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Titanium Containing Solid Core Mesoporous Silica Shell: A Novel Efficient Catalyst for Ammoxidation Reactions

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Novel titanium containing solid core mesoporous shell silica has been synthesized by using octadecyltrichloro silane and triethylamine. The synthesized material was characterized by various physicochemical techniques. The mesoporous character of the material has been revealed from PXRD studies. The presence of octadecyltrichloro silane and triethylamine in the sample has been confirmed from EDAX studies. TG/DTA analysis reveals the thermal characteristics of the synthesized material. The presence of titanium in the frame work and its coordination state has been studies by UV-vis DR studies and XPS analysis. Chemical environment of Si in the framework of the material has been studied by ^{29}SiMASNMR studies. The surface area of the material is found to be around 550 m^2g^{-1} and pore radius is of nano range from BET analysis. The spherical morphology and particle size of the core as well as shell has been found to be 300 nm and 50 nm respectively from TEM analysis. The catalytic application of this material towards the synthesis of caprolactam from cyclohexanone in presence of hydrogen peroxide through ammoxidation reaction has been investigated. The optimum conditions for the reaction have been established. The plausible mechanism for the formation of core silica and conversion of cyclohexanone has been proposed.

Key Words : Titanium, Solid core mesoporous silica shell, Octadecyltrichloro silane, Triethylamine, Ammoxidation

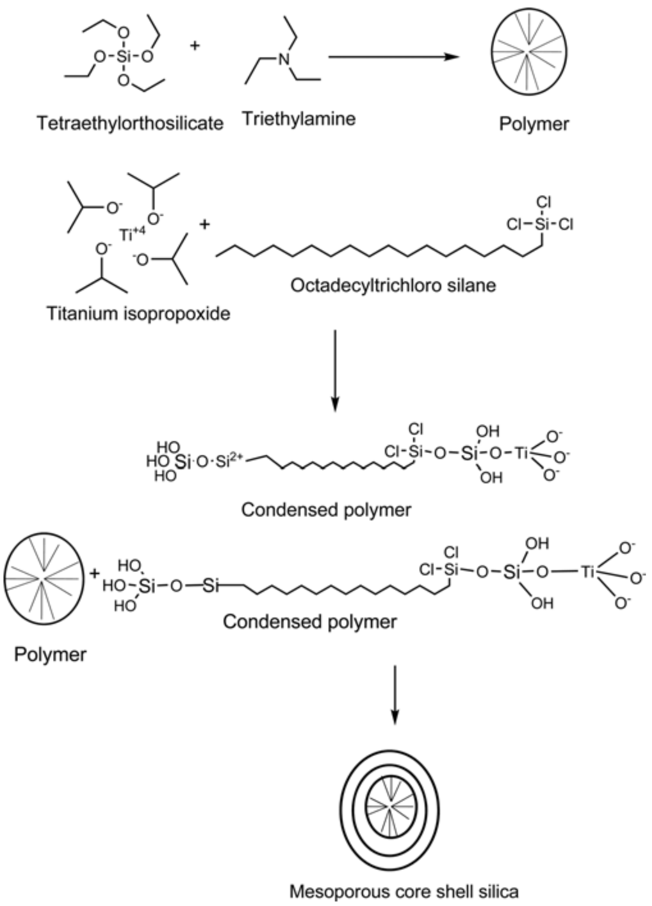
Introduction

Synthesis of novel metallo-silicates has attracted widespread attention since the eco-friendly, selective and industrially important oxidative organic transformations were first reported over titanium containing medium pore zeolite TS-1[1,2] in the presence of dilute H_2O_2 as oxidant. These catalytic reactions have been largely replaced the use of hazardous organic peracids, inorganic acids and other harmful oxidizing agents in various reactions. Among these selective partial oxidation reactions ammoxidation reaction is of particular interest. Caprolactam is an essential component of the versatile polymer nylon-6,6 and is largely produced today by the acid catalyzed Beckman rearrangement of the cyclohexanone oxime, which can be very efficiently and selectively produced by ammoxidation of cyclohexanone over TS-1[6] using dilute aqueous hydrogen peroxide and liquid ammonia. Restricted pore openings of these microporous titanium silicates (0.5-0.75 nm) emphasized the need to develop novel titanium silicates with pore dimensions of 1 nm or higher. Where the bulky organic ketones can easily penetrate to the active titanium sites located inside the channels. Thus highly ordered mesoporous silica[7] and its titanium silicate analog[8] have been synthesized. However, the large pore microporous and mesoporous titanium silicates[9] are found to be catalytically less active in ammoxidation of ketones because of their surface hydrophilicity associated due to the presence of excessive surface Si-OH groups. In the present study a novel titanium incorporated solid core mesoporous silica shell, is synthesized, characterized in detail and studied its catalytic properties over cyclohexanone and cyclododecanone ammoxidation.

Experimental

The titanium incorporated solid core mesoporous silica shell (TiMSS) was synthesized by using sol-gel method. In a typical procedure, 74 mL of acetone (99.5%, s.d.fine, India) was mixed with 6 mL of tetraethylortho silicate (98%, Aldrich, USA). 3.347 mL of triethylamine (98%, s.d.fine, India) and 10 mL of distilled water are mixed and stired for 1 h. Then 5 mL of tetraethylortho silicate and 2 mL of octadecyltrichlorosilane (Porogen, 98%, Aldrich, USA) were added to the above solution. A calculated quantity (Si/Ti = 100) of titanium tetraisopropoxide (98%, Aldrich, USA) was added drop wise to the above mixture and stirred well for about 2 h. The precipitate is centrifuged to separate the solid and washed with distilled water followed by methanol and dried at 383 K. A portion of the sample was calcined at 823 K for 5 h at a rate of 1.5 K/min from room temperature. The as-synthesized sample was subjected to various physicochemical characterizations to establish structural and morphological characteristics.

In a typical synthesis, tetraethyl orthosilicate condenses with triethylamine and forms a polymeric molecule. Octadecylttrichloro silane reacts with titanium isopropoxide and forms a condensed polymer and this condensed polymer which acts as a porogen. The formed condensed polymer



Scheme 1. Plausible mechanism for the synthesis of mesoporous core shell silica.

gets condensed on the surface of polymer and it forms a core shell silica structure. The pore structure of the material mainly depends on the nature of template. The plausible mechanism has been shown in Scheme 1.

Small angle X-ray diffraction analysis was carried out using Mac Science Co. Ltd., MO3XHF22 instrument in the 1-12° region. The particle size and shape were analyzed by a Leica Stereoscan - 440 electron microscope. The copper disc was pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in ionization chamber. Thermogravimetry/differential thermal analysis was carried out using Perkin Elmer, S11 Diamond TG/DTA analyzer. Fourier transform Infrared spectroscopic analysis was done using PerkinElmer spectrum one FT-IR spectrophotometer. The UV-vis diffuse reflectance spectra were recorded using a Pye Unichem (SP-8-100) instrument in 200-900 nm. X-ray photoelectron spectroscopic analysis carried out using ESCA-3000 (VG Scientific, UK) instrument. Cyclic voltammetric analysis carried out using Solartron S1 1287 Electrochemica interface and Solartron 1255B Frequency Response analyzer. Solid State Nuclear Magnetic Resonance spectrum is carried out using Bruker Avance 300 MHz instrument.

The liquid phase partial oxidation reactions were carried out in a two necked glass reactor fitted with a water condenser under N_2 atmosphere at an elevated temperature (343-353 K) with vigorous stirring. The substrate ketone and aqueous ammonia were taken in a required amount of solvent (*tert*-butanol) in the round bottomed flask maintaining at constant reaction temperature. Then the catalyst (20 wt % with respect to the substrate) was introduced into the mixture and the content was homogenized through constant stirring and finally dilute H_2O_2 was added dropwise for a period of 2 h through a slow feed-pump. At various reaction intervals the products were collected, catalyst was separated by centrifugation and the supernatant liquid was analyzed by a capillary gas chromatography (Agilent 4890, HP-1 column with flame ionization detector) to monitor the progress of the reaction. Products were identified through GC retention times and GC-MS (JEOL MS) splitting patterns of the authentic samples. When authentic samples were unavailable, identification was made through ^{1}H NMR spectroscopy.

Results and Discussion

The synthesis results, with and without octadecyltrichloro silane are given in Table 1. Use of octadecyltrimethoxy silane or methyltrimethoxy silane or octyltrimethoxy silane did not give any solid material in the present reaction condition. It is probably due to the poor hydrolyzing rate. It clearly indicates that good silica source is required to get homogenized solid material of mesoporous structure. The small angle X-ray diffraction pattern (Fig. 1) of the as- synthesized titanium containing solid core mesoporous silica shell shows that it is probably mesoporous. The presence of high intensity peak at a 2 theta less than 5^0 clearly indicates the mesoporous character of the synthesized material. On calcinations the peak positions did not change considerably, however a small line broadening occurs. Transmission electron micrograph (Fig. 2) of titanium containing solid core mesoporous silica shell shows that the particles are in spherical shape with uniform size with distinct particle sizes (particle size,

Table 1. Physical properties of titanium containing solid core mesoporous silica shell

No.	Gel composition	Product composition (2 h)	Particle size	Yield (%)
1	$0.01TiO_2$: SiO_2: 0.7 TEA: 0.1ODTCS: 11.5 H_2O: 1.25 Act	SiO_2: $0.06TiO_2$: 3.5TEA: 1.75 ODTCS	300 nm (shell size 100 nm dia)	85
2	$0.01TiO_2$: SiO_2: 0.7 TEA: 11.5 H_2O: 1.25 Act	SiO_2: $0.001TiO_2$: 0.08TEA	400 nm	70
3	$0.01TiO_2$: SiO_2: 0.7 TEA: 0.1 R: 11.5 H_2O: 1.25 Act	No precipitate	-	-

Synthesis conditions: duration = 2 h, temperature = 298 K, rotation = 650 rpm. TEA: triethylamine, DTCS: dodecyltrichloro silane, R: octadecyltrimethoxy silane, methyltrimethoxy silane, octyltrimethoxy silane

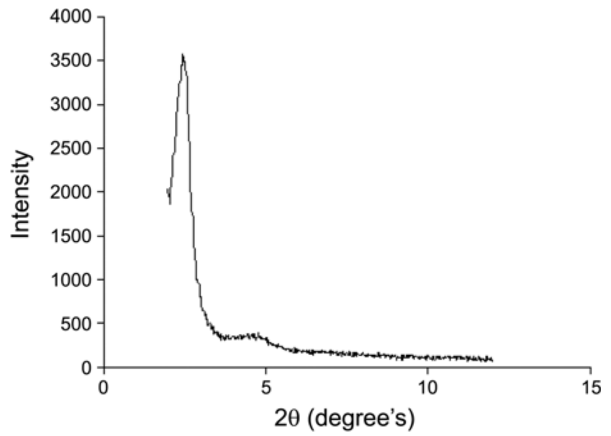


Figure 1. Small angle powder X-ray diffraction pattern of titanium containing solid core mesoporous silica shell.

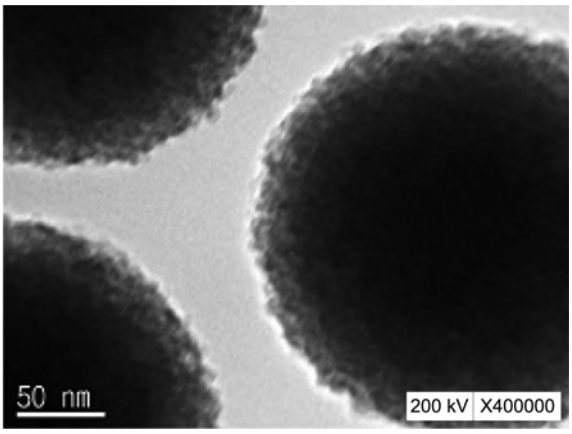


Figure 2. Transmission electron micrograph of titanium containing solid core mesoporous silica shell.

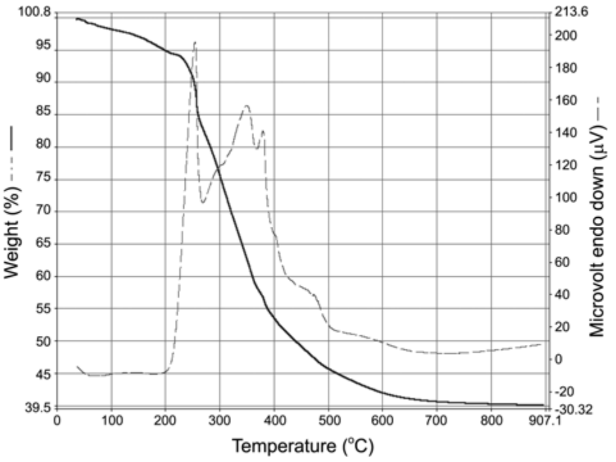


Figure 3. Thermogravimetry/differential thermal analysis of titanium containing solid core mesoporous silica shell.

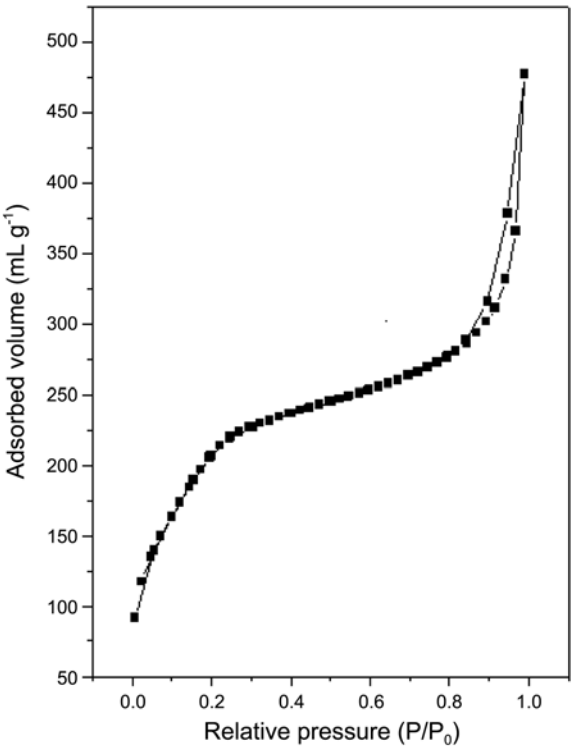


Figure 4. Nitrogen adsorption isotherm of titanium containing solid core mesoporous silica shell.

300 nm and shell size, 50 nm). E-DAX analysis (Table 1) of the as-synthesized samples shows that the presence of octadecyltrichloro silane and triethylamine on surface and which absent in calcined samples. This indicates that the higher surface area of the calcined samples is due to loss of surface adsorbed octadecyltrichloro silane and triethylamine.

The thermogravimetry/differential thermal analysis (Fig. 3) shows the 60% exothermic loss at 25-625 °C with peak positions at 255 & 350 °C due to the loss of occluded octadecyltrichloro silane and triethylamine. As it is a hydrophobic material, there is no endothermic loss due to physisorbed water. The Ti - nano silica samples synthesized using triethylamine only shows weight loss of about 23% with peak position at 330 °C.

Typical nitrogen adsorption isotherms at 77 K (Fig. 4) and the corresponding pore size distribution show a linear increase of the amount of adsorbed nitrogen at low pressures ($P/P_o = 0.35$). The resulting isotherm can be classified as a type II isotherm with a type H2 hysteresis, according to the IUPAC nomenclature.[10-13] The steep increase in nitrogen uptake at relative pressures in the range between $P/P_o = 0.40$ and 0.60 is reflected in a narrow pore size distribution. Thus, the variation of the catalyst in the solution during the growth process enables one to adjust and to control pore structural parameters such as the specific surface area is 550 m^2/g (Ti - nano silica = 152 m^2/g), specific pore volume is found to be 1.02 cm^3/g, and the average pore diameter is 210 Å and medium pore width is 250 Å.

Fourier transform infrared spectrum of the as-synthesized sample shows that peaks around 1700 and 3430 cm^{-1} corresponding to the carboxyl and hydroxyl groups[14] respectively. The absorption peak belonging to the Si-O stretching vibration of $Si\text{-}O^-M^+$ bond appears at 960 cm^{-1}.[15] The weak peaks around 2855 and 2920 cm^{-1} belong to the stretching vibrations of C-H bonds, which show a few organic groups are adsorbed on the spheres. The strong peaks near 1100, 802

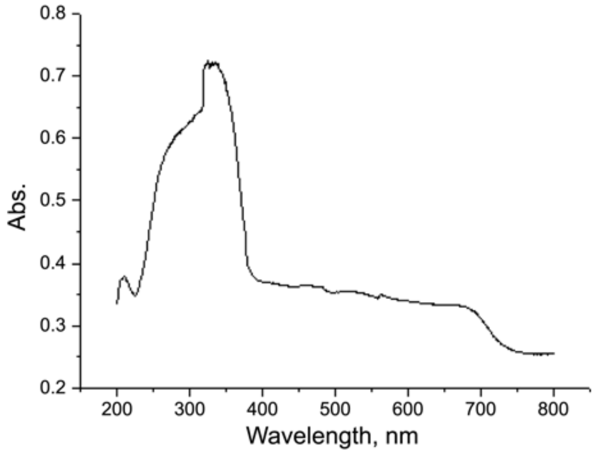


Figure 5. Ultraviolet - visible spectroscopic analysis of titanium containing solid core mesoporous silica shell.

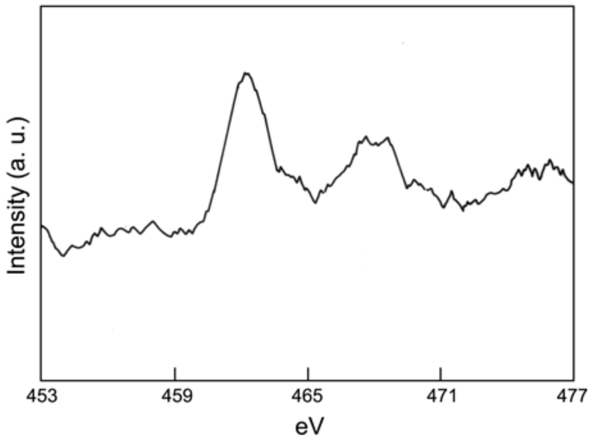


Figure 6. X-ray photoelectron spectroscopy of titanium containing solid core mesoporous silica shell.

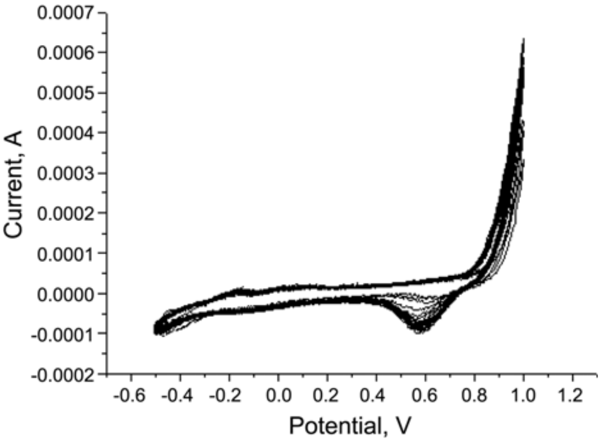


Figure 7. Cyclic voltammetric analysis of titanium containing solid core mesoporous silica shell.

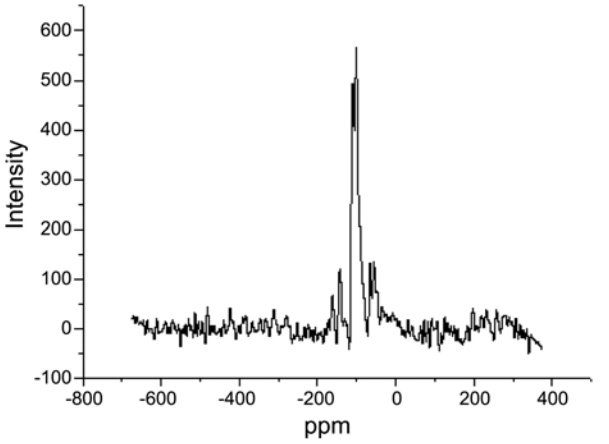


Figure 8. ^{29}Si Magic angle spinning nuclear magnetic resonance spectra of titanium containing solid core mesoporous silica shell.

and 467 cm^{-1} agree to the Si-O-Si bond which implies the condensation of silicon alkoxide.[16]

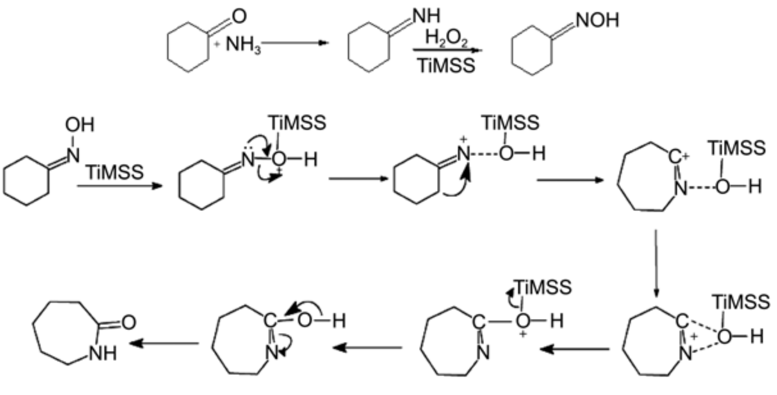
The ultraviolet - visible spectra of titanium containing solid core mesoporous silica shell (Fig. 5) shows two peaks at 350 and 220 nm. The peak at 220 nm may be due to Me-O$^-$ linkages. Peak at 350 nm indicates the presence of tetrahedrally co-ordinated Ti species in the matrix of mesoporous core shell silica material.[17,18]

The analysis of XPS intensity ratios indicates a surface enrichment of Titanium (Fig. 6). The surface concentration of Ti (Si/Ti = 80) is either equal or slightly higher than the bulk values reported for the titanium silicate. It is interesting to note that the Ti2p$_{3/2}$ binding energy is higher than the acceptable octahedral Ti^{4+} binding energy of 457.8-458.0 eV. It is believed that the increase in binding energy (462.2 and 468 eV) is associated with the tetrahedral co-ordination of titanium.[19] Based on the results from UV-vis DRS and XPS, it was clear that titanium is tetrahedrally co-ordinated in the matrix.

Castro-Martins *et al.*[20,21] have used cyclic voltammetric techniques to prove the presence of Ti^{4+} ions in the frameworks of TS-1 and TS-2. Titanium containing solid core mesoporous silica shell (TiMSS) produces (Fig. 7) one redox couple of peaks (between +0.6 V to −0.2 V). Figure 8 shows the ^{29}Si MASNMR spectrum of titanium containing solid core mesoporous silica shell. It shows three distinct lines (−108, −79 and −64 & −43 ppm) attributed to Si: Ti: 3Si, Si: 3Ti: Si, Si: 3Cl: C species respectively[22-25]

A plausible mechanism of titanium containing solid core mesoporous silica synthesis is given in Scheme 1. Triethylamine containing solid core nanosilica is formed by reaction of triethylamine and tetraethylorthosilicate. Octadecyltrichlorosilane, tetraethyl orthosilicate and titanium tetraisopropoxide reacted together formed as a layer around the solid core. The organic part over the mesoporous silica is removed on calcination.

Catalytic activity of titanium containing solid core mesoporous silica shell was studied under mild liquid phase reaction conditions. Ammoxidation of cyclic ketones was studied using dilute H_2O_2 and aqueous NH_3 as reagents (Scheme 2). The catalytic activity of different calcined solid core mesoporous shell titanium silica materials are shown in Table 2. As illustrated in the Table 2, cyclohexanone gave cyclohexanone oxime over different titanium containing solid



Scheme 2. Plausible mechanism for the conversion of cyclohexanone to caprolactam over Ti-containing mesoporous core shell silica.

Table 2. Ammoxidation of various ketones over various Ti-containing catalysts

No.	Catalyst	Reactant	Conversion (%)	Selectivity (%)
1	Ti-solid core mesoporous shell silica	Cyclohexanone	92.3	98
2	2nd cycle	Cyclohexanone	90.1	97
3	3rd cycle	Cyclohexanone	90.0	97
4	Ti-solid core mesoporous shell silica	Cyclododecanone	78	99
5	2nd cycle	Cyclododecanone	75	98
6	TS-1	Cyclohexanone	97	95
7	TS-1	Cyclododecanone	1	99
8	No catalyst	Cyclododecanone	-	-

Reaction condition : reactant : NH_3; H_2O_2; Solvent = tertiary butanol; Reaction temperature: 353 K, Reaction time = 6 h. TS-1 (Si/Ti = 30), Ti-MCM-41 (Si/Ti = 35)

core mesoporous silica shell catalysts after 6 h with moderate to excellent yields. In all the cases the yield was moderate to very good. Pure solid core mesoporous silica shell found to inactive towards the synthesis of caprolactam in this reaction. In the ammoxidation of bulky analogues such as cyclododecanone, cyclododecanone oxime was the sole product. A blank reaction for the ammoxidation of cyclododecanone was carried out in the absence of catalyst and found that no reaction was occurred even after 12 h. In contrast, other catalysts were used in the present study for comparison. TS-1 shows almost negligible amount of ammoxidation product.

Liquid phase oxidation reactions over novel mesoporous molecular sieves[28-30] have many unique advantage *viz.* easy work-up, separation and environment friendly. To test whether the high catalytic activity of this mesoporous titanium silicate originated due to the leaching of Ti from the catalyst during liquid phase reaction, controlled experiments were carried out for each of the samples. In each case after 2 h of reaction a part of the liquid was removed with a syringe, then the content were filtered and immediately transferred into another reaction vessel under identical reaction temperature. The composition of the reaction mixture was monitored periodically for another 4 h through the GC. It was seen that whereas the initital reaction mixture showed steady decrease of cyclohexanone and the increase in cyclohexanone oxime concentrations in the transferred solution showed almost no change in the concentrations of cyclohexanone and its oxime in 2-6 h reaction time. Further the absence of any leached Ti - species was confirmed from the UV-visible spectral data of this liquid reaction mixture collected after 6 h reactions in each case. This indicated that the liquid phase ammoximation reaction over Titano silicate was purely catalytic in nature and no leaching of Ti was observed to be responsible for such catalytic activity.

Conclusion

Novel titanium containing solid core mesoporous silica shell has been synthesized from octadecyltrichloro silane and triethylamine for the first time. Small angle powder X-ray diffraction analysis shows the synthesiszed material is probably mesoporous. Energy dispersive X-ray analysis shows that the sample contains Octadecyltrichloro silane and Triethylamine on surface. It is having spherical morphology with 300 nm particle size and 50 nm shell size. TG/DTA analysis shows that the sample lost almost half of its weight on calcinations. Nitrogen adsorption analysis shows it is having BET surface area of 550 m^2/g. The 960 cm^{-1} peak at fourier transform Infrared spectrum shows that titanium is incorporated inside the tetrahedral silica framework. UV-visible spectrum shows a peak at 300 nm for titanium in tetrahedral co-ordination. X-ray photoelectron spectrum shows a peak for titanium in tetrahedral co-ordination. ^{29}Si MASNMR spectrrum for as-synthesized sample shows the presence of Si: Ti: 3Si, Si: 2Ti: Si and Si: 3Cl: C species. It is found to be an effecient catalyst for synthesis of caprolactam from cyclic ketones *via* ammoxidation reactions.

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