



# Recent advances in the abatement of volatile organic compounds (VOCs) and chlorinated-VOCs by non-thermal plasma technology: A review

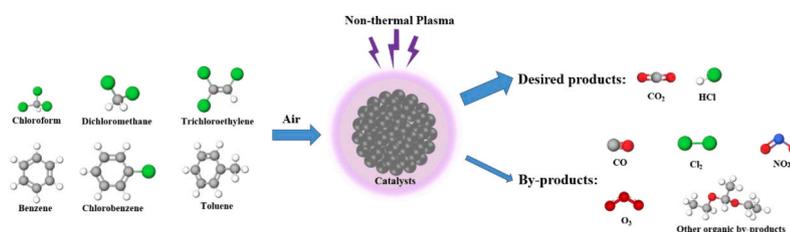
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## HIGHLIGHTS

- Catalytic degradation of Cl-VOCs under NTP condition is systematically reviewed.
- The different catalysts used in NTP for Cl-VOC control are covered.
- Formation and control strategies of hazardous by-products are reviewed.
- Techniques used for understanding the degradation mechanisms are reviewed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Most of the volatile organic compounds (VOCs) and especially the chlorinated volatile organic compounds (Cl-VOCs), are regarded as major pollutants due to their properties of volatility, diffusivity and toxicity which pose a significant threat to human health and the eco-environment. Catalytic degradation of VOCs and Cl-VOCs to harmless products is a promising approach to mitigate the issues caused by VOCs and Cl-VOCs. Non-thermal plasma (NTP) assisted catalysis is a promising technology for the efficient degradation of VOCs and Cl-VOCs with higher selectivity under relatively mild conditions compared with conventional thermal catalysis. This review summarises state-of-the-art research of the in plasma catalysis (IPC) of VOCs degradation from three major aspects including: (i) the design of catalysts, (ii) the strategies of deep catalytic degradation and by-products inhibition, and (iii) the fundamental research into mechanisms of NTP activated catalytic VOCs degradation. Particular attention is also given to Cl-VOCs due to their characteristic properties of higher stability and toxicity. The catalysts used for the degradation Cl-VOCs, chlorinated by-products formation and the degradation mechanism of Cl-VOCs are systematically reviewed in each chapter. Finally, a perspective on future challenges and opportunities in the development of NTP assisted VOCs catalytic degradation were discussed.

## 1. Introduction

Volatile organic compounds (VOCs) are those organic chemicals with boiling points between temperatures of 50 and 260 (Katsoyiannis et al., 2008). Chlorinated volatile organic compounds (Cl-VOCs), a major branch of VOCs, are widely used in industry as solvents for processes

such as metal degreasing (Tseng et al., 2010), dry cleaning (Su et al., 2013), production of pharmaceuticals (Priya and Philip, 2015) and adhesives (Kozicki and Guzik, 2021). In comparison with other VOCs categories, Cl-VOCs show a lower biodegradability, higher stability and toxicity. Table 1 lists the physicochemical properties of some common Cl-VOCs and their carcinogenicity. Most of the Cl-VOCs are recognised as major contributors (EPA, 2003; Parliament, 2008) to global air and

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**List of abbreviation**

BZ	Benzene
CB	Chlorobenzene
Cl-VOCs	Chlorinated volatile organic compounds
DBD	Dielectric barrier discharge
DCM	Dichloromethane
DRIFTS	Diffuse reflectance infrared Fourier transform spectrometer
IPC	In-plasma catalysis
MOFs	Metal organic frameworks
NTP	Non-thermal plasma
OES	Optical emission spectroscopy
PCE	Perchloroethylene
PPC	Post-plasma catalysis
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and furans
SIE	Specific input energy
SVUV-PIMS	Synchrotron vacuum ultraviolet photoionization mass spectrometry
TCE	Trichloroethylene
TOL	Toluene
VOCs	Volatile organic compounds
XYL	Xylene

water pollution as they are the precursors of ozone (Whalley et al., 2021), photochemical smog (Lin et al., 2021b) and secondary aerosols (Choi et al., 2020). The European Commission (Parliament, 2008) and the United States Environmental Protection Agency (EPA, 2003) have defined 14 Cl-VOCs as priority pollutants which are shown in Table 1. Moreover, most Cl-VOCs such as trichloroethylene, dichloromethane and chloroform are toxic and carcinogenic to human beings according to the classification by the International Agency for Research on Cancer (IARC) (Cancer, 2019). With the increasing attention to environmental protection, especially air pollution control, both the industries and research communities are facing great challenges to develop technologies to effectively remove the Cl-VOCs without generating toxic chemical pollutants and secondary pollutants.

For Cl-VOCs control, many methods have been reported such as

advanced oxidation (Vilve et al., 2010; Che et al., 2011; Che and Lee, 2011; Munoz et al., 2011; Karci et al., 2012; Li et al., 2015), adsorption (Shen et al., 2002; Lopez et al., 2004; Balamurugan and Subramanian, 2013; Apul and Karanfil, 2015; Miguet et al., 2015; Li et al., 2016; Valdés et al., 2021) and catalytic decomposition (Belkouch et al., 2009; Yang et al., 2015, 2018; Zhao et al., 2020). Although these methods are effective for Cl-VOCs control, each has its advantages and drawbacks. Advanced oxidation can eliminate the Cl-VOCs efficiently by generating powerful hydroxyl radicals, which possess strong oxidisability. However, the reaction of the advanced oxidation can only process the Cl-VOCs in the liquid phase and it is also a time-consuming process. Adsorption processes with zeolites (Lopez et al., 2004; Valdés et al., 2021), activated carbon (Miguet et al., 2015; Li et al., 2016), carbon nanotubes (Balamurugan and Subramanian, 2013; Apul and Karanfil, 2015), and polymeric adsorbents (Shen et al., 2002; Long et al., 2010) have been widely investigated for Cl-VOCs remediation. It has been confirmed that adsorption can capture the Cl-VOCs efficiently and provide the possibility to recover the Cl-VOCs. However, the major limitations of the adsorption process are the high cost of the adsorbents and the inevitable process of adsorbent regeneration (Kamal et al., 2016). Unlike adsorption that transfers the pollutants from one phase to another, catalytic decomposition can directly convert the Cl-VOCs into carbon dioxide and water. However, the chlorine substitution makes the Cl-VOCs exhibit stronger chemical stability in comparison with other VOCs, which restrains the catalytic decomposition process and produces more chlorinated by-products (Lin et al., 2021b). Moreover, these chlorinated species will deposit on the surface of the catalysts and reduce the longevity of the catalysts (Yang et al., 2013).

Non-thermal plasma (NTP) is a highly ionised gas which consists of electrons, various ions, radicals, excited species and neutral species (Chen et al., 2019a). NTP-assisted catalysis has been recently considered as an attractive alternative to conventional thermal activated catalysis due to its non-equilibrium character (Alexandrov and Hitchman, 2005), low energy cost (Zhang et al., 2017), and unique ability to initiate both physical and chemical reactions at low temperature (Chen et al., 2020; Mu et al., 2020). Therefore, NTP assisted catalysis can be an ideal method for the decomposition of Cl-VOCs as the active species can enhance the breaking of the chemical bonds of Cl-VOCs which results in higher conversion efficiency. Moreover, the interaction between NTP and the catalyst can also enhance the selectivity of the decomposition of

**Table 1**  
Physicochemical properties and carcinogenicity of Cl-VOCs.

Cl-VOCs	Formula	Boiling point °C	Vapour pressure At 25 °C (mm Hg)	Carcinogenicity <sup>a</sup> (Cancer, 2019)	Priority Pollutant (Parliament, 2008)
chloromethane	CH <sub>3</sub> Cl	-23.7	4300	N.A.	No
dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	39.6	435	Group 2A	Yes
chloroform	CHCl <sub>3</sub>	61.2	197	Group 2B	Yes
carbon tetrachloride	CCl <sub>4</sub>	76.7	115	Group 2B	Yes
chloroethane	C <sub>2</sub> H <sub>5</sub> Cl	12.3	1010 (20 °C)	N.A.	No
1,1-dichloroethane	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	57.2	227	N.A.	Yes
1,2-dichloroethane	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	84.0	78.9	Group 2B	Yes
1,1,1-trichloroethane	C <sub>2</sub> HCl <sub>3</sub>	74.0	124	Group 2A	Yes
1,1,2-trichloroethane	C <sub>2</sub> HCl <sub>3</sub>	114.0	23	Group 3	Yes
1,1,1,2-tetrachloroethane	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	130.5	12	Group 2B	No
1,1,2,2-tetrachloroethane	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	146.5	5.7	Group 2B	Yes
pentachloroethane	C <sub>2</sub> HCl <sub>5</sub>	162.0	3.5	Group 3	No
hexachloroethane	C <sub>2</sub> Cl <sub>6</sub>	186.8	53 (20 °C)	Group 2B	Yes
chloroethylene	C <sub>2</sub> H <sub>3</sub> Cl	-13.4	2980	N.A.	No
1,1-dichloroethylene	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	32.0	600	N.A.	Yes
1,2-dichloroethylene	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	55	201	N.A.	Yes
trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	87.2	69	Group 1	Yes
tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	121.1	18.5	Group 2A	Yes
chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	131.7	12.0	N.A.	Yes

Note.

<sup>a</sup>Data from the Hazardous Substances Data (HSD) Bank (2001).

<sup>b</sup>According to IARC, Group 1 represents those chemicals that are carcinogenic to humans. Group 2A is probably carcinogenic to humans and Group 2B stands for possibly carcinogenic to humans. While Group 3 is not classifiable as to its carcinogenicity to humans, and probably not carcinogenic to humans.

Cl-VOCs compared with plasma alone or thermal activated systems. Elimination of VOCs in a NTP assisted catalysis system has been reviewed from different perspectives in the literature (Xiao et al., 2014; Adelodun, 2020; Li et al., 2020b; Qu et al., 2021). However, a review paper related to the decomposition of Cl-VOCs with the NTP-assisted catalysis process is not available. The particular issues of Cl-VOCs abatement should not be ignored as more toxic chlorinated by-products, especially polychlorinated benzenes and dioxins (Weng et al., 2020; Lin et al., 2021b), are possible to be generated during the catalytic oxidation of Cl-VOCs. Therefore, in this review, we focus on the recent advances in the catalytic oxidation of both VOCs and Cl-VOCs under NTP conditions to achieve efficient abatement. Due to the importance of Cl-VOCs, we then discuss the pollutant by-products formed from NTP abatement technologies and the mechanism of Cl-VOC degradation.

## 2. Catalysts for VOCs and Cl-VOCs degradation by NTP activated catalysis

NTP is a non-equilibrium type of plasma which can be generated by applying a sufficiently strong electric field to a gas to make it discharge. In an NTP, the temperature of the electrons can reach an extremely high temperature in the range between 10,000 K and 250,000 K (1–25 eV) (Van Durme et al., 2008) while the heavier ions still remain at relatively low temperature, which makes the bulk temperature of the NTP, relatively cold. During the process of discharge, reactive species including ions and free radicals (such as OH• and O•) will be formed which are ideal for the conversion of environmental pollutants such as VOCs to CO<sub>2</sub>, H<sub>2</sub>O and other degradation products (Penetrante et al., 1997).

The plasma-alone system has been used for the decomposition of Cl-VOCs (Oda et al., 1995; Sugawara et al., 2010; Zhu et al., 2015; Song et al., 2018; Zadi et al., 2018). However, the selectivity of the plasma-alone system is unsatisfactory due to the incomplete oxidation of Cl-VOCs as they will lead to the formation of various unwanted by-products and intermediates (Vandenbroucke et al., 2011). It is generally accepted in the literature that the performance of the plasma-catalytic hybrid system can outperform the plasma-alone system as the presence of the catalysts have been shown to decrease the activation barrier (Neyts and Bogaerts, 2014; Mu et al., 2020), increase the conversion rate and improve the selectivity (Neyts and Bogaerts, 2014; Chen et al., 2019a, 2020).

In general, the plasma-catalytic hybrid system can be divided into two configurations by the position of the catalysts which are: (i) in-plasma catalysis (IPC) as shown in Fig. 1 (a) sometimes called one stage plasma catalysis and (ii) post-plasma catalysis (PPC) as shown in Fig. 1(b) which consists of two stages. The IPC system is similar to a

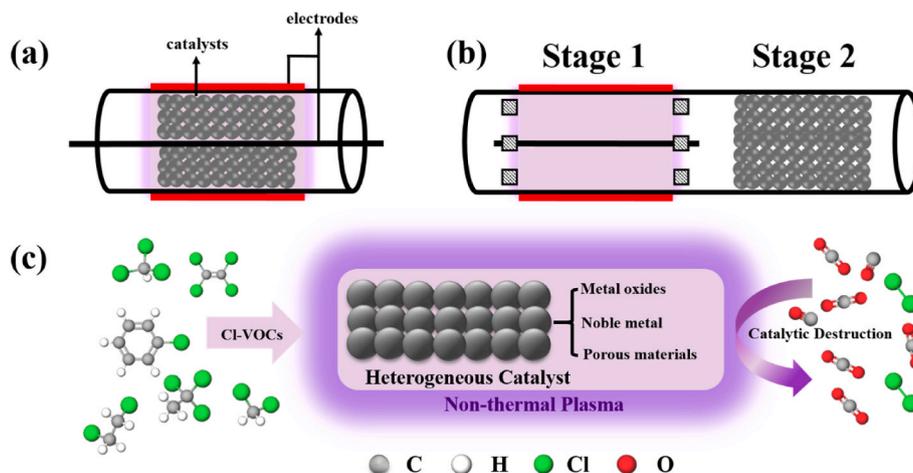
packed-bed reactor in which the catalysts are packed into the plasma discharge zone. In comparison, the PPC system comprises, the plasma reactor and a separate catalytic reactor in which the catalyst is located downstream of the NTP reactor. Both the IPC and PPC systems have been shown to enhance the removal efficiency and selectivity of the Cl-VOCs as well as inhibit the generation of unwanted by-products (Karupiah et al., 2013; Tang et al., 2013; Li et al., 2014b; Song et al., 2018). In comparison with PPC, the IPC system reportedly exhibits advantages such as lower energy consumption and easy installation (Bogaerts et al., 2020; Li et al., 2020a) and will be mainly reviewed in the following section.

Many different types of catalysts (such as supported noble metal catalysts, non-noble metal oxides, and zeolite) have been investigated for the decomposition of VOCs under NTP conditions. However, studies related to Cl-VOCs decomposition under NTP condition are limited. Chlorobenzene, the most 'dangerous' member of Cl-VOCs, attracts the highest research interests in Cl-VOCs because it is regarded as an important precursor for the formation of highly toxic dioxins (Yeh et al., 2020; Lin et al., 2021a). Consequently, a review based on the other aromatic VOCs (such as benzene, toluene, and xylene) which have similar chemical structures to chlorobenzene will aid future studies on the decomposition of chlorobenzene under NTP conditions. Herein, in this section, recent advances in relation to the catalysts used for the decomposition of Cl-VOCs and aromatic VOCs under the NTP reactor system will be reviewed in three different categories which are metal oxides, noble metal supported catalysts and porous material based catalysts as shown in Fig. 1(c).

### 2.1. Metal oxide catalysts

Metal oxides, a class of inorganic materials, have been widely used as catalysts in heterogeneous catalysis, especially in oxidation and acid-base reactions for more than 70 years (Védrine, 2017). Many metal oxides, mainly derived from elements (e.g. Al, Ti, Mn, Fe, Co, Cu) in groups II through III in the elemental periodic table, have been confirmed to be effective in NTP-assisted catalytic systems to decompose Cl-VOCs as summarised in Table 2. In addition, ceria-based oxides are also widely used in research into the decomposition of Cl-VOCs due to their great oxygen storage capacity which is shown particularly by Ceria oxides that can move between Ce(III) and Ce(IV) states (Yao and Yao, 1984; Montini et al., 2016).

Recently, mixed metal oxides have attracted much higher interest for the decomposition of Cl-VOCs assisted by NTP compared with single metal oxides. Many previous studies of VOC control under both plasma conditions and conventional thermal conditions have shown that mixed



**Fig. 1.** (a) In-plasma catalytic reactor (b) post-plasma catalytic reactor (c) schematic diagram of NTP-assisted catalysis for the decomposition of Cl-VOCs with metal oxides, noble metal supported catalysts and porous material based catalysts.

**Table 2**

Performance of VOCs decomposition by NTP over different metal oxides catalysts.

VOCs	Catalyst	Mass /volume	Concentration (ppm)	Flow rate (L min <sup>-1</sup> )	SIE (J L <sup>-1</sup> )	Removal efficiency (%)	CO <sub>x</sub> selectivity (%)	Ref	
DCM	γ-Al <sub>2</sub> O <sub>3</sub>	0.5 cm <sup>3</sup>	~500	1.00 <sup>a</sup>	54	43	–	Wallis et al. (2007c)	
	α-Al <sub>2</sub> O <sub>3</sub>	0.5 cm <sup>3</sup>	~500	1.00 <sup>a</sup>	54	34	–	Wallis et al. (2007c)	
	TiO <sub>2</sub>	0.5 cm <sup>3</sup>	~500	1.00 <sup>a</sup>	54	39	–	Wallis et al. (2007c)	
TCE	MnO <sub>2</sub>	10 g	250	0.50	240	99	60.6	Han and Oda (2007)	
	MnO <sub>2</sub>	–	1000	0.40	120	99	–	Oda et al. (2004)	
	Fe <sub>2</sub> O <sub>3</sub>	10g	250	0.50	240	99	52.5	Han and Oda (2007)	
	CuO	10g	250	0.50	240	99	48.5	Han and Oda (2007)	
	–	–	–	–	–	–	–	–	
CB	Al <sub>2</sub> O <sub>3</sub>	2 g	300	1.00	400	88	12.8	Li et al. (2021b)	
CB	MnO <sub>x</sub> /SMF	–	100	0.25	650	90	76	Karuppiyah et al. (2012)	
	AgO <sub>x</sub> /MnO <sub>x</sub> /SMF	–	100	0.25	650	95	88	Karuppiyah et al. (2012)	
	CoMn/TiO <sub>2</sub>	0.15 g	300	2.00	1080	97.1	97.2	Song et al. (2018)	
	CeMn/TiO <sub>2</sub>	0.15 g	300	2.00	1080	78	98.2	Song et al. (2018)	
	CuO/MnO <sub>2</sub>	0.3 g	163	1.00	–	76	56.9	Zhu et al. (2015)	
	CoO <sub>x</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	2 g	300	1.00	400	99.9	32.7	Li et al. (2021b)	
	FeO <sub>x</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	2 g	300	1.00	400	98.5	19.9	Li et al. (2021b)	
	MnO <sub>x</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	2 g	300	1.00	400	98	23.3	Li et al. (2021b)	
	CeO <sub>x</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	2 g	300	1.00	400	99	23.5	Li et al. (2021b)	
	CuO/γ-Al <sub>2</sub> O <sub>3</sub>	0.5 g	200	3.00	1100	85	48	Jin et al. (2021)	
	MnO <sub>x</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	0.5 g	200	3.00	1350	96.3	53	Yanghaichao et al. (2020)	
	–	–	–	–	–	–	–	–	
	–	CuO/α-Fe <sub>2</sub> O <sub>3</sub>	1.8 g	5623	16.70	9 kV	73.3	–	Xie et al. (2022)
	TCE	La <sub>0.8</sub> Ce <sub>0.2</sub> Mn <sub>0.8</sub> Ni <sub>0.2</sub> O <sub>3</sub>	–	150	0.50	16 kV	100	–	Pan et al. (2018)

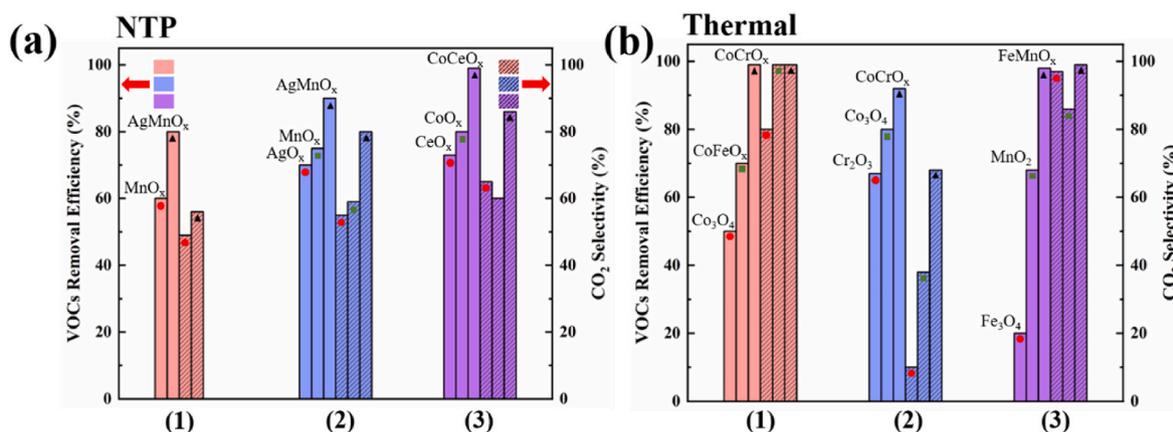
<sup>a</sup> represents the N<sub>2</sub> inlet gas into the plasma system; other inlet gas is dry air.

oxides usually exhibit higher activity and CO<sub>2</sub> selectivity compared with single oxides as shown in Fig. 2. This may be explained by the synergistic effect between two metal oxides that can increase the specific area, enhance the amount of oxygen vacancies and mobility and also provide more active sites for adsorption of surface active oxygen species (Karuppiyah et al., 2012; Bo et al., 2019; Jiang et al., 2019; Deng et al., 2020; Feng et al., 2020; Wang et al., 2020).

Li et al. (2021b) mixed different metal oxides MO<sub>x</sub> (M = Fe, Co, Mn, Ce) with γ-Al<sub>2</sub>O<sub>3</sub> for the decomposition of chlorobenzene to study the relationship between catalyst characteristics and the removal efficiency of chlorobenzene in a NTP. The results indicated that the reducibility and acidity of MnO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> determined the catalytic performance of the catalysts. Pan et al. (2018) reported three perovskite-type catalysts for the decomposition of trichloroethylene. The La<sub>0.8</sub>Ce<sub>0.2</sub>Mn<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3</sub> catalyst showed the best catalytic performance which could remove all the trichloroethylene under 16 kV plasma power. It was also observed that the formation of NO<sub>x</sub> and O<sub>3</sub> was inhibited with the existence of perovskite-type catalysts compared with the plasma alone system.

Karuppiyah et al. (2012) used metal oxides to modify sintered metal fibre (SMF) which could be directly used as an inner electrode in a dielectric barrier discharge (DBD) reactor. Different metal oxides including CoO<sub>x</sub>, MnO<sub>x</sub> and AgO<sub>x</sub> as well as CoO<sub>x</sub>/MnO<sub>x</sub> (Karuppiyah et al., 2013) and AgO<sub>x</sub>/MnO<sub>x</sub> (Karuppiyah et al., 2012) have been investigated to decompose different concentrations of chlorobenzene. The single metal oxide (MnO<sub>x</sub>) showed a reduced catalytic performance under low specific input energy (SIE) but the conversion rate could reach nearly 90% when increasing the SIE to 650 J L<sup>-1</sup>. With the deposition of AgO<sub>x</sub>, the catalyst could reach the same conversion rate (~90%) with a 20% lower SIE (520 J L<sup>-1</sup>).

As briefly mentioned before, the catalytic performance of mixed metal oxides is generally superior to single metal oxides and the following works give possible explanations from different aspects. Song et al. (2018) investigated CoMn/TiO<sub>2</sub> and CeMn/TiO<sub>2</sub> for NTP activated decomposition of chlorobenzene, in which the catalytic performance of CoMn/TiO<sub>2</sub> (with the highest removal efficiency at 97.1% and CO<sub>2</sub> selectivity at 65.5%) outperformed CeMn/TiO<sub>2</sub> due to better



**Fig. 2.** Catalytic performance of VOCs decomposition by single metal oxides and mixed metal oxides under (a) NTP and (b) thermal condition in the literature. (Experimental conditions are: (a1) VOC: CB, SIE: 390 J L<sup>-1</sup>, Flow Rate: 0.25 L min<sup>-1</sup>, Concentration: 100 ppm (Karuppiyah et al., 2012); (a2) VOC: xylene, SIE: 900 J L<sup>-1</sup>, Flow Rate: 0.3 L min<sup>-1</sup>, Concentration: 100 ppm (Jiang et al., 2019); (a3) VOC: Toluene, SIE: 400 J L<sup>-1</sup>, Flow Rate: 0.5 L min<sup>-1</sup>, Concentration: 210 ppm (Bo et al., 2019); (b1) VOC: CB, Temperature: 275 °C, Flow Rate: 0.1 L min<sup>-1</sup>, Concentration: 1000 ppm (Deng et al., 2020); (b2) VOC: DCM, Temperature: 375 °C, Flow Rate: 0.35 L min<sup>-1</sup>, Concentration: 1000 ppm (Feng et al., 2020); (b3) VOC: CB, Temperature: 280 °C, WHSV 20,000 h<sup>-1</sup>, Concentration: 600 ppm (Wang et al., 2020)).

reducibility and a much stronger enhancement of discharge of the plasma. To understand the activity difference, the dielectric constant and the physicochemical properties of the system were analysed. The dielectric constants of CoMn/TiO<sub>2</sub> and CeMn/TiO<sub>2</sub> were 10.9  $\epsilon$  and 6.1  $\epsilon$ , respectively. CoMn/TiO<sub>2</sub>, with a higher dielectric constant, could enhance the ionisation of the gas and also the electron energy (Mei et al., 2014; Wang et al., 2018). As a result, the oscillation currents of CoMn/TiO<sub>2</sub> were the most obvious in comparison with NTP-alone and CeMn/TiO<sub>2</sub> systems, which indicated a more stable discharge on the surface of the catalysts. On the other hand, more chlorobenzene would be dissociated by plasma into radical intermediates which would be beneficial to the catalytic performance. Furthermore, the H<sub>2</sub>-TPR analysis, showed that the first reduction peak of CoMn/TiO<sub>2</sub> located around 244 °C was shifted towards a lower temperature compared with CeMn/TiO<sub>2</sub> which indicated the interaction of the Co–Mn components (Mei et al., 2016). The interaction between metal oxides has a positive impact on the catalytic reaction and the work of Wang et al. (2017) on VOC decomposition elaborated on how the interaction make contributions to the reaction, using XPS results, it was reported that the mobility of oxygen in the CeO<sub>2</sub>-MnO<sub>x</sub> mixed oxides could be enhanced due to the existence of Mn<sup>2+</sup> and Mn<sup>3+</sup> in the catalysts which could bind with Ce<sup>4+</sup> to form Ce<sup>4+</sup>-O<sup>2-</sup>-Mn<sup>2+</sup> redox pairs. Furthermore, Mn<sup>2+</sup> (ionic radius, 0.091 nm) had a similar ionic radius as Ce<sup>4+</sup> (0.094 nm) facilitating isomorphous substitution of the Ce<sup>4+</sup> site and the oxygen vacancy would be formed to keep the balance of the charge. Indeed, the Ce1Mn1 catalyst with the highest Mn<sup>2+</sup>/(Mn<sup>2+</sup>+ Mn<sup>3+</sup>) ratio (29.4%) attained the best catalytic performance. The observation from Ramen spectroscopy was also consistent with the previous observation that the oxygen vacancies of Ce1Mn1 catalyst were the highest in comparison with the single oxide catalysts.

Metal oxides have been widely used in the degradation of Cl–VOCs under the NTP condition due to their strong oxidisability and high redox potential. Currently, most of the current metal oxides catalysts are designed to improve the conversion rate of the Cl–VOCs and the CO<sub>2</sub> selectivity. However, the selectivity of the HCl is ignored in most papers which is an important indicator to realise the complete degradation of Cl–VOCs. Therefore, more efforts should be taken on the design of proper catalysts to inhibit the formation of Cl<sub>2</sub> and other chlorinated organic by-products and enhance the selectivity of HCl. Furthermore, in

comparison with the single component system, the catalytic performance of the metal oxides under NTP condition with mixed VOCs systems should also be studied widely in the future which can provide useful information to the practical application.

## 2.2. Noble metal supported catalysts (Pt, Pd, Au, Ag)

Supported noble metals including Ag (Kim et al., 2005a, 2005b, 2006; Huang et al., 2015; Wang et al., 2015; Zhu et al., 2015; Dang et al., 2016; Pangilinan et al., 2016; Guo et al., 2018; Mustafa et al., 2018), Au (Magureanu et al., 2007; An et al., 2011; Zhu et al., 2020, 2021; Wu et al., 2022), Pt (Li et al., 2011, 2018; Chen et al., 2018), Ru (Fu et al., 2020) and Pd (Van Durme et al., 2009; Vandembroucke et al., 2016; Pham Huu et al., 2017; Mizushima et al., 2021) are widely used in the decomposition of VOCs due to their good catalytic activity (Abdelouhab-Reddam et al., 2015; Chen et al., 2019b) and high durability (Qin et al., 2019; Guo et al., 2021). Table 3 concluded the catalytic performance of the noble metal catalysts used for the decomposition of Cl–VOCs and aromatic VOCs.

Many different types of noble metal supported catalysts have been investigated for the decomposition of different aromatic VOCs and Cl–VOCs. Kim et al. (2006) deposited different metals (including Ag, Ni, Pt and Pd) on different supports (TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, HY and ferrierite) for the decomposition of toluene under NTP conditions. All the catalysts showed a high toluene conversion rate, in which the 0.5Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> performed the best, with CO<sub>2</sub> conversions of nearly 100% (under SIE = 210 J L<sup>-1</sup>). Ag/TiO<sub>2</sub> was also investigated by Kim et al. (2005b) in two different systems (N<sub>2</sub>-O<sub>2</sub>-benzene and Ar-O<sub>2</sub>-benzene NTP systems) to study the contribution of ultraviolet (UV) electromagnetic radiation generated by the NTP system. The emission of the excited Ar molecules ranged in the visible range, but the emissions of excited N<sub>2</sub> molecules (391.4 nm) ranged into the ultraviolet light range which theoretically could be used to activate TiO<sub>2</sub>. However, the results indicated the ultraviolet generated by the NTP was negligible to the activation of Ag/TiO<sub>2</sub>.

1Pt/0.5Sn/Al<sub>2</sub>O<sub>3</sub> was prepared by Mustafa et al. (2018) to decompose different types of Cl–VOCs and aromatic VOCs including tetrachloroethylene, toluene, trichloroethylene, and benzene. The results showed all the selected VOCs were fully decomposed under an SIE of

**Table 3**

Performance of aromatic VOCs and Cl–VOCs decomposition under NTP over different noble metal supported catalysts.

VOCs	Catalyst	Mass /volume	Concentration (ppm)	Flow rate (L min <sup>-1</sup> )	SIE (J L <sup>-1</sup> )	Removal efficiency (%)	CO <sub>x</sub> selectivity (%)	Ref
CB	1%Ag/TiO <sub>2</sub>	0.3 g	163	1	7 kV	88	51	Zhu et al. (2015)
BZ	3%Ag/TiO <sub>2</sub>	26.5 cm <sup>3</sup>	200	0.55	–	100	–	Pangilinan et al. (2016)
	1%Ag/TiO <sub>2</sub>	–	110	4	130	100	–	Kim et al. (2005b)
	1Pt/0.5Sn/Al <sub>2</sub> O <sub>3</sub>	–	100	4	987	100	–	Mustafa et al. (2018)
	0.5Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	24 cm <sup>3</sup>	200	4	210	95	–	Kim et al. (2006)
TCE	1Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	32 cm <sup>3</sup>	320	3	800	97	~78	Li et al. (2011)
	1Pt/0.5Sn/Al <sub>2</sub> O <sub>3</sub>	–	100	4	987	100	–	Mustafa et al. (2018)
	0.5%Au/GMS	34 cm <sup>3</sup>	430	0.51	670	99	95	Magureanu et al. (2007)
	0.5Pd/LaMnO <sub>3</sub>	0.5 g	560	2	460	82.3	–	Vandembroucke et al. (2016)
PCE	0.05%Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.5 g	600	2	300	80	–	Vandembroucke et al. (2010)
	1Pt/0.5Sn/Al <sub>2</sub> O <sub>3</sub>	–	100	4	987	100	–	Mustafa et al. (2018)
	1Pt/0.5Sn/Al <sub>2</sub> O <sub>3</sub>	–	100	4	987	100	–	Mustafa et al. (2018)
	13.5Ag-1.5Ce/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	–	100	1	800	100	48	Guo et al. (2018)
XYL	5%Ag/HY	0.5 g	100	0.3	700	97	98.1	Oda et al. (1995)
	13.5Ag-1.5Ce/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	–	100	1	800	95	58	Guo et al. (2018)
	1.5Au/CeO <sub>2</sub> - $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.15 cm <sup>3</sup>	100	0.2	1500	99	89	Zhu et al. (2020)
	0.1Au/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	–	300	0.3	80	100	68	Zhu et al. (2021)
TOL	1Au/CeO <sub>2</sub>	0.2 g	800	0.05	–	90	–	An et al. (2011)
	0.79Pt/CeO <sub>2</sub>	0.5 g	200	0.1	2880	~100	–	Chen et al. (2018)
	1Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2.2 g	1000	1	148	~90	48	Pham Huu et al. (2017)

987 J L<sup>-1</sup>. Zhu et al. (2020) a nano-catalyst (Au/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) that could totally decompose toluene with above 90% CO<sub>2</sub> selectivity. Furthermore, the hybrid system also showed a stable performance of both toluene conversion and CO<sub>2</sub> selectivity in a stability test (3 cycles and in total 54 h operation) because NTP conditions could activate the catalyst under mild reaction conditions which avoided irreversible Au particles aggregation. Zhu et al. (2021) studied the effect of the calcination temperature and time using Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and reported that the best catalyst calcination condition was a temperature of 300 °C for 5 h which maintained the size of Au particles at around 6 nm without sintering and with good dispersion on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and had the best catalytic decomposition performance (~100% conversion) of toluene under NTP conditions. In addition to the studies on the decomposition of single aromatic VOCs or Cl-VOCs, mixed VOCs were also investigated by Guo et al. (2018). They reported that a Ag-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst could decompose 68% benzene, 89% toluene and 94% xylene at the SIE of 800 J L<sup>-1</sup> in a ternary mixed VOCs NTP system in which the initial concentration of each VOCs was 100 ppm.

In general, the noble metal supported catalysts have excellent catalytic performance for both aromatic VOCs and Cl-VOCs under NTP conditions especially in improving the CO<sub>2</sub> selectivity and the suppression of by-products (Kim et al., 2005b; Li et al., 2011; Wu et al., 2022). However, for future studies, the following two main challenges still have to be investigated which are: (i) the cost of noble metal catalysts is expensive owing to the scarcity of noble metals, and (ii) the susceptibility of noble metal supported catalysts to poisoning by HCl, Cl<sub>2</sub> and other Cl-intermediates formed from Cl-VOC decomposition (Tidahy et al., 2006; Belkouch et al., 2009; de Rivas et al., 2011).

### 2.3. Porous material based catalysts

Zeolites may be used in different roles in the abatement of Cl-VOCs and aromatic VOCs including being used as adsorbents (Zaitan et al., 2016; Kraus et al., 2018; Li et al., 2020c), catalysts (Romero et al., 2015; Ikhlaq and Kasprzyk-Hordern, 2017; Boycheva et al., 2019) as well as the support material of catalysts (Chen et al., 2015; Liu et al., 2019; Li et al., 2021a) due to their excellent porous structure, acidic properties as well as hydrothermal stability. Table 4 shows recent porous material based catalysts used for the decomposition of Cl-VOCs and aromatic VOCs.

The hybrid zeolite-NTP system for the decomposition of aromatic VOCs was investigated by Ogata et al. (2001) who used commercial molecular sieves (-3A, -4A, -5A and -13X) to remove benzene under NTP conditions. The removal efficiency of the benzene had a two-fold improvement in comparison with the plasma reactor packed with

BaTiO<sub>3</sub>. Different zeolites (HZSM-5, NaZSM-5 and NaA) were also investigated by Wallis et al. (2007a) for the decomposition of dichloromethane. In addition to the enhancement of removal efficiency, it was also found that the participation of zeolites could inhibit the formation of NO<sub>x</sub> in comparison to the plasma alone system. Furthermore, the pore size of the zeolites also played an important role in the decomposition of VOCs. Different pore size HZSM-5 were synthesised by Xu et al. (2019) for the decomposition of toluene. The HZSM-5 with pore size being similar to the kinetic diameter of toluene showed the best toluene adsorption capacity and toluene decomposition efficiency (85% under 8 kV plasma power). In addition, it was also observed that the adsorption and catalytic performance of the HZSM-5 decreased simultaneously with the decrease of the pore size of the zeolite, and the gas diffusion resistance was considered as the major contributor to this phenomenon.

In recent studies, the research interests of using zeolites for the abatement of VOCs under NTP conditions have been mainly focused on doping noble metals/metal oxides with zeolites due to the relatively low selectivity of zeolite only systems. Yao et al. (2018b) doped MnO<sub>x</sub> with different zeolites (MCM-41, ZSM-5 and 13X) and showed that the best catalysts, MnO<sub>x</sub>/MCM-41, could remove 99.4% toluene with 73% CO<sub>2</sub> selectivity and with a 99.5% carbon balance. Notably, the catalytic performance of all the Mn-doped zeolites surpassed the zeolite only catalysts. Various zeolites were chosen by Huang et al. (2015) to study the decomposition of toluene under NTP conditions. The catalytic activity was found to take place in the following order: Ag/HY > HY > HZSM-5 > 5A, which was consistent with the ability of adsorption of the toluene. Loading 5 wt% Ag on the HY made the CO<sub>2</sub> selectivity significantly increase by 55% compared with the pure HY. Zhu et al. (2015) systematically investigated 3 different catalysts (CeO<sub>2</sub>/HZSM-5, CuO/MnO<sub>2</sub> and Ag/TiO<sub>2</sub>) under NTP conditions for the decomposition of chlorobenzene. The CeO<sub>2</sub>/HZSM-5 catalyst produced the best catalytic performance which could remove ~93% chlorobenzene under 7 kV plasma power with 60% CO<sub>x</sub> selectivity. Jiang et al. (2017) synthesised CeO<sub>2</sub>/HZSM catalysts with excellent stability for the decomposition of chlorobenzene which could operate for around 78 h without compromising the removal efficiency of chlorobenzene (~78%). Qin et al. (2021) mechanically mixed ZSM-5 with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a ratio of 1:2 to remove toluene, which significantly improved the mineralisation rate to 80%. Hossain et al. (2022) made an attempt to generate a large volume of uniform plasma at atmospheric pressure in a large-scale honeycomb catalyst. A Pd/HZSM-5 catalyst was coated on the honeycomb monolith, and the structured catalyst could remove.

85% toluene with 76% CO<sub>2</sub> selectivity at an SIE of 60 L min<sup>-1</sup> under NTP conditions. Metal organic frameworks (MOFs), are a new class of

**Table 4**

Performance of Cl-VOCs and aromatic VOCs decomposition under NTP conditions over different porous material catalysts.

VOCs	Catalyst	Mass/volume	Concentration (ppm)	Flow rate (L min <sup>-1</sup> )	SIE (J L <sup>-1</sup> )	Removal efficiency (%)	CO <sub>x</sub> selectivity (%)	Ref
CB	CeO <sub>2</sub> /HZSM-5	0.3 g	163	1	7 kV	93	60	Zhu et al. (2015)
	CeO <sub>2</sub> /HZSM-5	0.3 g	272	-	3500	72.6	36	Jiang et al. (2017)
DCM	HZSM-5	5 cm <sup>3</sup>	512	1	66	36	-	Wallis et al. (2007a)
	NaZSM-5	5 cm <sup>3</sup>	503	1	66	32	-	Wallis et al. (2007a)
	NaA	5 cm <sup>3</sup>	500	1	66	32	-	Wallis et al. (2007a)
	HZSM-5	0.9 cm <sup>3</sup>	100	0.3	700	78	39	Huang et al. (2015)
TOL	HZSM-5	0.15 g	100	100	-	85%	-	Xu et al. (2019)
	HY	0.9 cm <sup>3</sup>	100	0.3	700	82	60	Huang et al. (2015)
	5A	0.9 cm <sup>3</sup>	100	0.3	700	76	24	Huang et al. (2015)
	5%Ag/HY	0.9 cm <sup>3</sup>	100	0.3	700	98	93	Huang et al. (2015)
	Pd/HZSM-5	-	15	60	84	85	76	Hossain et al. (2022)
	Co/13X	2 cm <sup>3</sup>	150	0.4	3000	99	~48	Yi et al. (2017)
	MnO <sub>x</sub> /MCM-41	0.5g	110	1	500	99.4	73	Yao et al. (2018b)
	MnO <sub>x</sub> /ZSM-5	0.5g	110	1	500	89	64	Yao et al. (2018b)
	MnO <sub>x</sub> /13X	0.5g	110	1	500	84	63	Yao et al. (2018b)
	TiO <sub>2</sub> /ZIF-8	0.1 g	27	0.1	507	91.1	76.5	Li et al. (2022)
	BZ	MnO <sub>2</sub> -TiO <sub>2</sub>	-	400	0.5	1200	82	50

porous materials, with extra-high porosity, high gas adsorption and large surface area and have been for the abatement of aromatic VOCs (Ren et al., 2018). Li et al. (2022) developed a novel MOF catalyst TiO<sub>2</sub>/ZIF-8 which encapsulated ultra-small TiO<sub>2</sub> nanoparticles (~6.6 nm) into the framework of the ZIF-8. The toluene conversion efficiency was improved to 91.1% with 76.5% CO<sub>x</sub> selectivity. The catalysts also presented good stability, which catalytic performance maintained with no significant change in a 36 h stability test. Currently, porous material based catalysts are mainly used to degrade the VOCs like toluene and benzene, and there are few studies of using porous materials to degrade Cl-VOCs under NTP. Thus, more study of degradation of Cl-VOCs by porous materials under NTP condition should be carried out in the future. In addition, the pores of the zeolites and MOFs will also affect the molecule transport, the lifetime of active species and microdischarges under NTP condition. Therefore, the future studies also need to reveal the influence of pores to the deep degradation of VOCs and Cl-VOCs in detail.

In addition to catalytic oxidation, NTP-assisted VOCs adsorption/oxidation has been investigated as another alternative abatement process for Cl-VOCs and aromatic VOCs. NTP has been used for VOCs abatement and also coupled with adsorbent regeneration, as shown in Fig. 3. The adsorbents will firstly adsorb the VOCs then be regenerated by the NTP with the decomposition of the adsorbed VOCs. As mentioned in the introduction, one major limitation of the adsorption process is the regeneration of adsorbents. Therefore, plasma-assisted regeneration provides a possibility of using NTP technology to realise the regeneration of adsorbents and the decomposition of VOCs in the same process. Wang et al. (2015) used adsorbent/catalytic material (Ag-Mn/HZSM-5) for the decomposition of gas phase low concentration toluene (3 ppm). The addition of Ag increased the adsorption capacity of the HZSM-5 due to the formation of  $\pi$ -complexation between Ag and molecular toluene (Takahashi et al., 2000; Hernández-Maldonado and Yang, 2003). The positive synergistic effect of Ag and Mn also led towards complete toluene oxidation as well as the suppression of by-products formation. Qin et al. (2019) mixed 13X with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support at a ratio of 1:4 to adsorb and decompose toluene under NTP conditions. The results indicated that the plasma oxidation performance of 13X/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> outperformed the HY/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ZSM-5/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the decomposition of toluene with fewer by-products formed. A kinetic analysis also indicated that the mineralisation of the adsorbed toluene under NTP was well-fitted with a pseudo-second-order kinetic model. Fe/ZSM-5 catalysts were investigated by Youn et al. (2018) for toluene capture and decomposition. It was determined that ZSM-5 with low Si/Al ratios was beneficial to product selectivity, where it was reported that the CO<sub>2</sub> selectivity drop from 84.5 to 75.1 when the Si/Al ratio was increased from 11 to 140. Bahri et al. (2017) studied three different MOFs (MIL101, MIL-53 and CPM-5) in a toluene adsorption/desorption two-step system. The MIL-101 possessed the best adsorption performance and could remove 90% toluene.

### 3. Strategies of deep catalytic degradation and by-products inhibition of Cl-VOCs in NTP-catalytic system

The presence of Cl in the VOCs chemical structure increases the complexity of the final products formed from Cl-VOCs decomposition compared with other VOCs. The formation of polychlorinated by-

products may even show higher toxicity than the original Cl-VOCs. Furthermore, the NTP system will also generate two inevitable contaminants (NO<sub>x</sub> and O<sub>3</sub>) as air polluting process by-products. Therefore, the deep catalytic degradation and by-products inhibition strategies are also key points to be considered in the research of Cl-VOCs degradation. In general, the products of the degradation of Cl-VOCs include CO<sub>2</sub>, CO, HCl, Cl<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub> and organic products, particularly chlorinated organic products. In all the above-mentioned products, CO<sub>2</sub> and HCl are regarded as expected final products for the carbon and chlorine in the Cl-VOCs structure. In addition, the other products are undesirable by-products due to their toxicity or/and high oxidation capacity. Herein, the formation behaviours of CO<sub>2</sub>, HCl and inhibiting strategies of the above-mentioned by-products to realise the deep catalytic degradation will be discussed and summarised in the following section.

### 2.4. CO<sub>2</sub> selectivity

In all the case of Cl-VOCs decomposition under NTP-alone conditions, CO is a dominant by-product whereas the concentration of CO<sub>2</sub> is extremely low compared with the NTP-catalytic system (Zhu et al., 2015; Jiang et al., 2017; Song et al., 2018). It indicates the catalysts that exist in the NTP system are conducive to the conversion of CO to CO<sub>2</sub>. Therefore, the CO<sub>2</sub> selectivity of Cl-VOCs decomposition is mainly determined by the property of the catalysts and synergistic effect between catalysts and plasma.

Zhu et al. (2015) found that the CO<sub>2</sub> selectivity of a CeO<sub>2</sub>/HZSM-5 catalyst outperformed Ag/TiO<sub>2</sub>, CuO/MnO<sub>2</sub> and plasma only NTP conditions. The CeO<sub>2</sub>/HZSM-5 contributed the better performance due to the presence of more oxygen vacancies and reactive oxygen on the surface of the CeO<sub>2</sub> and the Brønsted acid sites of the HZSM-5 which both enhanced the adsorption ability of the catalysts and increased the degree of oxidation. Yao et al. (2018a) synthesised a mixed metal oxide (Co/Mn) catalyst which showed better CO<sub>2</sub> selectivity performance for VOCs degradation compared with the single Co and Mn oxides. The better redox properties of the Co-Mn oxide were believed to be the main reason for the promotion of CO<sub>2</sub> selectivity. The adsorption capacity was another important factor that can affect CO<sub>2</sub> selectivity. Ag-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was synthesised by Jiang et al. (2016), in which the CO<sub>2</sub> selectivity of benzene degradation could reach nearly 80% under SIE of 400 J L<sup>-1</sup>. It was suggested that the greater adsorption capacity of the catalyst enabled the extension of residence time which increased the collision probability between intermediates and active species.

In addition to the properties of the catalysts, the effect of other compounds on CO<sub>2</sub> selectivity has also been investigated. Zhou et al. (2021) introduced water into the NTP system for the decomposition of chlorobenzene. The results showed clearly that the humidity conditions can promote the yield of CO<sub>2</sub> under the same input energy and that the presence of OH radicals were regarded as the major contributor to the oxidation of CO to CO<sub>2</sub>. Furthermore, compounds like SO<sub>2</sub> and heavy metal (Pb) were also studied for the degradation of chlorobenzene by Sun et al. (2020). They reported that with Pb and SO<sub>2</sub> in the reaction system, CO<sub>2</sub> selectivity decreased as a result of the loss of redox property and acidity of the Mn-based catalysts used in the NTP process.

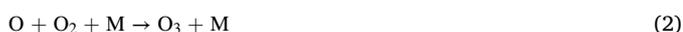


Fig. 3. Schematic of NTP-assisted VOCs adsorption/oxidation system.

## 2.5. HCl selectivity

The presence of chlorine is a problematic by-product of the NTP abatement process since the absorbed Cl<sub>2</sub> on the surface of the catalysts may also lead to the deactivation of catalysts because of the occupation of the active sites by Cl<sub>2</sub> (de Rivas et al., 2009; Xingyi et al., 2009; Kan et al., 2017). Moreover, Cl<sub>2</sub> with high oxidising property will aggravate the chlorination reaction resulting in higher generation of more chlorinated organics such as 1,1,3-Trichloro-2-methyl-1-propene (C<sub>4</sub>H<sub>5</sub>Cl<sub>3</sub>), 1,1-Dichloroacetone (C<sub>3</sub>H<sub>4</sub>Cl<sub>2</sub>O), and dichloro(nitro)methane (CHCl<sub>2</sub>NO<sub>2</sub>) (Li et al., 2021b; Lin et al., 2021b). Consequently, suppression of the formation of Cl<sub>2</sub> and promoting the selectivity of HCl is a vital challenge for the degradation of Cl-VOCs. Abedi et al. (2018) investigated the relationship between relative humidity and the selectivity of HCl in the process of chloroform decomposition under NTP conditions. The results showed that the introduction of water into the system could dramatically improve the selectivity for HCl. H radicals formed from the decomposition of water under NTP were regarded as an important role in the capture of chloride atoms from the catalyst surface. A similar finding was obtained by Zhou et al. (2021) in the process of decomposition of chlorobenzene under NTP conditions. The optimal experimental condition was 40% relative humidity which produced ~50% HCl selectivity in the final chlorinated products. However, the selectivity of HCl dropped to ~40% when the relative humidity was increased to 80%. In addition to relative humidity, the acidity of the catalysts will also affect the selectivity of HCl. Yang et al. (2017) synthesised a series of (Ce,Cr)<sub>x</sub>O<sub>2</sub>/HZSM-5 composite catalysts for the decomposition of dichloromethane. With higher (Ce,Cr)<sub>x</sub>O<sub>2</sub> loading, both the weak and strong acid sites decreased which led to the selectivity of HCl dropping from nearly 100% to 75%. Theoretical calculations and modelling were carried out by Cen et al. (2014) to understand the transformation of Cl species on ceria (111) model catalysts. The results indicated that the surface hydroxyl groups on the catalysts played an important role in promoting the selectivity of HCl, which could provide a H source to react with dissociated Cl species for HCl formation.

Ozone is an unavoidable by-product in air plasma reactors (Dang et al., 2016) and the formation of O<sub>3</sub> is through the following reactions (eq. (1) and eq. (2)).



Where M is a third collision partner such as (O<sub>2</sub> and N<sub>2</sub>).

It is generally accepted that O<sub>3</sub> concentration has a positive relationship with the SIE and more O<sub>3</sub> will be generated in NTP non-catalytic system compared with NTP-catalytic systems (Zhu et al., 2015; Dang et al., 2016; Jiang et al., 2021; Li et al., 2021b). However, this relationship will not be always maintained with the increasing SIE. In most studies, the concentration of O<sub>3</sub> has a point of inflexion to a lower concentration. This observation is normally explained in the following three views which are; (i) increasing the SIE will simultaneously increase the temperature of the plasma which results in the dissociation of O<sub>3</sub>; (ii) the competitive consumption of O atoms will be severe under high SIE due to the enhanced oxidation of Cl-VOCs and; (iii) O<sub>3</sub> will be dissociated on the surface of the catalysts and forms active oxygen species according to the following equations (from eq. (3) to eq. (5)).



Where \* is an adsorption site of catalyst.

The active atomic oxygen species are more chemically active compared with O<sub>3</sub>, which can promote the degradation of Cl-VOCs.

Therefore, an ideal catalyst should be designed to facilitate the full decomposition of O<sub>3</sub> to form active oxygen species, thereby contributing to the degradation of Cl-VOCs. In addition to the SIE, humidity is another factor that will affect the generation of O<sub>3</sub>. Zhou et al. (2021) found that increasing the humidity could inhibit the O<sub>3</sub> generation which was explained as the water-related species tending to consume atomic O leading to the reduction of O<sub>3</sub> generation.

## 2.6. Nitrogen oxides (NO<sub>x</sub>)

NO<sub>x</sub> (NO, NO<sub>2</sub> and N<sub>2</sub>O) is also an inevitable by-product of an air DBD plasma due to the reaction between oxygen radicals and excited-state nitrogen atoms (Kim and Ogata, 2011). The NO<sub>x</sub> in an air DBD plasma is mainly in the form of N<sub>2</sub>O because NO can be easily oxidised to NO<sub>2</sub> by oxidative species (such as O<sub>3</sub> and ·O) and further reacted with atomic nitrogen to N<sub>2</sub>O (Wallis et al., 2007b). The concentration of the NO<sub>x</sub> is strongly related to the input energy of the NTP and in all cases, higher input energy will enhance the formation of NO<sub>x</sub>. Jiang et al. (2021) found that a manganese-based catalyst, OMS-2, could suppress NO<sub>x</sub> formation more efficiently compared with LaMnO<sub>3</sub> due to the presence of more O<sub>ads</sub> on the OMS-2 catalyst surface which was beneficial to converting NO<sub>x</sub> to NO<sub>3</sub><sup>-</sup>. The NTP non-catalytic system was also individually investigated and the results indicated the NTP-catalytic system formed less NO<sub>x</sub> compared with the NTP non-catalytic system under the same input energy. Different results were obtained by Song et al. (2018) and Tang et al. (2017) which showed that the reactor system with packing materials generated more NO<sub>x</sub> compared with the NTP alone system. It was suggested that the packing materials could promote the electric field intensity resulting in the ionisation of N<sub>2</sub> and O<sub>2</sub> molecules to generate more NO<sub>x</sub>. The study of Cen et al. (2014) also noted that the concentration of NO<sub>x</sub> showed a monotonic increase with increasing concentration of O<sub>2</sub> and residence time.

## 2.7. Chlorinated organic by-products

At present, the research interest in the formation of the organic by-products generated from the abatement of Cl-VOCs under NTP conditions is mainly focused on chlorobenzene as it can potentially form more toxic organic by-products like dioxins. For the other Cl-VOCs, such as chloroform, dichloromethane and trichloroethylene, the generated organic by-products have been detected and defined by the GC-MS or FT-IR without further investigation of the effect of experimental parameters or quantitative identification. Herein, we summarise the by-products distribution during Cl-VOCs degradation under NTP conditions, Table S2 lists all the reported by-products formed from the decomposition of Cl-VOCs in NTP-non-catalytic systems or NTP-catalytic systems with identification nomenclature shown in Table S1. In addition, the organic by-product formation behaviours of chlorobenzene are also detailed and reviewed in the following section.

Mn-based cryptomelane-type octahedral molecular sieve (OMS-2) catalyst was used for chlorobenzene degradation under NTP processing by Jiang et al. (2021). The mutual exchange of Mn<sup>3+</sup> and Mn<sup>4+</sup> offered a constant supply of O<sub>ads</sub> according to the Mars-Van Krevelen mechanism, which was an important active species driving the surface reaction, and finally enhanced deep oxidation of chlorobenzene with less organic by-products formation. A similar observation was also confirmed by Li et al. (2021b) using MO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (M: Mn, Ce, Co, Fe) catalysts. Furthermore, by-products of C<sub>3</sub>H<sub>4</sub>Cl<sub>2</sub>O, CHCl<sub>2</sub>NO<sub>2</sub> and C<sub>4</sub>H<sub>5</sub>Cl<sub>3</sub> were detected on the surface of the catalysts. The formation of these by-products could not originate from the degradation of chlorobenzene as only one chlorine atom is found in chlorobenzene. Therefore, strategies including controlling the acidity of the catalysts can be used to accelerate the desorption of Cl species on the surface of the catalyst to reduce the formation of Cl<sub>2</sub> as well as the possibility of chlorination (Weng et al., 2018).

Humidity has a great impact on the formation of by-products

according to the study of Zhou et al. (2021). In general, fewer by-products were formed with the addition of water to the NTP system. The by-products,  $C_4H_8O_2$ ,  $C_4H_5NO_2$ ,  $C_8H_{15}ClN_2O_4$ ,  $C_{16}H_{32}O_2$  and  $C_{11}H_{24}O_4$ , could only be found under the dry air conditions. In addition, less chlorinated organic intermediates were formed in the presence of water as it could produce more OH radicals which were beneficial for the conversion of Cl atoms to HCl compared to that in the dry air system. With these observations and supported by results from GC-MS, the by-products formation pathways under dry air and also humid air were proposed. In addition, the molecular structure of VOCs will also affect the formation of by-products (Chung et al., 2019; Lei et al., 2019; Liang et al., 2022). For example, the degradation of toluene and benzene only share 14 gaseous decomposition species due to the substitution of methyl and the distribution of the shared decomposition species also has a great influence (Liang et al., 2022).

Yu et al. (2022) coupled a DBD plasma with 10 wt% Co/ $\gamma$ - $Al_2O_3$  catalyst to degrade chlorobenzene. After 10 h of discharge, 3 types of PCDD/Fs (2,3,7,8-TCDF, 1,2,3,4,6,7,8-HCDF and OCDD) were detected on the surface of the catalyst. In the thermal catalysis of Cl-VOCs, the temperature determined the formation of PCDD/Fs and PCDD/Fs and are unlikely to be formed under low temperature ( $<200$  °C) conditions (Wang et al., 2016) because the generation of active oxygen species is affected by the temperature. However, various active oxygen species can be generated at near room temperature under NTP conditions. Therefore, the PCDD/Fs formation under NTP conditions cannot only be determined by temperature based on previous experience obtained from thermal combustion/catalysis processing. Although PCDD/Fs could not be detected on the surface of the catalyst with a 3 h discharge, chlorinated phenols were detected, which are the most important structurally related precursors for the formation of PCDD/Fs (Altarawneh et al., 2009). According to the results reported from high-resolution GC-MS, the possible formation pathways of PCDD/Fs under NTP conditions were also proposed as shown in 11. Furthermore, this also proved that the formation of PCDD/Fs required the accumulation of a certain amount of precursors on the surface of the catalyst. In the study of Li et al. (2021b), various PCDD/Fs were also detected on the surface of the catalysts,  $MnO_x/Al_2O_3$  catalyst generated the most PCDD/Fs compared with Co, Ce and Fe catalysts.

#### 4. Mechanistic study of NTP-catalysis systems for VOCs and Cl-VOCs degradation

In general, the NTP catalysis system is highly complex which includes plasma discharge, ionisation of molecules, species transport/collisions, surface reaction and adsorption/desorption processes (Neyts and Bogaerts, 2014; Mehta et al., 2019). In such a complex system, the degradation mechanism of Cl-VOCs and aromatic VOCs are still not

completely understood. The main findings related to the decomposition mechanism of Cl-VOCs and aromatic VOCs under NTP conditions are summarised in the following section.

*In situ* diffuse reflectance infrared Fourier transform spectrometer (DRIFTS) as shown in Fig. 4 is an important technique used to measure the surface reactions on the microscopic scale under NTP conditions, which can facilitate an understanding of the relevant reaction mechanisms. By combing the *in-situ* DRIFTS analysis with mass spectroscopy, Wu et al. (2022) found Au/ $\gamma$ - $Al_2O_3$  catalyst could inhibit the further oxidation of benzaldehyde to benzoic acid or promote the decomposition of benzoic acid to  $CO_2$  and  $H_2O$  in comparison with  $\gamma$ - $Al_2O_3$ , which resulted in a higher selectivity. Also, the formation of bidentate carbonate on the surface of the Au/ $\gamma$ - $Al_2O_3$  catalysts was less than on the  $\gamma$ - $Al_2O_3$  which was beneficial to the longevity of the catalysts. Furthermore, Li et al. (2014a) confirmed  $O_3$  played an important role in the decomposition of toluene, in that intermediates such as benzaldehyde, benzoic acid and maleic anhydride could only be found in the presence of  $O_3$ . Different from *in-situ* DRIFTS, operando DRIFTS can collect the information from the surface of the catalyst in practical catalytic operations. By using operando DRIFTS, Rodrigues et al. (2016) identified the possible intermediate species on the catalyst surface and suggested mechanism pathways of toluene oxidation under NTP conditions.

In addition to *in situ* DRIFTS, Optical emission spectroscopy (OES) is another important technique that can be used to measure electron temperature and identify reactive species in the gas phase. Various active substances including  $\bullet NO$ ,  $\bullet NO_2$ ,  $H_2O_2$ ,  $O_3$ ,  $\bullet OH$  and  $O_2^- \bullet$  have been confirmed in an air DBD plasma system (Ma et al., 2017). To understand the contribution that these species played in the decomposition of chlorobenzene, the interactions of these active substances were explored using OES by Cheng et al. (2021). The amount of these active substances was controlled by adding radical scavengers to remove them, in addition different atmospheres ( $N_2$ ,  $O_2$  and air) were also investigated. The results showed  $O_2^- \bullet$  played the dominant role in the generation of  $\bullet OH$  (the oxidation potential = 2.8 eV) which could react with most organic compounds (Pare et al., 2008; Bilea et al., 2019). It was also found that  $\bullet NO$  and  $\bullet NO_2$  species were important to form the  $O=NOO^- \bullet$  where the oxidation capacity was close to the  $O_3$ , and 75%  $O=NOO^- \bullet$  was generated from  $\bullet NO$ .

Recently, synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) combined with molecular-beam sampling technique was successfully applied to measure active intermediates in the process of benzene decomposition under NTP conditions by Liang et al. (2021). In comparison with OES, Raman scattering and FT-IR, this technique can selectively and sensitively measure complex intermediates and reactive intermediates. Over 20 intermediates were identified by the PIMS analysis of which phenol, acetylene and acrolein were recognised as the main products of the decomposition of benzene.

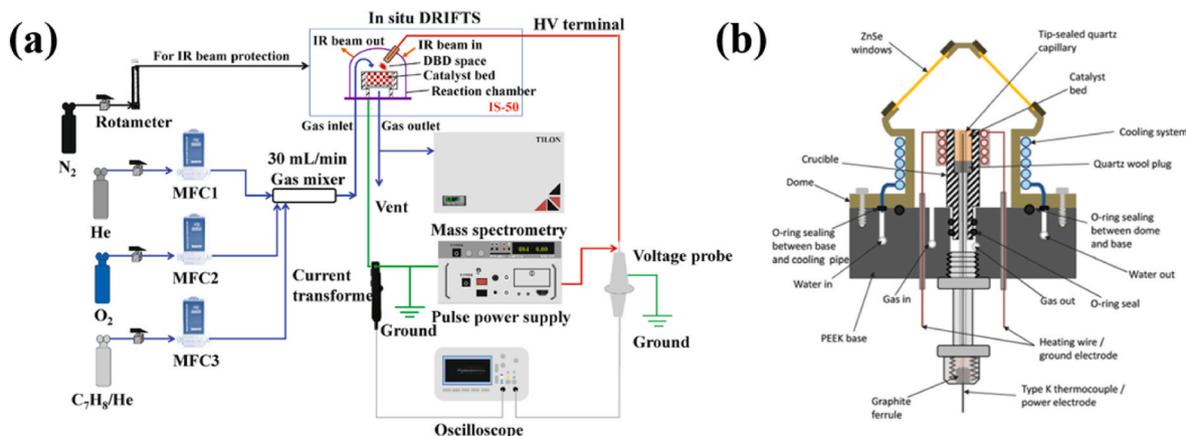


Fig. 4. (a) schematic of in situ plasma DRIFT system (Wu et al., 2022), (b) schematic of in situ plasma flow cell for a DRIFTS study (Stere et al., 2020).

Interestingly, acrolein as one of the main products in this study was usually ignored in previous studies. With the detailed information from SVUV-PIMS results and calculation of reaction enthalpy change, the key reaction pathway of the decomposition of benzene under NTP was also summarised. Based on the above-mentioned findings, Liang et al. (2022) did a further study by SVUV-PIMS combining theoretical calculations to reveal the difference between the degradation of benzene and toluene. The results showed toluene was much easier to be degraded in NTP due to the generation of abundant methyl radicals which could promote the decomposition of some intermediates. The findings indicated the substitution of a methyl group in the benzene ring not only changed the stability of molecules but also participated in the reaction pathway.

Kinetic studies are another useful tool to facilitate understanding of the interplay and mechanisms of plasma-catalyst systems, enabling an understanding of the effect of relevant variables such as discharge power, reactance concentration and catalysts on the reaction process. The pioneering work of Zhu et al. (2021) identified that O<sub>2</sub> concentration was the most sensitive parameter for the decomposition of toluene compared with discharge power and total flow rate. The kinetic study of adsorbed toluene over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> hybrid with different zeolites were carried out by Qin et al. (2019). They showed that for all the packing materials tested, the decomposition of toluene had a good match with a pseudo-second-order kinetic model, and the results also indicated that the packing materials would significantly affect the overall reaction constant (*k*).

Moreover, useful information can also be collected from modelling and simulation in addition to experimental investigations. Cheng et al. (2021) investigated the decomposition of chlorobenzene under NTP conditions using a zero-dimensional reaction kinetics model. The model suggested that the concentration of active substances O<sub>2</sub><sup>•</sup>, O<sub>3</sub> and •OH would significantly affect the removal efficiency of chlorobenzene in an air atmospheric NTP system, which was consistent with findings from the experimental study. The relationships between active substances and the chlorobenzene removal efficiency were also investigated under N<sub>2</sub> and O<sub>2</sub> atmospheres. At present, research based on the modelling and simulations of Cl-VOCs and aromatic VOCs are still limited. More research should be focused on the modelling and simulations to have a better understanding and control of the reaction pathway of the decomposition of Cl-VOCs and aromatic VOCs in the NTP reaction system in the future.

### 3. Conclusion and perspectives

This review was aimed at providing a comprehensive overview on the NTP-assisted catalytic degradation of VOCs and Cl-VOCs. Firstly, different types of catalysts including metal oxide catalysts, noble metal supported catalysts and porous materials based catalysts in relation to VOCs plasma-catalytic degradation have been summarised in this review. Metal oxides are widely used in the catalytic degradation of VOCs and Cl-VOCs under NTP condition due to the high activity and durability. In general, the binary mixed metal oxides have better catalytic performance in comparison with monometallic oxides. Noble metal supported catalysts can efficiently improve the degradation performance of VOCs and Cl-VOCs especially the enhancement of the CO<sub>2</sub> selectivity and the suppression of by-products. Previous studies have shown that the metal particle size and dispersion dominate the performance of noble metal supported catalysts. However, the noble metal supported catalysts still attract less interest compared with the metal oxides catalysts because their high price and easy deactivation with the presence of -S and -Cl make them become difficult to be used in industrial practical applications. The current study of porous material based catalysts for the VOCs degradation under NTP conditions are mainly focused on zeolite due to their excellent porous structure, acidic properties as well as hydrothermal stability. The pore size of the zeolites plays an important role in VOCs and Cl-VOCs degradation as it affects gas diffusion resistance and the adsorption performance of the

zeolites. However, the zeolite catalysts have poor CO<sub>2</sub> selectivity, thus zeolites are normally doped with noble metals and metal oxides to achieve a better catalytic performance.

Moreover, the by-product formation and inhibition strategies are also summarised and discussed. Compared with conventional thermal activation catalytic oxidation, degradation of VOCs under NTP conditions will generate two unique by-products which are O<sub>3</sub> and NO<sub>x</sub>. Moreover, due to the substitution of Cl, the specific by-products related to Cl-VOCs were also summarised. In general, catalysts with better redox properties and high adsorption capacity can inhibit the formation of CO and convert the VOCs into CO<sub>2</sub>. The formation of O<sub>3</sub> and NO<sub>x</sub> are strongly related to the SIE. The presence of water can improve the selectivity of HCl, promote the CO<sub>2</sub> selectivity and also inhibit the formation of O<sub>3</sub>. To reduce the formation of other chlorinated organic by-products, the acidity of catalysts can also be adjusted to accelerate desorption of Cl species on the surface of the catalyst.

Finally, a mechanistic study of the NTP-assisted catalytic degradation of VOCs and Cl-VOCs was summarised based on studies of *in-situ* analysis, catalytic oxidation kinetics and theoretical simulation and calculation. *In-situ* DRIFT is used to define the intermediate species and the possible reaction pathways are suggested based on the defined intermediates. OES is used to understand the contribution of various radicals in the system. Kinetic studies are carried out to understand the effect of relevant variables such as discharge power, reactance concentration and catalysts on the reaction process. Although plentiful efforts have been made to develop and understand the degradation of VOCs and Cl-VOCs under NTP conditions, there still exist many challenges for the efficient elimination of VOCs under NTP conditions;

- (i) Currently, the study of VOCs, including Cl-VOCs degradation under NTP conditions are mainly focused on single components. However, in real applications, VOCs are always mixed with other industrial emissions. Therefore, it is necessary for oxidation of mixed VOCs to be taken into consideration in future studies to have a better understating of the interaction among simultaneous oxidation of VOCs mixtures.
- (ii) Compared with thermal catalysis, the NTP catalytic system is much more complex, as heterogeneous catalysis proceeds not only with the chemisorption of reactants on the catalyst surface but also plasma-induced reactive species in the gas phase. *In-situ* techniques such as OES, FT-IR/DRIFT, GC-MS, SVUV-PIMS as well as advanced modelling methods have been used to understand the plasma-catalyst interactions. However, most of these technologies have their own limitations in that DRIFT cannot accurately quantitate the concentrations of functional groups, OES cannot detect complex heavy species selectively and sensitively and GC-MS can hardly identify the structures of complex species clearly (Du et al., 2017; Rostami et al., 2019; Saleem et al., 2019; Liang et al., 2022). Currently, most mechanism discussions in the published literature are based on one of the single techniques. Therefore, the above-mentioned techniques and methods should be combined to have a comprehensive and in-depth understanding of catalytic mechanism of VOCs degradation under NTP conditions which can aid the understanding of the degradation pathways, the reason for catalyst poisoning and to reduce formation of undesirable by-products.
- (iii) The trade-off between energy efficiency and VOCs and Cl-VOCs degradation still needs further investigation. It is important to develop the design of the reactors and optimise operating conditions to achieve a high energy efficiency. Currently, many efforts have been made on the improvement of the energy efficiency in VOCs degradation under NTP condition (Santos et al., 2020; Chang et al., 2022; Wu et al., 2022), but the comparison of energy efficiencies between the NTP system and other systems (e.g. thermal activated degradation and photocatalytic degradation) is still insufficient. Furthermore, structured

catalysts can also be investigated in the future for the practical industrial reactors since most of the catalysts used for study currently are in the form of loosely packed particle beds.

## Author statement

**Yibing Mu:** Investigation, Writing-original draft preparation. **Paul T. Williams:** Supervision, Writing - Reviewing and Editing, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

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