Synthesis and Characterization of Titanium-Containing Mesoporous Silica by a Non-Hydrothermal Microwave Method

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We report on a new method for preparing mesoporous silica and titanium-containing mesoporous silica using microwave (MW) synthesis under non-hydrothermal conditions. The materials were characterized by XRD, nitrogen adsorption, UV-vis and FTIR techniques, and compared with a sample prepared by the conventional method. A single peak at $2\theta = 2.4°$ in the XRD pattern showed the formation of mesoporous silica. A typical isotherm, characteristic of a mesoporous material where pore filling occurred at p/p_0 in the range of 0.2—0.3 was obtained for nitrogen sorption. UV-vis diffused reflectance spectra showed bands at 210—220 nm and a shoulder at 270 nm, indicating the presence of Si–O–Ti bonds for titanium-containing mesoporous silica. This new method has been observed to have inherent advantages over reported methods, such as instant start up, a short heating time and low cost. These mesoporous titanosilicates prepared using a microwave heat energy source are active in the oxidation of 2,6-diisopropylphenol (DIPP) and 2,6-di-*t*-butylphenol (DTBP) with hydrogen peroxide as an oxidant.

New synthesis routes have been undertaken for increasing the pore diameter of molecular sieves in order to extend their use to process bulkier molecules in catalytic reactions. Recently, scientists from Mobil Research Corporation invented mesoporous molecular sieves, M41S.[1] These materials were synthesized hydrothermally in the presence of surfactant supramolecular templates, and their pore diameter could be obtained in the range of 15—100 Å.

The hydrothermal crystallization of molecular sieves at various temperatures in the presence of structure guiding agents has been reported. 5owever, very few reports mention the use of microwaves as a heat energy source.[2,3,4] Wha-Seung Ahn and many others have prepared Ti-MCM-41 by the MW hydrothermal synthesis method, in which a gel is transferred in a Teflon® autoclave and kept in an MW oven from 10 min to a few hours at different temperatures.[5] The main reaction during the crystallization process is that of oligomerization of the type (–OH–Si–OH–Si–) forming –Si–O–Si– linkages. Also, it is reported that 2460 MHz frequency is selectively absorbed by the R–OH type of dipoles. MW application is likely to accelerate the molecular-sieve framework formation through such oligomerization. Conventionally, HMS is synthesized[6] by an aging process under specific preparation conditions. In the present paper we report on the synthesis of mesoporous silica by the application of MW, which does not involve a hydrothermal or aging step of crystallization, and only three minutes are required for the synthesis.

Experimental

Materials were synthesized according to the neutral templating mechanism. The gelation procedure used to synthesize siliceous and metal-containing mesoporous silica was similar to that described in the literature.[6,7] In a typical preparation, 2 g dodecylamine (DDA) was dissolved in 12 g of ethanol. The solution was added to 8.37 g of tetraethyl orthosilicate (TEOS) under stirring. Three ml of 0.4 M HCl (1 M = 1 mol dm^{-3}) was added so that the pH became 8—9. The reaction mixture was kept for aging for two days, or exposed to MW radiation for 3 min when there was no hydrothermal treatment. After the aging/MW treatment the solid product was collected by filtration and washed with ethanol. More than 85% of the template could be removed by Soxhlet extraction. The solid was then calcined at 550 °C in air for 12 h. The yield of the product was 95% on the basis of Si. Ti was incorporated by adding titanium tetrabutoxide (Si/Ti = 50, 30, 20) in isopropyl alcohol as a source material into the starting mixture.

All of the reactions were carried out batch wise in a 100 ml round-bottom flask fitted with a reflux condenser with continuous stirring. In a typical run, 100 mg of a catalyst was dispersed in a solution containing 1.35 g (10 mmol) of 2,6-diisopropylphenol, 3.4 g, 30 wt% H_2O_2 (30 mmol) and 7.0 ml acetone. The mixture was vigorously stirred and heated under reflux for 5 h. After the reaction, the catalyst was filtered off and the products were analysed in a gas chromatograph (Shimadzu GC 15A fitted with a capillary column (HPI) and FID detector. The identity of the product was confirmed by GC-FTIR and GC-MS.

The X-ray powder diffraction spectra (XRD) were recorded on a Philips instrument using Cu-$K\alpha$ radiation (1.5404 Å). Nitrogen adsorption-desorption isotherms were obtained using a Coulter Omnisorp 100 CX. The FTIR spectra were recorded on a Shimadzu-8300 spectrometer in a Nujol matrix, and the UV-vis diffused reflectance spectra were recorded on a UV-2101 pc UV-vis scanning spectrophotometer (Shimadzu). MW synthesis was carried out us-

ing a domestic microwave heater (BPL model BMO 100T-2460 MHz).

Results and Discussion

The XRD pattern of mesoporous silica prepared by a MW treatment shows a single peak at $2\theta = 2.4°$ with a d-spacing of 36.4 Å, and is comparable to the XRD pattern of HMS reported by Tanev et al.[7] (Fig. 1). Such a single peak in XRD is characteristic of mesoporous silica, unlike the XRD spectrum of MCM-41, which shows weak reflections of planes corresponding to 110, 200 and 210. The XRD pattern of mesoporous silica is broad compared to the XRD pattern of MCM-41. The XRD patterns of mesoporous silica and Ti-containing mesoporous silica prepared by the MW method are almost identical.

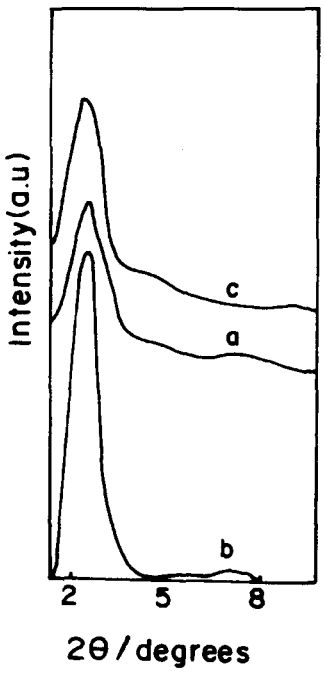

Fig. 1. X-ray diffraction patterns of a) mesoporous silica prepared by conventional method, b) mesoporous silica prepared by microwave method, and c) Ti-containing mesoporous silica prepared by microwave method.

UV-vis diffused reflectance spectra of Ti-containing mesoporous silica (Si/Ti = 20, 30, 50) along with TS-1 are shown in Fig. 2. A broad band at 210—220 nm can be assigned to absorption due to the isomorphous substitution of Ti in a mesoporous silica matrix, as reported in the literature.[8] A shoulder at about 270 nm has been assigned to partially polymerized penta and hexacoordinated Ti species which contain Ti–O–Ti bonds.[8]

The nitrogen adsorption-desorption isotherm at 77 K for calcined mesoporous silica, prepared by MW synthesis, is shown in Fig. 3, and is comparable to that reported by Tanev

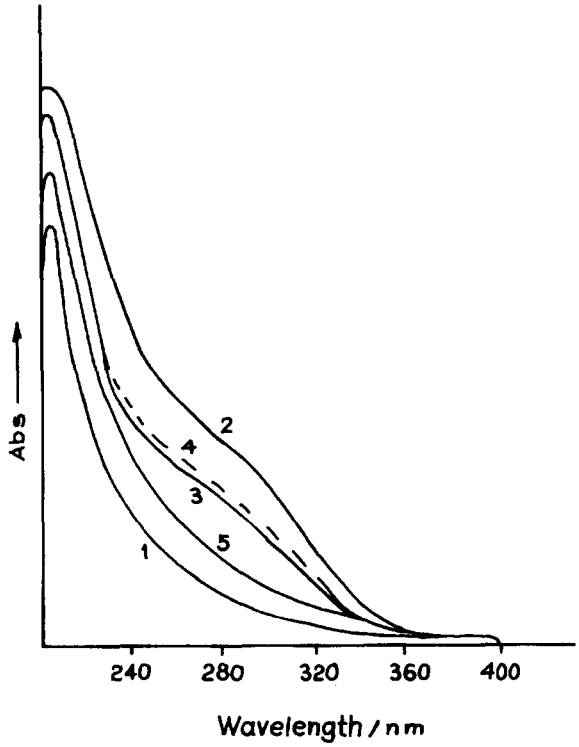

Fig. 2. Diffused reflectance UV-vis spectra of calcined 1) TS-1, Si/Ti = 30, 2) Ti-containing mesoporous silica, Si/Ti = 20, (MW), 3) Ti-containing mesoporous silica, Si/Ti = 30 (MW), 4) Ti-containing mesoporous silica, Si/Ti = 30 (aging), 5) Ti-containing mesoporous silica, Si/Ti = 50 (MW).

Table 1. Physico-Chemical Properties of Mesoporous Silica and Ti-Containing Mesoporous Silica

Sample	Si/Ti ratio	Method	$S_{BET}/m^2\,g^{-1}$	Pore diameter/Å	A_{963}/A_{800}[a)]
Mesoporous silica	—	aging	922	20	0.79
Mesoporous silica	—	microwave	809	20	0.73
Ti-containing mesoporous silica	30	aging	1211	14	2.18
Ti-containing mesoporous silica	30	microwave	1186	14	2.36

a) The ratio of the IR absorption areas of the bands at 963 and 800 cm^{-1}. See the text.

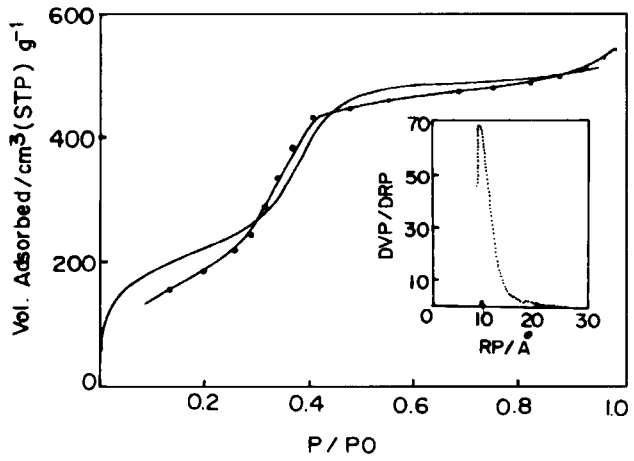

Fig. 3. Nitrogen adsorption (—), desorption (····) isotherm of nitrogen at 77 K for calcined mesoporous silica (MW). The inset shows the BJH pore size distribution.

et al.[6] The isotherm is of type IV. The pore filling starts from p/p_0 in the range of 0.2 to 0.3. This filling is due to the presence of mesopores. The pore-size distribution is measured by the BJH method (desorption), which is 2 nm for mesoporous silica (inset of Fig. 3). The BET surface area of calcined mesoporous silica and Ti-containing mesoporous silica (Si/Ti = 30) prepared by aging/MW synthesis are comparable (Table 1). Tanev et al.[6] have reported an increase in the pore diameter of Ti–HMS, as compared to HMS. However, our present studies show that the pore diameter decreases after the incorporation of Ti in mesoporous silica. This might be due to the presence of extra-framework Ti.

The FTIR spectra of mesoporous silica and Ti-containing mesoporous silica (Si/Ti = 50, 30, 20) prepared by MW synthesis were recorded in Nujol mull (Fig. 4). The peaks at about 1087, 721 and 459 cm^{-1} can be ascribed to Si–O–Si asymmetric internal stretching, the Nujol band and T–O–T bending vibration, respectively. Titanium-containing mesoporous silica exhibits a medium band at 963 cm^{-1}. The presence of this band is considered to be strong evidence for the incorporation of Ti in the framework. However, a similar band is also observed in mesoporous silica, assigned to the δ Si–OH vibration. The ratio of the areas of the band at 963 cm^{-1} (δ Si–OH + ν Si–O–Ti) to the band at 800 cm^{-1} (ν Si–O–Si symmetric) is higher in the case of Ti-containing mesoporous silica (1.96—2.3) than that found in mesoporous silica (0.79), as shown in Table 1. This shows the presence of an isomorphous substitution of Ti in Ti-containing mesoporous silica, as reported earlier.[9] However, there is no 1 : 1 corelation between the Si/Ti ratio and the titanium content.

Oxidation of 2,6-Diisopropylphenol. In order to evaluate the catalytic activity of Ti-containing mesoporous silica catalysts, the oxidation of aromatic compounds, like 2, 6-diisopropylphenol and 2,6-di-*t*-butylphenol, were carried out. Tanev et al. reported[6] on the oxidation of such bulkier aromatic compounds over Ti–HMS catalysts. The catalytic activity data of various Ti-containing mesoporous silica catalysts with different Ti contents in the oxidation of 2,6-diisopropylphenol is depicted in Table 2. Ti-containing mesoporous silica prepared by the microwave method is also compared with that prepared by the conventional aging method. It can be seen that the higher Ti content (Si/Ti = 20) leads to a higher conversion of DIIP. No other products were detected. The selectivity for H_2O_2 remained almost the same in all cases.

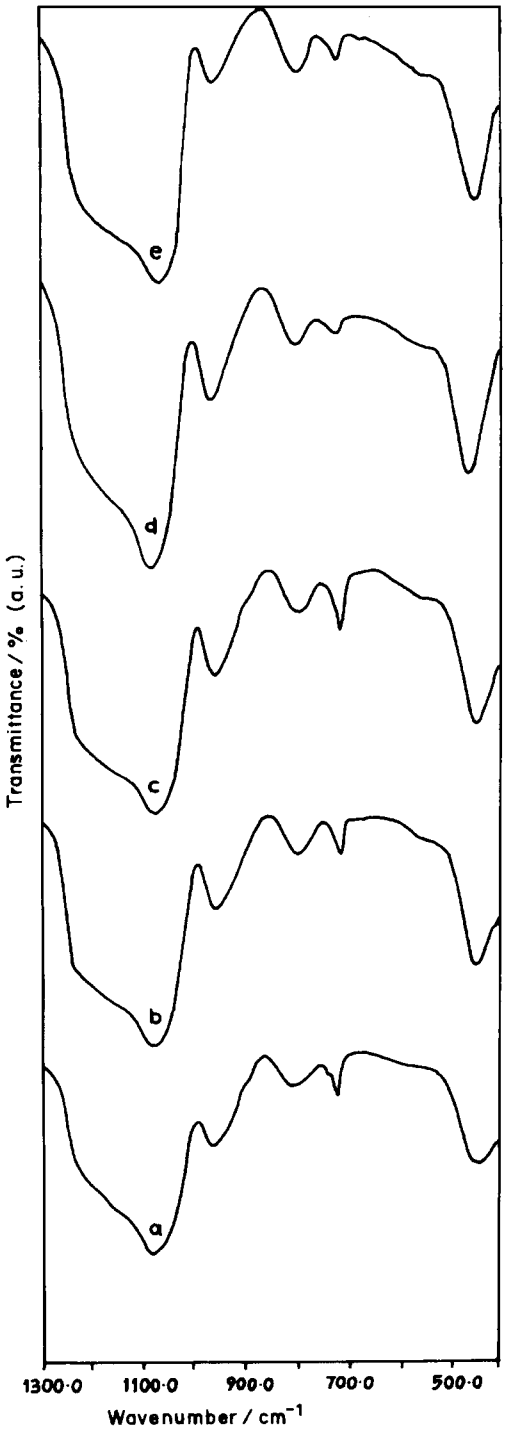

Fig. 4. FTIR spectra of Ti-containing mesoporous silica, a) Si/Ti = 50 (MW), b) Si/Ti = 30 (MW), c) Si/Ti = 30 (aging), d) Si/Ti = 20 (MW), e) mesoporous silica (aging).

Table 2. Catalytic Activity of Different Ti-containing Mesoporous Silica Samples in the Oxidation of Substituted Phenols

Substrate	Si/Ti ratio	Method	Quinone yield %
2,6-DIPP	30	Aging	13.8
2,6-DIPP	30	Microwave	14.1
2,6-DIPP	50	Microwave	10.2
2,6-DIPP	20	Microwave	19.5
2,6-DTBP	20	Microwave	19.1
2,6-DTBP	No catalyst		2.0

Reaction conditions: 100 mg catalyst, 1.35 g DIPP, 3.4 g H_2O_2 (30 wt %), 7 ml acetone, temp 335 K, time 5 h, H_2O_2 selectivity 90—95% (H_2O_2 utilized in moles for the formation of quinone/H_2O_2 converted × 100), Quinone yield = selectivity of quinone × conversion/100. Quinone is 2,6-diisopropylbenzoquinone and 2,6-di-*t*-butylbenzoquinone.

Since oxidation reactions require the presence of isolated metal sites, the higher conversion of 2,6-diisopropylphenol over the catalyst samples with higher titanium contents (Si/Ti = 20) gives indirect evidence concerning the formation of the framework Ti atoms in tetrahedral coordination. However, the conversion does not increase proportionately. This may be attributed to the extra-framework Ti in the case of higher Ti loadings, as indicated by the UV-vis spectra. Thus, these titanium species may not be as catalytically active as isomorphously substituted titanium. Ti-containing mesoporous silica catalysts prepared by the present non-hydrothermal microwave method have comparable activity to that prepared by the conventional method. The activity of these materials in the oxidation of bulkier molecules is ascribed to the free accessibility of Ti active sites in the pores of mesoporous silica.

Conclusions

A comparison of mesoporous silica and Ti-containing mesoporous silica prepared by MW synthesis without using an autoclave or the conventional method shows that the material prepared by the new method is competitive with respect to the surface area, yield, catalytic activity etc., and that considerable time can be saved. The other advantages are instant heating, easy heat control and homogeneous nucleation. The material can be used for oxidation reactions involving bulky molecules, like DIPP and DTBP, due to the mesoporosity.

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