



## REVIEW

### Catalytic Combustion of Volatile Organic Compounds (VOCs) over Perovskite Oxides: A Review

MADHAB DULE<sup>1</sup>, BIDYAPATI KUMAR<sup>1</sup> and RAJIB MISTRI<sup>\*,1</sup>

Department of Chemistry, Achhruram Memorial College, Jhalda, Purulia-723202, India

\*Corresponding author: E-mail: rajibmistri@yahoo.co.in

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Volatile organic compounds (VOCs) are one of the crucial outdoor as well as indoor air pollutants. Recently, the elimination of volatile organic compounds is become more attractive due to its potentiality of long-term human health effects. Among the different existing methods for the removal of VOCs, the catalytic combustion is the best convenient method due to its operational simplicity, cost effectiveness, high efficiency and industrial acceptability. Various perovskite oxides have been widely studied as suitable catalysts for the removal of VOCs because of their tunable physico-chemical properties, compositional/structural exibility and high thermochemical stability. The morphology, material composition and surface as well as bulk properties of perovskite oxides is the key determining factors for catalytic efficiency. The suitable metal or non-metal doping, controlling morphology (nano-structuring, three-dimensional ordered microporous (3DOM) building) and hybrid construction (perovskite as support for other active catalysts and other oxides as support for active perovskite catalyst) may have a remarkable effect on the surface as well as bulk properties and consequently the catalytic efficiency for ther removal reactions of VOCs are also effected. In this review article, different aspects of the current development in perovskite oxides catalysts for VOCs combustion with a special highlighting on the material designing, like doping, morphology controlling, surface modification and hybrid construction are presented.

**Keywords:** Volatile organic compounds, Oxidative combustion, Catalyst, Perovskite oxides.

## INTRODUCTION

The sustainable development of our society is mainly depend on the healthy ecosystem. Though, the rapid growth of civilization and industrialization can cause a serious damage to the ecosystems for the sustainable development of human society. In particular, atmospheric pollution like the water, earth and air pollutions has recently become one of the major apprehensions for safest as well as supportable ecosystem for mankind. Volatile organic compounds (VOCs) are mainly hydro-carbon compounds and also their oxygenated or halogenated derivatives with lower boiling points (50 to 260 °C) [1]. Recently, VOCs are received a particular interest as they recognized as the primary atmospheric air pollutants. Maximum VOCs are dangerous to the environment as they damage the ozonosphere and produces photochemical smog as well as they can cause a wide range of adverse health effects [2,3]. Some aromatic VOCs are harmful for human body even at  $\sim 0.2 \text{ mg m}^{-3}$  concentration and some VOCs, common in petrochemical industry, such as

ethylene, propylene are less toxic to the human body [4]. Thus new developed technologies for controlling and monitoring of VOCs became essential for establishment of rigid environment regulations.

Volatile organic compounds (VOCs) emissions are generally controlled by two common scheme *viz.* (i) recovery and (ii) destruction. The condensation, absorption, adsorption and membrane separation technologies are mainly used for the recovery of VOCs. The condensation and absorption process are comparatively simpler as well as mature methods than the other two methods. The adsorption is the most useful recovery technology for recycling of VOCs at low concentration in the atmospheric pollution controlling, petrochemical and other fields [5-8]. The porous activated carbon and carbon fiber with high surface area are mainly used as adsorbent in this adsorption method but the inferior reproducibility restricts the utilizations of this type of adsorbents. Recently, some work has been done to increase the adsorption capacity as well as selectivity

by modification of activated carbon [9-12]. Membrane separation method is potentially applied for removal of VOCs where the selective permeable polymer membrane is used in this technology. The membrane separation process is preferably used for highly concentrated organic solvents recovery. The low energy consumption, high efficiency and effective recycling ability makes the membrane separation route more useful than the other traditional recovery methods but the poor stability as well as high cost restricting its applications in large-scale [13,14]. Incompatible to recovery scheme, the oxidative destruction route is successfully used to convert VOCs into CO<sub>2</sub> and H<sub>2</sub>O under oxygenic conditions. Thermal incineration is one of this method where the combustible VOCs pollutants are burning as fuel. The method is most effectively used for the removal of highly concentrated VOCs as well as VOCs with complex composition but around 1100 °C requires for this process which limits the application of this method [15]. The catalytic pathway is one of the best practical alternative methods for VOCs removal and become hot spot for the researchers during last few decades. The plasma degradation, catalytic oxidation and photocatalysis are commonly used as catalytic methods for the removal of VOCs. In case of plasma degradation method, the chemical bonds are broken by the inelastic collision of high-energy electrons in the plasma with VOCs molecules and finally produces CO<sub>2</sub> and H<sub>2</sub>O [3]. However, the lower concentration of VOCs, high-energy consumption and generation of other pollutants like NO<sub>2</sub> limit its applications [16]. In photocatalysis route the VOCs are eliminated by oxidation or reduction under irradiation of sunlight. However, limited VOCs can be treated by this method and the poor catalytic stability as well as low efficiency make this method unfavourable for practical application [17]. The catalytic combustion is more environmental friendly method than the thermal incineration due to consumption of lower temperature or energy as well as lesser formation of toxic products and the method is also applicable for removal of various types of VOCs under mild conditions [18]. Thus, the removal of VOCs by catalytic method has become more interesting for the researchers during last few decades. Considering various VOCs in compare to their concentrations and compositions, it is important to prepare an efficient stable catalyst for elimination of several VOCs. In case of catalytic removal method, the complete VOCs oxidation can perform in oxygen-rich condition at elevated temperatures. Therefore, the thermal and chemical stability of the catalysts should have been higher under oxidizing environment. Besides this, sulfur poisoning is also an important factor for the catalytic combustion of VOCs. Various metal catalysts (particularly noble metals) in compare to the metal oxides show higher catalytic efficiency for elimination of VOCs by forming H<sub>2</sub>O and CO<sub>2</sub> [19-22]. However, inadequate resources of costly noble metals limited its application for large scale practical purpose. In recent times, some simple and complex transition metal oxides have successively used as catalysts for the catalytic elimination of VOCs due to their high thermal stability, low cost and appreciable chemical stability under oxidizing conditions [23-29].

Perovskite oxides (ABO<sub>3</sub>) are the important type of non-noble metal based complex metal oxides and they can also form

stable composition by substituting either A or B-sites as well as both sites with suitable other ions. The superior to simple perovskite oxides have some exceptional features such as rich defects, adjustable metal-oxygen bond length or strength and high redox capability of the B-site cations, *etc.* Therefore, perovskite oxides have been used comprehensively in many environmental and energy-related fields such as electro-catalysts [30-37], solid oxide fuel cells (SOFCs) [38-49], electrochemical sensors [50-54], solar cells [55-59], wastewater remediation [60-64], three-way catalysts [65-67] and catalysts for VOCs combustion [68-70]. The compositional as well as structural exibility, tunable redox capability and high thermal stability makes the perovskite oxides so important for catalytic combustion of VOC [71]. Usually, the B-site cations and O<sup>2-</sup> ions are the active sites of perovskite catalysts but the change in the A-site cation can also affect the catalytic performance [16]. Many researchers have been reported that the perovskite oxides are comprehensively used as catalysts for VOCs elimination and other connected applications, such as ameless combustion and de-NOx [72-74]. Yet, until now, limited reviews particularly concentrating on the development and design of perovskite oxides catalysts for VOCs removal have been published [16,75].

In this review article, the latest improvements of perovskite oxides based catalyst for VOCs combustion are highlighted. At first, the essential requirements of catalytic combustion for VOCs removal are discussed. Then, the features and superiority of perovskite oxides as catalyst in VOCs removal are also emphasized. In addition, the dependency of catalytic activity and stability of perovskite catalysts for VOCs combustion reactions with their structural modification are also summarized. This review mainly focuses on the designing highly efficient as well as stable perovskites catalyst for VOCs removal.

**Essence of VOCs catalytic combustion:** Volatile organic compounds have different type of chemical bonds like C-C, C=C, C-H, C-Cl, C-N, *etc.* and also contain different elements such as C, O, H, S, N, Cl, *etc.* Thus preparation of an efficient catalyst for the non-selective dissociation of all the chemical bonds is a big challenging. The catalytic reaction for VOCs removal predominantly occurs on the active sites of the catalyst surface and selectivity of the product mostly depends on the nature of the catalyst. The intrinsic activity and the active sites number are play the vital role for the catalytic efficiency. The number of active sites may be increases by building porous structure or forming nanostructure but sintering is a big problem in this cases. The physico-chemical properties of the catalyst such as composition, lattice structure, bond energy and amount of defect are largely related to the intrinsic catalytic activity. The selectivity of the catalyst is one more big part for oxidative VOCs removal and deep oxidation products of CO<sub>2</sub> and H<sub>2</sub>O is more preferred instate of different partial oxidized products. The higher catalytic activity and low selectivity is the key part for an ideal catalyst in this case. Durability of the catalysts is another important factor for catalytic VOCs removal. A highly oxidizing environment is mainly used for the catalytic VOCs elimination reaction thus the catalyst must be highly oxidative corrosion resistant and high coking resistant or avoid any carbon deposition on the surface. Thus, the ideal catalysts

should be cleaned during the reaction to avoid any deactivation of the catalyst and the activity as well as stability of the catalyst can be significantly maintained by controlling carbon deposition [76].

Some of the VOCs may contain sulfur as well as chlorine impurities, which can degrade the catalytic efficiency. Sulfur containing VOCs are moderately toxic but may have unpleasant odors at very low concentration. On the other hand, chlorinated volatile organic compounds (CVOCs) are highly toxic, poor degradable and forming highly toxic polychlorinated byproducts, which makes them the most difficult VOCs to be removing. Generally, noble and non-noble metal based as well as supported catalysts are mainly used as catalyst for removal of VOCs and metal-based catalysts for sulfur-containing VOCs [16]. Thus development of sulfur-tolerant and chlorine-tolerant catalysts are become most important topics for the researchers.

**Main aspects of perovskites as catalysts for the removal of VOCs:** Perovskite oxides having structural formula  $ABO_3$  where a lanthanide or an alkaline earth metal or both are occupied the A-site and the B-site is occupied by transition metal. The A-site is twelve-coordinated and B-site is six-coordinated with the oxygen. The outstanding compositional flexibility of perovskite oxides give them high catalytic properties, photovoltaic properties as well as cation, proton, electronic and oxygen ion diffusion capability [77-87]. Individually the A, B, even O-site [77-80] and two [83-86] or all the sites at same time [87] can be incorporated by various dopants in perovskite oxides lattice. The variable oxidation states of B-site cations are forming oxygen vacancies or interstitial oxygen to maintain the electric neutrality and the perovskite oxides become oxygen ion conductive at higher temperature. The B-site elements and  $O^{2-}$  are mainly affecting the perovskite oxide activity whereas the A-site may be inert for the catalytic reaction but it can regulate the catalytic performance by influencing the electronic nature of the B-site, surface properties and defect structure. Therefore, precisely controlled doping site and amount can make perovskite oxide so important for different applications [88].

Typically, perovskite oxides are capable some degree of cation or anion deficiency by maintaining their original lattice structure. Generally, the perovskites are maintaining their original lattice structure for cationic defect in A-site (even more than 30%) under certain condition [89,90] but defect in B-site cation is less favourable. The efficiency of perovskite oxides for different catalytic reactions could be influenced by such cationic deficiency due to change in their bulk as well as surface properties [91-94]. Furthermore, some perovskite oxides may form nanoparticles on their surface by maintaining their original structure under certain conditions due to change in the intrinsic properties after doping [95-98]. The thermal stability and activity of these nanoparticles could significantly increase for some reactions [95,97]. Some perovskite oxides can also be formed nanocomposite with other oxides through one-step synthesis method [44,45]. The strong interaction among the secondary phase and the perovskite phase could change the surface properties as well as the electronic structure of the perovskite phase and the composite may give some unique properties due to cation exchange among these two phases at high temperature.

Perovskites have been comprehensively used as electrodes for electrocatalysts [31,35-37], SOFCs [41,42,46,48-50] and three-way automobile catalysts [65-67]. Generally, perovskite oxides are synthesized in aerobic atmosphere and the catalytic removal of VOCs is also done in presence of oxygen, so using perovskite catalysts in VOCs removal have numerous benefits. In addition, the high thermal as well as chemical stability of perovskite oxides make them more efficient catalyst for VOCs removal. In case of catalytic VOCs removal, VOCs and oxygen both are first absorbed on the surface of the catalyst by forming catalyst surface-carbon or hydrogen and surface-oxygen bond. Thus, the C-C- or C-H bonds in VOCs are become weaker through adsorption on catalyst surface, which support the combustion of VOCs and consequently promote the carbon deposition on the surface of catalyst. Thus the activation of absorbed oxygen is more preferable, which is also favourable for non-selective combustion of VOCs [99-101]. Therefore, perovskite oxide catalysts provide excellent coking resistance in fuel oxidation at high temperatures [102]. The coking resistance or sulfur tolerance of perovskite catalysts can increase by improving the water and oxygen storage capability [103-106]. Notably, the exceptional structural as well as compositional flexibility and variable physicochemical properties make perovskite oxides as an efficient catalyst for VOC removal reactions. Previously the perovskite oxides cannot be used as catalyst for oxidative VOCs removal but high diverseness of catalytic activity for various perovskite oxides make them interesting for researcher to design a highly active as well as stable perovskite oxide catalyst for the removal of VOCs.

## Recent development of perovskites as catalysts

### Composition designing

**B-site doping:** The physical properties and stability of perovskites are mainly depended on the B-site metal ions, which also have a great impact on the catalytic efficiency for the VOCs removal. Thus, several researchers have attempted to improve the catalytic efficiency of perovskite catalysts for VOCs removal by doping different transition metals (Fe, Mn, Cu, Ni and Co) with various oxidation state at the B-site. For example, hydrothermally synthesized  $SrTi_{0.86}Mn_{0.14}O_3$  and  $SrTi_{0.89}Cu_{0.11}O_3$  were used for the toluene oxidation and result shown that catalytic activity increases in case of Mn doping due to increasing the ratio of adsorbed and lattice oxygen ( $O_{ads}/O_{latt}$ ) on the surface [107]. Alvarez-Galvan *et al.* [108] reported that  $LaBO_3$  (B = Ni, Co, Cr, Mn) perovskites are effectively used for the methyl ethyl ketone (MEK) oxidation and among the metals Mn and Co are the preferred for this reaction.

Besides the catalytic activity, the impurity tolerance and durability of perovskite catalysts also related to the B-site cation. B-site doped  $LaB_{0.2}Mn_{0.8}O_3$  (B = Fe, Ni, Co) perovskites have been studied for the oxidation of vinyl chloride and the results showed that Ni doped catalyst give high activity due to highest improved oxygen mobility and reducibility [109]. Some non-metallic element also used as dopants for the structural stability and the electrical conductivity improvement of perovskite [110, 111]. A particular amount ( $x = 0.03$ ) of phosphorous doped

LaCo<sub>1-x</sub>P<sub>x</sub>O<sub>3</sub> ( $x = 0$  to 0.05) catalysts was effectively increasing the catalytic efficiency for propane oxidation by increasing surface-reactive oxygen [112]. Zheng *et al.* [113] reported that boron doped LaCo<sub>0.93</sub>B<sub>0.07</sub>O<sub>3</sub> perovskite showed the best catalytic performance for oxidation of propane due to presence of more active sites and better reducibility. Interestingly, the outstanding thermal stability make this non-metal doped perovskite catalyst for industrial application of VOCs combustion.

**A-site doping:** The A-site cation of perovskite principally does not directly take part in the catalytic reaction, but it can alter the catalytic efficiency by varying B-site cations electronic structure, surface properties and defects. Different Sr doped La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> ( $x = 0, 0.1, 0.2$ ) perovskite oxides effectively increased the catalytic performance for methane oxidation as well as enhance sulfur tolerance by forming stable sulfates on surface of the catalyst and La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> catalyst gave best catalytic performance [114]. In the same way, sol-gel methodically synthesized Sr-doped LaMnO<sub>3</sub> perovskite catalysts used as an efficient catalyst for vinyl chloride combustion due to higher oxygen activation capability and better redox properties in presence of higher Mn<sup>4+</sup> concentration. Alternatively, the stronger basic Sr cations preferred to form Sr-Cl bond and keeping the active Mn species chlorine free [115].

Ce doped La<sub>1-x</sub>Ce<sub>x</sub>MnO<sub>3</sub> ( $x = 0-0.5$ ) perovskites effectively used for styrene oxidation and the catalytic activity increases due to change the valency of Mn ions and surface area [116]. Another A-site doped La<sub>0.8</sub>A<sub>0.2</sub>MnO<sub>3</sub> (A = Mg, Ce, Sr) also successively used for vinyl chloride catalytic oxidation and La<sub>0.8</sub>Ce<sub>0.2</sub>MnO<sub>3</sub> showed highest activity due to availability of more adsorb oxygen on this larger catalyst surface [117]. The activity of perovskite catalysts for VOCs oxidation effectively enhances by introducing noble metals in the catalyst and many researches are doped precious metals in the A-site of perovskites. One-pot sol-gel methodically synthesized silver-doped La<sub>1-x</sub>Ag<sub>x</sub>CoO<sub>3</sub> ( $x = 0-0.05$ ) perovskite showed better activity for toluene oxidation than the impregnation methodically prepared catalyst. However, LaCoO<sub>3</sub>-supported Ag catalyst calcined at 250 °C shows best activity compare to the other catalysts investigated for this reaction due to formation of more Ag<sup>0</sup> species in this supported catalyst [118]. Another Ag-doped La<sub>1-x</sub>Ag<sub>x</sub>FeO<sub>3</sub> ( $x = 0-0.25$ ) perovskite was comprehensively used as catalysts for methane and hexane oxidation and higher methane oxidation activity was found for  $\geq 0.05$  doping whereas  $\geq 0.1$  doped catalyst showed highest hexane oxidation activity [119]. The catalytic activity of Ca<sup>2+</sup> substituted LaFeO<sub>3</sub> and LaNiO<sub>3</sub> were significantly changed for ethanol and acetyl acetate combustion due to change of the electronic properties [120]. Similarly, Ca<sup>2+</sup> doped LaCoO<sub>3</sub> was also revealed better oxidation activity for propane due to change in crystal structure [121]. The same observation was found for La<sub>1-x</sub>Ca<sub>x</sub>CoO<sub>3</sub> catalyst in toluene oxidation [122] and La<sub>0.8</sub>Al<sub>0.2</sub>MnO<sub>3</sub> catalyst for 1,2-dichloroethane oxidation [123].

**A- and B-site co-doping:** The A-site and B-site both are simultaneously doping or co-doping approach was also extensively used to fabricate effective perovskites as catalyst for VOCs removal. The cerium for A-site and Ni for B-site co-doped La<sub>0.8</sub>Ce<sub>0.2</sub>Mn<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3</sub> catalyst showed the highest oxidation

activity for trichloroethylene (TCE) due to the enlarged specific surface area, Mn<sup>4+</sup>/Mn<sup>3+</sup> ratio and active oxygen amount [124]. Similarly, La<sub>0.7</sub>Sr<sub>0.3</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> perovskite showed significantly increased toluene oxidation activity due to change in morphology as well as decreased particle sizes [125]. Deng *et al.* [126] reported that Ce, Fe co-doped La<sub>1-y</sub>Ce<sub>y</sub>Co<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> ( $x = 0-1.0$ ;  $y = 0-0.1$ ) catalyst used comprehensively for CH<sub>3</sub>OH and CH<sub>4</sub> oxidation. Hydrothermally prepared La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3</sub> and La<sub>0.6</sub>Sr<sub>0.4</sub>Mn<sub>1-y</sub>Fe<sub>y</sub>O<sub>3</sub> ( $y = 0, 0.1, 1.0$ ) were examined for toluene oxidation and found that La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> showed highest activity by formation of Fe<sup>3+</sup>-O-Fe<sup>4+</sup> couples [127]. LaMnO<sub>3</sub> by Fe<sup>3+</sup> and Sr<sup>2+</sup> co-doped La<sub>0.9</sub>Sr<sub>0.1</sub>Mn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> catalyst was exhibited analogous toluene oxidation activity to some noble metal-based catalysts [128]. The details of several perovskite oxides catalyst with different doping for oxidation of VOCs are summarized in Table-1.

**Morphology controlling:** The amount of active sites and intrinsic activity also play a key role for the catalytic performance of perovskite oxides in the VOCs oxidation. The morphology and structure are depended on the number of active sites, whereas the crystal structure, material composition, oxygen vacancy and valence state are depended on the intrinsic activity. Thus, making nanostructures, morphology altering and specific surface area expanding are beneficial methods to increase the number of active sites.

The perovskite oxides with a nanobber morphology has been extensively fabricated by using electrospinning method. Different LaCoO<sub>3</sub> based perovskite with nanorod and nanobber morphology were synthesized by an electrospinning method and this perovskite are efficiently used as catalyst for benzene oxidation [129-131]. In general, LaCoO<sub>3</sub> based catalysts with nanorod morphology was more efficient than the catalyst with nanobber morphology in the catalytic benzene combustion. On the other hand, Sr doped LaCoO<sub>3</sub> perovskite with nanorod morphology exhibited lesser catalytic activity in compare to the catalyst with lamellar morphology for ethyl acetate oxidation [132]. Hydrothermally synthesized LaNiO<sub>3</sub> with nanocage structure gave excellent activity for CO oxidation [133] and solvothermally prepared hollow multishelled spherical PrMnO<sub>3</sub> was also successfully applied for CO and toluene catalytic oxidation [134]. The nano-mesoporous LaMnO<sub>3</sub> perovskite with large surface area also fabricated by nanocasting method and effectively used as catalyst for methanol conversion than the catalyst synthesized by other methods [135]. Cerium doped SrMnO<sub>3</sub> nanoparticle also effectively used for catalytic combustion of acetone [136]. Different catalytic VOCs oxidation reactions over perovskite oxide with various morphology are summarized in Table-2.

The fabrication of three-dimensional ordered microporous (3DOM) perovskite by templating route is also a useful scheme to enhance the specific surface area as well as activity of the catalyst. Different SrFeO<sub>3- $\delta$</sub>  and LaMnO<sub>3</sub> based perovskite with 3DOM morphology were prepared by this method and successively used for toluene oxidation [137-142]. LaCoO<sub>3</sub> perovskite with 3DOM morphology synthesized by nanocasting method also showed a superior activity for methane oxidation [143]. But the amount and type of additive and calcination tempera-

TABLE-1  
PEROVSKITE OXIDES CATALYST WITH DIFFERENT DOPING FOR OXIDATION OF VOCs

Catalysts	Preparation method	BET specific surface area	VOC	T <sub>max</sub>	Ref.
B-site doping					
SrTi <sub>0.86</sub> Mn <sub>0.14</sub> O <sub>3</sub>	Hydrothermal	22	Toluene	350	[107]
LaBO <sub>3</sub> (B = Ni, Co, Cr, Mn)	Citrate decomposition	4.4-14.4	Methyl ethyl ketone	270 (for Mn)	[108]
LaB <sub>0.2</sub> Mn <sub>0.8</sub> O <sub>3</sub> (B = Fe, Co, Ni)	Co-precipitation	11-25	Vinyl chloride	210-240	[109]
LaCo <sub>0.07</sub> P <sub>0.03</sub> O <sub>3</sub>	Sol-gel	15-27	Propane	376-483	[112]
LaCo <sub>0.93</sub> B <sub>0.07</sub> O <sub>3</sub>	Sol-gel	27.7	Propane	405	[113]
A-site doping					
La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub>	Sol-gel	23.4	Methane	300	[114]
HCl modified La <sub>0.5</sub> Sr <sub>0.5</sub> MnO <sub>3</sub>		21.8	Vinyl chloride	300	[115]
La <sub>1-x</sub> Ce <sub>x</sub> MnO <sub>3</sub> (x = 0–0.5)	Sol-gel	10.5-30.7	Styrene	321-358	[116]
La <sub>0.8</sub> Ce <sub>0.2</sub> MnO <sub>3</sub>	Co-precipitation	35.5	Vinyl chloride	213	[117]
La <sub>1-x</sub> Ag <sub>x</sub> CoO <sub>3</sub> (x = 0–0.05)	One-pot sol-gel	–	Toluene	239-300	[118]
La <sub>1-x</sub> Ca <sub>x</sub> CoO <sub>3</sub>	Citrate method	7.3-19.1	Propane	333-413	[121]
La <sub>0.5</sub> Ca <sub>0.5</sub> CoO <sub>3.6</sub>	Sol-gel	9.3	Toluene	218	[122]
La <sub>0.8</sub> Al <sub>0.2</sub> MnO <sub>3</sub>	Sol-gel	43.6/47.3	1,2-Dichloroethane	330	[123]
A- and B-site Co-doping					
La <sub>0.8</sub> Ce <sub>0.2</sub> Mn <sub>0.8</sub> Ni <sub>0.2</sub> O <sub>3</sub>	Citric sol-gel	15.66	Trichloroethylene	379	[124]
La <sub>0.7</sub> Sr <sub>0.3</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>	Sol-gel	22.2	Toluene	250	[125]
La <sub>0.91</sub> Ce <sub>0.10</sub> Co <sub>0.99</sub> O <sub>3</sub>	Reactive grinding	31	CH <sub>3</sub> OH and CH <sub>4</sub>	142 and 365	[125]
La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.9</sub> Fe <sub>0.1</sub> O <sub>3</sub>	Hydrothermal	24	Toluene	245	[126]
La <sub>0.9</sub> Sr <sub>0.1</sub> Mn <sub>0.9</sub> Fe <sub>0.1</sub> O <sub>3</sub>	Hydrothermal	67	Toluene	213	[128]

TABLE-2  
PEROVSKITE OXIDES CATALYST WITH VARIOUS MORPHOLOGY FOR OXIDATION OF VOCs

Catalysts	Morphology	Preparation method	BET specific surface area	VOC	T <sub>max</sub>	Ref.
La <sub>1-x</sub> Ce <sub>x</sub> CoO <sub>3</sub>	Nanofibers	Electrospinning	43	Benzene	415	[129]
LaCoO <sub>3</sub>	Nanorod	SBA-15-assisted electrospinning	177	Benzene	425	[130]
LaCoO <sub>3</sub>	Nanorod	NaOH etching	44	Benzene	350	[130]
LaCoO <sub>3</sub>	Nanorod	Electrospinning NaOH corrosion (3 h)	38.7	Benzene	388	[131]
SmMnO <sub>3</sub>	Net-like	One-step molten polymerization	27.7	Toluene	215	[70]
SrFeO <sub>3-δ</sub> -3EG	3DOM	Citric acid-assisted polytemplating	33.7	Toluene	347	[137]
CeMnO <sub>3</sub> /600	3DOM	Hard templating/excessive impregnation	39	Toluene	205	[138]
PrMnO <sub>3</sub> -HoMSs	Hollow multishelled	Polymer-derived	30	Toluene	249	[134]
SrMn <sub>0.8</sub> Ce <sub>0.2</sub> O <sub>3</sub>	Nanoparticle	Self-combustion	2.8	Acetone	200	[136]
LaCoO <sub>3.6</sub>	Rod	Citric acid complexing coupled with hydrothermal	26.4	Ethyl acetate	235	[132]
LaMnO <sub>3.6</sub>	Rod	Citric acid complexing coupled with hydrothermal	32.5	Ethyl acetate	203	[132]
La <sub>0.6</sub> Sr <sub>0.4</sub> CoO <sub>3.6</sub>	Lamellar	Citric acid complexing coupled with hydrothermal	20.2	Ethyl acetate	175	[132]
La <sub>0.6</sub> Sr <sub>0.4</sub> MnO <sub>3.6</sub>	Lamellar	Citric acid complexing coupled with hydrothermal	31.5	Ethyl acetate	190	[132]

tures used for the synthesis of catalyst was played vital roles on activity of catalyst [137,138,141]. Thus, the effect of the morphology was different on the different VOCs combustion and further work is required for clarification.

**Hybrid construction:** The removal of VOCs can also effectively increase by using perovskite oxides supported over other oxide supports with high surface area such as CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub>, MnO<sub>2</sub>, *etc.* than the perovskite oxide alone due to afford some additional interfacial and physio-chemical properties [144-150]. The high oxygen storage potentiality and exceptional redox properties make CeO<sub>2</sub> as an important support for perovskite in VOCs removal [151]. La<sub>0.8</sub>Ce<sub>0.2</sub>MnO<sub>3</sub> perovskite supported over three different kinds of CeO<sub>2</sub> with respect to their morphologies (cube, rod and polyhedron) have studied for toluene oxidation and result shown that polyhedron CeO<sub>2</sub>

support gave highest activity due to its high specific surface area, small particle size and more oxygen vacancies [152]. The catalytic efficiency of LaMnO<sub>3</sub> supported over CeO<sub>2</sub> can also enhance for chlorobenzene oxidation in compare to LaMnO<sub>3</sub> alone due to decrease the carbon deposition and increase the redox capability [145]. Similarly, LaCoO<sub>3</sub> perovskite supported over Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (x = 0-0.3) was also shown higher activity than bulk LaCoO<sub>3</sub> for benzene and toluene combustion due to enhanced oxygen mobility and more exposed surface area [148]. Various Mn-based perovskites supported over MnO<sub>2</sub> was also improve the catalytic efficiency for different VOCs removal like toluene, benzene, *o*-xylene and ethylbenzene oxidation [144]. LaMnO<sub>3</sub> with various supports like TiO<sub>2</sub>, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (YSZ) catalysts were investigated for 1,2-dichloropropane and toluene oxidation [153,154].

The hybrid construction can also be done by using perovskite oxides as a support for other active composition. Transition metal supported over various perovskites have shown high catalytic activity towards catalytic removal of VOCs by increasing the number of active sites. Commonly, Pd based catalysts are used most efficiently for VOCs removal. The Pd/LaBO<sub>3</sub> (B = Fe, Co, Ni, Mn) catalysts were designed for toluene oxidation and among the composites Pd/LaFeO<sub>3</sub> displayed higher activity due to increased particle size as well as well-dispersed Pd nano-particles [155]. Similarly, Pd/LaBO<sub>3</sub> (B = Fe, Co, Ni, Mn) catalysts were tested for chlorobenzene combustion in air and Pd/LaMnO<sub>3</sub> combination showed best activity because of synergistic effect between perovskite and Pd [156]. Ultrasonic treated Pd/CeMnO<sub>3</sub> catalyst also reported as an efficient catalyst for oxidation of benzene due to the surface pores formation and high number of active sites [157]. The Pd/Cu-doped LaCoO<sub>3</sub> and Au/LaMnO<sub>3</sub> were also reported for oxidation of benzene [158] and toluene [159], respectively due to strong metal-support interaction and modified surface area. Ag-modified La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub> perovskite catalysts was also enhancing their catalytic efficiency for methanol oxidation due to anionic vacancies formation by partial oxidation of Mn<sup>3+</sup> to Mn<sup>4+</sup> [160]. Different methodically synthesized Pt/LaCoO<sub>3</sub> were investigated for catalytic propane oxidation and the results shown that electrospinning methodically prepared catalyst exhibited a higher activity because of the synergetic effect of bulk Pt species and the catalyst surface [161,162]. The MnO<sub>2</sub>/LaMnO<sub>3</sub> composite have also prepared by different methods and successfully used for the removal of VOCs [146,163-165].

## Conclusion

Perovskite oxides have become more interesting because of their promising activity, cost-effective, extraordinary stability, compositional/structural exibility and tunable physiochemical properties. In last few decades, the designing and developing of perovskite-based catalysts for volatile organic compounds (VOCs) removal have become a hot topic for many researchers and they also have been achieved some encouraging results. Numerous techniques such as individual or co-doping, controlling morphology, constructing hybrid and surface modernization have been employed to increase the catalytic efficiency. The catalytic efficiency of perovskites has satisfyingly increased by either A, B or both at same time doping. Nano-structuring and three-dimensional ordered microporous (3DOM) morphology building scheme can also create an enlarge specic surface area as well as large number of active sites in perovskite catalysts and the enhance activity for VOCs combustion is also anticipated. The surface area as well as overall catalytic efficiency of perovskite can also increase by construction of hybrid structure either using different other metal oxides as support for perovskite or perovskite as support for different metals. Though great enhancement has been attained to the improvement of perovskite oxides for VOCs removal catalyst at ambient condition but further upgradation is still needed for practical application.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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