Catalysis Science & Technology

PAPER

View Article Online View Journal | View Issue

Cite this: *Catal. Sci. Technol.*, 2013, **3**, 2340

Received 1st May 2013, Accepted 29th May 2013

DOI: 10.1039/c3cy00306j

www.rsc.org/catalysis

1. Introduction

The selective oxidation of ethylbenzene to acetophenone is an important reaction as the product is the raw material for the production of fine chemicals and pharmaceuticals.^{1,2} Conventional oxidation reactions employ toxic solvents and metal salts as the catalysts. Such drastic reaction condition, and difficult separation of products from the reaction mixture make the process tedious on the industrial scale. Transition metal complexes are also used as the catalyst but the problem of reusability limits their application. Hence researchers are constantly trying to find a suitable heterogeneous catalytic system for the oxidation of ethylbenzene. Mesoporous materials possess well ordered arrangement of pores, high surface area, large pore volume and uniform pore size distribution.³⁻⁶ Hence these materials find a variety of applications in the field of catalysis, adsorption, sensors, fuel cells and solar cells.⁷⁻¹¹

In the family of mesoporous materials, SBA-15 possesses large pore size and thicker walls compared with M41S family members such as MCM-41 and MCM-48. However, siliceous SBA-15 mesoporous materials do not find application in catalysis due to lack of active sites in their framework.^{12,13} In view of this deficiency, creation of active sites in mesoporous SBA-15 is a

Direct synthesis of Mn-Ti-SBA-15 catalyst for the oxidation of ethylbenzene

P. Visuvamithiran, K. Shanthi, M. Palanichamy and V. Murugesan*

Bimetallic Mn-Ti-SBA-15 materials were prepared by direct hydrothermal method with appropriate pH adjustment. The materials were characterized by low and wide angle XRD, N₂ sorption studies, DRSUV-Vis, XPS, ESR, SEM and TEM. The XRD and BET results clearly demonstrated the incorporation of manganese and titanium species in the SBA-15 framework without affecting the mesoscopic nature of the material. The oxidation state and coordination environment of the active sites were confirmed by DRSUV-Vis, XPS and ESR. The results revealed that Mn^{2+} is in octahedral geometry whereas Mn^{3+} and Ti⁴⁺ are in tetrahedral coordination in the SBA-15 framework. The O1s XPS spectrum well established the framework incorporation of manganese and titanium species. The catalytic activity of Mn-Ti-SBA-15 materials was evaluated in the oxidation of ethylbenzene with TBHP as the oxidant under optimized reaction condition. It was found that Mn-Ti-SBA-15(50) catalyst showed high catalytic activity with a rate constant of 7.155 $\times 10^{-3}$ min⁻¹. The synergetic effect of Mn^{2+}/Mn^{3+} and Ti⁴⁺ sites in Mn-Ti-SBA-15 is a promising catalyst for the oxidation of ethylbenzene and other alkylbenzenes.

major challenge for catalytic applications. Since the incorporation of heteroatoms in SBA-15 is very difficult under strongly acidic condition due to the hydrolysis of the M–O–Si network, most researchers have introduced active sites on SBA-15 by a post-synthetic grafting method.^{14,15} These grafted active sites in mesoporous materials showed lot of inconvenience while in use as catalyst due to reduction of surface area, pore diameter and pore volume. Therefore, the introduction of active sites in the silica framework by direct synthesis gained importance. Wu *et al.*¹⁶ reported the incorporation of heteroatoms such as Al and Ti into SBA-15 by direct synthesis with suitable pH adjustment. Recently several reports are available on the incorporation of metal ions such as Al, Ti, V, Cr, Mn and Fe into SBA-15 framework by direct method under suitable pH condition.^{17–23}

Manganese is particularly attractive as a donor because many of its oxidation states possess redox potential that are suitable to drive demanding organic transformations.²⁴ Porous titanosilicates continue to attract considerable attention due to their remarkable catalytic efficiency in the oxidation of a wide variety of small chain hydrocarbons.^{25,26} Recently bimetals such as Ti–Co and Ti–V incorporated AlPO-5 molecular sieves have been found to exhibit good catalytic activity due to oxophilic centre of Ti(rv) active sites located in close proximity to another species, thus facilitated synergistic influence both from structural and catalytic perspective.^{27,28} The incorporation of two different metal ions into mesoporous materials may create new functional material with different or new redox and

Department of Chemistry, Anna University, Chennai-600 025, India. E-mail: v_murugu@hotmail.com; Fax: +91-44-2220066/22201213; Tel: +91-44-22358641

View Article Online Catalysis Science & Technology

acidic properties. However, only a few reports are available on bimetal incorporated mesoporous materials, demonstrating higher catalytic activity than monometal incorporated mesoporous materials.^{29–38} Based on this useful previous report, it was attempted to incorporate both Mn and Ti into SBA-15 framework. It was presumed that bimetal incorporated SBA-15 can create new redox sites compared to mono metal substituted SBA-15, and hence it was expected to display different catalytic activity.

In the present study, Mn-Ti-SBA-15 material was synthesized by direct hydrothermal method with careful pH adjustment. The catalyst was thoroughly characterized by various techniques as discussed in the following sections. The catalytic activity of Mn-Ti-SBA-15 was evaluated in the oxidation of ethylbenzene. The effects of reaction temperature, time, solvent and amount of catalyst on conversion and products' selectivity were also examined and discussed.

2. Experimental

2.1. Chemicals

Tetraethylorthosilicate (TEOS) (Aldrich) and triblockcopolymer (poly(ethylene glycol)-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123) of molecular weight 5800 (Aldrich) were used as silicon source and structure directing agent respectively. Titanium tetraisoproxide (Aldrich) and manganese nitrate (Aldrich) were used as Ti and Mn sources respectively. *tert*-Butyl hydroperoxide (TBHP) (Merck) was used as the oxidant. Ethylbenzene (Fluka) and all other solvents (Merck) were used without further purification.

2.2. Synthesis of bimetallic Mn-Ti-SBA-15

The bimetallic Mn-Ti-SBA-15(25) was prepared as follows: Pluronic P123 (4 g) was dissolved in 30 ml distilled water and stirred for 2 h. Then 2 M HCl (120 ml) was added to it and the stirring continued for another 2 h after the pH was adjusted to 3 by adding dilute ammonium hydroxide (solution A). Subsequently, TEOS (9 g), manganese nitrate (0.867 g) and titanium tetraisoproxide (0.982 g) were added to deionized water (5 ml) and stirred for 30 min to form a clear solution (solution B). The solution B was added dropwise to solution A and stirred at 40 °C for 24 h. The resulting mixture was aged at 100 °C for 24 h. The solid product was recovered by filtration and dried at 100 °C overnight. The template was removed by calcination at 550 °C for 6 h at a heating rate of 2 °C min⁻¹. The prepared sample was denoted as Mn-Ti-SBA-15(25).

2.3. Characterization of the catalyst

The small angle X-ray diffraction (XRD) pattern of the material was recorded on a Bruker D8 advanced powder X-ray diffractometer using Cu K α (λ = 1.54 Å) as the radiation source in the 2θ range 0.5–6° with a step size of 0.01° and a step time of 1s. The wide angle X-ray diffraction patterns were recorded on a PANalytical X pert PRO diffractometer equipped with Cu K α (λ = 1.54 Å) as the radiation source in the 2θ range of 5–80° with a step size of 0.02° and a step time of 1s. The nitrogen sorption

isotherms were recorded at 77 K on a Micromeritics ASAP 2020 volumetric adsorption analyzer. Prior to each adsorption measurement, the sample was degassed at 350 °C for 3 h under vacuum ($p < 10^{-5}$ mbar) in the degas port of adsorption analyzer. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated using Barrett-Joyner-Halenda (BJH) method. The DRSUV-Vis absorption spectra were recorded between 190 and 800 nm on a UV-Vis spectrophotometer (Shimadzu model 2450) using BaSO₄ as the reference. The X-ray photoelectron (XPS) spectrum was recorded using MS Omicron nanotechnology with XM-1000 monochromator and AlKa as the radiation source operated at 200 W. The ESR spectrum was recorded on a varian E-112 at room temperature with a modulation frequency of X-band (8.5-9.5 GHz). The morphology of the materials was examined by scanning electron microscope (SEM) after gold coating using SEM-JEOL, JSM-5600 model with an accelerating voltage of 20 keV. High-resolution transmission electron microscopic (HR-TEM) images were captured using JEOL JEM 2100 with an accelerating voltage of 200 keV.

2.4. Catalytic studies

Mn-Ti-SBA-15 (75 mg) was dispersed in 5 ml acetonitrile taken in a 100 ml round bottom flask. Ethylbenzene (3 mmol) and TBHP (5 mmol) were added to it dropwise. The reaction mixture was stirred magnetically at 80 °C for 2 h. The product was filtered, and the residue washed thoroughly with water and extracted with ether. The products so collected were analyzed by a gas chromatograph (Shimadzu GC-17A model) equipped with DB-5 capillary column (30 m \times 0.25 mm \times 0.25 μ m) and a flame ionization detector. The products were also identified by a gas chromatograph coupled with mass spectrometer (Perkin Elmer Clarus 500) using helium as the carrier gas at flow rate of 1 mL min⁻¹.

3. Results and discussion

3.1. Mechanism for the formation of Mn-Ti-SBA-15

The incorporation of an heteroatom (transition metal) in mesoporous SBA-15 is very difficult under highly acidic condition due to easy hydrolysis of the M–O–Si network. However, the rate of hydrolysis of the M–O–Si bond was decreased by lowering the acidity of the solution. The XRD patterns of Mn-Ti-SBA-15(25) at pH 2, 2.5 and 3 are shown in Fig. 1. The intensity of the XRD peaks increased with increase of pH from 2 to 3. The results revealed that high amount of manganese and titanium species were incorporated in SBA-15 at moderately low acidic pH. It is found that pH 3 of the gel mixture is higher than the isoelectric point of silica and hence it formed negatively charged silica species. The resulting negatively charged silica species interacted with M–OH species *via* hydroxyl group condensation catalyzed by nitrate ion.^{23,39} It was observed that pH 3 of the gel is found to incorporate high metal ion species into SBA-15 without loss of its mesoporous nature.

3.2. Characterization

3.2.1. XRD. The small angle XRD patterns of SBA-15 and Mn-Ti-SBA-15 with Si/(Mn + Ti) ratios of 25, 50, 75 and 100 are



Fig. 1 Small angle XRD patterns of Mn-Ti-SBA-15(25) at pH (a) 2, (b) 2.5 and (c) 3.



Fig. 2 Small angle XRD patterns of (a) SBA-15, (b) Mn-Ti-SBA-15(25), (c) Mn-Ti-SBA-15(50), (d) Mn-Ti-SBA-15(75) and (e) Mn-Ti-SBA-15(100).

shown in Fig. 2. The small angle XRD patterns of SBA-15 showed characteristic reflections in the 2θ range of 0.5-5, exhibiting a sharp intense peak below 1° (2 θ) corresponding to (100) and small humps at 1.65° and 1.8° (2 θ) corresponding

| Table 1 | Textural properties of Mn-Ti-SBA-15 |
|---------|-------------------------------------|
| | |

to (110) and (220) respectively. These characteristic diffraction patterns well supported the hexagonal ordered mesoporous structure with space group of P6mm.40 The small angle XRD patterns of Mn-Ti-SBA-15 exhibited similar characteristics of SBA-15. The intensity of the peaks increased with increase of metal content. It was also noticed that the unit cell parameters increased with increase of metal content from 100 to 25, and the results are presented in Table 1. The increase of unit cell parameters is due to higher ionic radii of Ti⁴⁺ and Mn²⁺/Mn³⁺ than Si⁴⁺ as well as higher bond length of Ti-O and Mn-O than Si-O. This suggested that manganese and titanium species were incorporated into SBA-15 framework. The wide angle XRD patterns of Mn-Ti-SBA-15 are shown in Fig. 3. There was no distinct diffraction pattern corresponding to metal oxides such as TiO₂ and MnO₂ or Mn₃O₄. This confirmed the incorporation of manganese and titanium species into SBA-15 framework without affecting the mesoporous silica.

View Article Online

Paper

3.2.2. N₂ sorption studies. The nitrogen adsorptiondesorption isotherms of SBA-15 and Mn-Ti-SBA-15 are shown in Fig. 4. The isotherms of Mn-Ti-SBA-15 samples exhibited type IV adsorption with H1 hysteresis loop in the relative pressure range of 0.6 and 0.8, which is similar to that of parent SBA-15. The textural properties such as surface area, pore volume and pore diameter of SBA-15 and Mn-Ti-SBA-15 with Si/(Mn + Ti) ratios of 25, 50, 75 and 100 are given in Table 1. All textural parameters increased with increased incorporation of metal content, as a consequence adsorption of nitrogen increased with increase of metal content. The surface area increased from 692 to 729 m² g⁻¹ and pore volume increased from 0.74 to 0.93 cm³ g⁻¹ due to expansion of mesopores and increase of pore diameter. The pore size distribution of SBA-15 and Mn-Ti-SBA-15 materials is shown in Fig. 5. Although SBA-15 showed very narrow pore size distribution, metal ions incorporated SBA-15 showed a slightly broad distribution which indicated well dispersion of metal ions into SBA-15 framework, and thus increased the pore diameter.

3.2.3. DRSUV-Vis spectroscopy. DRSUV-Vis spectra (Fig. 5) was useful to understand the coordination environment of Mn²⁺/Mn³⁺ and Ti⁴⁺. The DRSUV-Vis spectra of Mn-Ti-SBA-15 materials showed four distinct absorption bands at 210, 270, 305 and 513 nm. The bands at 270 and 513 nm were assigned to Mn²⁺/Mn³⁺ ions in SBA-15 framework.^{41–43} The band at 270 nm indicated the charge transfer transition of O²⁻-Mn³⁺ with tetrahedral coordination. The broad band centered at 513 nm was assigned to the d–d transition of Mn^{2+} in ${}^{6}A_{1g}$ – ${}^{4}T_{2g}$ crystal

| Indice 1 Textural properties of Min-11-SBA-15 | | | | | | | | | |
|---|---|---------------------------------|---|---|-----------------------------|--|--|--|--|
| Catalyst | Unit cell parameter <i>a</i> _o (nm) | Surface area BET $(m^2 g^{-1})$ | Pore volume $V_{\rm p}$ (cm ³ g ⁻¹) | Pore diameter <i>D</i> _p (nm) | Pore wall thickness (nm) | | | | |
| SBA-15 | 11.01 | 685 | 0.74 | 7.09 | 3.92 | | | | |
| Mn-Ti-SBA-15(25) | 11.32 | 729 | 0.93 | 7.29 | 4.03 | | | | |
| Mn-Ti-SBA-15(50) | 11.22 | 721 | 0.87 | 7.23 | 3.99 | | | | |
| Mn-Ti-SBA-15(75) | 11.20 | 715 | 0.81 | 7.21 | 3.99 | | | | |
| Mn-Ti-SBA-15(100) | 11.08 | 692 | 0.74 | 7.14 | 3.94 | | | | |

 $a_{\rm o}$ calculated from $a = 2d_{100}/3^{1/2}$. Pore wall thickness = $a_{\rm o} - D_{\rm p}$.



Fig. 3 XRD patterns of (a) Mn-Ti-SBA-15(25), (b) Mn-Ti-SBA-15(50), (c) Mn-Ti-SBA-15(75) and (d) Mn-Ti-SBA-15(100).

field transition.^{44,45} This confirmed that Mn^{2+} as well as Mn^{3+} ions coexist in SBA-15 framework. The peaks at 210 and 305 nm were assigned to Ti^{4+} in tetrahedral coordination.⁴⁶⁻⁴⁸ The first band is due to the charge transfer between O^{2-} and Ti^{4+} , and the latter band at 305 nm was assigned to the tetrahedral coordination with tripodal nature of Ti^{4+} in $(SiO)_3Ti=O.^{49,50}$ The results confirmed the octahedral coordination of Mn^{2+} and tetrahedral coordination of Mn^{3+} and Ti^{4+} ions in the mesoporous SBA-15.

3.2.4. XPS. The XPS spectra (Fig. 6) clearly revealed the oxidation state and chemical environment of the metal ions in SBA-15. All the binding energies are with reference to 1s spectrum of elemental carbon with a binding energy of 287.5 eV. The survey spectrum of Mn-Ti-SBA-15 (Fig. 6a) showed binding energy peaks for 2p of Mn and Ti and also O1s. Fig. 6b shows the XPS spectrum of the doublet spin states of Mn2p with their binding energies of 641.53 and 653.04 eV for Mn2p3/2 and Mn2p_{1/2} respectively.⁵¹ The FWHM of the Mn doublet state is found to be 1.4 eV, which provides good evidence for the presence of both Mn²⁺ and Mn³⁺ in the silica framework. The corresponding spin orbit coupling energy difference is found to be 11.51 eV. 52 The XPS spectrum of Ti 2p of Ti⁴⁺ is shown in Fig. 6c. The binding energies of 464.11 and 458.39 eV are attributed to Ti 2p1/2 and Ti 2p_{3/2} signal respectively, which is in good agreement with the binding energies of Ti⁴⁺ incorporated SBA-15.^{53,54}

The framework incorporation of metal ions was verified by the O1s XPS spectrum shown in Fig. 6d. The XPS spectrum of O1s showed three distinct deconvolute peaks which are assigned to Si–O, Mn–O and Ti–O with their corresponding binding energies of 533.2, 532.1 and 533.92 eV respectively.^{55–57} This result confirmed the incorporation of manganese and titanium species in SBA-15 framework. It was also noticed that O1s binding energies of manganese and titanium are different from TiO₂ (anatase), MnO₂ and Mn₃O₄. The framework incorporation of metal ions is well established by the O1s spectrum.



Fig. 4 (a) N₂ adsorption–desorption isotherms of (a) SBA-15, (b) Mn-Ti-SBA-15(100), (c) Mn-Ti-SBA-15(75), (d) Mn-Ti-SBA-15(50) and (e) Mn-Ti-SBA-15(25). (b) Pore size distribution of (a) SBA-15, (b) Mn-Ti-SBA-15(100), (c) Mn-Ti-SBA-15(75), (d) Mn-Ti-SBA-15(50) and (e) Mn-Ti-SBA-15(25).

The surface composition of the elements in wt% is O (68.4), Si (23.9), Mn (1.3) and Ti (1.1). These results also confirmed that manganese and titanium ions are present in the framework of SBA-15.

3.2.5. ESR spectrum. The oxidation state and coordination environment of Mn and Ti in Mn-Ti-SBA-15 were analyzed by its ESR spectrum. The ESR spectrum of Mn^{2+} showed weak sextet splitting with a *g* value of 2.0031 and hyperfine coupling constant around 97 G (Fig. 7). This provides good evidence for the presence of Mn^{2+} with octahedral coordination in Mn-Ti-SBA-15.⁴¹ The observed weak ESR sextet line may be due to the presence of Mn^{3+} . It is reported that Mn^{3+} is more opt than Mn^{2+} to be substituted for Si⁴⁺ in the framework position of zeolite and MCM-41.⁵⁸ It is therefore concluded that Mn^{2+}/Mn^{3+} ions coexist in SBA-15 framework, and not as Mn^{4+} ion. This is in good agreement with the DRSUV-Vis spectra.

Catalysis Science & Technology



Fig. 5 UV-DRS spectra of (a) Mn-Ti-SBA-15(25), (b) Mn-Ti-SBA-15(50), (c) Mn-Ti-SBA-15(75) and (d) Mn-Ti-SBA-15(100).

3.2.6. SEM and TEM. The morphology of Mn-Ti-SBA-15 materials was revealed by the SEM images as shown in Fig. 8. The morphology of the materials with different amount of metal ions loading at moderately low acidic condition (*i.e.* at pH 3) showed a worm-like structure.^{59,60} All the materials showed rope-like hexagonal structures of several hundred micrometers bundled together. The TEM images of SBA-15 and Mn-Ti-SBA-15 with various Si/(Mn + Ti) ratios are shown in Fig. 9. The images clearly demonstrated the uniform pores formed even after incorporation of the metal ions, and the estimated diameter of the pores is around 7 nm. It is inferred that the mesoporous structure was not affected during the synthesis under low acidic condition. This is in good agreement with the results of XRD and BET analysis.

3.3. Catalytic activity of Mn-Ti-SBA-15

The catalytic activity of Mn-Ti-SBA-15 was evaluated in the oxidation of ethylbenzene using TBHP as the oxidant. The influence of reaction parameters such as solvent, ratio of Si/ (Mn + Ti), temperature and time of the reaction was also studied to optimize the reaction conditions to obtain high conversion with high selectivity of the product. The results are presented in Table 2. The entries 1 to 4 in Table 2 revealed the influence of the solvent in the oxidation of ethylbenzene. Solvents such as dichloromethane, acetone, methanol and acetonitrile were used as the reaction medium for ethylbenzene oxidation. Among these solvents, acetonitrile exhibited the highest conversion with high selectivity of acetophenone. This is due to the high polar nature of the solvent that led to a partial decomposition of TBHP. The entries 5 to 7 in Table 2 show the results of Mn-SBA-15, Ti-SBA-15 and a physical mixture of these two monometallic SBA-15 as catalysts in the same oxidation which resulted low conversion. It contrast Mn-Ti-SBA-15 showed higher activity than monometallic substituted SBA-15 as well as physically mixed Mn-SBA-15 and Ti-SBA-15. The high catalytic activity of Mn-Ti-SBA-15 is ascribed to the synergetic



Fig. 6 XPS spectrum of Mn-Ti-SBA-15(50): (a) survey spectrum, (b) Mn 2p spectrum, (c) Ti 2p spectrum and (d) O 1s spectrum.

catalytic activity of Mn^{2+} and Ti^{4+} centers. The synergistic activity ascertained the simultaneous incorporation of Mn^{2+} and Ti^{4+} species in close proximity into the SBA-15 framework. The synergetic effect of Mn-Ti-SBA-15 is attributed to the



Fig. 7 ESR spectrum of Mn-Ti-SBA-15(50).



Fig. 8 SEM images of (a) Mn-Ti-SBA-15(25), (b) Mn-Ti-SBA-15(50), (c) Mn-Ti-SBA-15(75) and (d) Mn-Ti-SBA-15(100).

oxophilic centre of Ti⁴⁺ which easily coordinates with TBHP, and Mn^{2+}/Mn^{3+} species may be involved in the redox activity, which enhanced the catalytic activity. The entries 8 and 9 in Table 2 show the results of other oxidants used in the oxidation of ethylbenzene. When molecular O₂ was used as the oxidant, the conversion was found to be very low due to easy expulsion of O₂ from the reaction mixture. Similarly when H₂O₂ was used as the oxidant, it was decomposed easily and evolved oxygen rapidly due to the high exothermic nature, which resulted in a low conversion of ethylbenzene. In the case of TBHP as the oxidant, it generated active oxygen species on the redox sites and formed transition state on the catalyst which prevented expulsion of O₂ from the reaction mixture.

The effect of Si/(Mn + Ti) ratios of 25, 50, 75 and 100 incorporated into SBA-15 on the catalytic activity is depicted

Catalysis Science & Technology



Fig. 9 TEM images of (a) SBA-15 (b) Mn-Ti-SBA-15(25), (c) Mn-Ti-SBA-15(50), (d) Mn-Ti-SBA-15(75) and (e) Mn-Ti-SBA-15(100).

in Fig. 10. The ethylbenzene conversion increased with increase of metal content from 100 to 50, and further increase of metal content decreased the conversion due to limitation of reactant molecule diffusion caused by the pore blocking effect, which resulted small reduction of micropores in mesoporous SBA-15. So the reactants could not freely access the reactive sites, and hence a higher amount of Mn and Ti incorporated SBA-15 showed relatively low conversion. The order of activity for different ratios of Si/(Mn + Ti) in Mn-Ti-SBA-15 catalyst is 50 > 25 > 75 > 100. The rate of reaction for the oxidation of ethylbenzene was evaluated by the apparent rate constant, and the order for Si/(Mn + Ti) ratios of 50, 25, 75 and 100 is 7.155 × $10^{-3} \min^{-1} > 3.815 \times 10^{-3} \min^{-1} > 2.667 \times 10^{-3} \min^{-1} > 2.325 \times 10^{-3} \min^{-1}$.

3.3.1. Effect of temperature. Fig. 11 depicts the influence of the reaction temperature on ethylbenzene oxidation and acetophenone selectivity over Mn-Ti-SBA-15(50) using TBHP as the oxidant. The results revealed that the increase of the reaction temperature from 50 to 80 °C increased the ethylbenzene conversion and selectivity of acetophenone. This may be attributed to an enhanced decomposition of TBHP with the increase of temperature. It is concluded that higher temperature favored high conversion and selective oxidation. The activation energy was calculated from the Arrhenius equation, and it was found to be

Mn-Ti-SBA-15(50)d

11

 Table 2
 Ethylbenzene oxidation under different reaction conditions^a

| | | Solvent | Conversion ^e (%) | Selectivity ^e (%) | | |
|-------|---|--------------------|-----------------------------|------------------------------|------------------|------------------|
| Entry | Catalyst | | | Acetophenone | 1-phenyl ethanol | 2-phenyl ethanol |
| 1 | Mn-Ti-SBA-15(50) | CH_2Cl_2 | 59 | 29 | 59 | 12 |
| 2 | Mn-Ti-SBA-15(50) | Acetone | 52 | 39 | 46 | 15 |
| 3 | Mn-Ti-SBA-15(50) | CH ₃ OH | 34 | 47 | 22 | 31 |
| 4 | Mn-Ti-SBA-15(50) | ACN | 92 | 87 | 09 | 04 |
| 5 | Mn-SBA-15(50) | ACN | 52 | 62 | 31 | 07 |
| 6 | Ti-SBA-15(50) | ACN | 63 | 68 | 21 | 11 |
| 7 | Mn-SBA-15 + Ti-SBA-15 ^{b} | ACN | 67 | 53 | 29 | 18 |
| 8 | _ | ACN | 02 | 10 | 58 | 32 |
| 9 | Mn-Ti-SBA-15(50) | _ | 21 | 47 | 36 | 17 |
| 10 | Mn-Ti-SBA-15(50) ^c | ACN | 16 | 52 | 37 | 11 |

^a Reaction conditions: Catalyst (100 mg), ethylbenzene (3 mmol), TBHP (5 mmol), time 2 h, temperature 80 °C, and solvent (5 ml). ^b Physical mixture. ^c O_2 as oxidant. ^d H_2O_2 as oxidant. ^e Determined by GCACN = Acetonitrile.

31



ACN

21

Fig. 10 Effect of Si/(Mn + Ti) ratios in the oxidation of ethylbenzene.



45.14 kJ mol⁻¹ (Fig. 12). The results revealed that ethylbenzene oxidation over Mn-Ti-SBA-15 (50) at 80 °C showed high conversion with high selectivity of the product.



41

3.3.2. Effect of reaction time. The influence of reaction time on conversion and selectivity was studied between 1 and 3 h over Mn-Ti-SBA-15(50) catalyst using TBHP as the oxidant at 80 °C in acetonitrile, and the results are depicted in Fig. 13. The ethylbenzene conversion increased with the increase of reaction time up to 2 h whereas the selectivity of acetophenone did not change. The conversion and selectivity of the product were not alerted after 2 h reaction time. The results revealed that the reaction was almost completed in about 2 h, when the TBHP efficiency reached a maximum. This result also clearly revealed that the catalytic activity of Mn-Ti-SBA-15 was not affected by a longer reaction time. Based on the results, it is concluded that the optimal reaction time for high conversion of ethylbenzene is 2 h.

3.3.3. Reusability. The recyclability of Mn-Ti-SBA-15(50) catalyst was examined in ethylbenzene oxidation using TBHP as the oxidant in acetonitrile medium at 80 °C for 2 h. The used catalyst in the first cycle was recovered by filtration, activated at 300 °C and reused in the second cycle. This was repeated for 5 cycles and the results are depicted in Fig. 14. The results clearly showed that the reused catalyst did not show a significant loss in

28



Fig. 13 Effect of the reaction time on the oxidation of ethylbenzene.



activity up to 5 cycles. It is concluded that Mn-Ti-SBA-15 is a highly active and recyclable catalyst for oxidation reactions.

4. Conclusion

Mn-Ti-SBA-15 catalyst was synthesized by direct hydrothermal method with moderately low acidic condition. The pH adjusting method is found to be attractive to create multi-functional active sites in the mesoporous silica. The XRD and nitrogen sorption studies supported the framework incorporation of the metal ions without affecting the mesoporous structure. The oxidation state and coordination environment of Mn^{2+}/Mn^{3+} and Ti^{4+} are well established by DRSUV-Vis, XPS and ESR. The results evidently proved octahedral coordination for Mn^{2+} and tetrahedral coordination for Mn^{3+} and Ti^{4+} ions are present in the silica framework. The catalytic activity of Mn-Ti-SBA-15 in the oxidation of ethylbenzene using TBHP as the oxidant showed enhanced catalytic activity. The catalytic activity and

recyclability of the catalyst up to 5 cycles indicated that manganese and titanium species are intact in the mesoporous framework without leaching.

Acknowledgements

The authors gratefully acknowledge the financial support from the Department of Science and Technology (DST) (Sanction No. SR/S1/PC-10/2009, Dated 28.10.2009). One of the authors, Visuvamithiran is thankful to DST for the award of SRF position in this project. The authors are also thankful to UGC-DRS scheme and DST-FIST programme for creating infrastructural facilities.

References

- 1 R. A. Sheldon and J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- 2 R. Alcantara, L. Canoira, P. G. Joao, J. M. Santos and I. Vázquez, *Appl. Catal.*, *A*, 2000, **203**, 259–268.
- 3 A. Corma, Chem. Rev., 1997, 97, 2373-2419.
- 4 R. Chakravarti, P. Kalita, S. T. Selvan, H. Oveisi, V. V. Balasubramanian, M. L. Kantam and A. Vinu, *Green Chem.*, 2010, **12**, 49–53.
- 5 Z. Luan, M. Hatmann, D. Zhao, W. Zhou and L. Kevan, *Chem. Mater.*, 1999, **11**, 1621–1627.
- 6 R. M. Martín-Aranda and J. Cejka, *Top. Catal.*, 2010, 53, 141–153.
- 7 K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji and J. P. Hill, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 1–32.
- 8 M. Claudia Marchi, J. J. S. Acuna and C. A. Figueroa, *J. Nanosci. Nanotechnol.*, 2012, **12**, 6439–6444.
- 9 M. B. Zakaria, N. Suzuki, K. Shimasaki, N. Miyamoto, Y. T. Huang and Y. Yamauchi, *J. Nanosci. Nanotechnol.*, 2012, **12**, 4502–4507.
- 10 W. Xuan, C. Zho, Y. Liu and Y. Cui, *Chem. Soc. Rev.*, 2012, 41, 2590–2604.
- 11 Z. Li, J. C. Barnes, A. Bosoy, J. F. Stoddart and J. I. Zink, *Chem. Soc. Rev.*, 2012, **41**, 1677–1693.
- 12 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. Fredrikson,
 B. F. Chemelka and G. D. Stucky, *Science*, 1998, 279, 548–552.
- 13 R. Ryoo, J. M. Kim, C. H. ko and C. H. Shin, *J. Phys. Chem.*, 1996, **100**, 17718–17721.
- 14 R. R. Murugavel and H. W. Roesky, *Angew. Chem.*, 1997, **109**, 491–494.
- 15 A. Vinu, V. Murugesan and M. Hartmann, *Chem. Mater.*, 2003, **15**, 1385–1393.
- 16 S. Wu, Y. Han, Y. C. Zou, J. W. Song, L. Zhao, Y. Di, S. Z. Liu and F. S. Xiao, *Chem. Mater.*, 2004, **16**, 486–492.
- 17 A. Vinu, G. Sathish Kumar, K. Ariga and V. Murugesan, J. Mol. Catal. A: Chem., 2005, 235, 57–66.
- 18 G. Chandrasekar, M. Hartmann, M. Palanichamy and V. Murugesan, *Catal. Commun.*, 2007, 8, 457–461.
- 19 F. Berube, A. Khadhraoui, M. T. Janicke, F. Kleitz and S. Kaliaguine, *Ind. Eng. Chem. Res.*, 2010, **49**, 6977–6985.
- 20 M. Selvaraj and D. W. Park, Appl. Catal., A, 2010, 388, 22-30.

- 21 G. Sathish Kumar, M. Palanichamy, M. Hartmann and V. Murugesan, *Catal. Commun.*, 2007, **8**, 493–497.
- 22 M. Selvaraj and T. G. Lee, J. Phys. Chem. B, 2006, 110, 21793-21802.
- 23 A. Vinu, D. P. Sawant, K. Ariga, K. Z. Hossain,
 S. B. Halligudi, M. Hartmann and M. Nomura, *Chem. Mater.*, 2005, 17, 5339–5345.
- 24 A. J. Bard, R. Parsons and J. Jordan, *Standard Potential in Aqueous Solution*, Marcel Dekker, New York, 1985, p. 429.
- 25 B. Notari, Adv. Catal., 1996, 41, 253-334.
- 26 I. W. C. E. Arends, R. A. Sheldon, M. Wallau and U. Schuchardt, Angew. Chem., Int. Ed. Engl., 1997, 36, 1144–1163.
- 27 J. Paterson, M. Potter, E. Gianotti and R. Raja, *Chem. Commun.*, 2011, 47, 517–519.
- 28 S. Maurelli, M. Chiesa, E. Giamello, R. M. Leithall and R. Raja, *Chem. Commun.*, 2012, 48, 8700–8702.
- 29 V. Parvulescu, C. Anastasescu, C. Constantin and B. L. Su, *Catal. Today*, 2003, **78**, 477–485.
- 30 A. Vinu, K. Ariga, S. Saravanamurugan, M. Hartmann and V. Murugesan, *Microporous Mesoporous Mater.*, 2004, 76, 91–98.
- 31 M. Karthick, A. K. Tripathi, N. M. Gupta, A. Vinu, M. Hartmann, M. Palanichamy and V. Murugesan, *Appl. Catal.*, A, 2004, 268, 139–149.
- 32 Y. Zhang, F. Gao, H. Wan, C. Wu, Y. Kong, X. Wu, B. Zhao, L. Dong and Y. Chen, *Microporous Mesoporous Mater.*, 2008, 113, 393–401.
- 33 F. Adam and R. Thangappan, Chem. Eng. J., 2010, 160, 249-254.
- 34 S. Varghese, C. Anand, D. Dhawalea, A. Mano, V. V. Balasubramaniana, G. A. Gnana Raj, S. Nagarajana, M. A. Wahab and A. Vinu, *Tetrahedron Lett.*, 2012, 53, 5656–5659.
- 35 S. Varghese, S. Nagarajan, M. R. Benzigar, A. Mano, Z. A. Alothman, G. A. Gnana Raj and A. Vinu, *Tetrahedron Lett.*, 2012, 53, 1485–1489.
- 36 M. Severaj, D. W. Park, I. Kim, S. Kawi and C. S. Ha, *Dalton Trans.*, 2012, **41**, 14197–14203.
- 37 H. Zhang, C. Tang, C. Sun, L. Qi, F. Gao, L. Dong and Y. Chen, *Microporous Mesoporous Mater.*, 2012, **151**, 44–55.
- 38 H. Maneesuwan, R. Longloilert, T. Chaisuwan and S. Wongkasemjit, *Mater. Lett.*, 2013, 94, 65–68.
- 39 H. P. Lin, C. P. Mou and S. B. Liu, J. Phys. Chem. B, 2000, 104, 7885–7894.
- 40 A. Takai, Y. Doi, Y. Yamauchi and K. Kuroda, *J. Phys. Chem. C*, 2010, **114**, 7586–7293.

- 41 Q. Zhang, Y. Wang, S. Itsuki, T. Shishido and K. Takehira, J. Mol. Catal. A: Chem., 2002, 188, 189–200.
- 42 M. Selvaraj, P. K. Sinha, K. Lee, I. Ahn, A. Pandurangan and T. G. Lee, *Microporous Mesoporous Mater.*, 2005, **78**, 139–149.
- 43 S. Vetrivel and A. Pandurangan, *J. Mol. Catal. A: Chem.*, 2006, **246**, 223–230.
- 44 S. Velu, N. Shah, T. M. Jyothi and S. Sivasanker, *Microporous Mesoporous Mater.*, 1999, 33, 61–75.
- 45 A. Ramanathan, T. Archipov, R. Maheswari, U. Hanefeld,
 E. Roduner and R. Gla1ser, J. Phys. Chem. C, 2008, 112, 7468–7476.
- 46 C. Yu, H. Chu, Y. Wan and D. Zhao, *J. Mater. Chem.*, 2010, 20, 4705–4714.
- 47 C. Anand, P. Srinivasu, G. P. Mane, S. N. Talapaneni, D. S. Dhawale, M. A. Wahab, S. Vishnu Priya, S. S. Varghese, Y. Sugi and A. Vinu, *Microporous Mesoporous Mater.*, 2007, **100**, 20–26.
- 48 L. Kumaresan, A. Prabu, M. Palanichamy and V. Murugesan, J. Taiwan Inst. Chem. Eng., 2010, 41, 670–675.
- 49 V. A. de la Pena OShea, M. C. Capel-Sanchez, G. Blanco-Brieva, J. M. Campos- Martin and J. L. G. Fierro, *Angew. Chem., Int. Ed.*, 2003, 42, 5851–5854.
- 50 K. Choi, T. Yokoi, T. Tatsumic and K. Kuroda, *J. Mater. Chem. A*, 2013, **1**, 2485–2494.
- 51 P. Van Der Voort, M. Morey, G. D. Stucky, M. Mathieu and E. F. Vansant, *J. Phys. Chem. B*, 1998, **102**, 585–590.
- 52 I. Fechete, O. Ersen, F. Garin, L. Lazar and A. Rach, *Catal. Sci. Technol.*, 2013, **3**, 444–453.
- 53 C. Yu, H. Chu, Y. Wan and D. Zhao, J. Mater. Chem., 2010, 20, 4705–4714.
- 54 *Handbook of X-ray photoelectron spectroscopy*, ed. J. Chastin and R. C. King Jr, Physical Electronics. Inc., Minneapolis, Minnesota, 1995.
- 55 T. L. Barr, Zeolites, 1990, 10, 760.
- 56 A. Miyakoshia, A. Uenob and M. Ichikawac, *Appl. Catal.*, A, 2001, 219, 249–258.
- 57 Z. H. Luan, E. M. Maes, P. A. W. van der Heide, D. Y. Zhao, R. S. Czernuszewicz and L. Kevan, *Chem. Mater.*, 1999, **11**, 3680–3686.
- 58 Q. Zhang, Y. Wang, Y. Ohishi, T. Shihido and K. Takehira, J. Catal., 2001, 202, 308–318.
- 59 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, J. Am. Chem. Soc., 1998, 120, 6024–6036.
- 60 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson,
 B. F. Chmelka and G. D. Stucky, *Science*, 1998, 279, 548–552.