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Transformative process: Crafting imines from nitrobenzene and benzyl alcohol coupling with cerium oxide modified mesoporous SBA-15

Soumini Chandralayam[1*] and Sugunan Sankaran[2]

[1] Department of Chemistry, Mes Keveeyam College Valanchery Keveeyam College, **India**
[2] Department of Applied Chemistry, Cochin University of Science and Technology, **India**

* Corresponding Author: souminic@meskeveeyamcollege.ac.in

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Abstract: A low-cost and eco-friendly cerium oxide modified mesoporous SBA-15 catalyst was developed by wet impregnation. It enables sequential oxidation of benzyl alcohol and reduction of nitrobenzene, followed by imine formation in a single and solvent-free system. Characterization confirms homogeneous cerium oxide dispersion, high stability, and enhanced redox properties. The optimized catalyst demonstrates excellent conversion and selectivity, attributed to the mesoporous SBA support, acidic properties, and cerium's redox functionality. Elevated temperatures enhance benzyl alcohol dehydration and hydrogen diffusion, facilitating intermediate aniline formation by a borrowing-hydrogen mechanism and followed by imine synthesis. It eliminates solvents, reduces byproducts, and achieves high atom economy and renewability. It presents a significant advance in sustainable catalysis. The catalyst's robustness and ease of recovery strengthen its practicality for repeated cycles. The findings provide a scalable and energy-efficient solution for greener imine synthesis with potential applications in industrial processes requiring efficient and eco-friendly chemical production. It ensures minimal environmental impact and offers a cost-effective pathway for high-value chemical synthesis. This study supports the SDGs by promoting sustainable industrial practices through the development of a low-cost and eco-friendly catalyst that reduces environmental impact, enhances energy efficiency, and contributes to greener chemical production.

Keywords: mesoporous SBA-15; imine formation; ceria; catalyst development

1. Introduction

Imines serve as crucial intermediates in various industrial applications such as pharmaceuticals, fragrances, dyes, fungicides, and agricultural chemicals. While the synthesis of imines from nitro compounds and alcohols typically involves multi-step processes, there is growing interest in one-pot methods for their production [1]. It involves the chemoselective synthesis of imines by a greener approach, emphasizing atom economy, and energy efficiency. This process relies on a tandem reaction, beginning with the catalytic oxidation of alcohols to generate aldehydes and release hydrogen. The released hydrogen subsequently aids in converting nitro compounds into amines with the assistance of a catalyst. The amines and aldehydes undergo coupling to form imines. Depending on reaction conditions and catalyst properties, the resulting imines can be further transformed into secondary amines through reduction or alkylated to yield tertiary amines [2]. This versatile methodology offers potential for efficient and modified synthesis of valuable chemical compounds.

Several studies have explored the utilization of noble metals, transition metals, and other catalytic systems for the production of imines and amines. The subsequent section delves into the specifics of Au-supported catalytic systems for imine/amine synthesis. A high yield of imines can be crafted from the reaction between benzyl alcohol and amines utilising an Au-supported hydroxyapatite

(Au/HAP) catalyst under liquid-phase conditions at 60°C in the presence of oxygen [3]. The synthesis of imines from amines and alcohols using an Au/TiO_2 catalyst system was investigated under ambient conditions in the presence of oxygen. These reactions occurred at room temperature and atmospheric pressure with the addition of a base. The reaction's versatility was explored across a range of alcohol-amine combinations, achieving moderate conversion rates (10–65%) and high selectivity (>98%) for various substrates. It involved studies on the influence of parameters such as temperature, base concentration, and reaction time. In this context, the base acted as a promoter with different bases ($KOCH_3$, $NaOCH_3$, $LiOCH_3$). Potassium methoxide was identified as the most effective promoter that attributed to the enhancing effect of potassium ion [4].

A chemoselective method for synthesizing substituted imines, amines, and α,β-unsaturated imines by cascade reactions involving nitro and carbonyl compounds under mild conditions was developed. This process employed a nanogold catalyst (Au/TiO_2) in the presence of H_2, enabling efficient product formation [5]. Imine formation was achieved using transition metal catalysts that showcasing their effectiveness in facilitating these reactions [6]. In 2021, a study demonstrated the formation of imines from amines and alcohols through oxidation using a manganese–zirconium solid solution catalyst [7]. Other previous studies in 2016 explored both monometallic and bimetallic (Au-Pd, Ru-Pd). TiO_2 systems for coupling nitrobenzene with benzyl alcohol where the bimetallic systems showed superior yields in imine synthesis [8]. A comparative study on various gold-based catalysts highlighted their high activity and selectivity for converting amines to imines through oxidation under ambient conditions [9]. Three nanogold catalyst systems were developed using a solid grinding method with porous coordination polymers such as MOF-5, Al-MIL53, and CPL-2 serving as supports [10]. Among these, the Au/Al-MIL53 system (with Au particle size 1.6 nm) exhibited superior activity and selectivity for the formation of secondary amines by the condensation of primary amines. This reaction proceeded by a two-step process involving oxidative coupling to produce imine, followed by a reduction step leading to secondary amine formation. The Au/Al-MIL53 catalyst demonstrated applicability for the oxidative coupling between alcohol and amines in a basic medium, yielding secondary amines in moderate yield without requiring hydrogen or oxygen. This reaction also followed a two-step process.

Various metal oxide-stabilized gold nanoparticles were explored as catalyst for the oxidative coupling between equal amounts of benzyl alcohol and aniline that leading to imine and amine production. The Au/Co_3O_4 catalyst exhibited better selectivity towards imines, while the Au/ZrO_2 system showed better selectivity towards secondary amines. The Au/CeO_2 catalyst displayed enhanced activity towards the oxidation of benzyl alcohol in the absence of aniline but showed decreased activity for the coupling between alcohol and aniline compared to Au/ZrO_2. The decline in activity was associated with the Au/CeO_2 catalyst's insufficient capacity to adsorb aniline by hydrogen bonding. Thus, besides the basic or acidic properties of the catalyst surface, the aniline adsorption capacity significantly influences imine or secondary amine formation by promoting hydrogen transfer. Thereby, enhancing the yield of secondary amines [11]. Au/Fe_2O_3 catalysts with varying gold concentrations were employed for the direct synthesis of N-alkylated anilines from diverse nitrobenzenes and alcohols under ambient conditions [12]. Similarly, Au/Al_2O_3 catalysts were used to produce substituted secondary amines from nitroarenes and aldehydes with hydrogen acting as the reducing agent [13]. Nanogold supported on various metal oxide catalysts was employed for the oxidative coupling between benzyl alcohols and nitrobenzene. Au/ZnO catalysts exhibited better selectivity (62%) to imines, while Au nanoparticles on TiO_2 catalysts (Au/TiO_2-VS) demonstrated superior selectivity (>99%) to secondary amines with both systems achieving complete conversion. The Au/TiO_2-VS catalyst exhibited remarkable performance, achieving superior selectivity toward secondary amines while ensuring complete conversion of substrates [14].

Another catalyst in amine synthesis has been conducted by comparing the activity of Pd/TiO_2, Pt/TiO_2, Au/TiO_2, and Ag/TiO_2 by the reaction between nitrobenzene and benzyl alcohol. The Pd/TiO_2 catalyst exhibited better selectivity for amines and was found to be reusable under mild conditions. Various types of secondary amines were synthesized by using different alcohols and nitro compounds as substrates [15]. The effectiveness of silver (Ag) catalysts supported on alumina (Al_2O_3) for the reaction between nitro compounds and alcohols was demonstrated with a focus on the coupling of benzyl alcohol and nitrobenzene. This catalyst showed remarkable catalytic performance, achieving 100% conversion and 98% selectivity toward N-alkylated aniline (a secondary amine). The same catalyst was also applied to the reaction between various nitro compounds and alcohols [16]. Recyclable Ag nanoparticles on mesoporous polyacrylic acid stabilizers were also successfully synthesized for the coupling of aromatic alcohols and nitro compounds in equimolar ratios. It produces imines and secondary amines with secondary amines as the major product under certain conditions [17].

A Pt-Sn/γ-Al_2O_3 catalyst was reported for the synthesis of imines or secondary/tertiary amines in excellent yields through the N-alkylation of primary/secondary amines with alcohols under liquid phase conditions [18]. A selective method for the formation of secondary amines from nitro compounds and alcohols using Ru-based catalysts was also reported [19]. Copper-based catalysts (Cu/Fe_3O_4) were successfully employed for imine synthesis from alcohols and amines/nitro compounds [20]. A nanomagnetically recyclable copper catalyst was utilized for imine formation under basic conditions. Cu-MOF was employed as a catalyst for imine synthesis in THF solvent [21]. In 2022, Nb_2O_5/Co_3O_4 catalysts were used for imine synthesis [22]. It also focused on nickel (Ni)-based catalyst for synthesizing imines and amines by the oxidative coupling of aldehydes and nitro compounds. A Ni/SiO_2 was utilized for the selective formation of imines from various aldehydes and nitro compounds [23].

The synthesis of imines from nitroarenes and alcohols was demonstrated in a one-pot process utilizing Ir-Pd complexes [24]. A method for synthesizing imines with good yields was developed by reacting aldehydes with alkyl bromides/epoxides in the presence of aqueous ammonia [25]. CeO_2-MnO_2 binary oxides were employed for the synthesis of amines from alcohols and amines [26]. Furthermore, cerium oxide-doped mesoporous carbon was utilized for the formation of imines from alcohols and amines [27].

For the oxidative coupling of alcohols and nitro compounds to produce imines, a cost-effective heterogeneous catalyst capable of activating both oxygen and hydrogen is highly desirable. Therefore, this study employed cerium oxide modified mesoporous silica (SBA) catalysts for imine synthesis using benzyl alcohol and nitrobenzene as substrates under vapor-phase conditions. Many previous studies relied on noble metals, solvents, and precursors such as amines and alcohols or aldehydes and amines. Previous studies have explored similar borrowing hydrogen methods challenges such as high energy inputs, stoichiometric reagents, or excessive catalyst loading have limited their efficiency and environmental sustainability. However, this study introduces a novel cerium oxide modified mesoporous SBA catalyst which enhances the reaction's efficiency by improving the catalyst's redox properties and stability. It enables the reaction to proceed under milder conditions without the need for external hydrogen donors or solvents. In this process, excess benzyl alcohol serves as both the solvent and hydrogen donor, simplifying the system. As a novelty, this study utilizes benzyl alcohol and nitrobenzene enabling an in situ process. This eliminates the requirement for solvents, making the reaction more efficient and environmentally friendly. The silica-based system facilitates the uniform dispersion of cerium oxide and enhances the adsorption of aniline on the surface through hydrogen bonding. It will improve the rate of the coupling reaction between the in situ-formed benzaldehyde and aniline as their proximity to the catalyst surface promotes efficient interaction. Thus, the cerium oxide modified mesoporous SBA offers a robust, cost-effective, and sustainable catalytic platform for transformations.

The objective of this research is to develop a more sustainable, efficient, and scalable catalytic process for imine formation, reducing waste and energy consumption while maintaining high selectivity and yield. Byproducts such as benzaldehyde, aniline, and benzyl benzoate are also generated in this process. The conversion and selectivity to N-benzylidene aniline relative to nitrobenzene are calculated to assess the reaction's efficiency. Optimization of reaction parameters including catalyst weight, weight hourly space velocity (WHSV), benzyl alcohol to nitrobenzene molar ratio, temperature, and reaction time are carried out to determine the optimal conditions for the reaction.

2. Material and methods

2.1 Preparation of synthesizing SBA-15

SBA-15 was synthesized following a previously described procedure [28]. In summary, 4.4 g of the triblock copolymer P123 (from Sigma Aldrich) was dissolved in 30 ml of distilled water and stirred for 1.5 hours. After that, 120 g of 2 M HCl (from Nice Chemicals) was added while continuing to stir for another 2 hours. Then, 9 g of tetraethyl orthosilicate (TEOS, Sigma Aldrich) was gradually added to the mixture which was allowed to age at room temperature for 24 hours. The resulting solution was subjected to hydrothermal treatment at 100 °C for 48 hours. Once the treatment was completed, the product was filtered, washed with distilled water, and air-dried for a full day. It was then placed in an air oven at 70 °C for 12 hours before being calcined at 450 °C for 8 hours. The prepared mesoporous SBA-15 was ready to apply in next step.

2.2 Modifying SBA-15 with cerium oxide

Prepared SBA-15 underwent modification with cerium oxide by a straightforward impregnation method. Cerium nitrate hexahydrate (Loba Chemie Pvt. Ltd., Mumbai) served as the precursor for this process. Initially, the precursor was dissolved in water to create an approximately 0.1 M solution. The prepared SBA-15 was then immersed in this solution, after which the mixture was heated to 80°C to facilitate solvent evaporation. The resulting concentrated sample underwent drying in an oven at 85°C overnight, after which it was calcined at 450 °C for 3 hours. Cerium oxide was loaded onto prepared SBA-15 at weight percentages of 10%, 20%, and 30%. The resulting modified systems were labelled as x CeO_2/SBA, where x represents the weight percentage of cerium oxide loaded onto SBA-15.

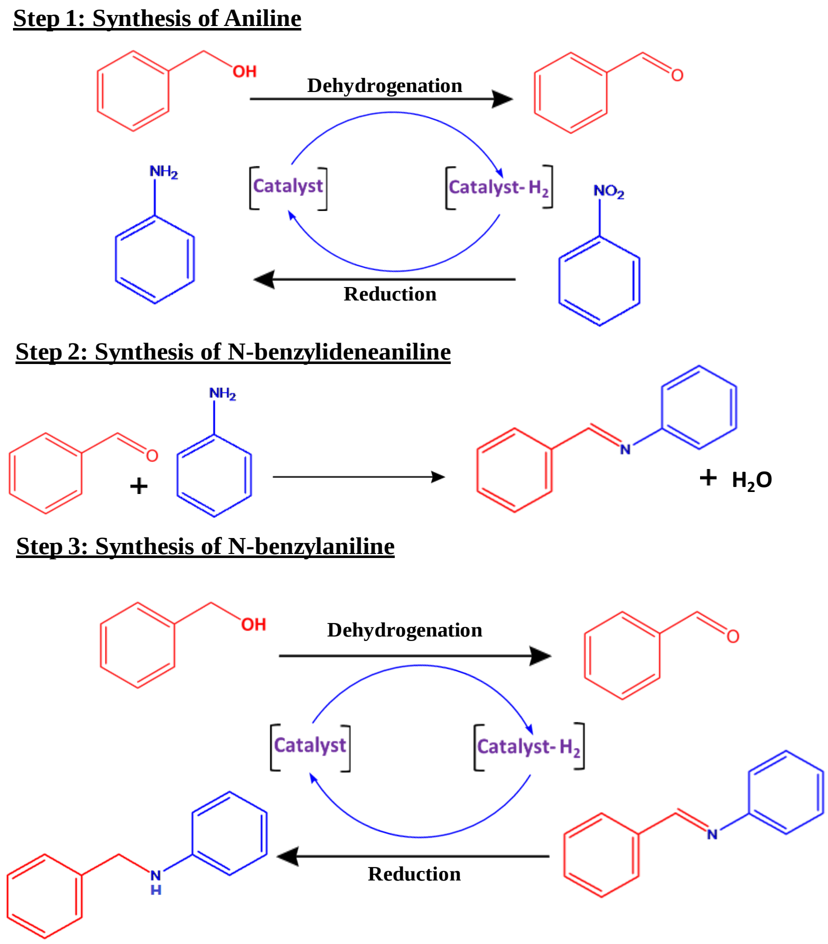
2.3 Catalyst characterization

The synthesized catalysts underwent a comprehensive analysis using a range of physico-chemical techniques. These included methods to assess elemental composition, crystalline structural and morphological characteristics, surface area, and optical properties. The instrument involved are ICP-AES for elemental composition, TEM for morphological characteristics, XRD for crystalline structure, BET for surface area and pore volume, UV-vis DRS for optical properties. ICP-AES measurements were done using Perkin Elmer Optima 5300 DV instrument. SEM analysis is done using JEOL Model JSM-6390LV with tungsten filament with a resolution of 1.38 eV. The samples are powdered and placed on a double sided carbon tape on a metal stub. TEM analysis was performed using ultra high resolution analytical electron microscope Jeol/JEM 3010 (Source: LaB6, Voltage: 200 kV, Point to point resolution: 0.23 nm; Lattice resolution: 0.14 nm, Magnification: 2000 X–1500000 X, camera length: 80–2000 mm). Prior to the analysis, the sample is sonicated in isopropanol and is allowed to evaporate on the TEM grid to form a dry film which made them electron transparent. The amorphous/crystalline nature of the prepared catalysts were identified by wide angle XRD technique using Bruker AXS D8 Advance diffractometer employing a scanning rate of 0.02° s^{-1} at room temperature with Ni filtered Cu Kα radiation source (λ=1.54

Å) in the range of 10–80° using Si(Li) PSD detector. Surface area, pore volume, and pore size distribution of the samples were analyzed using Micromeritics Tristar 3000 surface area and porosity analyzer. Prior to the analysis, the samples were degassed at 90°C for half an hour and 300°C for three hours. UV-vis DRS of the prepared samples were taken on Labomed UV-vis Double beam UVD-500 spectrophotometer equipped with an integrating sphere assembly with a charge coupled device detector. The scan range was 200–800 nm using $BaSO_4$ as internal standard.

2.4 Imine crafting by the coupling of nitrobenzene with benzyl alcohol

Imines were synthesized in the vapor phase using a fixed-bed tubular glass reactor with 1.2 cm in internal diameter and 40 cm in length utilizing 0.30 g of catalyst under atmospheric pressure and at 350°C (Scheme 1, Figure 1) for 2 hours. The tubular reactor was packed with glass beads. The catalyst positioned in the middle by sandwiching it between glass wool layers. Pure nitrobenzene and benzyl alcohol in 1:4 molar ratios were introduced into the reactor using a syringe pump with a WHSV: 7.17 h^{-1}. Following the reaction, the product and any unreacted reactants were cooled and collected in a collection tube at regular intervals. Subsequently, the products were analyzed using GCMS.



Scheme 1: Proposed reaction pathways for the coupling between benzyl alcohol and nitrobenzene

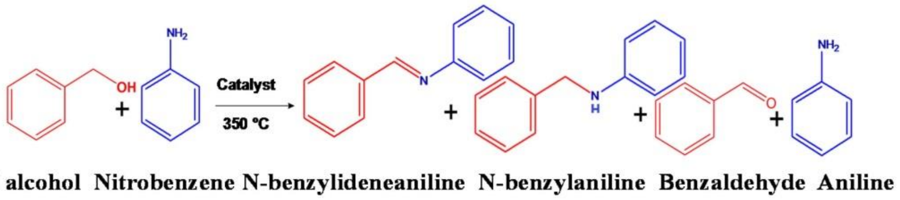


Figure 1. Reaction between benzyl alcohol and nitrobenzene

The gas-phase reaction between benzyl alcohol and nitrobenzene, proceeds by several steps as illustrated in Scheme 1. It employs a borrowing hydrogen methodology. Initially, benzyl alcohol undergoes oxidation in the presence of the catalyst, yielding benzaldehyde along with the liberation of hydrogen. Subsequently, the liberated hydrogen participates in the reduction of nitrobenzene to aniline via a borrowing hydrogen mechanism. The next stage involves the coupling between benzaldehyde and aniline, resulting in the formation of N-benzylidene aniline. Further, hydrogenation of N-benzylidene aniline may occur leading to the generation of N-benzylaniline.

3. Results and discussion

3.1 Element composition

Table 1 presents both the theoretical and experimental percentage compositions of different percentages of cerium oxide modified SBA systems. The results demonstrate the successful incorporation of metals into the parent system, with a significant amount of metal being incorporated across the systems. However, it was observed that the calculated amount of metals present was generally lower than the theoretical values.

Table 1. Elemental compositions of cerium oxide modified mesoporous SBA-15

Catalysts	Metal Composition (Weight %)	
	Theoretical	Experimental
10 Ce/SBA	10.00	8.29
20 Ce/SBA	20.00	15.41
30 Ce/SBA	30.00	22.58

3.2 Crystalline structure

The peaks observed near 2θ values of 28.1°, 32.6°, 47.0°, 55.9°, 58.8°, 69.0°, 76.2°, and 78.5° (Figure 2) corresponded to the diffraction peaks of cerium oxide with a fluorite structure, representing the (111), (200), (220), (311), (222), (400), (331), and (420) planes, respectively [29], [30]. These peak positions were consistent with fluorite CeO_2, exhibiting a face-centered cubic lattice (JCPDS No. 34-0394). The results indicated a rise in peak intensity as metal loading increased, likely due to improved crystallinity of the metal oxides at elevated metal concentrations. Furthermore, the Scherrer equation was applied to determine the average crystallite size of the samples.

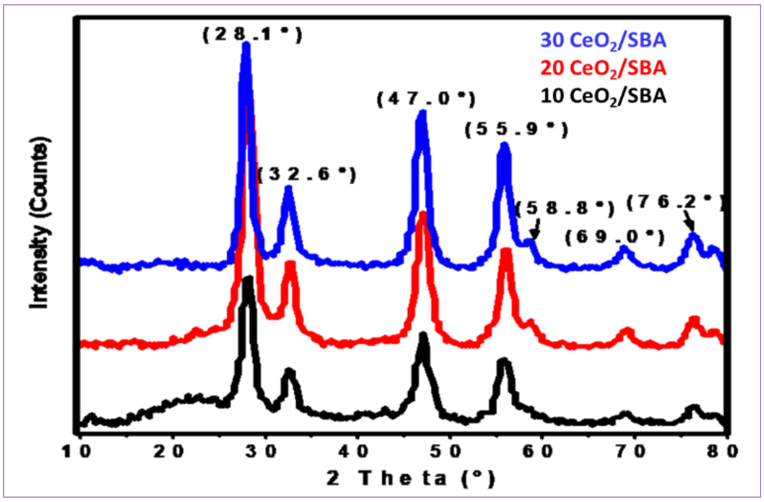


Figure 2. Crystalline structure of cerium oxide modified mesoporous SBA-15

Table 2. Crystallite size cerium oxides in various loading

Sample	Average crystallite size (nm)
10 Ce/SBA	6.3
20 Ce/SBA	6.2
30 Ce/SBA	7.5

3.3 Surface area and porosity of catalyst

N_2 adsorption-desorption analysis was performed to assess the surface area and porosity of the synthesized catalysts. Figures 3 and Figure 4 present the adsorption-desorption isotherms and pore size distributions, respectively, for each sample. Table 3 provides a summary of the textural characteristics, including BET surface area (m^2/g), total pore volume (cm^3/g), and mean pore diameter (nm).

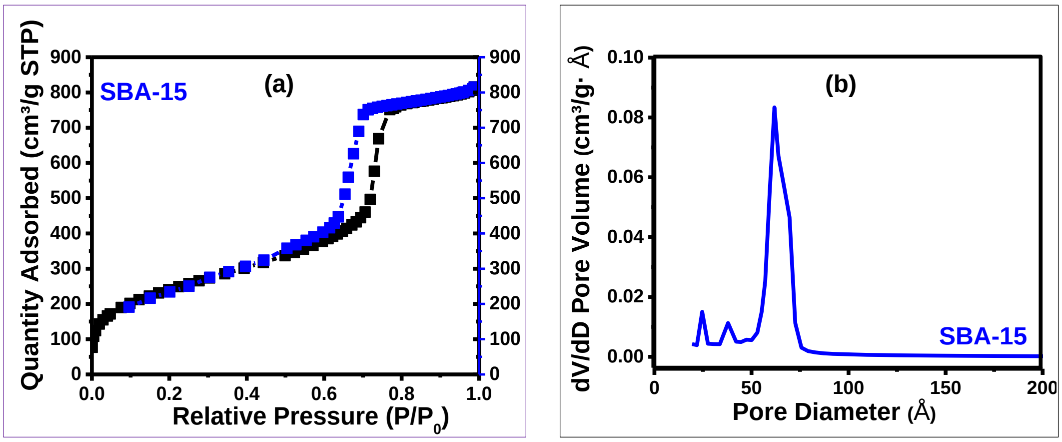


Figure 3. (a) Nitrogen adsorption desorption isotherm and (b) pore size distribution curve of pure SBA

The adsorption-desorption isotherms for both pure SBA (without cerium oxide) and cerium oxide modified SBA samples displayed a characteristic type IV profile with an H1 hysteresis loop, where the two branches remained nearly parallel across a wide range of relative pressures (Figures 3 and Figure 4) [31]. A sharp rise in P/P_0 values beyond 0.60 was attributed to nitrogen capillary condensation within the mesoporous silica channels. This is typical of hexagonal mesoporous structures which feature large pores and a narrow pore size distribution. It indicates uniform pore diameters. The BET surface area of pure SBA was measured at 872.9 m^2/g with a pore volume of 1.26 cm^3/g and an average pore diameter of 5.78 nm (Table 3).

Table 3. Textural properties of pure and cerium oxide modified mesoporous SBA-15

Systems	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SBA	872.9	1.26	5.78
10 Ce/SBA	650.0	0.96	5.48
20 Ce/SBA	581.5	0.80	5.13
30 Ce/SBA	484.5	0.65	4.99

Retention of the isotherm shape in cerium oxide modified mesoporous SBA-15 suggested the mesostructure was preserved post-modification [32]. Generally, the shift of the isotherm and capillary condensation to lower pressures in cerium oxide modified mesoporous SBA-15 is likely due to mesochannel contraction following modification of pure SBA [33].

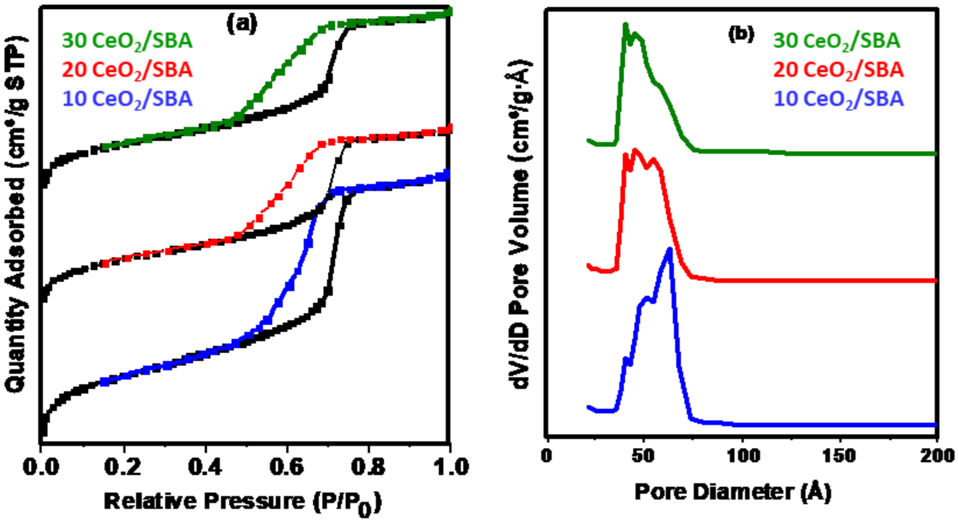


Figure 4. (a) Nitrogen adsorption desorption isotherms and (b) pore size distribution curves of cerium oxide modified mesoporous SBA-15

3.4 Optical properties

The UV-vis diffuse reflectance spectra (DRS) for cerium oxide modified mesoporous SBA-15 reveal two notable peaks around 215 nm and 295 nm (Figure 5). These spectra show the characteristic absorption bands that indicate the presence of cerium oxide on the SBA framework. The former peak is attributed to the charge transfer interaction between Ce^{3+} and oxygen ligands ($O^{2-}\rightarrow Ce^{3+}$), while the peak at 295 nm corresponds to the charge transfer between Ce^{4+} and oxygen ligands ($O^{2-}\rightarrow Ce^{4+}$) [34]. It's noteworthy that there is a noticeable blue shift in the bands for the charge transfer transitions for Ce^{4+} coordinated systems over the SBA matrix (295 nm), compared to those of pure cerium oxide systems (343 nm) [35], [36]. This change could be linked to the existence of finer cerium oxide particles that consistent with findings from the XRD analysis.

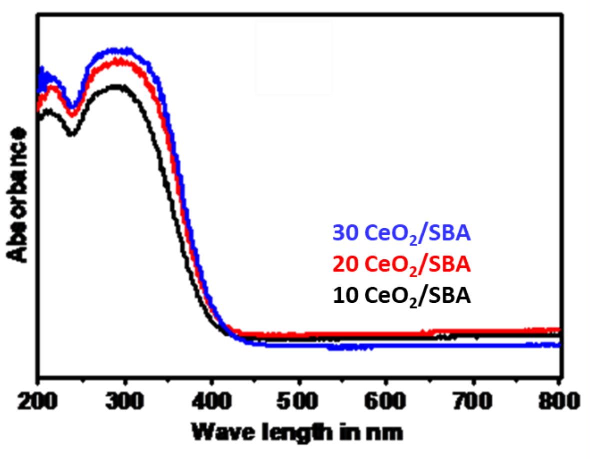
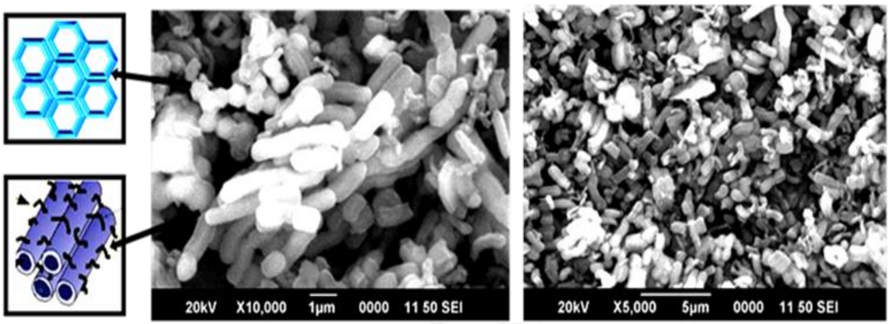


Figure 5. UV-vis absorbance spectra of cerium oxide modified mesoporous SBA-15

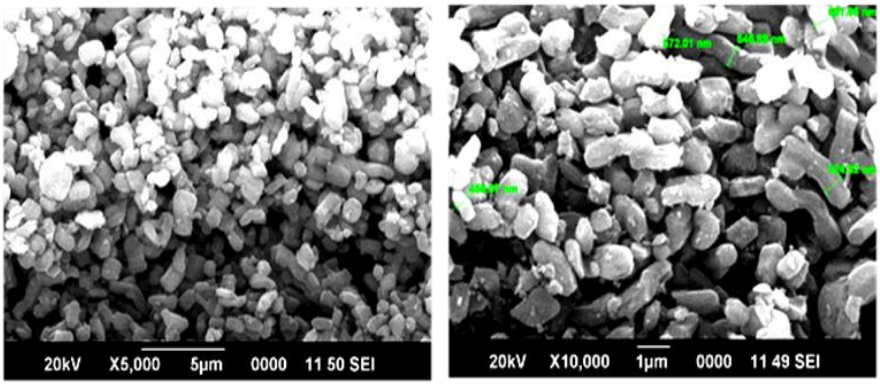
Regarding ligand-to-metal charge transfer interactions, the nature, number, and coordination position of ligands around the central metal ion significantly influence the intensity and position of the spectra. The peak observed at 295 nm is associated with the transfer of charge from oxygen ligands to cerium ions present in a tetra-coordinated environment, requiring higher energy compared to cerium ions embedded in a hexa-coordinated one (approximately 400 nm) [33]. Consequently, the lack of an absorption peak at 400 nm may indicate the absence of hexa-coordinated Ce^{4+} species. The peaks corresponding to the presence of cerium (III) oxides were not observed in the XRD profile of the cerium oxide modified mesoporous SBA-15. Hence, the band observed at 215 nm in the UV-vis spectra may be ascribed to the charge migration interactions between Ce^{3+} and O^{2-} ($O^{2-} \rightarrow Ce^{3+}$) which are created by the oxygen vacancy defects of fluorite CeO_2 [34].

3.5 Morphology and structural of catalyst

The morphology and structural arrangement of the materials under analysis. Figure 6 shows the morphology and structural of catalyst of pure SBA by SEM analysis which exhibit a rod-like structure when the electron beam from the source aligns with the mesochannels. Furthermore, hexagonal shapes were detected when the electron beam was oriented at a right angle to the primary direction of the mesochannels.



Pure SBA



20 CeO_2/SBA

Figure 6. Morphology and structural by SEM of pure SBA and 20 CeO_2/SBA

Figure 7 presents the morphology of catalyst by TEM analysis. The pure SBA reveal a well-organized structure of hexagonal mesopores arranged uniformly when the tubular pores align with the emitted electron beam [37], [38], [39]. A parallel configuration of tubular pores exhibiting long-range order was seen when the electron beam was positioned at a right angle to the orientation of these pores.

The TEM images for selected cerium oxide modified mesoporous SBA-15 indicate that the mesostructure of the original SBA remains intact after the incorporation of metal. These observations were corroborated by the N_2 adsorption-desorption isotherm results. Hence, the preparation methods employed were deemed conducive to the formation of highly ordered one-dimensional mesostructures with long-range order.

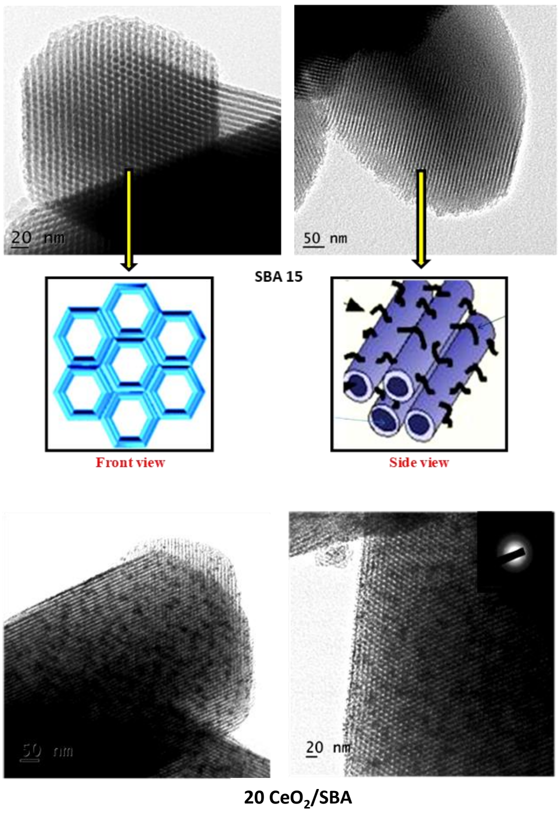


Figure 7. TEM images of pure SBA and cerium oxide modified mesoporous SBA-15

3.6 Effect of catalyst weight on conversion/selectivity

Figure 8 highlights the impact of catalyst weight on the reaction rate with weights ranging from 0.20 to 0.35 g. The conversion increased with catalyst weight. It peaks at 92.6% at 0.30 g, beyond which no further improvement occurred. Selectivity remained constant indicating the reaction pathway was unaffected by catalyst quantity with 0.30 g being the optimal weight for efficient active site utilization.

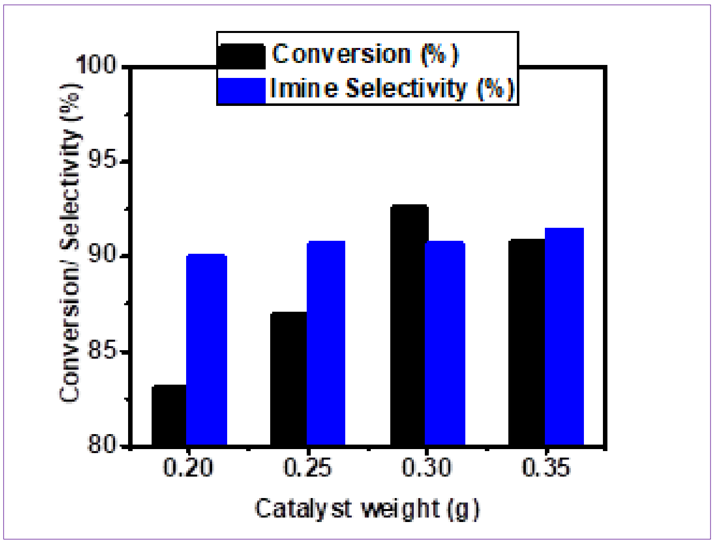


Figure 8. Effect of catalyst weight on conversion/selectivity (Reaction conditions: Temperature: 350°C, Nitrobenzene: Benzyl alcohol: 1:4, Flow rate: 1.8 mL/h, Time: 2 h, Catalyst: 20CeO_2/SBA)

3.7 Effect of nitrobenzene to benzyl alcohol molar ratio on conversion/selectivity

Figure 9 illustrates the impact of the nitrobenzene-to-benzyl alcohol ratio on the coupling reaction. At a 1:2 ratio, the conversion was relatively low (76.5%) due to limited benzyl alcohol availability. It reduces hydrogen generation needed for nitrobenzene reduction. Increasing the benzyl alcohol ratio enhanced conversion by improving aniline formation and imine synthesis efficiency.

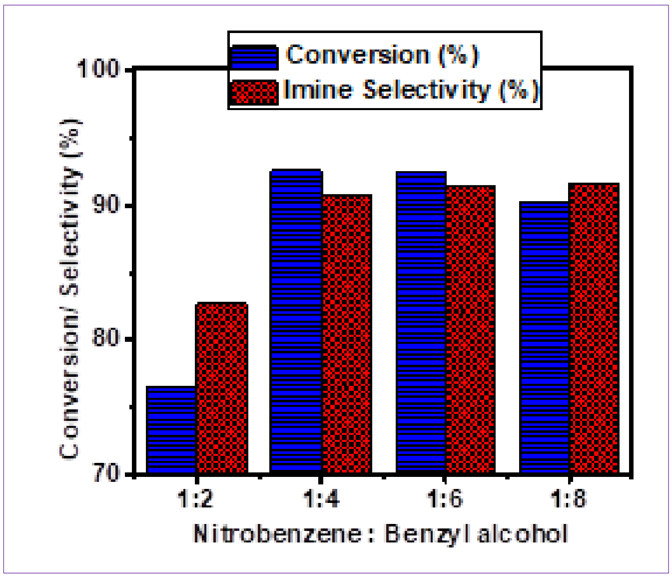


Figure 9. Effect of nitrobenzene to benzyl alcohol molar ratio on conversion/selectivity. (Reaction conditions: Temperature: 350°C, Catalyst: 0.3 g $20CeO_2$/SBA, WHSV: 7.17 h-1, Time: 2 h)

3.8 Effect of WHSV on conversion/selectivity

Figure 10 shows the effect of weight hourly space velocity (WHSV) on nitrobenzene conversion. The highest conversion occurred at a WHSV of 7.17 h^{-1}, after which it declined due to reduced contact time between reactants and the catalyst. Selectivity, however, remained consistent across all WHSV values.

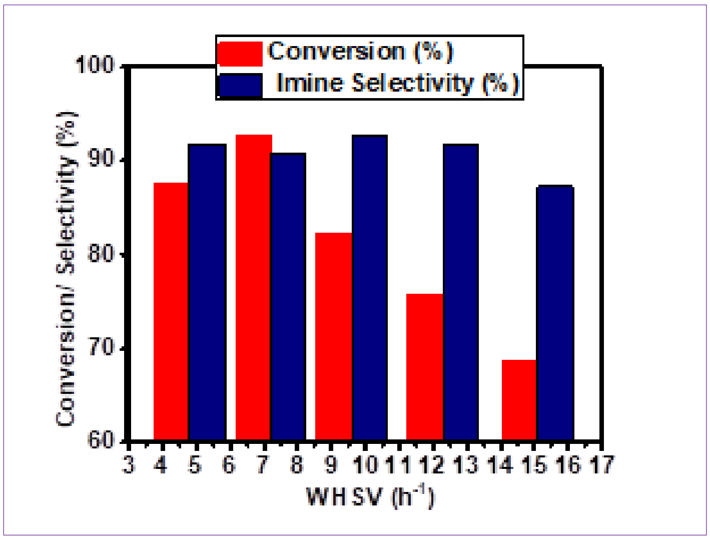


Figure 10. Effect of WHSV on conversion/selectivity. (Reaction conditions: Nitrobenzene: benzyl alcohol: 1: 4, Temperature: 350°C, Catalyst: 0.3 g $20CeO_2$/SBA, Time: 2 h)

3.9 Effect of temperature on conversion/selectivity

The influence of temperature on the imine formation reaction was studied across a range of 250–400°C (Figure 11). Maximum conversion was achieved at 300°C. However, deactivation studies at this temperature showed a faster decline in activity compared to 350°C. This accelerated deactivation at 300°C is likely due to slower diffusion of high-boiling-point products, such as N-benzylideneaniline (300°C) and N-benzylaniline (306–307°C), from the catalyst surface. The accumulation of these products, along with coke formation, may block active sites and hindering fresh reactant interaction. At 350°C, the rate of deactivation was slower, making it the optimal temperature for sustained catalyst performance.

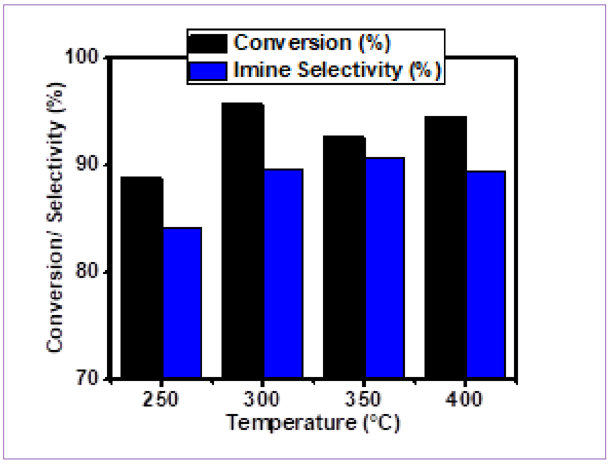


Figure 11. Effect of temperature on conversion/selectivity. (Reaction conditions: Nitrobenzene: benzyl alcohol: 1: 4, Catalyst: 0.3 g 20CeO_2/SBA, WHSV: 7.17 h^{-1}, Time: 2 h)

3.10 Effect of time (deactivation) on conversion/selectivity

Deactivation studies for the catalyst at 300°C and 350°C (Figure 12) revealed better resistance to deactivation at 350°C. This improvement is likely due to enhanced diffusion of products at higher temperatures and more efficient coke removal from the catalyst surface. The slight activity decline observed at 350°C may result from gradual coke deposition which can partially block active sites during the reaction.

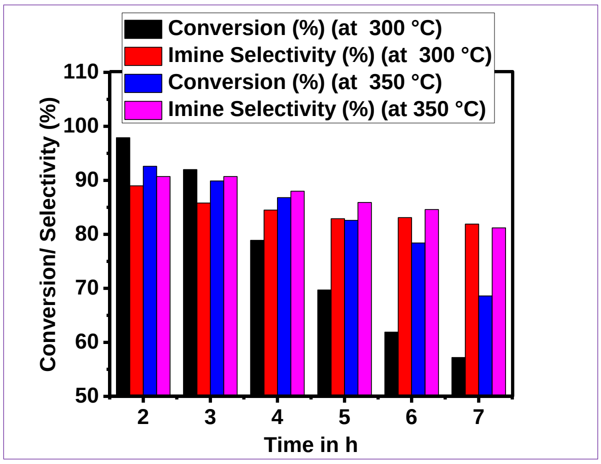


Figure 12. Deactivation for the imine formation reaction using 20CeO_2/SBA systems. (Reaction conditions: Nitrobenzene: Benzyl alcohol: 1: 4, Temperature: 300 and 350°C, Catalyst: 0.3 g 20CeO_2/SBA, WHSV: 7.17 h^{-1})

Figure 13 compares deactivation studies of the $xCeO_2$/SBA catalysts. The $10CeO_2$/SBA catalyst showed higher initial activity but deactivated faster, despite better imine selectivity. In contrast, the $20CeO_2$/SBA demonstrated superior activity and resistance to deactivation. It attributes to the optimal dispersion of cerium oxide on SBA-15's high surface area. The $30CeO_2$/SBA catalyst suffered rapid deactivation due to reduced surface area and increased cerium oxide crystallinity. The mesochannels in the $20CeO_2$/SBA catalyst facilitated effective reactant interactions. The silica's acidity helped retain intermediates like aniline, promoting coupling with benzaldehyde for efficient imine formation. Table 4 summarizes the optimized conditions for this system.

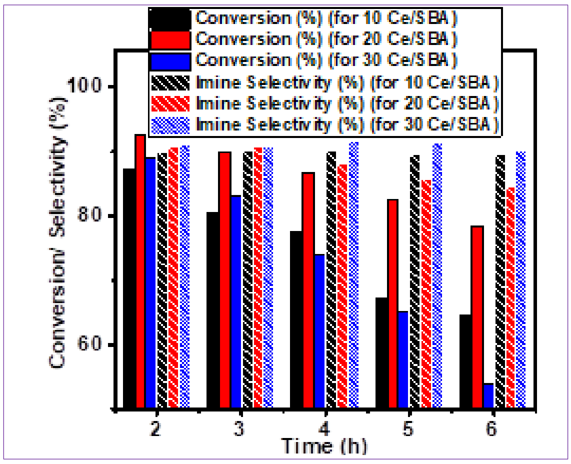


Figure 13. Deactivation for the imine formation reaction using xCeO2/SBA systems. (Reaction conditions: Nitrobenzene: benzyl alcohol= 1: 4, Temperature: 50°C, Catalyst: 0.3 g $20CeO_2$/SBA, WHSV: 7.17 h^{-1})

Table 4. Optimized conditions for the coupling reaction between nitrobenzene and benzyl alcohol

Time	2 h
Catalyst weight	0.30 g
Catalyst	20 CeO_2/SBA
Nitrobenzene: Benzyl alcohol	1:4 molar ratio
WHSV	7.17 h^{-1}
Temperature	350°C

3.11 Regeneration

Table 5 outlines the regeneration of the $20CeO_2$/SBA catalyst for the initial five cycles. Following the reaction, the catalyst underwent treatment with a flow of air for approximately 12 hours at 350°C until it was free from coke. Subsequently, it was utilized for the subsequent catalytic run using fresh reactants with deactivation being monitored in each cycle. Remarkably, the system demonstrated outstanding activity, regenerability, and resistance to deactivation over the course of five cycles. Only a slight decrease in activity was observed.

Figure 14 showcases the TEM images of the $20CeO_2$/SBA catalysts following its fifth regeneration. These images clearly reveal the presence of cerium oxide species and mesochannels, indicating the stability of the system post-regeneration.

Table 5. Regeneration studies for the coupling between nitrobenzene and benzyl alcohol using 20 CeO_2/SBA

Sl. No.	Time in h	Number of cycles									
		1		2		3		4		5	
		Conversion (%)	Selectivity to imine (%)	Conversion (%)	Selectivity to imine (%)	Conversion (%)	Selectivity to imine (%)	Conversion (%)	Selectivity to imine (%)	Conversion (%)	Selectivity to imine (%)
1	2	92.6	90.7	87.3	91.8	86.3	89.0	88.5	93.7	88.3	88.7
2	3	89.9	90.7	79.3	91.0	76.4	88.7	78.4	90.4	77.4	87.3
3	4	86.8	88.0	72.4	90.6	66.8	60.5	67.0	90.3	65.9	87.6
4	5	82.6	85.9	65.8	90.1	60.5	86.2	56.8	92.5	58.8	87.9
5	6	78.4	84.6	57.1	90.5	50.9	89.8	50.6	92.7	51.6	85.4
6	7	68.6	81.2	53.4	87.4	50.3	87.3	47.2	92.2	46.9	88.2

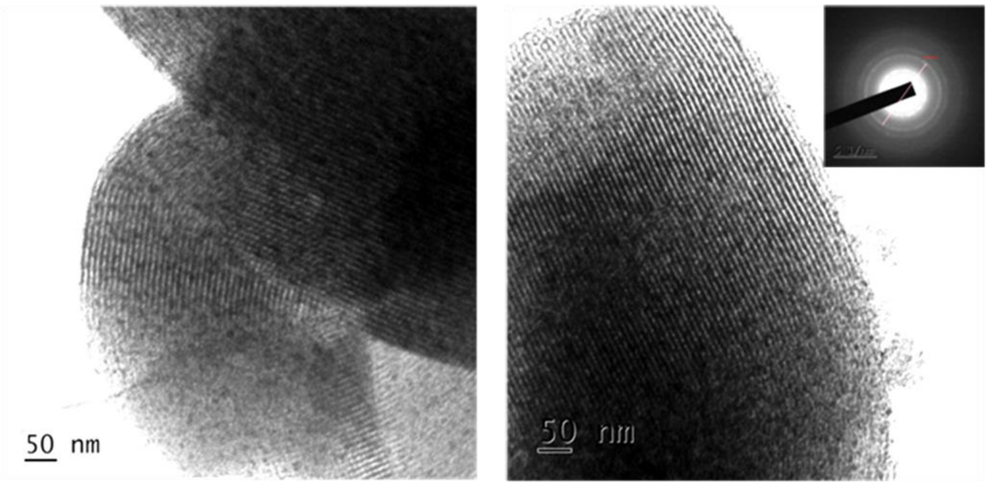


Figure 14. TEM images of 20 CeO_2/SBA after the fifth regeneration

3.12 Effect of various cerium oxide loading

Table 6 presents the performance of various cerium oxide loading in imine synthesis by the reaction of nitrobenzene with benzyl alcohol. Notably, the activity of the system was significantly reduced when number of catalysts was used or when bare SBA-15 was employed. This emphasizes the critical role of cerium oxide in improving both conversion and selectivity. The cerium oxide modified mesoporous SBA-15 catalysts (10CeO_2/SBA, 20CeO_2/SBA, and 30CeO_2/SBA) showed significantly higher activity compared to the bare SBA-15 support. The improvement can be attributed to the dual redox functionality of cerium oxide, which facilitates the sequential oxidation of benzyl alcohol to benzaldehyde and reduction of nitrobenzene to aniline. Both of these intermediates are critical for imine formation. The presence of cerium oxide on SBA-15 enhances these processes by providing:

1. **Oxygen Storage Capacity (OSC):** Cerium oxide possesses a unique ability to switch between Ce^{4+} and Ce^{3+} oxidation states, enabling it to participate in redox reactions effectively. This oxygen vacancy formation and replenishment mechanism facilitates both the oxidation of benzyl alcohol and the reduction of nitrobenzene in a single catalytic

system. Similar dual redox behavior has been reported in studies where cerium oxide based catalysts showed excellent performance in oxidation-reduction reactions [40].

2. **Dispersion and Surface Area:** The $20CeO_2$/SBA system demonstrated superior catalytic performance due to the optimal dispersion of cerium oxide on the high-surface-area SBA-15 support. BET and TEM analyses confirmed that cerium oxide nanoparticles are evenly distributed within the mesochannels of SBA-15. This dispersion ensures efficient reactant-catalyst interaction and minimizes the aggregation of cerium oxide particles which could otherwise reduce catalytic efficiency [41].
3. **Impact of Cerium Oxide Content:** A comparison between $10CeO_2$/SBA, $20CeO_2$/SBA, and $30CeO_2$/SBA reveals the importance of cerium oxide loading. The $10CeO_2$/SBA exhibited high initial activity. Its performance declined faster due to insufficient cerium oxide coverage which limited redox activity. In contrast, $30CeO_2$/SBA showed rapid deactivation despite good initial conversion. It is because of the excessive cerium oxide loading which reduced the overall surface area and increased cerium oxide crystallinity. This observation aligns with previous reports where excessive metal oxide loadings led to pore blockage and reduced catalyst efficiency.
4. **Synergistic Role of SBA-15 Support:** The mesoporous SBA-15 support provides a high-surface-area framework that facilitates the uniform dispersion of cerium oxide. Moreover, the mild acidity of SBA-15 helps retain intermediates like aniline, promoting efficient coupling with benzaldehyde to form imine. The synergy between cerium oxide's redox activity and SBA-15's structural properties contributes to the observed high conversion and selectivity.

This study represents a novel approach to achieve solvent-free and selective imine synthesis in the vapor phase under mild conditions. By carefully tuning the cerium oxide content, the $20CeO_2$/SBA system demonstrated the best performance. It offers a promising strategy for green and efficient imine production.

Table 6. Effect of various cerium oxide loading for the coupling between nitrobenzene and benzyl alcohol

Sl. No.	Cerium oxide loading	Conversion (%)	Selectivity to imine (%)
1	Without catalyst	18.5	100
2	With SBA	26.2	100
3	10 CeO_2/SBA	87.3	90.0
4	20 CeO_2/SBA	92.6	90.7
5	30 CeO_2/SBA	89.0	91.1

3.13 Comparison with various reported systems

Comparison was made among various catalytic systems for imine/amine formation through the reaction between nitro/amine compounds with aldehyde/alcohols [8], [11], [12], [17], [18], [21], [22], [23], [27], [28], [42], [43], [44], [45], [46], [47], [48]. In numerous documented instances, the reactions were performed with the inclusion of additives, inert atmospheres, and/or solvents which are not environmentally friendly. Moreover, these reactions often require prolonged durations for completion. Additionally, many of these systems utilize high-cost metals.

In this study, a low-cost and environmentally friendly catalyst has been introduced for the vapor-phase coupling of nitrobenzene and benzyl alcohol. The catalyst demonstrates high conversion efficiency, improved selectivity towards imine formation, minimal deactivation, and enhanced regenerability. It is a promising solution for sustainable catalytic processes. The exceptional activity of the catalyst is linked to the efficient distribution of the active component on the mesoporous silica substrate. The improved catalytic performance of the synthesized systems can be attributed to a combination of factors, such as the high surface area of the support featuring uniform mesochannels, its acidic properties, and the redox capabilities of the incorporated metal oxide.

4. Conclusion

This study represents novel imine synthesis in the vapor phase using nitrobenzene and benzyl alcohol with a cerium oxide modified mesoporous SBA-15 catalyst. The reaction showcases energy efficiency, atom economy, and environmentally friendly characteristics, leveraging a borrowing-hydrogen methodology. The mesochannels within the catalyst promote effective reactant-catalyst interactions and facilitating efficient product formation. The elevated synthesis temperature enhances the dehydration of benzyl alcohol, allowing hydrogen molecules to diffuse through the catalyst sites. It promotes the formation of intermediate aniline. This intermediate then reacts with benzaldehyde to yield the desired imine product.

The enhanced catalytic activity can be attributed to several factors, including the elevated temperature, moderate surface area, mesoporous structure, and the redox properties of cerium oxide. The study objectives are developing a more sustainable, efficient, and scalable method for imine synthesis-have been successfully met. These findings offer significant implications for greener chemical processes, providing a promising strategy for synthesizing imines with minimal waste, and energy consumption. Future applications of this methodology could extend to other industrial syntheses where imines or related compounds are key intermediates. Further, it enhances the sustainability and efficiency of chemical manufacturing.

Author's declaration

Author contribution

Soumini Chandralayam: Conducted the research, performed experiments, and analyzed the results. **Sugunan Sankaran**: Provided guidance, supervision, and critical insights throughout the study.

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Competing interest

There are no conflicts of interest in this research.

Ethical clearance

This research does not involve humans or animals as subjects.

AI statement

The grammatical structure of this article was corrected by using ChatGPT and the authors have rechecked the accuracy and correctness of the sentences with the topic and data of this study. Furthermore, the data and language used in this article have been validated and verified by an English language expert and none of the AI-generated sentences is included in this article. However, the authors are fully responsible for the whole content of this article.

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