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Research on Chemical Intermediates

ISSN 0922-6168

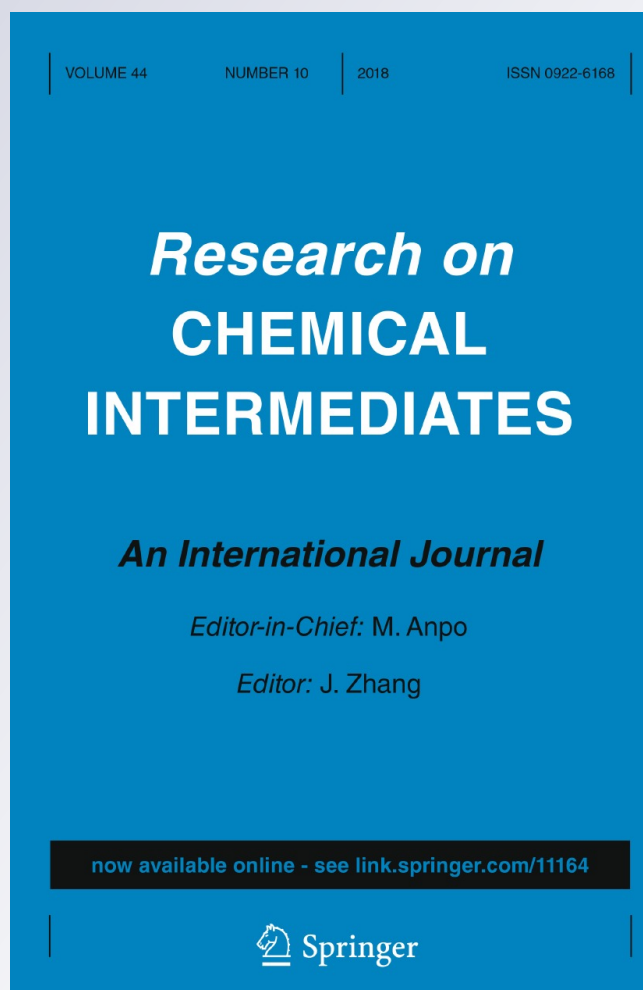
Volume 44

Number 10

Res Chem Intermed (2018)

44:6151-6168

DOI 10.1007/s11164-018-3482-1



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Selective allylic oxidation of cyclohexene over a novel nanostructured $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalyst

Bolla Govinda Rao^{1,2} · Putla Sudarsanam^{1,3} · P. R. G. Nallappareddy^{1,2} · M. Yugandhar Reddy¹ · T. Venkateshwar Rao^{1,2} · Benjaram M. Reddy^{1,2} 

Received: 24 January 2018 / Accepted: 21 May 2018 / Published online: 29 May 2018
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Abstract Selective allylic oxidation of cyclohexene was investigated over nanostructured $\text{CeO}_2/\text{SiO}_2$ and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts synthesized by a feasible deposition precipitation method. The $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalyst showed excellent catalytic efficiency with ~89 % cyclohexene conversion and ~90 % selectivity for allylic products (i.e., 2-cyclohexen-1-ol and 2-cyclohexene-1-one), while only ~50 and ~35 % cyclohexene conversion was observed, respectively, over $\text{CeO}_2/\text{SiO}_2$ and CeO_2 catalysts. Systematic characterization of the designed catalysts was undertaken to correlate their catalytic activity with the physicochemical properties using X-ray diffraction (XRD) analysis, Brunauer–Emmett–Teller (BET) surface area measurements, Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and NH_3 -temperature programmed desorption (TPD) techniques. The results revealed that doping of Sm^{3+} into the ceria lattice and simultaneous dispersion of resultant Ce–Sm mixed oxides on the silica surface led to improved structural, acidic, and catalytic properties. The better catalytic efficiency of $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ was due to high specific surface area, more structural defects, and high concentration of strong acid sites, stimulated by synergistic interaction between various oxides in the catalyst. The cyclohexene conversion and selectivity for allylic products depended on the reaction temperature, nature of solvent, molar ratio of cyclohexene to oxidant, and reaction time.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11164-018-3482-1>) contains supplementary material, which is available to authorized users.

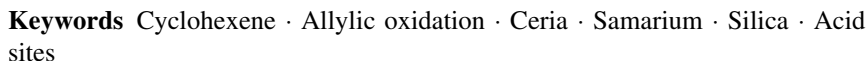
✉ Benjaram M. Reddy
bmreddy@iict.res.in; mreddyb@yahoo.com

¹ Inorganic and Physical Chemistry Division, CSIR–Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500 007, India

² Academy of Scientific and Innovative Research, CSIR-IICT, Hyderabad, India

³ Center for Surface Chemistry and Catalysts, KU Leuven, Celestijnenlaan 200f, Box 2461, 3001 Louvain, Belgium

Graphical Abstract SiO₂-supported CeO₂-Sm₂O₃ nanocatalyst exhibited outstanding catalytic performance with superior selectivity for allylic products in liquid-phase selective oxidation of cyclohexene under mild reaction conditions.



Selective oxidation of olefins has attracted significant research interest owing to the numerous applications of the resultant oxygenated products in chemical industry [1–4]. In particular, selective oxidation of cyclohexene is a vital chemical transformation, since it contains two reactive centers (allylic C–H and olefinic C=C). Therefore, controlling the oxidation at one of these positions is a key step for synthesis of desired products [5]. Direct epoxidation of cyclohexene at olefinic C=C bond yields cyclohexene oxide, whereas 2-cyclohexen-1-ol and 2-cyclohexen-1-one are obtained as products of allylic oxidation of cyclohexene. 2-Cyclohexen-1-ol and 2-cyclohexen-1-one are important intermediates in production of spices, pesticides, medicines, and insect pheromones [6–9]. Also, cyclohexene oxide can be used as a monomer in synthesis of polymers and as a key intermediate in the coatings industry [10, 11].

N-tert-Butylphenylsulfonimidoyl chloride and 2-iodoxybenzoic acid are oxidizing agents typically employed for selective oxidation of cyclohexene [12]. However, these oxidants are highly toxic and generate large amounts of undesirable side products and hazardous organic waste [13, 14]. Alternatively, some other oxidants including H₂O₂, *tert*-butyl hydroperoxide (TBHP), and O₂ have been explored, yielding quite positive results. Generally, catalysts based on homogeneous systems are reported to be efficient for oxidation of cyclohexene. However, application of such liquid-phase catalysts on industrial scale is often hindered by various problems, such as difficulty in catalyst separation from the reaction mixture and recycling, and generation of large amounts of unwanted products which exhibit strong corrosion

[15], among others. To overcome these issues, a wide variety of heterogeneous catalysts, especially based on metal nanoparticles dispersed on various supports, such as SiO_2 , TiO_2 , graphite, polyoxometalates, carbon nanotubes, zeolites, and metalorganic frameworks (MOFs), have been investigated [12, 16–21]. Among the various catalysts examined, supported noble metals (e.g., Au, Pd, and Ru) have been found to show excellent catalytic performance [22–24]. In spite of their high catalytic activity, use of noble metals is strongly discouraged in chemical industry due to their high cost and limited availability. Against this background, development of cost-effective and highly efficient noble-metal-free catalysts is highly desirable for oxidation of cyclohexene and related reactions.

Ceria has been recognized as a promising catalyst component in many organic reactions, such as dehydration of alcohols, hydrolysis of nitriles, C–C coupling, C–O cleavage, oxidation of olefins, oxidative coupling of amines, oxidation of alcohols, etc. [25–30]. The widespread application potential of ceria is due to its facile redox couple ($\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$) and abundant oxygen vacancies (structural defects) [31]. In addition, dual acid–base nature is another characteristic feature of ceria-based oxides. As is known from literature, the acidic property of catalysts plays a crucial role in oxidation of cyclohexene [32]. It is therefore believed that, by appropriately modifying its redox and acidic properties, the catalytic efficiency of ceria for oxidation of cyclohexene could be improved. Several promising strategies to tune the structure–activity relationship of ceria have been reported, including doping of suitable cations into the ceria lattice, dispersion of the resultant mixed oxide on a high-surface-area support, and tailoring of the oxygen vacancy population [33, 34]. Incorporation of an aliovalent cation such as Sm^{3+} is expected to introduce strain into the ceria lattice due to the difference in ionic radius between the Sm^{3+} (1.08 Å) and Ce^{4+} (0.97 Å) cations. Stimulation of lattice strain contributes to formation of unusual structural and redox properties in the final mixed oxides, resulting in unusual catalytic performance [35]. Furthermore, homogeneous dispersion of nanooxides on a high-surface-area support (e.g., SiO_2) can lead to enhanced textural and redox properties due to synergistic metal oxide–support oxide interactions. It is therefore highly desirable to investigate the characteristics of ceria after simultaneous incorporation of Sm cations and SiO_2 support, and their ensuing role in selective oxidation of cyclohexene. The present investigation was undertaken against the aforesaid background. Accordingly, systematic structure–activity relationship investigation is expected to provide useful information for development of feasible and selective catalytic protocols for not only oxidation of cyclohexene but also other industrially important chemical reactions.

In this work, nanosized $\text{CeO}_2/\text{SiO}_2$ and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts were synthesized and evaluated for oxidation of cyclohexene using TBHP as oxidant. Physicochemical characterization of the developed catalysts was carried out using X-ray diffraction (XRD) analysis, Brunauer–Emmet–Teller (BET) surface area measurements, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and ammonia-temperature programmed desorption (NH_3 -TPD) techniques. The effect of reaction temperature, nature of solvent, molar ratio of cyclohexene to oxidant, and reaction time were also investigated to optimize the reaction conditions. Efforts were also made to correlate

the catalytic activity results with the physicochemical properties of the synthesized catalysts.

Experimental

Catalyst preparation

CeO₂/SiO₂ catalyst (CeO₂:SiO₂ = 1:1 mol ratio based on oxides) was prepared by deposition precipitation method. Briefly, estimated stoichiometric amounts of colloidal silica (Ludox, 40 wt%, Aldrich) and Ce(NO₃)₃·6H₂O [Aldrich, analytical reagent (AR) grade] were dissolved separately in deionized water then mixed together under stirring. Subsequently, the precipitating agent, i.e., aqueous NH₃ solution, was added dropwise to the above solution until the pH of the solution reached ~8.5. The resultant slurry was filtered off and washed several times with double-distilled water until free from anion impurities. The obtained sample was oven-dried at 120 °C for 12 h and finally calcined at 500 °C for 5 h at heating rate of 5 °C min⁻¹ in air atmosphere.

CeO₂–Sm₂O₃/SiO₂ catalyst (CeO₂:Sm₂O₃:SiO₂ = 0.8:0.2:1 mol ratio based on oxides) was prepared by deposition coprecipitation method. In a typical procedure, colloidal SiO₂ was dispersed in deionized water and stirred for 2 h. Desired amounts of Ce(NO₃)₃·6H₂O (Aldrich, AR grade) and Sm(NO₃)₃·6H₂O (Aldrich, AR grade) were dissolved in deionized water and mixed together under mild stirring conditions. The resultant Ce–Sm nitrate solution was added to the dispersed solution of SiO₂ support. Subsequently, aq. NH₃ solution was added dropwise to the above mixture solution until the pH of the solution reached ~8.5. The resulting slurry was filtered off, washed with double-distilled water, and oven-dried at 120 °C for 12 h. The resulting cake was calcined at 500 °C for 5 h at heating rate of 5 °C min⁻¹ in air atmosphere. For comparison, pure CeO₂ was also prepared following the same procedure under identical conditions and calcined at 500 °C for 5 h.

Catalyst characterization

Powder XRD patterns were recorded on a Rigaku diffractometer using Cu K_α radiation (1.540 Å), operated at 40 kV and 40 mA. Diffractograms were recorded in the 2θ range of 10–80° with 2θ step size of 0.02° and step time of 2.4 s. XRD phases present in the samples were identified with the help of Powder Diffraction Files (PDFs) from the International Centre for Diffraction Data (ICDD). The average crystallite size of ceria in various samples was calculated using the Scherrer equation, and the lattice parameter was estimated by standard cubic indexation method using the intensity of the most prominent peak (111).

The BET surface area of various samples was determined by N₂ adsorption–desorption measurements using a Micromeritics Gemini 2360 instrument. Prior to analysis, the samples were oven-dried at 150 °C for 12 h and flushed with argon gas for 2 h to remove any surface-adsorbed residue. Surface area was calculated by

utilizing the desorption data. A Horiba Jobin–Yvon HR800 Raman spectrometer equipped with a liquid-nitrogen-cooled charge-coupled device (CCD) detector and confocal microscope was used to obtain Raman spectra of various samples. The emission line at 638 nm from an Ar⁺ laser (Spectra Physics) was focused on the sample under a microscope with diameter of the analyzed spot being $\sim 1\ \mu\text{m}$, under ambient conditions. The acquisition time was adjusted according to the Raman scattering intensity.

TEM/high-resolution electron microscopy (HREM) studies were carried out using a Tecnai G2 TEM microscope equipped with a slow-scan CCD camera at accelerating voltage of 200 kV. Carbon-coated Cu grid was used for preparation of samples for TEM analysis. Preparation of samples for TEM-HREM analysis involved sonication in ethanol for 2–5 min followed by deposition of a drop on a copper grid. The specimen was examined under vacuum at room temperature. XPS measurements were performed using a PHI 5400 instrument with an Al K α (1486.6 eV) X-ray source at pressure below 10^{-7} Torr [36]. Sample preparation for XPS analysis involved mounting of a few milligrams of sample on carbon tape supported by silica plate, which was placed in the vacuum chamber of a Thermo K-Alpha XPS instrument before starting analysis. Thermo Advantage software was used for XPS analysis of the prepared samples. The binding energies of Ce, Sm, and O were charge-corrected with respect to the adventitious carbon (C 1s) peak at 284.6 eV. We used a flood gun to remove static charge that developed on the sample surface during XPS analysis.

NH₃-temperature programmed desorption experiments were carried out on a Auto-Chem 2910 instrument (Micromeritics). Approximately 30 mg sample was placed in a quartz tube and degassed up to 300 °C under He flow. Then, anhydrous NH₃ gas was passed over the sample surface for 30 min, followed by flushing with helium gas to remove physisorbed gas. Then, the amount of chemisorbed NH₃ was estimated in He gas flowing at rate of 20 mL min⁻¹ from 50 to 800 °C at heating rate of 10 °C min⁻¹.

Activity measurements

Liquid-phase oxidation of cyclohexene was carried out using TBHP and acetonitrile as oxidant and solvent, respectively. In a typical experiment, 0.1 g catalyst, 4 mmol cyclohexene, and 5 ml solvent were charged into a 25-ml three-necked round-bottomed flask equipped with a condenser. Then, the required amount of TBHP was slowly added to the reaction mixture under vigorous stirring (~ 600 rpm). The mixture was then heated to the desired temperature in an oil bath. After reaction completion, the liquid products and the catalyst were separated by centrifugation. The derived products were further diluted with acetonitrile solvent and analyzed by gas chromatography (GC) using a BP-20 (wax) capillary column and flame ionization detector. The products were confirmed by GC–mass spectroscopy (MS) using a DB-5 capillary column and mass detector. Reaction products were also confirmed by injecting corresponding authentic compounds into the GC. The obtained cyclohexene conversion and product selectivity values are within the experimental error of ± 2 percent.

Results and discussion

Catalyst characterization

Figure 1 shows the XRD profiles of the CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts. All samples exhibited fluorite-structured ceria, as evidenced by the observation of characteristic diffraction peaks of (111), (200), (220), (311), (420), and (422) in Fig. 1 [37]. This indicates that addition of the dopant (Sm) and support (SiO_2) did not alter the structure of CeO_2 . The absence of XRD peaks pertaining to Sm_2O_3 for the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ sample can be attributed to several factors, including incorporation of Sm^{3+} ions into the ceria lattice, amorphous nature of Sm_2O_3 , or high dispersion of Sm_2O_3 species [38, 39]. Also, no XRD peaks corresponding to the SiO_2 support were observed in the case of the $\text{CeO}_2/\text{SiO}_2$ and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ samples, indicating amorphous nature of SiO_2 . Close inspection of Fig. 1 reveals that the XRD profiles of the $\text{CeO}_2/\text{SiO}_2$ and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ samples were quite different compared with that of pristine CeO_2 in terms of peak position and intensity. Changes in the ceria crystallite size and lattice parameter after addition of Sm and SiO_2 are a probable reason for this observation. As presented in Table 1, the $\text{CeO}_2/\text{SiO}_2$ (8.1 ± 1 nm) and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ (5.2 ± 1 nm) samples showed smaller crystallite size compared with pristine CeO_2 (8.8 ± 1 nm). This observation indicates a favorable role of the dopant and support in controlling crystal growth of ceria during high-temperature calcination. Nanoparticles are likely to undergo aggregation at elevated temperatures because of their exceptional surface energy. Incorporation of a dopant could reduce the surface energy of the ceria nanoparticles due to formation of strong metal–metal interactions, hence controlling the particle size, as clearly evidenced in the present work and in good agreement with literature [40]. The lattice parameter was found to be 0.540, 0.542, and 0.544 nm for the CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ samples, respectively.

Fig. 1 Powder XRD patterns of CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts

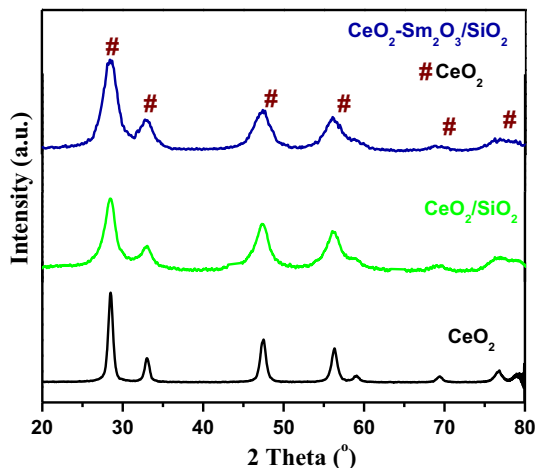


Table 1 BET surface area (S), average crystallite size (D), lattice parameter (LP), pore volume (V), and pore size (P) of CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalysts

Sample	S ($\text{m}^2 \text{ g}^{-1}$) ^a	D (nm) ^b	LP (nm) ^b	V ($\text{cm}^3 \text{ g}^{-1}$) ^c	P (nm) ^c
CeO_2	40 ± 2	8.8 ± 1	0.540 ± 0.05	0.114 ± 0.01	9.84 ± 1
$\text{CeO}_2/\text{SiO}_2$	120 ± 2	8.1 ± 1	0.542 ± 0.05	0.462 ± 0.02	7.53 ± 1
$\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$	193 ± 2	5.2 ± 1	0.544 ± 0.05	0.383 ± 0.01	5.40 ± 1

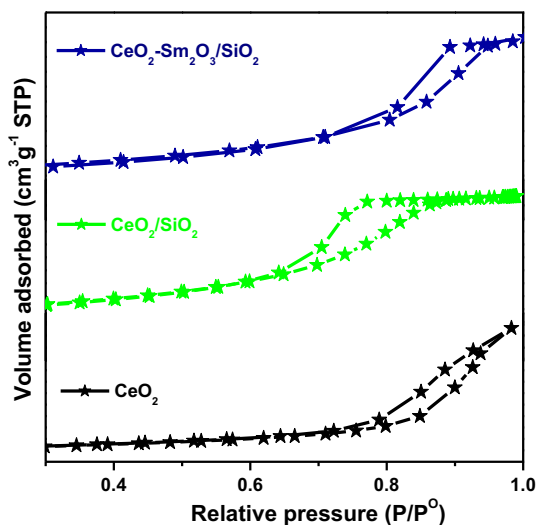
^aFrom BET analysis

^bFrom XRD analysis

^cFrom Barrett–Joyner–Halenda (BJH) analysis

Figure 2 shows the N_2 adsorption–desorption isotherms of the CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalysts; the corresponding BET surface area, pore diameter, and pore volume values are presented in Table 1. As shown in Fig. 2, the pure CeO_2 and $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ samples exhibited a type IV isotherm with H1 hysteresis loop, attributed to formation of mesopores. Unlike the pure CeO_2 and $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ samples, the $\text{CeO}_2\text{-SiO}_2$ sample showed a H2 hysteresis loop, indicating formation of pores with narrow necks and wide bodies. This is probably due to segregation of silica particles inside pores of ceria ($\text{CeO}_2/\text{SiO}_2$), resulting in the H2 isotherm and wide pore size distribution. The BET surface area of pristine CeO_2 was found to be $\sim 40 \text{ m}^2/\text{g}$, increasing significantly to $\sim 120 \text{ m}^2/\text{g}$ after addition of SiO_2 , indicating the favorable role of the support in enhancing the BET surface area of CeO_2 . Interestingly, simultaneous addition of Sm and SiO_2 to CeO_2 remarkably enhanced the specific surface area from ~ 40 to $\sim 193 \text{ m}^2/\text{g}$ (Table 1), indicating a synergetic effect of Sm and SiO_2 in improving the textural properties of the CeO_2 . The pore size distribution profiles of CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{-}$

Fig. 2 N_2 adsorption–desorption isotherms of CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalysts

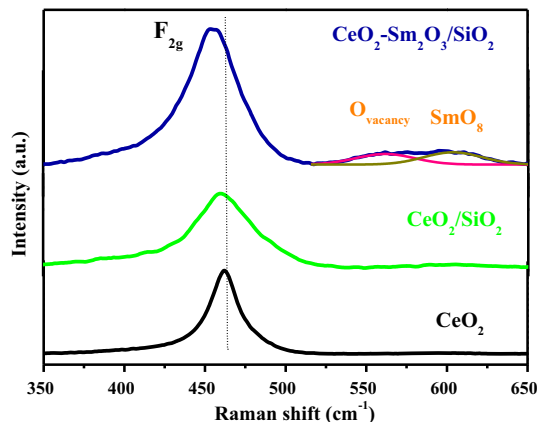


$\text{Sm}_2\text{O}_3/\text{SiO}_2$ catalysts are shown in Fig. S1. A unimodal pore size distribution was observed for the CeO_2 and $\text{CeO}_2/\text{SiO}_2$ catalysts, whereas a bimodal distribution was noted for the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalyst. The obtained pore volume and pore size values for pure CeO_2 were $\sim 0.114 \text{ cm}^3 \text{ g}^{-1}$ and $\sim 9.84 \text{ nm}$, respectively (Table 1). Also, the pore size and pore volume values of $\text{CeO}_2/\text{SiO}_2$ and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ samples were $\sim 7.53 \text{ nm}$ and $\sim 0.462 \text{ cm}^3 \text{ g}^{-1}$, and $\sim 5.40 \text{ nm}$ and $\sim 0.383 \text{ cm}^3 \text{ g}^{-1}$, respectively.

Figure 3 shows the Raman spectra of the CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ samples. A major Raman band centered at $\sim 465 \text{ cm}^{-1}$ was observed for all catalysts, attributed to the F_{2g} Raman-active mode of fluorite-structured CeO_2 in space group $Fm\bar{3}m$ [41, 42]. No Raman bands were found for Sm_2O_3 , in line with the XRD results (Fig. 1). Thus, the XRD and Raman results confirm incorporation of Sm into the ceria lattice, forming a homogeneous ceria solid solution. A noticeable shift of the F_{2g} peak towards lower wavenumber as well as peak broadening were observed for the $\text{CeO}_2/\text{SiO}_2$ and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ samples compared with pure CeO_2 . Variation in the Ce–O frequencies is one of the key reasons for this observation [43]. In addition to the F_{2g} band, two more Raman bands were noticed for the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ sample: The appearance of a band at $\sim 560 \text{ cm}^{-1}$ is attributed to presence of oxygen vacancies, whereas the band at $\sim 606 \text{ cm}^{-1}$ corresponds to SmO_8 defect complex [44, 45]. Since no oxygen vacancy band was observed for the $\text{CeO}_2/\text{SiO}_2$ catalyst, the dopant Sm^{3+} appears to play a unique role in generating oxygen vacancies in the cerium oxide lattice.

Formation of oxygen vacancies in the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ sample can be attributed to the charge compensation mechanism, due to the difference in ionic radius between the Sm^{3+} (1.08 Å) and Ce^{4+} (0.97 Å) cations. Figure 4 shows TEM and HREM images of the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ sample. Note that the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ sample contained sphere-shaped particles and the particle size was found to lie in the range of 6–8 nm. The particle size distribution histogram for the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ sample estimated from TEM analysis is shown inset to Fig. 4a. Lattice d -spacing of $\sim 0.31 \text{ nm}$ was also estimated, corresponding to the distance between adjacent (111) crystal planes of fluorite-structured CeO_2 [46].

Fig. 3 Raman spectra of CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts



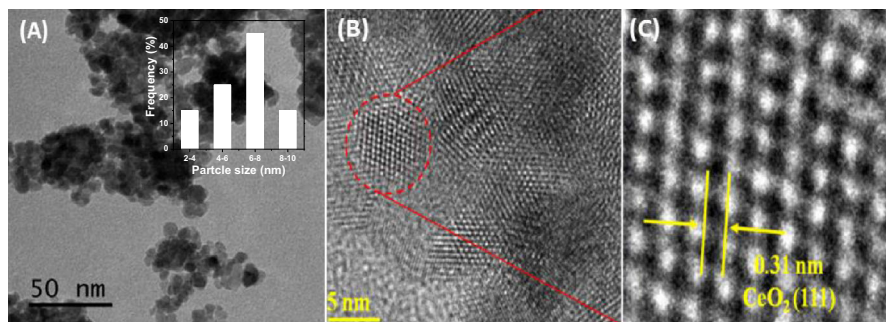
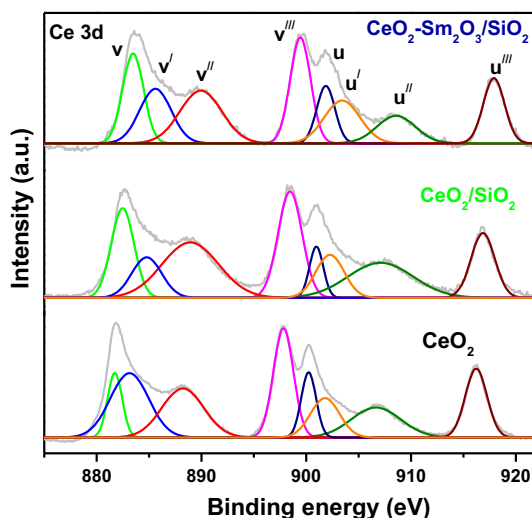


Fig. 4 TEM and HREM images of **a–c** $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalyst

Figure 5 shows the Ce 3d XP spectra of the pure CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ samples. It is well known from literature reports [47, 48] that Ce 3d XP spectra are complex, due to coexistence of multiple oxidation states as well as mixing of O 2p and Ce 4f levels in the primary photoemission process. Peaks labeled u correspond to Ce $3d_{3/2}$ spin-orbit states, while those labeled v correspond to Ce $3d_{5/2}$ contributions. As shown in Fig. 5, peaks labeled u' and v' belong to Ce^{3+} with electronic configuration $3d^{10} 4f^1$ whereas other bands labeled u, u'', u''', v, v'', and v''' belong to the $3d^{10} 4f^0$ electronic state corresponding to Ce^{4+} . The presence of all these peaks reveals coexistence of Ce^{4+} and Ce^{3+} species over the catalyst surface, indicating the redox nature of the as-prepared catalysts [49–51]. The binding energy of all the peaks observed for the CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ samples are presented in Table S1. The Ce 3d spectrum of the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ sample is notably different from those of the $\text{CeO}_2/\text{SiO}_2$ and CeO_2 samples (Fig. 5). Much higher binding energy was noted for the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalyst compared with the $\text{CeO}_2/\text{SiO}_2$ and CeO_2 samples, which is probably due to

Fig. 5 Ce 3d XP spectra of CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts

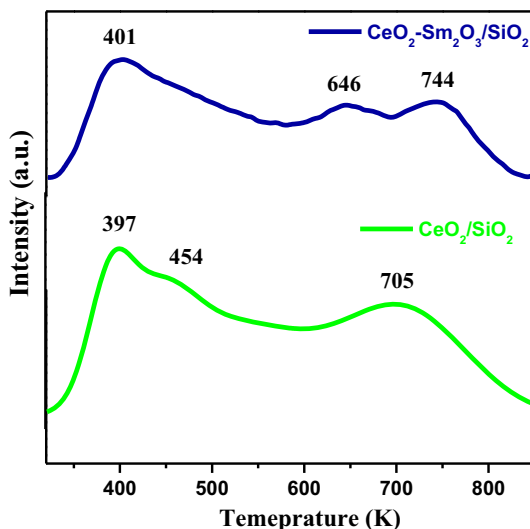


the fact that the dopant and support could influence the chemical environment of CeO_2 . Strong synergetic interaction of ceria with the dopant and support could be the reason for this influence on the chemical environment of CeO_2 [52–54]. Furthermore, we estimated the relative percentage of cerium species using the area ratio of $\text{Ce}^{3+}/\text{Ce}^{3+} + \text{Ce}^{4+}$; the obtained values are presented in Fig. S2, revealing an order of the samples of $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ (23.1 %) > $\text{CeO}_2/\text{SiO}_2$ (20.3 %) > CeO_2 (18.0 %). This trend clearly demonstrates that the fraction of Ce^{3+} was remarkably enhanced by simultaneous introduction of the dopant and support into ceria.

The $\text{Sm } 3d_{5/2}$ XP spectrum of the $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ sample shows a peak on the higher binding energy side (~ 1109.2 eV), which reveals presence of Sm in 3+ oxidation state (Fig. S3). Another peak was found at lower binding energy (~ 1082.3 eV), which is due to the charge transfer effect of the unpaired 4f electrons in Sm_2O_3 [55]. The deconvoluted O 1s spectra of all samples are presented in Fig. S4. The appearance of a peak at ~ 529.2 eV (O_I) can be attributed to ceria lattice oxygen. On the other hand, the presence of a peak at $\sim 530\text{--}531$ eV (O_{II}) is due to adsorbed oxygen species of hydroxyl groups. Another peak at $\sim 531.8\text{--}533.2$ eV (O_{III}) can be ascribed to adsorbed molecular water and carbonate species. The Si 2p core-level XP spectra of the $\text{CeO}_2/\text{SiO}_2$ and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts show a peak at ~ 102.8 eV, which is attributed to Si^{4+} species (Fig. S5) [56, 57].

NH_3 -TPD analysis was undertaken to estimate the acidic properties of the catalysts. As shown in Fig. 6, various desorption peaks were observed for the $\text{CeO}_2/\text{SiO}_2$ and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts. This is due to variation in the activation energy of NH_3 molecules desorbed from different acidic sites present on the catalyst surface [25, 58]. The NH_3 desorption profiles could be divided to above and below desorption temperature of 400°C , corresponding to the low-temperature (LT) and

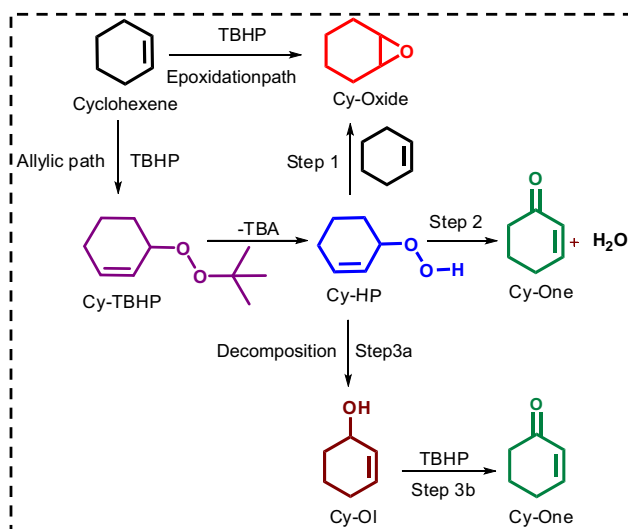
Fig. 6 NH_3 -TPD profiles of $\text{CeO}_2/\text{SiO}_2$, $\text{CeO}_2\text{--Sm}_2\text{O}_3$, and $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalysts



high-temperature (HT) region, respectively. The LT region peaks indicate desorption of NH_3 molecules from weak acidic sites present on the catalyst surface, whereas the HT region peaks correspond to presence of strong acidic sites. The $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalyst exhibited three peaks, with two peak maxima at higher temperatures (373 and 471 $^\circ\text{C}$), while only one peak was found for the Ce/SiO_2 catalyst at higher temperature (432 $^\circ\text{C}$). This observation indicates that the $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalyst contains a large amount of strong acid sites. It is therefore clear that simultaneous addition of Sm and SiO_2 results in improved acidic strength of CeO_2 , which could play a key role in oxidation of cyclohexene, as discussed below.

Catalytic activity results

Based on the activity results obtained in this work and from literature reports [59, 60], plausible reaction pathways can be proposed for oxidation of cyclohexene. As shown in Scheme 1, oxidation of cyclohexene using TBHP proceeds via two pathways, namely allylic and epoxidation. Initially, cyclohexene reacts with TBHP to give cyclohexene oxide (Cy-Oxide) and 3-(*tert*-butylperoxy) cyclohex-1-ene (Cy-TBHP) through epoxidation and allylic pathways, respectively. 2-Cyclohexen-1-hydroperoxide (Cy-HP) could also be obtained from Cy-TBHP with elimination of tertiary butyl alcohol. However, 2-cyclohexene-1-hydroperoxide is quite unstable and immediately reacts with cyclohexene to yield cyclohexene oxide (Cy-Oxide) via the epoxidation route (step 1). In parallel, 2-cyclohexen-1-hydroperoxide (CY-HP) can decompose upon heating to yield 2-cyclohexen-1-ol (Cy-OI, step 3a) as well as cyclohexen-1-one (Cy-One, step 3a) with release of water, which is an acid-



Scheme 1 Plausible reaction pathways for oxidation of cyclohexene

catalyzed reaction [18, 61]. Cyclohexen-1-one (Cy-One) can also be formed via oxidation of 2-cyclohexen-1-ol (Cy-OL, step 3b) with water as byproduct.

The results achieved for oxidation of cyclohexene over the CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalysts are shown in Fig. 7. Catalyst screening was conducted at 70 °C using TBHP and acetonitrile as oxidant and solvent, respectively, for 4 h. It is obvious from Fig. 7 that CeO_2 alone showed reasonable conversion of cyclohexene ($\sim 35\%$), indicating the oxidizing ability of pure CeO_2 for this reaction. High selectivity for allylic products ($\sim 78\%$) but poor selectivity for cyclohexene oxide (12 %) and Cy-TBHP ($\sim 10\%$) was found with CeO_2 . This observation indicates that the allylic oxidation pathway is favored when using the CeO_2 catalyst. Interestingly, considerable enhancement in cyclohexene conversion ($\sim 50\%$) and selectivity for allylic products ($\sim 81\%$) was observed when using the $\text{CeO}_2/\text{SiO}_2$ catalyst. On the other hand, the conversion of cyclohexene was significantly increased to $\sim 89\%$ when using the $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalyst, with high combined selectivity ($\sim 90\%$) for Cy-OL and Cy-One products. These results indicate a cooperative effect of Sm and SiO_2 in enhancing the catalytic strength of CeO_2 for oxidation of cyclohexene. As shown in Scheme 1, the allylic oxidation pathway of cyclohexene could be enhanced by the dehydration steps of 2-cyclohexen-1-hydroperoxide (step 3a) and 2-cyclohexen-1-ol (step 3b). The dehydration is a typical acid-catalyzed reaction. Based on the $\text{NH}_3\text{-TPD}$ results (Fig. 6), the $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalyst contained a large number of strong acidic sites, hence exhibiting higher catalytic efficiency for allylic oxidation of cyclohexene. In addition, the high BET surface area of the $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalyst (Table 1) is expected to play a crucial role in the cyclohexene oxidation reaction, because a high-surface-area catalyst can provide a greater number of active surface sites to promote oxidation of cyclohexene molecules, resulting in high conversion of cyclohexene.

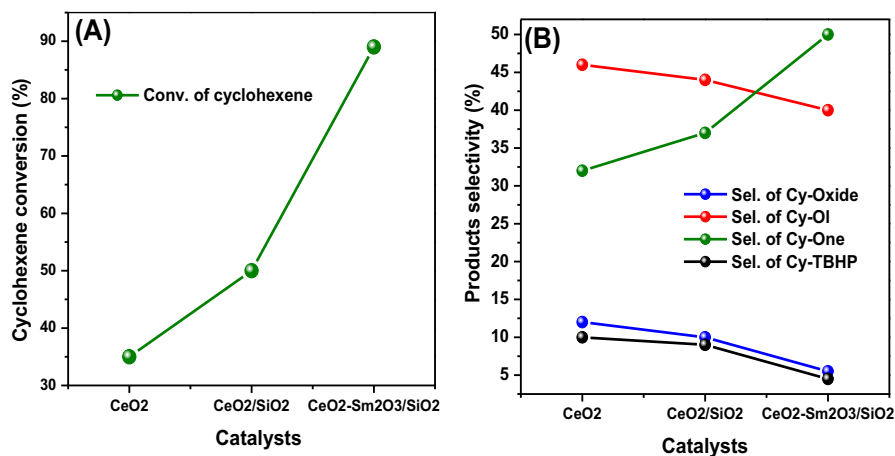


Fig. 7 Selective oxidation of cyclohexene over CeO_2 , $\text{CeO}_2/\text{SiO}_2$, and $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalysts: **a** conversion of cyclohexene and **b** selectivity for cyclohexene oxide (Cy-Oxide), 2-cyclohexen-1-ol (Cy-OL), 2-cyclohexen-1-one (Cy-One), and 3-(*tert*-butylperoxy) cyclohex-1-ene (Cy-TBHP)

To optimize the reaction conditions, the effect of various reaction parameters was investigated for oxidation of cyclohexene using $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalyst. The effect of reaction temperature on the cyclohexene conversion and product selectivity was investigated by varying the temperature from 40 to 70 °C for the reaction over $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$; the results are presented in Fig. 8. The conversion of cyclohexene and the selectivity for allylic products gradually increased with increase of the reaction temperature. When the reaction was performed at room temperature, very low conversion of cyclohexene was found ($\sim 10\%$) for time of 4 h, revealing the necessity for higher temperature to activate cyclohexene molecules to participate in the oxidation reaction. When the reaction was conducted at 40 °C, the cyclohexene conversion was about $\sim 28\%$, which increased to $\sim 89\%$ when the temperature was increased from 40 to 70 °C. This result confirms the crucial role of reaction temperature in the oxidation of cyclohexene. Also, the selectivity for allylic products, i.e., Cy-Ol and Cy-One, was found to increase from ~ 80 to $\sim 90\%$, while the selectivity for Cy-Oxide decreased from ~ 12 to $\sim 5.5\%$, with increase of the temperature from 40 to 70 °C.

Figure 9 shows the effect of reaction time (from 1 to 4 h) on the cyclohexene conversion and product selectivity over $\text{Ce--Sm}/\text{SiO}_2$ catalyst at 70 °C. Reasonable conversion of cyclohexene ($\sim 28\%$) was observed at 1 h of reaction time. Also, high selectivity for allylic products ($\sim 76\%$) but poor selectivity for Cy-Oxide ($\sim 15\%$) was observed at 1 h of reaction time, indicating a favorable role of the $\text{Ce--Sm}/\text{SiO}_2$ catalyst in selective oxidation of cyclohexene even for shorter reaction time. The conversion of cyclohexene was observed to be ~ 28 , ~ 50 , ~ 70 , and $\sim 89\%$ for reaction time of 1, 2, 3, and 4 h, respectively. The selectivity for Cy-Oxide and Cy-TBHP products decreased considerably with increase of the reaction time. On the other hand, high selectivity for allylic products was found for all reaction times (~ 76 , ~ 81 , ~ 84 , and $\sim 90\%$ at 1, 2, 3, and 4 h, respectively).

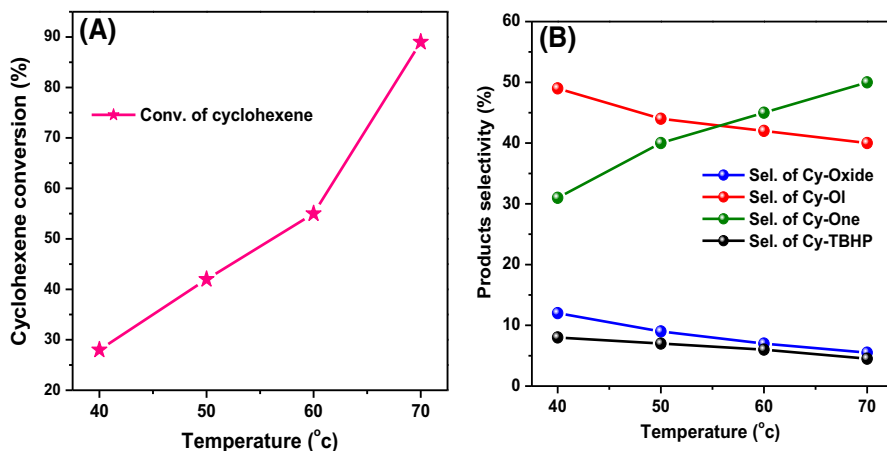


Fig. 8 Effect of reaction temperature on selective oxidation of cyclohexene over $\text{CeO}_2\text{--Sm}_2\text{O}_3/\text{SiO}_2$ catalyst: **a** conversion of cyclohexene and **b** selectivity for cyclohexene oxide (Cy-Oxide), 2-cyclohexen-1-ol (Cy-Ol), 2-cyclohexen-1-one (Cy-One), and 3-(*tert*-butylperoxy) cyclohex-1-ene (Cy-TBHP)

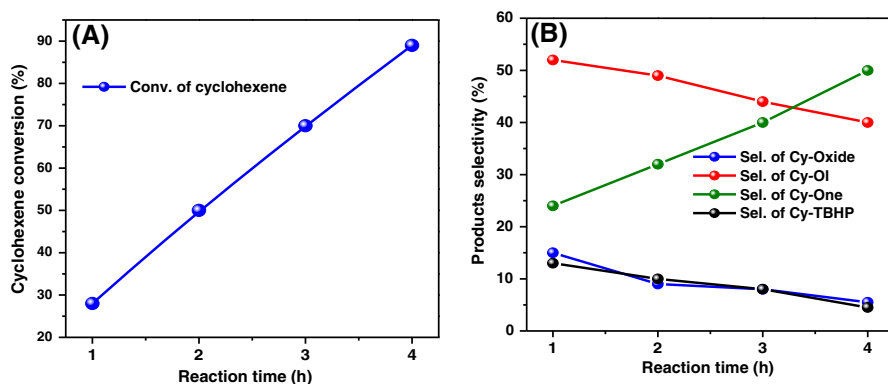


Fig. 9 Effect of reaction time on selective oxidation of cyclohexene over $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalyst: **a** conversion of cyclohexene and **b** selectivity for cyclohexene oxide (Cy-Oxide), 2-cyclohexen-1-ol (Cy-Ol), 2-cyclohexen-1-one (Cy-One), and 3-(*tert*-butylperoxy) cyclohex-1-ene (Cy-TBHP)

Figure 10 shows the effect of the molar ratio of cyclohexene/TBHP on oxidation of cyclohexene over $\text{Ce-Sm}/\text{SiO}_2$ catalyst under optimized reaction conditions. Very low cyclohexene conversion ($\sim 24\%$) was observed at 1:0.25 molar ratio of cyclohexene/TBHP, which is due to insufficient accessibility of TBHP molecules to interact with cyclohexene molecules. The conversion of cyclohexene was considerably increased with increase of the cyclohexene/TBHP molar ratio. The achieved cyclohexene conversion was ~ 24 , ~ 50 , ~ 75 , and $\sim 89\%$ for cyclohexene/TBHP molar ratio of 1:0.25, 1:0.50, 1:0.75, and 1:1, respectively. At molar ratio of cyclohexene/TBHP of 1:0.25, a considerable amount of epoxidation product (Cy-Oxide; $\sim 28\%$) was obtained, which decreased to 5.5% with increase of the molar ratio of cyclohexene/TBHP to 1:1. In parallel, the selectivity for allylic products

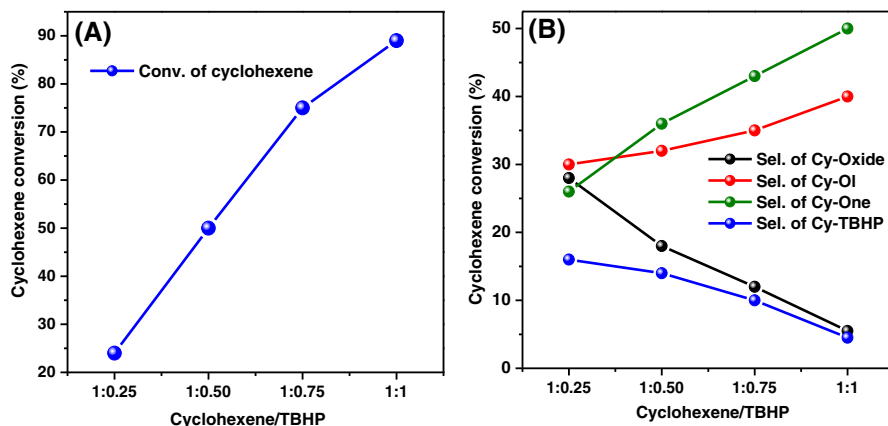


Fig. 10 Effect of mole ratio of cyclohexene/TBHP on selective oxidation of cyclohexene over $\text{CeO}_2\text{-Sm}_2\text{O}_3/\text{SiO}_2$ catalyst: **a** conversion of cyclohexene and **b** selectivity for cyclohexene oxide (Cy-Oxide), 2-cyclohexen-1-ol (Cy-Ol), 2-cyclohexen-1-one (Cy-One), and 3-(*tert*-butylperoxy) cyclohex-1-ene (Cy-TBHP)

was found to increase from ~ 56 , ~ 68 , ~ 78 to ~ 90 % with increase of the molar ratio of cyclohexene/TBHP from 1:0.25, 1:0.50, 1:0.75 to 1:1, respectively.

The effect of different solvents on the cyclohexene conversion and product selectivity was investigated using the Ce–Sm/SiO₂ catalyst; the results are shown in Fig. 11, revealing that both the cyclohexene conversion and product selectivity were highly dependent on the nature of the solvent. High conversion of cyclohexene (~ 89 %) with superior selectivity (~ 90 %) for allylic products was found when using acetonitrile as solvent. On the other hand, ~ 35 , ~ 45 , and ~ 61 % conversion of cyclohexene was noted when using dimethylformamide (DMF), ethanol, and chloroform, respectively, as solvent under similar reaction conditions. Interestingly, high selectivity for oxidation of cyclohexene to allylic products, namely 2-cyclohexene-1-ol (40 %) and 2-cyclohexene-1-one (50 %), was achieved when using acetonitrile compared with other solvents under identical conditions. The selectivity for allylic products with different solvents was as follows: acetonitrile (90 %) > DMF (70 %) > EtOH (67 %) > CHCl₃ (59.3 %). It can therefore be concluded that acetonitrile could be the best solvent to attain high conversion with superior selectivity for allylic products.

To understand the significance of the CeO₂–Sm₂O₃/SiO₂ catalyst, a comparison against recently reported catalysts for oxidation of cyclohexene is presented in Table 2. Various supported noble-metal catalysts, such as PdO/SiO₂, Au/SiO₂, Ru/CeO₂, and Ru/H-Mont, have been investigated, showing cyclohexene conversion of 71, 67.6, 38.1, and 22 %, respectively. Compared with these noble-metal-based catalysts, much higher cyclohexene conversion (89 %) was observed when using the CeO₂–Sm₂O₃/SiO₂ catalyst. On the other hand, very low cyclohexene conversion was reported when using Co/CeO₂ (36.9 %) or Cu-MOF (33 %) catalysts with TBHP as oxidant (entries 5 and 6). Also, the VO₂/SiO₂ and VO₂/TiO₂ catalysts showed low catalytic performance in terms of both cyclohexene conversion and selectivity for allylic products (entries 7 and 8) [62, 63]. Overall,

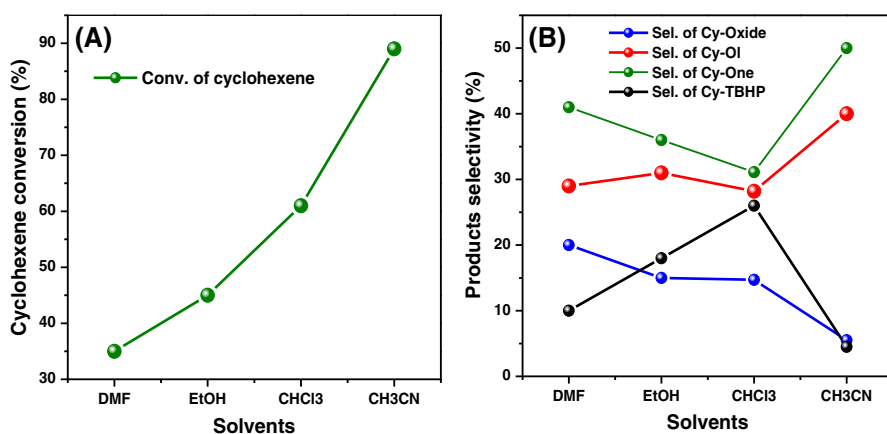


Fig. 11 Effect of solvent on selective oxidation of cyclohexene over CeO₂–Sm₂O₃/SiO₂ catalyst: **a** conversion of cyclohexene and **b** selectivity for cyclohexene oxide (Cy- Oxide), 2-cyclohexen-1-ol (Cy-Ol), 2-cyclohexen-1-one (Cy-One), and 3-(*tert*-butylperoxy) cyclohex-1-ene (Cy-TBHP)

Table 2 Comparison of activity of various catalysts for oxidation of cyclohexene

Entry	Catalytic system	Oxidant	Cyclohexene conversion	Selectivity for allylic products	Ref.
1	2.14 % PdO/SiO ₂	TBHP	71	81	22
2	1 % Au/SiO ₂	H ₂ O ₂	67.6	80.2	63
3	Ru/CeO ₂	TBHP	38.1	90.1	15
4	5 % Ru/H-Mont	TBHP	22	100	24
5	Co/CeO ₂	TBHP	36.9	87.5	15
6	Cu-MOF	TBHP	33	96	62
7	5 % VO ₂ -SiO ₂	TBHP	21	17	63
8	5 % VO ₂ -TiO ₂	TBHP	13	79	63
9	CeO ₂ -Sm ₂ O ₃ /SiO ₂	TBHP	90	89	This work

excellent cyclohexene conversion and high selectivity for allylic products were noted when using the CeO₂-Sm₂O₃/SiO₂ catalyst. Further studies are essential to exploit the present catalyst in place of noble-metal catalysts for not only selective oxidation of cyclohexene but also other industrially important oxidation reactions.

Conclusions

Highly promising nanostructured CeO₂/SiO₂ and CeO₂-Sm₂O₃/SiO₂ catalysts were synthesized by a facile deposition precipitation method and explored for selective liquid-phase oxidation of cyclohexene using TBHP as oxidant. The catalytic activity order of the employed catalysts for allylic oxidation of cyclohexene was found to be CeO₂ < CeO₂/SiO₂ < CeO₂-Sm₂O₃/SiO₂. All the catalysts showed high selectivity for allylic products, indicating that the ceria-based nanooxide catalysts favor the allylic oxidation pathway. The reaction temperature, reaction time, cyclohexene/TBHP molar ratio, and nature of solvent showed a notable influence on the cyclohexene conversion and selectivity for allylic products. The strong acidic nature of the CeO₂-Sm₂O₃/SiO₂ catalyst associated with large BET surface area facilitated its outstanding performance for allylic oxidation of cyclohexene. This noble-metal-free catalyst is expected to find numerous applications in other oxidation reactions of commercial significance. Further work is under active progress aimed at large-scale application of this catalyst.

Supplementary data

Pore size distribution profiles, Ce⁺³ concentration, and XP spectra of the catalysts.

Acknowledgements B.G.R and P.R.G.N. thank the Council of Scientific and Industrial Research (CSIR), New Delhi for research fellowships. B.M.R. thanks the DAE, Mumbai for the award of a Raja Ramanna Fellowship.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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