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Efficient degradation of multiple Cl-VOCs by catalytic ozonation over MnO_x catalysts with different supports



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ABSTRACT

This paper investigated catalytic ozonation of different Cl-VOCs (chlorobenzene (CB), dichloroethane (DCE), dichloromethane (DCM) and trichloroethylene (TCE)) over series of supported MnO_x catalysts. These Cl-VOCs with different molecule structures exhibited obviously difference in catalytic performances and byproducts formation. Interestingly, the correlation between catalytic behaviors and surface properties of catalysts was inconsistent for different Cl-VOCs. In comparison, Mn/HZSM-5(27) presented a better conversion and mineralization rate (MAR) for most of Cl-VOCs due to its abundant surface acidity and excellent pore structures. Catalytic co-ozonation of mixed Cl-VOCs over Mn/HZSM-5(27) showed co-existence of inhibitive and promotive effects. For instance, CB conversion occupied priority compared with DCE and TCE, and MAR was enhanced in the mixture. Thereafter, the temperature programmed desorption results of mixed Cl-VOCs degradation were the determining factors in catalytic co-ozonation of Cl-VOCs. Besides, catalytic co-ozonation of Cl-VOCs with presence of H₂O exhibited negligible impact. These observations provide valuable reference for industrial application with co-presence of multiple Cl-VOCs and water vapor.

1. Introduction

Among various types of volatile organic compounds (VOCs), chlorinated VOCs (Cl-VOCs) have attracted widely attention around the world due to its highly environmental toxicity and persistent damage [1,2]. Dichloromethane (DCM), 1,2-dichloroethane (DCE), vinyl chloride (VC), trichloroethylene (TCE), and chlorobenzene (CB) etc. are typical Cl-VOCs that generally emit from solid waste treatment, pharmaceutical and chemical industry [3,4]. Emission of Cl-VOCs into atmosphere will generate ozone, photochemical smog, and second organic aerosol generation under atmospheric photochemistry [3,5]. Besides, Cl substitution in Cl-VOCs contributes to its complicated transformation process and highly toxic risks in second pollutants, such as polychlorinated compounds and dioxins [6,7]. Therefore, exploitation of Cl-VOCs treatment technologies should consider these special issues relating to Cl migration pathway. Catalytic oxidation of Cl-VOCs exhibits particular superiority due to its high efficiency and stability at the acceptable temperature range, ca. 200 \sim 500 °C [3,8]. Nevertheless,

several bottleneck problems also restrict its industrial application, especially including relatively high temperature for desirable efficiency due to degradation difficulty, catalyst deactivation originating from Cl deposition, and complicated Cl-containing byproducts formation [5,9-12]. In other words, high temperature, undesirable conversion, worse stability, and incomplete degradation are common problems for catalytic oxidation of Cl-VOCs. Nowadays, catalytic ozonation might be potential to be an alternative approach for elimination of Cl-VOCs, which resorts the superiority of O₃ in accelerating conversion rate and decreasing apparent activation energy [13,14]. Especially, O₃ molecules can be decomposed into more strongly oxidizing radicals and active oxygen species on catalyst surface to promote further degradation of intermediates and organic byproducts. Lin et al reported that catalytic ozonation over simple MnO_x supported catalysts could achieve CB conversion of > 90% at ~ 120 °C with no deactivation during long-term stability tests [15,16]. Accordingly, catalytic ozonation possesses obvious advantages in Cl-VOCs treatment and enormous potentiality in practical application.

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MnO_x based catalysts attracted high level of concern in catalytic oxidation of Cl-VOCs due to its low price, variable valance states, polycrystalline phase, excellent redox properties, and certain resistance to Cl poisoning [8,17-19]. Weng et al. achieved exceed 95% CB conversion over γ -MnO₂ with high stability, while α -MnO₂ and δ -MnO₂ exhibited obviously deactivation [20]. MnOx loading on supports of CeO₂, TiO₂, ZrO₂, Al₂O₃, and HZSM-5, could enlarge the specific surface area and promote metal dispersion, thus enhancing the adsorption capacity and catalytic properties [15,21,22]. Especially, several solid acid support materials, such as HZSM-5, USY, and Al₂O₃, were frequently selected in view of their favourable pore structure and abundant surficial acidity [1,23,24]. Previous literatures have summarized that catalytic oxidation of Cl-VOCs is mainly correlated with the surface acidity, redox ability, and oxygen species of catalysts [5,25]. Among them, surface acidity including Lewis and Brønsted acidity are strongly associated with catalytic performances. For instance, Lewis acidity could accelerate the destruction of C-C and C-Cl bonds, while adsorption of Cl-VOC molecules, oxidation of intermediates, and Cl species desorption are mainly correlated with Brønsted acidity [25–28].

Our previous investigations have verified the superiority of catalytic ozonation for single Cl-VOCs, including DCE and CB elimination, CB and NO simultaneous removal, and CB degradation under complicated components (H₂O, SO₂, and NO) [15,26,29]. However, the correlations between catalytic ozonation and catalyst properties still exist unclear points. Ozone decomposition and Cl-VOCs oxidation occur simultaneously on catalyst surface. Besides, multiple Cl-VOCs, such as CB, DCM, DCE, and TCE, are co-existed in the practical flue gas and waste gas components [3,5]. Various Cl-VOCs possess different properties in structure, molecular polarity, and physicochemical property, which might cause great difference in catalytic performances and interactions. So far, catalytic co-ozonation of various Cl-VOCs simultaneously has

acquired seldom research. Based on above issues, this paper focused on the basic investigations on catalytic ozonation of DCM, DCE, TCE, and CB over series of supported MnO_x catalysts (Mn/SiO_2 , Mn/HZSM-5(27), Mn/HZSM-5(200), Mn/USY(11), and Mn/Al_2O_3)). The correlations between catalytic performances and catalysts properties were constructed. Next, catalytic co-ozonation and adsorption properties of mixed Cl-VOCs were also conducted to obtain the interaction effect. Finally, H_2O was introduced into catalytic co-ozonation of mixed Cl-VOCs for practical applications.

2. Experimental section

2.1. Catalyst preparation

The supported MnO_x catalysts were synthesized by simple impregnation method [15]. Al_2O_3 (γ -phase), SiO_2 , HZSM-5 ($SiO_2/Al_2O_3 = 27$ and 200), and USY ($SiO_2/Al_2O_3 = 11$) were selected as the support materials. Typically, 1 g support material was immersed into a 15 mL ethanol solution with 0.2228 g of $Mn(CH_3COO)_2 \cdot 4H_2O$ and stirring for 30 min at room temperature. The mixture was gradually heated to 70 °C in the water-bath until obtaining pasty solid, which was then dried at 90 °C overnight. Finally, the solid was calcined at 400 °C for 2 h in static air atmosphere and marked as Mn/Al_2O_3 , Mn/HZSM-5(27), Mn/HZSM-5(20), Mn/USY(11), and Mn/SiO_2 , respectively.

2.2. Catalyst characterization

The chemical/physical properties of catalysts were measured by X–ray diffraction (XRD), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), NH₃ temperature-programed desorption (NH₃-TPD), and pyridine adsorbed IR spectroscopy (Py-IR). The detailed



Fig. 1. Catalytic ozonation of various Cl-VOCs over supported MnO_x catalysts (conversion efficiency). (a) DCM, (b) DCE, (c) TCE and (d) CB. Temperature: 120 °C, catalyst dosage: 50 mg.



Fig. 2. Catalytic ozonation of various Cl-VOCs over supported MnO_x catalysts (MAR based on CO₂). (a) DCM, (b) DCE, (c) TCE, and (d) CB. Temperature: 120 °C, catalyst dosage: 50 mg.

procedure has been described in our reported work [26]. The temperature programmed desorption tests of mixed Cl-VOCs (Cl-VOCs-TPD) over Mn/HZSM-5(27) were conducted on the catalytic ozonation system described below. Initially, ~1.0 g of catalyst was loaded into the tube, and then purged under pure N₂ with a flow rate of 100 mL·min⁻¹ for 1 h at room temperature. Thereafter, two types of Cl-VOCs with equal concentration of 50 ppm were injected into the reactor for 1 h. After adsorption saturation, the Cl-VOCs were stopped and the catalyst was purged with N₂ for 30 min. Ultimately, the tube furnace was heated to 800 °C with a heating rate of 5 °C·min⁻¹, and the desorbed Cl-VOCs were monitored online by gas chromatograph (GC) [30].

2.3. Activity measurements

The catalytic ozonation system contained several mass flow controllers (MFCs, Sevenstar Electronics Co., Ltd., Beijing), an ozone generator, a quartz tube reactor (QTR, i.d. 8.0 mm), an inlet ozone concentration analyzer (BMT-964BT, OSTI, Inc., $0 \sim 100 \pm 0.1 \text{ g} \cdot \text{Nm}^{-3}$), an online GC (GC9790II, Zhejiang Fuli Co., Ltd), and an outlet ozone concentration analyzer (HGA600-O₃) [15,26]. CB was injected into the catalytic system by bubbling the liquid CB at $-5 \pm 3 \,^{\circ}$ C with N₂ as the carrier gas. DCM, DCE, and TCE were all supplied from the standard gas cylinder (500 ppm with N₂ balance). The pipeline was wrapped with heat tapes and maintained at 120 °C, which could avoid condensation of these Cl-VOCs and byproducts. The total gas flow rate was maintained at 100 mL·min⁻¹ and the O₂ concentration was 10 vol% with N₂ balance. For all the measurements, the catalyst loading amount was kept at 50 mg with the corresponding gas hourly space velocity (GHSV) of 24, 000 h⁻¹.

concentration was divided equally during co-ozonation of two types of Cl-VOCs. Meanwhile, O₂ flowed into the ozone generator firstly to generate O_3 with varied concentration ranging in 50 \sim 1500 ppm. Generally, the reaction temperature was fixed at 120 °C expect for the investigation of its effect. The effluent gas was directly injected into GC to monitor the outlet concentration of Cl-VOCs and CO/CO2 in two flame ionization detectors (FID). One of the FID detectors was connected to a Nickel conversion furnace, which could convert the CO/CO2 into combustible gas CH₄, and then realized the quantitative measurement. The separation column could control the entering order of CO and CO_{2} , thus acquiring different peaks in FID. The Cl-VOCs conversion and mineralization rate (MAR) were calculated by the Eqs. $(1) \sim (2)$. The activity results have been repeated for more than twice and the average values were presented. The effluent gas from catalytic ozonation of Cl-VOCs over Mn/HZSM-5(27) was collected by an adsorption tube (Tenax TA) for 20 min when the conversion efficiency maintained at 70 \sim 80%. Afterwards, the adsorbed byproducts could be detected by a thermal desorber equipped with a Gas Chromatography-Mass Spectrometer (GC-MS) [31,32].

Cl-VOCs conv. = ([Cl-VOCs]_{ini.} – [Cl-VOCs]_{out.}) / [Cl-VOCs]_{ini.}
$$\times$$
 100%(1)

$$MAR = [CO_2]_{out.} / ([Cl-VOC_s]_{ini.} \times n) \times 100\%$$
(2)

where $[Cl-VOCs]_{ini.}$ and $[Cl-VOCs]_{out.}$ are the initial and outlet concentration of Cl-VOCs (DCM, DCE, TCE, and CB, ppm), respectively; $[CO_2]_{out.}$ is the CO₂ outlet concentration (ppm); n represents the carbon number in the Cl-VOC molecules.

3. Results and discussions

3.1. Catalytic ozonation of different Cl-VOCs over supported MnO_x catalyst

Catalytic ozonation of DCM, DCE, TCE, and CB over series of MnOx supported catalysts, including Mn/Al₂O₃, Mn/HZSM-5(27), Mn/HZSM-5(200), Mn/USY(11), and Mn/SiO2, were conducted respectively and the conversion curves as a function of O3/Cl-VOCs are presented in Fig. 1. For comparison, the pristine support of optimal catalyst for each type of Cl-VOCs was also evaluated. Apparently, Cl-VOCs conversion strongly depended on O3/Cl-VOCs, but the correlations between different types of Cl-VOCs were also significantly variable. Interestingly, DCM possesses the simplest molecules but exhibited the highest difficulty as the lower conversion efficiency over same catalyst compared with other three Cl-VOCs, which should ascribe to its C-H bonds with much higher binding energy than C-C and C-Cl bonds [25,33,34]. As presented in Fig. 1(a), Mn/Al₂O₃ demonstrates excellent DCM conversion, attaining \sim 90% DCM conversion at a low molar ratio of O₃/DCM (O_{90}) , ca. 7.6. However, the other catalysts could not achieve 90% conversion despite enlarging O_3/DCM to 12.5. The pristine Al_2O_3 exhibited much lower DCM conversion but also reached 40% conversion finally, indicating Al₂O₃ with large surface area could also work as a catalyst but Mn loading played more critical role in catalytic ozonation of DCM. The DCM conversion over other catalysts decreased as the following order: Mn/HZSM-5(27) > Mn/HZSM-5(200) > Mn/SiO₂ > Mn/USY. Next, DCE possesses one more C-C bond with lower energy than DCM, thus trending to be easily oxidized by O3 compared with DCM [15,25]. As shown in Fig. 1(b), Mn/Al₂O₃, Mn/HZSM-5(27), and Mn/HZSM-5(200) achieve over 90% DCE conversion finally. Among them, Mn/HZSM-5(27) possessed the highest DCE conversion for with the lowest O_{90} , ca. 5.5. When the molar ratio of O_3 /DCE exceeded 8.0, Mn/Al₂O₃ performed a similar DCE conversion with Mn/HZSM-5(27). The two catalysts both achieved near 100% DCE conversion when O₃/ DCE reached 12.0. Interestingly, pristine HZSM-5(27) could also exhibit considerable DCE conversion, which was even better than Mn/USY as O₃/DCE exceeding 8.0. Diversely, TCE molecular consists of three C-Cl bonds and one C = C bond, which is quite different from DCE and DCM. C-Cl bond is easier broken than C-C, C = C, and C-H bond [25]. In comparison, TCE only possesses one C = C bond and C-H bond, which are much less than DCM and DCE, contributing to the much better TCE conversion than others with very low O_3 input (Fig. 1(c)). TCE conversion stabilized at 97%~100% over Mn/Al₂O₃ and Mn/USY catalyst with the wide range of O3/TCE from 2 to 13. Mn/HZSM-5(27) and Mn/ HZSM-5(200) displayed similar catalytic performances for TCE ozonation, while Mn/SiO2 was relatively inert compared with others. However, all these catalysts achieved 100% TCE conversion finally. Notably, pristine USY also exhibited excellent TCE conversion, which just ranked behind Mn/Al₂O₃ and Mn/USY. This demonstrated that TCE was so easy to be oxidized by ozone that Mn played relatively weak function in catalytic ozonation, which further implied the superiority of USY in catalytic ozonation of TCE. CB molecular contains an p-π conjugate of aromatic ring that increases the complexity of degradation process. Nevertheless, CB conversion still achieved over 90% with the increase of O3 injection over all these catalysts. As presented in Fig. 1(d), Mn/ HZSM-5(200) shows the optimal catalytic performance for CB ozonation. Its corresponding O₅₀ and O₉₀ value of CB ozonation reached to 2.8 and 7.7, respectively, which were relative lower than other catalysts. Conversely, Mn/HZSM-5(27) exhibited poorer performance than Mn/ HZSM-5(200) for CB conversion, which was different from other three types of Cl-VOCs. Interestingly, pristine HZSM-5(200) was superior to the rest of all supported MnOx catalysts for CB conversion, verifying its superiority in degradation of aromatic ring compounds.

The corresponding MAR values of these Cl-VOCs over various of catalysts are illustrated in Fig. 2. The MAR values increased continuously but with varied degrees along with the molar ratio of O_3 /Cl-VOC

for all conditions. Besides, the catalysts with the highest conversion might not exhibit same excellent MAR values. For instance, although Mn/Al₂O₃ possessed the best performance for DCM conversion, its MAR value was far lower than the other catalysts, which could not achieve 50% MAR at the highest O₃/DCM. Especially, pristine Al₂O₃ only attained $\sim 20\%$ MAR within the whole range of O₃/DCM. Mn/HZSM-5 (27) attained the more complete degradation of DCM as its high MAR values. Similarly, Mn/HZSM-5(27) also presented higher MAR in DCE ozonation, which echoed its excellent DCE conversion (Fig. 1(b) and Fig. 2(b)). Meanwhile, only Mn/HZSM-5(27) and Mn/HZSM-5(200) achieved over 80% MAR at high molar ratio of O3/DCE among all these catalysts. The pristine HZSM-5(27) also candidly admitted defeat. The molar ratio of O3/DCE reaching 50% MAR (M50) decreased as the following order: Mn/USY (7.2) > Mn/Al₂O₃ (5.1) > Mn/SiO₂ (5.0) > Mn/HZSM-5(200) (3.7) > Mn/HZSM-5(27) (3.3). Interestingly, the MAR of TCE maintained relatively low values within the whole range of O₃/TCE over all these catalysts and could not obviously elevate with increasing of O_3 input, which was similar to DCM. As shown in Fig. 2(c), Mn/USY possessed the poorest MAR among these supported catalysts, which was totally different with its performance in TCE conversion. The pristine USY also exhibited very poor performance in MAR. Other catalysts presented different order in MAR with that in TCE conversion. In comparison, CB exhibited the most linear curves than other Cl-VOCs and finally attained the highest MAR values (Fig. 2(d)). All these catalysts including pristine HZSM-5(200) obtained over 80% MAR finally during CB conversion.

Fig. S1 presents the catalytic ozonation of various Cl-VOCs with the variation of temperature. Clearly, the conversion of Cl-VOCs exhibited slightly decline when temperature elevated from 120 to 150 °C, and the MAR values were also in agreement with conversion expect for DCM exhibiting slight increase. Our previous literatures also reported similar results [15,36]. Higher temperature accelerates catalytic ozonation rate, but it also promotes ozone decomposition. Therefore, large amounts of ozone were diminished without participating in catalytic ozonation process. Fig. S2 presents the CO₂ selectivity during catalytic ozonation. Herein, CO2 selectivity was calculated based on the total formation of CO and CO₂, while MAR was calculated based on CO₂ formation divided by total C atom concentration in original Cl-VOC molecules. Most conditions maintained CO2 selectivity between 60%~70%, while DCE exhibited increasing tendency in CO2 selectivity with elevation of temperature. Future work should devote to develop novel catalysts with specific structure to provide new CO oxidation sites and prolonged reaction time, such as hollow and core-shell structures. The carbon balance was satisfied that could reach 95 \sim 100% for all conditions expect for TCE. TCE exhibited relatively lower carbon balance, ca. $80 \sim 100\%$, especially at low ratio of O3/TCE, corresponding to its lower MAR values. Nevertheless, the carbon balance at high ratio of O₃/Cl-VOCs could reach almost 100% over optimal catalysts for all these Cl-VOC molecules. These results demonstrated complete degradation with less byproducts formation.

In summary, there are several points should be mentioned: (I) DCM exhibited the most distinct difference over these supported catalysts and Mn loading played critical role in catalytic ozonation for chlorinated alkanes (DCM and DCE); (II) TCE could be oxidized at very low molar ratio of O_3 /TCE, which attained almost 80% conversion at O_3 /TCE of ~ 2.0. DCE followed the order, but DCM and CB were relatively hard to be oxidized; (III) The conversion of these Cl-VOCs over different catalysts decreased as the order: Mn/Al₂O₃ > Mn/HZSM-5(27) > Mn/HZSM-5 $(200) > Mn/SiO_2 > Mn/USY(11) > Al_2O_3$ (DCM), Mn/HZSM-5(27) > SiO₂ (DCE), Mn/USY(11) \sim Mn/Al₂O₃ > USY(11) > Mn/HZSM-5(200) > Mn/HZSM-5(27) > Mn/SiO₂ (TCE), Mn/HZSM-5(200) > HZSM-5 $(200) > Mn/USY(11) > Mn/HZSM-5(27) > Mn/SiO_2 > Mn/Al_2O_3$ (CB); (IV) High conversion efficiency did not mean high MAR value. DCM and TCE attained relatively low MAR than DCE and CB. In comparison, Mn loading played more critical role in mineralization than conversion. Mn/



Fig. 3. (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of synthesized fresh catalysts.

 Table 1

 Textual properties of synthesized catalysts.

Samples	BET surface area/ $m^2 \cdot g^{-1}$	Pore volume ^a / cm ³ ·g ⁻¹	Avg. pore diameter ^b / nm
Mn/Al ₂ O ₃	281.12	0.51	6.67
Mn/HZSM-5 (27)	394.02	0.08	2.06
Mn/HZSM-5 (200)	394.23	0.13	2.49
Mn/USY(11)	703.29	0.25	2.64
Mn/SiO ₂	328.73	1.50	18.09

^a BJH desorption cumulative pore volume.

^b BJH desorption average pore diameter.

HZSM-5(27) attained the highest MAR for DCM and DCE and also exhibited desirable performance for TCE and CB.

3.2. Crystal structures, textural properties, surface elements, and acidity

The XRD patterns of these synthesized catalysts and their corresponding supports, including Al_2O_3 , HZSM-5(27), HZSM-5(200), USY, and SiO₂, are presented in Fig. S3. The catalysts after Mn loading exhibited no obvious variation in crystal structures compared with

pristine supporting materials, implying excellent dispersion of MnO_x on the surface. In comparison, the intensity of diffraction peaks slightly declined due to the covering of MnO_x , indicating weakening of crystallinity.

The N2 adsorption/desorption isotherms and BJH pore size distribution (PSD) of these supported MnO_x catalysts are presented in Fig. 3. Table 1 tabulates the textual properties of these synthesized catalysts. All these catalysts presented a sharp climb at relative pressure P/P_0 < 0.1 in the isotherms of adsorption/desorption (Fig. 3(a)), verifying the existence of micropore structure, which was critical for adsorption of Cl-VOC molecules [29,37]. The overlap of adsorption/desorption isotherms for Mn/HZSM-5(27) and Mn/HZSM-5(200) at $P/P_0 < 0.8$ originated from the multilayer adsorption, indicating nonporous or macroporous structures [37,38]. Accordingly, Mn/HZSM-5(27) and Mn/HZSM-5(200) exhibited the narrow PSD within $0 \sim 5$ nm (Fig. 3) (b)). In comparison, Mn/HZSM-5(200) possessed a slightly stronger peak within 3 \sim 5 nm, contributing to its higher pore volume and average pore diameter than Mn/HZSM-5(27), ca. 0.13 > 0.08 cm³·g⁻¹ and 2.49 > 2.06 nm. The adsorption/desorption isotherms of Mn/Al₂O₃ and Mn/USY(11) should belong to type IV with an obvious H2 type hysteresis loop, indicating existence of mesoporous structure. The distinct peak of PSD for Mn/Al₂O₃ and Mn/USY(11) in Fig. 3(b) also verified this point. Mn/USY(11) possessed prominent specific surface



Fig. 4. XPS spectra of the synthesized MnO_x supported catalysts.

Table 2

Distribution of Mn ions, O species and surficial acid amount of synthesis catalysts.

Samples	XPS						Py-IR (μ mol \cdot g _{cat} ⁻¹)		
	Mn ³⁺ (%)	Mn ⁴⁺ (%)	O _L (%)	O _C (%)	O _{OH} (%)	B acid	L acid	B/L acid	
Mn/Al ₂ O ₃	54.77	45.23	8.12	91.88	/	4.19	123.84	0.03	
Mn/HZSM-5(27)	73.62	26.38	36.78	63.22	/	337.56	231.50	1.46	
Mn/HZSM-5(200)	67.82	32.18	14.05	85.95	/	12.65	133.42	0.09	
Mn/USY(11)	48.84	51.16	6.05	62.67	31.68	69.98	125.73	0.56	
Mn/SiO ₂	66.91	33.09	9.06	89.07	1.87	9.60	111.34	0.09	



Fig. 5. NH₃-TPD and Pyridine-IR profiles of synthesized catalysts.

area (BET) among these catalysts, ca. 703.29 $m^2 g^{-1}$, while Mn/Al₂O₃ had the smallest specific area, ca. 281.12 $\text{m}^2 \cdot \text{g}^{-1}$. However, Mn/Al₂O₃ possessed much higher pore volume than others expect for Mn/SiO₂ due to broad PSD in mesopore region. Diversely, Mn/SiO_2 displayed a type II isotherm with H3 hysteresis loop when P/P_0 reached to 0.9 ~ 1.0, reflecting its macroporous structure. Accordingly, Mn/SiO₂ exhibited much broad PSD in mesopore region, and its pore volume and average pore diameter were extremely larger than the others. The pore structures affect catalytic ozonation of Cl-VOCs to some extent. Mn/Al2O3 possessed abundant microporous and mesoporous structures was better for DCM and TCE catalytic degradation (Fig. 1). CB and DCE conversion exhibited positive correlation with the microporous structure but negative correlation with mesoporous structures. Therefore, both Mn/ HZSM-5(27) and Mn/HZSM-5(200) achieved excellent CB and DCE conversion as well as higher mineralization rate (Fig. 1 and Fig. 2). Overall, HZSM-5 supported catalysts presented desirable mineralization for all these Cl-VOCs, attributing to their excellent microporous structures (Fig. 2).

Surficial chemical states of Mn elements and surficial oxygen species of these synthesized catalysts were analyzed by XPS measurements and deconvoluted by Gaussian functions, as illustrated in Fig. 4. The proportion of each species could be calculated by integrated area and presented in Table 2. All catalysts had two characteristic peaks of Mn 2p_{3/2} around at the binding energy of 641.83 and 644.56 eV, ascribing to Mn³⁺ and Mn⁴⁺, respectively (Fig. 4(a)). Apparently, Mn/HZSM-5(27) and Mn/HZSM-5(200) exhibited much higher ratio of Mn³⁺, ca. 73.62% and 67.28%, respectively. Generally, more Mn^{3+} signifies the abundant oxygen vacancies to maintain charge balance, which are favorable for ozone decomposition [29]. Clearly, Mn/USY(11) possessed the lowest ratio of Mn³⁺, which might directly cause its undesirable activity for DCM and DCE conversion as well as the mineralization of DCM, DCE, and TCE. Fig. 4(b) presents three types of oxygen species in O 1 s spectra, i.e., lattice oxygen (OL), chemisorbed oxygen (OC), and hydroxyl oxygen (O_{OH}) from low to high binding energy [29,39]. Interestingly, the binding energy of O_C for HZSM-5 and USY supported catalysts shifted towards lower values compared with Al₂O₃ and SiO₂ supported catalysts. Besides, the proportion of O_C also exhibited lower

value. Apparently, O_C occupied the dominant proportion for all catalysts, which is regarded to be favorable for ozone decomposition [3,29]. Mn/Al₂O₃ exhibited the highest O_V proportion, ca. 91.88%. However, there was no certain correlations between oxygen species and catalytic activity. Fig. S4 and Table S2 present the variation of Mn species and O species of Mn/HZSM-5(27) after catalytic ozonation. Clearly, the proportion of Mn³⁺ and lattice oxygen O_L declined a lot for all these spent Mn/HZSM-5(27) catalysts. The consumption of oxygen vacancies (Mn³⁺) and ozone oxidation contributed to the elevation of average valance state of Mn, which further validated the critical role of oxygen vacancies in catalytic ozonation of Cl-VOCs. The decline in O_L should mainly originate from elevation of chemisorbed oxygen species O_C due to accumulation of active oxygen radicals from ozone decomposition and oxygenated intermediates from Cl-VOC oxidation.

NH₃-TPD and Py-IR were conducted to investigate the surface acidity of synthesized catalysts, as illustrated in Fig. 5. Generally, the NH₃-TPD profiles can be divided into three regions: weak (<280 °C), moderate (280 °C \sim 450 °C), and strong acidity (>450 °C) [21,29]. Obviously, all these catalysts exhibited a distinct desorption peak centralized at relatively low temperature. The weak acidity was dominant for all these catalysts. As expected, Mn/SiO₂ possessed the poorest acidity among these catalysts due to its inert property of SiO₂. Zeolite supported catalysts exhibited much higher acidity, which even surpassed Al₂O₃ supported catalyst, especially for weak acidity. Reducing the ratio of SiO₂/ Al₂O₃ further elevated the acidity [6,23]. Besides, Mn/Al₂O₃ demonstrated much more strong acidity with an obvious broad desorption peak at 505 °C, and Mn/HZSM-5(27) also had some moderate and strong acidity with the desorption peak centralized at 452 °C. Previous literature reported that moderate acidity was more critical for catalytic ozonation than strong acidity, and too strong acidity even caused negative effect on catalytic ozonation [40]. Fig. 5(b) and Table 2 concretely described the type of acidic sites and their amount based on the analysis of Py-IR measurement. All these catalysts displayed several obvious desorption peaks around at 1447 and 1602 cm⁻¹, corresponding to Lewis acidic sites [29,41]. The bands at ~ 1546 cm⁻¹ should be assigned to Brønsted acid sites, and the bands at $\sim 1491 \text{ cm}^{-1}$ demonstrated the coexistence of Brønsted and Lewis acidic sites [32]. Mn/



Fig. 6. GC–MS spectra and quantitative concentration of gaseous organic byproducts during catalytic ozonation of different Cl-VOCs over Mn/HZSM-5(27) with O_3/Cl -VOC of each Cl-VOCs obtained 70 ~ 80% conversion (DCM(8.0), DCE(4.0), TCE(4.0) and CB(8.0)).

Al2O3 and Mn/SiO2 were dominant in Lewis acidic sites, while Mn/ Al₂O₃ possessed slightly higher acidity than Mn/SiO₂. Zeolite supported catalysts exhibited much higher acidity than Mn/Al₂O₃ and Mn/SiO₂, in consistent with NH3-TPD results. Mn/HZSM-5(27) possessed the highest Brønsted acidic sites as well as Lewis acidic sites, ca. 337.56 and 231.50 $\mu mol \cdot g_{cat}{}^{-1}\!,$ respectively. The ratio of Brønsted acidic sites vs Lewis acidic sites (B/L) reached to 1.46. With elevating the ratio of SiO₂/Al₂O₃ to 200, Mn/HZSM-5(200) possessed much lower total amount of acidic sites than Mn/HZSM-5(27) and the Brønsted acidic sites almost disappeared. Mn/USY(11) had lower ratio of SiO₂/Al₂O₃, but its acidic sites were lower than Mn/HZSM-5(27), which should attribute to different pore structures (Y type and Z type). As reported, Lewis acidic sites mainly affect the breakage of C-C/C-Cl bonds of Cl-VOCs molecules and alleviate coke problem [29,32], while Brønsted acidic sites are favorable for migration of Cl species to weaken Cl poisoning [20,41]. Accordingly, Mn/HZSM-5(27) with abundant Lewis and Brønsted acidic sites contributed to its excellent Cl-VOCs conversion and mineralization.

3.3. Byproducts distribution in effluent gas

Organic byproducts generation is a typical problem in Cl-VOCs catalytic degradation. Besides, considering the difference of degradation processes between various types of Cl-VOCs, such as DCM, DCE, TCE, and CB, the byproducts formation and distribution could be similar or totally different. Therefore, the effluent gas during catalytic ozonation over Mn/HZSM-5(27) with the O₃/Cl-VOCs of each Cl-VOCs obtaining $70 \sim 80\%$ conversion (8.0 for DCM, 4.0 for DCE, 4.0 for TCE and 8.0 for CB) was collected and detected. The GC-MS spectra and quantitative concentration of each byproducts are presented in Fig. 6. Table S1 lists the molecular formula and structure of byproducts. Chlorinated organic compounds were dominant in all these Cl-VOCs ozonation byproducts. DCM possessed such simple molecule structure, therefore its byproducts mainly contained small and simple molecules. Chlorinated methane compounds, including chloromethane (CH₃Cl), trichloromethane (CHCl₃), and tetrachloromethane (CCl₄) occupied dominant position among all these byproducts. Hydrodechlorination of DCM caused formation of CH₃Cl firstly. Methoxy radicals were the critical intermediates during DCM oxidation, which produced chloromethoxy $(-O - CH_2Cl)$ by chlorination and finally generated CH₃Cl by interacting with hemiacetal species [5]. Subsequently, chlorination reactions produced a certain number of polychlorinated byproducts, i.e., CHCl3 and CCl4. Besides, slight amount of chlorinated ethylene and several oxygencontaining organic species were also detected. As for DCE ozonation, the byproducts distribution was much more complicated. Noticeably, all the byproducts of DCM ozonation were involved in DCE byproducts, which was inconsistent with previous conclusion [5]. Besides, several

polychlorinated alkanes and alkenes were also detected in the effluent gas of DCE ozonation, such as 1,1,2-trichloroethane (C2H3Cl3), 1,1,2,2tetrachloroethane (C2H2Cl4), 1,1-dichloroethylene (C2H2Cl2), and trichloroethylene (C₂HCl₃). These observations indicated complicated steps during catalytic ozonation of DCE, including dehydrochlorination to generate vinyl chloride (C₂H₃Cl) and hydrodechlorination with C-C cleavage to form chloromethane (CH₃Cl) [5]. Next, chlorination occurred for C2H3Cl and CH3Cl to produce above mentioned polychlorinated byproducts. C₂H₂Cl₄ should be originated from direct chlorination of DCE. Similarly, TCE, as one of the byproducts during catalytic ozonation of DCE, also showed some certain relevance with DCE ozonation in terms of byproducts distribution. However, TCE tended to be easily degraded due to the existence of C = C bonds, and more chlorinated alkanes were generated rather than chlorinated ethylene. Diversely, except for chlorinated alkanes, CB ozonation generated a few polychloride benzenes, including 1,2-dichlorobenzene (1,2-C₆H₄Cl₂), 1,3-dichlorobenzene (1,3-C₆H₄Cl₂), 1,4-dichlorobenzene (1,4-C₆H₄Cl₂), and 1,2,4-dichlorobenzene (1,2,4-C6H3Cl3). These polychloride benzenes mainly caused by the electrophilic substitution reaction between Cl species and H atom of benzene ring. Besides, several oxygen containing byproducts were also formed during the opening of benzene ring, i.e. (Z)-butenedioic anhydrides (C₄H₂O₃) and cis-3-chloroacrylic acid (C₃H₃ClO₂).

The quantitative analysis of the main byproducts from GC-MS spectra is presented in Fig. 6(b). Obviously, only a few chlorinated methane species, i.e., CHCl₃ and CCl₄, occupied the dominant position in DCM byproducts, and their corresponding concentration was 12.04 and 2.45 mg \cdot m⁻³ respectively. Similarly, chlorinated methane species were also the dominant byproducts in DCE ozonation. DCM became the dominant byproducts as its concentration came to 40.02 mg·m⁻³ that was ~ 3.5 times higher than CHCl₃, ca. 11.43 mg·m⁻³. Meanwhile, several polychlorinated ethane species were also formed due to the electrophilic substitution of Cl_·, including $C_2H_3Cl_3$ (8.36 mg·m⁻³) and $C_2H_2Cl_4$ (5.72 mg·m⁻³). Besides, a few chlorinated ethylene species caused by dehydrochlorination and chlorination, including C₂H₃Cl, C₂HCl₃, and C₂Cl₄. Among them, C₂H₃Cl and C₂Cl₄ presented a similar concentration with CH₃Cl, ca. 11.41 and 11.99 mg·m⁻³, respectively, while C_2HCl_3 concentration was half of them, ca. 4.34 mg·m⁻³. CHCl₃ and CCl₄ were the two dominant byproducts during catalytic ozonation of TCE, and their concentrations had reached to 22.34 and 61.24 $mg \cdot m^{-3}$, respectively, surpassing all other byproducts in TCE. CCl₄ even exceeded all other byproducts in DCM, DCE, and CB, causing its undesirable mineralization. It could be speculated that the initial stage of C = C cleavage in TCE ozonation was relative completely, while the further degradation process from intermediates to final products was not expectable. Posteriorly, a few chlorinated ethylene species were



Fig. 7. Catalytic co-ozonation of mixed Cl-VOCs over Mn/HZSM-5 (27). (a) CB and DCE, (b) CB and TCE, (c) DCE and DCM, (d) DCE and TCE conversion, Temperature: 120 °C, catalyst dosage: 50 mg, Cl-VOCs concentration: 100 ppm (50 ppm + 50 ppm).



Fig. 8. Mixed Cl-VOCs-TPD on Mn/HZSM-5 (27). (a) CB + DCE, (b) CB + TCE, (c) DCE + DCM, (d) DCE + TCE.

generated as well via hydrodechlorination, including C₂H₃Cl (4.34 mg·m⁻³) and C₂H₂Cl₂ (11.99 mg·m⁻³). As for CB ozonation, the total byproducts production was the lowest among these Cl-VOCs, verifying its excellent degradation potential by ozonation. The total concentration of chlorinated methane and chlorinated ethylene species came to 10.43 and 3.76 mg·m⁻³, respectively, which were much lower the corresponding byproducts of DCE and TCE. Furthermore, a certain amount of polychloride benzene formation was inevitably with electrophilic substitution between C–H of benzene ring and Cl-. Especially, 1,4-C₆H₄Cl₂ was much more dominant with the concentration of 10.02 mg·m⁻³. The concentration of 1,2-C₆H₄Cl₂, 1,4-C₆H₄Cl₂, and 1,2,4-C₆H₃Cl₃ was 4.32, 0.63, and 0.52 mg·m⁻³ respectively.

3.4. Catalytic co-ozonation of mixed Cl-VOCs

Multiple Cl-VOCs are usually co-existed in the practical flue gas and waste gas, therefore the interactions between each other during catalytic ozonation cannot be ignored. Fig. 7 presents the behaviors during catalytic co-ozonation of two types of Cl-VOCs. DCE and TCE could promote CB conversion especially at low O₃ input, but DCE and TCE both suffered slight inhibition at the same time (Fig. 7(a)~(b)). Actually, it was more accurate to describe that O3 preferentially reacted with CB compared with DCE and TCE. The O₃ molecules originally belonging to DCE and TCE were grabbed by CB. In comparison, TCE conversion exhibited more severe attenuation than DCE. For instance, when O₃/Cl-VOCs came to $4.4 \sim 4.6$, CB conversion increased from 48% to 58% and 61% by comparing single CB ozonation with co-ozonation of CB/DCE and CB/TCE, respectively. However, DCE conversion decreased from 90% to 84% and TCE conversion declined from 95% to 43%. The excellent TCE conversion during single ozonation at low O₃ input was completely destroyed during co-ozonation of CB/TCE. Therefore, in terms of conversion efficiency, CB occupied preferential position compared with TCE, but it was uncertain when compared with DCE which still had higher conversion than CB before the molar ratio of O₃/ Cl-VOC reaching 10.0. The MAR in CB + DCE mixture was approximately equal to the average value of CB and DCE single at low O₃ input, but it exhibited higher value than both CB and DCE single finally. Fortunately, the MAR in CB + TCE mixture had exceeded the average value of CB and TCE single along the full O3 input range, indicating improvement for deep oxidation during catalytic co-ozonation. Next, catalytic co-ozonation of chlorinated alkanes and alkenes exhibited different performance. DCE conversion was improved a lot with presence of both DCM and TCE, which attained almost completely conversion at much lower O₃ input, ca. O₃/Cl-VOC of ~ 4.5 (Fig. 8(c)~(d)). Conversely, DCM and TCE conversion were inhibited severely, which violently dropped from 45% and 91% to 5% and 66%, respectively, at the initial O_3 /Cl-VOC of ~ 2.5. Therefore, DCE occupied preferential position compared with DCM and TCE in terms of conversion efficiency in catalytic co-ozonation. As expected, the MAR of catalytic coozonation of DCE/DCM and DCE/TCE both decreased a lot compared with single ozonation, indicating incomplete degradation causing by the interaction between each other. If taking the degradation of total Cl-VOCs into consideration, co-existence of DCE/DCM and DCE/TCE exhibited negative effect. There are several points can be summarized: (I) CB exhibited superiority in catalytic ozonation compared with DCE and TCE, while TCE failed miserably during the competition; (II) DCE won the priority in catalytic ozonation in presence of DCM and TCE, but DCM and TCE conversion suffered violent attenuation; (III) The competition between TCE and CB was more severe compared with TCE and DCE, which should attribute to the more O3 molecules requirement of CB; (IV) CB + DCE and CB + TCE attained higher MAR than average value, whilst the mineralization was prevented in the system of DCE + DCM and DCE + TCE.

Adsorption is the first step of catalytic ozonation. Higher adsorption capacity enhances the intimate contact between Cl-VOC and O_3 molecules, as well as other active species on catalyst surface, thus attaining

higher activity. To evaluate the effect of competitive adsorption on catalytic performance, co-adsorption ability was measured. Fig. 8 displays the temperature programmed desorption of mixed Cl-VOCs over Mn/HZSM-5(27). Clearly, CB exhibited much higher adsorption capacity than both DCE and TCE. Interestingly, the initial and final desorption temperature of CB were very close for CB/DCE and CB/TCE in Fig. 8(a)~ (b), but there was a large gap between the maximum concentration. The integrated adsorption amount of CB was 12.06 and 90.36 mmol·g⁻¹, respectively. Visibly, DCE distinctly weakened CB adsorption, which was almost 7.5 times lower than TCE. In comparison, the adsorption capacities of DCE and TCE were much lower than CB, ca. 3.94 and 14.61 mmol·g⁻¹, respectively. The priority of CB in adsorption should be one of the reasons for its higher conversion in mixture than that in single CB system. The gap of adsorption capacity between DCE and CB was much less than that between TCE and CB, contributing to the violent drop in TCE conversion in Fig. 7(b). Nevertheless, TCE surpassed DCE a lot in adsorption capacity due to the stronger polarity of TCE than DCE. On the contrary, although DCE conversion obtained promotion when the coozonation of DCE/DCM and DCE/TCE, its adsorption capacities were both lower than DCM and TCE as exhibited in Fig. $8(c) \sim (d)$. The calculated DCE capacities were 1.71 and 3.03 mmol·g⁻¹ in DCE/DCM and DCE/TCE mixture, respectively, which were even lower than that in CB/DCE mixture, ca. 3.94 mmol \cdot g⁻¹. In comparison, DCM brought stronger competition on DCE adsorption than TCE. However, DCM and TCE conversion were both inhibited by DCE, while DCE conversion acquired superiority in catalytic co-ozonation. That's to say, adsorption might not be the determining factor for the competition during catalytic co-ozonation of DCE/DCM and DCE/TCE. Interestingly, TCE exhibited much higher adsorption capacity in DCE/TCE mixture than that in CB/ TCE mixture, ca. $22.08 > 14.61 \text{ mmol} \cdot \text{g}^{-1}$. TCE possesses stronger polarity than DCE but lower than CB, which caused these variations. Therefore, TCE conversion in DCE/TCE mixture was much higher than that in CB/TCE mixture.

There are several points from the catalytic ozonation of single compound can be adopted to interpret the catalytic co-ozonation results. DCM and DCE had higher difficulty in catalytic ozonation that required higher ozone input than stoichiometric ratio and Mn loading also played critical role in catalytic ozonation apart from support. In comparison, TCE and CB were liable to be degraded with less ozone input and exhibited weak correlation with catalysts. However, the MAR values of TCE were unsatisfactory. Therefore, catalytic ozonation of TCE and CB should mainly abide by L-H (Langmuir-Hinshelwood) mechanism that adsorption was the critical factor, while DCM and DCE might follow MvK (Mars and van Krevelen) mechanism that active oxygen species from ozone decomposition were the determining factor. CB possesses a big π bond conjugated system, strong molecular polarity, and higher boiling point than DCE and TCE, causing preferential adsorption [42]. Accordingly, CB conversion exhibited priority in CB + DCE and CB + TCE system. DCE provided additional H sources, thus promoting deep oxidation to obtain higher MAR value. TCE conversion was inhibited significantly, therefore the total MAR value also elevated with less negative impact from TCE. Apparently, both DCE and DCM belong to chlorinated alkanes with similarities in physical or chemical properties, thus existing strong competitive adsorption. Besides, DCM was inherently more difficult to be degraded than DCE as exhibited in Fig. 1. Meanwhile, Mn/HZSM-5(27) was not the optimal catalyst for catalytic ozonation of DCM. Consequently, DCM conversion was retarded and inhibited obviously. Although TCE could be degraded effectively with very less ozone input (Fig. 1(c)) and possessed stronger adsorption than DCE (Fig. 8(d)), the different reaction mechanism caused ozone derived active oxygen species accessed DCE molecules preferentially. TCE with more chlorine atoms might also bring a certain obstacle. Besides, it can acquire some valuable information from Fig. 6 that TCE was one of the critical byproducts of DCE. Similarly, DCM was the predominant byproducts during catalytic ozonation of DCE. This should be an important reason causing decline in DCE and TCE conversion during



Fig. 9. Catalytic co-ozonation of CB/DCE and CB/TCE at 120 °C with O₃/Cl-VOC of 12.5 under humidity of 5 vol%.

catalytic co-ozonation. Accordingly, it's possible to speculate that catalytic ozonation of CB might produce more byproducts relating to DCE and TCE, which caused the deactivation in DCE and TCE conversion. In conclusion, benzene ring structure exhibited better competitive adsorption that could be further degraded by active oxygen species on catalyst surface, while the degradation difficulty should play more determining role in competitive ozonation. Overall, catalytic coozonation for different combination of Cl-VOCs exhibited complicated performance due to their various physical and chemical properties. Sometimes, it's possible to develop new routes for saving ozone input by screening the combination of Cl-VOCs. Even more, introduction of other types of Cl-VOCs, or VOCs, maybe feasible to improve catalytic ozonation performance.

3.5. Effects of H₂O

Humidity is a critical factor for catalytic ozonation in practical application. Our previous investigations have reported the effects of H₂O on catalytic ozonation of single CB and catalytic co-ozonation of CB/NO, and obtained serval interesting observations [16,26,29]. For comparison, the further investigation of H₂O introduction into catalytic co-ozonation of CB/DCE and CB/TCE was conducted. Fig. 9 demonstrates the catalytic co-ozonation of CB/DCE and CB/TCE under water content of 5 vol%. Both CB, DCE, and TCE conversion could maintain stability of exceeding 90% in the initial dry stage. Thereafter, CB conversion exhibited fluctuation but elevated slightly in the CB/DCE mixture under humidity, while both CB and TCE conversion increased to 100% in the CB/TCE mixture. Conversely, DCE conversion appeared a certain decline in the humid atmosphere. Interestingly, the total MAR value of CB/DCE increased from \sim 82% to \sim 90% with reaction time over 200 min in the humid atmosphere, indicating the degradation of surficial intermediates was promoted. The slow decrease in MAR value after removing humidity further verified the washing and promoting degradation effect of water on intermediates [5,26]. However, the total MAR value of CB/TCE had dropped a lot along with reaction time under dry atmosphere, and then suffered violent fluctuations at the range of 75% to 95% with the introduction of H_2O . Fortunately, the total MAR value recovered to higher than 95% as the reaction time coming to 330 min, and even illustrated about 10% promotion compared with the initial stage. Interestingly, expect for DCE conversion in CB/DCE mixture, all other five values in Fig. 9 declined a lot and finally maintained at a stable level after entering back into dry atmosphere. This phenomenon might demonstrate that H₂O had participated into catalytic ozonation with the hydroxyl radicals produced from H₂O and O₃.

4. Conclusions

This paper investigated catalytic ozonation of various Cl-VOCs (DCM, DCE, TCE, and CB) over series of supported MnO_x catalysts

(Mn/SiO₂, Mn/HZSM-5(27), Mn/HZSM-5(200), Mn/USY(11), and Mn/ Al₂O₃)). Catalytic ozonation of DCM and DCE required higher ozone input than stoichiometric ratio and Mn loading also played critical role in catalytic ozonation apart from support materials. In comparison, TCE and CB were liable to be degraded with less ozone input than stoichiometric ratio and even exhibited desirable conversion with pristine support. Al₂O₃ and HZSM-5 with abundant acidic sites presented much higher activity than other supports. Interestingly, the optimal catalysts in terms of conversion did not necessarily exhibited the highest MAR. which is the important index to evaluate the thoroughness of catalytic ozonation. Mn/HZSM-5(27) with abundant Lewis/Brønsted acidic sites and microporous structure contributed to its excellent Cl-VOCs adsorption, conversion, and mineralization. The byproducts distribution during catalytic ozonation was also compared. Clearly, DCM with a simple structure only produced serval chlorinated alkanes, while others generated large amounts of chlorinated alkanes and alkenes. TCE conversion was accompanied by large amounts of byproducts, especially CHCl3 and CCl4, indicating incomplete degradation. Chlorinated aromatics were only detected in catalytic ozonation of CB. Although CB exhibited much lower byproducts production, but several polychlorinated aromatics were detected, such as 1, 2-C₆H₄Cl₂ and 1, 2-C₆H₃Cl₃. Polychlorinated byproducts from chlorination could not be ignored.

Catalytic co-ozonation of mixed Cl-VOCs over Mn/HZSM-5(27) presented diverse variations. Catalyst possessed much higher adsorption capacity of CB, contributing to its superiority in catalytic ozonation compared with DCE and TCE. The degradation difficulty of DCM and TCE as well as the byproducts formation of DCE caused the inhibition effect on DCM and TCE. However, catalytic co-ozonation might bring higher mineralization rate. Finally, the introduction of H₂O caused negligible effect on catalytic co-ozonation of Cl-VOCs, which further implied the superiority and potential of catalytic ozonation in multiple Cl-VOCs treatment of practical flue gas.

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.

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Appendix A. Supplementary data

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