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Catalytic combustion of VOCs on non-noble metal catalysts

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ABSTRACT

Volatile organic compounds (VOCs) are toxic and contribute significantly to the formation of the photochemical smog, which has remarkable impact to the air quality; therefore, the research on the removal of VOCs has attracted increasing interests during the last decade. This review covers the recent developments in catalytic combustion of VOCs over non-noble metal catalysts including mixed metal oxide catalysts, perovskite catalysts and Au-containing catalysts. The effect of water vapor, coke formation and the effect of supports on the catalytic combustion process will be discussed. The concept of an adsorption/catalytic combustion dual functional system is introduced and several examples of such systems are evaluated. To develop efficient and cost effective VOC removal technologies, further research in catalytic combustion needs to develop novel non-noble metal catalysts and adsorbents, and improve the understanding of catalytic mechanisms involved.

1. Background

Volatile organic compounds (VOCs) are the major components in air pollutants, which are organic compounds with the boiling points in the range of 50–260 °C at room temperature and atmospheric pressure of 133.322 Pa. VOC pollutants can come from indoor and outdoor sources. Indoor VOCs pollution often originates from household products such as office supplies, insulating materials, cleaning products, and pressed woods, and so on; On the other hand, outdoor VOCs pollution is mainly from emissions of industrial processes and automobile exhausts. VOCs are recognized as major contributors to air pollution because of their toxicity to human health and their involvement in the formation of photochemical smog.

The conventional approach for treatment of high concentration VOC streams is thermal incineration, but incineration has high operating costs, as temperatures exceeding 800–1200 °C are required to achieve complete VOC destruction. Incomplete, or poorly controlled combustion process produces undesirable by-products such as dioxins and nitrogen oxides in the incinerator flue gas. Several alternative VOC removal technologies are available and each technology has practical limitations for different organic compounds, concentrations, and emission sources [1]. For example, low-temperature condensation is energy intensive and limited to treatment of evaporative solvents [2]; biochemical methods are selective and concentration sensitive [3–4]; adsorption-based techniques are favorable for the treatment of highly diluted VOCs [5] but may simply transfer the environmental burden from the gas phase to a solid phase. One of the most effective and economically feasible VOC removal technologies is catalytic combustion [6], because catalytic oxidation can operate with dilute VOCs effluent streams ($<1\%$ VOCs) and at much lower temperatures than conventional thermal incineration. Additionally, catalytic combustion targets destruction of the pollutant compounds rather than transferring the pollutant to another phase, as is the case for condensation and adsorption technologies.

The development of noble metal catalysts and transition metal oxides for catalytic oxidation of VOCs has been widely reported in the literature [7–11]. The review paper published in 1987 by Spivey presents a good overview of catalytic combustion of VOCs [7]. A more recent review, focusing on catalytic combustion of chlorinated VOCs, was published by Everaert and Baeyens in 2004 [9]. This research field continues to be very active and in this paper we describe the progress over the past five years in the development of non-noble metal oxide catalysts for catalytic combustion of VOCs. Advances in mixed oxides, perovskite and gold catalysts will be described, followed by discussions on the effects on catalyst performance of water vapor, coke deactivation, and catalyst support. Finally, dual function adsorption/catalytic combustion systems will be discussed.

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2. Newly developed non-noble catalysts with high activity

Noble metal-based catalysts such as supported platinum and palladium show good activity at low temperatures for the complete oxidation of VOCs. Typical examples include Pd/Mg–Al hydrotalcite [12], Pd/Al_2O_3 [13], Pd/ZrO_2 [14,15] PdO/SnO_2 [16], platinum-containing monolithic carbon aerogels [17], Pt/Al_2O_3 [18,19]. However, the industrial application of platinum and palladium catalysts for VOC control is limited by cost and sensitivity of the noble metal catalysts to poisoning, especially by chlorine/chloride products when oxidizing chlorinated VOCs [20–23]. Thus, non-noble metal oxide catalysts have been considered as low cost alternatives to platinum and palladium. Researchers have looked to improve the oxidation activity, and resistance to poisoning of metal oxide catalysts such as Cu–CuNaHY [24], Cu/Mg/Al hydrotalcites [25], Cu/TiO_2 [26], Zn–Co/Al_2O_3 [27], gold/cerium oxide [28], gold/iron oxide [29], silica-supported U_3O_8 [30], V/$MgAl_2O_4$ [31], Co–Fe–Cu mixed oxides [32], Mn-doped ZrO_2 [6], Fe-doped ZrO_2 [33] and V_2O_5–WO_3/TiO_2 [9].

Although significant progress has been made towards developing non-noble metal oxide catalysts for VOCs combustion, several challenges still require further investigation. For example, chromium trioxide supported on porous carbon is very active [21], but the high toxicity of chromium causes serious catalyst disposal problems. In another example, supported vanadia catalysts offer excellent activity, selectivity, and resistance to sulfur dioxide poisoning [22]. Additionally, vanadia catalysts show good stability in the Cl_2–HCl environment, so they have potential for use in the simultaneous removal of NOx and chlorinated VOCs [9,22], which obviously enhances the economic advantages for the treatment of industrial flue gases. Despite these advantages, the corrosive properties of vanadia catalysts present a problem for their wide spread application, particularly for wet flue gas streams. To overcome the environmental and material handling issues associated with chromium- and vanadia-based catalysts, many novel catalysts have been developed in the past five years to deal with a variety of VOCs from both outdoor and indoor sources. Table 1 lists some of the typical non-noble catalysts as evidence of the possible directions for innovation in this field.

As shown in Table 1, cerium oxide prepared by combustion or precipitation method is very active for the VOCs combustion. Moreover Ce–Zr mixed oxides show an improved performance on the activities. Manganese-based catalysts have also attracted a great attention due to high activity towards total oxidation reactions, low cost and low toxicity. Perovskite catalysts are still in the spot because of their easily tunable redox properties. Au or Ag-supported catalysts are reported to be very effective for catalytic combustion of toluene, *n*-hexane, butyl acetate and methylethylketone. In addition to the extensively investigated Cr-based catalysts, it is noted that Ce and Mn-based catalysts are also very active for the chlorinated VOCs. The following sections will give the details on the development of the mixed metal oxides, perovskite, and gold catalysts.

2.1. Mixed metal oxides

There have been a number of reports on catalytic oxidation of VOCs on transition metal oxides [9,11,22]. According to the literature survey, ceria-based catalysts are very active in VOC oxidation because of the unique features of their oxygen storage capacity. The mechanism of VOC oxidation reactions over ceria is generally considered to be a redox type mechanism, in which the key steps are the supply of oxygen by the readily reducible oxide and its re-oxidation by oxygen [28].

Dai et al. [34] reported a very active CeO_2 catalyst prepared by thermal decomposition of cerium nitrate, followed by calcination at 550 °C. As shown in Table 1, this catalyst achieved 90% conversion of trichloroethlyene (TCE) at 205 °C. However, the catalyst was not thermally stable and deactivated in just a few hours due to the strong adsorption of HCl and Cl_2 species.

Table 1

Catalytic conversion for VOC combustion on non-noble metal catalysts reported in the recent literatures.[a].

Catalyst	VOC concentration in volume[b]	VOC conversion	Reference	Publication year
CeO_2	TCE (1000 ppm)	90% at 205 °C	[34]	2008
CeO_2	TCE (1000 ppm)	90% at 490 °C	[38]	2006
ZrO_2	TCE (1000 ppm)	90% at 500 °C	[38]	2006
$Ce_{0.5}Zr_{0.5}O_2$	TCE (1000 ppm)	90% at 465 °C	[38]	2006
$Ce_{0.15}Zr_{0.85}O_2$	TCE (1000 ppm)	90% at 450 °C	[38]	2006
CeO_2	Toluene (0.7 vol.%)	50% at 600 °C	[28]	2003
Au/CeO_2	Toluene (0.7 vol.%)	100% at 360 °C	[28]	2003
Au/TiO_2	*n*-hexane (125 ppm)	98% at 340 °C	[58]	2007
Au/γ-MnO_2	*n*-hexane (125 ppm)	100% at ~170 °C	[58]	2007
Cr–Cu/HZSM	TCE (2500 ppm)	94.2% at 400 °C	[63]	2006
γ-MnO_2	*n*-hexane (125 ppm)	100% at 180 °C	[42]	2006
$Mn_{0.4}Zr_{0.6}O_2$	DCE (1000 ppm)	100% at 450 °C	[49]	2007
$Mn_{0.4}Zr_{0.6}O_2$	TCE (1000 ppm)	100% at 550 °C	[49]	2007
Mn–Zr	Toluene (0.35%)	100% at 260 °C	[6]	2004
$Mn_{0.67}$–$Cu_{0.33}$	Toluene (0.35%)	100% at 220 °C	[6]	2004
Mn–Ce	Ethanol (1600 ppm)	100% at 170 °C	[45]	2008
Mn–Cu	Ethanol (1%)	100% at 210 °C	[48]	2008
$LaFe_{0.7}Ni_{0.3}O_3$	Ethanol (1%)	50% at 220 °C	[50]	2008
$LaFe_{0.7}Ni_{0.3}O_3$	Acetyl acetate (1%)	50% at 282 °C	[50]	2008
20%$LaCoO_3$/$Ce_{0.9}Zr_{0.1}O_2$	Toluene (1000 ppm)	50% at 192 °C	[51]	2007
10%$LaCoO_3$/$Ce_{0.9}Zr_{0.1}O_2$	Toluene (1000 ppm)	50% at 268 °C	[51]	2007
$Ce_{0.9}Zr_{0.1}O_2$	Toluene (1000 ppm)	50% at 295 °C	[51]	2007
Cr–PILC	CB (0.57%)	100% at 600 °C	[66]	2008
Cr–PILC	Xylene (0.57%)	100% at 600 °C	[66]	2008
Ag–HY	BA (1000 ppm)	100% at 400 °C	[72]	2008
Ag–HZSM-5	BA (1000 ppm)	100% at 400 °C	[72]	2008
Ag–HY	Toluene (1000 ppm)	100% at 290 °C	[76]	2004
Ag–HY	MEK (1000 ppm)	100% at 260 °C	[76]	2004

[a] *Note*: 1,2-dichloroethane (DCE), trichloroethlyene (TCE), Al pillared bentonite clay (PILC), chlorobenzene (CB), butyl acetate (BA), methylethylketone (MEK).

[b] Numeric data in the parenthesis stand for the VOCs concentration used in the related work.

Modifying CeO_2 with other metal oxides, for instance by the partial substitution of Ce^{4+} with Zr^{4+} in the lattice structure, can improve the catalyst's oxygen storage capacity, redox properties and thermal resistance, and enhance catalytic activity at low temperatures [35–37].

Gutiérrez-Ortiz et al. [38] investigated ceria, zirconia, $Ce_{0.5}Zr_{0.5}O_2$ and $Ce_{0.15}Zr_{0.85}O_2$ mixed oxides as catalysts for the complete oxidation of *n*-hexane, 1,2-dichloroethane and trichloroethylene in air. They reported the structural doping with Zr ions improved catalyst activity by increasing zirconia content. A possible reason for the catalytic enhancement may be that insertion of ZrO_2 into the cubic CeO_2 distorted on the mixed oxide structure, which allows greater lattice oxygen mobility [39]. Consequently, the reduction step was no longer confined to the surface but extended deep into the bulk, and hence significantly decreased the light-off temperatures of the chlorinated hydrocarbons as shown in Table 1 [38]. Furthermore, it was clearly observed that mixed oxides with high zirconia content, $Ce_{0.5}Zr_{0.5}O_2$ and $Ce_{0.15}Zr_{0.85}O_2$, showed the highest activity, which was associated with a suitable combination of surface acidity on the ceria–zirconia mixed oxide with a higher mobility of the lattice oxygen and relatively accessible lattice oxygen species [39]. Accordingly, it is suggested that the first stage of the TCE oxidation process is the adsorption of the chlorinated molecule on a strong acid site [40], which subsequently can be attacked by mobile oxygen species from the solid solution through a Mars–van Krevelen mechanism [41].

The polyvalent character of γ-MnO_2 makes this metal oxide a promising candidate to oxidize VOCs [42], including *n*-hexane and trimethylamine. Further fundamental investigation of the reaction kinetics could help to understand the behavior of manganese oxides (Mn_2O_3, Mn_3O_4 and β-MnO_2) for the VOC oxidation mechanism and reaction pathway [42–44].

Many research groups report Mn-containing mixed oxides to be effective for VOC combustion. For example, Delimaris and Ioannides [45] found that MnOx–CeO_2 catalysts, prepared by a urea combustion method, were superior for toluene oxidation than Mg/Mn/Al catalysts prepared from LDH precursors [46], with the MnOx–CeO_2 catalyst achieving complete toluene conversion at 260 °C (SV = 50,000 h^{-1}). The activity for complete ethanol conversion to CO_2 on MnOx–CeO_2 catalysts was available at 200 °C, which compares favorably with the supported 0.3 wt.% Pt/Al_2O_3 catalyst achieving complete ethanol oxidation conversion at 270 °C [47].

The incorporation of small amounts of copper in MnOx catalyst was reported to improve ethanol combustion to CO_2 [48]. Morales et al. [48] suggested that the addition of copper reduced the crystalline structure of manganese oxide, and thus increased the number of oxygen vacancies [48]. Likewise, Mn–Zr mixed oxides with 40 mol.% manganese content have been found to be an effective catalyst for the combustion of chlorinated VOCs. For example, Table 1 shows $Mn_{0.4}Zr_{0.6}O_2$ achieved 100% conversion of 1,2-dichloroethane (DCE) and trichloroethylene (TCE), at 450 and 550 °C, respectively [49]. The enhanced catalytic activity of Mn–Zr mixed oxides was attributed to increased surface acidity and availability of accessible active oxygen species.

Li et al. reported a series of manganese oxides mixed with Zr, Fe, Co, and Cu oxides, prepared by a reverse microemulsion method, for catalytic combustion of toluene [6]. The results are summarized in Table 2. These manganese oxides containing mixed oxides show very good activity for the catalytic combustion of toluene, indicating that the reverse microemulsion method is an effective method to incorporate highly active species into the combustion catalyst and hence highlight some potential active species for catalytic combustion.

Table 2

Activity of toluene oxidation over manganese oxides mixed with Zr, Fe, Co, and Cu oxides prepared in reverse microemulsions [6].

Sample	Molar ratio	Activity of toluene oxidation	
		Ignition temperature[a] (°C)	Combustion temperature[b] (°C)
$Mn_{0.4}Zr_{0.6}$	Mn/Zr = 2:3	255	280
Mn_2O_3	–	260	280
$Mn_{0.4}Fe_{0.6}$	Mn/Fe = 2:3	280	300
$Mn_{0.4}Co_{0.6}$	Mn/Co = 2:3	250	270
$Mn_{0.4}Cu_{0.6}$	Mn/Cu = 2:3	230	240
$Mn_{0.67}Cu_{0.33}$	Mn/Cu = 2:1	210	220

[a] Ignition temperature is referred to the temperature where the toluene conversion reaches around 3%.

[b] Combustion temperature is referred to the temperature where the toluene conversion reaches above 98%.

2.2. Perovskite catalysts

Perovskites have been widely investigated as the oxidation catalysts. For a perovskite represented by the general formula ABO_3, a partial substitution of the cation B by B′ of similar oxidation state and ionic ratio (to create a perovskite described as $AByB'_{1-y}O_3$) may improve the stability or enhance the redox efficiency of the catalyst. Pecchi et al. recently reported the catalytic activity for VOCs combustion over $LaFe_{1-y}Ni_yO_3$ perovskite oxides [50]. The substitution of iron by nickel significantly enhanced the combustion of ethanol and acetyl acetate. However, if the substitution of iron by nickel is complete the reaction rate decreases. Pecchi et al. [50] claimed that the cooperative effect of a $LaFe_{1-y}Ni_yO_3$ and NiO phases determines the oxygen activation capability, and hence their reactivity, and that the activity of $LaFe_{1-y}Ni_yO_3$ is related to the metal–oxygen bond and to the free energy of reduction of the cation placed at Fe and Ni sites.

Since the specific surface area of perovskites is typically low, another approach to improve perovskite catalyst activity is loading the perovskite species onto higher surface area active supports. For example, Alifanti et al. loaded 10 and 20 wt.% $LaCoO_3$ perovskites on $Ce_{1-x}Zr_xO_2$ (x = 0–0.3) supports. The ceria–zirconia-supported $LaCoO_3$ catalyst was reported to be very active for combustion of benzene and toluene in diluted streams. The highly dispersed $LaCoO_3$ species on the surface of ceria–zirconia support decreases the light-off temperatures and increases the reaction rates by an order of magnitude compared to bulk perovskite catalysts [51].

2.3. Au-containing catalysts

Since the pioneering work on Au catalysts by Haruta [56] many studies of gold catalysts and gold-supported catalysts (including Fe_2O_3, Co_3O_4, TiO_2, and Mn_2O_3 supports) for VOCs oxidation have been reported, with some reports of catalyst activities exceeding those of Pt/Al_2O_3 catalysts. The performance of gold catalysts for VOC combustion is highly dependent on the size of the gold particles, as well as the nature of the support [56], and thus strongly affected by the preparation method and the pretreatment conditions [52–55]. Moreover, Scirè et al. [57] have also suggested that gold could increase the oxygen mobility of the support and thus the overall activity of the catalysts towards VOC oxidation.

Cellier et al. prepared Au/MnO_2 and Au/TiO_2 as catalysts by the deposition–precipitation method [58], and investigated their activity in the total oxidation of *n*-hexane. The conversion of *n*-hexane into CO_2 on Au/MnO_2 is much higher than Au/TiO_2 for this reaction. However, Au/MnO_2 is also slightly less active than the original γ-MnO_2 support.

Gold/cerium oxide catalysts [28] show higher activity on catalytic combustion of toluene than cerium oxide, as presented in

Table 1. For an Au/Ce–DP catalyst prepared by deposition–precipitation (DP), toluene conversion starts at about 200 °C and 100% was achieved at 360 °C. In contrast, for an Au/Ce–CP catalyst prepared by co-precipitation (CP) and a CeO_2 catalyst the light-off temperatures are, respectively, 200 and 300 °C higher than for the Au/Ce–DP catalyst. These results indicate that gold is more effective in improving the catalytic behavior of cerium oxide-based catalysts when the gold is added to ceria by deposition–precipitation (DP) because DP promotes the formation of smaller gold particles (6 nm) than the CP method (8 nm). Scirè et al. [57] proposed that the presence of gold causes a decrease in the strength of the surface Ce–O bonds adjacent to gold atoms, thus leading to higher surface lattice oxygen mobility and a higher reactivity of these oxygens, and hence affects catalytic activity towards the oxidation of VOCs.

3. Effect of water vapor

Most of industrial oxidation processes produce flue gases containing water vapor, thus the effect of water vapor on VOC oxidation process always needed careful investigation. Although water is commonly regarded as a poison for the catalytic combustion of VOCs [59,60], in some cases the presence of water vapor may be beneficial. For example, in combustion of chlorobenzene on VOx/TiO_2, $VOx–WOx/TiO_2$ and $VOx–MoOx/TiO_2$ catalysts, water could play a positive role in removing Cl^- from the catalyst surface after the oxidation of the aromatic ring [23,62]. On the other hand, water can also react with chlorine to produce HCl by the Deacon [61] reaction and change the selectivity HCl/Cl_2.

Water vapor can act as hydrolysis agent and hydrogen-supplying agent to decrease by-product formation. Abdullah et al. [63] investigated the combustion of dichloromethane (DCM), trichloromethane (TCM) and TCE over chromium and copper catalysts supported on H-ZSM-5 (Si/Al = 240) modified with silicon tetrachloride. The treatment with silicon tetrachloride improves the chemical resistance of H-ZSM-5 against HCl. A water vapor concentration of 9000 ppm in the VOC stream was found to decrease the TCE conversion from 94.2 to 88.5% at 400 °C with 2500 ppm of trichloroethylene (TCE) and a gas hourly space velocity (GHSV) of 32,000 h^{-1}, but led to an increase in the carbon dioxide yield from 47.5 to 68.4%. The increased carbon dioxide yield was attributed to water acting as hydrogen-supplying agent to suppress chlorine-transfer reactions [63].

Xia et al. [64] reported an increase in hydrophobicity and hydrothermal stability of Pt/MCM-41 catalysts for toluene oxidation when the MCM-41 was prepared in a fluoride medium. This catalyst showed remarkable hydrothermal stability with 100% conversion of 4340 ppm toluene at 200 °C for 15 days in a stream containing 21,000 ppm of H_2O with VHSV of 15,000 h^{-1}. It was assumed that the water resistance of the catalyst was attributed to an increase in hydrophobicity, and therefore was capable to preserve the catalyst activity.

Kullavanijayam et al. reported that water enhanced the catalytic oxidation of cyclohexene over the Pt and Rh catalysts on ceria–alumina supports, but it had a negative effect on the oxidation of cyclohexane over a Pd loaded ceria–alumina catalyst [65]. In this case, the inclusion of water improves the activity of both Pt and Rh for the oxidation of cyclohexene possibly due to high activity of Rh and Pt for steam reforming [65].

Apparently, the role of water in VOC oxidation is a complex phenomenon [62,63,65], particularly at lower temperatures. Therefore, the effect of water should not be overlooked in the design of industrial pilot plants for potential VOC catalytic oxidation systems.

4. Coke formation

Carbonaceous deposits (coke) on the catalyst often occurred with the oxidation of VOCs and led to the loss in the oxidation activity of the catalysts, and therefore it always drew a great attention. Loading different metal active species onto the similar catalytic supports would lead to the significant difference in coke formation.

As reported by Antunes et al., the carbonaceous deposits, mainly composed of aromatic hydrocarbons and oxygenated aromatic compounds, are generally found retained inside the zeolite pores for catalytic deep oxidation of toluene in air at temperatures between 150 and 500 °C over CuNaHY zeolites with different copper contents [24]. The increase of copper content from 1 to 8 wt.% promotes the oxidation of toluene and facilitates the removal of coke formed in the course of reaction.

Both Cr-impregnated bentonite and the Pd-impregnated bentonite showed high activity for the total oxidation of cholorobenzene and xylene [66]. However, the dark color and thermogravimetric analysis (TGA) of the catalyst after reaction suggested the deposition of coke on the Cr-impregnated bentonite surface after several hours of operation at 600 °C. The deactivation was explained by coke formation, combined with the loss of Cr from the catalyst surface resulting from the formation of the volatile CrO_2Cl_2. The Pd-impregnated pillared bentonite was more robust, and catalytic activity was maintained for more than 70 h during reaction with chlorobenzene or xylene.

Li et al. recently reported that choosing an appropriate catalyst support for the same active catalyst material can minimize coke formation [67]. Fig. 1 shows the effect of catalyst supports on toluene conversion over Cu–Mn catalysts at 400 °C [67]. The Cu–Mn loaded on MCM-41 shows better catalyst stability over 50 h than the Cu–Mn loaded on Beta zeolite. TGA profiles (Fig. 2) confirmed that coke formation was substantially greater on the microporous Cu–Mn/Beta zeolite catalyst than on the mesoporous Cu–Mn/MCM-41 catalyst. The larger pores of the mesoporous MCM-41 facilitate the diffusion of aromatic intermediates in the coke formation process and reduce pore blockage by coke, as illustrated by the schematic in Fig. 3.

In addition to the carbonaceous coke, the formation of "sulfur-containing coke" is of interest in the catalytic combustion of malodorous sulfur-containing VOCs. Kucherov et al. [68] reported that Au/HZSM-5 and (Au + Pd)/HZSM-5 demonstrated a gradual loss of the catalytic efficiency after 6 h on stream in the combustion of 1100 ppm CH_3OH + 1060 ppm of $(CH_3S)_2$ at 320 °C. The VOC

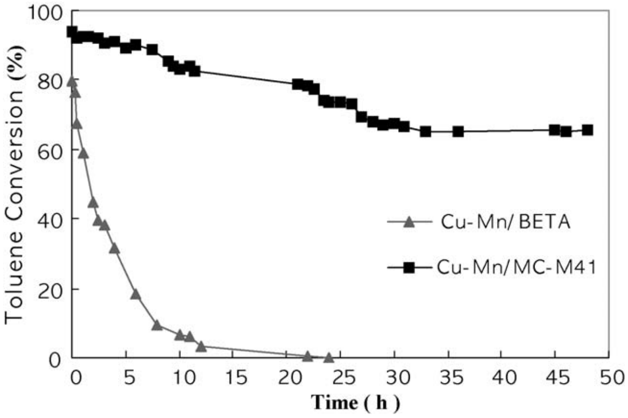

Fig. 1. Toluene conversion as a function of time-on-stream on Cu–Mn/βzeolite at 400 °C (A) and Cu–Mn/MCM-41 at 320 °C (B). Reaction conditions: 3500 ppm toluene, 8.8% oxygen, gas flowrate of 60 ml/min, balance gas as Ar and 0.1 g of catalyst [67].

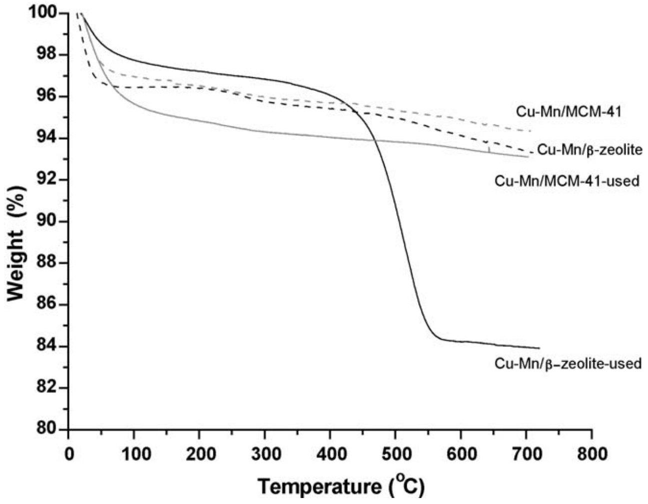

Fig. 2. TGA profiles of Cu–Mn/βzeolite-used (A) Cu–Mn/βzeolite (B) Cu–Mn/MCM-41-used (C) and Cu–Mn/MCM-41 (D) [67].

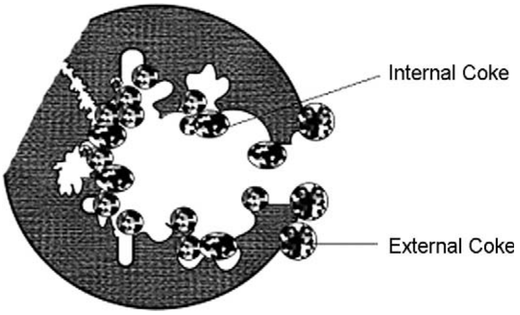

Fig. 3. Scheme of coke formation on a single pore of molecular sieves.

conversion to CO_2 fell from 95 to 65% and the spent catalysts were dark-gray color due to a substantial coke deposition. Coke burning from the spent Au-Pd/HZSM-5 catalysts by Temperature-programmed oxidation (TPO) released a considerable amount of SO_2 at temperatures above 400 °C. This TPO result indicates only a part of sulfur of $(CH_3S)_2$ was converted into SO_2, and some $(CH_3S)_2$ was fixed in the coke residue formed on these catalysts operating at 320 °C. However, these samples were able to provide efficient removal of $(CH_3S)_2$ and reduced coke formation when operated at higher temperatures (500 °C), which increases the energy cost of the process. Kucherov et al. also reported that Rh/HZSM-5 and (Rh + Au)/HZSM-5 demonstrated high efficiency and reduced coke formation at 320 °C, an improvement that results from an increase in the catalyst costs for Rh.

5. Effect of supports

The hydrophobicity, acidity and pore characteristics of the catalyst support are very important for catalytic combustion. Several research groups pointed out that the hydrophobicity of the support [69,70] will reduce the adsorption of water vapor, both from the atmosphere and formed as a reaction product on the catalyst, particularly at low reaction temperatures. The competitive adsorption between the organic and water molecules on the active sites of the catalyst always results in lower catalytic activity [69,71].

Both Ag/HY (Si/Al = 80) and Ag/HZSM-5 (Si/Al = 280) zeolites, prepared by ion exchange, exhibited high catalytic activity for the oxidation of butyl acetate, with 100% butyl acetate conversion achieved at temperatures above 400 °C [72]. Although the AgY catalyst contained less silver, this catalyst showed better oxidation activity, which was attributed to better metal dispersion, surface acidity and pore characteristics of the HY zeolite.

Imamura et al. reported that the order of activity of a series of mixed oxide catalysts was in close agreement with the strong acidity of the samples [73]. The function of surface acidity in chlorocarbon destruction was consistent with previous reports on zeolites, alumina, TiO_2/SiO_2, ZrO_2/SO_4, or TiO_2/ZrO_2-based catalysts. The promoting effect of acid sites was found to be associated with the composition of the mixed oxide. Accordingly, it is suggested that the first stage of the oxidation process is the adsorption of the chlorinated molecule on a strong acid site, which can subsequently be attacked by mobile oxygen species from the solid solution through a Mars–van Krevelen mechanism [73].

The supports have also been regarded as a factor to affect the activity of gold-supported catalysts. The catalytic behavior of the support was often reported as the stabilization of the small gold particles against coalescence [74]. The activity of VOC oxidation on gold catalysts supported on Co_3O_4, Fe_2O_3, MnOx was reported to exceed the activity of Pt/Al_2O_3 catalysts, where gold could increase the oxygen mobility of the support and thus the overall activity of the catalysts towards VOC oxidation [52].

6. Adsorption/catalytic combustion dual functional system

Although catalytic combustion is an effective way for complete destruction of VOCs, it is sometimes not economically feasible for the treatment of very low concentration VOCs. Combined with energy saving adsorption process, catalytic combustion can be even more effective for the control of such lower concentration VOCs. The concept of adsorption/catalytic combustion can be further extended by the dual functional adsorbent/catalyst system, which integrates the adsorption and catalytic combustion into a single control unit [75].

The dual functional adsorbent/catalyst system was operated in a process as reported by Kullavanijayam et al. [65], where 3000 ppm cyclohexene, 2800 ppm thiophene, 7000 ppm diethylamine and 2000 ppm methyl methacrylate streams were first concentrated by adsorption on activated carbon, 13× zeolite or γ-alumina. The adsorption step was followed by desorption of adsorbed gases by heating to 270 °C or above, then catalytic combustion of the desorbed gases was examined over Pt, Pd and Rh-based catalysts. The Pd-based systems offered the optimum configuration, with all pollutants converted at temperatures below 380 °C.

For the control of the low concentration VOCs, a good combined adsorbent/catalyst dual functional system was reported by Baek et al. [76]. Catalytic activity tests over various transition metal catalysts (Mn, Fe, Co, Ni, Cu, Zn, Ag) loaded on zeolite HY (Si/Al = 160, surface area = 681 m^2/g, pore volume = 0.47 cm^3/g) were carried out. Among these catalysts Ag/HY catalyst showed the lowest conversion temperatures, for example 330 and 310 °C for toluene and methylethylketone (MEK) oxidation, respectively. Baek et al. [76] therefore claimed this dual functional Ag/HY adsorbent/catalyst system as one of the most effective methods for the removal of low concentration VOCs.

Another good dual functional adsorbent/catalyst system design was reported for the removal of tetrachloroethylene (PCE) and MEK by Guillemot et al. [77]. Here, the adsorption/catalysis experiments were performed in a single reactor vessel containing two beds; first the adsorbent bed and then a catalyst bed, as shown in Fig. 4. The adsorption step was carried out at the ambient temperature 30 °C and GHSV of 15,300 h^{-1} until the beginning of the VOC breakthrough. And then VOCs gas flow was switched off, and replaced by wet reconstituted air (GHSV of 6120 h^{-1}). VOCs desorption on the first bed is obtained by lowering the reactor into an oven so that the two beds are heated at the oxidation

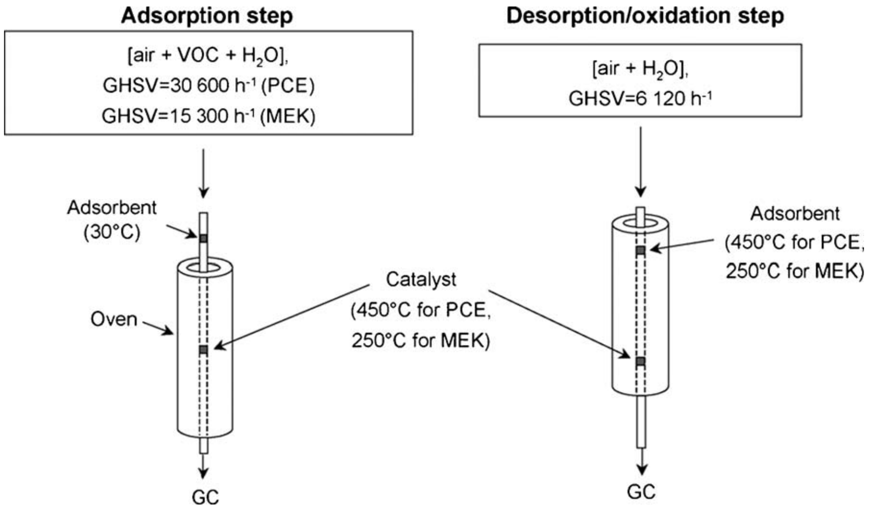

Fig. 4. Scheme of adsorption/oxidation apparatus [77].

temperature. VOC desorbed is then carried to the second bed, and converted to CO_2, and HCl in the case of PCE destruction.

As mentioned above, the combined dual function system appeared to be a plausible design to treat very low concentration VOCs, and it is reasonable to draw an increasing attention in terms of a practical point of view.

7. Summary

Catalytic combustion is a very effective route for the abatement of VOCs over non-noble metal catalysts although some other techniques such as heterogeneous catalysts combined with non-thermal plasma [78] and photocatalytic decomposition [79] are also very useful for VOCs treatment in certain cases. Mixed metal oxides, supported perovskites and Au-containing catalysts show a strong potential for the improvement of activity in catalytic combustion. The effects of water, catalyst supports, and coke formation continue to pose practical challenges for VOC catalytic combustion and should be investigated further. The dual functional adsorbent/catalyst system was suggested as an effective design for the removal of low concentration VOCs.

As summarized in this research, although significant progress has been made in development of VOCs oxidation techniques in the past five years, it is clear that further research is needed to develop novel non-noble metal catalysts and related designs with the target to improve removal efficiencies and reduce costs for the treatment of a wide variety of VOCs from outdoor and indoor sources. In addition, more fundamental research to understand the mechanisms involved is also crucial to the objective of developing appropriate industrial materials for VOCs removal.

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