Catalytic Oxidation of Chlorinated Organics over Lanthanide Perovskites: Effects of Phosphoric Acid Etching and Water Vapor on Chlorine Desorption Behavior

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ABSTRACT: In this article, the underlying effect of phosphoric acid etching and additional water vapor on chlorine desorption behavior over a model catalyst La$_3$Mn$_2$O$_7$ was explored. Acid treatment led to the formation of LaPO$_4$ and enhanced the mobility of lattice oxygen of La$_3$Mn$_2$O$_7$ evidenced by a range of characterization (i.e., X-ray diffraction, temperature-programmed analyses, NH$_3$-IR, etc.). The former introduced thermally stable Brønsted acidic sites that enhanced dichloromethane (DCM) hydrolysis while the latter facilitated desorption of accumulated chlorine at elevated temperatures. The acid-modified catalyst displayed a superior catalytic activity in DCM oxidation compared to the untreated sample, which was ascribed to the abundance of proton donors and Mn(IV) species. The addition of water vapor to the reaction favored the formation and desorption of HCl and avoided surface chlorination at low temperatures. This resulted in a further reduction in reaction temperature under humid conditions (T$_{90}$ of 380 °C for the modified catalyst). These results provide an in-depth interpretation of chlorine desorption behavior for DCM oxidation, which should aid the future design of industrial catalysts for the durable catalytic combustion of chlorinated organics.

1. INTRODUCTION

Chlorinated volatile organic compounds (CVOCs) are well-known to have deleterious effects on human health because of their inherent bioaccumulation and potential carcinogenicity; many CVOCs have been listed as priority pollutants worldwide.\(^1,2\) The efficient catalytic combustion of CVOCs usually encounters the problem of the lack of reliable catalysts to ensure durable operation in industrial applications. In general, there are two steps involved in CVOC oxidation: the scission of the C–Cl bond (i.e., adsorption/hydrolysis) at acidic sites or superficial oxygen vacancies, followed by the deep oxidation of adsorbates/intermediates at redox sites.\(^3,4\) The first step, however, tends to cause reversible or irreversible deactivation of the applied catalysts through surface chlorination. Therefore, efficient chlorine desorption from the applied catalyst is integral to the durable operation of catalytic CVOC oxidation in industry, and the study of chlorine desorption behavior to guide catalyst design is highly required.

Rare earth perovskites have been widely studied in CVOC oxidation due to their favorable structural and thermal stability which makes them well suited to thermocatalysis under industrial conditions (i.e., thermal shock, chlorine poisoning, water vapor, etc.). Many efforts have been devoted to improving redox abilities and surface acidities via substitution of A/B cations,\(^5,6\) introduction of acidic supports (i.e., Al$_2$O$_3$, TiO$_2$, acidic zeolite)\(^7\) and loading noble metals.\(^8\) The deactivation of rare earth perovskites, particularly lanthanide perovskites, has been reported to be caused by the interaction with dissociated chlorine. This has been found to accelerate the lanthanum migration to the surface, leading to the formation of inactive LaOCl.\(^9\) The inhibited redox ability by surface chlorination was another factor considered to be the cause of deactivation.\(^10\) To date, there is little knowledge on how to facilitate desorption of chlorine (in the form of either HCl or Cl$_2$) from lanthanide perovskites. In addition, the concentrated water vapor in industrial waste gases is reported to compete with reactants or become aggregated as clusters.
that block the access of applied catalysts to reactants, therefore leading to catalytic deactivation.\textsuperscript{11-13} However, the underlying effect of water vapor on the chlorine desorption behavior still lacks unified interpretation. As such, the deactivation behavior of lanthanide perovskites in CVOC oxidation (with or without water vapor) still requires further exploration, with the aim to clarify their causes and guide the catalyst design for industrial applications.

In this article, a Manganese layered perovskite (La$_3$Mn$_2$O$_7$) with high thermal stability and enriched oxygen species was studied as a model catalyst. Phosphoric acid etching was conducted to form insoluble lanthanum phosphate (LaPO$_4$, a solid acid that has unique characters in thermal stability. Bronsted acidity and hydrophilidad and expose Mn species at the surface. Unlike the HNO$_3$ and HF treatment,\textsuperscript{17,18} the H$_3$PO$_4$ etching could induce excess phosphorus and acidity by coordination of phosphorus species via the hydroxyl groups.\textsuperscript{19} Phosphoric acid treatment has been previously applied to Pt/MCM-41 to study its effect on Pt species. It was found that the increased acidity and oxidized Pt benefited CVOC oxidation. In this paper, phosphoric acid was expected to remove superficial La cations and form a combined catalyst (LaPO$_4$–La$_3$Mn$_2$O$_7$) that might benefit chlorine desorption (via the formation of HCl) and divert water molecules from active sites in catalytic CVOC oxidation. The aim was to explore the effect of phosphoric acid etching and water vapor on chlorine desorption behavior.

A range of analytical techniques have been employed to reveal the structural and chemical properties of fresh and used catalysts in catalytic dichloromethane (DCM) oxidation (note: the DCM is a typical chlorinated organic that is abundant in the pharmaceutical industry exhaust gas). The behavior of the chlorine desorption and the solid–gas–liquid reaction (to simulate industrial operation condition) was analyzed.

### 2. EXPERIMENTAL PROCEDURE

2.1. Preparation of the Catalyst. The La$_3$Mn$_2$O$_7$-\textit{g} catalyst was synthesized using a modified citric acid route as reported by Du et al.,\textsuperscript{20} denoted as La$_3$Mn$_2$O$_7$ (details are provide in Section S1 in the Supporting Information (SI)). The acid modification was conducted by treating portions (1 g) of La$_3$Mn$_2$O$_7$ in a 30 mL of 0.1 M H$_3$PO$_4$ solution with ultrasonic shaking for 40 min at room temperature. The solid products were washed with deionized water three times and then dried in a vacuum oven at 40 °C for 24 h. The resulting sample was denoted as La$_3$Mn$_2$O$_7$-\textit{g}.

2.2. Characterization of Catalysts. Details of characterization techniques, including XRD, HR-TEM, XPS, DRIFTS, TPR/TPD, etc. are provided in SI Section S2. Temperature-programmed desorption (TPD), temperature-programmed reduction (TPR) and temperature-programmed surface reaction (TPSR) were conducted using an automatic multi-purpose adsorption instrument TP-5079 (Tianjin Xianquan, China) equipped with a thermal conductivity detector (TCD) and a portable mass spectograph (MS) QGA (Hiden Analytical, UK).

Density functional theory (DFT) study was performed using the Vienna ab initio Simulation Package (VASP-5.4).\textsuperscript{21} A plane-wave basis set with a cutoff energy of 400 eV within the framework of the projector-augmented wave (PAW) method was employed. Each atom was converged to 0.05 eV Å$^{-1}$ for geometry optimization. A unit cell (a = b = 3.98 Å, c = 20.92 Å) with 24 atoms (6 La, 4 Mn, 14 O)\textsuperscript{20} and a 2 x 2 x 1 supercell with 96 atoms was used as the modeled catalyst La$_3$Mn$_2$O$_7$. A 3 x 3 x 1 Monkhorst-pack k-point mesh for geometry optimization of the La$_3$Mn$_2$O$_7$ composites was applied. Lanthanum etching was simulated by removing all the La atoms deposited at the exposed facet (1 0 0) (SI Figure S1).

2.3. Catalytic Test. The catalytic activities were evaluated in terms of DCM and CO$_2$/CO conversion as a function of temperature. The feed gas (100 mL/min) was comprised of 0.1 vol % DCM, 10 vol % oxygen and N$_2$ (as the inert diluent gas and/or carrier gas for steam), giving a constant gas hourly space velocity (GHSV) of 12 000 mL g$^{-1}$ h$^{-1}$. The decomposition of DCM by homogeneous gas reactions was neglected for temperatures under 600 °C, and the characteristic $T_X$ (the temperature when x % DCM conversion or CO$_2$ generation was reached in the light-off curves) was used as an indicator for activity. Conversion data were collected after an initial period of 40 min for each temperature to obtain a nearly constant reaction rate. The desorption plot of HCl or Cl$_2$ was recorded using MS. Further details are provided in SI Section S2.

### 3. RESULTS AND DISCUSSION

3.1. XRD, Surface Area, and HR-TEM Measurements. As identified through XRD analyses (SI Figure S2), trace amount of LaPO$_4$-0.5H$_2$O (JCPDS 46-1439) with the characteristic reflections at 20 of 19.9°, 25.1°, 29.0°, 31.2°, and 48.1° was observed in La$_3$Mn$_2$O$_7$-\textit{g} apart from the main structure of La$_3$Mn$_2$O$_7$. This result implied that a reaction between the surface La$^{3+}$ cations and PO$_4^{3-}$ occurred during the phosphoric acid etching generating insoluble LaPO$_4$-0.5H$_2$O. Surface area measurements demonstrated that each catalyst displayed a type II N$_2$ adsorption–desorption isotherm with a H$_3$-type hysteresis loop in the relative pressure (p/p$_0$) range of 0.2–1.0 (SI Figure S3), thereby revealing the existence of slit pores (originating from particles stacking) in La$_3$Mn$_2$O$_7$ and La$_3$Mn$_2$O$_7$-\textit{g}.$^22$ The phosphoric acid treatment was found to increase the surface area from approximately 18.8 m$^2$ g$^{-1}$ (for La$_3$Mn$_2$O$_7$) to 90.1 m$^2$ g$^{-1}$ (for La$_3$Mn$_2$O$_7$-\textit{g}). This increment was attributed to the reduction of particle size (from 24 to 35 nm), accompanied by the enlargement of pore size (from 8.9 to 15 nm, SI Table S1) and the formation of LaPO$_4$-0.5H$_2$O. As evidenced in HR-TEM analyses (SI Figure S4), the La$_3$Mn$_2$O$_7$ displayed uniform spherical particles with a size of 35 ± 7 nm (based on 150 particles, as shown in the size distribution), whereas the La$_3$Mn$_2$O$_7$-\textit{g} was characterized by much smaller spherical particles of 24 ± 5 nm, tangled with needle-like crystals that were characteristic of rhombohedral LaPO$_4$-0.5H$_2$O.$^25,24$ After being subjected to DCM oxidation, the structures of both La$_3$Mn$_2$O$_7$ and La$_3$Mn$_2$O$_7$-\textit{g} were not changed, and no phase transformation occurred during the reaction. The large increment in the surface area of La$_3$Mn$_2$O$_7$-\textit{g} would be expected to provide higher access to reactants such as DCM, oxygen and water molecules, and therefore result in superior activity.
3.2. Catalytic Activity Measurements. The light-off curves of DCM oxidation over the La$_3$Mn$_2$O$_7$ and La$_3$Mn$_2$O$_7$−P catalysts are illustrated in Figure 1. For La$_3$Mn$_2$O$_7$, the T$_{50}$ over the used sample (at ca. 435 °C) was 45 °C higher than that of the fresh counterpart (at ca. 390 °C). Such an obvious decline in DCM conversion over the used catalyst indicated that La$_3$Mn$_2$O$_7$ experienced deactivation due to chlorine poisoning. In comparison, a distinct promotion in the catalytic activity of the acid-modified catalyst La$_3$Mn$_2$O$_7$−P was observed, revealing a consistent T$_{50}$ of DCM conversion at 355 °C and a much lower T$_{90}$ at 420 °C over the fresh and used catalysts. A decline in DCM conversion was still observed over La$_3$Mn$_2$O$_7$−P, however the transition temperature related to Cl poisoning was much lower than that of La$_3$Mn$_2$O$_7$ (ca. 14.8%). This result suggested that the chlorine might be effectively desorbed from the catalyst surface that possessed the Mn(IV). Indeed, XPS measurements on the used catalyst displayed a retained low-temperature redox ability of the catalyst was inhibited after DCM oxidation. In particular, most of the Mn(IV) (ca. 390 °C in Figure 2(b)) in the La$_3$Mn$_2$O$_7$ was found to be reduced to Mn(III) (ca. 495 °C in Figure 2(b)). This result suggested that the dissociative chlorine interacted with the Mn(IV) species (Lewis acidic sites) and reduced the Mn valence. In contrast, the used La$_3$Mn$_2$O$_7$−P displayed a retained low-temperature redox ability with most of the active oxygen and Mn(IV) species (centered at 320 °C, 410 and 465 °C in Figure 2(b)) still present. This result suggested that the chlorine might be effectively desorbed from the catalyst surface that possessed the Mn(IV). Indeed, XPS measurements on the used catalyst revealed that the used La$_3$Mn$_2$O$_7$−P had ca. 5% residual Cl on the surface, that is, much lower than the used La$_3$Mn$_2$O$_7$ (at ca. 14.8%).

For the used catalysts, the H$_2$ reduction peaks both shifted toward higher temperature range, implying that the redox ability of the catalyst was inhibited after DCM oxidation. In particular, most of the Mn(IV) (at ca. 390 °C in Figure 2(b)) in the La$_3$Mn$_2$O$_7$ was found to be reduced to Mn(III) (at ca. 495 °C in Figure 2(b)). This result suggested that the dissociative chlorine interacted with the Mn(IV) species (Lewis acidic sites) and reduced the Mn valence. In contrast, the used La$_3$Mn$_2$O$_7$−P displayed a retained low-temperature redox ability with most of the active oxygen and Mn(IV) species (centered at 320 °C, 410 and 465 °C in Figure 2(b)) still present. This result suggested that the chlorine might be effectively desorbed from the catalyst surface that possessed the Mn(IV). Indeed, XPS measurements on the used catalyst revealed that the used La$_3$Mn$_2$O$_7$−P had ca. 5% residual Cl on the surface, that is, much lower than the used La$_3$Mn$_2$O$_7$ (at ca. 14.8%).

In the literature, Mn(IV) was proposed to be the most active species for low-temperature CVOC oxidation. Here, the regeneration of Mn(IV)−O center via chlorine removal was considered to be the rate-determining step for CVOC.
oxidation. In general, a dual active center was involved in the CVOC oxidation process over perovskites: an acidic site (electrophile) for attacking chlorine, and a basic site (nucleophile) for attacking carbon, followed by the adsorbates being oxidized at redox sites to form CO₂ and H₂O. In La₃Mn₂O₇, the Mn(IV)-O species acted as both the adsorption center and redox site. As such, the accumulation of dissociated chlorine on the redox site that led to the reduction of Mn(IV) to Mn(III) would cause catalyst deactivation.

XPS analysis of the fresh La₃Mn₂O₇ catalyst revealed a lanthanum enrichment feature with 40% La excess on the surface. The semiquantitatively measured La/Mn atomic ratio (2.1) was much higher than the theoretical value (1.5). After acidic treatment, a peak at ca. 133.4 eV was observed in the XPS spectra of P 2p (SI Figure S6) which suggested the formation of LaPO₄ in La₃Mn₂O₇-P (with the surface atomic ratio of La: Mn: P at 2.3:1:1:1). This resulted in the reduction of the La/Mn atomic ratio in the main phase La₃Mn₂O₇ to 1.2 (as LaPO₄-0.5H₂O has an atomic ratio La/P of 1). The even lower La/Mn ratio than the theoretical datum suggested that many manganese species had been exposed to the catalyst surface after acid etching. Such an exposure, leading to transition metal-rich termination, is expected to induce enriched oxygen vacancies on the catalyst surface. Indeed, the O 1s XPS revealed that the O₃/Ö₄ atom ratio in the La₃Mn₂O₇-P was measured at 1.0, much higher than that of La₃Mn₂O₇ (0.4) (SI Figure S7). Notably, the La₃Mn₂O₇-P displayed distinct OH⁻ and adsorbed H₂O species at the surface; these species should originate from the increased surface area and the P=OH or water (crystal water or "zeolitic" water²⁴,3¹) residing in the LaPO₄·0.5H₂O structure.

3.4. O₂-TPD Analyses and DFT Calculations. In the O₂-TPD profile, the desorbed oxygen species can be categorized into chemisorbed oxygen species (α-O) at 100–300 °C, superficial lattice oxygen (β-O, including the nonstoichiometric oxygen α'-O) at 300–600 °C and bulk lattice oxygen (β-O) above 600 °C. As shown in Figure 3(a), the fresh La₃Mn₂O₇ displayed three desorption peaks with maxima at approximately 150 °C, 590 °C (with a shoulder at 445 °C) and 1000 °C. The low-temperature peak α-O at 150 °C was assigned to the oxygen chemisorbed on oxygen vacancies; the α'-O peak at 590 °C was the superficial lattice oxygen generated from grain boundaries and dislocations, and the shoulder at 445 °C originated from the over-stoichiometric oxygen (α'-O) in manganese-based layered perovskites. The β-O peak at 1000 °C was mainly the bulk oxygen desorbed via vacancy migration inwards with the increase of temperature. For La₃Mn₂O₇-P, the oxygen desorption peaks appeared at approximately 150 °C, 573 °C (with a shoulder at 400 °C) and 715°C, all of which experienced a lower temperature shift in comparison with that of La₃Mn₂O₇. In particular, the amounts of α'-O (α'-O) and β-O were found to be both distinctly increased in the La₃Mn₂O₇-P, suggesting that the acidic treatment had effectively improved the lattice oxygen mobility in the catalyst. In the used La₃Mn₂O₇, the chemisorbed (α-O) and over-stoichiometric oxygen (α'-O) disappeared, whereas those still existed in the used La₃Mn₂O₇-P. This result indicated that the La₃Mn₂O₇-P had a better redox cycle in...
DCM oxidation. The ability for efficient chlorine desorption should account for such an enhanced redox cycle. Notably, for the used La$_3$Mn$_2$O$_7$ (Figure 3(b)), the peak corresponding to the subsurface lattice oxygen species (at 675 °C) merged into the superficial ones (605 °C). This indicated that the lattice oxygen migrated outwards, leaving vacancies at the subsurface during the DCM oxidation.

DFT calculation was used to verify the enhanced oxygen mobility of the modified catalyst after La etching. After stripping La from the first layer, the exposed oxygen at the surface (i.e., O$^1$ and O$^2$) was found to bond tightly with Mn. However, the oxygen anion at the shared vertex site of two MnO$_6$ (i.e., O1, O2, and O3) was easier to lose with enhanced mobility because of the adjacent Mn–O bonds (Mn1–O1) being elongated to ca. 2.304 Å from the original 1.984 Å. The electronic localization function (ELF, Figure 4b) also confirmed the existence of less covalent interactions between the Mn sites and their adjacent O atoms after La removal.

According to Kagomiya et al.,$^{33,34}$ the oxygen atoms at the shared vertex could be easily liberated at elevated temperatures, leaving oxygen vacancies, which enhanced the mobility of superficial and subsurface oxygen as reflected in O$_2$-TPD profiles. Actually, the La cation was inclined to attract oxygen and elongate the Mn–O bond as reported,$^{35}$ so the superficial Mn–O bond being released from La attraction became stronger while those in the second and third layers were weakened due to residual La cations, leading to easier oxygen desorption and facilitated oxygen mobility.

3.5. Surface Acidity Assessment. In the NH$_3$-TPD profile, the acidic sites can be generally divided into weak acidity (<200 °C), moderate acidity (200–400 °C) and strong acidity (>400 °C). As shown in Figure 5, the fresh La$_3$Mn$_2$O$_7$ displayed a weak ammonia desorption peak below 400 °C that mainly originated from the Lewis acid sites of Mn with an
Scheme 1. The Chlorination and Dechlorination Process for DCM Oxidation over Applied Catalysts$^a$

![Diagram of the Chlorination and Dechlorination Process](image)

A. The migration of lattice oxygen pushed the Cl atoms out of the occupied sites, and its mobility affects the Cl2 formation in step 3; the structural -OH or water could react with Cl to form HCl, and its effective supply affects the HCl formation in step 4.

empty orbital 36,37 After phosphoric acid treatment, an intense ammonia desorption peak ca. 214 °C with a shoulder ca. 303 °C appeared that possibly originates from the exposure of Mn(IV) with Lewis acidity at 1628 cm$^{-1}$ in NH3−IR (Figure 5(b)) and the formation of LaPO4·0.5H2O with Brønsted acidity at 1437 and 1668 cm$^{-1}$, 38,39 in NH3−IR (Figure 5(a,b)). In the used catalysts (Figure 5(d)), the total acidity of LaMn2O7−P was retained, along with the moderate acidity increasing and the weak acidity decreasing. This result indicated that the acidity in the LaMn2O7−P was very stable in DCM oxidation. As reported, 33 the LaPO4·0.5H2O associated with H3PO4 at the surface forming LaPO4·0.5H2O (H3PO4·xH2O) that was stable up to 1400 °C. This result explains why the acidity of LaMn2O7−P could be stable up to high-temperatures in DCM oxidation. Note that such a highly stabilized Brønsted acidity is particularly beneficial for industrial applications because it can consistently benefit the DCM adsorption 40 and provide protons for efficient DCM oxidation, even under the frequent thermal shock during operation conditions.

3.6. Cl Removal Capacity Measurements. To confirm the enhanced chlorine removal ability in the LaMn2O7−P catalyst, temperature-programmed surface reaction (TPSR) measurements with an inlet of 1000 ppm DCM and 10 vol % O2 in He were conducted.

For LaMn2O7 as shown in Figure 6, no obvious desorption of HCl and Cl2 was observed in the first run as the temperature elevated. However, desorption was observed for both as the temperature was maintained at 600 °C. This behavior should be ascribed to the retention of Cl on the surface of LaMn2O7 in the fast heating process. In the second run, initial temperature for HCl desorption appeared at approximately 500 °C and that of Cl2 was at approximately 450 °C. This result indicated that the chlorine desorption only occurred at temperatures above 450 °C in this catalyst and explains why the catalyst inevitably experienced deactivation due to chlorination at temperatures lower than 450 °C (Figure 1). For LaMn2O7−P, the HCl started to desorb at 400 °C (note: there were a trace amount of HCl desorbed at 100−350 °C, as shown in the enlarged figure of SI Figure S8), and the Cl2 began desorption at approximately 350 °C in both runs. Likewise, the LaMn2O7−P would not desorb Cl until the temperature reached 350 °C, in agreement with the activity measurements. Notably, the amount and the desorption rate of chlorine in terms of HCl or Cl2 from the LaMn2O7−P was much higher than those from LaMn2O7 in both runs. This result verified that the LaMn2O7−P was indeed efficient for the formation and desorption of Cl2. This desorption ability was effectively retained in the used catalyst. The efficient chloride desorption was also found to suppress the chlorination of intermediate products (i.e., electrophilic chlorination) as the generation of CHCl3 was limited in both the fresh and used La3Mn2O7−P (SI Figure S9).

3.7. Proposed Reaction Mechanism. In DCM oxidation over the La3Mn2O7 type catalysts, a surface chlorination process of the catalyst was observed that had been proven to originate from the formation of Mn−Cl bonds (as evidenced by H2−TPR, XPS and DCM-TPSR analyses), leading to catalyst deactivation. Such a chlorination process was proposed to occur through the extraction of Cl from DCM molecules at Lewis acidic sites or oxygen vacancies (steps (1−2), Scheme 1). With the temperature elevating, the Mn−Cl bond tended to break to form Cl2 or HCl (as shown in DCM-TPSR, steps (3−4), Scheme 1). The generation of Cl2 was strongly relevant to the mobility of lattice oxygen species, for example, α′-O and β-O. The isolated Cl atoms captured in metal oxide oxygen vacancies preferred to move toward the surface upon heating. This is due to the acceleration of the lattice oxygen migration via the oxygen released from subsurface. This then results in the pushing outward of the superficial trapped Cl (i.e., the Deacon process), the aggregation of which would form molecular-like species such as Cl2 (step (3), Scheme 1). As such, the accelerated oxygen diffusion due to the shared vertex oxygen removal in La3Mn2O7−P could favor the Cl removal from the catalyst surface and thus cause the release of more Cl2 than that of La3Mn2O7 (Figure 6). This process would leave vacancies in the subsurface layer according to Amrute et al. and Yang et al., 42−44 as confirmed by the reduced desorption of subsurface lattice oxygen on the after-test La3Mn2O7−P in Figure 4(b). Given that the amount of HCl generation (assisted by proton donor, for example, water and hydroxyl groups) from La3Mn2O7−P was four times higher than that of Cl2, the dissociative Cl appears to prefer being trapped by hydroxyl groups or water in the vicinity via hydrogen bonding, forming molecular-like HCl (step (4), Scheme 1). Similar results in DFT calculations and experiments have been reported by Cen et al. and Dai et al., 45,46 respectively.

In Scheme 1, steps 1−4 only showed the HCl formation (hereafter denoted as Type I HCl) originating from the regeneration of chlorinated surface (i.e., the Cl was extracted from the Lewis sites or oxygen vacancies). However, in the DCM−TPSR measurements (Figure 6), we also observed small amounts of HCl desorbed at 100−350 °C (SI Figure S8) in the La3Mn2O7−P catalyst. This HCl should originate from the Brønsted acid sites that provided protons to form HCl directly (hereafter denoted as Type II HCl, as shown in step...
The Type II HCl was even liberated at room temperature once the DCM comes into contact with the La₃Mn₂O₇−P (SI Figure S10).

To further evaluate the possibility of Type II HCl dissociation on catalyst surface that might also cause the catalyst chlorination (as shown in step (2') in Scheme 1), HCl-TPSR was conducted, in which a flow of HCl in He was continuously purged onto the La₃Mn₂O₇ and La₃Mn₂O₇−P catalysts, followed by the recording of HCl, Cl₂, and H₂O desorption from 100 to 600 °C. As shown in Figure 7, the observation of Cl₂ formation suggested that the Type II HCl was indeed dissociated over the La₃Mn₂O₇ and La₃Mn₂O₇−P catalysts. Hisham et al.⁴⁷ had reported that the HCl dissociation over metal oxides was an exothermic reaction, which suggested that the dissociation process could occur easily on the La₃Mn₂O₇ and La₃Mn₂O₇−P catalysts. The dissociated Cl from the Type II HCl might further cause the catalyst chlorination that would be eventually transferred into type I HCl at high temperatures.

In the HCl-TPSR profile, it was also observed that the HCl desorption coincided with the H₂O in both the La₃Mn₂O₇ and La₃Mn₂O₇−P catalysts. This suggested that the HCl might adsorb on the surface H₂O sites and desorb with the H₂O at elevated temperatures. We first analyze the different types of H₂O on the catalyst surface. As shown in Figure 7c, the H₂O-TPD revealed three types of H₂O in the catalysts. The first peak centered at ca. 220 °C is ascribed to the adsorbed H₂O molecules that are directly contacted with the catalyst surface,⁴⁸ denoted as Type I; the second peak is associated with the dehydration of structural hydroxyl group clusters (denoted as Type II), and the third peak at 477 °C and the tail above 500 °C corresponds to the dehydration of strongly bonded hydroxyl groups (via the interaction of migrated vicinal and spaced groups, denoted as Type III).

Figure 7. (a) and (b) Profiles of H₂O, HCl and Cl₂ desorption from La₃Mn₂O₇ and La₃Mn₂O₇−P in a stream of HCl (50 ppm in He). The baselines were calibrated by a blank experiment. (c) TPD spectra of H₂O (m/z = 18) for La₃Mn₂O₇ and La₃Mn₂O₇−P after purging at 100 °C in He for 1 h. The peaks correspond to (I) desorption of adsorbed molecular H₂O; (II) associative desorption from hydroxyl group clusters; (III) and its trail from vicinal and spaced hydroxyl groups.

Figure 8. Overall conversion rates of DCM ( ), CO₂ (□) and CO (○) over the catalysts (a) La₃Mn₂O₇ and (b) La₃Mn₂O₇−P in DCM oxidation with 1.5 vol % water vapor.
The water clusters (denoted as Type IV) interacting via hydrogen bonding would be removed during sample pretreatment step (at the 100 °C), which did not appear in the H2O-TPD profile.

Accordingly, the H2O desorption peak(s) centered ca. 120–220 °C in the HCl-TPSR profile (Figure 7a,b) should be ascribed to H2O clusters (Type IV) and H2O molecules (Type I), and the peak above 300 °C should be assigned to structural hydroxyl (Type II). According to other studies,50,51 the HCl inclined to dissociate on H2O clusters (n ≥ 4) or interact with H2O molecules via hydrogen bonding. This explained why the HCl would be desorbed with water simultaneously. In the H2O-TPD profile, it was also noted that the La3Mn2O7–P produced larger amounts of Type I and Type II H2O than those of the La3Mn2O7. The former should be mainly from "zeolitic" water,24,31 residing in the LaPO4·0.5H2O structure and the hydrogen bonding (with the oxygen of H2O molecule) at Brönsted acidic sites.

3.8. Water Vapor Effect. As either the H2O molecules or hydroxyl groups (~OH) could promote HCl desorption, it is likely that additional water vapor (which exists in many industrial waste gases) might be able to inhibit the catalyst chlorination by facilitating HCl desorption. Indeed, as shown in Figure 8, with the addition of 1.5 vol % vapor, the values of T30 of DCM conversion in La3Mn2O7 and La3Mn2O7–P were both effectually reduced to approximately 300 °C, which was nearly 85 °C lower than those in dry condition. As the temperature increased, La3Mn2O7 exhibited a plateau in DCM conversion up to 450 °C and La3Mn2O7–P showed a consistently increasing activity. The latter yielded the T90 of DCM conversion at approximately 380 °C and no obvious deterioration was observed after repeated usage in four runs (SI Figure S11). This activity is comparable to that of the Pt/CeO2–Al2O3 catalyst reported in the literature.52

The additional water vapor increased the concentration of molecular H2O and hydroxyl groups (~OH, via the dissociation of H2O on M-(OH)n sites, that is, acid–base centers according to Gun’ko et al. and Yin et al.49,53) which favored HCl formation and desorption. This was consistent with many other studies,12,54 which all demonstrated that the addition of H2O could lead to the generation of more HCl in CVOC oxidation. As such, the catalyst chlorination could be inhibited, thus enabling the catalytic activity in DCM oxidation to be maintained.

To verify the cause of the plateau in DCM conversion in the La3Mn2O7 catalyst, another H2O-TPD measurement was conducted in which the catalyst was preheated at 500 °C for 1 h and then rehydrated at 100 °C for 1 h.

As shown in Figure 9a, La3Mn2O7 exhibited a lack of Type I H2O and was inclined to form a stable hydroxyl layer on the surface. The ~OH species appeared to be uniformly distributed as both Type II and Type III H2O revealed a plateau-like desorption curve. As reported,55,56 the reactivity of hydroxyl groups in the vicinity of Cl determined the reaction rate for HCl formation. Therefore, the stable hydroxyl layer would impair the formation of HCl and the subsequent desorption from the La3Mn2O7, leading to the occurrence of a plateau in DCM conversion. This plateau would diminish until the reaction between Cl and hydroxyl groups recovered at a high temperature (herein, ca. 450 °C for La3Mn2O7, Figure 8).

In La3Mn2O7–P, the presence of "zeolitic" channels in LaPO4·0.5H2O would be able to store the additive vapor, and the proton in the Brönsted acidic sites could activate the vapor (via formation of H3O+ or H5O257). As such, the Type I H2O in the La3Mn2O7–P is distinct, which ensured sufficient H and H2O molecules react with dissociated Cl and desorb the HCl, respectively. Moreover, the Brönsted acidity in the La3Mn2O7–P catalyst might be capable of hydrolyzing the intermediates (i.e., chloromethoxy group) and further prevent the chlorination of the catalyst.58

It was also found that further increasing the amount of additive water to 5 vol % did not cause obvious deactivation in DCM oxidation for the La3Mn2O7–P catalyst (SI Figure S12). The catalyst could retain high DCM conversion after aging at 340 °C for approximately 850 min in the presence of 5 vol % H2O. This result revealed an excellent water-resistant ability of the catalyst, making it very promising for use in industrial applications (Figure 9b).

## ASSOCIATED CONTENT

* Supporting Information

Catalyst syntheses and characterizations, DCM-TPSR analyses, HCl generation curves and light-off curves in repeated runs (PDF)

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The authors declare no competing financial interest.

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References


(24) Colomer, M. T.; Mosa, J. Thermal evolution, second phases, and sintering behavior of LaPO4·nH2O nanorods prepared by two different chemical synthesis routes. Ceram. Int. 2015, 41 (6), 8080–8092.


(28) Zhao, B.; Ran, R.; Sun, L.; Guo, X.; Wu, X.; Weng, D. NO catalytic oxidation over an ultra-large surface area LaMnO3+δ perovskite synthesized by an acid-etching method. RSC Adv. 2016, 6 (74), 69655–69660.


(31) Mesbah, A.; Clavier, N.; Elkaim, E.; Szenknect, S.; Dacheux, N. In pursuit of the rhabdophane crystal structure: from the hydrated monoclinal LaPO4·0.667H2O to the hexagonal LaPO4 (Ln = Nd, Sm, Gd, Eu and Dy). J. Solid State Chem. 2017, 249, 221–227.


(40) Afanasiev, P. Non-aqueous preparation of LaPO₄ nanoparticles and their application for ethanol dehydration. RSC Adv. 2015, 5 (53), 42448–42454.


