

Research progress of molecular sieve supported catalysts in catalytic oxidation of chlorine-containing volatile organic compounds

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Abstract: Chlorinated Volatile Organic Compounds (CVOCs) come from a wide range of sources and are common precursors of PM_{2.5} and ozone pollution, which pose a serious threat to the environment and have adverse effects on human health. Catalytic degradation is one of the effective methods to solve CVOCs pollution, which has the advantages of low operating temperature, less chlorine-containing by-products and high degradation efficiency. The core of this technology is to design and develop catalyst materials with excellent stability and catalytic performance. At present, molecular sieve catalysts have attracted extensive attention because of their acidity and unique pore structure. In this paper, the current research status of catalysts supported by molecular sieve, such as noble metals, transition metal oxides and perovskites, and their activity, acidity, stability and selectivity in CVOCs catalytic reactions were summarized and analyzed, and the future development direction of CVOCs molecular sieve supported catalysts was prospected.

Keywords: CVOCs; Molecular sieve; Catalytic oxidation; Synergistic effect; Catalyst

1. Introduction

Volatile Organic Compounds, (VOCs) are all kinds of organic compounds that exist in the air in the form of vapor at room temperature with boiling point of 50°C to 260°C. Chlorinated volatile organic compounds (CVOCs) are volatile organic compounds with one or more chlorine atoms, which are highly stable and difficult to degrade. CVOCs are important precursors of PM_{2.5} and ozone pollution. Under the irradiation of high temperature and ultraviolet rays, their concentrations rise sharply, forming photochemical smog, which leads to low atmospheric visibility, poor breathing of organisms, muscle weakness and even paralysis [1-3]. The sources of CVOCs are extensive, and industrial sources account for the largest proportion. Common CVOCs, such as dichloromethane (DCM), chlorobenzene (CB), vinyl chloride (VC) and dichloroethane (DCE), are mostly by-products produced by organic solvents and thermal conductivity liquids from industrial sources[4]. At present, CVOCs have been listed as key pollutants by many countries in the world, and the first 12 persistent organic pollutants in the international treaties of the United Nations environmental projects are all chlorine-containing organic compounds[5]. In addition, dichloromethane, chloroform, trichloroethylene and tetrachloroethylene are all listed in the List of Toxic and Harmful Air Pollutants issued by China in early 2019. Therefore, it is urgent to control the CVOCs problem. At present, catalytic oxidation is one of the most common means for the degradation of CVOCs. However, in the combustion process of CVOCs, if the incineration temperature is lower than 800°C, chlorine atoms are prone to incomplete combustion, producing highly toxic by-products such as dioxins, which are highly carcinogenic to organisms[6, 7]. If CVOCs cannot be effectively adsorbed on the catalyst, the C-Cl bond will be incompletely broken, and chlorine-containing by-products will be produced, which will poison and deactivate the catalyst[8], but the acid site of Brønsted can improve the adsorption of CVOCs on the catalyst. Based on the above characteristics, the design core of chlorine-containing volatile organic compounds catalyst is to organically combine surface acidity and redox ability. At present, the catalyst design for CVOCs includes

noble metals, transition metal oxides and perovskite catalysts. In view of the particularity of chlorine species in chlorine-containing pollutants, these single catalysts cannot completely eliminate CVOCs, and the catalytic oxidation effect is inferior to that of molecular sieve supported catalysts, because molecular sieve supported catalysts can have both the characteristics of single catalysts and the excellent acidity of molecular sieves. In this study, the design schemes of supported catalysts based on molecular sieves in recent years are reviewed, the formation of by-products in oxidation reaction of CVOCs and the causes of catalyst deactivation are analyzed, and the future development trend of catalytic oxidation technology of CVOCs is prospected.

2. Molecular Sieve Catalysts

Molecular sieves mainly include X-type, Y-type and HZSM-5, all of which have large pore size, specific surface area and good acidity. Adjusting the particle size of molecular sieve can effectively adjust its diffusion performance and acidity performance, thus improving its catalytic performance[9]. Among them, X-type molecular sieve has strong Brønsted acid sites. Y-type molecular sieve has strong Brønsted acid sites, good thermal stability, high adsorption and catalysis, and high activity and selectivity for the degradation of CVOCs[10]. HZSM-5 molecular sieve is rich in Lewis acid sites and Brønsted acid sites, which can crack CVOCs into small molecular organic compounds, make chlorine atoms react with protons at acid sites, and then dechlorinate, effectively inhibiting the formation of chlorine-containing by-products[11]. Therefore, X-type, Y-type and HZSM-5 molecular sieves are widely used in the catalysis of CVOCs.

2.1. Molecular sieve supported noble metal catalysts

Nobel metal catalysts such as Pd, Pt, Ru, Ce, etc., have low ignition temperature, complete combustion, high activation ability for hydrocarbon molecules, rapid removal of chlorine atoms, and high product CO₂ selectivity, and are often used in the catalyst design of CVOCs[12]. However, the acidity of the carrier is not conducive to the dispersion of noble metal catalysts, and the molecular sieve supported noble metal catalysts can use the interaction between them to prevent the sintering and agglomeration of noble metals and maintain the catalytic characteristics of noble metals and molecular sieve catalysts[13].

2.1.1. Molecular sieve supported Pt catalyst

Pt has remarkable reducibility at low temperature and has been successfully popularized and applied in business. However, Pt is expensive and easily attacked by chlorine atoms, which leads to carbon deposition[14]. In order to study the performance of molecular sieve supported Pt catalyst, Li et al. [15] began to study the stability, durability, toluene conversion and CO₂ production of molecular sieve supported Pd catalyst. The results, as shown in Fig. 1, demonstrate that molecular sieve supported Pt catalyst is more beneficial to the catalytic oxidation of toluene, in which Pt/Beta-260 catalyst completely oxidizes toluene to CO₂ at about 160°C (Fig. 1 (a)). What is more noteworthy is that after a period of time, the toluene conversion rate and CO₂ production remained stable at T_{50%} and T_{90%} (Fig.1 (b)and(c)), and the catalytic activity of toluene was improved when steam was introduced (Fig.1 (d)and(e)and(f)), which indicated that the addition of molecular sieve could improve the carbon deposition phenomenon caused by Pt catalyst.

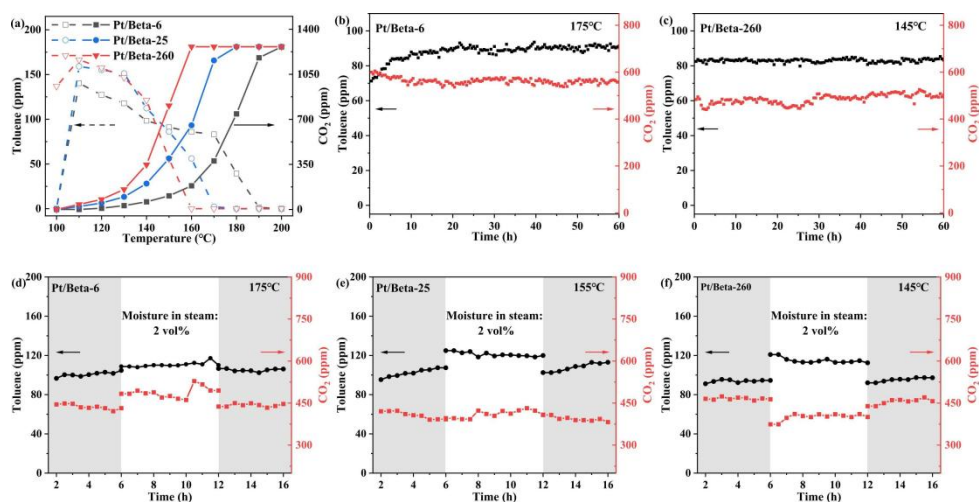


Fig.1. Bate molecular sieves with different Si/Al ratios supported Pt:(a)Toluene conversion and carbon dioxide production vary with temperature; (b),(c)Catalyst durability; (d),(e),(f)Toluene conversion and carbon dioxide production vary with 2v% steam[15]

Adding other metal modified molecular sieves supported Pt catalyst can further promote the dissociation and deep oxidation of CVOCs and reduce the formation of chlorine-containing by-products. Wang [16] found that the higher the proportion of $\text{CeO}_2\text{-ZrO}_2$, the better the dispersion state of Pt particles, and the $T_{90\%}$ value of Pt/CeZr/HZSM-5 catalyst for DCE can be reduced by about 110°C compared with that of Pt/CeZr catalyst, which shows that most Pt particles on Pt/CeZr/HZSM-5 catalyst can be dispersed in CeZr, and cooperate with molecular sieve to improve the mobility of active oxygen species on $\text{CeO}_2\text{-ZrO}_2$ and increase the number of active oxygen species. Su[17] et al. doped a small amount of Pt with 20% Co and loaded it on HZSM-5, and found that $T_{90\%}$ at this time was 67°C lower than Pt with the same mass fraction and 42°C lower than Co with the same mass fraction. Moreover, the chlorine-containing by-product produced in the process of catalytic oxidation of DCM by this catalyst is only CH_3Cl . It shows that under the synergistic effect of the three factors, Co can effectively anchor Pt atoms and realize the monoatomic dispersion of Pt, and DCM is completely oxidized by Pt and Co after being adsorbed on the acidic site of HZSM-5 molecular sieve.

2.1.2. Molecular sieve supported Pd catalyst

Pd has attracted much attention in the catalyst design of CVOCs because of its high activity and thermal stability[13]. When the same noble metal is supported on different carriers, it shows different catalytic activities and has a significant impact on the distribution of Cl by-products. Li et al. [18] used Pd as the catalytic active center and ZSM-5, $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 as carriers respectively, and found that HZSM-5 molecular sieve was the best catalyst. Moreover, the PhCl_x concentrations of Pd/ZSM-5(25) and Pd/ $\gamma\text{-Al}_2\text{O}_3$ are higher than those of Pd/ZSM-5(200) and Pd/ SiO_2 . The key point is that the Si/Al ratio can affect the Lewis acidity in the carrier. The lower the Si/Al ratio, the stronger the Lewis acidity in the carrier, which is more conducive to the adsorption of chlorinated organic molecules on the catalyst surface. However, at 600°C , the chlorine concentration in Pd/ZSM-5(25) catalyst product was about 700ppm, while the initial chlorine concentration was about 900ppm, which indicated that Cl deposited or formed polychlorinated organic by-products on the catalyst surface, and with the increase of temperature, the chlorination degree of organic by-products became higher and higher.

Compared with the single catalyst of molecular sieve, the catalytic performance of catalytic oxidation of DCM with trace Pd supported on molecular sieve is greatly improved. R et al. [19] studied Pd/HZSM-5, and found that the $T_{50\%}$ of the catalytic oxidation of DCM by Pd/HZSM-5 decreased significantly compared with the $T_{50\%}$ at the homogeneous catalysis, and the selectivity of oxidation products Cl_2 and CO_2 increased from 40% and 60-70% when HZSM-5 was only added to 70-80% and 80-90%.

2.1.3 Molecular sieve supported Ru catalyst

Compared with other noble metals, Ru is cheaper, has good stability in catalytic oxidation of CVOCs, has high conversion rate of CVOCs, and can convert HCl into Cl₂ for removal in Deacon reaction, which has good chlorine resistance and can reduce environmental pollution[20].

Different molecular sieves loaded on the same active center show different catalytic activities. Chen[21] conducted XRD tests on Ru/m-HZSM-5, Ru/m-HTS-1 and Ru/m-HSilicate-1, and found that the diffraction peaks of the three catalysts were highly consistent with those of MFI molecular sieve, and the crystallinity was good. Only Ru/m-HZSM-5 had two NH₃ adsorption peaks by NH₃-TPD test. In the process of DCM catalysis, the temperatures reaching T_{50%} and T_{90%} are 260°C and 299°C, respectively, which are lower than those of Ru/m-HTS-1 and Ru/m-HSilicate-1. It shows that Al contained in the catalyst can easily enter the molecular sieve skeleton, replacing Si atoms to make the skeleton charge uneven and form hydroxyl groups, which enables m-HZSM-5 strong acidity and optimal activity, and still have good catalytic performance at high temperature.

Adding a small amount of noble metal or transition metal oxide into Ru catalyst supported on molecular sieve to form noble metal/transition metal oxide -O-Ru structure can improve the catalytic activity (Fig. 2 (a)), characterize the activity (Fig. 2 (b)) and maintain the stability of the catalyst (Fig. 2 (c)). In the H₂-TPR spectrum recorded by Wang et al.[22], with the increase of Ru content, the area of the first reduction peak also increases. And when Pt₁/HZSM-5 catalyzes CVOCs, the reduction of oxygen mainly concentrates at 311°C and 345°C, which is 175°C higher than that of Pt_{0.5}Ru_{0.5}/HZSM-5. At the same time, the T_{50%} when Pt_{0.5}Ru_{0.5}/HZSM-5 catalyzes CB is about 234°C, which is lower than that when Pt₁/HZSM-5 and Ru/HZSM-5 catalyze CB. It is worth noting that when the conversion rate of CB is less than 20%, the oxidation reaction of CB shows that the activation energy (E_a)Pt_{0.5}Ru_{0.5}/HZSM-5(23kJ/mol) is easier to achieve than Pt₁/HZSM-5(50kJ/mol). Thanks to the Pt-O-Ru structure, Pt_{0.5}Ru_{0.5}/HZSM-5 catalyst can generate available surface oxygen with high mobility (which plays a leading role in oxidizing CB and removing Cl), and has high toxicity to Cl, which can promote the activation of gaseous oxygen into surface active oxygen and increase the catalyst activity. Chen et al. [21]observed by HRTEM and EDS mapping technology that CeO₂ existed in the form of tiny particles during the reaction of CeRu@m-HZ catalyst, which could be coated in the molecular sieve framework and fully enter the internal pores to form the Ce-O-Ru structure. H₂-TPR technology was used to explore the redox of the catalyst. It was found that the first reduction peak in the range of 100~240°C was Ru/HZSM-5, and the catalytic temperature was 179°C higher than CeRu@m-HZ(153°C). The catalytic performance of the catalyst was tested under the conditions of 600ppm DCM and GHSV = 25,000 ml/(g h). In addition, CeRu@m-HZ still has excellent catalytic activity between 100°C and 200°C. The results show that the Ce-O-Ru interface in CeRu@m-HZ catalyst can enhance the electron transfer ability on the catalyst surface and the circulation of oxygen species, and reduce the formation of by-products in the oxidation process.

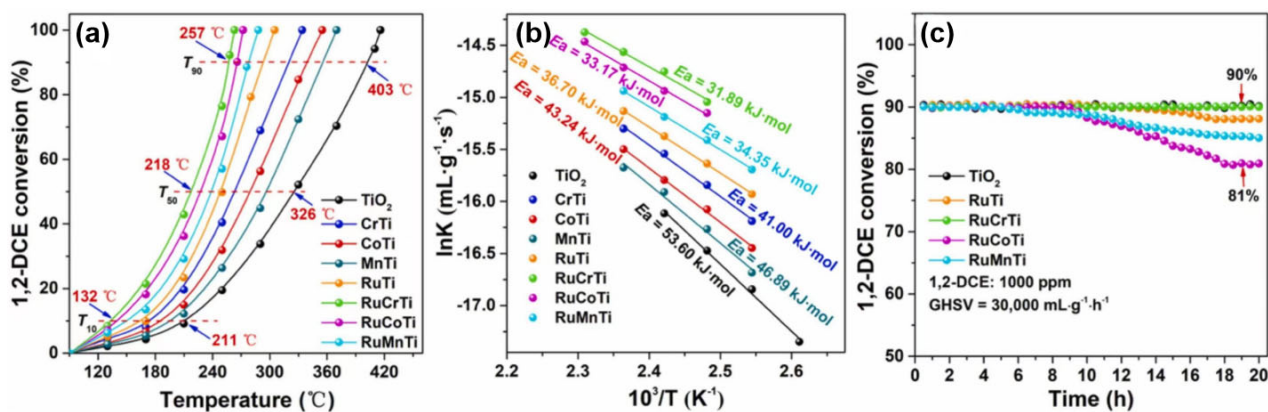


Fig.2. (a)1, 2-DCE catalytic activity under different catalysts; (b)activation energy of different catalysts; (c)Stability of 1, 2-DCE decomposition with different catalysts[23]

2.2. Molecular sieve supported transition metal oxide catalysts

Transition metal oxides mainly include Ce, Mn, Cu, Fe and Co. They can break the C-Cl bond during the catalytic oxidation of CVOCs, and have strong catalytic activity for CVOCs. After repeated use, they still maintain good catalytic activity, can reduce the use cost of the catalyst, and resist the poisoning caused by intermediate products or impurities produced during the catalytic oxidation of CVOCs. In recent years, they have become the research focus of CVOCs catalytic oxidation. Compared with noble metals, transition metal oxides are cheaper and more practical, so researchers began to study transition metal oxides step by step, hoping to design a substitute for noble metals or a catalyst superior to noble metals[24].

2.2.1. Molecular sieve supported Ce catalyst

In the process of catalytic oxidation of CVOCs, Ce has attracted wide attention of researchers because of its excellent redox property and strong oxygen storage capacity. The USY molecular sieve supported Ce catalyst combines the strong oxidation of Ce with the acid center on the surface of molecular sieve, which can inhibit the formation of chlorine-containing by-products and improve the selectivity of CO₂. Wang et al.[25] found that the catalytic oxidation ability of USY molecular sieve supported Ce catalyst for DCE was significantly higher than that of USY and CeO₂ alone, and it gradually increased with the increase of Ce content. According to the research results of pyridine adsorption infrared technology, Ce doping can enhance the Lewis acid characteristic band (1455cm⁻¹) and Brnsted acid characteristic band (1545cm⁻¹), that is, enhance the Lewis and Brnsted acid sites on the catalyst surface, improve the adsorption of DCE, and reduce the T_{max} (reaching the maximum concentration temperature) values of intermediate products CH₃Cl and C₂H₃Cl.

The synergistic effect among supported catalysts will affect the redox performance of catalysts, product selectivity, substrate conversion rate and so on. Huang et al. [26]found that under the condition of 360°C, CeO₂-USY catalyst can completely convert DCE, and when T_{90%}, the conversion rate of CeO₂/USY (1: 8) (245°C) is the highest, followed by CeO₂-USY(8:1)(273 °C)、USY(310 °C)、CeO₂(334 °C) respectively. By analyzing the intermediates of DCE oxidation under different catalysts, it was found that the T_{max} of the intermediates C₂H₃Cl, CH₃CHO and CH₃COOH was lower than that of CeO₂. The TPSR method confirmed that the amount of CO₂ and HCl produced by CeO₂-USY catalyst was higher than that by USY catalyst (Fig.3 3.). It shows that CeO₂-USY catalyst has higher selectivity for CO₂ and HCl, which is more conducive to the migration of oxygen.

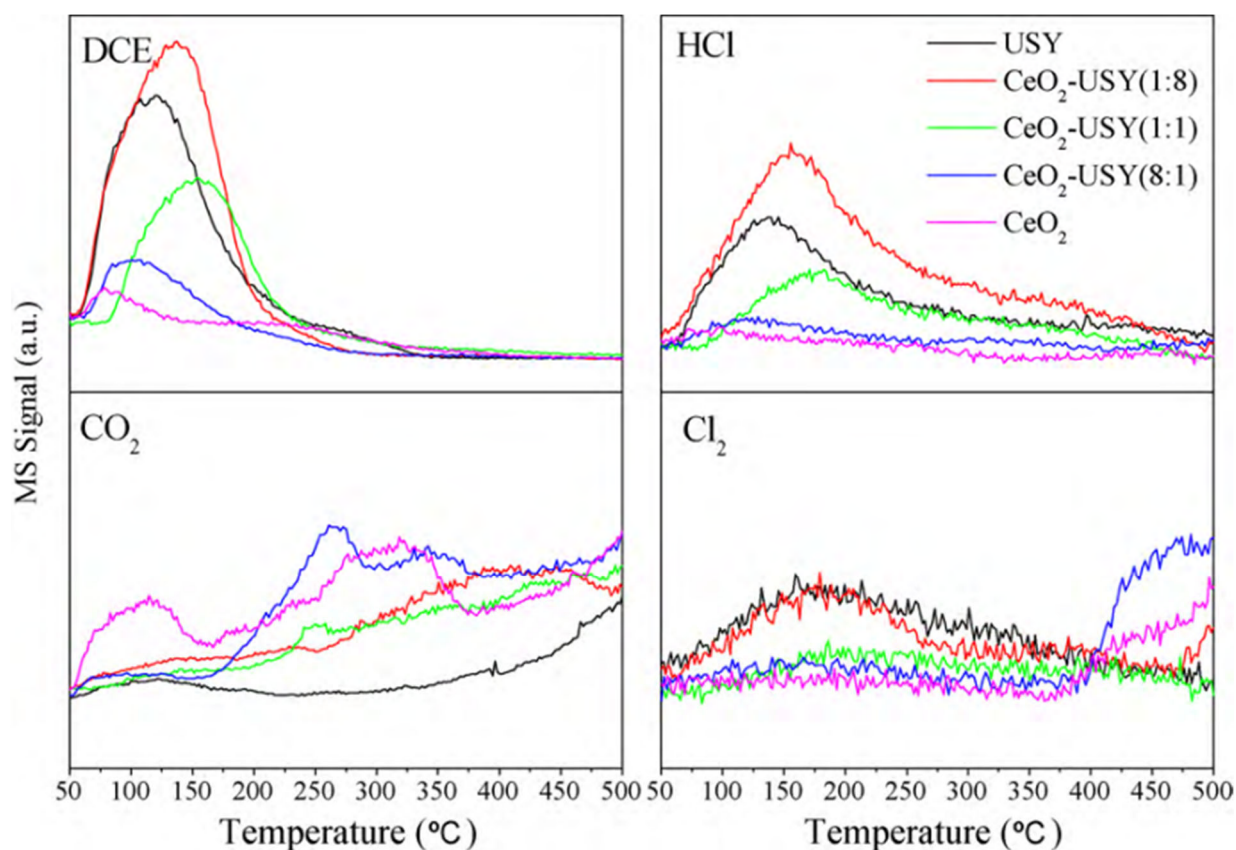


Fig.3. TPSR spectra of DCE decomposed on USY, CeO₂ and CeO₂-USY catalysts [26]

The doping of trace noble metals can promote the catalytic effect of molecular sieve supported Ce catalyst. Liu et al. [27] studied the combustion of DCM on $Ce_yV_{1-y}O_x/HZSM-5$, and found that when the molar ratio of Ce to V was 0.7: 0.3 and the temperature was 325 °C, DCM was almost completely transformed, and the selectivity of Cl₂ reached 7.1%. When the loading capacity is 15%, the conversion rate of dichloromethane reaches 98.5%, and most of Cl is converted into HCl. At 400 °C, 15% $Ce_yV_{1-y}O_x/HZSM-5$ can continuously catalyze DCM for 300 h, and the conversion rate of DCM is always above 95%, with a Cl₂ selectivity of 98.3%. It shows that doping a small amount of V into Ce-HZSM-5 can improve DCM conversion, CO₂ selectivity, catalyst stability and acidity.

The ratio of different substances in the same carrier has a significant effect on the catalytic activity of the catalyst. Qian et al. [28] conducted DCE oxidation experiments for different molar ratios of Cr and Ce, and found that Cr-Ce/H-MOR was the best ratio of activity, and its T_{90%} was 279.4 °C, which was lower than the temperature of other catalysts when T_{90%} was used. BET and SEM showed that the peak value of oxygen consumption of 2.5%Cr/H-MOR catalyst for trichloroethylene (TCE) shifted to low temperature after adding Ce crystal. Zhou et al. [29] characterized by NH₃-TPD and found that Cr-Ce/H-MOR had a certain strong acidity. After the catalyst was regenerated, TCE was oxidized, and the conversion rate of TCE was still about 88.6%, and its stability and reactivity were higher than those of pure Cr₂O₃ or pure CeO₂ catalyst. It is proved that the interaction between Ce and Cr can improve the stability of catalyst, oxygen fluidity and catalytic oxidation ability of TCE.

2.2.2 Molecular sieve supported Mn catalyst

As a transition metal oxide, Mn gene has a great research prospect in CVOCs catalytic oxidation because of its excellent redox property and fast lattice oxygen migration rate [30]. Mn has many valence states, such as +2, +3, +4, +7, and manganese-containing oxides include Mn₃O₄, Mn₂O₃ and MnO₂, etc. The loading capacity of MnO_x can increase the number of acidic sites and active

oxygen on the catalyst surface, and promote the adsorption and oxidation of CVOCs on the catalyst surface[31], among which MnO₂ has the highest catalytic activity. In the process of oxidation of CVOCs, manganese catalyst can follow Mars-Van Krevelen mechanism (substances are adsorbed on the catalyst surface and oxidized by lattice oxygen on the catalyst surface), which shows that manganese catalyst has a large specific surface area, many defect sites and good redox property[32]. However, deactivation may occur when single manganese is used as catalyst, and Mn supported on molecular sieve can reduce the weakness of single manganese as catalyst.

The structure, ion types and properties of the carrier have an impact on the redox and acidity of the catalyst, thus affecting the performance of the catalyst. Shi[33]observed the first H₂ reduction peak, and found that the lowest reduction peak temperature of different molecular sieve supported manganese catalysts was different, among which Mn/ZSM-5 had the lowest reduction peak temperature (367°C) and the strongest redox ability. When T_{90%} in the activity diagram of catalytic oxidation of 1, 2-DCE, the temperature of Mn/ZSM-5 in each molecular sieve supported manganese catalyst is also the lowest and the activity is the strongest. In addition, Shi also investigated the yield of CO₂ and HCl. Relevant data showed that Mn/ZSM-5 catalyzed the oxidation of 1, 2-DCE with the highest yield of CO₂ and HCl, reaching 83% and 100% at 500°C. Comprehensive characterization and analysis show that Mn/ZSM-5 contains a large number of Mn³⁺ (main active sites), strong acidity, more oxygen adsorbed on the surface and special three-dimensional cross-channel structure, which are beneficial to the catalytic oxidation of chlorine-containing volatile organic compounds.

Chang et al.[34] studied the catalytic performance of Mn-Ce/HZSM-5, MnO_x/HZSM-5 and CeO₂/HZSM-5 for the oxidation of trichloroethylene (TCE), and found that Mn-Ce/HZSM-5 had the strongest catalytic activity. With different Ce/Mn catalysts, the ratio of TCE increases gradually from 0.4 to 1.2, and the catalyst activity first increases and then decreases, reaching the peak at 0.8, that is, the removal rate of TCE reaches 97.6% and the selectivity of CO₂ reaches 96.7% at 500°C. H₂-TPR analysis of Mn-Ce/HZSM-5 shows that the catalyst has two broad peaks, the reduction temperature is lower than that of MnO_x and CeO₂, and the removal rate of TCE and CO₂ selectivity remain unchanged at 77% and 70% throughout the catalytic oxidation stage. Through the above series of experimental studies, it is shown that the synergistic effect between Mn and Ce accelerates the migration of oxygen, accelerates the formation of active oxygen through the adsorption of oxygen by oxygen vacancies and active metal sites and the transformation of lattice oxygen species, thus improving the stability of the catalyst and promoting the deep oxidation of TCE, and finally generates the final products CO₂ and H₂O through the action of active oxygen on the catalyst surface.

2.2.3 Molecular sieve supported Cu catalyst

As one of the important catalysts used in the catalytic oxidation of CVOCs, Cu has low temperature oxidation reducibility, low toxicity and high selectivity. However, during the catalytic oxidation of CVOCs, the Cu catalyst is easily deactivated by chlorine atoms. Banerjee et al.[35] found that the synergistic effect of Cu ions and BETA can improve the catalytic activity of catalytic oxidation of TCE. More researchers [36-38] chose molecular sieve mixed with Cu, and oligomeric copper and Cu²⁺/Cu⁺ as the dominant species of Cu can convert CH₂Cl₂ into HCl, which can avoid catalyst chlorine poisoning. However, with the increase of Cu content, the proportion of massive CuO_x increased. In the process of DCM reaction, massive CuCl_x and Cu_x(OH)_yCl are generated during chlorination of massive CuO_x, which leads to the rapid deactivation of the catalyst at the initial stage of the reaction (Fig.4).

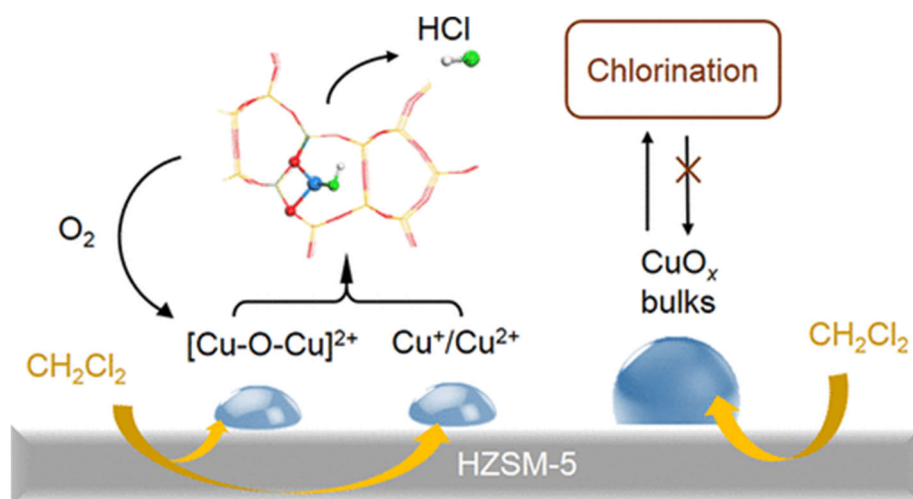


Fig.4. Cu/HZSM-5 Catalytic oxidation mechanism[38]

There are significant differences in stability and oxidation of Cu/HZSM-5 catalysts with different contents. Liu et al. [38] explored the activity of Cu/HZSM-5 catalysts with different contents at the same temperature, and found that the activity of Cu/HZSM-5 increased with the increase of Cu content, and the activity of Cu/HZSM-5 catalysts with different contents decreased rapidly at first and then stabilized with time. The conversion rate of DCM was the highest at 2.5Cu/HZSM-5, and it remained at 90% at 180°C. In the UV-vis-DR spectrum of Cu/HZSM-5 catalysts with different contents, the content of copper oxide on the surface of 10Cu/HZSM-5 is the highest, and the reduction peak of CuO crystal gradually increases with the increase of Cu content from 2.5% to 10wt% (Fig.5. (a) and (b)). 2p XPS spectrum shows that CuO crystal and Cu ion coexist in 10Cu/HZSM-5. As a catalyst, Cu can resist chlorine poisoning due to the fact that the oligomeric copper and $\text{Cu}^{2+}/\text{Cu}^+$ obtained in the catalytic process can release chlorine in the form of HCl. However, large Cu crystals will be attacked by Cl, forming by-products such as copper chloride. Under low copper loading, Cu/HZSM-5 may also lack redox ability due to coke deposition, so the research on Cu/HZSM-5 catalyst needs to be improved.

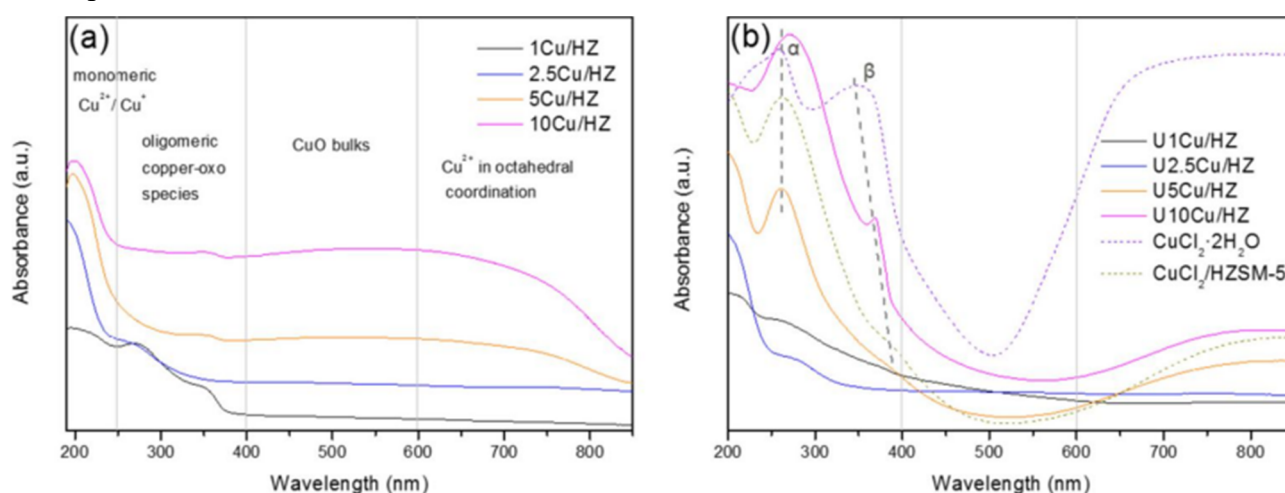


Fig.5. UV-vis-DR spectra of modified HZSM-5 with different copper contents before (a) and after (b) reaction with DCM at 320°C for 3h[38]

Researchers added other transition metal oxides to Cu/HZSM-5 catalyst to solve the problem of easy deactivation of Cu/HZSM-5. Wang et al.[39] improved the catalytic oxidation performance of CuCr/HZSM-5 for TCE by metal organic chemical vapor deposition, and found that the highest conversion rate of TCE was 90% at 338°C, which was significantly lower than that of the

intermediate products C_2Cl_4 of Cu/HZSM-5 and Cr/HZSM-5, but it could solve the problem that Cu/HZSM-5 was quickly inactivated at the initial stage of the reaction due to high copper content.

The doping of copper oxide can promote the stability, acidity, redox and DCE conversion of CeO_2 -USY catalyst. Huang et al.^[40] found through NH_3 -TPD spectrum analysis that when CuO- CeO_2 -USY was used as catalyst, the peak b moved to a low temperature range and a third reduction peak with weak and strong acidity appeared in a higher temperature range. The reduction peak-to-peak temperature of CuO-USY in H_2 -TPR curve is higher than that of CuO- CeO_2 -USY. Compared with CeO_2 -USY, the reduction peak-to-peak values of surface oxygen and volume oxygen of CuO- CeO_2 -USY move to a lower temperature range. After adding CuO and CeO_2 into USY catalyst, the analytical strength of TCE is enhanced and the peak of analytical peak moves to a higher temperature, and CO_2 can be seen when the temperature is as low as $250^\circ C$. After USY catalyst was used for 100h, the conversion rate of DCE decreased directly from 87% to 27%. After adding CuO and CeO_2 , the conversion rate of DCE could be kept above 70%, which was higher than that when CeO_2 -USY was used as catalyst. It can be inferred that the addition of CuO and CeO_2 in USY leads to the decrease of total acidity, but the strong acid sites and acidity increase, and the redox property is also enhanced, which can promote the improvement of TCE adsorption-desorption-catalysis process and the enhancement of CO_2 selectivity. Moreover, as a catalyst, CuO-USY is often deactivated due to coke deposition, and CuO- CeO_2 -USY catalyst can effectively inhibit the generation of coke and let the catalyst have good catalytic activity.

2.2.4 Molecular sieve supported Fe catalyst

Fe in molecular sieve supported Fe catalyst can enter the outer framework of molecular sieve, which improves the degradation of TCE by the molecular sieve[41]. Duraiswami Divakar et al.[42] studied Fe/HZSM-5 by impregnation method. Under the same conditions, the initial conversion of TCE with Fe/HZSM-5 catalyst was 88%, higher than that with HZSM-5. After 14 h of reaction, the conversion of TCE with Fe/HZSM-5 was 75%, and the conversion of HZSM-5 was only 10%. It shows that Fe/HZSM-5 has certain stability and activity, which reduces the $T_{50\%}$ of HZSM-5 by $125^\circ C$ and improves the stability by 51%, thus alleviating the problem of coke deposition when pure HZSM-5 is used as catalyst[43].

Compared with ordinary Fe/HZSM-5, microfiber composites have larger specific surface area and porosity, and the three-dimensional structure can increase the contact area and improve its heat transfer. This material was used to combine Fe/HZSM-5, which was studied by Chen et al.^[44]. It was found that 10% Fe/HZSM-5 can exert its highest activity under CVD method, showing lower $T_{90\%}$ and chlorination by-product selectivity, adsorbing trichloroethylene, promoting the fracture of C-Cl bond, and degrading intermediate products through iron oxide.

2.2.5 Molecular sieve supported Co catalyst

The oxides of Co mainly include Co_3O_4 , Co^{3+} with octahedral coordination and Co^{2+} with tetrahedral coordination, among which Co^{2+} is easily oxidized by oxygen to form chemisorbed oxygen, which reacts with CVOCs to generate deep oxidation products. Moreover, the bond energy of Co-Cl is 117KJ/mol, which is lower than that of metal oxides such as V-Cl, which is more conducive to the transfer of Cl on the catalyst surface[45].

Single catalyst has a certain oxidation effect on DCM, but its effect is generally inferior to that of supported catalyst. In the spectrum recorded by Zhang et al.[46], compared with the pure Co_3O_4 catalyst, the Alg band of the Co_3O_4 /ZSM-5 ratio shifts to a lower frequency, and the analytical peak is about $550^\circ C$, which is lower than that of the pure Co_3O_4 catalyst. During the oxidation process, DCM will be adsorbed by acid sites on the surface of molecular sieve, and chlorine atoms will be removed in the form of HCl. According to NH_3 -TPD spectrum, compared with other samples, Co_3O_4 /ZSM-5 has the highest number of acid sites, more Brønsted acid sites, stronger acidity, the most HCl production and the best catalytic performance. The molecular sieve supported Co_3O_4 can completely convert DCM at $480^\circ C$, but the pure Co_3O_4 catalyst cannot

completely convert DCM even at 480°C, and the $T_{90\%}$ of $\text{Co}_3\text{O}_4/\text{ZSM-5}$ is lower than that of other molecular sieves supported Co_3O_4 at 370°C. Different from pure Co_3O_4 catalyst, $\text{Co}_3\text{O}_4/\text{ZSM-5}$ has higher $\text{Co}^{2+}/\text{Co}^{3+}$, can form more highly active O^{2-} and O_2^{2-} , has better lattice oxygen mobility, and can show higher catalytic activity. $\text{Co}_3\text{O}_4/\text{ZSM-5}$ did not detect obvious by-products such as CHCl_3 and CCl_4 in the process of catalytic oxidation of DCM, and it had certain chlorine poisoning resistance.

Yuan et al. [47] prepared $\text{Co}_9\text{CrO}_z/\text{HZSM-5}$ by impregnation method, and found that 30CoCr/HZSM-5 had the highest catalytic activity, while T_{50} and T_{98} were the lowest (183°C and 242°C) (Fig. 6. (b)), and the selectivity for CO_2 reached 95.5% and that for HCl reached 91.6. In NH_3 -TPD spectrum, the total acidity of $\text{Co}_9\text{CrO}_z/\text{HZSM-5}$ is higher than that of pure Co_9CrO_z (Fig.6.(a)). It shows that the synergy of Co_9CrO_z and HZSM-5 makes the catalyst not only have rich surface acidity, which is beneficial to the formation of HCl, but also have high selectivity of CO_2 and HCl, which can show the best effect in the process of catalytic oxidation of VC.

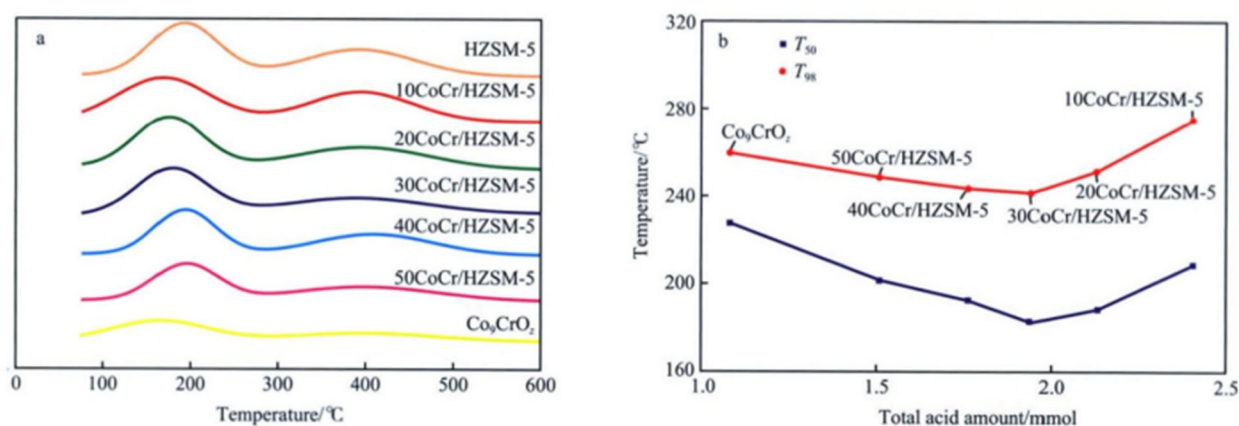


Fig.6. $\text{Co}_9\text{CrO}_z/\text{HZSM-5}$ Series catalysts: (a) NH_3 -TPD spectrogram; (b) T_{50} 、 T_{98} Relationship with total acid content[47]

2.3. Molecular sieve supported perovskite catalysts

In addition to noble metals and transition metal oxide catalysts, perovskite, as a new material, has become a research hotspot at present. As ABO_3 type composite oxide (A refers to alkaline earth metal element, lanthanide or rare earth metal, and B refers to transition metal oxide), perovskite is rich in source, low in price, high in temperature resistance, good in stability and unique in structure. Compared with noble metals and transition metal oxides, perovskite is not easy to be poisoned by carbon deposition and has better stability. Chen[48]found that $\text{Al}_{0.2}\text{La}_{0.8}\text{MnO}$ has strong activity, large specific surface area, high acid strength, low reduction temperature and strong redox ability. $T_{70\%}$ is 330°C and $T_{50\%}$ is lower than that of other $\text{Al}_x\text{La}_{1-x}\text{MnO}$ catalysts. And at the same temperature, the hydrogen consumption of oxidation-reduction CVOCs by $\text{Al}_{0.2}\text{La}_{0.8}\text{MnO}$ is the largest. When DCE is catalytically oxidized at 500°C, only CO_2 , HCl and Cl_2 are produced, and no other chlorine-containing by-products are generated except the unreacted DCE, which inhibits the formation of chlorine-containing by-products to some extent[49]. Up to now, there are few studies on the cooperation of perovskite and molecular sieve as catalysts for chlorine-containing volatile organic compounds, which need further research and discussion by subsequent scholars to prepare perfect catalysts.

3. Reasons for Catalyst Deactivation

Generally, the factors that affect the deactivation of catalyst are crystal pore and structure, carbon black, the amount of chlorine-containing by-products, CO₂, temperature, water vapor, etc.

3.1. Effect brought by crystal channel and structure

The blockage of crystal channels will reduce the catalyst activity. Compared with MnO_x/HZSM-5 and CeO₂/HZSM-5, the peak strength of all Mn-Ce/HZSM-5 catalysts is weakened. This is because Mn and Ce in MnO_x/HZSM-5 and CeO₂/HZSM-5 catalysts exist in the form of oxides, which leads to the blockage of some pore structures, while Mn and Ce in Mn-Ce/HZSM-5 catalysts interact with each other^[9, 50, 51](Fig.7.(a)).

3.2. Effect brought by carbon black

With the step-by-step reaction, the carbon black formed during the reaction is also one of the reasons for the deactivation of the catalyst. With the increase of carbon black content, the required temperature of 0.4Ru-1.0Ce-based catalyst increased gradually at the same conversion rate, indicating that the catalytic activity of the catalyst decreased[52]. 4.0Ce-USY lost 4.7% mass in the range of 350-650°C due to the influence of carbon deposition, and obvious CO signal peak can be detected in the exhaust gas detection[25].

3.3. Effect brought by temperature

High temperature is also one of the important factors affecting the activity of the catalyst. When the temperature of Mn-Ce/HZSM-5 catalyst is higher than 225°C, the conversion of TCE decreases [51](Fig.7.(c)). In the process of DCE catalyzed by CeO₂-USY catalyst, the intermediate CH₃Cl produced by cracking at strong acid sites exists at about 200°C, but when the temperature is above 360°C, CH₃Cl can hardly be detected. This shows that the activity of Mn-Ce/HZSM-5 catalyst decreases at high temperature. The strong acid site on CeO₂-USY catalyst lost its function, and DCE could not be split to produce the intermediate CH₃Cl[26].

3.4. Effect brought by water vapor

Water vapor has a great influence on the catalytic performance of the catalyst. Excessive water vapor will seize the acidic sites on the catalyst, making TCE unable to be adsorbed by the acidic sites and reducing the catalytic oxidation efficiency[34]. As shown in Fig.7.(d), with the increase of H₂O concentration from 1vol.% to 5vol.%, the activity of the catalyst is increasingly lower, and the conversion rate of 1, 2-DCE is also increasingly lower[23].

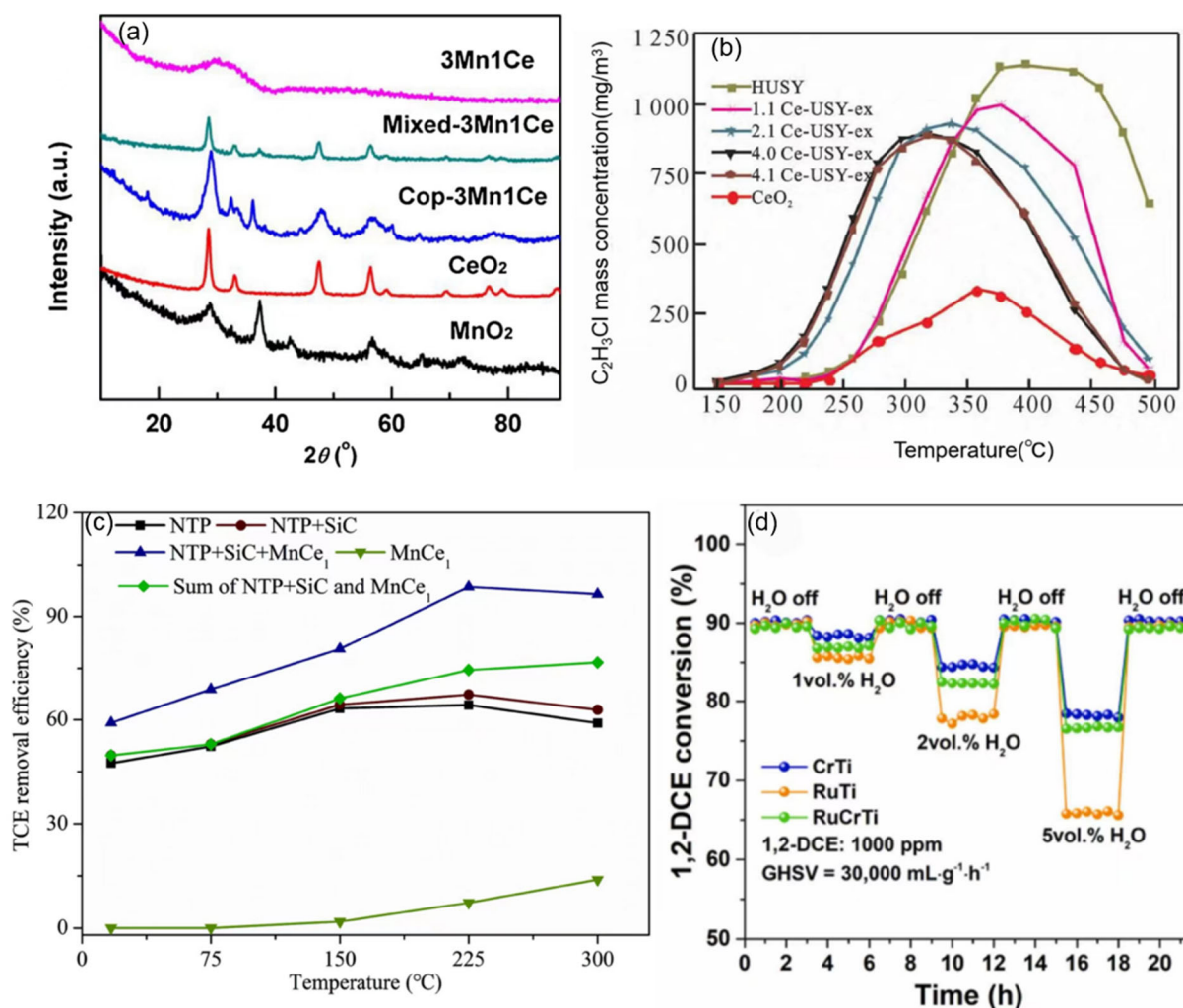


Fig.7. (a)The intensity of different catalysts varies with the lattice[9]. (b)The C₂H₃Cl mass concentration of different catalysts varies with the temperature[26]. (c)The TCE removal efficiency of different catalysts varies with the temperature[9]. (d)The influence of different water vapor on 1, 2-DCE conversion[38].

4. Conclusion and prospect

Catalytic combustion of CVOCs is by far the most common method for the degradation of CVOCs, with low energy consumption, high efficiency and no secondary pollution to the environment under complete combustion. In this paper, the catalysts for chlorine-containing volatile organic compounds are summarized, starting with three kinds of catalysts supported by molecular sieves, namely noble metals, transition metal oxides and perovskite. A series of molecular sieves such as Pt/CeZr-HZSM-5, Pt/H-ZSM-5 and Cr-Ce/H-MOR are discussed in terms of their catalytic activity, redox, acidity, stability, selectivity to CVOCs and HCl, and the formation of chlorine-containing by-products. Although the molecular sieve supported noble metal catalysts have complete light-off, high volatility and strong specific activity, they are expensive and prone to chlorine poisoning. The molecular sieve supported transition metal oxide catalysts have strong catalytic oxidation, which can break C-Cl bond, and its price is low, but they have high toxicity. So far, there is little research on molecular sieve supported perovskite catalysts, but the perovskite itself has high temperature resistance, strong stability and low price.

Although there has been a lot of research on chlorine-containing volatile organic compounds catalysts, there are still some challenges in the efficient catalytic oxidation of CVOCs. It is still a challenge to develop catalysts with strong acid sites, strong chlorine toxicity resistance, strong

redox, strong stability and strong catalytic activity. In the future, we can start from the direction of molecular sieve supported perovskite catalysts and design new catalysts to minimize the harm of CVOCs to the environment. In addition, in the actual industrial treatment, CO_x, NO_x, SO_x, etc. will be released while CVOCs are released. Hence, how to oxidize CVOCs without oxidizing other harmful gases into pollutants is also one of the problems we need to further discuss.

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