Catalytic destruction of chlorobenzene over mesoporous ACeO_x ($A = \text{Co}, \text{Cu}, \text{Fe}, \text{Mn}, \text{or Zr}$) composites prepared by inorganic metal precursor spontaneous precipitation

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ABSTRACT

Mesostructured ACeO_x ($A = \text{Co}, \text{Cu}, \text{Fe}, \text{Mn}, \text{or Zr}$) composites with large specific surface area and developed mesoporosity were prepared by inorganic metal precursor spontaneous precipitation (IMSP) method. Influences of catalyst surface area, pore structure, reducibility, and active oxygen concentration on catalytic performance were studied. Both preparation route and metal precursor type affect metal active site dispersion, and the IMSP is a desirable approach for synthesis of metal composites with homogeneous active phase distribution. The original crystalline structure of CeO_2 is well maintained although parts of transition metal cations are incorporated into its framework. The forming of $\text{A}^{n+}-\text{O}^{2-}-\text{Ce}^{4+}$ connections in ACeO_x catalysts could reduce the redox potential of metal species, allowing effective redox cycles during oxidation reactions. CuCeO_x demonstrates powerful catalytic efficiency with 99% of chlorobenzene (CB) destructed at 328 °C, which is much lower than the other ACeO_x oxides and Cu-doped catalysts synthesized via the incipient impregnation and coprecipitation methods ($T_{99} > 405$ °C). The active site reducibility is the foremost activity determining factor for CB destruction.

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1. Introduction

Volatile organic compounds (VOCs) emitted from industrial manufacturing and municipal burning are an important class of air pollutants [1,2]. Among them, chlorinated volatile organic compounds (CVOCs) are considered as the most harmful organic contaminants due to their acute toxicity and strong bioaccumulation potential [3]. Catalytic oxidation is an effective, energy-saving, and environment-friendly approach for CVOC elimination [4]. Supported noble metal catalysts and transition metal oxides are usually employed for arene elimination. The high cost, inferior thermal stability and low resistance to poisoning of noble metals limit their practical large-scale application, especially in the case of CVOC destruction [5,6]. Transition metal oxides are a proper alternative owing to their excellent thermal stability, superior durability against deactivation, and lower price [7]. Nonporous zirconia-based catalysts, manganese and copper oxides, have been claimed for their effectiveness in CVOC destruction or dechlorination reactions [8–10]. Besides, the superior catalytic performances of nanocrystalline

cobalt and iron metal oxides in CO and/or VOC oxidation have also been reported [11,12].

Ceria has recently attracted much attention as an efficient catalyst due to its abundant oxygen vacancy defects, high oxygen storage capacity, and relatively easy shuttles between Ce^{3+} and Ce^{4+} oxidation states [13,14]. However, CeO_2 deactivated quickly due to the strong adsorption of HCl or Cl_2 produced from CVOC decomposition [15]. Doping ceria with transition metals could modify the redox property of mixed oxides, enhancing the oxygen mobility and Cl species removal or transfer velocity, and thus, improving their catalytic activity and reaction stability during CVOC destruction. Wang et al. [16] have proposed that the $\text{MnO}_x\text{-CeO}_2$ catalysts with high Mn/(Ce + Mn) ratios presented a stable chlorobenzene (CB) oxidation performance due to the strong ability of Mn to remove Cl species. However, single or mixed metal oxides synthesized via the traditional methods possess nonporous structure and low active surface area, which greatly limit their low-temperature catalytic efficiency. Mesoporous transition metal oxides (MTMO) with d-shell electrons confined to nanosized walls and redox active internal surfaces show extreme fascinating prospects in VOC decomposition [17]. The synthesis of MTMO usually requires “soft” (e.g., surfactants or block copolymers) or “hard” (e.g., porous silica or carbon) structural templates [18–23]. For example, ordered mesoporous Co_3O_4 with high surface area (173 m^2/g) has been obtained by Garcia and coworkers

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through a nanocasting route using KIT-6 silica as the hard template, over which 100% propane could be totally oxidized at around 225 °C [22]. Nonetheless, the synthesis of mesostructured silica or carbon template is rather complex and time-consuming. Previously, we synthesized mesoporous $\text{CuO}_x\text{-CeO}_2$ catalysts with large surface area (up to 162.8 m^2/g) via a facile self-assembly method, and found that these materials possessed powerful catalytic activity for the oxidation of toluene and propanal [23]. However, the catalytic performances of mesoporous transition metal/ceria composites in CVOC oxidation were seldom considered.

Herein, mesoporous ACeO_x ($A = \text{Co}, \text{Cu}, \text{Fe}, \text{Mn}, \text{or Zr}$) composites were synthesized using cetyltrimethylammonium bromide (CTAB) as the soft template and urea as the precipitation inducer with the aim to explore the feasibility of mesostructured composite oxides in CVOC destruction. CB was adopted as the probe molecule as it's a typical aryl chloride and usually employed as the model reagent to predict the destruction behaviors of chlorinated aromatics and dioxins [9]. Physicochemical properties of all synthesized catalysts were characterized by XRD, N_2 sorption, FE-SEM, TEM, H_2 -TPR and O_2 -TPD. Furthermore, the influence factors such as surface area, mesoporosity, reducibility, and active oxygen concentration were discussed in detail with the catalytic activity.

2. Experimental

2.1. Catalyst preparation

Chemicals (without further purification) used in this work are cheap and easily available inorganic metal salts, cationic surfactant (CTAB), and urea. For a typical synthesis, 5 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 5.6 g CTAB, 7.7 g urea, and different amounts of inorganic metal precursors (metal loading = 30 wt.%) were dissolved in 190 mL deionized water. After stirring for 2 h, the metal ions, urea molecules, and CTAB micelles are homogeneous dispersed in the mixed solution. Then, the obtained mixed solutions were firstly aged in autoclaves at 80 °C for 24 h to make the inorganic metal precursors homogeneously precipitated around the CTAB/water micelles due to the persistent decomposition of urea, and the mixtures were further heated in autoclaves for 12 h at 120 °C for polycondensation and rearrangement of surfactant micelles. After that, 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 gain the mesostructured metal oxides.

For comparison, the CuCeO_x oxides with Cu loading of 30 wt.% were prepared by incipient impregnation (IM, named im- CuCeO_x) and coprecipitation (CO, named co- CuCeO_x) methods, and the preparation procedures can be found elsewhere [24,25]. Bulk CeO_2 was also synthesized through thermal calcination $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 550 °C for 4 h.

2.2. Catalyst characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert powder diffraction system using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) in the 2θ range of 10–80° with a scanning rate of 4°/min. N_2 sorption was collected on a Quantachrome NOVA 1200e gas sorption analyzer at 77 K. 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 at $P/P_0 = 0.05\text{--}0.25$ using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution and average pore diameter were derived from the desorption branch of the N_2 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. Temperature programmed reduction (H_2 -TPR) experiments were performed on a Micromeritics 2720 analyzer. Prior to reduction, 50 mg of the catalyst was heated in a 5% O_2/He flow (50 mL/min) from room temperature 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% H_2/He (50 mL/min) from 50 to 600 °C with a heating rate of 10 °C/min. The temperature programmed desorption of O_2 (O_2 -TPD) was carried out using the same apparatus as that for H_2 -TPR. 50 mg of the catalyst was preheated in a 5% O_2/He flow (50 mL/min) at 500 °C for 30 min, then the sample was heated from 50 to 700 °C at a heating rate of 10 °C/min under a stream of pure He.

2.3. Catalytic activity evaluation

The catalytic performances of all prepared catalysts for CB oxidation were performed in a continuous-flow fixed-bed reactor at atmospheric pressure, consisting of a stainless steel tube with an inner diameter of 6 mm. 300 mg of the catalyst (40–60 mesh) was used in each run. The reagent gas consisted of 500 ppm of CB, 21 vol.% of O_2 and balance N_2 at a flow rate of 200 mL/min, i.e., gas hourly space velocity (GHSV) of ca. 30,000 h^{-1} . The effluent gas composition was analyzed online by a gas chromatograph (GC9890A, Shanghai Linghua Co., China) equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD).

The CB conversion (X_{CB}) is calculated by Eq. (1),

$$X_{\text{CB}} = (C_{\text{CB,in}} - C_{\text{CB,out}}) / C_{\text{CB,in}} \quad (1)$$

where $C_{\text{CB,in}}$ and $C_{\text{CB,out}}$ are the CB concentration (vol.%) in the inlet and outlet stream, respectively.

The CO_2 selectivity (S_{CO_2}) is calculated according to Eq. (2),

$$S_{\text{CO}_2} = n_{\text{CO}_2} / (6 \cdot n_{\text{CB}}) \quad (2)$$

where n_{CO_2} and n_{CB} are mole of CO_2 produced in the outlet gas and mole of CB feed in the inlet gas, respectively.

The reaction rate (r_{AO_x}) is calculated with X_{CB} , as follows,

$$r_{\text{AO}_x} = F_{\text{CB}} \cdot X_{\text{CB}} / (W_{\text{cat}} \cdot W_{\text{AO}_x}) \quad (3)$$

where F_{CB} is the CB feeding rate (mol/s), W_{cat} is the catalyst weight used in the reaction (g), and W_{AO_x} is the metal oxide loading (wt.%) in the ACeO_x catalyst.

The effects of reaction products on the reaction rate may be ignored under differential conditions ($X_{\text{CB}} < 15\%$) [26], and the r_{AO_x} for CB destruction could be described as Eq. (4),

$$r_{\text{AO}_x} = A' \exp(-E_a/(R \cdot T)) \cdot P_{\text{CB}}^\alpha \cdot P_{\text{O}_2}^\beta \quad (4)$$

where A' is the pre-exponential factor, E_a is the apparent activation energy, R is the molar gas constant, T is the thermodynamic temperature, and P_{CB} and P_{O_2} are the partial pressures of CB and O_2 , respectively. The variations of the reactant component are negligible under differential reaction conditions, that is, A' , P_{CB}^α , and $P_{\text{O}_2}^\beta$ are nearly constant. Therefore, E_a can be obtained from the slope of the resulting linear plot of $\ln r_{\text{AO}_x}$ versus $1/T$ after taking the logarithm of Eq. (4).

3. Results and discussion

3.1. Structural and textural properties

As displayed in Fig. 1, both the preparation route and inorganic metal precursor type have evident effects on metal oxide dispersion.

Fig. 1. WA-XRD profiles of (a) CeO_2 , (b) CoCeO_x , (c) CuCeO_x , (d) FeCeO_x , (e) MnCeO_x , (f) ZrCeO_x , (g) co- CuCeO_x , and (h) im- CuCeO_x .

No CuO diffraction peaks can be found over CuCeO_x , which may be due to the high dispersion of Cu nanoparticles with too small particle sizes on the surface of the ceria support to be identified by XRD or the localization of Cu ions in the CeO_2 lattice [27]. However, a weak diffraction peak corresponding to the crystallized CuO phase can be noticed at $2\theta = 35.3^\circ$ over co- CuCeO_x and im- CuCeO_x (JCPDS No. 01-089-5898), indicating that the IMSP is a more desirable method than that of IM and CO for the synthesis of metal composites with homogeneous active phase dispersion. In addition, the distribution states of various metal oxides over the CeO_2 support differ from each other. Only one weak Co_3O_4 diffraction peak centered at 65.2° can be observed over CoCeO_x (JCPDS No. 01-078-1969), while there are respectively two MnO_2 ($2\theta = 55.1$ and 60.5° ; JCPDS No. 03-065-1298), three ZrO_2 ($2\theta = 29.6, 34.4$, and 49.3° ; JCPDS No. 01-079-1796), and four Fe_2O_3 ($2\theta = 35.7, 49.5, 54.1$, and 62.5° ; JCPDS No. 01-073-0603) diffraction peaks that can be detected over MnCeO_x , ZrCeO_x , and FeCeO_x , suggesting that the aggregation degree of MnO_2 , ZrO_2 , and Fe_2O_3 nanoparticles is probably more severe than that of CuO and Co_3O_4 . Table 1 lists the lattice parameter (a_{111}) of the synthesized catalysts. The slight decrease of a_{111} values after the introduction of metal species ($a_{111} = 5.4121$ – 5.4225 Å) provides the evidence that part of metal cations are incorporated into CeO_2 crystallites ($a_{111} = 5.4276$ Å) by considering that the radii of Co^{2+} (0.65 Å), Co^{3+} (0.54 Å), Cu^+ (0.96 Å), Cu^{2+} (0.73 Å), Fe^{2+} (0.61 Å), Fe^{3+} (0.55 Å), Mn^{2+} (0.67 Å), Mn^{3+} (0.58 Å), Mn^{4+} (0.53 Å), and Zr^{4+} (0.72 Å) ions are smaller than those of Ce^{3+} (1.10 Å) and Ce^{4+} (1.01 Å) ions. The main reflections at 2θ degree of 28.6, 33.2, 47.5, 56.4, 59.1, 69.6, 76.9, and 79.3 over ACeO_x catalysts are indexed well to the typical cubic fluorite-like structure of CeO_2 (JCPDS No. 03-065-5923), suggesting that the incorporation of transition metal ions has negligible influence on the original crystalline structure of the CeO_2 support.

Table 1
Physicochemical properties and hydrogen consumption of the synthesized catalysts.

Sample	a_{111} (Å)	S_{BET} (m^2/g)	D_v (cm^3/g)	D_p (nm)	$A_{\text{H}_2}^a$ ($\text{mmol}/\text{g}_{\text{cat}}$)
CeO_2	5.4276	61.5	0.18	6.23	
CoCeO_x	5.4145	126.3	0.17	4.42	0.28
CuCeO_x	5.4162	145.6	0.19	2.51	1.51
FeCeO_x	5.4179	107.8	0.21	3.73	0.06
MnCeO_x	5.4121	92.7	0.12	4.34	0.53
ZrCeO_x	5.4214	68.2	0.10	3.27	
co- CuCeO_x	5.4225	88.4	0.21	3.17	1.81
im- CuCeO_x	5.4151	59.5	0.16	5.58	0.11

^a Amount of H_2 consumption below 200 °C.

Fig. 2 shows that all composite metal oxides exhibit typical irreversible type IV shape isotherms with well expressed hysteresis loops at relative pressures P/P_0 of 0.45–1.0. The condensation step on the isotherm at low relative pressure ($P/P_0 = 0.45$ – 0.8) is characteristic of capillary condensation of framework-confined mesopores, and the condensation step on the isotherm at $P/P_0 = 0.8$ – 1.0 indicates the presence of a significant amount of textural pores contributing to the filling of interparticle spaces [28,29]. The above results indicate the coexistence of framework-confined and textural mesopores over CoCeO_x , CuCeO_x , MnCeO_x , ZrCeO_x , and co- CuCeO_x . However, for bulk CeO_2 , im- CuCeO_x and FeCeO_x , the so-called framework-confined mesoporosity is not observed as the hysteresis loops at $P/P_0 = 0.45$ – 0.8 are invisible (Fig. 2a). The BJH curves reveal that the pore size distributions of all ACeO_x samples are much narrower than those of im- CuCeO_x and CeO_2 support, suggesting the superior mesoporous homogeneity of ACeO_x (Fig. 2b). As listed in Table 2, the IMSP is an effective approach for the preparation of mixed metal oxides with large specific surface area (S_{BET}), while the S_{BET} values are varied for different inorganic metal precursors with the S_{BET} sequence decreases as CuCeO_x ($145.6 \text{ m}^2/\text{g}$) > CoCeO_x ($126.3 \text{ m}^2/\text{g}$) > FeCeO_x ($107.8 \text{ m}^2/\text{g}$) > MnCeO_x ($92.7 \text{ m}^2/\text{g}$) > ZrCeO_x ($68.2 \text{ m}^2/\text{g}$). The S_{BET} of all ACeO_x catalysts (68.2 – $145.6 \text{ m}^2/\text{g}$) are higher than the bulk CeO_2 ($61.5 \text{ m}^2/\text{g}$), while the average pore diameter (D_p) of ACeO_x samples (2.51 – 4.42 nm) are a little lower than the CeO_2 support (6.23 nm). Besides, the IMSP protocol is more valid for the synthesis of mixed metal oxides with larger S_{BET} than the conventional CO and IM methods by comparing the remarkably enhanced S_{BET} of CuCeO_x ($145.6 \text{ m}^2/\text{g}$) with co- CuCeO_x ($88.4 \text{ m}^2/\text{g}$) and im- CuCeO_x ($59.5 \text{ m}^2/\text{g}$).

As shown in Fig. 3, CoCeO_x , CuCeO_x , and MnCeO_x oxides feature shaggy surfaces, composed of crumb-like particles (30–150 nm) with a large degree of porosity. FeCeO_x consists in particles with more regular diameter (around 100 nm), and some particle aggregates can be found (Fig. 3d). ZrCeO_x shows a relatively smooth surface with rather limited mesopores, and most of metal nanoparticles over which are severely aggregated (Fig. 3f), in agreement with the XRD and N_2 sorption results (Figs. 1 and 2). As Fig. 4 shows, no well-defined mesoporous structure, like those in Si-based molecule sieves, could be found in all ACeO_x catalysts, suggesting that these mesopores are randomly distributed among a mixture of small nanoparticles. CoCeO_x and CuCeO_x compose of circle-like and rectangle-like nanoparticles with a disordered mesopore structure (Fig. 4b and c). MnCeO_x mainly composes of rectangle-like and pentagon-like nanoparticles (Fig. 4e). A little portion of particles are agglomerated over the FeCeO_x catalyst, while the metal precursors are prone to agglomerate into clusters over ZrCeO_x and im- CuCeO_x (Fig. 4f and h).

3.2. Reducibility and oxygen species mobility

As displayed in Fig. 5, CeO_2 shows two weak reduction peaks centered at around 415 and 517 °C, attributing to the reduction of surface oxygen and bulk oxygen, respectively [30,31]. The reduction of pure Co_3O_4 ($\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$: ≈ 280 °C; $\text{CoO} \rightarrow \text{Co}$: ≈ 350 °C), CuO (≈ 373 °C), Fe_2O_3 ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$: ≈ 390 °C; $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$: > 600 °C), MnO_2 ($\text{MnO}_2 \rightarrow \text{MnO}$: ≈ 365 °C; $\text{MnO} \rightarrow \text{Mn}$: ≈ 500 °C), and ZrO_2 (> 800 °C) oxides can be found elsewhere [32–35]. The H_2 -TPR results demonstrated that partial incorporation of A^{n+} metal cations into the CeO_2 crystallites can enhance the reducibility of corresponding AO_x metal oxides, which should be attributed to the appearance of abundant interfaces between related mixed metal oxides as this intergranular layers possess very high oxygen species adsorption ability [36]. For instance, the reduction peaks for CoCeO_x shift to the low-temperature side (> 40 °C), and more than 100 °C of temperature reductions are achieved for those of FeCeO_x , CuCeO_x , and MnCeO_x . Besides, the preparation method also has obvious effects on transition metal cations' incorporation degree and further their reduction behaviors (Figs. 1 and 5). Li et al. [37] reported

Fig. 2. N₂ adsorption/desorption isotherms and pore size distribution of (a) CeO₂, (b) CoCeO_x, (c) CuCeO_x, (d) FeCeO_x, (e) MnCeO_x, (f) ZrCeO_x, (g) co-CuCeO_x, and (h) im-CuCeO_x.

that CeO₂ promotes the reduction of finely dispersed CuO surface species, and the smaller the CuO particles, the easier they are to reduce. Bulk CuO is reducible at higher temperatures, and has a small contribution to catalytic activity. As demonstrated in Fig. 5, the first peak at about 103 °C over the CuCeO_x catalyst is attributed to the reduction of surface oxygen species, while no H₂ consumption peak for surface oxygen reduction can be detected over co-CuCeO_x and im-CuCeO_x. The H₂ consumption peaks at around 211 °C result from the reduction of CuO_x over CuCeO_x and co-CuCeO_x, however, much higher CuO_x reduction temperature (around 256 °C) is required for im-CuCeO_x. CuCeO_x and co-CuCeO_x are easily reduced than im-CuCeO_x due to the better dispersion of copper species, in accordance with the XRD and TEM results (Figs. 1 and 4). The forming of Aⁿ⁺–O^{2–}–Ce⁴⁺ connections after the incorporation of Aⁿ⁺ metal cations over ACeO_x catalysts could reduce the redox potential of metal species as well as act as a bridge for O transfer between A and Ce, and thus allowing effective redox cycles during oxidation reactions. As listed in Table 1, the H₂ consumption amounts (A_{H2}) of CuCeO_x (1.51 mmol/g_{cat}) and co-CuCeO_x (1.81 mmol/g_{cat}) below 200 °C are much higher than those of the other mixed oxides (<0.53 mmol/g_{cat}), suggesting the superior low-temperature reducibility of CuCeO_x and co-CuCeO_x. Moreover, the reducibility of a catalyst can be effectively evaluated by using the initial H₂ consumption rate (r_{H2}) when the

oxygen consumption of the catalyst is lower than 25% [38]. As Fig. 6 shows, the r_{H2} increases in the order of bulk CeO₂ ≤ ZrCeO₂ < im-CuCeO_x < MnCeO_x ≤ FeCeO_x < CoCeO_x < co-CuCeO_x < CuCeO_x. That is to say, the low-temperature reducibility of the synthesized catalysts decreased according to the sequence of CuCeO_x > co-CuCeO_x > CoCeO_x > FeCeO_x ≥ MnCeO_x > im-CuCeO_x > ZrCeO₂ ≥ CeO₂.

The adsorbed oxygen species over a catalyst changes according to the following procedures: O₂ → O₂[–] → O[–] → O^{2–}. The physically adsorbed oxygen (O₂, O_p) and chemically adsorbed oxygen (O₂[–]/O[–], O_c) species are much easier to desorb than that of the lattice oxygen (O^{2–}, O_L) species. As displayed in Fig. 7, the TCD signal according to the desorption of O_p is not observed over all catalysts as O_p species usually desorbs in the vicinity of 50 °C [5]. The desorption peaks centered at 306 °C over the CeO₂ support can be assigned to the O_c species. As is known, the incorporation of metal cations into CeO₂ could bring about structural deficiencies in the framework, which can adsorb oxygen molecules from the gas phase under real reaction conditions and be activated to form the active O_c (i.e., O₂[–] or O[–]) species, promoting the catalytic efficiency for CVOC oxidation. Herein, all mixed metal oxides have two to four oxygen desorption peaks, and the oxygen species desorption occurring at around 200 °C over ACeO_x and co-CuCeO_x catalysts could be correlated to the interaction between CuO and CeO₂ oxides. The total

Table 2
Catalytic activity, CO₂ selectivity, and reaction rate of ACeO_x catalysts.

Sample	T ₅₀ ^a (°C)	S ₅₀ ^b (%)	r _c × 10 ^{5c} (mol/(g _{cat} ·h))	r _A × 10 ^{5d} (mol/(g _{AOx} ·h))	r _s × 10 ^{7e} (mol/(m ² _{cat} ·h))	E _a (kJ/mol)
CeO ₂			1.78	5.93	2.89	147.9
CoCeO _x	304	99.3	5.04	16.79	3.99	101.4
CuCeO _x	259	99.8	8.21	27.41	5.64	89.7
FeCeO _x	348	97.7	2.84	9.46	2.63	121.8
MnCeO _x	345	98.1	3.62	12.05	3.91	107.3
ZrCeO _x	372	97.3	2.43	8.11	1.19	94.8
co-CuCeO _x	299	98.0	5.99	19.97	6.78	86.3
im-CuCeO _x	375	99.5	2.82	9.40	4.74	97.5

^a Temperatures at 50% conversion of CB.

^b CO₂ selectivity at 50% conversion of CB.

^c Reaction rate gained at 330 °C.

^d Reaction rate normalized to a specific rate per transition metal oxide mass unit.

^e Reaction rate normalized to a specific rate per catalyst surface area unit.

Fig. 3. FE-SEM images of (a) CeO_2 , (b) CoCeO_x , (c) CuCeO_x , (d) FeCeO_x , (e) MnCeO_x , and (f) ZrCeO_x .

amount of O_c species by deconvolving the peak areas under O_2 -TPD patterns below 500 °C [39] is in the order of $\text{FeCeO}_x > \text{CuCeO}_x > \text{co-CuCeO}_x > \text{CoCeO}_x > \text{CeO}_2 > \text{MnCeO}_x \approx \text{ZrCeO}_x > \text{im-CuCeO}_x$.

3.3. Catalytic destruction of CB

As shown in Fig. 8 and Table 2, CuCeO_x demonstrates a much higher catalytic activity ($T_{50} = 259$ °C) for CB destruction than the other catalysts ($T_{50} > 299$ °C) studied in this work. The catalytic activity order of all samples is $\text{CuCeO}_x \gg \text{co-CuCeO}_x > \text{CoCeO}_x > \text{FeCeO}_x > \text{MnCeO}_x > \text{im-CuCeO}_x > \text{ZrCeO}_x \gg \text{CeO}_2$. Besides, the preparation method significantly influences the catalytic performance of CuCeO_x catalysts. For deep catalytic destruction of CB over Cu-doped catalysts, the catalytic activity order is $\text{IMSP} > \text{CO} \gg \text{IM}$ (Fig. 8a). The catalyst prepared by the IMSP method exhibits the lowest CB total conversion temperature ($T_{99} = 328$ °C, even comparable to some noble metal-based catalysts [40–42]), which are much lower than the samples synthesized by the IM and CO methods ($T_{99} \geq 405$ °C). For example, Giraudon et al. found that the T_{90} temperatures for CB oxidation over various 0.5 wt.% Pd/ LaBO_3 catalysts (B = Co, Mn, Ni, and Fe) were in the range of 335–493 °C (CB concentration = 1000 ppm; GHSV ≈ 9000 h^{-1} ; $\text{O}_2 = 21$ vol.%) [41]. No organic reaction byproducts can be detected over CuCeO_x ($\text{S}_{\text{CO}_2} > 99\%$) and co-CuCeO_x ($\text{S}_{\text{CO}_2} > 98\%$), while a little

amount of aldehyde and acetic acid can be detected over the other metal oxides (Fig. 8b and c).

Results listed in Table 2 reveal that the E_a for CB combustion over various ACeO_x catalysts is 89.7–121.8 kJ/mol, and the mesostructured CuCeO_x possesses much higher reaction rate (8.21×10^{-5} mol/(g_{cat}·h)) for CB oxidation than the other ACeO_x catalysts (2.43×10^{-5} – 5.04×10^{-5} mol/(g_{cat}·h)), co-CuCeO_x (5.99×10^{-5} mol/(g_{cat}·h)), im-CuCeO_x (2.82×10^{-5} mol/(g_{cat}·h)), and CeO_2 (1.78×10^{-5} mol/(g_{cat}·h)). Among the Cu-doped catalysts, the mesoporous CuCeO_x catalyst shows a much higher catalytic activity for CB destruction than the co-CuCeO_x and im-CuCeO_x catalysts, and its reaction rate reaches 27.41×10^{-5} mol/(g_{cat}·h) at 330 °C, obviously higher than the co-CuCeO_x (19.97×10^{-5} mol/(g_{cat}·h)) and im-CuCeO_x (9.40×10^{-5} mol/(g_{cat}·h)) catalysts. The r_c values for CB combustion are ranked as $\text{CuCeO}_x > \text{co-CuCeO}_x > \text{CoCeO}_x > \text{MnCeO}_x > \text{FeCeO}_x > \text{im-CuCeO}_x > \text{ZrCeO}_x > \text{CeO}_2$, and the same order is also observed as normalized to a specific rate per oxide mass unit or surface area unit (Table 2). In addition, the E_a value of the CuCeO_x catalyst is lower than that of the other ACeO_x samples. The above results demonstrate that the mesostructured CuCeO_x catalyst is a very promising catalyst for CB deep oxidation.

Numerous parameters of the transition metal loaded catalysts such as specific surface area, pore structure, active site reducibility, and active oxygen species concentration are thought to affect the catalytic activity

Fig. 4. Representative TEM images of (a) CeO_2 , (b) CoCeO_x , (c) CuCeO_x , (d) FeCeO_x , (e) MnCeO_x , (f) ZrCeO_x , (g) co-CuCeO_x , and (h) im-CuCeO_x .

for CB destruction [43,44]. Although the catalytic activity increases with an increase in the specific surface areas of CuCeO_x (145.6 m^2/g), CoCeO_x (126.3 m^2/g), FeCeO_x (107.8 m^2/g), MnCeO_x (92.7 m^2/g), ZrCeO_x (68.2 m^2/g), and pure CeO_2 (61.5 m^2/g) samples, the co-CuCeO_x catalyst with a small specific surface area (88.4 m^2/g) exhibits a much higher activity ($T_{50} = 299^\circ\text{C}$) than the CoCeO_x ($T_{50} = 304^\circ\text{C}$), FeCeO_x ($T_{50} = 348^\circ\text{C}$), and MnCeO_x ($T_{50} = 345^\circ\text{C}$) catalysts, indicating that the catalytic activity could not directly correlate to the specific surface area (Table 1). Similarly, any relationship between total pore volume, average pore diameter and CB oxidation is not observed, suggesting that the both abovementioned parameters are not key factors governing the catalytic performance although the pore structure of a catalyst can affect the mass and thermal transfer during oxidation reactions. It is generally

accepted that the presence of oxygen vacancy facilitates the activation of oxygen molecules to active oxygen adspecies, and a good reducibility of the catalysts can provide a facile redox process that would lead to an enhanced catalytic performance [43]. Herein, the active oxygen adspecies over various catalysts is varied in the order of $\text{FeCeO}_x > \text{CuCeO}_x > \text{co-CuCeO}_x > \text{CoCeO}_x > \text{CeO}_2 > \text{MnCeO}_x \approx \text{ZrCeO}_x > \text{im-CuCeO}_x$ according to the O_2 -TPD result, much differing from the activity sequence (Figs. 7 and 8). As can be seen in Figs. 5 and 6, the reducibility of the synthesized catalysts decreased according to the sequence of $\text{CuCeO}_x > \text{co-CuCeO}_x > \text{CoCeO}_x > \text{FeCeO}_x \geq \text{MnCeO}_x > \text{im-CuCeO}_x > \text{ZrCeO}_2 \geq \text{CeO}_2$, which is in well accordance with the catalytic activity order reported in Fig. 8. We can infer that the excellent low-temperature reducibility is the primary factor deciding the catalytic activity during CB destruction.

Fig. 5. H₂-TPR profiles of (a) CeO₂, (b) CoCeO_x, (c) CuCeO_x, (d) FeCeO_x, (e) MnCeO_x, (f) ZrCeO_x, (g) co-CuCeO_x, and (h) im-CuCeO_x.

4. Conclusions

In summary, IMSP is an efficient route to synthesize composite metal catalysts with large specific surface area and developed pore structure. The type of metal precursors can obviously influence the textural properties of the final products. A part of metal cations (A^{n+}) are incorporated into CeO₂ crystallites, and the interaction of A^{n+} and Ce has synergistic effects for the reduction of the mixed oxides due to the appearance of abundant interfaces between related mixed metal oxides. CuCeO_x demonstrates a much higher catalytic activity ($r = 8.21 \times 10^{-5} \text{ mol}/(\text{g}_{\text{cat}} \cdot \text{h})$) for CB destruction than the other catalysts ($r = 1.78 \times 10^{-5} - 5.04 \times 10^{-5} \text{ mol}/(\text{g}_{\text{cat}} \cdot \text{h})$). The excellent catalytic activity of CuCeO_x catalysts can be primarily attributed to the superior reducibility of the active phase during CB oxidation. The mesostructured CuCeO_x oxide is a promising catalyst for CVOC elimination.

Nomenclature

A'	pre-exponential factor
A_{H_2}	H ₂ consumption amount below 200 °C
a_{111}	lattice parameter

Fig. 6. Initial H₂ consumption rate as a function of inverse temperature of various samples.

Fig. 7. O₂-TPD patterns of (a) CeO₂, (b) CoCeO_x, (c) CuCeO_x, (d) FeCeO_x, (e) MnCeO_x, (f) ZrCeO_x, (g) co-CuCeO_x, and (h) im-CuCeO_x.

BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CB	chlorobenzene
$C_{CB,in}$	chlorobenzene concentration in the inlet stream
$C_{CB,out}$	chlorobenzene concentration in the outlet stream
CO	coprecipitation
CTAB	cetyltrimethylammonium bromide
CVOCs	chlorinated volatile organic compounds
D_p	average pore diameter
D_v	total pore volume
E_a	apparent activation energy
F_{CB}	chlorobenzene feeding rate
FE-SEM	field emission scanning electron microscopy
FID	flame ionization detector
GHSV	gas hourly space velocity
H ₂ -TPR	temperature programmed reduction
IM	incipient impregnation
MTMO	mesoporous transition metal oxides
n_{CB}	mole of chlorobenzene feed in the inlet gas
n_{CO_2}	mole of CO ₂ produced in the outlet gas
O ₂ -TPD	temperature programmed desorption of O ₂
O _C	chemically adsorbed oxygen
O _L	lattice oxygen
O _P	physically adsorbed oxygen
P_{CB}	chlorobenzene partial pressure
P_{O_2}	O ₂ partial pressure
R	molar gas constant
r_A	reaction rate normalized to specific rate per transition metal oxides mass
r_{AO_x}	catalyst reaction rate
r_c	reaction rate at 330 °C
r_{H_2}	initial H ₂ consumption rate
r_s	reaction rate normalized to catalyst surface area
S_{BET}	specific surface area
S_{CO_2}	CO ₂ selectivity
S_{50}	CO ₂ selectivity at which 50% conversion of chlorobenzene
T	thermodynamic temperature
TCD	thermal conductivity detector
TEM	transmission electron microscopy
T_{50}	temperature at which 50% conversion of chlorobenzene
VOCs	volatile organic compounds
W_{AO_x}	metal oxide loading in catalyst
W_{cat}	catalyst weight used in the reaction
XRD	powder X-ray diffraction

Fig. 8. CB conversion and primary reaction byproduct distribution over synthesized catalysts (300 mg catalyst, 500 ppm CB, 21 vol.% O_2 , N_2 balance; GHSV = 30,000 h^{-1}).

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