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Unraveling the role of a Cu dopant in formaldehyde catalytic oxidation over a $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ perovskite: an experimental and theoretical study

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A series of $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ perovskite-type catalysts were prepared through a sol-gel method and evaluated for formaldehyde catalytic oxidation. Experimental and DFT studies were performed to reveal the role of the Cu dopant on formal dehyde oxidation over $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ catalysts and determine the optimal doping amount of Cu. The perovskite with a Cu substitution content of 0.2 exhibited the highest catalytic activity and good thermal stability for formaldehyde oxidation. The degree of Cu substitution significantly influenced the textural properties of the catalysts. The La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ catalyst exhibited the highest specific area, pore volume, and crystalline degree, which enabled the availability of more active sites for formaldehyde adsorption. The introduction of bivalent Cu²⁺ resulted in a charge imbalance that was compensated by the increased Mn⁴⁺/Mn³⁺ ratio of the perovskite. Partial substitution of Mn by Cu cations enhanced the oxygen mobility of perovskites, which was ascribed to a synergy between surface Cu and Mn atoms. The La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ catalyst presented excellent oxygen mobility and thus promoted formaldehyde catalytic oxidation. DFT calculation results indicated that the absolute value of the formaldehyde adsorption energy on the surface Cu-O site was higher than that on the Mn-O site. The Cu dopant facilitated formaldehyde adsorption and promoted the transfer of more electrons from formaldehyde to the catalyst, which was beneficial for formaldehyde activation and subsequent oxidation. Finally, combining the in situ FTIR measurements with DFT calculations revealed the reaction mechanism of formaldehyde oxidation on the $La_0 s Sr_0 2 Mn_{1-y} Cu_y O_3$ perovskite. Based on the experimental and theoretical methods, herein, the corresponding reaction cycle of formaldehyde oxidation is proposed. The reaction cycle contained seven elementary reaction steps, in which O_2 dissociation was the rate-limiting step with the highest energy barrier of 1.47 eV.

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1. Introduction

Formaldehyde is a typical oxygenated volatile organic compound (VOC).¹ It has been classified as a human carcinogen (group 1) by the International Agency for Research on Cancer (IARC) as the long-term exposure to formaldehyde increases the risk of getting affected by cancer and even myeloid leukemia.² The primary industrial emission sources of formaldehyde are fuel combustion,³ biomass burning,⁴ and petrochemical facilities.⁵ Unlike other pollutants, such as SO₂ and NO_x, emissions of VOCs have continued to increase over the past few years.⁶ Therefore, more efforts should be made to reduce the emission of VOCs.

Catalytic oxidation is considered a prospective technique to convert formaldehyde into CO₂ and H₂O, which are unharmful.⁷ A variety of catalysts have been studied for formaldehyde

^aState Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China. E-mail: liujing27@mail.hust.edu.cn; Fax: +86-27-87545526; Tel: +86-27-87545526 ^bState Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, PR China oxidation, including supported noble metals⁸ and non-noble metal oxides.⁹ However, the catalysts reported thus far have shown poor catalytic activity and product selectivity. Among these catalysts, the lanthanum-manganese perovskite (LaMnO₃) is regarded as a promising material in the field of catalysis owing to its thermal stability, environmental friendliness, and low-cost properties.¹⁰ For example, the LaMnO₃ perovskite was found to exhibit the highest activity for the oxidation of methanol¹¹ and methyl ethyl ketone (MEK)¹² among LaBO₃ (B = Cr, Co, Ni, Mn, and Fe) perovskites. Normally, the formation of the perovskite structure needs a relatively high calcination temperature (above 600 °C) at the cost of the surface area, leading to poor reducibility and activity at low-temperatures. Therefore, the low-temperature catalytic performance of LaMnO₃ perovskites should be further enhanced.

It is well known that the catalytic performance can be modified by doping a foreign element in the A site of the perovskite (formula of ABO₃). The substitution of La by Sr atoms in the LaMnO₃ perovskite proved to be favorable for formaldehyde oxidation.¹³ However, a gradual deactivation with reaction time was observed for the substituted catalysts, which was correlated with the accumulation of intermediates on the active sites. Thus, exploring the active center of A-site substituted LaMnO₃ is crucial to improving its catalytic behavior for formaldehyde oxidation. Normally, the A-site cations tend to not directly participate in catalytic reactions. For example, Raman spectra showed that the Sr dopant promotes the Jahn–Teller distortion in the MnO₆ octahedral structure, and further affects the charge transfer between the surface Mn cations and reactants (CH₄ and CO).¹⁴ Accordingly, Sr cations acted as a promoter, whereas the Mn cation served as an active site in the Sr-doped LaMnO₃ catalyst. Nevertheless, there are limited studies on the interaction mechanism between the active center of the A-doped LaMnO₃ perovskite and formaldehyde molecules.

In addition to the A-site substituted strategy, partial replacement in the B site by other elements can also modulate the catalytic performance of the perovskite, since the activity of the perovskite-type catalyst is mainly determined by component B.¹⁵ By selecting the appropriate B-site dopant, the stability and activity of the perovskite may be further improved for formaldehyde catalytic oxidation. Cu is considered as a potential B-site dopant that can promote the transfer of active oxygen species during redox reactions.16 Thus, it is feasible to design a catalyst based on the LaMnO₃ perovskite with the A- and B-site cations simultaneously substituted by Sr and Cu cations, respectively. However, no research studies have been performed on formaldehyde removal over A- and B-sites doped LaMnO₃ perovskite. Moreover, the active center and the role of the B-site dopant on formaldehyde oxidation over the A- and B-doped LaMnO₃ perovskite should be further clarified.

In this work, a series of $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ perovskites were prepared by the sol-gel method and evaluated for formaldehyde catalytic oxidation. The roles of the Cu dopant on the physicochemical properties and catalytic performance of the catalyst were unraveled based on a variety of characterizations. A long-term catalytic experiment for formaldehyde oxidation was conducted to evaluate the catalyst stability. Furthermore, density functional theory (DFT) calculations were performed to provide mechanistic insight into the effects of the Cu dopant on the interaction between the catalyst and formaldehyde molecule. Finally, the reaction mechanism of formaldehyde oxidation on $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ perovskites was proposed according to the *in situ* FTIR measurement and DFT calculation.

2. Methods

2.1 Catalyst synthesis

The La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO₃ (x = 0, 0.2, 0.5, 1) perovskite-type catalysts were prepared by a conventional sol–gel method, in which x represents the molar ratio of Cu/(Cu + Mn). La(NO₃)₃··6H₂O, Sr(NO₃)₂, Cu(NO₃)₂·3H₂O, Mn(NO₃)₂, and citric acid (C₆H₈O₇·H₂O) were dissolved in deionized water. The $n_{La}: n_{Sr}: n_{Mn}: n_{Cu}$ molar ratio used in the study was 0.8: 0.2: 1 - x: x. The proportion of the total metal ions to citric acid was maintained at 1: 1.2. After stirring for 1 h at 30 °C, the above solutions were gradually heated to 80 °C to form gels. The resulting sol–gels were dried at 100 °C for 12 h, and then calcined in

a muffle oven in two steps: 400 °C for 1 h, and 700 °C for 4 h with at heating rate of 10 °C min⁻¹.

2.2 Catalyst characterization

The specific surface area (S_{BET}) of the catalysts was determined through N2 adsorption and Brunauer-Emmett-Teller (BET) theory with a surface area analyzer at liquid N₂ temperature ($-196 \circ C$) on a 3H-2000PM2 instrument (BeiShiDe, China). Before each adsorption, the catalyst powder was degassed for 3 h at 300 °C under vacuum of typically 10⁻³ Pa in order to remove adsorbed species. The pore size distribution was conducted using a Barrett-Joyner-Halenda (BJH) model. The crystal structure of the catalysts was characterized by powder X-ray diffraction (XRD) analysis on a diffractometer (D8ADVANCE, Bruker Inc., Germany) in the range of $2\theta = 5^{\circ}-85^{\circ}$ at room temperature with a scanning rate of 8° min⁻¹, using filtered Cu K α radiation, operating at 40 kV and 10 mA. The morphology of the prepared samples was observed by scanning electron microscope (SEM) (Thermo Scientific Apreo 2C, United States). The chemical composition analysis was performed on an X-ray photoelectron spectroscopy (XPS) instrument (ESCA-LAB Xi+, Thermo Fisher Scientific, United States) with an exciting source of Al Ka X-ray beam ($h\nu = 1486.6$ eV). H₂-temperature programmed reduction (H2-TPR) was carried out on a chemisorption instrument (TP-5080, Xianquan, China) under the mixture of 10% H₂/Ar (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹ from 50 °C to 900 °C. The in situ FT-IR spectra of the formaldehyde oxidation process was obtained on a Nicolet iS50 spectrophotometer from thermo electron.

2.3 Catalytic activity measurement

The catalyst activities of $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ for formaldehyde oxidation were evaluated in a fix-bed reactor under atmospheric pressure with the reaction temperature ranging from 80 °C to 300 °C. 0.5 g of the catalyst and 1.5 g of quartz sand were fed into a quartz reactor with an inner diameter of 10 mm. Quartz wool was placed above the catalyst to prevent the airflow from carrying the catalyst out of the reactor and affecting subsequent experiments. The feed gas contained 0.3 vol% formaldehyde and 20 vol% O₂ balanced with N₂. The feed gas flow rate was set at 100 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of



Fig. 1 (a) Side view and (b) top view of the slab model of $\mbox{SrCu}-\mbox{La}\mbox{MnO}_3.$

5000 h⁻¹. The formaldehyde concentration was maintained by flowing a constant O_2/N_2 mixture over the paraformaldehyde. The outlet gas was monitored online using a gas chromatograph (GC) (Clarus 590, PerkinElmer, United States). The catalytic activity was measured in the temperature range of 80–300 °C. Conversion measurements and product profiles were taken after being maintained for 10 min at each test temperature. The conversion of formaldehyde was calculated based on the yield of CO_2 . The equation for the CO_2 conversion is listed below:

$$\eta_{\rm HCHO} = (C_{\rm CO}/C_{\rm HCHO}) \times 100\%$$
(1)

where $\eta_{\rm HCHO}$ is the conversion of formaldehyde, $C_{\rm HCHO}$ is the initial formaldehyde concentration, and $C_{\rm CO_2}$ is the formation concentration of CO₂.

2.4 Computational method

Spin-polarized DFT calculations were implemented using the CASTEP program.¹⁷ The exchange–correlation interaction was described by the Perdew–Burke–Ernzerhof (PBE) function of generalized gradient approximation (GGA).¹⁸ The ultra-soft pseudopotential method was used to describe the core electrons of the transition metals.¹⁹ The cutoff energy of the plane-wave basis set was set to 340 eV. A $4 \times 4 \times 1$ Monkhorst–Pack *k*-points scheme was used in the Brillouin zone. The self-consistent field (SCF) tolerance was set to 1×10^{-6} eV per atom in the electronic calculation. The bulk LaMnO₃ with an orthorhombic structure in the *Pnma* space group was used for the model construction. The convergence criteria of the optimized structures were based on the force, energy and displacement, which were set as 0.03 eV Å⁻¹, 1.0×10^{-5} eV per

Table 1 Textural properties of the prepared catalysts				
Samples	$S_{\rm BET} \left({{{\rm{m}}^2}\;{{\rm{g}}^{ - 1}}} ight)$	$V_{\rm t} \left(\rm cm^3 \ g^{-1} \right)$	$D_{\rm p}({\rm nm})$	
La _{0.8} Sr _{0.2} MnO ₃	26.555	0.230	34.570	
$La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$	37.554	0.282	29.984	
$La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O_3$	18.180	0.130	28.668	
$La_{0.8}Sr_{0.2}CuO_3$	16.524	0.043	10.288	

atom, and 0.001 Å, respectively. The calculated lattice parameters (a = 5.826 Å, b = 7.872 Å, c = 5.710 Å) of the LaMnO₃ unit cell have less than 3% deviation from the experimental parameters (a = 5.747 Å, b = 7.693 Å, c = 5.537 Å).²⁰ Consequently, the calculation results are in good agreement with the experimental data, which indicates that the DFT calculations are reliable. The 2 × 2 supercell cut from the LaMnO₃(010) facet was adopted to model the undoped La–Mn perovskite, labeled as SrCu–LaMnO₃. In the SrCu–LaMnO₃ structure, the Sr and Mn atoms were replaced by La and Cu atoms, respectively.

Results and discussion

3.1 Catalyst characterization

The influence of Cu substitution on the textural properties was obtained from N₂ adsorption–desorption isotherms. The structural parameters of La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO₃, including the specific surface area (S_{BET}), pore volume (V_t), and average pore size (D_p), are summarized in Table 1. The results show that the textural property of the catalyst is notably dependent on the degree of Cu substitution. Partial substitution of Mn by Cu cations with the Cu ratio up to 20% increases S_{BET} from 26.555 to 37.554 m² g⁻¹, while further Cu substitution drastically decreases S_{BET} . A similar tendency is observed for V_t , and La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ has the largest pore volume of 0.282 cm³ g⁻¹. The pore diameters (D_p) decrease from 34.57 to 10.288 nm as the Cu content increases from 0 to 1.

The morphologies of the $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ catalysts are displayed in Fig. 2. In the case of the Cu-undoped catalyst, the $La_{0.8}Sr_{0.2}MnO_3$ sample presents sphere-like particles with nonuniform size. The Cu substitution leads to the aggregation of perovskite particles to some extent. Rod-like clusters can be observed for the $La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$ catalyst, and a multifaceted morphology is observed for the $La_{0.8}Sr_{0.2}CuO_3$ catalyst. Therefore, the introduction of Cu cations into the catalyst greatly influences the microstructures of perovskite.

The XRD profiles of the synthesized catalysts are shown in Fig. 3. The $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$ and $La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O_3$ catalysts show a typical pattern of the



Fig. 2 SEM images of (a and b) La_{0.8}Sr_{0.2}MnO₃, (c and d) La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃, (e and f) La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃, and (g and h) La_{0.8}Sr_{0.2}CuO₃.



LaMnO₃ perovskite structure (PDF #54-1275), indicating that the partial substitution does not alter the crystalline phase of LaMnO₃. The intensity of the diffraction peak at 32.4° for the La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ catalyst is higher than that for the La_{0.8}Sr_{0.2}MnO₃ and La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃ catalysts. The sharp diffraction peak of La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ reflects that the addition of a modest amount of Cu is beneficial for perovskite crystallization. For the La_{0.8}Sr_{0.2}CuO₃ sample, most of the peaks can be well indexed to the perovskite-phase with an orthorhombic crystal structure of La₂CuO₄ (PDF #82-2141). Weak peaks corresponding to CuO (PDF #48-1548) and La₂O₂CO₃ (PDF #37-0804) are also detected. The effect of the calcination temperature on the crystallinity of the La-based perovskite was investigated in the previous work,²¹⁻²³ and it was found that the sample exhibits a well-crystallized perovskite structure at the synthesis temperature of 700 °C.21 Moreover, the La-Mn perovskite samples calcined at 600 °C showed the pure perovskite crystalline phase.22,23

The catalyst chemical states and element content of the La_{0.8}Sr_{0.2}Mn_{1-r}Cu_rO₃ samples were determined by XPS characterization analysis. The Avantage program was used for data acquisition and analysis. To correct the charging effects, all binding energies were referenced to the energy of the C 1s peak positioned at 284.8 eV. For the fitting analysis, the smart background was used and fitting was performed with a Lorentzian-Gaussian mixed ratio of 30%. The spectral components of the signals can be found by fitting a sum of single-component lines to the experimental data by means of nonlinear leastsquares curve-fitting. The XPS spectra of Mn $2p_{3/2}$, Cu $2p_{3/2}$, and O 1s are depicted in Fig. 4. The corresponding state compositions derived from the integration of peaks, as well as the Cu doping ratio, are listed in Table 2. Fig. 4a displays the Mn $2p_{3/2}$ spectra of the La_{0.8}Sr_{0.2}Mn_{1-r}Cu_rO₃ catalysts. The binding energy can be divided into two peaks at 642.47 \pm 0.36 eV and 641.27 \pm 0.18 eV, which are assigned to Mn⁴⁺ and Mn³⁺, respectively.24 For the Cu 2p spectra (Fig. 4b), the peak at 933.85 \pm 0.05 eV is attributed to the Cu^{2+} cation, and the peak at a lower binding energy of 932.40 eV corresponds to Cu⁺.²⁵ Fig. 3c represents the O 1s spectra, in which three characteristic peaks are divided: the lattice oxygen (O_{latt}) at 528.85 \pm 0.43 eV, surfaceadsorbed oxygen (O_{ads}) at 530.98 \pm 0.31 eV, and surface hydroxyl





Fig. 4 XPS spectra of the $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ catalysts: (a) Mn $2p_{3/2}$, (b) Cu $2p_{3/2}$, and (c) O 1s.

 (O_{O-H}) at 533.45 \pm 0.69 eV.²⁶ As summarized in Table 2, quantitative analysis of the surface atomic ratio was carried out. It is noteworthy that the order of the Mn⁴⁺/Mn³⁺ ratio is La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃ (2.165) > La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ (1.312) > La_{0.8}Sr_{0.2}MnO₃ (0.592). The Mn⁴⁺/Mn³⁺ ratio increases with the increase of the Cu content. This result may be induced by a net charge imbalance with the addition of the lower oxidation state Cu²⁺. Substitution of low valence ions into the B-site of perovskite would lead to a modified electron effect to maintain charge neutrality.²⁷ Therefore, partial Cu²⁺ substitution may result in the oxidation of Mn³⁺ ions to Mn⁴⁺. Moreover, the surface amounts of Cu cations in the La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ and La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃ catalysts are 0.1659 and 0.3972, respectively, which are lower than the theoretical amount.

Table 2 Surface atomic ratio estimated using XPS analysis

Sample	Mn (%)	Mn (%)		Cu/(Mn	O (%)	O (%)		
	Mn ⁴⁺	Mn ³⁺	Mn ⁴⁺ /Mn ³⁺	+ Cu)	O _{latt}	O _{ads}	O _{latt} /O _{ads}	
La _{0.8} Sr _{0.2} MnO ₃	0.372	0.628	0.592	0	0.422	0.560	0.754	
La _{0.8} Sr _{0.2} Mn _{0.8} Cu _{0.2} O ₃	0.568	0.433	1.312	0.166	0.505	0.476	1.061	
La _{0.8} Sr _{0.2} Mn _{0.5} Cu _{0.5} O ₃	0.684	0.316	2.165	0.397	0.449	0.544	0.825	
$La_{0.8}Sr_{0.2}CuO_3$	0	0	0	1	0.744	0.247	3.012	



Since formaldehyde oxidation is a redox reaction, the reducibility of the La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO₃ catalysts was assessed by H₂-TPR, as given in Fig. 5. For the La_{0.8}Sr_{0.2}MnO₃ catalyst, the TPR profile shows three sets of reduction processes. The broad peak at 398 °C is associated with the reduction of $Mn^{4+} \rightarrow Mn^{3+}$ in the perovskite structure.²⁸ The peaks in the range of 668-778 °C are related to the reduction of $Mn^{3+} \rightarrow Mn^{2+}$.¹³ As Mn is substituted by Cu cations, a shift of the first peak to a lower temperature is observed. For La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ and La_{0.8}-Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃, the peaks with temperatures below 300 °C are correlated with the process of $Mn^{4+} \rightarrow Mn^{3+,29}$ Weak peaks in the temperature region of 449-720 °C (Fig. 5b) can be assigned to the stepwise reduction processes of $Cu^{2+} \rightarrow Cu^+ \rightarrow$ Cu.³⁰ The reduction temperature of $Mn^{3+} \rightarrow Mn^{2+}$ over the La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ and La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃ catalysts are similar to that over La_{0.8}Sr_{0.2}MnO₃.³¹ For the La_{0.8}Sr_{0.2}CuO₃

catalyst, there are two main reduction peaks at 288 °C and 791 °C, which are ascribed to the reduction processes of $Cu^{2+} \rightarrow Cu^+$ and $Cu^+ \rightarrow Cu$, respectively.³²

It was observed that the onset reduction temperature (T_{onset}) and the first reduction peak are in the order of La_{0.8}Sr_{0.2}-Mn_{0.8}Cu_{0.2}O₃ < La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃ < La_{0.8}Sr_{0.2}CuO₃ < La_{0.8}Sr_{0.2}MnO₃. Accordingly, the introduction of Cu cations promotes the mobility of the oxygen species of perovskites. The first reduction peak and T_{onset} values of La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ and La_{0.8}Sr_{0.2}MnO₃. Therefore, the synergy between Cu and Mn is responsible for the enhanced redox ability of the La_{0.8}Sr_{0.2}MnO₃. Particularly, the La_{0.8}Sr_{0.2}MnO₃ and La_{0.8}Sr_{0.2}MnO₃. Therefore, the synergy between Cu and Mn is responsible for the enhanced redox ability of the La_{0.8}Sr_{0.2}MnO₃. Particularly, the La_{0.8}Sr_{0.2}MnO_{3.8}Cu_{0.2}O₃ sample has the lowest T_{onset} , indicating its best low-temperature reduction performance.

3.2 Catalytic activity for formaldehyde oxidation

The formaldehyde catalytic oxidation on the La_{0.8}Sr_{0.2}Mn_{1-x}-Cu_xO₃ (x = 0, 0.2, 0.5, 1) catalysts is exhibited in Fig. 6a. The reaction temperatures of T_{50} and T_{90} , referring to the temperatures at which 50% and 90% formaldehyde are converted, are summarized in Table 3. The reactivity of the La_{0.8}Sr_{0.2}Mn_{1-x}-Cu_xO₃ catalysts for formaldehyde oxidation is in the order of La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ > La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}-O₃ > La_{0.8}Sr_{0.2}CuO₃. The La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ catalyst presents the best formaldehyde oxidation performance, which reaches 50% conversion at 127 °C and 90% conversion at 152 °C (Table 3). However, with a further increase of the Cu content, the formaldehyde conversion efficiency decreases. The La_{0.8}-Sr_{0.2}CuO₃ catalyst exhibits the worst catalytic performance, with



Fig. 6 (a) Catalytic activities of the $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ catalysts. (b) Stability test for the $La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$ catalyst.

Table 3 Comparison of the catalytic activity between the La_{0.8}Sr_{0.2}-Mn_{0.8}Cu_{0.2}O_3 catalyst obtained in this work and Mn-based catalysts reported in the literature

Samples	T_{50} (°C)	T_{90} (°C)	Reference
LaSrMn _{0.8} Cu _{0.2} O ₃	127	152	This work
Mn–Cu mixed oxide	185-232	207-258	33
Mn–Fe spinel	195-227	244-329	34
Mn–Ce spinel	175-222	231-398	35
MnO ₂ -CeO ₂ -Al ₂ O ₃	190-240	210-245	36
Mn-Cu/HBC	_	>175	37
MnO _x -SnO ₂	$\sim \! 150$	$\sim \! 170$	38

Table 4 Catalytic activity of the $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ catalysts for formaldehyde oxidation

Samples	T_{50} (°C)	T_{90} (°C)	$E_{ m apparent} ({ m kJ} { m mol}^{-1})$
LaSrMnO ₃	133	168	33.89
LaSrMn _{0.8} Cu _{0.2} O ₃	127	152	29.51
LaSrMn _{0.5} Cu _{0.5} O ₃	156	177	30.31
LaSrCuO ₃	222	263	37.89

 T_{50} and T_{90} of 222 °C and 263 °C, respectively. The catalytic activity of the La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ catalyst obtained in this work was further compared with that of the Mn-based catalysts reported in other literature studies. The T_{50} and T_{90} data of the catalyst are shown in Table 3 It was found that the La_{0.8}Sr_{0.2}-Mn_{0.8}Cu_{0.2}O₃ catalyst prepared in this study demonstrated excellent catalytic oxidation activity of formaldehyde, and the removal efficiency of formaldehyde was superior to that of Mu–Cu, Mu–Fe, Mn–Ce, Mn–Sn and other mixed oxides.

The apparent activation energies ($E_{apparent}$, kJ mol⁻¹) of formaldehyde oxidation on the La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO₃ catalysts are calculated and given in Table 4. The values of $E_{apparent}$ are in the order of La_{0.8}Sr_{0.2}CuO₃ (37.89 kJ mol⁻¹) > La_{0.8}Sr_{0.2}MnO₃ (33.89 kJ mol⁻¹) > La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃ (30.31 kJ mol⁻¹) > La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ (29.51 kJ mol⁻¹). The La_{0.8}Sr_{0.2}Mn_{0.8}-Cu_{0.2}O₃ catalyst shows the lowest apparent activation energy.

In addition, continuous formaldehyde oxidation was performed to evaluate the stability of the prepared $La_{0.8}Sr_{0.2}$ - $Mn_{0.8}Cu_{0.2}O_3$ catalysts. Fig. 6b illustrates the formaldehyde conversion over time with the reaction temperature of 180 °C. The long-term stability test shows that the formaldehyde conversion efficiency remains above 95% for $La_{0.8}Sr_{0.2}Mn_{0.8}$ - $Cu_{0.2}O_3$ within 24 h. Therefore, this catalyst shows good stability for formaldehyde oxidation.

As discussed above, the $La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$ catalyst possessed the highest S_{BET} and V_t , while $La_{0.8}Sr_{0.2}CuO_3$ possessed the lowest values. The large surface area and pore volume enable more active sites to be exposed to adsorb reactants, and *vice versa*.³⁹ Therefore, the catalytic activity is probably associated with the physical properties of the catalyst. The Cu substitution at a moderate level of 20% contributes to the formation of a catalyst with a high surface area and pore volume, thus promoting formaldehyde adsorption and oxidation. Moreover, the H₂-TPR results indicated that introducing Cu cations can promote oxygen mobility of perovskite. The La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ sample shows the best low-temperature reduction performance, which would facilitate oxygen transfer and thus enhance formaldehyde oxidation performance. However, the better redox properties of the La_{0.8}Sr_{0.2}Mn_{0.5}-Cu_{0.5}O₃ and La_{0.8}Sr_{0.2}CuO₃ samples are not in accordance with their worse formaldehyde conversion efficiency. This disagreement may arise from the unsatisfactory textural properties of La_{0.8}Sr_{0.2}Mn_{0.5}Cu_{0.5}O₃ and La_{0.8}Sr_{0.2}CuO₃.

3.3 Mechanistic studies of formaldehyde adsorption

The high surface area is conducive to exposing more active sites for formaldehyde adsorption. Thus, the quality and quantity of the active site are determinants of the catalytic activity. It would be important to investigate the effect of the Cu dopant on formaldehyde adsorption and identify the corresponding active center at the microcosmic level. However, it is difficult to accurately determine the active sites in the formaldehyde oxidation process solely based on experiments. DFT calculations were thus carried out to elucidate the formaldehyde adsorption mechanism on the SrCu–LaMnO₃ surface. Meanwhile, the effect of the Cu dopant on the interaction between formaldehyde and the catalyst surface was further studied.

During the calculation, all possible adsorption sites were taken into consideration. Fig. 7a and b represent the optimized configurations and the corresponding adsorption energies (E_{ads}) , Mulliken charges (*Q*), and structural parameters of formaldehyde adsorption on the surface Cu–O and Mn–O sites, respectively. It was found that the formaldehyde molecule tends to adsorb on the surface metal and lattice oxygen atoms in a horizontal configuration. In Fig. 7a, the C and O atoms of formaldehyde respectively adsorb on the surface O and Cu atoms, forming the C–O bond (1.42 Å) and O–Cu bond (1.83 Å). Formaldehyde adsorbs on the surface Cu–O sites by releasing energy (1.88 eV) and donating 0.21 e electrons to the catalyst. In Fig. 7b, formaldehyde adsorbs on the Mn–O sites by releasing energy (1.52 eV). Meanwhile, C–O and O–Mn bonds are formed with the lengths of 1.42 Å and 1.95 Å, respectively.

The project density of state (PDOS) analysis was calculated to obtain an in-depth understanding of the interaction mechanism between formaldehyde and the SrCu–LaMnO₃ surface, as given in Fig. 8. Fig. 8a and b plot the PDOS of the bonding nature after formaldehyde adsorption on the surface Cu–O and



Fig. 7 Optimized configurations, adsorption energies (E_{ads}), Mulliken charges (Q), and structural parameters of formaldehyde adsorption on the surface (a) Cu–O and (b) Mn–O sites.



Fig. 8 PDOS analysis for formaldehyde adsorption on the (a) Cu–O and (b) Mn–O sites of the catalyst surface. The dashed line at 0 eV denotes the Fermi level.

Mn–O sites, respectively. A strong resonance between the C–p orbitals of formaldehyde and the surface O–p orbitals is observed in Fig. 8a and b. Meanwhile, the surface Cu–d orbitals mix with the O–p orbitals of formaldehyde in a wide energy range near the Fermi level (Fig. 8a). Nevertheless, the overlapping peaks of the surface Mn–d and O–p orbitals in Fig. 8b are weaker than that in Fig. 8a, suggesting that the hybridization interaction of formaldehyde with the Cu–O site is stronger than that of formaldehyde with the Mn–O sites.

The results show that formaldehyde adsorption on SrCu-LaMnO₃ is dominated by the chemisorption mechanism. The absolute value of the adsorption energy for formaldehyde on the Cu-O site is higher than that on the Mn-O site. Accordingly, the surface Cu and O atoms of perovskite serve as the active site for formaldehyde adsorption. The Cu dopant facilitates formaldehyde adsorption, and thus promotes the subsequent formaldehyde oxidation. The Mulliken population analysis indicates that the electrons are transferred from formaldehyde to the catalyst surface during formaldehyde adsorption. The catalyst surface serves as an acceptor to obtain electrons. Therefore, the surface cations with high valence states are conducive to accepting electrons and further formaldehyde adsorption. According to the XPS result, the Mn⁴⁺/Mn³⁺ ratio of La_{0.8}Sr_{0.2}-Mn_{0.8}Cu_{0.2}O₃ is higher than that of La_{0.8}Sr_{0.2}MnO₃, which may be one of the reasons contributing to the better catalytic performance of $La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$ than $La_{0.8}Sr_{0.2}MnO_3$. Previous studies revealed that the surface Mn⁴⁺ cation of the Mn-based perovskite is an important factor determining the catalyst reactivity,13 which is in accordance with our results.

3.4 Reaction cycle of formaldehyde oxidation

3.4.1 *In situ* **FT-IR measurement.** To further reveal the reaction mechanism of formaldehyde oxidation, *in situ* **FT-IR** characterization was performed. The surface chemical species of formaldehyde oxidation on the $La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$ catalyst were identified and analyzed. Fig. 9 shows the FT-IR spectra of the $La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$ catalyst. The peaks in the range of 800–1200 cm⁻¹ and 1449 cm⁻¹ are respectively attributed to the C–O and C–H vibrations of the dioxymethylene (DOM) species.⁴⁰



Fig. 9 Dynamic changes in the FT-IR spectra of the catalyst as a function of time in a flow of 3% formaldehyde + $20\% O_2 + N_2$ at 250 ° C.

The peaks at 1364 cm⁻¹ and 1600 cm⁻¹ can be respectively classified into the $v_s(COO)$ and $v_{as}(COO)$ vibrations of the formate species.^{41,42} The peaks at 2331 cm⁻¹ and 2362 cm⁻¹ can be assigned to the gas phase CO₂.⁴³ The peaks in the range of 3100–3700 cm⁻¹ are the typical characterized peaks of the hydroxyl groups.^{44,45}

Based on the characterization results, the DOM, formate and hydroxyl species are identified as the intermediates formed during formaldehyde oxidation on the $La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O_3$ catalysts. Furthermore, a possible reaction process of formaldehyde oxidation was speculated. First, the formaldehyde molecule is adsorbed on the catalyst surface, and then oxidized into the dioxymethylene species (DOM). The DOM subsequently reacts with activated oxygen species to form formate and hydroxyl on the surface. Then, formate is broken down into CO_2 in the last step.

3.4.2 DFT calculations. Based on the *in situ* FT-IR analysis, a reaction cycle of formaldehyde oxidation on the SrCu–LaMnO₃



Fig. 10 Reaction cycle, optimized structure, and energy profile of formaldehyde catalytic oxidation on the SrCu-LaMnO3 surface

catalyst is proposed, as shown in Fig. 10. The reaction cycle contains seven elementary reaction steps. Firstly, the gas-phase formaldehyde adsorbs on the surface Cu-O site with the adsorption energy of -1.88 eV (IS \rightarrow IM1). In the adsorption process, formaldehyde is attacked by the surface oxygen atom to form the DOM species. In step 2 (IM1 \rightarrow IM2), the DOM is dehydrogenated into the formate species with the energy barrier of 0.16 eV and reaction heat of -3.68 eV. In this process, DOM decomposed into the formate species with the breakage of one C-H bond. The dissociated H atom reacts with the neighbor activated oxygen species to form OH groups. In step 3 (IM2 \rightarrow IM3), the dehydrogenation reaction further proceeds for the formate species. The formate intermediate reacts with the OH group to form CO_2^* and H_2O^* . The energy barrier and reaction heat of this step are 1.18 eV and -0.9 eV, respectively. In step 4 (IM3 \rightarrow IM4), the intermediate CO₂^{*} desorbs from the catalyst surface by overcoming an energy of 0.05 eV and releasing an energy of 0.06 eV. Then, the H₂O* desorbs from the surface in step 5 (IM4 \rightarrow IM5) and absorbs an energy of 0.07 eV. It is noteworthy that the surface retains its oxygen vacancy (Ov) after CO₂ desorption (IM5). The gaseous O₂ adsorbs on the Ov site to replenish the vacancy in step 6 (IM5 \rightarrow IM6), and releases an energy of 0.96 eV. Finally, the adsorbed O_2^* dissociates into O^* , which then gets adsorbed on the surface Mn site (IM6 \rightarrow FS). The reaction heat and energy barrier of the O₂ dissociation reaction are 1.15 eV and 1.47 eV, respectively.

In the reaction cycle of formaldehyde oxidation, the O_2 dissociation process has the highest energy barrier of 1.47 eV. Therefore, the O_2 dissociation step is the rate-determining step of formaldehyde oxidation on the SrCu-doped LaMnO₃ surface. Our previous research study involved a theoretical and experimental investigation of the formaldehyde reaction over the Cu– Fe spinel catalyst.⁴³ The energy barrier of the O_2 dissociation on the CuFe₂O₄(100) surface is 341.08 kJ mol⁻¹ (3.54 eV), which is much higher than that on the SrCu–LaMnO₃ surface. Therefore, the Sr- and Cu-doped LaMnO₃ catalyst has potential industrial implications.

4. Conclusions

This work synthesized a series of $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ (x = 0, 0.2, 0.5, 1) perovskites for formaldehyde catalytic oxidation. The catalyst with a Cu substitution content of 0.2 presents the best formaldehyde oxidation performance with T₅₀ and T₉₀ of 127 °C and 152 °C, respectively. Long-term stability tests show that the formaldehyde conversion efficiency remains above 95% for La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ within 24 h. The excellent catalytic behavior of the La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ catalysts is closely associated with the higher surface area and pore volume, which enabled more active sites to be exposed for formaldehyde adsorption. Moreover, the TPR characterization results indicate that the enhanced reducibility and oxygen mobility of the La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ catalyst would accelerate formaldehyde oxidation. On the basis of the DFT calculation, it is concluded that the binding strength of formaldehyde on the surface Cu-O site is stronger than that on the Mn-O site. The substitution of Cu facilitates formaldehyde adsorption and promotes greater electron transfer from formaldehyde to the catalyst, which is beneficial for formaldehyde activation and subsequent oxidation. According to the in situ FTIR results, the DOM, formate and hydroxyl species can be identified as the intermediates formed during formaldehyde oxidation on the La_{0.8}Sr_{0.2}Mn_{0.8}-Cu_{0.2}O₃ catalysts. By combining the in situ FTIR and DFT calculation results, a reaction cycle for the formaldehyde

oxidation was proposed. The reaction cycle contains seven elementary reaction steps: formaldehyde adsorption, DOM dehydrogenation, formate dehydrogenation, CO_2 formation and desorption, H_2O desorption, O_2 adsorption and dissociation. O_2 dissociation has the highest energy barrier of 1.47 eV, and is identified as the rate-determining step in the reaction cycle. According to the characterization and experimental results, the catalytic activities of the $La_{0.8}Sr_{0.2}Mn_{1-x}Cu_xO_3$ catalysts were influenced by the Cu doping content. In the next work, further systematic calculation analysis will be carried out to better understand the influence of the Cu doping content on the adsorption energies, Mulliken charge, and the catalytic efficiency.

Data availability

The data supporting this article have been included in the tables and images presented in this article.

Conflicts of interest

There are no conflicts to declare.

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