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An overview on Metal doped / Supported Ceria Catalysts: Synthesis, Characterization and Applications

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Abstract

Design of viable catalysts that exhibits high catalytic activity and stability, as well as resistance against deactivation could be achieved by selecting the right active metal and support, understanding their structure, synergy or the metal support interaction and by employing the right preparation technique. Numerous studies and reviews have dealt with various aspects of CeO₂ based catalysts, with the sole target of understanding its activity in various reactions such as dry and steam reforming of methane. Good metal dispersion on CeO₂ surface is explained to be the reason for the promising activity of this systems. This review focuses on the synthesis, characterization and application of some CeO₂ doped/supported catalysts in hydrogen production by dry and steam reforming of methane, and other reactions. Various synthetic methods for the preparation of the metal doped/supported CeO₂ catalysts were introduced with a focus on how to effectively produce stable and efficient catalysts. Subsequently, some advanced characterization techniques were presented to precisely probe the metal and CeO₂ at the atomic level, which is critical in investigating the structure of the catalysts.

Key words : Ceria, Ruthenium, Iridium, Reforming, Hydrogen Production.

1.0 Introduction

Ceria (CeO₂) or cerium oxide, is a well-known cerium compound that has received considerable attention of researchers most

especially those in the field of catalysis and nanoscience. This is because both Ce³⁺ and Ce⁴⁺ ions can exist stably due to the unique nature of their electronic configurations⁴⁹. With high lattice ion mobility, redox property ($Ce^{3+} \rightleftharpoons Ce^{4+}$) along

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with high oxidizing power of Ce^{+4} cation, CeO_2 always exhibits superior and special catalytic properties in oxidation reactions^{5,22}. Because of the enormous number of lattice defects (grain and interphase borders, oxygen vacancies, dislocations, *etc.*) present at this scale, CeO_2 can operate as a catalyst in its own right, especially if its particles are in the nanometer range²⁷. The capacity of CeO_2 to release oxygen is crucial in catalytic applications⁴⁶. Furthermore, even after the removal of lattice oxygen, CeO_2 retains its crystal structure due to the development of oxygen vacancies and it can attain different shapes (nanorod, nanofibre, and nanocube structures *etc.*). Moreover, its activity can be further improved by the incorporation of different elements (dopants) into the crystal lattice. The doping of CeO_2 with noble metals is advantageous since only negligible amount of the noble metal is being used. Additionally, noble metals exist in multiple oxidation states exhibiting better redox properties⁵¹.

Noble metals (Ir, Ru, Rh, Pt) doped CeO_2 catalysts are key materials in advanced technology because they can be useful in a wide variety of reactions such as CO and formaldehyde oxidations, ammonia synthesis, combustion of chlorobenzene, methane dry/steam reforming among others. The size and shape of noble metal doped CeO_2 control their catalytic properties by affecting the surface structure and electronic state. For example, the ratio of noble metals atoms on the facets, edges, and corners are determined by the size and shape of the CeO_2 , resulting in different catalytic activities for structure-sensitive reactions³⁰.

Ruthenium and Iridium containing catalysts have attracted considerable interest for many reactions²¹. Among these catalysts, CeO_2 supported/doped ones have attracted much attention because of the formation of characteristic

surface metal species such as highly dispersed pentacoordinated ruthenium oxo species when compared to the Al_2O_3 and TiO_2 supported ones⁴⁵. At the same time, these strong metal-support interactions also contribute to noble metal atoms/clusters trapping or bonding onto the support surface, charge transferring and mass transporting (diffusion) between catalyst and support, defects and strain creating at the interface during catalysts preparation and post treatment under oxidizing or reducing conditions^{11,20}. It was reported by Satsuma *et al.*,³⁸ that self-dispersion of large-sized Ru particles into nanoparticles was caused by forming Ru-O-Ce bond during oxidation of Ru metal into Ru oxide in air.

On the other hand, Cheah *et al.*,⁴, reported a highly active CeO_2 doped Iridium (0.1wt%) and stabilized with gadolinium in methane reforming under gradual internal reforming condition. This catalyst is ten folds active than 1wt% Ru/ ZrO_2 . Postole *et al.*,³² has also given an overview for efficient hydrogen production from methane reforming using CeO_2 doped Ir catalyst prepared by combustion technique. Several other reports have demonstrated similar activity and usage Ir/ CeO_2 catalyst^{36,43}. In most of these reports, it has been demonstrated that the activity showed by Ir doped CeO_2 catalyst is associated to the support itself and then the synergy between the metal and the CeO_2 . For instance, equivalent amount of Ir/ CeO_2 and Ir/ Al_2O_3 doesn't induce the same activity.

In this review, we try to summarize some preparation method for some Ceria doped/supported metals (Ir, Ru), their characterization to probe the metal and CeO_2 at atomic level and finally some specific applications of the catalysts.

2.0 Synthesis of Ruthenium or Iridium Doped Ceria Catalyst (M/CeO_2 ; $M = \text{Ir or Ru}$) :

Depending on the factors that influence the catalytic activity of a given research, catalyst preparation method can range from simple process to a complex multi-step and time consuming one. In addition, a synthetic method can change as a function desired shape and structure of a catalyst. Nonetheless, a given preparation method contain one or more of the following unit operations; Precipitation, Gelation, hydrothermal transformation, decantation, filtration, centrifugation, washing, drying, crushing/grinding, calcination, reduction and activation³³.

2.1 Co-precipitation/Precipitation Method :

The oldest, simplest, and most often used synthetic approach is co-precipitation/precipitation. It is employed in the preparation of the metal supported catalyst and bulk oxides. It is known to occur in three different steps: supersaturation, nucleation and growth³³. By mixing the

precipitants' solutions together, two or more metals can be precipitated at the same time and in the resultant solid products, different active species are evenly dispersed^{49,50}. Precipitation/co-precipitation of M-CeO₂ (M= Ru or Ce) can be accomplished using precipitating agents such as NaOH, KOH, urea, and others. The appropriate amount of Cerium and metals salts are dissolved in deionized water and vigorously stirred followed by addition precipitating agents and stirring. The co-precipitate is filtered, washed several times with deionized water, and dried under inert flow. The collected powder is calcined in air at high temperature to obtain the active catalysts⁴⁰. Precipitation may be combined with other synthetic methods, such as hydrothermal, combustion or impregnation. For instance, CeO₂ is precipitated from Cerium salt, and the metal is impregnated on the formed precipitate^{6,23}. The **Fig.1** below represents a typical precipitation method.

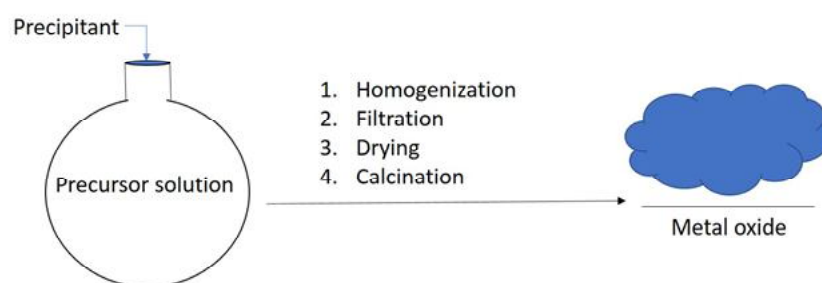


Fig. 1: Steps involved in precipitation.

2.2 Combustion Method :

Because it provides the finest catalytic performances, the combustion process is one of the best methods used in the preparation of M (Ru/Ir) doped CeO₂ catalyst. The combustion process, as described by Derk *et al.*,⁶ Upham *et al.*,⁴⁴ and Postole *et al.*,³² can be used to make Ru or Ir doped ceria. Aqueous solution of cerium and ruthenium salts, and urea (Millipore) are

mixed. The mixture is then heated at high temperature furnace to induce spontaneous combustion and produce an oxide. The combustion is incredibly fast, and it is thought that the metal atoms are unable to migrate and form a new phase in such a short period, and they become locked where they were when the combustion began. One of the most reliable approaches for manufacturing a substitutionally doped oxide is to use this procedure³².



Figure 2: Synthesis of M/CeO₂ by Combustion Method.

2.3 Hydrothermal Method :

An easy, one-pot batch synthesis approach of template-free nanostructured ceria is possible using a hydrothermal method for the synthesis of CeO₂ and CeO₂-based products. Hydrothermal method simply involves the transformation of a given precipitate or gels induced by temperature, under ageing in the presence of mother liquor³³.

To prepare Ru or Ir/CeO₂ using this approach, a salt solution of ceria is prepared and precipitated using NaOH. Varying temperatures can be used in the precipitation to obtain the desired nanostructured CeO₂. For instance, nanorods are obtained at 100°C and nanotubes 180°C. The produced nanostructured CeO₂ are then impregnated with the metal precursor (Ir or Ru), stirred, evaporate, and dry under inert flow (**Fig 3a**). The resulting powder is then reduced under H₂ to have the active catalysts^{24,42}.

2.4 Impregnation Method :

Impregnation is a preparation technique that involves bringing a solution of the active phase's precursor into contact with the support. The support (CeO₂) is contacted with a certain amount of the metal precursor, usually salts (nitrates, oxalates, formates or the chlorides). Impregnation can be dry (incipient wetness or the capillary) or wet (soaking) depending on the preparation conditions.

In dry impregnation, there is enough liquid

(precursor solution) to fill the pore volume of the support. Hence the volume of the liquid added should be the less than or equal to the pore volume. On the other hand, the support is dipped into an excess amount of solution (in respect to the pore volume of the support) containing the active phase precursor(s) in wet impregnation.

The formed slurry is then stirred to attain good homogeneity, evaporated and dried overnight under inert flow to have the powdered nanoparticles (**Fig 3b**). To have the active catalyst, the powdered catalysts is reduced under H₂ at high temperature^{4,6,37}.

2.5 Sol-Gel Method

In sol-gel synthetic methods, a starting material is converted into a colloidal solution (the 'sol'), which further forms 'gel'. This method requires either esters or salts soluble in weakly acidic organic solutions as new raw materials²⁹. A typical sol-gel process involves; hydrolysis, condensation, gelation, ageing and drying. Experimental procedures that affect the sol-gel process include the nature of the precursors, pH, amount of water used, temperature and ageing time.

In the sol-gel process, metal and the support salts in aqueous form are used and acidified nitric is added so as to reduce the pH of the salt's solutions to about 4.5. A solution of glucose-fructose mixture is then added to the prepared metal salts solution and stirred vigorously.

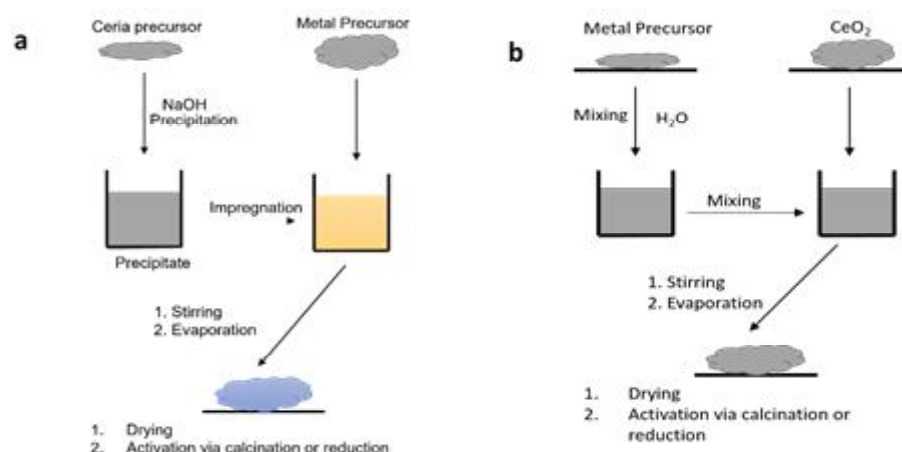


Figure 3:(a) Hydrothermal method (b) Impregnation Method for Metal/CeO₂ catalyst.

After this homogenization, the solution is stirred at room temperature for an hour to obtain the polymerized gel which is dried in an oven at 110°C. The dried sample is then calcined in a furnace with static air at high temperature⁴⁸.

support precursors are in solid state and the molecules require only mechanical and thermal activation to have reacts with each other. Apart from the above-mentioned methods for the synthesis of supported metal/ dopes catalyst, several other effective methods have also been reported. The microwave-assisted method is used to make noble metals doped ceria catalysts with a good yield and short reaction time⁵⁰. Ion-exchange, ultrasound assisted preparation methods and Electrospinning techniques was also reported by Liu, *et al.*,²¹.

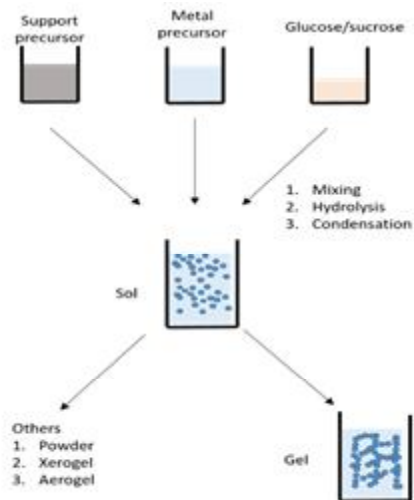


Figure 4: Sol-Gel Method for the synthesis of Metal Doped/Supported Catalyst

2.6 Solid state synthesis and other methods :

In solid state synthesis, both the metal and

A well-prepared and optimized catalysts is most often known to exhibits good catalytic activity in a given reaction. Different characterization techniques are set in place to understand the properties of a given catalyst (such as the morphology, surface chemistry) before and after a given reaction in other to come up with a satisfying arguments and explanations on the factors that influence its activity and/or its stability in a given reaction.

3.0 Characterization Ru/Ir doped Ceria Catalyst :

To attain a deep understanding of metal

support catalyst, it is important to verify the structure and the atomic states of both the dopant and the support, and the factors that influence its activity in different reactions. A series of advanced characterization techniques have been developed to probe and analyze metal (Ir, Ru) doped CeO₂ catalyst, understand their shape, surface states and the metal-support interactions. These techniques includes; powder x-ray diffraction (XRD), nitrogen physisorption – BET surface area, Raman spectroscopy, transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy, X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction techniques, inductive coupled plasma technique (ICP-OES) among others. In this review, we report some major characterizations techniques for Ru and Ir doped/supported CeO₂ catalysts.

3.1 XRD Analysis :

Powder x-ray diffraction (XRD) is used to analyze the structure of crystalline materials²⁶. The most common source of radiation in a powder XRD machine is a Cu K α x-ray tube, which produces x-rays with a wavelength of 1.5406 Å. The important features obtained from XRD include, the diffraction patterns lattice constant and average crystallite sizes of the catalysts. Wu *et al.*, (2021) reported the X-ray diffraction (XRD) executed on a Panalytical X'Pert³ powder diffractometer and found that the adjunction of Ru could slightly affects the textural property of the CeO₂ based catalysts. The XRD pattern of both fresh and reduce sample of Ru/CeO₂ revealed only patterns from CeO₂ support's diffraction peaks, with no peaks attributed to Ru species (Ru⁰, RuO₂, or RuO₃), showing the low metal loading and that the Ru species were well distributed on the CeO₂ support³⁴. The XRD spectra of Ru_{0.05}Ce_{0.95}O₂ also shows no diffraction peaks attributable to RuO₂ or metallic Ru²⁵.

In another report, some minor peaks that could be related to the hcp-phase of metallic Ru could be detected in bulk peak of CeO₂ according to Derk *et al.*, (2014). Hence the XRD patterns for the various Ru/CeO₂ catalysts are more or less identical, and no or minor diffraction peaks related to the Ru species (metallic Ru: 44°; RuOx: 35° and 54°) were observed. Its noteworthy, the absence of Ru peaks could result from the good dispersion that the Ru attain on the CeO₂ support, or as a result of small loading of the Ru on the CeO₂ Surface. The absence of the peak also signifies the small metal crystallite (< 1nm) on the support surface.

Like the Ru/CeO₂ catalyst, Ir/CeO₂ also showed no diffraction peaks due to Ir in the Ir doped CeO₂ catalysts is observed. Postole *et al.*,³² mentioned that, when Ir content in a given catalysts is low, and a good dispersion is achieved, hardly a peak attributed to a given metal is diffracted. The XRD study on 0.1 wt% Ir/CeO₂ (before catalytic test) revealed a diffraction pattern similar to cubic fluorite like structure of CeO₂, and that the addition of the of the Ir didn't affect the lattice parameter but however, influence the formation of slightly different CeO₂ crystallites. For instance, fresh CeO₂ showed an average crystallite size of 50nm which reduces to 37 nm after doping the CeO₂ with 0.1 wt% Ir³².

3.2 Nitrogen physisorption – BET

The specific surface areas of nano powders and mesoporous materials can be determined by determining nitrogen adsorption on the surface of porous materials at 77 K (nitrogen's boiling point). The Brunauer-Emmett-Teller (BET) method calculates how much adsorptive gas is needed to completely cover the external surface and any internal pores with a single monolayer of adsorbed gas.

Li *et al.*,²⁰ reported the influence of oxidation and reduction on the BET surface areas of 5wt% Ru/CeO₂. Most of catalysts showed low surface areas upon oxidation or reduction treatment when compared to the actual surface areas of the support (CeO₂). For instance, CeO₂ (nanotetrahedral) support showed a surface area of 45.9 m²/g. However, incorporating the Ru (5wt %) and treatment (oxidation/reduction), reduces the surface area to 33.8 m²/g (for oxidation) and 38.8 m²/g (for reduction) respectively. In the case of 5wt% Ru/CeO₂ (nanorods) an increase in surface was observed after reduction and oxidation. It is clarified that the differences in the surface areas of oxidation and reduction treatment is as a result redispersion of RuO_x species on the CeO₂, hence the reason for the increase in surface area after reduction. In addition, the average crystallite size of CeO₂ increases from 16.6nm to 17.7 and 18nm for the oxidation and reduction treatments respectively.

Qin *et al.*,³⁴ reported the specific surface areas (BET), average pore diameters, and total pore volumes (94 m² g⁻¹, 0.4 ml g⁻¹, and 16.2 nm for fresh Ru/CeO₂ and 95 m² g⁻¹, 0.4 mlg⁻¹ and 15.1 nm for reduces Ru/CeO₂). Using the BET method, Manaka *et al.*, (2020) estimated the particle surface areas (Ru/CeO₂) and discovered that the specific surface areas of the samples (CeO₂) did not increase when Ru was added.

Surface area decrease (47 to 19 m²/g) was also observed in CeO₂ stabilized gadolinium support (Ce_{0.9}Gd_{0.1}O₂) after treatment at high 1173K. The surface area decrease was attributed to the formation of large Ce_{0.9}Gd_{0.1}O₂ particles upon heating at high temperature.

To finalize on the surface area, doping CeO₂ with trace of noble metal such as Ru or Ir,

doesn't significantly affect the original CeO₂ surface area. However, different preparation methods and conditions can influence the surface area of the given material. Yahi *et al.*,⁴⁸ found that the BET surface areas of catalysts prepared by microemulsion are much higher than those prepared by the sol-gel method, with a large pore volume and pronounced mesoporosity.

3.3 Raman Spectroscopy

Raman spectroscopy is a vibrational technique that uses lasers in the visible, near-infrared, or near-ultraviolet wavelength range to analyze materials. Raman spectroscopy is used to measure the nature of these molecular vibrations, which are sensitive to changes in the structure and chemistry of crystal lattices (Larkin, 2017). Gupta *et al.*, (2017) states that Raman spectroscopy can be used in determining the local crystal symmetry, defects and disorders in oxides. It has been used to demonstrate the presence of oxygen vacancies in CeO₂. The investigation by Raman spectroscopy could give information on the incorporation of noble metal into the ceria lattice that could not be detected by XRD and STEM, XEDS and XPS¹.

Huang *et al.*, (2021) reported Raman spectra of 1 wt %Ru doped CeO₂ catalyst for chlorobenzene oxidation. All the CeO₂ (nanoparticles)-based samples present a strong band at about 460 cm⁻¹, which is attributed to the Raman-active vibrational mode (F_{2g}) of fluorite-type structure. It can be considered as a symmetrical stretching vibration of the oxygen atoms around Ce ions. Furthermore, another weak band appears at around 600 cm⁻¹, which is related to oxygen vacancies due to the presence of Ce³⁺ ions in CeO₂ lattice. Pure RuO₂ is known to exhibits bands at 528, 644, and 716 cm⁻¹ which can be assigned E_g, A_{1g}, and B_{2g} modes of

vibration (Satsuma *et al.*, 2012).

For the 1wt% Ru/CeO₂ samples, only bands from CeO₂ vibrations are observed strongly, notably the strong band at 460 cm⁻¹. However new additional bands than can be attributed to Ru-O-Ce bond appeared at 695 at 974 cm⁻¹. Thus, these Raman peaks are commonly designated to the Ru-O-Ce bond formed as a result of the interaction between Ru species and CeO₂ and could not be assigned to either single-phase CeO₂ or RuO₂.²¹.

3.4 Transmission Electron Microscopy :

Transmission electron microscopy (TEM) is a microscopic technique that transmits a beam of electrons through a sample to generate an image. TEM has been used to analyze the noble metal particle size and help in distinguishing the noble metal particles and the support¹⁵.

Fang *et al.*,⁸ shows that Ru clusters of around 1.26 nm are distinctly observed in the TEM images of the sucrose impregnated 1wt% Ru/CeO₂ catalyst. The average sizes of Ru clusters based on CO chemisorption are 1.9 and 1.4 nm for Ru/CeO₂ and the sucrose impregnated Ru/CeO₂. The difference in the sizes of Ru clusters might be as a result of the change in the strong metal support interaction between Ru species and CeO₂.

It is evident that small metal loading possesses no significant effect on the actual support particle size. Huang *et al.*,¹³ illustrated that no evident change in morphology could be observed when different CeO₂ supports (nanorods, nanocubes etc) are impregnated with Ru loading 0.5 wt%. All impregnated supports showed equivalent particle size as their independent. The same results were observed with a high-resolution

transmission electron microscopy (HRTEM).

In their work Manaka *et al.*,²⁵ carried out TEM measurements for the Ru dispersion and found that no particles were clearly observed perhaps due to the small loading. Hence in Ru/CeO₂ catalysts, Ru is considered to be in a highly dispersed state (below 1 nm), even if the metal (Ru) precursor is changed. This results further corroborate that Ru species (small loading) has a limited influence on their surface area morphology of the support material^{23,47}.

Very similar atomic-scale morphology of CeO₂ before and after methane steam reforming was reported for 0.1 wt% Ir/CeO₂. The fresh sample before the testing showed Ir particles in a mean size of 1.3 nm. Upon the activity testing in steam reforming, the TEM image revealed scarce Ir particle and the average particle size changes to greater than 1.6 nm³².

3.6 X-ray Photoelectron Spectroscopy :

XPS is a powerful quantitative spectroscopic technique that provides information about surface and near-surface chemistry and can provide additional information about oxidation states⁴.

Two Ru 3d_{5/2} peaks at 279.8 and 280.8 eV for Ru/CeO₂ and sucrose impregnated Ru/CeO₂ catalysts were reported by Fang *et al.*,⁷. These peaks were assigned to the Ru metal (Ru⁰) and Ru oxide (Ruⁿ⁺), respectively. The ratios of Ru⁰/(Ru⁰ + Ruⁿ⁺) are 0.72 and 0.81 for Ru/CeO₂ and sucrose impregnated Ru/CeO₂, respectively, revealing that a large amount of Ru⁰ existed in sucrose impregnated Ru/CeO₂. The ratio of the Ru⁰ in the two catalysts were further confirmed by the H₂ Temperature programmed analysis at 150°C. Moreover, the ratios of the Ru 3d to Ce

3d peak are 0.010 and 0.012 for Ru/CeO₂ and sucrose impregnated Ru/CeO₂, revealing that there is a larger number of the exposed Ru species for the catalyst prepared with the sacrificial sucrose strategy.

Carrillo *et al.*,³ analyzed the oxidation state of Ru, by comparing the Ru_{3p} spectra for Ru–CeO₂ before and after exsolution (*i.e.*, for exRuCeO₂). It was found that the Ru_{3p_{3/2}} binding energy for Ru–CeO₂ to be 463.26 eV, and shifted to 461.64 eV after exsolution, indicative of the Ru metal is in the 4+ oxidation state. There is little presence of Ce³⁺ in the surface of Ru–CeO₂, which slightly increases after exsolution, as revealed for exRuCeO₂.

The XPS spectra of Ru 3d and O1s obtained from 1 wt%Ru–CeO₂ catalysts was reported by Huang *et al.*,¹³ with the value of [Ce³⁺] in the catalyst being estimated to be 11.8 percent. The two peaks in the Ru 3d_{5/2} area at 281.8 and 283.0 eV, as well as the equivalent peaks in the Ru 3d_{3/2} region at 285.9 and 287.1 eV, were attributed to hydrated RuO₂ and Ru⁶⁺, respectively. O1s have a single peak at 529.3 eV, which is attributed to lattice oxygen. Two shoulder peaks are seen at ca. 531 and 533 eV, which can be attributed to adsorbed oxygen or/and weakly bonded oxygen species, or to surface oxygen in the form of hydroxyl species and/or adsorbed water species as surface pollutants. Furthermore, the 1wt% Ru–CeO₂ has a large amount of surface oxygen species at 531 eV, indicating that it has a better oxidation performance.

Sharma *et al.*,³⁹ reported the Ru(3p) core level spectrum of Ce_{0.95} Ru_{0.05}O₂ as prepared. The binding energy of Ru(3p_{3/2}) is 463.1 eV (the Ru(3p) region is investigated because Ru(3d_{5/2,3/2}) states coincide with C(1s) states). Ru(3p_{3/2})

binding energy in RuO₂ is 462.7 eV, which differs by 0.4 eV from Ru(3p_{3/2}) binding energy in Ce_{0.95}Ru_{0.05}O₂. This discrepancy is most likely due to differences in the environment: in Ce_{0.95}Ru_{0.05}O₂, the Ru oxygen distance and the placement of the oxygen atoms differ from those in RuO₂. If we must give the Ru dopant a formal charge, we choose +4 because Ru oxides with greater formal charges are unstable. When compared to the as-prepared catalyst, the XPS spectra of the catalyst after the process showed no change in the Ru(3p_{3/2}) binding energy. This means that the ionic Ru state at the surface region does not change.

The binding energies of Ru_{0.05}Ce_{0.95}O₂ and Ru/CeO₂, both as prepared and after the reaction, demonstrated that Ru atoms in the two catalysts differ: Ru in Ru_{0.05}Ce_{0.95}O₂ is more oxidized than Ru in Ru/CeO₂ or RuO₂. This could be due to a size effect (Ru clusters are small) or the oxidation of the Ru clusters by ambient oxygen prior to obtaining the XPS spectra (Derk *et al.*, 2014).

The XPS analysis of 0.1wt % Ir/CeO₂ reveal no evidential Ir–O–Ce species in the Ir/CeO₂ system, this could result from the low metal loading (0.1 wt %) of Ir in the catalysts.

3.5 Energy-dispersive X-ray Spectroscopy :

The technique of energy-dispersive x-ray spectroscopy (EDX) is used in elemental analysis to identify specific emitted x-rays from a sample specimen. When a substance is attacked with high-energy particles, it produces x-rays that may be identified and attributed to certain elements⁴¹. EDX analysis can be used to locate noble metal particles and recommend particle sizes. It also aids in determining the distribution of ruthenium and cerium throughout the particle volume²⁸.

Carrillo *et al.*, 2021 demonstrated for the first time that EDX provided confirmation of Ru nanoparticle exsolution and anchoring on CeO₂, which were well disseminated across the oxide surface.

3.8 Other Techniques :

Besides the above-mentioned main characterization techniques, various other techniques could use to further provide more key information for understanding ruthenium doped ceria catalysts.

TGA is another efficient technique used to measure the mass of a sample over time, with changing temperature. This analysis can be used to quantify characteristics such as the loss of water, loss of solvent, oxidation, carbon content, or decomposition vs. temperature. Fang *et al.*,⁸ reported the thermogravimetric analysis (TGA) of Ru/CeO₂ and SCRu/CeO₂ which was conducted in a 9% O₂/N₂ mixture on a Setsys Evolution (Setaram) thermal analyzer.

SEM and HRTEM like the TEM, the SEM and HRTEM techniques have been employed to characterize the morphology of the synthesized catalysts. Corrilla *et al.*,³ analyzed the structure of Ru–CeO₂ using SEM and the result showed that all the Ru at the surface is in the metal state. Cheah *et al.*,⁴ performed STEM and HRTEM on Ir/CeO₂ stabilized gadolinium catalyst with the aim of explaining the nature of the active sites of the catalyst, and the factors that are responsible for the enhanced behavior of the catalysts.

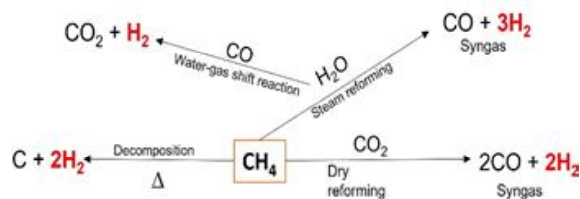
4.0 Applications :

The catalytic applications of Ru/CeO₂ and Ir/CeO₂ catalysts are versatile. In the following

sections, a few typical applications of the catalysts in the hydrogen production by dry and steam reforming of methane, CO and NH₃ oxidation is highlighted.

4.1 Methane Reforming :

Methane reforming process generally makes use of carbon dioxide (CO₂ for dry reforming)/ steam (H₂O, for steam reforming) and methane (CH₄) to produce syngas (H₂ + CO) which can be valued into different oxygenated chemicals (**Scheme 1**). The ability of the process to simultaneously utilize two greenhouse gases (CH₄ and CO₂), is environmentally and economically attractive and several catalysts have been reported in this regard^{17,31}. In addition to sustainable environment, steam reforming process offer the advantage of maximizing hydrogen production efficiently⁴⁹. The hydrogen economy is being pursued quite vigorously since hydrogen is an important and green energy source with a variety of applications as fuel for transportation, fuel cell, feedstock, energy vector reforming in refineries, carbon dioxide valorization, metallurgy, ammonia production, biomass conversion, *etc.*³⁵.



Scheme 1: Routes for Hydrogen production from Methane reforming process.

Nonetheless, the non-polar and chemical nature of methane (C-H bond energy: 104 kcal/mol), along with the highly endothermic character of the reaction enthalpy ($\Delta H_{298} = 246$ kJ/mol) make the methane reforming reaction a challenging task. The partial redox balance of the

reaction requires a catalyst that can take advantage of the activation of both difficult reactants. The penalty for this is the need to undertake the reaction at high temperature, requiring thermally stable catalysts with good selectivity (Fan *et al.*, 2020).

Another obstacle encountered during a reforming process is the deactivation of the catalyst by carbon deposition (coke), metal sintering, and metal oxidation. These are most often linked to the intrinsic nature of the metal catalyst. Designing catalysts with enhanced activity, high thermal stability and resistance to carbon deposition has been the topic in numerous studies of methane reforming^{4,7,22,32}. Noble metals (Ru, Ir) and Ni were highly active for this reaction with high resistance to carbon formation¹⁴.

Liu *et al.*, (2019) reported a highly active and stable 0.5 wt% CeO₂ supported Ru-nanocluster (<1nm) catalyst for dry reforming of methane. The catalyst prepared by impregnation method showed remarkable catalytic performance with a conversion rate of 343 and 394 micromol/g/s for CH₄ and CO₂ respectively, given syngas (CO + H₂) as the key products. It is demonstrated that, the reaction rate increases steadily with increasing temperature of the reaction given a H₂/CO ratio of 0.8 at 700°C. The activity reported for the 0.5 wt% CeO₂ supported Ru-nanocluster surpasses the conversion rate of 0.5wt% Ru/Al₂O₃ and 0.5wt% Ru/TiO₂ prepared using the same method. The result clearly showed how the support materials influences the activity of the catalysts. The *in-situ* X-ray diffraction (XRD) corroborated the influence of the support material by showing no diffraction peak in relation to the Ru which illustrates the good dispersion that was attained, in addition to the small nanoparticles of Ru (<1nm).

The influence of preparation methods on the catalytic activity of Ru doped CeO₂ was investigated by Derk *et al.*, (2014). Incredibly, the two-catalyst showed equivalent performance; 48% methane conversion for the catalysts prepared by combustion method, and 46% methane conversion for the catalyst prepared by impregnation respectively. However, the two catalysts showed different physical properties (XRD, Ru-XPS, and the IR spectrum of CO adsorbed on them) despite essentially their same catalytic chemistry and catalytic activity. The transient reaction experiments using oxygen pulses suggest strongly that methane is more readily activated by the partially reduced catalyst (for both catalyst preparations).

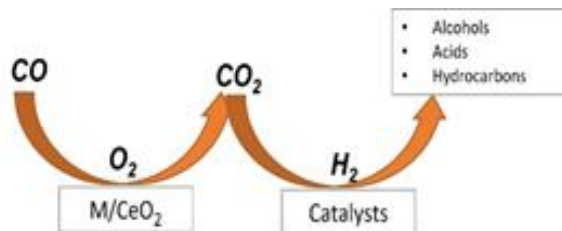
Despite the attentions received by Ni-based catalysts in methane steam reforming, the catalysts deactivation in water deficient system through metal sintering and coke deposition is considered as a key setback that needs to be addressed⁹. Noble metals (Pt, Rh, Ru and Ir) doped/supported on various oxides such as CeO₂ have been extensively studied in the past for MSR. Though not as active as the Ni based catalysts for steam reforming, but they resist deactivation by coke, with added advantage of low metal loading noticeably lower than 30–40 wt% typically used in Ni systems. It has been shown that pure CeO₂ and doped CeO₂ are active for CH₄/H₂ reactions and particularly resistant to carbon formation under gradual internal reforming conditions^{4,27}.

The influence of support material in methane reforming for hydrogen production was reported by Postole *et al.*,³². The CeO₂ based ones showed more activity and resistance to carbon and sulfur poisoning when compared to SiO₂-Al₂O₃ supported catalysts. In addition, the activity of 0.1 wt% Ir/CeO₂ prepared by solution

combustion synthesis surpasses that of 0.1 wt% Ir/CeO₂ prepared by incipient wetness impregnation and 0.1wt% Rh/CeO₂ prepared by solution combustion synthesis. As reported elsewhere (Mosqueda *et al.*, 2009; Cheah *et al.*, 2018), the promising results shown by CeO₂ based system in reforming comes from its ability to anchor metals and donates oxygen readily since it possessed an incredible oxygen storage capacity (Bunluesin *et al.*, 1997). Apart from reforming processes, the application of CeO₂ based system oxidation of CO and formaldehyde is well known.

4.1 CO, NH₃ and formaldehyde oxidation :

From the environmental perspective, CO is quite poisonous and deadly gas produced from incomplete combustion of fossils fuels such as coal. CO is most often oxidized to CO₂ which can be further valorized to oxygenated hydrocarbons catalytically via hydrogenation (Li *et al.*, 2017) (**Scheme 2**). From the research perspective, CO oxidation is a good cheap technique to evaluate a catalytic performance.



Scheme 2: CO oxidation to CO₂

1wt% Ru support CeO₂ nano fibers and 1wt% Ru support CeO₂ nanoparticles prepared by electorspinning technique were reported to have 85 and 76 % conversions at 130°C in CO oxidation (Liu *et al.*, 2020). It is mentioned that this activity comes from the synergy between the metal and the support because independent testing of the support and the metal doesn't show equivalent activity. The good activity reported here isn't surprising on because it is mentioned that Ru

catalyst supported on CeO₂ nanorods can exhibit ~9% CO conversion at near ambient temperature¹⁸. When compared to other metal oxides (ZrO₂, TiO₂, SiO₂, SnO₂, Al₂O₃ etc) support Ru, Ru/CeO₂ prepared by impregnation method was shown to offer better activity toward CO conversion at low temperature. The good activity was attributed to the good dispersion of Ru nanoparticles on the CeO₂ surface (Satsuma *et al.*, 2012).

CeO₂ based catalysts are also known for their good activity in formaldehyde oxidation to CO₂ and H₂O. A detailed overview on the recent advances of CeO₂ and other supported catalysts for formaldehyde oxidation was given by Guo *et al.*,¹⁰. Recently, 130ppm formaldehyde conversion was achieved using 1 wt% Ru/CeO₂ prepared by impregnation³⁴. The prepared catalyst showed better activity the 1 wt% Ru/Al₂O₃ prepared under the same condition. From the physical characterization data that was obtained, it is explained that the activity is attributed to the good dispersion induced by the good metal support interaction. The combustion of chlorobenzene¹³ and ammonia synthesis were reported for Ceria based system^{7,25,47}.

5.0 Conclusion and Recommendation :

The synergetic effect between the isolated metal atoms and support plays a significant role in improving the catalytic performance. The good synergy between supported/doped metals with CeO₂ coupled with good dispersion of the metals is explained to be the key secret of the practical application and the promising activity of the CeO₂ system. In this review, we have surveyed the synthesis, characterization and some application of CeO₂ based catalysts for hydrogen production by dry and steam reforming of methane, oxidation of CO and formaldehyde using metal (Ru, Ir) doped ceria/ruthenium supported

ceria catalysts. Significant advances have been made in preparing very-well controlled shapes of ceria crystallites (nanorods, cubes and octahedral) in order to study the effect of the exposed crystallographic facets of the support, will be prepared. Hydrothermal methods to prepare ceria with control crystal size and morphology and the combustion techniques have proven to be very useful. Furthermore, an overview of some characterization techniques (XRD, BET, Raman spectroscopy, TEM, EDX, XPS TGA) that can help in understating the surface chemistry and reasons for the enhanced activity are presented.

Furthermore, detailed characterization and theoretical calculations that are based on computational analysis are very important in understanding the mechanism of the catalyst performance.

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