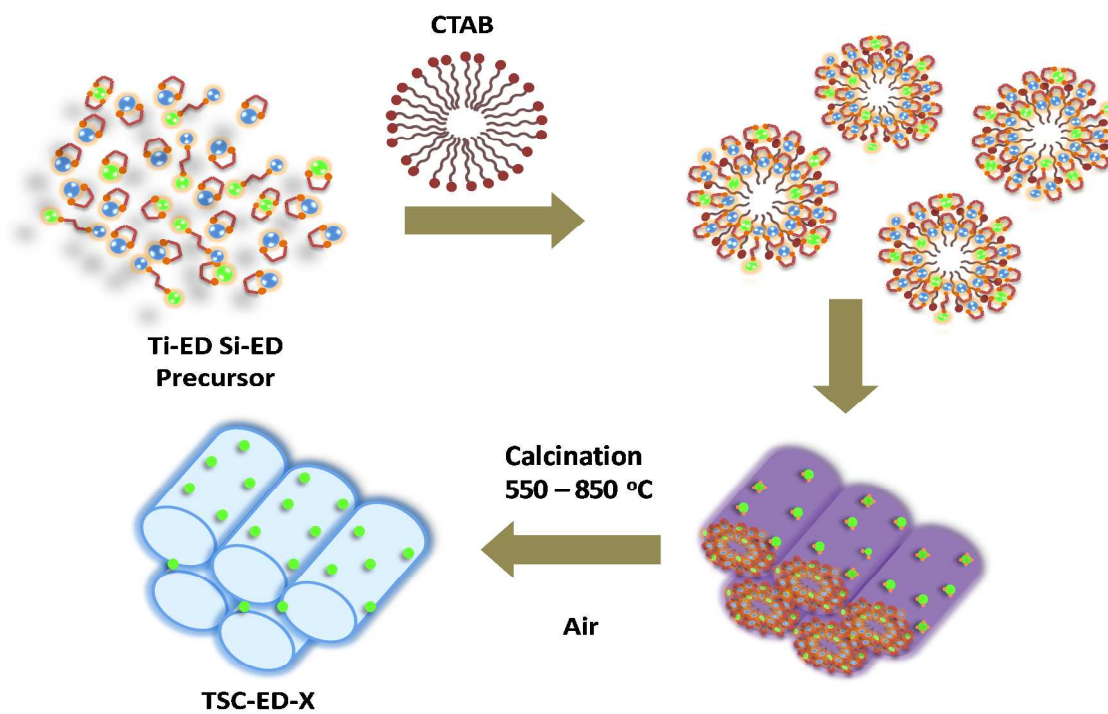




Preparation of mesoporous titanosilicate with isolated Ti active centers for cyclohexene oxidation

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Graphical abstract



**Preparation of mesoporous titanosilicate with isolated Ti active centers for cyclohexene
oxidation**

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Abstract

We report the preparation of mesoporous titanosilicate with active Ti centres using CTAB as the structure directing agent and ethylenediamine as the complexing agent (TSC-ED). The final material contained isolated Ti^{+4} centres substituting Si^{+4} in the mesoporous silica framework. The crucial role played by ethylenediamine in complexing with Ti^{+4} during sol-gel process and preventing the phase segregation of TiO_2 was studied systematically. Textural parameters, structural order, morphology, nature and co-ordination of Ti species were analyzed using various techniques such as X-ray diffraction (XRD), UV-vis diffused reflectance spectroscopy (UV-vis DRS), UV resonance Raman spectroscopy, Fourier transformed Infra-red spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), transition electron microscopy (TEM), Raman spectroscopy and X-ray photoelectron spectroscopy. Finally, the catalysts were tested for the catalytic activity in the oxidation of cyclohexene using various oxidants.

Introduction

Transition metal ions play an important role in catalyzing mild and selective oxidation reactions.^{1, 2} Metalloporphyrins of the transition metal, transition metal complexes have been used for the catalytic oxidation of organic substrates.^{3, 4} Porous solids containing isolated metal active sites are excellent and emerging heterogeneous catalysts due to advantages such as easy recovery, high surface area, easy accessibility to active centres and better reactivity.⁵ The discovery of titanium containing silicate (TS-1) catalysts, where Ti^{+4} substitutes Si^{+4} of crystalline silicates catalysts is significant for hydroxylation and epoxidation.⁶ However, difficulties due to poor mass transfer of large reactant molecules in microporous TS-1 catalysts lead to the development of amorphous versions, wherein Ti^{+4} centres are located in mesostructured SiO_2 matrix. The presence of a uniform and homogeneous distribution of Ti^{+4} active sites in silica matrix has been shown to be crucial to the performance of the catalyst.⁷ One of the crucial challenges in the synthesis of these catalysts is to prevent the phase separation of TiO_2 . This requirement reduces the scope of the widely used sol-gel technique and warrants for suitable modifications. The idea is to control the relative rates of hydrolysis and condensation of Ti and silica precursors so that TiO_2 formation is prevented. The synthetic strategies to prepare isolated Ti^{+4} containing mesoporous silica involve the use of pre-hydrolysed silica⁸, use of single Si-Ti alkoxide precursor⁹ and post grafting of Ti on condensed SiO_2 phases.^{10, 11} Although the methods demonstrated the formation of isolated Ti^{+4} sites, stability, requirement of multiple steps to prepare the precursor reagents and high processing costs are disadvantageous. In addition, using pre-hydrolysed silica method, the maximum Si:Ti ratio that can be achieved without phase separation of TiO_2 was only Si/Ti of 20.¹² On the other hand, single precursor method produces Ti centres deeply buried in the silica matrix remaining inaccessible to reactant molecules.¹³ It is known that pyrolysis of

organometallic atrane complexes in the presence of surfactants is an effective strategy to produce heterometallic homogeneous mixtures in oxides.¹⁴ In such works, triethanolamine is commonly used as a ligand to bind to the metal ions through N and O atoms. This forms an alkoxide-like precursor complex with an advantage of slow hydrolyzing rates. However, there were disadvantages with this method as it invariably led to the phase separation of TiO₂ with Si/Ti below 25. By replacing both the donor atoms with N as in case of ethylenediamine, we have shown that we could increase the tolerance of Si/Ti to as low as 10 without TiO₂ formation. The importance of our work lies in its facile approach based on a simple tweak in its chemistry and unambiguous characterization of site isolated nature.

More recently, Ti-complex was used as a precursor to produce isolated Ti centres.¹⁵ An efficient, cost effective and scalable method to produce high surface area mesoporous silica containing isolated Ti⁺⁴ centres remains a challenge. In this work, we have explored the Ti-complex method further to produce a precursor that is stable and can condense with silica precursor. Ethylenediamine (ED) used as a ligand to complex Ti condensed with hydrolysed silica. The ligand acts as the protection group for Ti centres and does not allow the formation of Ti-O-Ti species during the entire course of synthesis. The method has the advantages of using a bulk chemical such as ED which is a major advantage for scaling up of these industrially important catalysts. The resultant material contains isolated Ti centres without phase separated TiO₂ for a Si/Ti as high as 10. Besides, owing to the moderate stability of Ti-ED complex, the temperature needed for incorporation was only 550 °C. After successfully preparing the mesoporous SiO₂ containing isolated Ti centres using this method (TSC-ED-X), where X = Si:Ti, we tested their utility in the oxidation of cyclohexene, which is an industrially important chemical reaction used in the preparation of adipic acid, perfumes and pharmaceuticals.¹⁶

Experimental section

Chemicals

Tetraethyl orthosilicate (TEOS, Sigma Aldrich), Titanium (IV) isopropoxide (TIP, Sigma Aldrich), Ethylenediamine (EDA, Fluka), N-cetyltetraamine bromide (CTAB, Thomas Baker), Cyclohexene (Himedia), and ethanol were purchased from Thomas Baker and used without further purification.

Synthesis

The mesoporous TSC-ED-X was prepared through sol-gel method where CTAB was used as the structure directing agent to form mesoporous structure. Briefly, 10 mmol of TEOS and 20 mmol of ED were dissolved in 20 mL ethanol and stirred for 30 min. To this, 5 ml ethanol solution containing 0.25 mmol of TIP was added. The resulting light yellow solution was continuously stirred at room temperature for 2 h. In another beaker solution containing 5 mmol of CTAB in 56.8 ml of water heated to 80 °C for 2 h with stirring then cool to 50 °C. After that ED precursor solution was added drop wise to CTAB solution with vigorous stirring for 4 h. The resulting white gel was kept for aging overnight at room temperature. The resultant dry gel was collected by centrifuge, washed with water and ethanol, and dried in oven at 50 °C. To obtain the final mesostructured material as synthesised dry solid was calcined in air at different temperature ranging from 550 °C to 850 °C. For comparison TSC-25 was also synthesized via sol-gel method by adding NH₃ (20 mmol) as catalyst for hydrolysis and condensation without addition of ED.

Catalyst characterization

Low angle powder X-ray diffraction patterns of as-synthesized and calcined samples were recorded on a Phillips PAN analytical diffractometer, Ni-filtered CuK α radiation, $\lambda = 1.5404$ Å, between 0.5° and 10° (2 θ) with a scan rate of 1°/min. While wide angle XRD patterns of samples having different Si:Ti molar ratio and calcination temperature were recorded on a

recorded on a Rigaku D MAX CuK α radiation, $\lambda = 1.5404 \text{ \AA}$, between 10° and 80° (2θ) with a scan rate of $3^\circ/\text{min}$. Characterization of morphology of the synthesized TSC-ED having different nSi/nTi ratio was performed with a field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). SEM micrographs of the mesoporous titanosilicate samples were obtained on JEOL-JSM-5200 instrument while the TEM images were obtained on a TECNAI S-20 instrument. Infrared Spectroscopy measurements were done using Bruker FT-IR. The samples were analyzed as KBr pellets. Diffuse reflectance UV-Vis spectra were recorded in the range of 200–800 nm with a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment, using BaSO₄ as the reference. The UV-resonance Raman spectra were measured using 273.8 nm excitation wavelength generated by tuneable Ti-Sapphire laser (Indigo, Coherent Inc.). The average power used was $\sim 0.6 \text{ mW}$. Calibration was done by recording spectra of dimethylformamide, cyclohexane, indene, acetonitrile, trichloroethylene, and isopropanol with the known band positions.

Catalytic oxidation of Cyclohexene

The catalytic oxidation of cyclohexene was carried out in 25mL two-neck round bottom flask equipped with a reflux condenser. In a typical reaction, 50mg of catalyst was mixed with 5mL of solvent (acetonitrile), 0.5 ml of cyclohexene (4.9 mmol) and 5 mmol of TBHP (70% aqueous) or H₂O₂ (30% aqueous) as oxidant and stirred magnetically for 4 h at 60°C at atmospheric pressure. In case of O₂ as an oxidant, reflux condenser was fitted with O₂ balloon. The reaction mixture contained 25 μL of TBHP (5 mol% of reactant) as an initiator. For the recyclability tests, the catalyst was filtered off, washed twice with fresh solvent, calcined at 500°C for 4 h in air, cooled down to room temperature and reused under the same conditions. After reaction, catalyst was separated from product mixture by centrifugation and

the products were analyzed by Agilent Gas chromatograph equipped with HP-5 column and flame ionization detector.

$$\text{Conversion (\%)} = 100 \times \frac{[\text{C}_6\text{H}_{10}]_0 - [\text{C}_6\text{H}_{10}]_t}{[\text{C}_6\text{H}_{10}]_0}$$

$[\text{C}_6\text{H}_{10}]_0$ = Initial conc. of cyclohexene

$[\text{C}_6\text{H}_{10}]_t$ = Conc. of cyclohexene at time t.

$$\text{Selectivity (\%)} = 100 \times \frac{\text{moles of individual product}}{\text{moles of total products}}$$

Result and discussion

Morphology of calcined TSC-ED-25 was analysed using SEM (Fig.1a). TSC-ED 25 appeared as aggregation of spherical particles. The presence of Ti^{+4} can influence the final morphology of silica.¹⁷ The formation of various periodic mesoporous materials starts with nucleation, which involves the assembly of surfactant micelles and silicate species in a stable packing. However, the presence of foreign ions in the synthesis gel altered the action of the structure directing template. Small-angle X-ray diffraction pattern for the as-synthesized TSC-ED-25 (Fig. 1.b.(i)) showed well-resolved peaks at low angle value that can be indexed as (100) reflection associated with the ordered mesoporosity. From the 2θ value, the d-spacing corresponding to ordered pores was calculated to be 8.5 nm. Two well resolved reflections of low intensity corresponding to (110) and (200) were also observed that were characteristic of ordered hexagonal pore system. Notably, after calcination in air at 550 °C for 6 h, trace ii in Fig. 1.b confirmed mesostructured pores in TSC-ED-25. TSC-ED-X samples exhibited a high surface area in the range of 840 - 860 m^2g^{-1} as compared to 512 m^2g^{-1} for TSC-25. The pore size distributed from 2 - 24nm in TSC-ED-25. The higher surface area of TSC-ED-X could have been contributed by the thermal decomposition of ED ligands during calcinations. TEM images of TSC-ED-25 are provided in Fig.1 c) and d) where long channels

of pores are clearly seen. There was no direct evidence for formation of TiO₂ nanoparticles or aggregates blocking the pores from the microscopy images.

Wide angle powder XRD was used to study the crystalline phases in the sample and more importantly to evaluate the efficiency of the method to prevent the formation of TiO₂. The patterns presented in Fig. 2a correspond to TSC-ED with different values of X namely i) 40, ii) 25 and iii) 10 respectively. It can be observed that the diffraction peaks corresponding to crystalline TiO₂ phase are absent in the samples synthesized in the presence of ED for different ratios of X. This shows that TSC-ED-X samples are non-phase separated even for a high Ti content of X = 10 suggesting the efficiency of the method used. The trace iv) corresponding to X = 25 synthesized without using ED, however showed crystalline phase of TiO₂ with peaks indexed to (101), (200) and (204) of anatase phase. The data suggests the important role of ED in retaining the isolated Ti⁺⁴ centres on SiO₂ framework without formation of TiO₂. In order to probe the efficiency of the catalysts, the samples were synthesized at higher temperatures such as 550, 700 and 850 °C. The data presented in Fig 2b shows that even at high calcination temperatures phase separation to crystalline TiO₂ did not occur in TSC-ED-X. A mild reduction in the surface area was observed in TSC-ED-25 calcined above 700 °C probably due to crumbling of pores.

FT-IR spectra of TSC-25 and TSC-ED-X (X = 10, 25 and 40) catalysts are shown in Fig 2c. In order to confirm the substitution of Ti in silica framework, it was expected intensity of bands corresponding to the vibration modes of Si-O-Ti should increase with increasing concentration of Ti. The absorption band at 960 cm⁻¹ often assigned to the bending vibration of Si-O-Ti in the framework was observed in all the samples.¹⁸ However, the band at 960 cm⁻¹ is also usually prominent in the FT-IR spectrum of pure silica due to the bending vibration of Si-O-Si.¹⁹ The ratio of the intensity of shoulder at 970 cm⁻¹ due to Si-OH to the absorption band at 1086 cm⁻¹ due to the asymmetric stretching of Si-O-Si was observed for TSC-ED-X

samples. It was observed that as the value X decreased from 40 to 10 (high concentration of Ti), the ratio of area of bands increased from 0.68 to 1.46. In comparison to TSC-25, TSC-ED-25 showed a higher band ratio (1.03 to 1.12) suggesting a higher amount of successful incorporation of Ti^{+4} in the SiO_2 framework. A band at 810 cm^{-1} and a broad band about 1086 cm^{-1} with a shoulder at 1225 cm^{-1} corresponded to symmetric and asymmetric stretching of Si-O group respectively.²⁰

In order to rule out the formation of TiO_2 cluster formation or amorphous TiO_2 that may have been undetected by X-ray diffraction technique, solid-state UV-vis DRS spectra of TSC-ED 25, TSC-ED 10 and TSC-25 were analyzed and the results are shown in Fig 2d. The UV-vis spectra of the samples showed an absorption band centered at 220 nm associated with tetrahedral co-ordinated isolated framework Ti^{+4} species^{21, 22} and a band at 260 nm corresponding to multiple (penta or octahedral) coordinated Ti^{+4} species²³ in both TSC-ED 25 and TSC 25. However, exclusive formation of TiO_2 in TSC-25 was confirmed due to the presence of the band near 330 nm which indicated the presence of extra framework (phase separated) Ti^{+4} species.²⁴ The band at 330 nm was absent in TSC-ED-25 and TSC-ED-10, confirming the absence of phase separated TiO_2 . In Fig 2e and 2f, UV-resonance Raman spectra of TSC-ED-X (X = 10, 25 and 40) and TSC-25 samples recorded at room temperature using 273.8 nm are shown. It was observed that TSC-ED-X samples showed bands at 498 cm^{-1} and 1115 cm^{-1} representing framework tetrahedral Ti species.²⁵ A slight shift in the position of bands by 10 cm^{-1} in comparison to crystalline titanosilicate samples is probably due to the amorphous nature of the silica framework. Another sharp band between $680 - 695\text{ cm}^{-1}$ was also observed for TSC-ED-X samples representing isolated octahedral TiO_6 species.²³ On increasing the concentration of Ti, a red shift was observed which we are not able to explain at the moment. Interestingly, in TSC-25 which was prepared in the absence of ethylenediamine, a band at 710 cm^{-1} which is assigned for amorphous TiO_2 species was

clearly observed.²⁶ Thus, we can conclude that TSC-ED-X samples prepared using ethylenediamine contain tetrahedral and octahedral Ti species in the SiO₂ framework and formation of amorphous or crystalline TiO₂ can be ruled out. Using ED as an additive was helpful in maximising the incorporation of Ti⁺⁴ in SiO₂ framework without formation of TiO₂ for a high concentration of Ti with high thermal stability.

In order to interpret the synthesis mechanism of mesoporous TSC-ED-X, we propose the formation of coordination complex of Ti and ED. ED can form monomeric or dimeric complex with Si and Ti. The complex with Ti may be more favoured acid-base interaction. The dimeric species acts as the cross linking agent that is instrumental in incorporation of Ti into the silica framework. The complex precursors gradually condense with hydrolysed TEOS precursors around the mesophases formed by CTAB micelles which is also catalyzed by ED. Although this model will also support the cross linking between two Ti species, the probability is reduced because of large excess concentration of Si in the reaction medium. Thus, formation of TiO₂ is avoided. Stronger binding of ED with Ti also ensures the complete isolation of the Ti sites even at higher temperature of calcinations. XPS analysis showed traces of N species in the calcined TSC-ED-X samples suggesting the presence of N species in the vicinity of Ti⁺⁴ sites.

The catalytic activity of TSC-ED-X (X = 10, 25, 40 and 70) was tested in the oxidation of cyclohexene with different oxidants and the results are summarized in Table 1. The efficiency of TSC-ED-X catalysts are compared with TSC-25 catalysts which were prepared in the absence of ED. Oxidation of cyclohexene with TBHP and H₂O₂ as oxidants gave 1,2-epoxycyclohexane and 1,2-cyclohexanediol as major products. The epoxide which is formed undergoes hydrolysis on acidic Si-OH groups present on the surface to form diol. TSC-25 gave a conversion of 34 and 41 % with TBHP and H₂O₂ as oxidants respectively. In comparison, TSC-ED-X gave higher conversion and selectivity clearly showing the presence

of higher number of isolated Ti^{+4} active sites compared to TSC-25 catalyst. Among the TSC-ED-X samples, the difference in catalytic activity cannot be accounted with the minor changes in the surface area suggesting that isolated Ti centres play a major role in the catalytic activity. Also, it was observed that the conversion was usually maximum for $X = 25$. Low concentration of Ti^{+4} was not very active due to the sub-critical number of active sites. While, high concentration of Ti^{+4} accelerates the decomposition of the oxidants to transient active surface TiOOH species which rapidly decompose in futility in the absence of substrate molecule. An optimal value of $X = 25$ was therefore found to be active under the following conditions. Thus improved catalytic results obtained with this mesoporous titanosilicate are attributed to the combined advantages of isolated Ti^{+4} sites and high surface area of TSC-ED-X samples. Unlike MCM type mesoporous materials, TSC-ED-X samples with shorter channels have improved diffusion of bulky products towards the active sites preventing the deactivation of the catalyst due to poor mass transfer.²⁷ Efficiency of TSC-ED-X samples were also tested using molecular O_2 as the oxidant. Interestingly, an increase in the conversion was observed with TSC-ED-X samples compared to TSC-25 indicating the activation of O_2 . In the presence of O_2 , 2-cyclohexen-1-ol and 2-cyclohexen-1-one were also observed in addition to epoxide and diol products. It has been reported that the deactivation of some mesoporous titanosilicates occurs during oxidation due to leaching of Ti.^{28,29,30} To complete the evaluation of catalyst TSC-ED-25, the catalyst was subjected to five cycles of 4 h-catalytic reaction using TBHP and H_2O_2 as oxidants and the results are shown in Fig.3. The conversion did not change in a significant manner in both oxidants suggesting the stability of active sites.

In conclusion, preparation of Ti-silicate mesoporous materials with incorporation of isolated Ti^{+4} centres into the SiO_2 framework has been described using a Ti-ethylenediamine complex as the precursor. There was no phase separation of TiO_2 in amorphous or crystalline

forms when synthesized using ethylenediamine as ligand for Si:Ti as high as 10. The non-phase separated materials were unambiguously characterized using various spectroscopic techniques. The as-prepared materials were found to be very stable as oxidation catalysts for the oxidation of cyclohexene using various oxidants such as H₂O₂, TBHP and O₂. It may be extremely important to study and improve the activation of O₂ on these catalysts so that greener catalysts may eventually be developed. One of the ways to improve would be to control the coordination environment of Ti centres on these catalysts. We also believe this method could be developed as a versatile method to prepare other atom isolated catalysts for catalytic applications.

Acknowledgement

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Figure Captions

Fig.1(a). SEM images of TSC-ED-25 **b)** Low angle XRD pattern of (i) TSC-ED-25 uncalcined (ii) TSC-ED-25 calcined at 550 °C **c)** and **d)** TEM images of TSC-ED-25

Fig.2a) Wide angle XRD pattern of (i) TSC-ED-40, (ii) TSC-ED-25, (iii) TSC-ED-10 and (iv) TSC-25. **b)** Wide angle XRD pattern of TSC-ED-25 samples calcined at different temperature (i) 550 °C, (ii) 700 °C and (iii) 850 °C **c)** FTIR spectra of (i) TSC-ED-40 (ii) TSC-ED-25 (iii) TSC-ED-10 and (iv) TSC-25 **d)** UV-vis DRS spectra of (i) TSC-ED-25 (ii) TSC-ED-10 and (iii) TSC-25 **e) and f)** UV-resonance Raman spectra of (i) TSC-25, (ii) TSC-ED-10, (iii) TSC-ED-25, and (iv) TSC-ED-40 excited at 273.8 nm in different regions of Raman shift.

Fig.3 Recyclability of TSC-ED-25 catalysts for epoxidation of cyclohexene with H₂O₂ (and TBHP at 60 °C for 4 h.

Scheme

Scheme shows the ED complexes of Ti and Si (Ti-ED and Si-ED) and its self assembly over the CTAB micelles. On calcinations in air TSC-ED-X samples with isolated Ti⁺⁴ species incorporated on SiO₂ matrix is obtained.

Table

Table1 Catalytic result of TSC-ED-X (X=10, 25, 40 and 70) and TSC-25 using different oxidant for the oxidation of cyclohexene ^a.

List of Figures

Fig.1.

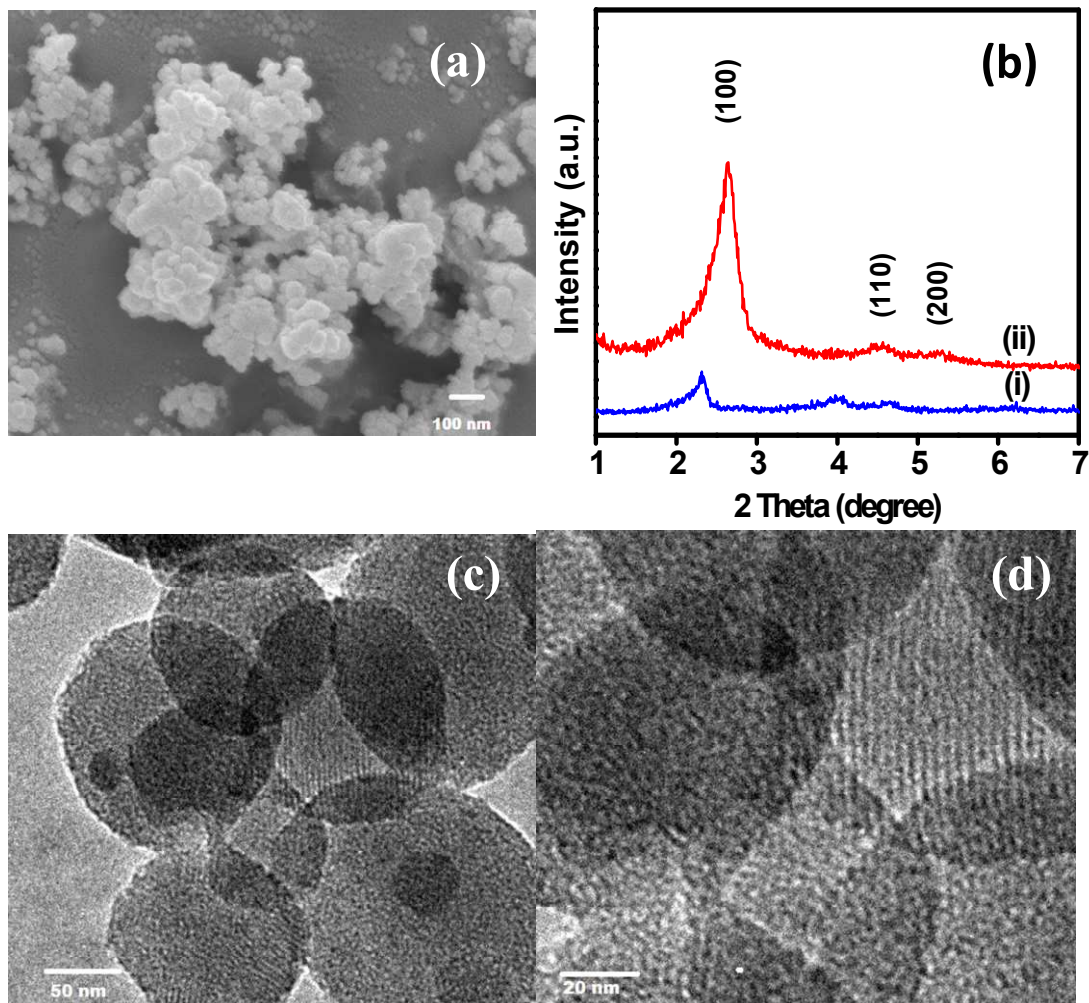


Fig.2.

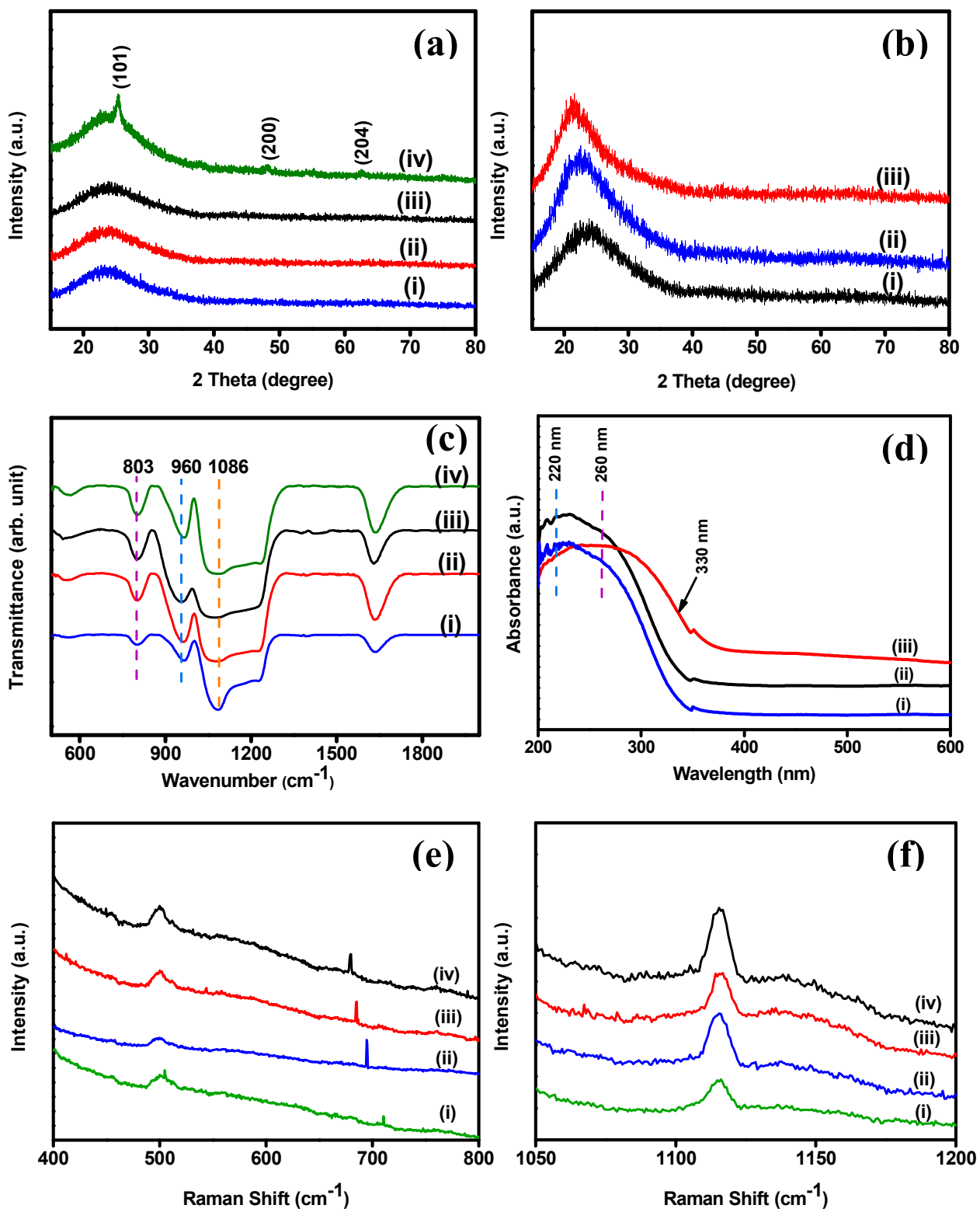
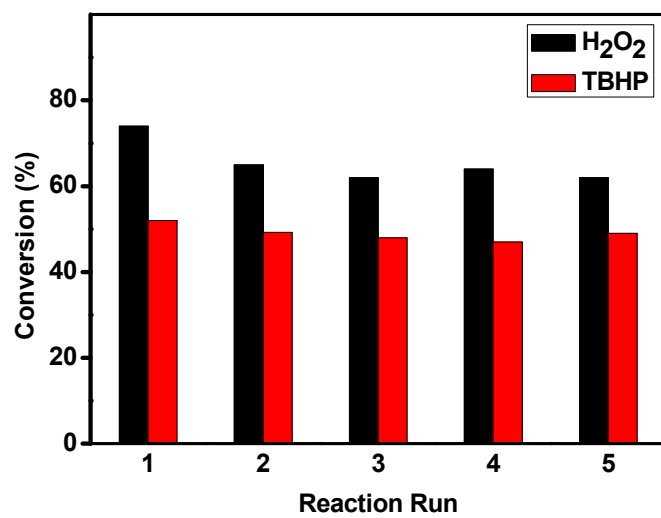


Fig.3



Scheme

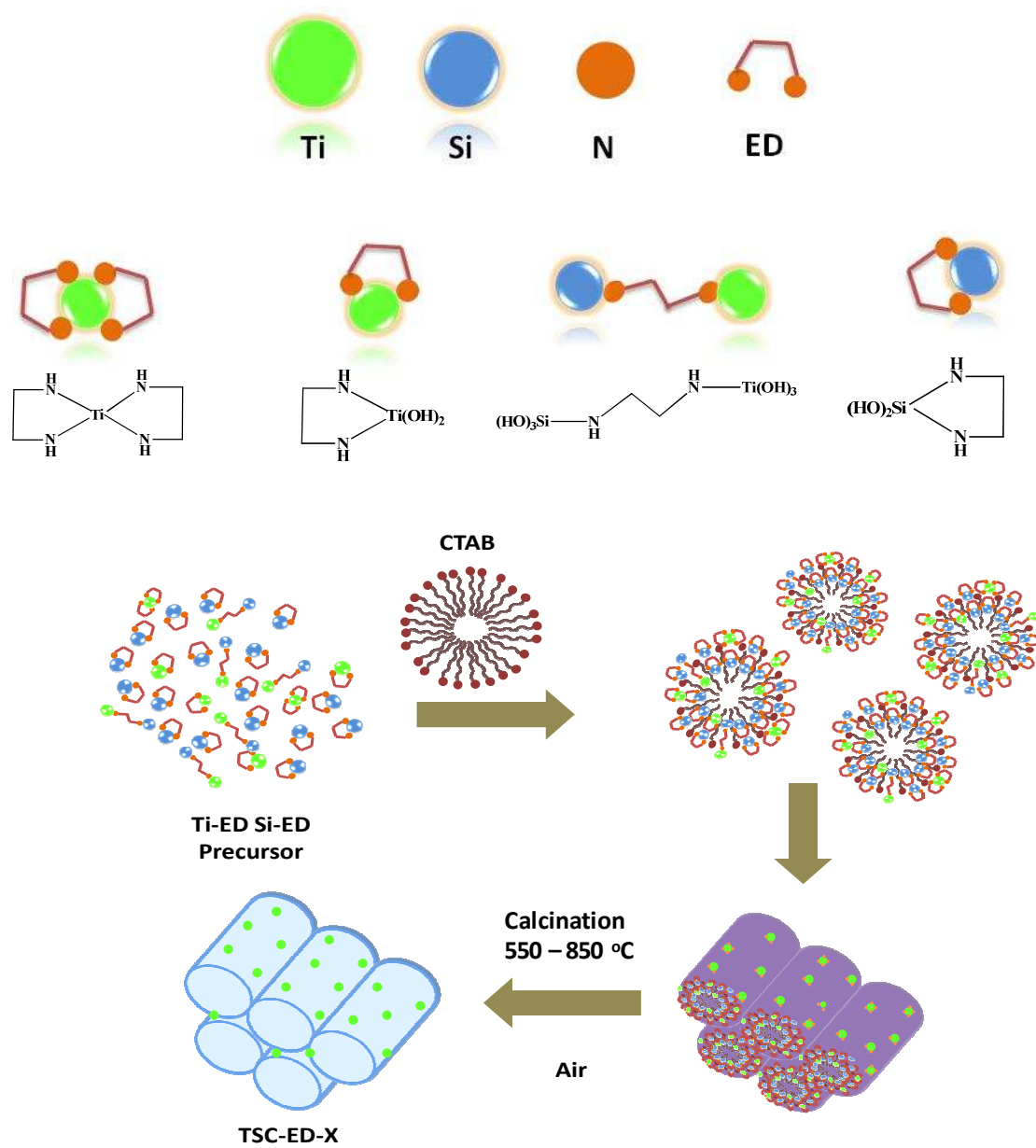


Table 1

| Entry | Catalyst | Oxidant | Conversion (%) | Selectivity (%) | |
|-------|------------------------|-------------------------------|----------------|-----------------|------|
| | | | | epoxide | diol |
| 1 | TSC-ED-10 ^b | TBHP | 41 | 70 | 25 |
| 2 | TSC-ED-25 ^b | TBHP | 52 | 73 | 10 |
| 3 | TSC-ED-40 ^b | TBHP | 45 | 64 | 15 |
| 4 | TSC-ED-70 ^b | TBHP | 40 | 62 | 31 |
| 5 | TSC-25 ^b | TBHP | 34 | 68 | 20 |
| 6 | TSC-ED-10 ^b | H ₂ O ₂ | 54 | 28 | 66 |
| 7 | TSC-ED-25 ^b | H ₂ O ₂ | 74 | 20 | 65 |
| 8 | TSC-ED-40 ^b | H ₂ O ₂ | 63 | 9 | 87 |
| 9 | TSC-ED-70 ^b | H ₂ O ₂ | 45 | 6 | 85 |
| 10 | TSC-25 ^b | H ₂ O ₂ | 41 | 6 | 83 |
| 11 | TSC-ED-25 ^c | O ₂ | 20 | 25 | 32 |
| 12 | TSC-ED-40 ^c | O ₂ | 16 | 18 | 35 |
| 13 | TSC-25 ^c | O ₂ | 4 | 45 | 16 |

^a reaction condition: temperature 60 °C, time 4h, catalyst wt. 50mg, 5 mmol cyclohexene, 5 mL acetonitrile, ^b Oxidant: 5 mmol, ^c TBHP as initiator (5 mol% of substrate), O₂ as oxidant in balloon, more selectivity towards allylic products (2-cyclohexen-1-ol and 2-cyclohexen-1-one)