Non-Thermal Synthesis of Mesoporous Zirconium Silicate and its Characterization

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A simple and rapid method for synthesis of mesoporous zirconium silicate with high thermal stability has been developed using sodium silicate in place of costly silicon alkoxides as a silica source. The product was characterized by means of X-ray diffraction, Nitrogen sorption isotherms, FT-IR spectroscopy, transmission electron microscopy (TEM) and thermogravimetry analysis (TGA).

INTRODUCTION

Synthesis of a new family of mesoporous molecular sieves with exceptionally large uniform pore structures were reported by Mobil researches in year 1992 [1-3]. Due to their high surface area they have found widespread use as catalysts [4,5] and efficient adsorbents [6]. Transition metal ions isomorphously substituted into the framework of mesoporous molecular sieves makes them more efficient catalysts for selective oxidations and as adsorbents for selective separations. Many elements, such as aluminum, titanium, iron, boron, niobium and vanadium have been incorporated into the framework of MCM-41 type material [7-10]. Microporous zirconium silicate was synthesized under hydrothermal condition [11-13]. Also zirconium substituted SBA-15 mesoporous silica was synthesized under microwave-hydrothermal conditions [14]. Different procedures of preparation for mesoporous materials have been proposed [15]. A large number of procedures utilize expensive organic

silicon compounds like tetraethylorthosilicate (TEOS) as a silicon source. In this work we report the preparation and properties of a new phase of mesoporous zirconium silicate using sodium silicate as the source of silicon and small amount of surfactant, at ambient temperature.

EXPERIMENTAL

Chemicals

All the chemicals used were of analytical grade from E. Merck (Germany) except Cetyltrimethylammonium bromide (CTMABr) which was supplied by Aldrich (UK).

Synthesis

In a typical synthesis, 0.6 g CTMABr was dissolved in 23 g of demineralized water, the mixture was stirred for 15 min (140 rpm) after that 3 g of sodium silicate was added to the mixture and it was further stirred for 30 min. The pH value of mixture was 11.5 which was decreased to 9 by adding sulfuric acid (2 M) solution. Then solution of $ZrOCl_2.8H_2O$ (0.45 g in 50 ml demineralized water) was added drop wise. The molar

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composition of the resultant mixture was SiO_2:0.12 CTMABr:0.1 ZrO_2:0.03 H_2SO_4:100H_2O. The stirring was continued for 4 h. A bulky white precipitate was formed. It was filtered, washed five times with demineralized water and dried in air oven at 50 °C for 48 h. Small portion of this material was calcined at 600 °C for 6 h.

Characterization

XRD was performed using a Philips X'pert powder diffractometer system with Cu-Kα (λ = 1.541 Å) radiation from 1.5° (2θ) to 10.0° (2θ). The adsorption isotherm of N_2 at 77 K was determined using a Micromeritic ASAP 2010 instrument. Specific surface area was determined by applying the BET equation to the isotherm [16]. Mesopore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula [17]. FT-IR was done using a Bruker FT-IR spectrophotometer model Vector-22. TEM image was taken by JEM-1200 EX with 100 kV acceleration voltages. Thermal analysis was done on a Rheometric Scientific modal STA-1500.

RESULTS AND DISCUSSION

X-ray Diffraction

The XRD patterns of the synthesized zirconium silicate and calcined sample are presented in Fig. 1. The spectra showed XRD patterns similar to MCM-41 materials [1-3]. The d_{100} reflection corresponds to a hexagonal unit cell, the parameter of which was calculated from the equation $a_{\circ} = 2d_{100}/\sqrt{3}$ [1]. The XRD pattern of the calcined sample is nearly similar to the uncalcined sample but on calcination, the peak (d_{100} spacing) is shifted to lower value probably due to condensation of internal Si-OH groups giving rise to a contraction of the unit cell [14]. This shows that the structure
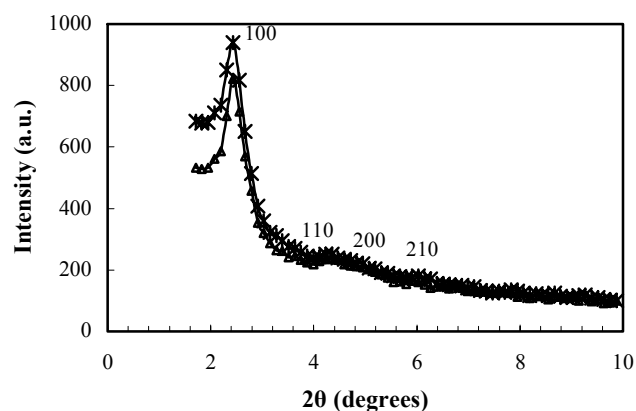

Fig. 1. XRD patterns of the synthesized mesoporous zirconium silicate: (∗) Calcined, (Δ) Uncalcined.

does not change at high temperature due to high thermal stability. The unit cell parameter and d-spacing of the synthesized zirconium silicate are given in Table 1.

Nitrogen Sorption Isotherms

Nitrogen sorption isotherm and corresponding pore size distribution of the synthesized zirconium silicate is given in Fig. 2. This shows a typical IV-type adsorption profile consisting of a step condensation behavior due to the formation of mesopores. As the relative pressure increases ($P/P_o > 0.4$), the isotherm shows inflection, where the P/P_o position of the sharpness of the isotherm in range $0.4 < P/P_o < 0.5$ corresponds to uniformity of mesopore size. Because the zirconium content in the synthesized zirconium silicate is high (mole ratio Si/Zr = 10), the amount of adsorbed nitrogen is low [18]. Pore size distribution of the synthesized zirconium silicate is shown in Fig. 2b.

Pore size distribution indicates that the pore size is about

Table 1. Properties of the Synthesized Mesoporous Zirconium Silicates

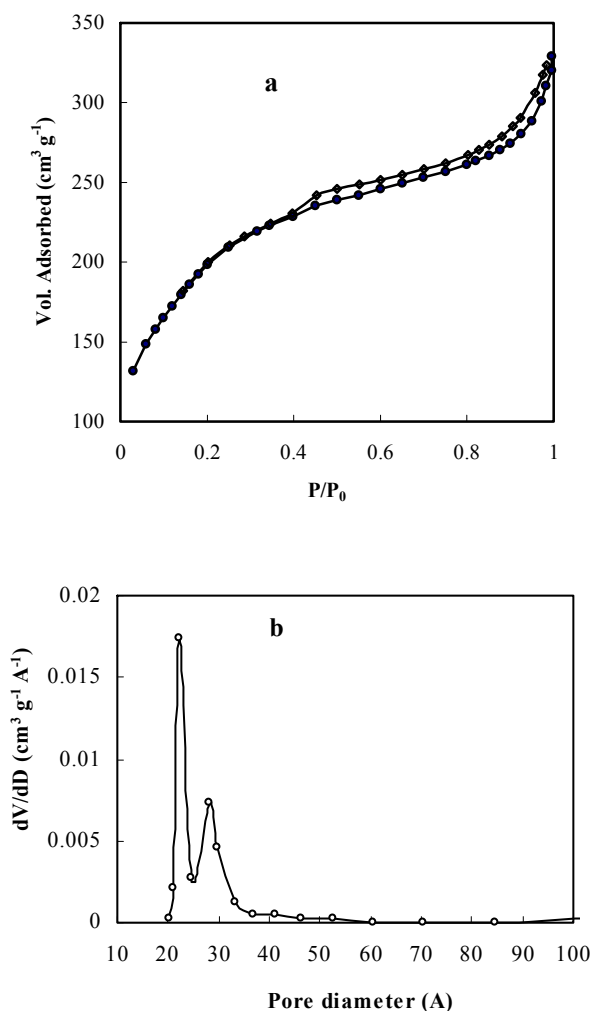| Si/Zr ratio		XRD d_{100} (Å)		Unit cell parameter[a] (a_o) (Å)	Pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	Pore diameter (Å)
Gel	Product	Uncalcined	Calcined				
10	3.68	35.5	32.1	37	0.51	788	25

[a]Determined as $a_{\circ} = 2d_{100}/\sqrt{3}$.

Fig. 2. Nitrogen adsorption/desorption isotherm (a) and pore size distribution of the synthesized mesoporous zirconium silicate (b).

Fig. 3. Transmission electron micrograph of the synthesized mesoporous zirconium silicate.

25 Å. Also BET surface area and pore volume of the synthesized zirconium silicate here are 788 m^2 g^{-1} and 0.51 cm^3 g^{-1}, respectively. This is an improvement over the reported value of pore diameter, BET surface area and pore volume of mesoporous zirconium silicates (with mole ratio Si/Zr about 10) that have been synthesized previously were between the range 19-28 Å, 641-766 m^2 g^{-1} and 0.38-0.51 cm^3 g^{-1}, respectively [11-13].

Transmission Electron Microscopy (TEM)
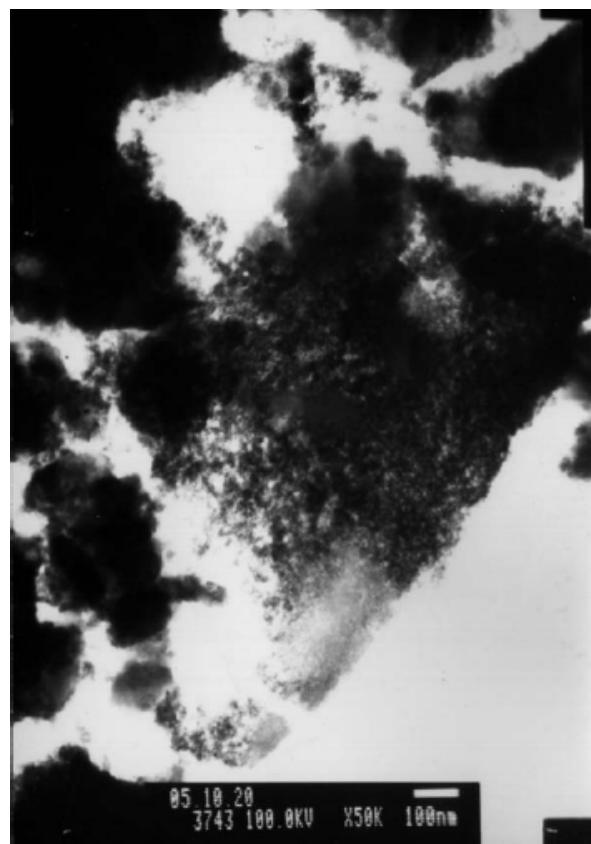
The transmission electron micrograph of the synthesized

zirconium silicate is given in Fig. 3. It shows that the pore diameter of the channels calculated from N_2 sorption measurement of the material is about 25 Å, which is consistent with the position of the first peak (d_{100}) in the X-ray diffraction pattern of this material. The pore diameter of the sample synthesized by thermal method is reported to be 19 Å [13]. Therefore the pore diameter is enhanced with non-thermal synthesis.

FT-IR Spectroscopy

The infrared spectrum of the synthesized mesoporous zirconium silicate is given in Fig. 4. The peaks appeared in the region of 400-1300 cm^{-1} is similar to vibrations of the framework structure of zeolites [19]. Similarly, mesoporous molecular sieves also show series of bands that are characteristics of the SiO_4 tetrahedral unit and its modification
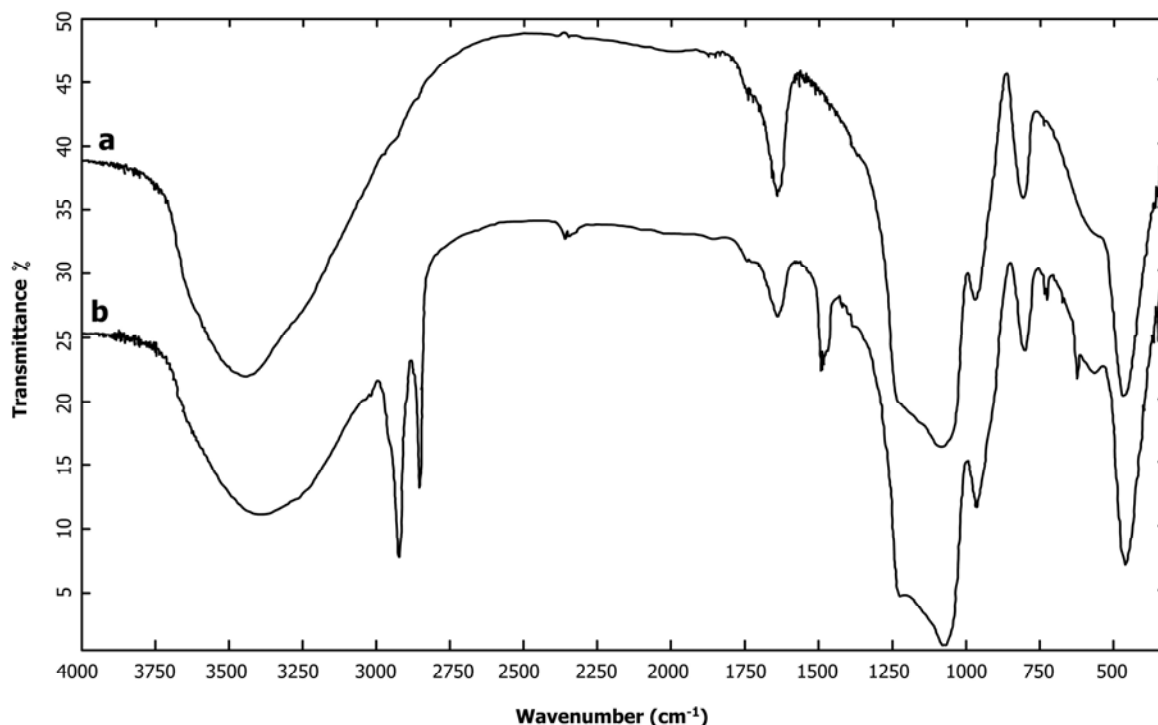
Fig. 4. FT-IR spectrum of the synthesized mesoporous zirconium silicate: (a) calcined, (b) uncalcined.

by introduction of metal ions. The spectrum shows five main absorption bands between the regions 3000-3700, 1055-1090, 960-970, 790-850, 440-465 cm^{-1}, similar to amorphous fumed silica [20-22]. The band in region 1055-1090 cm^{-1} due to internal asymmetric stretching mode of SiO_4 (TO_4) skeleton, appears to be the strongest band in the spectra of all silicates [22]. The peak in region 960-970 cm^{-1} is generally considered as a proof for the incorporation of the heteroatom into the framework [23]. Camblor *et al*. have proposed that the band at 960 cm^{-1} is due to the Si-O stretching vibrations of Si-OH groups present [23]. The Si-O-Si lattice vibrations are found to shift to lower wavenumbers probably due to the incorporation of Zr into the channel walls, as Zr-O bond is longer than Si-O bond.

Thermogravimetric Analysis

TGA curves of the synthesized zirconium silicates and calcined sample are presented in Fig. 5. The TGA curve of uncalcined sample shows a gradual weight loss up to 900 °C. The first step (below 130 °C) in the TGA profile is due to weight loss from the desorption of physisorbed water held in
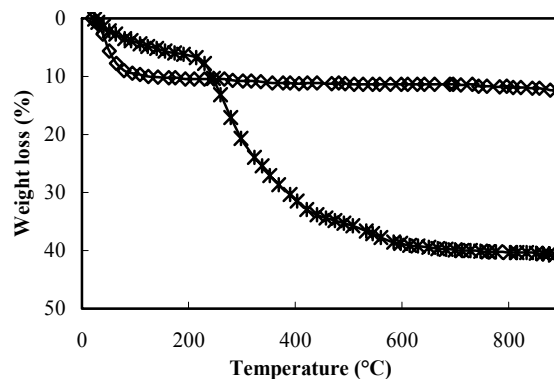

Fig. 5. Thermograms of the synthesized mesoporous zirconium silicate: (◇) Calcined, (✱) Uncalcined.

the pores. The weight loss in the temperature range of 130-320 °C followed by slow weight loss in the temperature range of 300-650 °C is mainly due to oxidative decomposition of templates and also loss of water molecules due to condensation of silanol groups. The TGA curve of synthesized zirconium silicate and its calcined sample show that both

samples (Fig. 5) have high thermal stability which has been confirmed by XRD pattern.

CONCLUSIONS

A simple, rapid and low cost non-thermal method has been developed to synthesize zirconium silicate incorporated mesoporous molecular sieves with high thermal stability and high surface area and pore volume.

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