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

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Mesoporous ACeO\textsubscript{x} (A = Co, Cu, Fe, Mn, 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\textsubscript{2} is well maintained although parts of transition metal cations are incoroporated into its framework. The forming of A\textsuperscript{3+}−O\textsuperscript{2−}−Ce\textsuperscript{4+} connections in ACeO\textsubscript{x} catalysts could reduce the redox potential of metal species, allowing effective redox cycles during oxidation reactions. CuCeO\textsubscript{2} demonstrates powerful catalytic efficiency with 99% of chlorobenzene (CB) destructed at 328 °C, which is much lower than the other ACeO\textsubscript{x} oxides and Cu-doped catalysts synthesized via the incipient impregnation and coprecipitation methods (T\textsubscript{99} > 405 °C). The active site reducibility is the foremost activity determining factor for CB destruction.

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 VOC 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\textsuperscript{3+} and Ce\textsuperscript{4+} oxidation states [13,14]. However, CeO\textsubscript{2} deactivated quickly due to the strong adsorption of HCl or Cl\textsubscript{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 MnO\textsubscript{1.97}−CeO\textsubscript{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\textsubscript{3}O\textsubscript{4} with high surface area (173 m\textsuperscript{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 CuO–CeO2 catalysts with large surface area (up to 162.8 m²/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 ACeO₅ (A = Co, Cu, Fe, Mn, 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, N₂ sorption, FE-SEM, TEM, H₂-TPR and O₂-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 Ce(NO₃)₃·6H₂O, 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 CuCeO₅ oxides with Cu loading of 30 wt.% were prepared by incipient impregnation (IM, named im-CuCeO₅) and co-impregnation (CO, named co-CuCeO₅) methods, and the preparation procedures can be found elsewhere [24,25]. Bulk CeO₂ was also synthesized through thermal calcination Ce(NO₃)₃·6H₂O 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 Cu Kα radiation (λ = 0.15418 nm) in the 2θ range of 10–80° with a scanning rate of 4°/min. N₂ sorption was collected on a Quantachrome NOVA 1200e 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/P₀) of ca. 0.99. The specific surface area was calculated at P/P₀ = 0.05–0.25 using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution and average pore diameter were derived from the desorption branch of the 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. Temperature programmed reduction (H₂-TPR) experiments were performed on a Micromeritics 2720 analyzer. Prior to reduction, 50 mg of the catalyst was heated in a 5% O₂/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% H₂/He (50 mL/min) flow from 50 to 600 °C with a heating rate of 10 °C/min. The temperature programmed adsorption of O₂ (O₂-TPD) was carried out using the same apparatus as that for H₂-TPR. 50 mg of the catalyst was preheated in a 5% O₂/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 reaction gas consisted of 500 ppm of CB, 21 vol.% of O₂ and balance N₂ 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),

\[ X_{\text{CB}} = \left( \frac{C_{\text{CB, in}} - C_{\text{CB, out}}}{C_{\text{CB, in}}} \right) \times 100\% \]

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

The CO₂ selectivity (S_CO₂) is calculated according to Eq. (2),

\[ S_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{(6 \cdot n_{\text{CB}})} \]

where \( n_{\text{CO}_2} \) and \( n_{\text{CB}} \) are mole of CO₂ produced in the outlet gas and mole of CB feed in the inlet gas, respectively.

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

\[ r_{\text{AO}} = F_{\text{CB}} \cdot X_{\text{CB}} / \left( W_{\text{cat}} \cdot W_{\text{AO}} \right) \]

where \( F_{\text{CB}} \) is the CB feeding rate (mol/s), \( W_{\text{cat}} \) is the catalyst weight used in the reaction (g), and \( W_{\text{AO}} \) is the metal oxide loading (wt.%) in the ACeO₅ catalyst.

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

\[ r_{\text{AO}} = A' \exp \left( -E_a / (R \cdot T) \right) \cdot P_{\text{CB}} a \cdot P_{O_2} b \]

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 \( P_{\text{CB}} \) and \( P_{O_2} \) are the partial pressures of CB and O₂, respectively. The variations of the reactant component are negligible under differential reaction conditions, that is, \( A' \cdot P_{\text{CB}}^a \cdot P_{O_2}^b \) are nearly constant. Therefore, \( E_a \) can be obtained from the slope of the resulting linear plot of \( \ln r_{\text{AO}} \) 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. 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 narrow than those of im-CuCeO$_x$ and CeO$_2$ support, suggesting the superior mesoporous homogeneity of CeO$_2$ (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 CeO$_2$ (<145.6 m$^2$/g) > CoO (<126.3 m$^2$/g) > FeO (<107.8 m$^2$/g) > MnO (<92.7 m$^2$/g) > ZrO$_2$ (<68.2 m$^2$/g). The $S_{BET}$ of all ACeO$_x$ catalysts (<145.6 m$^2$/g) are higher than the bulk CeO$_2$ (<61.5 m$^2$/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 CeO$_2$ (<145.6 m$^2$/g) with co-CuCeO$_x$ (<88.4 m$^2$/g) and im-CuCeO$_x$ (<59.5 m$^2$/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. Reductibility 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 CoO$_x$ (CoO$_4$ → Co$^2+$ + 2O) occurs at <280 °C; CoO → Co$^3+$ at <350 °C; Cu$^0$ (<373 °C); FeO$_2$ (Fe$^3+$ + 2Fe$^2+$) at <390 °C; FeO$_2$ → FeO at >600 °C), MnO$_2$ (MnO$_2$ → Mn$^2+$ at 280 °C; MnO → Mn$^2+$ at <500 °C), and ZrO$_2$ (<800 °C) oxides can be found elsewhere [32,33]. The H$_2$-TPR results demonstrated that partial incorporation of A$^{2+}$ metal cations into the CeO$_2$ crystallites can enhance the reducibility of corresponding A$^{2+}$ metal oxides, which should be attributed to the appearance of abundant interfaces related 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

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_{111}$ (Å)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$D_r$ (nm)</th>
<th>$D_p$ (nm)</th>
<th>$N_2$ (mmol/g·ce)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>5.4276</td>
<td>61.5</td>
<td>0.18</td>
<td>6.23</td>
<td></td>
</tr>
<tr>
<td>CoCeO$_x$</td>
<td>5.4145</td>
<td>126.3</td>
<td>0.17</td>
<td>4.42</td>
<td>0.28</td>
</tr>
<tr>
<td>CuCeO$_x$</td>
<td>5.4162</td>
<td>143.6</td>
<td>0.19</td>
<td>2.51</td>
<td>1.51</td>
</tr>
<tr>
<td>FeCeO$_x$</td>
<td>5.4179</td>
<td>107.8</td>
<td>0.21</td>
<td>3.73</td>
<td>0.66</td>
</tr>
<tr>
<td>MnCeO$_x$</td>
<td>5.4121</td>
<td>92.7</td>
<td>0.12</td>
<td>4.34</td>
<td>0.53</td>
</tr>
<tr>
<td>ZrCeO$_x$</td>
<td>5.4214</td>
<td>68.2</td>
<td>0.10</td>
<td>3.27</td>
<td></td>
</tr>
<tr>
<td>co-CuCeO$_x$</td>
<td>5.4225</td>
<td>88.4</td>
<td>0.21</td>
<td>3.17</td>
<td>1.81</td>
</tr>
<tr>
<td>im-CuCeO$_x$</td>
<td>5.4151</td>
<td>59.5</td>
<td>0.16</td>
<td>5.38</td>
<td>0.11</td>
</tr>
</tbody>
</table>

* Amount of H$_2$ consumption below 200 °C.
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 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 and im-CuCeO. The H₂ consumption peaks at around 211 °C result from the reduction of CuO over CuCeO and co-CuCeO, however, much higher CuO reduction temperature (around 256 °C) is required for im-CuCeO, CuCeO, and co-CuCeO, are easily reduced than im-CuCeO due to the better dispersion of copper species, in accordance with the XRD and TEM results (Figs. 1 and 4). The formation of A⁵⁺–O²⁻–Ce⁴⁺ connections after the incorporation of A⁵⁺ metal cations over ACeO catalysts could reduce the redox potential of metal species as well as act as a bridge to O transfer between A and Ce, and thus allowing effective redox cycles during oxidation reactions. As listed in Table 1, the H₂ consumption amounts (AH₂) of CuCeO (1.51 mmol/gcat) and co-CuCeO (1.53 mmol/gcat) below 200 °C are much higher than those of the other mixed oxides (<0.53 mmol/gcat), suggesting the superior low-temperature reducibility of CuCeO and co-CuCeO. Moreover, the reducibility of a catalyst can be effectively evaluated by using the initial H₂ consumption rate (fiH₂) when the oxygen consumption of the catalyst is lower than 25% [38]. As Fig. 6 shows, the fiH₂ increases in the order of bulk CeO₂ ≤ ZrCeO₂ < im-CuCeO < MnCeO₂ < FeCeO₂ < CoCeO₂ < co-CuCeO < CuCeO. That is to say, the low-temperature reducibility of the synthesized catalysts decreases according to the sequence of CuCeO > co-CuCeO > CoCeO > FeCeO ≥ MnCeO ≥ im-CuCeO > im-CuCeO > ZrCeO ≥ CeO₂.

The adsorbed oxygen species over a catalyst changes according to the following procedures: O₂ → O²⁻ → O⁻ → O²⁻. The physically adsorbed oxygen (O₂, O²⁻) and chemically adsorbed oxygen (O₂⁻, O⁻) species are much easier to desorb than that of the lattice oxygen (O²⁻, O⁻) species. As displayed in Fig. 7, the TCD signal according to the desorption of O₂ is not observed over all catalysts as O₂ 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 O₂ 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 O₂⁻ (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 and co-CuCeO 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 catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{\text{np}} ) (°C)</th>
<th>( S_{\text{a,b}} ) (%)</th>
<th>( r_\text{c} \times 10^{12} ) (mol/(gₐₜ-cat·h))</th>
<th>( r_\text{s} \times 10^{12} ) (mol/(gₐₜₖₒ₂ₜₜ·h))</th>
<th>( r_\text{i} \times 10^{12} ) (mol/(gₐₜₖₒ₂ₜₜ·h))</th>
<th>( E_\text{a} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>304</td>
<td>99.3</td>
<td>1.78</td>
<td>5.93</td>
<td>3.89</td>
<td>147.9</td>
</tr>
<tr>
<td>CuCeO</td>
<td>259</td>
<td>99.8</td>
<td>5.04</td>
<td>16.79</td>
<td>3.99</td>
<td>101.4</td>
</tr>
<tr>
<td>CoCeO</td>
<td>348</td>
<td>97.7</td>
<td>8.21</td>
<td>27.41</td>
<td>5.64</td>
<td>89.7</td>
</tr>
<tr>
<td>FeCeO</td>
<td>345</td>
<td>98.1</td>
<td>2.84</td>
<td>9.46</td>
<td>2.63</td>
<td>121.8</td>
</tr>
<tr>
<td>MnCeO</td>
<td>372</td>
<td>97.3</td>
<td>3.62</td>
<td>12.05</td>
<td>3.91</td>
<td>107.3</td>
</tr>
<tr>
<td>ZrCeO</td>
<td>299</td>
<td>98.0</td>
<td>5.99</td>
<td>19.97</td>
<td>6.78</td>
<td>86.3</td>
</tr>
<tr>
<td>co-CuCeO</td>
<td>375</td>
<td>99.5</td>
<td>2.82</td>
<td>9.40</td>
<td>4.74</td>
<td>97.5</td>
</tr>
<tr>
<td>im-CuCeO</td>
<td>345</td>
<td>98.1</td>
<td>3.62</td>
<td>12.05</td>
<td>3.91</td>
<td>107.3</td>
</tr>
</tbody>
</table>

\( ^a \) 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.
amount of O₂ species by deconvolving the peak areas under O₂-TPD patterns below 500 °C [39] is in the order of FeCeO₅ > CuCeO₅ > co-CuCeO₅ > CeO₂ > MnCeO₅ ≈ ZrCeO₅ ≈ im-CuCeO₅.

3.3. Catalytic destruction of CB

As shown in Fig. 8 and Table 2, CuCeO₅ demonstrates a much higher catalytic activity (T₅₀ = 259 °C) for CB destruction than the other catalysts (T₅₀ > 299 °C) studied in this work. The catalytic activity order of all samples is CuCeO₅ ≫ co-CuCeO₅ > CeO₂ > MnCeO₅ > im-CuCeO₅ > ZrCeO₅ > FeCeO₅. Besides, the preparation method significantly influences the catalytic performance of CuCeO₅ catalysts. For deep catalytic destruction of CB over Cu-doped catalysts, the catalytic activity order is IMSP ≫ CO ≫ IM (Fig. 8a). The catalyst prepared by the IMSP method exhibits the lowest CB total conversion temperature (T₉₀ = 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 (Tₙ₉ ≥ 405 °C). For example, Giraudon et al. found that the T₉₀ temperatures for CB oxidation over various 0.5 wt.% Pd/LaBO₃ catalysts (B = Co, Mn, Ni, and Fe) were in the range of 335–493 °C (CB concentration = 1000 ppm; GHSV ≈ 9000 h⁻¹; O₂ = 21 vol.%) [41]. No organic reaction byproducts can be detected over CuCeO₅ (Sₐldehyde > 99%) and co-CuCeO₅ (Sₐcetic acid > 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 Eₐ for CB combustion over various ACeOₓ catalysts is 89.7–121.8 kJ/mol, and the mesostructured CuCeO₅ possesses much higher reaction rate (8.21 × 10⁻⁵ mol/(gcat·h)) for CB oxidation than the other ACeOₓ catalysts (2.43 × 10⁻⁵–5.04 × 10⁻⁵ mol/(gcat·h)), co-CuCeO₅ (5.99 × 10⁻⁵ mol/(gcat·h)), im-CuCeO₅ (2.82 × 10⁻⁵ mol/(gcat·h)), and CeO₂ (1.78 × 10⁻⁵ mol/(gcat·h)). Among the Cu-doped catalysts, the mesoporous CuCeO₅ catalyst shows a much higher catalytic activity for CB destruction than the co-CuCeO₅ and im-CuCeO₅ catalysts, and its reaction rate reaches 27.41 × 10⁻⁵ mol/(gCeO₂·h) at 330 °C, obviously higher than the co-CuCeO₅ (9.40 × 10⁻⁵ mol/(gCeO₂·h)) catalysts. The rₐ values for CB combustion are ranked as CuCeO₅ > co-CuCeO₅ > CeO₂ > MnCeO₅ > FeCeO₅ > im-CuCeO₅ > ZrCeO₅ > CeO₂, 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 Eₐ value of the CuCeO₅ catalyst is lower than that of the other ACeOₓ samples. The above results demonstrate that the mesostructured CuCeO₅ 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...
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 ($T_{50} = 299$ °C) than the CoCeO$_x$ ($T_{50} = 304$ °C), FeCeO$_x$ ($T_{50} = 348$ °C), and MnCeO$_x$ ($T_{50} = 345$ °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 FeCeO$_x$ > CuCeO$_x$ > co-CuCeO$_x$ > CoCeO$_x$ > CeO$_2$ > MnCeO$_x$ ≈ ZrCeO$_x$ > 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 CuCeO$_x$ > co-CuCeO$_x$ > CoCeO$_x$ > FeCeO$_x$ ≥ MnCeO$_x$ > im-CuCeO$_x$ > ZrCeO$_2$ ≥ 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.
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\textsuperscript{n+}) are incorporated into CeO\textsubscript{2} crystallites, and the interaction of A\textsuperscript{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\textsubscript{x} demonstrates a much higher catalytic activity (r = 8.21 × 10\textsuperscript{-5} mol/(g\textsubscript{cat}·h)) for CB destruction than the other catalysts (r = 1.78 × 10\textsuperscript{-5}–5.04 × 10\textsuperscript{-5} mol/(g\textsubscript{cat}·h)). The excellent catalytic activity of CuCeO\textsubscript{x} catalysts can be primarily attributed to the superior reducibility of the active phase during CB oxidation. The mesostructured CuCeO\textsubscript{x} oxide is a promising catalyst for CVOC elimination.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>A'</td>
<td>pre-exponential factor</td>
</tr>
<tr>
<td>ΔH\textsubscript{H2}</td>
<td>H\textsubscript{2} consumption amount below 200 °C</td>
</tr>
<tr>
<td>α\textsubscript{111}</td>
<td>lattice parameter</td>
</tr>
<tr>
<td>A\textsuperscript{H2}</td>
<td>initial H\textsubscript{2} consumption rate</td>
</tr>
</tbody>
</table>

Fig. 5. H\textsubscript{2}-TPR profiles of (a) CeO\textsubscript{2}, (b) CoCeO\textsubscript{x}, (c) CuCeO\textsubscript{x}, (d) FeCeO\textsubscript{x}, (e) MnCeO\textsubscript{x}, (f) ZrCeO\textsubscript{x} (g) co-CuCeO\textsubscript{x} and (h) im-CuCeO\textsubscript{x}.

Fig. 6. Initial H\textsubscript{2} consumption rate as a function of inverse temperature of various samples.

Fig. 7. O\textsubscript{2}-TPD patterns of (a) CeO\textsubscript{2}, (b) CoCeO\textsubscript{x}, (c) CuCeO\textsubscript{x}, (d) FeCeO\textsubscript{x}, (e) MnCeO\textsubscript{x}, (f) ZrCeO\textsubscript{x}, (g) co-CuCeO\textsubscript{x}, and (h) im-CuCeO\textsubscript{x}.
Fig. 8. CB conversion and primary reaction byproduct distribution over synthesized catalysts (300 mg catalyst, 500 ppm CB, 21 vol.% O2, N2 balance; GHSV = 30,000 h−1).

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