**Plasma-Catalysis: the known knowns, the known unknowns and the unknown unknowns**

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**Abstract**

This review describes the history and development of plasma-assisted catalysis focussing mainly on the use of atmospheric pressure, non-thermal plasma. It identifies the various interactions between the plasma and the catalyst that can modify and activate the catalytic surface and also describes how the catalyst affects the properties of the discharge. Techniques for *in situ* diagnostics of species adsorbed onto the surface and present in the gas-phase over a range of timescales are described. The effect of temperature on plasma-catalysis can assist in determining differences between thermal catalysis and plasma-activated catalysis and focuses on the meaning of temperature in a system involving non-equilibrium plasma. It can also help to develop an understanding of the gas-phase and surface mechanism of the plasma-catalysis at a molecular level. Our current state of knowledge and ignorance is highlighted and future directions suggested.

**Keywords**

Plasma catalysis: catalysis: non-thermal plasma: adsorption: plasma physics: plasma chemistry: plasma diagnostics

**1. Introduction**

Plasma-catalysis, sometimes described as plasma-assisted catalysis, plasma-enhanced catalysis, plasma-driven catalysis or plasma-catalysis coupling, refers to the combination of a gaseous discharge or plasma heterogeneously with a material that has catalytic properties. This hybridisation can produce outcomes that are enhanced in some way and that sometimes cannot be achieved by plasma or catalysis separately. Most commonly, we are dealing with non-thermal, atmospheric pressure plasma where a breakdown in a gas or mixture of gases produces partial ionisation causing non-equilibrium between the temperature of the electrons (104 – 105 K) and that of the heavy particles (ions, atoms, molecules and radicals) which remain close to the ambient temperature of the gas (300 -1000 K). This plasma is often referred to as being low temperature and because it contains ionised and excited states of atoms and molecules and radicals not normally present at thermal equilibrium at ambient temperatures, it possesses reactive properties that are only seen in combustion systems and thermal discharges at much higher temperature (> 1000 K). Thus chemical processes can occur in non-thermal plasma at low temperatures that would not normally be possible in a system at thermal equilibrium. The introduction of a catalyst accelerates a chemical reaction whilst itself undergoing no chemical change by providing an alternative reaction pathway with a lower energy barrier. This can also result in a lowering of the temperature at which a chemical process takes place. The nature of the catalytic material in terms of its physical, structural and chemical properties is key to its effectiveness for a particular process. Reactions take place between species adsorbed onto the catalytic surface with either other adsorbed species or with species in the gas-phase. The activity of these adsorption sites determines the mechanisms that provide the lower energy reactive pathways.

Simple considerations will show that when discussing plasma-catalysis, the baseline or reference state is important. We could modify a reactive plasma system by the addition of a catalyst and observe any effects that the catalyst produces or we could take a catalytic process and subject the gas (and also the catalyst) to the effect of plasma. We understand each baseline system with a reasonable degree of certainty but the mutual interaction of plasma upon catalysis and *vice versa* is complex and varied and has still much that is not understood. Adapting Donald Rumsfeld’s description of the state of US military intelligence in 2002 [[1](#_ENREF_1)] to the field of plasma-catalysis, there is also much that we know we know, things that we know that we still do not know and most likely a range of things that we do not even know that we need to know. As Rumsfeld commented “it is the latter category that tends to be the difficult one.” This review attempts to summarise our present state of knowledge and provide some pointers for the future.

The history of the study of plasma-catalysis applied to reactive systems goes back at least sixty years. Probably the first reported observation of plasma-catalysis comes from a study in 1954 of the formation of hydrazine in a low pressure d.c. discharge of ammonia [[2](#_ENREF_2)] where a coating of platinum on the discharge tube walls was found to increase the overall yield of hydrazine by the catalytic removal of hydrogen atoms. The first account of the use of an atmospheric pressure plasma with a catalyst comes from 1992 reported by Mizuno et al. [[3](#_ENREF_3)] who investigated the synthesis of methanol (CH3OH) from CH4 and CO2 in a dielectric barrier discharge with a ZnO-CrO3-H2O catalyst and found that the catalyst “improved the efficiency of the synthesis”. There have been extensive studies during the following two decades focussing mainly on the use of atmospheric pressure, non-thermal plasma-catalysis and considerable progress has been made in assembling a knowledge base and developing an understanding of the processes. Recent reviews will give the reader access to much of that material and the recent historical development of the subject. [[4-23](#_ENREF_4)]

**2. Atmospheric pressure, non-thermal plasma production and properties**

Non-thermal plasma operating at atmospheric pressure has been successfully used for over one hundred and fifty years following the work by Siemens in 1857 on the production of ozone in a silent discharge (a form of dielectric barrier discharge) from air or oxygen. [[24](#_ENREF_24)] Non-thermal plasma can be produced using a range of experimental techniques. These include dielectric barrier discharges (DBD) where the gas passes between two electrodes at least one of which is shielded from the gas by a layer of dielectric material and are characterised by the formation of micro-discharges or streamers. [[25](#_ENREF_25)] Similar behaviour is found in corona, packed-bed and surface discharge reactors. [[26](#_ENREF_26)] These devices are driven by pulsed or a.c. power sources and their performance can be controlled by the power supplied, the frequency and pulse shape. Microwave and radio frequency excitation can also be used to generate a discharge often using an electrode-less configuration that can assist the incorporation of a catalyst. [[27](#_ENREF_27), [28](#_ENREF_28)] Gliding arc discharges are also finding increasing use for gas processing and are characterised by a warmer discharge than the dielectric and corona-like systems. [[29](#_ENREF_29)] In general, most of the work done so far on the combination of plasma and catalyst has been performed using corona, dielectric barrier and packed bed reactors.

As mentioned before, it is the non-equilibrium nature of the cold, low temperature or non-thermal plasma that offers opportunities for the plasma-catalyst hybridisation. The high energy of the electrons produced in the discharge allows for a range of electron collision processes with the gases that are being processed. These electron-atom and electron-molecule collisions can create a range of species in the gases including positive and negative ions, electronically excited states of the atomic and molecular species and dissociated fragments such as atoms and radicals that may be in their ground or higher energy electronic states. The disparity in mass between the electron and the gaseous species means that little kinetic energy is transferred between them and heavy atomic and molecular species remain close to their ambient temperature. Thus, the non-thermal discharge can create excited and reactive species that can only be produced in an equilibrium system such as an arc or flame at very high temperatures. This means that we can have an ionised, excited and reactive gas interacting with the catalyst at temperatures at which conventional thermal catalysis would be inactive. In addition, the radiation produced from the decay of electronically excited states produces photons, which can be of high energy in the vacuum ultraviolet. However, the photon flux from typical, non-thermal, atmospheric pressure plasma is assessed as being several orders of magnitude too small to activate a catalytic material allowing photocatalysis to take place. [[15](#_ENREF_15)]

The excited electronic species in the plasma include ions and neutral atoms and molecules in electronically excited states. In general, at atmospheric pressure the ionic and excited states have short radiative lifetimes (*τ*0)or are rapidly quenched or neutralised and do not play a significant role in the chemistry. An important exception is a group of metastable excited states where a radiative transition to the ground state is spin-forbidden. These “dark” states have long radiative lifetimes, *τ*0, and act as energy reservoirs providing energy to enable reactive and dissociative collisions. Examples include atomic and molecular states of oxygen (O 1D, *E* = 1.967 eV, *τ*0= 150 s: O2 *a*1Δ, *E* = 0.977 eV, *τ*0= 64.6 min) and nitrogen (N 2D, *E* = 2.38 eV, *τ*0~ 17 h: N 2P, *E* = 3.576 eV, *τ*0~ 12 s : N2 *A* , *E* = 6.224 eV, *τ*0= 2 .0 s ). [[30](#_ENREF_30), [31](#_ENREF_31)] The high reactivity of O 1D, for example, reduces its lifetime to 1 ns in a humid atmospheric pressure, air plasma due to quenching with air molecules and reaction with water to form the radical OH. [[32](#_ENREF_32)]

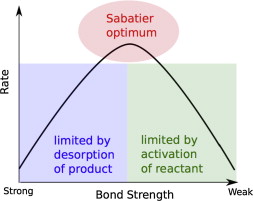
In addition to excitation in the form of ionisation and electronic state formation, much of the plasma energy can create vibrational excitation of the gas molecules. It was recognised at an early stage of the development of plasma-catalysis that the non-equilibrium nature of the discharge in terms of vibrational excitation could provide enhanced adsorption onto catalyst surfaces and increase the reactivity for endothermic processes such as the production of NO from N2 and O2 on WO3 and MoO3 catalysts. [[33](#_ENREF_33)] This is an extension of Polanyi’s Rules for the effectiveness of vibrational or translational energy in the reagents for promoting endothermic and exothermic processes. [[34](#_ENREF_34)] Currently, there is much interest in the possibility of vibrational excitation of CO2 promoting its decomposition or conversion on catalytic surfaces. [[35](#_ENREF_35), [36](#_ENREF_36)]

Particularly at atmospheric pressure, it can be difficult to maintain the non-equilibrium nature of the plasma. The excited ionic species produced in the discharge will rapidly recombine and become neutralised either in the gas-phase or upon surfaces. Collisional intermolecular energy transfer between plasma-created excited species and ground state atoms or molecules will tend to thermalize the non-equilibrium energy distributions of the different degrees of freedom that are initially formed. Electronically excited species can be quenched to their ground states with an efficiency that depends on the nature of the collision partner and the extent and lifetime of the excited state. Vibrationally and rotationally excited molecules will be thermalized by collisions with only tens of collisions being required to rotationally relax a typical molecule or a few hundred collisions for vibrational relaxation depending on the magnitude of the rotational and vibrationally energy spacing and anharmonicity of the molecule and the nature of the collisional partner. Vibrationally relaxation can be especially effective when there is a near resonance between the vibrational spacing of the excited molecule and the collision partner as occurs between N2 (*v* = 1) and CO2 (001) where one quantum of asymmetric vibration is excited. Thermalisation can also occur when an excited species collides with a surface. The extent to which the non-equilibrium nature of the plasma is maintained is strongly dependent of the nature of the electrical excitation of the plasma where direct supply of the electrical power in a pulsed mode or the pseudo-pulsed nature of a dielectric discharge and the formation of nanosecond duration streamers greatly facilitates non-equilibrium in the gas.

**3. Catalysis and catalytic materials: mechanisms and properties**

As Thomas reports [[37](#_ENREF_37)], the first observation of a heterogeneous catalytic process was by Humphry Davy in 1817 who noted that heated platinum gauze or foil would bring about the slow combustion of vapours such as alcohol, ether, coal gas and methane below their ignition temperature.[[38](#_ENREF_38)] This discovery was acknowledged by the Swedish chemist, Berzelius, in his treatise on catalysis where that word was first used. He recognised the existence of a catalytic force that “is reflected in the capacity that some substances have, by their mere presence and not by their own reactivity, to awaken activities that are slumbering in molecules at a given temperature”. [[39](#_ENREF_39)] We now understand that the presence of a catalyst can provide alternative reaction pathways with lowered energy barriers. Kinetically, these lowered barriers can increase the rate of the reaction increasing the degree of destruction or conversion of the reagents and enable the processing to occur at a lowered temperature. Mechanistically, these alternative reaction pathways may also improve the yield or selectivity for particular products and different catalysts can be used to favour particular outcomes.

A typical heterogeneous catalyst might be composed of a metal oxide or sulphide used in its own right or acting as a support for some form of active metal. More complex catalysts may involve mixtures of oxides and metals blended to achieve specific performance or utilise microporous species such as zeolites whose structure allows for selectivity on the basis of molecular size. Species in the gas phase are in continual collision with the surface and for catalysis to take place species have to become bound to the surface in some way. The nature and strength of this bonding is what lies at the heart of the catalytic process. Species can be bound to a surface either weakly by long-range physical forces (physisorption) or more strongly with bonding equivalent to chemical bonding (chemisorption). Upon adsorption, the atom or molecule may remain intact or become dissociated into fragments in a process called dissociative chemisorption. This may require the overcoming of an energy barrier. These adsorbed fragments will often be more reactive than their parents and can diffuse across the surface of the catalyst to react forming new species that can then desorb from the surface. When all the reactants involved in the catalytic reaction are adsorbed onto the surface prior to reaction, this is known as the Langmuir Hinshelwood mechanism where the rate determining step is assumed to be the surface reaction rather than the adsorption or desorption steps. An alternative mechanism, the Eley-Rideal mechanism, involves reaction by the collision of a gaseous reagent with a species that is already adsorbed on the surface. Careful examination of the temperature and pressure behaviour of the catalytic reaction can be used to distinguish between the two mechanisms. The kinetics of both mechanisms can be complicated if a reaction product (or intermediate) is strongly adsorbed onto the surface and the reaction becomes poisoned as fewer surface sites become available for adsorption. The relative binding energies to the surface (enthalpies of adsorption) for the reagents, intermediates and products are key in determining the effectiveness of the catalytic process. If the reagents are too weakly bound, then there will be low coverage of the surface and surface reactivity will be low. As the bonding to the surface becomes stronger, there will be greater surface coverage and the adsorbate will become too stable to decompose or react. Between these two extremes, is an optimum that depends on the nature of the catalyst and the adsorbing species often displayed as a “volcano plot” describing catalytic activity as a function of the strength of adsorption. This is called the Sabatier principle and is schematically depicted in Figure 1.



**Figure 1** Schematic representation of the qualitative Sabatier principle. Reproduced from Ref [[40](#_ENREF_40)] with permission from Elsevier.

The strength of bonding of an adsorbate to the catalyst surface is a critical parameter as it determines its kinetics for adsorption, desorption, diffusion and surface reaction upon which the overall yields and selectivity of the catalytic process depend. Understanding the bonding requires detailed knowledge of the electronic structure of both the adsorbate and the surface. Transition metals are commonly used as catalysts and the respective occupancy of *d-*orbitals as given by their position in the periodic table taken together with the orbital structure of the adsorbate will determine the nature and strength of the bonding of the adsorbate to the metal surface. This is the two dimensional, surface analogue of the binding of a ligand to an isolated transition metal. The heats of adsorption of oxygen and hydrogen on a metal correlate with the heats of formation of the corresponding metal oxides and hydrides. [[41](#_ENREF_41)] For the classic case of adsorption of CO, stronger bonding is associated with metals having fewer *d* electrons where the orbitals formed between the CO and the metal are principally bonding in character giving stronger chemisorption that can lead to dissociative adsorption. For metals with more *d* electrons, antibonding orbitals are also occupied giving weaker chemisorption. Dissociative chemisorption can produce atomic or radical fragments on the surface that are much more reactive than the undissociated molecule because of their zero or very low activation energies for reaction with other radicals and molecules.

Another commonly used class of catalyst are metal oxides. Binding of the adsorbate to the surface involves the transfer of either an electron or a proton and for this reason metal oxide catalysts are commonly referred to as being acidic or basic depending on their ability to donate or accept these charged species. For the transfer of an electron, we call a site a Lewis acid site if it is capable of receiving an electron pair from the adsorbate whereas a Lewis base site has a free pair of electrons that it can donate to the adsorbate. A surface site that can transfer a proton to the adsorbate is designated a Brønsted acid and a site that can accept a proton a Brønsted base. In general, Brønsted acidity depends on the strength of the metal-oxygen bond and acidity increases with the charge on the metal ion.

Metal oxides also show a wide variation in their work function. This is effectively the ionisation energy of the surface and is changed upon adsorption for both physisorption and chemisorption; although the largest changes are seen for chemisorption. This depends upon the relative position of the highest occupied molecular orbital (HOMO) of the adsorbate and the Fermi level of the metal oxide. For electropositive adsorbates, the HOMO lies above the Fermi level and an electron is transferred from the adsorbate to the metal oxide surface resulting in a positive charge on the adsorbate. For electronegative adsorbates, the HOMO is below the Fermi level and an electron is transferred from the surface to the adsorbate, which becomes negatively charged. The work function can also be changed by the surface roughness of the catalyst, the size of the catalyst particles and by the presence of oxygen vacancies in the metal oxide lattice.

Another class of materials that are commonly used as heterogeneous catalysts are zeolites, which are crystalline, hydrated, aluminosilicate materials. They form a framework with cavities and channels of mesoscale dimensions (1 μm – 1 mm) that can be precisely controlled providing a large surface area and enabling size and shape selective adsorption of molecular species. The properties of zeolites and their performance under plasma-activation can be controlled by the ratio of Si to Al and by the addition of alkali ions such as sodium or potassium or of protons. [[42](#_ENREF_42)] Metal-exchanged zeolites are commonly used as oxidation or reduction catalysts whilst hydrogen-exchanged zeolites are used for organic reactions such as hydrocarbon cracking and fuel synthesis. The acidity of the zeolite in terms of the Lewis and Brønsted acid sites can be controlled in its synthesis allowing considerable specificity in its catalytic behaviour.

Many simple theories of the mechanism of catalysis depend on the assumption that the surface of the catalyst is uniform and homogeneous and that all possible sites are equivalent. However, real catalytic surfaces are far from uniform and the effectiveness of the catalyst can depend significantly on its local molecular structure which may contain defect sites such as steps, edges, vacancies of atoms or ions and impurities with rates being greatly enhanced on features such as steps and edges. Geometric effects are also important with certain adsorbed species being “good fits” to a particular catalytic surface because of the molecular structure of the adsorbate and possible modification of the surface due to local vacancies or impurities. [[41](#_ENREF_41)]

**4. The mutual interaction or coupling of plasma with a catalyst**

Now that we have looked at some basic properties of plasma and catalyst separately, we will consider how they may be combined and what may be the nature of any interactions that result from this hybridisation. In general terms, there are two ways in which plasma and catalyst can be configured. In the first, the catalytic material (or a mixture of catalysts) is placed directly into the discharge region of the plasma: this is commonly called a one-stage plasma-catalytic system or in-plasma catalysis (IPC). In the second, the catalytic material is placed downstream of the plasma: a two-stage arrangement or post-plasma catalyst (PPC). The two-stage arrangement can also be extended to have more than one catalyst in sequence: a multistage plasma-catalysis processing where each of the catalysts might be different and have a different functionality and can be used to treat different components of the gas stream. There have been only a few reports of such “chaining” of downstream catalysts or the addition of a downstream catalyst to a one-stage configuration [[43](#_ENREF_43), [44](#_ENREF_44)] but it can be imagined that this may represent a pragmatic solution to treating complex gas mixtures in the future.

The way in which the catalytic materials are introduced into the plasma plays an important role in determining the interaction and the nature of the plasma-catalyst interaction. Commonly, the catalyst is used in a powdered form and placed between the electrodes in the case of a DBD reactor. This is a very simplistic statement and it has been noted that the particle size of the powder, the amount used and the way in which it is packed can significantly alter the performance of the plasma-catalyst processing as was seen for the dry reforming of CH4 with CO2 in a DBD reactor. [[45](#_ENREF_45)] In a packed-bed reactor, the void between the pellets can be filled with the catalyst in a fine powder form [[46](#_ENREF_46)] and this configuration has been successfully employed for a range of fundamental studies. However, packed-bed reactors have been difficult to scale-up and can suffer from a pressure drop due to the packing. Several workers have used ceramic monoliths that have been coated or impregnated with a catalytic material. Hensel [[47](#_ENREF_47)] has described the use of both a.c. and d.c. discharges in ceramic foams and honeycombs where the size of the microporous channels affects the formation of surface microdischarges within the pores. Kraus et al. [[48](#_ENREF_48)] used Ni- and Rh-coated, reticulated alumina ceramic foams inside a DBD reactor for the dry reforming of methane with carbon dioxide. The foam had a promoting effect on the chemistry and also improved the temperature control in the reactor. The small pore size of 420 μm gave a reduced gap size for the discharge increasing the breakdown field and giving an increased concentration of high energy electrons producing enhanced destruction of the CO2. Studies show that for nanoporous materials (pore size < 0.8 μm), the electrical discharge does not penetrate into the pores but for mesopororus materials (≥ 15 μm) it is possible for microdischarges to penetrate into the pores and that excited species can be stabilised in the pores giving enhanced reaction times. [[49](#_ENREF_49)]

Some types of plasma reactor present particular difficulties in incorporating a catalyst directly into the discharge region. This is particularly the case for a gliding arc discharge where supporting a catalyst between the electrodes is challenging. A novel solution comes from the work of Schmidt-Szaloskwi et al. [[50](#_ENREF_50)] who used a sprouted bed for the conversion of methane. Gaseous reagents are introduced at the bottom of the reactor, lifting the powdered catalyst into the discharge region between the electrodes giving an effective gas-surface interaction. Lee and Sekiguchi [[51](#_ENREF_51)] used a sprouted bed with a gliding arc for the direct conversion of methane into higher hydrocarbons and a similar arrangement has been employed with a DBD reactor by Wang *et al.* [[52](#_ENREF_52)] for the dry reforming of methane.

There will be distinct physical and chemical ways in which the interaction between plasma and catalyst occurs in a one-stage and two-stage arrangement. In a one-stage arrangement, all of the species (e.g. electrons, photons, ions, atoms, radicals, electronically and vibrationally-excited species) can activate the catalyst whereas in a two-stage arrangement, only relatively stable species (long-lived intermediates or reactive species such as ozone) exiting from the discharge will reach the catalyst. Plasma-catalyst interactions in the one-stage hybrid arrangement can broadly be described as resulting either from the plasma affecting the performance of the catalyst or the catalyst changing the discharge characteristics depending whether it is the presence of plasma or the catalyst that is the dominant perturbation resulting from the hybridisation. In reality, this may be too much of a generalisation and the plasma-catalysis interaction is more multifaceted and subtle.

As well as creating reactive species above the catalyst surface, plasma might also change the surface properties by ion, electron or photon interactions. Packing catalytic materials into the discharge may modify its electrical properties for example through changing dielectric effects or by altering its nature, e.g. from filamentary microdischarges to surface discharges. [[53](#_ENREF_53), [54](#_ENREF_54)] These different interactions may combine to improve the overall processing performance compared with using either plasma or catalyst separately. In some cases, there may even be a synergistic improvement where the overall effect using plasma-catalysis is greater that the sum of the individual effects of the plasma and catalyst taken separately. This synergy may be seen in some properties such as product yields, selectivities or energy efficiency but not universally. It should be stressed that plasma-catalysis is not inherently a synergistic process but may be in some cases. Vandenbroucke et al. [[55](#_ENREF_55)] have defined a “synergy factor” in their study of the plasma-catalytic decomposition of the decomposition of trichloroethylene (TCE). It is equal to the ratio of the degree of destruction of TCE by plasma-catalysis to the sum of the degree of destruction of TCE by plasma alone and the degree of destruction of TCE by catalyst alone. A synergy factor will be greater than 1 in a synergistic system. In their study, the factor ranges from 0.78 to 4.78 in a range of experiments with changing parameters demonstrating that synergy only exists under certain experimental conditions in this system. This measure deserves adoption as it is an unambiguous indication of synergy.

We shall now look at some of the generic effects of plasma interactions on the functioning of the catalysis process and the converse effects of the addition of a catalytic material upon the performance of a discharge.

**4.1 Using plasma to prepare catalysts**

Whilst we will be mainly concerned with the processing power of plasma and catalyst combined, it should be noted that plasma is increasingly being used as a tool for preparing catalysts for conventional thermal processing. [[56](#_ENREF_56)] For example, using a low pressure glow discharge or radio frequency plasma with Ar, He, N2 or air as a source of energetic electrons, it is possible to reduce a metal in a more environmentally sustainable way than with conventional thermal or chemical processing. [[57](#_ENREF_57), [58](#_ENREF_58)] The electron-assisted reduction produces a rapid nucleation of the metal at room temperature initiated by electrons without any additional heating. In this way it is possible to prepare coatings of metallic nanoparticles on a range of substrates including thermally unstable ones such as porous organic polymers with high loadings, much higher dispersion and smaller nanoparticles than by conventional means. This technique has been applied to prepare a Ni / Al2O3 catalyst for use in the thermal catalytic dry reforming of CO2 with methane [[59](#_ENREF_59)] where the Ni was found to be highly dispersed and the plasma-prepared catalyst was more stable in operation and the deposition of carbon was inhibited.

Plasma-assisted catalyst preparation has also been performed at atmospheric pressure using a plasma jet to prepare a Ni / SiO2 catalyst for dry reforming of methane where the Ni (NO3)2 impregnated SiO2 support was treated with a H2 / Ar plasma jet. [[60](#_ENREF_60)] A similar method was used by Qin *et al.* [[61](#_ENREF_61)] to produce a Ni / MgO2 catalyst for the same process giving improved surface content and dispersion of the Ni providing more actives sites for reaction and showing reduced carbon deposition enabling the reforming to take place at reduced temperature with enhanced catalyst stability. We have also demonstrated that it is possible to reduce a commercial NiO / Al2O3 catalyst using a DBD in an atmospheric pressure flow of pure methane [[62](#_ENREF_62)] or H2 in Ar [[63](#_ENREF_63)] at much lower temperatures than are used in the conventional thermal reduction with the same gases. The Ni / Al2O3 catalyst produced by methane reduction was found to have a coating of carbon nanofibres which appear to protect the catalyst from oxidation in air whereas the H2 in Ar reduced Ni was pyrophoric when exposed to air.

A novel class of materials called core-shell nanoparticles (CSNs) have attracting attention in arrange of catalytic applications. [[64](#_ENREF_64)] These advanced nanomaterials are constructed with inner cores and outer shells which either partially or wholly cover the core and be synthesised in a range of types *e.g.* inorganic / inorganic, organic / organic or mixtures. Lllorca *et al.* [[65](#_ENREF_65)] have produced dodecanethiol-stabilized core-shell gold nanoparticles which were treated with an oxygen plasma and found to give superior results for the selective conversion of methane into formic acid in a CH4 / H2 / O2 system at temperatures as low as 413 K.

Recently, an atmospheric pressure, dielectric barrier discharge in helium was used *in situ* to continuously activate an Ag / Al2O3 catalyst that was being used for the selective catalytic reduction of NOx in the presence of hydrocarbons (toluene or *n*-octane). [[66](#_ENREF_66)] They reported that a strong enhancement in activity was observed when compared with conventional thermal activation with high conversions of both NOx and hydrocarbons obtained at temperature ≤ 250 °C at which the silver catalyst would normally be inactive. Li *et al.* [[67](#_ENREF_67)] have also shown that the *in situ* or auto-reduction of a Ni / CeO2 / Al2O3 catalyst by the processing gases in the reforming of biofuels using a gliding arc discharge gave almost identical results to using a conventionally pre-reduced catalyst with a slightly smaller size of Ni particles.

The use of plasma plays an important role in tailoring the properties of a catalyst by the selective doping of a material with heteroatoms or by the modification of the band gap of a substance which can affect binding to the surface in a selective way. . The doping of a material can also give a selective control of the different functional groups on its surface and their acidic or basic nature. The low pressure N-atom doping of carbon nanotubes (CNT) can be achieved by treating the nano-material in a low pressure radio frequency or microwave plasma of nitrogen. This will increase the catalytic activity of the CNTs by creating electron donor states in the conduction band near the Fermi limit and by generating N-containing functional groups (*e.g.* amine, amide, pyridinic and pyrrolic). Altering the plasma conditions can selectively control these features. [[68](#_ENREF_68)] Titania, TiO2, can be similarly doped by nitrogen in a low pressure radio frequency discharge bringing about band gap narrowing. [[69](#_ENREF_69)] Hu *et al.* [[70](#_ENREF_70)] have used an a.c. plasma discharge in nitrogen and carbon tetrachloride to give mixed N- and Cl-doping of TiO2. The N-doping does not change the crystalline structure of the TiO2 but does modify the electron density around the titanium which increases the concentration of hydroxyl on the surface. The Cl ions do not dope into the TiO2 lattice but bind to the surface by coordinating with the Ti4+ ions, which has the effect of displacing the hydroxyl groups. This ratio of surface Cl to OH species is found to affect the catalytic oxidation of the TiO2. Liquid-phase plasma methods can also be used to dope and modify catalytic surface *e.g.* fluorination of carbon nanoparticles [[71](#_ENREF_71)] and modification of TiO2 with cobalt oxide nanoparticles. [[72](#_ENREF_72)]

It seems clear that if plasma can be used to prepare a catalyst in isolation under controlled conditions, then with the normal operating conditions of one-stage plasma-catalysis processing some of the plasma activity may be resulting in a continual dynamic modification of the catalytic surface. Marinov et al. [[73](#_ENREF_73)] have noted this for a SiO2 surface under exposure to a low pressure nitrogen plasma commenting that the surface under contact with the plasma is not static and suggesting that this type of behaviour is expected for a range of surfaces and plasma chemistries. The extent to which this dynamic interaction is beneficial in terms of reduced poisoning or coking and increased stability and activity can be inferred from some accounts of plasma-catalytic processing where studies of these properties are described and where the properties of the catalyst are characterised before and after processing. [[74](#_ENREF_74)]

**4.2 Adsorption and Desorption during Plasma-catalysis**

In plasma-catalysis, as in conventional thermal catalysis, the essential prerequisite to a reaction on the catalyst surface is that something must first be adsorbed onto the surface. Figure 2 is taken from a paper by Kim, Ogata and Futamura [[75](#_ENREF_75)] and is a graphical description of the many processes that can occur during plasma catalysis in a single stage configuration.

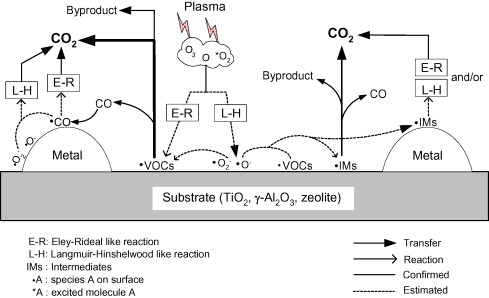


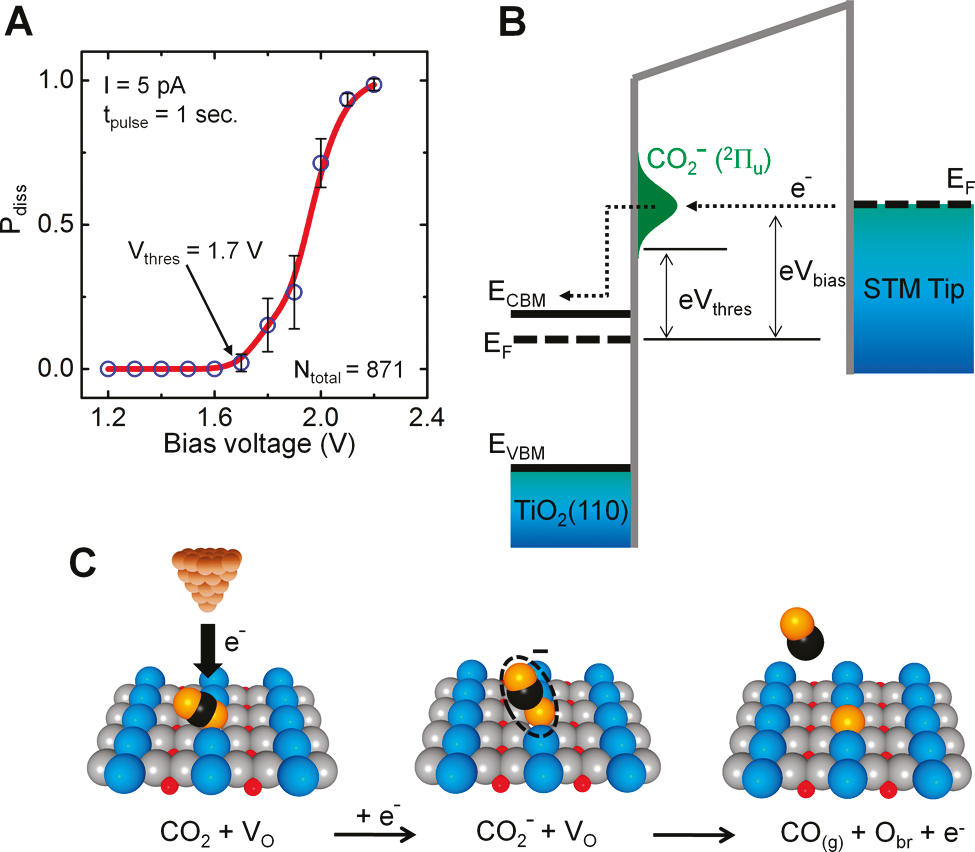
Figure 2. Possible mechanisms for the plasma-driven catalysis of volatile organic compounds in an air plasma. Reprinted with permission from Ref. [[75](#_ENREF_75)]. Copyright 2008, Elsevier.

It focuses on the oxidation of a volatile organic compound using oxygen plasma and a catalyst that consists of metal particles dispersed on an oxide or zeolite substrate to ultimately form carbon dioxide and water. Species are adsorbed either onto the metal or the substrate and can be in the form of stable molecules from the gas stream or fragments (atoms or radicals) formed by the action of plasma. Whether the species are adsorbed onto the metal or the substrate will depend on the nature and strength of their bonding to the metal or the substrate and the size of any energy barriers that must be overcome before adsorption. The temperature of the surface will also be an important parameter in determining the probability for absorption. After adsorption, the species may undergo dissociation or remain intact. They may migrate across the surface, penetrate into any pores in the catalyst or diffuse into the bulk of the catalyst. Electronically excited or vibrationally excited species created in the plasma may become quenched or relaxed by the surface. [[76](#_ENREF_76), [77](#_ENREF_77)] Under certain circumstances, species may spill over onto the substrate following adsorption on the metal. [[78](#_ENREF_78)] They may react with other species on the surface or suffer a collision with a gas-phase reagent. The reaction products may remain on the surface or may desorb back into the gas-phase. Some species may desorb in a different state *e.g.* vibrationally excited products can formed by the combination of atoms or molecules on the surface. [[79](#_ENREF_79)] A significant and beneficial outcome of combining a catalyst into a plasma system come from the increased reaction time and hence improved yield of products that comes from the adsorption of the reactant onto the surface and the selective adsorption of some species such as reactants as opposed to the carrier species (*e.g.* nitrogen or inert gases). [[32](#_ENREF_32)]

In a one–stage, plasma-catalysis configuration, the range of species that can be adsorbed from the gas phase is increased by the plasma action that creates excited species, radical and fragments. Many of these species will be extremely short-lived and can only be adsorbed unchanged if they are produced close to the surface of the catalyst. Otherwise, they may be collisionally quenched or removed by recombination or reaction on the surface. The mean free path at atmospheric pressure and room temperature is typically less than 100 nm and the time between collisions is less than 1 ns. The lifetime of a ground state oxygen atom, O 3P, in an atmospheric pressure plasma in dry air is about 14 μs [[32](#_ENREF_32)] and that of a ground state OH radical depends on the gas composition but is typically 100 μs in an air plasma although this reduces to about 20 μs when 500 ppm of trichloroethylene is added [[80](#_ENREF_80)] but increases in nitrogen with increasing humidity. [[81](#_ENREF_81)] These relatively short lifetimes for reactive species in the plasma means that there will only be a narrow layer immediately above the catalyst surface from which plasma-created species can be adsorbed. Kim *et al.* [[15](#_ENREF_15)] have calculated that for ground state oxygen atoms or OH radicals this layer will have a thickness of 50 μm. Outside of this layer, species produced by the plasma will react in the gas-phase in the same way that they do in the absence of the catalyst. In the optimal design of a plasma-catalyst reactor, careful thought must be given to concentrating the plasma-created species in the boundary layer to maximise the plasma-catalyst interaction. Reactors where the plasma is created either in very close proximity to the catalytic surface or even on its surface will be optimal.

There are some immediate differences in the surface chemistry that might be expected in a one-stage plasma-catalyst experiment compared to the corresponding conventional catalytic experiment. In the conventional experiment, the only source of radicals adsorbed upon the surface comes from dissociative chemisorption from a suitable precursor. In contrast, plasma-created radicals in the boundary layer can be adsorbed directly and it is likely that this will require a much lower energy. In the hybrid plasma-catalyst arrangement, there is the possibility of a direct Eley-Rideal reaction of a gas-phase, plasma-produced radical with an adsorbed species. There can be no such process in thermal catalysis except at very high temperatures. Thus there is the possibility of additional reaction pathways in plasma-catalysis that have lower energy barriers and higher rates than in the conventional catalytic process.

In a single-stage arrangement, the normal process of desorption can beinfluenced by the electrons that are created in the discharge. Electron-stimulated desorption is a well-known process in surface science. [[41](#_ENREF_41)] This can arise due to local heating of the surface by electron impact leading to thermal desorption. It is also possible that electron impact can affect the bonding between a molecular adsorbate and the surface creating repulsive interactions leading to desorption of a molecule or a molecular ion. For electrons typically found in the high energy tail of the plasma electron energy distribution, the dominant process will be *via* dissociative electron attachment giving an anion that then dissociates. In the case of CF2Cl2 adsorbed onto Ru, Cl- and F- ions are produced. [[82](#_ENREF_82)] An STM study [[83](#_ENREF_83)] has shown that electron attachment to a CO2 molecule that is adsorbed onto an oxygen vacancy on a TiO2 surface brings about dissociation of the anion to give CO and the filling of the oxygen vacancy by the O- ion. The CO will desorb from the surface or migrate to another region. This is shown diagrammatically in Figure 3. The threshold for this process is found to be 1.4 eV. It terms of plasma-catalytic dissociation of CO2 by this mechanism, there will need to be a process that can regenerate the oxygen vacancies.



**Figure 3 Schematic** of the electron-induced dissociation of CO2 adsorbed at an oxygen vacancy, VO, on a TiO2 surface. This proceeds *via* dissociative electron attachment producing CO and an oxygen which fills the vacancy. Reprinted with permission from Ref. [[83](#_ENREF_83)]. Copyright 2011, the American Chemical Society.

Recently, Mei et al. [[84](#_ENREF_84)] have demonstrated how oxygen vacancies generated under plasma action on the surface of TiO2 and BaTiO3 packed in a DBD reactor can facilitate the dissociation of CO2. Using XPS, they have shown the existence of Ti3+ and Ti4+ in the barium titanate sample. The Ti3+ is attributed to the formation of a lattice vacancy through the reaction

Ti4+ + O2- → V0 + Ti3+ + ½O2

where O2- is a lattice oxygen. Electron (*e*−) – hole (*h*+) pairs are generated by highly energetic electrons from the discharge,

*e* (> 3.0 eV) + BaTiO3 → *e*− + *h*+

and are moved in the opposite direction by the electric field, which reduces the probability of their recombination. The CO2 can then be dissociated on the surface as in Figure 3.

In a two-stage plasma-catalyst configuration, there is no direct interaction of the plasma with the catalyst surface that is positioned downstream of the discharge. However, species produced in the plasma that are sufficiently long-lived (> 1ms) will be able to reach the surface and possibly initiate some catalytic activity. Typically, the species that reach the surface are reaction intermediates or stable but potentially reactive molecules such as ozone, NO and NO2 which are commonly produced by plasma in air. In some plasma processes (e.g. oxidative conversion or mineralisation of volatile organic species), there can be a release of chemical energy that can raise the temperature of the gas facilitating catalytic action. The non-equilibrium nature of the plasma can also mean that vibrationally excited molecules are formed and depending on the rate of vibrational relaxation, these species may be able to reach the catalyst.

A downstream catalyst is commonly used to remove undesirable by-products following plasma processing. Considerable amount of work has been undertaken on the removal of NOx species in this way. Tonkyn *et al.* [[85](#_ENREF_85)] describe a system of two sequential, two-stage plasma catalysts for the removal of NOx from diesel exhaust. In both cases, the catalyst was a barium-Y zeolite that can be heated and the plasma was a double dielectric barrier discharge. The simulated exhaust gas mixture contained NO, O2, H2O and propene in a balance of nitrogen with the composition being representative of diesel exhaust. In the first stage, the plasma converted the NO into NO2 and partially converted some propene into acetaldehyde according to the overall reaction

C3H6 + 2O2 + 2NO → CH2O + CH3CHO + 2NO2.

This process proceeds byreactions of OH radicals produced in the plasma. When the resulting gas mixture is passed over the Ba-Y zeolite, NO2 is reduced to a mixture of N2 , N2O, HCN and NO. The combination of NO and acetaldehyde on the catalyst acts as a selective catalytic reduction process giving mainly N2 with small amounts of N2O and HCN. The second plasma-catalysis stage improves the NOx reduction up to 90% by regenerating the NO to NO2 and enhancing the amount of acetaldehyde.

Adsorption onto an appropriate material followed by plasma processing has been presented as an effective and energy efficient way of using plasma for the remediation of waste gases and has been applied to a range of species such as VOCs and NOx. These pollutants are adsorbed and concentrated onto an adsorbent catalytic material in one of two identical chambers arranged in parallel. When one adsorbent is nearly saturated, the gas stream is diverted into the other adsorption chamber whilst the saturated one is treated using plasma in a one- or two-stage configuration. The process is the repeated for the second chamber. This has been demonstrated with an oxygen discharge for a range of VOCs adsorbed onto TiO2, γ–Al2O3 and zeolites. [[75](#_ENREF_75), [86](#_ENREF_86)] Zeolites were recently used in a cycled storage-discharge process to remove formaldehyde with an oxygen or air plasma. [[87](#_ENREF_87)] This technique offers many advantages over a continuous processing system as the plasma only needs to be used for a small percentage of the time required to saturate the adsorbent catalytic material, giving significant energy saving.

An ingenious analytical application of two-stage plasma-catalysis worthy of mention can be found in the work of Han *et al.* [[88](#_ENREF_88), [89](#_ENREF_89)] is the process of cataluminescence which is chemiluminescence resulting from reaction of excited states produced by the discharge on the catalyst. This can be used as a sensor for CO in air. The mixture of CO and air is passed through a non-thermal DBD and than onto a catalyst composed of alkaline earth nanoparticles doped with a metal such as Ag or of Mn / SiO2 giving a weak chemiluminescence whose intensity can be used to give a quantitative measure of the amount of CO present.

**4.2 The role of active oxygen and ozone in plasma-catalysis**

The adsorption of oxygen onto a catalytic surface is key for the application of plasma-catalysis as an advance oxidation process for the treatment of volatile organic compounds in waste gas streams. [[90](#_ENREF_90)] This field in conventional catalysis has been reviewed by Panov *et al.* [[91](#_ENREF_91)] who suggested following the work of Bukhtiyarov *et al.* [[92](#_ENREF_92)]that on a metal oxide surface, the active oxygen is atomic oxygen produced by dissociative chemisorption of molecular oxygen which can then accept electrons from the surface in a stepwise manner until it is fully reduced to O2-. Four active oxygen species can be identified: terminal M=O and bridging M–O–M species, called lattice oxygen, and two anion radicals, molecular O2- and atomic O-. Terminal chemisorption bonding is stronger than the lattice bonding (200 kJ mol-1 compared to 80 kJ mol-1). The former is associated with oxides such as V2O5, MoO3 and Sb2O5 andthe latter with the oxides of Mn, Co, Ni and Cu.

EPR spectroscopy was used to identify oxygen species produced when non-thermal plasma was in contact with a porous γ-Al2O3 surface. [[93](#_ENREF_93)] O- and O2- could not be detected but a signal associated with an Al-O-O\* aluminium peroxyl group formed from OH groups under the plasma action was identified independent of the O2 content of the discharged gas. There are reports of lattice oxygen in BaTiO3 being the origin of CO when methane in nitrogen is treated in a packed bed discharge [[94](#_ENREF_94)] and lattice oxygen in Al2O3 and TiO2 being the source of extra O2 when remediating chlorofluorohydrocarbons in a surface discharge plasma reactor. [[95](#_ENREF_95)]

When active oxygen is produced by plasma and then chemisorbed, the adsorbed oxygen can be extremely persistent under a wide range of conditions. Guaitella and co-workers [[96](#_ENREF_96)] have shown that TiO2 and SiO2 pre-treated with a plasma of oxygen or air can catalyse the oxidation of C2H2 up to 10 minutes after the plasma treatment has ceased. It is found that additional surface coverage of 5 × 1014 cm-2 oxygen atoms can be “grafted” onto the SiO2 surface by the O2 plasma pre-treatment. [[97](#_ENREF_97)] Teramoto *et al.* [[98](#_ENREF_98)] have looked at the surface oxygen produced by an oxygen plasma and fixed onto the surface of zeolite supported Ag-nanoparticle catalyst and found that under conditions of dry air or nitrogen that 70 – 90% of the fixed oxygen was still present after 1000 minutes. It was noted that the amount of surface oxygen fixed was proportional to the square of the amount of silver on the zeolite.

Ozone is a common constituent in oxygen and air plasma and is a powerful oxidising agent. It is commonly formed in the gas-phase by a three-body recombination reaction of plasma-produced oxygen atoms with oxygen molecules

O + O2 + M → O3 + M.

The possibility that ozone can be formed in a plasma-catalytic process has been investigated using an air plasma with α- and γ-Al2O3, quartz and silica gel finding that there was only evidence for ozone production over γ-Al2O3. [[32](#_ENREF_32)] Conversely, catalytic surfaces are well known for their ability to decompose ozone and are commonly used to remove ozone from various processes. For a range of metal oxide catalysts, *e.g.* MnO2-CuO / TiO2, Mn2O3, Ba-CuO Cr2O3 / Al2O3, [[86](#_ENREF_86)] it is found that their use in a two-stage arrangement where plasma-generated ozone is combined with a stream of a VOC onto a catalyst is particularly effective in removing it. The presence of CuO in the catalyst converts CO formed from incomplete oxidation into CO2. [[99](#_ENREF_99)] The catalyst converts the ozone into a surface-bound active oxygen atom, O(S),

O3 + S → O(S) + O2

which can either deactivate a further ozone molecule [[100](#_ENREF_100), [101](#_ENREF_101)]

O3 + O(S) → S+ 2O2

or can react with a VOC that is adsorbed onto the surface and initiate the oxidation of the VOC *via* a Langmuir-Hinshelwood mechanism. Einaga et al. have studied the decomposition of benzene by ozone on a MnO2 / Al2O3 catalyst and find that the rate of destruction of the benzene and the rate of decomposition of the ozone are correlated and that there is a linear relationship between the rate of formation mineralisation products, CO and CO2, and the rate of decomposition of the ozone. [[102](#_ENREF_102)] Benzene has a negligible rate of reaction with ozone in the gas phase. Holzer *et al.* [[32](#_ENREF_32)] have found that catalysts in a porous form are more effective at decomposing a VOC than in a non-porous form, which they attribute to a longer residence time for the organic molecules due to diffusion into the pores before adsorption where short-lived species from the plasma are available for reaction. This also gives enhanced production of CO2 over CO. However, not all of the removed VOC is converted into gaseous end products and some of the removed carbon content remains on the surface. This build-up of intermediate compounds contributes to severe deactivation of the catalyst where in the case of benzene oxidation, species such as formic and acetic acid, phenol and surface formates remain strongly bound to the catalyst. [[102](#_ENREF_102)]

Barakat *et al.* [[103](#_ENREF_103)] have investigated the oxidation by plasma-produced ozone of isopropanol and acetone pre-adsorbed onto a TiO2 catalyst. They show that ozone can be adsorbed on TiO2 according to the scheme of Bulanin *et al.* [[104](#_ENREF_104)] in three ways: weakly physisorbed to an –OH or bound to either weak or strong Lewis acid sites. Only ozone adsorbed onto the strong Lewis acid site can decompose to give the surface oxygen atom that can oxidise the VOC. For the reaction with isopropanol, they monitor both the gaseous products and adsorbed species on the surface and observe the gas-phase evolution of CO2 and to a lesser extent CO with a rate of formation that is limited by the rate of oxidation of the acetone intermediate, which saturates the surface.

**4.3 Direct *in situ* detection of adsorbed intermediates**

In order to completely understand and describe the chemistry of plasma-catalysis, it is vital to be able to identify the species that are present on the catalytic surface during the plasma processing. Ideally, this should be performed *in situ* in real time during the processing. It is possible to remove the catalyst at various times during the processing and perform *ex situ* analysis of the catalyst surface using a range of surface analysis techniques such as infrared, Raman, thermal desorption spectroscopy and X-ray photoelectron spectroscopy. This has been applied in several plasma-catalysis studies indicating the change in important functional groups on the surface such as H2O, CO, CO2 and many organic species. [[105](#_ENREF_105)] But this will only give an indication of very strongly adsorbed species that remain on the surface long enough for remote analysis and will not identify the short-lived intermediates that may play an important role in the mechanism of plasma-catalysis. We can probably class these as “known unknowns”. There is a wide range of surface analytical techniques that have been used to provide *in situ* probing of surface intermediates in conventional thermal catalysis but few of these have so far been applied to the more hostile environment of plasma-catalysis, which presents additional experimental challenges.

One technique that has been applied to *in situ* detection of species at the surface in plasma-catalysis is diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in which infrared radiation is reflected from the surface and collected allowing time-resolved analysis of the surface coverage of reagents, intermediates and products to be performed by identifying the vibrational frequencies characteristic of various chemical bonds and functional groups on the surface or immediately below the surface.. Whilst this technique has been widely used for studying conventional catalysis [[106](#_ENREF_106), [107](#_ENREF_107)], it has only recently been applied to plasma-catalysis. An example can be found in the work of Stere *et al.* [[108](#_ENREF_108)] who used DRIFTS to examine the selective catalytic reduction (SCR) of NOx on a Ag / AlO2 catalyst in the presence of toluene and *n*-octane where the catalyst was activated by an atmospheric pressure, helium plasma jet. The experimental arrangement is shown in Figure 4 where the infrared radiation enters and exits through the zinc selenide windows. For the reaction with *n*-octane, an isocyanate intermediate is identified from the growth of –NCO bands observed in the infrared spectrum on a timescale of about 10 minutes following plasma activation of the catalyst as the adsorbed *n*-octane disappears. In contrast, for the toluene-SCR of NOx, there was no evidence of isocyanate formation and the observed intermediate was cyanide deduced from the detection of the –CN band. In thermally-activated SCR with *n*-octane, both isocyanate and cyanide intermediates are found suggesting that plasma-activated SCR with *n*-octane favours the isocyanate reaction pathway associated with the formation of an organic nitrate, R-NO2. The authors also report that a critical role of the non-thermal plasma in this process is in keeping the surface clean, which can be attributed to plasma-generated species such O and O3 and also OH, HO2 in the presence of any moisture.

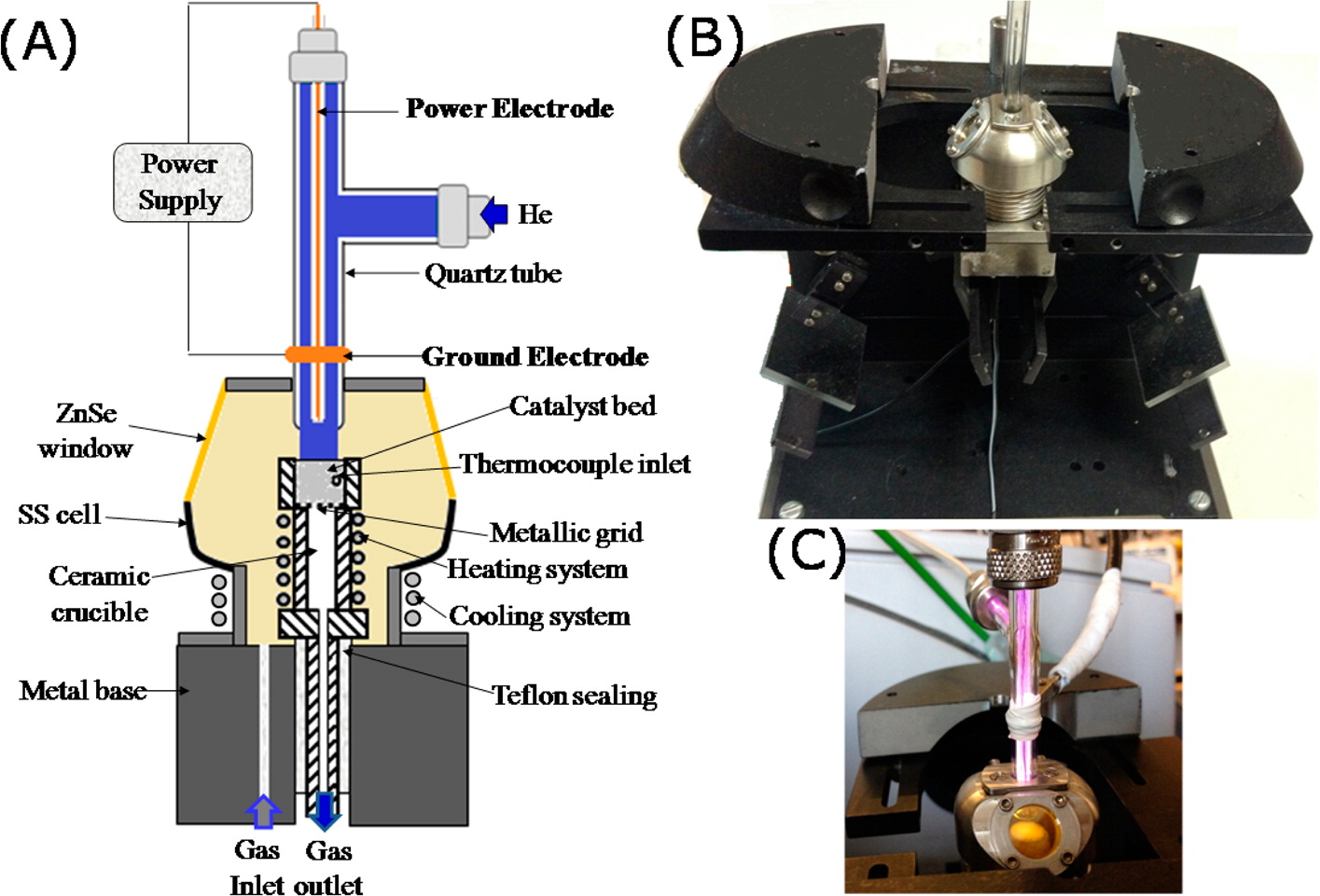


Figure 4. Schematic view of the diffuse reflectance infrared (DRIFTS) cell designed for the investigation of plasma-assisted, gas-phase catalysed reactions. Reprinted from Ref. [[108](#_ENREF_108)] with permission. Copyright 2015, the American Chemical Society.

Another example of DRIFTS applied to plasma-catalysis comes from the work of Barakat *et al.* [[103](#_ENREF_103)], mentioned in the previous section, on the oxidation of isopropanol and acetone adsorbed on TiO2 by ozone produced in a downstream plasma in a two-stage plasma-catalysis arrangement. The sensitivity of the DRIFTS analysis in identifying the species on the surface and their time-dependent behaviour can be seen in the study on acetone. In the initial step, acetone is adsorbed onto the TiO2 and Figure 5 shows the time evolution of two adsorbed species that can be detected. Firstly, bands characteristic of adsorbed acetone can be observed. They grow in and then decrease as the surface becomes saturated. The second species grows in slightly slower than the acetone after about three minutes. This is identified as mesityl oxide, which is a α, β-unsaturated ketone with the formula CH3CCH=C(CH3)2. This is formed on the surface by a condensation reaction of two acetone molecules, which releases a water molecule creating –OH groups on the surface. It is estimated that about 50% of the adsorbed acetone is converted to mesityl oxide. When ozone is admitted to the saturated surface, the adsorbed acetone and mesityl oxide are rapidly oxidized and CO and CO2 and observed in the gas-phase peaking after about 10 minutes. Adsorbed products, formic acid and formates, are also formed on the surface but over a longer time scale of up to 60 minutes. The time resolution of the DRIFTS analysis is 1 minute.

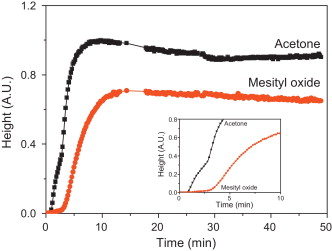


Figure 5. Evolution of acetone and mesityl oxide surface coverages on TiO2 during the adsorption of acetone detected by DRIFTS. Reprinted from Ref. [[103](#_ENREF_103)] with permission. Copyright 2014, Elsevier.

A related technique based on infrared spectroscopy that could have considerable potential as a diagnostic tool for real time, *in situ* surface analysis in plasma-catalysis is attenuated total reflectance (ATR) spectroscopy in which infrared radiation passes through a crystal in such a way as to reflect from a surface attached to the crystal. It has a penetration depth into the surface of about 0.5 – 2.0 μm. Following multiple such reflections through the crystal, the infrared radiation is analysed giving similar information to the DRIFTS experiment. This has been used in conventional catalysis experiment to study adsorbed species in methanol synthesis using nickel-based [[109](#_ENREF_109)] or Pt catalysts [[110](#_ENREF_110)]. ATR-FTIR has been adapted for use in a plasma experiment in which film growth was monitored [[111](#_ENREF_111)] but there have been no reports yet of the application of ATR-FTIR to plasma-catalysis. Non-linear optical techniques (e.g. Second Harmonic Generation) have also been applied to studying adsorbates on catalytic surfaces in situ for a full range of pressure conditions allowing the mechanism of catalytic reactions to be determined [[112](#_ENREF_112)] but there are no reports of this technique being applied to plasma-catalytic studies.

Another promising technique that has recently been applied to the *in situ* analysis of a catalytic surface is that of near-ambient-pressure x-ray photoelectron spectroscopy (NAP-XPS) using synchrotron radiation [[113](#_ENREF_113)]. X-ray photoelectron spectroscopy (XPS) is a well-established and highly surface sensitive technique giving information on the chemical states of both catalysts and adsorbates but is commonly restricted to working under ultra high vacuum conditions. Recent developments have enabled the technique to be used at near atmospheric pressure enabling *in situ* probing of thermal catalytic processes. Examples are given of the oxidation of CO on Pt-group metal catalysts and the catalytic conversion of hydrocarbons. Whilst these studies are time-averaged and give information only on the most thermodynamically stable adsorbed species, the technique has also been developed to give time resolved information using a laser pulse-probe XPS method for the decay of excited Ti species on a photo-excited TiO2 surface. [[114](#_ENREF_114)] The decay processes are typically on a timescale of 50 - 100 ns and the resolution allows dynamics on the nanosecond timescale to be resolved. [[115](#_ENREF_115)] It is suggested [[113](#_ENREF_113)] that “similar time-resolved experiments under the presence of gases of O2 and organic molecules may provide information on evolution of a photocarrier-induced oxygen radical species and decomposition dynamics of adsorbed organic molecules”. These could then be adapted to plasma-catalytic studies involving plasma-induced oxygen radical species.

Moving from time-resolved experiments on the timescale of minutes (DRIFTS , ATR) to nanoseconds or less is an exciting prospect for the study of the dynamics of plasma-catalysis at an atomistic level that could be achieved within the next few years. Adaption of this pump-probe technique to a plasma-catalyst environment will again be challenging probably needing a short duration (1ns), pulsed plasma source as the pump stage. The “unknown unknown” in this area is the timescale upon which significant surface processes take place in plasma-catalysis. Short-lived, weakly bound intermediates (atoms, radicals) will certainly play important roles in the mechanisms and we need molecular dynamics simulations to inform us about the timescales that are necessary to probe unstable transient as well as more stable adsorbed species in plasma-catalysis. We can be guided by recent studies from the group of Nilsson [[116](#_ENREF_116)] using a time-resolved study of the desorption of CO from a Ru(001) surface under high vacuum conditions using a femtosecond laser pump and X-ray absorption and emission spectroscopy. The optical laser pump causes vibrational excitation of the adsorbate within a picosecond which then weakens the CO-Ru bond and as the CO-metal distance increases, it forms a short-lived precursor state (> 2 ps) from which it diffuses or desorbs from the site. [[117](#_ENREF_117)]

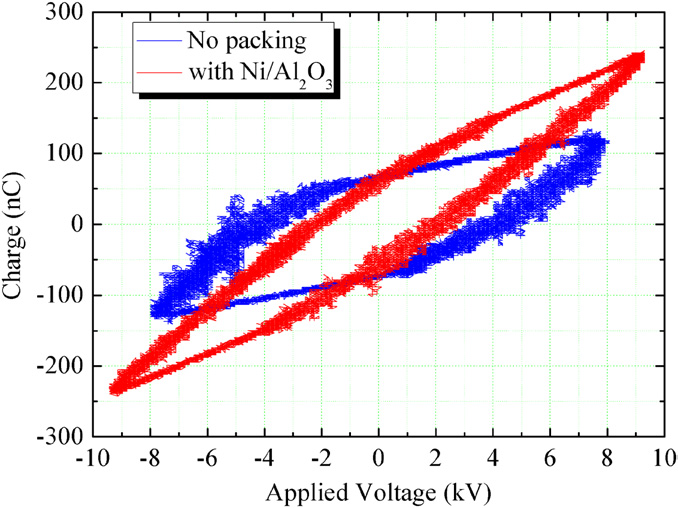
**5. The effect of a catalyst on the plasma discharge**

If the interactions of plasma on a catalyst broadly affect the chemistry or properties of the catalyst, then the reverse interaction of the catalyst on the plasma largely brings about changes to physical or electrical properties of the discharge. The packing material may change the nature of the discharge. For example, Tu *et al.* [[118](#_ENREF_118), [119](#_ENREF_119)] have noted that the presence of a surface (BaTiO3 or TiO2) within an Ar or N2 DBD (a single-stage arrangement) changes the discharge from being formed of microdischarges or streamers to one in which the microdischarges become more spatially confined and there is a transition to surface discharges on the catalyst. This causes a modification of the electron energy distribution in the plasma enhancing the concentration of higher energy electrons and increasing the vibrational temperature of the N2 gas. [[119](#_ENREF_119)] In the dry reforming reaction of CH4 in the presence of CO2, packing the DBD plasma reactor with quartz wool, a non-catalytic material, increases the conversion of CH4 and CO2 compared with the empty reactor due solely to the transition from microdischarges to a surface discharge on the quartz. [[45](#_ENREF_45)]

When a dielectric material is placed into a plasma reactor such as a DBD reactor, the capacitance of the reactor will be changed. The resultant capacitance of the packed reactor, *C*cell, depends on the capacitance of the dielectric material, *C*d, and the capacitance of the gas, *C*g,

.

*C*cell can be determined from the measured Lissajous figures using the method of Manley [[120](#_ENREF_120)] where the area of charge *versus* voltage corresponds to the capacitance of the reactor. Figure 6 shows the Lissajous figures measured for a DBD with no packing and also when packed with a Ni / Al2O3 catalyst. [[53](#_ENREF_53)] From this figure, it can be deduced that there is an increase in the capacitance from 7.5 to 18.5 pF when the catalyst is added to the reactor due to its dielectric properties (ε 50). From the shape of the figures, it can be deduced that there is a lowering in the breakdown voltage upon adding the catalyst (from 3.3 to 0.75 kV) meaning that the discharge can be initiated at lower voltages giving a potential improvement in energy efficiency. This is attributed to a transition in discharge mode from filamentary with no packing to a combination of filamentary and surface discharge with the packing. [[54](#_ENREF_54)] It should be noted that the efficiency and conversion achieved also depends on the morphology, porosity and chemical activity (acid-base properties) of the packing material as well as its dielectric properties as noted by Yu *et al.* [[121](#_ENREF_121)]and Duan *et al.* [[122](#_ENREF_122)] in their studies of CO2 decomposition on materials such as quartz, alumina, CaO and MgO. Holzer *et al.* [[123](#_ENREF_123)]found that the magnitude of the dielectric constant for two ferroelectric materials (Al2O3, ε 5, compared with TiO2, ε > 40) does not effect the selectivity for the oxidation of either acetone or toluene in an acetone-toluene-air mixture. Hung *et al*. [[124](#_ENREF_124)] find that CO2 and CH4 conversions and H2 selectivity in the dry reforming of methane using a ferroelectric-packed bed DBD reactor (packed with either BaFe0.5Nb0.5O3 or BaZr0.75Ti0.25O3) were greater for the material with the higher dielectric constant (BaFe0.5Nb0.5O3). Packing the DBD with glass beads produced an outcome that was poorer than using a DBD by itself.



**Figure 6.** Lissajous figures of a CH4 / CO2 DBD with and without a reduced Ni / Al2O3 catalyst at a constant discharge power of 50 W. Reproduced from Ref. [[53](#_ENREF_53)]. Copyright, 2011 IOP Publishing.

The technical advantages of using ferroelectric materials with high dielectric constants in terms of lower operating voltages and enhanced fields that give higher concentrations of reactive species have been employed to study plasma-catalysis by interspersing catalytically-active species amongst the ferroelectric materials. Holzer *et al.* [[123](#_ENREF_123)] used an arrangement to investigate the decomposition of methyl tertiary-butyl ether (MTBE) in air that had two regions of packing with BaTiO3 at the inlet side of the plasma reactor followed by a second region formed of LaCoO3. They found that this arrangement gave a conversion to COx (CO + CO2) products that was only slightly higher than that given by using only BaTiO3. However, if the same components of BaTiO3 and LaCoO3 were homogeneously mixed, there was a lower conversion of MTBE but a higher selectivity for the formation of CO2. If LaCoO3 was used by itself, there was an even lower conversion of MTBE but the selectivity for CO2 was higher. They interpret this finding by suggesting that MTBE can be efficiently oxidised on BaTiO3 to COx and some reactive intermediates and these species are then further oxidised by the LaCoO3 catalyst. Goḿez-Ramírez and co-workers [[125](#_ENREF_125)] report that a small amount of a vanadium / alumina catalyst dispersed onto a barium titanate ferroelectric packed bed substantially increased the yield of formaldehyde obtained from carbon dioxide and ethane. Rico et al. [[126](#_ENREF_126)] have added a copper-manganese catalyst to a DBD packed with BaTiO3 and find that there is a modest increase in the already high decomposition rate for methanol for (92 – 97%) but that there is a significant change in the end-products formed. With BaTiO3, the products are exclusively H2 and CO but upon the addition of the catalyst CO2 and H2O are also formed reducing the selectivity for H2 and CO to 36 and 80%, respectively. We have also used the technique of mixing small amount of catalysts in a barium titanate packed bed plasma reactor to study the temperature dependence of plasma-catalysis for a wide range of systems. [[9](#_ENREF_9)]

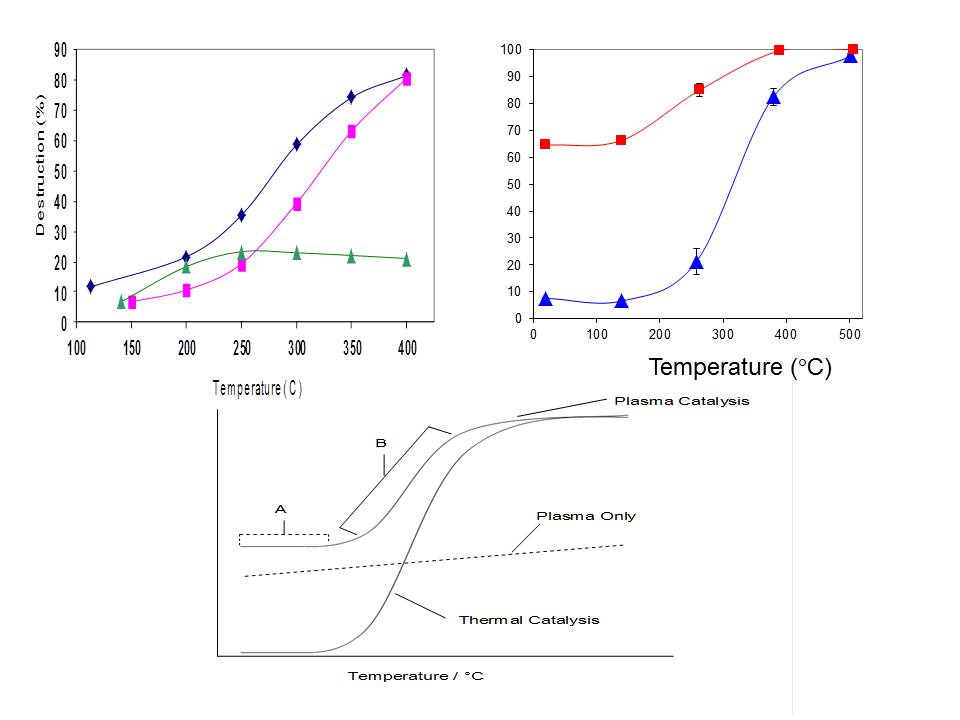
Li *et al.* [[127](#_ENREF_127)] have shown that in a dielectric barrier discharge reactor that is packed with γ-Al2O3, it is possible to have a difference in temperature between the gas which is hotter by up to 10°C than the alumina pellets for relatively low discharge powers (2 W). The mechanism by which the electrical energy of the plasma is converted into heat in the gaseous and solid phases differs. In the gas, it is the energy absorbed by the electrons that is transferred to the heavy species through the various collisional processes in the plasma. The heating of the pellets comes from electrical energy consumed via dielectric polarisation loss, which depends on the nature of the material. The γ-Al2O3 used in their modelling has a relatively low dielectric constant compare to materials such as BaTiO3 where it might be expected that dielectric heating will consume more of the electrical energy of the plasma. They also point out that the size of the pellets and the spacing between the electrodes containing the pellets will affect the dielectric polarisation loss.

The nature of the catalyst surface can have an effect on the electric field in the discharge and irregularities in the surface such as roughness or the presence of pores can create local variations in the electric field. These can be very important as the electron energy distribution (EED) in the discharge is determined by the electric field strength and local regions of field intensification can become a source of high energy electrons. The EED determines the yield of chemical species in the discharge. [[123](#_ENREF_123)] In packed bed reactors filled with spherical beads, there is an intense field at the points of contact of the beads [[128](#_ENREF_128)], which affects the formation of the microdischarges. The higher the dielectric constant of the beads, the stronger is the intensification of the electric field due to effective polarisation. This increases the electron density, which will lead to the creation of more reactive species close to the surface. The islands of nano-sized dispersed metals on a support will also encourage enhanced electric fields [[86](#_ENREF_86)] as will edges, steps or other irregularities in the crystalline structure of the catalyst and features such as pores and roughness.

The way in which the discharge area is packed with the catalyst can affect the outcome of the plasma processing. For example, a DBD reactor that is only partially filled with a catalyst has been shown to double the CH4 conversion and H2 yield during the dry reforming of CH4 with CO2 compared to when the reactor is completely filled. [[45](#_ENREF_45)] The size of the catalytic particles is also an important processing parameter.

**6. Temperature effects in plasma-catalysis**

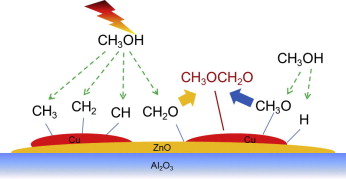
Looking at how temperature affects plasma-catalysis can be very revealing in terms of understanding the mechanism of the coupling between plasma and catalyst. Variation of temperature can be a probe of the kinetics and of the thermodynamics or energetics of the processes involved. The discharge is a source of energy that can be transformed into heat. It has been found that the temperature change of a plasma reactor increases almost linearly with the applied energy. [[15](#_ENREF_15)] The overall reaction that is being studied may be exothermic as for VOC oxidation or endothermic as for hydrocarbon reforming or decomposition. In the latter case, energy must be supplied. In non-thermal plasma, the gas temperature is normally close to ambient (< 300 K) whereas the normal threshold or lift-off temperature for a catalyst to become activated is generally much higher than this. Most plasma-catalytic processing is performed at near to ambient temperatures to achieve improved energy efficiency where the catalyst is not thermally activated. Two different types of behaviour found when studying the temperature dependence of plasma-catalysis are illustrated in the upper panels of Figure 7. On the left, the results for the removal of 100 ppm dichloromethane in air in an AC-powered, heated BiTiO3 packed bed reactor, with and without the addition of a TiO2 catalyst is compared with the results for thermal catalysis. [[129](#_ENREF_129)] When the experiment is performed in the BaTiO3 reactor without a catalyst, there is only a small degree of destruction which shows a small temperature dependence increasing to 20% by 250°C. This can be attributed to the production of electrons in the plasma and the subsequent electron-induced processes, which have only a slight temperature dependence. [[130](#_ENREF_130)] The destruction curve for thermal catalysis shows the typical “lift-off” shape where the catalyst only becomes active for temperatures greater than 150 - 200°C. When the TiO2 catalyst is added to the packed bed, the curve resembles that for thermal catalysis but is shifted to lower temperatures by about 50°C. There is no evidence of strong synergy in this behaviour except perhaps at temperature < 150°C, which suggests that the mechanism of thermal and plasma-catalysis are similar in this case except for the lowering of some energy barrier by the plasma interaction which might result from the direct adsorption of a plasma-dissociated species (possibly an oxygen atom) rather than the dissociative chemisorption of molecular oxygen. Alternatively, the plasma treatment of the TiO2 might have created more oxidative sites on the surface as was discussed in Section 4. A pronounced synergistic effect is seen at low temperatures (< 200°C) when 500 ppm of toluene in air is treated in an AC-powered, heated BaTiO3 packed bed to which a 0.5% Ag / γ-Al2O3 catalyst has been added [[131](#_ENREF_131)] as shown in the upper right hand panel of Figure 7. The toluene destruction curve for thermal catalysis shows that the catalyst only becomes active for temperatures greater than 150 - 200°C whereas the plasma-activated catalysis is able to destroy > 60% of the toluene from 20°C and is more effective than thermal catalysis until 500°C. In this case, it would seem that there has been a much more significant change in the reaction mechanism resulting from the coupling of plasma and catalyst.

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**Figure 7** Top (left): Comparison of thermal catalysis (), plasma alone () and plasma-catalytic destruction () of 100 ppm dichloromethane in air as a function of temperature using a TiO2 catalyst. Adapted from Ref [[129](#_ENREF_129)] with permission. Copyright 2007 Wiley. Top (right): Comparison of thermal catalysis () and plasma-catalysis () for the destruction of 500 ppm toluene in air as a function of temperature, using a Ag/γ-Al2O3 catalyst, in a one-stage configuration. Adapted from Ref. [[131](#_ENREF_131)] with permission. Copyright 2008 Elsevier. Lower: Schematic diagram showing the trends in pollutant destruction observed between thermal catalysis, plasma-catalysis and plasma alone operation in a one-stage configuration. Reproduced from Ref. [[132](#_ENREF_132)] with permission. Copyright 2009 Springer.

We have attempted [[132](#_ENREF_132)] to crudely deconstruct the form of these plasma-catalysis temperature profiles into two portions as shown in the lower panel of Figure 7. The portion marked **B** is a replica of the curve found for thermal catalysis with the same catalyst shifted to lower temperature and is the only identifiable component in the plasma-catalytic processing of dichloromethane on TiO2. However, in the case of the processing of toluene on a Ag / Al2O3,we find an additional contribution at lower temperatures marked **A** in Figure 7. It is possible that all plasma-catalysis temperature profiles can be deconvoluted into different proportions of these two components, **A** and **B**. At high enough temperatures, it is impossible to distinguish the plasma-catalytic and thermal curves as they both converge to the same level of destruction implying that the mechanism for these temperatures and above is essentially thermal and unhindered by inaccessible energy barriers. The component, **B**, which represents essentially catalytic behaviour modified by the plasma can come about from processes which might include the increased concentration of reactive radicals such as O and OH formed in the discharge or by the creation of additional reactive species on the surface from plasma-created intermediates such as ozone and excited species (electronic or vibrational). If a species delivered to the surface is already dissociated then the adsorption step is easier resulting in a lower temperature threshold but essentially the same form of temperature dependence. The portion of the curved marked **A** represents some or all of the processes and mechanisms described in Sections 4 and 5. It could simply come from increased residence times on the surface due to adsorption of reactive species onto plasma-created sites on the surface or into pores where surface discharges can create excited states. Increased residence times for adsorbed reactive species will increase the overall reactivity. It is possible that there are different and low energy reaction pathways available for some plasma-created species or plasma-created surface sites that give alternative routes for the conversion and possibly different final products which will modify the selectivities for certain products as is sometimes observed. The possibility of additional reaction pathways that become operative only under the conditions of plasma-activated catalysis is a big unknown and will be a challenge to the computational chemists and modellers to investigate.

As an example of changing reaction pathways resulting from plasma excitation, a recent paper by Kim *et al.* [[133](#_ENREF_133)] on the methanol steam reforming process performed in a heated DBD reactor packed with a Cu / ZnO / Al2O3 catalyst postulates that the process involves the adsorption of radicals produced in the plasma rather than the adsorption of methanol as in the thermal catalysis which then dissociates to a methoxy radical, CH3O. The subsequent dehydrogenation reaction of the methoxy radical on the surface is a rate-determining step in the thermal mechanism that ultimately produces H2 and CO. However, the plasma produces a different set of radical species such as CH3, CH2, CH2O and OH in the gas-phase that can be adsorbed and undergo other reactions bypassing the thermal rate-determining step and yielding H2,CO and a trace of CH4 at an enhanced rate. This is shown in cartoon form in Figure 8.

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**Figure 8.** Adsorption of radicals produced by an electric discharge as intermediate species on the catalyst surface in the steam reforming of methanol by plasma-catalysis on a Cu / ZnO / Al2O3. Reproduced from Ref. [[133](#_ENREF_133)] by permission. Copyright 2014, Elsevier.

Studying the temperature dependence of a plasma-catalytic reaction can be a means of obtaining kinetic information for the overall reaction. The rate constant for the overall process can be determined for a range of temperatures and used to determine an activation energy. There will be many elementary reactions contributing to the overall process but one will be slowest, the rate determining step, and the derived activation energy will reflect this process. The kinetics of rate determining step will depend on the reaction conditions such as the pressure, the nature of the catalyst, the type of plasma excitation and the occupancy of the surface sites on the catalyst. The rates of the plasma-catalysed reactions will usually be determined by measuring the concentrations of reactants or products under steady state conditions, which gives little information about the detailed dynamics of the elementary reactions. [[41](#_ENREF_41)] Mok and co-workers [[134](#_ENREF_134)] have studied non-thermal plasma methanation of CO with H2 using a Ru / TiO2 / Al2O3 catalyst over the temperature range 240 - 300°C giving an activation energy ranging from 76 – 115 kJ mol-1 that depended on the applied plasma voltage. Vandenbroucke *et al.* [[55](#_ENREF_55)] studied the oxidation of trichloroethylene (TCE) in dry air using a corona / glow discharge plasma with a MnO2 catalyst in a down-stream, two-stage arrangement over the temperature range 300 - 500°C. They found that the activation energy for the abatement of TCE was reduced from the thermal catalytic value of 36 to 6 kJ mol-1 by plasma-catalysis, which they attribute to more efficient oxidation of plasma-created intermediates. Demidyuk and Whitehead [[135](#_ENREF_135)] investigated the difference in overall activation energy for the destruction of toluene in air using a BaTiO3  packed bed plasma reactor where a AuO2 / Al2O3 or MnO2 catalyst was either placed into the packed–bed in a one-stage arrangement or was placed separately downstream. In both configurations, the catalyst was heated between 115 and 400°C. When using the catalyst in the two-stage arrangement, they found that the activation energy for the plasma-catalytic two-stage arrangement and thermal catalysis was similar. However, plasma treatment decreased the activation energy for the silver oxide catalyst in the one-stage arrangement from 63 to 49 kJ mol-1. For the manganese dioxide catalyst in the one-stage arrangement, plasma-activation accelerated the oxidation of toluene but the activation energy was unchanged and the gain came from an increase in the number of active sites (the pre-exponential factor in the Arrhenius expression). This was attributed to a possible change of the oxidation state of the Mn ions, under the influence of the plasma or the action of plasma-created species (*e.g.* ozone, atoms, and radicals) with the catalyst surface that can promote electron transfer from Mn sites.

Simplified kinetic models have been applied to plasma-catalytic systems to explain the experimental observations. Kim *et al.* [[136](#_ENREF_136)] developed a generalised model for the oxidation of a volatile organic compound (VOC) on a catalyst where the plasma created activated sites on the surface. The concentration of these activated sites was proportional to the plasma power density. The activated sites “react” with adsorbed VOC molecules to produce intermediates or products. They showed that the rate of removal of the adsorbed VOC obeys zeroth order kinetics agreeing with their experimental results for a range of VOCs in atmospheric pressure air using surface discharge plasma with a Ag / TiO2 catalyst. No gas-phase chemistry initiated by the plasma was included. A more extensive kinetic model was presented by Tochikubo [[137](#_ENREF_137)] who modelled the plasma-enhanced selective catalytic reduction of nitrogen oxides with a hydrocarbon additive. The action of a dielectric barrier plasma discharge was represented by modelling a single microdischarge to calculate the yield of ions, radicals and excited states as a function of specific energy density involving 33 different electron impact, ionisation, recombination and electron attachment processes. This then provided the input for modelling the gas-phase chemistry which involved 20 reactions [[138](#_ENREF_138)]. The reactions at the catalytic surface were modelled using a simple mass balance model with a set of 17 reactions representing a range of adsorption, desorption and surface processes. The concentrations of species as a function of specific energy density were modelled giving predictions of the removal of NO and NO2 for a range of temperatures This model did not include any effects of the discharge on the surface reactivity during the plasma processing.

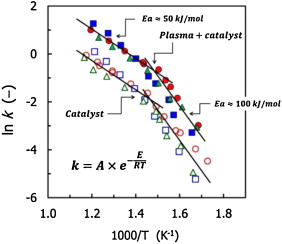
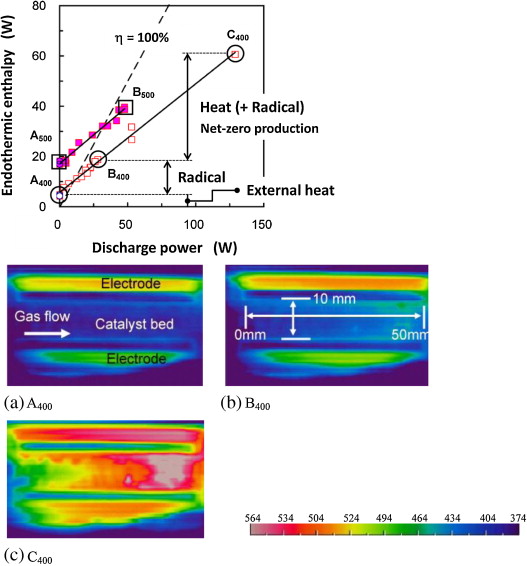
The concept of temperature in the non-equilibrium system of plasma-catalysis using non-thermal plasma can be vague and ambiguous. Whilst the energy deposited into the plasma can be determined with a high degree of certainty, it is not clear *a priori* how this will affect the temperature of the plasma and the different degrees of freedom in the plasma are usually associated with a range of temperatures rather than a single value. The temperature characterising the electron energy distribution (if it can be represented as Maxwellian) is considerably larger than the temperatures for the different degrees of freedom associated with gas due to inefficient momentum transfer. For the gas, there is often a hierarchy of values such that temperature describing electronic excitation is larger than that for vibration, which in turn is larger than for rotation and translation. It is often assumed that the rotational temperature and the translational or gas temperature have the same value in a non-thermal plasma operating at atmospheric pressure because of rapid R-T collisional energy transfer and this is the basis of the determination of gas temperature by emission or absorption spectroscopy [[139](#_ENREF_139)] or Raman scattering. [[140](#_ENREF_140)] However, it is not always the case that complete thermalisation of rotation will have occurred in every gas mixture used in plasma studies and the two temperatures will then differ with Trot > Tgas. There are also examples in which the observed rotational distributions are non-Boltzmann and cannot be described by a single temperature. [[139](#_ENREF_139)]

Non-equilibrium in the degrees of freedom of the plasma gas, particularly for vibration, is can be of advantage in some examples of plasma-catalysis. For example, in the steam reforming of methane with water, it has been suggested that vibrational excitation of the CH4 and H2O will facilitate the process. [[35](#_ENREF_35)] It has been shown [[141](#_ENREF_141)] that vibrationally excited CH4 chemisorbs with more than three orders of magnitude greater efficiency on a Ni surface than does methane in its ground vibrational state although the nature of the vibrational mode is found to be more important than its vibrational energy with the *ν3* stretching mode of CH4 being more effective than the *ν4*bending mode. [[142](#_ENREF_142)] Nozaki and co-workers have investigated the steam reforming of methane in a DBD reactor with a Ni / SiO2 catalyst and showed that the conversion of methane exceeded the thermal equilibrium conversion and that there was a distinct synergistic effect from the coupling of plasma and catalyst above 400°C [[143](#_ENREF_143)] Electron impact processes in the plasma create vibrationally-excited methane and enhanced chemisorption on the Ni is the origin of the improved conversion of methane seen in the plasma-catalysis compared to thermal catalysis (50% *versus* 20% at 400°C). They investigated the effect of both catalyst and gas temperature on the processing showing that even when the gas temperature reached 400 - 500°C, a synergistic coupling of the plasma and catalyst was not achieved unless the catalyst bed temperature exceeded 200°C. [[144](#_ENREF_144)]

This study was extended by Nozaki and Okasaki [[35](#_ENREF_35)] to the steam reforming of methane in a flow of N2 and H2O using a DBD reactor packed with a Ni / Al2O3 catalyst and equipped with external heating. The temperature distribution in the reactor is shown in the left hand panel of Figure 9. In the sequence (a) (b) (c), the input power to the plasma is increased. Between (a) and (b), the conversion of methane increases substantially from 3 to 13% due to the production of radical species by the plasma but there is no significant increase in the bed temperature which stays at about 420°C. At (a), the energy efficiency exceeds 100% because steam reforming of methane is enabled by the external heat source. At (b), the energy efficiency drops to 80% as the conversion of methane reaches chemical equilibrium. By (c), the methane conversion is determined by chemical equilibrium giving a conversion of 40% and the extra plasma energy produces excess radicals that are not required and eventually that energy is converted into thermal energy. This raises the temperature of the bed as can be seen in Figure 9 with significant increase in the downstream region of the catalyst bed. At this point the energy efficiency falls to 50%. In the right hand panel of Figure 9, we see the Arrhenius plots for the temperature dependence of the conversion of methane where the rate-determining step is taken to be the activation of methane on the Ni catalyst. The curves for both the thermal catalysis and the hybrid plasma-catalysis show evidence of two distinct pathways with different activation energies. In low temperature region, the process is limited by the rate of surface reactions but in the higher temperature region, surface diffusion is limiting. The transition between these two pathways occurs at 460°C for thermal catalysis but at the lower value of 420°C for plasma-catalysis. The obtained activation energy of 100 kJ mol-1 corresponds to the limiting surface reaction step being the dehydrogenation of methane and is unaffected by the action of plasma. For both pathways, the pre-exponential factor is greater in the case of the plasma-catalytic system by up to 50 times for the methane activation stage and by a factor of 7 in the diffusion regime. This could be interpreted as the plasma increasing the number of active sites associated with chemisorbed carbon produced in the reforming that can be removed via the Boudouard reaction

C + CO2  CO + CO

which is facilitated by plasma action through the production of radicals such O and OH. In addition, local heating of the Ni nanoparticles in the catalyst can cause melting and diffusion of the carbon into the particle where it can be oxidised by adsorbed CO2. [[145](#_ENREF_145)]



**Figure 9.** The plasma reforming of CH4 in a DBD reactor packed with 12% Ni / Al2O3 catalyst. Left hand panel: Temperature distribution of the bed. Right hand panel: Arrhenius plot for forward methane reaction rate constant. Reproduced from Ref. [[35](#_ENREF_35)] by permission. Copyright 2015 Elsevier.

Local heating of different regions of the surface, which could imply locally high temperatures can arise through a variety of reasons. The electric field can be intensified by surface irregularities creating discharge hotspots. The inhomogeneity of the discharge temperature within a DBD can be seen quite clearly in the thermal imaging experiments of Tirumala et al. [[146](#_ENREF_146)] The electrical conductivity of the surface due to the dispersed metallic particles can cause the discharge to spread over the surface causing Joule heating. [[86](#_ENREF_86), [145](#_ENREF_145)] The impact of energetic ions, electrons and electronically excited species colliding with the surface can also be a cause of hotspots. Temperature gradients on a La2O3 / CeO2 catalyst surface can be observed in microwave plasma reforming of methane. [[147](#_ENREF_147)] Kim *et al.* [[23](#_ENREF_23)] have pointed out that the rate of heating of the nanoscale metal clusters on a support can be very much faster than that for the support due to the difference in the heat capacities of the two materials. For a 10 nm Ag particle on a 2mm support, the silver reaches a stable temperature in 1 ps whereas several seconds are required for the support to come to equilibrium which could cause rapid temperature fluctuations to occur in the surface temperature of the metal during the plasma-catalytic processing. Neyts and Ostrikov [[148](#_ENREF_148)] have drawn attention to the necessity to consider the nanoscale thermodynamics of plasma catalysis where the systems may be affected by localised fluctuations and that many of the thermodynamic properties including chemisorption energies will have a dependence on the size of the nanocrystals of the catalyst as well their physical states (liquid or solid).

**7. Selection of catalysts**

Whilst a wide range of catalysts have been used in plasma-catalytic experiments (*e.g.* see comparative tabulations for specific systems in recent reviews [[8](#_ENREF_8), [19-21](#_ENREF_19)]), it is not yet possible to recommend *a priori* the best choice of catalyst for use in a particular plasma-catalyst discharge configuration for a particular reactive system under defined conditions to produce a specified outcome. It will probably be a long time before we can make a selection that will satisfy even some of those aspirations. It has been inevitable that almost all the catalytic materials that have been used so far in successful plasma-catalytic experiments are the same materials that have been used in the corresponding thermal catalysis experiments. That means that thermal and plasma-assisted catalyst experiments require many of the same properties in their choice of catalytic materials. In essence, the catalyst must allow for the adsorption of the reagents and provide reaction pathways that achieve the conversions and transformations that are required. How might this differ between thermal and plasma catalysis? We have seen that plasma can make adsorption more effective by lowering energy barriers and increasing the number of active sites. This will increase the yield under plasma excitation and also reduce the operating temperature. Effective adsorption is also important as it increases the residence time of the adsorbed species in the plasma region and thereby increases reaction yields. Thus many materials like alumina and zeolites that might not be conventionally classed as catalysts improve the performance when added to a plasma system. The physical state of the catalyst in terms of particle size and porosity will affect the adsorption probability and may also increase the conversions by modifying the discharge properties. The ability of the plasma to increase the dispersion of metals on supports will also enhance performance and modify the nature of the discharge.

It may also be that the reagent species that are adsorbed are different or in different states following plasma excitation *e.g.* dissociated fragments (atoms and radicals) of the supplied reagents are adsorbed or that the reagents are in excited states (vibrational or electronic). This may simplify or modify the reaction pathways but the use of a particular catalyst in both thermal and plasma-catalysis implies that much of the surface and heterogeneous chemistry must be common to both systems. We can think of differences due to different species being adsorbed in plasma-catalysis and hence surface reactions (Langmuir-Hinshelwood) may be different. The gas-phase species in contact with the surface are changed under plasma action particularly by the creation of atoms and radicals and so gas-surface reactions (Eley-Rideal) will be different. Zaharia et al. [[149](#_ENREF_149)] have recently demonstrated that Eley-Rideal reactions become more important than Langmuir-Hinshelwood when considering the reaction of nitrogen atoms with a Ru surface covered with O atoms. Consideration of the different binding energies involved (N − Ru ∼ 5.6 eV, O− Ru ∼ 5.5 eV, N − O ∼ 6.5 eV, N − N ∼ 9.8 eV) indicates that the formation of NO by an Eley-Rideal reaction is exothermic by ∼ 1 eV whereas by Langmuir-Hinshelwood would be endothermic by ∼ 4.6 eV and this is confirmed experimentally.

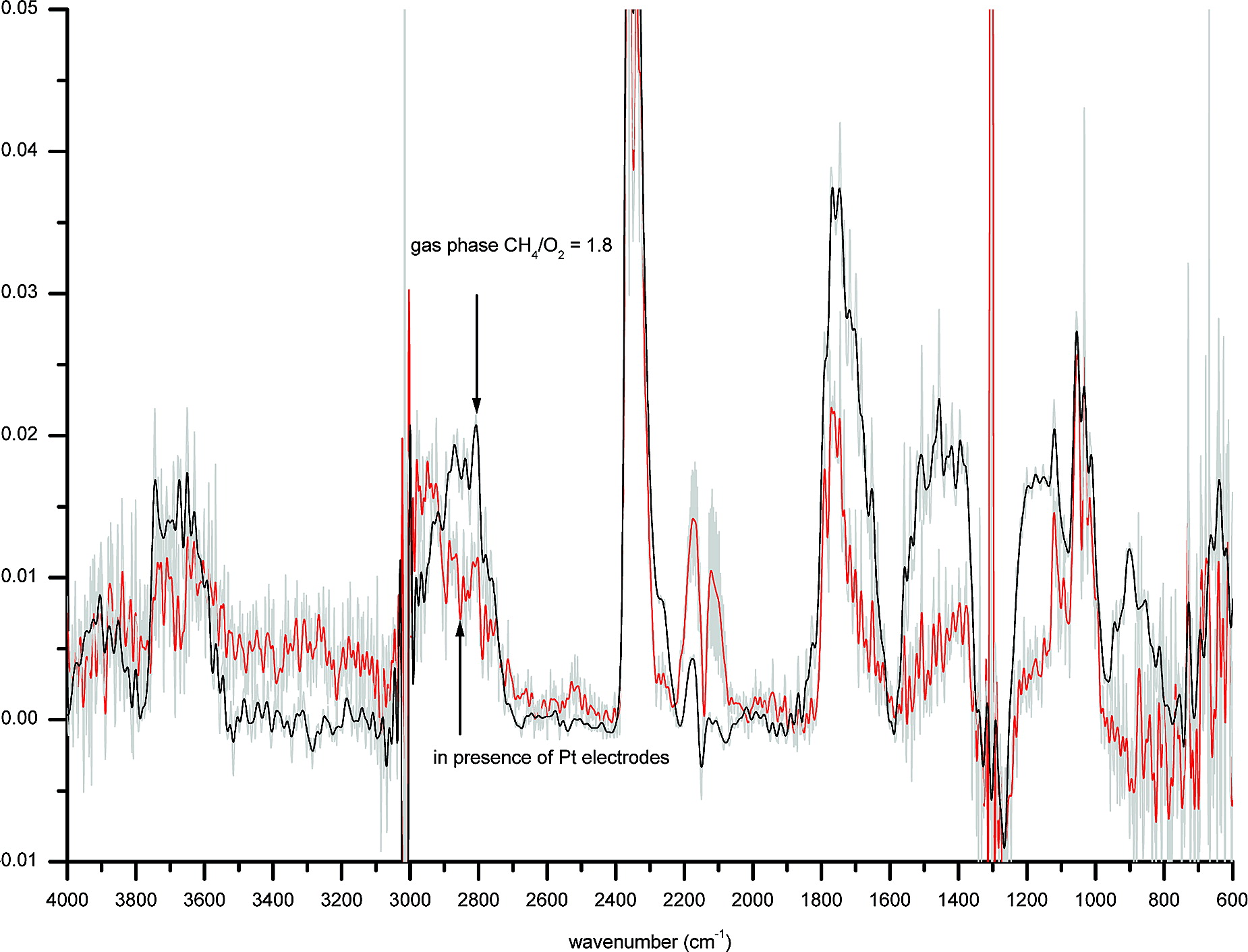
But experience tells us that the changes resulting from plasma activation are often not very profound but are subtler in terms of outcomes *e.g.* different products or improved selectivities than they are in terms of overall conversions. There are reports of conventional catalytic materials that are inactive in terms of improving the performance of a plasma process and we may learn as much by analysing these failures as we can from successful systems. It is the case, that there are very few materials, if any, that are active for plasma-catalysis that are inactive as thermal catalysts which suggests that plasma-catalysis can be regarded as a perturbation of conventional catalysis rather than a novel process.

However, we are at the point where there is already a tremendous wealth of experimental results from plasma-chemical experiments on a wide range of systems studied under various conditions with different catalysts that should be capable of producing more information and yielding more understanding than we have at present. All of these results constitute a very large dataset which is an issue faced in many areas of science at the moment ranging from astrophysics, biological science, medicine to social science and economics. There are statistical and computational tools available for cataloguing and analysing such data and for finding connections and dependencies between the various parameters in the data; often called data mining. The tools of chemometrics that extract information from chemical systems by data-driven means could be applied to this universal dataset or appropriate subsets. These tools include multivariate analysis, principal component analysis, pattern recognition, classification and clustering. A simplified example of this approach can be found in the recent work of Tu and co-workers [[150](#_ENREF_150)] who analysed the results of experiments for the conversion of methanol in air using a DBD reactor with a range of Mn-Ce oxide catalysts of different composition using an artificial neural network (ANN) analysis to gain a better understanding of the role of the different processing parameters and the catalyst performance. They found the optimum conditions for the methanol removal efficiency and the energy efficiency in terms of the catalyst composition, methanol concentration, discharge power and gas flow rate. The analysis showed that in terms of methanol removal efficiency, the catalyst composition was the most important variable but for energy efficiency the discharge power was the most influential parameter. The ANN method can be used to give fast and accurate prediction of the optimal conditions that give particular outcomes that can aid the design of new systems.

As well as this global rationalisation of existing and future experimental data, our ability to select and design optimised catalysts for particular systems will require us to understand the mechanism of plasma-catalysis at an atomic and molecular level both in terms of the heterogeneous and surface reaction chemistry and also in terms of the effect of the discharge on different materials properties of the catalyst. The kinetics studies referred to the previous section produced information about the activation energies for the overall process that can be identified with a rate determining step which is part of a much larger set of reaction pathways. The *in situ* spectroscopic analysis referred to in section 4.3 can identify species adsorbed on the surface which may be reagents or intermediates and may give additional insight into the dynamics of the reactive processes by measurement of the time profiles for particular species. Experiments have also been performed to directly monitor the steady state concentration of species formed in the gas-phase region of the plasma in plasma-catalysis rather than the more usual downstream analysis of the products that exit from the reactor. Nair *et al.* [[151](#_ENREF_151)] have used *in situ* FTIR spectroscopy to study the conversion of methane with O2 into oxygenated species in a DBD reactor with and without the presence of a platinum catalytic surface. Figure 9 shows the difference between the FTIR spectra for the plasma-only and the plasma-assisted catalysis. Differences are seen in several regions of the spectrum. For example, a pronounced CH3 adsorption at 2985 cm-1 in the presence of the catalyst can be observed in the gas-phase compared to the adsorption at 2803 cm-1 that is associated with the C-H stretch in aldehyde intermediates seen in the absence of the catalyst. The platinum catalyst can accelerate oxidation reactions of aldehydes and alternative oxidation steps forming CO and CO2 may become available. In addition, O-O absorptions at 800 – 900 cm-1 from peroxy species, RO2, are reduced upon the introduction of the Pt catalyst. The peroxy intermediates come from gas-phase recombination reactions of radicals with O2 in a three-body process

R + O2 + M → RO2 + M

suggesting increased oxidation of these intermediates on the catalyst surface. This type of measurement looking at the gas-phase species with and without a catalyst is a very powerful way to drawing inferences about the effect of the catalyst on the chemistry and deserves to be much more widely employed.

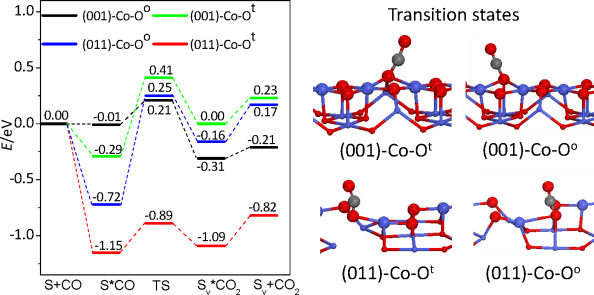


**Figure 10**. FTIR absorption spectra in a gas mixture with CH4/O2 ratio = 1.8 and in the presence of platinum sputtered electrodes. Input energy = 70 kJ/(mol CH4). Reproduced from Ref. [[151](#_ENREF_151)] by permission. Copyright 2007, American Chemical Society.

In addition to *in situ* FTIR absorption spectroscopy, other spectroscopic methods for determining the identity of gaseous species in the plasma can be used to gain information about the gas-phase plasma chemistry and how it is modified when a catalyst is introduced to the system. A recent review of optical absorption and emission techniques for probing plasma has been presented by Ono [[152](#_ENREF_152)] and the reader will find there detailed critical descriptions of a wide range of methodologies. Other absorption-based methods include ultraviolet – visible absorption and a range of laser-based techniques operating in the infrared and ultraviolet – visible region such as laser-induced fluorescence (LIF), two-photon absorption laser-induced fluorescence (TALIF) [[153](#_ENREF_153)], tuneable diode laser absorption spectroscopy (TDLAS). [[154-156](#_ENREF_154)] A detailed review focussed on absorption methods for probing plasma comes from Reuter *et al.* [[157](#_ENREF_157)] These methods allow for the determination of the concentrations of a wide range of atomic, radical and molecular species; generally in their ground electronic states but also in electronically excited states, in a few cases. In many of the experiments, these measurements represent averaged concentrations along the absorption path through the plasma but in some cases, spatially resolved maps of concentration can be obtained as in the work of Teramoto [[158](#_ENREF_158)] using LIF to look at OH *X* radicals in a humid air DBD. Absorption methods that use pulsed detection can also be synchronised to the discharge source giving time-resolved concentration measurements. Such data that contains both temporal and spatial information about species in plasma provides valuable experimental data against which chemical models and simulations can developed and validated. We are still a long way from being able to produce information of this richness in a plasma-catalytic system.

Optical emission spectroscopy, OES, is also commonly used as an *in situ* technique to detect electronically excited atoms, radicals and molecules from their ultraviolet and visible emission. This is a very sensitive technique that is often used to obtain estimates of the gas temperature by determining the rotational temperature of excited N2 or OH radicals assuming that their creation by electron impact excitation reflects the temperature of the corresponding ground state species. [[139](#_ENREF_139)] Care must be taken in making this correspondence between the gas temperature and the rotational temperature because the electronically excited state can be modified by subsequent collisions *e.g.* OH\* emission from electron impact excitation of ground state OH *X* radicals can be enhanced by excitation energy transfer from metastable species such as CO *a*3Π or N2 *A*  and CH\* and C2\* emissions can be boosted by chemiluminescent reactions between, for example, C2H radicals and O atoms, or C atoms and CH radicals, in hydrocarbon systems. [[159](#_ENREF_159)] The ratio of the concentration of electronically-excited species compared to that of ground state species in a plasma depends on the relative cross-sections for the production of electronically excited fragments by electron impact collision with a molecule compared to those for the production of the corresponding ground state fragments and on the excited state lifetimes and collisional quenching rates. Generally speaking, this ratio will be very small implying that electronically excited species whilst readily visible are in the minority and our interpretation of the plasma chemistry should not be biased towards these species as collisions involving ground state species will constitute the majority of the reactive processes. However, the reactions of energy-rich metastable species such as N2 *A* can play an important role in some plasma systems as mentioned in Section 2.

The experimental information obtained from *in situ* measurements on the gaseous and surface species can be used in conjunction with quantum mechanical calculations of the reaction pathways in terms of their energetics and configurations coupled with modelling and simulations of the dynamics on such reaction pathways to gain an understanding of the reaction dynamics in these plasma-catalytic systems. Neyts and Bogaerts have recently reviewed this topic and the reader is referred to that source for more detail of what is a challenging and very time-intensive activity. [[12](#_ENREF_12)] As an example of what is presently possible, we describe recent theoretical calculation by Wang *et al.* of the energetics of the thermal oxidation of CO on a Co3O4 catalyst, using density functional theory (DFT) methods. [[160](#_ENREF_160)] They calculate the energetics for the different stages in the process on the surface from the CO through various intermediates or transition states to the final CO2 product. This is shown in Figure 11 where the different stages are described in terms of the energetics and molecular structures of the various intermediate states on the catalyst surface focussing on the binding of the CO to different oxygen lattice sites on the Co3O4 for its different crystal faces. The Co firstly adsorbs onto a Co-O pair state and then interacts to form an adsorbed CO2 that then desorbs into the gas phase. A barrier separates the adsorbed CO state from the adsorbed CO2 corresponding to a transition state that must passed in order to proceed from reactants to products. This study is for a simplified sequence of reactions taking place only on the surface and involving no other adsorbed species and no gas-surface collisions. These calculations can provide the intermolecular potentials and geometries for a molecular dynamics simulation that could describe the timescales and probabilities for reactions to match the experimental methods outlined above.



**Figure 11.** Pathways and energies for CO oxidation with the lattice oxygen ion in the Co3O4 catalyst including the structures of the transition states. The Co atoms are coloured blue, O in red and C in black. There are two possible O ion states: Ot is bound to a Co2+ ion and O0 to a Co3+ ion. Reproduced from Ref. [[160](#_ENREF_160)] by permission. Copyright 2015 Elsevier.

Hensen and co-workers have developed a microkinetic methodology for describing the mechanism of catalytic reactions that makes use of DFT quantum calculations of the surface reaction potential energies for the intermediates and calculates the kinetics without any assumptions of the critical reaction pathway incorporating the dynamic changes of the surface during the reaction. This has been applied to systems such as the Fischer-Tropsch process and its optimisation. [[161](#_ENREF_161), [162](#_ENREF_162)] For the purposes of describing a plasma-catalytic process, it would be necessary to incorporate in a dynamic manner the effect of the plasma on the binding of species to the surface and on the nature of the transition state. This would allow comparison between the measured energetics of the catalytic process and the plasma-assisted process and the effect that this has on the dynamics of the process. At present, there is no computational methodology that has been used to incorporate the effects of the plasma on the catalyst.

In selecting a catalyst for a particular processes, it is important to use a benchmark to assess its performance. This is commonly given in terms of the extent of the conversion of a reagent or the selectivity or yield of a particular product. Another very important benchmark when assessing the effectiveness of a plasma-catalytic process is the energy efficiency, which can be expressed in terms of the rate of conversion of reagents (useful for environmental clean-up applications destruction of dilute toluene in an air stream) or the selectivity of a particular product (useful for plasma-catalytic synthesis of a particular substance e.g. hydrogen from the dry reforming of methane with carbon dioxide) as a function of the input power. This can have a bewildering range of units *e.g.* kg J-1, mol J-1, molecule eV-1, mol kWhr-1 *etc.*, but they can be interconverted! The reciprocal of the energy efficiency is sometimes and called the specific energy. Gutsol et al. have provided a very useful review with summaries of different ways of describing energy efficiency in plasma systems. [[163](#_ENREF_163)]

These benchmark parameters are important in allowing different plasma-catalysis experiments to be compared amongst themselves in terms of the effectiveness of different plasma types, different catalysts and other system variables and should always be given as an outcome of an experiment. But it is equally important to use these parameters, especially the energy efficiency, as the means of comparing plasma-catalysis with other competing technologies. For example, the production of ammonia from N2 and H2 by the commercial Haber-Bosch process has a specific energy cost of 30 – 35 GJ ton-1 [[164](#_ENREF_164)]. Mizushima *et al.* [[165](#_ENREF_165)] have used a DBD reactor with catalytic metallic membranes to produce ammonia from N2 and H2.  They have investigated a wide range of metals (Ru, Pt, Ni and Fe) and have demonstrated a clear advantage from using plasma-assisted catalysis making useful contributions to the understanding of the mechanism at a molecular level. However, the specific energy cost even for their most efficient configuration is 25,000 GJ ton-1 indicating that in this case, plasma-catalysis is a long way from providing an alternative solution. Bai *et al.* [[166](#_ENREF_166)] have used an alumina-coating in a micro-gap DBD to produce ammonia from methane and nitrogen achieving up to 8000 ppm of NH3 and a 9.1% yield of H2 at an energy cost of 5,200 GJ ton-1. Despite these large energy costs, it is felt that plasma-catalysis can ultimately provide an energy efficient method for nitrogen fixation if it can approach the theoretical thermodynamic limit. [[164](#_ENREF_164), [167](#_ENREF_167)]

When considering possible scale-up and industrial applications of plasma-catalysis, a whole life cost analysis must be performed to determine if the process will be economically competitive. [[168](#_ENREF_168)] There can be additional costs associated with separating a range of products such as the use of pressure swing adsorption or membranes that require additional capital and energy input. A promising recent development has been the hybridisation of a DBD reactor with a solid oxide electrolyser cell (SOEC) for the conversion of CO2 into CO and O2 where the SOEC removes oxygen from the reactor as it is formed, preventing the back reaction of CO and O2 to reform CO2 allowing complete conversion of the CO2. [[169](#_ENREF_169)] The costs of the selected catalyst will be important as many of the examples described here use scarce and expensive metals and alternative, more sustainable materials must be sought. The lifetime and durability of the catalyst will be critical and there have been very few studies of the effects of the ageing of the catalysts used; certainly not lasting for thousands of hours or more that will be necessary to judge realistic running costs. One of the “best” so far is 150 hours of testing performed by Kim et al. [[136](#_ENREF_136)] There is already some activity looking specifically at the degradation of catalysts in a plasma environment (*e.g.* [[170](#_ENREF_170)]) but this will become more important if plasma-catalysis is to move from the laboratory into a commercial environment. There is evidence that poisoning and coking of catalysts is minimised when used in a plasma environment compared to thermal catalysis during partly to the reduced operating temperatures and enhanced surface oxidation during plasma-catalysis (see Section 4.1).

**8. Concluding Remarks: The Way Forward.**

Inevitably, most of this review has been concerned with describing the things that we already know: the “known knowns”. However, many of these “known knowns” are essentially phenomenological observations, some of incredible intricacy and precision requiring the utmost level of experimental skill and imagination in their devising and performance. However, they must really still be classed as “known unknowns” if we continue to lack an interpretive or theoretical framework with which to fully describe them. It is because of the continuing development and adoption of innovative experiments with improved resolution and precision that we are able to make progress in our understanding by observing things and making measurements that would not previously have been possible. For example, a major “known unknown” concerns the timescales involved in the production and removal of species in the gas and surface phase in plasma catalysis and how and where are these species distributed on the catalytic surface and within the plasma volume with particular emphasis on the gaseous boundary layer immediately adjacent to the surface. To answer to these questions requires us to be able measure the spatial and temporal behaviour of species adsorbed and adsorbing onto the surface and also in the gas phase over a wide range of timescales ranging from sub-nanosecond to seconds. It is a gradation from describing dynamical behaviour at the atomic or molecular level that takes place at the shortest timescale and the slower bulk kinetic behaviour at the longest. It requires input about the binding energies and collisional behaviour of the transient, radical and excited species uniquely created by plasma with the catalytic surface and the gas phase for which there may be no experimental studies and theoretical calculation and modelling may be the only way of providing answers. We need to understand issues of heat and mass transfer in plasma catalytic systems both at the molecular and bulk level. What are the concentration gradients for key species within the plasma volume and on the surface? With an ever improving level of detail, we can develop and test more sophisticated hypotheses by devising further experiments and developing new theoretical tools involving quantum electronic structure calculations, scattering calculations, non-equilibrium thermodynamics, molecular simulations and big data analytics. This will transform many “known unknowns” into “known knowns”. Further studies of plasma-catalysis that are merely incremental and not innovative will not make significant additional contributions to our understanding. All experiments can provide new information but the best experiments also produce questions. What is needed is to identify the unknowns for which we need to know answers and devise the appropriate experiments to specifically to give those answers. Many of these experiments will need to borrow techniques from other areas some of which have been described above. Some will require the design of really novel and innovative experiments from scratch.

What then are the “unknown unknowns”? Well, of course, nobody knows. They could include being able to answer questions such as: “Will it be possible to design a catalyst that can be activated by plasma but is inactive thermally?” or “Will it ever be possible to scale up plasma-catalysis to compete with the throughput and economics of thermal catalysis?” or ….. However the unknown unknowns will reveal themselves to those who study hard, who can see obscure connections, indulge in lateral thinking and who might even just get lucky and find some serendipity! Donald Rumsfeld also had some advice that could be applied to research in plasma-catalysis: “*Plan backwards as well as forward. Set objectives and trace back to see how to achieve them. You may find that no path can get you there. Plan forward to see where your steps will take you, which may not be clear or intuitive.*” Retracing our steps may let us find things that we have overlooked, make new connections and postulate different directions of enquiry. The answers to the known unknowns and the unknown unknowns may already be there in the work of others in this field and seemingly unrelated fields just waiting for us to stumble upon them. The path forward that has the greatest potential of making a significant breakthrough probably is not clear or intuitive but it is there.

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**References**

[1] Rumsfeld D H and Myers R *US Department of Defense Briefing, 12 February 2002* 2002 <http://www.defense.gov/Transcripts/Transcript.aspx?TranscriptID=2636>.

[2] Devins J C and Burton M *Journal of the American Chemical Society* 1954 **76** 2618-2626

[3] Mizuno A, Chakrabarti A and Okazaki K "Application of Corona Technology in the Reduction of Greenhouse Gases and other Gaseous Pollutants" In: B. M. Penetrante and S. E. Schultheis, eds. *Non-Thermal Plasma Techniques for Pollution Control*. Berlin: Springer-Verlag 1993:165-185.

[4] Kim H H *Plasma Processes and Polymers* 2004 **1** 91-110

[5] Hammer T, Kappes T and Baldauf M *Catal. Today* 2004 **89** 5-14

[6] Kim H-H, Ogata A and Futamura S "Applications of Plasma-Catalyst Hybrid Processes for the Control of NOx and Volatile Organic Compounds" In: L. B. Bevy, ed. *Trends in Catalysis Research*. New York: Nova Science Publishers Inc. 2006:1-50.

[7] Mizuno A *Plasma Physics and Controlled Fusion* 2007 **49** A1-A15

[8] Chen H L, Lee H M, Chen S H, Chang M B, Yu S J and Li S N *Environ. Sci. Technol.* 2009 **43** 2216-2227

[9] Whitehead J C *Pure and Applied Chemistry* 2010 **82** 1329-1336

[10] Van Durme J, Dewulf J, Leys C and Van Langenhove H *Applied Catalysis B: Environmental* 2008 **78** 324-333

[11] Samukawa S, Hori M, Rauf S, Tachibana K, Bruggeman P, Kroesen G, Whitehead J C, Murphy A B, Gutsol A F, Starikovskaia S, Kortshagen U, Boeuf J P, Sommerer T J, Kushner M J, Czarnetzki U and Mason N *Journal of Physics D-Applied Physics* 2012 **45**

[12] Neyts E C and Bogaerts A *J. Phys. D: Appl. Phys.* 2014 **47** 224010/1-224010/18, 18 pp.

[13] Arai H, Ogata A, Yamasaki A, Kim H-H and Yanagisawa Y *Kagaku Kogaku Ronbunshu* 2010 **36** 310-316

[14] Thevenet F, Sivachandiran L, Guaitella O, Barakat C and Rousseau A *Journal of Physics D-Applied Physics* 2014 **47**

[15] Kim H-H, Teramoto Y, Negishi N and Ogata A *Catal. Today* 2015 **256** 13-22

[16] Neyts E C, Ostrikov K K, Sunkara M K and Bogaerts A *Chemical reviews* 2015 **115** 13408-46

[17] Mizuno A *Catalysis Today* 2013 **211** 2-8

[18] Schmidt-Szalowski K, Jodzis S, Krawczyk K, Mlotek M and Gorska A *Curr. Top. Catal.* 2006 **5** 39-68

[19] Xiao G, Xu W, Wu R, Ni M, Du C, Gao X, Luo Z and Cen K *Plasma Chemistry and Plasma Processing* 2014 **34** 1033-1065

[20] Vandenbroucke A M, Morent R, De Geyter N and Leys C *Journal of Hazardous Materials* 2011 **195** 30-54

[21] Chen H L, Lee H M, Chen S H, Chao Y and Chang M B *Appl. Catal. B Environ* 2008 **85** 1-9

[22] Neyts E C *Plasma Chem. Plasma Process.* 2016 **36** 185-212

[23] Kim H-H, Teramoto Y, Ogata A, Takagi H and Nanba T *Plasma Chem. Plasma Process.* 2016 **36** 45-72

[24] Siemens W *Poggendofl's Ann. Phys. Chem.* 1857 **102** 66

[25] Kogelschatz U, Eliasson B and Egli W *Pure and Applied Chemistry* 1999 **71** 1819-1828

[26] Chang J-S "Energetic Electron Induced Plasma Processes for Reduction of Acid and Greenhouse Gases in Combustion Flue Gas" In: B. M. Penetrante and S. E. Schultheis, eds. *Non-Thermal Plasma Techniques for Pollution Control*. Berlin: Springer-Verlag 1993:1-32.

[27] Laroussi M and Akan T *Plasma Processes and Polymers* 2007 **4** 777-788

[28] Niu J, Peng B, Yang Q, Cong Y, Liu D and Fan H *Catalysis Today* 2013 **211** 58-65

[29] Fridman A, Nester S, Kennedy L A, Saveliev A and Mutaf-Yardimci O *Progress in Energy and Combustion Science* 1999 **25** 211-231

[30] Golde M F *International Journal of Chemical Kinetics* 1988 **20** 75-92

[31] Golde M F and Thrush B A *Reports on Progress in Physics* 1973 **36** 1285-1364

[32] Holzer F, Roland U and Kopinke F D *Applied Catalysis B-Environmental* 2002 **38** 163-181

[33] Gicquel C, Cavadias S and Amouroux J *J. Phys. D: Appl. Phys.* 1986 **19** 2013-2042

[34] Anlauf K G, Maylotte D H, Polanyi J C and Bernstei.Rb *Journal of Chemical Physics* 1969 **51** 5716-&

[35] Nozaki T and Okazaki K *Catalysis Today* 2013 **211** 29-38

[36] Yang Y-C, Lee B-J and Chun Y-N *Energy* 2009 **34** 172-177

[37] Thomas J M *Philos Trans A Math Phys Eng Sci* 2015 **373**

[38] Davy H *Phil. Trans. R Soc. London A* 1817 **107** 77-85

[39] Berzerlius J J *Edinburgh New Philosophical Journal* 1836 **21** 223

[40] Medford A J, Vojvodic A, Hummelshoj J S, Voss J, Abild-Pedersen F, Studt F, Bligaard T, Nilsson A and Norskov J K *Journal of Catalysis* 2015 **328** 36-42

[41] Somorjai G A *Introduction to Surface Chemistry and Catalysis*. New York: John Wiley & Sons, 1994

[42] Kim H-H, Teramoto Y, Sano T, Negishi N and Ogata A *Applied Catalysis B-Environmental* 2015 **166** 9-17

[43] Harling A M, Glover D J, Whitehead J C and Zhang K *Applied Catalysis B: Environmental* 2009 **90** 157-161

[44] Hung Quang T and Mok Y S *Chemical Engineering Journal* 2014 **251** 199-206

[45] Tu X and Whitehead J C *Applied Catalysis B-Environmental* 2012 **125** 439-448

[46] Wallis A E, Whitehead J C and Zhang K *Catalysis Letters* 2007 **113** 29-31

[47] Hensel K *European Physical Journal D* 2009 **54** 141-148

[48] Kraus M, Eliasson B, Kogelschatz U and Wokaun A *Physical Chemistry: Chemical Physics* 2001 **3** 294-300

[49] Roland U, Holzer F and Kopinke F D *Catalysis Today* 2002 **73** 315-323

[50] Schmidt-Szalowski K, Gorska A and Mlotek M *Journal of Advanced Oxidation Technologies* 2006 **9** 215-219

[51] Lee H and Sekiguchi H *Journal of Physics D-Applied Physics* 2011 **44**

[52] Wang Q, Cheng Y and Jin Y *Catalysis Today* 2009 **148** 275-282

[53] Tu X, Gallon H J, Twigg M V, Gorry P A and Whitehead J C *Journal of Physics D-Applied Physics* 2011 **44** 274007 - 274010

[54] Mei D, Zhu X, He Y-L, Yan J D and Tu X *Plasma Sources Science & Technology* 2015 **24**

[55] Vandenbroucke A M, Mora M, Jimenez-Sanchidrian C, Romero-Salguero F J, De Geyter N, Leys C and Morent R *Applied Catalysis B-Environmental* 2014 **156** 94-100

[56] Witvrouwen T, Paulussen S and Sels B *Plasma Processes and Polymers* 2012 **9** 750-760

[57] Liu C-J, Zhao Y, Li Y, Zhang D-S, Chang Z and Bu X-H *ACS Sustainable Chemistry & Engineering* 2014 **2** 3-13

[58] Cheng D G *Catal. Surv. Asia* 2008 **12** 145-151

[59] Cheng D, Zhu X, Ben Y, He F, Cui L and Liu C *Catalysis Today* 2006 **115** 205-210

[60] Liu G H, Li Y L, Chu W, Shi X Y, Dai X Y and Yin Y X *Catal. Commun.* 2008 **9** 1087-1091

[61] Qin P, Xu H, Long H, Ran Y, Shang S, Yin Y and Dai X *Journal of Natural Gas Chemistry* 2011 **20** 487-492

[62] Gallon H J, Tu X, Twigg M V and Whitehead J C *Applied Catalysis B: Environmental* 2011 **106** 616-620

[63] Tu X, Gallon H J and Whitehead J C *Catalysis Today* 2013 **211** 120-125

[64] Gawande M B, Goswami A, Asefa T, Guo H, Biradar A V, Peng D-L, Zboril R and Varma R S *Chemical Society Reviews* 2015 **44** 7540-7590

[65] Llorca J, Casanovas A, Domínguez M, Casanova I, Angurell I, Seco M and Rossell O *Journal of Nanoparticle Research* 2007 **10** 537-542

[66] Stere C E, Adress W, Burch R, Chansai S, Goguet A, Graham W G, De Rosa F, Palma V and Hardacre C *Acs Catalysis* 2014 **4** 666-673

[67] Li K, Liu J-L, Li X-S, Zhu X and Zhu A-M *Chemical Engineering Journal* 2016 **288** 671-679

[68] Hussein L *Rsc Advances* 2016 **6** 13088-13100

[69] Lee H U, Lee Y-C, Lee S C, Park S Y, Son B, Lee J W, Lim C-H, Choi C-J, Choi M-H, Lee S Y, Oh Y-K and Lee J *Chem. Eng. J. (Amsterdam, Neth.)* 2014 **254** 268-275

[70] Hu S, Li F and Fan Z *Appl. Surf. Sci.* 2013 **286** 228-234

[71] Panomsuwan G, Saito N and Ishizaki T *J. Mater. Chem. A* 2015 **3** 9972-9981

[72] Lee H, Park Y-K, Kim S-J, Kim B-H and Jung S-C *Journal of Industrial and Engineering Chemistry* 2015 **32** 259-263

[73] Marinov D, Guaitella O, de los Arcos T, von Keudell A and Rousseau A *Journal of Physics D-Applied Physics* 2014 **47**

[74] Lee H M, Juan L-K, Yeh F-M, Li H-Y, Chen H-L, Chang M B, Chen S-H and Tzeng C-C *Ieee Transactions on Plasma Science* 2009 **37** 2213-2220

[75] Kim H H, Ogata A and Futamura S *Applied Catalysis B: Environmental* 2008 **79** 356-367

[76] Marinov D, Lopatik D, Guaitella O, Ionikh Y, Roepcke J and Rousseau A *Journal of Physics D-Applied Physics* 2014 **47**

[77] Boubert P and Vervisch P *Journal of Chemical Physics* 2000 **112** 10482-10490

[78] Conner W C and Falconer J L *Chemical Reviews* 1995 **95** 759-788

[79] Purvis G D, Redmon M J and Woken G *Journal Of Physical Chemistry* 1979 **83** 1027-1033

[80] Hibert C, Gaurand I, Motret O and Pouvesle J M *Journal of Applied Physics* 1999 **85** 7070-7075

[81] Rudolph R, Francke K P and Miessner H *Plasmas and Polymers* 2003 **8** 153-161

[82] Lu Q B, Ma Z and Madey T E *Physical Review B* 1998 **58** 16446-16454

[83] Lee J, Sorescu D C and Deng X *Journal of the American Chemical Society* 2011 **133** 10066-10069

[84] Mei D, Zhu X, Wu C, Ashford B, Williams P T and Tu X *Applied Catalysis B-Environmental* 2016 **182** 525-532

[85] Tonkyn R G, Barlow S E and Hoard J W *Applied Catalysis B-Environmental* 2003 **40** 207-217

[86] Kim H H and Ogata A *Eur. Phys. J.: Appl. Phys.* 2011 **55** 13806/p1-13806/p11

[87] Zhao D-Z, Li X-S, Shi C, Fan H-Y and Zhu A-M *Chemical Engineering Science* 2011 **66** 3922-3929

[88] Han J, Han F, Ouyang J, He L, Zhang Y and Na N *Nanoscale* 2014 **6** 3069-3072

[89] Han F, Yang Y, Han J, Jin O and Na N *Journal of Hazardous Materials* 2015 **293** 1-6

[90] Whitehead J C "Plasma catalysis for volatile organic compounds abatement": Imperial College Press 2014:155-172.

[91] Panov G I, Dubkov K A and Starokon E V *Catalysis Today* 2006 **117** 148-155

[92] Bukhtiyarov V I, Kaichev V V and Prosvirin I P *Journal of Chemical Physics* 1999 **111** 2169-2175

[93] Roland U, Holzer F, Poppl A and Kopinke F D *Applied Catalysis B-Environmental* 2005 **58** 227-234

[94] Ogata A, Mizuno K, Kushiyama S and Yamamoto T *Plasma Chemistry and Plasma Processing* 1998 **18** 363-373.

[95] Ogata A, Kim H H, Futamura S, Kushiyama S and Mizuno K *Applied Catalysis B-Environmental* 2004 **53** 175-180

[96] Guaitella O, Lazzaroni C, Marinov D and Rousseau A *Applied Physics Letters* 2010 **97**

[97] Guerra V, Marinov D, Guaitella O and Rousseau A *Journal of Physics D-Applied Physics* 2014 **47**

[98] Teramoto Y, Kim H-H, Ogata A and Negishi N *Catalysis Letters* 2013 **143** 1374-1378

[99] Harling A M, Glover D J, Whitehead J C and Zhang K *Applied Catalysis B-Environmental* 2009 **90** 157-161

[100] Li W, Gibbs G V and Oyama S T *Journal of the American Chemical Society* 1998 **120** 9041-9046

[101] Li W and Oyama S T *Journal of the American Chemical Society* 1998 **120** 9047-9052

[102] Einaga H and Futamura S *J. Catal.* 2004 **227** 304-312

[103] Barakat C, Gravejat P, Guaitella O, Thevenet F and Rousseau A *Applied Catalysis B-Environmental* 2014 **147** 302-313

[104] Bulanin K M, Lavalley J C and Tsyganenko A A *Journal of Physical Chemistry* 1995 **99** 10294-10298

[105] Wallis A E, Whitehead J C and Zhang K *Applied Catalysis B-Environmental* 2007 **72** 282-288

[106] Guo J, Lou H, Mo L and Zheng X *Journal of Molecular Catalysis a-Chemical* 2010 **316** 1-7

[107] Gonzalez-Delacruz V M, Pereniguez R, Temero F, Holgado J P and Caballero A *Acs Catalysis* 2011 **1** 82-88

[108] Stere C E, Adress W, Burch R, Chansai S, Goguet A, Graham W G and Hardacre C *ACS Catalysis* 2015 **5** 956-964

[109] Ohyama S *Applied Catalysis a-General* 2006 **313** 58-62

[110] He R, Davda R R and Dumesic J A *Journal of Physical Chemistry B* 2005 **109** 2810-2820

[111] Klages C-P, Hinze A and Khosravi Z *Plasma Processes and Polymers* 2013 **10** 948-958

[112] Eisert F, Elg A P and Rosen A "In situ investigation of catalytic reactions with second-harmonic generation" In: H. L. Dai and H. J. Freund, eds. *Laser Techniques for Surface Science Iii* 1998:7-14.

[113] Toyoshima R and Kondoh H *Journal of Physics-Condensed Matter* 2015 **27**

[114] Ozawa K, Emori M, Yamamoto S, Yukawa R, Yamamoto S, Hobara R, Fujikawa K, Sakama H and Matsuda I *Journal of Physical Chemistry Letters* 2014 **5** 1953-1957

[115] Ogawa M, Yamamoto S, Kousa Y, Nakamura F, Yukawa R, Fukushima A, Harasawa A, Kondoh H, Tanaka Y, Kakizaki A and Matsuda I *Review of Scientific Instruments* 2012 **83**

[116] Oberg H, Gladh J, Dell'Angela M, Anniyev T, Beye M, Coffee R, Foehlisch A, Katayama T, Kaya S, LaRue J, Mogelhoj A, Nordlund D, Ogasawara H, Schlotter W F, Sellberg J A, Sorgenfrei F, Turner J J, Wolf M, Wurth W, Ostrom H, Nilsson A, Norskov J K and Pettersson L G M *Surface Science* 2015 **640** 80-88

[117] Beye M, Anniyev T, Coffee R, Dell'Angela M, Foehlisch A, Gladh J, Katayama T, Kaya S, Krupin O, Mogelhoj A, Nilsson A, Nordlund D, Norskov J K, Oberg H, Ogasawara H, Pettersson L G M, Schlotter W F, Sellberg J A, Sorgenfrei F, Turner J J, Wolf M, Wurth W and Ostrom H *Physical Review Letters* 2013 **110**

[118] Tu X, Gallon H J and Whitehead J C *Ieee Transactions on Plasma Science* 2011 **39** 2172-2173

[119] Tu X, Gallon H J and Whitehead J C *Journal of Physics D: Applied Physics* 2011 **44** 482003

[120] Manley T C *Transactions of the Electrochemical Society* 1943 **84** 83-94

[121] Yu Q, Kong M, Liu T, Fei J and Zheng X *Plasma Chemistry and Plasma Processing* 2012 **32** 153-163

[122] Duan X, Hu Z, Li Y and Wang B *Aiche Journal* 2015 **61** 898-903

[123] Holzer F, Kopinke F D and Roland U *Plasma Chemistry and Plasma Processing* 2005 **25** 595-611

[124] Chung W-C, Pan K-L, Lee H-M and Chang M-B *Energy & Fuels* 2014 **28** 7621-7631

[125] Gomez-Ramirez A, Rico V J, Cotrino J, Gonzalez-Elipe A and Lambert R M *Acs Catalysis* 2014 **4** 402-408

[126] Rico V J, Hueso J L, Cotrino J, Gallardo V, Sarmiento B, Brey J J and Gonzalez-Elipe A R *Chemical Communications* 2009 6192-6194

[127] Li S, Zheng W, Tang Z and Gu F *Heat Transfer Engineering* 2012 **33** 609-617

[128] Zhang Y, Wang H Y, Jiang W and Bogaerts A *New Journal of Physics* 2015 **17** 12

[129] Harling A M, Wallis A E and Whitehead J C *Plasma Processes and Polymers* 2007 **4** 463-470

[130] Harling A M, Kim H-H, Futamura S and Whitehead J C *J. Phys. Chem. C* 2007 **111** 5090-5095

[131] Harling A M, Demidyuk V, Fischer S J and Whitehead J C *Applied Catalysis B-Environmental* 2008 **82** 180-189

[132] Blackbeard T, Demidyuk V, Hill S L and Whitehead J C *Plasma Chemistry and Plasma Processing* 2009 **29** 411-419

[133] Kim T, Jo S, Song Y-H and Lee D H *Applied Energy* 2014 **113** 1692-1699

[134] Mok Y S, Kang H-C, Koh D J, Shin D N and Baik J H *J. Korean Phys. Soc.* 2010 **57** 451-457

[135] Demidyuk V and Whitehead J C *Plasma Chemistry and Plasma Processing* 2007 **27** 85-94

[136] Kim H H, Ogata A and Futamura S *Journal of Physics D-Applied Physics* 2005 **38** 1292-1300

[137] Tochikubo F *Thin Solid Films* 2009 **518** 957-961

[138] Tochikubo F, Uchida S, Yasui H and Sato K *Japanese Journal of Applied Physics* 2009 **48**

[139] Bruggeman P J, Sadeghi N, Schram D C and Linss V *Plasma Sources Science & Technology* 2014 **23**

[140] Klarenaar B L M, Brehmer F, Welzel S, van der Meiden H J, van de Sanden M C M and Engeln R *Review of Scientific Instruments* 2015 **86**

[141] Juurlink L B F, McCabe P R, Smith R R, DiCologero C L and Utz A L *Physical Review Letters* 1999 **83** 868-871

[142] Juurlink L B F, Smith R R, Killelea D R and Utz A L *Physical Review Letters* 2005 **94** 208303

[143] Nozaki T, Muto N, Kado S and Okazaki K *Catalysis Today* 2004 **89** 57-65

[144] Nozaki T, Muto N, Kadio S and Okazaki K *Catalysis Today* 2004 **89** 67-74

[145] Kameshima S, Tamura K, Ishibashi Y and Nozaki T *Catalysis Today* 2015 **256** 67-75

[146] Tirumala R, Benard N, Moreau E, Fenot M, Lalizel G and Dorignac E *Journal of Physics D-Applied Physics* 2014 **47** 255203

[147] Zhang X L, Lee C S M, Mingos D M P and Hayward D O *Applied Catalysis A* 2003 **249** 151-164

[148] Neyts E C and Ostrikov K *Catal. Today* 2015 **256** 23-28

[149] Zaharia T, Kleyn A W and Gleeson M A *Physical Review Letters* 2014 **113** 053201

[150] Zhu X, Liu S, Cai Y, Gao X, Zhou J, Zheng C and Tu X *Applied Catalysis B-Environmental* 2016 **183** 124-132

[151] Nair S A, Nozaki T and Okazaki K *Industrial & Engineering Chemistry Research* 2007 **46** 3486-3496

[152] Ono R *Journal of Physics D-Applied Physics* 2016 **49** 083001

[153] Klochko A V, Lemainque J, Booth J P and Starikovskaia S M *Plasma Sources Science & Technology* 2015 **24**

[154] Welzel S, Rousseau A, Davies P B and Roepcke J "Kinetic and diagnostic studies of molecular plasmas using laser absorption techniques" In: Z. L. Petrovic, N. J. Mason, S. Hamaguchi and M. RadmilovicRadenovic, eds. *Radicals and Non-Equilibrium Processes in Low-Temperature Plasmas* 2007.

[155] Rond C, Hamann S, Wartel M, Lombardi G, Gicquel A and Roepcke J *Journal of Applied Physics* 2014 **116** 093301

[156] Roepcke J, Engeln R, Schram D, Rousseau A and Davies P B "Kinetic and Diagnostic Studies of Molecular Plasmas Using Laser Absorption Techniques" In: M. Bonitz, N. Horing and P. Ludwig, eds. *Introduction to Complex Plasmas* 2010:315-343.

[157] Reuter S, Sousa J S, Stancu G D and van Helden J-P H *Plasma Sources Science & Technology* 2015 **24**

[158] Teramoto Y, Kim H-H, Ogata A and Negishi N *Journal of Applied Physics* 2014 **115**

[159] Richley J C, Kelly M W, Ashfold M N R and Mankelevich Y A *Journal of Physical Chemistry A* 2012 **116** 9447-9458

[160] Wang Y-G, Yang X-F and Li J *Chinese Journal of Catalysis* 2016 **37** 193-198

[161] van Santen R A, Markvoort A J, Filot I A W, Ghouri M M and Hensen E J M *Physical Chemistry Chemical Physics* 2013 **15** 17038-17063

[162] Filot I A W, van Santen R A and Hensen E J M *Angewandte Chemie-International Edition* 2014 **53** 12746-12750

[163] Gutsol A, Rabinovich A and Fridman A *Journal of Physics D-Applied Physics* 2011 **44**

[164] Patil B S, Wang Q, Hessel V and Lang J *Catalysis Today* 2015 **256** 49-66

[165] Mizushima T, Matsumoto K, Ohkita H and Kakuta N *Plasma Chemistry and Plasma Processing* 2007 **27** 1-11

[166] Bai M, Zhang Z, Bai M, Bai X and Gao H *Plasma Chemistry and Plasma Processing* 2008 **28** 405-414

[167] Cherkasov N, Ibhadon A O and Fitzpatrick P *Chemical Engineering and Processing* 2015 **90** 24-33

[168] Hessel V, Cravotto G, Fitzpatrick P, Patil B S, Lang J and Bonrath W *Chemical Engineering and Processing* 2013 **71** 19-30

[169] Mori S, Matsuura N, Tun L L and Suzuki M *Plasma Chem. Plasma Process.* 2016 **36** 231-239

[170] Lee D H and Kim T *Plasma Processes and Polymers* 2014 **11** 455-463

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