Phase Transfer Ceria-Supported Nanocatalyst for Nitrile Hydration Reaction

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ABSTRACT: The present study elaborates the catalytic effect of rare-earth metal oxides (Sm2O3 and La2O3) over ceria as a support phase transfer catalyst. The synthesized catalysts have been subjected to different characterization techniques, such as field-emission scanning electron microscopy, high-resolution transmission electron microscopy, powder X-ray diffraction, N2 adsorption–desorption (BET surface analysis), temperature-programmed desorption study (NH3/CO2-TPD), Fourier transform infrared, Raman analysis, and X-ray photoelectron spectroscopy to get better insights into the catalytic activity of the catalysts for hydration of nitrile.

1. INTRODUCTION

Elemental cerium exhibiting ([Xe] 4f5d6s2) electronic configuration is normally found in both +3 ([Xe] 4f5d6s6) and +4 ([Xe] 4f5d6s6) oxidation states; it received considerable attention in the past several decades owing to its excellent catalytic performance in various heterogeneous catalytic reactions involving redox chemistry. More specifically, the high oxygen storage capacity (OSC) associated with the valence change between Ce3+ and Ce4+, a surface charge with acidic and basic sites as well as the high-level crystal phase stability of the material make it as an excellent choice to exploit various catalytic applications. CeO2 plays a pivotal role in automotive pollution control. The development of the three way catalysts was to treat the tailpipe exhaust gas from automobiles to oxidize the product, mainly to control the pollutants and to convert gases like CO, volatile organics, and NOx present in the automotive exhaust to H2O, CO2, and N2. CeO2 is also used to remove SOx from the fluidized catalytic cracking process and several oxidation reactions.

Though the CeO2 catalyst is having acid/base and redox properties, it also had been explored for various organic reactions; for example, Tamura et al. reported a simple ceria catalyst for hydration of nitrile in aqueous conditions to form amides. In this process, the Lewis acidic sites and basic sites of the low-coordinated CeO2 helps the reaction to process easily. It is observed that among the various oxide supports, ceria-based catalysts were found to be highly active and selective toward amide formation. The hydration of nitriles to generate the corresponding amides is an important transformation from both academic and industrial points of view. Amides not only constitute versatile building blocks in synthetic organic chemistry but also have a wide range of industrial applications and biologically active and pharmacological interests.

In this work, the production of such organic substances from dual immiscible reactants is highly affected by using ceria-supported phase transfer catalysts (PTCs). When the reactants are mixed in immiscible phases, PTCs carry active species which penetrates another phase, where the reaction occurs and produces a selectively high yield. Because of the presence of PTCs, reactions generally work up under ambient conditions with easy work-up processes, and hence these catalysts are commercially very significant. Currently, PTC is an ingenious process, which is also environmentally benign. The reaction mechanism indicates that the reaction pathway proceeds through the formation of hydroxyl ions over the “Ce”-supported catalyst, to enhance the formation of such reactive ions and several organic reactions both microwave irradiation and ultrasound used. High temperature and local pressure are induced with ultrasonic waves to increase the mass transfer and flow of the reactants, and this helps in reducing the reaction time and increase the yield.

Although ceria depicts excellent activity in several catalytic applications, which are assigned to a relative alloy of oxygen vacancy constitution and enhanced in surface area than that of the bulk form, but it has some limitations as ceria has less thermal constancy ensuing in the release of OSC, surface area, and in turn, its catalytic activity. It is known that the addition of the second oxide relatively in trace amounts and...
the catalytic activity of the primary component are affected considerably.\textsuperscript{22–26}

The rare-earth oxides such as Ce, “Sm, La”, and “Ru” have been chosen for the current work, as they have vivid applications in catalysis. They depict good catalytic properties in various organic reactions, also in the synthesis of ammonia and oxidative coupling of methane, and so forth.\textsuperscript{26–29} The wide range of the surface area to the pore volume of the nanoparticle assures to enhance their catalytic properties, especially in the number of surface oxygen species.\textsuperscript{30} The other reported catalysts for the hydration process are mainly CeO$_2$, MnO$_2$, TiO$_2$, CaO, Y$_2$O$_3$, La$_2$O$_3$, and ZrO$_2$; however, they have few drawbacks, such as high retention time for the reactant adsorption—desorption (BET surface analysis), high-resolution transmission electron microscope (HR-TEM), and temperature-programmed desorption study for probe molecules (TPD of NH$_3$ and CO$_2$), Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), and laser Raman spectra analysis.

XRD of the catalysts was carried out using a X’Pert Pro diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) with a proportional counter as the detector. The profiles of the catalysts were recorded in theta ranging from 10 to 90° at a scanning rate of 4°/min. The mean crystal size (\textit{d}) was calculated by the line broadening method with the Scherrer equation $d = K\lambda/\beta \cos \theta$, where \textit{K} is the Scherrer constant (0.89), \textit{\lambda} is the wavelength of the X-ray, \textit{\beta} is the full width of peak at half-maximum height (fwhm), and \textit{\theta} is the diffraction angle of CeO$_2$(111).

Microstructure studies for the catalysts were carried out by FE-SEM, and it was carried out on an accelerating voltage of 10 kV. The samples were mechanically deposited on the holders and subsequently gold-coated to reduce charge buildup.

The typical operating conditions of the HR-TEM instrument (Jeol JEM 200) is 200 kV electrons (field emission gun), 10–6 mbar vacuum, and 0.1 nm resolution. HR-TEM was used for imaging of the microstructure and compositional analysis of the PTC catalyst. The bright field image is studied from the diffracted electron beams, which shows a little decrease in the angle from the transmitted beam.

\subsection*{2.1. Catalyst Synthesis.}

This study provides a process for the preparation of the Ce-supported PTCs denoted as CSR (Ce−Sm−Ru) and CLR (Ce−La−Ru), which are mixed metal oxide catalysts. Ce−La/Sm−Ru (90:9.5:0.5) wt % were synthesized and characterized by using various characterization techniques, and these catalysts are subjected to catalytic activity with and without ultrasonic cavitation influence.

The catalyst synthesis was done in a three-step process:

Step 1: solution A: cerium precursor [cerium(III) nitrate hexahydrate-99.99% (Sigma-Aldrich)] was taken and dissolved in 5 mL of deionized water and held under continuous stirring at 550 rpm.

Step 2: solution B: ruthenium precursor [ruthenium(III) chloride-99.98% hydrate solution-Sigma-Aldrich] was added dropwise to solution A with constant stirring at 85 °C, where yellowish slurry was formed. The formed slurry was aged at 150 °C for 5 h with stirring at 700 rpm. After the completion of aging, catalyst slurry was subjected for drying at 180 °C for 6 h. The dried catalyst was calcined by heating at a ramp rate of 2 °C/min and heated to 200 °C for 3 h, further heated to 500 °C for next 3 h, and then calcined to 900 °C for 12 h. Calcined catalysts were denoted as CSR and CLR, respectively.

\subsection*{2.2. Catalyst Characterization.}

The synthesized catalysts were characterized by using powder X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDAX), field emission scanning electron microscope (FE-SEM), N$_2$ adsorption—desorption (BET surface analysis), high-resolution transmission electron microscope (HR-TEM), and temperature-programmed desorption study for probe molecules (TPD of NH$_3$ and CO$_2$), Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), and laser Raman spectra analysis.

\subsection*{2.3. Catalytic Activity Study.}

Starting materials such as 2-cyanopyridine (99%) and product standards such as 2-picolinamide (2-PA) 98% and extraction solvents such as dichloromethane (DCM, AR grade) were procured from Sigma-Aldrich. The catalyst activity was tested for the hydration reaction of 2-cyanopyridine with water to form 2-PA as the selective product. This reaction was conducted in a round-bottom flask connected with a reflux condenser. The required energy for the reaction was supplied by a heating bath. The effect of ultrasonic cavitation was also tested for the same for which the round-bottom flask was submerged in an ultrasonic cavitation bath. Nitrite conversion and yield of the reaction were determined by GC Agilent (model number-7890 A) using an HP-5 capillary column (length-30 m × 250 μm × 0.25 μm) (Scheme 1).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{scheme1.png}
\caption{Scheme 1. Hydration Reaction Pathway}
\end{figure}

\subsection*{3. RESULTS AND DISCUSSION}

Ceria is utilized as the support and acts as a reaction initiator which adsorbs and dissociates water molecules, forming the Ce−hydroxyl complex; at the same time, it is also forming a Ce−nitrite complex which further initiates the reaction. Sm/La and Ru oxides act as the promoter and co-promoter, respectively, for this reaction as they provide acidic sites for the reactant adsorption.

\subsection*{3.1. X-ray Diffraction.}

XRD patterns revealed (Figure 1) that the CSR and CLR exhibit a cubic fluorite structure\textsuperscript{32} with unit cell parameters of 0.5427 nm (CSR) and 0.5432 nm (CLR), respectively. The average crystallite size of catalysts was determined using Debye—Scherer equation from the (111) peak of CeO$_2$ which were found to be 10.6 and 12.3 nm, respectively. The different diffraction angles for Sm/La and Ru were identified with the help of X’pert Pro software. The diffraction peaks of all samples could be indexed to 111, 200, 311, 222, 400, 331, 420, and 422 crystal faces, attributed to the lantanides as promoters and ruthenium as the co-promoter have been successfully evaluated for the hydration of nitrile in the presence of ultrasonic cavitation.
face-centered cubic phase of CeO$_2$ (JCPDS 34-0394). As shown in Figure 1, the peaks of CeO$_2$ exhibit (a) poor crystallinity with smaller crystallite size in CSR, and this catalyst shows the existence of many lattice defects having a pure cubic fluorite structure (JCPDF04-0593) and space group $Fm\overline{3}m$ (225).

3.2. Morphological (FE-SEM) Study. The FE-SEM profile shows platelets and irregular shape with an edge length of 5–10 $\mu$m (Figure 1a,b); despite the distribution of the crystals in high density, the presence of agglomeration demonstrates the homogeneous solid solution formation by the dispersion of Sm/La and Ru oxide over the CeO$_2$ surface. This result of SEM indicated that defects sites of the CeO$_2$-supported catalyst might perform a better activity for the hydration reaction, which is also confirmed by XRD. The bulk portion was taken for elemental quantification analysis for CSR and CLR catalysts, respectively.

3.3. Energy-Dispersive X-ray Spectroscopy. Table 1 and Figure 2c,d represent the EDAX spectrum of Ce, Sm, La, Ru, and O peaks which are related to its respective metal oxide presence in the CeO$_2$-supported PTC oxide catalysts. The EDAX data are also agreeing with HR-TEM (Figure 3c–e) and elemental mapping data (Figure 5a,b), where the homogenous dispersion of Ce, Sm, La, Ru, and O has been found.

3.4. High-Resolution Transmission Electron Microscope. Figure 3a–e shows HR-TEM for CSR and CLR catalysts. The oxides of Ce, La/Sm, and Ru are distinctly seen in close proximity. This demonstrates the solid solution nature of the reported catalysts in this communication. The marginal shift in d-spacing values (shown in HR-TEM images) is attributed to the stress of accommodating La/Sa and Ru oxides in the ceria crystallites. In Figure 3c, La$_2$O$_3$ and CeO$_2$ exhibited the overlapped lattice fringes for CLR oxides (d—0.34 nm), and Figure 3c,d also shows the overlapped lattice fringes for CSR oxides (d—0.34 nm) and individually for Sm$_2$O$_3$ (d—0.228 nm). The bulk portion was taken for elemental mapping for CSR and CLR catalysts, respectively.

3.5. Elemental Mapping. Figure 3f,g clearly shows the formation of a homogenous solid solution of (Ce-Sm/La-Ru) oxides and dispersion of elements on the ceria surface. It is evenly representing the elemental mapping of CeO$_2$ supported PTC oxide catalyst, respectively.

3.6. Fourier-Transform Infrared Spectroscopy. Figure 4a,b shows the FT-IR spectra of the bands at 1638 and 3200 cm$^{-1}$ which represents the water and the hydroxyl stretches, respectively. The intensive band at 1400 cm$^{-1}$ represents the N–O stretch due to the presence of nitrate. The strong absorption band observed below 600 cm$^{-1}$ represents the Ce–O stretch. No vibrational features were observed due to the presence of Sm–O and La–O, which indicated the formation of a homogeneous solid solution. XRD and HR-TEM results were also evident for the abovementioned conclusion.

3.7. NH$_3$/CO$_2$-TPD. The PTC catalysts exhibited nearly equal acidic and basic (bifunctional) properties for CSR and CLR catalysts (Table 2). Table 2 also provides other physicochemical characteristics.

However, the absolute values of acidity/basicity are significantly different for CSR and CLR catalysts. The present work exemplified that CeO$_2$/Sm/La$_2$O$_3$/Ru$_2$O$_3$ phases are synergistically responsible for the activation of various nitriles.

The density of acid/base sites on CeO$_2$-supported catalysts was quantified by NH$_3$/CO$_2$-TPD at different desorption peaks at 50–200, 200–400, and 400–800 °C which represents the weak, medium, and strong sites, respectively (Figures 5 and 6a,b) (Table 2). The PTC catalysts are having a large amount of acidity/basicity at the strong (400–800 °C) site. CSR and CLR are amphoteric in nature as it is has an acidity of 0.43 and 0.49 mmol/g and a basicity of 0.41 and 0.49 mmol/g, respectively. This amphoteric nature might be responsible for the high selectivity of hydration of nitrile toward their corresponding amide.

3.8. X-ray Photoelectron Spectroscopy. Figure 7a–c reveals the X-ray photoelectron spectra of the Ce 3d and La 3d core levels with six and eight peaks corresponding to Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ spin–orbit components. The peaks ranging from $u'$ (905.9–907.83) and $u''$ (915.37–916.13) corresponds to Ce$^{4+}$ 3d$_{5/2}$, while $v'$ (886.04–886.61) and $v''$ (897.58–897.92) corresponds to Ce$^{3+}$ 3d$_{5/2}$, and the peaks assigned to $u'$ (900–901.2) and $v'$ (881.76–882.01) describes to Ce$^{4+}$ 3d$_{3/2}$ species. Figure 7c shows only one spectrum at 838.5 eV, which is addressed to La 3d$_{5/2}$, and according to the literature, it shows the defected ceria sites (Ce$^{3+}$ and lanthanum (La$^{3+}$). These indicate that our synthesized ceria-supported PTC has high OSC because of the presence of Ce$^{4+}$ and La$^{3+}$.

No significant intensity for Sm 3d and Ru 3d spectra was observed, indicating that the contribution of these elements on the surface under XPS conditions is insignificant. A small amount of Ru 3d could be a possible reason for not observing the Ru core-level spectrum. Sm may form a homogeneous solid solution with Ce$_2$O$_3$, or it may be present as elemental Sm; therefore, no spectrum corresponds to the same observed in this XPS profile.

3.9. N$_2$ Adsorption–Desorption (BET Surface Analysis). Figure 8a,b represents the N$_2$ adsorption–desorption

Table 1. EDAX Data of CSR and CLR  
| catalyst | CSR | CLR |
|----------|-----|-----|
| element  | Ce  | Sm  | Ru  | O  |
| wt %     | 17.77 | 16.87 | 52.87 |
| at %     | 3.49  | 3.09  | 90.95  |
isotherms at \(-196\, ^\circ\text{C}\) and the pore size distribution according to the Barrett–Joyner–Halenda method for the PTC samples. According to IUPAC, it classified the shapes of the adsorption isotherms for samples as type IV with a hysteresis loop, which is associated with capillary condensation in the mesopores. It was observed that the initial part of the isotherm where the relative pressure \(p/p^\circ \approx 0.3\) of CSR/CLR catalysts can be attributed to monolayer adsorption. Total pore volume, specific surface area \((S_{\text{BET}})\), and average pore size for CSR/CLR were found to be 86.75 and 79 m\(^2\)/g; 0.105 and 0.106 cc/g; and 24 and 26.9 Å, respectively.

3.10. Raman Spectra. The cubic fluorite phase formed in the commercial CeO\(_2\) catalyst (Figure 9) has been confirmed by the high intense peak at 460 cm\(^{-1}\) observed in Raman spectra which describe the vibrational mode of the above type of structure, also confirmed by XRD. The structure conformation conveyed that the symmetric breathing mode of oxygen atoms present around Ce ions is sensitive to the sub lattice oxygen from any nonstoichiometry. The band at 460 cm\(^{-1}\) is not changed in intensity but shifted to a lower frequency for CSR and CLR sample (450.89 and 448.74 cm\(^{-1}\)), respectively. The insertion of (Sm/La)Ru ions into

![Figure 2. SEM profiles of CSR (a) and CLR (b) catalysts. (c,d) SEM-EDAX profiles of PTCs CSR and CLR catalysts.](image1)

![Figure 3. (a–e) TEM images of CeO\(_2\)-supported PTC oxide CSR and CLR catalysts (a) pure CeO\(_2\), (b) Ru\(_2\)O\(_3\), (c) CSR with 5 nm, (d) CSR with 20 nm, and (e) CLR with 20 nm. (f) CSR and (g) CLR TEM elemental mapping of PTC.](image2)
CeO₂ which decreases the vibrational frequency of the metal–anion band accredited to the larger atomic mass of Sm, La, and Ru than that of Ce and the variation of the lattice parameter. The shift in the frequencies in both catalysts reveals the formation of ceria solid solution with (Sm/La)Ru ions, resulting in different oxidation states for ceria (Ce⁴⁺ and Ce³⁺), samarium (Sm³⁺), and lanthanum (La²⁺), where the Ru-oxidation state disappeared as its weight percentage is very low.

4. EXPERIMENTAL SECTION AND ACTIVITY STUDIES

4.1. Hydration of Nitrile Catalyzed by CSR/CLR and Commercial CeO₂ Catalyst without Cavitation Influence. The reaction was conducted at 140 °C for 3 and 6 h, and the resulting mixture was extracted with DCM (30 mL) and used for GC analysis by following reaction conditions: 2-CP/H₂O molar ratio (1:1), where 2-CP is 50.41 mmol and H₂O is 55 mmol with 10 wt % of CSR/CLR and commercial ceria (approximately 0.52 g). Reaction results in Figure 10.
show that amongst the CSR, CLR, and pure CeO$_2$ (commercial), the CSR catalyst is more active for the hydration. This higher activity of CSR can be justified with the help of the physical properties of the catalyst which we studied during this work. The characterization data reveals that the CSR is having a higher surface area when compared to CLR (Table 2) and reported commercial CeO$_2$. Apart from this, CSR is also having an appropriate ratio of acidic to the basic site. The other reason for the higher activity of the CSR catalyst can be substantiated with the help of elemental mapping (Figure 3f) which reveals the uniform dispersion of the elements over the catalyst surface and the formation of homogenous solid solution which makes this catalyst superior to the other tested catalysts.

4.2. Effect of Temperature Using CSR without Cavitation Influence. The effect of temperature on the reaction between 2-CP and water (molar ratio of 1:10) to form 2-PA with 10 wt % catalyst loading for 6 h by varying the temperature from 30 to 140 °C. It is demonstrated that the reactivity is enhanced with rise in the temperature. The collision of the reactants at higher temperature is also increased. Hence, the apparent yield of the amide is increased at a higher temperature. These results are demonstrated in Figure 11, which is plotted against temperature and yield of amide (2-PA).
4.3. Effect of Ultrasound and without Ultrasound on the Reaction. The effect of cavitation for the hydration of nitrile to the corresponding amide was performed for different intervals of time 1–6 h. The reaction temperature was maintained at 45 °C for cavitation experiments and 60 °C for without cavitation experiments. The result indicates that the conversion increases linearly over time with or without ultrasonic irradiation. It is to be noted that the cavities release highly unstable OH ions in the solution, which helps the reaction in the presence of the catalyst. However, with ultrasonic cavitation, high rate of reaction is observed at 45 °C in comparison to the reaction conducted under the conventional reflux method (without ultrasonication) over time (Figure 12).

Figure 12. Influences of ultrasonic cavitation.

The influences of ultrasonic cavitation have been studied with the following reaction condition: 2-cyanopyridine/H2O (molar ratio) 1:10, catalyst loading −10 wt % (with respect to 2-cyanopyridine loading). The reaction mixture was stirred at 600 rpm, and the reaction temperature for cavitation experiments was 45 and 60 °C without cavitation experiments.

5. CONCLUSIONS

The characterization data suggest that the Ce-supported Sm and La oxide catalyst is better for the hydration of nitriles as these compositions can successfully eliminate the drawbacks of the known catalyst. Catalysts have appropriate acidic and basic sites and can also form homogeneous distribution of active metals on the CeO2 support. The catalytic activity is tested at various temperatures under the influence of ultrasonic cavitation, which helps for the formation of highly unstable hydroxyl ions. PTC exhibits efficient catalytic activity for the hydration of nitriles to produce corresponding amides. Experimental results show the yield of 2-PA at 45 °C under the influence of ultrasonic cavitation, where it increases linearly over time.

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Notes

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