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Development of Quinary Layered Double Hydroxide-Derived High-Entropy Oxides for Toluene Catalytic Removal

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Abstract: In this work, a novel method for the preparation of high-entropy oxides (HEO) was successfully developed using multivariate composition layered double hydroxides (LDHs) as precursor. Thermal treatment over 600 °C led to the complete transformation of LDHs to single spinel phase HEOs. The performance of the obtained HEO catalysts in the removal of volatile organic compounds (VOCs) was studied with the catalytic oxidation of toluene as the probe reaction. The optimized HEO-600 catalyst showed impressive activity and stability over toluene catalytic oxidation, which resulted from the vast quantity of surface oxygen vacancies and the relative variable metal valence. The T_{50} and T_{90} values of HEO-600 were 246 and 254 °C, and the T_{90} value only presented a slight increase to 265 °C after a 10-cycle test. This work developed a simple way to obtain HEO materials and provide technical support for the application of HEO catalysts for VOCs removal.

Keywords: high-entropy oxides; layered double hydroxides; VOCs; catalytic oxidation; toluene



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1. Introduction

The industrial emission of volatile organic compounds (VOCs) is one of the main reasons for the excessive ozone in the atmospheric environment [1,2]. Regenerative catalytic oxidation (RCO) technology has a great potential for the deep treatment of VOCs due to its advantages of high purification rate, low energy consumption and controllable by-products [3,4]. In practical applications, catalysts applied using the RCO technique are faced with the crucial work conditions of high temperature and water vapor. Thus, the stability of the catalysts is directly related to the operating cost of the RCO.

High-entropy oxides (HEO) have been widely observed by researchers since their identification [5]. By incorporating five or more different transition metals into a single-phase oxide system, a HEO is able to maintain an entropy-stable structure through the formation of the joint lattice between the metal elements [6]. Rost and his group reported an entropy-stable metal oxide ceramic with a rock salt structure, which was the first confirmed case of a single-phase system formed by an entropy-driven transition [7]. With the deepening of the research, more structures, such as perovskite, fluorite and spinel have been explored and employed in different fields, such as in sodium or lithium ion batteries, oxygen evolution reactions and high temperature CO₂ hydrogenation [8]. Pan and his group [9] designed a series of CoFe₂O₄-type spinel HEO catalysts and tested their activation of the oxygen evolution reaction. The disordered occupation of the metal cations facilitated the formation of structurally stable, high-density oxygen vacancies on the exposed surface, resulting in the efficient and stable catalytic oxygen evolution of the optimized (Co_{0.2}Mn_{0.2}Ni_{0.2}Fe_{0.2}Zn_{0.2}) Fe₂O₄ spinel catalyst. Dai et al. [10] reported a new strategy of the (NiMgCuZnCoO_x)-supported Pt catalyst for the CO oxidation. The selected 0.3 wt.% Pt NiMgCuZnCoO_x sample showed superior activity even after 900 °C calcination.

The entropically-driven stability is the key to maintain high activity and survive the tough conditions when applied. By now, the synthesis methods for HEOs mainly consist of a solid-state reaction [11], hydrothermal [12] and sol-gel auto combustion [13]. A thermal treatment ranging from 700 to 1500 °C is a necessary step to obtain the HEO for each method [14,15]. The complexity and high energy cost of fabricating HEOs limit their promotion and application.

Layered double hydroxides (LDHs) are ionic layered compounds with brucite-like laminates constituted by adjustable metal elements. This material can be prepared at a large scale and using industrialization. The catalysis of LDH-derived oxides (LDO) with different active components and uniformly dispersed elements can be obtained by adjusting the preparation conditions and materials [16]. LDO catalysts have been deeply studied in the field of the catalytic removal of VOCs. It has been proved that LDO can efficiently remove benzene, toluene, formaldehyde and other VOC pollutants under laboratory conditions [17–19].

In this work, we propose a new way to prepare HEO materials by adjusting the preparation conditions of multi-component LDH precursors. Because the metal elements of LDH precursors are highly dispersed, we inferred that the HEO catalyst may be formed under heat treatment at lower temperatures than with the traditional way of milling mixed oxides. Furthermore, by adjusting the metal composition of LDHs, the derived HEO catalysts could be optimized to acquire high catalytic activity and excellent stability for VOC catalytic combustion. Toluene was chosen as the target pollutant to test the efficiency of HEO catalysts because of its large emissions, high toxicity and photochemical activity. Compared with traditional precious metal-based catalysts, the application of an HEO catalyst with excellent stability and activity can reduce the operation cost of RCO technology, which technically supports the development of VOC catalytic oxidation technology.

2. Results and Discussion

Structure and Morphology of Catalysts

Figure 1A presents the XRD patterns of the CuCoMnNiFe-LDH precursor and its calcined products. The diffraction peaks of the obtained CuCoMnNiFe-LDH precursor were observed at 11.5°, 23.4°, 34.1°, 39.1°, 59.3° and 61.1°, corresponding to the (003), (006), (012), (015), (110) and (113) crystal planes of typical LDHs [20,21]. It is proven that LDHs with a uniform structure and integrity crystal phase can still be formed when there are five kinds of metal elements on the laminates. After calcination at 400 °C, the formed mixed oxides were in an amorphous state and no apparent peaks were observed in the related XRD patterns. When calcination temperature increased to 500 °C, all diffraction peaks of obtained HEOs were in strong agreement with the characteristic diffraction peaks of the spinel and no impurities were detected, in which $2\theta = 18.4^\circ, 30.6^\circ, 35.9^\circ, 37.5^\circ, 43.6^\circ, 54.3^\circ, 57.5^\circ, 63.4^\circ$ corresponded to (111), (220), (311), (222), (400), (422), (511), (440) crystal planes of spinel structure [14,22–25]. Therefore, it turns out that the spinel HEOs could be formed by the calcination of LDHs at 500 °C. Compared with the LDH-derived spinel reported in the literature [26–29], the existence of five metal elements on the laminates makes the conversion temperature from LDHs to spinel lower. Zhao et al. also reported that high-entropy composition facilitated the formation of a single-phase spinel structure [30]. The diffraction peak intensity of the HEOs increased with the increase in the calcination temperature, indicating the crystallinity of the samples improved. However, a small diffraction peak near 38.8° was formed as the impurity phase when the calcination temperature was further increased to 700 °C. The TGA-DSC test for the LDH precursor was carried out to study the transformation of the CuCoMnNiFe-LDHs precursor to HEOs, and the results are shown in Figure 1B. The TGA curve of the CuCoMnNiFe-LDHs has three obvious thermal decomposition stages distributed at room temperature: 152 °C, 152–415 °C and 415–580 °C. The first stage, with an exothermic peak at 130 °C, is related to the removal of physical adsorbed water and water molecules between laminates. The mass loss in the second stage, with a less-obvious exothermic peak at around 240 °C, can be attributed to the

dehydroxylation of the LDH layers and the decarbonization of the interlayer CO_3^{2-} [31]. The third stage, with a small mass loss (3.2 wt.%), can be ascribed to the elimination of the interlayer residual CO_3^{2-} . The evolution of the interlayer CO_3^{2-} was also investigated with XPS, and the peak of C 1s at about 288.8 eV attributed to the carbonate species [32] appears in HEO-400 and HEO-500 and disappears in HEO-600, HEO-700 and HEO-800 (Figure S1), indicating that the interlayer CO_3^{2-} was almost completely removed when the calcination temperature was increased to 600 °C. The above results indicated that, after calcination at 600 °C, the CuCoMnNiFe-LDH precursors have completely transformed to spinel-type HEOs.

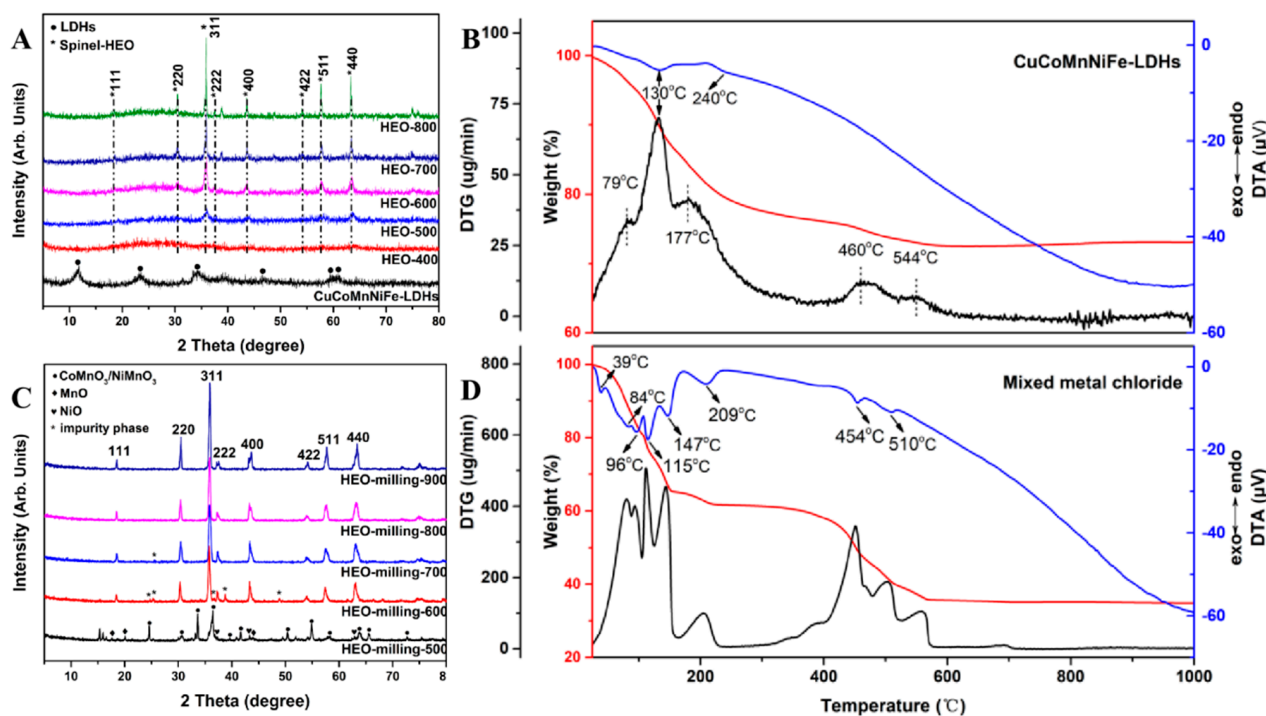


Figure 1. (A) XRD patterns of CuCoMnNiFe-LDHs precursor and LDHs derived HEOs; (B) TGA-DSC profiles of CuCoMnNiFe-LDHs precursor; (C) XRD patterns of HEO-milling-T; (D) TGA-DSC profiles of mixed metallic chloride.

Figure 1C shows the XRD patterns of HEO-milling samples calcined at different temperatures. The HEO-milling-500 showed a complex composition, including CoMnO₃ (JCPDS 12-0476), NiMnO₃ (JCPDS 48-1330), MnO (JCPDS 04-0326), NiO (JCPDS 47-1049) and other metal oxides. When the calcination temperature was increased to 600 °C, the characteristic diffraction peaks of the spinel appeared, accompanied by the impurity phase (marked by * in the Figure 1C). The impurity phase disappeared until the calcination temperature was increased to 800 °C, indicating the successful transformation into spinel HEOs. Compared with the LDH precursor, mixed metal chlorides need higher calcination temperatures to be converted into HEOs. The TGA-DSC curves of the HEO-milling sample are shown in Figure 1D. The weight loss was a continuous occurrence at 25–220 °C with a 38.2% mass loss, which attributed to the removal of the surface adsorbed water and crystal water of mixed metal chloride. At 220–575 °C, metal chlorides were decomposed successively with the obvious exothermic peaks at 454 and 510 °C, which resulted in the formation of metal oxides. It also can be seen from the TGA-DSC curves that, compared with the LDH derivation method, the synthesis of HEOs using the solid-phase reaction method requires a higher temperature.

The SEM images of LDHs and their derived HEOs are shown in Figure 2. The LDH precursor exhibited typical nanosheet morphology (Figure 2A) with a homogeneous distribution of the constituent metal elements Cu, Co, Mn, Ni and Fe (Figure 2G,H). After

calcination, the nanosheet structure of the catalyst becomes gradually loose and changes into a nanosphere structure with the further increase of calcination temperatures. For HEO-400 and HEO-500, the morphology still appeared as nanosheets. When the calcination temperature reached 600 °C, the obtained HEO started to form nanosphere-like structures co-existing with the nanosheet structure. The particle size of the nanospheres gradually increased with the further increase in temperature, which was caused by the agglomeration and fusion of the oxides. The above results indicated that the calcination treatments with different temperatures have obvious influences on the sample morphology. Combined with the XRD and TGA-DSC results, the morphological change from LDHs to HEOs was due to the collapse of the LDH laminate structure. The microstructure of HEO-600 was further characterized by TEM. The TEM image in Figure 3A showed the nanosheet structure and some dotted particles. As shown in the HRTEM image in Figure 3B, the lattice fringes with inter-planar distances of 0.254, 0.292 and 0.480 nm ascribed to the (311), (220) and (111) crystal planes of spinel respectively, which is consistent with the XRD results. The obtained SAED pattern (Figure 3C) indicated the polycrystalline features of HEO-600 [33]. The EDS results (Figure S2 and Table S1) show that each element was highly dispersed, similarly to those in the LDH precursor with an equimolar ratio of metal elements, indicating that 600 °C calcination did not lead to the agglomeration of individual metal elements.

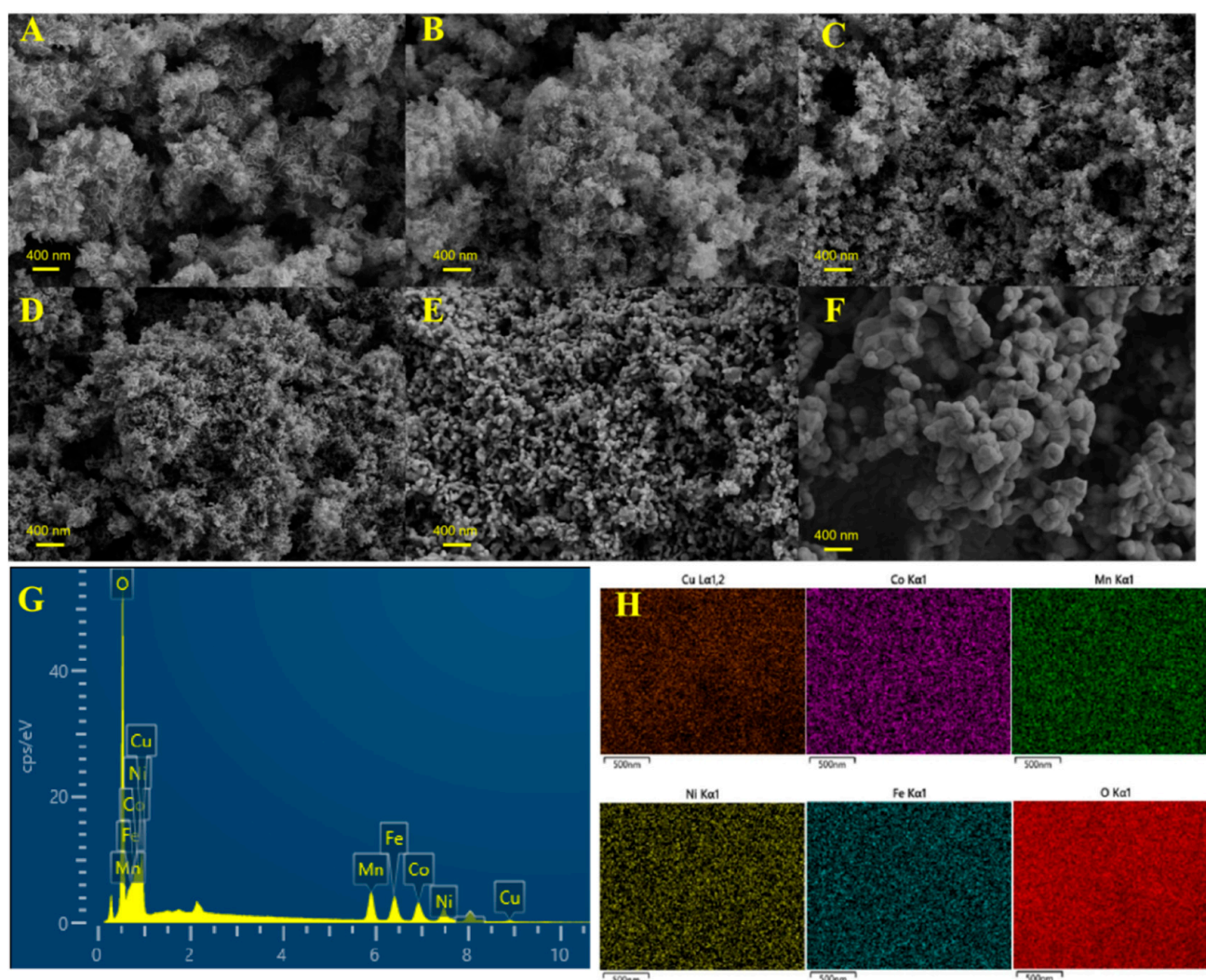


Figure 2. SEM images of (A) CuCoMnNiFe-LDHs; (B) HEO-400; (C) HEO-500; (D) HEO-600; (E) HEO-700 and (F) HEO-800. (G) EDS spectrum of CuCoMnNiFe-LDHs; (H) elements mapping of CuCoMnNiFe-LDHs.

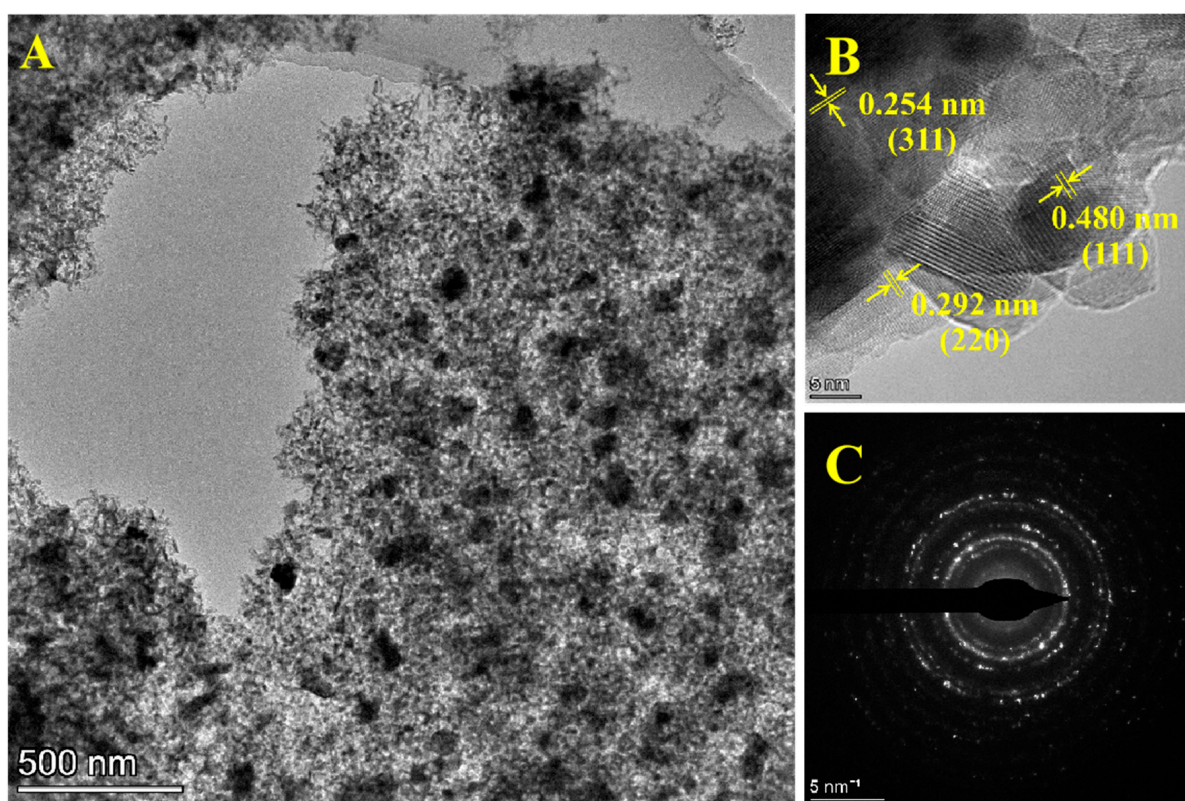


Figure 3. (A) TEM image; (B) HRTEM image and (C) SAED pattern of HEO-600.

N₂ adsorption/desorption isotherms of the HEOs in Figure S3A are identified as type IV isotherms with H3 type hysteresis loops without the adsorption saturation in the region of high relative pressure, indicating the existence of irregular pore structures related to the nanosheet structure [34]. The associated Barrett–Joyner–Halenda (BJH) pore size distribution in Figure S3B also indicated that all the samples show a mesoporous structure, but only HEO-400, HEO-500 and HEO-600 show an obvious pore size distribution above 10 nm. The amount of mesoporosity gradually decreased with the increase in the calcination temperature, and the mesopores of HEO-700 and HEO-800 that, below 10 nm, should arise from the voids between particles. As summarized in Table 1, the specific surface area, average pore diameter and pore volume of HEOs showed a downward trend along with the increasing calcination temperatures. The decrease of the BET surface area and pore volume of the samples from 140.0 to 9.4 m²/g and 1.35 to 0.05 cm³/g, respectively, occurred when the calcination temperature increased from 400 to 800 °C, which could be attributed to the morphology change from nanosheets to nanospheres. In the gas phase reaction, the specific surface area of the powder catalyst is usually related to the activity of the catalyst. The larger specific surface area can provide more reaction sites for the reaction, and the appropriate pore size distribution can ensure full contact between the active components of the catalyst and reaction gas.

Table 1. Results of N₂ adsorption-desorption test for HEOs.

Samples	BET Surface Area (m ² /g)	Average Pore Diameter (nm)	Pore Volume (cm ³ /g)
HEO-400	140.0	38.6	1.35
HEO-500	79.6	27.8	0.55
HEO-600	49.2	23.9	0.29
HEO-700	16.7	23.4	0.12
HEO-800	9.4	22.2	0.05

The XPS characterization of HEOs was conducted to investigate the surface state of constituent elements of HEOs, and the XPS spectra after deconvolution are shown in Figure 4. As shown in Figure 4A, the XPS peak of Cu 2p_{3/2} could be deconvoluted into two peaks at 934.3 and 931.0 eV, which were attributed to Cu²⁺ and reduced copper species, respectively. Reduced copper species were further identified by Auger electron spectroscopy (AES) (Figure S4) and the peak at 574.1 eV in the Cu LMM Auger spectra confirmed the existence of Cu⁺ [35]. Figure 4B shows the Co 2p XPS spectra, the peaks with a binding energy of 780.2 and 795.3 eV assigned to Co³⁺, and the peaks at 781.7 and 796.8 eV which could be ascribed to Co²⁺ [36,37]. The XPS spectra of the Mn 2p region are shown in Figure 4C, and the deconvolution results show that Mn existed with a mixed valence state of Mn²⁺, Mn³⁺ and Mn⁴⁺ for all HEOs [38]. Ni 2p spectra in Figure 4E display the co-existence of divalent and trivalent species in HEOs, in which two fitted peaks at 854.5 and 855.9 eV in the Ni 2p_{3/2} region could be assigned to Ni²⁺ and Ni³⁺, respectively [39]. Fe 2p XPS spectra in Figure 4D also indicated the co-existence of Fe²⁺ and Fe³⁺ in the HEOs. Two major peaks in the Fe 2p_{3/2} region located at 710.4 and 712.7 eV were attributed to Fe²⁺ and Fe³⁺, respectively, and the Fe 2p_{1/2} peaks could be deconvoluted into two peaks at 723.9 eV for Fe²⁺ and 726.4 eV for Fe³⁺, respectively [40]. The spectra of O 1s shown in Figure 4F were resolved into three individual peaks at 529.7, 531.4 and 533.5 eV, corresponding to lattice oxygen (O_α), surface hydroxyl groups (O_β) and absorbed water, respectively [41,42].

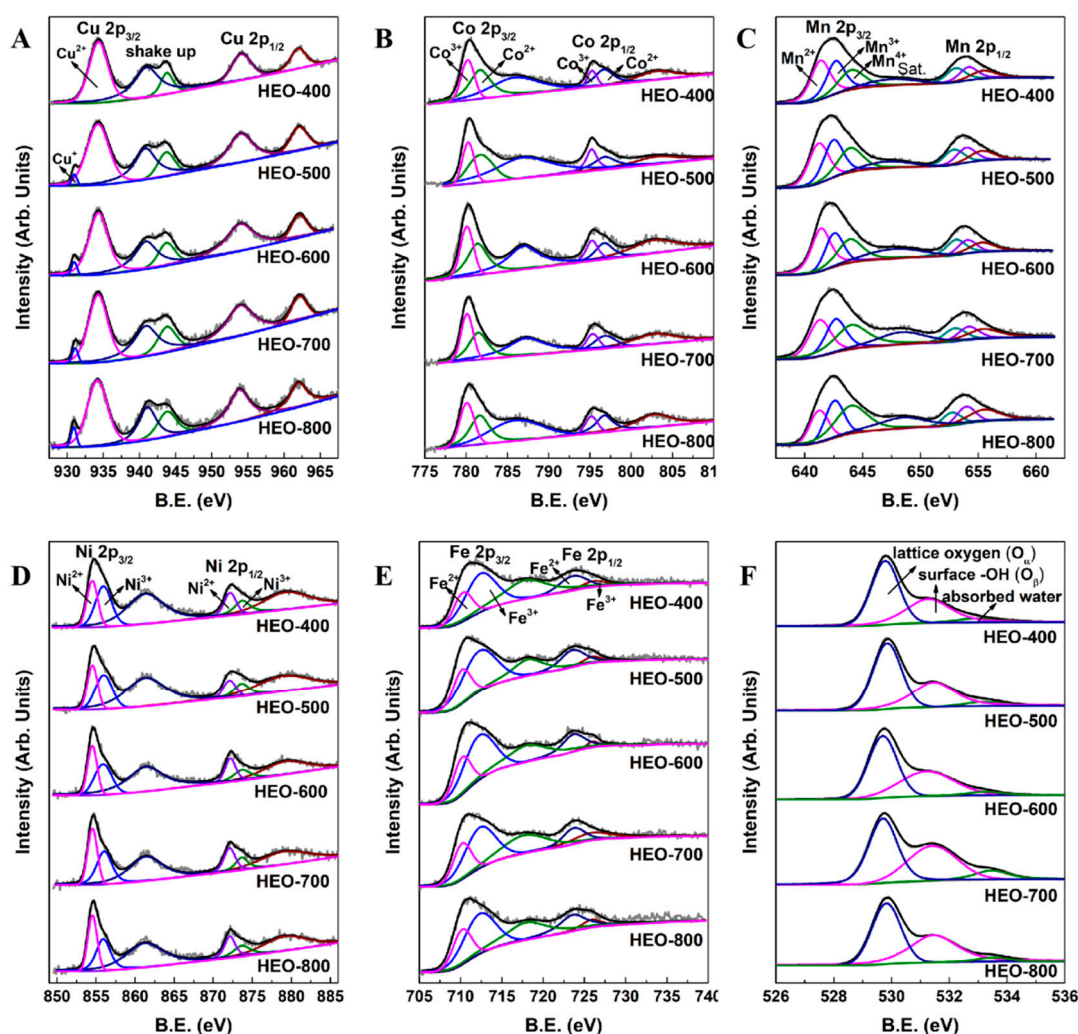


Figure 4. XPS spectra of (A) Cu 2p; (B) Co 2p; (C) Mn 2p; (D) Ni 2p; (E) Fe 2p and (F) O 1s of LDHs derived HEOs.

The relative proportion of different existing forms of HEO constituent elements were calculated through the peak area after the deconvolution, and the results are shown in Table 2. When calcination increased from 400 to 600 °C, the ratios of $\text{Co}^{3+}/(\text{Co}^{2+} + \text{Co}^{3+})$ and $\text{Mn}^{4+}/(\text{Mn}^{2+} + \text{Mn}^{3+} + \text{Mn}^{4+})$ increased significantly, but the content of Ni^{3+} and Fe^{3+} exhibited the contrary trend. In addition, Cu mainly existed in the form of Cu^{2+} , and the content of Cu^+ increased slightly with the increase in calcination temperature. During the calcination process, both the effect of oxygen in the air atmosphere and the redox reaction between different metal species resulted in the above valence changes [43]. Liu et al. also reported similar valence changes in the NiMnFe-Mixed Oxides during calcination, and that the redox reaction between the Ni and Mn ions resulted in an increase in Mn^{4+} content and a decrease in Ni^{3+} content [44]. When the calcination temperature was higher than 600 °C, the ratio of Co^{3+} , Ni^{3+} and Fe^{3+} changed slightly, because the complete formation and structural ordering of the spinel phase makes the oxidation-reduction between the metals less likely to occur. However, the content of Mn^{4+} still increased with the further increased temperature, which reflected the fact that Mn can easily be oxidized [45]. The calcination temperature had a significant influence on the relative intensity of the oxygen vacancy; $\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$ increased from 0.413 to 0.478 when the calcination temperature was increased from 400 to 800 °C. From the XPS analysis, it can be concluded that the calcination temperature had a direct effect on the existing forms of the metal elements and oxygen species of the HEOs.

Table 2. XPS analysis of surface Cu, Co, Mn, Ni, Fe, and O elements for LDHs derived HEOs.

Samples	$\text{Cu}^{2+}/(\text{Cu}^+ + \text{Cu}^{2+})$	$\text{Co}^{3+}/(\text{Co}^{2+} + \text{Co}^{3+})$	$\text{Mn}^{4+}/(\text{Mn}^{2+} + \text{Mn}^{3+} + \text{Mn}^{4+})$	$\text{Ni}^{3+}/(\text{Ni}^{2+} + \text{Ni}^{3+})$	$\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$	$\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$
HEO-400	~1	0.392	0.262	0.584	0.707	0.413
HEO-500	0.962	0.407	0.293	0.566	0.694	0.421
HEO-600	0.950	0.432	0.306	0.532	0.682	0.442
HEO-700	0.944	0.444	0.396	0.524	0.671	0.454
HEO-800	0.933	0.449	0.454	0.515	0.671	0.478

The catalytic activity over the toluene removal of the LDH-derived HEOs was investigated, and the results are shown in Figure 5A. In all test processes, the products of toluene oxidation were CO_2 and H_2O . The T_{50} values of HEO-400, HEO-500, HEO-600, HEO-700 and HEO-800 were 232 °C, 239 °C, 246 °C, 300 °C and 407 °C, respectively. The T_{90} values for toluene combustion on the HEO catalysts were 274 °C, 288 °C, 254 °C, 344 °C and 486 °C. Interestingly, the optimum catalytic activity was presented by HEO-600, with the lowest T_{90} value. The shoulder peaks from HEO-400 and HEO-600 at around 150 °C were caused by the adsorption and desorption of toluene on the surface of the porous catalysts. In most research on LDH-derived mixed oxides, the most suitable calcination temperature was selected as 400 °C or 500 °C, and the catalytic activity declined noticeably when the temperature was exceeded. In this work, the LDH precursor composed of multiple metals was transformed into a single spinel phase after its calcination at 600 °C, and gradually gathered into larger nano-sized nanospheres with the increase of the calcination temperature deduced from the XRD results and SEM images. For comparison, the catalytic activity of HEO-milling-600 and HEO-milling-800 were tested under the same initial conditions. The results shown in Figure S5 indicated that the T_{50} values were 372 °C for each sample, and the T_{90} values far exceed 400 °C. Combined with the characterization results, the poor performance of the HEO-milling-600 sample in toluene oxidation was probably caused by the antagonistic effects of the mixed oxides.

To evaluate the stability of the optimal catalyst, HEO-600, 10 cycles of catalytic activity tests were carried out (Figure 5B). For each cycle, the temperature was programmed from 20 to 600 °C at a rate of 2 °C/min and maintained at 600 °C for 3 h before it was cooled down to room temperature. In the stability test, the gas-flow always contained 800 ppm gas-phase toluene during the heating and cooling process, so the catalyst could maintain in the state of adsorption saturation, which reduced the effect of toluene adsorption. The

results showed that after the 10 cycle-test, the T_{90} value of HEO-600 only presented a slight increase to 265 °C. The above demonstrates the outstanding stability of the HEO-type catalyst and its potential for use in large-scale industrial VOC emissions.

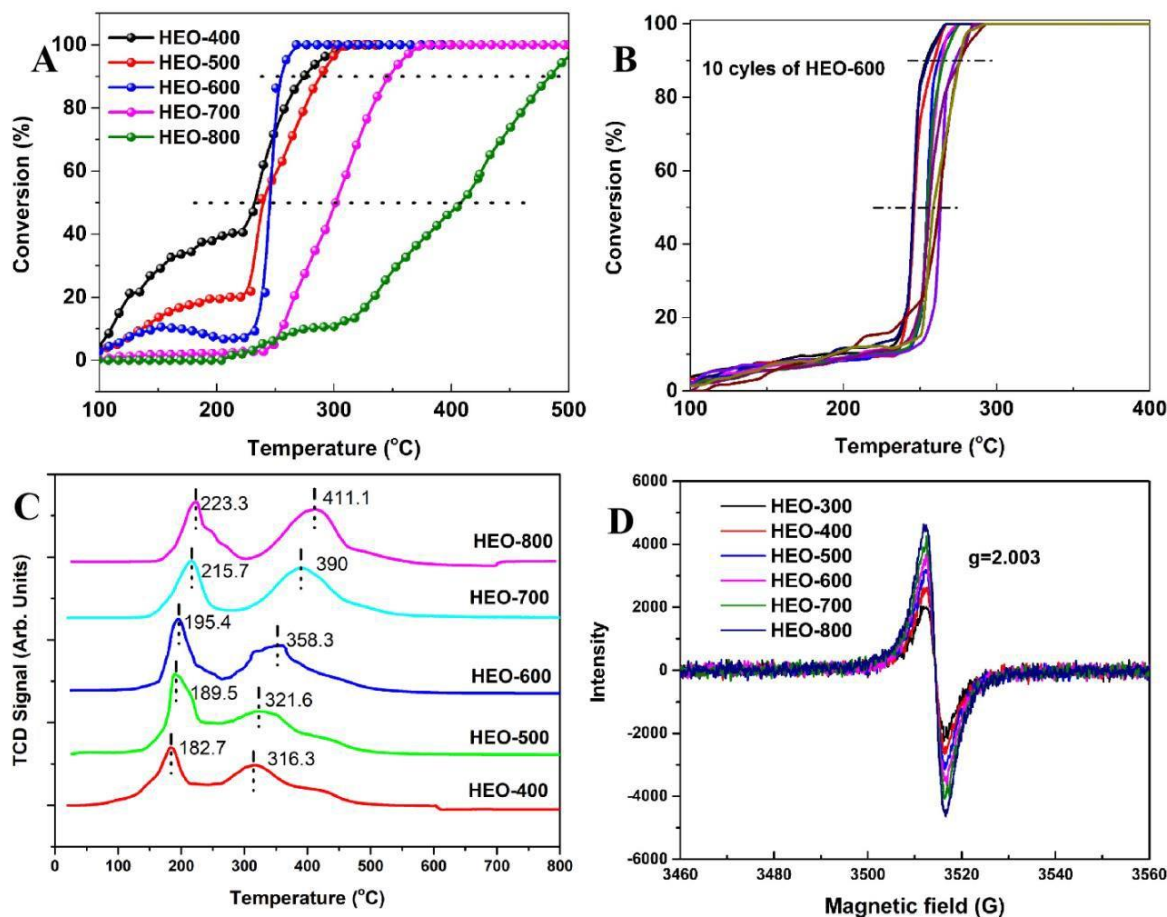


Figure 5. (A) Catalytic removal of toluene by HEOs with various calcination temperatures; (B) 10 cycles of activity test of HEO-600; (C) H_2 -TPR profiles of HEOs; (D) ESR spectra of HEOs.

Figure 5C presented the H_2 -TPR profiles of HEO catalysts. For each sample, two main reduction peaks could be observed at the T_{max} of 174–223 °C (low-temperature) and 316–411 °C (high-temperature), respectively, which are related to the reduction processes of $Mn^{4+} \rightarrow Mn^{3+}$, $M^{3+} \rightarrow M^{2+}$ ($M = Co, Mn, Ni$ and Fe), $M^{2+} \rightarrow M^0$ ($M = Co$ and Ni), and $Cu^{2+}/Cu^+ \rightarrow Cu^0$ [35,44]. The T_{max} of the two reduction peaks gradually moved to higher temperatures with the increase in the calcination temperature from 400 to 600 °C, which was probably caused by the increased content of the high valence metal demonstrated by XPS. As the calcination temperature further increased, the T_{max} of the reduction peaks shifted notably to higher temperatures, especially in the high-temperature region. The poor reducibility of the HEOs obtained at temperatures above 600 °C was probably due to the agglomerated nanoparticle structure and high crystallinity [46]. Therefore, the suitable calcination temperature could promote the interaction between the different metal species to facilitate the reducibility.

Figure 5D shows the EPR spectra of the HEO catalysts. The signal at $g = 2.004$ was observed for each catalyst and discerned as trapped electrons on surface oxygen vacancies. As the calcination temperature increased, the signal intensity became stronger, suggesting more oxygen vacancies were possessed. The signal intensity illustrates that HEOs obtained via high-temperature calcination have more oxygen vacancies. According to the Mars van Krevelen mechanism [47], the toluene molecules adsorbed on the catalyst surface are oxidized and degraded by the lattice oxygen components in the metal oxide, and the

defective parts of the catalyst surface can continuously adsorb gas oxygen molecules to supplement the consumed lattice oxygen. The higher concentration of oxygen defect sites can adsorb more oxygen species, and then accelerate the consumption and supplement of the lattice oxygen, thus improving the activity of the catalyst. The mobility of the oxygen adsorbed on the surface has a great influence on the activity of the catalyst. Metal oxide catalysts continuously accept the adsorption and activation of gas-phase oxygen on their surface oxygen vacancies to produce surface-adsorbed oxygen, which accelerates the participation of lattice oxygen in reaction and regeneration. On the other side, the surface morphology and pore structure were changed with the calcination temperature; the agglomeration of nanoparticles leads to less contact between the catalyst and reaction gas, thus the catalytic activity significantly decreased after 700 or 800 °C calcination.

3. Materials and Methods

3.1. Chemicals

All the chemicals used were of analytical reagent and without further treatment. Na_2CO_3 , NaOH, nitrates including $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and metallic chlorides, such as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, MnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, were purchased from Sinopharm Chemical Reagent limited corporation.

3.2. Catalysts Synthesis

CuCoMnNiFe-LDHs precursor were prepared by a simple co-precipitation method. In detail, 0.01 mol of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 50 mL water. The evenly mixed nitrate solution was slowly dropped into 0.1 mol/L of Na_2CO_3 solution with system pH = 10 ± 0.2 adjusted by 4 mol/L NaOH solution. The product was filtrated after 12 h aging and dried in 60 °C oven. To obtain spinel HEO, the CuCoMnNiFe-LDHs precursor were transferred to muffle furnace for 5 h calcination at 400–800 °C with heating rate of 5 °C/min, and obtained catalysts were named as HEO-400, HEO-500, HEO-600, HEO-700 and HEO-800, respectively. For comparison, HEO with same composition was synthesized by a traditional high-energy ball milling method. Same mole amount of metallic chloride (including $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, MnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was put into the ball mill after uniform mixing. The mass ratio of ball milling beads to mixed oxides was 8:1. After 5 h milling under 200 r/min, the mixture was calcined at 500–900 °C for 5 h with heating rate of 5 °C/min and denoted as HEO-milling-T (T = calcination temperature).

3.3. Characterization

X-ray diffraction (XRD) patterns of LDH precursors and HEOs were characterized by a Shimadzu XRD-7000 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The 2 θ pattern ranging from 5° to 80° (5°·min^{−1} scanning rate, 40 KV, 30 mA) was displayed in the test. Thermogravimetric analysis-differential scanning calorimetric (TGA-DSC) curves of as-synthesized samples were determined from 25 to 1000 °C with the heating rate of 10 °C/min under air condition by Hitachi STA7300. The specific surface areas of samples were calculated from the adsorption isotherm under 0.05–0.30 relative pressure (P/P_0) by Brunauer–Emmett–Teller (BET) method. Morphology of the samples was viewed using scanning electron microscopy (SEM, ZEISS 300, Oberkochen, Germany). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images, and selected area electron diffraction (SAED) patterns, were recorded on JEM 2100F microscope (JEOL, Tokyo, Japan). The H₂-temperature-programmed reduction (H₂-TPR) analysis of samples was carried out using a chemisorption analyzer (PCA-1200). 50 mg sample was placed in a quartz tube and preheated at 400 °C for 30 min under Ar flow. After cooled down to 25 °C, a flow of reductive gases (N₂/H₂ = 95/5 vol.%) passed through samples with a heating rate of 10 °C/min to 700 °C. The surface state of constituent elements of catalysts was determined by X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi

analyzer, Thermo Fisher, Waltham, MA, USA). The obtained XPS spectra were corrected by the standard binding energy of C1s (284.5 eV) and then deconvoluted by XPS PEAK 41 software. Electron paramagnetic resonance (EPR) spectra of samples were obtained by a Bruker A300-10 instrument to analyze the surface oxygen vacancies.

3.4. Catalytic Activity Test

During the test, the simulated gas flow consisted of 800 ppm toluene and 20 vol.% O₂/Ar was regulated as 100 mL/min. 0.1 g of catalyst was placed in the reaction furnace and temperature programmed from room temperature to 500 °C with a heating rate of 2 °C/min. The content of VOCs in the gas before and after the reaction was detected in real time by a gas chromatograph (Agilent GC7890A) connected to the micro reaction device. The recycle test of selected sample was operated from room temperature to 600 °C and maintained at 600 °C for 3 h with same simulated atmosphere and catalyst dosage.

4. Conclusions

A series of spinel type high-entropy oxides were successfully prepared using multi-variate composition LDHs as precursors. Thermal treatment over 600 °C led to the complete transformation of the LDHs to single-phase HEOs. The calcination temperature significantly affects the crystal structure, morphology and existing form of the constituent metals of the synthesized HEOs, which further affects the catalytic activity. The optimal HEO-600 catalyst showed impressive activity and stability during toluene catalytic oxidation, which resulted from the vast quantity of surface oxygen vacancies and the relative variable metal valence. The T₅₀ and T₉₀ values of HEO-600 were 246 and 254 °C, and the T₉₀ value only presented a slight increase to 265 °C after the 10-cycle test. The entropy-stable state of the as-synthesized catalyst was the key factor for operating under harsh conditions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13010119/s1>, Figure S1. c 1s xps spectra of heos. Figure S2. eds spectrum and elements mapping of heo-600. Figure S3. (a) n₂ adsorption/desorption isotherms and (b) bjh pore size distribution of heos. Figure S4. cu aes spectra of heos. Figure S5. catalytic performance of heo-milling-600 and heo-milling-800. Table S1. The obtained atomic percentage from eds spectrum.

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