and (f) ∞ obtained under M−H conditions. (B) High-angle X-ray diffraction data for calcined Ti−SBA-15 sample with a bulk Si/Ti ratio of 10.

Raman spectra were generated on a conventional scanning Raman instrument, ISA U1000, at room temperature in the wavelength range from 200 to 1300 cm^{-1} using a 514 nm line from a Coherent 90-6 Ar^+ ion laser. The spectrophotometer was advanced in 1 cm^{-1} increment during the scan.

Results and Discussion

A minimum crystallization time of 2 h has been reported for the preparation of a highly ordered SBA-15 molecular sieve under microwave−hydrothermal conditions.[29] Hence, all syntheses were performed for 2 h and crystallized samples were subjected to characterization. The obtained results are discussed in the following sections, and the Si/Ti ratios of the prepared samples are treated on a bulk basis.

X-ray Diffraction Analysis. Calcined siliceous SBA-15 and Ti−SBA-15 samples with varying titanium loading displayed a well-resolved pattern with a sharp peak at about 0.8° and two weak peaks at about 1.6° and 1.7° that matched well with the reported pattern[15] (Figure 1A). However, the intensities of the peaks are found to decrease with an increase in titanium loading.

The XRD peaks are indexed to a hexagonal lattice with $d(100)$ spacing corresponding to a large unit cell parameter (a_0). The estimated unit cell parameters for the calcined samples are given in Table 1. The unit cell parameters for Ti−SBA-15 (Si/Ti = 20, 30, and 40) samples are found to be higher compared to nonsubstituted SBA-15 sample. Such expansion of the unit cell parameter may indicate the successful incorporation of titanium (up to Si/Ti = 20) in the framework. However, parameters under high titanium loading (Si/Ti= 5, and 10) are found to be similar to those of siliceous SBA-15 sample. Hence, the formation of titanium dioxide is anticipated during syntheses at higher loading. To learn more about the state of the formed titanium dioxide, X-ray diffraction data of the corresponding high-angle region ($2\theta = 20°-60°$) is collected. Typical XRD data in the high angle region for the sample having Si/Ti = 10 is shown in Figure 1B. The measured data showed a band corresponding to the trace Ti(IV) in anatase at about $2\theta \sim 25°$, and those of Rutile phase ($2\theta \sim 54$ and 56°) are absent.[11] These bands are not observed for samples having Si/Ti ratios of 20, 30, and 40. Additional evidence for the presence of anatase phase is also obtained from UV−vis diffuse reflectance, and Raman spectroscopies.

Nitrogen Adsorption. Figure 2 shows nitrogen adsorption/desorption isotherms for siliceous SBA-15 and various Ti−SBA-15 samples. The estimated textural parameters such as specific surface area, S_{BET}, external surface area, S_{ex}, primary mesopore volume, v_p, and micropore volume, v_{mi}, total pore volume, V_p, and mesopore size, W_{KJS}, for various samples are compiled in Table 1. The obtained mesopore size distribution based on the KJS approach for each sample is shown in Figure 3. All of the nitrogen adsorption/desorption isotherms are found to be of Type IV in nature as per the IUPAC classification and exhibited a H1 hysteresis loop which is typical of mesoporous solids.[30] Furthermore, the adsorption branch of each isotherm showed a sharp inflection at a relative pressure value of about 0.68. This is a characteristic of capillary condensation within uniform pores.[26] The position of the inflection point is clearly related to a diameter in the mesopore range, and the sharpness of these steps indicates the uniformity of the mesopore size distribution.[26] A good match between the points of inflection on the adsorption branch of each isotherm suggests that all of the samples have similar pore size. The pore size distribution curves shown in Figure 3 show an average pore size of about 76 Å for samples having Si/Ti ratios of 5, 10, 20, and 30, whereas an average pore size of about 73 Å is obtained for samples with Si/Ti ratios of 40 and ∞. Furthermore, a narrow pore size distribution is observed for all of the samples except for the sample with the highest titanium loading wherein the presence of smaller pores of about 32, 40, and 52 Å are noticed. Interestingly, an increase in the mesopore size is noticed with an increase in titanium loading. Such a trend may correspond to a decrease in wall thickness of the crystallized samples with an increase in titanium loading. These results indicate that the titanium-substituted SBA-15 could be crystallized without any decrease in mesopore size via a direct synthesis approach under microwave−hydrothermal conditions. Also, a good agreement of the textural

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Table 1. Structural Parameters for Various Ti–SBA-15 Samples Prepared under Microwave–Hydrothermal Conditions[a]

Si/Ti ratio	d_{100} (Å)	a_o[b] (Å)	BET spec. surf. area S_{BET}, (m^2/g)	ext. surf. area S_{ex}, (m^2/g)	prim. mesopore vol. V_p (cm^3/g)	pore vol. V_t,[c]	prim. mesopore size W_{KJS} (Å)
5	89.96	103.9	767.1	15.8	0.78	0.83	76.2
10	89.96	103.9	860.5	24.0	0.86	0.91	76.0
20	90.92	104.9	830.4	18.7	0.95	1.01	76.1
30	93.95	108.5	859.5	26.7	0.95	1.04	76.4
40	93.95	108.5	844.7	16.7	0.87	0.96	73.2
∞	89.01	102.7	811.2	25.8	0.91	0.98	73.4

[a] Syntheses are performed at 373 K for 2 h. [b] $a_o = 2/(3)^{1/2} \times d_{100}$. [c] At $p/p_o = 0.95$ (cm^3/g)

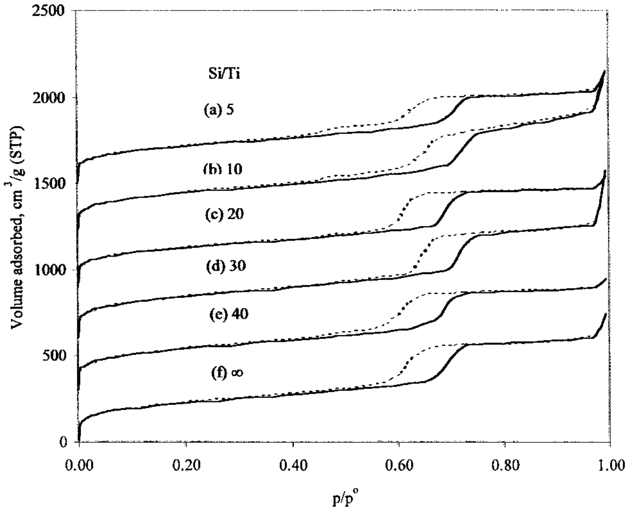

Figure 2. Nitrogen adsorption (–)/desorption (·) isotherms for various Ti–SBA-15 samples obtained under M–H conditions at 77 K. The adsorption/desorption isotherms for samples with bulk Si/Ti ratios of (a) 5, (b) 10, (c) 20, (d) 30, (e) 40, and (f) ∞ are shifted by 1500, 1200, 900, 600, 300, and 0 cm^3 STP/g, respectively.

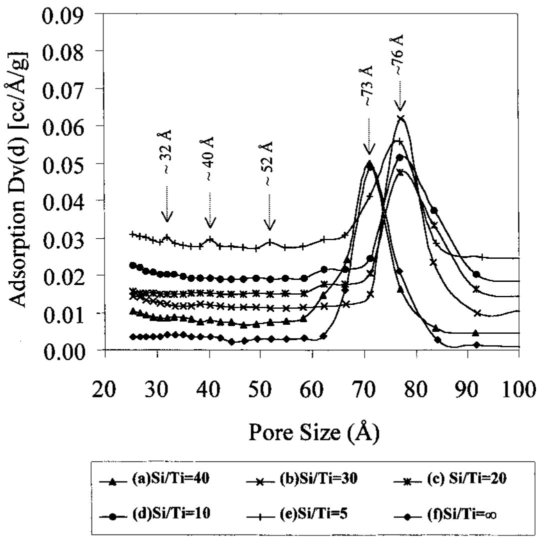

Figure 3. Pore size distribution for various Ti–SBA-15 samples with Si/Ti ratios. The adsorption/desorption isotherms for samples with bulk Si/Ti ratios of (a) 40, (b) 30, (c) 20, (d) 10, (e) 5, and (f) ∞ are shifted by 0.004, 0.008, 0.012, 0.016, 0.024, and 0 cm^3/Å/g, respectively.

properties such as specific BET surface area, primary mesopore volume, external surface area, and total pore volume for Ti–SBA-15 samples and the siliceous SBA-15 sample (Table 1) has further reinforced this observation. This is in contrast to the postsynthesis approach wherein a gradual decrease in mesopore size has been reported with an increase in titanium loading.[17]

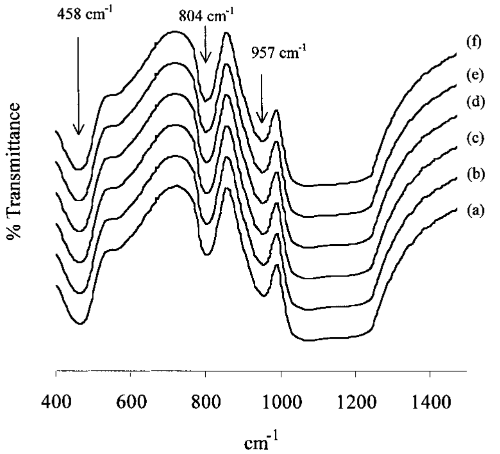

Figure 4. FTIR absorption spectra in the 1500–400 cm^{-1} region of various calcined Ti–SBA-15 samples with different titanium loading corresponding to bulk Si/Ti ratios of (a) 5, (b) 10, (c) 20, (d) 30, (e) 40, and (f) ∞.

Fourier Transform Infrared Spectroscopy. Figure 4 shows the spectra of the siliceous and Ti-containing SBA-15 samples in the region 1500–400 cm^{-1}. The IR spectra for Ti–SBA-15 and pure SBA-15 samples show characteristics absorption bands at ca. 457, 804, and 957 cm^{-1}. These bands are usually assigned to δ(Si–O–Si), ν_s(Si–O–Si), and ν_{as}(Si–O–Ti), respectively.[11]

It is well-known that an absorption band in the 950–975 cm^{-1} region characterizes the vibrational spectrum of titanium silicate and may be considered the fingerprint of framework titanium.[31] It was first assigned to Ti=O groups.[1] However, such assignment has been discounted and interpreted in terms of Si–OH groups and Ti–O–Si bonds.[32] Its exact position depends on many parameters such as the amount of adsorbed water, crystallite size, etc.[33] This band is at ca. 957 cm^{-1} for all of the titanium-substituted SBA-15 samples (Figure 4). A similar absorption band is also found to be present for the siliceous SBA-15 sample, and its presence can be attributed to the silanol groups (band at ca. 3613 cm^{-1}, not shown in Figure 4) present in the siliceous sample even in the absence of Ti (IV) species. Therefore, on the basis of IR spectrometry, framework titanium may be considered as a structural defect rather than an atom isomorphously substituted for silicon in the silica framework of SBA-15.

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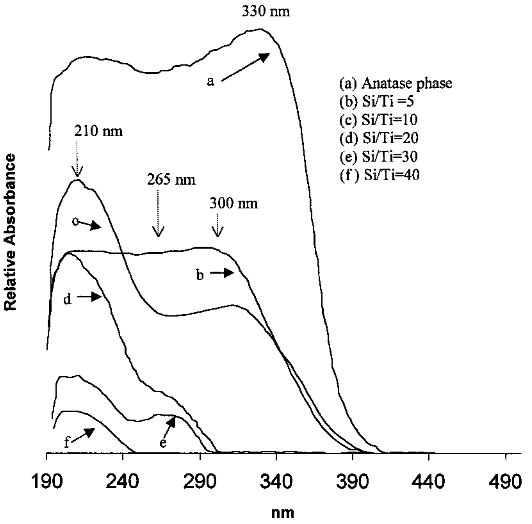

Figure 5. Diffuse reflectance UV−visible spectra of anatase phase (a) and calcined Ti−SBA-15 samples with different titanium loading corresponding to bulk Si/Ti ratios of (b) 5, (c) 10, (d) 20, (e) 30, and (f) 40.

Diffuse UV−vis Reflectance Spectroscopy (DRUV) and Raman Spectroscopy. UV−vis diffuse reflectance spectroscopy is extensively used and is perhaps one of the best technique to detect the framework and extraframework titanium species.[31] In addition to this, X-ray absorption spectroscopy is also a powerful technique to distinguish the state and coordination of titanium ions present in micro- and mesoporous titanium-substituted molecular sieves.[31] The DRUV spectrum of Ti-containing materials has two important regions; the first area, with a maximum at about 200−220 nm and absorption onset at about 290 nm, is due to a charge-transfer process in isolated [TiO_4] or [$HOTiO_3$] units.[31] This charge transfer occurs with electron excitation from the ligand oxygen to an unoccupied orbital of the central titanium ion. Therefore, it is directly connected with the framework Ti^{4+} with tetrahedral coordination, and any changes of its position or intensity during treatments are related to changes of the state or coordination of these ions.[31] Furthermore, a low-energy charge-transfer transition between tetrahedral oxygen ligands and central Ti^{4+} ions is also reflected in the absorption band at 265 nm.[34] The second band is characteristic for Ti(IV) particles (anatase) with a maximum at about 330 nm and absorption onset at about 390 nm.[31]

Figure 5 shows the ultraviolet spectra of a series of Ti−SBA-15 samples and TiO_2 anatase phase. The absorption band maximum is observed at about 210 nm for samples having Si/Ti ratios of 20, 30, and 40, and its intensity is found to decrease monotonically with an increase in Si/Ti ratio. Interestingly, a second absorption band maxima at about 265 nm is also noticed for the sample having a Si/Ti ratio of 30. Such a band is also observed to be present in the form of a shoulder for the sample having a Si/Ti ratio of 20. This has suggested the presence of a low-energy charge-transfer transition process as described above. This shows successful isomorphic substitution of titanium inside siliceous framework SBA-15. Interestingly, the sample with a Si/Ti ratio of 10 shows the presence of absorption band maxima at about 210 and 300 nm, which correspond to the presence of framework as well as extraframework titanium species and represent the partial isomorphic substitution. A further increase in titanium loading (Si/Ti = 5) also shows a broad absorption band at about 300 nm. The bands near 290 nm represents a blueshift from the 330 nm band for bulk TiO_2 anatase.[34,35] Such a blueshift has been reported for dispersed TiO_2 nanoparticles on silica and is so interpreted here. Therefore, higher titanium loading leads to the formation of TiO_2 nanoparticles. These results were further confirmed with the help of Raman spectroscopy (see below).

When extraframework titanium oxide species are present, they can belong to a segregated phase such as anatase TiO_2 and can be detected with Raman spectroscopy as it is extremely sensitive to TiO_2 nanoparticles with minimum detection limit of 0.05 wt % due to their strong scattering properties[36,37] Raman spectra for SBA-15 samples with higher titanium content (Si/Ti = 5 and 10) show bands at 394, 517, and 643 cm^{-1} (figure not shown) which are characteristic of a TiO_2 anatase phase.[34] This follows the reported trend for the postsynthesis preparation of Ti−SBA-15.[17] Furthermore, the intensities of these bands were not found to increase with an increase in titanium loading. To confirm the formation of particles within the pores, additional information (e.g., from TEM) is required. In addition, this would lead to a reduced pore diameter and smaller specific surface area with a higher degree of titanium loading; both effects were not observed in the materials presented in this study. Therefore, the formation of a titanium oxide film inside the mesoporous channels could not be confirmed. No such bands, however, are observed for Ti−SBA-15 with low titanium loadings (Si/Ti = 20, 30, and 40), which in turn suggest successful titanium incorporation (up to Si/Ti = 20) into the silica framework of SBA-15 under microwave−hydrothermal conditions. This is a substantial improvement compared to the postsynthesis method that reports a framework substitution of titanium at very low loading (Si/Ti = 80) inside the silica framework of SBA-15.[17]

Mechanism of Titanium Substitution. The above characterization results suggest a successful isomorphous substitution of titanium inside the siliceous framework of SBA-15 under microwave−hydrothermal conditions. Hence, attempts are made to investigate the mechanism of formation of Ti−SBA-15 under microwave−hydrothermal conditions.

It has been proposed that the assembly of the mesoporous silica organized by triblock copolymer species in acid media occurs through a $(S^{\circ}H^{+})(X^{-}I^{+})$ pathway.[15] Furthermore, the relative times required for silica mesophase precipitation to occur depend on the acid anion and are found to be the shortest in the presence of Cl^{-} anion when used in the form of hydrochloric acid.[15] The precipitation time was also found to decrease with an increase in Cl^{-} concentration.[15] Thus, the use

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of $TiCl_4$ as a titanium source in the present study seems to be critical for the successful incorporation of titanium into the SBA-15 framework. $TiCl_4$ used under acidic conditions is proposed to undergo hydrolysis to produce a highly reactive titanium oxychloride and hydrochloric acid. This in turn is expected to undergo a heterocondensation polymerization reaction with partially hydrolyzed alkoxysilane (TEOS) to produce additional hydrochloric acid as per the following reaction:

$$(EtO)_3Si{-}OH + Cl{-}TiO{-}Cl + HO{-}Si(OEt)_3 \rightarrow (EtO)_3Si{-}O{-}TiO{-}O{-}Si(OEt)_3 + 2HCl$$

Such heterocondensation polymerization reactions are reported to be fast with respect to homocondensation reaction between partially hydrolyzed silica species.[38] This would lead to an increase in Cl^- anion concentration and would eventually decrease precipitation time for the mesophase silica formation which is expected to follow the proposed reaction mechanism.[15] Under the influence of microwaves, the polymerization of these reactive species is believed to be fast due to rapid heating and fast supersaturation. Hence, the role of titanium source as well as microwave heating happens to be critical for a successful incorporation of a titanium-substituted mesoporous SBA-15 molecular sieve.

Conclusions

Direct synthesis of titanium-substituted molecular sieve SBA-15, up to Si/Ti = 20, has been achieved using titanium chloride as a titanium source under microwave–hydrothermal conditions within 2 h at 373 K without any loss in textural properties. The higher titanium loading (Si/Ti = 5 and 10) leads to the formation of titanium dioxide, apparently an anatase phase within the mesoporous channels of SBA-15. The role of the titanium source is believed to be important for successful incorporation as well as rapid precipitation of Ti–SBA-15 under microwave–hydrothermal conditions. On the basis of the obtained results, the microwave–hydrothermal synthesis approach is believed to be an ideal way to prepare titanium-substituted SBA-15 mesoporous molecular sieve, which is expected to be useful as a selective oxidation catalyst for large organic molecules.

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