An efficient, reusable heterogeneous Ceria pramoted lanthanum catalyst developed for the synthesis of (e)-1-(Arylmethylene)-2-phenylhydrazines

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Abstract

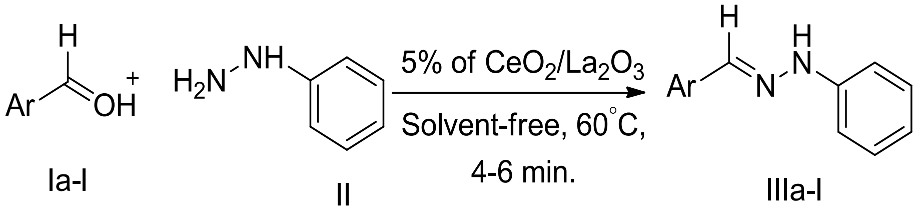
An efficient, reusable heterogeneous ceria promoted Lanthanum catalyst was developed for the synthesis of (E)-1-(Arylmethylene)-2-phenylhydrazine derivatives by condensation of aromatic aldehydes and phenyl hydrazine under solvent-free condition. The catalyst was characterized by using X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface Area, Energy Dispersive X-*ray Spectrometry* (*EDS) and UV-Visible DRS.*

Keywords: Schiff's bases, phenyl hydrazine, Ceria promoted Lanthanum catalyst, solvent-free reactions.

Introduction

Schiff bases are most extensively studied in medicinal chemistry due to their wide variety of pharmacological activities such as antimicrobial[15], anticancer[7], anti-inflammatory[11], anti-tuberculosis[1], antioxidant[16], anticonvulsant[4] and antihelmintic[2] activities etc. Schiff bases are also used as dyes, catalysts, intermediates in organic synthesis and also used as polymer stabilisers[5]. Imine or azomethine groups are present in various natural, natural-derived and non-natural compounds. Furthermore, the hydrazones derivative shows many physiological activities such as antimicrobial[13], antibacterial[12], antifungal[3], antitubercular[6], anti-HIV[10] and anticancer activities[8]. Hydrazones constitute an important class of biologically active drug molecules, for example, iproniazide just like isoniazide used as antitubercular drug[14]. Nifuroxazide is an oral nitrofuran antibiotic, used in anti-dehydration and colitis treatment[9].

Moreover, the previous methodologies for synthesis of hydrazones have various drawbacks as long reaction times, work up complexity, tedious reaction conditions, low yields and especially non eco-friendly. The chemistry of metal catalysts uses in organic syntheses has been developed rapidly. Nowadays, many organic chemists synthesized organic compounds by using recyclable and reusable metal catalysts due to advantages like less reaction time and more eco-friendliness. Hence, we have focused selection and preparation of reusable metal catalysts with low toxicity and more selectivity. In the view of green chemistry protocol and metal catalyst properties, we have developed a new solvent-free approach (E)-1-(Arylmethylene)-2-phenylhydrazine by using 5% of CeO_2/La_2O_3 reusable heterogeneous catalyst.



Scheme 1: Synthesis of 1-(Arylmethylene)-2-phenylhydrazines (IIIa-l)

Table 1
Optimization of catalyst with different organic solvents.

Entry	Reagent	solvent	Reaction time (min.)	Yield[a]
1	CeO_2/La_2O_3	Acetonitrile	20	<80%
2	CeO_2/La_2O_3	Chloroform	10	85%
3	CeO_2/La_2O_3	Acetic acid	10	88%
4	CeO_2/La_2O_3	Ethanol	8	90%
5	CeO_2/La_2O_3	*t*-butanol	8	86%
6	CeO_2/La_2O_3	Neat	5	99%
7	CeO_2/La_2O_3	water	10	82%

[a] isolated yield

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Material and Methods

FTIR (KBr) spectra were recorded on a Shimadzu FT-IR-8400s spectrophotometer. The powder X-ray diffraction pattern has been recorded on a Siemens D-5000 diffract meter by using Cu K radiation source and a scintillation counter detector. The XRD phases present in the samples were identified with the help of JCPDS data files. The BET surface area was determined by nitrogen physisorption at liquid nitrogen temperature on a Micromeritics Gemini 2360 instrument.

Prior to measurements, samples were oven-dried at 393°K for 10 h and flushed with argon gas for1 hr. Melting points were determined in open capillary tubes and are uncorrected. The purity of the compounds was checked by TLC using precoated silica gel plates 60_{254}(Merck). ^{1}H NMR spectra were recorded on Bruker Avance II 400 MHz spectrometer using tetramethylsilane as an internal standard.

Preparative method for 5% of CeO_2/La_2O_3: Dissolve lanthanum nitrate hexahydrate (50 gm) in distilled water 0.1 M ammonium hydroxide was added up to white precipitate formation. The precipitated compound was filtered using Buchner funnel and washed with ammonium hydroxide, then the compound was dried under oven at 150°C for 12 hr. The pulverised lanthanum (III) hydroxide (25 gm) was dissolved in distilled water. Ceric ammonium nitrate $[(NH_4)_2Ce(NO_3)_6]$ is added and then heated on water bath up to dry precipitate formation. The compound was dried under oven 150°C for overnight and further calcined at 650°C for 4 hours to obtain pure pulverised 5% of CeO_2/La_2O_3.

General procedure for the synthesis of (E)-1-(arylmethylene)-2-phenylhydrazine (IIIa-l): A mixture of aldehydes (Ia-l) (1 mmol), phenyl hydrazine (II) (1mmol) and 5% of CeO_2/La_2O_3 (30 mg) was taken into round bottom flask, then it was mixed well and stirred at 60°C for 4-5 min (Table 1). After completion of the reaction, formation of crystalline precipitate was observed.

Then the catalyst was separated out by using organic solvent as ethyl acetate (the catalyst dried in an oven at 100-120°C for 8 hr and reused for 8-10 consecutive reaction runs without significant decrease in its activity). The organic layer was concentrated under reduced pressure and then concentrated to afford pure Schiff's bases (IIIa-l).

Spectral data

IIIa. 1-Benzylidene-2-phenylhydrazine: IR (KBr, cm^{-1}): 1647 and 3328. ^{1}H NMR ($CDCl_3$, ppm): δ 6.87-6.90 (m, 1H, ArH), 7.14-16 (m, 2H, ArH), 7.28-7.40 (m, 7H, ArH), 7.63-7.66 (m, 3H, ArH).

IIIb. 1-(4-methoxybenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1645 and 3322. ^{1}H NMR ($CDCl_3$, ppm): δ 3.84 (m, 3H, OCH_3), 6.85-6.71 (m, 3H, ArH), 7.10-12 (d, 2H, ArH), 7.29-7.39 (m, 4H, ArH), 7.63-7.66 (m, 3H, ArH).

IIIc. 1-(4-Chlorobenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1640 and 3324. ^{1}H NMR ($CDCl_3$, ppm): δ 6.87-6.90 (m, 1H, ArH), 7.11-7.13 (d, 2H, ArH), 7.28-7.36 (m, 3H, ArH), 7.55-7.61 (m, 5H, ArH).

IIId. 1-(2-Chlorobenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1647 and 3331. ^{1}H NMR ($CDCl_3$, ppm): δ 6.86-6.89 (m, 1H, ArH), 7.10-7.12 (d, 2H, ArH), 7.28-7.45 (m, 5H, ArH), 7.63-7.65 (m, 3H, ArH).

IIIe. 1-(4-methybenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1645 and 3322. ^{1}H NMR ($CDCl_3$, ppm): δ 2.41 (m, 3H, CH_3), 6.88-6.91 (m, 1H, ArH), 7.12-14 (d, 2H, ArH), 7.29-7.37 (m, 5H, ArH), 7.64-7.67 (m, 3H, ArH).

IIIf. 1-(2-methybenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1647 and 3328. ^{1}H NMR ($CDCl_3$, ppm): δ 2.41 (m, 3H, CH_3), 6.87-6.90 (m, 1H, ArH), 7.11-13 (d, 2H, ArH), 7.29-7.43 (m, 6H, ArH), 7.71-7.4 (m, 2H, ArH).

IIIg. 1-(4-bromobenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1642 and 3335. ^{1}H NMR ($CDCl_3$, ppm): δ 6.88-6.91 (m, 1H, ArH), 7.10-7.12 (d, 2H, ArH), 7.29-7.39 (m, 3H, ArH), 7.53-7.59 (m, 5H, ArH).

IIIh. 1-(2-Bromobenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1651 and 3328. ^{1}H NMR ($CDCl_3$, ppm): δ 6.89-6.91 (m, 1H, ArH), 7.11-7.13 (d, 2H, ArH), 7.29-7.48 (m, 5H, ArH), 7.65-7.67 (m, 3H, ArH).

IIIi. 1-(4-Nitrobenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1655 and 3341. ^{1}H NMR ($CDCl_3$, ppm): δ 6.93-6.95 (m, 1H, ArH), 7.18-7.20 (d, 2H, ArH), 7.30-7.42 (m, 3H, ArH), 7.73-7.78 (m, 5H, ArH).

IIIj. 1-(2-Nitrobenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1652 and 3337. ^{1}H NMR ($CDCl_3$, ppm): δ 6.92-6.94 (m, 1H, ArH), 7.15-7.17 (d, 2H, ArH), 7.31-7.40 (m, 4H, ArH), 7.75-7.80 (m, 4H, ArH).

IIIk. 1-(3,4-dimethoxybenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1644 and 3326. ^{1}H NMR ($CDCl_3$, ppm): δ 3.80 (m, 3H, OCH_3), 3.84 (m, 3H, OCH_3), 6.87-6.90 (m, 3H, ArH), 7.11-13 (d, 2H, ArH), 7.29-7.39 (m, 3H, ArH), 7.57-7.59 (m, 3H, ArH).

IIIl. 1-(2,4-dimethoxybenzylidene)-2-phenylhydrazine: IR (KBr, cm^{-1}): 1644 and 3326. ^{1}H NMR ($CDCl_3$, ppm): δ 3.81 (m, 3H, OCH_3), 3.84 (m, 3H, OCH_3), 6.89-6.91 (m, 1H, ArH), 7.05-7.08 (m, 3H, ArH), 7.29-7.39 (m, 3H, ArH), 7.53-7.56 (m, 3H, ArH).

Results and Discussion

FT-IR spectrum: The FT-IR spectrum of La_2O_3 and CeO_2/La_2O_3 shows two characteristic stretching frequencies peaks around 1462 and 854 cm^{-1} (Figure 1). The peak around 1462 cm^{-1} is representing presence of oxide and the peak found at 854 cm^{-1} is characterizing the crystalline La_2O_3. Based on FT-IR data, it is concluded that the crystalline La_2O_3 does not changes with Ceria.

X-ray diffraction: The compounds La_2O_3 and CeO_2/La_2O_3 calcined at 650°C are shown in figure 2. The strongest three intense peaks appeared at 2θ values 25.34, 30.08 and 44.14 which are associated with (111) (200) (201) h, k, l planes respectively which indicate that CeO_2 doped La_2O_3 is in hexagonal phase. The average particle size was calculated using the Scherer equation $D=0.9\ \lambda/\beta\ \cos\theta$ (where D is the average crystalline size, λ is x-ray wavelength, β is (FWHM) diffraction line and θ is the diffraction angle). The average crystalline size is below 50 nm.

Scanning Electron Microscopy (SEM): In SEM images of La_2O_3 and CeO_2/La_2O_3 (Figure 3) similar to each other, the average crystalline size of the particles was also found to be same in both images. It indicates that the particles were uniformly distributed all over the surface and spherical in shape and this result was in agreement with XRD results of hexagonal phase with same crystallite size.

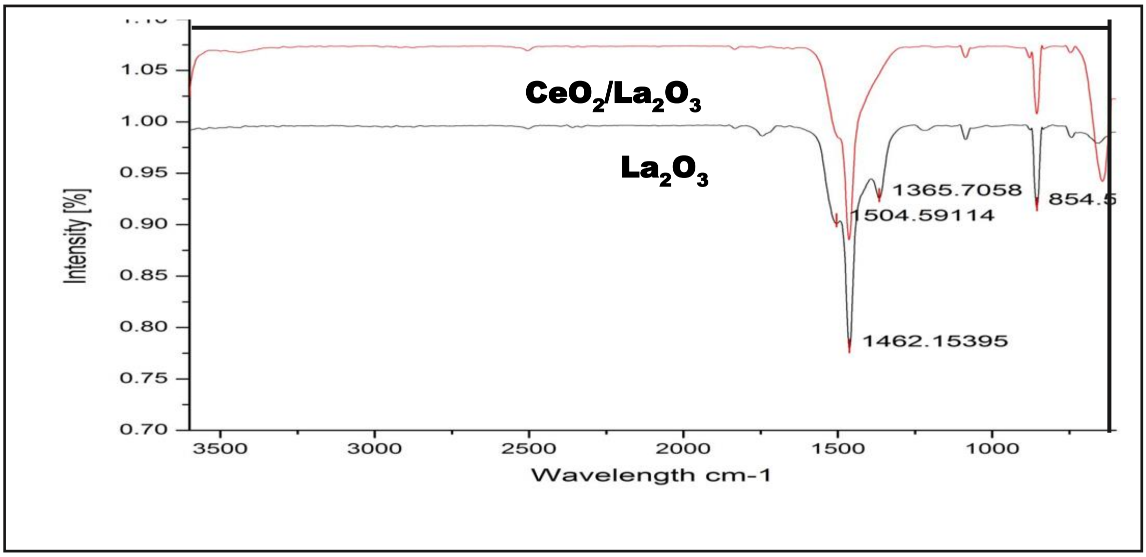

Figure 1: IR spectra of La_2O_3 and CeO_2/La_2O_3

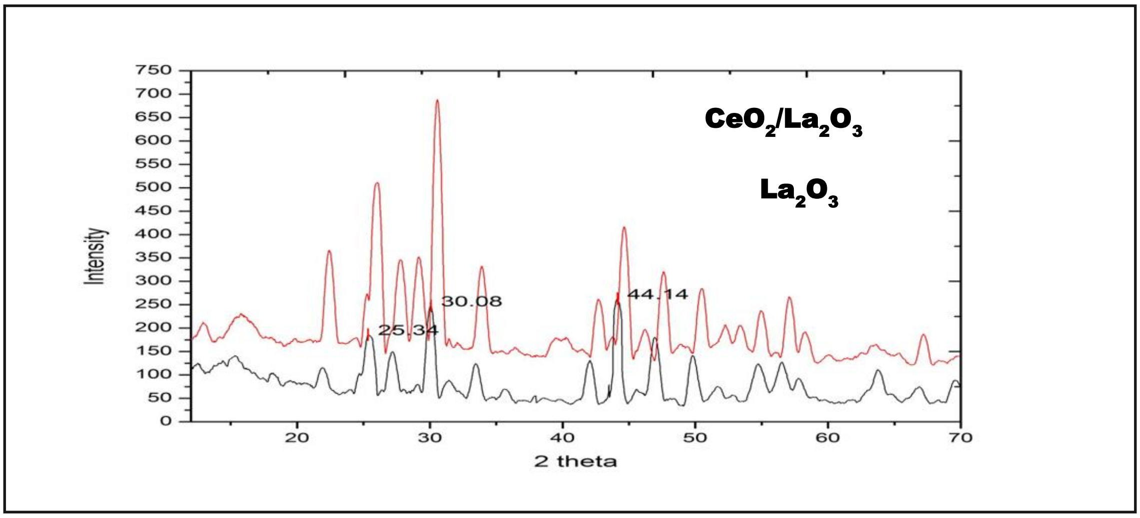

Figure 2: XRD spectra of La_2O_3 and CeO_2/La_2O_3

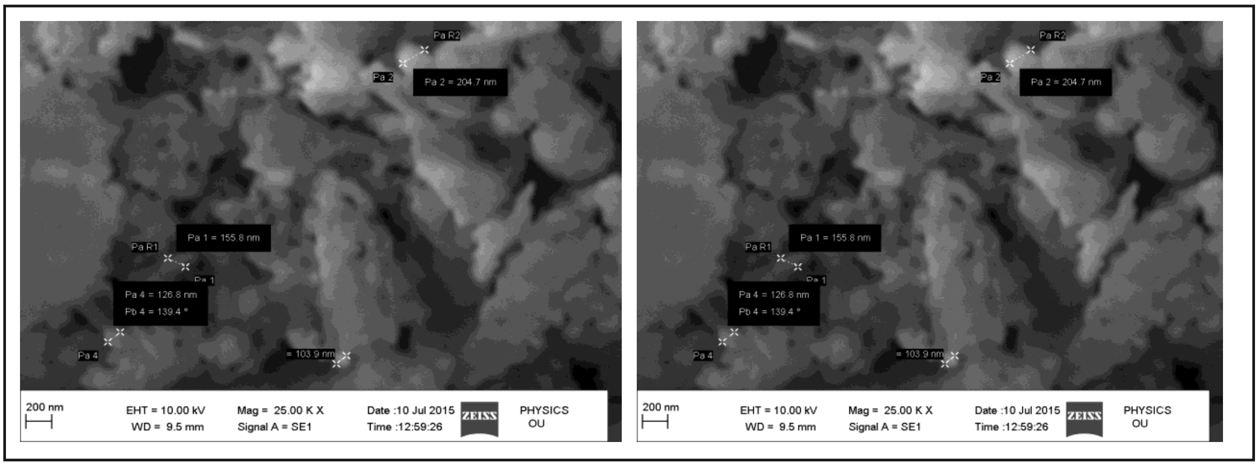

Figure 3: SEM images of La_2O_3 (image 1) and CeO_2/La_2O_3 (image 2)

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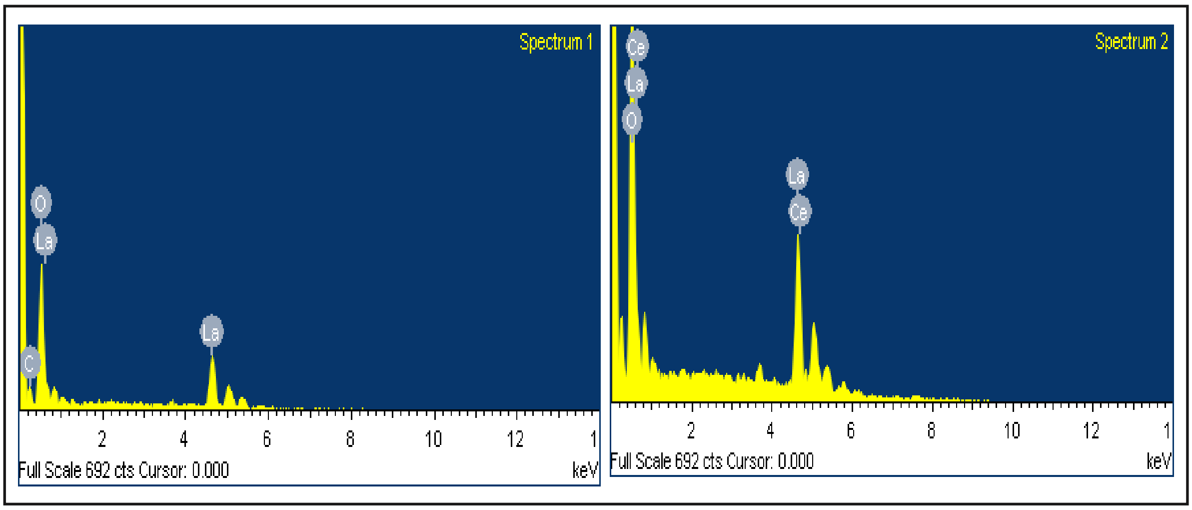

Figure 4: EDX images of La_2O_3 (Spectrum 1) and MgO/La_2O_3 (Spectrum 2)

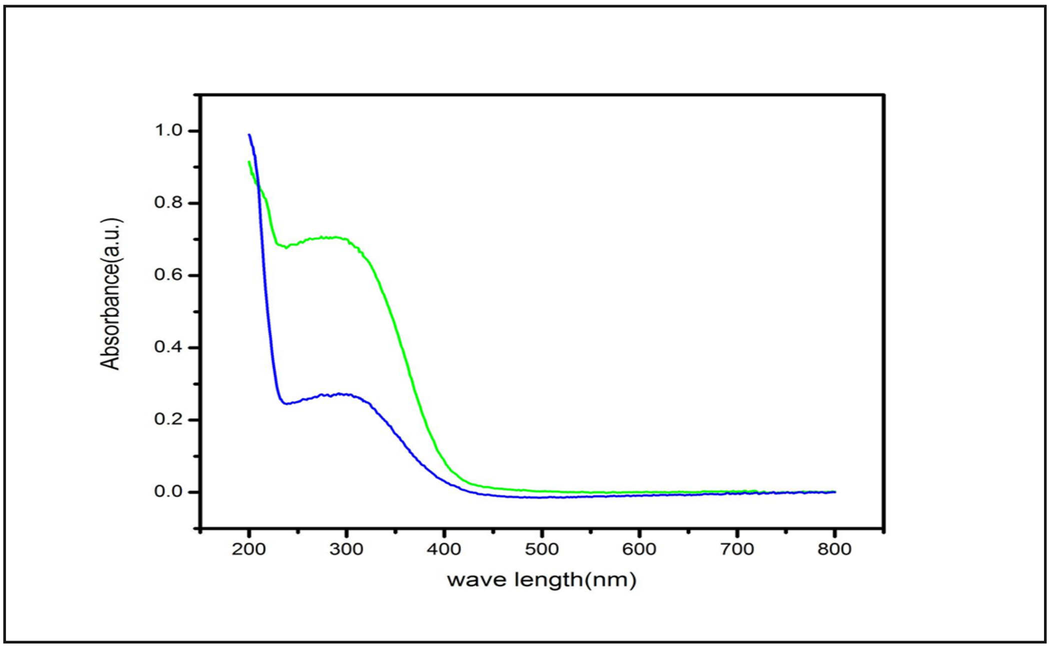

Figure 5: UV-Visible DRS spectra of La_2O_3 and CeO_2/La_2O_3

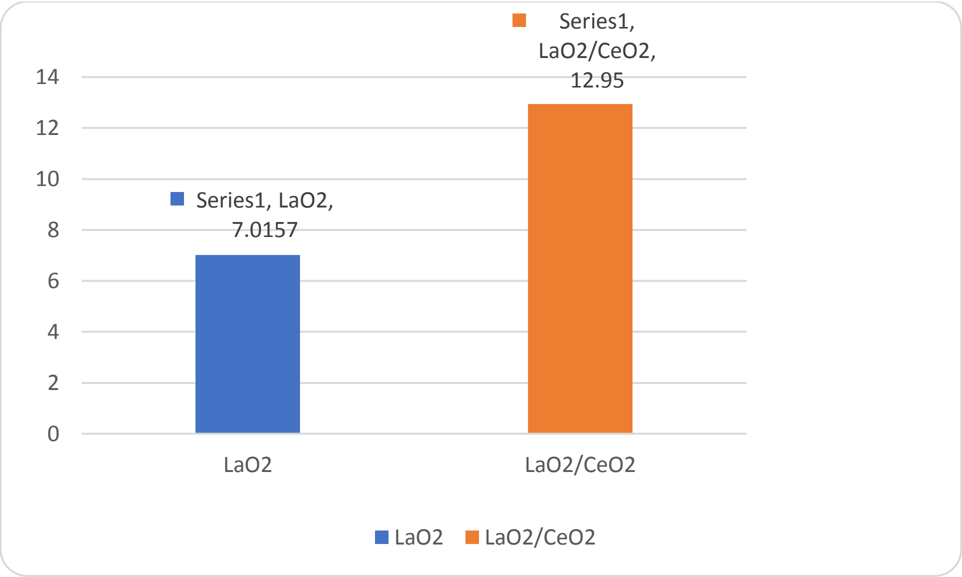

Figure 6: images of BET surface area comparison with La_2O_3 and CeO_2/La_2O_3

Energy DispersIIIe X-ray Spectrometry (EDS): EDX figure image 1 shows two characteristic signals which correspond to La and O (Oxygen), it confirms the presence of the compound La_2O_3 without any impurity and the image 2 shows La, Ce and O (Oxygen) characteristic signals which confirm Cerium incorporation of on La_2O_3.

UV-Visible DRS spectrum: The UV–Visible DRS spectrums of La_2O_3 and CeO_2/La_2O_3 are presented in figure 5. The absorption edges are obtained from the plots of absorbance *vs.* wavelength. (The interception of the tangent on the descending part of the absorption peak of the wavelength axis gives the value of diffuse absorption edge in nm). The UV-visible DRS spectrum of La_2O_3 shows absorption peak in visible region, wavelength was observed at 380 nm with band gap 3.26 eV (The band gap was measured using $Eg=1240/\lambda$ formula where Eg is the band gap energy and λ is the wavelength of the absorption edge). The UV-visible DRS spectrum of CeO_2/La_2O_3 shows a red shift compared to La_2O_3 at observed wavelength at 410 nm with band gap of 3.02 eV. The red shift in UV-visible DRS spectrum clearly indicates incorporation of Ceria on La_2O_3.

Brunauer-Emmett-Teller (BET) Surface Area: In the BET surface area calculation, the specific surface area of Lanthanum was found to be 7.0157 m^2/g and the Ceria promoted Lanthanum was found 12.95 m^2/g (Figure 6). The specific surface area of CeO_2/La_2O_3 was heavier than that of pure La_2O_3 surface, the higher surface area may be due to impression of Ceria on surface of the Lanthanum. It clearly represents that the Ceria strongly influences the surface area of pure La_2O_3.

Conclusion

The heterogeneous metal catalyst was successfully prepared by using Lanthanum nitrate hexahydrate and Ceric ammonium nitrate with good yield and the catalyst was characterized on the basis of FTIR, XRD, SEM and UV-DRS spectrums. The catalyst shows similar properties with the pure La_2O_3 and the EDX spectrum confirms presence of La and Ce. It confirms the Cerium doped on lanthanum. (E)-1-(arylmethylene)-2-phenylhydrazine has synthesized with excellent yield using heterogeneous CeO_2/La_2O_3 catalyst and the structures of title compound confirmed by using spectral data.

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