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Catalyst preparation using plasma technologies

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Abstract

This paper discusses catalyst preparation using thermal and cold plasmas. In general, there are three main trends in preparing catalysts using plasma technologies: (1) plasma chemical synthesis of ultrafine particle catalysts; (2) plasma assisted deposition of catalytically active compounds on various carriers, especially plasma spraying for the preparation of supported catalysts; (3) plasma enhanced preparation or plasma modification of catalysts. Compared to conventional catalyst preparation, there are several advantages of using plasmas, including: (1) a highly distributed active species; (2) reduced energy requirements; (3) enhanced catalyst activation, selectivity, and lifetime; (4) shortened preparation time. These advantages are leading to many potential applications of plasma prepared catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Plasma preparation; Catalyst; Plasma modification; Plasma spraying; Thermal plasma; Cold plasma

1. Introduction

Catalysts are of great importance in the modern world. At present, almost all major chemicals are produced by catalytic processes. Among these catalytic processes, heterogeneous catalysis plays a very active role, because of environmental concerns: in the near future, non-environmentally friendly liquid acid catalysts will be replaced by green solid acid catalysts. To ensure an efficient reaction in heterogeneous catalysis, the active phase (usually the metal) on the catalyst surface must be highly dispersed over a large specific surface area and the specific activity maximized. To achieve this objective, catalytically active species are usually deposited as very fine particles on the surface of a highly porous support material (such as alumina, silica, titania, and zeolites) with high thermostability, high surface area, and suitable mechanical strength. The conventional preparation of dispersed catalysts usually requires a combination of several unit operations, including (i) introduction of the metal precursor on the support using ion-exchange, impregnation, co-precipitation, and deposition; (ii) drying; (iii) calcination; and (iv) if necessary, reduction. However, the present state-of-the-art status of technologies for catalyst preparation is far from perfect. Some of these unit operations are not well understood. There exist some catalytic reactions, for example, oxidative coupling of methane, partial oxidation of methane, CO_2 reforming of methane, and Fischer–Tropsch synthesis, are challenging chemists all over the world to seek a better catalyst or a more effective catalyst preparation method. Recently, using plasmas for catalysis has attracted a lot of attentions [1–18]. Some unusual chemical activities have been achieved when plasma species were involved in the catalyst surface reactions, which have led to efforts to apply plasmas directly to prepare more effective catalysts. In general, there are three main trends in catalyst preparation using plasmas:

1. plasma chemical synthesis of ultrafine particle catalysts;

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2. plasma assisted deposition of catalytically active compounds on various carriers, especially plasma spraying for the preparation of supported catalysts using thermal plasmas and
3. plasma enhanced preparation or plasma modification of catalysts.

The objective of this review paper is to summarize the present status of plasma technologies for catalyst preparation.

2. The performances of various plasma techniques

In general, plasma is an ionized gas that can be generated by a number of methods, including electric discharges (glow, microwave, plasma jet, radio frequency and so on). Depending on their energy level, temperature, and ionic density, plasmas are usually classified as high temperature plasmas (for nuclear applications) and low temperature plasmas (including thermal and cold plasmas). The low temperature plasmas have been used in catalyst preparation. In thermal plasmas, like plasma jet, the gas bulk temperature is close to the electron temperature (up to several tens of electron volts). Therefore thermal plasmas are also named as equilibrium plasmas. On the other hand, the bulk temperature in cold plasmas can be as low as room temperature, while the electron temperature can reach as high as 10,000–100,000 K (1–10 eV). Thus the cold plasmas are so-called non-equilibrium plasmas. Some of the characteristics of thermal and cold plasmas have been given in Table 1. Electrode configuration of plasmas (used for catalyst preparation) has also been shown in Fig. 1.

3. Plasma chemical synthesis of ultrafine particle catalysts

The theory and practice of heterogeneous catalysis have demonstrated that the activity of solid-phase catalysts is determined by their chemical and phase composition, crystal structure, and active specific surface. A close relation has been observed between the catalyst activity and the specific surface of catalysts. In this regard, the ultrafine particle catalysts attract special attention because of their large specific surface and less-perfect crystal lattice with a large number of vacancies [18]. These induce a high catalytic activity. One of the most efficient methods for producing ultrafine particles has been the plasma technique [12–25]. Thermal plasmas are known to be excellent in the production of ultrafine particle catalysts of the order of a few tens of nanometers with a highly developed specific surface and a high catalytic activity [12–25]. When the plasma chemical synthesis of ultrafine particles is accompanied by an effective quenching of products at a rate of 10^5–10^6 K/s that leads to an extra high energy over-saturation, then conditions are created for condensation of ultrafine particles with an unusual distribution of the additives [26,27], degenerated crystal structure, and numerous defects in crystal lattice that result in a high catalytic activity [13,15,16,26,27]. The mean particle size of plasma synthesized particles is 5–500 nm (specific surface is less than 100 m^2/g). Moreover, quenching determines the phase content of the produced ultrafine particles. The purities of the ultrafine particles are simply determined by the starting materials used [18].

According to Roginskiy's theory of over-saturation [28], catalysts obtained under energy over-saturation conditions must demonstrate an increased activity. The

Table 1
Characteristics of thermal and cold plasmas used for catalyst preparation

	Thermal plasma	Cold plasma
Pressure	Atmospheric or higher	Low (<0.1 bar) for most cases
Appearance	Filamentary inhomogeneous	Homogeneous
Temperatures	High electron temperature High gas (bulk) temperature	High electron temperature Low gas temperature
De-excitation rate in gas phase	High	Low
Types	Plasma jet; dc corona torch; arc	Glow; radio frequency; microwave
Uses	Ultra-fine particles spraying; sputtering	Modification or treatment of catalyst surface

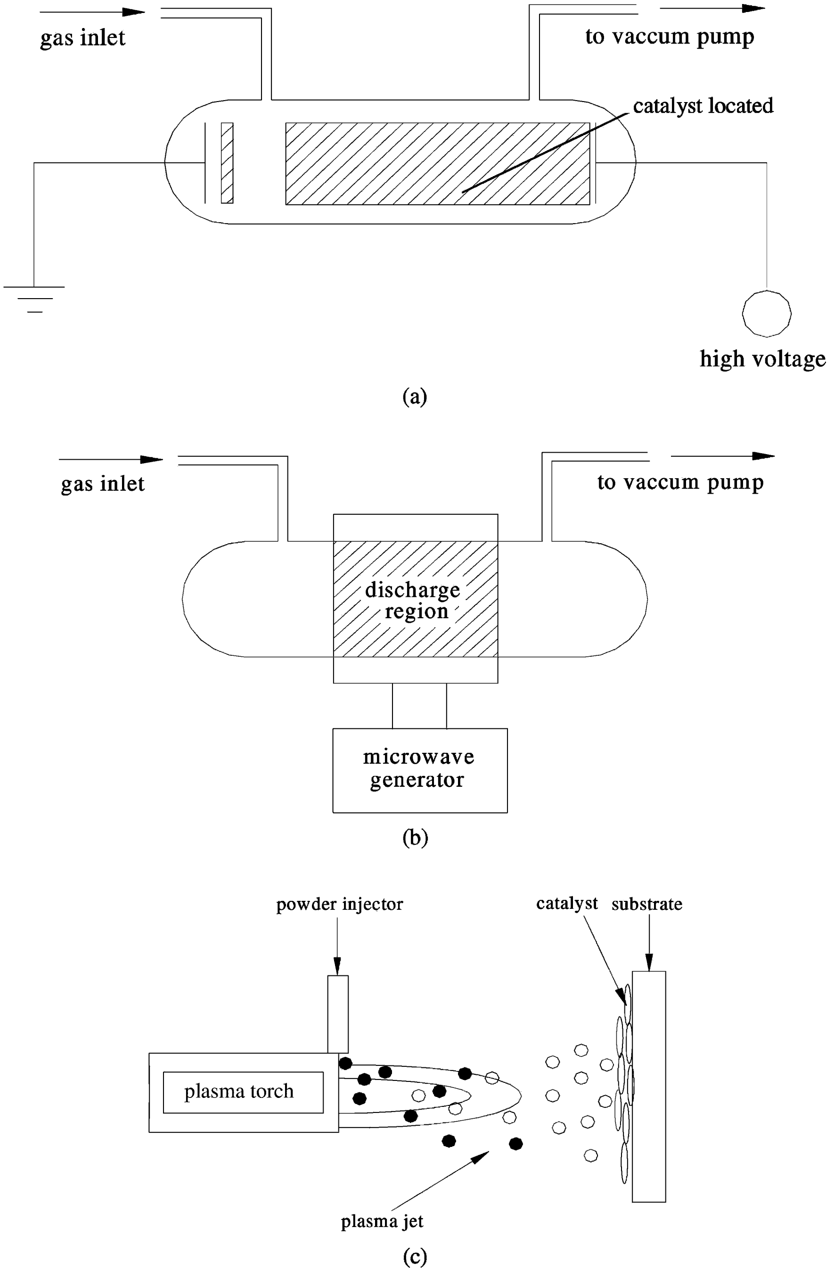

Fig. 1. Schematically representatives of electrode configurations of discharge phenomena applied for catalyst preparation: (a) glow discharge; (b) microwave plasma; (c) plasma spraying.

extent of energy over-saturation of a system increases with an increasing rate of heat transfer to it

$$\frac{\mathrm{d}Q}{\mathrm{d}\tau} = \alpha(T_1 - T_2)\mathrm{d}F_1 \qquad (1)$$

where T_1 is the temperature of heat carrier (plasma in the case considered here), T_2 the temperature of the substance heated (micrometer-size particles), and dF is the surface separating them. If one assumes that the material treated is spherical with radius R, then the specific surface of particles belonging to different fractions will be inversely proportional to their radii

$$\frac{F_1}{F_2} = \frac{R_2}{R_1} \tag{2}$$

or the smaller the particles, the higher will be their specific surface. However, decreasing the particles size is only reasonable to a certain limit, defined by Biot's criterion

$$\mathrm{Bi} = \frac{\alpha R}{\lambda} = \frac{R/\lambda}{1/\alpha} \tag{3}$$

where λ is the particle coefficient of heat conductivity and α is the coefficient of heat transfer from the heat carrier to the particle.

The numerator in Eq. (3) characterizes the resistance to heat propagation from the surface to the center of the particle, and the denominator characterizes that to heat transfer from the heat carrier to the particle surface. When R is large, the heat-transfer process is limited by the heat resistance of the particle and, inversely, for small R, by the heat resistance of the phase interface. There obviously exists a value of R for which the two quantities are equal ($\mathrm{Bi} = 1$)

$$R = \frac{\lambda}{\alpha} \tag{4}$$

To create maximal energy over-saturation, the raw material must be pre-dispersed to a particle size as close as possible to that defined by Eq. (4). The calculations for the case of, for example, elemental Fe or iron oxides yield a value of approximately 50 μm.

Table 2 shows some illustrative catalysts prepared using plasmas. Processes involved included ammonia synthesis, ethylene production, natural gas reformation, low temperature steam conversion of carbon monoxide, methanol formation, nitrogen oxide production, methane conversion, photo-catalytic decomposition of water and so on (Table 2).

A good catalyst must have certain characteristics. The catalyst should:

1. provide a sufficiently high reaction rate under the specific reactive conditions;
2. sustain its activity over a long period of time;
3. exhibit low sensitivity to poisons, such as sulfur compounds;
4. have good mechanical strength;
5. show selectivity, it should accelerate the desired reaction only and
6. be reduced before use since most of catalysts are produced as oxides. The reduction period should be as short as possible in order to avoid a decrease in the production efficiency.

Obviously, these requirements are quite contradictory. For example, high activity cannot always be combined with good stability, whereas a stable catalyst may be difficult to reduce. In addition, mechanical strength is usually inherent to high-density catalysts that are less active. In this regard, the catalyst prepared using thermal plasma shows better comprehensive performances [15,16,22–25,27]. The unique distribution of active components on the plasma prepared catalysts reduces its sensitivity to poisons. The high specific surface of ultradispersed plasma prepared catalysts, together with the numerous defects in their crystal structure, is conducive to their fast reduction.

Kinetic studies were also conducted on plasma synthesized catalysts under conditions similar to industrialized catalysts [26,27]. It has been demonstrated that the increased catalytic activity is due to an increase in the pre-exponential factor in the Arrhenius equation at constant activation energy, i.e. to an increase in the number of active centers per catalyst weight.

It is a common misconception that plasma synthesized catalysts are expensive. If one takes into account the main characteristics of plasma synthesized catalysts, including one-step production, simplicity, short preparation period, miniaturization of equipment, and so on, it is safe to predict plasma chemical synthesis of catalysts will soon prove its advantages. Note that the cost of catalysts is a small fraction of the total cost of production (for example, 2–3% for ammonia production).

4. Plasma assisted deposition of catalytically active compounds on various supports

There are some reports in the literature on plasma assisted deposition of catalytically active compounds on various supports. Plasma spraying [7,12,39–46] (some illustrative tests have been shown in Table 3),

Table 2
Illustrative catalysts prepared using plasmas

Catalyst	Plasma	Composition (%)/active substance/specific surface ($m^2\,g^{-1}$)	Application/remark	Reference/patent
Catalyst for NH_3 synthesis	Electric arc LTP, gas: Ar, H_2, N_2, (N_2 + O_2), air	(Fe_3O_4 + Fe_2O_3 + FeO)-94; Al_2O_3-3; K_2O-0.8; CaO-2; SiO_2-0.2/α-Fe, γ-Fe/up to 40	Ammonia synthesis: the reduction rate is three to five times faster; 15–25% higher catalytic activity at 673–823 K and higher thermal stability at 1073 K than fresh conventional catalyst type SA-1	[14–16,23,26,27,29,30]/ Bulg. P 35353 (1982)
Catalyst for ammonia	High enthalpy air	Fe oxides-84.6–92.6; Al_2O_3-3.9–9.8; CaO-2.5; K_2O-1–3;/α-Fe and 10% γ-Fe	Ammonia synthesis: the catalytic activity is higher at the interval 673–823 K than industrial catalyst type SA-1; $d_p \approx 35$ nm	[31]
W or Mo oxides	H plasma discharge	W and Mo oxides	C_2H_4 synthesis	CSP 243932 (1987)
Catalyst for natural gas reforming	Electric arc LTP, gas: Ar, H_2, N_2, (N_2 + O_2), air	NiO-8.5–12.8; Al_2O_3-85.7–88.9; CaO-0.7–1.3; MgO-0.2–0.4/Ni/19–58	Natural gas reforming (steam conversion of methane) (873–1123 K); the catalytic activity is higher than conventional fresh catalyst type G56A or G56H	[12,15,16,26,27,32–35]/ Bulg. P 35353 (1982)
Catalyst for low-temperature steam conversion of CO	Electric arc LTP, gas: air	LTC-8P: CuO-37.3; Al_2O_3-24.5; ZnO-28.2; LTC-4P: CuO-54.0; Al_2O_3-21.0; ZnO-11; Cr_2O_3-14.0/Cu/65–127	Low temperature (473–453 K) steam conversion of carbon monoxide; the catalytic activity is higher with 15–20% that conventional fresh catalyst type LTC; spherical particles with $d_p \approx$ 10–50 nm	[36]
Catalyst for synthesis of CH_3OH	Electric arc LTP, gas: air	$2CuO{\cdot}ZnO{\cdot}0.16Al_2O_3$	Catalyst for synthesis of methanol, thermal stability catalyst; the particles size of CuO are 30–40 nm; ZnO-40–70 nm	[37]

Table 2 (*Continued*)

Catalyst	Plasma	Composition (%)/active substance/specific surface ($m^2\,g^{-1}$)	Application/remark	Reference/patent
MoO_3	N and O plasma	MoO_3	Synthesis of nitrogen oxides; manufacture of HNO_3	FP 2549459 (1985)
Th–La–Ga–Zr	H plasma	Th–La–Ga	Conversion of natural gas; low-temperature reaction	WO 8604054 (1985)
Al_2O_3	Ar and H plasma		Conversion of CH_4 or light alkanes into unsaturated hydrocarbons; selectivity for C_2H_2 is 71%	EP 370909 (1990)
$CaO{\cdot}SiO_2$	Ar plasma	$CaO{\cdot}SiO_2$	Manufacture of α-olefins	FP 2639346 (1990)
Ni particles on a carbonaceous residue	Electrical condensation	Ni-20; carbonaceous-80/Ni-35 nm	Hydro-conversion of heavy feeds process	EP 429132 (1991)
β-SiC powder	Arc plasma, Ar, Ar/He, Ar/H_2 or Ar/N_2	Si-10	Photocatalytic decomposition of water	[38]

Table 3
Illustrative catalysts prepared using plasma spraying

Catalyst	Plasma	Composition (%)/active substance/specific surface ($m^2\,g^{-1}$)	Application/remark	Reference/patent
Metal and metal oxides of Fe, Ni, Cr, Cu, Au: supported on a supports	Plasma plating	Ni, Fe, Cr, Au, Cu/(NiO, Fe_2O_3, Fe_3O_4, Cr_2O_3, CuO)	Reduction of NO_2 to NO; auto exhaust treatment	JP 53004791 (1978)
Fe–Cr or Fe–Cr–Ni/support	Plasma sprayed alloy	Fe–Cr; Fe–Cr–Ni	Reduction of NO_2 to NO; NO removal from flue gases	JP 57197024 (1982)
Co and Cu oxides on Al_2O_3 fiber sheet	Plasma vapor deposition	Co, Cu	Catalytic combustion/household heater	JP 61249541 (1986)
Pt supported on porous Ni–Cr alloy	Thermal plasma spraying	Dispersed Pt on Ni or Cr/Pt	Oxidation processes/high oxidation activity at low temperatures	JP 62144750 (1987)
Dual-layer ceramic coated surface	Plasma deposition	Ni, Al powder on Al_2O_3, SiO_2, or ZrO_2	Removal of CO (99.5%)/treatment of car exhaust gases	JP 63044944 (1988)
Honey Pt support plasma, coated with Pd	Plasma deposition	Pt support, coated with mixture of Pd and Ag, Co, Ni, Fe, Cr, Mn, Cu	Combustion of natural gas (CH_4); efficiency 99.8% after 1000 h	JP 011058346 (1989)
Catalyst for combustion (Pt, Au)	Plasma spraying on a metal support	Pt, Au or Pt–Au alloy, Al_2O_3, ZrO_2, NiO, Cr_2O_3, SiO_2, MgO	Combustion exhaust gas treatment	JP 05103996 (1993)
α-Al_2O_3 and γ-Al_2O_3 supported on Ni, Ti, Co–La	Electric-arc plasma torch	Al_2O_3, La–Co-γ-Al_2O_3/0.4–0.6	Conversion of CH_4 in air	[39]
Ni catalyst for hydro-treating	High frequency plasma	Ni particles supported on carbon	Hydro-conversion of deasphalted vacuum residue	[40]
Co–Fe	Plasma spraying	$CoO \cdot Fe_2O_3$ supported on the tube	Syngas conversion to hydrocarbons	[48]

plasma sputtering [49], and plasma assisted CVD [50] have been employed for it, although more concerns have been given to plasma spraying.

The unique characteristics of thermal plasma (high effective temperature, energetic particles, etc.) make it very suitable to prepare membrane catalysts on various supports, especially metals. Metals have some advantages (like high mechanical strength, good heat conductivity, and others) that make their application in catalysis more attractive than ceramic supports for the use of the membrane catalyst. A typical example is the catalytic treatment of automobile exhausts. The conventional preparation of metal-supported catalysts poses some serious problems, including (1) protecting catalytic membranes from mechanical shock and chemical exposure to the reaction medium; and (2) maintaining catalytic activity at high temperatures. It is also very difficult to prepare a catalytic membrane with a strong contact between the membrane and the metal surface at high temperatures. Plasma spraying is already widely applied for the preparation of thick coatings of refractory materials and is one of the prime candidates for producing effective anti-corrosion coatings, especially for high temperature applications [51]. As is shown in Fig. 1, powder is heated to near or above its melting point in a plasma torch and then is accelerated by a plasma gas stream toward the substrate. The powder used for plasma spraying is between 5 and 60 μm in diameter. The size distribution of the powder should be narrow to achieve a uniform heating and acceleration. Fine powders are heated and accelerated more rapidly, but they tend to lose momentum quicker when sprayed at longer distances from the torch. This usually leads to a denser coating, which is less favorable for catalyst preparations. A porous structure of sprayed membranes or coatings is necessary for catalytic applications. Changing the particle size of the powder sprayed allowed the physicochemical characteristics of the catalytically active layer to be regulated (phase composition, porosity, specific surface, thermal conductivity, etc.) [36,43].

Several papers have shown that the porous structure of sprayed membranes depends significantly on the jet outflow regime (laminar, transient, or turbulent), the components and the flow rate of the plasma forming gas, the applied power (or the average bulk temperature), the spraying distance, and so on [36,41,42]. For example, an increase in the plasma-forming gas flow rates leads to a growth of the porosity of the catalytic membranes.

Two different approaches have been used for the synthesis of catalyst membranes using plasma spraying: (1) preliminary spraying of a gradient layer with various additives, followed by the deposition of the catalytically active components; and (2) direct spraying of the catalytically active components on a support surface [36,44–46]. Khan and Frey [45] prepared perovskite oxide $LaMO_x$ films (where M is Co, Mn, or Ni) deposited on Al_2O_3 by a plasma spray deposition.

There have been studies of applications of direct-current plasma torchs with interelectrode inserts for atmosphere plasma spraying Al_2O_3 (α-Al_2O_3 and γ-Al_2O_3) coatings on different geometry (plates/foams) metal substrates [36]. Experiments performed on metal supports of different geometries have shown that a sprayed Al_2O_3 layer demonstrates a strong and uniform adhesion to the metal surface. The gradient layer sprayed successfully solves two different problems [36,47]: (1) it serves as a washcoat on which a catalyst can subsequently be synthesized; and (2) it protects the metal surface from oxidation at high temperatures.

The effectiveness of plasma sprayed membrane catalysts has also been confirmed by a conversion of syngas to hydrocarbons in a tube-wall reactor using a Co–Fe plasma sprayed catalyst, reported by Dalai et al. [48]. The plasma sprayed catalyst layer is 0.16 mm thick and consists of a mixture of metal oxide particles ($CoO\cdot Fe_2O_3$, principally) that are fairly uniformly distributed on the tube surface as well as in the cross-section of the plasma sprayed catalyst layer. The uptake of hydrogen and carbon monoxide of plasma sprayed Co–Fe bimetallic catalysts was found to be higher (8.0 and 7.4 μmol/g, respectively) than the uptake of powdered bimetallic catalysts (0.8 and 2.0 μmol/g, respectively). The experiments showed that the catalytic activity of the plasma sprayed catalyst was a strong function of the operating conditions and a maximum CO conversion of 98.5% was achieved. The selectivity of $C_5{}^+$ hydrocarbons was over 40% when produced in the pressure range of approximately 0.69–1.03 MPa.

5. Plasma enhanced preparation or plasma modification of catalysts

5.1. Plasma heat treatment

The plasma enhanced preparation or plasma modification of the catalyst is usually performed after the supported catalyst (which is made of metal oxides in most cases) is dried. There are two techniques regarding plasma enhanced preparation or plasma modification of a catalyst: plasma heat treatment and plasma chemical treatment (modification). The first technique usually employs microwave plasma at low-pressures [52–55] or atmospheric pressure [56]. Plasma heat treatment is conducted to replace the thermal calcination of a catalyst. In principle, the microwave plasma heat treatment of a catalyst is similar to the microwave heat treatment [55–57], but it is combined with the chemical treatment from the active plasma species. These catalysts prepared using the plasma heat treatment are very different from those calcined conventionally. Sugiyama et al. [52] reported a plasma heat-treated Nb_2O_5 catalyst for the vapor-phase Beckmann rearrangement reaction. It has been found that a plasma heat-treated catalyst shows weakened acid strength and better selectivity. From XPS characterization of catalysts, Nb^{4+} and Nb^{2+} species have been detected on the surface, in addition to Nb^{5+} that was known to exist. It is clear that the catalyst has been reduced by the plasmas. It has even been observed that the surface color of Nb_2O_5 changed from white to blue after it was plasma treated. It is apparent that the effect of active plasma species cannot be ignored during the plasma heat treatment.

Zhang et al. [58] reported plasma activation of a $Ni/\alpha\text{-}Al_2O_3$ catalyst for methane conversion to syngas that is a typical example of combining plasma heating and chemical treating of the catalyst. First, the radio frequency ($f = 13.56\,\text{MHz}$) plasma with argon as plasma forming gas has been used for the decomposition of $Ni(NO_3)_2$ into black Ni_2O_3. In this step, plasma serves as a special energy supply. Then hydrogen plasma at the same frequency has been applied for the reduction of catalyst. The catalyst becomes green at the first ($Ni_2O_3 \rightarrow NiO$), then changes to black ($NiO \rightarrow Ni$) again by hydrogen plasma. This represents an intensive interaction of the plasma with the surface of the supported catalyst. The plasma prepared catalyst shows a better activity and stability, compared to the catalyst prepared conventionally. The total treatment time is less than 3 h (1.5 h for plasma heat treatment and 65 min for plasma reduction) at the discharge tube temperature of 65 °C, while the conventional preparation of catalyst needs 10 h of calcination at 900 °C and 1 h of reduction at 600 °C.

A potential important application of plasma heat treatment is for the preparation of zeolite catalysts [59]. The principal objectives of thermal treatment of zeolites at elevated temperature include template removal from as-synthesized materials and activation in catalyst preparation. Various reactions such as ultra-stabilization, cation redistribution, and de- and re-alumination may take place in the zeolite, based on the temperature applied. Maesen et al. [59] have explored the application of a radio frequency dry air plasma treatment for low temperature oxidation of combustibles in various zeolites. It has been found that such plasma treatment does not impair the zeolite structure since the gas temperature during plasma treatment is approximately 45 °C. The IR and TGA analysis of plasma treated zeolites confirms that the plasma has removed most of the template [59]. In addition, it has been concluded that the plasma treatment, as the conventional calcination does, affects the long-range ordering but, in contrast to heat treatment, plasma treatment leaves the local ordering unaffected.

5.2. Plasma chemical treatment or modification

The plasma chemical treatment or modification of a catalyst is a process in which gases are partly broken down into chemically active species in plasma, which then flow to, and physically or chemically react at, the catalyst surface [60]. Plasma itself is a complex mixture that contains electrons, ions, photons, neutral species, excited species (including vibrationally, rotationally, and translationally excited species) and so on. Different plasma species affect the heterogeneous surface in very different ways. There has been considerable interest in investigating the role of plasma surface interaction in the chemical reactions under the influence of various plasma species. Regarding the reactivity of each plasma species toward surfaces, Tas [61] summarized it and concluded that only radicals and vibrationally excited molecules need to be considered for surface reactions in atmospheric non-thermal plasmas. Ions and detectable electronically excited molecules are already de-excited before they start to interact strongly with the surface, although they may be highly vibrationally excited as a result of de-excitation. The effect of rotational and translational excitation can be ignored in non-thermal plasmas at atmospheric pressure. For the case of low pressure plasmas, such as glow discharge, electrons will become more important [62], in addition to radicals and excited molecules. Exactly, it has been observed that the interaction of active plasma species with the catalyst surface has led to some unusual catalytic activity for waste treatment or methane conversion or the others [1–11]. Kameoka et al. [63] reported formation of a novel Al_2O_3 surface with Al–O* by plasma excited nitrogen N_2^*. The following reactions are presented to explain the observed phenomena:

$$N_2^* + 6\text{Al–OH} \rightarrow 2NH_3 + 6\text{Al–O}^* \quad (5)$$

$$6\text{Al–O}^* + 3H_2O \rightarrow \tfrac{3}{2}O_2 + 6\text{Al–OH} \quad (6)$$

The total reaction is

$$N_2^* + 3H_2O \rightarrow 2NH_3 + \tfrac{3}{2}O_2 \quad (7)$$

Reaction (3) is a thermodynamically unfavored reaction ($\Delta G_{298\,\mathrm{K}} = 162$ kcal/mol), while this reaction can take place on the Al_2O_3 surface activated by nitrogen plasma. The unusual capability of plasma species in the treatment or modification of a catalyst for the conventional chemical processes has also been established. Yagodovskaya and co-workers [64–66] reported a preparation of Fe_2O_3/ZSM-5 catalyst for hydrogenation of carbon monoxide using glow discharge of oxygen and argon. The major objective of that investigation was to develop a low-temperature preparation of the Fe_2O_3/ZSM-5 catalyst to avoid the reduction in both activity and selectivity of catalysts due to a noticeable segregation of the metal phase on the outer zeolite surface that occurs in the conventional calcination thermally. They applied a low-pressure (1 Torr) glow discharge to treat the ZSM-5 zeolite impregnated by a solution of Fe(III) nitrate for approximately 5–20 min. The total decomposition of iron nitrate into the amorphous Fe_2O_3 and NO_2, as a result of treatment by oxygen or argon glow discharge, has been achieved. This prepared catalyst showed a well-developed surface. The specific surface increases with the surface enriched by iron [65], after glow discharge treatment. The reduction of iron oxide on the prepared catalyst to Fe^0 by hydrogen was facilitated. Such a plasma prepared catalyst showed higher activity and better selectivity of $C_2{}^+$–$C_4{}^+$ alkene, compared to the catalyst prepared conventionally.

Diamy et al. [67,68] reported a preparation of gold-based metallic catalysts using a dihydrogen microwave plasma afterglow. An interesting application of gold in heterogeneous catalysis is its association with group VIII metals, such as platinum [69] and palladium [70,71] for the preparation of supported bimetallic catalysts. Gold is introduced either for the enhancement of the dispersion of the more active metal or for the improvement of selectivity or stability of catalysts. However, the conventional reduction of gold in hydrogen at high temperature leads very often to large particles, especially with zeolites as supports. The use of the afterglow of a microwave plasma (2450 MHz) of dihydrogen has led to a better preparation of gold-based metallic zeolite catalysts. The afterglow is a medium that contains active hydrogen atoms, which works at sufficiently low temperatures that the formation of large particles can be avoided. Based on the analysis using transmission electron microscopy, most of the particles produced in the afterglow of dihydrogen are less than 5 nm in diameter.

Furukawa et al. [60] also reported a plasma modification of an H–Y zeolite by a radio frequency CF_4 plasma. A novel surface with new zeolite functionalities (e.g. hydrophobic surfaces) has been achieved. The infrared absorption analyses clarified that the replacement of –OH groups of zeolite by $–CF_3$ or –F groups on the micropore surface of the zeolite are responsible for the formation of the hydrophobic surface.

An important application of plasmas in the preparation of zeolite catalysts is modifying zeolite acidity. Takeuchi [72] showed that the water and the OH group on the HY zeolite can be removed after the 5-min treatment using microwave discharge. Lewis acid is thereby efficiently formed in the HY zeolite. The discharge-treated HY zeolite used for *iso*-butane catalytic cracking showed a higher activity compared to the catalyst prepared using conventional calcination for 2 h at 600 °C. Moreover, the investigation showed the framework of the zeolite would be destroyed during conventional calcination at high temperatures, which can be avoided in plasma preparation.

Using low-pressure glow discharge plasmas [73,74], a simple and novel preparation of bi-functional catalysts for converting methane to aromatics has also been developed. Infrared (IR) analysis shows this preparation significantly enhances in Brönsted acidity, which plays an important role in methane aromatization. The intensity of Brönsted acidity of Fe–Mo/HZSM-5, for example, increases more than 265%, compared to the same zeolite prepared conventionally. The enhanced Brönsted acidity induces a significant increase in the conversion of methane (from approximately 11–24%) without increasing the selectivity of coke formation. Because of the importance of acidity of zeolites in catalyzing a great number of hydrocarbon transformation reactions, the plasma enhanced acidic properties of zeolites will lead to many other applications, either in the petroleum or chemical industries.

6. Conclusions

Plasma technology is an established key technology in microelectronic fabrication and in modern surface treatment. New applications of plasma catalyst preparations have emerged as a promising future approach. The advantages of the plasma approach include the following.

- Ultra-dispersed catalysts are obtained with high specific surfaces.
- The homogeneous distribution of the components in the specimens contributes to a decreased sensitivity to poisons.
- Its strictly constant composition is assured for selectivity.
- The catalyst preparation period is short.
- The dispersion and composition of the samples can be controlled within wide limits via variation of the plasma chemical parameters.

To develop plasma's potential for preparing catalysts, future efforts should address: (1) designing plasma chemical installations that would ensure complete evaporation of ingredients; (2) studying condensation and crystallization of nano-dispersed phases simultaneously with plasma chemical reactions under highly non-equilibrium conditions; and (3) investigating the fundamental properties of plasma modified catalysts.

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