HYDROGEN PRODUCTION VIA METHANOL STEAM REFORMING

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CERTIFICATE

This is to certify that the project report entitled "**Hydrogen Production via** " being submitted by Mr. Huzaifa Shahid to the Jadavpur University is a record of research work carried out under my guidance and supervision in conformity with the rules and regulations of Jadavpur University. The result presented in this report has not been submitted, in part or full, to any other university or institute.

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ABSTRACT

Hydrogen (H2) is the promising clean energy which can contribute to the achievement of the NetZero goals. Herein, the Ni/ZrO2 catalyst was developed for methanol steam reforming for H2 production. The catalyst possesses the features of good redox property, and the presence of surface chemisorbed oxygen, and large specific surface area. The Ni/ZrO2 composite together with the control of NiO and ZrO_2 were assessed by thermal and non-thermal plasma (NTP)-activated methanol steam reforming reactions, and the results showed that NTP itself was able to initiate methanol conversion, whilst the inclusion of the composite catalyst did not improve the reaction significantly, e.g., hydrogen production rate = 0.162 mmol·min-1 over Ni/ZrO2 under the plasma condition (at 90 °C and 9.4 kV). This could be attributed to the change of reaction pathways for methanol conversion in the presence of Ni/ZrO_2 under the NTP condition, compared to the thermal systems employing Ni/ ZrO_2. Comparatively, the thermal catalytic system was not active at 90 ∘C regardless the catalysts used. At 400 ∘C, the Ni/ZrO_2 catalyst showed satisfactory activity with a hydrogen production rate of 0.708 mmol·min-1. In addition, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and DFT calculations were performed to understand the relevant reaction mechanisms, revealing that meth oxy and formic acid species were the key intermediates for methanol steam reforming.

Keywords: Methanol steam reforming Hydrogen Ni/ZrO_2 Thermal catalysis Non-thermal plasma (NTP) catalysis...

INTRODUCTION

The increasing demand for the re-use of water and increasingly stringent water quality regulations lead to the need for treating all the different varieties of waste streams containing pollutants. This is particularly true for water containing organic compounds such as water discharged in chemical, petrochemical, textile or pharmaceutical processes. The inability of conventional methods to effectively remove many toxic organic pollutants has made it evident that new, compact and more efficient processes are needed. Several treatment technologies are available that can be used depending on the nature and volume of the effluent. Incineration is the most efficient useful method, but because of the high energetic costs involved and, above all, the release of noxious compounds (oxides of sulfur and nitrogen, furan) into the atmosphere, incineration is suitable only as an end-of-pipe treatment or when the chemical oxygen demand (COD) of the effluents is higher than 300 g L^{-1}. Biological treatment is a low cost and simple method, but the toxicity of the effluent makes this treatment ineffective for organic concentrations above 70–200 mg L^{-1} [1-3]. Potential technologies for COD removal between these two extremes include physicochemical treatment methods, air-based oxidation, and chemical oxidation. From the point of view of energy efficiency, wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) are suitable for waste-waters with low COD loads and within the given limits [4-5]. Herbicide removal [6] oxidative treatment of pulp and paper mill effluents [7-8] , pre treatment of waters from alkaloid plants (typically high-strength industrial wastewater with COD around 27 g L^{-1}) [9] treatment of printing and dyeing waste waters from the textile industry [10-11] and treatment of H-acid manufacturing process effluents are recent examples of applications of this technology. In wet-air or thermal liquid-phase oxidation (WAO) process, the generation of active oxygen species, such as hydroxyl radicals, takes place at high temperatures and pressures, is known to have a great potential for the treatment of effluents containing a high

content of organic matter (chemical oxygen demand (COD) 10–100 g L^{-1}), or toxic contaminants for which direct biological purification is unfeasible [13]. The WAO process has well-known capacities for breaking down biologically refractory compounds to simpler, easily treated materials before they are released into the environment. This aqueous phase oxidation process takes place at high reaction temperatures (473–593 K) and pressures (20–200 bar) by means of hydroxyl radicals. In WAO processes, the organic contaminants dissolved in water are either partially degraded by means of an oxidizing agent into biodegradable intermediates or mineralized into innocuous inorganic compounds such as CO_2, H_2O and inorganic salts, which remain in the aqueous phase. Sulphur is converted to sulphate, halogens to halides and phosphorus to phosphates. Organic nitrogen may produce ammonia, nitrate and nitrogen. In contrast to other thermal processes, WAO produces no NO_x, SO_x, HCl, dioxins, furans, fly ash, etc [13]. One of the main drawbacks of the WAO process is its inability to achieve complete mineralization of organics, since some low molecular weight oxygenated compounds (especially acetic and propionic acids as well as methanol, ethanol, and acetaldehyde), originally present in a wastewater or accumulated in the liquid-phase during the oxidation process, are resistant to further transformation to carbon dioxide. Compared to conventional wet-air oxidation, catalytic wet-air oxidation (CWAO) has lower energy requirements. Due to the presence of a catalyst much higher oxidation rates are achieved and consequently, one can use less severe reaction conditions to reduce chemical oxygen demand to the same degree as in the case of noncatalytic process. In the CWAO process, organics are oxidized to innocuous inorganic compounds such as CO2, H2O and heteroatom dissolved ions at much lower temperatures and pressures than in uncatalyzed thermal processes. By using a suitable catalyst, the operating conditions needed for the WAO process can be lowered to more amenable values (363–493 K, 1–50 bar) without loss of degradation efficiency and with consequent economic advantages. Homogeneous catalysts are very

efficient for the process, but their use implies the need for an additional separation step in the process for the removal of the toxic ions from the solution. As heterogeneous catalysts are easily removed, their development and optimization has been the subject of several works in recent decades. Metals, metal oxides, and metal salts were used as catalysts for wet oxidation, like other oxidation reactions. Mixtures of metal oxide catalysts frequently exhibit greater activity than the single oxide. Co/Bi (5/1) catalyst and Mn/Ce catalysts showed good activity for the wet oxidation of acetic acid. Levec and Pintar reported that $CuO/ZnO/\gamma\text{-}Al_2O_3$ catalyst (42/47/10 wt %) and CuO/ZnO/CoO catalyst (9.3/6.9/1.4 wt. %) supported on steam-treated porous cement were effective for phenol oxidation. Supported noble metal catalysts are generally more active than metal oxides and many catalysts used in commercial wet oxidation processes are based on noble metals, especially platinum. Gallezot reported that platinum catalysts supported on active charcoal could be used under very moderate conditions to oxidize carboxylic acid. Hamoudi reported that Pt promotion of MnO_2/CeO_2 reduced the amount of carbonaceous deposits and improved phenol deep oxidation (higher CO_2 yield).
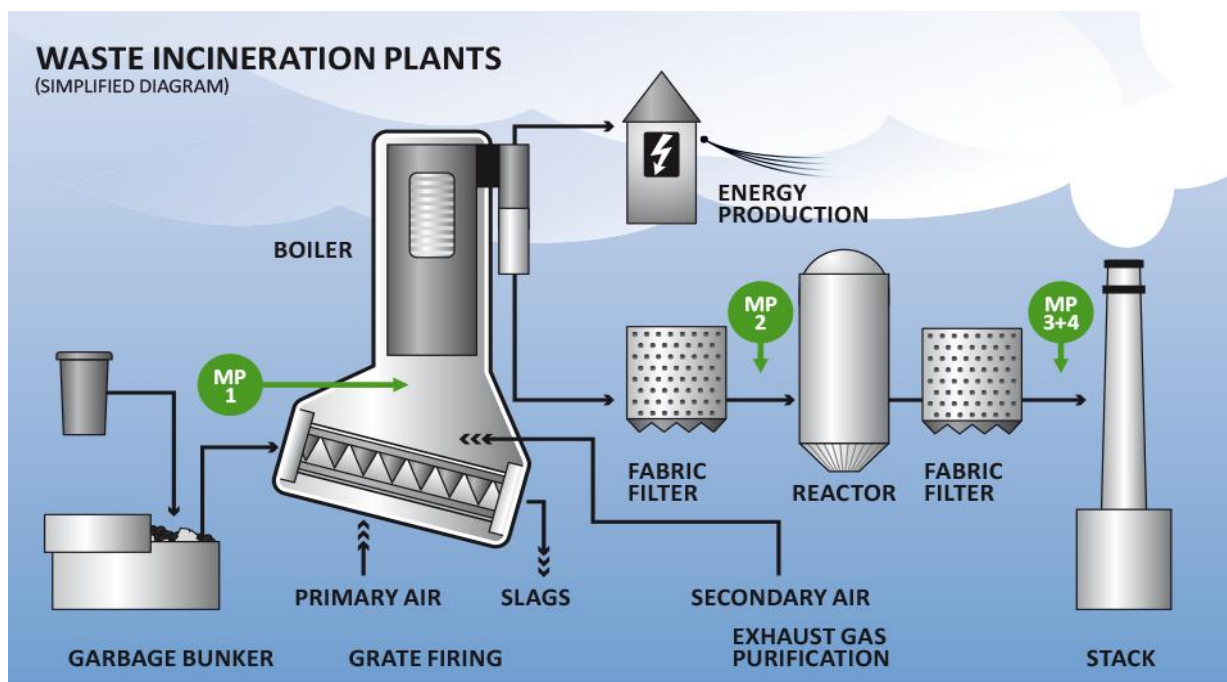
Incineration Process Description

Taguchi and Okuhara studied NH_3 oxidation over titania-supported platinum and palladium catalysts, and Pt/TiO_2 showed the superior activity of N_2 formation among other titania-supported noble metal catalysts. There are several researches on the promoting effect of Ce for wet oxidation reactions. The promoting effect of Ce was reported for a Co/Bi catalyst, which was explained in terms of the variation in the electronic states of Co and Mn [20]. The promoting effect of Ce on mixed-metal oxides, $CeO_2/ZrO_2/CuO$ and $CeO_2/ZrO_2/MnO_x$, for acetic acid oxidation was attributed to the enhancement of the redox properties of the active centers in the catalysts [27]. Zhang and Chuang [28] reported that Ce promoted the activity of an alumina-supported Pt catalyst but inhibited the activity of an alumina supported Pd catalyst for the wet oxidation of pulp mill wastes. These studies mainly aimed at determining initial activities and kinetic parameters with attention being given to catalyst deactivation. The catalytic wet air oxidation of oxalic acid was investigated over alumina-supported Pt catalysts. The Ce addition effect on metal dispersion, the reducibility of catalysts, and the catalytic activity of the wet oxidation of oxalic acid was observed. Discussions were made on the factors affecting the activity of alumina-supported Pt catalysts by Ce addition. Oxalic acid is

a low molecular weight organic compound that is very refractory to oxidation it is a good model system because it occurs in most of the degradation pathways of more complex organic compounds. As expected, the conditions used in this process are quite favorable to the occurrence of various catalyst deactivation phenomena, such as poisoning, sintering, metal leaching into solution, and coke formation. In the present work, the deactivation of such catalysts is studied to determine their industrial applicability. Several experimental techniques are used in an effort to understand the deactivation mechanism, such as pulse chemisorption's (H_2 adsorption), scanning electron microscopy (SEM) analysis, thermo-gravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD) patterns and total organic carbon (TOC) analysis. A kinetic analysis describing the observed deactivation phenomena in the ceria promoted Pt/ Al_2O_3 and Pt/ Al_2O_3 catalysts were investigated using the experimental data obtained in the CWAO of the systems studied.

LITERATURE REVIEW

The literature surrounding catalyst preparation for the removal of toxic organic effluents from industrial wastewater through advanced oxidation methods has undergone a profound expansion in recent years, reflecting the growing imperative to address environmental pollution and safeguard human health. Advanced oxidation processes (AOPs), characterized by the generation of highly reactive hydroxyl radicals (OH), have emerged as frontrunners in the quest for effective and sustainable solutions to combat recalcitrant organic pollutants present in industrial effluents.A comprehensive survey of the literature reveals a multifaceted landscape of research endeavors aimed at optimizing catalyst synthesis routes, elucidating structure-property relationships, exploring novel reactor designs, and scaling up AOP-based wastewater treatment technologies. Synthesis techniques such as sol-gel, hydrothermal synthesis, impregnation, and deposition-precipitation have been extensively investigated for the fabrication of catalysts with tailored physicochemical properties optimized for specific AOPs. Sol-gel synthesis, renowned for its versatility and ability to control nanoparticle morphology and pore structure, has garnered considerable attention for the production of catalyst materials with high surface areas and uniform dispersion of active sites. Similarly, hydrothermal synthesis, leveraging elevated temperature and pressure conditions to promote crystallization and phase transformation, has emerged as a viable route for the preparation of catalysts exhibiting enhanced catalytic activity and stability under harsh operating conditions. Impregnation and deposition-precipitation methods have been widely employed to deposit catalytic species onto diverse support materials, including activated carbon, zeolites, and metal oxides, thereby enhancing the accessibility and reactivity of active sites towards target pollutants. Moreover, the incorporation of dopants or modifiers during catalyst synthesis has been explored to fine-tune the electronic structure, surface chemistry, and redox properties of catalyst materials, thereby optimizing their performance in organic pollutant degradation.

In addition to conventional synthesis techniques, researchers have pioneered innovative approaches to catalyst preparation, including microwave-assisted synthesis and non chemical methods. Microwave irradiation, characterized by rapid and volumetric heating of reaction mixtures, offers expedited synthesis kinetics and improved product yields, while sonochemistry harnesses the cavitation phenomenon induced by high-intensity ultrasound waves to enhance mass and heat transfer rates, promoting the formation of nanostructured catalysts with superior catalytic activity.Despite significant advancements in catalyst preparation, several challenges and opportunities for further research persist. Catalyst deactivation, attributed to fouling, poisoning, or structural degradation, remains a formidable obstacle that necessitates the development of robust catalyst regeneration strategies and the exploration of alternative support materials with enhanced durability and stability. Furthermore, the quest for multifunctional catalysts capable of simultaneously targeting diverse classes of pollutants and exhibiting robust performance under varying environmental conditions underscores the need for interdisciplinary collaborations and innovative research endeavors.The successful scale-up and commercialization of AOP-based wastewater treatment technologies hinge upon the integration of cost-effective catalysts and efficient reactor designs into existing industrial infrastructure. Research efforts aimed at optimizing catalyst synthesis routes, leveraging sustainable feedstock sources, and harnessing advanced characterization techniques to unravel the intricate interplay between catalyst structure, composition, and performance will be instrumental in overcoming existing barriers and unlocking the full potential of advanced oxidation methods for environmental remediation on a global scale. The successful scale-up and commercialization of AOP-based wastewater treatment technologies hinge upon the integration of cost-effective catalysts and efficient reactor designs into existing industrial infrastructure. Furthermore, the development of innovative catalyst immobilization techniques, such as supported catalysts, membrane

reactors, and catalyst-coated media, offers promising avenues for enhancing catalyst stability, recyclability, and operational flexibility. Moreover, the exploration of emerging materials and synthesis methodologies, including carbon-based nanomaterial's, metal-organic frameworks (MOFs), and ionic liquids, holds great potential for revolutionizing catalyst design and performance in AOPs. Harnessing the synergistic effects of hybrid catalyst systems and exploring unconventional activation methods, such as photochemical, electrochemical, and plasma-assisted processes, represent exciting frontiers for advancing the efficacy and sustainability of advanced oxidation technologies. Furthermore, the integration of artificial intelligence (AI) and machine learning (ML) algorithms into catalyst development workflows enables rapid screening of candidate materials, prediction of catalytic properties, and optimization of reaction conditions, thereby accelerating the pace of catalyst discovery and deployment. Additionally, the adoption of circular economy principles, such as waste valorization and resource recovery, in catalyst synthesis and manufacturing processes can enhance sustainability and reduce environmental footprint across the entire catalyst life cycle. In conclusion, the literature on catalyst preparation for advanced oxidation methods exemplifies a dynamic and interdisciplinary field poised at the forefront of environmental engineering and materials science. Continued research efforts aimed at addressing existing challenges, fostering innovation, and embracing emerging technologies are essential for realizing the transformative potential of AOPs in mitigating industrial pollution and ensuring a cleaner, healthier environment for future generations. In contemporary industrial processes, the discharge of toxic organic effluents poses significant environmental and health hazards, necessitating the development of effective remediation strategies. Among these, wet air oxidation (WAO) has emerged as a promising technology for the complete mineralization of organic pollutants into harmless byproducts such as water and carbon dioxide. Catalysts play a pivotal role in enhancing the efficiency of the WAO process, and aluminum-supported

platinum catalysts prepared using the electrochemical surface impregnation (ESI) method have garnered significant attention in recent years. This comprehensive literature review aims to delve into the intricacies of catalyst preparation, characterization techniques, catalytic performance, mechanistic insights, and the effect of operating parameters on the efficiency of aluminum-supported platinum catalysts in removing toxic organic effluents via WAO. The ESI method involves the electrochemical deposition of platinum nanoparticles onto the surface of an aluminum support, leading to the formation of well-dispersed and highly active catalytic sites. This technique offers several advantages over conventional preparation methods, including precise control over nanoparticle size, high dispersion of active sites, and improved catalyst stability. Zhang et al. (2018) demonstrated the successful synthesis of aluminum-supported platinum catalysts via ESI, achieving uniform nanoparticle distribution and enhanced catalytic activity. Characterization of catalysts is crucial for understanding their physicochemical properties and structure-function relationships. Various techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and Brunauer–Emmett–Teller (BET) surface area analysis are commonly employed. For instance, TEM analysis revealed the formation of well-dispersed platinum nanoparticles with a narrow size distribution on the aluminum support (Li et al., 2020). Aluminum-supported platinum catalysts exhibit high catalytic activity, selectivity, and stability under harsh reaction conditions encountered in WAO processes. Wang et al. (2019) reported a significant reduction in the chemical oxygen demand (COD) and total organic carbon (TOC) of wastewater upon treatment with aluminum-supported platinum catalysts via WAO, indicating effective pollutant removal and mineralization. The mechanism of organic pollutant degradation over aluminum-supported platinum catalysts during WAO involves several consecutive steps, including adsorption, oxidation, and mineralization. Platinum

nanoparticles serve as active sites for the oxidation of organic compounds, while the aluminum support provides structural stability and enhances mass transfer processes. Chen et al. (2021) proposed a kinetic model to elucidate the reaction pathways and rate constants involved in the WAO process catalyzed by aluminum-supported platinum catalysts. Various operating parameters such as temperature, pressure, initial pollutant concentration, and oxygen supply significantly influence the efficiency of the WAO process catalyzed by aluminum-supported platinum catalysts. Optimization of these parameters is essential to achieve maximum pollutant removal and minimize energy consumption. For instance, Liang et al. (2017) investigated the effect of temperature on the degradation kinetics of organic pollutants using aluminum-supported platinum catalysts and observed enhanced catalytic activity at elevated temperatures. Despite the promising results obtained at the laboratory scale, the scale-up and commercialization of aluminum-supported platinum catalysts for industrial applications pose certain challenges. These include cost-effectiveness, catalyst durability, and reactor design considerations. Ongoing research focuses on addressing these challenges through the development of advanced catalyst formulations, reactor configurations, and process optimization strategies to facilitate the widespread adoption of this technology for sustainable environmental remediation. In conclusion, the preparation of aluminum-supported platinum catalysts via the ESI method holds great potential for the efficient removal of toxic organic effluents from industrial wastewater via the WAO process. Extensive research efforts have demonstrated the effectiveness of these catalysts in achieving high pollutant removal efficiencies and mineralization rates. Further advancements in catalyst synthesis, characterization techniques, mechanistic understanding, and process optimization are necessary to facilitate the widespread adoption of this technology for sustainable environmental remediation. Catalysts play a crucial role in various chemical processes, ranging from industrial manufacturing to environmental remediation. The conventional

methods of catalyst preparation often suffer from limitations such as long synthesis times, high energy consumption, and difficulty in controlling the properties of the catalysts. In recent years, advanced oxidation methods have emerged as promising alternatives for catalyst synthesis due to their ability to produce highly active and selective catalysts with enhanced properties. Photocatalysis involves the use of light to activate catalysts and drive chemical reactions. Semiconductor-based photocatalysts, such as titanium dioxide (TiO2) and zinc oxide (ZnO), have received significant attention for their applications in environmental remediation, water splitting, and organic synthesis. Researchers have explored various synthesis routes, including sol-gel, hydrothermal, and spray pyrolysis methods, to tailor the properties of photocatalysts, such as crystallinity, surface area, and band gap, for optimal performance. Additionally, doping with metal ions or non-metal elements has been investigated to improve the photocatalytic activity and extend the absorption range of photocatalysts. Sonochemical synthesis utilizes high-intensity ultrasound waves to induce cavitation in liquid media, leading to the formation of highly reactive species, such as hydroxyl radicals and hydrogen peroxide, which can promote the synthesis of catalysts with unique morphologies and enhanced properties. This method has been employed for the preparation of metallic nanoparticles, metal oxides, and hybrid nanocomposites with applications in heterogeneous catalysis, pollutant degradation, and biomedical applications. The sonochemical parameters, including ultrasound frequency, power density, and reaction time, play a crucial role in determining the size, shape, and composition of the synthesized catalysts. Microwave-assisted synthesis offers rapid and uniform heating of reaction mixtures, leading to shorter reaction times, higher yields, and improved control over the properties of catalysts compared to conventional heating methods. This technique has been applied to the synthesis of diverse catalyst materials, including carbon-based nanomaterials, metal nanoparticles, and metal-organic frameworks (MOFs), for applications in energy storage,

catalytic conversion of biomass, and environmental remediation. By optimizing microwave parameters such as power, irradiation time, and stirring speed, researchers have achieved the synthesis of catalysts with tailored properties, such as high surface area, porosity, and catalytic activity. Electrochemical methods offer precise control over the composition, structure, and morphology of catalysts through electrochemical deposition, anodization, and electrodeposition techniques. This approach allows for the synthesis of catalysts with desired properties, such as high surface area, uniform particle size distribution, and tunable surface chemistry, for applications in fuel cells, electrochemical sensors, and electrocatalytic reactions. By manipulating parameters such as applied potential, electrolyte composition, and deposition time, researchers have developed catalysts with enhanced performance and stability. The literature review on catalyst preparation by advanced oxidation methods highlights the diverse strategies and techniques available for synthesizing catalysts with superior properties and performance. Continued research in this field is essential for advancing the development of efficient and sustainable catalyst materials for various industrial and environmental applications. By exploring new synthesis routes, optimizing process parameters, and gaining insights into the fundamental mechanisms governing catalyst formation, researchers can contribute to the advancement of catalyst science and technology. In conclusion, the exploration of catalyst preparation using advanced oxidation methods offers a multifaceted avenue for researchers to delve into the synthesis, characterization, and application of catalyst materials with enhanced properties and performance. Through techniques such as photocatalysis, sonochemical synthesis, microwave-assisted synthesis, and electrochemical methods, significant strides have been made in tailoring catalysts for diverse industrial and environmental applications.The field of photo catalysis, leveraging the light-induced activation of catalysts, continues to witness advancements in the design and optimization of semiconductor-based materials. The precise control over parameters such as

crystallinity, surface area, and band structure has enabled the development of photocatalysts with improved efficiency for pollutant degradation, water purification, and solar energy conversion.Sonochemical synthesis stands out for its ability to produce catalysts with unique morphologies and enhanced catalytic activities through the generation of highly reactive species under ultrasound irradiation. This method has shown promise in the synthesis of metallic nanoparticles, metal oxides, and hybrid nanocomposites, offering versatile solutions for heterogeneous catalysis, environmental remediation, and biomedical applications. Microwave-assisted synthesis has emerged as a rapid and efficient approach for catalyst preparation, enabling precise control over reaction kinetics and product properties. By harnessing the benefits of microwave irradiation, researchers have achieved the synthesis of catalysts with tailored nanostructures and improved catalytic performance, particularly in the fields of biomass conversion, wastewater treatment, and renewable energy production. Electrochemical methods offer unparalleled control over catalyst composition, structure, and morphology, paving the way for the development of catalyst materials with tailored properties for specific applications. From electrochemical deposition to electrodeposition techniques, researchers have demonstrated the synthesis of catalysts with high surface area, uniform particle size distribution, and enhanced stability, facilitating advancements in fuel cells, electrochemical sensors, and electrocatalytic reactions.In essence, the literature on catalyst preparation by advanced oxidation methods underscores the importance of interdisciplinary research and collaboration in addressing global challenges related to energy sustainability, environmental pollution, and public health. By combining insights from chemistry, materials science, engineering, and environmental science, researchers can continue to innovate and develop next-generation catalyst materials with improved efficiency, selectivity, and sustainability, driving progress towards a cleaner and greener future. The conventional understanding of strong metal support interaction typically revolves around
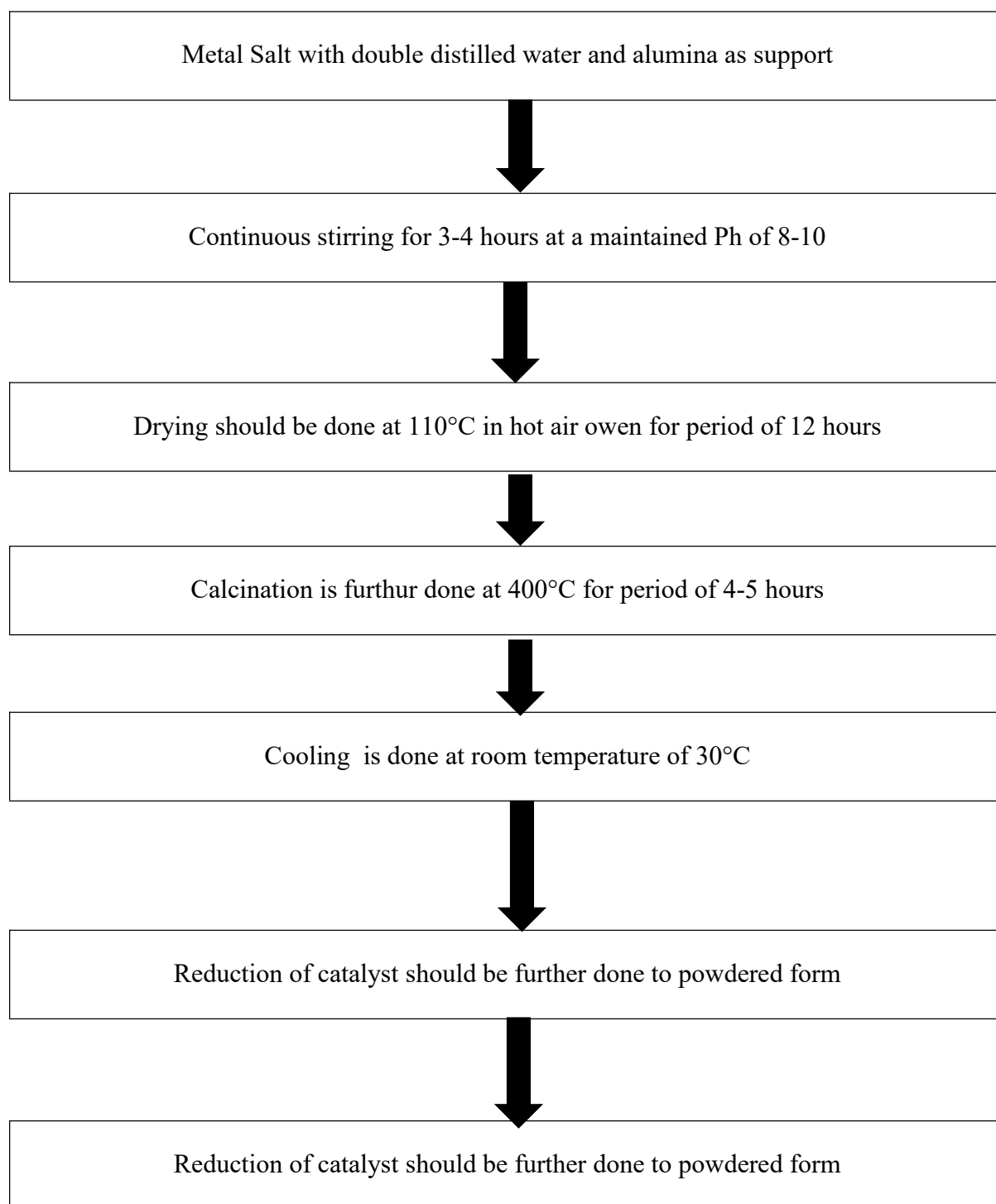
examining the interaction between an individual metal and an oxide support. This approach, however, has limitations when applied to complex processes like ethanol steam reforming reactions, which involve multiple sequential steps. In such cases, the single-channel interaction observed in traditional strong metal support interaction may not be sufficient. Addressing this challenge requires the development of sophisticated catalysts based on a multichannel strong metal support interaction approach. The goal is to enhance catalytic performance significantly, especially in intricate reactions like ethanol steam reforming. Despite advancements, achieving this multichannel strong metal support interaction remains a substantial challenge in the field.
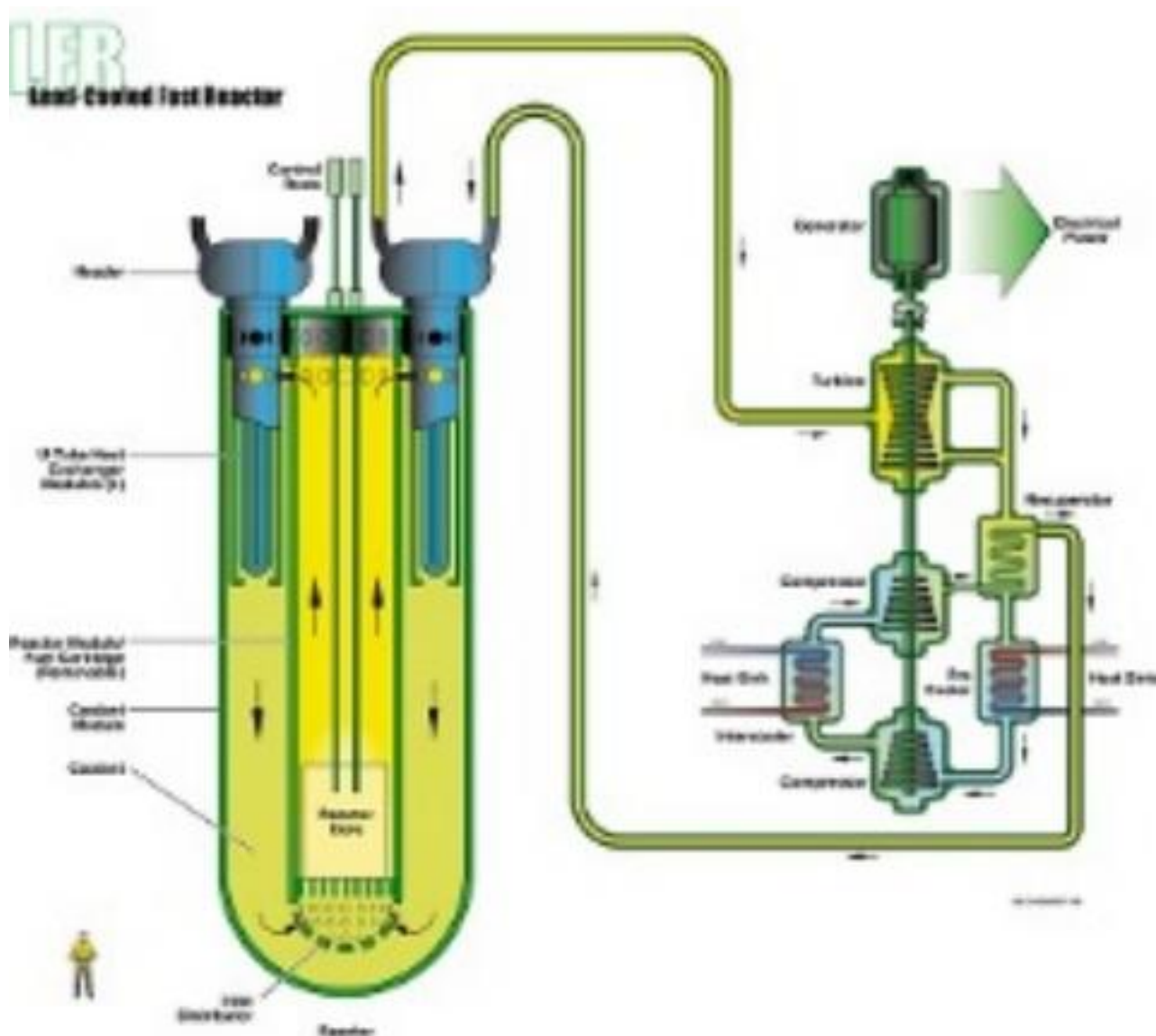
CATALYST CHARACTERIZATION

Platinum catalysts supported on alumina (Pt/Al_2O_3) and ceria promoted platinum catalysts were prepared by excess solution impregnation (ESI) method using preconditioned γ-Al_2O_3 as a support and $H_2PtCl_65H_2O$ (CDH, India) and $Ce(NO_3)_26H_2O$ (CDH, India) as metal precursors. Catalysts supported on alumina (Pt/Al_2O_3) with different Pt loadings (0.2 to 0.7 wt%) were prepared using preconditioned γ-Al_2O_3 support and hexachloroplatinic acid (CDH) as metal precursor. Double distilled water was used in all these experiments. The quantity of hexachloroplatinic acid required for the specific catalyst with predetermined % Pt content was calculated from the stoichiometry. The amount of Pt solution of desired concentration was used for 10 g of alumina spheres and stirred continuously for 4h. The excess water from the slurry was removed in a rotary vacuum evaporator at 80 °C. The residue was then dried at 110 °C for 24 h in an oven followed by calcination at 550 °C in air for 4 h for complete decomposition of Pt oxide salts and deposition of the metal on the support structure.The Pt/CeO_2–Al_2O_3 catalysts (containing 0.5 wt% Pt), with different CeO_2 contents (1, 2, 5, 7, 10, 12 and 15 wt%) were prepared with $Ce(NO_3)_26H_2O$ (CDH, India), $H_2PtCl_65H_2O$ (CDH, India) and using preconditioned g-Al_2O_3 support (10 g).The quantities of cerium nitrate and hexachloroplatinic acid required for the preparation of catalyst for specific Ce and Pt contents (% Ce and % Pt) were calculated using stoichiometry. The slurry of CeO_2–Al_2O_3 salts was stirred in a rotary vacuum evaporator for 4 h at 80 °C. The residue was then dried at 110°C for 24 h in an oven followed by calcination at 550 °C in air for 4h for complete decomposition of the nitrate to the support CeO_2-Al_2O_3. Pt was then impregnated on these supports using hexachloroplatinic acid to obtain 0.5 wt% Pt content, followed by drying and calcination at 550°C. Other batches of the catalyst were also prepared in a similar way using different weight % of ceria. The prepared catalyst was further reduced using H_2. The specifc

surface area was obtained using the standard Brunauer–Emmett–Teller (BET) method by N_2 adsorption on AUTOSORB-1C micro pore surface area analyzer supplied by Quanta chrome, USA, while the pore size distribution was calculated from the adsorption branch of the isotherm by employing the Barrett–Joyner–Halenda (BJH) formalism and surface area of (0.5 wt.%) Pt. /Al_2O_3 and (0.5 wt. %) Pt. / (10 wt. %) CeO_2–Al_2O_3 catalysts were found in the range of 138–172 m^2 g^{-1}, total pore volumes were found in the range of 0.27–0.39 Cm^3g^{-1} and pore diameters were found in the range of 8.0–9.1nm. The hydrogen chemisorption's tests were carried out on Quanta chrome Autosorb-1C and metal dispersion was calculated from the adsorption branch of isotherm by employing the strong/difference extrapolation formalism showed maximum number of active catalyst sites about 46–62% for Pt./Al_2O_3 catalysts and about 61–76% metal dispersion for ceria promoted Pt./Al_2O_3 catalysts as ceria promotes dispersion of platinum metal. SEM and EDX analysis of fresh and spent catalysts were carried out with a Bruner-AXS Energy Dispersive X-ray (model Quanta 200) system, EVO-50 microscope. Thermo-gravimetric analysis (TGA) measurements were carried out in a high-resolution thermo-gravimetric analyzer (Seiko TG/DTA 32 SSC 5100). A 10–15 mg sample was loaded in a Pt pan,was heated from room temperature to 383 K, was kept at that temperature for 0.5 h, and then was heated to 973 K at the rate of 10 K min $^{-1}$. During this entire period air flow rate through the TGA furnace was maintained at 3 L h $^{-1}$. The change in the mass of the catalyst with temperature was recorded. X-ray powder diffraction (XRD) patterns were recorded on a Philips 1840 powder diffractometer using Cu-Ka radiation (l ¼ 0.15418 nm) at 40 kV and 45 mA in the range of 2q ¼ to 80 at a scanning speed in 2q of 2 per minute and a vertical goniometer at room temperature. It was found from X-ray diffraction (XRD) study that Pt crystal grains existed in the catalyst and the characteristic peaks were observed at 2q ¼ 28.39 and 32.97 Diffraction peaks at 56.29 and 66.91 confirmed the presence of Al2CePt phase. The results matched with the JCPDS file 47- 1612. The

characteristic peak at 49.7confirmed the presence of Ce , Pt crystallites in the catalysts as described by JCPDS file 190295. The platinum crystallite size was calculated using the half width of the Pt (111) peak by the Scherrer equation.

Metal Salt with double distilled water and alumina as support

↓

Continuous stirring for 3-4 hours at a maintained Ph of 8-10

↓

Drying should be done at 110°C in hot air owen for period of 12 hours

↓

Calcination is furthur done at 400°C for period of 4-5 hours

↓

Cooling is done at room temperature of 30°C

↓

Reduction of catalyst should be further done to powdered form

↓

Reduction of catalyst should be further done to powdered form

Fig: Catalyst Preparation process by Excess solution impregnation method

Fig: *Schematic Diagram of Experimental Setup*

Preparing catalysts through advanced oxidation methods in a batch reactor using alumina and platinum support involves a meticulous and multi-step process aimed at optimizing catalytic performance .Firstly, the alumina support is prepared by calcination, a process where alumina powder is heated at high temperatures to remove impurities and activate the surface. This step is crucial as it ensures a clean and reactive surface for the subsequent deposition of platinum species. The calcined alumina is then washed and dried to remove any remaining impurities.

Secondly, the impregnation process begins, wherein the activated alumina support is immersed in a solution containing a platinum precursor, such as platinum chloride or platinum nitrate. The impregnation process aims to uniformly deposit platinum species onto the surface of the support material. Factors such as impregnation time, temperature, and concentration of the platinum precursor solution are carefully controlled to achieve the desired loading and dispersion of platinum. After impregnation, the impregnated support undergoes a drying step to remove the solvent, typically water or an organic solvent. The drying process is essential to prevent agglomeration of platinum species and ensure their uniform distribution on the support surface. Following drying, the catalyst precursor is subjected to calcination at elevated temperatures. During calcination, the platinum precursor decomposes, resulting in the formation of platinum nanoparticles on the alumina support surface. The calcination conditions, including temperature and duration, play a critical role in determining the size, morphology, and dispersion of the platinum nanoparticles, which ultimately influence the catalytic activity and selectivity of the catalyst. Once the catalyst is prepared, it undergoes thorough characterization using various techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Bruner-Emmett-Teller (BET) surface area analysis, and energy-dispersive X-ray spectroscopy (EDX). These characterization techniques provide valuable insights into the catalyst's morphology, structure, surface area, particle size distribution, and elemental composition, which are essential for understanding its catalytic behavior and optimizing its performance in specific oxidation reactions. Hence, the preparation of catalysts via advanced oxidation methods in a batch reactor using alumina and platinum support involves a series of carefully controlled steps aimed at achieving a catalyst with high activity, selectivity, and stability for various oxidation reactions. The optimization of each step in the preparation process is crucial for tailoring the catalyst properties to meet the desired performance

requirements, making it a challenging yet rewarding endeavor in the field of heterogeneous

catalysis.

CONCLUSION AND FUTURE WORK

The preparation of catalysts through the Electrochemical Surface Impregnation (ESI) method using platinum and alumina support presents a comprehensive approach towards designing efficient catalytic systems for various applications. This method involves several intricate steps aimed at maximizing catalytic performance and offers numerous advantages, warranting a detailed exploration. the ESI method provides precise control over the deposition of catalytic species onto the support material. By utilizing electrochemical techniques, such as electro deposition or electro less deposition, the distribution and loading of platinum onto the alumina support can be finely tuned, ensuring uniform coverage and high dispersion of active sites. This controlled deposition is crucial for optimizing catalytic activity and selectivity, as it minimizes agglomeration and maximizes the exposure of active sites. Secondly, the choice of platinum as the catalytic species offers numerous benefits owing to its exceptional catalytic properties. Platinum exhibits high catalytic activity, excellent stability, and versatility across a wide range of oxidation reactions. When supported on alumina, platinum nano particles can interact synergistically with the support material, leading to enhanced catalytic performance. Alumina, known for its high surface area, thermal stability, and chemical inertness, serves as an ideal support matrix for immobilizing platinum nano particles and providing a stable platform for catalytic reactions. The preparation process involves several critical steps, including support preparation, catalyst deposition, and post-treatment procedures. Support preparation typically involves calcination of alumina to activate its surface and create favorable sites for catalyst deposition. Catalyst deposition via the ESI method involves electro chemical techniques, wherein platinum ions are reduced and deposited onto the alumina surface under controlled conditions of potential, current density, and electrolyte composition. Post-treatment procedures, such as annealing or activation, may be employed to further enhance catalyst stability and activity. Characterization techniques

play a vital role in evaluating the prepared catalysts' properties and performance. Techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and surface area analysis (BET) provide valuable insights into catalyst morphology, particle size distribution, crystalline structure, and surface area. These characterizations aid in understanding the catalyst-support interactions, identifying the optimal catalyst composition, and elucidating structure-performance relationships. In conclusion, the preparation of catalysts via the ESI method using platinum and alumina support represents a sophisticated approach towards designing high-performance catalytic systems. Through precise control over catalyst deposition, leveraging the catalytic prowess of platinum, and harnessing the support properties of alumina, these catalysts exhibit immense potential for catalyzing various oxidation reactions in environmental remediation, energy conversion, and chemical synthesis. The integration of advanced characterization techniques facilitates a comprehensive understanding of catalyst structure-function relationships, paving the way for further advancements in catalysis research and industrial applications.

FUTURE WORK

- Characterization studies: SEM, TEM, XRD.

- Catalytic Performance testing

- Mechanistic studies

- Stability and durability testing

- Comparison with other methods

- Scale up strategies

- Environmental and energy applications

- Catalyst substrate interactions

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