

Catalytic Oxidation of BTX (Benzene, Toluene, and Xylene) Using Metal Oxide Perovskites

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The high toxicity, volatility, and dispersion of the light aromatics, benzene, toluene, and xylene (BTX) pose a serious threat to the environment and human health. Compared to incineration, catalytic oxidation technologies for BTX removal offer benefits such as low energy consumption, high efficiency, and low pollution. ABO_3 -type perovskite catalysts (ABO_3 -PCs) are particularly promising materials for the catalytic oxidation of BTX due to their high activity and thermal stability, as well as their adjustable elemental composition and flexible structure allowing their properties to be improved. Nonetheless, the full potential of ABO_3 -PCs for the oxidation of BTX has yet to be reached. This review systematically and critically analyses progress in the catalytic oxidation of BTX by ABO_3 -PCs. Catalytic performance is assessed for each category of perovskite, including non-doped, doped (A-, B-, or A/B-site doped), and loading type (noble metal, metal oxide, and matrix composite), with structure-activity relationships are established. A kinetic model and proposed mechanism for the catalytic oxidation of BTX are also presented. Finally, the challenges and opportunities of ABO_3 -PCs applied to BTX oxidation and other reactions are highlighted.

to photochemical reactions and ozone pollution.^[2] As industrial VOC emission regulations become more stringent, the reduction and control of VOCs in many countries has become a key priority in air pollution management.^[3] Notably, BTX, primarily originating from industrial processes such as synthetic rubber manufacture, paint and dye production, fiber synthesis, petroleum processing, semiconductor fabrication, and fuel production, have garnered attention due to their high toxicity and facile entry into the human body through inhalation or contact with skin.^[4]

Recycling and removal are the two main methods of disposing BTX.^[5] Recovery technologies are ideal for removing low-concentrations of BTX and offer advantages such as high efficiency and operational simplicity.^[6] Nevertheless, additional treatments may be required to address potential secondary contamination.^[7]

Destruction technologies effectively treat BTX across a wide concentration range, completely breaking them down into harmless small molecules.^[8] Biological and photocatalytic approaches remain in the development stages, and direct oxidation is only suitable for treating exhaust gases with a high combustible content.^[9] Considering the economic and technical advantages of various treatment methods, catalytic oxidation has consistently offered low costs and high removal rates, positioning

1. Introduction

Volatile organic compounds (VOCs) are typically toxic and pathogenic, posing significant threats to both the natural environment and human health.^[1] VOCs comprise hydrocarbons, ketones, aldehydes, etc. Among them, a group of light aromatic hydrocarbons known as BTX (benzene, toluene, and xylene) is considered highly polluting due to their significant contribution

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it as an efficient, environmentally friendly, and cost-effective approach for BTX removal.^[10]

Catalytic oxidation methods offer a means of achieving complete oxidation, utilizing a catalyst to accelerate the oxidation process of BTX at temperatures of 300–500 °C.^[11,12] This approach reduces energy consumption and allows the treatment of a wide range of BTX concentrations.^[13] Typically, catalytic oxidation technologies achieve organic waste gas degradation rates exceeding 95%, with CO₂ and H₂O serving as the final decomposition products. Additionally, the lower reaction temperatures employed in catalytic oxidation significantly suppresses NO_x production, thereby surpassing other treatment methods.^[14]

In recent years, there has been growing interest on the full oxidation of BTX, with a particular emphasis on developing novel catalysts.^[15] Various catalysts, including noble metal-based and non-precious metal oxide catalysts, have been reported. However, there is a need for further improvement in terms of low-temperature catalytic activity and enhanced stability.^[16,17] ABO₃-PCs have attracted attention as they possess high activity at low-temperatures, high stability and have easily adjustable redox properties.^[18,19] Metal oxide perovskites follow the general formula ABO₃, where A represents rare earth (La³⁺, Sr²⁺, Ce⁴⁺, Sm²⁺, Gd²⁺ etc.), alkali metal ions (K⁺, Rb⁺, Cs⁺ etc.), or alkaline-earth ions (Be²⁺, Mg²⁺, Ca²⁺, Ba²⁺ etc.) and B represents transition metal ions (Co²⁺, Mn³⁺, Ni³⁺, and Fe²⁺ etc.).^[20] The unique ABO₃ crystal structure, electronic structure, and other properties, make them highly promising as alternative catalysts due to their comparatively low cost.^[21] There has been a steady increase in studies focusing on ABO₃-catalyzed oxidation of BTX,^[22] with research focusing on understanding the factors that influence activity, providing mechanistic insights and ultimately catalyst design strategies. Notably, substitution of cations, either on the A- or B-site, with cations with similar radii, is a common strategy used to generate defects and oxygen vacancies that enhance catalytic performance.^[23] Compared to many noble metal-based catalysts, ABO₃-PCs have large specific surface areas, rendering them highly active and cost-effective.^[24]

Previous reviews on catalytic oxidation of VOCs have primarily focused on noble metal catalysts and non-precious metal catalysts.^[25] A systematic review of the catalytic oxidation of BTX pollutants by ABO₃-PCs is lacking.^[14] In this review, we address this gap by covering the advances made in the oxidation of BTX using ABO₃-PCs since the year 2000, providing a comprehensive understanding of the fundamental principles governing the catalytic oxidation of BTX.^[26] The review begins by summarizing the sources and hazards of BTX and highlights the key features and advantages of ABO₃-catalyzed oxidation as a method to eliminate them. We evaluate the catalytic performance of ABO₃-PCs based on various categories, including non-doped, doped (A-site, B-site, and A/B-site doped), and different loading types (noble metal, metal oxide, and matrix composite). Additionally, the effects of overall morphology, structure, water vapor, and sulfur species on ABO₃-PCs are examined. The review also presents a systematic summary of the kinetic model and possible oxidation mechanism of BTX catalytic oxidation. Current issues and challenges are highlighted. Special emphasis is placed on outlining future research directions and prioritizing work in the field of BTX removal using ABO₃-PCs. By providing a comprehensive and insightful overview, we believe the review will unlock addi-

tional opportunities to deepen the understanding of ABO₃ oxidation principles and lay the theoretical groundwork for developing new high-performance ABO₃-PCs.

2. BTX Sources and Hazards

BTX (benzene, toluene, and xylene) are a class of highly irritating and toxic organic compounds that fall under the category of volatile organic compounds (VOCs). These compounds are structurally stable aromatic compounds and are either non-polar (benzene) or weakly polar (toluene and xylene). The emission of BTX contribute significantly to global atmospheric pollution.^[27] Consequently, BTX pose a threat to the environment and human health.^[28]

2.1. Benzene

Benzene emissions primarily originate from industrial activities, transportation, and fuel consumption.^[29] There are three main sources of benzene:

- i) Production processes – benzene is extensively used in the manufacture of synthetic rubber, plastics, paints, dyes, and other chemicals. Significant amounts of benzene are also generated during oil refining and fuel processing.^[30]
- ii) Transportation – benzene is present in vehicle exhaust, and is particularly prevalent in urban areas with a high traffic density.
- iii) Tobacco – smoking releases benzene and other harmful substances, making it a significant sources of benzene emissions.

Benzene has various detrimental effects on the human body.^[31] Benzene is myelotoxic and increases the risk of leukemia, lymphoma, and other forms of cancer. Long-term exposure to benzene can result in neurological damage, decreased mental capacity, and impaired immune system function, leading to the development of allergies, asthma, and other respiratory diseases.^[32] Prolonged exposure to benzene during pregnancy can cause fetal malformations and miscarriages. Benzene can adversely affect the central nervous system, cardiovascular health, liver, lungs, kidneys, and other vital organs, giving rise to various secondary effects.^[33,34]

2.2. Toluene

Toluene is primarily released through industrial pollution and urban traffic. Petrochemical processes, automobile exhaust, printing and lacquer industry, and synthetic wood and furniture panels, are among the sources of toluene emissions.^[35] Toluene is carcinogenic and can cause irritation to the eyes and throat, respiratory irritation, as well as cause sensory abnormalities.^[26] Exposure to high concentrations of toluene can result in symptoms such as headaches, dizziness, nausea, vomiting, and weakness, affecting the nervous system, liver, kidneys, immune system, and other organs. Prolonged exposure to toluene can lead to neurological and immune system disorders, including epilepsy, neuralgia, and anemia.^[36]

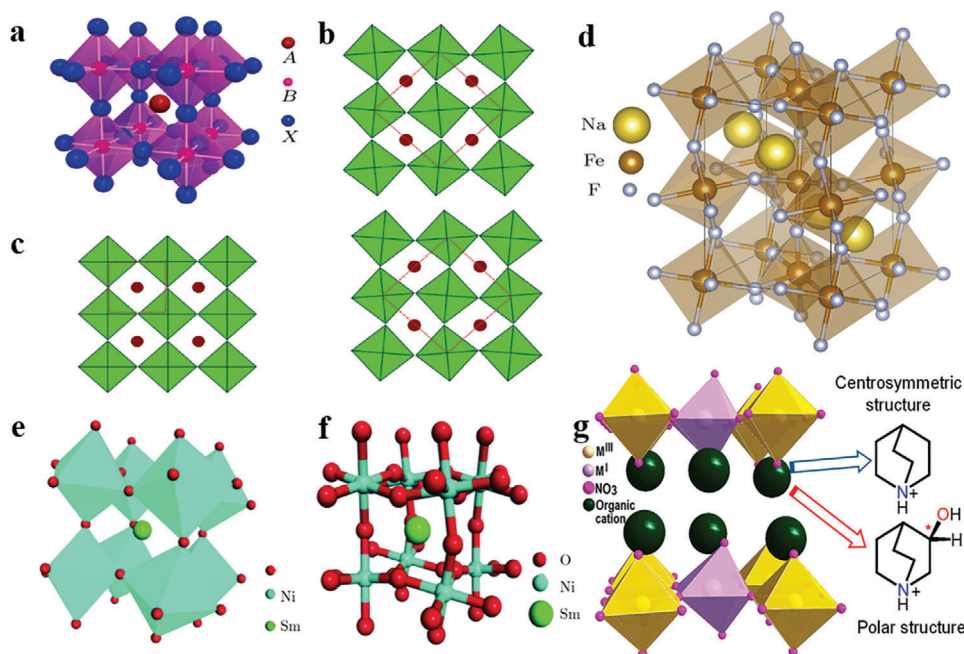


Figure 1. a–c) Three typical structures of ABO_3 -type perovskites, d,e) inorganic, f) organic, and g) organic–inorganic perovskites.^[40,41]

2.3. Xylenes

Xylene (*o*-, *m*- and *p*-xylene) is sourced from petroleum refining, printing and dyeing, plastic processing, and paint production.^[6] It is also present in household items including perfumes, paints, and cleaners as well as in gasoline and diesel fuels. Exposure to xylene in the atmosphere poses risks to the central nervous system, respiratory system, and eyes.^[25] Longer-term exposure to xylene can result in nausea, insomnia, headaches, and gastrointestinal discomfort,^[37] and ultimately causes organ damage, cancer, and immunosuppression.^[38] Xylene is also released into aquatic environments through industrial wastewater and municipal sewage, posing a threat to aquatic organisms and other ecological environments. It can also interact with other hazardous substances, leading to synergistic effects that pose an even greater threat to human health.^[39]

3. Characteristics and Advantages of ABO_3 -Type Perovskites

The general formula for a typical chalcogenide oxide is ABO_3 , where lanthanide and/or alkaline earth metal ions, primarily located in the A-site, are combined with transition metal ions in the B-site, see Figure 1a–c. ABO_3 -type perovskites have been evaluated in many fields, such as electrode materials in electrochemistry, advanced oxidation catalysis and as automotive exhaust gas catalysts.^[40,41] Figure 1d–g illustrates typical inorganic, organic and organic–inorganic ABO_3 structures. With their unique structures and properties, ABO_3 -type perovskites are promising catalysts for BTX oxidation.

ABO_3 -PCs have the following characteristics that make them ideally suited to BTX oxidation.

- i. High flexibility in composition. Studies have shown that approximately 90% of the metal ions in ABO_3 -PCs can be substituted without altering the lattice structure, allowing for a certain degree of anionic or cationic defects.^[42] The A- and B-sites of ABO_3 allows various types of dopants to be incorporated, so different types of functional catalysts may be prepared by doping different metal ions at the A- and B-sites.^[43] Even the oxygen vacancies can be doped to some extent with F^- , Cl^- , and S^{2-} , further enhancing the flexibility of their components and thus potentially improving the performance in catalytic oxidation reactions.^[44]
- ii. Tunable redox properties. The excellent redox properties of ABO_3 -PCs are predominantly associated with the rich valency of B-site transition metal ions,^[45] which gives rise to lattice vacancies and/or alterations in the valence state of B-site ions upon substitution, providing ABO_3 -PCs with a flexible and adjustable electronic structure.^[46] Furthermore, although the A-site cation in ABO_3 is typically considered inert in catalytic reactions, it can influence the redox properties of ABO_3 by affecting the electronic structure, defect structure and surface properties of the B-site cation.^[47]
- iii. Oxygen migration properties.^[48] ABO_3 -PCs possess a high oxygen adsorption capacity affording two oxygen species, i.e., α - and β -oxygen. α -Oxygen refers to oxygen weakly adsorbed on the ABO_3 surface and β -oxygen corresponds to lattice oxygen within ABO_3 . Due to the flexible composition and abundant defects in ABO_3 , both α - and β -oxygen can undergo rapid migration on the surface and in the bulk phase, thus improving the catalytic reaction rate of oxidation reactions. Moreover, oxygen mobility in ABO_3 -PCs can be significantly enhanced by substitution of A and B sites. By increasing the oxygen mobility, the concentration of α -oxygen

- at the interface can be elevated, further improving catalytic activity.^[49]
- iv. Versatile surface properties. The ABO_3 -PC motif can serve as a substrate for the generation of nanoparticles (NPs).^[50] Specifically, selected metal elements can be initially doped into the chalcogenide lattice, and then, through reduction or high temperature processes, NPs can be formed on the ABO_3 surface.^[51] Alternatively, ABO_3 can be loaded onto the surface of other substrates, such as zeolites, polymers and other metal oxides, taking advantage of the strong interactions between ABO_3 and other substances, thereby enhancing their performance as heterogeneous catalysts for the oxidation of pollutants.^[52]
 - v. Anti-coking and anti-poisoning properties. ABO_3 -PCs exhibit exceptional anti-coking properties during catalytic oxidation, ensuring thorough pollutant oxidation.^[53] Notably, even when pure methane is used as a substrate, coke formation is not observed at high temperatures when employing ABO_3 -PCs. Moreover, doping anions into the oxygen sites enables the chalcogenide lattice to act as a storage material for impurities such as sulfide and chloride, removing these species from the ABO_3 surface and improving tolerance to these catalyst poisons.^[54] The outstanding oxygen and water storage capacity of ABO_3 -PCs also contributes to their anti-coking and anti-poisoning properties.^[55]

ABO_3 -PCs offer several advantages for the catalytic oxidation of pollutants.

- i. Facile and inexpensive preparation. The methods used to prepare ABO_3 -PCs are straightforward and the preparation costs are relatively low.^[56] Typically, hydrothermal, sol-gel and precipitation methods are used and require inexpensive precursors. Moreover, the methods are scalable, allowing ABO_3 -PCs to be produced in large quantities.
- ii. High activity. Due to the unique crystal structure and abundant oxygen vacancies, ABO_3 -PCs exhibit remarkable oxidation activity and enable catalytic reactions to proceed at comparatively low temperatures and pressures.^[57]
- iii. Outstanding stability. ABO_3 -PCs demonstrate exceptional stability even at high temperatures and pressures, ensuring sustained catalytic efficiency over extended periods and enabling recycling and reuse,^[58] including under oxidative environments.^[59]
- iv. Sustainability. ABO_3 -PCs are often free from toxic and harmful components, and their application also eliminates the need for using corrosive reagents, thereby ensuring an environmentally benign approach.^[60]

4. ABO_3 -PCs for BTX Oxidation

4.1. Non-Doped ABO_3 -PCs

Non-doped perovskites, particularly La-based ABO_3 -PCs, have been extensively investigated for their structural stability and compositional versatility. La-based ABO_3 -PCs are excellent catalysts for various reactions, principally in the reduction of aldehydes and ketones, but also in the oxidation of BTX. Spinicci et al. investigated the oxidation of benzene using $LaMnO_3$ and

$LaCoO_3$, with the former having a higher activity (a 20 °C difference in $T_{50\%}$). Redox analysis confirmed that cobalt in $LaCoO_3$ is exclusively in the Co^{3+} oxidation state, whereas $LaMnO_3$ contains 35% Mn^{4+} in addition to Mn^{3+} . Hence, the metal ion and valence state in the B-site have a significant influence on catalytic performance.^[61] In a related study, Zhang et al. synthesized $LaMnO_3$ (LMO) using citric acid sol-gel (SG), glycine oxidation (GC) and co-precipitation (CP) techniques, and applied the perovskites in the oxidation of toluene. The catalytic activity followed the trend LMO-SG > LMO-CP > LMO-GC, aligning with the specific surface area of the catalyst and concentration of surface adsorbed oxygen species.^[62] Rezlescu et al. compared $GdAlO_3$, $SrMnO_3$, $SrCoO_3$, and $MnFeO_3$ prepared using a sol-gel auto-combustion method in the complete oxidation of benzene. $SrMnO_3$ showed the highest catalytic activity at low temperatures. The differences in catalytic activity were attributed to the distinct reactivity of oxygen species involved and/or variations in the number of active sites on the perovskite surface.^[63] **Table 1** provides an overview of non-doped ABO_3 compounds evaluated as catalysts for benzene and toluene oxidation over the past two decades. $LaCoO_3$, $LaMnO_3$, and $LaFeO_3$ have been extensively investigated, and further development of other non-doped ABO_3 species appear warranted. As observed from **Table 1**, the conversion temperature and performance of non-doped ABO_3 -PCs differ, primarily influenced by the air velocity, benzene and toluene concentrations and other reaction conditions.

4.2. Stoichiometrically Doped and Defective ABO_3 -PCs

The catalytic activity of ABO_3 -PCs may be improved by replacing ions with radii similar to those in the A-, B-, and O-sites.^[90] Catalytic activity is primarily attributed to the B-site cations, whereas the A-site cations mainly play a role in stabilizing the structure.^[91] However, substituting an A-site cation with other metal ions potentially leads to an alteration in oxidation state, oxygen vacancies, and cation defect density of the B-site cation, ultimately affecting the catalytic performance. Therefore, the catalytic activity of ABO_3 -PCs can be modified by introducing other ions through partial or simultaneous substitution of A- and B-site cations.^[92] **Table 2** summarizes all doped ABO_3 -PCs evaluated in the catalytic oxidation of BTX.

4.2.1. A-Site Cation Doping

The A-site ions of ABO_3 -PCs play a pivotal role in stabilizing the structure by controlling the dispersion state and atomic valence of the active B-site component.^[60] Despite the A-site ions having little direct involvement in chemical reactions, the substitution of the A-site ions indirectly influences the valence state of the B-site ions.^[120] They can also introduce lattice defects and modify the chemical sites of the lattice oxygen, influencing the reactivity at B-sites.^[121] A-site ions and O^{2-} form a dense stacking layer dominated by ionic bonding.^[122] Transition metals have multiple valences, which facilitates the variable substitution of the A-site ions, but can induce a change in the coordination number or lead to other structural changes.^[123]

Parvizi et al. investigated the catalytic activity of $La_{0.8}A_{0.2}MnO_3$ (A: Co^{2+} , Zn^{2+} , Mg^{2+} , and Ba^{2+}) nanocatalysts in toluene

Table 1. Non-doped ABO₃-PCs evaluated in the catalytic oxidation of benzene and toluene.

Catalyst	Reactant composition	Space velocity/flow rate	T _{50%} [°C]	T _{90%} [°C]	References
LaMnO ₃	C ₆ H ₆ /O ₂ :1/100	14100 mL g ⁻¹ h ⁻¹	301	–	[61]
LaCoO ₃	C ₆ H ₆ /O ₂ :1/100	14100 mL g ⁻¹ h ⁻¹	323	–	[61]
GdAlO ₃	1–2% C ₇ H ₈	5100 mL g ⁻¹ h ⁻¹	350	–	[61]
SrMnO ₃	1–2% C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	325	–	[64]
LaCoO ₃	500 ppm C ₆ H ₆	96000 mL g ⁻¹ h ⁻¹	266	331	[65]
LaCoO ₃	500 ppm C ₆ H ₆	96000 mL g ⁻¹ h ⁻¹	288	388	[66]
LaNiO ₃	400 ppm C ₆ H ₆	100 mL min ⁻¹	≈350	–	[67]
LaMnO ₃	400 ppm C ₆ H ₆	100 mL min ⁻¹	≈250	–	[67]
LaFeO ₃	400 ppm C ₆ H ₆	100 mL min ⁻¹	≈420	–	[67]
LaCoO ₃	400 ppm C ₆ H ₆	100 mL min ⁻¹	≈390	–	[68]
LaCoO ₃	500 ppm C ₇ H ₈	192000 mL g ⁻¹ h ⁻¹	–	275	[69]
LaMnO ₃ -SG	1000 ppm C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	204	224	[62]
LaMnO ₃ -GC	1000 ppm C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	245	274	[62]
LaMnO ₃ -CP	1000 ppm C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	214	257	[62]
LaFeO ₃	210 ppm C ₇ H ₈	138 mL min ⁻¹	506	545	[70]
LaCoO ₃ -acetic acid	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	–	223	[71]
LaFeO ₃ -5	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	255.9	277.3	[72]
LaFeO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	–	243	[63]
LaFeO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	308.1	333.3	[73]
SrTiO ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	370	385	[74]
LaMnO ₃	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	229	298	[75]
LaMnO ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	295	332	[76]
LaFeO ₃	4000 ppm C ₇ H ₈	47000 mL g ⁻¹ h ⁻¹	323	–	[77]
LaNiO ₃	4000 ppm C ₇ H ₈	47000 mL g ⁻¹ h ⁻¹	297	–	[77]
LaMnO ₃	5 g m ⁻³ C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	170	250	[78]
LaCoO ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	268	411	[79]
Bulk-LaMnO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	263	300	[80]
SmMnO ₃	1000 ppm C ₇ H ₈	48000 mL g ⁻¹ h ⁻¹	223	258	[81]
SmMnO ₃	1000 ppm C ₇ H ₈	24000 mL g ⁻¹ h ⁻¹	–	<240	[82]
LaMnO ₃	1000 ppm C ₇ H ₈	40000 mL g ⁻¹ h ⁻¹	281	290	[83]
LaFeO ₃	0.2 mol% C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	268	400	[84]
GdMnO ₃ (SY)-0.05	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	240	260	[85]
GdMnO ₃ (SY)	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	244	276	[85]
LaMnO ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	349	416	[86]
LaFeO ₃	0.1 vol% C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	200	253	[87]
LaCoO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	–	>280	[88]
LaCrO ₃	1000 ppm C ₇ H ₈	9600 mL g ⁻¹ h ⁻¹	352	445	[89]

if oxygen is not mentioned in the list, then the reaction system uses air.

oxidation and found that La_{0.8}Zn_{0.2}MnO₃ exhibited the highest activity (Figure 2a).^[124] Similarly, Liu et al. synthesized La_{1-x}Ce_xMnO₃ (x = 0–10%) doped perovskites and observed that Ce⁴⁺ substitution increased the Mn⁴⁺/Mn³⁺ ratio and oxygen species, resulting in enhanced catalytic activity (Figure 2b).^[93] In another study, Liu et al. prepared La_{1-x}Ce_xMnO₃ (x = 0–10%) using flame spray pyrolysis and investigated their activity in the catalytic oxidation of benzene at temperatures ranging from 100 to 450 °C. The introduction of Ce⁴⁺ resulted in a change in the chemical state of B-site ions and oxygen species, with the ratios of Mn⁴⁺/Mn³⁺ and the adsorbed oxygen/lattice oxygen

(O_{ads}/O_{latt}) ratio on the catalyst surface increasing, and enhancing catalytic activity.^[125]

SmMnO₃, Sm_{0.8}A_{0.2}MnO₃ (A = Ce, Sr, and Ca), and Sm_{1-x}Ca_xMnO₃ (x = 0.0, 0.1, 0.2, and 0.3) were synthesized via a sol-gel method and evaluated in the catalytic oxidation of toluene in a fixed-bed reactor. Substitution of Ce⁴⁺ and Ca²⁺ positively influences the catalytic performance in toluene oxidation,^[94] whereas the substitution of Sr²⁺ has a negative effect (Figure 2c). Zhao et al. used porous La_{1-x}Co_xFeO₃ (x = 0–0.4) for toluene oxidation.^[126] Partial substitution of La³⁺ by Co³⁺ in LaFeO₃ induced structural deformations, increasing its specific surface

Table 2. Doped ABO₃-PCs employed in the catalytic oxidation of BTX.

Catalyst	Reactant composition	Space velocity/flow rate	T _{50%} [°C]	T _{90%} [°C]	References
La _{0.8} Sr _{0.2} MnO _{3-δ}	500 ppm C ₆ H ₆	20000 mL g ⁻¹ h ⁻¹	520	–	[33]
LaCoO ₃	500 ppm C ₆ H ₆	96000 mL g ⁻¹ h ⁻¹	266	331	[65]
La _{1-x} Sr _x MnO ₃	400 ppm C ₆ H ₆	100 mL min ⁻¹	≈270	–	[68]
SrTi _{1-x} CuXO ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	348	412	[74]
SrTi _{1-x} MnXO ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	305	335	[74]
La _{0.8} Ca _{0.2} FeO ₃	4000 ppm C ₇ H ₈	47000 mL g ⁻¹ h ⁻¹	289	–	[77]
La _{0.8} Ca _{0.2} NiO ₃	4000 ppm C ₇ H ₈	47000 mL g ⁻¹ h ⁻¹	333	–	[77]
La _{0.6} Ca _{0.4} NiO ₃	4000 ppm C ₇ H ₈	47000 mL g ⁻¹ h ⁻¹	346	–	[77]
LaCo _{0.6} Fe _{0.4} O ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	218	363	[79]
LaCo _{0.6} Cr _{0.4} O ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	242	384	[79]
LaCo _{0.6} Cu _{0.4} O ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	261	410	[79]
LaZn _{0.01} Fe _{0.99} O ₃	0.2 mol% C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	235	363	[84]
LaZn _{0.05} Fe _{0.95} O ₃	0.2 mol% C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	233	356	[84]
LaZn _{0.1} Fe _{0.9} O ₃	0.2 mol% C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	230	335	[84]
LaZn _{0.2} Fe _{0.8} O ₃	0.2 mol% C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	226	327	[84]
LaZn _{0.3} Fe _{0.7} O ₃	0.2 mol% C ₇ H ₈	15000 mL g ⁻¹ h ⁻¹	222	323	[84]
La _{0.67} Ca _{0.33} CrO ₃	1000 ppm C ₇ H ₈	9600 mL g ⁻¹ h ⁻¹	302	381	[89]
La _{0.8} Ca _{0.2} CrO ₃	1000 ppm C ₇ H ₈	9600 mL g ⁻¹ h ⁻¹	354	424	[89]
La _{0.5} Ca _{0.5} CrO ₃	1000 ppm C ₇ H ₈	9600 mL g ⁻¹ h ⁻¹	295	374	[89]
La _{1-x} Ce _x MnO ₃	1000 ppm C ₆ H ₆	60000 mL g ⁻¹ h ⁻¹	–	450	[93]
Sm _{0.8} Ca _{0.2} MnO ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	–	238	[94]
La _{0.9} Sr _{0.1} CoO ₃	1000 ppm C ₇ H ₈	100 mL min ⁻¹	219	–	[95]
LaNi _{0.75} Co _{0.25} O ₃	1000 ppm C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	–	225	[96]
La _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	1000 ppm C ₇ H ₈	30000 mL g ⁻¹ h ⁻¹	251	270	[97]
La _{0.8} Ce _{0.2} Mn _{0.8} Ni _{0.2} O ₃	1000 ppm C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	–	295	[98]
La _{0.7} Sr _{0.3} Co _{0.8} Fe _{0.2} O ₃	500 ppm C ₇ H ₈	5700 mL g ⁻¹ h ⁻¹	>243	–	[99]
La _{0.8} Zn _{0.2} MnO ₃	1393 ppm C ₆ H ₆	200 mL min ⁻¹	≈400	–	[100]
La _{0.8} Zn _{0.2} MnO ₃	498 ppm C ₆ H ₆	200 mL min ⁻¹	≈500	–	[100]
La _{0.8} Zn _{0.2} MnO ₃	149 ppm <i>o</i> -Xylene	200 mL min ⁻¹	≈550	–	[100]
La _{1-x} Ce _x CoO _{3-δ}	500 ppm C ₆ H ₆	90000 mL g ⁻¹ h ⁻¹	308	–	[101]
La _{0.9} Sr _{0.1} Mn _{0.9} Fe _{0.1} O ₃	500 ppm C ₇ H ₈	30000 mL g ⁻¹ h ⁻¹	213	236	[102]
LaFe _{0.27} Mn _{0.73} O ₃	1000 ppm C ₇ H ₈	40000 mL g ⁻¹ h ⁻¹	–	<280	[103]
La _{0.8} Ce _{0.2} Mn _{0.3} Fe _{0.7} O ₃	1000 ppm C ₇ H ₈	6000 mL g ⁻¹ h ⁻¹	179	202	[104]
La _{0.8} Sr _{0.2} MnO _{3-δ}	0.6% C ₇ H ₈	2000 mL g ⁻¹ h ⁻¹	260	–	[105]
LaNi _{0.5} Co _{0.5} O _{3-δ}	500 ppm C ₇ H ₈	100 mL min ⁻¹	221	239	[106]
La _{0.6} Ce _{0.4} Co _{0.6} Fe _{0.4} O ₃	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	190	318	[107]
La _{0.82} Sr _{0.18} CoO ₃	600 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	–	210	[108]
Eu _{0.6} Sr _{0.4} FeO ₃	500 ppm C ₇ H ₈	22500 mL g ⁻¹ h ⁻¹	279	305	[109]
La _{0.8} Cu _{0.2} MnO ₃	6000 ppm C ₇ H ₈	5000 mL g ⁻¹ h ⁻¹	–	–	[110]
La _{0.8} Sr _{0.2} MnO ₃	6000 ppm C ₇ H ₈	5000 mL g ⁻¹ h ⁻¹	–	–	[110]
La _{0.8} Sr _{0.2} CoO ₃	0.1 mol% C ₇ H ₈	7200 mL g ⁻¹ h ⁻¹	163	–	[111]
LaMn _{0.5} Co _{0.5} O ₃	0.2 mol% C ₇ H ₈	5000 mL g ⁻¹ h ⁻¹	200	–	[112]
LMNi _{4.50}	900–1200 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	234	278	[113]
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.2} O ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	–	>219	[114]
La _{0.5} Sr _{0.5} MnO _{3-δ}	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	250	255	[115]
La _{0.6} Sr _{0.4} MnO _{3-δ}	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	299	310	[115]
La _{0.4} Sr _{0.6} MnO _{3-δ}	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	218	255	[115]
La _{0.5} Ca _{0.5} CoO _{3-δ}	2000 ppm C ₇ H ₈	12000 mL g ⁻¹ h ⁻¹	183	218	[116]
La _{0.9} Ca _{0.1} CoO ₃	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	–	220	[117]
Acid-etched LaCoO ₃	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	–	215	[117]

(Continued)

Table 2. (Continued)

Catalyst	Reactant composition	Space velocity/flow rate	T _{50%} [°C]	T _{90%} [°C]	References
La _{0.99} Ag _{0.01} CoO ₃	1000 ppm C ₇ H ₈	30000 mL g ⁻¹ h ⁻¹	275	300	[118]
La _{0.98} Ag _{0.02} CoO ₃	1000 ppm C ₇ H ₈	30000 mL g ⁻¹ h ⁻¹	265	290	[118]
La _{0.97} Ag _{0.03} CoO ₃	1000 ppm C ₇ H ₈	30000 mL g ⁻¹ h ⁻¹	249	284	[118]
La _{0.95} Ag _{0.05} CoO ₃	1000 ppm C ₇ H ₈	30000 mL g ⁻¹ h ⁻¹	238	268	[118]
La _{0.75} Sr _{0.25} CoO _{3-δ}	500 ppm C ₇ H ₈	30000 mL g ⁻¹ h ⁻¹	212	–	[119]

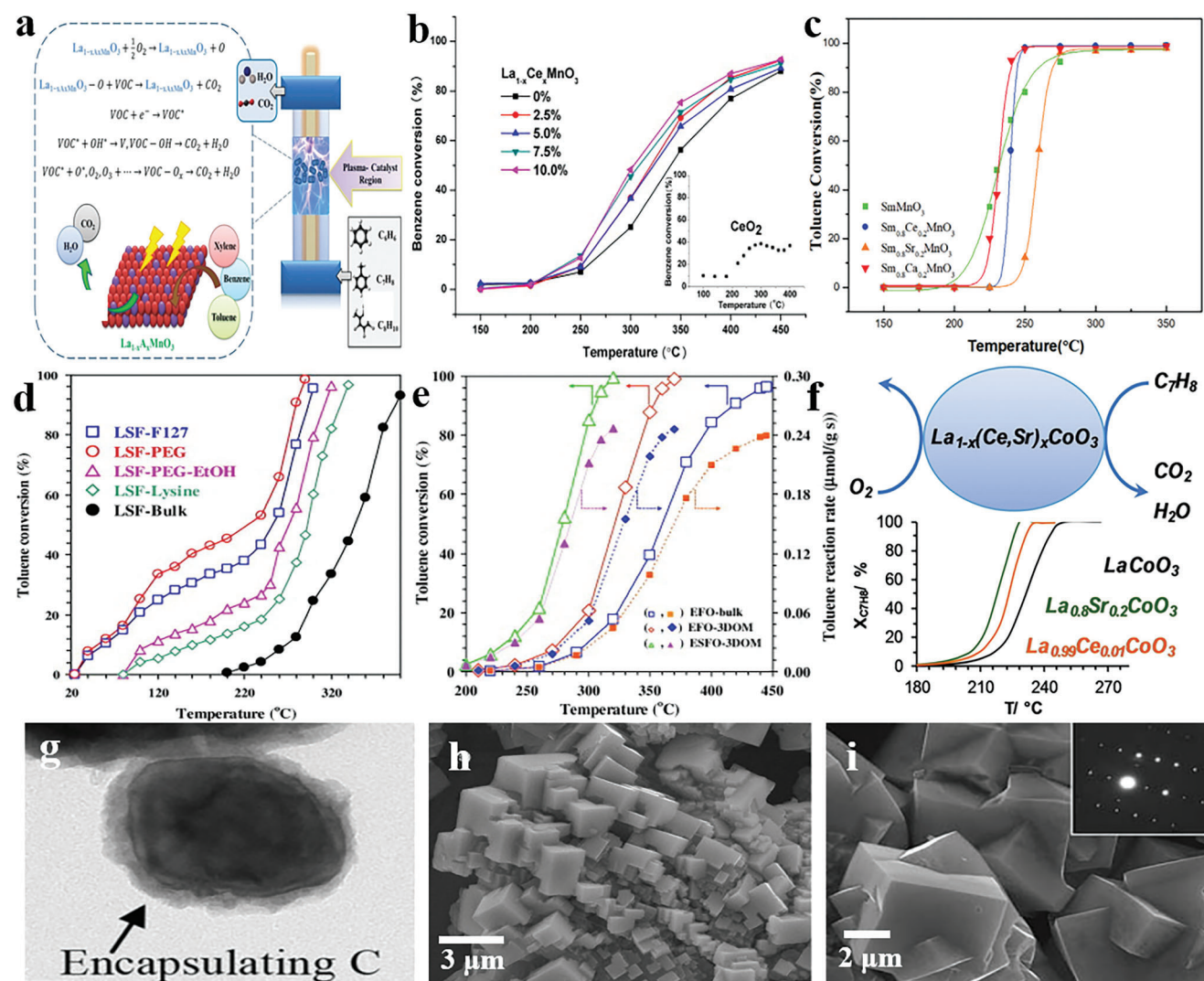


Figure 2. a) La_{1-x}(Co, Zn, Mg, and Ba)_xMnO₃ for BTX degradation.^[124] b) Benzene conversion of La_{1-x}Ce_xMnO₃. Reproduced with permission.^[93] Copyright 2015, The Royal Society of Chemistry. c) Performance of Sm_xA_{1-x}MnO₃ (A = Ce, Sr, and Ca) perovskite for efficient catalytic oxidation of toluene.^[94] d) Toluene conversion of the La_{0.6}Sr_{0.4}FeO_{3-δ} catalysts.^[127] e) Toluene conversion and the corresponding reaction rate versus reaction temperature catalyzed by Eu_{1-x}Sr_xFeO₃-bulk, 3D ordered macroporous materials (3DOMs) Eu_{1-x}Sr_xFeO₃, and 3DOM Eu_{1-x}Sr_xFeO₃ catalysts.^[125] f) La (Sr and Ce) CoO₃ and their properties in toluene catalytic total oxidation.^[95] g) TEM image of used catalysts after steam reforming at 800 °C for 1 h.^[74] h) SEM image of La_{0.4}Sr_{0.6}MnO_{3-δ}.^[128] i) SEM image and selected area electron diffraction patterns (inset) of La_{0.6}Sr_{0.4}MnO_{3-δ}-270-50-0.35. Reproduced with permission.^[129] Copyright 2013, Elsevier.

area, and promoting the exposure of active sites. This generated a large amount of lattice oxygen and more surface-adsorbed oxygen, resulting in a significant improvement in the catalytic activity. Zhao et al. prepared A-site substituted $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$, which showed excellent catalytic performance in toluene oxidation ($T_{10\%} = 54\text{ }^\circ\text{C}$, $T_{50\%} = 225\text{ }^\circ\text{C}$, and $T_{90\%} = 280\text{ }^\circ\text{C}$).^[127] The high performance of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ catalyst (Figure 2d) is related to its larger specific surface area. Inspired by this work, Ji et al. substituted Sr^{2+} by Eu^{2+} to afford $\text{Eu}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0$ and 0.4), which showed a greater surface oxygen concentration and remarkable activity in the oxidation of toluene (Figure 2e).^[125] Heidinger et al. explored the oxidation of toluene with Sr^{2+} and Ce^{4+} substituted LaCoO_3 .^[95] The stability of the catalyst was improved, with substitution by Sr^{2+} significantly altering the reduction and oxygen desorption properties of Co^{3+} , whereas substitution by Ce^{4+} had only a limited effect (Figure 2f).

Soongprasit et al. synthesized $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0, 0.2$, and 0.4) using a sol-gel method and found that Ce^{4+} doping afforded filamentary carbon on the surface with Co located at the top of the carbon filament.^[74] This structure was proposed to result in higher catalytic activity compared to the undoped catalyst (Figure 2g). A $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3-\delta}$ catalyst prepared by Deng et al. has a microcubic structure,^[128] as shown in Figure 2h. Hydrothermally prepared $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta}$ for toluene oxidation, along with SEM and TEM image analysis of Sr-substituted LaMnO_3 , revealed minimal morphological variation among catalysts.^[129] The particles showed an interwoven microcubic shape, with $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta}$ exhibiting the highest catalytic activity (Figure 2i). Thus, elemental doping produces varying effects on the morphology and structure of the catalysts, which can affect the catalytic activity of ABO_3 -PCs.

4.2.2. B-Site Cation Doping

When the B-site ion of ABO_3 -PCs is replaced by an ion of a different valency, it can cause lattice vacancies or a change in the valence state of the B-site ion, enabling the B-site ion a focal point for designing or improving ABO_3 -PCs.^[130] Transition metals such as Fe, Co, Ni, Mn and Cu can oxidize to unstable higher valence states, thereby altering catalytic activity. In addition, B-site substitution in ABO_3 -PCs is more intricate compared to the A-site ions and warrants a thorough investigation. The catalytic activity of the ABO_3 -PCs is determined by the nature of the excess metal cations at B site.^[131] B-site transition metal ions exhibit a wide range of oxidation states, adding to the complexity of their substitution effects, surpassing those of the A-site ions.^[132]

B-site doping in ABO_3 -PCs has a profound effect on their catalytic properties and despite the complexity of synthesizing B-site doped materials,^[133] it is an excellent approach to enhance catalyst performance. Hosseini et al. synthesized nanostructured LaFeO_3 and $\text{LaZn}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0.01, 0.05, 0.1, 0.2$, and 0.3) perovskites and evaluated them in the catalytic oxidation of toluene (Figure 3a). Characterization data revealed that the total insertion of zinc into LaFeO_3 takes place when $x \leq 0.1$. However, ZnO segregation occurs to some extent, especially at $x > 0.1$. The catalytic activity increases with the zinc content, attributed in part to the presence of zinc oxide. The proportion of $\text{LaZn}_x\text{Fe}_{1-x}\text{O}_3$ and zinc oxide influences the oxygen activation capacity and re-

activity of the catalyst.^[84] Lv et al. examined the catalytic performance of $\text{LaCo}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Fe, Cr, and Cu}$) under identical conditions and observed that introducing an appropriate proportion of specific metal cations at the B site of ABO_3 -PCs could improve the catalytic activity, primarily through modifications in the oxidation state of the B site cations and oxygen vacancy content (Figure 3d,e).^[79] Qi discovered that the doping of a small amount of Co^{3+} at the B site of LaNiO_3 significantly enhances the catalytic oxidation of toluene,^[96] while substituting Ni^{3+} with Cu^{2+} did not improve activity (Figure 3f,g). Among all the catalysts tested, $\text{LaNi}_{0.75}\text{Co}_{0.25}\text{O}_3$ exhibited the highest activity, achieving a relatively low temperature ($T_{90\%} = 225\text{ }^\circ\text{C}$) for toluene oxidation. Sahin et al. demonstrated that LaMnO_3 catalysts are more active than LaFeO_3 for toluene oxidation, with lower $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ values (Figure 3h).^[70]

In addition to catalytic activity, B-site cations are also closely related to the durability of the perovskite and resistance to impurities (potential catalyst poisons). Vazquez et al. explored the effect of B-site cations in SrTiO_3 on catalytic behavior in toluene oxidation reactions (Figure 3b,c).^[134] The addition of metal dopants ensured good stability over three catalytic cycles and lifetime tests. However, CuO deposition was observed on the surface of the Cu-doped catalyst. Incorporation of Mn^{4+} into the Ti^{4+} site in SrTiO_3 enhances the $O_{\text{ads}}/O_{\text{latt}}$ ratio and catalytic performance. Notably, $\text{SrTi}_{1-x}\text{B}_x\text{O}_3$ doped with Mn^{4+} and Cu^{2+} exhibited the highest catalytic activity for complete conversion of toluene to CO_2 at temperatures below $350\text{ }^\circ\text{C}$. Giraudon et al. loaded Pd NPs onto the surface of ABO_3 -PCs using a hydrogen reduction calcination method and investigated the catalytic activity of Pd/ LaB_3 ($B = \text{Co, Fe, Mn, and Ni}$) in the oxidation of toluene, with the following trend observed: Pd/ $\text{LaFeO}_3 > \text{Pd}/\text{LaMnO}_{3-\delta} > \text{Pd}/\text{LaCoO}_3 > \text{Pd}/\text{LaNiO}_3$.^[135] The higher activity of Pd/ LaFeO_3 for the total oxidation of toluene was attributed to a low amount of calcination and to the remarkable high stability of the perovskite lattice whatever the nature of the gas stream, which allowed the same palladium dispersion to be maintained at the different stages of the process and was stable under the oxidizing conditions. In contrast, phase transformations for the other perovskite lattices led to increases in the palladium particle size and was considered responsible for the lower activity (Figure 3i).

4.2.3. A/B-Site Cation Doping

The A-site cations of ABO_3 -PCs indirectly influence the valence state of the B-site ions and the oxygen vacancies within the catalyst, resulting in changes in the electronic state of the B-site ions and the B-O bond lengths,^[136] with the B-site cations serving as the active catalytic centers in oxidation reactions.^[137] In addition, the co-doping can realize the tuning of structural and electronic properties of ABO_3 -PCs at the same time. Consequently, partial substitution of both A-site and B-site ions can be employed to improve the catalytic performance of ABO_3 -PCs.^[138]

Oskoui et al. used artificial neural networks to model the correlation between catalytic performance in toluene oxidation and catalytic parameters (the mole fraction of La, the mole fraction of Fe, calcination temperature ($^\circ\text{C}$), and molar ratio of citric acid to the total nitrates in the precursor solution) using $\text{La}_x\text{Sr}_{1-x}\text{Fe}_y\text{Co}_{1-y}\text{O}_3$ catalysts. They achieved 100% toluene

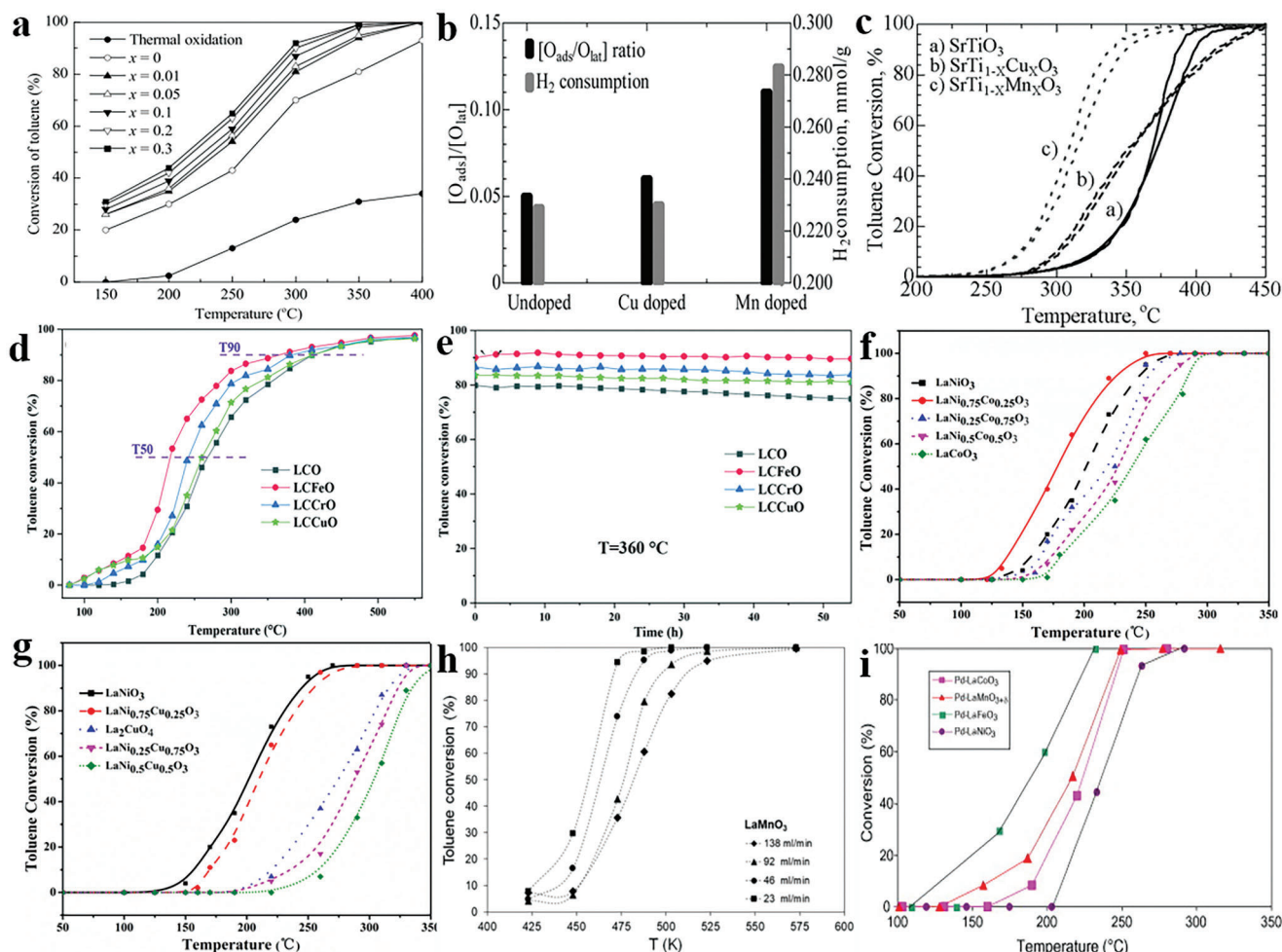


Figure 3. a) Performance of LaMnO_3 perovskites in the catalytic oxidation of toluene.^[84] b,c) Catalytic oxidation of toluene using $\text{SrTi}_{1-x}\text{B}_x\text{O}_3$ ($\text{B} = \text{Cu}$ and Mn). Reproduced with permission.^[134] Copyright 2018, John Wiley and Sons. d,e) Catalytic performance of $\text{LaCo}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}, \text{Cr},$ and Cu), $\text{LaNi}_x\text{B}_{1-x}\text{O}_3$ ($\text{B} = \text{Co}$ and Cu).^[79] f,g) LaMnO_3 ($\text{B} = \text{Co}$ and Cu).^[96] h) LaMnO_3 .^[70] i) Pd/LaBO_3 ($\text{B} = \text{Co}, \text{Fe}, \text{Mn},$ and Ni)^[135] in the catalytic oxidation of toluene. Reproduced with permission.^[135] Copyright 2007, Elsevier.

conversion for dual doped $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_3$ at total conversion temperatures (T_c) = 700 and 800 °C, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.82}\text{Co}_{0.18}\text{O}_3$ at $T_c = 700$ °C, and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.66}\text{Co}_{0.34}\text{O}_3$ at $T_c = 650$ °C. A/B substitution strongly impacts on $\text{La}_x\text{Sr}_{1-x}\text{Fe}_y\text{Co}_{1-y}\text{O}_3$ catalyst performance.^[139] Li et al. employed an active milling method to prepare $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ perovskites and evaluate their catalytic properties in toluene oxidation (Figure 4a). $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) demonstrated remarkable catalytic activity with a $T_{90\%}$ of 270 °C (Figure 4b–c), attributed to improvements in redox ability through A/B site doping,^[97] oxygen vacancy enrichment, and activation of lattice oxygen species. Yuan et al. investigated the impact of Ce^{4+} and Ni^{3+} doping in $\text{La}_{1-x}\text{Ce}_x\text{Mn}_{1-y}\text{Ni}_y\text{O}_3$ perovskites on catalytic toluene oxidation, with $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ exhibiting the highest conversion for toluene oxidation (Figure 4d,e).^[98] XPS analysis revealed that $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ possesses a higher lattice oxygen content and a lower redox onset temperature, both of which contribute to the catalytic oxidation of toluene (Figure 4f–h).

Co-doping is an efficient approach for generating active sites and enhancing the catalytic performance of ABO_3 -PCs

(see above). Moreover, several ABO_3 -PCs with the composition $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ ($x = 0$ and 0.3 ; $y = 0, 0.2,$ and 0.5) were prepared using a sol-gel method and their catalytic activity was studied in toluene oxidation.^[99] Doping with Sr^{2+} resulted in a flaccid morphology with reduced particle size and increased specific surface area. The study revealed that the catalytic activity was significantly increased with 30% Sr^{2+} substituted in the A site, whereas a slight improvement was observed with 20% partial substitution of Fe^{4+} at B site. Among the catalysts tested, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ was the most active, attributed to the reduced particle size, increased specific surface area, the formation of Fe^{4+} ions and the presence of electrophilic O-species, which serve as active sites that activate the substrate.

4.2.4. ABO_3 -PCs with Anion/Cation Defects

Due to the structural stability of ABO_3 -PCs they can withstand the removal of ions to afford crystal defects that can be exploited as active sites in catalytic processes.^[140] For example, Sun et al.

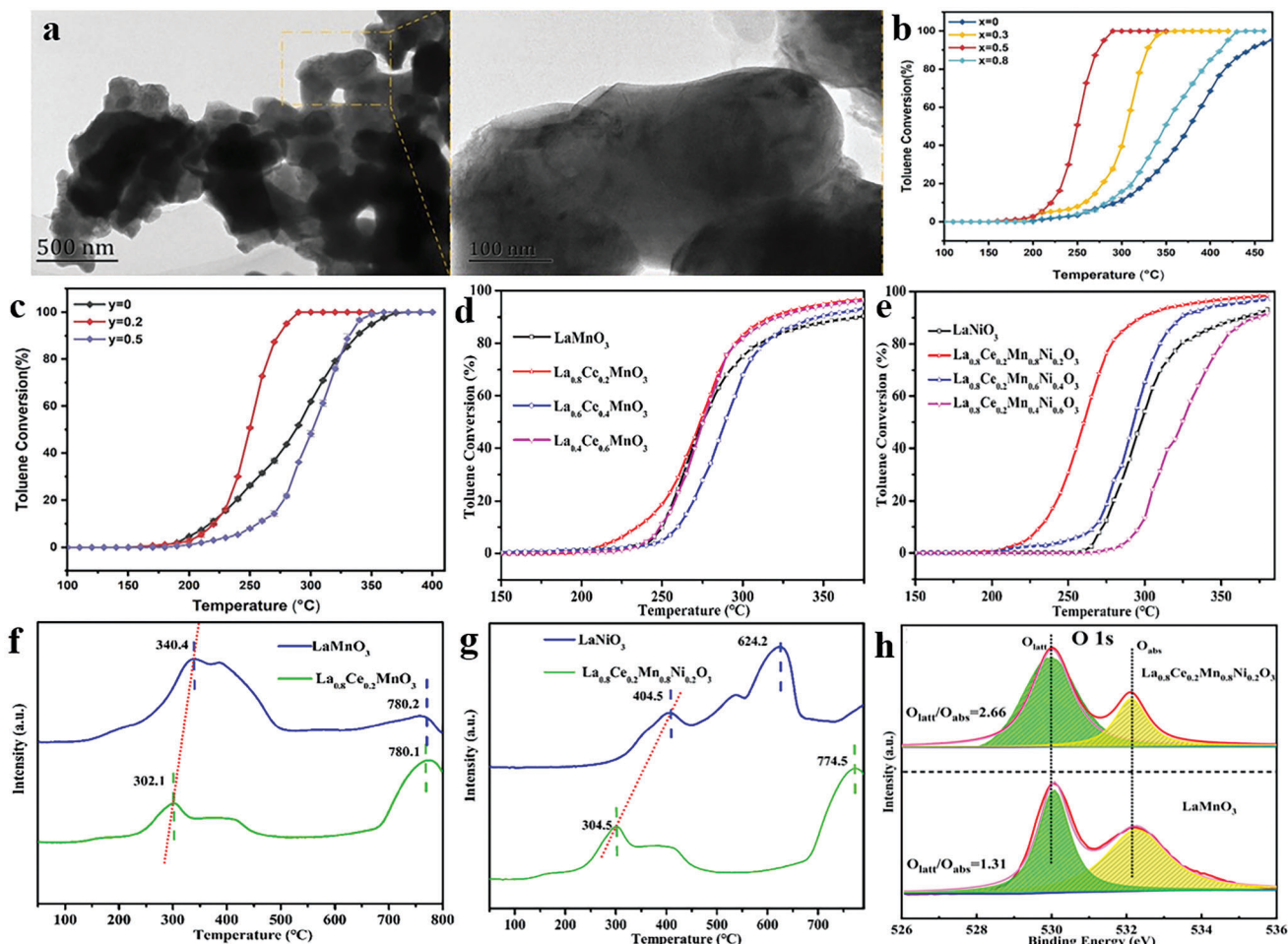


Figure 4. a) TEM of the LSCF catalyst. Toluene conversion using b) $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($x = 0, 0.3, 0.5,$ and 0.8) and c) $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-y}\text{Fe}_y$ ($y = 0, 0.2,$ and 0.5) catalysts. Reproduced with permission.^[97] Copyright 2023, Elsevier. d) Catalytic activity of (d) $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ perovskites ($x = 0, 0.2, 0.4,$ and 0.6) and e) LaNiO_3 , $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{1-y}\text{Ni}_y\text{O}_3$ ($y = 0, 0.2, 0.4,$ and 0.6). f) H_2 -TPR of LMO and $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$, and g) LaNiO_3 and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$. O 1s analysis of LMO and $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$. Reproduced with permission.^[98] Copyright 2023, American Chemical Society.

doped ABO_3 -PCs with Ca^{2+} ions which leads to an increase in the number of oxygen vacancies and valency changes on the surface of the catalysts, resulting in a more active catalyst.^[141] In addition, adjusting the ratio of A/B site cations can also promote the formation of oxygen vacancies on the surface to expose more active sites, e.g. Vincent et al. investigated the structure of $\text{La}_{0.8}\text{MnO}_{3-\delta}$, and found that varying the ratio of La/Mn affects the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ and generates vacancies.^[142] Wu et al. synthesized a series of A-site cation-deficient LaFeO_3 PCs using the Pechini method, and evaluated them in the oxidation of toluene in the temperature range of 200–400 °C. Toluene conversion was maintained at 80% in a long cycle. Studies indicate that the introduction of A-site cation deficiencies affects the surface physicochemical properties of the PC, including enhanced oxygen vacancies, surface valence state, and surface oxygen content.^[73] Indeed, Xu et al. designed a series of $\text{La}_{1-x}\text{MnO}_3$ and found that the La^{3+} defects induce oxygen vacancies and adjust the electronic structure, significantly improving catalytic activity.^[143]

An alternative way to generate defects is to dope the oxygen vacancies of ABO_3 -PCs with F^- , Cl^- , Br^- , S^{2-} etc., thus modifying

the lattice structure, concentration of oxygen vacancies, specific surface area, etc., which in turn influences the electronic structure, oxygen diffusion properties, metal–oxygen bond strength, etc.^[144] although further studies are required to fully understand these features.

4.3. Complexes Containing ABO_3 Compounds

4.3.1. Noble Metal Composite ABO_3 -PCs

Incorporating noble metal NPs into ABO_3 -PCs is an effective approach to improve their catalytic performance.^[145] Dai et al. prepared LaMnO_3 and $x\text{Au}/\text{LaMnO}_3$ ($x = 1.4, 3.1,$ and 4.9 wt.%) with chain-ordered macroporous structures, the latter with Au NPs dispersed on the surface.^[146] Of the hybrid materials, $4.9\text{Au}/\text{LaMnO}_3$ demonstrated the highest catalytic activity, achieving a $T_{50\%}$ and $T_{90\%}$ of 201 and 226 °C, respectively, for toluene oxidation. The high activity was attributed to high surface area and elevated O_{ads} concentration, enhanced low-temperature

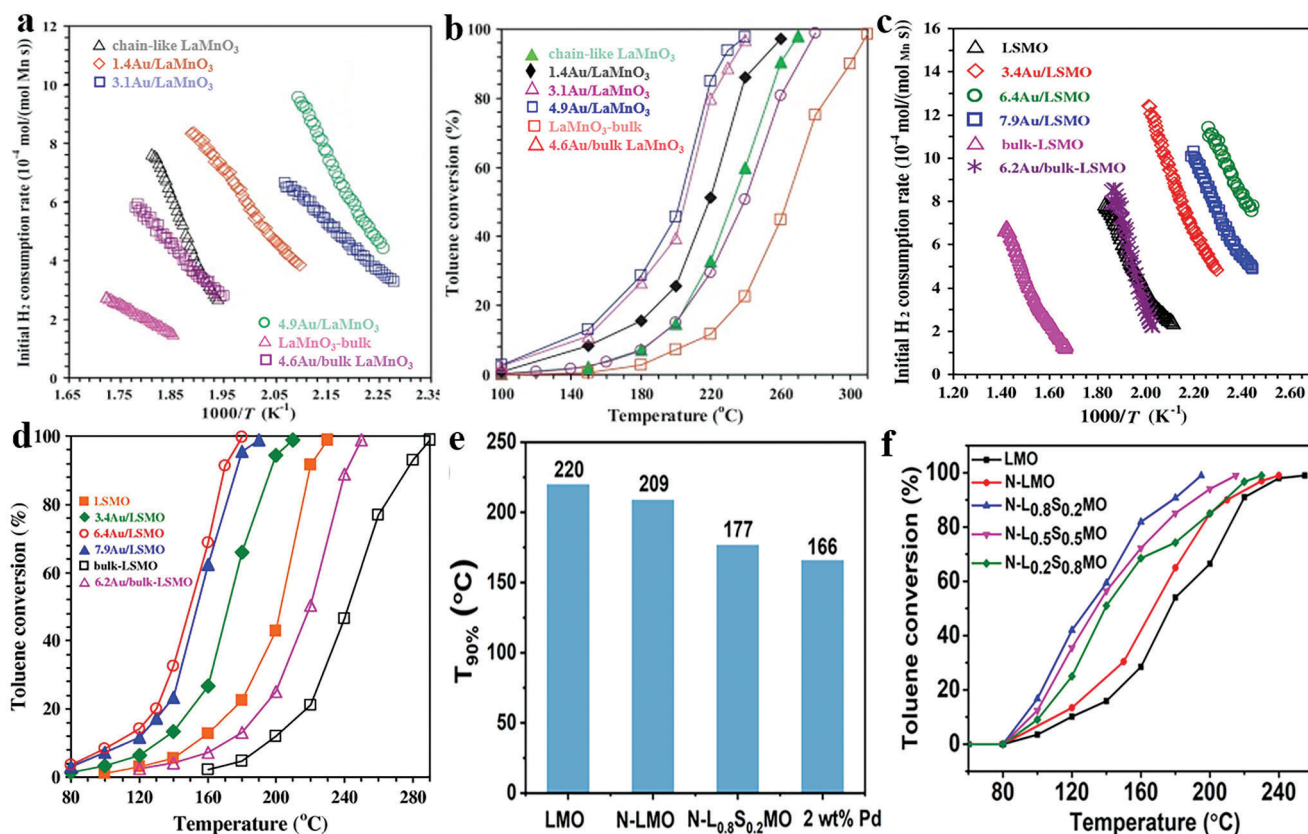


Figure 5. a) Initial H₂ consumption rate as a function of inverse temperature of chain-like LaMnO₃, 1.4Au/LaMnO₃, 3.1Au/LaMnO₃, 4.9Au/LaMnO₃, LaMnO₃-bulk, and 4.6Au/bulk LaMnO₃. b) Toluene conversion as a function of reaction temperature with the catalysts listed in (a).^[146] c) Initial H₂ consumption rate as a function of inverse temperature of the LSMO and xAu/LSMO samples. d) Toluene conversion as a function of temperature with La_{0.6}Sr_{0.4}MnO₃ and xAu/LSMO catalysts.^[147] e) The temperature difference of each catalyst when the toluene conversion rate reaches 90%. f) Toluene conversions as function of reaction temperature with LaMnO₃, N-LMO, N-L_{0.8}S_{0.2}MO, N-L_{0.5}S_{0.5}MO, and N-L_{0.2}S_{0.8}MO.^[148] Copyright 2021, Elsevier.

reducibility, due to strong interactions between the Au NPs and LaMnO₃ support (Figure 5a,b). Similarly, Dai et al. fabricated 3DOM La_{0.6}Sr_{0.4}MnO₃ (LSMO) and its xAu/LSMO (x = 3.4–7.9 wt.%) catalysts.^[147] They found that 6.4Au/LSMO exhibited the best catalytic activity, with T_{50%} and T_{90%} values for toluene oxidation at space velocity (SV) = 20000 mL g⁻¹ h⁻¹ reaching 150 and 170 °C, respectively (Figure 5c,d). The high activity was associated with a higher concentration of O_{ads}, improved low-temperature reducibility, and strong interaction between the Au NPs and LSMO.

Chen et al. used a nanocast array method to prepare Pd/La_{0.8}Ce_{0.2}MnO₃ catalysts, with optimal activity for the oxidation of toluene obtained using Pd/La_{0.8}Ce_{0.2}MnO₃/ZSM-5, attributed to higher acidity of the ZSM-5 support (Figure 5e,f). The Pd is highly dispersed on the surface of the La_{0.8}Ce_{0.2}MnO₃ perovskite, and the sample demonstrated a T_{50%} at 112 °C and T_{90%} at 227 °C for toluene oxidation.^[148] Another related study using ABO₃-PC as a support material showed that it prevents Pd from sintering. Nishihata et al. reported the remarkable catalytic activity of Pd-LaFeO₃, which was attributed in part to the reversible movement of Pd in and out of the perovskite lattice under oxidizing and reducing atmospheres, respectively, effectively inhibiting the growth of Pd NPs. This finding was further confirmed in another study, stemming from the homogeneous distribution

of Pd and the prevention of sintering. Consequently, Pd/LaFeO₃ exhibited a significantly higher catalytic activity in the oxidation of toluene compared to other composites.^[135]

Liang et al. synthesized Ag/LaCoO₃ catalysts using an impregnation method,^[118] and observed that the catalytic activity of Ag/LCO-250, Ag/LCO-450, and Ag/LCO-700 in toluene oxidation exceeded that of LaCoO₃. The enhanced catalytic performance was attributed to the interaction between the Ag/Ag₂O and LaCoO₃ perovskite, as well as to differences in surface oxygen composition and reactivity. Li et al. prepared catalysts such as 3DOM LaCoO₃ and its xAu/3DOM LaCoO₃ (x = 0–7.63 wt.%) catalysts, finding that 7.63Au/3DOM LaCoO₃ displayed the most favorable catalytic performance for toluene oxidation. This PC benefited from a high surface area (24–29 m² g⁻¹), a high concentration of adsorbed oxygen species and optimal low-temperature oxidation.^[149]

4.3.2. Metal Oxide Composite ABO₃-PCs

The formation of chalcocite typically requires high calcination temperatures, which leads to a sacrifice of the specific surface area and therefore a lower number of active catalytic sites, typically reducing catalytic activity. It was found that loading

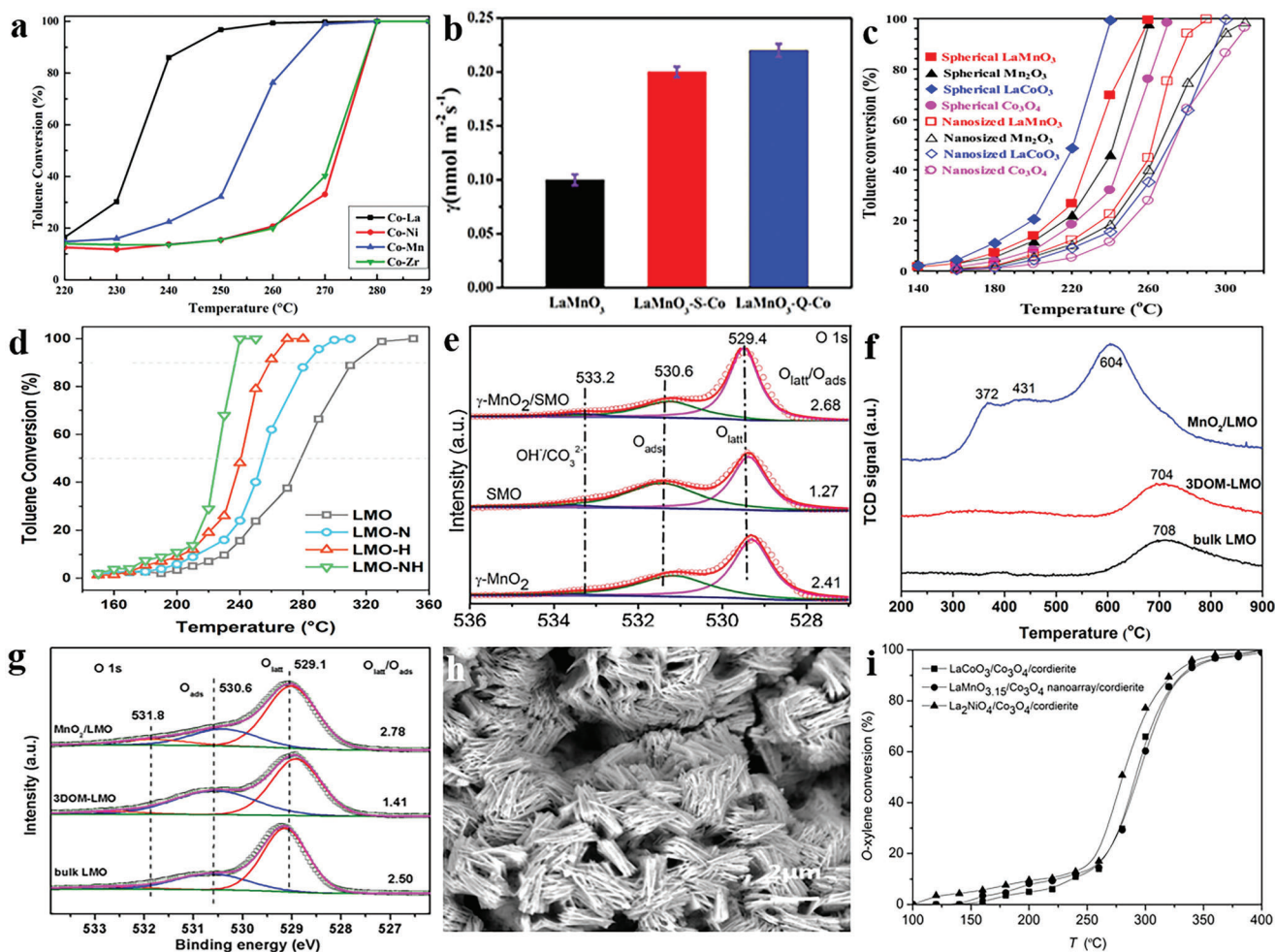


Figure 6. a) The effect of different metal oxides on the catalytic activity of $\text{LaCo}_3\text{Mn}_{1-x}\text{O}_3$ in the oxidation of toluene. Reproduced with permission.^[153] Copyright 2022, Elsevier. b) Toluene consumption rates at 250 °C and of different catalysts.^[154] c) Catalytic oxidation activity of spherical and nano-sized LaMnO_3 and MO_x catalysts on toluene. Reproduced with permission.^[155] Copyright 2013, American Chemical Society. d) Oxidation of toluene using LaMnO_3 catalysts.^[156] e) O 1s XPS spectra of $\gamma\text{-MnO}_2/\text{SMO}$, SMO , and $\gamma\text{-MnO}_2$.^[157] f) O_2 -TPD profiles and g) O 1s XPS spectra of the MnO_2/LMO , 3DOM-LMO, and bulk LMO catalysts.^[158] h) SEM image of $\text{LaCoO}_3/\text{Co}_3\text{O}_4$ nanowires. i) Oxidation of *o*-xylene catalyzed by LaBO_3 (B = Mn, Co, and Ni)/ $\text{Co}_3\text{O}_4/\text{cordierite}$ with different B types.^[159]

ABO_3 -PCs onto metal oxides is an effective approach for enhancing activity.^[16] Co_3O_4 and MnO_x are the most commonly used metal oxides combined with ABO_3 -PCs.^[150–152]

Wu et al. synthesized ultrafine Co_3O_4 decorated $\text{Co}_3\text{O}_4/\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$, exhibiting significantly improved catalytic performance at a concentration of 1000 ppm and SV of 72000 $\text{mL g}^{-1} \text{h}^{-1}$, resulting in a $T_{90\%}$ of 269 °C. The high catalytic activity may be attributed to the substantial surface area, abundant oxygen vacancies, and excellent reducibility (Figure 6a). Moreover, density functional theory calculations revealed that Co_3O_4 doping and interfacial effects of $\text{Co}_3\text{O}_4/\text{LaCo}_x\text{Mn}_{1-x}\text{O}_3$ result in lower activation energies for C–H cleavage.^[153] In another study by Zhang et al., Co_3O_4 catalysts were modified with different metals M (M = La, Mn, Zr, and Ni) for the catalytic oxidation of toluene. They found that $\text{Co}_3\text{O}_4\text{-LaCo}_3$ exhibited excellent catalytic performance with a $T_{90\%}$ of 243 °C and higher conversion rate (Figure 6b). Analysis suggests that the excellent activity of $\text{Co}_3\text{O}_4\text{-LaCo}_3$ may be attributed to its

high specific surface area with many Co^{3+} species and abundant adsorbed oxygen species.^[154] Dai et al. also discovered that hollow spherical LaCoO_3 and solid spherical Co_3O_4 outperformed their nano-sized counterparts in toluene oxidation.^[155] Their outstanding catalytic properties were attributed to their large surface area, high oxygen adsorption concentration, and better low-temperature oxidation (Figure 6c).

Wang et al. obtained a MnO_2/LMO material with a rod-like morphology through an alkaline hydrothermal treatment with acid etching (Figure 6d), with the material catalyzing the oxidation of toluene with a $T_{90\%}$ of 236 °C.^[156] Compared with bulk LMO, LMO with an alkaline hydrothermal treatment (LMO-N) and LMO with an acid treatment (LMO-H), LMO with an alkaline hydrothermal treatment with acid etching (LMO-NH) has a higher ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ions on the surface, which significantly improves the low-temperature catalytic activity by lowering the apparent activation energy ($< 38.6 \text{ kJ mol}^{-1}$) of the reaction. LMO-NH also has a high lattice oxygen

concentration and surface oxygen vacancy density, thus accelerating the adsorption and reaction of toluene. In another study, γ -MnO₂, SmMnO₃, and γ -MnO₂/SmMnO₃ were synthesized, and compared with γ -MnO₂/SmMnO₃ formed from the situ growth of γ -MnO₂ on the surface of SmMnO₃. Of the three materials, γ -MnO₂/SmMnO₃ was found to have the highest activity in BTX oxidation in wet air (10 vol.%), attributed to a higher molar ratio of surface lattice oxygen to adsorbed oxygen ($O_{\text{latt}}/O_{\text{ads}}$) (Figure 6e) and improved low-temperature processing.^[157] Li et al. reported MnO₂/LaMnO₃, which at 290 °C could completely oxidize toluene to CO₂ and H₂O, with a toluene/oxygen molar ratio of 1/100 and a space velocity of 120000 mL g⁻¹ h⁻¹. Based on O₂-TPD and O 1s XPS data (Figure 6f,g), it was found that the catalyst has abundant oxygen species and high lattice oxygen mobility.^[158]

ABO₃-PCs have also been immobilized on a range of materials. Sun et al. successfully integrated different perovskite/hybrid perovskites onto the surface of cordierite honeycomb ceramics and evaluated them in the catalytic oxidation of xylene. The La₂NiO₄/Co₃O₄ composite exhibited a unique 3DOM hierarchical hollow microsphere structure composed of nanowires (Figure 6h). Compared with LaCoO₃/cordierite, Co₃O₄/cordierite, LaMnO_{3.15}/Co₃O₄/cordierite and LaCoO₃/Co₃O₄/cordierite, the La₂NiO₄/Co₃O₄/cordierite catalyst displayed superior catalytic performance, achieving a T_{90%} for *o*-xylene of 299 °C (Figure 6i). The high catalytic activity of La₂NiO₄/Co₃O₄/cordierite catalysts was attributed to the high specific surface area, large oxygen storage capacity, and synergistic effects between La₂NiO₄ and Co₃O₄.^[159]

4.3.3. Other Composite ABO₃-PCs

ABO₃-PCs are often limited by their low specific surface areas and low mechanical strength, which impacts on their activity and lifetime. Incorporating dispersed ABO₃-PCs on or within a support material can overcome these limitations. Various support materials have been evaluated including Al₂O₃, CeO₂, MgO, MnO₂, and ZrO₂.

Si et al. reported that 3DOM LaMnO₃ dispersed and immobilized on MnO₂ results in better catalytic performance in the oxidation of toluene compared to the unsupported catalyst.^[158] Similarly, Wang et al. found that La_{0.8}Ce_{0.2}MnO₃/CeO₂ nanocubes exhibit high catalytic efficiency in the oxidation of toluene due to having a high specific surface area, more oxygen vacancies, better low-temperature reduction, and highly active oxygen species.^[160] Composite catalysts have also shown promising results, as demonstrated by Alifantim et al., who immobilized 10–20 wt.% LaCoO₃ on Ce_{1-x}Zr_xO₂ (x = 0–0.3) and observed significant activity in the oxidation of benzene and toluene in the temperature range 100–500 °C. In contrast, bulk LaCoO₃ catalysts were less active and required higher temperatures.^[161] Giroir-Fendler et al. drew similar conclusions, highlighting the influence of the interaction between LaMnO₃ and the substrate on oxygen diffusion and catalytic performance in toluene oxidation.^[62] Xue et al. supported La_{0.8}Sr_{0.2}MnO₃ and La_{0.8}Sr_{0.2}CoO₃ on γ -Al₂O₃ via an impregnation method, with the catalysts achieving 90% xylene conversion at 260 °C.^[162]

Table 3 summarizes the ABO₃-PCs immobilized on various support materials and their performance in the catalytic oxidation of BTX. In general, the immobilized catalysts exhibit superior oxygen exchange capacity and catalytic activity compared to dispersed ABO₃-PCs. Furthermore, certain supports compensate for the surface properties lacking in ABO₃, thereby enhancing catalytic activity. The morphology, crystallinity, reducibility, acidity, hydrophobicity, and other physicochemical properties of the support affect catalytic activity. For example, a hydrophobic surface repels water and favors interactions with hydrophobic BTX leading to improved catalytic performance.^[153]

5. Factors Affecting Catalytic Activity

5.1. Effect of Morphology

Controlling and optimizing the morphology of ABO₃-PCs is important due to the impact that catalyst morphology has on performance, and the route used to prepare ABO₃-PCs plays a key role in governing their morphology.^[183] Currently, the main approaches used to modulate the morphology ABO₃-PCs involves utilizing templates with high specific surface areas and well-defined channel structures in their synthesis. For example, Chen et al. fabricated catalysts comprising Pd supported on La_{1-x}Sr_xMnO₃ mesoporous nanotube arrays using SBA-15 as a hard template (Figure 7a). The morphological control results in catalysts with a very high specific surface area, ordered hollow orifices, and large pore size. Notably, compared to La_{0.8}Sr_{0.2}MnO₃, the 2 wt.% Pd@La_{0.8}Sr_{0.2}MnO₃ catalyst exhibits outstanding catalytic performance in the oxidation of toluene (T_{90%} = 177 °C) and shows excellent stability. Such improved catalytic activity can primarily be attributed to the high surface area, high Mn⁴⁺/Mn³⁺ ratio, and abundant lattice oxygens exhibits outstanding catalytic performance in the oxidation of toluene and shows excellent stability.^[148]

Hydrothermal methods, melt polymerization and template methods have been employed to modulate the morphology of ABO₃-PCs.^[184,185] Liu et al. proposed an industrially scalable one-step melt polymerization strategy to prepare SmMnO₃ with distinct morphological structures.^[186] Through citric acid polymerization (Figure 7b), they were able to produce SmMnO₃ with three different morphologies, i.e. reticular, granular, and bulk. Among these catalysts, reticular SmMnO₃ with a porous structure (Figure 7f,g) showed the highest activity, being able to completely oxidize toluene, benzene, and *o*-xylene at 240, 270, and 300 °C, respectively. Benzene and *o*-xylene were completely converted into carbon dioxide and water at these temperatures, demonstrating comparable activity to noble metal catalysts. The remarkable catalytic efficiency of reticulated SmMnO₃ for BTX was attributed to its distinctive structure, high surface Mn⁴⁺/Mn³⁺ ratio, and $O_{\text{latt}}/O_{\text{ads}}$ composition and strong reduction properties. In another study conducted by Deng et al., single-crystal microcubic La_{0.5}Sr_{0.5}MnO_{3- δ} was prepared by a hydrothermal method (Figure 7c). The temperature used was found to have a significant effect on the morphology and properties of the La_{0.5}Sr_{0.5}MnO_{3- δ} catalyst. The catalysts hydrothermally treated at 250 °C showed the optimal activity in toluene oxidation, attributed to surface Mn enrichment, a high Mn⁴⁺/Mn³⁺ ratio, and extensive surface oxygen vacancies provided by the

Table 3. Composite and immobilized ABO₃-PCs evaluated in the catalytic oxidation of BTX.

Catalyst	Reactant composition	Space velocity/flow rate	T _{50%} [°C]	T _{90%} [°C]	References
Mn-LaNiO ₃	400 ppm C ₆ H ₆	200 mL min ⁻¹	≈280	–	[67]
LaCoO ₃ /MgO	500 ppm C ₇ H ₈	192000 mL g ⁻¹ h ⁻¹	–	248	[69]
La _{0.9} Ca _{0.1} CoO ₃ /MgO	500 ppm C ₇ H ₈	192000 mL g ⁻¹ h ⁻¹	214	228	[69]
LaMnO ₃ /LaMn ₂ O ₅	210 ppm C ₇ H ₈	138 mL min ⁻¹	481	515	[70]
La _{0.75} Ag _{0.25} MnO ₃	5 g m ⁻³ C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	140	230	[78]
LaMnO ₃ /0.5% Pt	5 g m ⁻³ C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	160	220	[78]
LaMnO ₃ /0.2% Pt	5 g m ⁻³ C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	170	230	[78]
LaMnO ₃ /0.1% Pt	5 g m ⁻³ C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	170	230	[78]
LaMnO ₃ /0.02% Pt	5 g m ⁻³ C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	165	230	[78]
LaMnO ₃ /0.5% Pd	5 g m ⁻³ C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	175	250	[78]
LaMnO ₃ /0.1% Pd	5 g m ⁻³ C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	165	260	[78]
5 wt.%MnO _x /3DOM LaMnO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	210	228	[80]
8 wt.%MnO _x /3DOM LaMnO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	208	225	[80]
12 wt.%MnO _x /3DOM LaMnO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	203	222	[80]
16 wt.%MnO _x /3DOM LaMnO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	193	215	[80]
MnO ₂ /LaMnO ₃	1000 ppm C ₇ H ₈	40000 mL g ⁻¹ h ⁻¹	225	234	[83]
LaMnO ₃ /TiO ₂	1000 ppm C ₇ H ₈	100 mL min ⁻¹	278	303	[86]
Pd/ LaCoO ₃	1800 ppm C ₇ H ₈	3000 mL g ⁻¹ h ⁻¹	223	–	[135]
Pd/LaFeO ₃	1800 ppm C ₇ H ₈	3000 mL g ⁻¹ h ⁻¹	185	–	[135]
Pd/LaMnO _{3-δ}	1800 ppm C ₇ H ₈	3000 mL g ⁻¹ h ⁻¹	217	–	[135]
Pd/LaNiO ₃	1800 ppm C ₇ H ₈	3000 mL g ⁻¹ h ⁻¹	234	–	[135]
Au/LaMnO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	201	226	[146]
Pd-La _{0.8} Sr _{0.2} MnO ₃	50 ppm C ₇ H ₈	36000 mL g ⁻¹ h ⁻¹	–	166	[148]
Au/3DOM LaCoO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	188	202	[149]
Co ₃ O ₄ /LaCoO ₃	500 ppm	100 mL min ⁻¹	–	243	[154]
Co-LaMnO ₃	1000 ppm C ₇ H ₈	72000 mL g ⁻¹ h ⁻¹	–	269	[153]
γ-MnO ₂ /SmMnO ₃	1000 ppm <i>o</i> -Xylene	60000 mL g ⁻¹ h ⁻¹	232	250	[157]
LaMnO _{3,15} /Co ₃ O ₄ /cordierite	<i>o</i> -Xylene	–	–	330	[159]
LaCoO ₃ /Co ₃ O ₄ /cordierite	<i>o</i> -Xylene	–	–	331	[159]
La ₂ NiO ₄ /Co ₃ O ₄ /cordierite	<i>o</i> -Xylene	–	–	320	[159]
La _{0.8} Ce _{0.2} MnO ₃ /CeO ₂	300 ppm C ₇ H ₈	12000 mL g ⁻¹ h ⁻¹	–	<240	[160]
Pd-CeMnO ₃	500 ppm C ₆ H ₆	20000 mL g ⁻¹ h ⁻¹	139	186	[163]
Pd-CeMnO ₃	500 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	145	186	[67]
Pd-CeMnO ₃	500 ppm C ₆ H ₆	19200 mL g ⁻¹ h ⁻¹	139	184	[164]
CeO ₂ /LaCoO ₃	500 ppm C ₆ H ₆	80 mL min ⁻¹	288	–	[165]
Bulk SmMnO ₃	12000 ppm C ₆ H ₆	100 mL min ⁻¹	237	275	[166]
γ-MnO ₂ /SmMnO ₃	1000 ppm C ₆ H ₆	60000 mL g ⁻¹ h ⁻¹	213	226	[166]
γ-MnO ₂ /SmMnO ₃	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	187	208	[166]
CuO/Zr _x Ce _{1-x} O _y	1000 ppm C ₆ H ₆	96000 mL g ⁻¹ h ⁻¹	–	<300	[167]
Cordierite-NiMnO ₃	1000 ppm C ₆ H ₆	15000 mL g ⁻¹ h ⁻¹	–	275	[168]
Pd-LaCoO ₃ -cordierite	1500 ppm C ₆ H ₆	20000 mL g ⁻¹ h ⁻¹	≈280	–	[169]
Cu-LaCoO ₃ -cordierite	1500 ppm C ₆ H ₆	20000 mL g ⁻¹ h ⁻¹	≈300	–	[169]
Ceria-based-LaCoO ₃	1700 ppm C ₆ H ₆	60000 mL g ⁻¹ h ⁻¹	330	–	[170]
Ceria-based-LaCoO ₃	1700 ppm C ₆ H ₆	60000 mL g ⁻¹ h ⁻¹	244	–	[170]
SmMnO ₃ / cordierite	1000 ppm C ₆ H ₆	20000 mL g ⁻¹ h ⁻¹	≈285	≈345	[171]
γ-MnO ₂ /SmMnO ₃	1000 ppm C ₇ H ₈	60000 mL g ⁻¹ h ⁻¹	187	208	[171]
γ-MnO ₂ /SmMnO ₃	1000 ppm <i>o</i> -Xylene	60000 mL g ⁻¹ h ⁻¹	232	250	[171]
LaMnO ₃ /δ-MnO ₂	1000 ppm C ₇ H ₈	30000 mL g ⁻¹ h ⁻¹	–	258	[172]
Pd/La _{0.8} Ce _{0.2} MnO ₃ /ZSM-5	3 mg L ⁻¹ C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	–	285	[173]
La _{0.75} Ce _{0.25} MnO ₃ /CeO ₂	1000 ppm C ₇ H ₈	18000 mL g ⁻¹ h ⁻¹	–	250	[174]

(Continued)

Table 3. (Continued)

Catalyst	Reactant composition	Space velocity/flow rate	T _{50%} [°C]	T _{90%} [°C]	References
LaCoO ₃ /ZrO ₂ /cordierite	1000 ppm C ₇ H ₈	100 mL min ⁻¹	159	216	[175]
LaCoO ₃ /r-Al ₂ O ₃ /cordierite	1000 ppm C ₇ H ₈	100 mL min ⁻¹	180	220	[175]
LaCoO ₃ /TiO ₂ /cordierite	1000 ppm C ₇ H ₈	100 mL min ⁻¹	206	233	[175]
LaCoO ₃ /cordierite	1000 ppm C ₇ H ₈	100 mL min ⁻¹	210	240	[175]
Mn ₃ O ₄ -Au 3DOM La _{0.6} Sr _{0.4} CoO ₃	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	214	230	[176]
Au/MnO _x /La _{0.6} Sr _{0.4} MnO ₃ 3DOM	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	205	220	[177]
80Co-20La	500 ppm C ₇ H ₈	100 mL min ⁻¹	230	242	[178]
LaCoO ₃ /SBA-15	1000 ppm C ₇ H ₈	20000 mL g ⁻¹ h ⁻¹	284	320	[179]
EuCoO ₃ /LaCoO ₃	1700 ppm C ₇ H ₈	100 mL min ⁻¹	256	-	[180]
Fe doped LaMnO ₃ /Al ₂ O ₃	200 ppm o-Xylene	200 mL min ⁻¹	744 J/L	-	[181]
SmMnO ₃ /SmMn ₂ O ₅	1000 ppm o-Xylene	100 mL min ⁻¹	-	280	[182]

microcubic structure.^[128] Wang et al. developed a molten salt route to control the morphology of porous LaMnO₃ NPs, i.e. spherical and cubic, using porous Mn₂O₃ spheres as a template (Figure 7d,e). These catalysts exhibit high catalytic performance in the oxidation of toluene, with the cubic structure having the highest activity. The T_{10%}, T_{50%} and T_{90%} temperatures for toluene oxidation in the presence of cubic LaMnO₃ are 110, 170, and 220 °C, respectively, at a toluene/oxygen molar ratio = 1/400 and SV = 20000 mL g⁻¹ h⁻¹. It was inferred that the high surface Mn⁴⁺/Mn³⁺ molar ratio and facile low-temperature oxidation of cubic LaMnO₃ enhance the catalytic performance.^[187] Rahemi et al. synthesized La_{0.8}Zn_{0.2}MnO₃ using a sol-gel method with different citric acid to metal nitrate ratios with lanthanum, manganese, and zinc (La/Zn/Mn molar ratio of 0.8/0.2/1). With the increase of calcination temperature, La_{0.8}Zn_{0.2}MnO₃ shows a spongy porous structure (Figure 7h), attributed to the large amount of gas generated during the calcination process. At a calcination temperature of 550 °C the particles vary in size and shape and are aggregated, whereas at calcination temperatures of 600 and 650 °C spherical NPs are formed. At a calcination temperature of 700 °C the particles are spherical and dispersed, which facilitates mass transfer to enhance the activity of the catalyst.^[100]

5.2. The Impact of Structural Regulation

Nano-structuring, such as building 3DOM or core-shell structures can generate ABO₃-PCs with large specific surface areas and stabilities that are conducive to high catalytic performance. Table 4 summarizes catalyst structures and how structure influences the catalytic oxidation of benzene and toluene. Hollow multishell structures are particularly active catalysts for the oxidation of BTX due to their porous nature and mutual interactions between different shells. This arrangement results in a relatively large effective speciated surface area with excellent resistance to sintering. For example, Chen et al. synthesized spherical PrMnO₃ hollow multishells (PrMnO₃-HoMSs) and evaluated them as catalysts in the oxidation of toluene (Figure 8a,b). Compared with the catalysts (PrMnO₃-PC) synthesized by a co-precipitation method, PrMnO₃-HoMSs exhibit higher catalytic performance in toluene oxidation. The activity

was attributed to the high specific surface area of the porous, polycrystalline structure, and an abundance of reactive oxygen species.^[188]

3DOM structures have high porosities characterized by tunable pore sizes (> 50 nm) and a regular, uniform arrangement of pores that allows for tight pore connectivity and high porosity. Such structures facilitate gas diffusion and enhances contact efficiency during the catalytic BTX oxidation treatment, resulting in significantly improved gas diffusion efficiency. Zhao et al. synthesized cordierite-supported 3DOM La_{0.8}Ce_{0.2}MnO₃ (Figure 8c,d) using a PMMA template method. The catalysts calcined at 600 °C show optimal performance (T_{50%} = 147 °C; T_{90%} = 217 °C; Ea = 27.01 kJ mol⁻¹; SV = 6000 mL g⁻¹ h⁻¹).^[189] Ji et al. produced 3DOM cubic SrFeO_{3-δ} using citrate acid-assisted poly (methyl methacrylate)-templating in the presence of surfactants (ethylene glycol, sucrose, or l-lysine). They observed variations in the catalytic activity of the samples, which were correlated with surface area, oxygen adsorption concentration, and low-temperature reduction. Catalytic activity followed the order of SrFeO_{3-δ}-ethylene glycol > SrFeO_{3-δ}-lysine > SrFeO_{3-δ}-glucose (Figure 8e), which correlates with the porosity of the SrFeO_{3-δ} catalyst.^[190] 3DOM CeMnO₃ (Figure 8f), 3DOM LaCoO₃,^[191] and SmMnO₃ sheets (Figure 8g) with mesoporous structures display excellent catalytic activity and stability in BTX oxidation.

5.3. Effect of Surface Modification

Surface modification of ABO₃-PCs using acids, bases, and salts is also an effective approach to enhance catalytic activity.^[204-206] Treatment with acids, bases, and salts can increase the specific surface area of the catalyst, etching pores to enhance porosity, and removing the A-site ions to expose active sites.^[207]

Acetic acid, citric acid, and nitric acid are commonly employed to improve the performance of ABO₃-PCs. Wu et al. investigated the impact of acid treatment on SmMnO₃/cordierite monolithic catalysts (Figure 9a,b). A series of experiments showed that the catalyst treated with 1.0 mol L⁻¹ HNO₃ for 6 h and calcined at 450 °C for 1 h has the best performance (Figure 9c), which was attributed to the increase of the specific surface area,

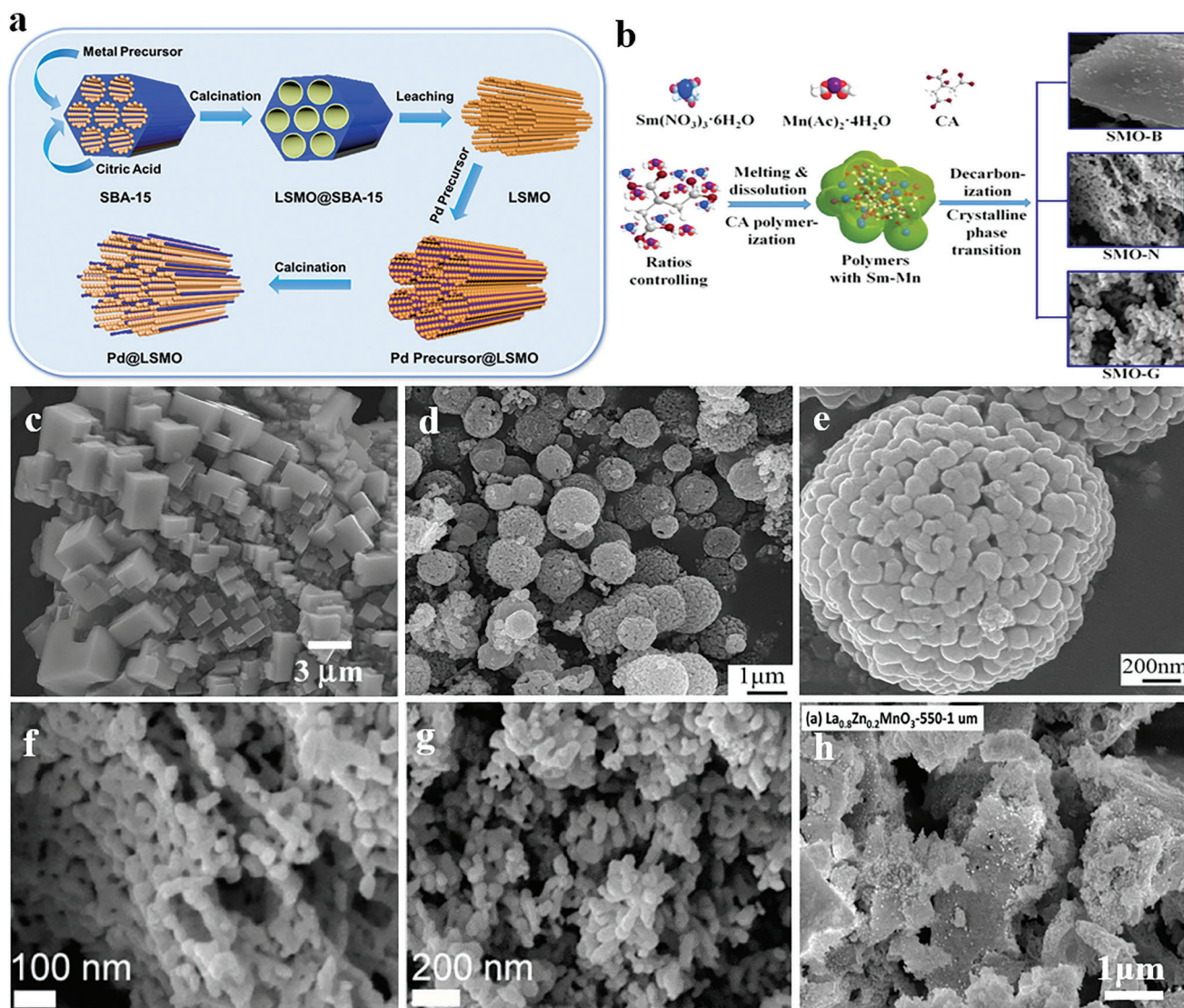


Figure 7. a) Route used to prepare Pd/La_{0.8}Sr_{0.2}MnO₃ mesoporous nanotube arrays. Reproduced with permission.^[148] Copyright 2021, Elsevier. b) Synthesis pathway and SEM images of SmMnO₃ with netlike (SMO-N), granular-like (SMO-G), and bulk (SMO-B) structures.^[186] Copyright 2018, American Chemical Society. c) SEM image of La_{0.5}Sr_{0.5}MnO_{3-δ}-250. Reproduced with permission.^[128] Copyright 2008, Elsevier. d,e) SEM images of the porous spherical LaMnO₃ obtained after calcination at 550 °C for 4 h. Reproduced with permission.^[187] Copyright 2014, The Royal Society of Chemistry. f) SEM and g) TEM image of SmMnO₃ with bulk structures.^[186] h) Field emission scanning electron microscopy (FESEM) image of La_{0.8}Zn_{0.2}MnO₃-550. Reproduced with permission.^[100] Copyright 2021, Elsevier.

pore volume and the mechanical stability of the catalyst.^[171] Yang et al. treated LaCoO₃ with acetic acid and observed a 40 °C reduction in the temperature required for 90% toluene conversion (Figure 9d–f).^[71] Peng et al. modified Sr-doped LaCoO₃ using dilute nitric acid and found that the acid treatment improved the stability of the catalyst. Similarly, Li et al. achieved high catalytic activity and stability for toluene oxidation by treating bulk LaMnO₃ perovskite with an acidic KMnO₄ solution (Figure 9g,h).^[156] In the report of Sun et al., citric acid treatment of GdMnO₃ resulted in a higher specific surface area, a rich pore structure, abundant high-valent metal ions (Figure 9i) and active oxygen species, consequently improving low-temperature catalytic performance.^[85]

Hydrothermal treatment under alkaline conditions may also be used to increase the specific surface area and enrich the oxygen species of the catalyst. As a post-treatment method, Wang et al. obtained rod-like MnO₂/LaMnO₃ composite catalysts by combining both alkaline hydrothermal and acid-etching techniques, achieving a T_{90%} of 236 °C. The MnO₂/LaMnO₃ catalyst surface exhibited an elevated Mn⁴⁺/Mn³⁺ ratio in comparison to the bulk LaMnO₃ catalyst. It significantly improved the low-temperature catalytic activity, thus exhibiting a low apparent activation energy of 38.6 kJ mol⁻¹. Additionally, alkali-acid treatment increased the concentration of lattice oxygen on the catalyst surface and generated a high oxygen vacancy density, which facilitates the adsorption of toluene and its subsequent oxidation.

Table 4. Shape controlled and structurally optimized ABO₃-PCs employed in the catalytic oxidation of benzene and toluene.

Catalyst	Reactant composition	Space velocity [mL g ⁻¹ h ⁻¹]	T _{50%} [°C]	T _{90%} [°C]	References
3DOM EuFeO ₃	1000 ppm C ₇ H ₈	20000	276	322	[125]
3DOM Eu _{0.6} Sr _{0.4} FeO ₃	1000 ppm C ₇ H ₈	20000	278	305	[125]
3D-La _{0.6} Sr _{0.4} FeO _{3-δ}	1000 ppm C ₇ H ₈	20000	225	280	[127]
Ni/La _{0.7} Sr _{0.3} AlO _{3-δ}	1.5% C ₇ H ₈	6000	–	300	[134]
3DOM Co ₃ O ₄ /Eu _{0.6} Sr _{0.4} FeO ₃	1000 ppm C ₇ H ₈	20000	251	269	[109]
Au/3DOM La _{0.6} Sr _{0.4} MnO ₃	1000 ppm C ₇ H ₈	10000	150	170	[147]
Hollow spherical LaCoO ₃	1000 ppm C ₇ H ₈	20000	220	237	[155]
Rod-like MnO ₂ /LaMnO ₃	1000 ppm C ₇ H ₈	60000	–	236	[156]
3D-MnO ₂ /LaMnO ₃	2000 ppm C ₇ H ₈	120000	263	279	[158]
SmMnO ₃ -B	1000 ppm C ₆ H ₆	32000	190	215	[186]
SmMnO ₃ -N	1000 ppm C ₆ H ₆	32000	206	228	[186]
SmMnO ₃ -G	1000 ppm C ₆ H ₆	32000	223	258	[186]
3DOM-SrFeO _{3-δ}	1000 ppm C ₇ H ₈	20000	292	340	[190]
3D-LaCoO ₃	100 ppm C ₆ H ₆	40000	–	305	[193]
3D-La _{0.8} Ce _{0.2} MnO ₃ /cordierite	500 ppm C ₇ H ₈	6000	147	217	[189]
Cubic LaMnO ₃	1000 ppm C ₇ H ₈	20000	170	220	[187]
Rod-like MnO ₂ /LaMnO ₃	1000 ppm C ₇ H ₈	60000	–	236	[156]
GdAlO ₃	1–2% C ₆ H ₆	–	259	–	[194]
3DOM La _{0.7} Ce _{0.3} CoO ₃ /Ce _{0.75} Zr _{0.25} O ₂ -Al ₂ O ₃ /cordierite	1000 ppm C ₇ H ₈	6000	103	218	[195]
3D-LaMnO ₃	1000 ppm C ₇ H ₈	20000	222–232	243–253	[196]
3D-LaMnO ₃	1000 ppm C ₇ H ₈	20000	226	249	[197]
Hollow spherical LaCoO ₃	1000 ppm C ₇ H ₈	20000	220	237	[155]
3D-EuFeO ₃	1000 ppm C ₇ H ₈	20000	312	347	[198]
3DOM CeMnO ₃	300 ppm C ₇ H ₈	15000	–	172	[192]
3D-Eu _{0.6} Sr _{0.4} FeO ₃	1000 ppm C ₇ H ₈	20000	250	270	[199]
Spherical PrMnO ₃	1000 ppm C ₇ H ₈	60000	>230	<250	[200]
Cobalt-Enriched LaCoO ₃	1000 ppm C ₇ H ₈	15000	184	206	[201]
La _{0.6} Sr _{0.4} MnO _{3-δ} Microcubes	1000 ppm C ₇ H ₈	20000	283	–	[202]
3DOM-La _{0.7} Ce _{0.3} CoO ₃	1000 ppm C ₇ H ₈	6000	103	218	[203]

5.4. Effect of Humidity

Water vapor is one of the products of BTX oxidation and is also commonly present in exhaust gases,^[208,209] and has two key effects on the catalyst.^[210] Water can adsorb onto active sites of the catalyst, competing with BTX for adsorption and inhibiting the oxidation process, and can also act as an efficient cleaning agent, removing byproducts from the surface of the catalysts.^[211,212]

Zhao et al. confirmed that humidity has an inhibitory effect on toluene oxidation,^[126] consuming the active oxygen atoms adsorbed by the catalyst and blocking the active sites through the generation of surface bound OH species (Figure 10a). In another study, water vapor was introduced into the reaction using 6.4Au/LSMO PC a 2% decrease in the T_{90%} for toluene oxidation was observed.^[147] However, deactivation of the 6.4Au/LSMO catalyst is reversible, with activity restored when the water is removed from the system (Figure 10b). Additionally, the impact of water on LSMO was investigated, revealing a decrease in conversion of toluene to 95 and 86% when 5 and 10 vol.% of water were introduced, respectively.^[97] Upon the removal of water, toluene conversion returned to the initial level (Figure 10c). Similar to the above results, in other study wa-

ter was shown to reduce the activity of 1.67Mn₃O₄-2Au/3DOM La_{0.6}Sr_{0.4}CoO₃, 5.92Au/8MnO_x/3DOM La_{0.6}Sr_{0.4}CoO₃ (x = 2–4), SmMnO₃ cordierite monolithic and LaCoO₃ PCs (Figure 10d,e).

In addition to inhibiting the activity of ABO₃-PCs, the introduction of water vapor may also affect the CO₂ yield. For instance, Sun et al. found that different humidity conditions (0, 50, and 100% relative humidity) did not affect the conversion of toluene but led to a decrease in the yield of CO₂ at 230 °C (Figure 10f),^[186] with the oxidation of carboxyl group-containing and carbonate intermediates being incomplete. Water vapor may also promote the conversion of CO to CO₂ through the water-gas shift reaction (WGS) to improve the CO₂ yield.^[213,214]

5.5. Effect of Sulfur Species

It is widely recognized that many industrial emissions often contain a diverse range of sulfur species,^[215] with many sulfur species acting as catalyst poisons.^[216–218] Various sulfur species (SO₂, SO₃, SO₃²⁻, SO₄²⁻, and S²⁻) can deposit on a catalyst surface to block active sites,^[219] preventing the adsorption and diffusion of BTX and catalyst deactivation.^[220,221] Not surprisingly,

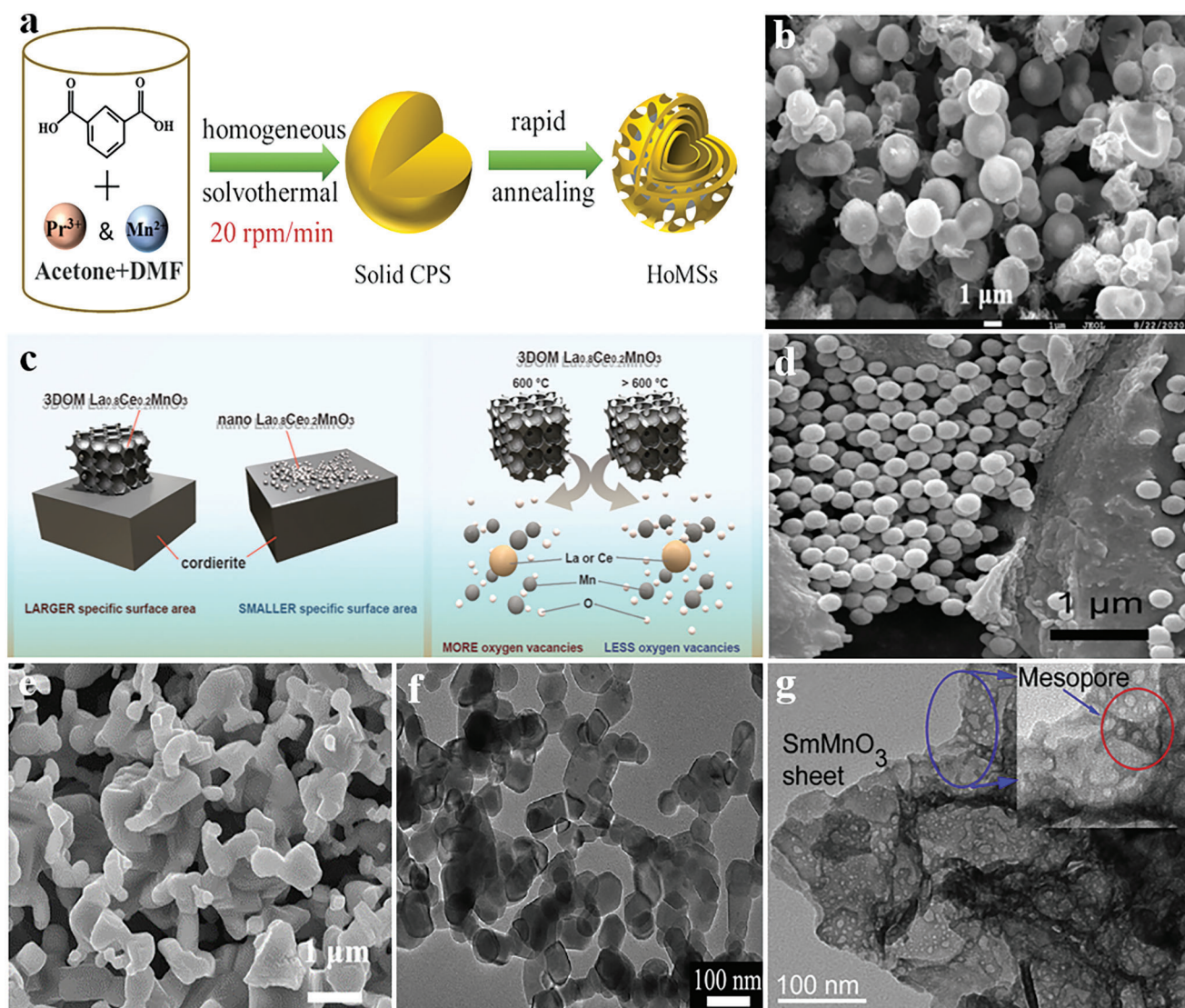


Figure 8. a) Hollow multishell spherical PrMnO_3 -HoMS PC that efficiently catalyzes oxidation of toluene. b) FESEM image of the PrMnO_3 -HoMSs. Reproduced with permission.^[188] Copyright 2021, Elsevier. c) Comparison of 3DOM $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ /cordierite and nano $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ /cordierite catalysts. d) SEM image of 3DOM-LCM/cordierite. Reproduced with permission.^[189] Copyright 2019, Elsevier. e) SEM image of $\text{SrFeO}_{3-\delta}$ -bulk-900 PCs.^[190] f) HRTEM of 3DOM CeMnO_3 . Reproduced with permission.^[190] Copyright 2021, Elsevier. Reproduced with permission.^[192] Copyright 2020, Elsevier. g) Mesoporous structured SmMnO_3 sheets. Reproduced with permission.^[82] Copyright 2018, Elsevier.

extensive research has been conducted to investigate the impact of SO_2 on the activity of ABO_3 -PCs.

Hu et al. used a sol-gel method to prepare $\text{La}_{1-x}\text{Ce}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ ($x = 0, 0.2, 0.4, \text{ and } 0.6$; $y = 0, 0.2, 0.4, \text{ and } 0.6$) catalysts, with Ce^{4+} or Fe^{3+} doped LaCoO_3 showing improved the catalytic activity in the oxidation of toluene and resistance to sulfur poisoning (Figure 11a).^[107] Analysis of sulfate species in sulfur-aged catalysts during the temperature-programming stages revealed Ce^{4+} substitution improved catalytic activity, whereas Fe^{3+} substitution enhanced resistance to poisoning by sulfur (Figure 11b). During the oxidation of toluene, sulfate concentrations were observed to decrease with increasing temperatures, suggesting that heating caused sulfate poisoning and the adsorption of gaseous SO_2 on surface anion vacancies, forming sulfite or sulfate via

continuous oxidation.^[222] The process of catalyst poisoning by SO_2 was evident via the formation of lanthanum sulfate and sulfite species, i.e. extracting an active component from the PC. However, by substituting B-site cations (i.e. $\text{LaCo}_{1-x}\text{M}_x\text{O}_3$), Chen et al. showed that the negative effects of SO_2 poisoning could be reduced.^[79] Metal ions influence factors such as lattice stability and sulfur adsorption (Figure 11c). Fe^{3+} doping was found to afford a more effective catalyst compared to catalysts doped with Cr^{3+} or Cu^{2+} , improving the tolerance to sulfur compounds (Figure 11d).

Huang et al. examined the influence of SO_2 and dodecyl mercaptan on $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.8}\text{Cu}_{0.2}\text{MnO}_3$ PCs during the oxidation of toluene.^[110] They observed that the PCs were poisoned in the presence of SO_2 . In the presence of dodecyl mercaptan

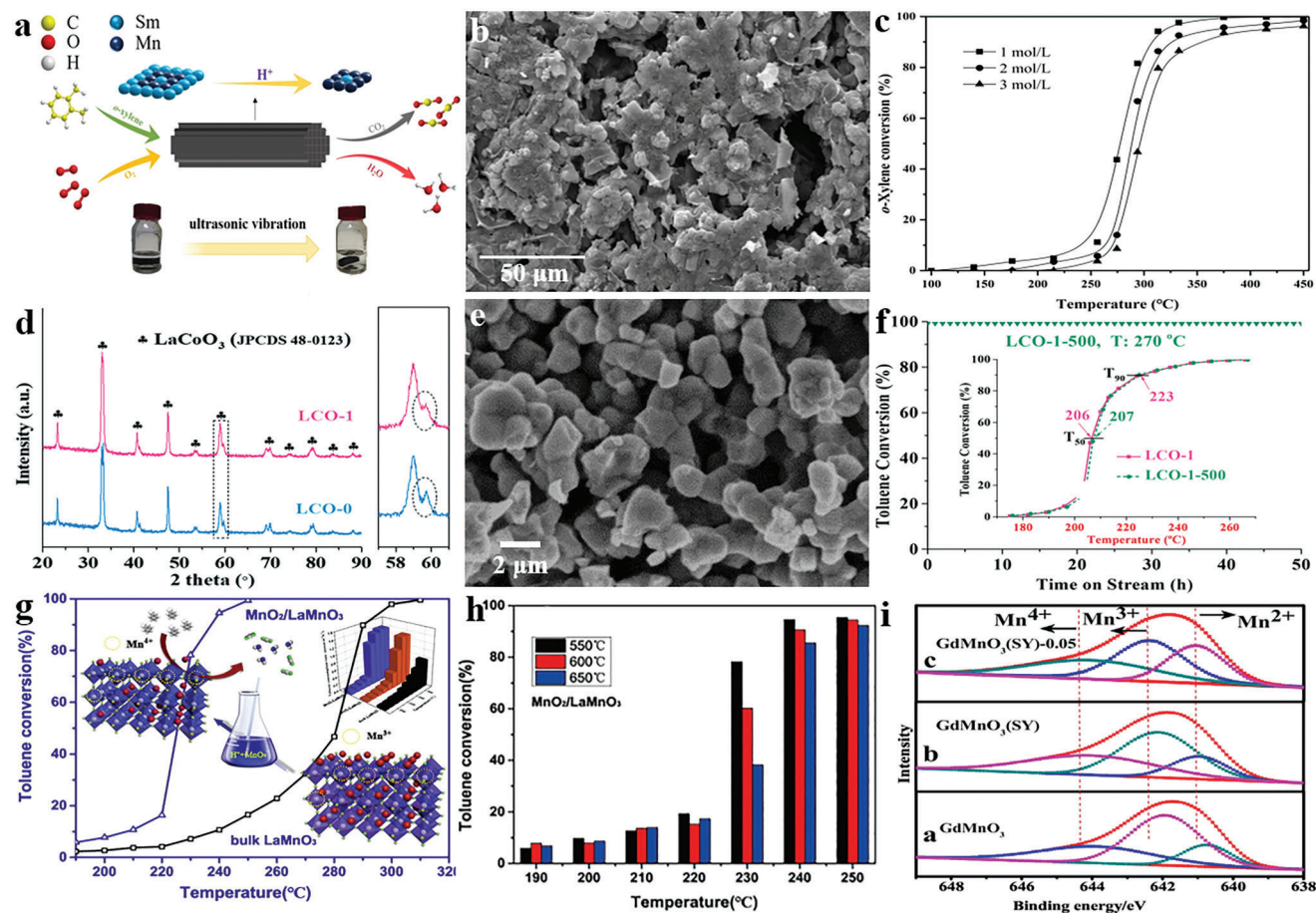


Figure 9. a) Preparation and application of the SmMnO_3 /cordierite monolithic catalyst. b) SEM image of the SmMnO_3 /cordierite catalyst treated with $1 \text{ mol L}^{-1} \text{ HNO}_3$ for 6 h. c) Catalytic activity of the SmMnO_3 /cordierite acid-treated with different concentrations of HNO_3 . Reproduced with permission.^[171] Copyright 2021, Chemistry Europe. d) XRD patterns of raw LaCoO_3 catalyst (LCO-0) and the LaCoO_3 treated with acetic acid for 1 h (LCO-1). e) SEM image of LCO-1. f) Toluene conversions of LCO-1-500 at 270°C . Reproduced with permission.^[71] Copyright 2018, John Wiley and Sons. g) Catalytic activity of $\text{MnO}_2/\text{LaMnO}_3$ and bulk LaMnO_3 catalysts in the oxidation of toluene. h) Toluene conversions catalyzed by $\text{MnO}_2/\text{LaMnO}_3$.^[156] i) XPS spectra of $\text{Mn}2p_{3/2}$: a– GdMnO_3 , b– $\text{GdMnO}_3(\text{SY})$, and c– $\text{GdMnO}_3(\text{SY})-0.05$. Reproduced with permission.^[156] Copyright 2019, Elsevier.

($\text{C}_{12}\text{H}_{25}\text{SH}$), $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ exhibits better resistance to sulfur poisoning than $\text{La}_{0.8}\text{Cu}_{0.2}\text{MnO}_3$. It was found that the SO_2 deactivation is due to the formation of CuSO_4 on the catalyst surface (Figure 11e,f).

6. Mechanistic Insights

There is a lack of consensus on the reaction mechanism of catalytic oxidation by ABO_3 -PCs catalysts. Proposed kinetics encompass Langmuir Hinshelwood (L-H), Eley Rideal (E-R), and Mars van Krevelen (MvK) mechanisms. The L-H mechanism implies that the catalytic reaction occurs between adsorbed oxygen and adsorbed BTX. The E-R mechanism implies that the reaction takes place between adsorbed oxygen and gaseous substrates. The MvK mechanism is widely used to rationalize the low-temperature-catalytic oxidation of BTX, and involves a dynamic cycle where the catalyst undergoes simultaneous reduction and oxidation. This mechanism relies on chemisorbed oxygen and lattice oxygen in the catalyst, in contrast to the L-H and

E-R mechanisms that rely on adsorbed oxygen species on the catalyst surface.

In the vast majority of current studies, the oxidation of BTXs over ABO_3 -PCs catalysts mainly follows the redox mechanism (MvK) and is divided into two main steps:

- 1) BTXs diffuse and adsorbed on the catalyst surface where they are oxidized to CO_2 and H_2O by reaction with the lattice oxygens on the catalyst surface, and at the same time, the catalyst surface is reduced due to the generation of oxygen vacancies.
- 2) The oxygen adsorbed by the catalyst dissociates and fill the oxygen vacancies to re-oxidize the surface atoms.

This mechanism achieves the oxidation of BTXs by changes of the metal valence states, O_{latt} and O_{ads} , in the catalyst. As shown in Figure 12, usually a series of intermediates are formed followed by further chemical bond breaking and reorganization, resulting in the full conversion of BTXs to CO_2 and H_2O . This mechanism has been confirmed by many studies. For example, Xiang et al. explored the mechanism of toluene oxidation by

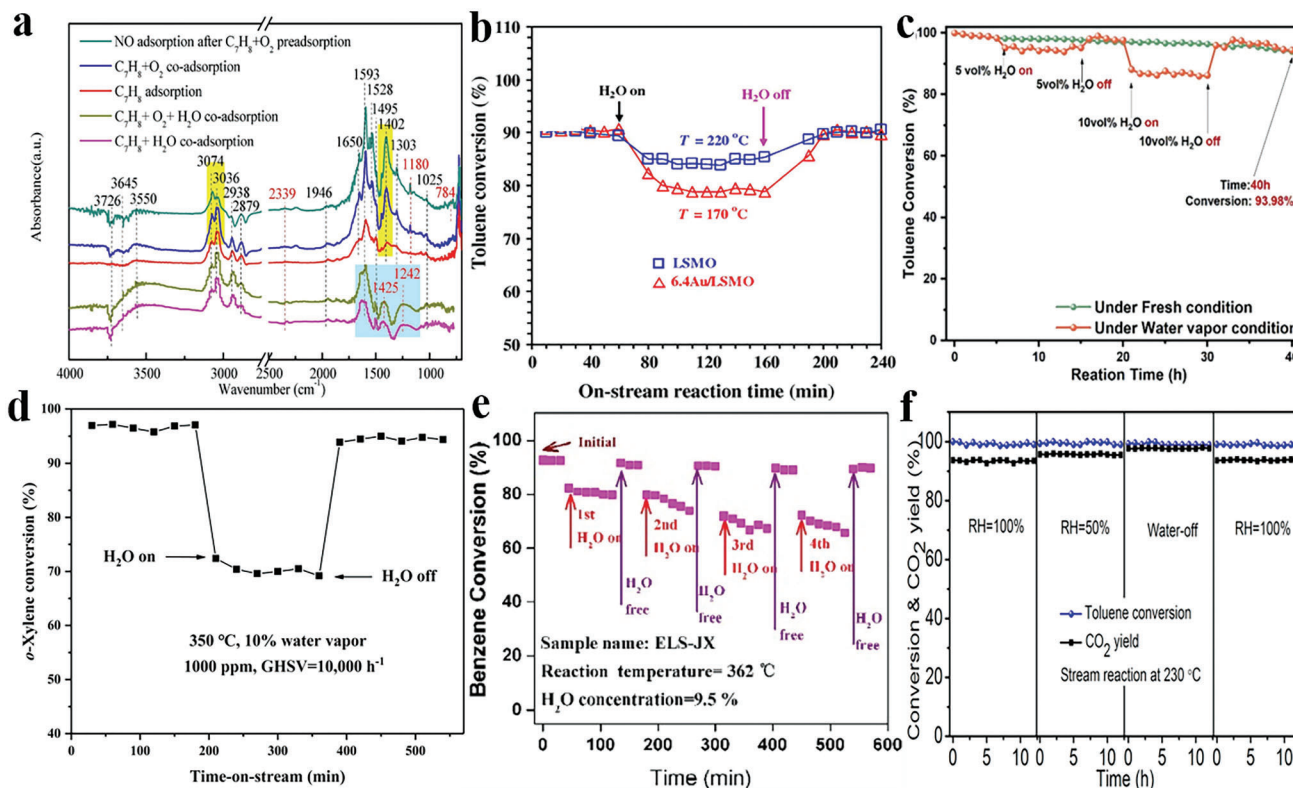


Figure 10. a) In situ DRIFTS of $\text{La}_{0.65}\text{Co}_{0.35}\text{FeO}_3$ in the presence of toluene, toluene and O_2 , toluene and O_2 and H_2O , and toluene and O_2 and H_2O .^[126] Impact of H_2O on toluene oxidation using b) the Au/3DOM $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ catalyst and c) the La–Sr–Co–Fe–O perovskite-type oxides. Reproduced with permission.^[97] Copyright 2023, Elsevier. d) Impact of H_2O on *o*-xylene oxidation using the SmMnO_3 cordierite monolithic catalyst. Reproduced with permission.^[171] Copyright 2021, John Wiley and Sons. e) Impact of H_2O on benzene oxidation using the $\text{LaCo}_3/\text{SBA}-15$. Reproduced with permission.^[65] Copyright 2017, Elsevier. f) Impact of H_2O on toluene oxidation using the SmMnO_3 with a netlike structure. Reproduced with permission.^[186] Copyright 2018, American Chemical Society.

LaFeO_3 and showed that toluene is adsorbed on the surface of the LaFeO_3 catalyst, with the chemisorbed species then reacting with ambient oxygen atoms to form carbonates, which are then converted to CO_2 and desorbed.^[72] During the oxidation of BTX, a series of intermediates such as benzoic acid, maleic anhydride and carboxybenzene species are generated.^[116] A variety of intermediates were identified from the oxidation of BTX catalyzed by $\gamma\text{-MnO}_2/\text{SmMnO}_3$, including 5-hexen-1-ol, ethanedioic acid, acetic acid, n-butyric acid, phenol, and malic acid for benzene oxidation; acetic acid, benzaldehyde, 2-(5H)-furanone, citric acid and benzoic acid for toluene oxidation and acetic acid, citric acid, and 1,3-isobenzofurandione for *o*-xylene.

During the reaction, ABO₃-PC catalysts may degrade and deactivate, primarily through mechanisms such as poisoning, coking, plugging, and sintering.^[45] Catalyst poisons such as sulfides or chlorides can form strong chemical bonds with the active components of ABO₃-PC, thereby reducing or eliminating its activity.^[229] Simultaneously, during the catalytic process, the deposition of carbon-containing substances or other intermediates in the pores of the catalyst can coat the active catalytic sites and block micropores, hindering the diffusion of BTX molecules into the pores, resulting in catalyst inactivation.^[230] Moreover, high temperatures can induce structural and performance changes in the catalyst. Elevated temperatures can lead to sintering, reduc-

ing catalytic efficiency, as well as altering the chemical and phase composition of the catalyst.^[231] These changes may include grain growth, burial of active components by the carrier, and loss of active components due to the generation of volatile or sublimable substances.^[232] Further research is required to understand the intricate decomposition and deactivation processes, as well as the catalytic mechanisms during reactions more thoroughly.

7. Conclusion and Outlook

Catalytic oxidation is an important process for the elimination of organic pollutants such as BTX, especially when the concentration of these pollutants is low. Generally, the most active catalysts are based on precious and expensive noble metal oxides. However, in recent years, ABO₃-PCs have been widely studied as BTX oxidation catalysts, and are particularly versatile due to their flexible composition, abundant defects, highly exposed active surfaces, and tunable redox properties. Moreover, ABO₃-PCs display high activity and stability in the catalytic oxidation of BTX.

The main role of the A-site ions (La^{3+} , Ce^{4+} , Sr^{2+} , Ca^{2+} , etc.) of ABO₃-PCs is to stabilize the chalcogenide crystal structure. However, the A-site ions can introduce lattice defects and change the chemical sites of the lattice oxygens, affecting the dispersion and valence of the B-site ions, thus indirectly altering the activity

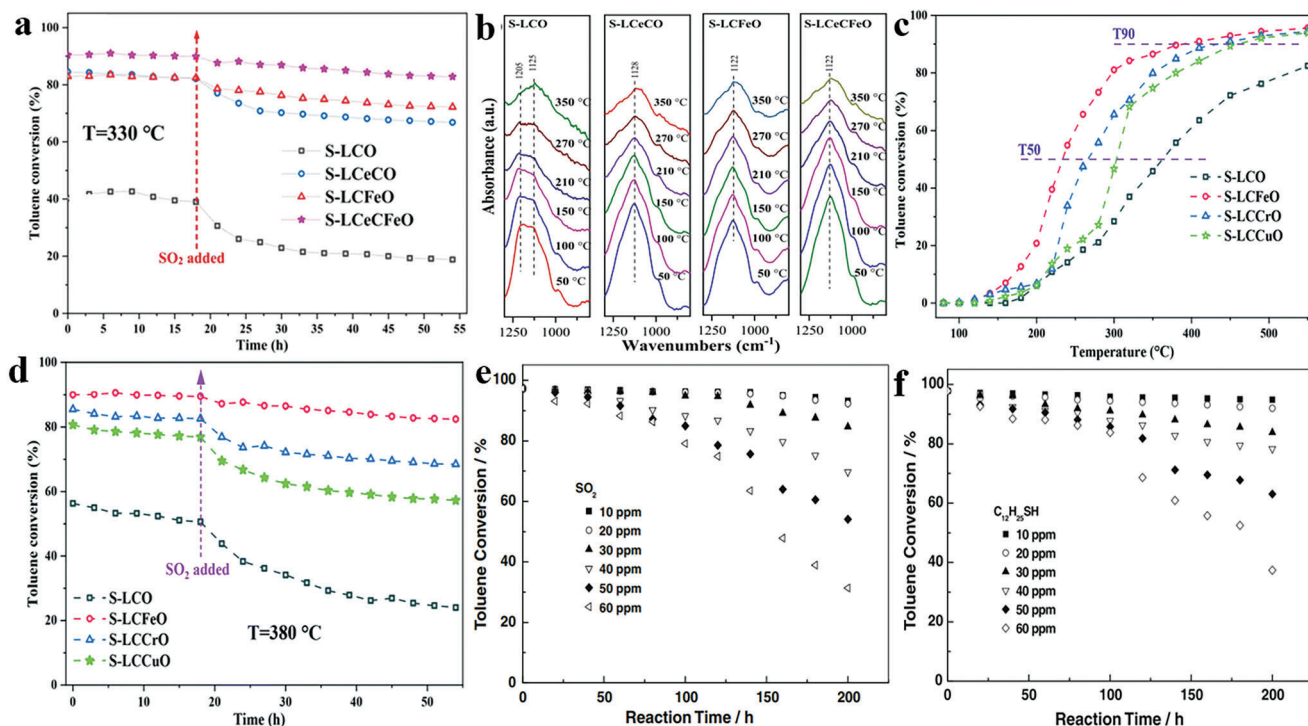


Figure 11. a) Impact of SO_2 on toluene oxidation of sulfur-aged catalysts.^[107] b) Infrared spectra of sulfate in the heating process of toluene oxidation for S-LCO, S-LCeCO, S-LCFeO, and S-LCeCFeO catalysts. c) Conversion of toluene as a function of temperature catalyzed by S-LCO, S-LCeFeO, S-LCCrO, and S-LCCuO. d) Catalytic stability test for toluene oxidation of sulfur-aged catalysts list in (c). e) Impact of SO_2 on the conversion of toluene catalyzed by $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ over time. f) Impact of $\text{C}_{12}\text{H}_{25}\text{SH}$ on the conversion of toluene by $\text{La}_{0.8}\text{Cu}_{0.2}\text{MnO}_3$. Reproduced with permission.^[110] Copyright 2010, Elsevier.

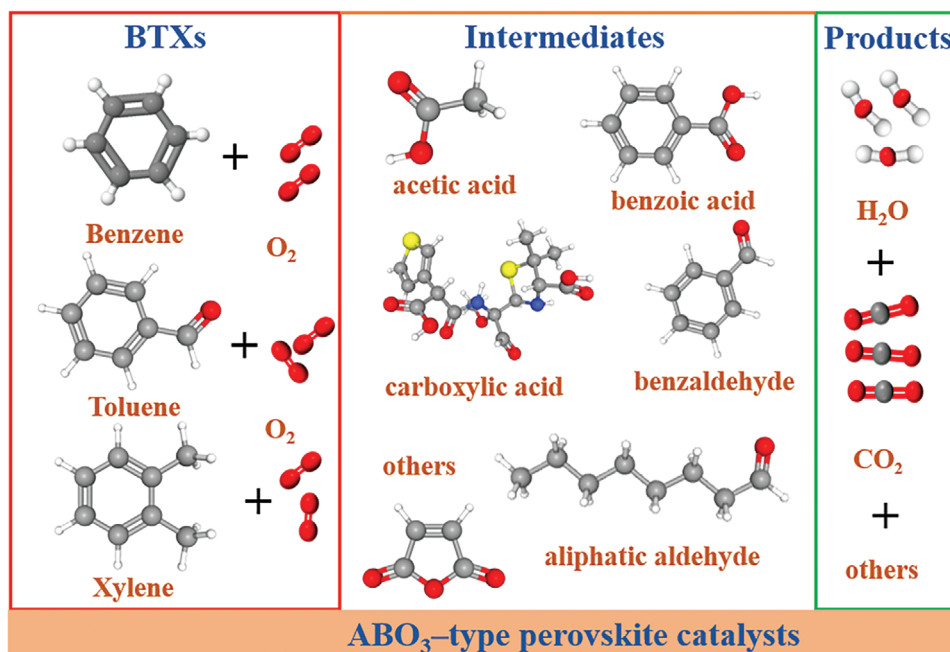


Figure 12. Intermediates observed in the catalytic oxidation of BTX by ABO_3 -PCs.

of ABO₃-PCs. Usually, the catalytic activity of ABO₃-PCs is determined by the B-site ions (Co²⁺, Fe³⁺, Mn³⁺, Ni³⁺, Cu²⁺, etc.), which exhibit a variety of oxidation states and have high structural/compositional flexibility and redox capacities.

ABO₃-PCs are often used as supports to immobilize noble metal particles or are themselves immobilized on metal oxides and other materials, increasing the specific surface area of the active catalyst, leading to improved activity. In addition, different morphologies and structures of ABO₃-PCs affect the packing density, porosity, specific surface area, and surface energy of the catalyst, influencing catalytic activity.

The catalytic activity is also affected by water, sulfur species, and other impurities. Water can adsorb onto the active sites of the catalyst, competing with BTX for adsorption and inhibiting the oxidation process. Sulfur species tend to deposit on the surface of ABO₃-PCs, blocking the active sites, hindering the adsorption and diffusion of BTX, and extruding metal ions that react to form catalytically inactive sulfates.

The mechanism of benzene and toluene oxidation by ABO₃-PCs mainly follows the MvK mechanism, whereas the oxidation mechanism of xylene and BTX mixtures, has not been fully explored and there are a lack of mechanistic studies exploring real flue gases contain BTX. In addition to A-site, B-site doping, and A/B-site co-doping, anion doping on the O-site has recently emerged as an alternative approach to tune the electronic structure of ABO₃-PCs to improve catalytic performance, and further studies are required in this nascent area.^[144] In situ spectroscopic and theoretical studies are required to further clarify BTX oxidations using ABO₃-PCs, and upscaling is also essential, to better understand potential problems such as coking, poisoning, and sintering. Employing in-situ characterization techniques, like in situ Raman spectroscopy.

Although challenges persist, ABO₃-PC are promising candidates for application as real-world BTX oxidations. As ABO₃-PCs continue to improve, they are likely to contribute to pollution control and the preservation of health and the environment. Combining ABO₃ perovskite oxidation processes with lead halide perovskite photovoltaics^[223–226] would also provide a sustainable way to achieve BTX oxidation and capturing the CO₂ generated would allow clean synthetic fuels to be obtained.^[227,228]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

BTX, catalytic oxidation, environmental sustainability, perovskites

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