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

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ABSTRACT

Mesoporous CuO-MnO_x-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 CuO_x, MnO_x, 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-MnO_x-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].

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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 CVOs 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 oxychloride 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 environmental 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 CVOs, 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 Ce^{3+} and Ce^{4+} 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_x-CeO₂ catalysts in epichlorohydrin (ECH) combustion was also observed in our group. Wang et al. [1] and Li et al. [9] have found that the MnO_x-CeO₂ mixed oxides showed high catalytic activity and stability for chlorobenzene (CB) and trichloroethylene (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 CuMnCeO_x catalysts possessed excellent CO oxidation performance. However, studies about the catalytic combustion of CVOs over mesoporous CuO-MnO_x-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/Ce_{0.8}Zr_{0.2}O₂, 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-assisted hydrothermal (UHT) protocol for the preparation of mesoporous CuO-MnO_x-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 CuMnCeO_x catalysts, and the chlorobenzene oxidation mechanism over CuMnCeO_x 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, 7.9 g of Ce(NO₃)₃·6H₂O, and 6.6 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 Cu_aMn_{0.3-a}Ce_{0.7}O_x (*a* = 0.1, 0.15, and 0.2).

For comparison, the Cu_{0.3}Ce_{0.7}O_x and Mn_{0.3}Ce_{0.7}O_x catalysts were also synthesized via the UHT procedure. In addition, the CuMnCeO_x 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, MnO_x 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 K α 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 samples 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/P*₀) 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 ChemBET 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 ($<5 \times 10^{-10}$ Torr) using Al K α 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 evaporation 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 CuMnCeO_x mixed oxides

3.1.1. Catalytic activity and organic byproducts distribution

The light-off curve and catalytic activity data (i.e., T₅, T₅₀, T₉₅, 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 CuMnCeO_x mixed oxides prepared via the UHT method possess much higher chlorobenzene destruction activity than those of the other catalysts, and appropriate amount of Cu/Mn doping is vital for the catalytic performance. Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x has the highest chlorobenzene combustion activity (T₉₅ = 264 °C), which is much higher than the Cu_{0.3}Ce_{0.7}O_x (T₉₅ = 315 °C), Mn_{0.3}Ce_{0.7}O_x (T₉₅ = 368 °C), and CuMnCeO_x-imp (T₉₅ = 346 °C) catalysts (see Table 1). The activity sequence of all samples is: Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x » Cu_{0.1}Mn_{0.2}Ce_{0.7}O_x » Cu_{0.3}Ce_{0.7}O_x » Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x » CuMnCeO_x-imp » Mn_{0.3}Ce_{0.7}O_x » CuO » MnO_x » CeO₂. Furthermore, the chlorobenzene combustion rates listed in Table 1 also confirm the superior activity of Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x. Catalytic

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).

Fig. 2. The reaction byproduct distribution over prepared catalysts (600 ppm of chlorobenzene, 21% of O₂, N₂ balance, GHSV of 30,000 h⁻¹).

activities of Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x and Cu_{0.1}Mn_{0.2}Ce_{0.7}O_x 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 Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x (T₉₅ = 264 °C). For instance, the T₉₅ temperatures of 0.5% Pd/ZrO₂-TiO₂ (T₉₅ = 370 °C), U₃O₈/SiO₂ (T₉₅ = 370 °C), 0.5% Pt/CrOOH (T₉₅ = 370 °C), Pt/BEA (T₉₅ = 370 °C), Pt/MFI (T₉₅ = 370 °C), and Ce₆-Co₆/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 VO_x-WO_x/s-TiO₂ (T₉₅ = 260 °C) and Mn_{0.8}La_{0.1}Ce_{0.1}O_x (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_x > CuO > Mn_{0.3}Ce_{0.7}O_x > Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x ≥ CuMnCeO_x-imp (Fig. 2). Absence of the aldehyde byproduct over the Cu_{0.1}Mn_{0.2}Ce_{0.7}O_x, Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x, and Cu_{0.3}Ce_{0.7}O_x probably due to their highly oxidation efficiency, namely, the oxidation reaction is too fast or the byproduct concentration is too low to find by the detector.

3.1.2. Effect of water feed concentration

Influence of water feed concentration on the combustion of chlorobenzene over most active Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x 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 Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x 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

Table 1
Catalytic performance and physicochemical characteristics of various catalysts.

Catalyst	T_5^a (°C)	T_{50}^a (°C)	T_{95}^a (°C)	r^b (μmol/g s)	S_{BET}^c (m ² /g)	D_v^d (cm ³ /g)	D_p^e (nm)	C_s^f (nm)	L_p^g (Å)
Cu _{0.1} Mn _{0.2} Ce _{0.7} O _x	204	259	312	19.9	95.4	0.27	5.5	9.1	5.4116
Cu _{0.15} Mn _{0.15} Ce _{0.7} O _x	166	225	264	26.8	98.7	0.22	4.5	8.6	5.4123
Cu _{0.2} Mn _{0.1} Ce _{0.7} O _x	203	262	336	15.9	108.1	0.21	4.2	10.1	5.4205
CuMnCeO _x -imp	165	261	346	15.1	42.9	0.12	6.0	14.9	5.4237
Cu _{0.3} Ce _{0.7} O _x	177	259	315	17.4	162.8	0.17	2.5	10.5	5.4169
Mn _{0.3} Ce _{0.7} O _x	159	281	368	12.9	113.4	0.19	2.9	7.2	5.4017
CuO	222	350	/	5.1	0.1	/	5.4	/	/
MnO _x	221	/	/	3.2	6.2	0.01	3.4	/	/
CeO ₂	201	/	/	1.4	60.8	0.18	6.1	16	5.4276

^a Temperatures at which 5%, 50%, and 95% conversion of chlorobenzene.

^b Chlorobenzene conversion rate gained at 300 °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 CeO₂.

^g Lattice parameter of the synthesized catalysts.

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

Catalyst	GHSV (h ⁻¹)	CB concentration (ppm)	T_{95} (°C)	Reference
Cu _{0.1} Mn _{0.2} Ce _{0.7} O _x	30,000	600	312	This work
Cu _{0.15} Mn _{0.15} Ce _{0.7} O _x	30,000	600	264	This work
2.0% Pt/γ-Al ₂ O ₃	8,000	300	285	[35]
0.5% Pd/TiO ₂	17,000	1000	320	[36]
0.5% Pd/ZrO ₂ -TiO ₂	17,000	1000	360	[36]
VO _x -WO _x /s-TiO ₂ ^a	37,000	100	260	[37]
U ₃ O ₈ /SiO ₂	70,000	10,000	395	[38]
0.5% Pt/CrOOH	46,000	7500	380	[39]
Mn _{0.8} La _{0.1} Ce _{0.1} O _x ^b	15,000	1000	220	[40]
Pt/BEA(75) ^c	18,600	2000	350	[41]
Pt/MFI(30) ^c	18,600	2000	370	[41]
Ce6-Co6/HMS	30,000	1000	445	[42]

^a s-TiO₂: sulfated containing TiO₂ support.

^b The catalyst calcinated at 550 °C for 5 h.

^c Number in the parentheses stands for the Si/Al molar ratio.

presented a major pathway for trichloroethylene destruction in dry air and in air containing low water concentrations, while hydrolysis was a favored route in the presence of excess water. As a consequence, the increase of chlorobenzene conversion under high water contents over Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x catalyst probably results from the adsorbed chlorine species removal ability of water and the hydrolysis of chlorobenzene molecules.

Fig. 3. The effect of variable water concentration (v/v) on chlorobenzene oxidation over Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x catalyst (600 ppm of chlorobenzene, 21% of O₂, N₂ balance, GHSV of 30,000 h⁻¹, 0–10.0% of H₂O).

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 Cu_{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 Cu_{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 CeO₂ 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. 4. The influence of organic reactant inlet concentration on chlorobenzene combustion over Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x catalyst (600–2000 ppm of chlorobenzene, 21% of O₂, N₂ balance, GHSV of 30,000 h⁻¹).

Fig. 5. The durability of representative $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ (hollow symbols) and $\text{CuMnCeO}_x\text{-imp}$ (solid symbols) catalysts in the catalytic combustion of chlorobenzene under conditions of 600 ppm of chlorobenzene, GHSV of $30,000\text{ h}^{-1}$, and reaction temperature of 300°C . (C_c , S_{CO_2} , and C_{bp} stand for the chlorobenzene conversion, CO_2 selectivity, and byproduct aldehyde concentration, respectively.).

3.2. Deactivation of the CuMnCeO_x catalysts

Fig. 5 shows the dependences of the catalytic performance (CO_2 selectivity, chlorobenzene conversion, and organic byproduct distribution) on reaction time in the combustion of chlorobenzene at 300°C over two representative catalysts (i.e., $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ and $\text{CuMnCeO}_x\text{-imp}$) 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 $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ catalyst with CO_2 selectivity higher than 99.5%. Both the activity (chlorobenzene conversion <80%) and CO_2 selectivity (<90%) of $\text{CuMnCeO}_x\text{-imp}$ are much lower than those of $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$, 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 $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ catalyst still shows nearly full conversion of chlorobenzene and more than 99.5% selectivity to CO_2 . However, the $\text{CuMnCeO}_x\text{-imp}$ catalyst just shows about 44.1% chlorobenzene conversion and 69.2% selectivity to CO_2 , and the concentration of byproduct aldehyde correspondingly increases to more than 60 ppm. These results indicate that $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ catalyst possesses much higher reaction durability than that of $\text{CuMnCeO}_x\text{-imp}$, which would be potentially important for practical applications of the catalyst for industry CVOs 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 CeO_2 at $2\theta = 28.6^\circ$ using the Scherrer equation are listed in Table 1. The main reflections at $2\theta = 28.6, 33.0, 47.5, 56.3, 59.2, 69.3$, and 76.7° over all CuMnCeO_x , CuCeO_x , and MnCeO_x catalysts are indexed well to the typical cubic fluorite-like structure of CeO_2 (JCPDS No. 81-0792). 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 $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$ and $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ 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 $\text{CuMnCeO}_x\text{-imp}$, diffraction peaks corresponding to ceria have the smallest values of full width at half maximum (FWHM), which indicates

Fig. 6. XRD patterns of (a) CeO_2 , (b) $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$, (c) $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$, (d) $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$, (e) $\text{Cu}_{0.3}\text{Ce}_{0.7}\text{O}_x$, (f) $\text{Mn}_{0.3}\text{Ce}_{0.7}\text{O}_x$, (g) $\text{CuMnCeO}_x\text{-imp}$, (h) CuO , and (i) MnO_x .

the presence of very big crystallites (14.9 nm). Furthermore, some diffraction peaks of crystalline copper oxides at $ca. 35.8^\circ$ 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 aforementioned diffraction peaks are also found over the $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$ 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 ceria. Aggregation of copper species on the surface of ceria 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 $\text{Cu}_{0.3}\text{Ce}_{0.7}\text{O}_x$ 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 $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$ (5.4116 Å) and $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ (5.4123 Å) catalysts are much smaller than that of pure CeO_2 (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 ($\text{Cu}^+ = 0.96\text{ Å}$, $\text{Cu}^{2+} = 0.73\text{ Å}$, $\text{Mn}^{2+} = 0.67\text{ Å}$, $\text{Mn}^{3+} = 0.62\text{ Å}$, and $\text{Mn}^{4+} = 0.56\text{ Å}$) than that of cerium oxides ($\text{Ce}^{3+} = 1.10\text{ Å}$, $\text{Ce}^{4+} = 1.01\text{ Å}$) [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 CeO_2 lattice,

Fig. 7. Representative FE-SEM and TEM images of $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ catalysts: (a, d) $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$, (b, e) $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$, and (c, f) $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$.

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 $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ 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 $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ 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 $\text{CuMnCeO}_x\text{-imp}$ 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 $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ as well as $\text{Cu}_{0.3}\text{Ce}_{0.7}\text{O}_x$ and $\text{Mn}_{0.3}\text{Ce}_{0.7}\text{O}_x$ samples possess large S_{BET} exceeding $95 \text{ m}^2/\text{g}$, indicating the effectiveness of the UHT method in the synthesis of high surface area metal oxides. The S_{BET} of $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ catalysts reach the maximum value when the Cu:Mn atomic ratio equal to 2:1 ($108.1 \text{ m}^2/\text{g}$), and the S_{BET} value decreases to some extent when further enhance the manganese contents. Besides, the $\text{Cu}_{0.3}\text{Ce}_{0.7}\text{O}_x$ and $\text{Mn}_{0.3}\text{Ce}_{0.7}\text{O}_x$ samples have larger S_{BET} than those of $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ 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 $\text{Cu}_{0.3}\text{Ce}_{0.7}\text{O}_x > \text{Mn}_{0.3}\text{Ce}_{0.7}\text{O}_x > \text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x > \text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x > \text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x > \text{CuMnCeO}_x\text{-imp}$, differing from the order of catalytic activity (Fig. 1). 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 $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ 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 polycondensation and rearrangement process of CTAB/water micelles will occur when CTAB micelles aged at 120°C , and the crystallized mesoporous metal oxides will be finally obtained after removing the CTAB organic residues by thermal calcination. Herein, the morphological properties of all $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ 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 $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ has a shaggy and porous surface, which is composed of ball-like nanoclusters with nonuniform size (Fig. 7b). Likewise, the $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$ sample also possesses a porous surface, while the metal nanoparticles seem

Fig. 8. Mn 2p XPS spectra of (a) $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$, (b) $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$, (c) $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$, (d) $\text{Mn}_{0.3}\text{Ce}_{0.7}\text{O}_x$, and (e) $\text{CuMnCeO}_x\text{-imp}$.

to be aggregation to some degree, and both ball-like and sheet-like nanoclusters can be observed (Fig. 7a). The $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$ 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 $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ 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 $\text{Cu}_a\text{Mn}_{0.3-a}\text{Ce}_{0.7}\text{O}_x$ 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 of nanoparticles assemble to some extent with the mean size of around ca. 50–100 nm over $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$ (Fig. 7d), in accordance with the SEM result (Fig. 7a). As for the $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$ 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 2p_{3/2}, Cu 2p_{3/2}, 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 2p_{3/2} 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 2p_{3/2} 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 $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$ (0.48) and $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$ (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 $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$ (2.34) and $\text{CuMnCeO}_x\text{-imp}$ (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 2p_{3/2} 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 Cu^{2+} . The weak shake-up peak at

Fig. 9. Cu 2p and Auger L₃VV spectra of (a) $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$, (b) $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$, (c) $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$, (d) $\text{Cu}_{0.3}\text{Ce}_{0.7}\text{O}_x$, and (e) $\text{CuMnCeO}_x\text{-imp}$.

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 2p_{3/2} binding energy cannot distinguish the Cu^+ and Cu^0 as they are essentially identical. According to literature, the Auger L₃VV

Fig. 10. Ce 3d XPS spectra of (a) $\text{Cu}_{0.1}\text{Mn}_{0.2}\text{Ce}_{0.7}\text{O}_x$, (b) $\text{Cu}_{0.15}\text{Mn}_{0.15}\text{Ce}_{0.7}\text{O}_x$, (c) $\text{Cu}_{0.2}\text{Mn}_{0.1}\text{Ce}_{0.7}\text{O}_x$, (d) $\text{Cu}_{0.3}\text{Ce}_{0.7}\text{O}_x$, (e) $\text{Mn}_{0.3}\text{Ce}_{0.7}\text{O}_x$, and (f) $\text{CuMnCeO}_x\text{-imp}$.

Table 3
Physicochemical properties of various catalysts.

Catalyst	Cu ^a (at.%)	Mn ^b (at.%)	Cu/Mn	Cu ^c (%)		Mn (%)			Ce ^{3+/d} (%)	O _{sur.} ^e (%)
				Cu ⁺	Cu ²⁺	Mn ²⁺	Mn ³⁺	Mn ⁴⁺		
Cu _{0.1} Mn _{0.2} Ce _{0.7} O _x	12.0	24.8	0.48	15.2	84.8	21.3	36.6	42.1	27.7	43.5
Cu _{0.15} Mn _{0.15} Ce _{0.7} O _x	17.7	16.6	1.06	21.8	78.2	16.1	35.4	48.5	33.8	46.9
Cu _{0.2} Mn _{0.1} Ce _{0.7} O _x	29.1	12.4	2.34	25.1	74.9	21.1	34.7	44.2	30.1	41.9
CuMnCeO _x -imp	34.6	22.7	1.52	11.8	88.2	22.1	37.2	40.7	21.4	41.3
Cu _{0.3} Ce _{0.7} O _x	21.2	/	/	19.2	80.8	/	/	/	29.2	40.6
Mn _{0.3} Ce _{0.7} O _x	/	23.3	/	/	/	19.2	37.5	43.3	31.3	26.4

^a The surface Cu content estimated by XPS analysis.

^b The surface Mn content estimated by XPS analysis.

^c Obtained from the deconvolution results of Auger L₃VV kinetic energy spectra of samples.

^d Ce³⁺ ratio obtained from the Ce 3d XPS result, $Ce^{3+} = \frac{u'+u''+u'''+v'+v''+v'''}{u+u'+u''+u'''+v+v'+v''+v'''} \times 100\%$.

^e Percentage of the surface oxygen species, $O_{sur.} = \frac{O_{sur.}}{O_{sur.} + O_{latt.}} \times 100\%$ (O_{latt.}: lattice oxygen).

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 curves 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 Cu_{0.1}Mn_{0.2}Ce_{0.7}O_x, Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x, Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x, and CuMnCeO_x-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 over 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 Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x (29.1%) and CuMnCeO_x-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 CuO_x, MnO_x, and CeO₂ species over Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x and CuMnCeO_x-imp samples may be weaker than those of the other catalysts (Table 3). Additionally, the Mn 2p_{3/2} result shows that the primary oxidation state of manganese in Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x catalyst is Mn⁴⁺ (Fig. 8 and Table 3). As a consequence, the capability of redox couple of Cu⁺-Cu²⁺ in Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x 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 *v* (ca. 882.2 eV), *v'*

(ca. 888.6 eV), *v''* (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 Ce⁴⁺ 3d states [55]. The high bind energy doublet (*u'''*/*v'''*) is attributed to the state of Ce(IV)3d⁹4f⁰O2p⁶, doublet (*u''*/*v''*) is assigned to the state of Ce(IV)3d⁹4f¹O2p⁵, and doublet (*u*/*v*) corresponds to the state of Ce(IV)3d⁹4f²O2p⁴. The bind energy couple corresponding to one of the two possible electron configuration of the final state of Ce³⁺ species (Ce(III)3d⁹4f²O2p⁵) are labeled as *u'* (ca. 903.4 eV) and *v'* (ca. 885.4 eV). The proportion of Ce³⁺ ions with regard to the total cerium is calculated from the ratio of the sum area of Ce³⁺ species to the sum area of total cerium species [56]. The relative content of Ce³⁺ 3d_{5/2} in cerium is calculated and listed in Table 3. It can be observed that the Ce³⁺ 3d_{5/2} concentration in the mixed metal oxide catalysts decrease in the sequence of Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x > Cu_{0.1}Mn_{0.2}Ce_{0.7}O_x > Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x ≥ CuMnCeO_x-imp > Cu_{0.3}Ce_{0.7}O_x » Mn_{0.3}Ce_{0.7}O_x. It is reported that the existence of Ce³⁺ 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 CuO_x, MnO_x, and CeO₂ species over the Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x and CuMnCeO_x-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 (O_{latt.}), while a shoulder peak at around ca. 531.6 eV belongs to the active surface oxygen (O_{sur.}) 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 O[•], O₂^{•-}, and O⁻. Table 2 lists the active O_{sur.} percentages of various catalysts. It can be observed that all the Cu_aMn_{0.3-a}Ce_{0.7}O_x catalysts have larger quantity of O_{sur.} 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

Fig. 11. O1s XPS spectra of (a) Cu_{0.1}Mn_{0.2}Ce_{0.7}O_x, (b) Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x, (c) Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x, (d) Cu_{0.3}Ce_{0.7}O_x, (e) Mn_{0.3}Ce_{0.7}O_x, and (f) CuMnCeO_x-imp.

Fig. 12. H_2 -TPR profiles of (a) $Cu_{0.1}Mn_{0.2}Ce_{0.7}O_x$, (b) $Cu_{0.15}Mn_{0.15}Ce_{0.7}O_x$, (c) $Cu_{0.2}Mn_{0.1}Ce_{0.7}O_x$, (d) $Cu_{0.3}Ce_{0.7}O_x$, (e) $Mn_{0.3}Ce_{0.7}O_x$, (f) $CuMnCeO_x$ -imp, (g) CuO , (h) MnO_x , and (i) CeO_2 .

latter being re-oxidized by the adsorbed oxygen [59,60]. Therefore, both the gas-phase oxygen adsorption capability and oxygen transfer rate between $O_{sur.}$ and $O_{latt.}$ are vital chlorobenzene oxidation influencing factors.

3.3.5. Temperature programmed reduction with H_2

Reducibility of the single/mixed metal oxides was investigated by 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 CuO , MnO_x , and CeO_2 . $Mn_{0.3}Ce_{0.7}O_x$ 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 $Cu_{0.3}Ce_{0.7}O_x$ catalyst. The reduction peak centered at about 142 °C is attributed to the reduction of CuO_x 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 Cu^+ species. The reduction peak centered at 184 °C is attributed to the reduction of dispersed CuO_x species on the ceria surface and the two-/three-dimensional copper clusters in small size [61]. All the $Cu_aMn_{0.3-a}CeO_x$ catalysts possess three reduction peaks in the temperature range of 150–360 °C. Fig. 12 reveals that the reduction temperatures of $Cu_aMn_{0.3-a}CeO_x$ 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 $Cu_{0.15}Mn_{0.15}CeO_x$ 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 $CuMnCeO_x$ solid solution (Fig. 6), leading to a improved reducibility of the catalyst as the Cu-Mn-O-Ce connection in the $CuMnCeO_x$ solid solution could reduce the redox potential of copper and manganese species as well as act as a bridge for 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 (O_2 -TPD), as shown in Fig. S2. As is known, the chemically adsorbed oxygen O_2^-/O^- species are much easier to desorb than that of the lattice O^{2-} species, and which are indispensable for the superior catalytic combustion performance [65]. It is shown that the $Cu_aMn_{0.3-a}CeO_x$ samples possess larger amounts of chemically adsorbed oxygen species than those of the other materials. Among them, the $Cu_{0.15}Mn_{0.15}CeO_x$ 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 Cl is very important for CVOs combustion as the adsorbed 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 Cl species, and therefore, the highest amount of chemically adsorbed oxygen species can clean the surface adsorbed Cl species over $Cu_{0.15}Mn_{0.15}CeO_x$ 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 V_2O_5/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 CVOs oxidation. Van de Brink and co-workers [67] also reported that the C–Cl bond scission is the first step for chlorobenzene oxidation over $Pt/\gamma-Al_2O_3$. 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 perdeuteriochlorobenzene, 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 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 $CuMnCeO_x$ 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 CuO_x , MnO_x , and 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

Fig. 13. Proposed chlorobenzene combustion route over CuO-MnO_x-CeO₂ composite catalysts.

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 CuMnCeO_x 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., CO_x, 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 molecules combustion is probably their dissociative adsorption on active copper and manganese sites via Cl abstraction. The adsorbed Cl species over Cu_{0.2}Mn_{0.1}CeO_x, Mn_{0.3}CeO_{0.7}O_x, CuMnCeO_x-imp, CuO, MnO_x, and CeO₂ samples may be difficult to remove until achieving the equilibrium of adsorbed and desorbed Cl species due to the absence 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 CO_x 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-MnO_x-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

CuMnCeO_x mixed metal oxides with mesoporous structure and high specific surface area were synthesized via a urea-assisted

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 Cu_{0.15}Mn_{0.15}CeO_x 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 CuMnCeO_x 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

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2014.01.076>.

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