Anionic starch-induced Cu-based composite with flake-like mesostructure for gas-phase propanal efficient removal

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ABSTRACT

Highly crystalline flake-like $\text{CuCeO}_{2-\delta}$ composites (strCCx) with large specific surface area and developed mesoporosity were prepared using an economic and effective bio-template route. Modified starch with abundant surface carboxyl groups was adopted as the chelating agent and template for metal cations immobilization via electrostatic attraction predominately based on the process of $-\text{COO}^- \cdots \text{Cu}^{2+}$ and $-\text{COO}^- \cdots \text{Ce}^{3+}$. Physicochemical properties of prepared materials were systematically explored by FT-IR, XRD, TG, N_2 adsorption/desorption, FE-SEM, TEM, H_2 -TPR, O_2 -TPD, XPS, DRUV-Vis, and XAFS techniques. Propanal as a typical oxygen-contained VOC was adopted as the probe pollutant to evaluate the catalytic performance of synthesized materials. Characterization results reveal that plenty of copper ions in composite oxides are incorporated into CeO_2 lattice, which produces oxygen vacancies and enhances metal reducibility. Both specific surface area and pore volume of strCCx samples decreased with the increasing of Cu loading. The flake-like $\text{CuCeO}_{2-\delta}$ sample ($\text{Cu}/(\text{Cu} + \text{Ce}) = 0.15$) with highest specific surface area ($108.2 \text{ m}^2/\text{g}$) and surface oxygen concentration is identified as the most active catalyst with propanal totally destructed at 230°C . The introduction of H_2O has a negative effect on propanal removal, and the synthesized catalyst has high tolerance to moisture. In conclusion, the specific surface area and surface oxygen density are two vital factors governing the catalytic activity of composite catalysts.

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1. Introduction

Volatile organic compounds (VOCs) emitted from many industrial processes are considered as great contributors to atmospheric pollution and to be dangerous to human health [1]. Catalytic oxidation offers interesting advantages toward conventional flame combustion or other treatment approaches. It is able to remove dilute VOCs from industrial effluents to very low levels, which may meet the stringent emission requirements in future. Moreover, this technique carries out at low temperature, thereby reducing or even avoiding the use of auxiliary fuel, and inhibiting the formation of toxic byproducts such as dioxin and NO_x [2]. Catalytic oxidation of VOCs has been performed either with noble-metal catalysts or with non-noble-metal catalysts, where the noble-metal catalysts generally exhibited better catalytic performances [3], but their applications have been hampered by the high cost of noble metals. Transition metal oxides have much lower cost and higher reaction resistance to thermal and heteroatom poisoning [4], while their limited activity at low temperatures does not make them competitive in comparison with the noble-metal catalysts [5]. Exploiting low cost noble-metal-free catalysts with high activity would be much more desirable.

Different protocols have been reported for the synthesis of transition metal oxide-contained catalysts in previous work, such as sol–gel, incipient impregnation, thermal combustion, one-pot polymeric precursor, co-precipitation, micro-emulsion, and spray pyrolysis, while the surface area and porosity of obtained catalysts were rather low [6–10]. Catalytic reactions always take place on the surface of catalyst and the reaction rates are usually in proportion to the molecule reachable surface area [11] though many other factors also have important effects on catalytic activity. Therefore, porous supports with high surface areas (e.g., $\gamma\text{-Al}_2\text{O}_3$, zeolite, porous carbon, and molecular sieve) were usually adopted, while the active phase loadings were always strictly controlled to avoid the aggregation of active sites [12–15]. In-situ creating mesoporous structures is a very favorable and feasible option to achieve metal oxides with high surface areas [16,17]. In addition, the mesostructure can also improve the diffusion of guest molecules. There are two representative routes to synthesize mesoporous metal oxides, that is, using the supramolecular surfactants as the soft templates and porous materials (e.g., silica or carbon-based materials) as the hard templates [18,19]. However, many shortcomings such as complex synthesis procedure, cost and availability of the templates, and treatment of secondary effluents limit the vast applications of above methods.

Among all transition metal oxides, copper loaded catalysts are known to be very active for oxidation reactions [20–22]. The use of metallic oxide promoters that are composed of rare earth elements can lead to an improvement in oxygen storage capability in solids, which evidently enhances the oxidation processes [23]. The most important property of ceria is to serve as an oxygen reservoir that stores and releases oxygen via the redox shift between Ce^{4+} and Ce^{3+} , which under oxidizing and reducing conditions leads to a high activity of catalysts [24]. CuCeO_x were found to be a kind of very powerful catalysts for oxidation reactions, even comparable to the supported noble-metal catalysts [25] as the introduction of ceria can stabilize the active Cu sites, affect the Cu redox property, and improve the oxygen diffusivity and storage capacity of the composite catalysts [26]. Mesoporous CuO-CeO_2 composite catalysts were prepared via soft or hard template approach in previous literature, while the synthesis procedures were either complicated or highly expensive as lots of surfactants were usually required [27,28]. Starch as a polysaccharide bio-template is more attractive for industrial use because of its renewability, biodegradability, simple chemical modification, and

low cost. Many porous metal oxides such as NiO and ZnO have been synthesized using soluble starch as template, based on the fact that polysaccharides can combine with metal cations in solution because of their coordinating functional groups [29,30]. Moreover, researchers have found that the surface modified starches containing surface carboxyl, amino, or hydrosulfuryl groups possessed much higher chelating capacity for metal ions [31,32], and water-soluble polymers are powerful tools for controlling particle shape, size, and size distribution [33,34].

In the present work, we demonstrate a low cost and effective route for the synthesis of metal composite oxides with mesoporous structure. The evident advantage of this method presents here is the simplicity and effectiveness of the synthesis process, and the abundant and inexpensive of the raw materials, which are very important for large-scale applications. Highly crystalline flake-like mesoporous $\text{CuCeO}_{2-\delta}$ oxides with high surface area and narrow pore size distribution were synthesized. Propanal was adopted as the probe pollutant to evaluate the catalytic efficiency of prepared catalysts, and the catalytic performance of all catalysts is correlated with their physicochemical parameters, namely, surface area, reducibility, oxygen distribution, and catalyst surface state. Moreover, the influences of H_2O concentration on propanal removal rate and long-term stability of composite catalyst were further studied.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of solid-state citric acid adduct

All materials and chemicals (maize starch in food grade; copper acetate, cerium acetate, and other routine reagents were analytical grade) were supplied by Sinopharm Chemical Reagent Co., Ltd. without any further purification. The 2-hydroxy-3-chloropropylcitric acid was prepared via reaction with monosodium citrate and epichlorohydrin ($n_{\text{monosodium citrate}}/n_{\text{epichlorohydrin}} = 9/10$) under reflux until one phase was formed. After partial cooling to 60°C , the above mixture was poured into a beaker containing large excess of absolute ethyl alcohol ($v_{\text{alcohol}}/v_{\text{mixture}} = 8/1$) to remove formed glycols and unreacted epichlorohydrin. Finally, the synthesized compound was filtered, and dried at 80°C for 10 h to obtain the solid-state citric acid adduct (SCA).

2.1.2. Synthesis of carboxyl contained starch chelating agent

The carboxyl contained starch was prepared according to the dry technique reported by Khalil and Aly [35]. Typically, native maize starch was thoroughly mixed with powdered NaOH for 5 min using mechanical stirring, and then the SCA was added at room temperature and mixed for another 5 min ($n_{\text{starch}}:n_{\text{SCA}}:n_{\text{NaOH}} = 11:8:1$). Then the mixture was transferred to a stoppered flask and kept in a thermostatic waterbath at 70°C for 2 h. After that, the as-synthesized product was poured into ethanol and the pH was adjusted to 8.0, filtered, and Soxhlet extracted for 12 h using an ethanol–water mixture ($v_{\text{ethanol}}:v_{\text{water}} = 4:1$). Finally, the product was dried at 80°C to obtain the starch-2-hydroxypropylcitric acid (str-CA).

2.1.3. Synthesis of metal ions-chelated starch and composite catalysts

To introduce metal ions, the prepared str-CA sample was firstly chelated with copper and cerium cations. Briefly, a mix solution (200 mL) of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3$ with a total metal ion concentration of 0.1 M ($\text{Cu}/(\text{Cu} + \text{Ce}) = 0.15, 0.3, \text{ and } 0.4$, atomic ratios) was treated with the str-CA sample (5.0 g) added as solid, and the pH of the mix solution was adjusted to 6.0 as the str-CA chelating agent was highly protonated in a strong acidic medium and could not effectively interact with the metal ions due to the

Fig. 1. Schematic synthesis mechanism of the mesostructured $\text{CuCe}_{2-\delta}$ composites.

loss of negative charge [36]. The mixture was then stirred at room temperature for 24 h, washed with distilled water, filtered, and dried at 60 °C to obtain the metal ions-modified starches (denoted as-strCCx, x is the nominal atomic percent of Cu in the composite) with different copper contents. Finally, the recovered products were calcined at 550 °C in air for 4 h to form the mesoporous composite catalysts (named strCCx). For comparison, the $\text{CuCe}_{2-\delta}$ catalysts with Cu loading of 30 at.% were prepared by the coprecipitation (cop), incipient impregnation (imp), and thermal combustion (tcb) methods according to the previous reports [37,38], and the obtained catalysts were respectively denoted as copCC, impCC and tcbCC. Additionally, pure CuO and CeO_2 were also synthesized through thermal calcination of their corresponding hydrated metal nitrates at 550 °C for 4 h.

2.2. Catalyst characterizations

X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert powder diffraction system using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) in the 2θ range of 10–80° (scanning rate of 4° min⁻¹). N_2 adsorption/desorption isotherms of catalysts at -196 °C were collected on a SSA-4000 gas sorption analyzer. All samples were degassed under vacuum at 300 °C for 3 h before the measurement. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.99. The specific surface area was calculated at P/P_0 of 0.05–0.25 using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was derived from the adsorption branch of the N_2 isotherm using the Barrett–Joyner–Halenda (BJH) method. Field emission scanning electron microscopy (FE-SEM) images were recorded on a JEOL JSM-6700F microscope. Transmission electron microscopy (TEM) images were collected on a Hitachi H-7650 microscope operating at an acceleration voltage of 80 kV. The actual Cu content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a PerkinElmer OPTIMA 7000 DV. Temperature programmed reduction (H_2 -TPR) experiments were performed on a Micromeritics ChemiSorb 2720 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 for 30 min, and then treated in a He stream at room temperature for 30 min to remove any residual oxygen. The sample was finally reduced under a 5% H_2/He (50 mL min⁻¹) from 50 to 700 °C with a heating rate of 10 °C min⁻¹. Temperature programmed desorption of O_2 (O_2 -TPD) was carried out on the same apparatus as that in 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, and then the sample was heated from 50 to 700 °C with a heating rate of 10 °C min⁻¹ in a pure He stream. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Kratos AXIS ULTRA instrument under high vacuum ($<5 \times 10^{-10}$ torr) using Al $\text{K}\alpha$ as the exciting radiation at a constant pass energy of 1486.6 eV. The C 1s peak was used to calibrate the binding energy. Diffuse reflectance UV–Vis (DRUV–Vis) spectra were recorded on a Shimadzu UV-3600 spectrophotometer under ambient conditions with the spectral grade BaSO_4 as the reference material. Fourier transform infrared spectra (FT-IR) were recorded using a Bruker Tensor27 IR spectrometer by measuring the absorbance of the KBr pellet (2 wt.% sample and 98 wt.% KBr).

2.3. Catalytic activity

All evaluation experiments were performed in a continuous-flow fixed-bed reactor at the atmospheric pressure, consisting of a quartz tube (4 mm i.d.) that was filled with the catalyst. The propanal-containing gas was generated by bubbling air through the VOC saturator, and then further diluted with another air stream (propanal concentration = 2500 ppm) before reaching the reaction bed. Water steam was introduced by delivering the liquid water with a syringe pump (WZ-50C6, Smiths Co., China) into dry air, and the injection point was electrically heated to ensure complete vaporization of the water. Temperatures of catalyst bed and tubular electric furnace were monitored automatically by E-type thermocouples. In each test, 50 mg of catalyst (diluted with 40–60 mesh quartz sand) was placed at the middle of the tube reactor and the total flow rate was kept at 60 mL min⁻¹ (gas hourly space velocity (GHSV) of ca. 36,000 h⁻¹). In each test, the catalyst bed temperature was first raised to 100 °C with the feed stream passing and stabilized for 30 min. Then the temperature was increased to the next point at a heating rate of 5 °C min⁻¹ and stabilized for 20 min prior to online analysis of the effluent gas composition in a gas chromatograph (GC9890A, Linying Co., China) equipped with the flame ionization detector (FID) and thermal conductivity detector (TCD). The conversion of propanal (X) is calculated by Eq. (1), and temperature at which 90% conversion of propanal are defined as T_{90} .

$$X = \frac{(C_{\text{in}} - C_{\text{out}})}{C_{\text{in}}} \quad (1)$$

where C_{in} and C_{out} are the propanal concentration in the inlet and outlet streams, respectively.

The reaction rate (r) is calculated with X , as Eq. (2),

$$r = \frac{F \cdot X}{W_{\text{cat}} \cdot W_{\text{Cu}}} \quad (2)$$

where F is the propanal feeding rate (mol s⁻¹), W_{cat} is the catalyst weight (g), and W_{Cu} is the copper loading in catalyst.

The effects of reaction products on the reaction rate may be ignored under differential conditions ($X < 15\%$), and the apparent active energy (E_a) for propanal destruction could be obtained according to Eq. (3),

$$r = A \exp\left(\frac{-E_a}{R \cdot T}\right) \cdot P_{\text{propanal}}^\alpha \cdot P_{\text{O}_2}^\beta \quad (3)$$

where A is the pre-exponential factor, R is the molar gas constant, T is the thermodynamic temperature, and P_{propanal} and P_{O_2} are the partial pressures of propanal and oxygen, respectively. Parameters of A , $P_{\text{propanal}}^\alpha$, and $P_{\text{O}_2}^\beta$ are nearly constants as the variations of reactant component are negligible under differential reaction conditions.

Fig. 2. FT-IR results of (a) native starch, (b) str-CA, and (c) as-strCC15.

The mass transfer limitation was evaluated via the Weisz–Prater criterion [39], as Eq. (4),

$$\phi_{WP} = \frac{r_a \cdot R_p^2}{C_a \cdot D_{eff}} \quad (4)$$

where ϕ_{WP} is the dimensionless WP parameter, r_a is the observed rate per catalyst volume ($\text{mol cm}^{-3} \text{s}^{-1}$), R_p is the radius of the catalyst particle (cm), C_a is the gas-phase concentration of propanal at catalyst surface (mol cm^{-3}), and D_{eff} is the effective diffusivity of propanal ($\text{cm}^2 \text{s}^{-1}$).

The effective diffusivity of propanal in Eq. (4) can be determined according to Eq. (5),

$$D_{eff} = \frac{1}{3} \nu d \quad (5)$$

where ν is the average velocity of propanal molecules in the microreactor (cm s^{-1}), and d is the average pore diameter of catalyst (cm).

3. Results and discussion

3.1. Metal cation chelating and porous composite formation

The schematic synthesis process of the mesoporous composite catalysts is shown in Fig. 1. Firstly, the maize starch with abundant surface hydroxyl was modified by solid-state citric acid adduct to form str-SCA, and then the carboxyl in str-SCA was ionized under weak acidic solution to form anionic starch intermediate. The ionized carboxyl over starch intermediate can interact with metal cations via electrostatic attraction predominately based on $-\text{COO}^- \cdots \text{Cu}^{2+}$ and $-\text{COO}^- \cdots \text{Ce}^{3+}$. Finally, the crystallized mesoporous metal composite oxides were obtained after removing the template at 550°C as all starch can be removed below 450°C (Fig. S1).

Fig. 2 displays the FT-IR spectra of native starch, str-CA, and as-strCC15. Native starch exhibits a broadly stretched intense peak at 3440 cm^{-1} , which is the characteristic adsorption of O–H. The weak peak at 1025 cm^{-1} is produced by the stretching vibration of secondary alcohol, and the one observed at 2930 cm^{-1} is due to the C–H stretching vibration [40]. Two IR peaks centered at 1675 cm^{-1} and 1580 cm^{-1} assigned to the stretching vibrations of the carboxyl can be found over str-CA, indicating that the 2-hydroxy-3-propylcitric acid group was successfully introduced to the native starch. After metal chelating reaction, the above peaks according to the carboxyl groups were disappeared. In addition, intensities of the O–H vibration peaks over as-strCC15 were

Fig. 3. XRD patterns of (a) strCC15, (b) strCC30, (c) strCC40, (d) copCC, (e) impCC, (f) tcbCC, (g) CeO_2 , (h) CuO , and (i) native starch.

Table 1
Physicochemical properties of synthesized catalysts.

Sample	CeO_2 crystallite size (nm)	Lattice microstrain ($\times 10^{-3}$)	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore diameter (nm)
strCC15	14.5	9.1	108.2	0.21	4.1
strCC30	17.8	9.9	92.6	0.18	4.4
strCC40	16.4	12.3	84.3	0.13	3.8
copCC	10.0	14.1	86.5	0.14	3.2
impCC	15.7	8.8	59.1	0.16	5.5
tcbCC	64.1	2.2	3.9	0.01	5.2
CeO_2	16	8.7	60.8	0.18	6.1
CuO	/	/	<1.0	/	5.3

Table 2
Characteristic data of synthesized catalysts.

Sample	Cu content (%)		Cu (%)	Ce (%)	O (%)	Ce^{3+} (%)	Oxygen distribution (%)		
	XPS	ICP-OES					O_{latt}	O_{surf}	O_{ads}
strCC15	12.8	12.1	6.0	25.9	68.1	34.2	56.9	41.9	1.2
strCC30	27.2	24.5	7.9	26.2	65.9	32.1	60.7	38.5	0.8
strCC40	37.5	30.7	8.8	24.4	66.8	28.0	62.9	35.9	1.2
copCC	32.2	31.1	8.0	16.8	75.2	33.5	58.3	35.4	6.3
impCC	37.1	29.3	6.4	18.1	75.6	31.3	64.3	31.5	4.2
tcbCC	42.6	30.5	15.6	21.0	63.4	23.3	67.8	25.3	6.9

weaker than those over str-CA and native starch, which suggests that parts of hydroxyl also combined with metal cations by host-guest interactions such as hydrogen bonding, Coulombic interaction, and van der Waals interaction [41].

3.2. Crystal structure and textural property

XRD patterns of all catalysts are shown in Fig. 3. Typical cubic fluorite-type structure of CeO_2 can be observed in all composite samples (JCPDS No. 81-0792). No diffraction peak of CuO (JCPDS No. 80-1268) can be found over strCC15, indicating the fine

Fig. 4. Representative FE-SEM images of (a) native starch, (b) CeO₂, (c) strCC15, (d) strCC30, (e) strCC40, (f) copCC, (g) impCC, and (h) tcbCC. EDX pattern of strCC15 (b, insert).

dispersion of CuO particles or the incorporation of copper phase into ceria lattice [28,42]. However, CuO diffraction peaks at 35.2° or/and 38.3° can be observed over the other composite catalysts, which suggests the partial aggregation of CuO particles. Furthermore, the Cu phase aggregation degree over tcbCC and strCC40 is higher than that over strCC30, copCC, and impCC. Meanwhile, the increase of lattice microstrain (calculated from the (111) reflection of CeO₂ using the Williamson–Hall plot method [13]) of composite samples also approves the incorporation of Cu phase, as listed in Table 1. Bulk Cu contents of composite catalysts are characterized by ICP–OES, as illustrated in Table 2. The actual Cu contents of copCC, impCC, and tcbCC are approximately equal to the theoretical Cu loadings. While the bulk Cu contents in all anionic starch induced composites are obviously lower than the theoretical values, suggesting that Ce³⁺ cation with more positive charge is easier to be chelated by the ionized carboxyl than that of Cu²⁺. The surface composition of synthesized catalysts is

further estimated by XPS, and the results reveal that Cu species are uniform distributed in strCC15 and copCC from surface to interior, while the enrichment of Cu species can be found over tcbCC and strCC40 (Table 2), in consistency with the XRD result (Fig. 3).

As can be seen in Fig. S2, copCC, impCC, and CeO₂ possess well expressed H1-type hysteresis loops at relative pressure of 0.8–1.0, corresponding to the presence of textural pores contributed to the filling of interparticle spaces [43]. All strCCx samples show typical IV shape isotherms with distinct H1-type hysteresis loops observed in the range of 0.45–1.0, indicating the coexistence of structural ($P/P_0 = 0.45–0.8$) and interparticle accumulation mesopores [27]. The pore diameter distribution curves of strCCx show one single peak at 4.0 nm (much narrower than those of copCC, impCC, and CeO₂), suggesting the good homogeneity of the mesopores. The BET surface areas of strCCx samples are measured to be 84.3–108.2 m² g^{−1}, obviously larger than those of CuO (<1.0 m² g^{−1}) and CeO₂ (60.8 m² g^{−1}). In addition, the decrease

of BET surface area and pore volume of strCCx composites can be noticed with the increasing of Cu content (Table 1).

Fig. 4a reveals that the native maize starch possesses sphere-like and spheroid-like granular structure in the size range of 8–30 μm , and CeO_2 nanoparticles with average diameter of ca. 30 nm can be observed in Fig. 5b. Morphology of strCCx are much different from those of the native starch and samples synthesized via the imp, cop, and tcb approaches (Fig. 4a, c–h). The strCCx composites have shaggy and flake-like micromorphologies with plenty of pores over their walls, and this porous structure with short pore channels should possess unique advantages in mass and heat transfer during oxidation reactions [44]. EDX result indicates that Cu content over strCC15 (13.89 at.%) is a little lower than the nominal value (Fig. 4c, insert), in agreement with the XPS and ICP–OES results (Table 2). In addition, a portion of particles over impCC and copCC aggregate to some degree, while these particles are badly aggregated over tcbCC (Fig. 4f and g). Microstructure of prepared composite catalysts is further studied by TEM (Fig. S3). Nanoparticles with diameter of 10–20 nm are well dispersed and lots of structural or interparticle accumulation mesopores can be found over strCC15. However, particles over strCC30 and strCC40 seems to agglomerate to some extent, especially for strCC40 sample (Fig. S3a–c). The copCC sample also presents a well dispersed morphology, while the metal particles are prone to aggregated to clusters over impCC (ca. 40 nm) and tcbCC (ca. 200 nm) (Fig. S3d–f), in consistent with the SEM result in Fig. 4.

3.3. Reducibility and oxygen mobility

Reducibility of synthesized catalysts were studied by H_2 -TPR (Fig. 5A). All composite samples have much better reducibility than that of CuO and CeO_2 due to the synergy effect between Cu and Ce components as the $\text{Cu}^{x+}-\text{O}^{2-}-\text{Ce}^{y+}$ connection could reduce the redox potential of metal species. Similar reduction behaviors can be noticed for strCCx samples with three reduction peaks below 320 $^\circ\text{C}$, and the reducibility of strCCx composites is continuously decreased when increases the Cu contents probably due to the reduction of H_2 accessible surface areas [27] or the aggregation of Cu species (Table 1 and Fig. 3). The first two H_2 consumption peaks (<200 $^\circ\text{C}$) over strCCx samples can be respectively assigned to the reduction of well-dispersed CuO and framework CuO in CeO_2 lattice, while the H_2 consumptions higher than 200 $^\circ\text{C}$ over strCC30 and strCC40 are attributed to the reduction of CuO cluster [2]. The copCC sample with a large portion of Cu species reduced at 169 $^\circ\text{C}$ shows much better reducibility than that of impCC and tcbCC due to better dispersion of Cu species. The H_2 consumption amounts below 300 $^\circ\text{C}$ over all composite catalysts are shown in Table S1. Overall considering the reduction temperature and low-temperature H_2 consumption amount, the reducibility of synthesized catalysts is in the order of copCC > strCC15 > strCC30 > impCC > strCC40 > tcbCC > CeO_2 > CuO .

As shown in Fig. 5B, the desorption of physically adsorbed oxygen (O_2) is not detected over all samples. The strCCx and copCC catalysts exhibit three oxygen desorption peaks, while impCC and tcbCC samples just present two oxygen desorption peaks centered at higher temperature range of 370–640 $^\circ\text{C}$. Three desorption peaks below 460 $^\circ\text{C}$ over strCCx and copCC samples could be assigned to the chemically adsorbed oxygen (O_2^-/O^- , ad) atom as the quick desorption of the oxygen species, and the unsymmetric desorption peaks higher than 570 $^\circ\text{C}$ over composite catalysts can be assigned to the lattice O^{2-} species [38]. It is worth noting that the a large number of catalytically active O_2^- or O^- species can desorb from strCCx catalysts at very low temperatures (<180 $^\circ\text{C}$). Furthermore, strCCx has larger quantity of O_2^- or O^- species than the other samples, and the concentration of O_2^- or O^- species is in the sequence of strCC15 > strCC30 > strCC40 > copCC > tcbCC $\approx$ impCC >

$\text{CeO}_2 \gg \text{CuO}$ according to the deconvolution peak areas under TPD curves.

3.4. Surface state and structural property

The surface state and composition of synthesized catalysts were investigated by XPS, as shown in Fig. 6 and Table 2. As is known, the presence of Ce^{3+} in CeO_2 means the formation of oxygen vacancy, which could accelerate oxygen transfer rate during oxidation reaction. Results in Fig. 6A and Table 2 reveal that the percentage of Ce^{3+} in strCCx decreases to some degree with the increasing of Cu contents according to the fitted peak areas underlying the original XPS curves ($\text{Ce}^{3+} = u' + u_0 + v' + v_0$), and the Ce^{3+} contents in all composite catalysts are following the sequence of strCC15 (34.2%) > copCC (33.5%) > strCC30 (32.1%) > impCC (31.3%) > strCC40 (28.0%) > tcbCC (23.3%). The Cu state was studied by Cu 2p and Cu LMM Auger lines, as demonstrated in Fig. 6B and C. Two peaks centered at 934.3 and 932.5 eV can be reasonably attributed to the existence of Cu^{2+} and reduced Cu species (i.e., Cu^{1+} and/or Cu^0), respectively [2]. Cu LMM Auger lines were further studied in order to clarify the composition of the reduced Cu species (Fig. 6C), and the peaks at 917.1 and 912.9 eV respectively correspond to the Cu^{2+} and Cu^{1+} [45]. The distribution of oxygen species was also investigated, as shown in Fig. 6D. XPS curves can be decomposed to three peaks with binding energies centered at 529.1, 531.4, and 532.4 eV, corresponding to the lattice oxygen (O_{latt}), surface oxygen (O_{surf}), and adsorbed oxygen (O_{ads}), respectively [9]. The O 1s core level of O_{latt} over all composite samples shifts to higher values due to “O $\rightarrow$ Cu” electron-transfer processes, which can create active oxygen species such as O, O_2^- , O^- , and O^{2-} [2]. The oxygen species distribution over different

Fig. 5. (A) H_2 -TPR and (B) O_2 -TPD profiles of (a) strCC15, (b) strCC30, (c) strCC40, (d) copCC, (e) impCC, (f) tcbCC, (g) CeO_2 , and (h) CuO .

Fig. 7. (A) Light-off curves of propanal oxidation in the presence of 1.0 vol.% of H_2O over synthesized catalysts, and (B) arrhenius plot of propanal oxidation; (C) long-term stability at $220\text{ }^{\circ}\text{C}$ in the presence of 3.0 vol.% of H_2O and effect of water feeding concentration (0–3.0 vol.%) on propanal oxidation for strCC15 catalyst; (D) relations between T_{90} and surface oxygen concentration and specific surface area.

Furthermore, the catalyst stability in dry or humid conditions is always a most important parameter for practical applications. Fig. 7C displays the oxidation behaviors of propanal over most active strCC15 catalyst in the presence of different water vapor concentrations. The water vapor has a negative effect on propanal removal, and the T_{90} temperatures increase $17\text{ }^{\circ}\text{C}$ when 3.0 vol.% of water vapor is added to the system. Besides, the inhibition effect of H_2O molecules on $\text{CuCeO}_{2-\delta}$ catalyst in this work seems much weak than that on Al-containing materials probably due to the hydrophobicity of metal composite [48]. The long-term durability of strCC15 catalyst at $220\text{ }^{\circ}\text{C}$ in dry and humid conditions was studied by stepwise addition and removal of water vapor (3.0 vol.%). The result in Fig. 7C reveals that the catalytic activity of strCC15 is inhibited by the water molecules as propanal conversion drops instantaneously when 3.0 vol.% of H_2O is introduced. Noticeably, after switching back to the water-free reaction conditions, the propanal conversion increases immediately and return to the initial value gradually, and this indicates that the synthesized catalyst has a high tolerance to moisture.

The XRD, XPS and copper K-edge XANES results reveal that a large amount of copper species migrated into CeO_2 lattice of the strCCx samples in the form of the $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution (Figs. 3 and 6, and S5). The $\text{Cu}^{x+}-\text{O}^{2-}-\text{Ce}^{y+}$ connection in the solid solution can reduce the redox potential of copper species as well as act as a bridge for O transfer between Cu and Ce phases. 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., $\text{Cu}^{2+}/\text{Cu}^{1+} \xrightleftharpoons[\text{O}_2^-]{2e^-} \text{Ce}^{4+}/\text{Ce}^{3+}$)

to occur during oxidation reactions. Researchers proposed that the activation of propane and propene over MnO_x and $\text{MnO}_x-\text{CeO}_2$ metal oxides is thought to occur by abstraction of the H atoms from the weakest C–H bonds, with a simultaneous reduction of the surface sites and successive formation of the surface hydroxide ions [49,50]. In the present work, it is inferred that the active oxygen can also preferentially extract the H atoms from the weakest C–H bonds in propanal molecules, and more active oxygen species should favor the activation of propanal. It is generally accepted that the specific surface area, active oxygen availability, and reducibility of a transition metal oxide are most important factors deciding its catalytic activity [51,52]. The oxidation reactions of organic compounds over the transition metal oxide catalysts are known to occur through two possible mechanisms, that is, the suprafacial and/or intrafacial mechanism [53]. The former mechanism is operative at reaction temperature (T) $< 400\text{ }^{\circ}\text{C}$ and involves oxygen species adsorbed over the surface oxygen vacancies of the catalyst. The latter one takes place at $T > 400\text{ }^{\circ}\text{C}$ and involves the lattice oxygen of the catalyst through a Mars–van Krevelen redox cycle [54,55]. In the latter case, a direct relation between the catalyst reducibility and the activity takes place [56]. Herein, the presence of oxygen vacancies due to the incorporation of copper species facilitate the activation of oxygen molecules to active oxygen adspecies, and reducibility of the synthesized composite catalysts is obviously improved (especially for the sample with large specific surface area) comparing with bulk CuO and CeO_2 oxides due to the $\text{Cu}^{x+}-\text{O}^{2-}-\text{Ce}^{y+}$ connection in $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution. The reducibility sequence of

Table 3
Catalytic performance of the synthesized catalysts.

Sample	T_{90} ^a (°C)	Reaction rate ^b (mmol g ⁻¹ h ⁻¹)	Activation energy (kJ mol ⁻¹)	R^2
strCC15	215	3.99	97.1	0.978
strCC30	236	3.31	101.8	0.998
strCC40	264	2.56	121.3	0.992
copCC	255	2.84	130.5	0.966
impCC	295	1.15	159.1	0.996
tcbCC	/	0.20	278.2	0.964
CeO ₂	/	0.01	511.5	0.968
CuO	/	0.23	372.4	0.962

^a Temperature at which 90% conversion of propanal.

^b Propanal reaction rate gained at 225 °C.

synthesized catalysts (copCC > strCC15 > strCC30 > impCC > strCC40 > tcbCC > CeO₂ > CuO) in this work is inconsistent with the catalytic activity result, as shown in Table S1, Figs. 5A and 7. For example, the copCC sample possesses the best reducibility, while the catalytic activity of copCC (T_{90} = 255 °C) is much lower than that of the strCC15 (T_{90} = 215 °C). That is to say, the redox property of prepared catalysts is probably not the most vital factor determining the overall catalytic activity, and propanal oxidation over synthesized catalysts should obeys the suprafacial mechanism. The O 1s XPS and H₂-TPR results reveal that the mesoporous CuCeO_{2- δ} catalysts possess higher surface oxygen concentrations (relevant to the oxygen vacancy density) than those of copCC, impCC, and tcbCC samples (Table 2, Figs. 5 and 6). In addition, the large specific surface area favors the dispersion of active phase, and hence promotes the catalytic process. The relations between T_{90} and surface oxygen concentration and specific surface area for all composite catalysts were studied (Fig. 7D). General linear relations of T_{90} versus O_{surf} content and T_{90} versus specific surface area could be established, namely, the temperatures of T_{90} increase with the decrease of O_{surf} concentration and specific surface area. Therefore, we can anticipate that the specific surface area and surface oxygen density are two foremost factors governing the catalytic activity.

4. Conclusions

Mesoporous CuCeO_{2- δ} composites with high specific surface area and developed mesoporosity were prepared by a low cost and effective metal cation chelating method with modified maize starch as the bio-template. The experimental results shows that all strCCx samples have shaggy and flake-like morphology. Large portion of Cu²⁺ ions are incorporated into CeO₂ lattice, which leads to structure defects and improved oxygen mobility. Cu species is well-dispersed in strCC15 and copCC samples, while the aggregation of Cu species can be found over tcbCC and strCC40. The catalyst reducibility is not the primary factor determining the catalytic performance. The strCC15 possesses the highest propanal destruction activity (reaction rate is 19.9 times higher than tcbCC at 225 °C), and propanal can be totally removed at 230 °C. In general, the superior activity of strCCx catalysts is ascribed to their large specific surface area and high surface oxygen concentration. We proposes that this protocol based on electrostatic attraction is a universal route for preparing mesostructured metal oxides with single or multiple components, which should have vast application prospects in catalysis, adsorption, separation processes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2015.05.021>.

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