Removal of VOCs from gas streams via plasma and catalysis

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Abstract

Emission of volatile organic compounds (VOCs) has resulted in various environmental issues. Therefore, development of effective VOCs removal technology is essential for reducing the adverse effects associated. This work provides a systematic review on VOCs removal from gas stream via catalytic oxidation, plasma degradation and plasma catalysis. For catalytic oxidation of VOCs, possible reaction mechanisms and how physicochemical properties of catalyst influences catalytic performance are presented and discussed, followed by plasma removal of VOCs,

VOC degradation and byproduct formation mechanisms. Next, interactions between plasma and catalyst are interpreted for comprehensive understanding. Last, perspectives are provided for further development of VOCs removal technology.

1　Introduction

Volatile organic compounds (VOCs) are organic chemicals with high volatility at room temperature and atmospheric pressure. In 2004, the Europe Union (EU) defined VOCs as organic chemicals having a normal boiling point lower or equal to $250^{o}C$ [1],[2], including alkanes, olefins, alcohols, ketones, aldehydes, ethers, aldehydes, esters, paraffins, aromatics, halogenated hydrocarbons and sulfides [3],[4]. Anthropogenic VOC emissions come from outdoor and indoor sources, the former includes industrial plants, power plants, pharmaceutical plants, petroleum refineries, traffic, food processing, automobiles and gas stations [5],[6], and the latter involves paintings, printings, furniture, textiles, cooking, insulating materials and tobaccos [7],[8]. VOCs can be the precursors of photochemical smog, tropospheric ozone and secondary aerosols once they are emitted into atmosphere [9]-[11]. Furthermore, emissions of VOCs result in climate change and acid rain [12],[13]. VOCs are also hazardous toward human health as exposure toward VOCs can result in acute and chronic respiratory, cardiovascular, neuro-, dermal, hepatic and gastrointestinal

diseases due to the nature of toxicity, carcinogenicity and mutagenesis [14]-[16]. In

recent years, concern of indoor VOCs emission and concentration has been increased

due to the enhanced public awareness of indoor air quality.

Table 1 lists physicochemical and thermodynamic properties of some important

VOCs [17]. Among them, benzene, toluene, ethylene and p-, m- and o-xylene (BTEX)

are the most important VOCs since they are categorized as group I (benzene)

carcinogenic pollutant, group IIB (ethylbenzene) carcinogenic pollutant and group III

neurotoxins (benzene and xylenes) by International Agency for Research on Cancer

(IARC). As a result, a large portion of VOCs abatement research is contributing for

BTEX removal. Besides, halogenated hydrocarbons such as trichloroethylene (TCE),

dichloromethane (DCM) are also frequently investigated due to their high toxicity

(both of VOCs and their byproducts during treatments). So far, various control

technologies have been applied for VOCs abatement, including absorption [18]-[20],

adsorption [21]-[24], condensation [25], biological degradation [26]-[28], thermal

incineration [5],[29], catalytic oxidation [30]-[36], photocatalytic oxidation [37]-[39],

ozone-catalytic oxidation [40]-[43], plasma oxidation [44]-[48] and plasma catalytic

oxidation [49]-[53]. Among them, absorption and adsorption are commercialized

techniques, nevertheless, absorption and condensation requires further treatment of

liquor or solid product and adsorption demands regeneration of adsorbent. The above

techniques are two-stage processes and lead to additional cost [54]. Condensation does not consume any chemical since condensation is a physical treatment, but the limitation is the treatment and disposal of coolants [54]. Biological processes can be operated at a mild condition and no subsequent process is needed, however, the operation must be well-controlled and the treatment period is longer than other processes [55]. Photocatalytic oxidation has the advantage of utilization of solar energy, which reduces the energy cost during VOCs abatement, but the low reaction rate is the major challenge. Furthermore, solar corrosion and poisoning of photocatalyst also reduce the lifetime of photocatalyst [56]. Thermal incineration can completely destroy VOCs with shorter operation time and complete mineralization into nontoxic products. Nonetheless, high energy demand is necessary for the high operating temperature, which results in tremendous demand of energy. Also, in field applications, incineration can result in secondary pollutant formation, e.g. NO_x [57].

Catalytic oxidation is also a traditional VOCs abatement technique. Both noble metal-based catalysts and transition metal-based catalysts are employed in catalytic oxidation of VOCs. Noble metal-based catalysts possess good catalytic activities and complete oxidation can be achieved with lower operating temperatures due to their high electron transfer capability [58]. Nonetheless, noble metal-based catalysts have the drawbacks of high cost and deactivation caused by coke deposition, halogen and

water vapor [59]. Transition metal-based catalysts are good alternatives for low-cost catalytic oxidation and their resistances toward poisoning and coke deposition are better than noble metal-based catalysts. But their mineralization rates are often lower than that of noble metal-based catalysts [60]. It is noted that some VOCs contain halogen and sulfur, thus, formation of byproducts during catalysis, e.g. chlorine radical, sulfur nanoparticles, can deactivate both noble metal-based and transition metal-based catalysts [61]. What is more, the practical operation of catalytic oxidation is companied with water vapor, acidic gases and other halogen- and sulfur-containing compounds, and the existence of those substances poisons the catalyst to limit the catalytic oxidation [54].

Nonthermal plasma stands for another promising alternative technique to remove VOCs from gas streams (herein we use the term plasma to substitute nonthermal plasma). Instead of thermal energy, plasma is driven by electrical energy. Hence, no external thermal energy is required [62]-[64]. During plasma operation, VOCs are degraded via electron impact reactions, i.e. vibrational excitations, dissociations and Penning dissociations [65]. Various plasma reactors including corona discharge [66],[67], gliding arc [68],[69], dielectric barrier discharge (DBD) [70]-[73], glow discharge [74],[75], atmospheric pressure glow discharge (APGD) [76] and microwave plasma [77],[78] have been investigated for their VOCs oxidation capacity,

and comparable removing efficiency of VOCs have been achieved. Being different from catalysis, kinetics of plasma oxidation is more complex since more species are generated during discharge, including cations, anions, atoms, excited molecules and atoms, electrons and radicals. Therefore, composition of effluent is usually more complicated than that treated with catalysis, resulting in lower mineralization rate [79],[80]. Occasionally, effluent stream may have even higher toxicity than influent stream, which also restrain the application of plasma [81],[82].

Combining plasma and catalyst to form a two-stage system or single-stage system is expected to solve the shortcomings of plasma and catalyst simultaneously. The former method (also called post-plasma catalysis, PPC) is to pack catalyst after the discharge volume of plasma reactor and in this configuration the active species participating in catalytic reactions are different from catalysis since plasma can generate various active species and intermediates. The latter method (also called in-plasma catalysis, IPC) is to place catalyst inside the discharge volume to induce interactions between plasma and catalyst. Compared to PPC system, IPC system is far more complicated since the existence of catalyst can influence plasma in the meantime. Generally speaking, plasma can influence physical, chemical and thermodynamic properties of catalyst by particle bombardments. On the other hand, catalyst can alter the electrical, magnetic and thermal nature of plasma and these

phenomena depend on the characteristics of plasma and catalyst, respectively. So far, many studies have been conducted to discuss the interactions between plasma and catalyst [83]-[95]. For VOCs abatements, the performance of plasma catalysis system and interactions between plasma and catalyst should be characterized to further improve the performance for VOCs removal.

This article aims to provide a systematic review of VOC removal via single technique and hybrid process, i.e. plasma catalysis. Major concepts of catalytic oxidation (Chapter 2), nonthermal plasma abatement (Chapter 3) and plasma catalysis process (Chapter 4) are discussed in detail including major oxidation mechanisms and factors influencing VOCs abatement. Byproduct formation is inevitable and is also included in nonthermal plasma oxidation. Detailed interactions between plasma and catalyst are provided in Chapter 4. Moreover, the impacts of plasma on catalyst and the influences of catalyst on plasma are elucidated comprehensively. Finally, some prospects are introduced for further modification of the hybrid VOCs removal system.

2 Catalytic oxidation of VOCs

Compared to thermal incineration, catalytic oxidation of VOCs can be operated at lower temperatures since catalytic oxidation provides different reaction routes. In catalytic oxidation processes, activation energy of oxidation can be reduced by

changing reaction mechanism and adsorbing VOCs, oxygen and other reactive species.

Up to date, noble metal-based catalysts (Pt, Au, Pd, Rh and Ag) and transition

metal-based catalysts (Mn, Co, Ti, Ni, V and Ce) coated on various supports have

been evaluated for their VOCs oxidizing capability. The performance of the catalytic

oxidation depends on the characteristics of catalyst, including specific surface area,

pore distribution, surface acidity, particle size, surface and lattice oxygen diffusivity,

electron transport capability and crystal structure, and nature of VOCs such as

molecular weight, molecular structure, polarity, acidity and redox potential. Hermia

and Vigneron (1993) applied a Pt-Pd/honeycomb catalyst to oxidize VOCs and they

established the order of VOC activity as: alcohols > aldehydes > aromatics > ketones

> alkenes > alkanes, indicating that molecular structure is a key factor influencing the

activity of VOCs oxidation [96]. Furthermore, Barresi and Baldi (1994) applied a

Pt/cordierite-γ-Al$_2$O$_3$ catalyst for the oxidation of a series of aromatics. The results

showed the ranking of aromatic oxidation capabilities is as following: benzene >

toluene > ethylbenzene > o-xylene > styrene, again it reveals that the molecular

structure plays an important role in catalytic oxidation of VOCs [97]. Besides,

reaction mechanism of catalysis, by-product formation and interactions among active

metal, modifier and support need to be taken into account in designing a catalysis

reactor.

2.1　Reaction kinetics of catalytic VOCs oxidation

Catalytic oxidation of VOC takes place between VOC molecule and oxygen

species which may originate from gas stream, catalyst surface and catalyst lattice,

depending on free energy and diffusivity. Hence, the reaction routes for VOC

oxidation among different VOCs and catalyst are not identical. Based on the sources

of oxygen, reaction routes and kinetics can vary and are generally divided into three

categories, i.e. Langmuir-Hinshelwood (L-H) model, Eley-Rideal (E-R) model and

Mars-van Krevelen (MVK) model, respectively. Those surface reaction mechanisms

are proposed for catalytic VOCs oxidation in previous experimental and theoretical

studies. Figure 1 presents the schematic concept of L-H model, E-R model and MVK

model, respectively [98]. Since L-H model, E-R model and MVK model have

different reaction pathways, reaction kinetics including reaction rate, activation

energy and reacting species are different [99]. Detailed mechanisms are introduced as

following:

L-H model, as illustrated in Figure 1 (a), can be described as following: two

reactants, VOC and oxygen are adsorbed on the catalyst surface firstly. Next, two

adsorbed species further react with each other to form products. The last step is

desorption of product from active sites [100]. For VOCs oxidation, VOC and oxygen

can be adsorbed on adjacent active sites (single-site L-H model) or different active sites (dual-site L-H model). For dual-site L-H model, the diffusivities of VOC and oxygen play important roles. The oxidation rates of single-site L-H model and dual-site L-H model can be expressed by Equations (1) and (2), respectively.

$$-r_{VOC,LHss} = \frac{kK_{O_2}K_{VOC}P_{O_2}P_{VOC}}{(1 + k_{O_2}P_{O_2} + k_{VOC}P_{VOC})^2} \tag{1}$$

$$-r_{VOC,LHds} = \frac{kK_{O_2}K_{VOC}P_{O_2}P_{VOC}}{(1 + k_{O_2}P_{O_2})(1 + k_{VOC}P_{VOC})} \tag{2}$$

where r_{VOC} stands for the reaction rate of VOC removal (mol/m^3·s), k stands for reaction rate, K_{O_2} and K_{VOC} stand for the equilibrium constants for the adsorption of oxygen and VOC, respectively, P_{O_2} and P_{VOC} stand for the partial pressures of oxygen and VOC, respectively, and k_{VOC} and k_{O_2} represent the rate constants for VOC oxidation and catalyst re-oxidation, respectively.

E-R model (Figure 1 (b)) contains two steps: the first is the adsorption of oxygen on catalyst surface and the second is the reaction between adsorbed oxygen and VOC in gas stream. During E-R mechanism reaction, the rate of VOC oxidation is the rate-limiting step [101]. Equation (3) expresses the rate of E-R mechanism.

$$-r_{VOC,ER} = \frac{kK_{VOC}P_{O_2}P_{VOC}}{(1 + K_{VOC}P_{VOC})} \tag{3}$$

MVK model (Figure 1 (c)) consists of two steps during VOC oxidation. Firstly, VOC is adsorbed on catalyst surface and then reacts with lattice oxygen. Secondly, the oxygen vacancy caused by step 1 can be reoxidized by free oxygen. Being different from L-H and E-R models, oxygen participating in oxidation is mostly attributed to lattice oxygen, instead of surface oxygen [102].

$$-r_{VOC,MVK} = \frac{k_{O_2} k_{VOC} P_{O_2} P_{VOC}}{\gamma k_{VOC} P_{VOC} + k_{O_2} P_{O_2}} \tag{4}$$

where γ is the stoichiometry coefficient of O_2 in the oxidation.

Table 2 lists postulated kinetics among previous studies on catalytic VOCs oxidations. L-H and MVK models are used to simulate reaction kinetics, however, there is no obvious relationship among VOC, catalyst and reaction model. For toluene oxidation, both L-H mechanism and MVK mechanism are possible, similar trend can be observed in benzene, propane and acetone oxidation, as indicated in Table 2. Besides, acetone oxidation with $Cu_xCe_{1-x}O_y$ follows different reaction route when Cu-Ce ratio is varied. Figure 2 shows two different reaction routes of catalytic oxidation of benzene. Li et al. (2016) applied $NiMnO_3/CeO_2/Cordierite$ catalyst to oxidize benzene and their kinetic study indicates that catalytic benzene oxidation

follows MVK mechanism. Benzene is firstly adsorbed on $NiMnO_3/CeO_2/Cordierite$ catalyst surface, and then oxidized by the oxygen originated from catalyst lattice. As a result, oxidation of benzene leaves oxygen vacancies in catalyst lattice and these oxygen vacancies can adsorb oxygen in gas stream to again form lattice oxygen [119]. Being different from this observation, Zeng et al. (2015) proposed an L-H model to explain benzene oxidation over MnO_x/TiO_2 catalyst. Oxygen and benzene are firstly adsorbed on catalyst surface, then, further substitute the hydrogen to form phenolate, benzoketone, and maleate. Total oxidation of benzene to CO_2 can be achieved via consequent oxidation [120]. It is worth noting that the oxygen species participating in oxidizing reaction sprang up from catalyst lattice and gas stream.

2.2 Features of catalytic oxidation

To date, catalysts with various active metals, modifiers and supports are investigated for their catalytic activity and durability toward VOCs oxidation. Various factors can influence catalysis performance including surface area, particle size, valance and redox potential of active metals, crystalline structure, acidity and basicity, diffusivity and amount of surface and lattice oxygen, pore structure, electron mobility and hydrophilicity [121],[122]. There is no certain dependence among catalyst properties and catalysis activities and durabilities, since characteristics of catalyst can

be easily adjusted via several ways such as partial substitution by metals, pretreatment via ultrasound, plasma, microwave, soaking in acid/base solutions, modification of preparation process and thermal oxidation/reduction. Fortunately, there are some relevance of catalyst characteristics and catalytic performances and herein we discuss their dependence.

Table 3 lists previous investigation results of catalytic oxidation of VOCs. It is obvious that both characteristics of catalyst and physicochemical properties of VOC can influence oxidation efficiency. Minicò et al. (2001) and Scirè et al. (2001) prepared two Au/Fe_2O_3 catalysts with the same preparation procedure while loading of gold is different (8.2 wt% and 3.5 wt%, respectively) and investigated their oxidizing capability toward acetone, methanol and toluene. The results indicate that 8.2%Au/Fe_2O_3 has the oxidizing capability ranking of acetone > methanol > toluene while 3.5%Au/Fe_2O_3 reveals different order of methanol > acetone > toluene [130],[131]. Based on the abovementioned results, many factors should be taken into account simultaneously in designing the catalysis system. According to previous studies, several factors are especially important to discuss in this review: size distribution of active phase particles, surface acidity, valence of surface metals, activity of surface oxygen and lattice oxygen and pore size distribution.

(1) Size distribution of active-phase particles. There are three major steps

influencing reaction kinetics regardless the reaction route it follows: adsorption of VOC and oxygen, oxidation of VOC and desorption of products. Although the rate of VOC oxidation is the rate-limiting step in catalytic VOC oxidation, the thermodynamic properties of adsorption and desorption strongly influence VOC oxidation rate. Therefore, adsorption kinetics of VOC is an essential step in catalytic VOC oxidation [132],[133]. Particle size distribution of adsorption sites (?or catalyst??) is a crucial role to determine the adsorption energy and further lead to reduced activation energies. Isaifan et al. (2013) prepared a series of Pt/C catalysts with different average Pt particle sizes on carbon surface and valuated their oxidation ability toward ethylene. They found that there was a strong relationship among average Pt particle size, activation energy and turnover frequency of ethylene oxidation, as illustrated in Figure 3 (a). It can be seen that activation energy decreases with smaller average Pt particle size and this may be attributed to the stronger chemical adsorption of VOC onto active phase and thus larger adsorption heat. As a result, the turnover frequency achieved with the catalyst having a smaller average Pt particle size can be increased since activation energy is reduced [134]. Furthermore, Chen et al. (2015) synthesized Pt/ZSM-5 catalyst to oxidize toluene and the relationship between average Pt particle size and T_5, T_{50} and T_{98} is revealed as depicted in Figure 3 (b). They found that conversion of toluene can be enhanced when

average Pt size is decreased from 2.3 nm to 1.9 nm due to the reduction of activation

energy. Nevertheless, oxidation of toluene is unexpectedly inhibited as the average Pt

size is further decreased from 1.9 nm to 1.3 nm, and authors attributed this

phenomenon to the fact that desorption rate is inhibited since the chemical adsorption

is stronger [135]. Yet this trend is observed only for Pt-based catalysts, other studies

pointed out that smaller average metal particle size is feasible for better VOC

oxidation due to lower activation energy [136]-[140].

(2) Surface acidity. Catalyst can have surface acidity or basicity, depending on the

nature of support and active phase and the interactions between support and active

phase. Table 4 lists the acidity and basicity of some supports [141]. Based on previous

investigations, some oxides possess acidity, e.g. γ-Al_2O_3, MoO_3, Nb_2O_5, Ta_2O_5, TiO_2,

and WO_3. Catalysts with those supports usually possess various degree of acidity and

this property can influence their catalytic activities. Surface acidity usually enhances

proton acceptability of catalyst but the adsorption capacity of oxygen can be inhibited

simultaneously. Okamura et al. (2003) synthesized the catalysts with palladium being

supported on Al_2O_3, MgO, Nb_2O_5, SiO_2, SnO_2, WO_3 and ZrO_2, respectively, to

evaluate their surface acidity and toluene oxidation efficiency. Results indicate that

higher surface acidity is unfavorable in toluene oxidation because of lower oxygen

affinity [146]. Yazawa et al. (2002) prepared platinum catalysts supported on Al_2O_3,

La_2O_3, MgO, SiO_2, ZrO_2, SiO_2-Al_2O_3 and SO_4^{2-}-ZrO_2 for propane oxidation. They found that the conversion of propane was dependent on the surface acidity of these catalysts, as shown in Figure 4. Propane conversion decreases with increasing surface basicity and the catalyst with the lowest surface acidity reveal the best propane oxidation ability [126]. However, for chlorinated volatile organic compounds (CVOCs), the tendency of oxidation capability is opposite to that of hydrocarbons. Stronger surface acidity can enhance adsorption rate and capacity toward CVOC, resulting in better CVOC oxidation efficiency [127],[147],[148].

(3) Metal can exist with single or multiple oxidation states, and the oxidation state of metal plays a crucial role in catalytic oxidation. Many studies point out that active metal with lower oxidation state possesses higher oxygen diffusivity and electron mobility to enhance the activities of catalysts, including Ce^{3+}, Co_3O_4, Mn^{3+}, Pt^0, Pd^0 and Au^0 [37],[58],[132],[149]-[151]. Additionally, some studies found that the coexistence of two or more oxidation states of metal on catalyst surface would further modify the catalytic performance for VOC oxidation. Mo et al. (2016) prepared CoO_x/LDH and $CoAlO_x$/LDH catalysts (layered double hydrotalcite) to convert benzene and toluene. Among them, CoO_x/LDH possesses the highest surface acidity and the smallest specific surface area, which is unfavorable for VOC oxidation. However, CoO_x/LDH has the highest capability for the oxidation of benzene and

toluene compared to CoAlO$_x$/LDH catalysts, authors attributed the results to the fact that CoO$_x$/LDH catalyst has dual oxidation states of cobalt, Co^{2+}/Co^{3+}, and the coexistence of cobalt cations leads to higher adsorption rate and reactivity of surface oxygen [152]. Liu et al. (2012) synthesized three-dimensionally ordered (3-DOM) macroporous Au/CeO$_2$ catalyst via a precursor complexion process to oxidize formaldehyde, and the activity test results show that formaldehyde can be oxidized with a reasonable efficiency even at room temperature. XPS result indicated that Au^0 and Au^{3+} coexisted on catalyst surface and authors pointed out that Au^{3+} has better catalytic activity than Au^0. Nevertheless, existence of Au^0 provides another oxidation route of formaldehyde, as illustrated in Figure 5. It is noted that during oxidation of formaldehyde with Au^{3+} particle, Au^{3+} site can be reduced to form Au^0 and the oxidation route can be altered to mechanism 2 in Figure 5. When formaldehyde oxidation takes place on Au^0 particle, the route can also be shifted from mechanism 2 to mechanism 1. Finally, the authors attributed the excellent oxidation capability of Au/CeO$_2$ catalyst to the dual gold oxidation states and reaction mechanism [153].

(4) Density and activity of surface and lattice oxygen. As described in the previous section, oxygen species participating in catalytic oxidation can be divided into surface oxygen, lattice oxygen and free oxygen in gas stream, depending on their reaction mechanism, i.e. L-H, MVK or E-R. However, E-R route is hardly induced

during VOC oxidation due to low temperatures. Hence, reactivity of surface and lattice oxygen is an important factor affecting catalytic VOC oxidation. Zeng et al (2015) proposed MVK mechanism for benzene oxidation with a series of MnO_x/TiO_2 catalysts, and test results show that catalytic activity of MnO_x/TiO_2 catalyst is strongly dependent on the loading of manganese, i.e. 20% MnO_x/TiO_2 has better catalytic activity than other MnO_x/TiO_2 catalysts. XPS results show that 20% MnO_x/TiO_2 has the largest relative density of lattice oxygen as shown in Table 5 and this can be the major cause since average particle size, acidity and oxidation state of Mn among catalysts are nearly identical [120].

In addition to above properties, other physicochemical properties also influence catalytic oxidation performances, e.g. pore size distribution, hydrophilicity, crystallinity and redox potentials. Among them, pore size distribution influences diffusion resistance of VOC and oxygen, which can further affect reaction rate of adsorption, oxidation and desorption. Hydrophilicity of catalyst leads to strong adsorption of water vapor and this might result in slower desorption of water molecules and hence affects catalysis performance. Crystallinity is also an important factor since the crystalline phase affects surface oxygen as well as electron diffusivity. Redox potential principally determines the tendency of donating electron or accepting electron. For p-type metal oxides, they are easily to donate electron and this

characteristic is favorable for oxidation reaction. As a result, those characteristics should be considered in designing a catalysis system, for a reasonable and economical treatment of VOCs in gas streams [154].

3   Nonthermal plasmas

Nonthermal plasma provides another efficient route to remove VOCs from gas streams. Nonthermal plasma utilizes electrical energy to drive free electrons to collide with and transfer energy to gas molecules. During collision, inelastic collisions are required to induce electron impact reactions including electron impact excitation, dissociation and ionization, to further destroy VOC molecules [155],[156]. Since the driving force of VOCs removal is electron energy, there is no need to heat up the gas stream. Hence, the energy consumption of VOCs abatement can be reduced. So far, various types of nonthermal plasma reactors have been developed for VOCs abatement [157]-[166]. Nonthermal plasma reactors can destroy VOC molecules with a lower operating temperature compared to catalytic oxidation. It is worth mentioning that removal efficiency of VOC via plasma depends on two factors: the first one is the nature of VOC to be removed, including bond strength, acidity and molecular structure, and the second is the physical properties of plasma. Karatum and Deshusses (2016) applied a DBD reactor with a specific input power ranging from 50 to 300 J/L

to treat the gas stream containing specific VOC. Various VOCs including benzene, toluene, ethylbenzene, n-hexane, methyl tert-butyl ether (MTBE), methyl ethyl ketone (MEK) and 3-pentanone are carried individually with a dry air flow with a flow rate of 6.6 L/min and the concentration of specific VOC is controlled at 95 ppm. Figure 6 illustrates the removal efficiencies of specific VOC compound achieved with DBD reactor. Removal efficiencies follow the trend as: n-hexane > MTBE > ethylbenzene > 3-pentanone > toluene > benzene > MEK. The reasons for this removal trend are structure of VOC molecular and hydrogen weight fraction. VOC with straight chain structure are most easily decomposed due to its lowest bonding energy, followed by branched chain. Aromatics are the VOCs most difficult to degrade due to its stable structure. However, as shown in Figure 6 some aromatics such as ethylbenzene are more easily degraded, authors attributed the result to the fact that VOC with higher hydrogen weight fraction can be easier reduced since hydrogen is feasible to generate free electrons and radicals [167],[168]. Next, different reactor geometries lead to various types of plasma reactor and hence varying physical properties, e.g. gas temperature, electron energy and electron density and current. Table 6 lists some physical properties among various nonthermal plasmas, including electron energy, electron density, current and gas temperature. The above characteristics depend on the power supply and structure of reactor and play crucial roles in VOC abatement. Since

plasma abatement of VOC is induced via electron collisions, electron energy and electron density are key factors to determine the overall operation efficiency. Higher electron energy and electron density may be feasible to induce electron impact vibrational and electron excitation and dissociation. Hence, from the viewpoint of electron collisions, plasmas with higher electron energy and electron density can be candidates, e.g. DBD, APPJ, spark discharge and microwave. Unfortunately, higher electron densities are more likely associated with elastic collisions, which are not ideal. Another factor which should be taken into account is the gas temperature. Average gas temperature in plasma reactor can be elevated via electron collisions if the electron energy is insufficient to induce electron impact reactions. As a result, higher average gas temperature is not favorable. From the viewpoint of energy efficiency, lower average gas temperature is suitable, e.g. corona discharge, DBD and APPJ. Herein we discuss principal VOC decomposition mechanism, influence of operation parameters and byproducts formation for specific VOC decomposition.

3.1　Decomposition mechanism

During discharge, free electrons are accelerated via external electric field to collide with particles. Energy can be transferred from electrons to particles and the degree of energy transfer plays a crucial role to influence consequent phenomena.

When the transferred energy from electrons to particles, e.g. gas molecules, exceeds the threshold energy, relevant reactions can be activated such as excitation, dissociation, electron attachment and dissociative electron attachment. Consequently, VOCs such as ethylene, benzene and trichloroethylene can be destroyed via electron impact reactions. The fastest channel of VOC destruction is mostly attributed to electron impact dissociation. When the transferred energy exceeds the bonding energy such as C–C, C–H, C–O, C=O and C–Cl bonds, VOC molecules can be destroyed via such dissociation [178],[179]. However, the threshold energy of electron impact dissociation is definitely high (usually higher than 10 eV) which is difficult to induce via atmospheric-pressure plasmas. On the other hand, electron impact electron and vibrational excitations stand for another reaction channel for VOC destruction. Electron impact vibrational excitation has a lower threshold energy compared to dissociation (usually lower than 3 eV), thus, the reaction rates of vibrational excitation are much higher than that of electron impact dissociations in nonthermal plasma [180],[181]. Similarly, some electron impact excitations have lower threshold energy than electron impact dissociation and are important and crucial reactions [182],[183]. The most important is that some vibrationally and electron excited states of VOCs are of considerably long lifetimes (hundreds of nanoseconds to tens of microseconds). Excited molecules can further absorb energy from electron collision and this process

can reduce the threshold energy needed to dissociate VOC molecule [184],[185].

In fact, aforementioned reactions account for less than 5% in VOC removal since the VOC concentration in gas stream is usually low. The most important reaction mechanism is radical production via electron collisions with neutral species in gas stream including oxygen, nitrogen and water vapor [186]. Table 7 lists some radical and intermediate species generated via collision between free electron and neutral species including O_2, N_2 and $H_2O_{(g)}$ [187]. Radicals and intermediate species can further react with VOCs to destroy them since radicals and intermediate species are of longer lifetimes than free electrons (up to μs). Excited oxygen atom ($O(^1D)$) and oxygen ions (O_2^-, O_2^+, O^+ and O_2^*) are active oxidizing agents, therefore, the collision with these so-called reactive oxygen species (ROS) induces oxidation of VOCs [188],[189]. Among the above oxygen species, ozone is the other oxidizing specie generated during discharge. In the presence of oxygen in gas stream, ozone can be generated and further dissociated into oxygen atom to further oxidize VOCs [190],[191]. Boganov et al. (2014) applied a pulsed glow discharge to treat benzene-containing gas stream diluted with Ar. Both gas streams without and with the existence of oxygen are simulated to distinguish the role of oxygen and Fourier-transform infrared (FT-IR) is used to investigate the intermediates and products formed during benzene abatement. Both carbon dioxide and water vapor can

be found regardless of the presence of oxygen, however, formation and distribution of intermediates and by-products are somewhat distinct between two reaction conditions (in case of oxygen-free condition, oxygen is speculated to be from microleaks in vacuum system). For benzene decomposition in the absence of oxygen, fulvene ($C_5H_4CH_2$) and benzvalene (C_5H_5CH) can be found and both are isomers of benzene. They can be formed via C–H and C–C bond breaking and subsequent bond formation. Next, acetylene (C_2H_2), butadiyne (C_4H_2), ethylene (C_2H_4) and methane (CH_4) are distinguished as stable products with comparable yield. The above products are speculated to be formed via dissociation of benzene, and authors attributed those dissociations to the collisions induced between free electron and benzene and between excited Ar and benzene. Followed by phenyl (C_6H_5), ethynyl (C_2H) and butadiynyl (C_4H) radicals can be recognized via FT-IR as intermediates. Also, argon clusters, e.g. Ar_nH^+, can be found and the formation of those intermediates can be attributed to the collision between Ar and hydrocarbons. The overall degradation of benzene in the absence of oxygen is summarized in Figure 7 (a). With the addition of oxygen, oxygen-containing products and intermediates including formaldehyde (HCHO), ketene (CH_2CO), formyl (HCO), ketenyl (HCCO), propadien-3-on-1-ilydene (C3O) and propadiene-1,3-dione (C_3O_2), carbon dioxide, water vapor, carbon monoxide, hydroperoxyl (HO_2), O_4^- and ozone are detected. Results of the above tests indicate

that oxygen species participated in benzene destruction via various reaction routes. More importantly, numerous oxygen species including O, O_2^-, O_2^+, O_3^-, O_4^-, O_4^+ and O_3 can be generated via plasma and induce oxidation of benzene, as indicated in Figure 7(b) [192].

Advanced oxidation process (AOP) is a well-developed technique and has been applied in many fields, e.g. water purification, sterilization and surface cleaning [193]. AOP is mainly induced by OH radical, to oxidize and destroy target reactant. AOP also takes place in plasma abatement of VOCs, as indicated in Table 7 [194]. OH radical can be generated during discharge in the presence of hydrogen and oxygen atoms, especially in humid gas stream since water molecules can be dissociated into OH and O radicals by electron impact dissociation [195],[196]. Bo et al. (2007) applied a gliding arc discharge reactor to treat the gas stream containing tetrachloromethane, n-butane or toluene and the influences of oxygen content and relative humidity on VOCs removal efficiency are further evaluated. They concluded that the addition of water vapor reduces electron density and suppresses ROS formation while gives rise to OH radical formation. Based on adverse effect of water vapor addition on ROS formation, the influences of humidity on VOCs removal are not identical among those three VOCs. For n-butane and toluene abatement, addition of water vapor enhances OH radical formation and hence AOP takes place for

n-butane and toluene oxidation, resulting in better removal efficiency. However, for tetrachloromethane destruction, oxidation by $O(^1D)$ has a much higher reaction rate constant than that by $O(^3P)$ and OH radical, thus the suppression of $O(^1D)$ formation by adding water vapor results in lower tetrachloromethane removal [197].

Accordingly, the roles of oxygen, water vapor and other components are not consistent and depend on the nature of VOCs and plasma reactor. Figure 8 shows several postulated degradation pathways for toluene removal. Figure 8 (a) depicts the speculated reaction routes of benzene via ozone as hypothesized by Baltaretu et al. (2009). Ozone can react with toluene, and tends to attract electrons near oxygen atom to form a C=C double bond. As a result, toluene ring is destroyed to form non-aromatic intermediates. Further dissociation can be induced by both free electron and ozone, to form oxygen-containing hydrocarbons. It is noticed that during this chain reaction, zwitterion polymers are generated via toluene ring destruction [199]. On the other hand, Bailey (1958) proposed that co-existence of hydroxyl radical and molecular oxygen plays an important role in toluene removal, as explained in Figure 8 (b). Hydroxyl radical can firstly attack toluene ring to form a hydroxyl-containing aromatics, those intermediates can further be dissociated to form water molecule via oxygen attack. Here many reaction routes are possible and depend on intermediate structure and oxygen collision mechanism. Still another important reactive species to

27

dissociate toluene is free electron. Free electron can dissociate toluene and release methyl radical or hydrogen atom if the kinetic energy of electron exceeds the threshold energy, it is noted that electron and hydroxyl radical can attack the intermediates to further dissociate them into fragments or to combine them into other aromatics [200]. Liang et al. (2013) developed a model to explain the degradation pathways of toluene as shown in Figure 8 (c). Figure 8 (c) indicates that toluene degradation is a sequence of electron/hydroxyl radical attack on toluene and intermediates, to further oxidize toluene into CO_2 [201]. Actually, in practical plasma operation, the above mechanisms can all be possibly induced, namely, electron impact excitation and dissociation, ROS and ozone oxidation and AOP are involved with and the rate constants of mentioned reaction are therefore dependent on many factors, including gas stream composition, electron density, electron energy, gas temperature, residence time and applied power.

Input power influences the plasma performance on VOCs removal since power plays a key role in active species generation. Marotta et al. (2008) investigated DC corona discharging for i-octane removal and the differences of +DC and −DC are distinguished via atmospheric pressure chemical ionization mass spectrometry (APCI-MS). Both +DC and −DC reactors show nearly identical energy consumption for i-octane-containing stream with the identical applied voltage as well as

comparable removal efficiency. However, APCI-MS spectra show different patterns between +DC and –DC plasmas. For –DC plasma, O_3^-, O_2^-, $O_2^-O_2$, $O_2^-H_2O$ and $O_3^-H_2O^-$ ions are distinguished as intermediates and oxidizing agents. For +DC plasma, positive ions instead of negative ions are dominating species, such as O_2^+, N_2^+, NO^+ and H_3O^+ ions, those ions can also degrade i-octane into intermediates, e.g. $C(CH_3)_3^+$ and $CH_2CH(CH_3)_2$. These intermediates are stable and are easily to be oxidized into CO and CO_2. Though positive ions are difficult to generate during discharge, reaction rates between positive ions and i-octane are much higher than that between negative ions and i-octane, results in comparable removal efficiencies between –DC and +DC reactors. Moreover, with the existence of water vapor, OH radicals can be generated via H_2O dissociations and participate in i-octane degradation [202].

Table 8 lists previous investigations on plasma removal of VOCs. In terms of energy utilization efficiency, here we introduce the term energy efficiency (g/kWh), being defined as the mass of VOC removed per kilo-watt hour input. In other words, higher energy efficiency indicates the better energy utilization efficiency during plasma operation. Table 8 indicates that for identical plasma reactor and VOC, operation parameters can be varied for a wide range, e.g. discharge power ranges from millis of Watt to thousands of Watt. Those variations further result in a wide range of

energy efficiency. For instance, the energy efficiency for toluene removal can be as high as 55.9 g/kWh while lower energy efficiency can be only 4.43 g/kWh for the inlet toluene concentrations in the ppm level [79],[205]. It is noted that higher input power does not necessarily lead to higher energy efficiency, and neither low VOC effluent concentration. Instead, how to effectively generate active species including ROS, hydroxyl radicals and energetic electrons is crucial to enhance plasma performance.

3.2 Formation of byproducts

Compared to catalytic oxidation of VOCs, generation of unwanted byproducts remains as the major challenge in plasma gas clean-up on a commercial scale since plasma reactions are not selective. The formation of byproducts can be attributed to two reasons: (1) plasma abatement of VOCs contains a series of oxidation, radical damage and electron impact reactions, as a result, the reaction routes of VOC would inevitably be complex. The multiple channels of VOC degradation such as toluene, propylene and trichloroethylene provide a variety of degradation pathways, however, many stable products can be generated through various channels, and a part of them are unwanted byproducts, (2) all components in gas stream can participate in plasma reactions, e.g. N_2, H_2O as well as Ar. Electron bombardments onto these reactants can

also generate different types of intermediates including ions, radicals and excited species such as $N_2(A_3\Sigma_u^+)$, $N_2(C_3\Pi_g)$, $N(^2D)$ and $N(^2P)$[213][213]-[215]. These active species can react with other active species in gas stream such as O, OH and hydrocarbons to form byproducts. This process is definitely different from catalytic oxidation that is called "cross coupling". Cross coupling can take place between C– N or H–N to form N–C and N–H functional group and hence byproducts, for example, products containing NH, NH_2 and CN groups can be generated as final products. Furthermore, N_2 coupling with O_2 to form NO_x stands for another important byproduct due to its role of secondary pollutant [77],[201].

Sobacchi et al. (2003) developed a pulsed corona discharge reactor for the decomposition of acetone, methanol and α-pinene. In the plasma degradation of acetone, methanol is found as the major byproduct when the initial concentration of acetone is increased to 200 ppm. The amount of methanol in the effluent also increases with increasing acetone inlet concentration and with increasing acetone degradation, i.e. higher discharge power. This result suggests that methanol is generated via the dissociation of acetone and stands for a stable intermediate in the destruction of acetone. However, for methanol oxidation, byproduct is not detected by gas chromatography. Moreover, CO concentration in effluent is quite low, indicating that the rate of methanol oxidation to CO_2 is high. The vital factor is that C–C

bonding is more difficult to dissociate than C–H bond which is more easily to be broken by oxygen. For α-pinene degradation, pinoacetaldehyde and pinonic acid are identified as the major byproducts and followed by acetone. The oxygenated byproducts are speculated to be produced from the dissociation of C–C bond and coupling of oxygen atom [216]. Gandhi et al. (2013) investigated the degradation of ethylene with a DBD reactor and found that the byproducts including C_2H_2 and CH_4 are inevitably formed in the plasma process. The formation of these byproducts can be attributed to the fact that electron impact dissociation is the dominant reaction to break C=C and C–H bonds. Nevertheless, CO_2 production is quite low due to insufficient contact between oxygen radical and CO, C and hydrocarbons [217]. Schiavon applied a DBD reactor to treat two mixtures of VOCs, i.e. ethanol and ethyl acetate for mixture 1 and benzene, toluene and octane for mixture 2, respectively. For plasma decomposition of mixture 1, acetaldehyde and acetic acid are the dominating byproducts. They concluded that acetaldehyde is mostly generated via ethanol oxidation while acetic acid is produced mainly via ethyl acetate degradation. In addition to the above byproducts, other trace compounds including methanol, formic acid, propionic acid, formamide, 2-methyl—propanol, 1,2-ethanediol monoformate and 1,2-ethanediol diformate are also detected as products. For mixture 2, other trace byproducts including benzaldehyde, phenol, o-cresol, p-cresol, benzyl alcohol,

octane-dione and benzyloxy-benzene are detected [218].

Generally speaking, it is more difficult to convert chlorine-containing VOCs into CO_2. C–Cl dissociation energy is lower than that of C–H bond. However, chlorine is electron-negative and tends to form Cl⁻. Hence, chlorine radicals tend to attack intermediates to form byproducts. Futamura and Yamamoto (2007) investigated the abatement of trichloroethylene with a pulsed corona reactor. Byproducts including trichloroethane, tetrachloroethylene and 1,2-dichloroethylene are observed in effluent stream [219]. Vandenbroucke et al. (2015) developed a DC corona discharge for the removal of trichloroethylene in a gas stream and analyzed the byproducts formed in the process via FT-IR. They proposed that oxygen is the key specie to determine the destruction rate of TCE. Nevertheless, formation of chlorine-containing species including Cl_2 and Cl also plays an important role in reacting with products and intermediates. Hence, chlorinated byproducts are further identified via FT-IR, such as dichloroacetylchhloride (DCAC), trichloroacetaldehyde (TCAA), $COCl_2$, $CHCl_3$ and HCl [220].

On the other hand, cross coupling between carrier gas and VOCs usually results in byproduct formation. Ognier et al. (2007) simulated a pure nitrogen gas stream mixed with benzene and the gas stream is treated with a corona discharge reactor to investigate the product distribution. Byproducts detected can be divided into several

groups including linear compounds, aromatic oxygenated compounds and aromatic nitrogenated compounds. Nitrogen is found to be coupled with linear and aromatic hydrocarbons to form hydrogen cyanide, isocyanomethane, 2-propenenitrile, pyridine, benzonitrile. Moreover, polymerization also takes place during corona discharge removal of benzene to form poly-aromatics, i.e. hydrocarbons containing two or three rings and nitrogen(s) [221]. Similar results are achieved with another corona discharge reactor as reported by Ondarts et al. (2017). With very low power and specific energy input (2 to 12 W and 3.5 to 6.8 J/L, respectively), various byproducts are identified by gas chromatography - mass spectroscopy (GC/MS) and are listed in Table 9 [187]. Some oxygen-containing aromatics are proposed to be generated via cross coupling between benzene associated intermediate and ROS, such as benzyl alcohol, phthalic anhydride and benzoic acid. Nitrogenated aromatics are simultaneously found and their formation is attributed to the cross coupling between reaction intermediates and active nitrogen species. It is noted that when relative humidity is elevated to 60%, aromatic formation is inhibited and it may be attributed to higher AOP rate.

4   Combination of plasma and catalysis

So far, we have discussed some features of catalytic oxidation and plasma

removal of VOCs. Generally speaking, both of nonthermal plasma and catalyst are two powerful measures to remove VOCs. Nonetheless, both of them still face some challenges, e.g. formation of unwanted byproducts, limited operation period and insufficient mineralization rate. To further increase the removal efficiency of VOCs, combination of nonthermal plasma and catalyst can be considered as a practical way. Up to date, two plasma systems are investigated including PPC system [222]-[224] and IPC system [225]-[229]. Since the driving forces of plasma and catalysis are completely different and reaction routes are dissimilar between two processes, combining them may induce synergies. Until now, detailed synergistic effects between the plasma and catalysis have not been explored and more research is needed to elucidate the physical and chemical interactions between the plasma and catalysts to further improve the performance of plasma-catalytic processes. It is worth mentioning that interactions firstly depend on combination form, i.e. PPC and IPC, and further depend on discharge nature of the plasma, thermodynamic, electrical and optical properties of the catalyst, surface structure of catalysts and thermodynamic properties of the plasma catalysis system. In this section, we will discuss possible interactions between the plasma and catalyst, and those interactions can be divided into two parts: plasma affecting catalyst and catalyst affecting plasma. Again, in addition to our discussion on discovered interactions, many unknown interactions exist between

plasma and catalyst.

4.1 Plasma for catalyst preparation

Being different from catalysis, a range of reactive species can be generated in

plasma including highly energetic electrons (up to 10 eV), radicals, and excited atoms,

metastables and ions. All of these species produced in the gas phase can collide with

catalyst to induce various types of interactions. For instance, during inelastic collision

between electron and catalyst, heat can be transferred from electron to bulk catalyst,

resulting in local high temperature, which is also called hot spot [154]. In order to

reduce free energy in bulk catalyst, recrystallization can take place to form a new

local structure. Jang et al. (2008) applied a 360°-rotating RF plasma to treat a

5%Ni/Al_2O_3 catalyst and estimated the Ni particle size loaded on Al_2O_3. They

prepared a series of Ni/Al_2O_3 catalysts and treated the catalysts with an air or H_2

plasma before calcination (denoted by (B) in Table 10) or after calcination denoted by

(A) in Table 10). Table 10 lists the results of Ni particle size among various

plasma-treated catalysts achieved with XRD analysis under different operating

temperatures. Among the Ni/Al_2O_3 catalysts treated with plasma and calcination, the

Ni particle size follows a trend: Air(B) > H_2(B) > Air(A) > H_2(A) > Air(B)H_2(A). This

trend can be attributed to the recrystallization of plasma treatment, resulting in even

smaller Ni particle sizes due to its higher energy density in a local volume. As the XRD analyzing period is elongated to more than 2 hours, the trend of Ni particle size vanishes since high XRD operating temperature and long operating period result in the aggregation of Ni particles on Al_2O_3 surface [230].

On the other hand, recrystallization can influence pore structures including pore size, pore volume and pore diameter. Tang et al. (2015) synthesized $Mn-CoO_x$ catalyst via solid phase reaction method and then treated with a nitrogen DBD at different applied voltages (5.6, 7.0 and 8.5 kV), as shown in Table 11. The original $Mn-CoO_x$ catalyst had a specific surface area, a total pore volume and a micropore volume of 254 m^2/g, 0211 cm^3 and 0.002 cm^3/g, respectively. After the N_2 plasma treatment with applied voltage of 7.0 kV on catalyst, the specific surface area and total pore volume of the catalyst are increased by about 30%. It is noticed that the enhancement of micropore volume of the plasma-treated catalysts is over 5 times of the $Mn-CoO_x$ catalyst without the plasma treatment, indicating that the number of micropores in the catalysts is increased and further reduced the average pore diameter. Furthermore, as the applied voltage is increased to 8.5 kV, the specific surface area and total pore volume of the catalysts are reduced. Although they did not give an explanation of this trend, this phenomenon could be attributed to the high energy input, leading to overheating of catalyst to cause sintering to block micropores. This explanation can

be supported by the increase of the average pore diameter of the catalysts, indicating that the number of micropores is reduced [231].

Accompanied with thermal energy transmission, ions bombardments can also take place to influence catalyst structure. Together with thermal energy dissipation, chemical bonding between metal and oxygen and between metal and support can be varied from untreated catalyst. The Mn-CoO$_x$ catalysts mentioned beforehand can be with different metal compositions after plasma treatment. Catalysts treated with the N$_2$ DBD had a higher Mn^{4+}/Mn^{3+} ratio, and the level of increase depends on the applied voltage and discharge time, as indicated in Table 12 [231]. It is noted that activities of Mn-based catalysts depend on Mn^{4+}/Mn^{3+} ratio, although low Mn^{4+}/Mn^{3+} ratio is favorable for VOC oxidation [232],[233]. Fortunately, other studies revealed that metal oxides can be reduced by H$_2$ or Ar plasmas due to ion bombardment, thermal dissipation and electron attachment [234]-[237]. Zhu et al. (2006) used an Ar atmospheric-pressure glow discharge (APGD) to treat Pt/Al$_2$O$_3$ catalyst and the results indicate that the APGD can partly reduce Pt^{4+} to form Pt^0 [238]. Bullard and Lynch (1997) employed H$_2$ microwave plasma to reduce FeO$^.$TiO$_2$ to yield iron [239]. Besides, Guo et al. (2006) investigated a wire-plate DBD reactor packed with manganese oxide and they found that Mn$_2$O$_3$ could be reduced into Mn$_3$O$_4$ with the plasma and the enhancement of toluene decomposition could be partly attributed to

the reduction of manganese [240].

4.2   Influence of plasma on catalyst

Another advantage of thermal energy dissipation is the plasma-driven activation of catalysis. Traditional catalysis is driven by thermal activation, and the activation energy can be reduced with the help of catalyst by shifting the reaction route. In plasma catalysis, thermal energy can be provided via inelastic collisions. Hammer et al. (2004) measured the temperature increase for a DBD reactor with a specific input energy density of 10 J/L and the average gas temperature during the discharge increased roughly by $10–15^{o}C$ [241]. Kim et al. (2006) also reported a temperature increase of approximately $70^{o}C$ with a specific input energy of 200 J/L [242].

However, those temperature increases are presented in the macroscopic view of average gas temperature. From microscopic view of catalyst surface, the temperature rising can be even higher since thermal energy can be accumulated on the catalyst surface. Based on temperature increase of gas stream and catalyst, thermal activation of catalysis is likely to occur during plasma catalysis operation.

In addition, plasma can generate various species during discharge, e.g. atoms, radicals, vibrationally excited species and electron excited species. These species can interact with catalyst during plasma catalysis process, resulting in different synergistic effects. Firstly, reaction rate can be increased with the help of plasma. Demidyuk and Whitehead (2007) investigated the decomposition of toluene over Ag_2O/Al_2O_3 and MnO_2/Al_2O_3 catalysts under three different operating modes: catalysis-alone, IPC and PPC. Packing Ag_2O/Al_2O_3 or MnO_2/Al_2O_3 catalyst into the discharge region to form an IPC system reveals a higher toluene decomposition than PPC and catalysis-alone systems, indicating that plasma-catalyst coupling generates synergistic effects for toluene removal. Furthermore, they applied Arrhenius plots to deduce plasma activations as listed in Table 13. For the Ag_2O/Al_2O_3 catalyst, the activation energies associated with catalysis alone and PPC mode are almost the same, indicating that the active species generated by the plasma cannot react with the catalyst in the PPC mode. Similar phenomenon can be found for the Ag_2O/Al_2O_3 catalyst. By contrast, the

activation energy for toluene decomposition in the IPC mode is decreased by 20% [243], which can be attributed to the change of the reaction mechanisms in the presence of the catalyst within the plasma process. Firstly, ozone can be generated by air plasma [244]-[246]. Ozone is a well-known strong oxidizing agent and is recognized as an important oxidizing specie during plasma oxidation of VOCs [246],[247]. Moreover, ozone-assisted catalytic oxidation (OZCO) of VOCs is another efficient process to oxidize VOCs [248],[249]. Secondly, singlet oxygen ($O_2(^1\Delta_g)$) can also be generated in the plasma. Singlet oxygen is a molecule with higher internal energy (0.98 eV) compared to triplet oxygen ($O_2(\Sigma_g^-)$) [250]-[252]. Singlet oxygen also plays a key role as an oxidizing agent in the oxidation of VOCs [253]-[255]. Lastly, vibrationally excited species can be generated in the plasma since the energy demand of electron impact vibrational excitation is lower than that of electron impact dissociation and ionization. Also, some vibrationally excited species have lifetimes over microseconds, which is long enough to react with other reactants. Once reactant is vibrationally excited, the activation energy can be decreased, as indicated in Figure 10 [256].

Another important aspect is that the oxidation of VOCs follows multi-channel. As discussed in Section 2, catalytic oxidation of VOCs follows L-H reaction route or MVK reaction route, depending on the nature of VOC and catalyst [257],[258]. When

packing a catalyst into the discharge zone, various reaction routes can be induced via several synergistic effects such as: (1) Catalysis activated by plasma can follow the catalysis route, principally L-H route. (2) Oxygen-related active species including ozone, singlet oxygen, triplet oxygen and oxygen atom, can be adsorbed onto catalyst to form surface oxygen and further react with adsorbed VOCs. At the subsequent stage, L-H or E-R route may be stimulated depending on whether VOC molecule is adsorbed onto catalyst surface or not. Incidentally, the above reactions are surface reactions, yet VOCs can be oxidized without the help of catalyst, i.e. plasma induced oxidations, as mentioned in Section 3. In summary, combining plasma and catalyst can stimulate various reaction mechanisms and both gas-phase reactions and catalytic surface reactions are altered. Catalytic surface reaction routes including L-H and E-R are possibly induced in plasma catalysis system.

4.3　Influence of catalyst on plasma

Along with catalyst modification by discharging, the existence of a catalyst inside a plasma reactor also influences physicochemical properties of the plasma as the plasma properties are strongly related to the geometry and configuration of the reactor. During discharge, electron density and electron energy play important roles in VOCs removal. Appropriate electron temperature is favorable to induce electron impact

dissociation of VOCs and to collide with carrier gas to generate reactive species, e.g. ozone, singlet oxygen and vibrationally excited species. Packing a catalyst into plasma reactor can change the above two properties, based on the electrical property of the catalyst, i.e. dielectric constant (ε_r). Dielectric can be polarized under an external electric field and the strength of polarization is expressed as dielectric constant or relative permittivity. Previous studies pointed out that higher dielectric constant of packing material results in higher electric current and thus elevate dissipating power in discharge zone [259]. Takaki and Chang (2004) simulated time averaged deposited power, current density and electron temperature inside a two-mesh N_2 plasma reactor packing with ferroelectric with a dielectric constant of 660, 5,000 and 10,000, respectively. Figure 11 (a) indicates that packing the material with a higher dielectric constant into the plasma reactor enhanced the power deposited into discharge zone. Another important point of using a packing bed is that packing higher dielectric constant material into the plasma can reduce the breakdown voltage of the plasma. For example, the reactor packed with dielectric material possessing a dielectric constant of 10,000 reduces the breakdown voltage by near 2 kV. Further simulation revealed that the time averaged current density (Figure 11 (b)) and time- and space-average electron temperatures (Figure 11 (c)) are increased by packing the pellets with a high dielectric constant into the discharge zone. Higher time averaged

current density, namely, number of free electrons in the discharge zone leads to higher

collision frequency between electrons and gas molecules [260]. On the other hand,

shorter rising time and higher space-averaged electron temperature result in effective

collision, i.e. electron impact excitation and dissociation instead of heat transfer which

is usually unfavorable. Ogata et al. (1999) investigated the decomposition of benzene

in a DBD reactor packed with Mg_2TiO_4, $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ with the

dielectric constants ranging from 20 to 15,000. Figure 12 (a) shows the dependence of

benzene removal on the field strength and dielectric constant and the removal

efficiency of benzene is proportional to the dielectric constant of the packing

materials. Possibly, packing the material with a higher dielectric constant leads to

enhanced local electric field, resulting in higher deposited energy inside discharge

zone, and consequently higher benzene removal efficiency. However, Figure 12 (b)

shows that packing the material with a higher dielectric constant also leads to higher

benzene removal per unit energy input. This phenomenon can be attributed to higher

electron energy, as discussed beforehand [261]. In fact, catalysts usually have

dielectric constants lower than 10, thus the influence of dielectric constant on

discharge behavior is negligible. Fortunately, some catalysts have relatively higher

dielectric constants such as TiO_2 and CeO_2 In fact, catalysts usually have dielectric

constants lower than 10, thus the influence of dielectric constant on discharge

behavior is negligible. Fortunately, some catalysts have relatively higher dielectric constants such as TiO_2 and CeO_2 [262], appropriate modification of such kind of catalyst may be beneficial for VOC oxidation.

Catalyst possesses rough surface, i.e. pores, sharp edge, crystal boundaries and particle boundaries. Firstly, sharp edge leads to point discharge, which usually results in electric arc. Hence, electron density could be higher near the sharp edge of the catalyst [263]. Secondly, catalyst pores provide smaller local volumes to induce electrical streamer, i.e. microdischarge [264],[265]. Microdischarge plays an important role in plasma catalysis based on two reasons: the first is that microdischarge leads to high electron density to enhance electron impact dissociation and the second is that pore diffusion is one of reaction stage of catalysis and microdischarge can influence molecular diffusivity inside pores. Since the plasma characteristics are strongly dependent on the geometry of a plasma reactor, pore structure of catalyst determines the characteristics of the plasma and microdischarge. Zhang et al. (2016) simulated a He plasma reactor packed with two dielectrics and one of the dielectrics is porous with various depth and width. Simulation results revealed that pores with large enough size (several times higher than Debye length) can actually induce microdischarge inside the pores. With appropriate pore size and discharge power, electrons can be accumulated inside the pore with high electron

temperatures (up to 6.3 eV for He plasma simulated). Also, ions can be concentrated inside the pore thanks to higher electron density and temperature inside the pore [266]. Moreover, the pore depth also influences plasma properties near the catalyst surface. Several catalysts with various pore depths are simulated and Figure 13 shows the simulation results of the dependence of electron and total ion density inside and near the pore. For those nonporous and porous catalysts with pore depths smaller than 100 μm, there is no obvious difference of electron density. However, for the catalysts having a pore depth larger than 200 μm, there is a peak value at the central of pore. The trend of electron density indicates that for catalyst with an appropriate pore depth, microdischarge can be effectively induced to enhance electron density inside the pore. On the other hand, total ion density can be effectively enhanced as long as the pore in the catalyst is larger than 20 μm, which can be attributed to the fact that not only electron density is enhanced but electron temperature is increased to promote electron impact ionization of He [266]. Accompanied by pore structure, dielectric constant of a catalyst also influences the characteristics of microdischarge. Zhang et al. (2016) conducted a similar simulation on a He plasma reactor with a pore depth of 0.194 mm and a pore diameter of 0.1 mm. In this case, dielectric constant of dielectric is varied from 25 to 1,000, to distinguish the influence of dielectric constant on discharge properties. Figure 14 shows the trend of varying dielectric constant. For the dielectric

with $\varepsilon_r = 25$, electrons with relatively high temperatures are concentrated inside the pore. Increasing dielectric constant leads to the thermal energy dissipation from pore to catalyst surface. In other words, for dielectric with $\varepsilon_r = 1,000$, high- temperature electrons are concentrated on catalyst surface near the pore, instead of being concentrated inside the pore. Generally speaking, varying the dielectric constant from 25 to 1,000 leads to the transformation of discharge behavior from inside-the-pore microdischarge to surface discharge [267].

Photocatalytic oxidation of VOCs has been investigated since 1990s because of the advantage of utilizing solar radiation [268],[269]. In addition, combination of plasma and photocatalyst has been studied recently to improve its performance. During photocatalysis, sufficient energy carried by photons can be absorbed by the valence electron to be excited to conduction band and leaves an electron hole in valence band in the meantime. The free electron in conduction band can react with VOCs easily since activation energy is reduced and the electron hole in valence band can trap an electron to maintain its electric neutrality. In addition, combining photocatalyst and plasma has also been proposed to remove VOCs in gas stream and various interactions have been discovered [270],[271]. During discharge, several kinds of species can be utilized to activate the creation of electron-hole pair to induce photocatalysis, e.g. photons, electrons and photons. Photons are effectively generated

in discharge zone and the energy can be absorbed by a photocatalyst to excite valence electron to form excitons, electron-hole pair, when photons are impinged onto the photocatalyst, if the energy of a photon is higher than the bandgap. However, there are several doubts to be resolved: the first one is that whether the amount of photons generated is sufficient to induce photocatalysis, the second one is that the potential of conduction is not necessarily negative enough to induce photocatalysis and the last one is that the quantum yield of traditional photocatalyst is insufficient [272]-[275]. Next, electrons can possess sufficient energy to activate valence electrons to form excitons. Being different from photons, incident electrons are electronic negative. Hence, the kinetic energy of electrons should be higher than the bandgap to overcome Coulomb force. Until now, the literature is lacking to elucidate the interactions between electron and photocatalyst and requires detailed investigations [276]. Moreover, photons can be generated via lattice vibration, and the energy of photons can be transferred to valence electron. Note that the energy of photon is much lower than the bandgap, as a result, the photocatalysis activation by photons must be a multistep process. Overall, the combination of photocatalyst and plasma provides a large variety of plasma-catalysis interactions, and this type of reactor demands more studies to further discover its mechanisms.

Figure 15 depicts the interactions between nonthermal plasma and catalyst.

Nonthermal plasma can modify catalyst characteristics via thermal dissipation, charge transfer and particle collision, hence catalytic performance can be improved. On the other hand, the presence of a catalyst in a nonthermal plasma influences the characteristics of the plasma simultaneously, depending on its electrochemical properties, surface structure and shape. To achieve better performance of VOC abatement via plasma catalysis, detailed reaction mechanisms and interactions between plasma and catalyst are required. Up to date, many unknowns require to be discovered for plasma catalytic systems [277].

5 Feasible developments for plasma catalysis system

It should be pointed out that byproduct formation and catalyst deactivation still limit the applicability of plasma catalysis for VOC abatement. To reduce this obstacle, selection of appropriate catalyst is essential and herein we provide some possibilities to further modify the system.

5.1 Microporous, mesoporous or macroporous?

Pore size and its distribution play an important role in both conventional catalytic process and plasma-catalytic process. From the viewpoint of catalysis, pore size can primarily influence mass transfer resistance to determine adsorption and desorption

rates. To achieve ideal catalytic oxidation, mesopores with high homogeneity is suggested. From the viewpoint of plasma-catalysis system, pore size and its distribution can further influence physical properties of the plasma, which in turn affect the plasma-catalytic chemical reactions. As discussed beforehand, microdischarge can be induced inside pores of a catalyst. The degree of microdischarge, e.g. electron density and temperature, is crucial to influence the decomposition of VOCs inside the catalyst pores. However, the induction of microdischarge is not certainly to take place. The reason is that streamers cannot be induced within the distance of Debye length. Therefore, pores smaller than a Debye sphere is unfavorable to induce microdischarge. For a typical atmospheric-pressure plasma reactor, Debye length is about 100 μm, which indicates that pores smaller than this size is unfavorable. Pores with a diameter of hundreds of micrometers can be favorable for both satisfying low mass transfer resistance and high degree of microdischarge.

5.2   Electrical properties of catalyst

Generally speaking, most of electron collisions are not effective due to low kinetic energy. In other words, lots of energy is lost during discharge in terms of thermal, optical and other forms of energy. To further improve the removal efficiency

of VOCs, effective utilization of the dissipated energy for chemical reactions is necessary. The first form and the most important part of energy is thermal energy. Catalyst can absorb heat to induce catalytic oxidation of VOCs, as introduced in Section 4.3. As a result, precise selection of an appropriate catalyst into the plasma reactor can well enhance thermal energy utilization and further improve VOC removal efficiency. The second form of energy is optical energy. During discharge, various photons can be generated via electron excitation-relaxation. Unfortunately, only a little part of photons participates in VOC degradation, i.e. UV photolysis of VOCs. Most of photons are wasted as optical energy since they are unable to participate in VOC decomposition. Photocatalyst provides an alternative way to further convert optical energy into electrochemical energy, i.e. in terms of electron-hole pair. However, the lifetime of electron-pair becomes a key factor to determine the utilization rate of optical energy. If the lifetime of electron-pair is insufficient, the electrochemical potential can be dissipated into photons, phonons or thermal fluctuation. Thus, well development and choice of photocatalyst is another issue in designing plasma photocatalysis system. Also, photocatalyst possessing good photocatalysis activity can further increase electron utilization rate since kinetic energy of electron can be absorbed by photocatalyst to induce further photocatalytic degradation of VOC.

Catalyst or photocatalyst possessing ferroelectricity can be a good candidate to enhance plasma catalysis reactor. As discussed in Section 4.3, catalyst with a high dielectric constant aids plasma performance via increasing electron temperature and electron density. Higher electron density and temperature is favorable for plasma reactor since ROS and hydroxyl radical generations can be enhanced. On the other hand, when dielectric constant exceeds a certain value, electrons tend to be concentrated on catalyst surface instead of inside the pore. From the viewpoint of reactions taking place inside the pore, this trend can be unfavorable due to lower electron temperature inside pores. Thus, dielectric constant of catalyst should be in an appropriate range, e.g. several hundreds, to further increase electron temperature and density inside the pores. In addition to ferroelectricity, ferroelectric always possess piezoelectricity and pyroelectricity. The former is the nature of piezoelectric to convert normal stress into electricity and the latter is the behavior of pyroelectric to convert thermal energy into electricity. In state-of-the-art, no literature discusses how the above properties affect plasma, and this may be an interesting topic for plasma catalysis system.

5.3   Oxidizing agent?

Oxygen plays a crucial role in VOC abatement. For catalysis, surface oxygen and

lattice oxygen play crucial roles in VOC oxidation. Whether surface oxygen or lattice oxygen is more important is dependent on the reaction route the catalytic oxidation follows. L-H mechanism requires surface oxygen to be adsorbed on surface and further oxidize VOCs while MVK mechanism needs lattice oxygen to react with adsorbed VOCs. For plasma, oxygen also plays an important role in terms of ROS and hydroxyl radical. In consequence, oxygen species inevitably play the most important role in plasma-catalytic processes. Firstly, the amount and activity of ROS and hydroxyl radical determine the oxidation rate and the degree of VOCs degradation. Secondly, insufficient oxygen species usually leads to incomplete oxidation of VOCs, i.e. byproduct formation. Existence of the catalyst in the plasma process may provide an effective way to enhance oxygen species utilization because catalyst can adsorb oxygen to produce surface oxygen or lattice oxygen. Catalyst possessing high capacity of oxygen adsorption and diffusion can be effective for the oxidation of VOCs, and hence to reduce the formation of by-products. Moreover, catalyst itself can provide ROS since catalyst is capable to dissociate O_2 into O to induce oxidation. In this manner, catalysts with strong oxygen storage capacity should be selected for plasma-catalysis system.

6 Conclusions

In this review, we discussed the state-of-the-art of catalysis and plasma performances on VOC removal, and some prospects of interactions between plasma and catalyst. In the viewpoint of catalysis, some relationship between physicochemical properties and catalytic performances are presented in Section 2. Firstly, size distribution of active phase has great impact on catalytic activity. Smaller particle is favorable due to the reduction of activation energy. However, desorption rate of product is also restricted due to the strong adsorption, as a result, appropriate particle size, e.g. few nanometers, is favorable. Secondly, surface acidity influences oxygen adsorption and storage capacity and previous studies indicate that strong acidity of catalyst results in lower VOC oxidation efficiency. Thirdly, metals with lower oxidation states usually leads to better VOC degradation performance due to better oxygen affinity. Multi-valence of metal can be a substitute, for example, gold possessing Au^{3+} and Au^{4+} simultaneously has the potential to improve catalytic activity since multiple oxidation routes are provided. Lastly, surface oxygen participates in reaction when VOC oxidation follows L-H mechanism while lattice oxygen is dominating when MVK route is followed. Catalyst has higher surface oxygen or lattice oxygen storage capacity and diffusivity is strongly required for better VOC oxidation efficiency.

In the viewpoint of plasma removal of VOC, electron density, electron temperature and gas stream composition are crucial factors for plasma. Direct electron impact dissociation of VOC is limited due to the requirement of energy, hence, generation rate of active species including ROS, hydroxyl radicals is a key factor to determine VOC degradation rate. Byproduct formation stands for the major obstacle during plasma removal of VOCs, and the formation mechanism can be divided into incomplete oxidation and cross coupling between VOC and background gas.

Being a potential solution for VOC abatement, packing catalyst into plasma reactor may induce various synergistic effects to improve VOC removal performance. During operation of plasma catalysis, features of plasma and catalyst can be altered by each other, and hence reaction mechanism, reaction rate and degradation efficiency can be modified. Plasma can affect catalyst for the particle size of metal clusters, pore size and volume, valence of metal and metal-support interactions via electron and ion bombardments. The degree of the above phenomena is strongly dependent on the discharge gas and treatment time and should be different for catalyst preparation and for plasma catalysis system. In the meantime, plasma provides various active species such as ROS, radicals and vibrationally excited species to react with catalyst, to provide other reaction routes. Thermal dissipation in plasma reactor may be utilized by catalyst, in terms of thermal activation of catalysis by plasma, and this

phenomenon can further enhance the energy utilization efficiency. Existence of catalyst can simultaneously influence plasma reactor for electron density, electron temperature and species distribution. Catalyst with a relatively high dielectric constant ($\varepsilon r \sim 10^2$) can increase electron density and temperature while discharge behavior can be shifted from microdischarge to surface discharge with a higher dielectric constant. Catalyst with photocatalytic activity can be a solution to further absorb optical energy, kinetic energy of electron and phonons to induce photocatalytic oxidation of VOCs. It should be pointed out that detailed interactions need to be elucidated to further develop an energy-saving and cost-effective technology for VOCs removal.

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