Catalytic behavior and synergistic effect of nanostructured mesoporous CuO-MnOₓ-CeO₂ catalysts for chlorobenzene destruction

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Abstract
Mesoporous CuO-MnOₓ-CeO₂ composite metal oxides with different copper and manganese loadings were prepared by a urea-assisted hydrothermal method, and were further adopted for the complete catalytic combustion of chlorobenzene. The effects of reaction conditions such as inlet reagent concentration and water feed concentration on chlorobenzene combustion were also studied. The structure and textural properties of the synthesized catalysts were characterized via the XRD, N₂ adsorption/desorption, FE-SEM, TEM, H₂-TPR, O₂-TPD, and XPS techniques. The characterization results reveal that the presence of a small amount of Mn species can facilitate the incorporation of Cu and Mn ions into ceria lattice to form Cu-Mn-Ce-O solid solution. The synergistic effect of Cu and Mn species can reduce the redox potential of the composite catalysts, and produce large amounts of oxygen vacancies in the interface of CuOₓ, MnO₂, and CeO₂ oxides. The catalyst with Cu/Mn atomic ratio of 1/1 exhibits the best chlorobenzene elimination capability, oxidizing about 95% of the inlet chlorobenzene at 264 °C with CO₂ selectivity higher than 99.5%. The concentration and mobility of the chemically adsorbed oxygen are vital for the effective removal of surface Cl species, which inhibits the dissociation of oxygen molecules and decreases the reducibility of the copper and manganese species. It can be rationally concluded that the superior catalytic performance and durability of the mesoporous CuO-MnOₓ-CeO₂ composite oxides are primarily attributed to the higher surface oxygen concentration and better active oxygen mobility.

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1. Introduction
Chlorinated volatile organic compounds (CVOCs) are released to the atmosphere from a wide range of industrial processes or incineration of municipal and medical wastes. Especially, aryl chlorides are hazardous pollutants that are considered among the most harmful organic contaminants due to their acute toxicity, strong bioaccumulation potential, and high environmental stability. Conventional thermal combustion technology for CVOCs destruction usually requires very high temperature (>850 °C), and leads to the formation of other more toxic reaction byproducts such as polychlorinated (PCDDs) and dibenzofurans (PCDFs) [1]. Low-temperature catalytic oxidation has been considered as a more proper approach for the decomposition of CVOCs compared with direct thermal combustion due to its less severe operation conditions, high catalytic efficiency for destruction of very dilute pollutants without additional fuel, and high selectivity to harmless byproducts [2]. The catalytic oxidation of CVOCs to CO₂, H₂O, HCl is the most desirable route for their elimination. As far as we are concerned, the key issue for such an approach is still the availability of the economic and efficient catalyst.

In the past decades, three types of catalysts, that is, noble metal-based catalysts, transition metal oxide catalysts, and solid acid catalysts [3–5], have been studied for the catalytic combustion of CVOCs. Although the noble metal catalysts are catalytically more active at low temperature in comparison with the other metal oxides, the high cost, limited availability, and low resistance to halide such as HCl and Cl₂, greatly restrict their large-scale application [6,7]. Solid acid catalysts such as metal-free zeolites (e.g., H-USY, H-Beta, and H-ZSM-5) and alumina-based materials have been adopted for CVOCs combustion in recent years, while their activities are relatively low and the Brønsted acid sites in H-zeolites usually lead to the coke deposition and catalyst deactivation [8].
Besides, plenty of higher chlorinated compounds are produced due to the co-presence of the Lewis acid sites in these solid acid catalysts [9]. In contrast, the transition metal oxide catalysts exhibit higher activity and superior durability against deactivation [10]. Among them, the copper, manganese, and chromium modified catalysts show excellent catalytic activities for CVOCs destruction. Although the good catalytic efficiency of chromium oxides, researchers have proposed that the chromium-based catalysts are prone to the formation of extremely toxic residues such as chromium oxchloride at low temperature [11]. Copper and its compounds have been widely applied to investigate the dechlorination reactions and achieved good results [12,13]. Huang and co-workers have reported that the CuO modified USY zeolite possessed good activity and high stability for 1,2-chloroethane (DCE) decomposition [14]. Manganese oxides are considered as environmentally friendly materials [15]. It has been verified that manganese oxides are highly active in hydrocarbons oxidation due to their high efficiency in the reduction/oxidation cycles [16]. Although pure copper/manganese oxides will deactivate during the combustion of CVOCs, their resistance to the attack by Cl species can be certainly promoted by the addition of other elements [17]. Ceria has recently attracted much attention as an efficient catalyst due to its abundant oxygen vacancy defects, high oxygen storage capacity, and the relatively easy shuttles between the Ce³⁺ and Ce⁴⁺ oxidation states [18,19]. Gamarra et al. [20] and Luo et al. [21] have reported that the CuO–CeO₂ materials are very powerful catalysts for oxidation reactions, which was even comparable to the supported noble metal catalysts. Besides, the superior low-temperature catalytic performance of ordered mesoporous CuO–CeO₂ catalysts in epichlorohydrin (ECH) combustion was also observed in our group. Wang et al. [21] and Li et al. [9] have found that the MnO₃–CeO₂ mixed oxides showed high catalytic activity and stability for chlorobenzene (CB) and trichloroethylen (TCE) oxidation. Manganese-copper mixed oxides have been widely employed as active catalysts for total oxidation reactions (e.g., CO, hydrocarbons, and methane) and selective catalytic reduction of NO [10,22,23]. Li and co-workers [24,25] have found that the CuMnCeO₃ catalysts possessed excellent CO oxidation performance. However, studies about the catalytic combustion of CVOCs over mesoporous CuO–MnO₂–CeO₂ mixed oxides were seldom reported. Different approaches such as urea-nitrate combustion, incipient impregnation, coprecipitation, and sol–gel have been studied for the synthesis of metal oxide catalysts, while the surface areas of the obtained catalysts were rather low [26–29]. Mesoporous transition metal oxides with d-shell electrons confined to nanosized walls, redox active internal surfaces, and connected pore networks show extreme fascinating prospects in catalysis, separation, and energy conversion and storage [30,31]. Recently, a new method involving a surfactant in the precipitation process was used, and the obtained catalysts show enhanced surface areas and improved catalytic performance. Mesoporous CuO–Fe₂O₃, CuO/Co(OH)₂/ZrO₂/Al₂O₃, and CuO–CeO₂ catalysts with large surface areas have been synthesized using CTAB as the soft template [32,33], and these material show high activity in oxidation reactions.

In this article, we report an economic and facile urea-assistant hydrothermal (UHT) protocol for the preparation of mesoporous CuO–MnO₂–CeO₂ mixed oxides. Chlorobenzene is a typical aryl chloride and usually employed as the model reagent to predict the destruction behaviors of chlorinated aromatics as well as dioxins [34], and the effects of chlorobenzene inlet concentration and water feed concentration on catalytic activity were also evaluated. The characterization results are correlated with the catalytic behavior of CuMnCeO₃ catalysts, and the chlorobenzene oxidation mechanism over CuMnCeO₃ catalysts is further simply discussed.

2. Experimental

2.1. Catalyst preparation

All chemicals used in the hydrothermal route are cheap metal nitrates, CTAB template, urea, and water. Typically, 9 g of urea was added to the mixed aqueous solution of different ratios of Cu(NO₃)₂·3H₂O and 50% Mn(NO₃)₂·6H₂O, and 6.8 g of CTAB. After stirring for 2 h, the solutions were aged in autoclaves at 90 °C for 24 h, and followed by 12 h at 120 °C. Then, the products were washed with distilled water and recovered by centrifugation. Finally, the recovered products were dried at 80 °C and calcined at 550 °C for 4 h to remove organic residues, and the obtained catalysts are denoted as CuMn₉₋₅₇Ce₅₋₅₂O₃ (α = 0.1, 0.15, and 0.2).

For comparison, the CuO₀.₃CeO₂O₃ and MnO₃–CeO₂O₃ catalysts were also synthesized via the UHT procedure. In addition, the CuMnCeO₃ mixed oxide (Cu: Mn: Ce = 1:5:1:5:7, atomic ratio) was also prepared by the traditional incipient impregnation (IMP) method [15]. Pure CuO, MnO₂, and CeO₂ were synthesized through thermal calcination their corresponding hydrous metal nitrates at 550 °C for 4 h.

2.2. Catalyst characterizations

X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert powder diffraction system using Cu Kα radiation (λ = 0.15418 nm) in the 2θ range of 0.7–5° (scanning rate of 0.5°/min) and 10–80° (scanning rate of 4°/min), respectively. N₂ adsorption/desorption isotherms of catalysts at 77 K were collected on a Quantachrome NOVA 1200e gas sorption analyzer. All experiments were degassed under vacuum at 300 °C for 3 h before the measurement. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P⁰) of ca. 0.99. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was derived from the desorption branch of the N₂ isotherm using the Barrett–Joyner–Halenda (BJH) method.

Field emission scanning electron microscopy (FE-SEM) images were recorded on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images were collected on a Hitachi H-7650 microscope operating at an acceleration voltage of 80 kV. The actual Cu and Mn contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a PerkinElmer OPTIMA 7000 DV, and the results show that the contents of both Cu and Mn in the final catalyst are nearly equal to the theoretical values.

Temperature programmed reduction (H₂-TPR) experiments were performed on a Quantachrome ChemiBET 3000 TPR–TPD analyzer. Typically, 50 mg of catalyst was heated in a 5% O₂/He flow (50 mL/min) from RT to 500 °C and held for 30 min, and then treated in a He stream at room temperature for 30 min to remove any residual oxygen. The sample was finally reduced under a 5% H₂/He (50 mL/min) from 50 to 700 °C with a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) were carried out on a Quantum 2000 instrument under high vacuum (<5 × 10⁻¹⁰ Torr) using Al Kα as the exciting radiation at a constant pass energy of 1486.6 eV. The C 1s peak was used to calibrate the binding energy.

2.3. Catalytic performance evaluation

All evaluation experiments were performed in a continuous-flow fixed-bed reactor at the atmospheric pressure, consisting of a stainless steel tube (6 mm i.d.) that was filled with the catalyst. The VOC-containing gas was generated by bubbling air through the VOC saturator, and then further diluted with another air stream before
reaching the reaction bed. Water steam was introduced by delivering the liquid water with a syringe pump (WZ-50C6, Zhejiang Smiths Co., China) into dry air, and the injection point was electrically heated to ensure complete vaporization of the water. The temperatures of the catalyst bed, vaporization, and tubular electric furnace were monitored by E-type thermocouples.

In each test, 300 mg of the catalyst (40–60 mesh) was placed at the middle of the tube reactor. The gas hourly space velocity (GHSV) and O2 feed concentration were kept at ca. 30,000 h⁻¹ and 21% (v/v), respectively. The catalyst bed temperature was first raised to 120°C with the feed stream passing and stabilized for 30 min. Then the temperature was increased to the next one at a heating rate of 5°C/min and stabilized for 20 min prior to online analysis of the effluent gas composition in a gas chromatograph (GC9890A, Shanghai Linghua Co., China) equipped with an electron capture detector (ECD) for the quantitative analysis of organic reactant and products, and a flame ionization detector (FID) for the quantitative determination of CO and CO₂ (convert to methane by a methanation reactor). Furthermore, the reaction byproducts and intermediates were identified by a Hiden QGA on-line mass spectrometer.

3. Results and discussion

3.1. Catalytic behavior of CuMnCeOₓ mixed oxides

3.1.1. Catalytic activity and organic byproducts distribution

The light-off curve and catalytic activity data (i.e., T95, T50, T05, and reaction rate) of all synthesized catalysts for chlorobenzene oxidation are respectively shown in Fig. 1 and Table 1. The blank tests were carried out with crushed quartz sand (40–60 mesh) packed in the reactor in order to check whether or not some reactions under thermal combustion condition could take place, and no thermal or homogeneous chlorobenzene destruction can be observed below 400°C. The CuMnCeOₓ mixed oxides prepared via the UHT method possess much higher chlorobenzene destruction activity than those of the other catalysts, and appropriate amount of CuMn doping is vital for the catalytic performance. Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ has the highest chlorobenzene combustion activity (T95 = 264°C), which is much higher than the Cu₀.₃Ce₀.₇Oₓ (T95 = 315°C), Mn₀.₃Ce₀.₇Oₓ (T95 = 368°C), and CuMnCeOₓ-imp (T95 = 346°C) catalysts (see Table 1). The activity sequence of all samples is: Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ > Cu₀.₁Mn₀.₂Ce₀.₇Oₓ > Cu₀.₃Ce₀.₇Oₓ > Cu₀.₂Mn₀.₁Ce₀.₇Oₓ > CuMnCeOₓ-imp > Mn₀.₃Ce₀.₇Oₓ > CuO > MnO > CeO₂. Furthermore, the chlorobenzene combustion rates listed in Table 1 also confirm the superior activity of Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ. Catalytic activities of Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ and Cu₀.₁Mn₀.₂Ce₀.₇Oₓ are comprehensively compared with the other representative catalysts used for chlorobenzene combustion in the literature [35–41] considering their conspicuous activity, as displayed in Table 2. The T95 temperatures for chlorobenzene oxidation over the majority of catalysts (either transition metals oxides or noble metals-supported materials) are much higher than that of the Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ (T95 = 264°C). For instance, the T95 temperatures of 0.5% Pd/ZrO₂-TiO₂ (T95 = 370°C), U₂O₉/SiO₂ (T95 = 370°C), 0.5% Pt/CrOOH (T95 = 370°C), Pt/BEA (T95 = 370°C), Pt/MFI (T95 = 370°C), and Ce₆-C₆H₆/HMS (T95 = 445°C) are much higher than 320°C [36,38,39,41,42]. Some transition metal oxides displayed in Table 2 also possess good chlorobenzene combustion activity, such as VOₓ-WO₅-xTiO₂ (T95 = 260°C) and Mn₀.₈La₀.₁Ce₀.₁Oₓ (T95 = 220°C), while either the GHSV or chlorobenzene inlet concentration is lower than that of the present work [37,40]. A little amount (<30 ppm) of aldehyde can be detected during chlorobenzene combustion with the concentration order of CeO₂ > MnO > CuO > Mn₀.₃Ce₀.₇Oₓ > Cu₀.₂Mn₀.₁Ce₀.₇Oₓ > CuMnCeOₓ-imp > Mn₀.₃Ce₀.₇Oₓ > CuO > MnO > CeO₂. Absence of the aldehyde byproduct over the Cu₀.₁Mn₀.₂Ce₀.₇Oₓ, Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ, and Cu₀.₃Ce₀.₇Oₓ probably due to their highly oxidation efficiency, namely, the oxidation reaction is too fast or the byproduct concentration is too low to be detected.

3.1.2. Effect of water feed concentration

Influence of water feed concentration on the combustion of chlorobenzene over most active Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ catalyst was studied due to the coexistence of chlorobenzene and vapor in most industry waste gases, as shown in Fig. 3. The presence of water evidently inhibits the catalytic activity of Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ oxides when the water feed concentrations lower than 6% due to the competition of water molecules with the chlorobenzene for adsorption on the active sites or water is dissociated on the surface of ceria into H⁺ and OH⁻ species so as to retard the adsorption of oxygen molecules [43]. However, the water inhibition effect weakens obviously when further increase the water amount to 8%, and the water introduction even shows some promotion effects on chlorobenzene combustion at high conversion range if the water feed concentration reach up to 10%. López-Fonseca et al. [44] has found that the presence of excess water in the gaseous stream exhibited substantial beneficial effects on the conversion of dichloromethane and trichloroethylene since the water could act as an efficient cleaning agent of chlorine species from the catalyst surfaces. González-Velasco et al. [45] has proposed that the oxidation

![Fig. 1. The light-off curves of chlorobenzene combustion over various catalysts (600 ppm of chlorobenzene, 21% of O₂, N₂ balance, GHSV of 30,000 h⁻¹).](image1)

![Fig. 2. The reaction byproduct distribution over prepared catalysts (600 ppm of chlorobenzene, 21% of O₂, N₂ balance, GHSV of 30,000 h⁻¹).](image2)
Table 1
Catalytic performance and physicochemical characteristics of various catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(T_{\text{R}}^\circ (^\circ \text{C}))</th>
<th>(T_{\text{SO}}^\circ (^\circ \text{C}))</th>
<th>(T_{\text{SO}}^\circ (^\circ \text{C}))</th>
<th>(s (\mu\text{mol/g s}))</th>
<th>(S_{\text{BET}} (\text{m}^2/\text{g}))</th>
<th>(D_p^\circ (\text{cm}^3/\text{g}))</th>
<th>(D_p^\circ (\text{nm}))</th>
<th>(C_1 (\text{nm}))</th>
<th>(L_p (\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO (0.15)Mn(0.15)Ce(0.7)O(_x)</td>
<td>204</td>
<td>259</td>
<td>312</td>
<td>19.9</td>
<td>95.4</td>
<td>0.27</td>
<td>5.5</td>
<td>9.1</td>
<td>5.4116</td>
</tr>
<tr>
<td>CuO (0.15)Mn(0.15)Ce(0.7)O(_x)</td>
<td>166</td>
<td>225</td>
<td>264</td>
<td>26.8</td>
<td>98.7</td>
<td>0.22</td>
<td>4.5</td>
<td>8.6</td>
<td>5.4213</td>
</tr>
<tr>
<td>CuO (0.15)Mn(0.15)Ce(0.7)O(_x)</td>
<td>203</td>
<td>262</td>
<td>336</td>
<td>15.9</td>
<td>108.1</td>
<td>0.21</td>
<td>4.2</td>
<td>10.1</td>
<td>5.4205</td>
</tr>
<tr>
<td>CuMnCeO(_{0.15})</td>
<td>165</td>
<td>261</td>
<td>346</td>
<td>15.1</td>
<td>42.9</td>
<td>0.12</td>
<td>6.0</td>
<td>14.9</td>
<td>5.4237</td>
</tr>
<tr>
<td>CuO (0.15)Mn(0.15)Ce(0.7)O(_x)</td>
<td>177</td>
<td>259</td>
<td>315</td>
<td>17.4</td>
<td>162.8</td>
<td>0.17</td>
<td>2.5</td>
<td>10.5</td>
<td>5.4169</td>
</tr>
<tr>
<td>Mn(0.15)Ce(0.7)O(_x)</td>
<td>159</td>
<td>281</td>
<td>368</td>
<td>12.9</td>
<td>113.4</td>
<td>0.19</td>
<td>2.9</td>
<td>7.2</td>
<td>5.4017</td>
</tr>
<tr>
<td>CuO</td>
<td>222</td>
<td>350</td>
<td>/</td>
<td>5.1</td>
<td>0.1</td>
<td>/</td>
<td>5.4</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Mn(0.15)Ce(0.7)O(_x)</td>
<td>221</td>
<td>/</td>
<td>/</td>
<td>3.2</td>
<td>6.2</td>
<td>0.01</td>
<td>3.4</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>CeO(_2)</td>
<td>201</td>
<td>/</td>
<td>/</td>
<td>1.4</td>
<td>60.8</td>
<td>0.18</td>
<td>6.1</td>
<td>16</td>
<td>5.4276</td>
</tr>
</tbody>
</table>

\(^a\) Temperatures at which 5\%, 50\%, and 95\% conversion of chlorobenzene.  
\(^b\) Chlorobenzene conversion rate gained at 30\(^0\)C.  
\(^c\) BET specific surface area calculated at \(P/P_0 = 0.05–0.25\).  
\(^d\) Total pore volume estimated at \(P/P_0 = 0.99\).  
\(^e\) BJH pore diameter calculated from the desorption branch.  
\(^f\) Crystallite size calculated by the Scherrer equation from the (1 1 1) reflection of CeO\(_2\).  
\(^g\) Latent parameter of the synthesized catalysts.

Table 2
Catalytic data in the oxidation of chlorobenzene over different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>GHSV (h(^{-1}))</th>
<th>CB concentration (ppm)</th>
<th>(T_{\text{SO}}^\circ (^\circ \text{C}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO (0.15)Mn(0.15)Ce(0.7)O(_x)</td>
<td>30,000</td>
<td>600</td>
<td>312</td>
<td>This work</td>
</tr>
<tr>
<td>CuO (0.15)Mn(0.15)Ce(0.7)O(_x)</td>
<td>30,000</td>
<td>600</td>
<td>264</td>
<td>This work</td>
</tr>
<tr>
<td>2.0% Pt/(\gamma)-Al(_2)O(_3)</td>
<td>8,000</td>
<td>300</td>
<td>285</td>
<td>[35]</td>
</tr>
<tr>
<td>0.5%Pt/TiO(_2)</td>
<td>17,000</td>
<td>1000</td>
<td>320</td>
<td>[36]</td>
</tr>
<tr>
<td>0.5%Pt/ZnO-TiO(_2)</td>
<td>17,000</td>
<td>1000</td>
<td>360</td>
<td>[36]</td>
</tr>
<tr>
<td>VO(_2)-WO(_3)/s-TiO(_2) (^d)</td>
<td>37,000</td>
<td>100</td>
<td>260</td>
<td>[37]</td>
</tr>
<tr>
<td>U(_3)O(_7)/SiO(_2)</td>
<td>70,000</td>
<td>10,000</td>
<td>395</td>
<td>[38]</td>
</tr>
<tr>
<td>0.5%Pt/CrOOH</td>
<td>46,000</td>
<td>7500</td>
<td>380</td>
<td>[39]</td>
</tr>
<tr>
<td>Mn(_2)O(_3)(NH(_3))(_2) (^a)</td>
<td>15,000</td>
<td>1000</td>
<td>220</td>
<td>[40]</td>
</tr>
<tr>
<td>Pt/BEA (^7) (^a)</td>
<td>18,600</td>
<td>2000</td>
<td>350</td>
<td>[41]</td>
</tr>
<tr>
<td>Pt/MFI (^3) (^a)</td>
<td>18,600</td>
<td>2000</td>
<td>370</td>
<td>[41]</td>
</tr>
<tr>
<td>Ce(_6)-Co6/HMS</td>
<td>30,000</td>
<td>1000</td>
<td>445</td>
<td>[42]</td>
</tr>
</tbody>
</table>

\(^a\) s-TiO\(_2\): sulfated containing TiO\(_2\) support.  
\(^b\) The catalyst calcinated at 550\(^0\)C for 5 h.  
\(^c\) Number in the parentheses stands for the Si/Al molar ratio.

3.1.3. Effect of reagent inlet concentration

The chlorobenzene concentrations in different industry waste gases are usually different from each other. The effect of chlorobenzene inlet concentration on the catalytic activity of CuO \(0.15\)Mn\(0.15\)Ce\(0.7\)O\(_x\) catalyst was further investigated, as exhibited in Fig. 4. Chlorobenzene conversion changes mildly with the increase of its inlet concentration from 600 to 2000 ppm, indicating that the CuO \(0.15\)Mn\(0.15\)Ce\(0.7\)O\(_x\) catalyst could be used for removing lower or higher concentration chlorobenzene waste gases. Fig. 4 also shows that the chlorobenzene conversion increases appreciably with the increase of its inlet concentration from 600 to 1500 ppm. As is known, the chlorobenzene molecules are probably adsorbed on the active sites in competition with oxygen during oxidation process, and the surface chlorobenzene concentration could be the reaction limiting factor when low contents of organic reagent are introduced, so higher feeding concentrations lead to a more chemisorbed chlorobenzene molecules, and hence a higher conversion. However, the surface oxygen concentration gradually becomes the reaction controlling factor if continuous increase the chlorobenzene inlet concentration, and therefore, the conversion of chlorobenzene is prohibited due to a higher feeding concentration. Similarly, the positive influences of trichloroethylene inlet concentration on its catalytic combustion over CeO\(_2\) and Pt-based catalysts were also found by Core et al. and Dai et al. [9,46]. Besides, the promotion effect of inlet ethyl acetate concentration on its catalytic destruction was also reported in our previous work [47].

Fig. 3. The effect of variable water concentration (v/v) on chlorobenzene oxidation over CuO \(0.15\)Mn\(0.15\)Ce\(0.7\)O\(_x\) catalyst (600 ppm of chlorobenzene, 21\% of \(O_2\), \(N_2\) balance, GHSV of 30,000 h\(^{-1}\), 0–10.0\% of \(H_2O\)).

Fig. 4. The influence of organic reagent inlet concentration on chlorobenzene combustion over CuO \(0.15\)Mn\(0.15\)Ce\(0.7\)O\(_x\) catalyst (600–2000 ppm of chlorobenzene, 21\% of \(O_2\), \(N_2\) balance, GHSV of 30,000 h\(^{-1}\)).
3.2. Deactivation of the CuMnCeO₅ catalysts

Fig. 5 shows the dependences of the catalytic performance (CO₂ selectivity, chlorobenzene conversion, and organic byproduct distribution) on reaction time in the combustion of chlorobenzene at 300 °C over two representative catalysts (i.e., Cu₀.₁₅Mn₀.₁₅Ce₀.₃O₅ and CuMnCeO₅-imp) respectively prepared via the UHT and IMP protocols. When the reaction time is less than 4.5 h, there is no significant catalytic performance variation over both studied catalysts. Chlorobenzene can be totally oxidized by Cu₀.₁₅Mn₀.₁₅Ce₀.₃O₅ catalyst with CO₂ selectivity higher than 99.5%. Both the activity (chlorobenzene conversion <80%) and CO₂ selectivity (>90%) of CuMnCeO₅-imp are much lower than those of Cu₀.₁₅Mn₀.₁₅Ce₀.₃O₅, and a small amount of aldehyde byproduct (around 15 ppm) can be detected. When the reaction time increases from 4.5 to 15 h, the Cu₀.₁₅Mn₀.₁₅Ce₀.₃O₅ catalyst still shows nearly full conversion of chlorobenzene and more than 99.5% selectivity to CO₂. However, the CuMnCeO₅-imp catalyst just shows about 44.1% chlorobenzene conversion and 69.2% selectivity to CO₂, and the concentration of byproduct aldehyde correspondingly increases to more than 60 ppm. These results indicate that Cu₀.₁₅Mn₀.₁₅Ce₀.₃O₅ catalyst possesses much higher reaction durability than that of CuMnCeO₅-imp, which would be potentially important for practical applications of the catalyst for industry CVOCs elimination.

3.3. Catalyst characterizations

3.3.1. Powder X-ray diffraction

Fig. 6 shows the wide-angle XRD patterns of various catalysts. The lattice parameter and corresponding crystallite size calculating from the (1 1 1) plane of CeO₂ at 2θ = 28.6° using the Scherrer equation are listed in Table 1. The main reflections at 2θ = 28.6, 33.0, 47.5, 56.3, 59.2, 69.3, and 76.7° over all CuMnCeO₅, CuOₓ, and MnCeO₅ catalysts are indexed well to the typical cubic fluorite-like structure of CeO₂ (JCPDS No. 01-0792). No diffraction peaks corresponding to manganese oxides (JCPDS No. 96-900-9082) can be found, indicating that the high dispersion of manganese oxides with too small particle sizes to be identified by the XRD or poorly crystallized or combined with the finely dispersed copper oxides and ceria to form Cu-Mn-Ce-O solid solution [48]. For the Cu₀.₁₅Mn₀.₂Ce₀.₃O₅ and Cu₀.₁₅Mn₀.₁₅Ce₀.₃O₅ catalysts, no crystalline peaks of copper species can be observed, suggesting that copper species are highly dispersed on the ceria surface and/or incorporated into ceria lattice to form ceria-based solid solution [49]. In the case of CuMnCeO₅-imp, diffraction peaks corresponding to ceria have the smallest values of full width at half maximum (FWHM), which indicates the presence of very big crystallites (14.9 nm). Furthermore, some diffraction peaks of crystalline copper oxides at ca. 35.8° and 38.9° (JCPDS No. 80-1268) are observed, arising from the aggregation of copper species on the surface of ceria, suggesting that the IMP process is not favorable for the dispersion of copper species. Likewise, the abovementioned diffraction peaks are also found over the Cu₀.₂Mn₀.₃Ce₀.₇Oₓ catalyst, which indicates that Mn species may affect the dispersion of copper oxides at relatively high Cu loading and probably lead to the aggregation of copper species on the surface of cerium oxide. Aggregation of copper species on the surface of cerium oxide is disadvantageous to chlorobenzene combustion as part of the surface active sites are covered by the bulk CuO particles [50]. The diffraction peaks are broadened in CuₓMn₀.₇₃₋ₓCe₀.₃ₓOₓ catalysts, indicating the occurrence of more defective cerianite lattice and smaller crystallite size. Additionally, Fig. 6 reveals that the diffraction peaks of all mixed metal oxides shift to higher 2θ value compared with that of the pure ceria. These phenomena imply that partial of active components enter ceria lattice to form solid solution, which can be confirmed from the variation of the corresponding cubic ceria lattice parameter (see Table 1).

As shown in Table 1, the lattice parameters of cubic ceria in the Cu₀.₁₅Mn₀.₂₃Ce₀.₇ₓO₅ (5.4116 Å) and Cu₀.₁₅Mn₀.₁₅Ce₀.₃ₓO₅ (5.4123 Å) catalysts are much smaller than that of pure CeO₂ (5.4276 Å), which suggests that some copper and manganese ions incorporate into the ceria lattice to form Cu-Mn-Ce-O solid solution as the smaller ionic radii of copper and manganese ions (Cu²⁺ = 0.73 Å, Mn²⁺ = 0.67 Å, Mn³⁺ = 0.62 Å, and Mn⁴⁺ = 0.56 Å) than that of cerium oxides (Ce³⁺ = 1.10 Å, Ce⁴⁺ = 1.01 Å) [51]. The more the copper and manganese ions incorporated into the cerium oxides are, the smaller the lattice parameter is and the more stable Cu-Mn-Ce-O solid solution is. The oxygen vacancy density and oxygen mobility would be increased with the distortion of CeO₂ lattice.
which are favorable for the redox properties of mixed metal oxides. Therefore, the existence of stable Cu-Mn-Ce-O solid solution and the synergistic effects of Cu, Mn, and Ce oxides are probably two of significant reasons for the superior catalytic performance of the Cu$_{0.15}$Mn$_{0.15}$Ce$_{0.7}$O$_x$ catalyst.

3.3.2. Nitrogen adsorption/desorption

The N$_2$ adsorption/desorption isotherms as well as the corresponding BJH pore size distribution of all synthesized catalysts are shown in Fig. S1. All Cu$_x$Mn$_{0.3}$Ce$_{0.7}$O$_x$ samples exhibit typical IV shape isotherms with the $P/P_0$ of the inflection point corresponding to a diameter in the mesoporous range [52], which are different from those of CuMnCeO$_x$-imp and pure cubic ceria (Fig. S1A). Table 1 displays the specific surface area ($S_{BET}$), total pore volume ($D_v$), and average pore diameter ($D_p$) of various catalysts. All the Cu$_x$Mn$_{0.3}$Ce$_{0.7}$O$_x$ as well as Cu$_{0.2}$Ce$_{0.7}$O$_x$ and Mn$_{0.3}$Ce$_{0.7}$O$_x$ samples possess large $S_{BET}$ exceeding 95 m$^2$/g, indicating the effectiveness of the UHT method in the synthesis of high surface area metal oxides. The $S_{BET}$ of Cu$_x$Mn$_{0.3}$Ce$_{0.7}$O$_x$ catalysts reach the maximum value when the Cu:Mn atomic ratio equal to 2:1 (108.1 m$^2$/g), and the $S_{BET}$ value decreases to some extent when further enhance the manganese contents. Besides, the Cu$_{0.3}$Ce$_{0.7}$O$_x$ and Mn$_{0.3}$Ce$_{0.7}$O$_x$ samples have larger $S_{BET}$ than those of Cu$_x$Mn$_{0.3}$Ce$_{0.7}$O$_x$ oxides, indicating that the codoping of copper and manganese oxides has a disadvantageous influence on $S_{BET}$ of the final composite metal oxides.

The $S_{BET}$ decreases in the order of Cu$_{0.3}$Ce$_{0.7}$O$_x$ > Mn$_{0.3}$Ce$_{0.7}$O$_x$ > Cu$_{0.2}$Mn$_{0.1}$Ce$_{0.7}$O$_x$ > Cu$_{0.15}$Mn$_{0.15}$Ce$_{0.7}$O$_x$ > Cu$_{0.1}$Mn$_{0.2}$Ce$_{0.7}$O$_x$. This result indicates that the BET specific surface area is not the primary factor determining the catalytic activity.

3.3.3. Scanning and transmission electron microscopy

The Cu$_x$Mn$_{0.3}$Ce$_{0.7}$O$_x$ catalysts were prepared via the UHT method in the present work, and urea is believed to play an indispensable role in the formation of mesoporous mixed metal oxides [53]. When the mixture is heated to 90 °C, urea starts to decompose and slowly releases ammonia into the aqueous solution, and OH$^-$ anions are gradually formed. Steady supply of the OH$^-$ anions causes a persistent precipitation of corresponding metal hydroxides, which grow around the CTAB/water micelles. The polycrystalline and rearrangement process of CTAB/water micelles will occur when CTAB micelles aged at 120 °C, and the crystalized mesoporous metal oxides will be finally obtained after removing the CTAB organic residues by thermal calcination. Herein, the morphological properties of all Cu$_x$Mn$_{0.3}$Ce$_{0.7}$O$_x$ catalysts are investigated by FE-SEM, as shown in Fig. 7a–c. The results show that the copper and manganese contents can remarkably affect the catalyst morphologies. The Cu$_{0.15}$Mn$_{0.15}$Ce$_{0.7}$O$_x$ has a shaggy and porous surface, which is composed of ball-like nanoclusters with nonuniform size (Fig. 7b). Likewise, the Cu$_{0.1}$Mn$_{0.2}$Ce$_{0.7}$O$_x$ sample also possesses a porous surface, while the metal nanoparticles seem

![Image](image-url)
to be aggregation to some degree, and both ball-like and sheet-like nanoclusters can be observed (Fig. 7a). The Cu0.2Mn0.1Ce0.7O3 presents a relatively smooth surface consisting of sheet-like nanoclusters (particles seriously aggregated), which is much different from those of the abovementioned catalysts. Information about the microstructure of the Cu0.2Mn0.1Ce0.7O3 mixed oxides is further studied by TEM, as displayed in Fig. 7d–f. Unlike those of Si-based molecules sieves, no well-defined mesoporous structure could be observed in all Cu0.2Mn0.1Ce0.7O3 catalysts, suggesting that these mesopores are randomly distributed among a mixture of small nanoparticles. As shown in Fig. 7e, the nanoclusters with average diameter of about ca. 20 nm is optionally distributed, forming large quantities of mesopores. Partial nanoparticles assemble to some extent with the mean size of around ca. 50–100 nm over Cu0.2Mn0.1Ce0.7O3 (Fig. 7d), in accordance with the SEM result (Fig. 7a). As for the Cu0.2Mn0.1Ce0.7O3 mixed metal oxide, a large portion of particles are seriously agglomerated, and nanoclusters with calculated diameter higher than 200 nm can be observed (Fig. 7f), in well consistent with the XED and SEM results (Figs. 6 and 7c).

3.3.4. X-ray photoelectron spectroscopy

The information of surface composition and chemical state of the synthesized catalysts was studied by XPS. Figs. 8–11 display the Mn 2p3/2, Cu 2p3/2, Ce 3d, and O 1s XPS spectra of synthesized catalysts. The corresponding chemical state composition as well as surface contents of Cu and Mn derived by XPS is listed in Table 3. Fig. 8 shows the Mn 2p3/2 region spectra of all Mn-containing mixed metal oxides. Mn ions in 2+ (639.9 eV), 3+ (641.0 eV), and 4+ (642.3 eV) oxidation states in cerium-free materials has been reported in the literature [50]. Herein, the Mn 2p3/2 region is presented as deconvoluted into all its components and its relative ion ratios are listed in Table 3. It can be observed that the actual ratios of copper to manganese on the surface of Cu0.1Mn0.2Ce0.7O3 (0.48) and Cu0.15Mn0.25Ce0.7O3 (1.06) are similar to the theoretical ratios (i.e., 0.5 and 1.0). However, the ratios of copper to manganese on the surface of Cu0.2Mn0.1Ce0.7O3 (2.34) and CuMnCeO4–imp (1.52) are higher than the theoretical ratios (i.e., 2.0 and 1.0). The above results suggest that manganese species is more favorable to migrate into the ceria lattice compared with that of copper, and the UHT is a more efficient approach to introduce metal ions into the lattice of ceria support than the IMP method.

The Cu 2p3/2 XPS spectra are shown in Fig. 9A. The principal peak at binding energy of 934.5 eV over all copper-containing catalysts indicates the presence of Cu2+. The weak shake-up peak at 940–948 eV and the peak at binding energy of 932.5 eV suggest the existence of reduced copper species [54]. As is known, the Cu 2p3/2 binding energy cannot distinguish the Cu+ and Cu0 as they are essentially identical. According to literature, the Auger L3VV

![Fig. 8. Mn 2p XPS spectra of (a) Cu0.1Mn0.2Ce0.7O3, (b) Cu0.15Mn0.25Ce0.7O3, (c) Cu0.2Mn0.1Ce0.7O3, (d) Mn0.3Ce0.7O3, and (e) CuMnCeO4–imp.](Image 8)

![Fig. 9. Cu 2p and Auger L3VV spectra of (a) Cu0.1Mn0.2Ce0.7O3, (b) Cu0.15Mn0.25Ce0.7O3, (c) Cu0.2Mn0.1Ce0.7O3, (d) Cu0.3Ce0.7O3, and (e) CuMnCeO4–imp.](Image 9)

![Fig. 10. Ce 3d XPS spectra of (a) Cu0.1Mn0.2Ce0.7O3, (b) Cu0.15Mn0.25Ce0.7O3, (c) Cu0.2Mn0.1Ce0.7O3, (d) Cu0.3Ce0.7O3, (e) Mn0.3Ce0.7O3, and (f) CuMnCeO4–imp.](Image 10)
Table 3
Physochemical properties of various catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu (at.%)</th>
<th>Mn (at.%)</th>
<th>Cu/Mn</th>
<th>Cu⁺ (%)</th>
<th>Mn⁺ (%)</th>
<th>Ce⁺⁺⁺ (%)</th>
<th>Osat⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₀.₂Mn₀.₁Ce₀.₇Oₓ</td>
<td>12.0</td>
<td>24.8</td>
<td>0.48</td>
<td>15.2</td>
<td>84.8</td>
<td>21.3</td>
<td>36.6</td>
</tr>
<tr>
<td>Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ</td>
<td>17.7</td>
<td>16.6</td>
<td>1.06</td>
<td>21.8</td>
<td>78.2</td>
<td>16.1</td>
<td>35.4</td>
</tr>
<tr>
<td>Cu₀.₂Mn₀.₁Ce₀.₇Oₓ</td>
<td>29.1</td>
<td>12.4</td>
<td>2.34</td>
<td>25.1</td>
<td>74.9</td>
<td>21.1</td>
<td>34.7</td>
</tr>
<tr>
<td>CuMnCeOₓ-imp</td>
<td>24.6</td>
<td>22.7</td>
<td>1.52</td>
<td>11.8</td>
<td>88.2</td>
<td>22.1</td>
<td>37.2</td>
</tr>
<tr>
<td>Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ</td>
<td>34.6</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Mn₀.₁₅Ce₀.₇Oₓ</td>
<td>/</td>
<td>23.3</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

* The surface Cu content estimated by XPS analysis.
* The surface Mn content estimated by XPS analysis.
* Obtained from the deconvolution results of Auger L₃VV kinetic energy spectra of samples.
* Ce⁺⁺⁺ ratio obtained from the Ce 3d XPS result, Ce⁺⁺⁺ = \frac{\text{Ce}^{2+}}{\text{Ce}^{3+}} × 100%.
* Percentage of the surface oxygen species, Osat⁺ = \frac{\text{O}^{−}}{\text{O}^{3−}} × 100% (Osat⁺: lattice oxygen).

The Cu⁺⁺⁺ electron lines of copper species are usually used to circumvent this problem in terms of the kinetic energy peaks of Cu²⁺ and Cu⁺⁺⁺ species at around 917 eV and 913 eV, respectively [24]. Fig. 9B displays the Auger L₃VV kinetic spectra of the prepared mixed metal oxides, and the deconvolution results are listed in Table 3. The peaks in the Auger kinetic spectra of 916.4 and 912.8 eV should respectively correspond to the Cu²⁺ and Cu⁺⁺⁺ species. The ratios of Cu⁺⁺⁺ to Cu²⁺ over the Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ, Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ, Cu₀.₂Mn₀.₁Ce₀.₇Oₓ, and CuMnCeOₓ-imp catalysts are 0.18, 0.27, 0.33, and 0.13, respectively. The above results indicate that the Cu⁺⁺⁺ species is easier to form on the catalysts synthesized by the UHT protocol, and the increase of manganese content is beneficial for the formation of low valence copper species. The surface copper contents over Cu₀.₂Mn₀.₁Ce₀.₇Oₓ (29.1%) and CuMnCeOₓ-imp (34.6%) catalysts are higher than those of the theoretical values (that is, 20% and 15%), which indicates that the copper nanoparticles aggregate to some extent. Li et al. [25] also found that doping a small amount of manganese can induce more copper species into ceria lattice, while presence of excessive manganese is unfavorable for the copper dispersion. The interaction of Cu₀.₂, Mn₀.₁, and Ce₀.₇Oₓ species over Cu₀.₂Mn₀.₁Ce₀.₇Oₓ and CuMnCeOₓ-imp samples may be weaker than those of the other catalysts (Table 3). Additionally, the Mn 2p₃/₂ result shows that the primary oxidation state of manganese in Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ catalyst is Mn⁴⁺ (Fig. 8 and Table 3). As a consequence, the capability of redox couple of Cu⁺⁻Cu²⁺ in Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ may be strongly enhanced by the large number of Mn⁴⁺ ions on the surface of ceria support, which is favorable for the chlorobenzene oxidation.

Fig. 10 presents the XPS spectra of the Ce 3d core levels of all mixed metal oxides. Six peaks labeled as ν (ca. 882.2 eV), ν" (ca. 888.6 eV), ν‴ (ca. 897.7 eV), u (ca. 900.7 eV), u" (ca. 906.9 eV), and u‴ (ca. 916.6 eV) refer to three pairs of spin-orbit doublets, which can be identified as characteristic of Ce⁺⁺⁺ 3d states [55]. The high binding energy doublet (u‴/u") is attributed to the state of Ce(V)3d⁴4p²O₂p⁵, doublet (u"/u′) is assigned to the state of Ce(V)3d⁴4p⁴O₂p³, and doublet (u/ν) corresponds to the state of Ce(V)3d⁴4p⁴O₂p⁴. The binding energy couple corresponding to one of the two possible electron configuration of the final state of Ce⁺⁺⁺ species (Ce(III)3d⁴4p²O₂p⁵) are labeled as u (ca. 903.4 eV) and ν (ca. 885.4 eV). The proportion of Ce⁺⁺⁺ ions with regard to the total cerium is calculated from the ratio of the sum area of Ce⁺⁺⁺ species to the sum area of total cerium species [56]. The relative content of Ce⁺⁺⁺ 3d⁵⁵₂ in cerium is calculated and listed in Table 3. It can be observed that the Ce⁺⁺⁺ 3d⁵⁵₂ concentration in the mixed metal oxide catalysts decrease in the sequence of Cu₀.₁₅Mn₀.₁₅Ce₀.₇Oₓ > Cu₀.₂Mn₀.₁Ce₀.₇Oₓ > Cu₀.₂Mn₀.₁Ce₀.₇Oₓ > CuMnCeOₓ-imp > Cu₀.₂Mn₀.₅Ce₀.₇Oₓ. It is reported that the existence of Ce⁺⁺⁺ in CeO₂ implies the formation of oxygen vacancy [33], and it can be inferred that the UHT method can create more oxygen vacancies than that of IMP approach. The oxygen vacancies could be the active centers in reaction as oxygen of the defective oxides tends to be readily released and transferred, which would enhance the catalytic activity [57]. XRD and XPS results reveal that the interactions of partial Cu₀.₂, Mn₀.₁, and Ce₀.₇Oₓ species over Cu₀.₂Mn₀.₁Ce₀.₇Oₓ and CuMnCeOₓ-imp catalysts are weak, and thus, the formation of oxygen vacancies over which may not fully improve the capability of the copper and manganese redox couples.

The O 1s XPS spectra of all synthesized catalysts were analyzed (see Fig. 11) in order to investigate the characteristic of surface oxygen species. The O 1s spectra of catalysts are fitted with two peak contributions. The primary peak with a binding energy of about ca. 529.2 eV is attributed to the lattice oxygen (Olat.), while a shoulder peak at around ca. 531.6 eV belongs to the active surface oxygen (Oox) resulting from the adsorbed oxygen and weakly bonded oxygen species [8]. In addition, the O 1s XPS spectrum of pure ceria can be divided into four peaks with the core level of lattice oxygen at ca. 528.9 eV [58]. Compared with pure ceria, the O 1s core levels of lattice oxygen over all mixed metal oxides shift to higher values due to "O→Cu" or "O→Mn" electron-transfer processes, which can create active oxygen species such as O²⁻, O³⁻, and O⁴⁻. Table 2 lists the active Oox percentages of various catalysts. It can be observed that all the CuMnCeOₓ-imp catalysts have larger quantity of Oox than those of the other samples, indicating that the coexistence of copper and manganese species could facilitate the adsorption of oxygen species (relevant to the oxygen vacancy density), in well agreement with the Ce 3d result (Fig. 10). It is well-known that the catalytic combustion of organic compounds over transition metal oxides involves a Mars–van Krevelen mechanism, where the organic molecules are primarily oxidized by the lattice oxygen of metal oxides, the
latter being re-oxidized by the adsorbed oxygen [59,60]. Therefore, both the gas-phase oxygen adsorption capability and oxygen transfer rate between \( \text{O}_\text{surf} \) and \( \text{O}_\text{latt} \) are vital chlorobenzene oxidation influencing factors.

### 3.3.5. Temperature programmed reduction with \( \text{H}_2 \)

Reducibility of the single/mixed metal oxides was investigated by \( \text{H}_2\)-TPR, as displayed in Fig. 12. Pure ceria shows two weak reduction peaks centered at around 415 and 517 °C, attributing to the reduction of surface oxygen and bulk oxygen, respectively [56]. Pure copper oxide shows a single reduction peak of maximum hydrogen consumption at about 373 °C, and pure manganese oxides present two reduction peaks centered at around 464 and 541 °C. Fig. 12 reveals that the reduction profiles of mixed metal oxides are much different from that of the pure \( \text{CuO} \), \( \text{MnO}_x \), and \( \text{CeO}_2 \). \( \text{Cu}_{0.3}\text{Mn}_{0.7}\text{CeO}_x \) shows a single reduction peak centered at 338 °C, which is lower than the reduction temperatures of single copper and manganese oxides. There are three reduction peaks between 100 and 300 °C can be observed over the \( \text{Cu}_{0.2}\text{Ce}_{0.8}\text{O}_2 \) catalyst. The reduction peak centered at about 142 °C is attributed to the reduction of \( \text{CuO} \) species which strongly interact with the ceria support, and the high-temperature reduction peak at about 256 °C can be assigned to the reduction of \( \text{Cu}^+ \) species. The reduction peak centered at 184 °C is attributed to the reduction of dispersed \( \text{CuO} \) species on the ceria surface and the two-/three-dimensional copper clusters in small size [61]. All the \( \text{Cu}_x\text{Mn}_{0.3-}\text{CeO}_x \) catalysts possess three reduction peaks in the temperature range of 150–360 °C. Fig. 12 reveals that the reduction temperatures of \( \text{Cu}_0.1\text{Mn}_{0.1}\text{CeO}_x \) samples are shift more or less to the higher temperature side, and this is probably ascribed to the lower reducibility of manganese oxides than that of copper oxides due to the more negative free energy of formation of manganese oxides [62]. Papavasiliou et al. [63] and Morales et al. [64] have proposed that the coexistence of copper species can mutually facilitate the reduction of each other, so their reduction peaks are difficult to distinguish. It can be noticed that the \( \text{Cu}_{0.15}\text{Mn}_{0.15}\text{CeO}_x \) catalyst has the best reducibility with most of reducible species over which reduced around 153 °C, and either further increase or decrease the atomic ratios of copper and manganese is disadvantageous to the redox property of the mixed metal oxides. The XPS results reveal that the presence of a small amount of manganese species can increase the number of copper ions as well manganese ions entering into the lattice of ceria support to form \( \text{CuMnCeO}_x \) solid solution (Fig. 6), leading to a improved reducibility of the catalyst as the \( \text{Cu-Mn-O-Ce} \) connection in the \( \text{CuMnCeO}_x \) solid solution could reduce the redox potential of copper and manganese species as well as act as a bridge for \( \text{O}^- \) transfer among copper, manganese, and cerium. Additionally, the oxygen species mobility over the synthesized catalysts was further studied by temperature programmed desorption of oxygen (\( \text{O}_2\)-TPD), as shown in Fig. 52. As is known, the chemically adsorbed oxygen \( \text{O}_2^-/\text{O}^- \) species are much easier to desorb than that of the lattice \( \text{O}^{2-} \) species, and which are indispensable for the superior catalytic combustion performance [65]. It is shown that the \( \text{Cu}_{x}\text{Mn}_{0.3-}\text{CeO}_x \) samples possess larger amounts of chemically adsorbed oxygen species than those of the other materials. Among them, the \( \text{Cu}_{0.15}\text{Mn}_{0.15}\text{CeO}_x \) catalyst has the largest quantity of chemically adsorbed oxygen owing to the abundant surface oxygen vacancy, in accordance with the XPS result (see Table 3). The rapid and effective removal of surface \( \text{Cl} \) is very important for CVOCs combustion as the adsorbed \( \text{Cl} \) species inhibit the dissociation of oxygen molecules and decrease the reducibility of the copper and manganese species. Dai et al. [40] suggested that the increase of active oxygen species can weaken the adsorption of \( \text{Cl} \) species, and therefore, the highest amount of chemically adsorbed oxygen species can clean the surface adsorbed \( \text{Cl} \) species over \( \text{Cu}_{0.15}\text{Mn}_{0.15}\text{CeO}_x \) as quickly as possible to maintain its high chlorobenzene oxidation activity.

### 3.4. Proposed chlorobenzene combustion scheme

The catalytic combustion mechanism of chlorinated benzene (chlorobenzene, 1,2-, 1,3-, and 1,4-dichlorobenzene) over \( \text{V}_2\text{O}_5/\text{TiO}_2 \) catalyst has been studied by Lichtenberger et al. [66] using the in-situ FT-IR technique, and the authors proposed that both the nucleophilic and electrophilic substitutions happened in sequence toward CVOCs oxidation. Van de Brink and co-workers [67] also reported that the C–Cl bond scission is the first step for chlorobenzene oxidation over \( \text{Pt}/\gamma-\text{Al}_2\text{O}_3 \). These researchers also proposed a substantial kinetic isotope effect for the combustion of the deuterated benzene, while only a tiny discrepancy could be observed in the case of perdeuterochlorbenezene, confirming the notion that the latter is activated by the weaker C–Cl bond and not the C–H bond. In our work, similar processes would occur for chlorobenzene combustion over the synthesized transition metals-based catalysts. Chlorobenzene molecules are firstly dissociative adsorption on the transition metal oxide sites via \( \text{Cl} \) abstraction. Then the electrophilic substitution step will take place for the adsorbed dechlorinated species before oxidized to the final products. Aldehyde is also detected over partial catalysts as the electrophilic substitution procedure could also result in the bond breaking of the aromatic ring [66]. According to the analysis above, a chlorobenzene catalytic combustion mechanism over \( \text{CuMnCeO}_x \) catalysts consisting of ten elementary steps is schematized, as shown in Fig. 13. Adsorption of gas-phase chlorobenzene molecules on the active copper and manganese sites locating at the gaps among \( \text{CuO} \), \( \text{MnO}_x \), and \( \text{Cu-Mn-Ce-O} \) solid solution (step (a)). A little amount adsorbed chlorobenzene species is oxidized by the active adsorbed oxygen from the gas-phase, which are activated
at catalyst surface to replenish the oxygen vacancies (step (b)), and by the oxygen releases from the ceria due to the excellent oxygen storage capability of cerium oxide (step (c)). The adsorbed chlorobenzene molecules are mainly oxidized by the active lattice oxygen releases from the CuMnCeO₄ oxides due to the formation of Cu-Mn-Ce-O solid solution. In Cu-Mn-Ce-O solid solution, the Ce⁴⁺ ions were substituted by the metal ions with lower valences (e.g., Mn³⁺ and Cu²⁺) to release lattice oxygen in order to balance charge (step (d)). The adsorbed chlorobenzene molecules are oxidized to the final products, i.e., CO₂, H₂O and HCl (step (e)). As is known, the energy of C–Cl bonds is weaker than that of C–H bonds, and hence, the C–Cl bonds are more prone to be attacked by nucleophiles. The first step in chlorobenzene molecular combustion is probably their dissociative adsorption on active copper and manganese sites via Cl abstraction. The adsorbed Cl species over CuₓMnₓCeₓO₄, MnₓCeₓO₄�, CuMnCeO₄–imp, CuO, MnOₓ, and CeO₂ samples may be difficult to move until achieving the equilibrium of adsorbed and desorbed Cl species due to the absence of active oxygen species or weak interaction between metal oxides and ceria. The laggard adsorbed Cl cleanup process mentioned above may retard of the overall reaction, and probably cause the formation of small amounts of organic reaction byproducts. The organic reaction byproducts are further oxidized by the active oxygen species to form CO₂ and H₂O (steps (e–g)). Simultaneously, a small portion of produced HCl may be back to the catalyst surface and adsorbed on the oxygen vacancies or some active sites (step (h)), and followed by the removal of adsorbed Cl species from catalyst surface by the active oxygen species in the form of Cl₂ (steps (i–j)). Finally, the consumed oxygen species are replenished by the gas-phase oxygen adsorbed on oxygen vacancies (step (k)). Obviously, the active oxygen quantity and mobility are the critical factors for chlorobenzene combustion over the mesoporous CuO–MnOₓ–CeO₂ composite metal oxides. The existence of Cu-Mn-Ce-O solid solution makes the oxygen atoms in the catalysts locating in an agitated chemical surrounding, leading to highly active oxygen mobility during chlorobenzene elimination.

4. Conclusions

CuMnCeO₄ mixed metal oxides with mesoporous structure and high specific surface area were synthesized via a urea-assistant hydrothermal protocol. The existence of a small amount of manganese species can introduce more Cu and Mn ions into ceria lattice in the form of Cu-Mn-Ce-O solid solution, leading to structure defects and surface oxygen vacancies. However, manganese species has a negative influence on copper dispersion at relative high copper loading. The interaction of among Cu, Mn, and Ce has synergistic effects for improving the reducibility of the mixed metal oxides. The Cu₀.₁₅Mn₀.₁₅CeO₄ catalyst shows the highest chlorobenzene oxidation activity with 95% of chlorobenzene conversion at 264 °C. The specific surface area is not the factors governing the catalytic activity, and both the concentration and mobility of chemically adsorbed oxygen are vital for the effective removal of surface adsorbed Cl species. The superior catalytic performance of the mesoporous CuMnCeO₄ oxides can be ascribed to higher surface oxygen concentration and better active oxygen mobility. Low concentration of water has a negative effect on chlorobenzene combustion, while high amount of water can accelerate the conversion of chlorobenzene. It can be expected that these mesoporous oxides are effective and promising catalysts in the low-temperature aryl chlorides and dioxins removal, and simultaneously have other potential applications in the field as catalysis, sensor, and separation.

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Appendix A. Supplementary data

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References
