ORIGINAL ARTICLE

Synthesis, characterization and catalytic application of silica supported tin oxide nanoparticles for synthesis of 2,4,5-tri and 1,2,4,5-tetrasubstituted imidazoles under solvent-free conditions

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Abstract   Highly efficient and eco-friendly, one pot synthesis of 1,2,4,5-tetra substituted imidazoles and 2,4,5-trisubstituted imidazoles was reported under solvent free conditions using nanocrystalline silica supported tin oxide (SiO_2:SnO_2) as a catalyst with excellent yield. The present methodology offers several advantages such as mild reaction conditions, short reaction time, good yield, high purity of product, recyclable catalyst without a noticeable decrease in catalytic activity and can be used for large scale synthesis. The synthesized SiO_2:SnO_2 nanocrystalline catalyst was characterized by XRD, BET surface area and TEM techniques.

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1. Introduction

Multisubstituted imidazole derivatives are an important pharmacophore in modern drug design and discovery (Lombardino and Wiseman, 1974). The substituted imidazole derivatives

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have been reported to have a wide range of applications in diverse therapeutic areas including anti-inflammatory, antiviral, antibacterial, anti-allergic, and antitumor (Mison, 2001; Black et al., 1974; Ucucu et al., 2001; Antolini et al., 1999; Wang et al., 2002). A wide variety of derivatives of this ring system have been used as heme oxygenase-1 inhibitors, HMG-Co A reductase inhibitors, hemeoxygenase inhibitors, fatty acid amide hydrolase inhibitors, γ-aminobutyric acid receptor agonists and P2X$_7$ receptor agonists (Nie et al., 2012) and also act as inhibitors of p38 and MAP kinase and glucagon receptors (Murry, 2003). Over the century, imidazoles have received significant attention due to their synthesis, reactions and biochemical properties. Even today, research in imidazole chemistry continues undebated.

There are many methods used for the synthesis of multisubstituted imidazoles, some imidazoles have been prepared by Ugi reaction and Davidson cyclization (Sung et al., 2002; Gulevich et al., 2007) or by reaction of imidazolium ylids and lithiated imidazoles (Zificsak and Hlasta, 2005; Torregrosa et al., 2005). The multisubstituted imidazoles also synthesized by condensation of 1,2-diketone or α-hydroxy ketone with aldehyde and ammonium acetate on a solid support by microwave irradiation, by heterocyclic cope rearrangement, condensation of a 1,2-diketone with an aryl nitrile and primary amine under microwave irradiation and N-alkylation of trisubstituted imidazoles (Sparks et al., 2004; Usyatinsky and Khmelnitsky, 2000). Tetra substituted imidazoles can be directly prepared from cycloaddition of munchnone derivatives but this methodology is limited to N-methyl imidazoles (Nagarapu et al., 2007). Recently, the synthesis of multisubstituted imidazole derivatives was reported by condensation of aryl aldehyde with 1,2-dicarbonyl compound, primary amine and ammonium acetate using Cu(II) nitrate impregnated zeolite, triphenyl (propyl-3-sulfonyl) phosphonium toluenesulfonate, $FeCl_3 \cdot 6H_2O$, $AlCl_3$, $MgCl_2$, $HClO_4$:SiO_2, SiO_2/$NaHSO_4$, sulfanilic acid, CAN, ionic liquids, p-toluene sulfonic acid and alum (Sharterian et al., 2011; Sivakumar et al., 2010; Heravi et al., 2008; Sadeghi et al., 2008; Karimi et al., 2006; Mohammed et al., 2008; Sangshetti et al., 2008; Khodaei et al., 2007; Mohammad et al., 2008; Kantevari et al., 2007). Despite their tremendous success, many of these methods have suffered from some drawbacks such as, low yield, long reaction time, harsh reaction conditions and tedious work up, some of the catalysts employed are expensive and toxic. Co-occurrence of several side reactions and in some cases more than one step is involved in the synthesis of compound. Hence, the challenge for a sustainable environment calls the use of alternative procedures avoiding the use of harmful solvents and catalysts. Keeping all these things in our mind, we report the efficient and recyclable SiO_2:SnO_2 nanocatalyst for the synthesis of multisubstituted imidazole derivatives.

Nowadays, the use of heterogeneous catalysts has gained more importance in various disciplines including organic synthesis (Henrich and Cox, 1994). Recently, mixed metal oxide as a solid heterogeneous catalyst would be an encouraging alternative owing to its eco-friendliness and easy synthesis. It has received more attention due to its high thermal stability, large surface area, easy recovery and good ability to perform organic reactions at lower temperatures. A mixed metal oxide represents one of the most important and widely employed categories of solid catalyst, either as active phase or support. A metal oxide and mixed metal oxides utilize both acid–base and redox properties and constitute the largest family of catalyst in heterogeneous catalysis (Noguera et al., 1996; Reddy, 2006; Feng et al., 2005). In the field of catalysis mixed metal oxides have been extensively used as a catalyst for various organic transformation reactions such as, oxidation reactions (Gawande et al., 2006), dehydrogenation and condensation reactions (Emrani et al., 2011), epoxidation reactions (Choudhary et al., 2006), photocatalytic reaction (Gambhire et al., 2008). In view of importance of mixed metal oxide catalysts in organic synthesis and for continuation of our work (Borhade et al., 2012) we now wish to report the preparation of an efficient and recyclable SiO_2:SnO_2 nanocrystalline catalyst by hydrothermal method for the synthesis of multisubstituted imidazole derivatives.

2. Materials and methods

All chemicals were purchased from Aldrich chemical company and were used without purification. The XRD patterns were acquired on a multi-purpose X-ray diffractometer (Philips-1710 diffractometer CuKα, λ: 1.5406 A°) at a scan rate of $0.17°\ 2\theta\ s^{-1}$. The nanosize and morphology of the SiO_2:SnO_2 nanocatalyst were observed under TEM with SAED (CM-200, Philips microscope). The surface area of the material was measured by N_2 adsorption–desorption isotherm, and was carried out on Quantachrome Autosorb Automated Gas Sorption System Autosorb-1, NOVA-1200 and Mercury Porosimeter Autosorb-1c. All yields refer to isolated products after purification using column chromatography. Column chromatography was performed on silica gel (120–240 mesh) supplied by Acme Chemical company. IR spectra were run on a 8400s Shimadzu FTIR Spectrophotometer (as KBr pellets). ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury XL-300 and Bruker spectrometer instruments using TMS as an internal standard and $CDCl_3$, DMSO-d_6 as a solvent. The mass spectra were recorded on Shimadzu GC–MS QP 2010A mass spectrometer with an ionization potential of 70 eV.

2.1. Preparation of SiO_2:SnO_2 nanoparticle

SiO_2:SnO_2 nanoparticles were synthesized by hydrothermal method. In typical experiments, 1.0 mmol of $SiCl_4$ and 1.2 mmol of $SnCl_2 \cdot 2H_2O$ (Merck > 99%) were added to 40 ml of distilled water. To basify the above solid solution

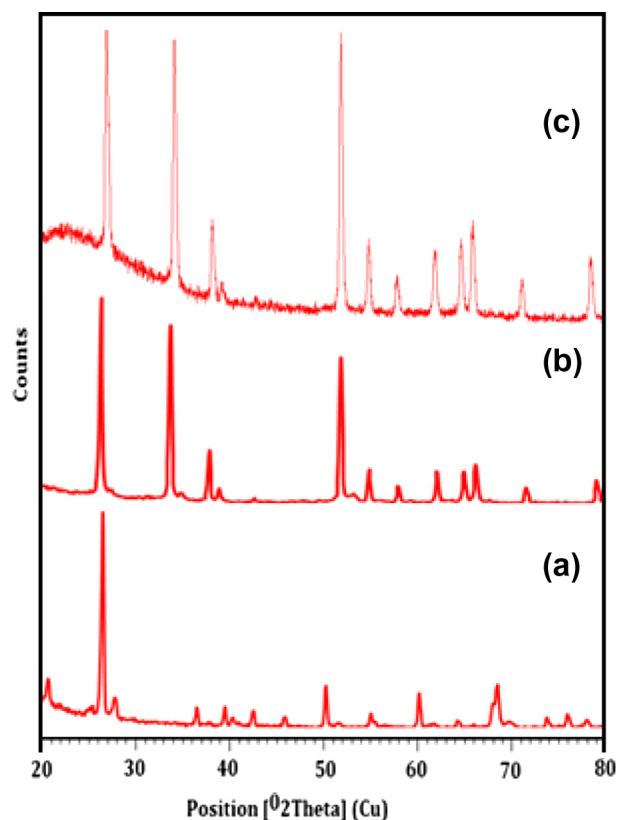**Figure 1** XRD pattern of (a) SiO_2, (b) SnO_2 and (c) SiO_2:SnO_2.

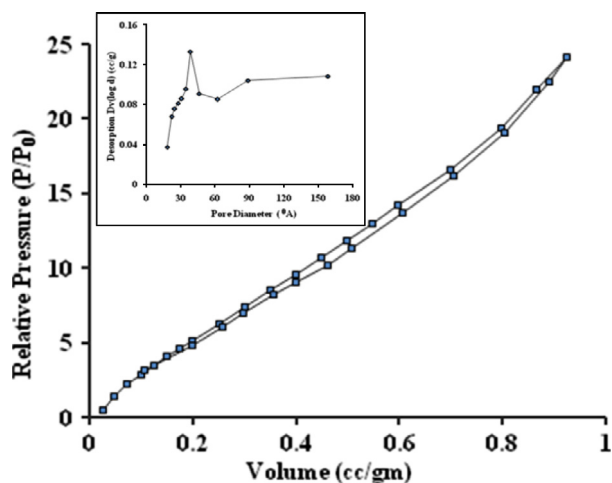**Figure 2** BET surface area of SiO_2:SnO_2.

mixture, 2 M NaOH solution was used. The mixture was then transferred to a Teflon-lined stainless steel autoclave and placed in the oven at 120 °C for 48 h. After 48 h, the Teflon bottle was cooled naturally at room temperature. The solid products obtained were filtered, washed with deionized water and dried in the oven at 100 °C for 24 h. Then, the final product was characterized by instrumental technique and used for reaction.

2.2. General procedure for the synthesis of 2,4,5-tri and 1,2,4,5-tetra substituted imidazoles

A mixture of benzil (1 mmol), an aromatic aldehyde (1.2 mmol), a primary amine (1.1 mmol), ammonium acetate (1 mmol) and SiO_2:SnO_2 (0.5 mmol) was heated in the oil bath at 80 °C for 30–120 min. The reaction progress was monitored by thin-layer chromatography (TLC) by using ethyl acetate–hexane (3:7 v/v) as the solvent system. After

completion, the reaction mixture was cooled up to room temperature; hot absolute ethanol was added and filtered to remove the catalyst. The catalyst was washed with a small portion of cold water (10 ml) and hot absolute ethanol (10 ml) respectively. The combined filtrate was concentrated to half and kept at room temperature. The precipitate was collected by filtration, dried overnight and recrystallized from absolute ethanol to give compounds in high yield. The separated catalyst was washed with cold water and hot absolute ethanol, dried at 120 °C under vacuum for 3 h and reused for another reaction. The catalyst could be used at least three times with only slight reduction in its catalytic activity. Similar procedure was employed for the synthesis of 2,4,5-trisubstituted imidazoles by using benzil (1 mmol), aromatic aldehyde (1.2 mmol), ammonium acetate (2.3 mmol) and SiO_2:SnO_2 (0.5 mmol) catalyst. All the products were characterized by IR, ^{1}H, ^{13}C NMR, Mass spectrometry and their melting points were identical to those of the known compounds reported in the literature.

2.3. Spectral data of selected and unknown compounds

2.3.1. 1,2,4,5-Tetraphenyl-1H-imidazole
FT-IR (KBr, cm^{-1}): 3350, 2870, 2295, 1636, 1216; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.08 (d, J = 6.4 Hz, 2H), 7.18 (m, 2H), 7.21–7.35 (m, 12H), 7.48 (m, 2H), 7.66 (d, J = 7.2 Hz, 2H); ^{13}C NMR (DMSO-d_6): 146.78, 136.12, 136.95, 134.28, 131.00, 130.75, 130.49, 130.36, 128.97, 128.86, 128.31, 128.25, 128.17, 128.07, 128.00, 127.87, 127.32, 126.52; EI-MS (m/z): 373 (M + 1).

2.3.2. 2-(3,4-Dimethoxyphenyl)-1,4,5-triphenyl-1H-imidazole
FT-IR (KBr, cm^{-1}): 3446, 1633, 1545; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 3.85 (s, 3H), 3.89 (s, 3H), 7.21–7.81 (m, 13H), 12.52 (br s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 59.2, 59.7, 106.8, 109.9, 112.1, 122.3, 124.2, 125.6, 129.1, 128.1, 128.4, 128.5, 129.1, 129.5, 129.9, 130.5, 130.9, 132.5, 135.6, 140.2, 143.4, 150.5, 152.2; EI-MS (m/z): 433.79 (M + 1).
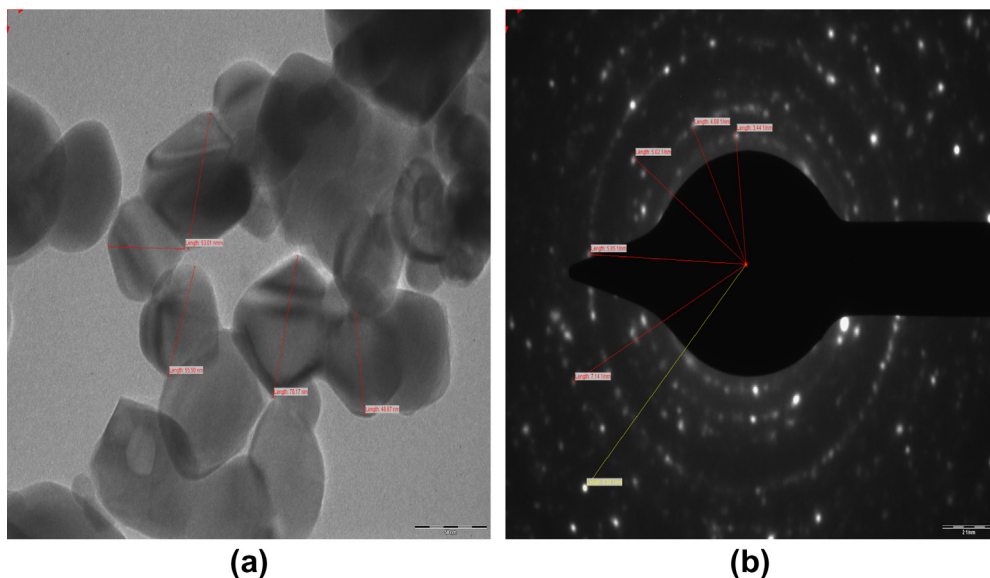

(a)

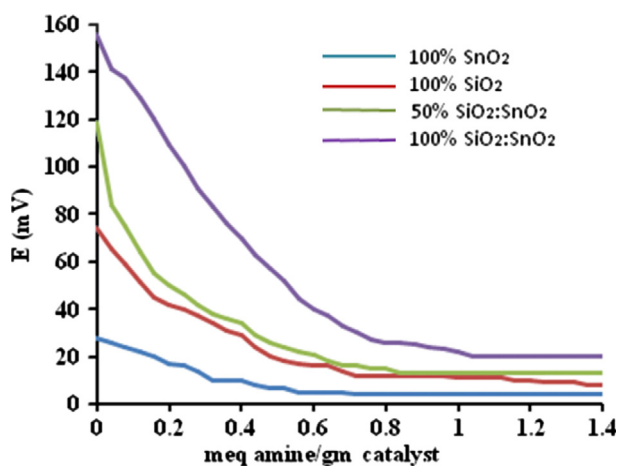**(b)**

Figure 3 TEM and SAED of SiO_2:SnO_2.

Figure 4 Potentiometric titration curves for SiO$_2$:SnO$_2$ catalysts.

Table 1 Effect of catalyst on reaction time and yield.

Entry	Catalyst	Time (min)	Yield (%)
1	SiO$_2$	90	64
2	SnO$_2$	80	48
3	25% SiO$_2$:SnO$_2$	50	69
4	50% SiO$_2$:SnO$_2$	40	71
5	75% SiO$_2$:SnO$_2$	30	79
6	100% SiO$_2$:SnO$_2$	25	94

Table 2 Effect of mole percentage of catalyst.

Entry	(mol) of SiO$_2$:SnO$_2$	Time (min)	Yield (%)
1	0.1	80	78
2	0.4	40	89
3	0.5	25	94
4	1.0	25	87

2.3.3. 2,4,5-Triphenyl-1H-imidazole

FT-IR (KBr, cm^{-1}): 3434, 2993, 2470, 1638 1216, ^{1}H NMR (DMSO-d_6 + CDCl$_3$, 300 MHz): δ 12.61 (br s, 1H), 7.42–8.12 (m, 15H). ^{13}C NMR (DMSO-d_6 + CDCl$_3$, 75 MHz): 136.5, 129.1, 128.5. 127.2, 122.1, EI-MS (m/z): 297.08 (M + 1).

2.3.4. 2-(4-Methoxy-phenyl)-4,5-diphenyl-1H-imidazole

FT-IR (KBr, cm^{-1}): 3428, 2893, 2465, 1636, 1216; ^{1}H NMR (DMSO-d_6 300 MHz): δ 3.85 (s, 3H), 12.52 (br s, 1H), 8.02–8.05 (d, 2H), 7.25–7.59 (m, 10H,), 6.93–6.96 (d, 2H), 3.85 (s, 3H); ^{13}C NMR (DMSO-d_6): 159.1, 145.7, 132.8, 127.6, 126.5, 126.3, 122.7, 113.2, 54.6; EI-MS (m/z): 327.50 (M + 1).

Table 3 Effect of Solvent on reaction.

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	Solvent free	60	45	83
2	Solvent free	80	25	94
3	Solvent free	100	25	92
4	Solvent free	120	20	89
5	MeOH	Reflux	25	87
6	EtOH	Reflux	45	86
7	DMF	Reflux	40	82
8	CH$_3$CN	Reflux	60	69
9	CH$_2$Cl$_2$	Reflux	50	72

3. Results and discussion

In this study, we have prepared the SiO$_2$:SnO$_2$ nanocatalyst by hydrothermal method. The XRD patterns of SiO$_2$:SnO$_2$ along with SiO$_2$ and SnO$_2$ are shown in Fig. 1. The peaks are sharp and fit well with the previous reported values of cassieeterite SnO$_2$ (JCPDS 1983 41-1445). These indicate that tin oxide is formed in the sample with small size. On the other hand, the XRD spectrum does not reveal any other phase except the characteristic peaks of tin oxide. This result shows that the direct chemical interaction of SnO$_2$ with SiO$_2$ does not occur in the composite metal oxide.

The particle size in the range of 60–70 nm was calculated from XRD data of the nanocrystalline SiO$_2$:SnO$_2$ using Scherrer equation. ($l = K\lambda/\beta\cos\theta$), where λ is the wavelength of the X-ray radiation (CuKα = 1.5406 Å), K is the constant taken as 0.89, β is the line width at half maximum height and θ is the diffracting angle.
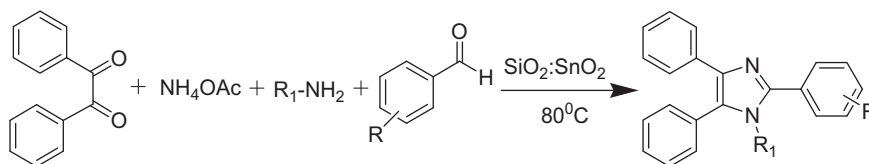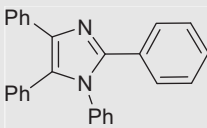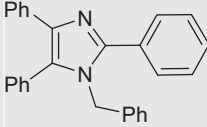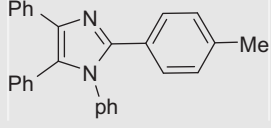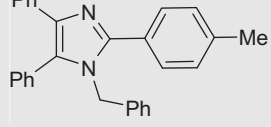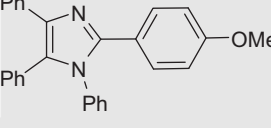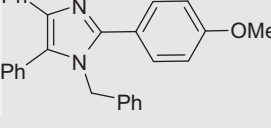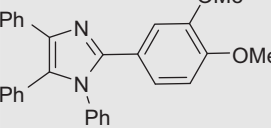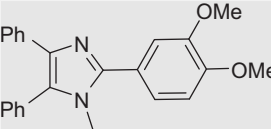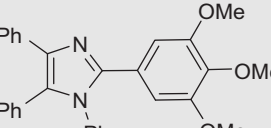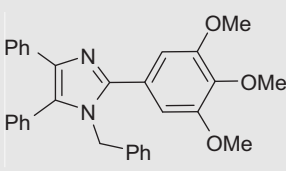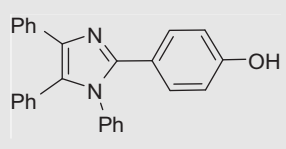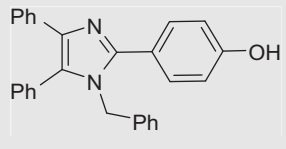

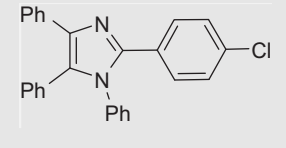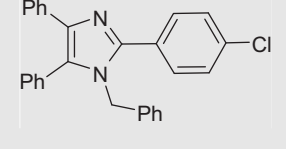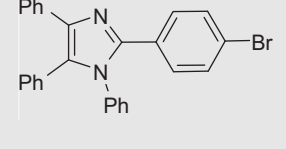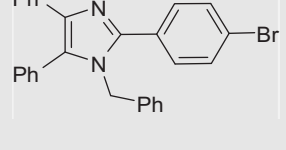**Scheme 1** Synthesis of 1,2,4,5-tetrasubstituted imidazole.
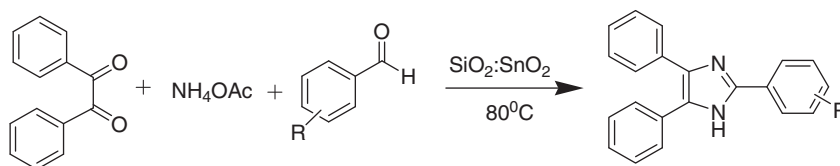
Scheme 2 Synthesis of 2,4,5-trisubstituted imidazole.

Table 4 Synthesis of 1,2,4,5-tetra substituted imidazoles.

Entry	Aryl aldehyde R	Primary amine R_1	Product	Time (min)	Yield[a] (%)	M.P. (reported M.P.)[b]
1a	C_6H_5	C_6H_5		25	94	217–220 (216–218)[32]
1b		$C_6H_5CH_2$		25	89	162–163 (165–167)[26]
2a	4-MeC$_6$H$_4$	C_6H_5		35	92	185–187 (185–188)[32]
2b		$C_6H_5CH_2$		40	95	168–170 (165–166)[26]
3a	4-MeOC$_6$H$_4$	C_6H_5		35	92	171–173
3b		$C_6H_5CH_2$		30	88	159–162 (157–160)[26]
4a	3,4-MeOC$_6$H$_3$	C_6H_5		50	92	175–178
4b		$C_6H_5CH_2$		45	90	183–184 (185–187)[33]
5a	2,3,4-MeOC$_6$H$_3$	C_6H_5		40	93	135–137

Table 4 (*continued*) Synthesis of 1,2,4,5-tetra substituted imidazoles.

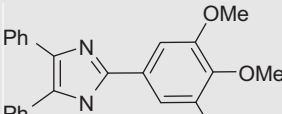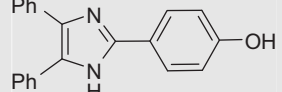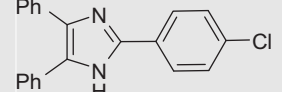|					
5b		$C_6H_5CH_2$		45	87	179–180 (184–186)[26]
6a	4-HO-C_6H_4	C_6H_5		30	94	276–278 (280)[17]
6b		$C_6H_5CH_2$		30	90	135–137 (134–135)[26]
7a	4-Cl-C_6H_4	C_6H_5		20	93	194–195 (189–192)[33]
7b		$C_6H_5CH_2$		25	91	156–158 (162–165)[26]
8a	2-Br-C_6H_4	C_6H_5		25	94	195–197
8b		$C_6H_5CH_2$		25	89	171–173 (170–172)[26]
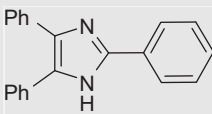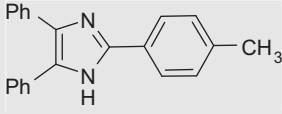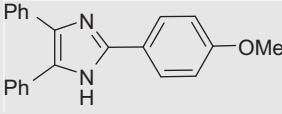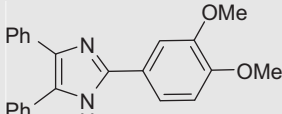
[a] All the products were characterized by ^{1}H NMR and MS spectral data and were compared with the reference compounds. The products were characterized by comparison of their spectroscopic and physical data with reference samples.
[b] References for known compounds.

Fig. 2 shows the N_2 adsorption–desorption isotherms and the BJH pore size distribution of SiO_2:SnO_2. It reveals that the samples have typical IV N_2 adsorption–desorption isotherms with H_1 hysteresis which indicates that the sample reserves the cylindrical mesopores. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Based on the N_2 adsorption–desorption isotherms, the specific surface area (S_{BET}), of SiO_2:SnO_2 obtained from BET method is 87.6 m^2/g, the average pore volume (V_P) and pore diameter (dp) were 0.110 cc/g and 70.12 Å.

The TEM image along with the selected area of the diffraction pattern (SAED) (Fig. 3a and b), was recorded for the sample corresponding to SiO_2:SnO_2. TEM reveals that the nanoparticles are tetragonal with several hexagonal shaped crystallites. The dark spot in the TEM micrograph can be alluded to the synthesized SiO_2:SnO_2 nanoparticles as SAED pattern associated with such spots reveals the occurrence of SiO_2:SnO_2 in total agreement with the XRD data. The average size of the SiO_2:SnO_2 nanocrystallite was found to be 62.3 nm.

Table 5 Synthesis of 2,4,5-tri substituted imidazoles.

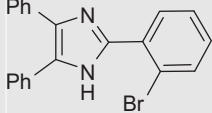| Entry	Aryl aldehyde R	Time (min)	Product	Yield[a] (%)	M.P. (reported)[b]
1	C_6H_5	25		94	270–272 (273–275)[17]
2	4-MeC_6H_4	20		93	232–233 (234–236)[17]
3	4-MeOC_6H_4	15		90	248–251 (256–257)[17]
4	$3,4\text{-(MeO)}_2C_6H_3$	30		91	210–211 (213)[17]
5	$2,3,4\text{-(MeO)}_3C_6H_2$	30		92	255–257 (259–261)[17]
6	4-HO-C_6H_4	25		89	260–261 (261–263)[17]
7	4-Cl-C_6H_4	20		91	250–252 (253–254)[17]
8	2-Br-C_6H_4	15		93	205–207

[a] All the products were characterized by ^{1}H NMR and MS spectral data and were compared with the reference compounds. The products were characterized by comparison of their spectroscopic and physical data with reference samples.
[b] References for known compounds.

The acidity of the catalysts was measured by potentiometric titration with n-butylamine. The n-butylamine is considered a strong base, so its adsorption could be expected on sites of different acid strengths. The total solid acidity without distinguishing the type of acidity is titrated. The potentiometric titration curves obtained for the supported catalysts during the n-butylamine are shown for $SiO_2:SnO_2$ in Fig. 4. This technique evaluated the total number of acid sites (meq amine/g

solid) and their strength (E_i) on the catalyst surface. The strength of the acid sites can be classified according to following scale: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ mV (weak sites), and $E_i < -100$ mV (very weak sites) (Cid and Pecci, 1985).

Fig. 4 shows the titration curves of some selected solid acid catalysts. According to this scale, SnO_2 and SiO_2 show strong sites at $E_i = 28$ and 74 mV respectively. While 50% and 100% SiO_2:SnO_2 show very strong sites at 119 and 156 mV with total number of acidic sites at 0.56, 0.67, 0.92 and 1.25 mmol g^{-1} respectively. It is observed that the strength of acid sites of SiO_2:SnO_2 is stronger than the others.

3.1. Catalytic results

In order to get effective results, the reaction conditions were optimized. For this purpose, benzil, an aromatic aldehyde, primary amine and ammonium acetate were used as the model substrate for the synthesis of 1,2,4,5-tetrasubstituted imidazoles (Scheme 1). Similarly benzil, aromatic aldehyde and ammonium acetate were used as the model substrate for the synthesis of 2,4,5-trisubstituted imidazoles (Scheme 2). The reaction was monitored by TLC technique using ethyl acetate–hexane (3:7 v/v) as the solvent system. The reaction conditions were optimized in terms of the following reaction variables.

Initially, a blank reaction was carried out using benzil, an aromatic aldehyde, primary amine and ammonium acetate for the synthesis of 1,2,4,5-tetrasubstituted imidazole. Similarly benzil, aromatic aldehyde and ammonium acetate were used for the synthesis of 2,4,5-trisubstituted imidazole at 80 °C which resulted in no formation of imidazole product even after 2 h. The same reaction was carried out using a catalytic amount of SiO_2:SnO_2 which afforded the desired substituted imidazole with 94% yield in 25 min.

To check the effectiveness of nanocrystalline SiO_2:SnO_2 with different catalysts we tried SnO_2, SiO_2, SiO_2:SnO_2, for the cyclization reaction of multisubstituted imidazoles. SnO_2 gave poor yield while SiO_2 and 50% SiO_2:SnO_2 gave good yield but required more time as compared to SiO_2:SnO_2. We observed that SiO_2:SnO_2 gave good yield with less time compared to 25%, 50% and 75% SiO_2:SnO_2 and the results are shown in Table 1. Thus, it is confirmed from our studies that SiO_2:SnO_2 was superior for the cyclization reaction with good yield in short time.

To optimize the amount of catalyst required for the cyclization we tried various mol equivalents of the catalyst compared to the quantity of the benzil (Table 2). It was found that when the reaction was carried out with 0.5 mol equivalents cyclization was 94%.

The cyclization reaction was carried out in different solvents such as DMF, MeOH, EtOH, and CH_3CN and the results clearly demonstrated that methanol was found to be the good choice which is shown in Table 3. The yields of the reaction under solvent free conditions were greater and the reaction times were generally shorter than the conventional method. The best result was obtained at 80 °C for 20 min under solvent free conditions. Increasing reaction time or temperature did not improve the yield. Subsequently, all the reactions were carried out at 80 °C under solvent free conditions.

The generality of the cyclization reaction of multisubstituted imidazoles was checked by treating it with a wide range of substituted primary amine and aryl aldehyde. The results
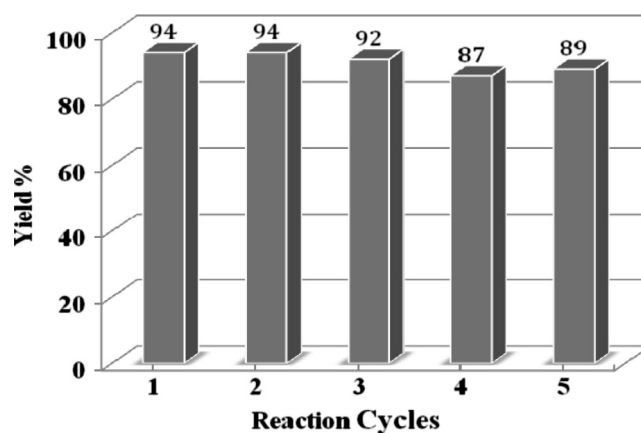

Figure 5 Results of the reaction run in the presence of recycled catalyst.

obtained are shown in Table 4. It is worthy to mention that present method provides for the synthesis of some new furnished multisubstituted imidazoles (Table 4 entries 3a, 4a, 5a, 8a and 8b, Table 5 entry 8) which have not been synthesized earlier.

The effect of electron donating and electron withdrawing substituents on the aromatic ring of aryl aldehydes on the rate of reaction was investigated. As Table 4 demonstrates electron donating groups influence the reaction and furnish the corresponding 1,3,4,5-tetrasubstituted imidazoles in high yield with less time (Table 4 entries 1–6), whereas electron withdrawing substituents need a longer reaction time with good yield (Table 4 entries 7 and 8). Moreover it has been observed that the electronic properties of the aromatic ring of aryl aldehyde have some effect on the yield and reaction time. Similar effects were observed for the synthesis of 2,4,5-trisubstituted imidazoles (Table 5).

In order to study the possibility of reusability, the catalyst was filtered, washed with methanol and calcined at 200 °C in an oven for 2 h. The reusability of the catalyst was checked for several successive runs under identical reaction conditions. The catalyst was found to be stable and reusable even after 5 cycles without appreciable loss in activity and are shown in Fig. 5.

In order to prove that reaction is heterogeneous, a standard leaching experiment was carried out. The catalyst was filtered during the reaction temperature and the reaction was allowed to proceed without a catalyst. There was no change in yield even after 12 h reflux, indicating that no homogeneous catalyst was involved.

4. Conclusion

The present work describes a new, efficient and eco-friendly SiO_2:SnO_2 catalyst for the synthesis of 2,4,5-tri and 1,2,4,5-tetrasubstituted imidazole. The SiO_2:SnO_2 catalyst exhibits excellent catalytic activity for the condensation. Most importantly this catalyst facilitates the reaction at 80 °C providing solid support in the reaction, enhances the reaction rate and thereby the excellent yields of the products. Therefore, we conclude that the SiO_2:SnO_2 is the best catalyst for the synthesis of 2,4,5-tri and 1,2,4,5-tetrasubstituted imidazole.

Acknowledgments

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