

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

An efficient noble metal-free Ce-Sm/SiO₂ nano-oxide catalyst for oxidation of benzylamines under ecofriendly conditions

Putla Sudarsanam, A. Rangaswamy and Benjaram M. Reddy*

Received (in XXX, XXX) XthXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Nanosized Ce-Sm/SiO₂ catalyst was found to show an outstanding performance in the oxidation of benzylamines into valuable dibenzylimine products with almost 100% selectivity with O₂ as the green oxidant under solvent-free conditions, which is attributed to the presence of abundant strong acidic sites, enhanced oxygen vacancy concentration, and superior BET surface area.

Selective oxidation reactions are the most fundamental functional group transformations in organic chemistry.¹⁻⁴ Particularly, the selective oxidation of amines into imines is a topic of significant research investigation in recent years due to extensive use of imines in the chemical industry.^{5,6} Imines are vital electrophilic reagents for a number of organic reactions, which include alkylation, condensation, reduction, cycloaddition, *etc.* Imines are also crucial intermediates for the synthesis of medicines and biologically active compounds.⁷ Several oxidation procedures that make use of hazardous stoichiometric oxidants, such as 2-iodoxybenzoic acid and N-tert-butylphenylsulfonimidoyl chloride, along with Ru-, Ir-, and Cu-based homogeneous catalysts have been reported for amine oxidation.⁷⁻¹⁰ Alternatively, numerous heterogeneous catalysts, especially based on precious metals (e.g., Au, Ru, and Pd) have been developed for amine oxidation.^{7,10,11-15} Although these methods are quite interesting, the combination of a promising noble metal-free heterogeneous catalyst with molecular O₂ as green oxidant is essential for amine oxidation from the viewpoints of both economical and environmental concerns.^{5,16,17}

Development of ceria-based materials with favourable properties is of immense research interest to the scientific community during the past few years, not only due to their commercial exploitation in auto-exhaust purification, but also due

Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Hyderabad – 500 007, India.

E-mail: bmreddy@iict.res.in; mreddyb@yahoo.com; Fax: +91 40 2716 0921; Tel.: +91 40 2719 3510.

†Electronic supplementary information (ESI) available: Details concerning the synthesis and characterization results of ceria-based materials; TEM, XPS, FTIR, time-on-stream and reusable analysis of the CeO₂-based samples for benzylamine oxidation.

to their significant use for various organic transformations.^{18,19}

One of the most notable features of ceria is that it easily forms ample oxygen vacancy defects by preserving its fluorite-structure when an appropriate metal ion (e.g., Sm³⁺, Fe³⁺, *etc.*) is introduced into the ceria lattice.²⁰⁻²² Consequently, the structural and redox properties of ceria are greatly improved, resulting in remarkable catalytic performance. Moreover, owing to their unique and fascinating physicochemical properties, the ceria-based oxides can selectively activate organic molecules to yield the desirable products.¹⁸ It was also shown that reducing the ceria particle size to nanoscale range leads to a decrease in oxygen vacancy formation energy and thereby, an improved catalytic activity towards oxidation reactions.²⁰ The dispersion of ceria-based mixed oxides on an inert support (e.g., SiO₂) is one of the efficient approaches to improve the CeO₂ properties further as well as to reduce its particle size.^{23,24}

Motivated by the above observations, we developed a novel and promising ceria-based catalyst i.e., Sm-doped CeO₂ dispersed on SiO₂ (Ce-Sm/SiO₂) for the aerobic oxidation of various benzylamines under ecofriendly reaction conditions. The selection of Sm in the present work is mainly due to its resemblance in the ionic radius and electro negativity with respect to Ce.²¹ The nano-structured Ce-Sm/SiO₂ catalyst showed an interesting performance in the aerobic oxidation of various benzylamines with ~100% selectivity to imine products. We employed a highly practicable synthesis procedure based on precipitation of metal nitrate precursors for the preparation of the investigated Ce-Sm/SiO₂ nano-oxides (Supporting Information, ESI†). For comparison purpose, pure CeO₂ and Sm-doped CeO₂ samples were also prepared by adopting the same synthesis procedure. A linear correlation was found between the concentration of strong acidic sites, BET surface area, oxygen vacancy concentration, and the oxidation performance of the synthesized catalysts. A thorough multi-technique analysis

detailing structural and electronic properties of the synthesized samples was also undertaken (ESI[†]).

The XRD and Raman profiles of the investigated CeO₂-based materials are shown in Figs. 1A and 1B, respectively. It was found that all samples exhibit the characteristic XRD patterns of fluorite-structured CeO₂.^{25,26} Raman spectra show a sharp peak at ~450-460 cm⁻¹ for all samples, attributed to Raman-active F_{2g} mode of fluorite-structured CeO₂, in line with the XRD results.²⁷ Interestingly, no XRD and Raman peaks corresponding to Sm₂O₃ were found, which confirm the doping of Sm cations into the CeO₂ lattice. It was obvious from Figs. 1A and 1B that the addition of dopant (Sm) and support (SiO₂) strongly modifies the XRD patterns as well as Raman spectrum of pristine CeO₂. The estimated lattice parameter, average crystallite size, and F_{2g} peak position of the samples confirm the above observations (Table 1). Hence, the incorporation of Sm³⁺ ions into the CeO₂ lattice could favourably modify its structural properties for the aerobic oxidation of benzylamines as discussed in the later paragraphs.

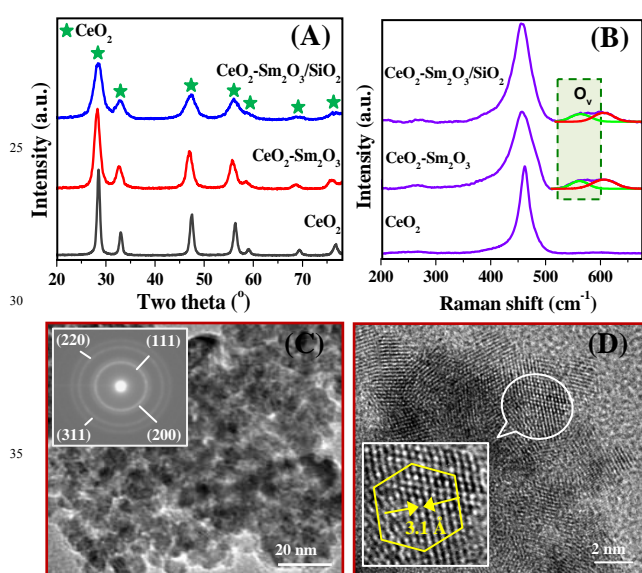


Fig. 1 (A) Powder XRD and (B) Raman profiles of CeO₂-based materials (O_v-oxygen vacancy band); (C) TEM image of Ce-Sm/SiO₂ and the corresponding selected-area electron diffraction (SAED) pattern; and (D) HRTEM image of Ce-Sm/SiO₂ (inset: enlarged view of selected area).

Table 1 BET surface area (BET SA), average crystallite size (D), lattice parameter (LP), and F_{2g} peak position of CeO₂-based catalysts. Standard deviations for BET SA and D values are ±5 m²g⁻¹ and ±0.5 nm, respectively.

Sample	BET SA (m ² g ⁻¹)	D (nm) ^a	LP (nm) ^a	F _{2g} peak position (cm ⁻¹) ^b
CeO ₂	41	8.9	0.541	461
CeO ₂ -Sm ₂ O ₃	84	7.6	0.545	456
CeO ₂ -Sm ₂ O ₃ /SiO ₂	188	5.1	0.543	454

^a From XRD studies. ^b From Raman spectra.

Two additional Raman bands are found for Ce-Sm and Ce-Sm/SiO₂ samples. The appearance of Raman band at ~560 cm⁻¹ indicates the presence of oxygen vacancies in the ceria-based materials, whereas the band at ~606 cm⁻¹ reveals the SmO₈ defect complex.²¹ We estimated the concentration of oxygen vacancies from the ratio of oxygen vacancy band (O_v) to F_{2g} band (O_v/F_{2g}) in such a way that a higher ratio means a higher oxygen vacancy concentration. It is interesting to note that the Ce-Sm/SiO₂ sample shows higher oxygen vacancy concentration (O_v/F_{2g} = 0.1053) than that of the Ce-Sm sample (O_v/F_{2g} = 0.0948). Moreover, the Ce-Sm/SiO₂ catalyst exhibits superior BET surface area (188 m²/g) compared with Ce-Sm (84 m²/g) and pristine CeO₂ (41 m²/g) samples (Table 1).

As can be noted from the Figs. 1C & 1D, the Ce-Sm/SiO₂ sample contains nearly spherical shaped particles and fall in the nanoscale range (~8-12 nm). The selected area electron diffraction patterns of Ce-Sm/SiO₂ reveal cubic structured CeO₂ with (111), (200), (220), and (311) planes, supporting the observations made from the XRD studies (Fig. 1A). The Ce-Sm/SiO₂ sample is well crystalline and the shape of the most crystallites is compatible with an octahedron defined by (111) facet at 3.1 Å (Fig. 1D). TEM and HRTEM images of the Ce-Sm sample provide evidence of the formation of nanosized particles in the range of 10-15 nm (Fig. S1, ESI[†]).

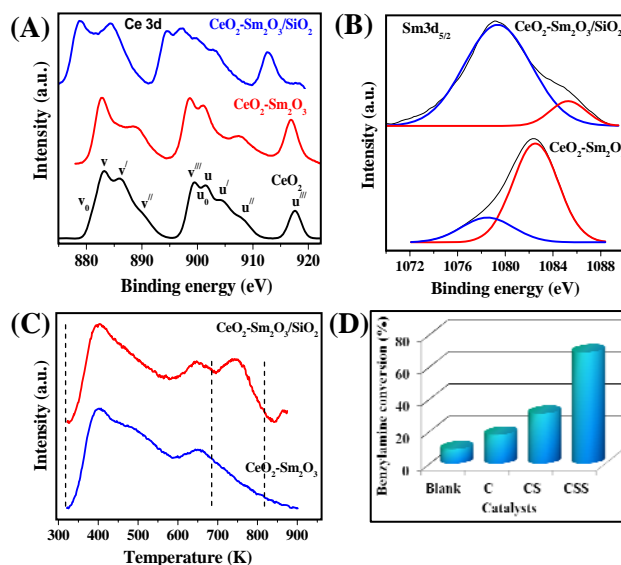


Fig. 2 (A) Ce 3d and (B) Sm 3d_{5/2} XPS spectra of CeO₂-based samples. (C) NH₃-TPD profiles of CeO₂-Sm₂O₃ and CeO₂-Sm₂O₃/SiO₂ samples, and (D) catalytic performance of CeO₂ (C), CeO₂-Sm₂O₃ (CS), and CeO₂-Sm₂O₃/SiO₂ (CSS) samples for aerobic oxidation of benzylamine. Reaction conditions: benzylamine (0.2 mmol), catalyst amount (0.2 g), O₂ bubbling rate (20 mL/min), reaction time (4 h), and temperature (393 K).

To our surprise, the Ce 3d spectrum of Ce-Sm/SiO₂ sample is noticeably different from that of the Ce-Sm and CeO₂ samples (Fig. 2A). Very much low binding energy of u^{III} peak (~912.6 eV) was found for the Ce-Sm/SiO₂ compared with Ce-Sm (916.9 eV) and CeO₂ (917.5 eV), which strongly indicates the facile reducible nature of the Ce-Sm/SiO₂ sample.²² It is generally

accepted that the reducible nature of CeO₂ (i.e., Ce⁴⁺ → Ce³⁺) highly depends on generation of oxygen vacancies.^{22,28} Hence, there is a huge possibility for the formation of more number of oxygen vacancies in the Ce-Sm/SiO₂ compared with the Ce-Sm oxide, in line with Raman results (Fig. 1B). Two peaks were found in the O 1s XP spectra of the ceria-based samples (Fig. S2, ESI†).^{28,29} The lower energy peak denotes the ceria lattice oxygen, which is considerably varied for the Ce-Sm/SiO₂ sample in comparison to Ce-Sm and CeO₂ samples. Appearance of another peak at higher binding energy side signifies adsorbed oxygen species of hydroxyl and carbonate groups on the catalyst surface, as confirmed by FT-IR study (Fig. S3, ESI†).

The Sm 3d_{5/2} XP spectra of Ce-Sm and Ce-Sm/SiO₂ samples show a peak at higher binding energy side, which confirm the presence of Sm in the 3+ oxidation state (Fig. 2B).³⁰ Another peak was found at lower binding energy side due to the strong charge transfer effect of the unpaired 4f electrons in Sm₂O₃. Interestingly, the intensity of the charge transfer band is much higher for the Ce-Sm/SiO₂ compared with that of the Ce-Sm sample.³⁰⁻³² This unusual observation reveals that the number of unpaired 4f electrons increases by more than one during the creation of the 3d¹ core hole in the Ce-Sm/SiO₂ sample, thus making it more positively charged. This result also explains the Sm 3d_{5/2} peak shift of the Ce-Sm/SiO₂ sample towards higher binding energy side. It is therefore expected that these unusual electronic modifications of Ce, Sm and O could improve the acidic properties of the Ce-Sm/SiO₂ sample. To understand this, the acidic properties of Ce-Sm and Ce-Sm/SiO₂ samples were investigated by means of NH₃-TPD analysis (Fig. 2C). The relative position of the peak maxima in Fig. 2C indicates the magnitude of NH₃ desorption activation energy, and therefore, the relative strength of the acidic sites.³³ As shown in Fig. 2C, the NH₃-TPD peaks can be assigned to before and after 673 K, corresponding to low-temperature (LT) and high-temperature (HT) regions, respectively.³⁴ The HT peak reveals NH₃ desorption from the strong acidic sites, whereas the LT peaks are attributed to release of NH₃ from the weak acid sites. It was apparent from Fig. 2C that the Ce-Sm/SiO₂ sample contains both strong- and weak-acidic sites, whereas the Ce-Sm sample has only weak acidic sites. This could be the reason for the observed high catalytic efficiency of the Ce-Sm/SiO₂ sample in the aerobic oxidation of benzylamine as discussed in the later paragraphs.

Fig. 2D shows the catalytic performance of CeO₂, Ce-Sm, and Ce-Sm/SiO₂ samples for the oxidation of benzylamine using O₂ as a green oxidant under solvent-free conditions. Very low benzylamine conversions were found for CeO₂ (~16%) and Ce-Sm (~31%) samples compared with the Ce-Sm/SiO₂ sample (~69%) for 4 h of reaction time. When the reaction time was increased to 6 h, almost 100% amine conversion was found for the Ce-Sm/SiO₂ sample (Fig. S4, ESI†). In contrast, ~38 and 72% of amine conversions were achieved with the bare CeO₂ and Ce-Sm samples for 6 h. However, it must be mentioned here that the activity of the Ce-Sm/SiO₂ sample is very much low at initial reaction times (i.e., ~12% amine conversion for 1 h of reaction time). A remarkable finding in the present investigation is that all samples exhibit superior selectivity of dibenzylimine product

(~100%). Interestingly, when the reaction was conducted in the absence of catalyst (blank test), only 9% of amine conversion was observed. This result indicates the significance of ceria-based catalysts in the aerobic oxidation of benzylamine. The presence of strong acidic sites, along with abundant oxygen vacancies and larger BET surface area are found to be the crucial factors for the observed enhanced activity of the Ce-Sm/SiO₂ catalyst.

Table 2 Aerobic oxidation of various substituted benzylamines over the Ce-Sm/SiO₂ catalyst

R = H, OMe, Me, Cl, F

Substituted dibenzylamines

Entry	Substrate	Time (h)	Amine conversion (%) ^a	Imine selectivity (%) ^b
1		4	69	99.9
2		6	~100	99.9
3		4	90	99.8
4		5	~100	99.6
5		4	53	99.9
6		6	91	99.7
7		4	45	99.9
8		6	85	99.7
9		4	65	99.8
10		6	96	99.6
11		6	93	99.7

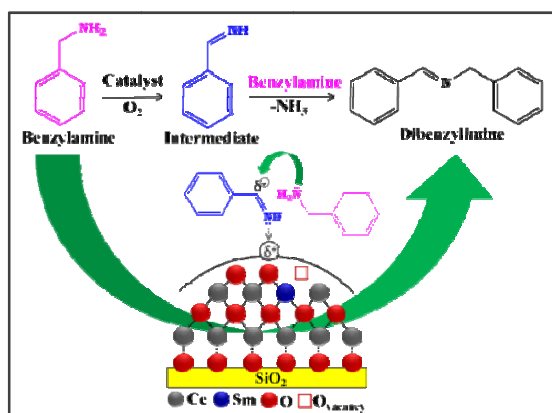
^a Reaction conditions: substituted benzylamine (0.2 mmol), catalyst amount (0.2 g), O₂ bubbling rate (20 mL/min), and temperature (393 K). ^b Very small amount of nitrile product was formed.

We investigated the scope of the Ce-Sm/SiO₂ catalyst for the aerobic oxidation of various substituted benzylamines. As summarized in Table 2, substituted benzylamines can also be selectively oxidized into the corresponding imines using the Ce-

Sm/SiO₂ catalyst. Amongst, the highest amine conversion was achieved with p-MeOPhNH₂ (Table 2, entries 3 & 4) attributed to more basic nature of the amine and thereby, strong interaction between the amine and Ce-Sm/SiO₂ catalyst, resulting in high amine conversion.¹¹ Very low amine conversion was found for 2-MePhNH₂ (Table 2, entries 7 & 8) compared with 4-MePhNH₂ (Table 2, entries 5 & 6), which might be due to steric hindrance of the methyl group at 2-position. Reasonable amine conversions were achieved in the case of halogen (Cl and F) substituted amines (Table 2, entries 9-11), which are highly useful synthons for the synthesis of chiral amines.³⁵

We also studied the reusability of the Ce-Sm/SiO₂ catalyst to understand its stability for the aerobic amine oxidation (Fig. S5, ESI†). The catalytic experiments were fixed as follows: benzylamine (0.2 mmol), catalyst amount (0.2 g), O₂ bubbling rate (20 mL/min), reaction time (6 h), and temperature (393 K). After each run, the catalyst was washed with acetone to remove reaction gradients and then pre-activated at 423 K for 2 h. It was found that the Ce-Sm/SiO₂ catalyst could be used repeatedly up to 4 cycles for amine oxidation without any significant loss of the activity, and ~100 and 90% benzylamine conversions were obtained for the 1st and 4th cycles, respectively. After 4th cycle, the performance of the Ce-Sm/SiO₂ catalyst was considerably decreased. Approximately, 72 and 59% amine conversions were obtained for the 5th and 6th cycles, respectively. Understanding the reasons for the decrease in activity of the Ce-Sm/SiO₂ catalyst after several recycling experiments are under further investigation. Despite the decrease in amine conversion with repeated use of the catalyst, no variation in the selectivity of the product was observed. On the whole, the Ce-Sm/SiO₂ is a promising and recyclable noble-metal-free catalyst for aerobic oxidation of benzylamine under eco-friendly reaction conditions.

Scheme 1 Possible mechanism for the aerobic oxidation of



benzylamine over the Ce-Sm/SiO₂ catalyst

The aerobic oxidation of benzylamine into dibenzylimine usually follows two steps (Scheme 1).^{10,11} First, an imine intermediate (PhCH=NH) is formed through the oxidative dehydrogenation of benzylamine. Afterward, the unstable imine intermediate reacts instantly with benzylamine to form an aminal followed by release of NH₃ to give the final dibenzylimine product. Alternatively, the dibenzylimine product can also be formed by the transformation of imine intermediate into

benzaldehyde, which subsequently reacts with the available benzylamine to give dibenzylimine. It was obvious from Scheme 1 that the intermediate imine has net positivity charge, thus there is a high possibility for the attack of benzylamine on imine intermediate due to the presence of lone pair on the nitrogen atom of the benzylamine rather than the formation of benzaldehyde from imine intermediate. As stated, no benzaldehyde was found in the present study, confirming the formation of imine product through the aminal formation followed by NH₃ release. It is a well-known fact in the literature that acid catalysts show remarkable efficiency in the amine oxidation through activation of C=N bond of imine intermediate.³⁶⁻³⁸ Hence, the strong acidic nature of the Ce-Sm/SiO₂ catalyst is a key factor for its exceptional performance in the aerobic oxidation of benzylamines.

In conclusion, we have developed a novel nanostructured Ce-Sm/SiO₂ catalyst for efficient aerobic oxidation of various benzylamines under ecofriendly conditions. The Ce-Sm/SiO₂ catalyst showed almost 100% benzylamine conversion with 100% selectivity to dibenzylimine for 6 h of reaction time. This catalyst also selectively converts various substituted benzylamines into the corresponding imines with moderate to excellent yields. A remarkably finding observed in the present study is that the Ce-Sm/SiO₂ catalyst can be used repeatedly up to 4 times without any significant loss of the activity and selectivity. The strong acidic nature of the Ce-Sm/SiO₂ catalyst along with superior BET surface area and enhanced concentration of oxygen vacancies are crucial factors for its outstanding performance in the aerobic oxidation of benzylamines.

Acknowledgements

P. S. and A. R. thank the Council of Scientific and Industrial Research (CSIR), New Delhi for research fellowships.

References

- X. F. Wu, C. B. Bheeter, H. Neumann, P. H. Dixneuf and M. Beller, *Chem. Commun.*, 2012, **48**, 12237–12239.
- Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang and Y. Yang, *Chem. Soc. Rev.*, 2014, **43**, 3480–3524.
- N. Dimitratos, J. A. Lopez-Sanchez and G. J. Hutchings, *Chem. Sci.*, 2012, **3**, 20–44.
- M. Sankar, E. Nowicka, E. Carter, D. M. Murphy, D. W. Knight, D. Bethell and G. J. Hutchings, *Nat. Commun.*, 2014, **5**, 3332–3337.
- S. Ahmad, K. Gopalaiah, S. N. Chandrudu and R. Nagarajan, *Inorg. Chem.*, 2014, **53**, 2030–2039.
- L. Tang, H. Sun, Y. Li, Z. Zha and Z. Wang, *Green Chem.*, 2012, **14**, 3423–3428.
- S. Furukawa, A. Suga and T. Komatsu, *Chem. Commun.*, 2014, **50**, 3277–3280.
- L. -P. He, T. Chen, D. Gong, Z. Lai and K. -W. Huang, *Organometallics*, 2012, **31**, 5208–5211.
- W. H. Bernskoetter and M. Brookhart, *Organometallics*, 2008, **27**, 2036–2045.
- M. T. Schümperli, C. Hammond and I. Hermans, *ACS Catal.*, 2012, **2**, 1108–1117.
- R. J. Angelici, *Catal. Sci. Technol.*, 2013, **3**, 279–296.

- 12 A. Gorrane, A. Corma and H. Garcia, *J. Catal.*, 2009, **264**, 138–144.
- 13 L. Aschwarden, T. Mallat, F. Krumeich and A. Baiker, *J. Mol. A: Chem.*, 2009,**309**, 57–62.
- 5 14 K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Ed.*, 2003, **42**, 1480–1483.
- 15 X. Jin, Y. Liu, Q. Lu, D. Yang, J. Sun, S. Qin, J. Zhang, J. Shen, C. Chu and R. Liu, *Org. Biomol. Chem.*, 2013, **11**, 3776–3780.
- 10 16 R. D. Patil and S. Adimurthy, *RSC Adv.*, 2012, **2**, 5119–5122.
- 17 R. D. Patil and S. Adimurthy, *Adv. Synth. Catal.*, 2011, **353**, 1695–1700.
- 18 L. Vivier and D. Duprez, *ChemSusChem*, 2010, **3**, 654–678.
- 19 C. Sun, J. Sun, G. Xiao, H. Zhang, X. Qiu, H. Li and L. Chen, *J. Phys. Chem. B*, 2006,**110**,13445–13452.
- 15 20 S. M. Kozlova and K. M. Neyman, *Phys. Chem. Chem. Phys.*,2014, **16**, 7823–7829.
- 21 K. Kuntaiah, P. Sudarsanam, B. M. Reddy and A. Vinu, *RSC Adv.*, 2013, **3**, 7953–7962.
- 20 22 P. Sudarsanam, B. Mallesham, D. N. Durgasri and B. M. Reddy, *RSC Adv.*, 2014, **4**, 11322–11330.
- 23 C. Sun, H. Lia and L. Chen, *Energy Environ. Sci.*, 2012, **5**, 8475–8505.
- 24 L. Katta, P. Sudarsanam, B. Mallesham and B. M. Reddy, *Catal. Sci. Technol.*, 2012,**2**, 995–1004.
- 25 25 P. Munusamy, S. Sanghavi, T. Varga and T. Suntharampillai, *RSC Adv.*, 2014, **4**, 8421–8430.
- 26 C. Sun and L. Chen, *Eur. J. Inorg. Chem.*, 2009, 3883–3887.
- 27 P. Bharali, P. Saikia and B. M. Reddy, *Catal. Sci. Technol.*, 2012, **2**, 931–933.
- 30 28 P. Sudarsanam, B. Mallesham, P. S. Reddy, D. Großmann, W. Grünert and B. M. Reddy, *Appl. Catal., B*, 2014, **144**, 900–908.
- 29 J. He, G. K. Reddy, S. W. Thiel, P. G. Smirnotis and N. G. Pinto, *J. Phys. Chem. C*, 2011, **115**, 24300–24309.
- 35 30 W. D. Zhang, B. S. Liu, Y. P. Zhan and Y. L. Tian, *Ind. Eng. Chem. Res.*, 2009, **48**, 7498–7504.
- 31 G. Attard and C. Burnes in *Surfaces, Spectroscopic Techniques for Probing Solid Surfaces*, Oxford University Press, Oxford,1998.
- 40 32 C. Suzuki, J. Kawai, M. Takahashi, A. -M. Vlaicu, H. Adachi and T. Mukoyama, *Chem. Phys.*, 2000,**253**, 27–40.
- 33 B. Mallesham, P. Sudarsanam and B. M. Reddy, *Catal. Sci. Technol.*, 2014, **4**, 803–813.
- 45 34 B. Mallesham, P. Sudarsanam, G. Raju and B. M. Reddy, *Green Chem.*, 2013, **15**, 478–489.
- 35 K. A. Nolin, R. W. Ahn and F. D. Toste, *J. Am. Chem. Soc.*, 2005,**127**, 12462–12463.
- 36 S. M. Landge, V. Atanassova, M. Thimmaiah and B. Török, *Tetrahedron Lett.*, 2007,**48**, 5161–5164.
- 50 37 S. Mallick, S. Rana and K. Parida, *Ind. Eng. Chem. Res.*, 2012, **51**, 7859–7866.
- 38 K. N. Tayade and M. Mishra, *J. Mol. Catal. A: Chem.*, 2014,**382**, 114–125.
- 55