

Atmospheric plasma in the preparation and pre-treatment of catalytic materials – A mini review

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ABSTRACT

This review paper presents a concise summary selected plasma-assisted catalyst preparation and pre-treatment methods. It provide classification of reported plasma techniques used for catalyst preparation and give examples for their applications. The paper also discusses the advantages and disadvantages of plasma-assisted methods for the synthesis of catalytic materials. The challenges associated with the use of plasma in the preparation of catalytic materials are also presented. The opportunities for the application of plasma in the preparation of catalysts for generation of advanced materials and improving industrial processes are also highlighted.

1. Introduction and scope of the review

Catalytic systems play a crucial role in the manufacture of key products that are essential for the prosperity of our civilisation such as chemicals, fuels, plastics and fertilizers. Catalysts allow for a chemical reaction to be carried out at a lower temperature and pressure, with higher yields and selectivity to the desired product(s). For a catalytic process to occur with maximum efficiency, catalyst preparation is of utmost importance [1–3]. However, there are many drawbacks to the conventional preparation methods that are currently used to prepare catalytic materials. The most important of these is the large number of chemicals required during catalyst synthesis and to precipitate or reduce the components of the active phase during the preparation step. The best known and most widely used methods of catalyst synthesis are impregnation, sol-gel, precipitation, and co-precipitation. All these methods generate enormous amounts of unnecessary chemicals. These chemicals generate chemical waste that needs to be treated at great cost and pollute the environment. If a more efficient process for catalyst preparation is available, these chemicals can be utilised in manufacture of other products that advance the society and industry, or not used at all, thus generating environmental and economic benefits [4–8].

One solution to this problem may be found in the utilisation of plasma technology. Plasma itself does not require the introduction of

additional chemicals during catalyst synthesis and to precipitate or dissolve the active phase components. Plasma is the fourth state of matter and is composed of charged species, electrons and ions. The excited species making up the bulk of plasmas provide high reactivity, effusion of radiation and capacity to direct and modulate by applying external electric and magnetic fields [7,9]. Plasma can be generated by various electrical discharges and can be classified into high and low-temperature plasma (thermal and cold plasma). Cold and thermal plasma are widely used in the production of various materials and catalysts. In the case of cold plasma, also called non-equilibrium plasma, the bulk temperature can be maintained even at room temperature while the electron temperature reaches a temperature between 10,000–100,000 K (1–10eV) [10]. In contrast, in thermal plasmas (equilibrium plasmas), the bulk gas temperature is close to the electron temperature, reaching tens of electron volts [7].

The use of plasma in the production of the catalytic materials allows to limit the number of preparation steps used in the synthesis of catalytic materials by conventional methods and to speed up the synthesis process itself. The use of plasma in the catalyst synthesis allows for production of metallic [11], bimetallic and even alloy systems with specific catalytic and physicochemical properties [12,13]. In addition, plasma pre-treatment of the catalyst allows for the reduction of the active phase component present on the catalyst surface at a much lower temperature

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compared to the conventional methods used for modification of catalyst surfaces. Plasma activation of the catalyst changes its electronic properties and thus has a direct effect on its adsorption properties. Heterogeneous catalysts prepared by plasma-assisted methods were shown to have a high metallic dispersion and to exhibit high activity and selectivity in the studied processes. The plasma-assisted synthesis of catalytic materials allows for the preparation of systems with defect-rich surfaces, heteroatom-doped catalysts, and controllable structure. Plasma is also used for the cleaning and special pre-treatment of catalyst surfaces. Furthermore, plasma is a well-suited technology for coating and etching of catalytic surface [12,14–19].

This concise review paper we summarize selected reports concerned with plasma technologies used in the preparation of the heterogeneous catalytic system and other materials that can potentially be used in catalytic systems. We provide classification of reported plasma techniques and give examples for their applications. We also discuss the challenges and opportunities for plasma techniques in catalysts preparation.

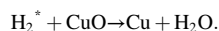
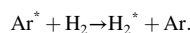
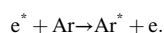
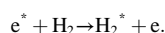
2. Preparation of the heterogeneous catalysts by means of plasma

The interaction of the plasma with the species present on the surface of a catalyst leads to the formation of particles which are predominantly negatively charged. This charge generation prevents agglomeration and allows for the synthesis of highly dispersed nanometre scale particle. The electrons that are created in the plasma can also lead to the reduction of metallic ions that are present on the surface of the catalyst to metallic particles. The reduction process itself takes place at a much lower temperature than when conventional thermal method. The electrons produced in the plasma are a cost-effective way for reducing metal ions with positive standard electrode potentials. The electrons can react with water to produce hydrated electrons and radicals that can reduce the metallic precursors. The interaction of electrons with molecules and/or precursors leads to irreversible growth of nanoparticles. In the case of the hydrogen-generated plasma, both hydrogen radicals and electrons can interact with the ionic species present on the catalyst surface, leading to the formation of reduced metallic particles. Molecules, atoms, and radicals are also involved in the plasma catalyst preparation. It should be noticed that various reactive and excited species are produced in addition to electrons, the type of which depends of the plasma atmosphere. The excited molecules/atoms or generated radicals may migrate to the inside or outside of the pores of the catalysts and change the phase composition and/or physicochemical properties of the treated catalysts. This effect can have an enormous impact on the activity of the catalyst material used during the process as well as its selectivity [14,20,21].

Activation of the surface by reactive radicals or by excited molecules or atoms can change the structural or electronic properties of the surface of the catalytic systems. The catalytic material whose surface has been activated can more readily adsorb reactants from the gas phase via the Langmuir-Hinshelwood or Eley-Rideal mechanism [22]. In addition, the use of plasma itself to activate or prepare the catalyst material leads to an improvement in the reactivity of the catalyst in various processes [4,19,23–26]. The activation of the surface or the preparation of the catalytic material in the contribution of the plasma lead to the reduction, oxidation, decomposition, deposition of the catalyst components or can also be carried out by doping or etching processes. One of the main advantages of the plasma-assisted catalyst synthesis method is the dynamics of the process. The plasma is used for a short period of time during the catalyst preparation step. This type of catalyst synthesis route does not require the application of chemicals to precipitate, dissolve or reduce the active phase species during the preparation step. In addition, plasma-assisted synthesis allows the cost of the catalyst preparation to be reduced [3,7,9,10,13,18,22,27].

2.1. DBD Plasma assisted pre-treatment method

Lan-Bo Di et al. [28] studied the plasma pre-treatment of copper catalysts. In their work, they used a DBD reactor to synthesize the catalyst using different gases with a constant flow between two stainless-steel electrodes. The distance between the electrodes was 4 mm. During the synthesis, a sinusoidal (36 kV) high voltage (14.1 kHz) was applied under atmospheric pressure at room temperature in a hydrogen or hydrogen-argon mixture gas mixture (H₂-Ar(N₂)). When pure argon or a nitrogen-argon mixture was used, the reduction process did not continue. However, when a mixture of H₂-Ar was applied, this resulted in a reduction of the CuO. A maximum reduction was seen in a mixture containing 20% of H₂. The authors explained these results by the collisions of the reactants in the plasma and, as a consequence, the generation of reactive hydrogen and energetic electrons. Optical emission spectroscopy (OES) measurements performed during the reduction process in different gases showed that excited hydrogen atoms radicals, heating effect or atomic hydrogen are responsible for the reduction of CuO. The authors proposed the possible mechanism of the process, which involves several steps:



According to the results obtained, the authors proposed that the first step involves the interaction of the hydrogen molecules with electrons, which generate excited hydrogen molecules. At the same time, argon flowing in the discharge zone generates metastable argon species, which in the next step, can interact with the hydrogen molecules and generate additional numbers of excited hydrogen molecules. The excited hydrogen radicals formed are consumed during the reduction of the CuO species to metallic Cu.

L.B. Di et al. [29] also investigated the possibility of plasma application in the preparation of bimetallic Pd-Cu heterogeneous catalysts. They simply applied an impregnation method to prepare a bimetallic Pd-Cu catalyst and then reduced this system using DBD atmospheric cold plasma. They produced highly active fine PdCu alloy which showed high performance in the CO oxidation process. The alloy formation between Pd and Cu was confirmed by XRD and XPS techniques. The high activity of the formed alloy was attributed to the fine-sized particles of the alloy phase and their dispersion on the catalyst surface. The authors highlighted the fact that the cold plasma DBD method allows for the preparation of the alloy phase during the rapid low-temperature reduction process. Zhicheng Tang et al. [30] studied Vulcan XC-72 carbon black as a support material for Pt catalyst. The pre-treatment of the support materials was carried out using a PGT-II plasma system with a frequency of 40 MHz and a power of 200 W. They reported that plasma treatment of the investigated carbon material using different atmospheres such as H₂, Ar and O₂ had a tremendous effect on the physicochemical properties of the catalytic material. The prepared materials were evaluated in the methanol electrooxidation process. The results showed that the Ar and H₂-treated plasma systems had fine Pt particles on their surface. In addition, the physicochemical measurements carried out on the carbonaceous material also showed that the microstructures and functional groups present on the surface of the plasma-treated supports were altered. The results confirmed that the plasma generated atmosphere plays a crucial role in the pre-treatment of the material. It was also found that the H₂-treated plasma gave the highest yield in the catalytic process studied, and resulted in the smallest Pt particles of 2.6 nm.

In another work [31], CeO₂ support was synthesized by

hydrothermal method and treated by dielectric barrier discharge plasma with AC frequency of 1.8 kHz. The final support was then impregnated with a significant amount of platinum salts. Part of the impregnated Pt catalyst was also activated in the plasma. During the discharge, a flow of 100 ml/min was applied with a mixture of 20% O₂ and 80% N₂. In the next step, the catalyst was dried and calcined and its properties were studied using various techniques. The discharge process was carried out for 30 min with an input power of 4.8 W. It was demonstrated that smaller particles were formed after a reaction performed in dry atmospheric plasma in a DBD reactor (see Fig. 1.) [31]. Pt particles can be recombined as a result of the reaction with energetic electrons to form smaller Pt particles on the catalyst surface [32]. Both catalysts and supports were both evaluated in toluene oxidation. The results showed that the plasma activated Pt system was the most active. The high activity of this system was attributed to the high dispersion of Pt on the surface and the highest concentration of oxygen vacancies in the catalytic system. In addition, the Pt/CeO₂-P (P stands for plasma treated) system showed the highest stability in the toluene oxidation process. It was also reported that the plasma discharge changes the oxidation state of Ce and Pt, which is also responsible for the easier oxidation of toluene.

Another possible method of producing metallic particles is low-temperature plasma reduction [33]. This is a new green synthesis method that can be used to produce metal nanoparticles without the use of chemicals. The species generated in the plasma, such as energetic electrons, hydrogen radicals and others, lead to the effective reduction of metal ions. The advantage of this method is the slow crystal growth at low temperatures and the rapid nucleation of the crystals in the plasma. Two methods of reduction can be distinguished. For the metal ions with positive standard electrode potential such as Pd, Au, Pt, and Ag, a non-hydrogen plasma technique can be used. On the other hand, for the metal ions with negative standard electrode potential, hydrogen plasma technology must be used. The authors of reference [33] synthesized metallic Ag particle using a hydrogen DBD cold plasma system on the

surface of N-doped TiO₂ nanotubes. N-doped TiO₂ nanotubes were obtained by an ion-exchange method. The authors reported the generation of metallic silver particles with an average particle size of 5.8 nm. The Ag/N-TiO₂ system formed showed adsorption capacity in the visible light region together with the lower recombination rate of charge carriers.

An HVACP (high-voltage atmospheric cold plasma) DBD system was applied in order to activate the Ru—Ni bimetallic catalysts and tested in the isomerization of grape seed oil. High alternating voltage in the range 0–130 kV was used during the experiments [34]. During the experiments two gases were used: pure hydrogen and a mixture of H₂/He. During each experiment firstly pure H₂ was flown through the DBD system (800 ml/min) in order to reduce oxygen. Then the placed into the HVACP system and a mixture H₂—He (100 ml/min) was passed through the system for 10 min. During the activation process a high voltage was applied (80 kV) to the electrodes to initiate the HVACP at 25 °C. An activation process was carried out for 60, 120, 180, 240 and 300 s using various power: 50, 100, 150, 200 and 250 W, respectively. During the activation process of the catalytic material the following gas composition was applied: 1% H₂/99% He, 3% H₂/97% He, 5% H₂/95% He, 7% H₂/93% He, and 9% H₂/91% He. The obtained results clearly indicate that the catalyst activated during plasma treatment for 180 s with the power 150 W using gas composition 5% H₂/95% He exhibited higher specific surface area, increased pore size distribution, better dispersion, a higher atomic ratio of Ru—Ni and higher activity in the tested reaction [35].

Gold nanoparticles (NPS) prepared using an atmospheric pressure Dielectric Barrier Discharge (DBD) plasma torch fed with a nebulized Au precursor solution was reported in the work [36]. According to Ghosh et al. Ni NPS were produced using the nickelocene vapor [36]. The literature data shows that the synthesis of the gold nanoparticles is possible using several configuration of the plasma torches. The gold nanoparticles were produced from Tetrachloroauric (III) acid trihydrate

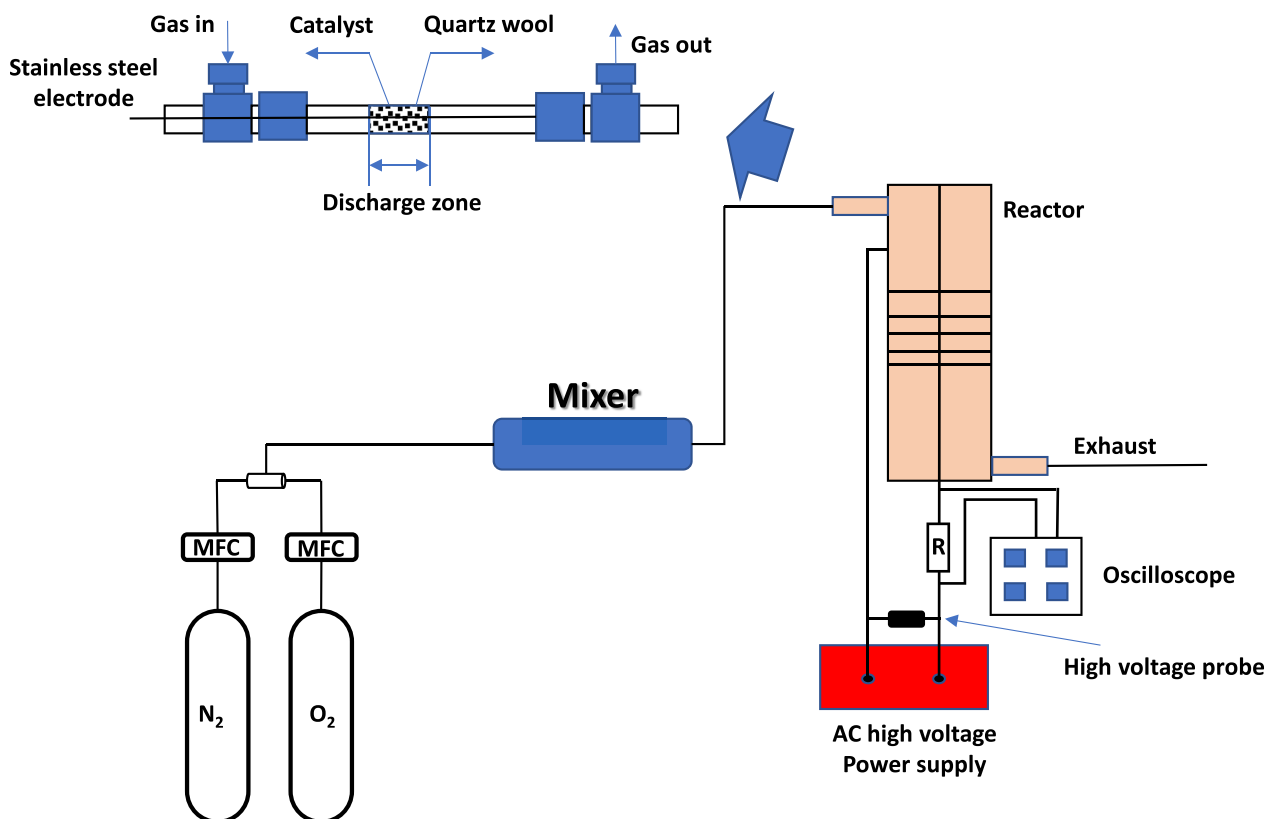


Fig. 1. Schematic of treatment of a DBD system; figure reconstructed from reference [31].

($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, >99.9%) precursor which was dissolved in a solvent mixture ethanol and/or water. The solution containing gold precursor was introduced into the plasma using ultrasonic nebulizer (Sono-Tek®, 1 W, $f = 120$ kHz) which generate the droplets size between 10 and 100 nm. Then the generated droplets were transferred near post-discharge using argon gas (10 slm flow rate). During the experiment the DBD system was used with a coaxial geometry containing 2 concentric hollow quartz tubes. The plasma was generated between the inner tube and the outer tube. It is also worth to indicate that the inner tube was coated on its outer surface by 300 nm Pt thick film and connected to the ground. While, the outer quartz tube was covered by a 5 cm long Al foil which was also connected to the high voltage generator (AFS generator, 52 kHz, 20 W) [37]. This configuration allow to generated the plasma between those two tubes. The authors also investigated various parameters of the Au deposition process. In dielectric discharge (DBD) plasma torch experiments, the precursor concentration was 0.25 g/L during the 10 min deposition. Pure ethanol, a mixture of ethanol and water (with 25 and 50 vol% water) and pure water were used as solvents during the deposition process. In addition, the deposition process was carried out with a precursor of the same concentration dissolved in ethanol at a concentration of 0.25 g/L for 1, 5, 10, 30 and 60 min. The results of their studies showed that the increasing of the water concentration in a mixture which was applied during the deposit process result in agglomeration tendency. TEM analysis performed for the sample obtained after deposition process of gold using gold precursor concentration equal 0.25 g/l in ethanol and for the 10 min of the conducting process with plasma enables to obtain a homogeneous dispersion of gold NPs. SEM measurements performed for the investigated gold containing materials generated after various deposit time showed that density of NPs was changed with increasing of the deposition time. Gold NPs with high dispersion of metal were created by plasma treatment. This results authors assigned to the carbon matrix formed on the surface of Au NPs produced from the ethanol solution. It was also found that carbon matrix prevents the Au NPs agglomeration [37].

In a non-equilibrium plasma, free electrons have an energy of several eV, which is sufficient energy to initiate dissociation, excitation and ionization processes and thus enable plasma chemical reactions. Organic metal compounds dissociate in the plasma to produce oversaturated metal vapours and other radicals or their fragments, which then subsequently condensing and/or coagulating to produce nanoparticles. For this reason, this method has recently been used to produce nanoparticles from metallocene precursors, including ferrocene [38–43]. Due to the very complex decomposition process in plasma, most studies in the literature only focus on optimizing processes and material properties without delving into the mechanism of the processes taking place. However, the optical emission spectroscopy (OES) technique can provide us with valuable information about the intermediate state of radicals occurring in the plasma process, which is difficult to obtain with other in situ or ex situ analyses. For this reason, OES studies can give us some clues about the dissociation of ferrocene vapours in the microplasma [44].

Optical emission spectroscopy (OES) technique is widely used to study in situ the mechanism of the plasma-assisted CO_2 hydrogenation in dielectric barrier discharge (DBD, 6 mm O.D. \times 4 mm I.D.) reactor under atmospheric pressure. In the work [45] OES of the gas phase generated during NTP process from the blank reactor without a catalyst and the NTP process performed over 2.5% Ru/MgAl-R300 and 2.5% Ru/MgAl-R600 catalysts were analysed in order to understand the nature of the excited species formed during NTP conditions with or without the catalyst. The recorded spectra in both studied processes showed specific bands assigned to the emission from plasma in a range of 180–450 nm and the characteristic electronically excited states of CO ($b^3\Sigma + \rightarrow a^3\Pi$), $\text{CO}_2 + (\text{B}: A^2\Sigma + \rightarrow X^2\Pi)$, OH ($A^2\Sigma + \rightarrow X^2\Pi$) and CH ($A^2\Delta \rightarrow X^2\Pi$) [45,46] were observed. An analysis of the obtained spectra confirmed that the identified bands in the case of the process performed in NTP catalytic process have higher intensity compared to the non-catalytic

process. This result is explained by the higher concentration of the reactive species in the excited states which leads to higher activity in CO_2 hydrogenation reaction. The electron temperature of the NTP is about 2.8 eV which means that they can activate the stable gas molecules [47,48]. In order to confirm the reaction pathway of hydrogenation of carbon dioxide assisted by NTP process, in situ DRIFTS measurements coupled with mass spectrometry (MS) detector were performed. In addition, to compare the obtained hydrogenation reaction performed in the participation of the plasma, conventional thermochemical process at 270 °C and NTP process using different feed gases were carried out. During the thermal process over heterogenous catalyst (2.5% Ru/MgAl-R300) typical CO pathway was observed through the formation of CO and CH_4 . While, in the case of the process performed on Ru/MgAl-R600 catalyst beyond of methane and carbon dioxide also formate species were detected on the recorded spectra. The observed specific bands located on the recorded spectra assigned to formate species did not change during the conducting process what indicates that those surface species did not take a part in a methane formation. Whereas, DRIFTS measurements carried out during NTP catalytic process proceeds via more complex pathway for CO_2 conversion through more carbon species. It was shown in the literature that both gas-phase and plasma-assisted surface reactions have impact on the conversion values of the CO_2 and selectivity towards methane formation [48,49]. The results of the DRIFTS and MS studies confirmed dissociation of CO_2 to CO in a mixture of 1% CO_2/Ar mixture under the NTP conditions over 2.5% Ru/MgAl-R300 catalyst. Further during the performed experiments the influence of the plasma treatment on the created on the catalyst surface species was investigated. The analysis of the process without the plasma treatment confirmed the lack of the surface species on the recorded spectra. Then, when the plasma was generated during the conducting process the specific bands in the range assigned to linearly adsorbed COad, bidentate carbonate species immediately were detected on the recorded spectra. This result confirmed the adsorption of the excited CO_2 species during the reaction. However, the switching off of the plasma did not result in disappearance of the surface species, indicating the strong adsorption of those species on the investigated catalytic surface. An application of the reaction 1% CO_2 /4% H_2 /Ar mixture during the DRIFTS and MS measurements during thermochemical process confirmed the formation of the presence of the specific bands assigned to CO_2 peaks and confirm, that the 2.5% Ru/MgAl-R300 catalyst was not active in CO_2 hydrogenation. When the plasma was reignition the appearance of the CH_4 and decreasing of the CO_2 ($m/z = 44$) signals in MS profile was observed. In addition, the specific bands assigned to the carbonyl, carbon-hydroxyl and formyl species and methoxy species were detected on the catalyst surface using DRIFTS technique [42]. The presence of the methoxy species indicate that methanol was also formed during NTP process the formation of which was also confirmed by the appearance of the MS signal $m/z = 31$ on the spectrum. Methane formation was not observed due to its fast desorption from the catalyst surface. After switch off the plasma system the catalyst was not active. In addition, the authors also studied the evolution of the surface species during the NTP process and they confirmed that increase of the surface CO_2 intensity was observed while CH_4 signal on the mass spectrum increased continuously. Furthermore, during the conducting process also MS signals attributed to CO together with MS CH_4 were increased as a result of the proceeding of NTP process or dissociation of CO_2 on the catalyst surface. It was also found that progressive increase of the HCO_{ad} and COH_{ad} species agree well with the rate of CH_4 formation indicate that the hydrogenation of CO_2 runs via HCO and COH pathway [50–52]. Take into consideration the formation energy for HCO_{ad} (~1.25 eV) and COH_{ad} (~1.42 eV) it was confirmed that concentration of HCO_{ad} on the surface was higher. Based on these results the mechanism of the CO_2 hydrogenation was proposed and it proceeds via dissociation of CO_2 over 2.5% Ru/MgAl-R300 catalyst to carbonyl (COad) and O^* species which are hydrogenated to formyl intermediate (HCOad and COHad) species as a result of the interactions with the OH and CH excited species

detected by OES in the gas phase. Then those surface species are further hydrogenated to methane or/and methanol. The CO_2 hydrogenation mechanism is more complex during its realized on Ru/MgAl-R600 system. During the thermochemical process with CO_2/Ar gas bicarbonate, carbonate species were formed on the catalyst surface as a result of interaction of CO_2 with hydroxyl groups. Whereas, during the plasma assisted process more surface carbon species were formed including bridged and linearly adsorbed CO_{ad} , bicarbonate, bidentate carbonate and CO with O_2 which was formed via dissociation of CO_2 . During the hydrogenation of CO_2 process with the plasma treatment realized in a mixture of (i.e. 1% $\text{CO}_2/4\%$ H_2/Ar) carbonyl and oxygenated species were formed and then within 5 min they disappeared after plasma was off. These results suggested that CHO and CO_{ad} species are active in hydrogenation of CO_2 hydrogenation reaction. The authors also confirmed that oxygenated species CH_xO comes from the reaction between CO^* and H^* , i.e. $\text{CO}^* + \text{H}^* \rightarrow \text{CHO}^*$, and then $\text{CHO}^* + \text{H}^* \rightarrow \text{OCH}_3$. Then, formed OCH_3 interact with H^* and produce CH_4 and H_2O . The small amount of the methanol formation was detected during the process. The bicarbonate species disappeared during the reaction under plasma conditions and were converted to monodentate formates [52]. It was also found that when the plasma was off the bicarbonate build up again mainly on the support surface. An application of the NTP during the catalytic process enables generation of alternative pathways of CO_2 hydrogenation. NTP treatment of the catalyst during the reduction process has influence on the metal-support interaction, sorption properties in relation to CO_2 on the catalyst surface and specific interaction between metal and support. The obtained results showed that plasma has huge impact on the intermediates formed during the investigated process.

2.2. Micro-plasma assisted method

Micro-plasma is one of the plasma technologies used to produce functional materials. It is a non-thermal gas discharge plasma. This type of plasma is also non-equilibrium, has a specific power density, and microscale dimensions [44,53,54]. This type of plasma system was used for the synthesis of the iron oxide, for example [44]. The scheme of the apparatus used in the preparation of the nanomaterial is shown in Fig. 2. In work [44] iron oxide was synthesized using argon micro-plasma method with ferrocene (29.0 ppm) as the precursor salt and a flow rate of 100 ml/min. During the iron oxide production, the plasma power was in the range of 1–2.5 W. The furnace temperature was 340 K. The iron oxides species were deposited directly onto the substrate. The resulting material showed that the lower power of the plasma allows to obtain more homogeneous material with smaller particles. On the other hand, higher electron temperatures and densities lead to the

agglomeration process of the oxides. Very similar results were obtained in the case of nickelocene [55]. It important to note that the concentration of the precursor salts used during the micro-plasma treatment played a crucial role in the particle size of the generated nanomaterial. Increasing the concentration of metal salt precursors in the solution leads to larger particles produced in the process.

Continuous-flow micro-plasma generated at atmospheric pressure was also used to produce nanomaterials [56]. Ni and Fe nanomaterials were prepared in the gas phase by non-thermal dissociation of metal organic salt precursors using micro-plasma. During the synthesis, the metal organic salts were sublimated at ambient temperature in an Ar stream at atmospheric pressure. The micro-plasma was maintained at a constant DC current of 5 mA, ballasted by a 160 k Ω resistor. The nanoparticles produced were homogeneously nucleated from the organic precursor salts by collisions of the vapours of the metallic solutions with electrons and/or radicals. As a result of this synthesis, metallic and even bimetallic nanoparticles can be deposited on the surface, depending on the solution used during the synthesis.

2.3. Atmospheric pressure plasma jet method

A cold atmospheric pressure plasma jet (APPJ) [20] was used for the deposition of gold nanoparticles from a water solution of gold salt. The efficiency of the reduction of gold nanoparticles from the HAuCl_4 solution was strongly dependent on the plasma input power. It was also shown that ethanol, due to its volatile properties, improves the reduction efficiency caused by free electrons and hydrogen peroxide generated in the plasma. During the atmospheric pressure plasma jet process, the electrochemical reduction of the liquid precursors is used to synthesize the nanoparticles. In the case of aqueous solution, highly reactive radicals H^* and OH^* facilitate the production of nanoparticles [57]. In another work [58], APPJ was used to prepare zeolite crystals with high crystallinity and uniform crystal size distribution. A highly reactive nitrogen plasma used in the APPJ process to treat an aged solution (see Fig. 3.). The aged solution was plasma treated for 30–60 s prior to the hydrothermal reaction. The zeolite suspensions were deposited onto the silica wafer using the spin-on deposition method. The deposited zeolite thin film had dense morphology and high Young's modulus.

Im and co-workers [59] also used atmospheric pressure argon plasma jet technique to prepare nano-sized SnO_2 particles from the SnCl_4 and O_2 . The SnCl_4 solution was introduced into the plasma using the bubbler feed system with an argon stream. O_2 was injected into the reactor also using Ar as a carrier gas. SEM and TEM measurements showed that the particle size of the produced SnO_2 was between 3 and 20 nm. The authors also reported that the produced particle size was dependent on the flow of the carrier gas applied during the synthesis. The size of the SnO_2

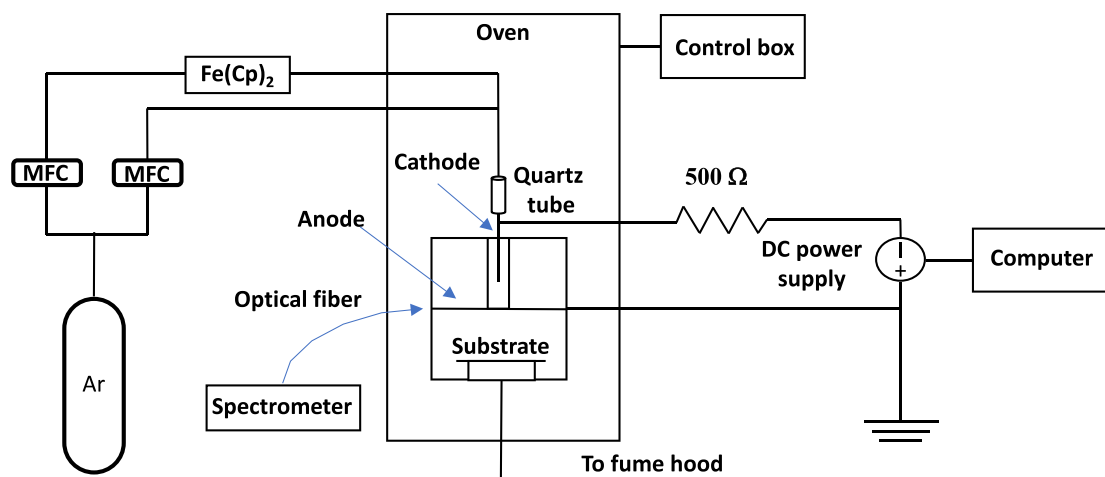


Fig. 2. Schematic diagram of the micro-plasma setup; figure was reconstructed from reference [55].

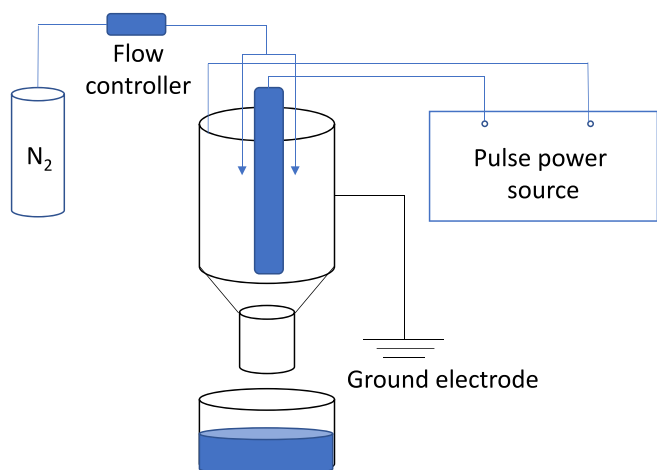


Fig. 3. Scheme of an APPJ setup; figure was reconstructed from reference [58].

particles decreased with decreasing of the carrier gas flow.

Other authors [60] used the APPJ method to prepare silver (Ag) electrocatalysts. The solution of AgNO_3 was used to decompose Ag particles on the solid YSZ electrolyte substrate. The water-silver solution was placed in a 2.45 MHz piezoelectric atomizer for generating small droplets. The vapor phase droplets of the precursor salts were transferred into the plasma head using argon carrier gas through a heated pipe ($150\text{ }^\circ\text{C}$). The atoms or molecules formed in the heated pipe travelled to the plasma head and recombined with reactive oxygen or nitrogen gas species. In the plasma head the complete decomposed process started and the deposition of decomposed particles on the electrolyte substrate took place. The DC power source was used during the deposition process, which operated at a constant current. The maximum working distance used to deposit the silver particles was 20 mm. The XRD analysis of the Ag electrocatalysts confirmed the formation of pure Ag particles with a size of 49.6 nm.

2.4. Atmospheric pressure glow discharge (APGD) plasma jet

Literature shows that reduction of metal ions is possible using plasma generated species such as: electrons, hydrated electrons, hydrogen radicals and other reducing species. Non-hydrogen glow discharge is a cast effective electron source capable of reducing metal ions with positive standard electron potentials even at room temperature. In the case of the metal ions with negative standard electron potentials, hydrogen plasma or other reducing agents are required for reduction. The application of the electron treatment method allows for the synthesis the small metallic particles on the surface using fast reduction and slow crystal growth. Recently, the possibility of forming bimetallic particles by electron reduction process has been reported. Recent reports suggest that plasma treatment can potentially replace the conventional high

temperature reduction process or the application of hazardous chemicals. This is due to the low energy input requirement and the lack of application of chemicals to reduce the metal ions to small particles in a plasma system [61].

In reference [62], the authors synthesizes $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts using plasma calcination and reduction processes and tested them in dry reforming of methane. Fig. 4 shows the schematic of the APGD system used in the preparation of the catalysts. As we can see, there was a copper rod connected to the high voltage supply inside of the reactor. The grand electrode was made of stainless steel. During the discharge process, AC voltage (20 kHz) and a gas containing 20% of H_2 in argon stream were applied to generate the plasma. During the catalyst synthesis the temperature of the catalyst bed was $527\text{ }^\circ\text{C}$. The catalytic activity and stability tests of the catalysts in the dry reforming of methane showed that the plasma synthesized Ni system exhibited higher activity, selectivity and stability. The high activity of the plasma treated system was explained by the greater dispersion of Ni particles on the surface. The size of the Ni particles was 5 nm.

In another work [8], a Ni catalyst supported on the SiO_2 was prepared by the impregnation method from a $\text{Ni}(\text{NO}_3)_2$ solution and then dried at $110\text{ }^\circ\text{C}$ for 5 h. The resulting precursor of $\text{Ni}(\text{NO}_3)_2/\text{SiO}_2$ was then introduced into the tube positioned after the discharge zone to decompose the nitrates and then reduced by plasma jet for 10 min in the system as shown in Fig. 4. A mixture of 20% H_2 -80%Ar and a 20 KHz AC voltage were used for plasma generation during the reduction process. The prepared catalysts were applied to a dry reforming process, which was carried out in the temperature range of $600\text{--}900\text{ }^\circ\text{C}$ using a gas mixture of $\text{CH}_4\text{-CO}_2$ with the molar ratio of CH_4/CO_2 equal to 4/6, the gas hourly space velocity (GHSV) was $30\text{ L}/(\text{g}\cdot\text{h})$. The catalytic activity studies carried out for the Ni catalyst showed high activity. The high activity of the Ni system was explained by the smaller size of the Ni particles generated by the plasma, which facilitates a higher dispersion of the metallic nickel on the catalyst surface. In addition, the BET measurements confirmed the higher specific surface area of the Ni system prepared by the plasma-assisted method. The TEM results also confirmed the absence of any agglomeration or sintering process in the plasma treated samples.

Ni/CeO_2 catalysts were prepared via the impregnation method and tested in steam reforming of glycerol production [3]. The catalysts were divided into two groups, one of which was dried and then the precursor salt (nickel nitrate or chloride) was decomposed by conventional thermal treatment. In the other group, the precursor salts were decomposed by plasma treatment. The reactivity results of the Ni catalysts tested in the steam reforming of the glycerol process showed that plasma treated catalyst had higher activity than the conventionally calcined systems. These results can be explained by the smaller crystallite size of the Ni particles and their greater dispersion on the catalyst surface. In addition, the high activity of these systems may also be explained by the specific interaction that occurs between Ni and Ce species. In addition, the plasma-treated catalytic material showed a higher selectivity towards hydrogen compared to the conventionally prepared catalysts. The

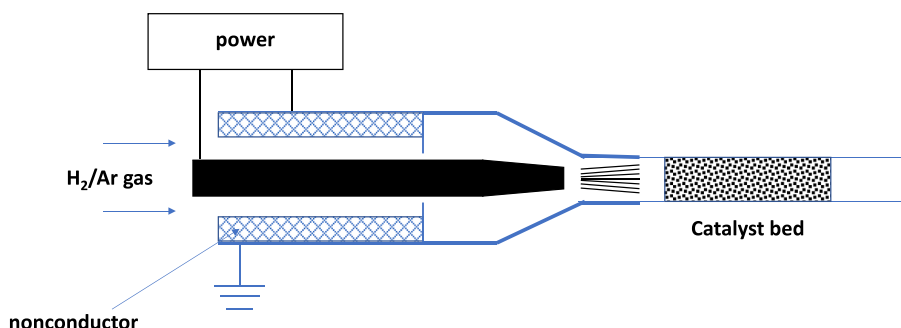


Fig. 4. Schematic of the atmospheric pressure glow discharge (APGD) plasma jet; figure was reconstructed from reference [62].

reaction tests carried out during the 8 h of the process confirmed the higher stability of the Ni catalyst treated by plasma. The catalysts treated by plasma showed higher resistance to carbon deposition. It was also observed that the nickel particles present on the surface of the catalyst did not undergo the sintering process.

2.5. Pulsed arc plasma

Pulsed arc plasma deposition is a promising method which enables to deposit of metal nanoparticles or nanofilms on the surface from the bulk metals or other electronic conducting materials [63]. Schematic of the Pulsed arc plasma is presented in Fig. 5. The system for generation of pulsed arc plasma is equipped with turbomolecular pump which generate vacuum in a special chamber, arc discharge source (Ulvac Inc., ARL-300) and a special container equipped with a rotating stirring mechanism using to introduce of raw material. In an arc discharge source, the column cathode, insulating tube, trigger electrode, and cylindrical anode are arranged coaxially. The cathode is in the form of a metal rod with a diameter of 10 mm and a length of 17 mm connected to a direct current source. However, the cylindrical anode is connected to ground and the trigger electrode is connected to a pulse power supply. An electrolytic capacitor is placed between cathode and the ground. An application of the high voltage (3 kV) pulse to trigger electrodes result in breakdown between trigger electrode and cathode which ignites pulse arc discharge. The pulse discharge duration with a period of 0.1 and 0.2 ms is generated between cathode and the anode. Due to high energy density of the arc discharge pulse the metal situated on the cathode surface proceed vaporisation and ionization resulting in the ejection of the plasma. As a result of the metal ions collide with the carrier powder, they lose their kinetic energy as they diffuse on the surface and finally deposited as nanoparticles [63].

2.6. Atmospheric plasma spray (APS)

Atmospheric plasma spray method used plasma spraying to deposit metals and metal oxides from a solid solution onto a surface of a material. The process is carried out in a high temperature plasma spray (see Fig. 6). The high temperature of the plasma causes the metals or metal oxides introduced in the plasma torch via a carrier gas to be melted and then deposited on the surface. The feed gas of the plasma torch used during the deposition process plays an important role in the melting and

deposition processes [64]. The authors of the reference [64] synthesized TiO₂ coatings on Inconel alloy substrates using thermal spray plasma process. Different mixtures of Ar/H₂ and commercial rutile and anatase TiO₂ phases were used in the process. The resultant coatings were tested as photoanodes in the solar photoelectrocatalysis treatment of an azo dye. It was shown that the coatings prepared with higher amounts of the crystalline phases (anatase and rutile) exhibited better performance in the process studied compared to the non-stoichiometric TiO₂ suboxides. The authors reported that the lower energy spraying conditions resulted in higher roughness and porosity of the coatings. While the higher energy spraying resulted in better melting of particles in the formed coating.

2.7. Suspension plasma spraying

Thermal plasma spraying technique has been widely used to synthesize titania-containing coatings. The available literature shows that thermal plasma spraying method allows to obtain effective materials for photocatalytic decomposition of organic chemicals [66–68]. This preparation method is extremely fast and accelerated by the flowing gas and flattened on the target substrate. To increase the thermal conductivity or viscosity of the plasma, hydrogen or helium can be added to a carrier gas as a secondary gas. The feedstock in a suspension plasma spraying system is usually a powder with a specific particle size typically ranging from 10 to 100 nm. It has also been reported that applying a liquid solution to a plasma spraying system may also be possible. Typical organometallic, inorganic solutions or even alcoholic suspensions can be used as feedstock for a suspension plasma spraying system [69].

Toma et al. [70] investigated the preparation of catalytic materials using a high temperature suspension plasma spraying method (see Fig. 7). In this work, TiO₂ P25 powder (Degussa AG), which was dispersed in water or ethanol solution, was injected into the plasma head. Plasma was generated in a mixture of hydrogen-argon or argon-hydrogen-helium at atmospheric pressure. The coatings formed were tested in a photocatalytic process. The results showed that the catalysts prepared from an alcohol suspension containing 23% of anatase exhibited a low photocatalytic decomposition yield. In comparison, the application of the aqueous solution of the suspension allowed to produce deposit with anatase phase with a smaller crystallites size. The presence of small crystallites size of anatase was attributed to the high performance of these deposits in the photocatalytic process.

The authors reported that the structure of the formed deposit, its characteristics and activity properties in the studied process depended on the suspension injected into the plasma.

2.8. Solution precursor plasma spray (SPPS)

The SPPS method uses a liquid precursor to deposit solid coatings. SPPS can also be used to prepare of the catalytic material (see Fig. 8). The application of this technique allows to use different type of liquid solution to introduce metal particles into the plasma [71–73]. The metal particles deposited on the surface by this method had nanometre size. The SPPS method can be used for both aqueous and non-aqueous solutions. The SPPS catalyst synthesis involves several steps including droplet break-up, evaporation of the solvent, pyrolysis of the solution, melting and then deposition on the surface. Prashant Nehe and co-workers [74] used solution precursor plasma spray technique to deposit catalyst on the fins of the reformer plates. The deposited catalyst using SPPS method was used in the methanol steam reforming process. As part of the work, the efficiency of the micro-reformer was examined. The conversion of methanol and the rate of hydrogen production were determined. The methanol conversion was 66% and the hydrogen production rate was 0.83 mol h⁻¹ at the inlet feed rate of 40 cm³ h⁻¹. The reaction was carried out at a temperature of 240 °C with a molar ratio of water to methanol equal to 1.1.

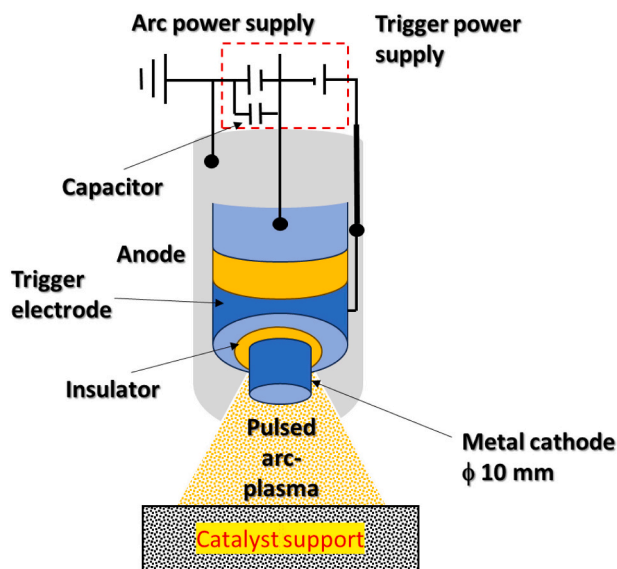


Fig. 5. Schematic of the Pulsed arc plasma; figure was reconstructed from reference [63].

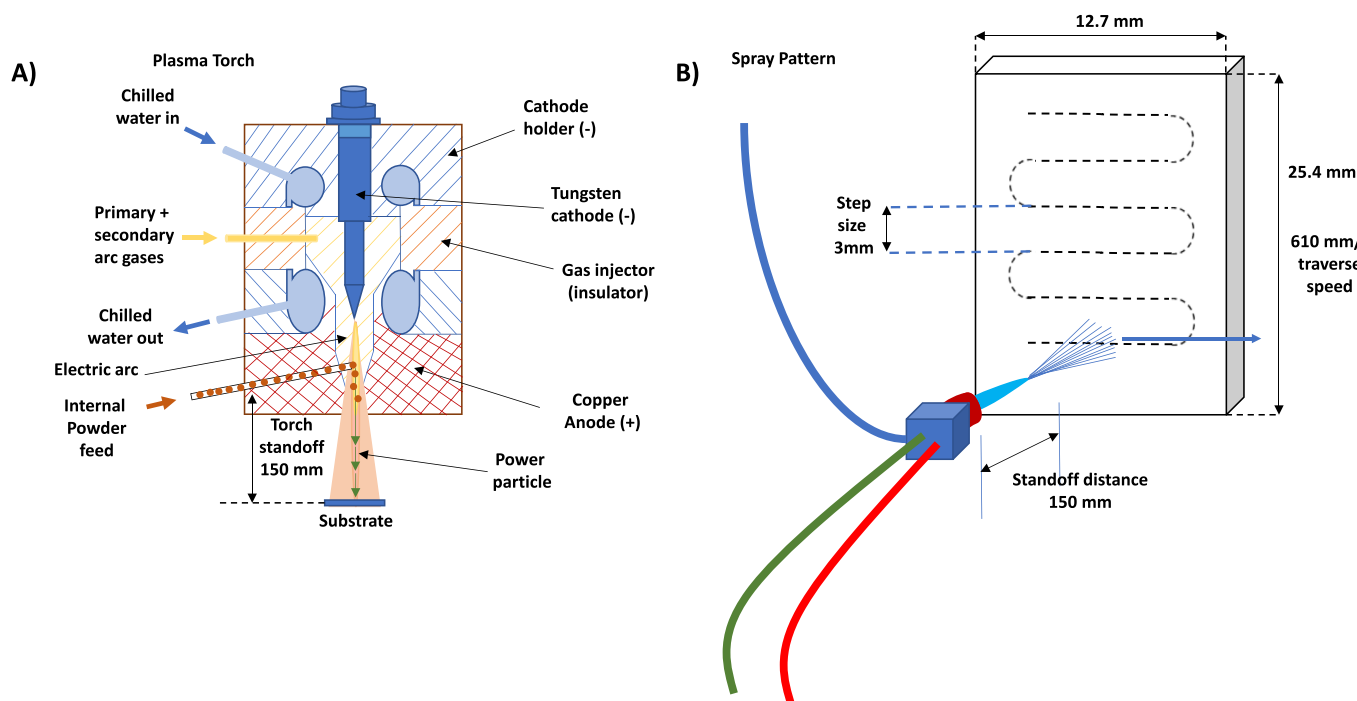


Fig. 6. A) Schematic of the plasma torch used in the Air Plasma Spray (APS) deposition process, B) Illustration of the spray pattern during the deposition process including the parameters applied during the deposition process; the figure has been reconstructed based on reference [65].

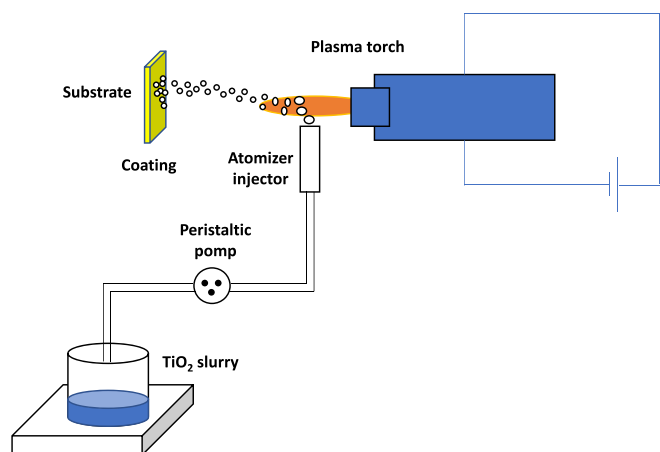


Fig. 7. Schematic diagram of a device for suspension plasma spraying; the figure was reconstructed on the basis of the reference [70].

2.9. Radio frequency (RF) plasma

Non-thermal plasma (NTP) activation process is an alternative method of catalyst activation compared to the conventional calcination of the catalytic material. This method of catalyst activation is characterized by the lower energy consumption and shorter process time compared to the conventional calcination methods [75–78]. Plasma activation of the catalytic material influence on pore structure, catalyst specific surface area, size of the grain and distribution of the active phase components. Activation process of the catalyst by plasma leads to improvement of the catalyst activity and stability in the investigated processes [79–81].

It was also shown in the literature that the non-thermal RF plasma treatment of the heterogenous catalysts leads to improvement of the catalyst activity and selectivity in relation to the non-treated systems [82–85].

In addition, it was found that catalyst treatment using RF plasma at room temperature allows to obtain high metal dispersion and various metal-support interfaces from catalysts. Therefore this method may be applied to the synthesis of the heterogenous catalysts and nanomaterials [86–88].

In order to improve the catalytic performance of the nickel-based catalyst for dry methane reforming, the Ni-imp catalyst with the addition of La was optimized using a plasma-assisted process. The catalysts were treated using RF plasma in N_2 atmosphere for 2 h using 200 W power (equipment number is ZK1048017). Before the plasma treatment Ni precursor salt (nitrate) was distributed on the surface of the support. Under the action of the plasma, reactive species generated in the plasma (ionized nitrogen atoms and electrons) bombarded the surface of the precursor. This activation process of the precursor leads to the decomposition of the precursor of the Ni salts into NiO and diffusion of this oxide phase into the pores of the support. Higher activity, stability and resistance to carbon deposit formation of the nickel catalyst with plasma-enhanced treatment was explained by the smaller nickel particles and the stronger interaction between metal and support [84].

Ni catalyst (10%Ni/MCM-41) was prepared via impregnation method and the dried at 80 °C for 12 h. After that the dried catalyst was treated by Radio Frequency plasma under vacuum conditions for 0.5 h (Ni–P0.5h). In addition, 10%Ni–3%Ce/MCM-41 catalyst was also prepared by the same procedure using different plasma treatment time (0.5 h, 1 h, 2 h and 3 h). The results of the catalytic activity performed in dry reforming of methane showed that Ce-doping Ni-based catalyst (Ni–Ce–P2h) exhibited excellent coke resistance and high activity in the studied process. The high activity of the plasma treated catalyst was explained by the small size of the active component, strong metal - support interaction and more abundant oxygen species [84,87].

2.10. Microwave-induced plasma jet irradiation

Jai Young Chung et al. [89] used plasma irradiation coupled with a fixed bed reactor system to synthesize catalyst materials. During the preparation of the catalytic material microwave-induced plasma jet irradiation was used. Pd/Al₂O₃ was dried at 110 °C for 12 h and then

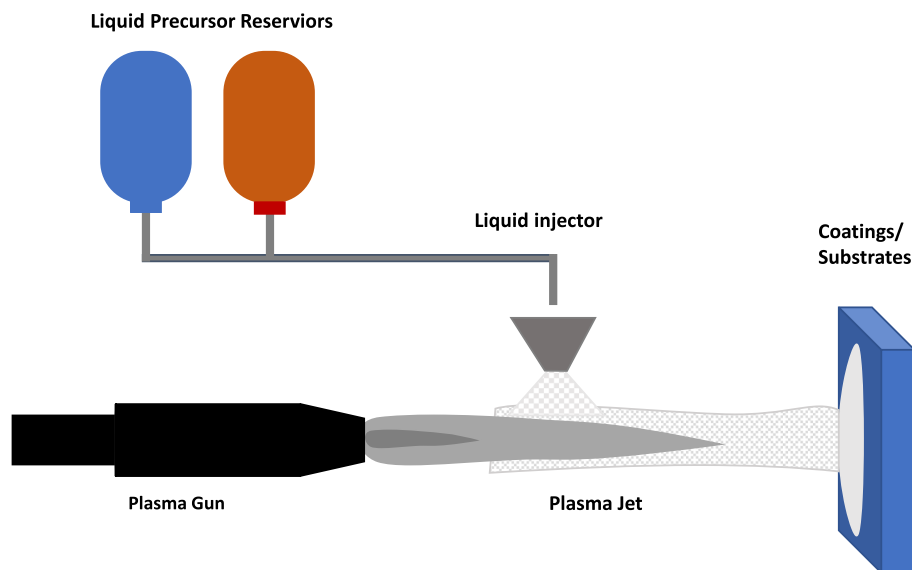


Fig. 8. Schematic of the solution precursor plasma spray process; figure reconstructed from reference [71].

crushed into fine particles. In the next step, the obtained material was placed in a fixed-bed reactor and treated by the plasma under the following plasma conditions: power = 270 W, Ar flow rate = 2.5–4 L/min, H₂ flow rate = 60 ml/min for 15 min (see Fig. 9). The physico-chemical properties of the Pd catalysts prepared by the plasma-assisted method were compared with the systems synthesized by the conventional method and reduced in a mixture of H₂–Ar at 500 or 900 °C, respectively. The XRD, SEM, TEM and chemisorption results showed that catalyst prepared by plasma treatment had higher metal dispersion and smaller metal particle size.

Furthermore, it was found that Pd catalyst prepared by microwave-induced plasma jet method coupled with fixed bed reactor exhibited metallic Pd on its surface in contrast to the Pd system which were prepared by a conventional method. The prepared catalysts were tested in an acetylene hydrogenation process and the reactivity results showed that Pd systems prepared by the plasma assisted method, for which the distance between the waveguide and the particles is shorter, showed

higher C₂H₂ conversion in the investigated process. Marjorie Foix et al. [35] also tested silver catalysts prepared by microwave fluidized bed plasma reactor treated with ethanol in SCR NO_x and compared their results with the thermally treated catalytic systems. The results showed that the Ag system prepared by plasma treatment showed higher NO_x reduction efficiency. They reported that the high activity of the plasma treated system was due to the formation of different and more reactive silver species on the catalyst surface.

Microwave plasma has been also applied for the preparation of Ag/Al₂O₃ catalyst. During this preparation method higher nitric oxide (NO_x) reduction efficiency was observed during the selective catalytic reduction of NO_x by ethanol [90]. In other work [89] a combination of the microwave-induced plasma jet with the spouted bed of Pd/Al₂O₃ catalyst lead to high yield in selective hydrogenation of acetylene to ethylene. An application of the Microwave-induced plasma can generated active species under atmospheric pressure.

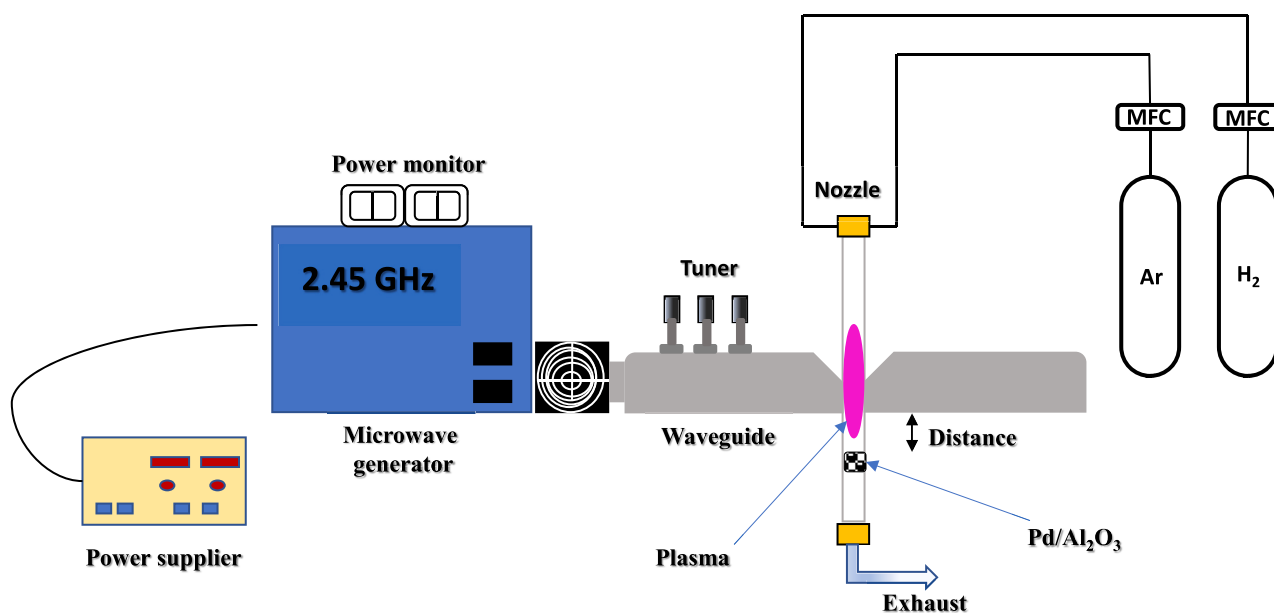


Fig. 9. A schematic diagram of the fixed-bed reactor with the microwave-induced plasma jet; figure was reconstructed from reference [89].

3. Challenges in plasma-assisted method of catalyst preparation

The use of plasma in the catalytic process allows for generating catalytic materials with specific properties. The plasma itself can reduce, oxidize or even change the structure of the catalytic material. The reduction process affects the phase composition of the active phase component present on the support surface and in some cases can even produce an alloy. In addition, the application of the plasma during the preparation of the catalytic material can alter the electronic states of the active phase components present on the catalyst surface. The challenge of the plasma assisted synthesis of catalyst material method is to optimize the effect of the plasma on the phase composition of the catalyst system and its physicochemical and catalytic properties. Another big challenge associated with the preparation of the catalytic materials using plasma is unravelling the mechanism of the plasma interaction with the catalyst surface. The possibility of stimulating the interactions of the plasma generated species with the components of the catalyst allows the production of the catalytic material with specific properties. In addition, the identification of the crucial stage of the catalyst preparation step and the understanding of the mechanism of the preparation method allow to develop of more active and selective catalytic material, which can be used in various catalytic processes. For the purpose of the plasma development, additional factors should be considered in order to achieve more active catalytic material. The next challenge in the development of plasma systems for catalyst preparation relates to the design of the reactors used during synthesis. The possibility of preparing the catalyst material by plasma treatment under high pressure is still a challenge. The capacity to synthesize catalysts under high pressure allows the use of special conditions, e.g. water under supercritical conditions. However, the application of supercritical conditions during the synthesis of catalyst materials is only possible in the case of specially designed equipment. This method can allow to avoid huge amount of the unwanted chemicals introduced into the environment and aligns with the principles of green chemistry.

4. Summary

This paper presents a concise summary of plasma-assisted synthesis methods for catalyst preparation. The literature survey shows that glow discharge and dielectric barrier discharge techniques are the most widely used plasma generation methods due to their simplicity. Different types of plasma deposition methods, which are extensively used in catalyst preparation, are also described. The advantages and disadvantages of the methods of plasma-assisted synthesis of catalytic materials were described. This review article shed light on the opportunities presented by the application of plasma techniques in the field of catalyst preparation. The catalysts prepared by the plasma-assisted method showed great potential for producing nanoparticles or nanolayers deposited on different supports. The nanoparticle systems obtained can also be modified by various plasma treatments, for example, by doping or etching processes. The catalytic systems obtained by plasma-assisted methods show higher activity and selectivity in the catalytic processes studied than the catalysts synthesized via conventional methods. The review of published literature indicates that catalysts prepared by the plasma-assisted method have a huge potential for industrial applications and may become one of the important methods of the catalyst preparation.

Author contributions

The work was designed and prepared by P.M., A.M-V., M.I-S-J. and K.V. All authors have read and agreed to the published version of the manuscript.

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CRediT authorship contribution statement

Pawel Mierczynski: Conceptualization, Funding acquisition, Visualization, Writing – original draft, Writing – review & editing. **Agnieszka Mierczynska-Vasilev:** Supervision, Writing – review & editing. **Malgorzata Szynkowska-Jozwik:** Supervision. **Krasimir Vasilev:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare no conflicts of interest.

Data availability

No data was used for the research described in the article.

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