Investigation of Zirconia Effect in Zr/CeO2- Al2O3 Catalyst for Diesel Soot Oxidation

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Abstract

The cost of diesel exhaust treatment is steadily rising, and soot particles in diesel engine exhaust have a negative impact on human health. The study uses efficient Zr/CeO_2-Al_2O_3 catalysts as a substitute for noble metal catalysts to lower the process cost.

A part of this is because of the ever-increasing scarcity of noble metal catalysts required for diesel oxidation catalysts. The current study focuses on an alternative diesel oxidation catalyst with efficiency similar to that of a noble metal catalyst but with a much lower cost. CeO_2-Al_2O_3 catalysts are known for their oxygen storage capacity and high redox activity, making them suitable for soot oxidation. The addition of Zr to these catalysts has been shown to influence their structural and chemical properties, which significantly affect their catalytic behavior.

Evaporation-induced self-assembly (EISA) was used to prepare 1, 3, and 5 wt% Zr supported mesoporous CeO_2-Al_2O_3 catalysts. Morphological, structural, and physicochemical properties of the synthesized catalysts were examined using BET, Absolute Isotherm, SEM, -XRD, FTIR, TPR, and NH3-TPD. XRD, BET, and SEM data confirmed that the catalysts were mesoporous and low-crystalline while having a high surface area. The loose contacts soot oxidation activity test using TGA suggested that 50% oxidation of soot occurred at 390^{o}C in the absence of a catalyst. T50 of CeO_2-Al_2O_3 catalyzed soot oxidation was 296 ^{o}C. We observed a further drastic change in T50 of soot over 1, 3, and 5% Zr/CeO_2-Al_2O_3, which were 220^{o}C, 210^{o}C, and 193^{o}C, respectively. According to these results, incorporating Zr into the CeO_2-Al_2O_3 catalyst greatly improved the oxidation process of soot.

Introduction

Diesel exhaust contains various harmful compounds such as carbon monoxide, nitrogen oxides, aldehydes, and particulate matter (such as sulphate). The release of these toxic compounds into the atmosphere without proper treatment increases toxicity in the air near the surroundings (Manju Dhakad Tanwar 2008). This could lead to adverse effects on human health and the environment (Bhardawaj 2017). Therefore, diesel exhaust treatment is something that cannot be looked upon lightly. The air-to-fuel exhaust ratio in Diesel exhaust is often too high, which hampers the efficiency of many current exhaust treatment methods (Bosch & Janssen 1988; F. Zhong 2011). On the other hand, researchers have found that Diesel Oxidation Catalysts (DOCs) are effective in treating diesel exhaust.

DOCs are an engine after-exhaust treatment technology that converts engine-exhausted harmful molecules (CO, NOx, SOx, etc.) into less harmful ones (CO_2, etc.) (Heywood 1988). DOC must possess high thermal and chemical stability with excellent catalytic activity at low temperatures. Noble metals (Pt and Pd) comprise DOCs and are highly effective in oxidizing toxic diesel exhaust (Johnson 2007; W. Tan 2021; Li-Hsin Chang 2006). However, the super-high cost and low abundance of these metals are the associated problems with these noble metal-based DOCs.

Transition metals such as aluminum, cerium, and zirconium are becoming a hope in current years to replace Pt and Pd in the diesel exhaust oxidation process. Alumina is used for its high specific surface area, which allows metal dispersion, and it is often used as a support material for active catalyst components such as transition metals (e.g., Fe, Zr, Co, Ni) (Li-Hsin Chang 2006; Khalil 2007). These composite catalysts exhibited enhanced activity compared to pure Al_2O_3. Alumina serves as a support for the dispersion or accumulation of active catalytic species, and its support-based active species, like metal oxide clusters or nanoparticles, are uniformly dispersed to ensure high catalytic activity and effective catalyst utilization. The catalytic activity and selectivity of the catalyst can be influenced by the surface characteristics of alumina, such as its acidity and basicity, which can affect reactant molecule adsorption and the activation of particular reaction pathways. Alumina-based catalysts are active because they can stabilise and support catalytic reactions while also offering an environment that is favourable for the dispersion and interaction of active catalytic species (Revana Chanerika 2022; Xianwei Wang 2019; Tzia Ming Onn 2017). These were simultaneously loaded during this step and were selected for their environmentally friendly acetate salt preparation and promising catalytic performance. Based on morphology and structure characterizations, tests against benchmarks, and discussions, the structure and performance of these support catalysts were examined (Trasatti 2005).

CeO_2 has also gained broad interest in scientific society because of its natural abundance and significant high activity, as DOC (Kajia Wei 2019). CeO_2 has two possible oxidation states, namely Ce^{3+} and Ce^{4+}. Therefore, CeO_2 can provide excellent electron mobility to the compound for oxidation on its surface (Aslam1 2020; Y. Madier 1999; A. Bueno - López 2005; A. Setiabudi 2004). To take advantage of both CeO_2 and Al_2O_3, researchers used mixed oxides of CeO_2 and Al_2O_3 for DOC. Al_2O_3 provides a large specific surface area for good metal dispersion, while Ceria facilitates oxidation reactions due to the ease of Ce^{3+}/Ce^{4+} interconversion (Marco Piumetti 2017). Moreover, CeO_2 concurrently improves the thermal stability of Al_2O_3 in these mixed oxides CeO_2-Al_2O_3 DOCs (Benjaram M. Reddy 2009). Previous studies on a reduced CeO2 surface showed the formation of active oxygens essential for soot oxidation. The best activity and stability in the catalytic combustion of carbon black have been studied for various stable oxides, such as Al_2O_3, ZrO_2, O_2, and CeO_2 in pure and supported copper (2 weight percent CuO) systems (Catherine Davies a 2018; Masato Machida 2008; C. Pruvost 2000).

Zirconium oxide and its compounds are also promised active components of DOCs catalytic materials. Well-distributed zirconia on high surface area support not only increased its catalytic activity but also improved thermal stability, oxygen storage capacity (OSC), and various other chemical properties (G.K. Chuah 1996; A.Calafat 1998; S. Abdollahzadeh-Ghom 2011). Studies on the oxidation of soot using ceria-zirconia catalysts in the past have demonstrated a significant improvement in catalytic activity due to the presence of more reactive oxygen vacancies from the bulk and surface provided by the zirconia. This stabilisation of performance after calcination and improved intrinsic activity of the catalyst are the results of the zirconia's addition. The Ce-Zr solid solution catalyst can successfully lower the temperature of the maximum oxidation rate of soot particles as well as the ignition temperature, according to the results of the TG-DSC analysis and platform testing (Alinezhadchamazketi 2013; Ai 2019; Andana 2016; Shukla 2022; Atribak 2008).

To take advantage of all three active components (ceria alumina and zirconia), we developed trimetallic catalysts. The study includes in-depth analyses of Ceria-Alumina catalysts with varying Zr loadings (1%, 3%, and 5% Zr on $CeO_2–Al_2O_3$) in order to investigate the quantitative impact of Zr content on soot oxidation. The incorporation of Zr into $CeO_2–Al_2O_3$ catalysts leads to structural modifications that enhance their redox activity and, consequently, their catalytic performance as shown in Fig. 1. These findings support the development of catalysts that effectively control particulate matter emissions, addressing critical environmental and health issues.

Materials and methods

Aluminum isopropoxide ($Al [OCH(CH_3)_2]_3$), zirconium oxynitrate hydrate ($ZrO (NO_3)_2 . xH_2O$), pluronic P_{123} and cerium nitrate hexahydrate ($Ce (NO_3)_3 .6H_2O$) were obtained from Sigma Aldrich. Nitric acid (HNO_3) was obtained from Merck, Germany.

Catalyst Preparation

Cerium nitrate hexahydrate (Sigma-Aldrich, purity of 99%) and Aluminium isopropoxide (Sigma-Aldrich ≥ 98%) were dissolved in ethanol as illustrated in Fig. 2. After that, dropwise addition of HNO_3 (Merck, purity of 69%) and then mechanically agitating the mixture to prevent precipitate formation, Solution A was prepared. Simultaneously, Solution B was obtained by dissolving $(EO)_{20}$ $(PO)_{70}$ $(EO)_{20}$ triblock copolymer material (Pluronic P_{123}, Sigma-Aldrich) in ethanol. After that, both the solutions were separately stirred for 4 hours. After stirring, both were mixed together and then again stirred overnight. To evaporate the solvent, the mixture was kept in the oven at 60^oC for 48 hours. The solid thus obtained was calcined in the furnace at 700^oC for 8 hours to remove the triblock copolymer material assembly of P_{123}, and hence Mesoporous CeO_2-Al_2O_3 support (CeO_2:Al_2O_3 = 1:9) was obtained.

For the impregnation of metal, a predetermined amount of $CeO_2–Al_2O_3$ was introduced to the precursor (Zirconium (IV) oxynitrate hydrate, Make Sigma-Aldrich, purity of 99%) solution. To achieve a dry solid, the mixture was successively stirred for an hour at ambient temperature and evaporated at 80^oC. At last, the material was calcined for four hours at 550^oC.

Catalyst Characterization Methodologies

The samples' specific surface areas, average-pore radius, and total pore volume were determined using N2 physisorption at -195.8°C using Quanta Chrome Instruments' Autosorb-IQ Station 1. The material was degassed for four hours at a temperature of 250°C before analysis. The sample's surface area was calculated using the BET (Brunauer, Emmett, and Teller) method, and its pore volume distribution and pore size distribution were assessed using the Barrett-Joyner-Halenda (BJH) method.

Scanning Electron Microscopy (SEM) images were obtained with the FEI Quanta 200 F by FSEM to study the morphological analysis. Using EDX microanalysis, the metal ion structure on the catalyst's surface was investigated.

Using D-8 Advance Bruker-Germany and CuKα radiation (a value of 0.15418), Powder X-ray diffraction patterns, were collected in order to analyze the synthesized catalyst and support structure. The XRD results were collected at an increment of 0.04∘ with an average counting interval of 1.99s/step, between 2^{o} and 80^{o}C.

Temperature-programmed reduction experiments were carried out using the Micromeritics Auto Chem II apparatus. The sample was placed in the TPR cell and flushed with argon for 30 min at 150°C. The sample was then subsequently cooled down to room temperature. Finally, the furnace temperature was increased at a ramp-up rate of 10°C/min in a 15 ml/min flow rate with the H_2/Ar mixture (10:90 ratios). NH_3- Temperature-programmed desorption (NH_3-TPD) studies were also carried out using an Autochem II chemisorption analyzer (Micromeritics, USA).

FTIR analysis was done using the Perkins Elmer-Spectrum Two Model with a range of 4000 to 400 CM^{-1} for the soot oxidation process on a zirconium-doped ceria Alumina (CeO_2-Al_2O_3) support to provide valuable insights into the surface properties, active sites, and interactions occurring during the catalytic reaction.

Catalytic activity measurements

The performance of the synthesized catalyst in oxidizing soot was evaluated by thermogravimetric analysis testing in an N2 and air environment using a Shimadzu DTG-60. For analysis, catalyst and soot were combined with a 10:1 catalyst-to-soot ratio using a spatula for loose contact. The mixture was heated in the oxidation experiment from 26°C to 898°C at an average rate of 10°C/min while being supplied with a flow of N2 or air at 100 ml/min. Carbon black was the form of soot used in the investigation, and good results can be anticipated because printer ink and diesel soot have similar compositions.

Results and Discussion

BET and Absolute Isotherm

Table 1
BET surface area and Average Pore Radius of the synthesized catalyst

Catalysts Samples	**BET Surface Area (m^2/g)**	**Average Pore Radius (A^o)**
CeO_2-Al_2O_3	110	67.5
1% Zr/CeO_2-Al_2O_3	367	33.5
3% Zr/CeO_2-Al_2O_3	318	21.9
5% Zr/CeO_2-Al_2O_3	304	23.7

The data of average pore radius and BET surface area is given in Table 1. The surface areas of 1%, 3%, and 5% Zr/ CeO_2-Al_2O_3 are 367 m2/g, 318 m2/g, and 304 m2/g, respectively, which reveals that, as Zr loading increases on the CeO_2-Al_2O_3, the catalyst's average pore radius and surface area decreases. This phenomenon can be associated with the pore-clogging of CeO_2-Al_2O_3 support with an increase in Zr content. For the same reason, the catalyst's surface area and pore radius with 1% Zr is greater than that of 3% Zr, and 5% Zr catalyst has the lowest surface area.

The adsorption isotherm of CeO_2-Al_2O_3 in Fig. 3 is classified as type IV by the IUPAC, which is associated with mesoporous material. Prepared catalysts have an H2 hysteresis loop type, which is connected to bottle-shaped ink pores with a comparatively uniform network of channel-like pores (Sing 2001; Shukla M. K 2021). The catalyst with 1% Zr has less impact on the catalyst's pore structure as compared to higher loadings, i.e., 3% or 5%, resulting in different adsorption properties and isotherm behaviour that reflect the variation in surface properties. Higher loadings of Zr lead to stronger interactions between the Zr species and the CeO_2-Al_2O_3 support, influencing the distribution and accessibility of active sites for adsorption.

SEM

SEM pictures (Fig. 4) were used to examine the catalyst's microstructure. These pictures help in identifying a network of pores on the catalyst's surface. These pores provide a large surface area for Zr dispersion. Pore size distribution and the BET isotherm also support this observation. Only one phase of CeO_2 was identified, indicating uniform dispersion of ceria dopant over Alumina.

Based on its morphology and phase, Al_2O_3 remains stable even at elevated temperatures. It is sintered when subjected to high temperatures, which reduces the surface area for use by itself. Despite the high calcination temperature, no such sintering can be observed in the SEM image of a ceria-catalyzed alumina solid solution, consistent with previous research. Images demonstrate the uniform distribution and large surface area for Zr dispersion over CeO_2-Al_2O_3 support. EDX was used to find out the catalyst's elemental composition. The percentage of elements found in the EDX data matched the catalyst's actual composition.

FT-IR

FT-IR analysis for the soot oxidation process on a zirconium-doped ceria Alumina (CeO_2-Al_2O_3) support can provide valuable insights into the surface chemistry and interactions occurring during the catalytic reaction. Figure 5 shows the FT-IR Spectra of zirconium-doped Ceria Alumina (CeO_2-Al_2O_3) support between 400 to 4000 cm^-1. The absorption band at 3400–3500 is the stretching 0-H bonds with a hydrogen bond, and the bands in the range of low-frequency area 1300-1700cm^-1 are assigned to carbonated species. The bending vibration appeared at 1628 cm^-1. The intense sharp bands at 1384 cm^-1 for 1, 3, and 5 wt% of Zr/CeO_2-Al_2O_3 were due to the CH_2 bending vibration of the template. The strong absorption in the region from 500 cm − 1 to 1000 cm − 1 is owing to the vibration modes of oxides of Al (Al − O), Ce (Ce − O), and Zr (Zr − O).

XRD

XRD, i.e., Powder X-ray diffraction patterns, were collected to analyze the catalyst and support structure using Cu K radiation (λ = 0.15418) on a D-8 Advance Bruker (Germany). Figure 6 represents the synthesized catalysts at 1%, 3%, and 5% Zr on CeO_2-Al_2O_3 XRD patterns, with an angle range of 2° to 80°.

The base peak looks completely flat, and it suggests that CeO_2-Al_2O_3 is amorphous. The peaks only appear after the addition of zirconium, indicating that zirconium can bring some crystallinity into the material. It is observed that after the addition of 1% zirconium, only peaks correlating to ceria and alumina are observed, which might be due to low rates of Zirconia impregnation on the compound. Ceria Peaks are visible at 28.6^o and 46.25^o (JCPDS no. 34–0394), which corresponds to the planes 111 and 220, respectively. The only single alumina peak visible is at 66.77^o (JCPDS 86-1410) (A.Calafat 1998) due to its amorphous nature. We can see zirconia peaks at 28.2, 38.6, and 50.1^o for the diffractogram of 3%, supported by CeO_2-Al_2O_3. This indicates that zirconium is present in monoclinic form inside the compound. The peaks correspond to planes − 111, 120, and 022, respectively. In the diffractogram of 5% zirconium, we notice that further addition of Zirconium into CeO_2-Al_2O_3 results in a widening and a less intense peak, which implies the suppression of crystal development.

TPR

H2-TPR profiles of 1%, 3%, and 5% Zr/CeO_2-Al_2O_3 are shown in Fig. 7. Cerium can oscillate between two stable oxidation states, namely Ce^{4+} and Ce^{3+}. This makes it possible for them to store oxygen easily in an oxidative environment and release it in a reductive one (Shukla 2022; Jeong 2015).

Figure 7 indicates that the initial addition of zirconium in CeO_2-Al_2O_3 increases the height of the peak, and a broad reduction peak can be seen near 540°C because of the reduction of the surface oxygen species. Furthermore, the 3% and 5% graphs show that an increase in zirconia to the catalyst support reduces the reduction potential as ceria alumina starts getting reduced at temperatures lower than previous peak heights. This suggests that doping Zr promotes the weak metal-metal interaction and surface reduction of Ce^{4+} between zirconium and alumina.

TPD

The NH3- TPD graph in Fig. 8 shows the profile of 1%, 3%, and 5% Zr/CeO_2-Al_2O_3 catalysts and the acidic strength of zirconium-added ceria alumina, with variation in temperature. For the base support, due to interaction between ceria and alumina, the ceria peak is shifted back to around 120°C, which is attributed to weak acidic sites, and the alumina peak is shifted forward to around 400, which is attributed to medium acidic sites. With the addition of zirconium, the locations of these peaks do not vary, indicating that zirconium addition does not affect the acidity of the compound. Comparing the size of the alumina and ceria peaks, we can conclude that the compound is most acidic when at around 400°C. The addition of zirconium initially increases acidity at sites, but the continuous addition of zirconium reduces the peak height and acidity (Glorius 2018; Uppara 2019).

Soot oxidation activity of catalysts

TGA in Air

(a)

Table 2

Normalised soot conversion% T50% (^{O}C)

Sample/Catalyst	**T50% (^{o}C)**
5% Zr CeO_2-Al_2O_3 + Printer soot (A)	193
3% Zr CeO_2-Al_2O_3 + Printer soot (B)	296
1% Zr CeO_2-Al_2O_3 + Printer soot (C)	210
CeO_2-Al_2O_3 + Printer soot (D)	220
Printer soot (E)	390

As a function of the temperature, it is shown in Fig. 9 that normalization of soot conversion occurs between CeO_2–Al_2O_3 mix oxides with 1%, 3%, and 5% Zr. The oxidation of the soot without a catalyst has also been investigated to obtain more precise comparisons. Catalytic oxidation activity can be estimated using T50 values with a temperature that indicates a 50% conversion rate. The activity of the prepared catalyst for soot oxidation was evaluated using TGA data.

It can be observed that the peaks in the TPR test for Zr/CeO_2-Al_2O_3 are broad in nature. This can be due to the amorphous nature of the support, which resulted in a bulk spread of Zirconium. (Shukla 2022) It can also be observed that the peak temperatures are reducing with the addition of Zirconia, indicating weak support metal bonding. The increase in area under the graph signifies an increase in H2 consumption, which means that the catalyst's oxidation potential is increasing with an increase in metal/support ratio.

The TGA profile showed that when using a catalyst, the soot oxidation T50 was significantly less than if no catalyst had been used. T50 values for catalyzed soot over 1%, 3%, and 5% Zr CeO_2-Al_2O_3 were 210^{o}C, 296^{o}C, and 193^{o}C, whereas 390^{o}C was the point at which 50% soot conversion was reached in the absence of the catalyst.

The catalytic activity of the synthesized catalyst towards soot oxidation was evaluated using TGA profiles in the air (Fig. 9) mixed with printer soot and printer soot alone. The Soot oxidation behavior of synthesized catalysts was compared by considering T50 (Temperature at which 50% conversion was achieved) values and percentage weight loss of the catalyst-soot mixture. The percentage weight loss for the uncatalyzed soot is about 21.32%. The catalyst and the printer soot have been mixed in 10:1 catalyst: soot) ratio. The percentage weight loss for 1%, 3%, and 5% Zr/CeO_2–Al_2O_3 catalyst-soot mixtures was 22.93%, 36.21%, and 26.48%, respectively. The data indicates that the percentage weight loss for the 3% Zr/CeO_2-Al_2O_3 catalyst is the largest among all the other catalysts, which might be because the surface oxygen vacancies and structural change in catalysts with Zr loading promoted the oxygen release from the surface/bulk of the catalysts. This results in the high activity performance of the catalyst.

Conclusions

Ceria Alumina has been synthesized by the EISA technique, and the catalyst zirconium was later added using wet impregnation. The method used helps to produce highly crystalline materials, as demonstrated by XRD. The catalysts prepared were characterized by BET, SEM, FTIR, and XRD. From XRD, we can see that the resulting compound is of low crystallinity. Results from TPR and NH3-TPD analyses show that although the metal-to-metal interaction between zirconium and Alumina is low, the acidity and ability to release oxygen for the compound increase. This implies the presence of large amounts of lattice oxygen in the compound. The oxidation ability of the catalyst has been examined using TGA for a soot catalyst combination during loose contact mode. The developed catalyst had a high surface area and was thermally stable, according to the results. The temperature at which 50% conversion was achieved for the soot oxidation behaviour of synthesised catalysts of 5% Zr/CeO_2-Al_2O_3 was T_{50} at 193^{o}C, 3% Zr/CeO_2-Al_2O_3 at 296^{o}C and 1% Zr/CeO_2-Al_2O_3 at 210^{o}C. The highest soot oxidation was observed in 3% Zr/ CeO_2-Al_2O_3, due to large particle size, oxygen vacancies, and high reducibility. In conclusion, Zr served as a superb stabiliser and encouraged distinct oxygen transfers in various environments to aid in the oxidation of diesel engine exhaust emissions. These characteristics suggest that Zr/CeO_2-Al_2O_3 could be a highly effective catalyst for the oxidation of diesel soot.

Declarations

Ethical Approval

The manuscript entitled " **Investigation of Zirconia Effect in Zr/CeO2- Al2O3 Catalyst for Diesel Soot Oxidation** " is submitted for consideration for publication in **"Environmental Science and Pollution Research."** This is to confirm that the research described in this manuscript did not involve human or animal participants and, therefore, did not require ethical approval from an ethics committee or institutional review board (IRB).

Consent to participate

All authors have agreed to the journal's terms and conditions, which may cover aspects such as originality of the work, ethical considerations, copyright, and permissions for the publication. We confirm that all the authors voluntarily participated, had the opportunity to ask questions, and received satisfactory answers.

Consent to publish

We, the researchers of CSIR-IIP, agree on the submission and publication of the paper. The submitted work is original and has not been published before. We confirm that the content of the paper and all information provided in the manuscript are accurate to the best of our knowledge.

Author Contributions

Dr. Mritunjay Kumar Shukla: The author was responsible for Conceptualization, Methodology, and experimental analysis.

Ms. Vibhuti Bangwal: The author conducted data analysis, draft preparation, writing, and editing.

Dr. Atul Dhar: Experimental analysis and data curation for the experimental results.

Dr. Thallada Bhaskar: Concept and Design of Experiments

Mr. Adarsh Kumar: Synthesizing the catalyst required for the study and editing of the final draft prepared.

Later on, the conclusions were thoroughly discussed among all the authors, and hence, they are mentioned according to the views of all the authors. This is the total contribution and combined effort of all the above-mentioned authors to take this research paper to the final stage.

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Competing Interests

The authors declare that they have no competing interests in this research paper.

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Figures

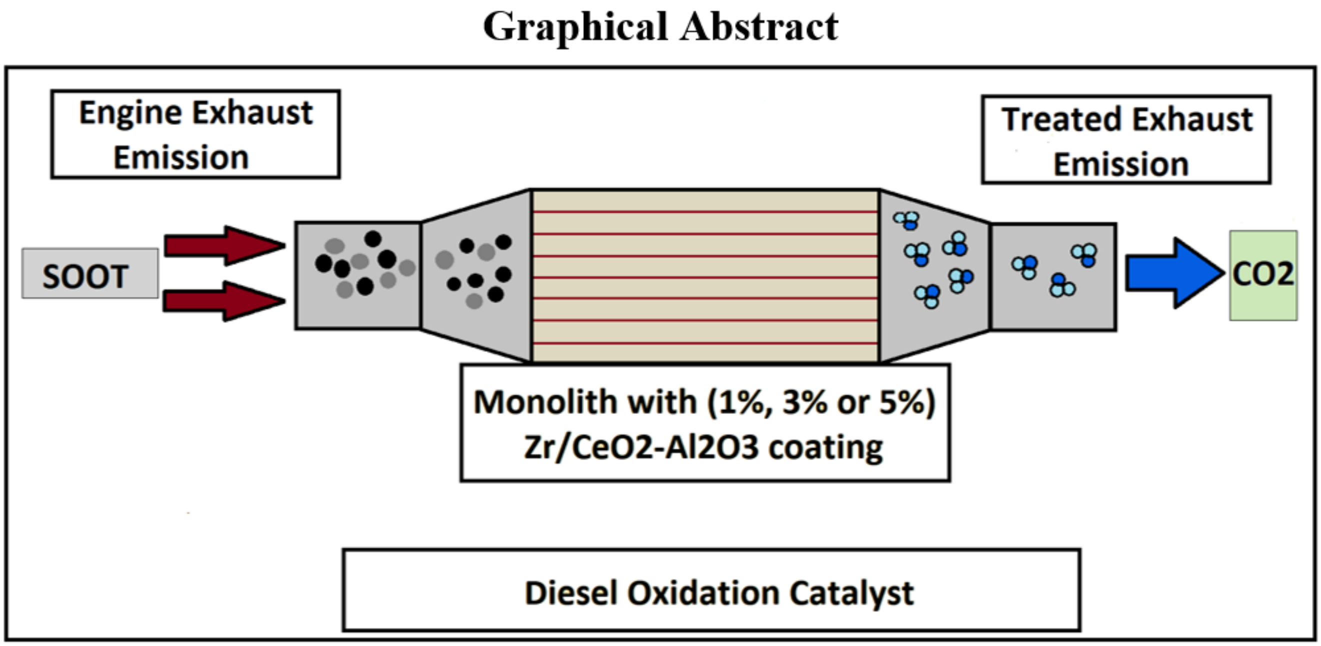

Figure 1

Graphical abstract of diesel oxidation catalyst

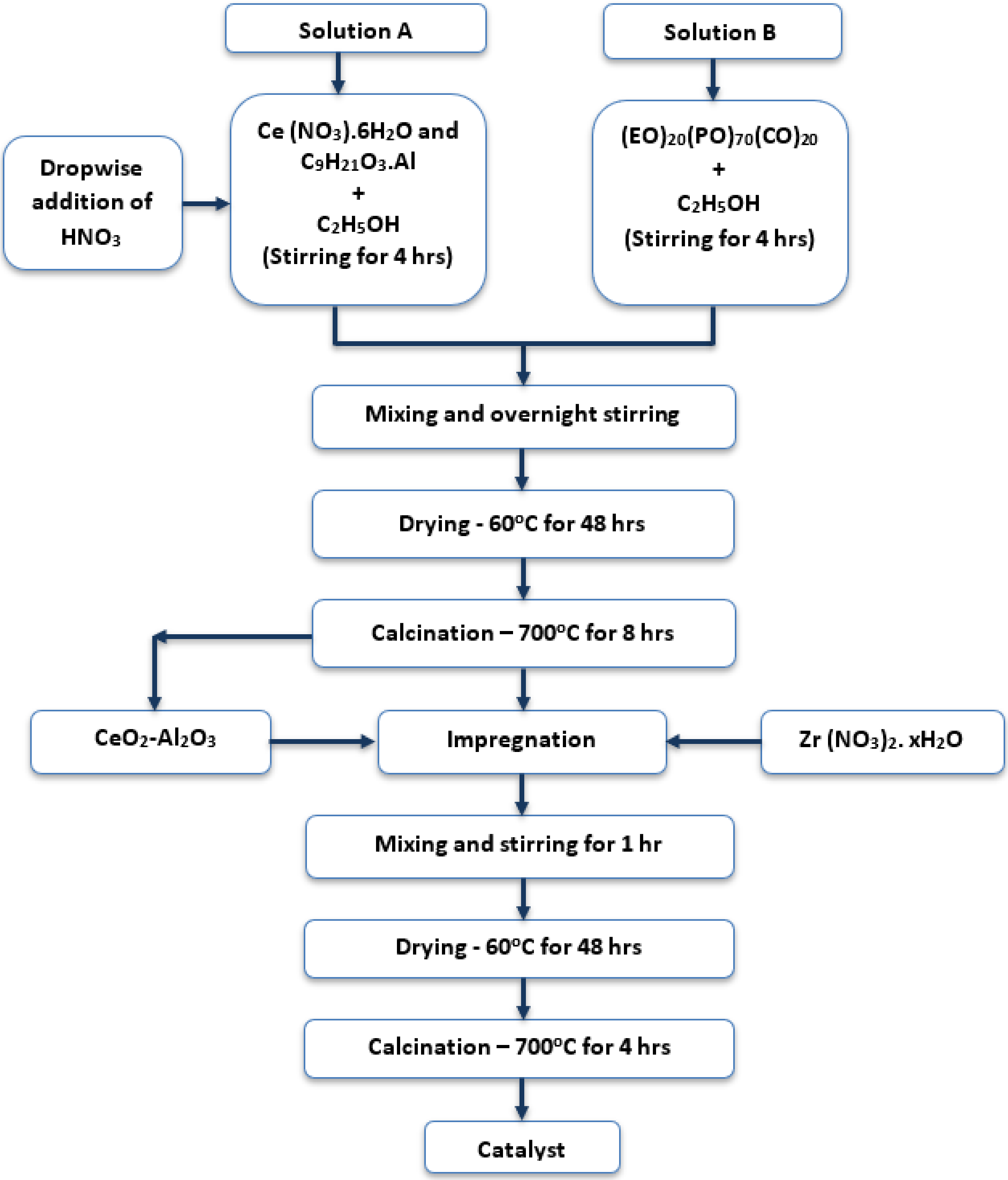

Figure 2

Flow diagram of catalysts synthesis procedure

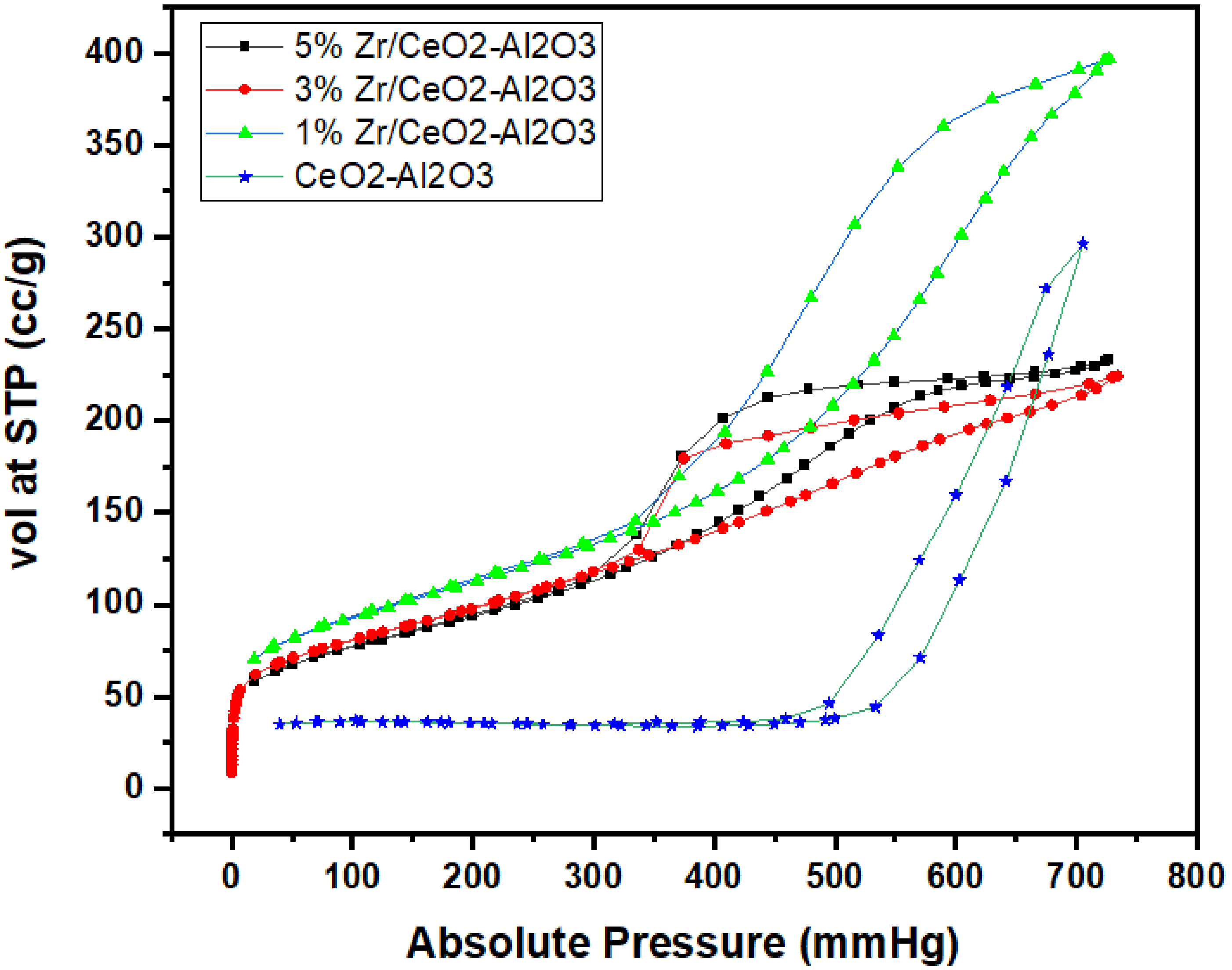

Figure 3

Adsorption Desorption isotherm of Nitrogen for 1%, 3% and 5% Zr /CeO_2-Al_2O_3

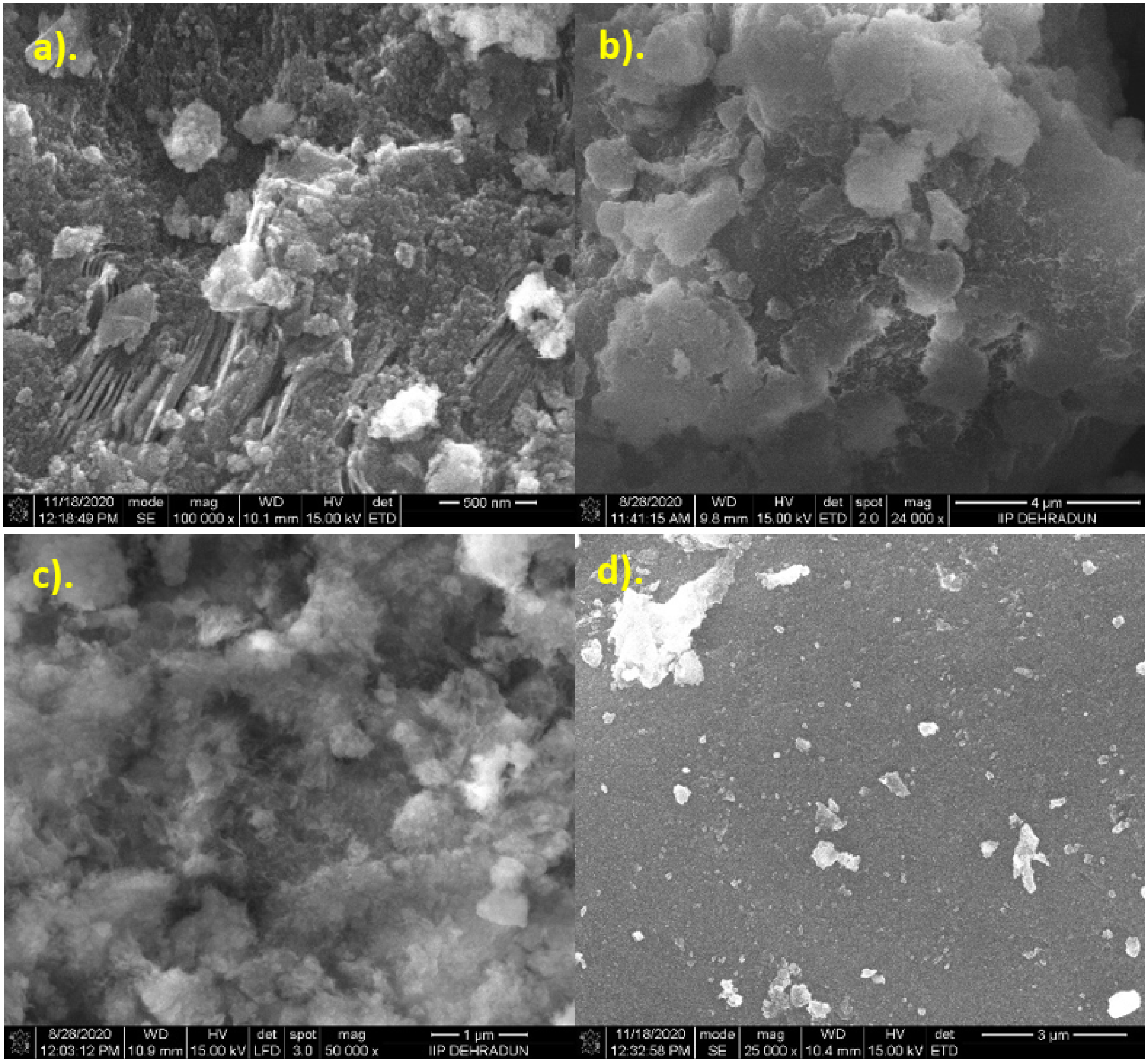

Figure 4

SEM pictures with EDX of a) CeO_2-Al_2O_3, b) 1% Zr /CeO_2-Al_2O_3, C) 3% Zr /CeO_2-Al_2O_3, d) 5% Zr /CeO_2-Al_2O_3

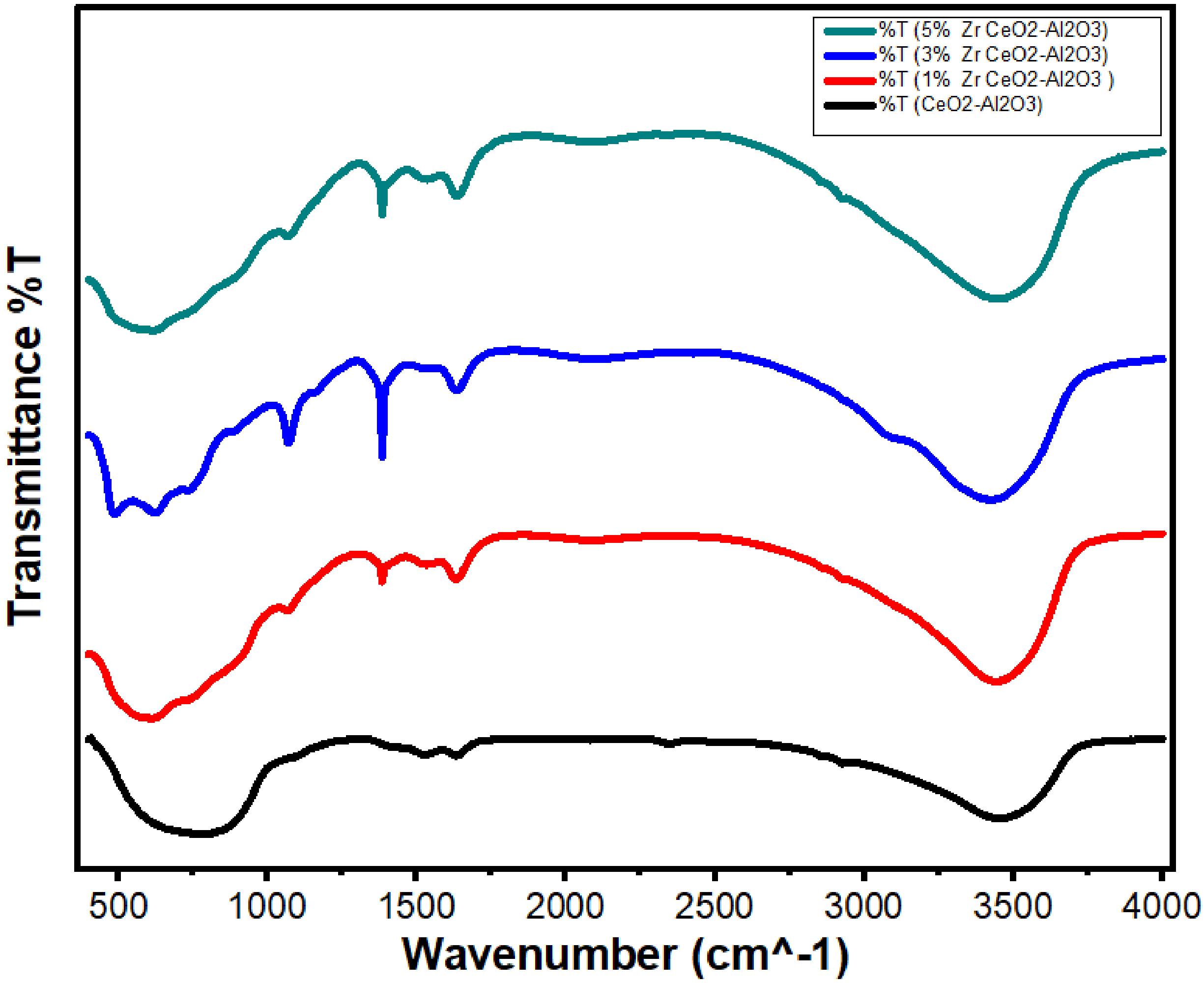

Figure 5

FT-IR spectra of 1%, 3% and 5% Zr /CeO_2-Al_2O_3

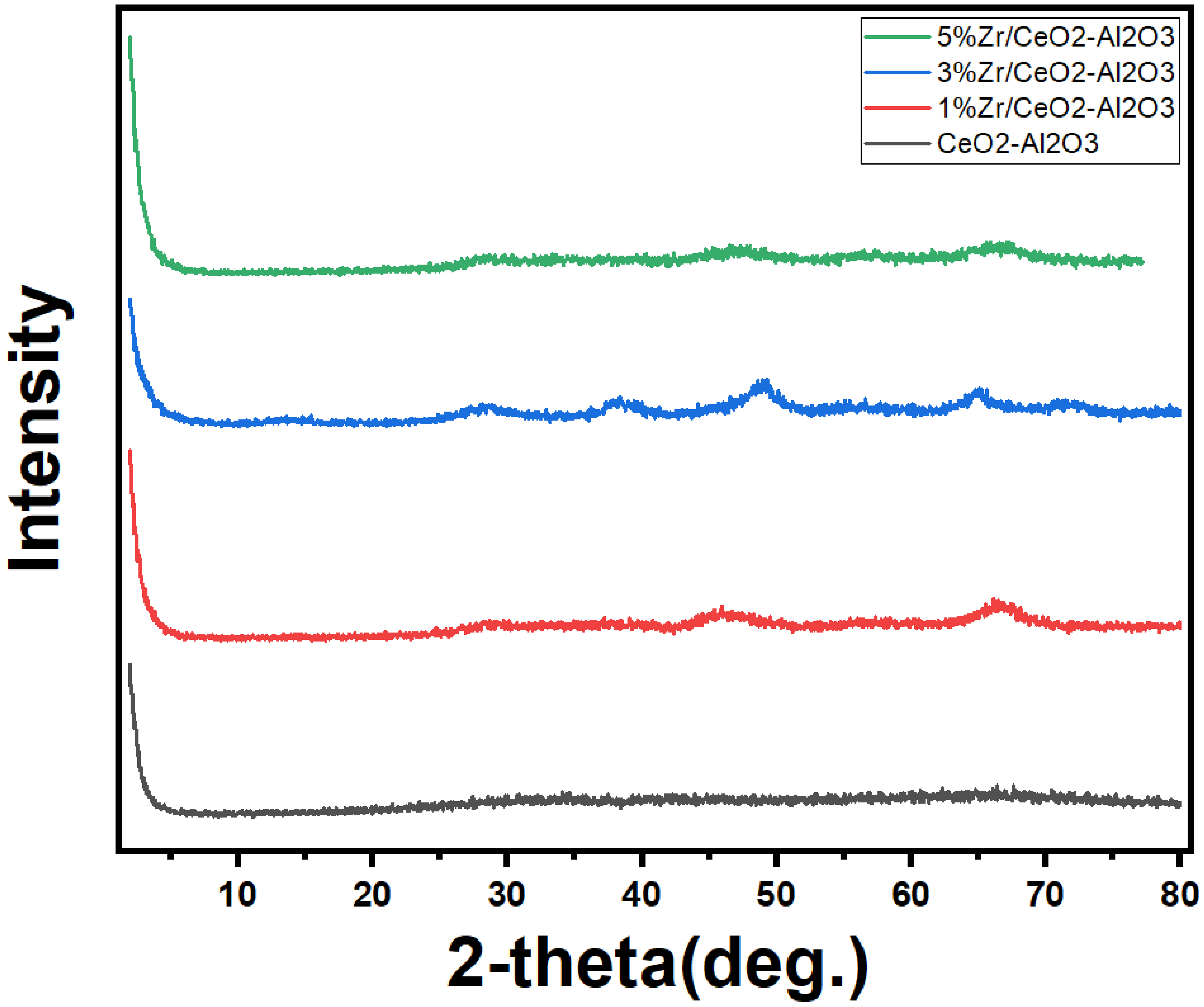

Figure 6

XRD patterns of 1%, 3% and 5% Zr/CeO_2-Al_2O_3

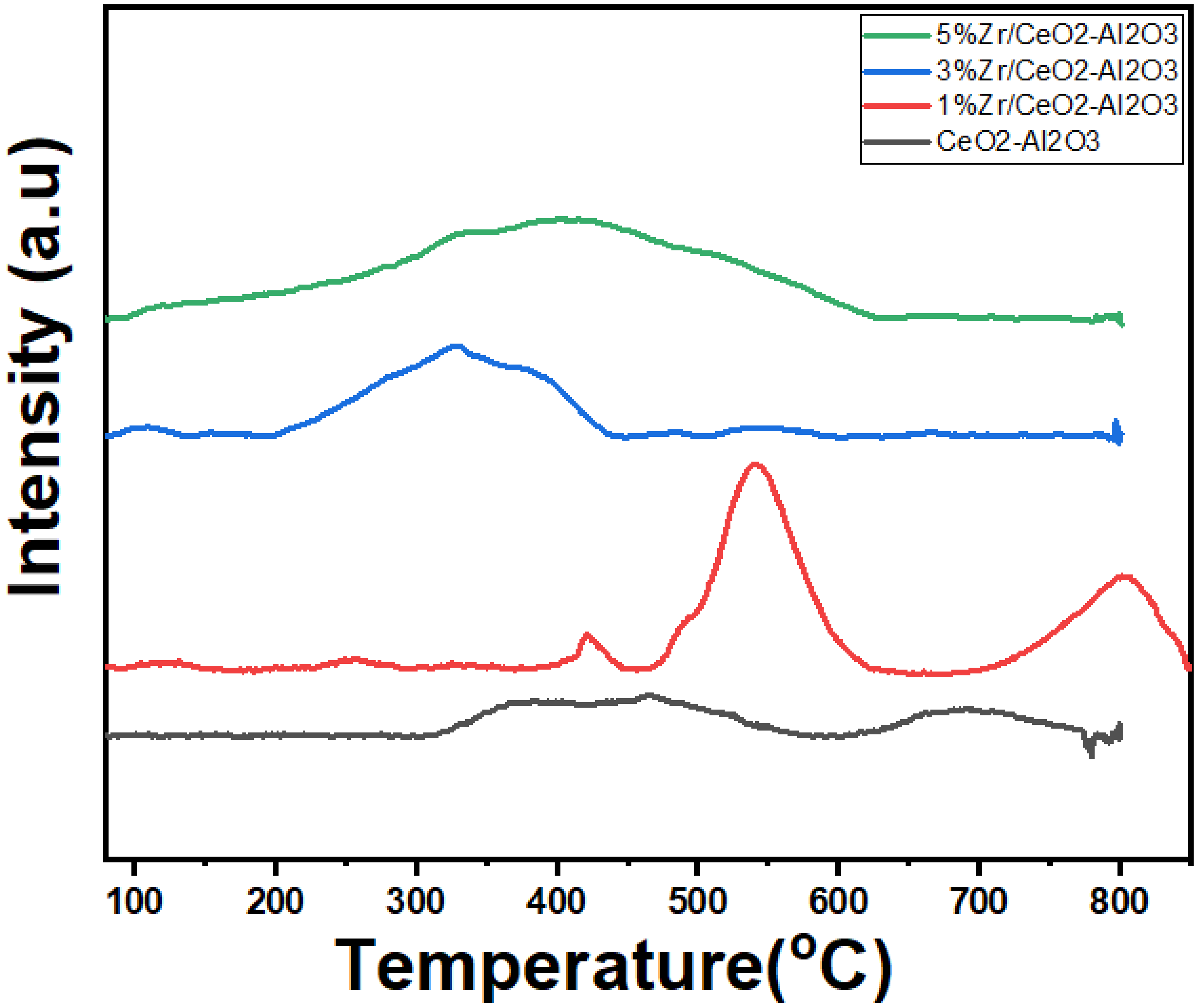

Figure 7

H2-TPR profiles of 1%, 3% and 5% Zr/CeO_2-Al_2O_3

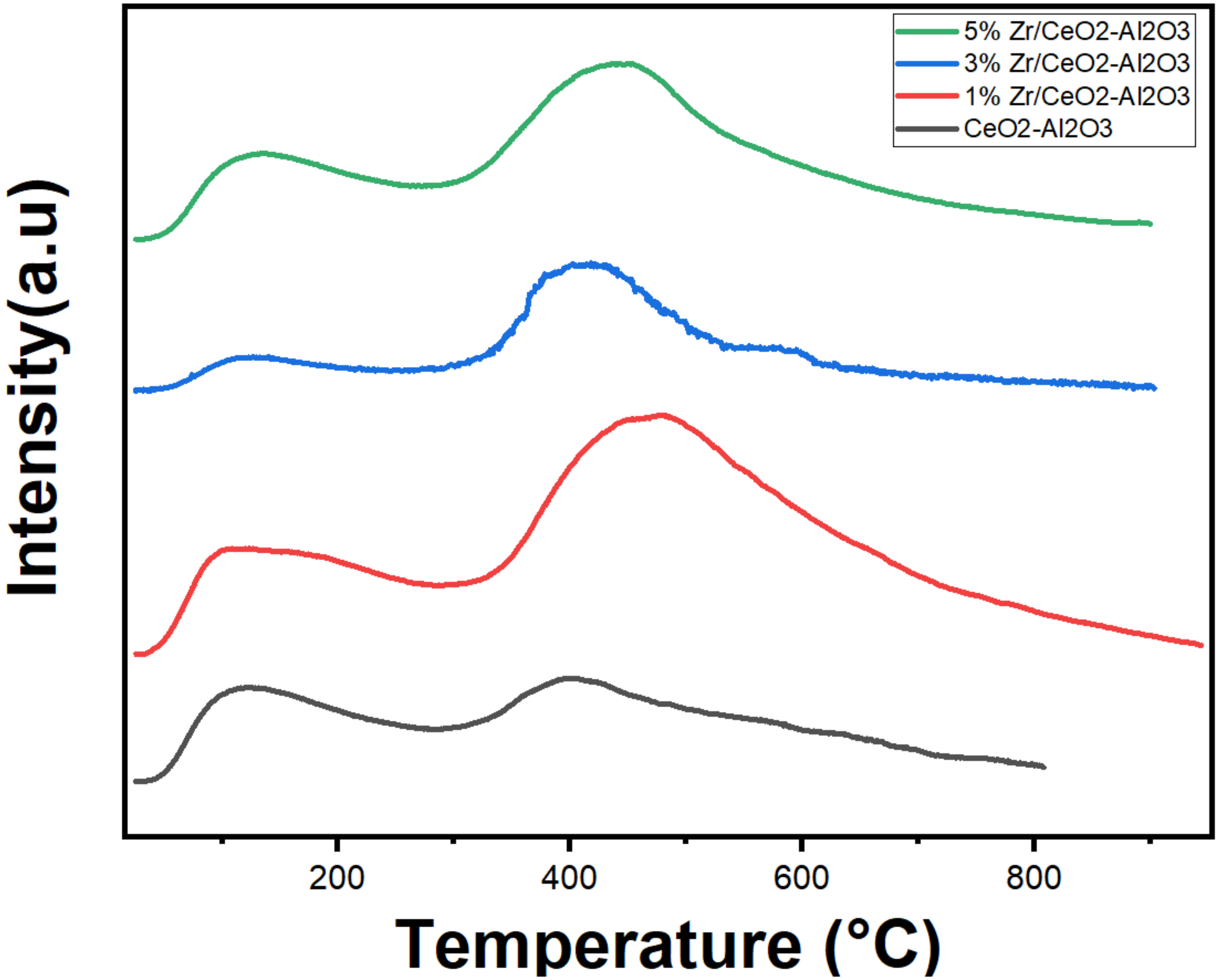

Figure 8

NH-3 TPD profiles of 1%, 3% and 5% Zr/CeO2-Al_2O_3

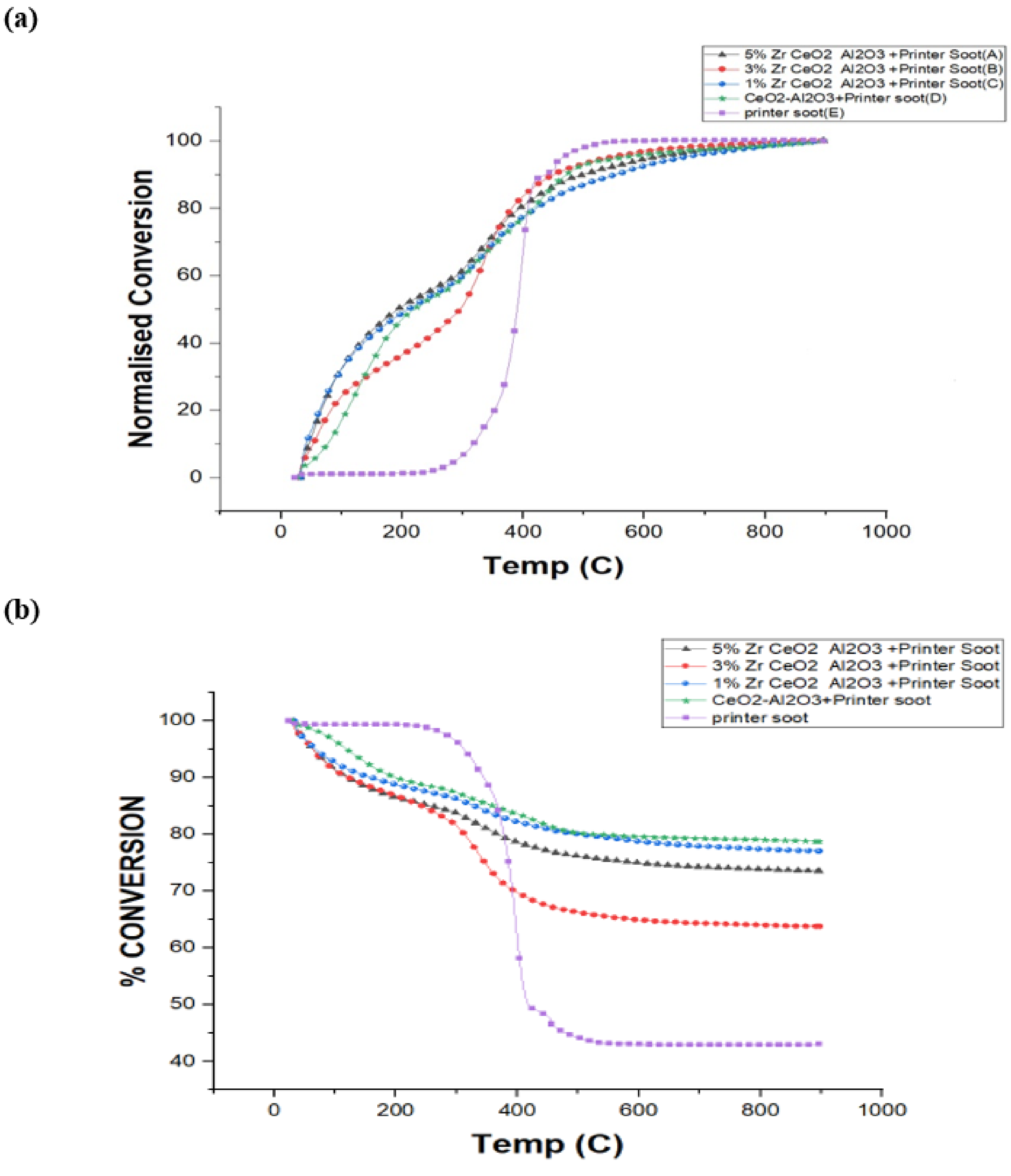

Figure 9

(a) Normalized soot conversion (%) (b) Percentage weight loss versus reaction temperature (^{O}C) for CeO_2-Al_2O_3, 1% Zr/CeO_2-Al_2O_3, 3% Zr/CeO_2-Al_2O_3, 5% Zr/CeO_2-Al_2O_3 and Uncatalyzed soot sample in loose contact mode.