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Facile preparation of 3D ordered mesoporous $\text{CuO}_x\text{-CeO}_2$ with notably enhanced efficiency for the low temperature oxidation of heteroatom-containing volatile organic compounds†

Chi He,^{ab} Yanke Yu,^a Changwei Chen,^a Lin Yue,^c Nanli Qiao,^c Qun Shen,^d Jinsheng Chen^{*a} and Zhengping Hao^{*c}

SBA-16 silica with intact surface hydroxyl groups was quickly obtained (5 min) via a fast-microwave-assisted method, and further adopted as an efficient template for the synthesis of three-dimensional (3D) ordered mesoporous $\text{CuO}_x\text{-CeO}_2$ catalysts (htpCCx) through a simple and reproducible host-guest interaction. XRD, XPS, H_2 -TPR, and Raman results reveal that many of the Cu^{2+} ions in htpCCx are incorporated into the CeO_2 lattice, leading to the formation of a $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution, which produces a large number of oxygen vacancies and enhances the reducibility of the metal. The interaction of Cu and Ce is essential to the reaction as it maintains the $\text{Cu}^{2+}/\text{Cu}^{1+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples. The catalyst has a 3D mesostructure and possesses remarkably enhanced low-temperature activity for the combustion of epichlorohydrin. HtpCC20 has been identified as the most powerful catalyst for this reaction, with the reaction rate at 165 °C being about 6.3 and 33.3 times higher than those of catalysts synthesized using conventional incipient impregnation and thermal combustion methods, respectively. Furthermore, htpCC20 shows superior CO_2 selectivity (>99%) and stability (no deactivation occurs after 50 h reaction). It is believed that the dispersion of the active phase, density of surface active oxygen, and low-temperature reducibility are the dominant factors governing the catalytic performance.

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1. Introduction

The development of effective methods for the environmentally friendly removal of VOCs emitted from industrial processes and municipal incineration is of great importance considering their high toxicity and contribution to major environmental problems such as ozone formation/depletion, aerosols, and global warming.¹ The catalytic oxidation of VOCs offers interesting advantages over conventional flame combustion or other treatment approaches. It can be carried out at low temperature, thereby reducing or even avoiding the use of an auxiliary fuel, as well as inhibiting the formation of thermal

NO_x and other more harmful by-products.² Moreover, catalytic oxidation techniques are feasible at any fuel-to-oxidant ratio, thus allowing for the treatment of streams with very low hydrocarbon concentrations.^{3,4} The key challenges are still how to design and prepare low-cost and highly efficient catalysts for the low-temperature catalytic combustion of VOCs, especially for heteroatom (Cl, N, S, *etc.*) containing pollutants.⁵ Supported or unsupported noble metal catalysts (mainly Pd and Pt) and transition metal oxides (Co, Cu, Mn, Cr and Ni) that can exist as single or mixed oxides are usually employed for the complete oxidation of VOCs. Noble metals are catalytically more active at low temperature in comparison to other metal oxides, however they are expensive and rapid deactivation by chlorine or sulfur poisoning greatly limits their large-scale application for the elimination of S-VOCs and Cl-VOCs.^{3,6,7} CeO_2 has recently attracted considerable attention as an efficient catalyst due to its abundant oxygen vacancy defects, high oxygen storage capacity and the relatively easy shuttle between its Ce^{3+} and Ce^{4+} oxidation states.^{8–10} However, CeO_2 is deactivated quickly when used for the decomposition of Cl-VOCs due to the strong adsorption of HCl or Cl_2 on to its surface, which blocks the active sites.¹¹ Researchers have found that the stability of CeO_2 could be

^aKey Lab of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, P. R. China. E-mail: jschen@iue.ac.cn; Fax: +86 592 6190765; Tel: +86 592 6190765

^bDepartment of Environmental Science and Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China

^cDepartment of Environmental Nano-materials, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China. E-mail: zpinghao@rcees.ac.cn; Fax: +86 10 62923564; Tel: +86 10 62923564

^dResearch Center for Greenhouse Gases and Environmental Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, P. R. China

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improved if the adsorbed Cl_2 or Cl^- was removed or transferred rapidly enough.^{1,9} Among transition metal oxides, chromium, manganese and copper oxides are estimated to be the most active catalysts for the oxidation of heteroatom-containing VOCs (HCVOs). Copper and its compounds have been widely applied in the study of dechlorination reactions and have achieved good results.^{12–14} For instance, Huang *et al.* have reported that a CuO modified USY zeolite possessed good activity and high selectivity for Cl-VOC decomposition.¹⁵ Adding ceria as a promoter to copper oxide has many advantages for catalytic performance: 1) it stabilizes the dispersion of the active Cu phase;¹⁶ 2) it acts as an oxygen storing phase ($\text{Ce}^{3+}/\text{Ce}^{4+}$) and strongly affects the copper redox properties;^{17–20} and 3) it creates structural defects and improves the oxygen storage capacity and diffusivity.^{19,21,22} However, studies concerning the low-temperature catalytic combustion of HCVOs using CuO–CeO₂ have seldom been reported, despite the material being proven to have excellent catalytic activities for the oxidation of many VOC pollutants.^{23,24}

At present, the primary issues for the oxidation of HCVOs using transition metal oxides are how to improve the catalytic activity, reaction durability, and thermal stability. Different protocols have been reported for the synthesis of highly efficient transition metal oxide-loaded catalysts in previous studies, such as sol-gel, incipient impregnation, urea-nitrate combustion, coprecipitation, and one-pot polymeric precursors, however, the surface areas and total pore volumes of the obtained catalysts were rather low.^{9,25–27} In order to overcome the aforementioned problems, porous supports (*e.g.*, $\gamma\text{-Al}_2\text{O}_3$ and USY zeolite) are usually adopted, however, the metal oxide content has to always be controlled in order to avoid aggregation of the active phase.^{15,28–30} Mesoporous transition metal oxides with d-shell electrons confined to nanosized walls, redox active internal surfaces, and connected pore networks demonstrate extremely fascinating prospects for use in catalysis, energy conversion and storage, as well as gas sensing, adsorption, and separation.^{31–33} The use of soft templates (*e.g.*, chelating agents and surfactants) and hard templates (*e.g.*, mesoporous materials and carbon nanotubes) has led to some wonderful contributions.^{34–36} Compared with soft templates, hard templates have some advantages for the preparation of ordered mesoporous arrays. Supramolecular mesoporous silica templates (MCM41S, SBA-15, KIT-6, SBA-16, *etc.*) have uniform mesocavities, high surface areas, and large pore volumes, which makes them the perfect candidates to serve as “hard templates”.^{35,37,38} Among these, SBA-16 has three-dimensional (3D) channels and a cubic *Im3m* (body-centered cubic arrangement of cages with 8 apertures to the nearest neighbors) structure, which could be more favorable for mass and thermal transfer than a unidirectional pore system.³⁹ In order to introduce the maximum quantity of metal precursors, as many silanol groups as possible must be retained during the preparation of the silica template. In our previous work, we found that the mesochannels of SBA-15 and KIT-6 were far from completely filled by metal precursors due

to a large loss of Si–OH groups during the organic template removal process that involved a thermal calcination,^{40,41} and this phenomenon has also been reported by other groups.^{35,42,43} Other approaches such as using solvents and supercritical fluid extraction require long periods of operation (>24 h) and it is difficult to remove the organic template completely.⁴⁴ Tian *et al.* proposed microwave irradiation as an effective technique for making organic templates such as Pluronic P123 quickly and with total removal of the one-dimensional (1D) SBA-15 material with the greatest preservation of the original mesoporous structure and surface hydroxyl groups.⁴⁵ In this work, we report a fast-microwave-assisted (FMA) method, which can completely remove triblock copolymers P123 and F127 within 5 min. We demonstrate that the obtained material is a powerful host for the production of crystalline 3D ordered CuO_x–CeO₂ with a high BET surface area (>100 m² g^{−1}) and large pore volume (>0.17 cm³ g^{−1}). Moreover, the application of this FMA technique for the convenient and fast preparation of other mesostructured metal oxides could be expected.

Numerous active materials such as porous clay/silica-supported catalysts and hydrotalcite-derived metal oxides have been successfully developed for the elimination of VOCs (*e.g.*, alkane and arene) in our previous work.^{46–50} Herein, for the first time, we have prepared a series of 3D ordered mesoporous CuO_x–CeO₂ catalysts through reverse replication of the structure of FMA-SBA-16 for use in the low temperature oxidation of epichlorohydrin (ECH: a representative and highly toxic HCVO widely used in industry) with the aim of developing a more efficient catalyst for HCVO removal. The catalytic performance of these materials was extensively compared to that of the corresponding single oxide, and the CuO_x–CeO₂ binary oxides synthesized *via* traditional incipient impregnation, coprecipitation and thermal combustion methods. The central issues addressed in this study include: 1) the proposition of a simple and reproducible approach for the synthesis of ordered mesoporous metal oxides; 2) the development of practical and highly effective transition metal-loaded catalysts for the low-temperature removal of HCVOs; 3) the illumination of the role and contribution of physico-chemical properties (*e.g.*, surface area, pore structure, surface state, reducibility, and active oxygen mobility) to the catalytic performance and durability; and 4) the investigation of the nature of the active sites and the role of copper and ceria in the binary metal oxides in order to elucidate a possible reaction mechanism.

2. Experimental

2.1. Synthesis of the SBA-16 silica template

Stucky *et al.*⁵¹ found that the EO/PO ratio of a Pluronic copolymer could be used to tailor the pore diameter, pore entrance size, and structural order of SBA-16. Ryoo *et al.*³⁸ proposed that the obtained SBA-16 possessed the largest possible pore diameter and pore window size as well as the

highest possibility of forming an ordered structure when a mixture of P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) with an EO/PO ratio of 16/7 was adopted. Therefore, in the present work, SBA-16 was prepared under acidic conditions using two poly(alkylene oxide)-type triblock copolymers, Pluronic 123 and F127, as structure-directing agents and tetraethyl orthosilicate (TEOS) as a silica source. Briefly, 0.48 g of P123 and 2.41 g of F127 were dissolved in 142 mL of 2 M HCl solution at 35 °C. Afterward, 11.6 mL of TEOS (98%) was added to the solution, and magnetic stirring was continued for 20 min at 35 °C. The mixture was kept under static conditions in an oven for 24 h at the same temperature, and then aged at 100 °C for 24 h. The recovered precipitate was filtered and dried at 100 °C without washing to obtain SBA-16. The P123 and F127 organic templates in the as-made SBA-16 were totally removed within 5 min with a FMA technique using an XT-9912 microwave preparation system (Shanghai Xintuo Co., China). Briefly, 1.0 g of as-made SBA-16, 6.67 mL of concentrated HNO_3 , and 3.25 mL of H_2O_2 (30 wt%) were digested in a Teflon vessel for 5 min using an operating power, reaction temperature and pressure of 1300 W, 250 °C and 2.0 MPa, respectively. The obtained sample was washed with deionized water and ethanol, and then dried at 40 °C in order to obtain FMA-SBA-16.

2.2. Catalyst preparation

$\text{CuO}_x\text{-CeO}_2$ catalysts with 3D ordered mesoporous structures were synthesized using a simple thermolysis process. Typically, different amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.13–0.41 g) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1.75–2.25 g) were dissolved in 18 mL of ethanol. Dry FMA-SBA-16 samples (0.43 g per group) were then added to the above solutions. After stirring for 6 h, the solutions were transferred to clean Petri dishes and the solvent was evaporated. Next, the hybrid samples were thermally calcined at 550 °C for 4 h at a heating rate of 2 °C min^{-1} . The metal oxides were obtained in very high yields by solution etching the silica framework using 0.1 M NaOH at 80 °C for 12 h. The $\text{CuO}_x\text{-CeO}_2$ materials were washed with distilled water and ethanol and then recovered using centrifugation. The final catalysts with different Cu content are denoted as htpCCx, while the used catalysts are denoted as htpCCxu. For comparison, $\text{CuO}_x\text{-CeO}_2$ binary oxides with Cu loading of 30 wt% were prepared using conventional incipient impregnation, coprecipitation, and thermal combustion methods following literature procedures,^{27,28,52} and the related catalysts are denoted as impCC30, copCC30 and tcbCC30, respectively. Moreover, bulk-CuO and bulk-CeO₂ single oxides were also synthesized by thermal calcination of the corresponding hydrated metal nitrates at 550 °C for 4 h.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using a Philips X'Pert powder diffraction system with Cu-K α radiation ($\lambda = 0.15418$ nm) in the 2θ ranges of 0.6–5° (scanning rate of 0.10° min^{-1}) and 10–80° (scanning rate of 4° min^{-1}). N_2 adsorption/desorption isotherms of the catalysts were measured at 77 K using a Quantachrome NOVA 1200e gas sorption analyzer. All samples were degassed under vacuum at 300 °C for 3 h before 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 N_2 isotherm using the Barrett-Joyner-Halenda (BJH) method. The actual Cu content was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) with a PerkinElmer OPTIMA 7000 DV spectrometer. Thermogravimetric analysis (TGA) was performed using a Netzsch 209 F3 Tarsus thermo-microbalance from 50 to 900 °C at a heating rate of 10 °C min^{-1} under a stream of O_2/N_2 . Fourier transform infrared spectra (FT-IR) were obtained using a Nicolet IS10 IR spectrometer by measuring the absorbance on KBr pellets (2 wt% sample and 98 wt% KBr). Transmission electron microscopy (TEM) images were obtained using a Hitachi H-7650 microscope operating at an acceleration voltage of 80 kV. Field emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi S-4800 microscope equipped with an EDX detector for composition analysis of the synthesized catalysts. Temperature programmed reduction (H_2 -TPR) experiments were performed using a Quantachrome ChemBET 3000 TPR-TPD analyzer. Prior to reduction, 50 mg of the catalyst was heated in a 5% O_2/He flow (50 mL min^{-1}) from room temperature to 500 °C and held at this temperature for 30 min, before treatment with a stream of He at room temperature for 30 min in order to remove any residual oxygen. Finally, the sample was reduced under a 5% H_2/He flow (50 mL min^{-1}) from 50 to 700 °C at a heating rate of 10 °C min^{-1} . 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 pre-heated in a 5% O_2/He flow (50 mL min^{-1}) at 500 °C for 30 min, then the sample was heated from 50 to 800 °C at a heating rate of 10 °C min^{-1} under a stream of pure He. X-ray photoelectron spectroscopy (XPS) experiments were carried out with 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. Raman spectra were obtained using a Horiba Jobin Yvon S.A.S. LabRAM Aramis spectrometer at ambient temperature and under moisture-free conditions. The emission line at 532 nm from an Ar⁺ ion laser was focused in order to analyze a spot of about 1 mm. The time for acquisition was varied according to the intensity of the Raman scattering, and the wave numbers obtained from the spectra were accurate to within 1 cm^{-1} . Diffuse reflectance UV-visible (DRUV-Vis) spectra were obtained using a Hitachi UV-3000 spectrophotometer under ambient conditions with spectral grade BaSO_4 as a reference material. X-ray absorption fine structure (XAFS) data for the htpCCx materials were measured using a 4W1B beam line at the Beijing Synchrotron Radiation Facility (BSRF). The spectral range from 8.820 to 9.640 keV for the K-absorption edge at 8.990 keV was collected under ambient conditions. A Si (111) monochromator crystal was used and the XAFS spectra of the adsorption samples were collected with a Lytle ionization detector in fluorescence mode. An average of three scans was performed in order to achieve an adequate signal/noise ratio, and the energy of the Cu K-absorption edge was calibrated with Cu foil. The XAFS data were processed

following the standard procedure of background absorption removal: normalization, conversion to k -space and Fourier transformation. Extended X-ray absorption fine structure (EXAFS) geometric information was extracted using WINXAS 3.1 software. A linear function fit for the pre-edge region and a second-order polynomial fit in the post-edge region were used for the normalization in order to remove the background absorption. The normalized EXAFS spectra were converted to the EXAFS function $\chi(k)$ (where k is the wavenumber of the photoelectron) using a cubic spline-fit and k^3 -weighting. The $k^3\chi(k)$ spectra were then converted into R space by Fourier transforming the region between 2.6 to 9.9 $\text{\AA}^{-1}$ without using a window function.

2.4. Catalytic activity measurement

All evaluation experiments were performed at atmospheric pressure in a continuous-flow fixed-bed reactor, containing a stainless steel tube (6 mm internal diameter) that was filled with the catalyst. VOC-containing gas was generated by bubbling air through a VOC saturator, which was then further diluted with another air stream, before reaching the reaction bed. The temperatures of the catalyst bed and tubular electric furnace were monitored automatically using E -type thermocouples. In each test, 300 mg of the catalyst (40–60 mesh) was placed at the middle of the tube reactor and the total flow rate was maintained at 200 mL min^{-1} , *i.e.*, a gas hourly space velocity (GHSV) of 18 400 h^{-1} , and the O_2 feed concentration was kept at about 21 v/v%. In each test, the catalyst bed temperature was first raised to 120 $^\circ\text{C}$ with the feed stream passing and stabilized for 30 min. The temperature was then increased to the next desired value at a heating rate of 5 $^\circ\text{C} \text{ min}^{-1}$ and stabilized for 20 min prior to online analysis of the effluent gas composition using a gas chromatograph (GC9890A, Shanghai Linghua Co., China) equipped with an electron capture detector (ECD) and flame ionization detector (FID). The concentrations of organic chlorinated compounds in the feed and effluent streams were determined and quantified by the ECD, while other by-products were identified by the FID and a Pfeiffer Omnistar online mass spectrometer.

3. Results

3.1. Template removal and preparation of 3D mesoporous $\text{CuO}_x\text{-CeO}_2$ oxides

FT-IR transmission spectra of the as-made SBA-16, FMA-SBA-16, and calcined SBA-16 samples are shown in Fig. 1. A broad band at around 3400 cm^{-1} that appears in all of the samples is partially caused by the O–H stretching vibration of adsorbed water molecules, whose bending vibration mode is also responsible for the band recorded at around 1630 cm^{-1} . The IR absorption bands centered at 2936 and 1466 cm^{-1} , shown in the spectrum of as-made SBA-16 can be assigned to the C–H bond stretching and bending vibrations of the P123 template,⁴⁵ however these absorptions are nearly indiscernible in the spectra of the FMA-SBA-16 and calcined SBA-16 samples. This suggests that both the FMA and calcination methods can efficiently remove the organic P123 template. Remarkably, the

Fig. 1 FT-IR spectra of (a) as-made SBA-16, (b) FMA-SBA-16, (c) calcined SBA-16, and (d) htpCC20.

relative intensity of the Si–OH bending vibrations centered at 957 cm^{-1} is almost the same for the as-made SBA-16 and FMA-SBA-16 samples, but much weaker for the calcined sample, indicating that a high level of silanol groups are preserved on the interior and exterior pore wall surfaces during the FMA process while the thermal calcination inevitably decreases their number. The thermal stability of the aforementioned samples was investigated using TGA (Fig. S1, ESI†). TGA curves reveal weight losses of approximately 9.0% for the FMA-SBA-16 and 7.9% for the calcined SBA-16, which are much lower than that of the as-made SBA-16 (about 34.8%). The results from the FT-IR spectra and TGA clearly indicate that the FMA technique leads to fast and thorough removal of the template, while simultaneously preserving the integrity of the surface hydroxyl groups.

Briefly, the formation of the final nanostructured mesoporous $\text{CuO}_x\text{-CeO}_2$ catalysts required the following four steps: firstly, the 3D mesoporous SBA-16 siliceous templates with abundant surface silanol groups were synthesized using the FMA approach. Secondly, the related hydrated metal nitrate precursors were introduced *via* highly enhanced host–guest interactions such as hydrogen bonding, Coulombic interactions, coordinating interactions, and van der Waals interactions.⁵³ Thirdly, the mesostructured pattern was formed and the guest materials crystallized using the thermal calcination method. Fourthly, the silica host was etched with a dilute NaOH aqueous solution in order to obtain the final mesostructured binary metal oxides. Fig. 2A shows the small-angle XRD (SA-XRD) patterns of the synthesized materials in the 2θ range of 0.7–5 $^\circ$. Both the calcined and FMA treated samples have one intense diffraction peak at around 0.8 $^\circ$, alongside two other weak peaks between 1.1–2.0 $^\circ$, which can be assigned to the (110), (200) and (211) reflections of the cubic $Im\bar{3}m$ mesostructure.³⁸ The htpCC10 and htpCC20 oxide catalysts possess (110) and (200) reflections between 0.7–1.1 $^\circ$, which indicate that the uniform pore structure of FMA-SBA-16 is well retained. Furthermore, the diffraction peaks appear to become

Fig. 2 (A) SA-XRD patterns of (a) calcined SBA-16, (b) FMA-SBA-16, (c) as-made SBA-16, (d) htpCC10, (e) htpCC20, and (f) htpCC30; (B) WA-XRD profiles of (a) bulk-CeO₂, (b) htpCC10, (c) htpCC20, (d) htpCC30, (e) copCC, (f) impCC, (g) tcbCC, and (h) bulk-CuO.

weaker or even disappear with increasing Cu content, which indicates that the ordered mesoporous structure decreases to some extent.

3.2. Crystal phase and textural properties of the prepared samples

Fig. 2B shows the wide-angle XRD (WA-XRD) patterns of the samples synthesised using different preparation methods and with differing Cu/(Cu + Ce) loading. The distinct fluorite-type oxide structure of CeO₂ was present in each sample (JCPDS No. 81-0792). No diffraction peaks corresponding to CuO or Cu₂O could be identified, except in the cases of impCC and tcbCC (JCPDS No. 80-1268). The absence of CuO peaks can probably be attributed to: 1) the fine dispersion of CuO in the form of

small clusters on the ceria surface, which cannot be detected using XRD;^{54,55} 2) the incorporation of CuO into the CeO₂ lattice, or a combination of these two phenomena.^{56,57} The lattice parameters of the CeO₂ unit cell were obtained from the position of the (111) diffraction peak and are listed in Table 1. The slight decrease in the bulk-CeO₂ (5.4276 Å) lattice parameter after the addition of the copper species is evidence that Cu ions are partly incorporated into the CeO₂ crystallites, probably forming Cu–O–Ce species, especially considering that the radius of a Cu²⁺ ion (0.073 nm) is smaller than that of a Ce³⁺ (0.110 nm) or Ce⁴⁺ ion (0.097 nm).⁵⁷ Additionally, the lattice microstrain was calculated, and the value related to bulk-CeO₂ (8.7×10^{-3}) was found to be somewhat lower than those of the CuO_x–CeO₂ binary oxides (8.8×10^{-3} – $14.3 \times$

Table 1 Physicochemical characteristics of the synthesized catalysts

Sample	Nom. ^a (wt%)	ICP ^b (wt%)	XPS ^c (wt%)	d_{110} ^d (nm)	a_{111} (Å)	C_s ^e (nm)	L_s ^f ($\times 10^{-3}$)	S_{BET} ^g (m ² g ⁻¹)	D_v ^h (cm ³ g ⁻¹)	D_p ⁱ (nm)
htpCC10	10	9.1	11.7	6.4	5.4217	15.6	8.9	128.8	0.28	5.2
htpCC20	20	20.6	22.5	6.1	5.4179	12.2	11.6	117.9	0.24	4.9
htpCC30	30	28.9	35.3	5.7	5.4173	10	14.3	108.2	0.17	4.0
copCC	30	31.1	32.2	—	5.4152	10	14.1	86.5	0.14	3.1
impCC	30	29.3	37.1	—	5.4148	15.7	8.8	59.1	0.16	5.5
tcbCC	30	30.5	42.6	—	5.4125	64.1	2.2	3.9	0.01	5.3
bulk-CeO ₂	—	—	—	—	5.4276	16	8.7	60.8	0.18	6.1
bulk-CuO	—	—	—	—	—	—	—	1.1	—	5.4

^a Nominal Cu content in the synthesized samples. ^b The Cu value estimated using XPS analysis. ^c Actual Cu content obtained from the ICP-OES analysis. ^d Interplanar spacing of the (110) plane, calculated using Bragg's law. ^e Crystallite size. ^f Lattice microstrain value calculated from the (111) reflection of CeO₂ using the Scherrer equation. ^g BET specific surface area calculated at $P/P_0 = 0.05$ – 0.25 . ^h Total pore volume estimated at $P/P_0 = 0.99$. ⁱ BJH pore diameter calculated from the desorption branch.

10^{-3}) due to the incorporation of Cu. The ICP-OES results listed in Table 1 reveal that the actual Cu content in the final catalyst is approximately equal to the theoretical Cu loading. Moreover, the surface composition of the synthesized samples was further estimated using XPS (Table 1). It can be concluded that the Cu species are uniformly distributed in htpCCx and copCC from the surface through to the interior. In contrast, there is a surface enrichment of Cu oxide for the impCC (37.1%) and tcbCC (42.6%) samples, which is consistent with the XRD results (Fig. 2B (f and g)).

The N_2 adsorption/desorption isotherms and pore size distribution of all of the synthesized catalysts are shown in Fig. S2 (ESI†), while the specific surface area (S_{BET}), mean pore diameter (D_p), and total pore volume (D_v) are listed in Table 1. It is clear that htpCC10 and htpCC20 possess type IV isotherms with a typical H2 type hysteresis loop, characteristic of an ordered mesoporous cage-like ($Im3m$) structure according to IUPAC classification.⁵⁸ This result demonstrates good reverse replication of the mesostructure of the FMA-SBA-16 template by the metal nitrate precursors *via* a simple host-guest interaction. However, the pore order is decreased when the Cu content is further increased, which is in good agreement with the XRD results (Fig. 2A (f)). In general, the D_v values (0.17 – 0.28 cm^3 g^{-1}) of the htpCCx catalysts are larger

than those of the samples synthesized *via* other approaches (0.01 – 0.16 cm^3 g^{-1}). However, the D_p values of the htpCCx samples (*ca.* 4.0 – 5.2 nm) are a little lower than those of impCC (*ca.* 5.5 nm) and tcbCC (*ca.* 5.3 nm). The values for the interplanar spacing (d_{110}) of the mesoporous $CuCeO_x$ samples are listed in Table 1, and the results reveal that the mesoporous mixed metal oxides possess larger interplanar spacings (*ca.* 5.7 – 6.4 nm) than that of the Si-based SBA-16 template (*ca.* 5.5 nm). Noticeably, the S_{BET} values (108.2 – 128.8 m^2 g^{-1}) of all of the htpCCx samples are much higher than those of the other catalysts and single metal oxides (0.1 – 86.5 m^2 g^{-1}). All of the S_{BET} , D_v , and D_p values are gradually reduced with the increasing copper loading, as shown in Table 1.

Further information about the microstructure of the as-prepared CuO_x – CeO_2 mixed oxides, as well as the FMA-SBA-16, is provided using TEM (Fig. 3). Long-range ordered pores arranged in a 3D mesoporous structure can be observed for FMA-SBA-16, htpCC10, and htpCC20, with average pore diameters of *ca.* 4.7 , 5.5 , and 5.2 nm, respectively (Fig. 3a–d). TEM also shows that htpCC30 has a smaller pore diameter (*ca.* 5.0 nm) and a lack of long-range order, which is consistent with the XRD and N_2 sorption results (Fig. 2, Fig. 3e, and Fig. S2, ESI†). The nanoparticles of the copCC sample, synthesized

Fig. 3 Representative TEM images of the various catalysts: (a) FMA-SBA-16, (b) htpCC10, (c) htpCC20 [100], (d) htpCC20 [111], (e) htpCC30, (f) copCC, (g) impCC, (h) tcbCC, and (i) htpCC20u.

Fig. 4 FE-SEM images of (a) FMA-SBA-16, (b) bulk-CeO₂, (c) htpCC20 (insets: magnified SEM patterns and EDS spectra), (d) copCC, (e) impCC, and (f) tcbCC.

using a coprecipitation protocol, exhibit a well dispersed morphology with an average crystallite size of *ca.* 17 nm (Fig. 3f), while the metal precursors are prone to agglomerate into clusters with calculated diameters greater than 40 and 200 nm for the impCC and tcbCC catalysts, respectively (Fig. 3g and h). Fig. 4 shows typical FE-SEM images of the prepared samples. The SEM image of FMA-SBA-16 (Fig. 4a) indicates that the most commonly observed particle morphology is that of rhombidodecahedron-shaped single crystals, which is in accordance with the crystal model of the cage-like *Im3m* structure.⁵⁹ The htpCC20 sample possesses a porous and coarse surface morphology, which is different to that of the pure siliceous FMA-SBA-16 template probably due to breakage of the long-range order of the original mesopores (Fig. 4c). EDX results reveal that the Cu content of htpCC20 (22.13 wt%) is close to the nominal value (Fig. 4c, inset). The copCC, impCC, and tcbCC samples are composed of nanocrystallites with diameters ranging from dozens to hundreds of nanometers, moreover these nanosized particles are badly aggregated in the tcbCC sample (Fig. 4d–f).

3.3. Surface composition and reducibility of the synthesized catalysts

The surface composition and chemical state of the elements that exist in the CuO_x–CeO₂ catalysts were further investigated using XPS. Fig. 5 shows a comparison of the Cu 2p, Ce 3d, and O 1s XPS binding energies (BE), as well as the Cu LMM Auger kinetic energy, of the catalysts with different Cu loadings and synthesis methods. The presence of a shake-up peak and a high Cu 2p_{3/2} binding energy (BE > 933.1 eV) are two major XPS features that are characteristic of Cu²⁺ species, while a lower Cu 2p_{3/2} binding energy (BE = 932.2–933.1 eV) and the absence of a shake-up peak are characteristic of reduced copper (Cu¹⁺ or Cu⁰).⁶⁰ The Cu 2p spectra of the CuO_x–CeO₂ (Fig. 5) catalysts possessed shake-up peaks of weak intensity (especially for the htpCCx samples) between 940–947 eV and Cu 2p_{3/2} binding energy peaks at 934.5 (the principal peak) and 932.4 eV. The lower Cu 2p_{3/2} binding energy (932.4 eV) and weak intensity of the shake-up satellite structure suggest the presence of reduced copper species. The degree of reduction of the Cu species can be studied by determining the *I*_{sat}/*I*_{pp} ratios (Table 2).⁶¹ The *I*_{sat}/*I*_{pp} values in this work are in the range of 0.11–0.37, which are between the values of 0.57 for pure Cu²⁺

Fig. 5 Cu 2p, Auger LMM kinetic energy, Ce 3d, and O 1s XPS spectra of (a) htpCC10, (b) htpCC20, (c) htpCC30, (d) copCC, (e) impCC, and (f) tcbCC.

and zero for pure Cu^{1+} ,⁶² indicating the presence of a reduced Cu phase in all of the samples. The Auger Cu LMM lines were further investigated for all of the $\text{CuO}_x\text{-CeO}_2$ samples in order

to clarify the composition of the reduced copper species as the Cu $2p_{3/2}$ binding energy cannot be used to distinguish between Cu_2O and Cu^0 . The broad features of the kinetic energy spectra

Table 2 Characteristic data and a summary of the XPS and H_2 -TPR analysis results

Sample	$I_{\text{sat}}/I_{\text{pp}}^a$	$\text{Ce}^{3+}/\text{Ce}_{\text{tot}}^b$	T_{fr}^c (°C)	$L_{\text{H}_2}^d$ ($\mu\text{mol g}^{-1}$)	$H_{\text{H}_2}^e$ ($\mu\text{mol g}^{-1}$)	Cu (%)	Ce (%)	O (%)	O_{sd}^f (%)		
									O_{latt}	O_{sur}	O_{ads}
htpCC10	0.17	0.37	159	194.3	679.9	2.2	15.1	82.7	61.1	36.5	2.4
htpCC20	0.14	0.39	103	868	1416.6	5.2	13.6	81.2	42	45.9	12.1
htpCC30	0.11	0.38	95	979.5	1547.3	7.7	14.1	78.2	51.4	42.1	6.5
copCC	0.22	0.33	99	693.7	1172.1	8.0	16.8	75.2	58.3	35.4	6.3
impCC	0.28	0.31	152	425.9	988.2	6.4	18.1	75.6	64.3	31.5	4.2
tcbCC	0.37	0.23	251	96.4	1014.3	15.6	21.0	63.4	67.8	25.3	6.9

^a The ratio of the Cu 2p satellite peaks to the principal peaks of the $\text{CuO}_x\text{-CeO}_2$ catalysts.

^b Ce^{3+} ratio = $\frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}} = \frac{u' + u_0 + v' + v_0}{u_0 + u + u' + u'' + u''' + v_0 + v + v' + v'' + v'''}$, and the related peak areas obtained from Fig. 6. ^c Temperature corresponding to the first reduction peak in the H_2 -TPR analysis. ^d H_2 consumption of the reduction peaks below 200 °C. ^e Total H_2 consumption of the reduction peaks from room temperature to 600 °C. ^f Oxygen species distribution in the various catalysts.

for the Auger Cu LMM electrons, shown in Fig. 5, are composed of the contribution from two Cu species. The peaks in the Auger kinetic spectra at 917.6 and 914.6 eV correspond to Cu^{2+} and Cu^{1+} species, respectively.⁶³ The coexistence of Cu^{1+} and Cu^{2+} ions in the CuO-CeO_2 catalysts prepared using various methods have been previously reported.^{27,60,62} Avgouropoulos *et al.*²⁷ and Flytzani-Stephanopoulos *et al.*⁶⁰ have proposed that Cu^{1+} species result from the strong interactions of the Cu clusters with Ce oxide. The formation of Cu^{1+} might be induced by substitution at the interface of the two oxide phases due to the similarity between the ionic radii of Cu^{1+} and Ce^{4+} .

The experimental and fitted Ce 3d spectra of the synthesized catalysts are shown in Fig. 5, and the calculated Ce^{3+} ratios are listed in Table 2. It should be noted that there is no significant difference in the $\text{Ce}^{3+}/\text{Ce}_{\text{tot}}$ ratios among the htpCCx samples with different Cu/Ce ratios, while the quantity of Ce^{3+} in the htpCCx catalysts (0.37–0.38) is slightly higher than in copCC (0.33), impCC (0.31), and tcbCC (0.23). Previous work has reported that the existence of Ce^{3+} in CeO_2 implies the formation of an oxygen vacancy, and thus, it can be inferred that the htpCCx samples possess more oxygen vacancies than the other catalysts. Furthermore, the ratios of Ce^{3+} for all of the prepared samples are much higher than that of pure CeO_2 reported in the literature ($\text{Ce}^{3+} = 0.067$), which leads to the larger lattice parameters of these samples compared to that of the reported one (Table 1). The corresponding O 1s XPS spectra of the synthesized catalysts can be resolved into three peaks by deconvolution (Fig. 5): 1) the lattice oxygen (O_{latt} , BE = 529.3 eV) and surface oxygen (O_{surf} , BE = 531.5 eV) assigned to the defect oxide or surface oxygen ions in low coordination situations and weakly bonded oxygen species; 2) adsorbed oxygen species (O_{ads} , BE = 532.8 eV) from hydroxyl species and adsorbed water as contaminants on the surface.^{9,64} Table 2 shows the oxygen species distribution in the various samples, and the results reveal that the O_{surf} values of htpCCx (>36.5%) are much higher than those of the other samples (25.3–35.4%). The htpCC20 sample has the highest percentage of O_{surf} (45.9%), followed by htpCC30 ($\text{O}_{\text{surf}} = 42.1\%$). In sharp contrast, tcbCC possesses the lowest amount of surface oxygen ($\text{O}_{\text{surf}} = 25.3\%$).

The H_2 -TPR profiles of the $\text{CuO}_x\text{-CeO}_2$ catalysts are shown in Fig. 6, and the reducibility of bulk- CeO_2 and bulk-CuO is also investigated for comparison purposes. The reduction of pure CuO commences at about 250 °C, and its reduction profile is characterized by a single peak centered at 373 °C (Fig. 6g). Pure CeO_2 shows two weak reduction peaks with apexes at 415 and 517 °C (Fig. 6h), which can be ascribed to the reduction of the surface capping and bulk oxygen of CeO_2 , respectively.⁶⁵ The reduction peaks of the $\text{CuO}_x\text{-CeO}_2$ mixed oxides are systematically shifted towards the lower temperature region compared with bulk- CeO_2 and bulk-CuO, implying that the reduction of copper and cerium oxide is promoted due to the interaction between the Cu and Ce oxide. The htpCCx catalysts have two to four reduction peaks below 500 °C, with the reductive peaks at around 100 and 170 °C attributed to the reduction of the well dispersed Cu species and Cu incorporated into the CeO_2 lattice, respectively.⁶⁶ The reduction peaks higher than 200 °C correspond to the contribution of crystal-

Fig. 6 H_2 -TPR profiles of (a) htpCC10, (b) htpCC20, (c) htpCC30, (d) copCC, (e) impCC, (f) tcbCC, (g) bulk-CuO, and (h) bulk- CeO_2 .

line CuO ,²³ and signal peaks centered at reduction temperatures exceeding 300 °C are probably associated with the reduction of CeO_2 surface oxygen. The first reduction peak decreases from 159 to 95 °C with the increasing Cu loading of the htpCCx samples (Fig. 6a–c). This is probably due to an increase in Cu–O–Ce species, which facilitate the reduction of copper species due to the reducibility of Cu–O–Ce.²² In addition, the copCC sample is more easily reduced than the impCC and tcbCC samples due to the better dispersion of the copper species,⁶⁷ which is in good agreement with the XRD and TEM results (Fig. 2 and Fig. 3). The H_2 consumption of the reduction peaks (the bulk-CuO reduction peak was used for calibration) below 200 °C and 600 °C, as well as the temperatures that correspond to the first reduction peaks are listed in Table 2. Taking into account both the H_2 consumption and reduction temperature, htpCC20 and htpCC30 possess superior reducibility compared to the other samples.

3.4. Structure characteristics of the $\text{CuO}_x\text{-CeO}_2$ catalysts

Fig. 7 shows the UV-Vis diffuse reflectance spectra of the prepared catalysts. Bulk- CeO_2 shows three characteristic peaks centered at 226, 281, and 345 nm, which can be assigned to the $f \rightarrow d$ transitions of Ce^{3+} species, low coordination $\text{Ce}^{4+}\text{-O}$ charge transfer, and interband transitions in CeO_2 , respectively.⁶⁸ The absorption peak at around 461 nm can be attributed to the emission and absorption of one photon by a Cu^{1+} complex,²⁵ indicating the presence of Cu^{1+} in the synthesised catalysts. The absorption in the 636–675 nm range corresponds to the $d\text{-d}$ transitions of Cu^{2+} in an

Fig. 7 DRUV-Vis profiles of (a) htpCC10, (b) htpCC20, (c) htpCC30, (d) copCC, (e) impCC, (f) tcbCC, and (g) bulk-CeO₂.

octahedral O_h configuration, which is more or less tetragonally distorted and the wavelength decreases as the distortion increases. For square pyramidal or tetrahedral complexes, the $d-d$ transitions are shifted towards higher wavelengths.⁶⁹ The above results indicate that the htpCC10 sample features square pyramidal or tetrahedral copper complexes, while htpCC20 and htpCC30 have copper species in octahedral O_h configurations.

The Cu K-edge XANES spectrum of the fresh htpCC20 catalyst is compared with that of the CuO, Cu₂O, and Cu foil standards in Fig. 8. The different edge energies and edge shapes of these standard materials provide important information, which can be used to identify the oxidation state and local structure of the Cu species. The weak pre-edge peak of the CuO standard at 8.978 keV can be ascribed to the dipole-forbidden electronic transition from $1s \rightarrow 3d$ in Cu²⁺, and the more intense peak between 8.982 and 8.987 keV can be attributed to dipole-allowed $1s \rightarrow 4p$ electron transitions in Cu¹⁺ and Cu²⁺, respectively.^{70,71} It can be observed that a small edge transition peak centered at about 8.981 keV appears in the spectrum of htpCC20, indicating the existence of Cu¹⁺ species. Additionally, the absence of the edge transition peaks (8.978 keV and 8.982–8.987 keV), the higher white line intensity (8.992–9.007 keV), and the different shape of htpCC20 XANES spectrum stems from the interaction between the copper species and CeO₂ because both the incorporation of Cu into the CeO₂ lattice and the strong interaction of isolated Cu and CeO₂ can lead to different electronic environments and structural properties.⁷² The inset of Fig. 8 shows the k^3 -

Fig. 8 Copper K-edge XANES spectra of htpCC20, CuO, Cu₂O, and Cu foil (inset: the Fourier transformed EXAFS spectra of htpCC20 and htpCC20u). The peak positions are uncorrected for phase shifts.

weighted Fourier transform magnitudes of the EXAFS spectra for the htpCC20 and htpCC20u catalysts. The tiny decrease of the Cu–O peak intensity after ECH oxidation at 1.5 Å suggests the reduction of a small fraction of Cu²⁺ to Cu¹⁺.⁷³ The tiny decrease of the Cu–O peak intensity during the oxidation reaction, indicating the loss of Cu–O bonds, was probably due to a small amount of the active oxygen (*O) being used to oxidize ECH without being replaced by gas phase oxygen. Moreover, no higher Cu–Cu shell peak was observed at 2.5 Å for the htpCC20u sample, indicating that the Cu ions could not be reduced to metallic Cu during the ECH oxidation, and that two redox couples, *i.e.*, Ce⁴⁺/Ce³⁺ and Cu²⁺/Cu⁺, coexisted within the htpCCx catalysts during the catalysis.

3.5. Catalytic activity and reaction by-product distribution

The catalytic behavior of the synthesized catalysts for ECH oxidation was evaluated, as shown in Fig. 9. In the temperature range of our experiments no thermal or homogeneous ECH destruction could be observed during the blank test. The CuO_x–CeO₂ catalysts have better catalytic activity for the ECH oxidation than bulk-CeO₂ and bulk-CuO. All of the htpCCx samples possess much higher low-temperature activities than those synthesized *via* other traditional protocols in this work. In particular, htpCC20 has the highest activity with the complete combustion of ECH achieved at *ca.* 204 °C, which is a much lower temperature than the other catalysts (Fig. 9A and Fig. S3, ESI†). Fig. S4 (ESI†) shows T_{10} , T_{50} , and T_{90} (the temperatures needed for the 10%, 50%, and 90% conversion of ECH) as a function of the catalyst. The temperature decrease at 50% ECH conversion for htpCC20 ($T_{50} = 143$ °C) is about 135 °C when compared with bulk-CeO₂ ($T_{50} = 278$ °C). The catalytic activity sequence of all of the prepared samples is as follows: htpCC20 > htpCC30 > htpCC10 > copCC > impCC > tcbCC > bulk-CuO > bulk-CeO₂. Fig. 9B shows Arrhenius plots for the ECH oxidation under different conditions (ECH conversion < 10%). The reaction rates (r) and activation energies (E_a) were

Fig. 9 (A) The r - T curves of ECH oxidation using the synthesized catalysts; (B) Arrhenius plot of ECH oxidation reaction (300 mg catalyst; 300 ppm ECH; 21% O₂ balanced with N₂; GHSV = 18 400 h⁻¹; reaction temperature: 120–195 °C).

estimated according to the slopes of the Arrhenius plots and are listed in Table 3. As can be seen, the htpCC20 sample possesses much higher ECH catalytic activity at low temperature. For instance, the reaction rate (r) of htpCC20 at 165 °C (r = 413.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$) is 4.04, 33.3, and 57.4 times greater than

that of htpCC10 (r = 93.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$), tcbCC (r = 12.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$), and bulk-CuO (r = 7.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$), respectively. Moreover, htpCC20 has the lowest E_a value (E_a = 113 kJ mol⁻¹) when compared to the other samples (E_a = 141.2–246.5 kJ mol⁻¹), which also indicates its superior low-temperature activity. The distribution of the reaction by-products and CO₂ selectivity using various catalysts were further investigated, as shown in Table 3 and Fig. 10. It was found that the primary reaction products were CO₂, H₂O, Cl₂, HCl, and a trace of CO. The organic chlorinated compounds could not be detected during the ECH oxidation under the reaction conditions, while a small amount of propanal and propanoic acid were observed as reaction intermediates with some of the prepared catalysts. It should be noted that there are no reaction by-products when htpCC20 and htpCC30 are used, and that the by-product concentration is directly proportion to the catalytic activity. In addition, the CO₂ selectivities listed in Table 3 prove that htpCC20 is a powerful catalyst for the oxidation of ECH at low temperature (S_{50} > 99%). The reaction determining factor and related ECH oxidation processes for the CuO_x-CeO₂ catalysts will be further discussed in the following section.

Some researchers have proposed that hydrocarbons could be used to remove the Cl species from the surface of Pt loaded catalysts and thus enhance the catalytic performance.⁷⁴ The effect of an additional hydrocarbon (hexane (HE) is selected as a typical VOC) on the activity of the most active catalyst was investigated in order to reveal the applicability of the related promotion effect in our work (Fig. 11 and Fig. S5, ESI†). For comparison purposes, the mutual effect of using ECH and HE over pure bulk-CeO₂ was also studied. The addition of HE has an obvious positive influence on ECH oxidation with the T_{50} temperature decreasing from 279 to 242 °C accordingly (Fig. S5, ESI†). This promotion effect may be explained as follows: an H-atom is abstracted from an HE molecule, which can then react with the strongly adsorbed Cl species on the surface of bulk-CeO₂ to form HCl, resulting in the recovery of some of the active sites for ECH oxidation. For htpCC20, the presence of HE has negligible influence on ECH conversion at low reaction temperatures (<150 °C), while the catalytic activity decreases at higher reaction temperatures with the T_{90} temperature increasing by about 17 °C. This decrease in the catalytic activity suggests that the consumption of surface oxygen during HE oxidation decreases the oxygen species needed to

Table 3 The catalytic performance and representative results of the kinetic measurements

Sample	T_{10}^a (°C)	T_{50}^a (°C)	T_{90}^a (°C)	S_{50}^b (%)	r^c ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	E_a^d (kJ mol ⁻¹)	R^2
htpCC10	146	191	215	98.1	93.9	170.1	0.975
htpCC20	126	143	174	99.4	413.3	113	0.986
htpCC30	135	144	195	99.2	351.7	141.2	0.927
copCC	141	198	225	97.4	120.7	159.3	0.968
impCC	152	208	240	92.3	66.1	201	0.982
tcbCC	183	232	—	89.9	12.4	205.5	0.998
bulk-CeO ₂	213	278	—	81.7	9.4	189.3	0.988
bulk-CuO	198	237	—	86.4	7.2	246.5	0.976

^a Temperatures at which 10%, 50% and 90% conversion of ECH occurred. ^b CO₂ selectivity at which 50% conversion of ECH occurred: $S_{50} = \frac{\text{mole number of CO}_2 \text{ produced}}{3 \times (\text{mole number of ECH fed})} \times 100\%$. ^c Reaction rate achieved at 165 °C. ^d Apparent activation energy obtained from the Arrhenius plot.

Fig. 10 Primary reaction product distribution: (A) propanal, and (B) propanoic acid.

remove the adsorbed Cl species, which blocks the active sites and probably deactivates the catalyst.

4. Discussion

It is generally accepted that there are many factors that influence the catalytic performance of a transition-metal oxide, including the specific surface area, pore structure, dispersion of the active phase, number of oxygen vacancies, and mobility of the active oxygen. Table 1 lists the related textural data of all of the synthesized catalysts. No relationship between S_{BET} , D_v , D_p and ECH oxidation is observed, indicating that both the surface area and pore structure are not key factors governing the catalytic performance, although the 3D mesoporous structure of the htpCCx samples could be favorable for mass and thermal transfer. It is known that the presence of oxygen vacancies favors the activation of oxygen molecules to give active oxygen adspecies, and that a good reducibility or oxygen mobility can provide a facile redox process that leads to

Fig. 11 The activity of htpCC20 and bulk-CeO₂ (300 mg catalyst; 300 ppm ECH; 1000 ppm *n*-hexane; 21% O₂ balanced with N₂; GHSV = 18 400 h⁻¹).

enhanced catalytic performance.⁷⁵ Herein, the role of each of these features is further elucidated on the basis of the experimental results.

4.1. Oxygen vacancies and the mobility of active oxygen in the composite oxides

The formation of oxygen vacancies has an important influence on catalytic activity. These defective sites can act as active centers in the catalytic reaction because the oxygen molecules of the defective oxides tend to be readily released and transferred, which can enhance the reactivity of the catalyst for HVOC oxidation.⁷⁶ The Ce 3d XPS spectra demonstrate that the htpCCx samples have larger numbers of Ce³⁺ ions, compared to copCC, impCC, and tcbCC (Table 2 and Fig. 5), indicating that there are more oxygen vacancies in the htpCCx catalysts. The oxygen vacancies in htpCCx as well as bulk-CeO₂ were further investigated using Raman spectroscopy, as shown

Fig. 12 Raman spectra of (a) htpCC10, (b) htpCC20, (c) htpCC30, and (d) bulk-CeO₂ (inset table: integrated areas for the peaks at 601 cm⁻¹).

Fig. 13 O₂-TPD patterns of (a) htpCC10, (b) htpCC20, (c) htpCC30, (d) copCC, (e) impCC, (f) tcbCC, (g) bulk-CeO₂, and (h) bulk-CuO.

in Fig. 12. Pure bulk-CeO₂ shows one sharp peak centered at 460 cm⁻¹, characteristic of the Raman shift of a fluorite-type structure.⁷⁷ The Raman spectra of bulk-CuO can be found in the literature, with three peaks at 295, 340, and 626 cm⁻¹.⁷⁸ All of the htpCCx samples exhibit the peak corresponding to bulk-CeO₂, which is shifted to lower frequencies as a result of changes to the cell parameters and the formation of oxygen vacancies in the lattice.⁷⁹ The oxygen vacancy concentration in pure CeO₂ and other CuO-CeO₂ catalysts has been indirectly measured in the literature to be in the region of 585 cm⁻¹.^{52,80} The relevant peaks of the htpCCx catalysts were deconvoluted using a Gaussian method, and the corresponding peak areas are shown in Fig. 12 (see the inset table). It can be seen that the oxygen vacancy concentration follows the order htpCC20 > htpCC30 > htpCC10 >> bulk-CeO₂, which correlates well with the catalytic performance (Table 3, Fig. 9, and Fig. 10). It is known that the higher the number of oxygen vacancies, the higher number of Cu species incorporated into the ceria lattice, which causes distortion and defective sites in the structure, according to the following equation:

where *□ is an oxygen vacancy.

O₂-TPD is an effective method to determine the mobility of oxygen species, and the results for all of the synthesized catalysts are shown in Fig. 13. Generally, the adsorbed (ad) oxygen species changes according to the following sequence:

O₂(ad) → O₂⁻(ad) → O⁻(ad) → O²⁻(lattice). The physically adsorbed oxygen O₂(ad) and chemically adsorbed oxygen O₂⁻/O⁻(ad) species are much easier to desorb than the lattice O²⁻ species.⁵⁰ The desorption of physically adsorbed oxygen is not observed for all of the catalysts. Bulk-CeO₂ shows two desorption peaks centered at 301 and 576 °C, assigned to the chemically adsorbed oxygen and lattice oxygen species, respectively, while there is no obvious oxygen species desorption from the bulk-CuO sample (Fig. 13g and h). The CuO_x-CeO₂ catalysts possess two to four oxygen desorption peaks. It is worth noting that the CuO_x-CeO₂ samples (except impCC) have oxygen species desorption peaks due to chemically adsorbed molecular oxygen, O₂⁻(ad), at very low temperatures (<220 °C), while no such desorption peak around this temperature is found for the pure bulk-CuO and bulk-CeO₂. Moreover, the htpCCx samples possess large quantities of chemically adsorbed oxygen (O₂⁻/O⁻(ad)) species in the present work is in the order htpCC20 > htpCC30 > htpCC10 > copCC > tcbCC ≈ impCC > bulk-CeO₂ >> bulk-CuO according to the deconvolution peak areas under the O₂-TPD curves below ca. 500 °C. It can be inferred that the desorbed oxygen species below 220 °C should be related to the interaction between the CuO and CeO₂ oxides. Ce 3d XPS and Raman spectra (Fig. 5 and Fig. 12) revealed that surface oxygen vacancies are always present in the CuO_x-CeO₂ oxides, which can be centers for oxygen activation. Oxygen molecules (O₂) from the gas phase can adsorb into the oxygen vacancies under the reaction conditions and be activated to form O₂⁻ or O⁻ species, which are easily desorbed below 500 °C⁸¹ and are important for the ECH oxidation reaction.

4.2. Redox properties and durability of the synthesized CuO_x-CeO₂ catalysts

The redox characteristics of the metal oxides (especially the active phase reducibility) are critical for the catalytic performance, according to the Mars-van Krevelen mechanism, which has been proven to be suitable for describing the VOC oxidation over CuO-CeO₂ type catalysts.^{82,83} According to the results of H₂-TPR and *in situ* XANES, Menon and coworkers²⁸ proposed that both Cu²⁺ and Ce⁴⁺ can be reduced during the reaction. A similar result was also found by Martinez-Arias *et al.* for CO/O₂ redox over a CuO-CeO₂ catalyst.⁸⁴ It is well-known that additional elements incorporated into a metal oxide can weaken the bonds between the metal and oxygen atoms, making the latter more reactive and mobile.²⁰ This effect will be even stronger if the added element has a lower valence than the cation it replaces (such as Cu²⁺ and Ce⁴⁺). The results of XRD, XPS and Raman spectroscopy have demonstrated that a portion of the Cu²⁺ ions (particularly in htpCCx) are incorporated into the CeO₂ lattice probably in the form of a Cu_xCe_{1-x}O_{2-δ} solid solution (Fig. 2, Fig. 5, and Fig. 12). The resulting Cu_xCe_{1-x}O_{2-δ} solid solution exhibits a lower Cu redox potential, *i.e.*, an enhanced reducibility, due to the Cu²⁺-O²⁻-Ce⁴⁺ connection, and the vacancy can be considered as a bridge for the transfer of O from Ce to Cu. Likewise, the reduction process of CeO₂ is also shifted towards lower temperatures when Ce⁴⁺ ions are substituted with Cu²⁺ ions. The H₂-TPR results in this work (Fig. 6) revealed that all of the

$\text{CuO}_x\text{-CeO}_2$ mixed oxides can be reduced at lower temperatures compared to bulk- CeO_2 and bulk- CuO . In addition, the htpCCx samples possess higher reducibilities than those of the other catalysts, which is in good agreement with the O_2 -TPD results (Fig. 13). Furthermore, the reduction temperature of copCC is much lower than that of impCC and tcbCC, which is probably due to the aggregation of CuO particles (monocrystalline CuO) on the surfaces of impCC and tcbCC (proven using WA-XRD, Fig. 2B). Huang and coworkers have proposed that the well dispersed Cu could be connected to CeO_2 via a so-called nested oxygen ion, which has a weakened Cu=O bond, thus allowing for easy reduction.⁸⁵ EXAFS spectroscopy of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ catalysts and the density functional theory (DFT) results of a $\text{Cu}_{0.25}\text{Ce}_{0.75}\text{O}_2$ catalyst from Hegde and coworkers²² have revealed the structure and chemical environment of Cu species in CeO_2 . They found that there are six O atoms around each incorporated Cu^{2+} , the nearest in the first shell at a distance of 1.92–1.95 Å. The rearrangement of the CeO_2 lattice around incorporated Cu^{2+} induces distortion and vacancies, leading to a weak Fourier transformed signal from the medium range shells.²² Likewise, the Cu^{2+} of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ in the present samples would weaken the surface oxygen bonds of the solid solution, making them more reactive and reducible (Table 2 and Fig. 6). The monocrystalline CuO particles on the impCC and tcbCC catalysts are reduced at relatively high temperatures (see Fig. 6 for the H_2 -TPR results), indicating that the monocrystalline CuO phase will only be active at higher reaction temperatures. This result suggests that the inferior catalytic performance of impCC and tcbCC can be partly ascribed to the inertia properties of crystalline CuO at low temperatures and the suppressive effect of monocrystalline CuO towards the surface active species.⁶¹

In general, catalyst deactivation is a hurdle in the commercial application of the catalytic elimination of HVOCs. The catalytic stability during the decomposition of ECH, as a function of the conversion *versus* time-on-stream,

Fig. 14 The conversion of ECH over htpCC20, copCC, impCC, tcbCC, and bulk- CeO_2 as a function of time-on-stream at various reaction temperatures (300 mg catalyst; 300 ppm ECH; 21% O_2 , balanced with N_2 ; GHSV = 18 400 h^{-1}).

was carried out by feeding a stream of gas containing 300 ppm of ECH and 21% O_2 at reaction temperatures of 225 and 300 °C (Fig. 14). As shown in Fig. 14, during the first 10 h, the ECH conversion over tcbCC and pure bulk- CeO_2 falls from 41% and 27% to about 32% and 11%, respectively, due to the strong adsorption of HCl or Cl_2 produced from the decomposition of ECH on the CeO_2 surface.⁹ However, the original activities of tcbCC and bulk- CeO_2 are rather low at 225 °C. An obvious activity drop during the first 15 h was noticed for the copCC and impCC catalysts, decreasing from 95% and 80% to 69% and 52%, respectively. ECH conversion over htpCC20 also decreases from 100% to 92% during the first 3 h, but this remains at about 91% for the rest of the reaction time. The lower activity loss (<10%) and faster ECH conversion equilibrium period (<3 h) of htpCC20 indicate that the 3D ordered mesostructures of the htpCCx samples evidently enhance the catalysts' durability. Wang *et al.* found that higher reaction temperatures have a significant positive effect on the removal of surface Cl species over $\text{MnO}_x\text{-CeO}_2$ catalysts in the combustion of chlorobenzene.^{1,9} Therefore, the durability of the catalysts with higher catalytic performance (*i.e.*, htpCC20 and copCC) was further evaluated at a reaction temperature of 300 °C. For copCC, stable activity can be achieved within 6 h, and less activity reduction (about 17%) is also observed. Noticeably, ECH conversion over htpCC20, is maintained at almost 98% or higher for 50 h. In addition, the ordered mesoporous structure of the used htpCC20 catalyst, shown in Fig. 3i, further confirms the high stability of the mesostructured copper and ceria composite metal oxide. Analysis with GC and online MS shows that the htpCC20 catalyst under study demonstrates more than 99.5% selectivity for CO_2 with no other C-containing by-products detected. Zhou *et al.* demonstrated that the interaction of CeO_2 and CuO can improve the stability of a $\text{CuO-CeO}_2\text{-USY}$ catalyst used in the oxidation of 1,2-chloroethane, and that the abundant oxygen species inhibit the production of coke during long time reaction.¹⁵ In the oxidation of ECH, ECH was first adsorbed on to the surface of the catalysts, then the C-Cl bond dissociation occurs, followed by the reaction of the dissociated fragments and active oxygen to produce CO_x and H_2O . Chlorine species, which can block the active sites and deactivate the catalysts, need to be removed from the catalyst surface in the form of Cl_2 or HCl . Highly dispersed CuO nanoparticles over the surface of CeO_2 can offer plenty of active sites for ECH oxidation. Moreover, the incorporation of Cu^{2+} into the lattice of CeO_2 results in a large number of oxygen vacancies in the $\text{CuO}_x\text{-CeO}_2$ catalysts, especially the htpCCx samples, and hence creates large quantities of active oxygen species (O^{2-}/O^-) that can efficiently react with the adsorbed chlorine species. As shown in Fig. 14, the htpCC20 catalyst possesses good durability for ECH combustion, suggesting that the removal of Cl species is rapid enough to maintain the active sites that are accessible to reactant molecules at 300 °C.

4.3. Proposed reaction process and mechanism for ECH oxidation

The results derived from XRD, H_2 -TPR, XPS and Raman spectroscopy (Fig. 2, Fig. 5, Fig. 6, and Fig. 12) reveal that a large amount of Cu^{2+} species migrated into the CeO_2 lattice of

Scheme 1 The formation of oxygen vacancies and proposed mechanism for ECH oxidation over the htpCCx catalysts.

the htpCCx catalysts in the form of a $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution. A schematic of the crystal structure of Cu substituted CeO_2 can be found in Scheme 1 (left image). The $\text{Cu}^{2+}-\text{O}^{2-}-\text{Ce}^{4+}$ connection in the $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution reduced the redox potential of Cu species as well as acting as a bridge for O transfer between Cu and Ce. Thus, the interaction between Cu and Ce in the solid solution ensures that the reducibility is enhanced for both compounds, and this allows an effective redox cycle (*i.e.*, $\text{Cu}^{2+}/\text{Cu}^+ \xrightleftharpoons[\text{O}^{2-}/\text{O}^-]{2e^-} \text{Ce}^{4+}/\text{Ce}^{3+}$) to occur during oxidation reactions. The proposed mechanism for low temperature ECH oxidation with the htpCCx catalysts is shown as a schematic in order to obtain deeper insight into this reaction process (Scheme 1), and the primary elementary reaction routes can be listed as follows:

Firstly, ECH molecules in the gas phase must come into contact and be adsorbed ($\text{ECH}(\text{ad})$) into the active Cu^{2+} sites (eqn (2)). $\text{ECH}(\text{ad})$ can then react with active oxygen species from the Cu sites to form CO_x , H_2O and HCl as well as

adsorbed Cl species (eqn (3)). Simultaneously, a portion of the HCl produced returns to the catalyst surface and is adsorbed into the oxygen vacancies or some of the active sites for the oxygen transformation (eqn (4)). After this, the reduced Cu sites can be recovered (Cu^{2+}) *via* migration of the adsorbed O^-/O^{2-} species or lattice oxygen from CeO_2 grains (eqn (5) and (6)). The role of Ce^{4+} in the ECH oxidation is similar to that of Cu^{2+} in the well-known Wacker reaction for the direct oxidation of alkenes to aldehydes or ketones, which is catalyzed by CuCl_2 and PdCl_2 . In the Wacker reaction, the reduced Pd^0 is re-oxidized by Cu^{2+} regenerating Pd^{2+} , *i.e.*, contact between Cu^{2+} and Pd^0 is essential in order to close the catalytic cycle of $\text{Cu}^{1+}/\text{Cu}^{2+} \rightleftharpoons \text{Pd}^0/\text{Pd}^{2+}$.⁸⁶ Reduced Ce^{3+} can be re-oxidized by the reduction of oxygen at the Ce sites or by $\text{CO}_2/\text{H}_2\text{O}$ in the gas phase (eqn (7) and (8)).²⁸ The reoxidized Ce^{4+} sites can then act as oxygen suppliers at the ECH oxidation sites for the re-oxidation of nearby reduced Cu^{1+} . As a consequence, the coexistence of Cu and Ce species is essential to the reaction, maintaining the $\text{Cu}^{2+}/\text{Cu}^{1+} \rightleftharpoons \text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycle according to the Mars-van Krevelen mechanism.⁸³ The consumed active oxygen species can be replenished from gas phase oxygen on the surface of the CeO_2 crystals, probably around the oxygen vacancies (eqn (9)), and the desorption of the adsorbed chlorine species (in the form of Cl_2) can be promoted by the active oxygen species (eqn (10)). Some partial oxidation products (*i.e.*, propanal and propanoic acid) were formed during ECH combustion, especially over tcbCC, bulk-CuO, and bulk- CeO_2 (Fig. 10). It is known that C-Cl bonds are weaker than C-H bonds, and hence, they are more prone to attack from nucleophiles.⁸⁷ Consequently, the first step in the oxidation of ECH molecules is probably their dissociative adsorption on to active Cu sites *via* Cl abstraction. The adsorbed Cl ($* \text{Cl}$) in the tcbCC, bulk-CuO, and bulk- CeO_2 samples may be difficult to remove until an equilibrium of adsorbed and desorbed Cl species is achieved due to the absence of oxygen vacancies and active oxygen species (Table 2 and Fig. 12). Therefore, the elementary reaction steps in eqn (7), (9), and (10) were slower for these catalysts than for the htpCCx catalysts, thus, resulting in the formation of small

amounts of organic reaction by-products. Obviously, the active oxygen species, reducibility, and oxygen vacancies are important for efficient ECH low-temperature combustion as well as for *Cl species removal.

5. Conclusions

3D ordered mesoporous $\text{CuO}_x\text{-CeO}_2$ catalysts (htpCCx) were prepared *via* a simple metal nitrate precursor host-guest interaction with SBA-16 silica as a hard template. We propose that the fast-microwave-assisted (FMA) method is a universal approach for the quick removal (about 5 min) of the organic template in the siliceous materials, and the employment of this FMA technique in the synthesis of other mesostructured metal oxides with widespread applications in energy and environmental fields can be anticipated. The experimental results show that Cu species are uniformly distributed over the mesoporous $\text{CuO}_x\text{-CeO}_2$ samples, and a large number of Cu^{2+} ions are incorporated into the CeO_2 lattice in the form of a $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution, leading to structural defects and improved oxygen mobility. The interaction of Cu and Ce increases the reducibility of the $\text{CuO}_x\text{-CeO}_2$ catalysts, and the coexistence of Cu and Ce is required in the reaction to preserve the two redox couples, *i.e.*, $\text{Cu}^{2+}/\text{Cu}^{1+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$. The surface area and pore structure are not the key factors governing the catalytic performance, although the 3D mesostructure could be favorable for mass and thermal transfer. The catalysts with 3D mesoporous structures have much higher low-temperature activity for epichlorohydrin oxidation, *e.g.*, the T_{50} temperature of htpCC20 decreases more than 130 °C compared to bulk- CeO_2 . HtpCC20 has been shown to be the most powerful catalyst for epichlorohydrin removal due to its superior activity, selectivity, and stability. The better activity of the htpCCx catalysts can be ascribed to the high dispersion of the active phase, improved mobility of oxygen species, and large amount of surface active oxygen. We can rationally expect these novel materials to be effective catalysts for the elimination of HVOCs, while simultaneously having other potential applications in catalysis, as well as separation and adsorption processes.

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